THE ELURA OREBODY

A MULTIDISCIPLINARY STUDY INVESTIGATING
GEOCHEMICAL, MINERALOGICAL & GEOMETALLURGICAL ORE
CHARACTERISTICS

GERNOT C. LOIDL (MSc)
SCHOOL OF EARTH & ENVIRONMENTAL SCIENCES
DEPARTMENT GEOLOGY & GEOPHYSICS
THE UNIVERSITY OF ADELAIDE

A THESIS SUBMITTED FOR THE DEGREE OF
Doctor of Philosophy
MARCH, 2012
Panel of supervisors

Principle supervisor: Ian R. Plimer

1. Co-supervisor: Oskar A.R. Thalhammer

2. Co-supervisor: Andreas Schmidt-Mumm

Date of submission: 12th of August, 2011

Principle supervisor
I, Gernot LOIDL, hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying, subject to the provision of the Copyright Act 1968.

I also give permission for the digital version of my thesis to be made available on the web, via the University’s digital research repository, the Library catalogue and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

ADELAIDE, 12th of March 2011

Gernot C. LOIDL
Dedicated to my family, ...

... my parents, Christa and Josef Leidl,
... my brother, Roland Leidl,
... and my grandmothers, Antonia Kofler and Margarete Leidl.

Your perpetual support, trust and love you endowed me with is exceptional.

My sincere thanks to all of you.
Acknowledgements

First and foremost, I would like to thank two persons who initiated my PhD venture via sparking the interest to further extent my geological knowledge, Oskar A.R. Thalhammer and Ian R. Plimer. Oskar Thalhammer taught me many important aspects of applied geosciences during my studies at the University of Leoben, Austria, and significantly contributed to my intellectual and personal growth. He furthermore introduced me to Ian Plimer, whom I met on a field trip to Milos, Greece. Ian Plimer’s incredibly enthusiastic way of teaching and explaining geology further advanced my interest, inquisitiveness in, and my understanding of geology. During this field trip he offered for me to come to Australia in order to undertake a PhD at the University of Adelaide under his supervision. This is how my Australian voyage began. Many thanks to both of you.

Secondly, my sincere thanks go to Bob Besley, the former Managing Director of CBH Resources Ltd., for offering me a graduate geologist position at the Endeavor Mine in Cobar. This work experience not only broadened my mind in many practical aspects of mining other than geology, it also allowed me to thoroughly study and gain a fundamental understanding of the geology of the Elura deposit prior to the commencement of my PhD studies. During this employment I was part of a team of great geologists. Every team member significantly contributed to an improved understanding of the mine geology and helped to advance the geological, structural and resource models. Many thanks to Peter Nicholson, Vanadis Mares, Don Smith, Rebecca Smart and Catherine Smith. In particular I would like to thank Peter Nicholson who took significant effort to train me in the manifold skills related to mine geology and trusted in my capabilities. He was a quite demanding supervisor, and a great mentor as his help, advice and support was never far away. I also would like to acknowledge the former general manager of Endeavor Operations Pty. Ltd. David Vink for his support during my employment and his backing of my PhD study plans.

This research project would not have been possible without the advice, help and support of many great people and companies. Therefore, I would like to convey my sincere thanks to:

... Andrew McCallum for passing on his experience related to mineral processing at Elura and for providing numerous data and information.

... Kylie Simmons for her help during my extensive sampling campaign.

... ALS Australia, in particular Stephen Finlayson and Shaun Kenny, for their financial support, great analytical service and advice on laboratory procedures.

... Federica Zaccarini and Helmut Mühlhans for their help, training and advice during my electron microprobe work, which was carried out at the Department of Applied Geosciences and Geophysics; chair of Resource Mineralogy; University of Leoben, Austria. I greatly appreciated Helmut Mühlhans’ extraordinary sample preparation skills of high quality polished thin-section.

... Thomas C. Meisel for his advice and training on rare earth and platinum group element analytic, and for access to the laboratory facilities at the Department of General, Analytical and Physical Chemistry, University of Leoben, Austria.

... Galen Halverson for providing training and support during my zinc isotope analytical work.

... Ronald Bakker for his interest and support during my fluid inclusion investigations and Raman analyses.

... Giorgio Garuti for his advice on chloride chemistry and geothermometry.

... Amdel Limited, in particular Kelly Jones, for organising the QEMSCAN® analyses, supplying essential information about the analytical technique and for giving me a crash-course in the iDiscover software package.

... FEI Australia, in particular Alan Butcher, for supplying the iDiscover software package and licenses.

... Benjamin Wade for his help during my LA-ICP-MS measurements at Adelaide Microscopy.

... Heinz Mali for access to his high quality photomicrographic imaging system.

... Nigel Cook for reviewing my LA-ICP-MS section, and

... Martin Griesmann and Marcus Kunzmann for many convivial gatherings, accompanied by productive and inspiring conversations.

I would like to thank the entire panel of supervisors, Ian R. Plimer, Oskar A.R. Thalhammer and Andreas Schmidt-Mumm, for their advice, guidance and support throughout my PhD studies, as well as for their editorial reviews, corrections and recommendations.

Last but not least, and most importantly, I would like to thank CBH Resources Ltd and Toho Zinc Co. Ltd. for their generous financial support and their interest in my PhD project.
# Contents

Table of Contents xi

Abstract xvii

List of Figures xix

List of Tables xxiii

1 Introduction 1
   1.1 Location, landform, climate and vegetation 1
   1.2 Mining history in the Cobar region 2
   1.3 Discovery of the Elura deposit 5

2 Regional Geology 7
   2.1 The Tasmanides 7
   2.2 The Lachlan Fold Belt 10
      2.2.1 Overview and geography 10
      2.2.2 Tectonic evolution of the Lachlan Orogen 10
      2.2.3 Stratigraphy 15
      2.2.4 Rifting induced basin development and subsequent igneous activity 17
      2.2.5 Metallogeny of the Lachlan Orogen 17
   2.3 The Cobar Basin 20
      2.3.1 Overview and basin formation 20
      2.3.2 Stratigraphy 21
      2.3.3 Structural setting 24
      2.3.4 Igneous activity within and proximal to the Cobar Basin 25
   2.4 Australian Zn-Pb-Ag ore systems 27
      2.4.1 History and current production 27
      2.4.2 The most important base metal deposit types 27
      2.4.3 Deposits in the Cobar region 31

3 The Elura Orebody 35
   3.1 Geological characteristics 35
      3.1.1 Host lithology 35
      3.1.2 Ore types and their zoning 39
      3.1.3 Wall rock alteration 44
      3.1.4 Structural setting 45
      3.1.5 Regolith expression 47
3.2 The current genetic model for the Elura deposit ........................................... 50
  3.2.1 Chronological overview ................................................................. 50
  3.2.2 Contributions to the genetic model for the Elura deposit ..................... 50
  3.2.3 Age, metal source and physiochemical fluid characteristics ................. 51
3.3 Research objectives and methodology ....................................................... 56
  3.3.1 Petrography and texture of the massive sulphide mineralisation ......... 57
  3.3.2 Mineral chemistry of sulphide ore phases ...................................... 57
  3.3.3 Whole rock geochemistry ............................................................. 58
  3.3.4 Fluid characteristics and timing of the ore forming event ................. 59
3.4 Sampling ..................................................................................................... 59

4 Ore mineralogy and petrography ................................................................. 63
  4.1 Microscopic observations ........................................................................ 63
    4.1.1 Sulphide gangue phases .............................................................. 64
    4.1.2 Base metal and silver phases ...................................................... 68
    4.1.3 Non-sulphide gangue phases and altered wall rock fragments .......... 69
    4.1.4 Ore type specific characteristics and textures ............................. 72
    4.1.5 Mineral paragenesis ................................................................. 76
  4.2 Electron microprobe analyses ................................................................ 79
    4.2.1 Compositional variability of sulphides throughout the Elura orebody 79
    4.2.2 Silver phases – their classification and alteration ......................... 93
    4.2.3 Chlorite chemistry .................................................................... 101
    4.2.4 Application of the sphalerite geobarometer ................................. 106
  4.3 Trace element composition derived from LA-ICP-MS ............................. 108
    4.3.1 Analytical background ............................................................... 108
    4.3.2 Overview of analytical results ...................................................... 110
    4.3.3 Trace elements in sphalerite ....................................................... 110
    4.3.4 Galena trace element composition ............................................. 114
    4.3.5 Trace elements incorporated in iron sulphides ............................. 119
  4.4 Fluid inclusion study in sphalerite ........................................................... 126
  4.5 Zinc isotopes of sphalerite ..................................................................... 129
    4.5.1 Analytical technique ................................................................. 129
    4.5.2 Results and discussion ............................................................... 131
  4.6 Summary of findings ............................................................................. 134

5 Geochemical ore characterisation ............................................................... 139
  5.1 Background and methodology ............................................................... 140
    5.1.1 Major and trace element whole rock geochemistry ....................... 140
    5.1.2 Rare earth element analysis ......................................................... 141
    5.1.3 Platinum group element determination (incl. rhenium) ................ 142
  5.2 Major elements, modal mineralogy and density estimation .................. 145
  5.3 Trace element signature - trends and element affinities ....................... 149
    5.3.1 Inter-element affinities ............................................................. 149
    5.3.2 Trace element concentrations and their spatial distribution .......... 151
    5.3.3 Element cross-plots ................................................................... 161
    5.3.4 Reconciliation between geochemistry and mineral chemistry for selected elements ................................................................. 162
  5.4 Host rock classification ......................................................................... 166
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>Mass/volume and element gain-loss estimation</td>
<td>170</td>
</tr>
<tr>
<td>5.5.1</td>
<td>The Isocon-method</td>
<td>170</td>
</tr>
<tr>
<td>5.5.2</td>
<td>The hypothesis</td>
<td>171</td>
</tr>
<tr>
<td>5.5.3</td>
<td>Results</td>
<td>172</td>
</tr>
<tr>
<td>5.6</td>
<td>Rare earth element signatures of different ore types</td>
<td>176</td>
</tr>
<tr>
<td>5.7</td>
<td>Platinum group elements and the time of ore formation</td>
<td>182</td>
</tr>
<tr>
<td>5.7.1</td>
<td>PGE concentrations and their fractionations</td>
<td>182</td>
</tr>
<tr>
<td>5.7.2</td>
<td>Principals of the Re-Os isotopic system</td>
<td>184</td>
</tr>
<tr>
<td>5.7.3</td>
<td>The isochron age and potential osmium sources</td>
<td>186</td>
</tr>
<tr>
<td>5.8</td>
<td>Summary of geochemistry and integration of ore petrology</td>
<td>190</td>
</tr>
<tr>
<td>6</td>
<td>Geo-metallurgical study via QEMSCAN®</td>
<td>195</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>195</td>
</tr>
<tr>
<td>6.2</td>
<td>Fundamentals of the QEMSCAN® technique</td>
<td>197</td>
</tr>
<tr>
<td>6.3</td>
<td>Sampling</td>
<td>199</td>
</tr>
<tr>
<td>6.3.1</td>
<td>The 5/5 Stope</td>
<td>199</td>
</tr>
<tr>
<td>6.3.2</td>
<td>Sample preparation</td>
<td>199</td>
</tr>
<tr>
<td>6.4</td>
<td>Investigations prior to QEMSCAN®</td>
<td>202</td>
</tr>
<tr>
<td>6.4.1</td>
<td>Ore petrology</td>
<td>202</td>
</tr>
<tr>
<td>6.4.2</td>
<td>Mineral chemistry</td>
<td>205</td>
</tr>
<tr>
<td>6.4.3</td>
<td>Whole rock geochemistry</td>
<td>207</td>
</tr>
<tr>
<td>6.5</td>
<td>QAQC and data processing</td>
<td>209</td>
</tr>
<tr>
<td>6.5.1</td>
<td>Adjustment of mineral list and pre-processing of raw data</td>
<td>209</td>
</tr>
<tr>
<td>6.5.2</td>
<td>Assay correlation</td>
<td>210</td>
</tr>
<tr>
<td>6.5.3</td>
<td>Important QAQC particle features</td>
<td>211</td>
</tr>
<tr>
<td>6.5.4</td>
<td>Limitations and analytical problems</td>
<td>211</td>
</tr>
<tr>
<td>6.6</td>
<td>QEMSCAN® results from PMA and field scans</td>
<td>213</td>
</tr>
<tr>
<td>6.6.1</td>
<td>General ore characterisation</td>
<td>213</td>
</tr>
<tr>
<td>6.6.2</td>
<td>Mineral specific characterisation</td>
<td>218</td>
</tr>
<tr>
<td>6.6.3</td>
<td>Grain size distributions</td>
<td>222</td>
</tr>
<tr>
<td>6.6.4</td>
<td>Particle liberation</td>
<td>225</td>
</tr>
<tr>
<td>6.6.5</td>
<td>Free particle surface</td>
<td>227</td>
</tr>
<tr>
<td>6.6.6</td>
<td>Mineral associations and locking</td>
<td>230</td>
</tr>
<tr>
<td>7</td>
<td>Interpretation and conclusions</td>
<td>233</td>
</tr>
<tr>
<td>7.1</td>
<td>Aspects to the genesis of the Elura orebody</td>
<td>233</td>
</tr>
<tr>
<td>7.1.1</td>
<td>The modified genetic model for the Elura orebody</td>
<td>236</td>
</tr>
<tr>
<td>7.1.2</td>
<td>Differences to previous genetic models and important new aspects</td>
<td>236</td>
</tr>
<tr>
<td>7.2</td>
<td>Important aspects for mineral processing</td>
<td>239</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>243</td>
</tr>
</tbody>
</table>
## CONTENTS

### Appendices 255

**A  Ore mineralogy and petrography** 257  
A.1 Sampling ........................... 258  
A.2 Photomicrographs .................. 270  
A.2.1 Massive pyrrhotitic ore (Po) 279  
A.2.2 Siliceous pyritic ore (SiPy) 291  
A.2.3 Siliceous pyrrhotitic ore (SiPo) 295  
A.2.4 Stringer and breccia style ore (VEIN) 299  
A.2.5 Tetrahedrite .......................... 301  
A.2.6 Arsenopyrite ....................... 304  
A.2.7 Miscellaneous ...................... 307  
A.3 Back scatter electron images .... 311  
A.4 Mineral chemistry ................. 322  
A.4.1 Element mapping and energy dispersive spectra 323  
A.4.2 Electron microprobe analytic 332  
A.4.3 Laser ablation ICP-MS analyses 379  

**B  Whole rock geochemistry** 477  
B.1 Analytical methods and detection limits 479  
B.2 Major element analytic ............ 480  
B.3 Trace element concentrations ...... 486  

**C  QEMSCAN® ore characterisation study** 492  
C.1 General ore characterisation ...... 493  
C.1.1 Measurement setup and RAW data 494  
C.1.2 Quality assurance quality control (QAQC) 504  
C.1.3 Particle size distributions ...... 507  
C.1.4 Ore characterisation ............... 510  
C.1.5 Theoretical grade/recovery diagrams 520  
C.2 Sphalerite (PMA) .................... 528  
C.2.1 Grain size ......................... 529  
C.2.2 Compositional variability ........ 531  
C.2.3 Particle liberation ................ 534  
C.2.4 Free particle surface .............. 545  
C.2.5 Mineral associations .............. 555  
C.3 Galena (PMA) ....................... 562  
C.3.1 Grain size ......................... 563  
C.3.2 Particle liberation ................ 566  
C.3.3 Free particle surface .............. 577  
C.3.4 Mineral associations .............. 588  
C.3.5 Grade/recovery graph including chalcopyrite 595  
C.4 Chalcopyrite (PMA) ................. 598  
C.4.1 Grain size ......................... 599  
C.4.2 Copper-bearing mineral phases 602  
C.4.3 Particle liberation ................. 604  
C.4.4 Free particle surface .............. 614  
C.4.5 Mineral associations .............. 623
C.5 Iron sulphides (PMA) ......................................................... 630
  C.5.1 Grain size distribution of pyrite ............................ 631
  C.5.2 Grain size distribution of pyrrhotite ..................... 633
  C.5.3 Grain size distribution of pyrrhotite ..................... 637
C.6 Silver-bearing mineral phases (PMA) ......................... 638
  C.6.1 Assay correlation and identified silver phases ........ 639
  C.6.2 Grain size ........................................................... 642
  C.6.3 Particle liberation .............................................. 644
  C.6.4 Mineral associations ........................................... 649
C.7 Field scan results .................................................... 650
  C.7.1 Measurement setup ............................................. 651
  C.7.2 General ore characterisation ............................... 653
  C.7.3 Mineral associations ........................................... 663
  C.7.4 Characterisation of iron sulphides ...................... 667
  C.7.5 Compositional variability of sphalerite ............... 670
  C.7.6 Characterisation of silver phases ...................... 673
  C.7.7 Bismuth mineral search ..................................... 675
  C.7.8 Grain size distributions ..................................... 676
C.8 Field scan images .................................................... 681
Abstract

The Elura Zn-Pb-Ag deposit 43 km NNW of Cobar, NSW, contained a pre-mining resource of 50.7 Mt at 8.8 wt% Zn, 5.6 wt% Pb, 107 g/t Ag and 0.2 wt% Cu. Sediment-hosted ore within a turbiditic sequence is strongly structural controlled. It is sheet-like with several elongated, sub-vertical massive zoned sulphide bodies with central pyrrhotitic cores surrounded by pyrite ore which is enclosed by semi-massive and breccia-stringer mineralisation.

This study showed pronounced grain sizes, texture, mineral composition and trace element geochemistry heterogeneity. The pyrite-pyrrhotite-galena-sphalerite ore has minor marcasite, chalcopyrite and arsenopyrite and trace tetrahedrite (± freibergite), native silver and magnetite. Enrichment trends towards the surface and peripheral pyrite-dominated ore zones are in Ag, As, Tl, Hg, Sb, Sn, Mo and Au.

The first Re-Os whole rock massive sulphide isochron age is 378 ±15 Ma. Initial $\gamma_{Os}$ of ~170 is either caused by juvenile continental crust of the Lachlan Fold Belt as metal source or by a contribution of primitive mantle Os. Zinc isotope compositions of sphalerite ($\delta^{66}Zn_{JMC}$ 0.220-0.450‰) suggest effectively leached average continental crust as the source for metals, chlorite thermometry showed temperatures at 314-343 °C, high Cu concentrations coincide with light Zn isotopes that define two major zones of fluid influx and the isocon method showed host lithology replacement was negligible during ore genesis.

Sulphides formed in sites of increased dilation and fracture-induced permeability during prolonged periods of fracturing and fluid pulses. Decreasing fluid pressure and adiabatic cooling initiated precipitation of sulphides. No evidence for fluid mixing was identified. Initially, lower parts of the orebody formed in dilational zones in sandstone-rich sequences along a transpressional fault corridor. Major fracturing then caused the formation of upper main lode and upgrading of the lower main lode ore zones. Changing fluid temperatures, internal refinement via dissolution-reprecipitation and temporal fluid composition change created vertical mineralogical and geochemical ore zonation. The orebody was modified during post-depositional compression during continued basin inversion resulting in sulphide remobilisation, upgrading and amplified ore zonation.

Zinc and, in particular, Pb recovery rates significantly fluctuated since production began in 1983. Fluctuating recovery rates resulted from grain size variability and subsequent poor particle liberation during grinding. Silver recoveries rarely exceeded 50%. Poor Ag recoveries were due to fine-grained argentian tetrahedrite, common associations with gangue phases and alteration of tetrahedrite. High concentrations of Bi were encountered recently in lead concentrate. A galenamatildite solid solution contains Bi (max. 5,645 ppm). High Bi is limited to the lowermost main lode ore zone.

Geometallurgical ore characterisation via QEMSCAN® was undertaken to predict mineral processing characteristics of ore sourced from parts of the same stope. On the stope scale there are significant variations in flotation characteristics from different parts of the stope which enables prediction of recoveries, concentrate qualities and mill throughput. Theoretical recovery calculations suggest that ore from the western part will have 10% lower recovery. Theoretical and long-term average recoveries are similar for Zn but not for Pb. Theoretical data may overestimate recovery because sample preparation may liberate more particles than plant grinding. An overview of mineralogy and trace elements allows geometallurgical ore characterisation on the stope scale to better predict mill performance. Investigation of geometallurgical ore characteristics and penalty element concentrations are recommended on a stope-by-stope basis within life-of-mine planning.
## List of Figures

1.1 Location of the Elura Orebody ........................................ 1
1.2 The township of Cobar in the late 1890s ............................... 3
1.3 Aerial photograph showing the footprint of the Endeavor Mine ...... 5

2.1 The Tasman Fold Belt on the eastern margin of Gondwana ............ 8
2.2 Regional extent of orogenic belts in the Tasmanides .................. 8
2.3 Proposed geodynamic mechanisms causing the orogenies in the Lachlan Fold Belt ................................. 11
2.4 Surface geology of New South Wales .................................. 12
2.5 Unconformities and timing of deformational events in the Lachlan Fold Belt ........................................ 14
2.6 The three subprovinces in the Lachlan Fold Belt ....................... 15
2.7 Occurrences and age of intrusives in the Lachlan Fold Belt .......... 19
2.8 Location of the Cobar Basin ........................................... 20
2.9 Geology of the Cobar Basin ........................................... 22
2.10 Stratigraphy of the Cobar Basin ....................................... 23
2.11 Deposits in the Cobar region .......................................... 33

3.1 Geology in the vicinity of the Elura Orebody .......................... 36
3.3 Example of tuff horizons within the Elura’s host rock sequence .... 37
3.2 Sedimentological variations of the host rock sequence ................ 37
3.4 Mine stratigraphy of the Elura deposit .................................. 38
3.5 The different mineralised zones of the Elura Orebody ................ 39
3.6 Hand specimen of massive/semi-massive ore ........................... 40
3.7 Sulphide stringer in silicified wall rock ................................ 41
3.8 Sphalerite replacing siderite in mudstone rich sequence .............. 42
3.9 Siliceous hydrothermal breccia with minor sulphides ................. 42
3.11 The spatial distribution of different ore types and their zoning .... 43
3.12 Siderite spotting adjacent to sulphide vein ............................ 44
3.13 Pyrite nodules in zone of intense quartz-siderite veining ............ 44
3.15 Major structures affecting the Elura deposit ........................... 46
3.17 The geometry of the Elura Orebody and spatial sample coverage .... 60

4.1 Locations of samples investigated via EMPA ........................... 63
4.2 Back scatter electron images of pyrite and its replacement .......... 65
4.3 Reflected light microphotographs of the four pyrite varieties ......... 66
4.4 Marcasite rich bands in massive pyritic ore ........................... 67
4.5 Euhedral zoned arsenopyrite ........................................... 68
4.6 Significant grain size variation of sphalerite and galena .............. 69
4.7 Occurrences of argentian-tetrahedrite ................................. 70
4.8 Various non-sulphide gangue phases ................................................. 71
4.10 Typical examples of massive pyrrhotitic ore .................................. 73
4.12 Typical examples of massive pyritic ore ........................................ 74
4.14 Photomicrographs of semi-massive ore types ................................ 75
4.15 Mineral paragenesis and hydrothermal stages .................................... 77
4.16 Iron content in sphalerite for different ore types ................................ 79
4.17 Iron concentration in sphalerite vs. depth ...................................... 80
4.18 Cadmium concentration in sphalerite vs. depth .................................. 80
4.19 Bismuth in galena for different ore types ....................................... 81
4.20 Bismuth concentration in galena vs. depth ..................................... 81
4.21 Search for Bi mineral phases .................................................... 82
4.22 Trace element mapping in galena ................................................ 83
4.23 Pyrite composition within the Co-Ni-As system ................................ 84
4.24 Gold concentration in chalcopyrite vs. depth .................................. 85
4.25 Silver concentration in pyrite vs. depth ........................................ 85
4.26 Gold concentration in chalcopyrite for different ore types .................. 86
4.27 Arsenic concentration in pyrite for different ore types ....................... 86
4.28 Silver concentration in pyrite for different ore types ......................... 86
4.29 Bismuth concentration in pyrite for different ore types ...................... 86
4.30 Iron-deficiency in pyrrhotite ..................................................... 87
4.31 As/S atomic ratio of arsenopyrite ................................................ 88
4.32 Arsenopyrite composition in the Fe-As-S system ................................ 88
4.33 Arsenopyrite zonation (WDS element mapping image) ....................... 89
4.34 Arsenopyrite zonation (BSE image) .............................................. 90
4.35 Magnetite intimately intergrown with pyrite type C ........................... 91
4.36 Compositional variability of Ag-sulfosalt phases ............................... 95
4.37 Comparison of Ag-phase composition in respect to silver and sulfur content .......................................................... 96
4.38 Alteration of Ag-rich tetrahedrite .................................................. 97
4.39 Chlorite classification ............................................................... 102
4.40 Comparison of temperature estimates of different geothermometers .......... 105
4.41 Chlorite temperature variability vs. depth ..................................... 105
4.42 Pressure estimates for different ore types ..................................... 107
4.43 Pressure estimates as a function of depth ..................................... 107
4.44 Sample locations for LA-ICP-MS study ......................................... 108
4.45 Trace element affinities to certain mineral phases (cluster analysis) ........ 110
4.46 Compositional variability of sphalerite vs. depth .............................. 111
4.47 Example of time-resolved intensity profile of sphalerite ..................... 112
4.48 Compositional variability of galena vs. depth .................................. 115
4.49 Intensity cross-plot between $^{111}$Cd and $^{114}$Cd for galena analyses ....... 116
4.50 Example of time-resolved intensity profile of galena ......................... 117
4.51 Galena composition in the Ag-Bi-Pb and Ag-Sb-Pb ternary systems .......... 119
4.52 Compositional variability of pyrite vs. depth .................................. 120
4.53 Pyrite classification based on cobalt, nickel and arsenic content .......... 120
4.54 Time-resolved intensity profile for gold in pyrite .............................. 122
4.55 Example of time-resolved intensity profile of pyrite ......................... 123
4.56 Example of time-resolved intensity profile of pyrrhotite ..................... 124
4.57 Element intensity (cps) cross-plots ............................................. 125
4.58 Images of fluid inclusions hosted by sphalerite ................................ 126
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.60</td>
<td>Raman spectra of sphalerite</td>
<td>127</td>
</tr>
<tr>
<td>4.59</td>
<td>Raman spectra of reference materials</td>
<td>127</td>
</tr>
<tr>
<td>4.61</td>
<td>Raman spectra of fluid inclusions hosted by sphalerite</td>
<td>128</td>
</tr>
<tr>
<td>4.62</td>
<td>Zinc isotope sample locations</td>
<td>129</td>
</tr>
<tr>
<td>4.63</td>
<td>Zinc isotope QAQC diagrams</td>
<td>131</td>
</tr>
<tr>
<td>4.64</td>
<td>Zinc isotope histogram</td>
<td>132</td>
</tr>
<tr>
<td>4.65</td>
<td>Zinc isotope variability vs. depth</td>
<td>132</td>
</tr>
<tr>
<td>5.1</td>
<td>Sample locations for major and trace element whole rock geochemistry</td>
<td>139</td>
</tr>
<tr>
<td>5.2</td>
<td>Samples selected for rare earth element study</td>
<td>141</td>
</tr>
<tr>
<td>5.3</td>
<td>Rare earth element standard analyses (Penrhyn Slate OU-6)</td>
<td>141</td>
</tr>
<tr>
<td>5.4</td>
<td>Samples selected for the determination of platinum group element content</td>
<td>143</td>
</tr>
<tr>
<td>5.5</td>
<td>Calculated modal mineral composition based on geochemical data</td>
<td>145</td>
</tr>
<tr>
<td>5.6</td>
<td>Comparison of calculated and measured density data of different ore types</td>
<td>146</td>
</tr>
<tr>
<td>5.7</td>
<td>Variability of modal mineralogy in respect to different ore types</td>
<td>148</td>
</tr>
<tr>
<td>5.8</td>
<td>Coordinate transformation for geostatistical modelling</td>
<td>149</td>
</tr>
<tr>
<td>5.9</td>
<td>Overview of trace element affinities according to cluster analysis</td>
<td>150</td>
</tr>
<tr>
<td>5.10</td>
<td>Grouping of trace elements related to base metal mineralisation (cluster analysis)</td>
<td>150</td>
</tr>
<tr>
<td>5.11</td>
<td>Trace elements relatively enriched in pyritic ore types</td>
<td>152</td>
</tr>
<tr>
<td>5.12</td>
<td>Trace elements relatively enriched in pyrrhotitic ore types</td>
<td>153</td>
</tr>
<tr>
<td>5.14</td>
<td>Spatial Ag distribution according to the resource block model</td>
<td>154</td>
</tr>
<tr>
<td>5.16</td>
<td>Spatial Cu distribution according to the resource block model</td>
<td>155</td>
</tr>
<tr>
<td>5.17</td>
<td>Trace element variabilities vs. depth (Hg, Tl)</td>
<td>156</td>
</tr>
<tr>
<td>5.18</td>
<td>Trace element variabilities vs. depth (As, Ag, Sb)</td>
<td>157</td>
</tr>
<tr>
<td>5.19</td>
<td>Trace element variabilities vs. depth (Co, Cu, In)</td>
<td>158</td>
</tr>
<tr>
<td>5.20</td>
<td>Trace element variabilities vs. depth (Se, Te, Bi)</td>
<td>159</td>
</tr>
<tr>
<td>5.21</td>
<td>Trace element variabilities vs. depth (Mo, Ga, Cd)</td>
<td>160</td>
</tr>
<tr>
<td>5.22</td>
<td>Important element cross-plots</td>
<td>161</td>
</tr>
<tr>
<td>5.23</td>
<td>Reconciliation of mineral chemistry (EMPA) to geochemical data for Bi</td>
<td>162</td>
</tr>
<tr>
<td>5.24</td>
<td>Reconciliation of mineral chemistry (LA-ICP-MS) to geochemical data (Cd, In)</td>
<td>162</td>
</tr>
<tr>
<td>5.25</td>
<td>Reconciliation of mineral chemistry (LA-ICP-MS) to geochemical data for Ag</td>
<td>163</td>
</tr>
<tr>
<td>5.26</td>
<td>Reconciliation of mineral chemistry (LA-ICP-MS) to geochemical data (Bi, Se, Te)</td>
<td>163</td>
</tr>
<tr>
<td>5.27</td>
<td>Wall rock discrimination of tectonic settings (K₂O/Na₂O vs. SiO₂)</td>
<td>166</td>
</tr>
<tr>
<td>5.28</td>
<td>Wall rock discrimination for source rock provenance (major element ratios)</td>
<td>167</td>
</tr>
<tr>
<td>5.29</td>
<td>Classification of wall rock for tectonic environments (trace elements)</td>
<td>168</td>
</tr>
<tr>
<td>5.30</td>
<td>Chondrite normalised REE distribution of wall rock</td>
<td>168</td>
</tr>
<tr>
<td>5.31</td>
<td>Multi-trace-element diagram comparing wall rock samples to reference data</td>
<td>169</td>
</tr>
<tr>
<td>5.32</td>
<td>Principles of the isocon method</td>
<td>170</td>
</tr>
<tr>
<td>5.33</td>
<td>Zirconium-hafnium cross-plot</td>
<td>171</td>
</tr>
<tr>
<td>5.34</td>
<td>Scaled isocon diagram for altered and minor mineralised wall rock</td>
<td>172</td>
</tr>
<tr>
<td>5.35</td>
<td>Scaled isocon diagram for breccia-stringer type ore</td>
<td>173</td>
</tr>
<tr>
<td>5.36</td>
<td>Scaled isocon diagram for semi-massive ore</td>
<td>174</td>
</tr>
<tr>
<td>5.37</td>
<td>Scaled isocon diagram for massive ore</td>
<td>175</td>
</tr>
<tr>
<td>5.38</td>
<td>LREE and HREE fractionation cross-plots</td>
<td>177</td>
</tr>
<tr>
<td>5.39</td>
<td>REE distributions of different ore types</td>
<td>178</td>
</tr>
<tr>
<td>5.40</td>
<td>Most characteristic REE patterns significantly different to CSA wall rock</td>
<td>179</td>
</tr>
<tr>
<td>5.41</td>
<td>The three distinct REE distributions in ore samples</td>
<td>180</td>
</tr>
<tr>
<td>5.42</td>
<td>REE content in carbonates</td>
<td>180</td>
</tr>
</tbody>
</table>
5.43 Normalised PGE distribution diagrams .......................................................... 182
5.44 Isotopic evolution of Os in continental crust relative to CHUR ..................... 185
5.45 Re-Os isochron diagram .................................................................................. 186
5.46 Os isotope variation (γ Os) in various lithologies/reservoirs compared to Elura .. 187
6.1 Thin-section sample locations for ore characterisation study ............................. 199
6.2 Ore types within the 5/5 stope .......................................................................... 200
6.3 Bulk sample locations for 5/5 stope ore characterisation study ....................... 200
6.4 Field scan image (BSE and sulphides) for sample DE377 ................................. 202
6.5 Field scan image (BSE and sulphides) for sample DE306 ................................. 203
6.6 Field scan image (BSE and sulphides) for sample DE381-1 .............................. 203
6.7 Field scan image (BSE and sulphides) for sample DE381-2 .............................. 204
6.8 Field scan image (BSE and sulphides) for sample DE398 ................................. 204
6.9 QEMSCAN® – chemical assay correlation ......................................................... 210
6.10 Particle size distribution for $PS + 3/ − 80 \mu m$ ............................................. 211
6.11 Average ESD grain sizes for sulphide phases ................................................... 214
6.12 Average ESD grain sizes for non-sulphide gangue phases ............................... 214
6.13 Theoretical grade-recovery diagram for Zn ...................................................... 216
6.14 Theoretical grade-recovery diagram for Pb ...................................................... 216
6.16 Theoretical grade-recovery diagram for copper .............................................. 217
6.15 Lead grade-recovery graphs (incl. chalcopyrite) .............................................. 217
6.17 Reconciliation of sphalerite composition (QEMSCAN® vs EMP) ...................... 218
6.18 Reconciliation of Ag and Sb between QEMSCAN® and chemical assay data .... 219
6.19 Classification of pyrite type A and B via QEMSCAN® ...................................... 221
6.20 Associations of pyrite type A and B with pyrrhotite ........................................ 222
6.21 Grain size distributions of galena ..................................................................... 222
6.22 Grain size distributions of pyrite type A and B ................................................ 223
6.24 Grain size distributions of argentian tetrahedrite ............................................. 224
6.23 Long-term Ag plant recoveries for different particle size fractions .................. 224
6.25 Particle liberation of sphalerite for different 5/5 Stope parts .............................. 225
6.27 Particle liberation of galena for different 5/5 Stope parts ................................. 226
6.26 Long-term Pb plant recoveries for different particle size fractions .................. 226
6.28 Lead recovery and corresponding particle liberation of galena for different particle size fractions ........................................................................................................ 227
6.29 Particle images for galena liberation ................................................................. 228
6.30 Particle sub-populations selected for recovery case calculations .................... 229
6.31 Important mineral associations of galena and contained Pb ............................. 232
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Orogenic events in the Lachlan Fold Belt</td>
<td>13</td>
</tr>
<tr>
<td>2.2</td>
<td>Important characteristics of subduction zones in the Lachlan Fold Belt</td>
<td>16</td>
</tr>
<tr>
<td>2.3</td>
<td>Major faults in the Cobar Basin</td>
<td>26</td>
</tr>
<tr>
<td>3.1</td>
<td>Deformational events and their structural elements</td>
<td>47</td>
</tr>
<tr>
<td>4.1</td>
<td>Number of samples taken from different ore zones and ore types</td>
<td>79</td>
</tr>
<tr>
<td>4.2</td>
<td>Summary of sphalerite composition determined via EMPA</td>
<td>82</td>
</tr>
<tr>
<td>4.3</td>
<td>Summary of galena composition determined via EMPA</td>
<td>82</td>
</tr>
<tr>
<td>4.4</td>
<td>Summary of chalcopyrite composition determined via EMPA</td>
<td>83</td>
</tr>
<tr>
<td>4.5</td>
<td>Summary of pyrite composition determined via EMPA</td>
<td>84</td>
</tr>
<tr>
<td>4.6</td>
<td>Summary of pyrrhotite composition determined via EMPA</td>
<td>86</td>
</tr>
<tr>
<td>4.7</td>
<td>Summary of arsenopyrite composition determined via EMPA</td>
<td>89</td>
</tr>
<tr>
<td>4.8</td>
<td>Composition of magnetite intergrown with pyrite type C</td>
<td>91</td>
</tr>
<tr>
<td>4.9</td>
<td>Standards and conditions for EMPA of sulphides</td>
<td>92</td>
</tr>
<tr>
<td>4.10</td>
<td>Standards and conditions for EMPA of Ag-phases</td>
<td>94</td>
</tr>
<tr>
<td>4.11</td>
<td>Representative Ag-rich tetrahedrite analyses</td>
<td>98</td>
</tr>
<tr>
<td>4.12</td>
<td>Composition of other Ag-rich sulfosalt phases (stylotypite)</td>
<td>99</td>
</tr>
<tr>
<td>4.13</td>
<td>Compositions of altered Ag-rich sulfosalt phases</td>
<td>100</td>
</tr>
<tr>
<td>4.14</td>
<td>Standards and conditions for EMPA of chlorite</td>
<td>102</td>
</tr>
<tr>
<td>4.15</td>
<td>Overview of chlorite composition and representative analyses</td>
<td>103</td>
</tr>
<tr>
<td>4.16</td>
<td>LA-ICP-MS MASS-1 standard analyses (RSDs, Data/Bkg, MDL)</td>
<td>109</td>
</tr>
<tr>
<td>4.17</td>
<td>Summary of trace element composition of sphalerite</td>
<td>113</td>
</tr>
<tr>
<td>4.18</td>
<td>Summary of trace element composition of galena</td>
<td>118</td>
</tr>
<tr>
<td>4.19</td>
<td>Summary of trace element composition of pyrite</td>
<td>121</td>
</tr>
<tr>
<td>4.20</td>
<td>Summary of trace element composition of pyrrhotite</td>
<td>122</td>
</tr>
<tr>
<td>4.21</td>
<td>Zinc isotope data</td>
<td>133</td>
</tr>
<tr>
<td>5.1</td>
<td>Number of samples for different ore types and ore zones</td>
<td>139</td>
</tr>
<tr>
<td>5.2</td>
<td>Summary of major element composition of different ore types</td>
<td>147</td>
</tr>
<tr>
<td>5.3</td>
<td>Summary of trace element composition of different ore types</td>
<td>165</td>
</tr>
<tr>
<td>5.4</td>
<td>Major and trace element composition of unaltered and altered wall rock</td>
<td>166</td>
</tr>
<tr>
<td>5.5</td>
<td>Summary of REE characteristics of different ore types</td>
<td>176</td>
</tr>
<tr>
<td>5.6</td>
<td>REE concentration data</td>
<td>181</td>
</tr>
<tr>
<td>5.7</td>
<td>PGE concentration data for massive sulphide ore samples</td>
<td>183</td>
</tr>
<tr>
<td>5.8</td>
<td>Naturally occurring isotopes of Re and Os</td>
<td>184</td>
</tr>
<tr>
<td>5.9</td>
<td>Data for Re-Os geochronology</td>
<td>188</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>6.1</td>
<td>Bulk samples for 5/5 stope ore characterisation</td>
<td>201</td>
</tr>
<tr>
<td>6.2</td>
<td>Thin-section samples for ore characterisation study</td>
<td>201</td>
</tr>
<tr>
<td>6.3</td>
<td>Tonnage and grade of the 5/5 stope</td>
<td>201</td>
</tr>
<tr>
<td>6.5</td>
<td>Mineral chemistry of galena (5/5 stope)</td>
<td>205</td>
</tr>
<tr>
<td>6.4</td>
<td>Mineral chemistry of sphalerite (5/5 stope)</td>
<td>205</td>
</tr>
<tr>
<td>6.6</td>
<td>Mineral chemistry of argentian-tetrahedrite (5/5 stope)</td>
<td>206</td>
</tr>
<tr>
<td>6.7</td>
<td>Mineral chemistry of chalcopyrite (5/5 stope)</td>
<td>206</td>
</tr>
<tr>
<td>6.8</td>
<td>Mineral chemistry of pyrite (5/5 stope)</td>
<td>206</td>
</tr>
<tr>
<td>6.9</td>
<td>Mineral chemistry of arsenopyrite (5/5 stope)</td>
<td>207</td>
</tr>
<tr>
<td>6.10</td>
<td>Mineral chemistry of pyrrhotite (5/5 stope)</td>
<td>207</td>
</tr>
<tr>
<td>6.11</td>
<td>Major element geochemistry of samples proximal to the 5/5 stope</td>
<td>208</td>
</tr>
<tr>
<td>6.12</td>
<td>Trace element geochemistry of samples proximal to the 5/5 stope</td>
<td>208</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Location, landform, climate and vegetation

The Elura Zn-Pb-Ag deposit, now known as Endeavor, is located approximately 43 km NNW of Cobar on the Eastern margin of the Cobar Basin, Central Western New South Wales (figure 1.1; 31.16° S and 145.65° E, COBAR SH55-14 1:250 000 map sheet). The orebody is currently being exploited by CBH Resources Limited, a wholly owned subsidiary of Toho Zinc Co., Ltd. The present total resource and reserve is estimated at 25.2 Mt at 6.5% Zn, 3.9% Pb, 55 g/t Ag, 0.2% Cu, and 8.4 Mt at 7.5% Zn, 4.8% Pb, 96 g/Ag, 0.2% Cu, respectively (CBH-Resources, 2008), with a pre-mining resource of 42 Mt at 8.6% Zn, 5.4% Pb and 96 g/Ag (Stegman, 2001). The Devonian Cobar Basin is part of the Lachlan Orogen and has a long history of mineral exploration and mining. Most of mineral occurrences are located on the eastern margin of the basin with a historical and present resource in the order of 431,000 t copper, 1,600,000 t lead, 2.5 Mt zinc, 4,050 t silver and 56 t gold (Glen et al., 1994).

The landscape is characterised by undulating colluvial and alluvial plains and rounded low relief rises (Gibson et al., 2003). Several creeks are located in the vicinity of the deposit and drain into the Darling River about 80 km distant.

The climate is semi-arid, characterised by a median annual rainfall of 390.2 mm (Bureau of Meteorology-Australian Government, 2011) with a slight increase in precipitation during the summer months. The evaporation is estimated at approximately 2000 mm per annum (Lorrigan, 2005). Monthly mean temperatures are cool to mild during winter ranging between 5.0 and 15.8 °C in July, and warm to hot in summer between 20.5 to 34.0 °C in January (Bureau of Meteorology-Australian Government, 2011).

The main vegetation consists of scattered mulga (Acacia aneura), white cypress pine (Callitris columellaris), belah (Casuarina cristata) in addition to a diversity of eucalypts (Gibson et al., 2003). Predominantly woody shrubs (e.g. Eremphila, Dondonea, Cassia) and...
grasses are undergrowth. Sparse occurrence of Bimble Box (*Eucalyptus popunea*) with an understory of woody shrubs is the dominating fauna at the mine site (Lorrigan, 2005). Overall, vegetation is relatively sparse, with denser vegetation found along creeks or pronounced incisions.

### 1.2 Mining history in the Cobar region

Three important mining belts are distinguished in the Cobar area: the Cobar Belt, the Canbelego Belt and the Girilambone Belt. Out of those three mineral belts, the Cobar Belt is the most important of these belts and represents the largest accumulation of Phanerozoic base metals in New South Wales. All major mining centres with important mineral deposits in the Cobar region, e.g. Cobar, Canbelego, Nymagee, Shuttleton and Mount Hope, are hosted in Early Devonian rocks of the Cobar Supergroup sediments. The leading base metal and gold producers are Endeavor, CSA, Great Cobar, Chesney, New Occidental and Mt Boppy Mines (Stegman and Stegman, 1996; Department of Primary Industries, 2007).

Advancing industrialisation, electrification and the railway in July 1892 led to increased production and profitability. In 1889 the copper price was £60 per ton, dropping down to £39 before steadily increasing to £75 per ton in 1899, with the copper consumption being above production by 1906. The copper price finally peaked at over £100 per ton in 1907 (Stegman and Stegman, 1996; Department of Primary Industries, 2007).

The fall of copper prices in 1908 lead to a halt of mining and depressed the flourishing exploration activities with particularly difficult times during 1920s to 1950s. Equally, copper price and demand fell by over 40% in 1919 after World War I, forcing Cobar mines to close. The only gleam of hope during this period was a strong renaissance of gold demand during the economic depression in the 1930s. No major mines were in operation between 1952 and 1965. The population of Cobar varied between a few hundred up to more than 10,000 during the first quarter of the 19th century due to significant fluctuations in production (Stegman and Stegman, 1996; Department of Primary Industries, 2007).

In 1962 a new deep shaft sinking began at the CSA mine, full scale mine development commenced in 1964 and production re-commenced in 1965. Since then, the CSA mine had been seriously affected by a drop in metal prices and...

---

* Summarised after:  
1.2 Mining history in the Cobar region

the mine closed in 1975 and again in 1985. After a mine closure in 1997/98 it was reopened by Glencore in 1999 and is now operated by Cobar Management Pty Ltd—a wholly owned Australian subsidiary of Glencore International AG (Switzerland) (Stegman and Stegman, 1996; Department of Primary Industries, 2007).

The Peak mining field, comprising The Peak, Perseverance, New Occidental, Chesney and New Cobar Mines, are operated by Peak Gold Mines Pty Ltd, a subsidiary of Goldcorp Inc.

The Elura Mine was initially discovered in 1973 and operated by Electrolyte Zinc Co. of Australasia Ltd before being taken over by North Broken Hill Holdings Ltd in 1984/85 which in turn merged with Riotinto of Australia Ltd in 1988 forming Pasminco Ltd. Consolidated Broken Hill Ltd (now CBH Resources), an ASX listed company, bought the Elura mine from the Administrators of Pasminco Ltd and renamed it into the Endeavor Mine in 2003. Upon acquisition of all CBH’s issued ordinary shares on 23rd September 2010, CBH Resources Limited became a wholly owned subsidiary of Toho Zinc Co., Ltd, a company listed on the Tokyo Stock Exchange. CBH Resources was delisted from the ASX on 30th September 2010 (Department of Primary Industries, 2007).

Rather early in the mining history of Cobar, several production problems and difficulties became apparent. The sudden decrease of the ore grade from the initial 9 to 11% copper in the supergene enriched zone down to 1 to 3% in the unweathered primary mineralisation was probably the most difficult. This problem was intensified by recovery issues due to the increased complexity in the sulphide mineralogy. Furthermore, the high consumption of timber for stopping and furnaces led to major shortages in the timber supply. Severe dust storms, water supply issues, rock creep and partial mine collapses also caused serious problems amongst the mining community (Stegman and Stegman, 1996; Department of Primary Industries, 2007).

Figure 1.2: Early settlements in the township of Cobar in the late 1890s. Marshall Street, nowadays the main street, is to the right of the photo. Photograph taken from Stegman and Stegman (2002).
Summary of ownerships:

- **1893** Great Cobar Syndicate organised by Swansea smelters (Longworth Bros.), later Great Cobar Ltd,
- **1930** Occidental Ltd, later reorganised as New Occidental Gold Mines NL,
- **1947** Enterprise Exploration Co. Pty Ltd, a subsidiary of Zinc Corporation Ltd (later Consolidated Zinc Pty Ltd), acquisition of CSA mine and extensive regional exploration (mapping of Cobar belt from CSA to Queen Bee in 1 : 4,800),
- **1955** Broken Hill South Ltd, secured an option over leases and other assets from New Occidental Gold Mines Ltd,
- **1956** Broken Hill South Ltd created two wholly owned subsidiaries, Cobar Mines Pty Ltd and Cobar South Pty Ltd,
- **1957** Broken Hill South purchased key Cobar leases from New Occidental Gold Mines Ltd,
- **1962** Cobar Mines Pty Ltd; operating CSA Mine,
- **1973** Electrolyte Zinc Co. of Australasia Ltd, discovery of the Elura deposit,
- **1980** Conzinc Riotinto of Australia Ltd, purchased Cobar Mines Pty Ltd and Cobar South Pty Ltd,
- **1983** Electrolyte Zinc Co. of Australasia Ltd, production commenced at Elura,
- **1984/1985** North Broken Hill Holdings Ltd, take-over of Electrolyte Zinc Co. of Australasia Ltd and acquisition of the Elura mine,
- **1988** Pasminco Ltd, merger with North Broken Hill Peko Ltd and Conzinc Riotinto of Australia Ltd,
- **1992** Golden Shamrock Mines; acquisition of the CSA mine,
- **1999** Glencore International AG; acquisition of the CSA mine,
- **2003** Wheaton River Minerals Ltd (now Goldcorp Inc); acquisition of the Peak Mines from Rio Tinto,
- **2003** Consolidated Broken Hill Resources Ltd; acquisition of the Elura mine (re-named in Endeavor mine) from Pasminco Ltd,
- **2010** Toho Zinc Co. Ltd; Consolidated Broken Hill Resources Ltd. is a wholly owned subsidiary.
1.3 Discovery of the Elura deposit

Cobar’s mining field with its potential extensions of identified mineral resources represented an excellent exploration target. It still does. In 1971, Electrolytic Zinc Co of Australasia successfully applied for two Exploration Licences in the area NW of Cobar. In previous exploration work the geologists had assumed, the Cobar Supergroup sediments, hosting the mineralisation of the CSA mine, would continue to the NE, towards Mt. Drysdale. A new hypothesis suggested that the particular lithology might as well continue N and possibly NW under soil cover. Most of the known mineral occurrences in the Cobar area exhibit a magnetic anomaly. That is due to the occurrence of either pyrrhotite or magnetite. Subsequently, airborne magnetometry was undertaken in order to test for potential extensions of the known mineralisation at the CSA Mine.

Several deep-seated and surface anomalies were identified. Despite the fact that Elura exhibited itself as a characteristic “bulls-eye” anomaly it was initially not considered to be of great potential because it was not associated with the highly prospective host lithology of the CSA mineralisation. However, it was decided later, to investigate all characteristic magnetic anomalies irrespective of their stratigraphic position.

Ground magnetic follow-up work at the Elura anomaly commenced in January 1973 resulting in a single positive anomaly of approximately 150 nT and extending over 500 m. The subsequent auger sampling revealed a strong Pb anomaly with values up to 3,000 ppm continuing over a strike-length of 1,200 m. A sample spacing of 5 to 10 m on grid lines 50 m apart were used with samples taken at a depth of 1.8 m. The original strategy was to plan and drill the first two diamond holes based on the magnetic survey and auger sampling results. However, due to delays in the processing of exploration tenements, the drilling program was deferred in favour of gravity and electromagnetic surveys. A well defined gravity anomaly in addition to a weak conductive zone in the vicinity of the ground magnetic anomaly was identified.

In February 1974, the first diamond drill hole E1 intersected gossan and sulphide mineralisation at a downhole depth of 102 m and 133.5 m, before being abandoned at 152.4 m. After the first drill hole, gossan was also found cropping out at the surface. The second diamond drill hole E2, designed to test the source of combined magnetic, gravity and induced polarisation, intersected 85 m of sulphide mineralisation. A total of 24 diamond drill holes and six wedged “daughter” holes were drilled during the main exploration phase resulting in an indicated resource potential of approximately 27 Mt at 8.4% zinc, 5.6% lead and 139 g/t silver. For the purpose of metallurgical bulk sampling, an exploration shaft was sunk to a depth of 165 m between 1976 and 1977. Mining by Electrolyte Zinc Co. of Australasia Ltd commenced at Elura in March 1983.

NOTE: This figure/table/image has been removed to comply with copyright regulations. It is included in the print copy of the thesis held by the University of Adelaide Library.

Figure 1.3: Aerial photograph showing the footprint of the Endeavor Mine (formerly known as Elura Mine). Photograph supplied by CBH Resources Ltd.

Chapter 2
Regional Geology

2.1 The Tasmanides

The Tasman Fold Belt system occupies the eastern third of the Australian continent, covering an area of approximately 3600 km by 1200 km (Glen, 2006). The Tasmanides are part of an enormous Orogen system along the eastern margin of Gondwana (figure 2.1) with an approximate extent of 20,000 km, and stretching from western Argentina via Antarctica to Australia. The origin of the Tasmanides was initiated by the break-up of the supercontinent Rodinia at approximately 750 Ma, followed by the growth of orogenic belts on the eastern margin of Gondwana. The convergent period is interpreted to have started in the Middle Cambrian at around 525 Ma and continued until the late Triassic (Glen, 2006).

Two further orogenic belts, the Thomson and the North Queensland, are found in Queensland, a small part of the former possibly occurring in northernmost New South Wales (Scheibner, 1996). Figure 2.2 shows the regional extent of the four largest orogenic belts, i.e. Thomson, Lachlan, New England and Delamarian. These five belts developed along an active plate margin. Lithologies occurring are: turbiditic sediments, collision related igneous rocks, minor occurrences of ophiolite and greenstone complexes, followed by molassic sediments, bimodal volcanics and post-orogenic intrusion of granites (Scheibner, 1996). The vast majority of the occurring lithologies follow a west to east directed younging trend, in agreement with the general accepted accretion model (Glen, 2006).

Four major orogenic fold belts, becoming progressively younger from west to east, are distinguished within the Tasmanides in New South Wales (e.g. Scheibner (1996); Glen (2005, 2006)):

- Kanmantoo,
- Lachlan,
- Hodgkinson-Broken River, and
- New England.


2. REGIONAL GEOLOGY

The Delamerian Supercycle commenced at around 750 Ma as a rather long-lived rifting event when Rodinia began to disintegrate. This initial phase of the Delamerian lasted for approximately 150 Ma, forming the amagmatic Adelaide Rift Complex, followed by the development of a major alkaline magmatic rift system between 580 to 600 Ma. The change of tectonic plate movement at around 520 Ma resulted in the establishment of a convergent margin, with a subsequent change in magmatism and the formation of the Kanmantoo Trough, a rift basin in back-arc position. The magmatic activity switched from alkaline to mafic and ultramafic and is reflected by the formation of boninitic fore-arc crust, which is preserved on the western part of Tasmania and Victoria. The supercycle ended at approximately 510 to 505 Ma when arc and fore-arc rocks were accreted, followed by extension, post-collision magmatism and deformation at the end of the Cambrian.

The Lachlan Supercycle started as an erosive event with the formation of molassic sediments on the Delamerian Orogen. However, the cycle was mainly dominated by highly convergent plate boundaries and the formation of the intraoceanic Macquarie Arc. During the Benambran Orogeny in the Late Ordovician to Early Silurian, several terranes consisting of turbidites, shales, subduction related blueschist facies metamorphic rocks, MORB-like mafic vol-
canics and cherts were imbricated and accreted together with the Macquarie Arc, leading to the closure of the ocean basins.

The subsequent Tabberabberan cycle commenced as a major phase of increased tension on the eastern part of Gondwana in the Early Silurian due to a rollback of the southern part of the Pacific Plate. This resulted in the development of an intraoceanic arc, led to the dismembering of the previously accreted Macquarie Arc and initiated the formation of sedimentary rift and trans-tensional basins, followed by the emplacement of I- and S-type granites. The cycle peaked in the Tabberabberan Orogeny via the accretion of the Bendigo Terrane in the Middle Devonian. This event led to the inversion of sedimentary basins and rifts, to the deformation of granitoids, and re-deformation and further imbrications of older rocks.

The **Hunter Bowen Supercycle**, mainly reflected in the New England Orogen, is characterised by the establishment of a continental margin arc, a forearc basin and subduction related complexes to the east. The convergent period lasted from Late Devonian to the Carboniferous and ended, probably triggered by accretion of an intraoceanic arc, in exhumation of the subduction complex, imbrications and uplift of the volcanic arc. The following extensional period in Early Permian led to basin formations and granite intrusions and is believed to reflect a rollback of the subduction zone. The formation of the Bowen-Gummedah-Sydney Basin System, consisting of a series of rift and trans-tensional basins, was initiated by a rifting process west of the New England Orogen in Early Permian. Due to increased crustal load during the continuing convergence and uplift of the arc, the basin converted to a foreland basin in the Late Permian to Triassic. The collision with an intraoceanic arc in the Middle to Late Triassic lead to the termination of the Hunter-Bowen super-cycle.

The **Kanimblan Cycle**, temporally overlapping with the Hunter-Bowen super-cycle of the New England Orogen, mainly affected areas which are now located in NSW and in Victoria. The cycle is characterised by the onset of narrow rifts and the formation of granites and volcanics, of A-type in NSW, S- and I-type in Victoria. This magmatic episode was followed by a period of sediment deposition, forming a 3 to 4 km thick cover of continental sedimentary rocks, extending across the Delamerian, the Lachlan and the Thomson Orogen. The cycle ended with regional deformation in the Early Carboniferous and the emplacement of post-tectonic granites.

The metallogeny of the Tasman Fold Belt, as described in Degeling *et al.* (1986), is manifold in respect to types and number of mineral deposits. Only limited economic mineralisation is found in the Kanmantoo Belt, mostly as stratabound copper deposits. During the Cambrian to the Ordovician, stratabound Cu and Mn deposits formed in the Lachlan Fold Belt within a volcanic arc setting. Porphyry Cu-Au deposits originated during the latest stages of this tectonic setting in the Silurian, as well as post-accretionary in the Early Devonian. Several major base metal deposits developed between the Middle Silurian and Early Devonian due to rifting and volcanism (Degeling *et al.*, 1986). Contemporaneous granite intrusions led to the formation of Sn-W, Mo and base metal-Au mineralisation. Early to Middle Carboniferous felsic plutonic activity caused the genesis of Mo-W and Sn deposits in the eastern part of the Lachlan Fold belt. Progressing further east, epithermal Au, associated with rifting and bimodal volcanism, formed in the Middle Devonian. Pre-accretionary stratabound Cu and Mn, exhalative Au (Early Devonian to Late Carboniferous), and quartz-magnetite deposits (Late Carboniferous) are present in the New England Fold Belt. Furthermore, vein style deposits (Sn and Au-As-Ag-Sb) originated due to S-type magmatism during the Late Carboniferous to the Early Permian.
2. REGIONAL GEOLOGY

2. The Lachlan Fold Belt

2.2 The Lachlan Fold Belt

2.2.1 Overview and geography*

The Lachlan Fold Belt of eastern Australia is a major structural unit occupying the south-eastern part of the composite Tasman Fold Belt System. It was part of the Palaeozoic convergent plate margin surrounding the supercontinent Gondwana (Foster and Gray, 2000). The Fold Belt extends from eastern Tasmania through Victoria to New South Wales, and is bounded by the Thompson Fold Belt in the north, the New England Fold Belt in the east and the Kanmantoo Fold Belt in the west (Suppel and Scheibner, 1990). The Orogen is dominated by turbiditic lithologies and developed due to step-wise continental accretion of oceanic sequences accompanied by imbrications and uplift. The major deformation and metamorphism occurred between the Late Ordovician and the Early Carboniferous, ~450 Ma and ~380 Ma, respectively (Foster and Gray, 2000). Based on mica crystallisation, Gray and Foster (2004) estimated the youngest deformation at 360 to 340 Ma.

Deep water quartz-rich turbidites, cherts, calc-alkaline volcanic and granitic rocks, comprise the major rock types within the Lachlan Fold Belt, which are overlain by a sequence of younger cover sediments (Suppel and Scheibner, 1990), as shown in figure 2.4. It has been suggested that the upper-crustal section consists of thin-skinned thrust belts which flatten with depth and link into a mid-crustal detachment. The lower crust is composed of imbricated oceanic crust, possibly containing fragments of continental crust (Foster and Gray, 2000). Significant structural thickening and shortening in the order of approximately 300% and 75%, respectively, led to the formation of 26 to 52 km thick crust during the Late Ordovician to the Devonian.

2.2.2 Tectonic evolution of the Lachlan Orogen†

Gray and Foster (2004) summarised four causes that have been proposed of being important for the genesis of the Lachlan Orogen (figure 2.3):

1. Plutonism-induced orogeny: deformation due to upwelling of hot asthenosphere caused by magmatic underplating, crustal extension, mantle plumes or delamination.

2. Intraplate convergence: deformation caused by a single subduction zone.

3. Slab rollback and extensional retreat: similarly to (2) with the difference being, that continuous slab pullback was repeatedly interrupted by short phases of contraction.

4. Multible subducting slabs: accretionary thrust belts and deformation caused by several subduction systems.

2.2 The Lachlan Fold Belt

Chronological evolution

The chronological evolution of the Lachlan Orogen is described in Gray and Foster (2004) and summarised below, beginning with the latest stages of the Delamerian supercycle:

Post Rodinia breakup (550 to 526 Ma)

This period commenced with the folding of the Neoproterozoic sedimentary cover in the northern Flinders Ranges (~550-540 Ma) and the deformation of the Upper Adelaidean metasediments. The sedimentation of the Kanmantoo Group sequence commenced at around 532 and lasted until 526 Ma. These sediments were deposited in a pull-apart basin, forming along rifts in a trans-tensional tectonic environment during the Rodinia breakup.

Major deformation and backarc spreading (520 to 495 Ma)

Earlier fold structures were overprinted by high temperature metamorphism and intense deformation in the southern Delamerian Orogen (~520-505 Ma). Obduction of oceanic crust occurred in Tasmania (~520-515 Ma) accompanied by strong deformation and metamorphism, followed by the exhumation of these metamorphic complexes between approximately 500 to 490 Ma. Post-tectonic alkaline plutons and rift-related volcanics mark a post-orogenic

The geologic situation at 450-440 Ma

![Diagram of geologic situations](image)

**Figure 2.3:** Proposed geodynamic mechanisms causing the orogenies in the Lachlan Fold Belt (after Gray and Foster (2004)). (a) Plutonism induced orogeny; deformation due to upwelling of hot astenosphere caused by magmatic underplating, crustal extension, mantle plumes or delamination. (b) Intraplate convergence; deformation caused by a single subduction zone. (c) Slab rollback and extensional retreat; similarly to (b), but continuous slab rollback was repeatedly interrupted by short phases of contraction. (d) Multiple subducting slabs; accretionary thrust belts and deformation caused by several subduction systems.
2. REGIONAL GEOLOGY

**Figure 2.4:** Map showing the surface geology of New South Wales. Yellow dashed line is the approximate outline of the Lachlan Fold Belt. Map is based on the 1:5,000,000 Surface Geology map of Australia.

extensional regime (~505-495 Ma). Contemporaneously, oceanic crust developed off the Gondwana margin, subsequently forming the basement of the Lachlan Orogen.

**Cratonisation of the Delamerian Orogen and turbidite deposition in the Lachlan back arc basin (490 to 460 Ma)**

At the start of this period, the Delamarian Orogen was further affected by post orogenic magmatism, followed by cooling and erosional exhumation (~490-480 Ma). Enormous turbiditic fans were deposited within a marginal oceanic basin in addition to minor quantities of deep marine cherts (~490-470 Ma). The Macquarie Volcanic Arc complex formed distal to the continental margin (~485 Ma). Subduction zones developed on both sides of this back arc basin, east of the Delamerian Orogen and inboard of the Macquarie Arc (~460 Ma).

**Back arc basin closure (450 to 410 Ma)**

The closure of the earlier described back arc basin commenced due to double divergent subduction causing the development of extensive thrust belts. Strong deformation (chevron-style folding) affected the turbiditic sequence and fragments of oceanic crust were imbricated. Extensive crustal thickening in the western Lachlan led to erosional exhumation of the turbities.
Docking, cratonisation of the western and central, and the development of an Andean-type continental margin for the eastern Lachlan Fold Belt (400 to 380 Ma)

During the basin closure (finalised at ~380 Ma), post-orogenic magmatism (~400 Ma) affected the western Lachlan Fold Belt, followed by amalgamation and cratonisation of the inner orogenic zone (western and central Lachlan Fold Belt). Magmatism, metamorphism (high temperature) and volcanism occurred along the Andean-type active continental margin in the eastern Lachlan Fold Belt.

Rollback and post-orogenic extension (360 to 320 Ma)

In-board convergence caused the inversion of former extensional basins in the eastern Lachlan Orogen. The post-orogenic magmatism prolonged and the cratonisation of the Orogen was finalised at around 330 Ma.

Orogenies

A total of six orogenies, ranging for over 100 Ma, are interpreted to have affected the Lachlan Fold Belt (Gray and Foster, 1997), the most important of them being the Benambran, the Tabberabberan and the Kanimblan Orogeny (Glen, 2005). All of them are predominantly defined based on unconformities in the rock record and/or changes in sedimentation style, and most of them are named after their type localities (table 2.1).

The timing of these six orogenic events is shown in table 2.1, their regional extent in figure 2.5. In the following, the orogenies are summarised after Gray and Foster (1997), beginning with the oldest:

The Benambran represents the oldest known orogenic event in the Lachlan Fold Belt and occurred in the Early Silurian, mainly affected the central parts of the belt. The orogeny is characterised by at least two phases of
2. REGIONAL GEOLOGY

deformation, accompanied by metamorphism and intrusive events. East-west trending folds and north-north-westerly striking structural elements are characteristic.

The Quidongan Orogeny (late Early Silurian) can’t be differentiated from the Benambran in most of the Fold Belt, in particular in Victoria. Therefore its regional importance is uncertain.

The Bowning Orogeny is of Late Silurian to Early Devonian age and caused wide spread deformation in the eastern Lachlan Fold Belt.

The Early Devonian Bindian Orogeny is locally defined by an angular unconformity between Early Devonian and Silurian volcanics, the latter characterised by intense foliation. Regionally, however, the Bindian and the Bowning Orogeny are indistinguishable, and are now viewed as the same event.

The Tabberabberan Orogeny was a major period of regional deformation during the Middle Devonian, and is the orogeny regionally most widely recognised in the Lachlan Fold Belt. This event was characterised by such a prolonged intensity that subsequently the sedimentary environment changed to non-marine. The strength of deformation decreased towards the northeast and caused open, close and tight chevron folding of turbiditic rock suites.

The Kaninblan Orogeny is the last event in the tectonic evolution of the Lachlan Fold Belt. It occurred during the Early Carboniferous and caused regionally extensive, although relative weak deformation. Generally open, locally tight folding due to reactivation of older faults, are the most important structural features.
2.2.3 Stratigraphy

Three subprovinces can be distinguished in the Lachlan Fold Belt, each with differences in rock type, metamorphic grade, structural history and geological evolution (Foster and Gray, 2000). The regional extent and metamorphic grade of the three subprovinces is shown in figure 2.6. Despite those differences, there is only little evidence suggesting that these three sub-provinces had travelled far with respect to each other. Most likely, they all had formed along the same Gondwana continent margin but at different distances from the active margin and in different depositional environments. The most characteristic structural features within the Lachlan Fold Belt are upright chevron folds, ranging from tight to open, and steep dipping fault systems (Foster and Gray, 2000). No simple accretionary trend is apparent in none of the three sub-provinces, nor is the orogen characterised by thrust-belts generally verging towards the craton. It is widely accepted within the research community that subduction played a very important role during the genesis of the Lachlan Fold Belt. However, the exact number of subduction zones is still disputed (Gray and Foster, 2004). The main features of subduction zones within the three subprovinces are described in detail by Gray and Foster (2004) and are summarised in table 2.2. Characteristic features of those three sub-provinces are described by Foster and Gray (2000) and summarised in the following.

The Western Subprovince

This part of the Lachlan Fold Belt is predominantly composed of folded turbidites, which are intersected by a succession of parallel, steeply westwards-dipping reverse faults. Highly deformed rocks, characterised by intense crenulation cleavage associated with meso- and micro folds, are developed within an approximately 2 km-wide zone along these major faults. In some areas, fault-bounded Cambrian metavolcanics, cherts and volcanoclastics are exposed, in addition to very minor blueschist facies assemblages in ultramafics. These rock types form the basement to the younger siliciclastic sediments and are interpreted to represent exorciated oceanic crustal fragments. The quartz-rich turbidites developed during the Ordovician to the Devonian and consist of chevron-folded interbedded sand- and mudstone layers, reflecting a shortening of up to 65%. Slaty cleavage is caused by mica growth. Based on deep seismic studies, a crustal detachment is interpreted at a depth of approximately 15 to 17 km. Metamorphism is predominantly sub- to lower green-
schist facies, with the exception being hornfels
contact zones in the vicinity of Devonian in-
trusions and unroofed amphibolite facies rocks
along the Moyston Fault, representing the west-
ern boundary of the subprovince.

The Central Subprovince

Most of this subprovince is occupied by the
metamorphic Wagga-Omeo Complex (figure
2.6). The Complex is fault-bounded and
consists of complexly deformed Ordovician
metasediments, which experienced greenschist
to upper amphibolite facies conditions. De-
formation occurred during the Early to Middle
Silurian accompanied or followed by the intru-
sion of large volumes of Silurian to Devonian
granites. The peak metamorphic conditions
are estimated at temperatures and pressures in
the order of approximately 700°C and 3.5 kbar,
causing local anatexis and the formation of
migmatites. The subsequent erosional unroof-
ing of the Wagga-Omeo Complex occurred dur-
ing the Middle to Late Silurian followed by the
emplacement as a crustal wedge during the Late
Silurian to Early Devonian. The complex is
truncated by major mylonitic strike-slip faults
to the east and the west. An ultramafic to mafic
melange zone, including blueschist facies com-
ponents, is developed along the western bound-
ary fault.

The Eastern Subprovince

In contrast to the other two subprovinces, here
folding is more open, characterised by an east-
wards trending fold tightening accompanied by
an increase in cleavage development. The sub-
province is composed of anticlinorial and syn-
clinorial zones, bounded by east and west dip-
ning reverse faults and underlain by calcalkaline
volcanic arc basement. The prevailing litholo-
gies are folded turbidites of Ordovician to Sil-
urian age. A Devonian belt of brittle thrusts is
developed in the eastern part of the subprovince,
containing a melange of a Late Ordovician to
Early Silurian accretionary complex, in turn
contained within a sequence of Late Cabrian
to Early Ordovician cherts, basalts and tur-
bitites. Several foliated granites intrude along
the thrust belt, causing relatively narrow low
pressure/high temperature metamorphic com-

NOTE:
The figure/table/image has been removed
to comply with copyright regulations.
It is included in the print copy of the thesis
held by the University of Adelaide Library.

Table 2.2: Important characteristics of subduction zones in the Lachlan Fold Belt (modified after Gray and Foster (2004))
plexes. Tectonic movement along these faults caused intense multiple deformation of the wall rock, gneissic banding, mylonitic layering and secondary foliation in the granites.

2.2.4 Rifting induced basin development and subsequent igneous activity

The Lachlan Orogen was affected by several extensional episodes leading to the development of rift basins and half grabens, involving granitic magmatism and silicic and bimodal volcanism (Foster and Gray, 2000). Major periods of basin formation occurred during the Early Silurian (~440 to 430 Ma) within the Wagga-Omeo-Complex (figure 2.6) and during the Late Silurian to Early Devonian (~420 to 400 Ma) east of the belt, e.g. causing the development of the Cobar Basin.

Granites mainly occur in the central and eastern subprovinces and comprise up to 36% of the exposed Lachlan Orogen (figure 2.7). Magmatism occurred over a prolonged time (440 to 340 Ma) culminating between 410 and 380 Ma (Gray and Foster, 1997). According to Foster and Gray (2000), syntectonic plutons formed in the high-grade metamorphic complexes of central and western subprovinces during 430 and 415 Ma (e.g. Bega batholiths), followed by an eastwards directed migration of the magmatic front towards the coastal areas between 405 and 390 Ma. Contemporaneous with the latter period, numerous high-level plutons intruded in the western, in addition to predominantly post-tectonic plutons in the central subprovinces. Post-tectonic granites, interpreted to be linked to the formation of caldera systems, developed between 370 and 360 Ma in central Victoria (Foster and Gray, 2000). A wide range of igneous rocks, ranging from basalt/gabbro to alkali-feldspar granites occur, with S-type (peraluminous, containing cordierite) as well as I-type (metaluminous, containing hornblende and biotite) geochemical signatures. The different types are interpreted to be caused by variations in the degree of mixing between two magma types: subduction related mantle-derived mafic magma and that from partial crustal melting. Mafic oceanic island arc basement and turbiditic rock suits are suggested as crustal components affected by partial melting. Based on outcrop pattern (e.g. shape, elongation and orientation), Foster and Gray (2000) suggested five major granite provinces. Chappell et al. (1988) on the other hand defined nine, potentially ten petrological granite suites characterised by common chemical features reflecting their source rock composition. He linked the source variation to blocks or terranes of continental and/or subcontinental lithosphere or basement. Variations in their fertility in respect to precious and base metal content might have had significant influence on the genesis of ore deposits.

2.2.5 Metallogeny of the Lachlan Orogen

Diverse metallogenic associations, significantly varying across the fold belt and comprising more than 22 mineral commodities, are found throughout the entire Lachlan Fold Belt (Hough et al., 2007). The vast majority of the mineral deposits formed between approximately 450 to 360 Ma. Many major porphyry copper-gold and orogenic gold deposits are interpreted to have formed during a metallogenically significant period at approximately 440 Ma.

From west to east, Bierlein et al. (2002)
defined five metallogenetic provinces: (1) turbidite-hosted orogenic lode gold (±As-Sb), (2) granite-related magmatic gold (±Mo-Sb-Cu-Te), (3) epigenetic sediment-hosted base metal and gold, (4) granite-hosted tin-tungsten and (5) porphyry copper-gold and volcanic-hosted massive sulphides. Spatially, the deposit types occurring throughout the Lachlan reflect the geotectonic setting in which they had formed (Hough et al., 2007). The western Lachlan Orogen is dominated by Silurian to Devonian orogenic and magmatic gold deposits developed within an accretionary collision zone. In the central Lachlan Orogen, (a) tin-tungsten deposits (Silurian) formed as a consequence of partial melting of the lower crust in a subduction setting; (b) orogenic gold is found in an accretionary collision zone; and (c) rifting and accompanying bi-modal volcanism led to the development of sediment-hosted copper-gold and base metal deposits (Late Silurian to Early Devonian). The eastern Lachlan Orogen accommodates (a) porphyry gold-copper deposits (Ordovician) related to oceanic island arc; (b) volcanic-hosted massive sulphide, sediment-hosted copper-gold and base metal deposits of Late Silurian to Early Devonian age in rift basins; and (c) orogenic gold deposits (Middle to Late Devonian) in an accretionary collision zone.

The sediment-hosted gold-copper-lead-zinc deposits of the central Lachlan Orogen (e.g. Elura, Cobar deposits and Queen Bee) occur in turbidites containing variable quantities of volcanics (Hough et al., 2007). They formed along or in the vicinity of the margin of sedimentary basins, developed in a rift-related extensional and transpressional tectonic regime. Typically, the sulphide ore is characterised by a paragenesis consisting of base metal sulphides, magnetite, pyrite, pyrrhotite, gold and/or silver, and occurs as massive lenses or subvertical pipes, stringer veins, or as stockwork. Alteration types (e.g. silicification, chloritisation, sericite, carbonate, iron sulphide and iron oxide alteration) and their intensities vary between deposits. Frequently, mineralisation is hosted in high-strain zones and truncated by deeply dipping faults. Most ore bodies exhibit at least to some extent a structural control and therefore have to be syn-deformational and epigenetic in nature. The exact timing of ore formation of several deposits is, however, still debated, consequently, the classification as syn- or epigenetic is equivocal (Bierlein et al., 2002; Hough et al., 2007).

The most important sediment hosted deposits of the Cobar region are described in more detail in chapter 2 on page 31.
2.2 The Lachlan Fold Belt

Figure 2.7: Occurrences of intrusives in the Lachlan Fold Belt and their age (map data based on the 1:5000000 Surface Geology Map of Australia.)
2. REGIONAL GEOLOGY

2.3 The Cobar Basin

2.3.1 Overview and basin formation

The Cobar Basin is located in central NSW and forms the eastern part of the composite Darling Basin in the central subprovince of the Lachlan Fold Belt (Suppel and Scheibner, 1990). Figure 2.8 shows the regional extent of the Darling Basin and the Cobar Basin. During Mid-Silurian to Mid-Devonian times, the Lachlan Fold Belt had experienced widespread extension leading to the formation of deep and shallow water clastic sediment basins, partially with occurrences of volcanics. The formation of the trans-tensional Cobar Basin, as one of many sedimentary basins in the Lachlan Orogen, is interpreted to have been initiated in the latest Silurian due to subduction roll back. Subsequent extension and rifting led to the formation of several back-arc, intracratonic, deep water basins at the start of the Tabbaerabberian cycle between the Pridolian to the Pragian (Glen, 1990). The Mount Hope and the Rast Troughs form the southern extensions of the Cobar Basin (figure 2.8), separated by the Crowl Creek Fault (Glen, 1990).

Glen et al. (1992) defined the Cobar Basin as an overlap/cover basin to the central Lachlan Fold Belt. The basin contains half-graben sequences and formed as a ramp basin above a mid-crustal detachment in an left-lateral trans-tensional stress regime (Glen et al., 1994). The subsequent basin inversion was caused by right-lateral transpression (Glen, 1990) and was accompanied by thin-skinned thrusting above relatively shallow detachments (Glen et al., 1994). They occur in the vicinity of the contact between basement and basin sediments or within the latter, and are interpreted to represent major pathways for mineralising fluid and therefore being of great importance for ore genesis. Based on K-Ar and \(^{40}\)Ar\(^{39}\)Ar whole rock dating, basin inversion and main cleavage development occurred at around 395 to 400 Ma (Glen et al., 1992). Lithologies deposited in the Cobar Basin experienced deformation and low-grade metamorphism. According to Brill (1988), metamorphic grades were anchizonal to epizonal close to the transition between prehnite-pumpellyite-greenschist facies.

Figure 2.8: The composite Darling Basin (dotted shape) in the central Lachlan Foldbelt and the extent of the Cobar Basin (yellow shape) and its southern extensions (green shape), the eastern Rast Trough and the western Mount Hope Trough (modified after Bull et al., 2008).

Glen, R. (1990). Formation and inversion of transtensional basins in the western part of the Lachlan Fold Belt, Australia, with emphasis on the Cobar Basin. Journal of Structural Geology, 12 (5-6), 601–620,
The geology of the Cobar Basin is presented in figure 2.9. The basin is truncated on the eastern margin as well as underlain by the Ordovician metasediments of the Girilambone Group and by Late Silurian granitoids (Glen, 1990). Those multiply-deformed Ordovician metasediments, which experienced metamorphic conditions between greenschist and lower amphibolites facies, were deposited in the back arc Wagga Basin (Suppel and Scheibner, 1990; Glen, 1990).

The Girilambone Group is divided into two subgroups according to their metamorphic grade and rock types (Fergusson et al., 2005). The western part, the Ballast Formation, consists of low grade metamorphic quartz-rich turbidites and bedded cherts of Middle to Late Ordovician age. The Ballast Formation forms the eastern Hinterland to the Cobar basin and therefore represents an important sediment source feeding into the basin during formation. Rocks of the eastern part of the Girilambone Group experienced slightly higher metamorphic grades up to the lowest amphibolite facies and are composed of phyllites as well as psammitic and mafic schists.

The Silurian granites intruded at approximately 420 Ma (figure 2.9) and are of post-tectonic origin and S-type in character (Glen, 1990). The Early Devonian rock sequences deposited in the composite Darling Basin and its flanking shelves comprise the Cobar Supergroup (Suppel and Scheibner, 1990). The Kopyje Shelf is developed at the northern and eastern, and the Winduck Shelf at the western basin margin (figure 2.9). The former is composed of siliciclastics and limestones of Lochkovian age. Pragian storm sediments and littoral sands are the main lithologies occurring in the Winduck Shelf (Glen, 1990).

The Cobar Basin is predominantly filled with turbiditic sediments sourced from the eastern, northern and western hinterland with only minor occurrences of volcanic rocks, mostly as tuff units. The maximum thickness has been estimated via deep-crustal reflection seismic at approximately 6 km (Glen et al., 1994). The depth is variable and is to some extent controlled by the presence of syn-deformational faults. The Cobar Basin is asymmetrical in shape, with the western edge steeper than the eastern edge, suggesting a higher importance of the western basin edge during basin opening.

2.3.2 Stratigraphy*

The earliest sediments deposited during synrift stages on a rapidly subsiding and unstable shelf are those of the Mouramba Group (Glen, 1990). The sediments were sourced from basement rocks to the southeast and east and consist of outwash fans and shallow water clastics, locally with minor felsic volcanics. The remaining syn-rift phase is characterised by the deposition of turbiditic sediments and minor felsic volcanics of the Nurri Group and turbidites from the lower Amphitheatre Group (figure 2.10). The sediment source is the main difference between those two units, with the Nurri Group sediments sourced from the Girilambone basement along the eastern basin margin, whereas the lower Amphitheatre Group sediments derived from the northwest and west from the Winduck Shelf, and to some extent from granites to the southwest (Glen, 1990). The difference in sediment source is also reflected by the occurrence of shallow water fossils in the westerly-derived turbidites in contrast to the fossil poor nature of easterly-derived sediments from the Girilambone metasediments. Furthermore, the Nurri Group is characterised by upward fining, whereas the Amphitheatre Group is an upward coarsening unit commensurate with shallow water deposition.

The Chesney Formation represents the lower

Figure 2.9: Geological map of the Cobar Basin; map data is from the 1:250 000 Australian National Grid Cobar SH/55-14 map sheet (Brunkor, 1969).
part of the Nurri Group (figure 2.10) and consists of litharenite, minor conglomerate and siltstone. It is overlain by the Great Cobar Slate (figure 2.10), composed of mud- and siltstone (Scott and Phillips, 1990). The lower Amphitheatre Group consists predominantly of the CSA Siltstone as the lower stratigraphic unit and is overlain by the sandstone-dominated Biddabirra Formation (figure 2.10). The CSA Siltstone is characterised by rhythmically thinly interbedded mudstones and siltstones, and sandstone beds at varying thicknesses occurring at mostly irregular intervals (Scott and Phillips, 1990).

The deposition of the upper Amphitheatre Group flags the commencement of the post-rift phase of basin development (figure 2.10). These turbiditic sediments are similar to those of the lower Amphitheatre Group. However, the abrupt change in bedding thickness and consistency of mud-, silt- and sandstone beds indicate a much more tectonically inactive depositional environment. The gentle subsidence during the sag-phase of the basin formation caused the deposition of the upward-shallowing part of the Winduck Group (figure 2.10). They were deposited over older Ordovician basement and Silurian granites west of the Cobar Basin and consist of turbidites and shelf sediments (Glen, 1990).

The two-stage sedimentary characteristics of the Amphitheatre Group and the occurrences of volcanic rock units in the early stage of basin development led to the interpretation of a rift related origin of the basins in the Cobar region (Glen, 1990). However, the occurrence of volcanic units is more the exception than the rule and they are commonly absent. Deep crustal seismic reflection data indicates a mid-crustal detachment formed between lower and upper

![Figure 2.10](image-url)
crust due to extension (Glen et al., 1994). The interpreted detachment plane surfaces not at the basin margin but west of it. The tectonically highly active initial stage of basin development, accompanied by pronounced subsidence, was followed by a quieter period. Glen et al. (1994) concluded that the Cobar Basin had developed as a ramp basin and the two-stage sedimentation characteristics can also be interpreted as a result of a regional thermal event during the basin formation that caused increased subsidence rates on the eastern basin margin.

2.3.3 Structural setting*

Several major syn-depositional fault systems developed during the basin formation and many of those were reactivated during basin inversion. The eastern margin of the Cobar Basin is defined by the Rookery Fault as shown in figure 2.10 (Glen, 1990). The fault activity was greatest during the initial stage of basin formation in the Lochkovian. The interpretation of faults on the western basin margin is difficult due to syn-rift sediments being covered by either post-rift or Tertiary lithologies. However, it seems likely, that the western margin corresponds to the Jackermaroo Fault, separating shallow-water sediments on the west, from turbidites on the east (Glen, 1990). The northern basin margin, which is inferred to be the Little Tank Fault, separates the northern Kopyje Shelf sediments from turbidites on the west, from turbidites on the east (Glen, 1990). The Crowl Creek Fault represents the southern boundary and separates the siliciclastic Cobar Basin from the southern Mount Hope Trough, dominated by deep-water sediments and volcanics, respectively. Sudden thickness changes in the Biddabirra Formation and to a lesser extent in the CSA Siltstone during Pragian times, suggests the development of intra-basinal fault systems (Glen, 1990), e.g. the Myrt Fault (figure 2.10), the Bundella Fault, the Amphitheatre Fault and the Buckwarroon Fault (figure 2.10). The most important faults are summarised after Glen (1990) in table 2.3.

Glen (1990) defined two zones of high and low strain defined by regional structures that had formed or were reactivated during the basin invasion (figure 2.10). A general trend is apparent, with high strain zones mainly occurring on the eastern basin margin and decreasing towards the centre and west-wards. An ill-defined third zone, characterised by low strain, occurs in the north-western part of the Cobar Basin.

Structural Zone 1

The D1 high-strain zone is confined by the Rookery Fault to the east, the Myrt-Thule Fault system to the west and by the Crow Creek Fault to the south. The following characteristic features can be summarised for this southwards widening zone: (1) regional intense sub-vertical S1 cleavage, overprinting an early cleavage oblique to bedding; (2) a regional down-dip extension lineation L1, meso- to macroscopic F1 folds. According to Glen (1990), these structures developed due to right-lateral transpression above a positive flower structure. The zone is highly imbricated and contains two internal NNW-trending faults – the Cobar and the Great Chesney Faults. The latter is a steeply E-dipping fault and represents the contact between the folded and imbricated Great Cobar Slate in the footwall to the west and the folded Chesney Formation in the hangingwall to the east. To the south, the Great Chesney Fault is lost in the Great Cobar Slate, whereupon the faulting seems to have been transferred southeast-wards to a zone of closely spaced ductile-brittle fault array in the Peak area – the Great Peak Fault, Blue Shear and Lady Greaves Shear (Glen, 1990).

Several mineral deposits are present in this structural zone. Most of deposits of the Cobar Gold Field, e.g. The Peak, New Occidental, Chesney and New Cobar are localised along regional NNW-trending faults, the Great Chesney and the Great Peak Faults. The CSA and the Great Cobar deposits formed on thrusts

within imbricated plates, the Cobar and Chesney plates, respectively (Glen, 1995).

Structural Zone 2

Most of the Cobar Basin was affected by much lower strain and can be summarised in the D1 low-strain zone, which in turn can be divided into five sub-zones or blocks. Those are from north to south: the Bundella Block, the Maryvale Block, the Olino Block and the Biddabirra Block. The low-strain zone extends from the Buckwaroon Fault in the west to the Myrt-Thule Fault system in the east and is confined by the Little Tank Fault in the north. The southern truncation is unclear. Two important structure sets were identified in this zone: (1) D2 structures, including variably developed S2 cleavage and variably plunging; (2) upright open F2 folds (variable in strike direction) which are refolding earlier F1 folds. F1 are accompanied by a subvertical S1 cleavage at times (Glen, 1990).

The Bundella Block is located in the northernmost part of the low-strain zone. It is confined by the Little Tank fault to the north and by the Bundella Fault to the south. Due to major thickening of the Biddabirra Formation, the Bundella Fault is interpreted as a re-activated syn-depositional growth fault. The Bundella Block is internally characterised by WNW-trending F1 folds with an accompanying subvertical S1 cleavage. These folds were affected by a later deformation D2. The overall occurrence of the S1 cleavage in the Bundalla Block is a significant difference compared with other areas in the low-strain zone, and indicates increased strain in this particular block. During the D2 event, the older structural elements were folded into NE-trending upright F2 folds, with a locally occurring subvertical NE-trending S2 cleavage (Glen, 1990).

The Elura deposit is located in this block. Glen (1990) interpreted several blind thrusts throughout the Cobar Basin. Glen (1995) suggested the deposit formed at the end of such a blind thrust, which acted as a major pathway of ascending mineralising fluids.

2.3.4 Igneous activity within and proximal to the Cobar Basin

Siliceous volcanics represent only a minor component of the exposed Cobar Basin. Several tuff layers have been identified in the Elura deposit since its discovery. Thicknesses of those tuffs vary, ranging between < 1 to ~20 cm. They display typical sedimentary features developed under subaqueous conditions, i.e. a sharp lower layer contact and an upper gradational zone into mud- and siltstone.

The Silurian Tinderra Granite (410 ±10 Ma; Pogson and Hilyard, 1981) is the only known intrusion proximal to the Elura deposit. The S-type granite is localised at the basin boundary at a distance of around 30 km in north-easterly direction from the deposit (figure 2.9 and figure 2.10). In the vicinity of the CSA deposit, a 30 m thick cherty bed is interpreted to represent a tuff unit (Scott and Phillips, 1990). Rhyolitic to rhyodacitic volcanics occur within the host rock sequence of the Peak deposit (Hinman and Scott, 1990).

By contrast, the southern extensions of the Cobar Basin, the Rast and the Mt Hope Troughs (figure 2.8), are characterised by significant igneous activity. The Ural Volcanics, contained within the Rast Trough around 200 km south of Cobar, predominantly comprise felsic porphyric facies and are cross-cut by very minor highly altered mafic and intermediate dykes and intrusives. The deposition of these volcanic rock suites occurred in a submarine environment. Concurrent eruptions were both, eruptive

---

and effusive in nature. Based on U-Pb zircon ages, deposition is interpreted to have occurred at approximately 411 to 395 Ma (Bull et al., 2008).

The Mt Hope Volcanics occur within the trough approximately 100 km south of Cobar. Most of exposed felsic volcanic facies are rhyolitic to dacitic in composition, porphyritic to aphanic and commonly feature spherulitic textures and flow-banding. They form sills, minor dykes and lava flows, which in places are auto-brecciated. Abundant, mostly syn-eruptive pyroclastics and minor mafic-intermediate cross-cutting dykes are present. The Mt Hope Trough is host to several granitic intrusions (e.g. Thule, Coan and Boolahbone Granites). The most prominent is the I-type Thule Granite, interpreted to underlie the volcanic rock sequence. An approximate age of the Mt Hope Volcanics has been estimated at 411 to 400 Ma. The age is constrained by K-Ar dating of the granite and the marine fossil-bearing cover sequence above the volcanics (Bull et al., 2008). The Boolahbone Granite is an A-type granite.

<table>
<thead>
<tr>
<th>Fault</th>
<th>Age</th>
<th>Activity</th>
<th>Type of fault</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rookery</td>
<td>Lochkovian</td>
<td>Separates shelf from basement; west-dipping. Eastern edge of Cobar basin in the north, hinge zone overlapped by inter-fingered facies in southeastern corner. Infra-basinal conglomerates and slumped blocks of limestone in basin sediments attribute to faulting.</td>
<td>Strike-slip, oblique-slip</td>
</tr>
<tr>
<td>Little Tank</td>
<td>Lochkovian</td>
<td>Separates shelf from basin</td>
<td>Extensional</td>
</tr>
<tr>
<td>Jackermaroo</td>
<td>Lochkovian</td>
<td>Separates basal Lochkovian shelf sediments from basal Lochkovian turbittes.</td>
<td>Strike-slip (inferred), oblique-slip</td>
</tr>
<tr>
<td>Myrt</td>
<td>Pragian</td>
<td>West dipping. Dramatic thinning of Biddabirra Formation and CSA Siltstone. Inactive before end of Biddabirra deposition</td>
<td>Strike-slip, oblique-slip</td>
</tr>
<tr>
<td>Bundella</td>
<td>Pragian</td>
<td>South dipping, confine Biddabirra formation to the south</td>
<td>Extensional</td>
</tr>
<tr>
<td>Crowl Creek</td>
<td>to Pragian</td>
<td>Separates southern volcanics from northern clastics</td>
<td>Extensional</td>
</tr>
<tr>
<td>Buckwaroon</td>
<td>Pragian</td>
<td>Thickening of the Biddabirra Formation to the east</td>
<td>Transfer fault</td>
</tr>
</tbody>
</table>

Table 2.3: Major syn-depositional faults in the Cobar Basin after (Glen, 1990).
2.4  Australian Zn-Pb-Ag ore systems

2.4.1  History and current production

At the end of the 18th century, the mining boom for base metals commenced in Australia (1880s and 1900s for Pb-Ag and Zn, respectively). Major discoveries in the Broken Hill region in western New South Wales caused Australia to become a major world-class producer of lead, silver and subsequently zinc. These discoveries were: Thackaringa-Silverton (1876) and shortly after the nearby Umbumberka deposit, followed by the "line of lodes" in Broken Hill itself in 1883 discovered by Charles Rasp (Mudd, 2007). Several mining companies were founded in Broken Hill (e.g. Pasminco Ltd – now Zinifex Ltd, Broken Hill Proprietary Company Ltd – now BHP Billiton). Initially, only silver and lead were produced due to the fact that zinc had no or only limited market potential and no economic recovery and concentration method was known at this time. The German brothers Bessel were the first to describe a process called differential froth flotation and patented this new technique in 1877 (Fuerstenau et al., 2007). In 1905, differential froth flotation for sulphide ore was simultaneously invented by A.H. Higgins in London and G.A. Chapman in Broken Hill (Fuerstenau et al., 2007). Nowadays, it is one of the most important mineral separation techniques (Mudd, 2007). Several other important Zn-Pb-Ag discoveries in Australia followed, e.g. Mt Isa (1923), Hilton and George Fischer (1947-1948), McArthur River (1955), Woodcutters (1964), Elura (1973), Century (1989) and Cannington (1990).

According to statistical data compiled by the U.S. Geological Survey (2010), Australia is the world fourth largest producer of zinc, the second largest of lead and ranks sixth for silver. An estimated total production of 1.300 kt zinc, 516 kt lead and 1,800 t silver were achieved throughout Australia in 2009. Mudd (2007) estimated an overall economically demonstrated resource of 22.9 Mt lead and 41.0 Mt zinc, in addition to an inferred resources of 21.6 Mt lead and 25.2 Mt zinc (as per data available in December 2004).

2.4.2  The most important base metal deposit types

Most of Australian Pb-Zn-Ag deposits developed temporarily in three events: 2.9 to 3.0, 1.5 to 1.7, 0.3 to 0.5 Ma. Approximately 75% of the entire zinc resource is contained in deposits that formed in a rather short time span between 1.58 to 1.69 Ma (Huston et al., 2006). Mineralisation occurred in various geological settings, some of them characterised by igneous activity, others entirely lacking of any volcanism or plutonism. Huston et al. (2006) described the four most important ore forming systems in great detail, i.e. volcanic-hosted massive sulphide (VHMS), Broken Hill (BHT), Mississippi Valley (MVT) and Mount Isa-type deposits (MIT). Several other deposit-types, apart from those mentioned above, have been described in the past, e.g. skarns, mantos, Irish-type, vein, epithermal and Elura-Woodcutters-type deposits. Only the latter is characterised by a large tonnage and contributes significantly to the Australian base metal production. Features of this deposit-type are described in detail in chapter 3 on page 35 on basis of the Elura orebody. Major characteristics of those four most important types were summarised after Huston et al. (2006) in the following.

---

Volcanic-hosted massive sulphide deposits∗

Compared to MIT and BHT deposits, australian VHMS deposits are relatively small in size and contain around 16.52 Mt zinc, 5.03 Mt lead and 19,730 t silver. Some large examples are Mt Lyell, Rosebery and Hellyer in the western Tasmania region, the Benambra district in Victoria, Mt Morgan in Queensland and Woodlawn in New South Wales.

Deposits of this style formed in submarine back-arc basins, characterised by significant volcanic activity, causing high heat flow subsequently driving large hydrothermal systems. Observed ore fluid temperatures are in the order of 200 to 350°C. Mostly polyphase subvolcanic intrusives, characterised by varying chemistry ranging from trondhjemitic, tonalitic to granitic and dioritic, represent the heat sources. The metals are predominantly leached from the volcanics via circulating seawater brines with a minor contribution of magmatic fluids. Sulphur is sourced from both, seawater and the leached volcanic rock sequences.

Massive sulphide lenses are developed above footwall alteration zones dominated by chlorite- and/or sericite and quartz alteration, and can containing significant quantities of copper. The regional alteration is semiconformable, indicating subhorizontal fluid flow direction. Transgressive alteration is developed at deposit scale as a consequence of ore forming fluids migrating and focussing along major fluid conduits (e.g. synvolcanic faults). The volcanic host sequences are characterised by epidote, hematite, albite and K-feldspar alteration. The extent of alteration varies in size ranging between 150 to 500 m. The apparent sulphide zoning is defined by temperature gradients with high-T assemblage (pyrite and Cu-bearing sulphides) at the base and lower-T mineral parageneses (Zn-Pb-Ag sulphides and minor barite) at the top of the deposits. The ore formation is controlled by local structures, providing fluid focus and pressure drop in dilational sites, as well as changes in the volcanic rock facies. Furthermore, replacement of host rocks and sub-seafloor hydrothermal-seawater mixing are important mechanisms for ore precipitation. Exhalites, such as banded iron formations and tourmalinites, precipitate on the seafloor around the outflow zone.

Broken Hill-type deposits†

Broken Hill and Cannington are economically the most important examples of this deposit style. The BHT mineral systems are famous for their large size and their high grade metamorphic ore (amphibolite facies or higher). The world’s largest Zn-Pb-Ag deposit, Broken Hill (Australia) has produced some 300 Mt of high-grade ore for 60 Mt of metal producing revenue of $350 billion. The wealth generated by the exploitation of the orebody significantly aided the industrialisation process of Australia, created Broken Hill Proprietary Company Limited (BHP) in 1885 and financed the precursor to Rio Tinto. The 1685 Ma orebody hosted by metasediments comprises nine masses of sulphide rocks that were affected by multiphase coeval high-grade metamorphism and intense deformation in the Olarian Orogeny (1600 Ma) and coeval lower grade metamorphism and deformation in the Delamerian Orogeny (500 Ma). In 2006, all Australian BHT deposits combined contain an estimated unmined resource of 26.25 Mt zinc, 33.92 Mt lead and 65,600 t silver.

The generalised current genetic model for BHT ore forming systems includes syngenetic or diagenetic deposition and syn- or post-tectonic replacement. The mineralisation is hosted by metamorphic overprinted upward coarsening siliciclastics within sediment-
dominated basins, which developed in a continental rift setting. These basins are characterised by elevated geothermal gradients and were affected by igneous activity, such as the intrusions of high Fe-high Ti tholeiitic basalt sills (1685 Ma) at Broken Hill. The formation of igneous rocks took place approximately contemporaneous to ore formation. Interbedded pelite and psammitic units constrained sulphur-poor geothermal systems that leached evaporites to provide hypersaline fluids, which subsequently leached metals from deeper rock units. Reactive minerals in basalt, felsic volcanics and felsic metasediments were altered and are now represented by an almandine-quartz-sillimanite overprint. Metasediments stratigraphically below the Broken Hill orebody show extensive premetamorphic hydrothermal alteration and now comprise blue quartz-manganoan garnet-ferroan gahnite-plumbian orthoclase assemblages with minor and variable amounts of sulphides.

Contrary to VHMS deposits, water was sourced from intercontinental fresh water lakes. A sudden deepening of the basin caused an over-pressurisation of oxidised metal bearing low-sulphur hydrothermal fluids circulating in aquifers. Fluid migration, focus and, subsequently the location of alteration and ore precipitation were mainly controlled by active structures enabling the breach of capping, impermeable rock units. Hydrothermal fluids released from their aquifers caused transgressive sulphide-bearing footwall alteration zones. Those zones subsequently acted as major fluid conduit for episodic pulses. Broken Hill’s C-Lode formed along such a conduit where the escaping fluids precipitated as iron formations on the seafloor, now comprising a thin finely laminated quartz-magnetite-spessartine-fluorapatite ± hyalophane-sphealerite-gahnite-plumbian orthoclase rock. Later, these fluids deposited stratiform base metal mineralisation, e.g. the zinc dominated B- and A-Lode, and No 1 Lens, as well as the stratigraphically higher lead dominated No 2 and No 3 Lenses in Broken Hill. Spessartine- and gahnite-bearing rocks stratigraphically equivalent to the Broken Hill orebody are interpreted as exhalites whereas strike equivalent tourmalinite and possibly some quartz-gahnite rocks may have formed from stratal flow and metal precipitation in psammitic aquifers. Ascending fluids, influxing and replacing permeable psammitic sequences, formed stratiform sub-seafloor base-metal mineralisation (e.g. Western Mineralisation in Broken Hill). Zones of mineralisation are commonly enveloped by a quartz-manganoan almandine-gahnite alteration assemblage (Broken Hill) or by quartzose biotite-sillimanite schists and feldspatic garnet-bearing psammites (Cannington). In Broken Hill, alteration associated with lead-dominated orebodies is mostly absent.

Deformation during the Olarian and Delamerian Orogenies remobilised the base metal sulphides into fold hinges and dilational jogs. Manganese, zinc and iron reacted with the enclosing metasediments to form spessartine- and gahnite-rich lithologies. Remobilised ore has a relative enrichment in Pb, Ag, Cu, As and Sb.

Zinc, lead, iron and silver occur as sulphides, silicates, spinels, oxides or as native phases. The mineral paragenesis and the fact that pyrite is absent in BHT deposits suggests formation in a sulphur-poor environment. Sulphur isotopes of various mineral phases are consistently at or close to $\delta^{34}\text{S} = 0\%$. Strontium, lead and boron isotopes suggest mantle, crustal and evaporitic sources. The genetic model proposed for the Broken Hill base metal deposit involves ore formation by replacement and lake floor hydrothermal sedimentation in a shallow fresh water rift lake.

Mississippi Valley type deposits*

Several Australian MVT deposits are found along the Lennard shelf and the Broom platform in Western Australia, the largest of them being the Admiral Bay deposit. The MVT deposits

are relatively small in size and contain a total of 10.7 Mt zinc, 5.89 Mt lead and 4,888 t silver.

The deposits are of epigenetic origin, stratabound and formed in intracratonic settings in sag or rift basins. Host lithologies are predominantly marine platform carbonates. The estimated depth of ore formation ranges between a few hundreds of metres and up to 2 km. The basinal rock sequences comprise carbonates, mudstones, evaporates, and calcareous/carbonaceous shales and siltstones. The basins tend to show weakly reducing conditions. Basal permeable sandstone layers and reactivated syn-depositional growth faults on basin margins act as major fluid conduits. Due to the historic complexity of intracratonic basin development, source rocks are not easily identified. Basinal fluids are either driven by the diagenetic compaction of the sediment column, hydraulically due to tectonic uplift, forced by orogenic compression or due to gas expulsion as a consequence of a drop in sea level. Metal was sourced and leached from the siliciclastic sediments and subsequently transported via chloride complexation. Seawater and/or evaporitic sequences are interpreted as chloride source. Sulphur is interpreted to be either transported via the basinal brine as \( \text{H}_2\text{S} \) or sulphate, or sourced locally at the site of ore precipitation from a second fluid or from evaporites. Hydrocarbons and/or organic matter genetically linked to the ore formation is interpreted to be sourced from deeper levels within the basin and not generated at the site of ore deposition.

Mineralisation generally occurred during the latest stages of main subsidence prior to exhumation. Temperature conditions (80 to 200 °C) reflect normal geothermal gradients without magmatic activity. Sulphide deposition occurred in or near reactivated basin-bounding faults as replacement of evaporates, hosted in hydrothermal solution breccias or in permeable reef carbonates. Most commonly, these depositional sites are truncated by sequences characterised by low permeability (e.g. granites, shales). The alteration haloes are characterised by mineral assemblages typically composed of quartz, siderite, gypsum, magnetite, marcasite, hydrocarbons, fluorite, dolomite, calcite and barite.

**Mount Isa-type deposits**

The four most important deposits of this style are HYC (Here’s Your Chance) deposit in the McArthur region, and the Hilton-George Fisher, the Mount Isa and the Century deposits in the western succession of the Mount Isa Inlier. With 77.09 Mt zinc and 34.44 Mt lead, the Australian MIT deposits contain the world’s largest base metal accumulations. The combined silver content of all MIT is 61,890 t, slightly lower compared to BHT deposits.

Despite their similar large size compared to Broken Hill-type deposits and the occurrence of volcanic rock suits within the basins in which they are hosted in, MIT deposits are interpreted to have formed without immediate and coeval contribution of volcanism or magmatism. They are hosted by pyritic and carbonaceous dolomitic siltstones developed within intracratonic extensional basins which formed due to tectonic activity along the North Australia craton. Rock types occurring in these basins are dominated by siliciclastics (laminated dolomitic siltstone and shale, quartzose sandy dolomite and sandstone), bimodal volcanics, felsic magmatic rock suits, platform and ramp carbonates. Similarly to MVT deposits, temperatures of ore formation were relatively low (70-240°C) and achievable without the need of an additional heat sources such as granitic intrusions. Metaliferous fluids migrated along major sandstone dominated aquifers contained within the basinal rock sequence and subsequently ascended along deep penetrating basin-scale faults. The flow of these brines was controlled similarly to MVT deposits, e.g. by over pressurisation of aquifers caused by extension. Evaporitic sequences are interpreted to represent the source for sulphur and chloride. Volcanic rocks contained in the basin sequence have been af-

---

2.4 Australian Zn-Pb-Ag ore systems

affected by hydrothermal alteration and are characterised by losses of zinc, lead and copper. These volcanics represent the most probable metal sources. Thermal sulphate reduction is described as the most likely and most important mechanism for the generation of $H_2S$ for base metal formation. Alteration is typical potassic in nature, characterised by mineral assemblages either composed of orthoclase-quartz ± sericite ± hematite ± dolomite ± anatase ± barite, or chlorite-orthoclase-quartz.

Syn-deformational and syngenetic models have been proposed for Mount Isa-type deposits in the past, however the age relationship between ore formation and the host lithologies are still debated. With an age discrepancy of 28 Ma, lead model age studies at the Mount Isa deposit demonstrated that the host lithology is significantly older then the sulphide mineralisation itself. Amongst many, this is probably one of the most important arguments supporting a diagenetic/epigenetic origin.

2.4.3 Deposits in the Cobar region

Several polymetallic base metal, copper-gold and gold deposits are found in the Cobar area. Schmidt (1990) estimated a total of 85 Mt of ore is contained in the known deposits with metal contents in the order of 2.6 Mt zinc, 1.6 Mt lead, 1.0 Mt copper, 4000 t silver and 70 t gold. Since that time, resources have grown as a consequence of near mine exploration and delineation drilling (no published data). The orebodies of the Cobar deposits show significantly different features compared to the other four major deposit types described in the previous chapter. The deposits themselves, excluding the McKin nons deposit located towards the western basin margin, however, have several characteristics in common (Lawrie and Hinman, 1998): (1) all deposits are hosted in siliciclastic marine turbidites of the Cobar Supergroup; (2) ore formation is strongly structurally controlled (dilation, competency contrast, fault jog); (3) the ore bodies are subvertically orientated and located in steeply-dipping high strain zones near the eastern Cobar basin margin; (4) geometries are similar, e.g. vertically elongated massive sulphide pipes, lenses or sulphides in stringer zones; (5) the mineralisation is exclusively discordant to host rock sequences; (6) genetic links to igneous activity have not been identified in any of the known Cobar deposits. However, there are some differences. The obvious north-south trending change of ore mineral paragenesis, characterised by metal assemblages dominated by Pb-Zn-Ag ±Cu at the Elura deposit via Cu-Zn-Pb-Ag to Cu & Au at Peak, Chesney, New Cobar, New Occidental and Great Cobar, is indicative for changes in fluid temperature, pH and redox condition, or, as suggested by Lawrie and Hinman (1998), for more than one metal source. Another difference is the occurrence of magnetite in some copper-gold systems, entirely absent in zinc-lead-copper dominated deposits. This feature indicate changes in the fluid chemistry during ore formation, e.g. redox condition or the amount of dissolved sulphur as described in Large (1977). The current genetic model of the Elura deposit also referring to the other Cobar deposits will be discussed in section 3.2 on page 50 and therefore is not described within this chapter. Important orebody features of the deposits beginning with the southernmost Peak gold deposit are summarised in the following.

The Peak Gold deposit•

The Peak gold and minor base metal deposit is located 8 km south-east of Cobar (figure 2.11) and is hosted by the Chesney Formation, part of the Nurri Group (Hinman and Scott, 1990). The deposit formed in a narrow high strain zone of strongly deformed host sediments. Siliceous volcanics of rhyolitic to rhyodacitic composition occur at depth. These rock types are variably pseudobreciated, partially chloritised and

• Summarised after

31
show flow banding (Hinman and Scott, 1990). The mineralisation occurs adjacent to the earlier described volcanics as veins, fracture filling or in a disseminated manner. The orebody consists of several zoned pods and lenses, characterised by a Cu-rich inner zone becoming Pb-Zn dominated towards the rim (Lawrie and Hinman, 1998). Only minor mineralisation is found in the volcanics themselves. Apparent cack-seal features indicate formation in a dilational environment. Hinman and Scott (1990) described five styles of mineralisation, comprising three lead-zinc and two copper dominated ones in the Peak deposit: (1) zones of strong silicification and disseminated sphalerite-galena; (2) folded and boudinaged quartz-sphalerite-galena veins; (3) black banded silver-rich mineralisation characterised by a paragenesis of chlorite-sphalerite-galena, and partially replacing style 1; (4) breccia-hosted high level gold chalcopyrite-pyrrhotite ±pyrite mineralisation at the contact between the Nurri Group and volcanics; (5) late quartz-chalcopyrite-iron sulphide vein-style mineralisation.

Other deposits in the Cobar Goldfield

The Cobar Goldfield consists of another four mineral deposits in addition to the Peak deposit (figure 2.11). The New Occidental represents a gold deposit whereas the remaining three are gold-copper systems. The ore bodies are sub-vertical orientated and steeply plunging to the north.

The Chesney deposit consists of two gold-rich pipe-like bodies connected by a copper-rich vein-style zone, and a thin lenticular body. The orebody is epigenetic and hosted by shear zones. The mineral paragenesis consists of chalcopyrite-pyrrhotite-magnetite-native Au-Ag-native Bi-bismuthinite and minor sphalerite-galena-pyrite. Alteration is characterised by early quartz veining and silicification followed by chloritisation.

The New Cobar deposit is characterised by fairly consistent metal ratios with an overall increase of gold content towards the surface. The four pipe-like orebodies are shear-hosted and developed due to strike slip reactivation of thrust faults. A halo of pyrite surrounds the zones of mineralisation. Mineral parageneses such as magnetite-Au-maldonite-native Bi-bismuthinite, chalcopyrite-pyrrhotite-pyrite and galena-sphalerite-pyrrhotite are found in the deposit. Early silicification, quartz veining and a syn-mineralising chloritisation are described as main alteration features.

The sulphide-poor New Occidental deposit consists of a disc-shape orebody containing six discrete ore lenses which are characterised by varying metal ratios. The richest gold zones are found in the upper parts of the mineralisation as Au-maldonite-Bi-magnetite ore. Other typical mineral assemblages are chalcopyrite-pyrrhotite-pyrite and galena-Au-sphalerite-pyrrhotite. The orebody is epigenetic in nature and hosted within shears developed at zones of rheology contrasts. Alteration is expressed as silicification, quartz veins and breccias, colloform banded quartz chlorite, carbonate veining and chloritisation.

Three vertical pipe-like ore lodes continue for more than 1000 m, and four smaller lenses are found at the Great Cobar deposit. The deposit is epigenetic and hosted in shear-zones. Three ore types are distinguished: (1) magnetite-pyrrhotite-chalcopyrite, hosted by silicified and chloritised slate; (2) quartz-chalcopyrite-pyrrhotite±magnetite and (3) lead-zinc mineralisation with accompanying chloritisation. The siliceous ore type (2) mainly occurs at depth.

The CSA base metal deposit

The polymetallic copper-lead-zinc CSA deposit is located 11 km NNW of Cobar (figure 2.11).

---


The orebody is hosted by the CSA Siltstone, which is a thinly bedded turbiditic rock sequence part of the Amphitheatre Group (Scott and Phillips, 1990). The host rocks experienced greenschist metamorphism accompanied by the development of a pronounced cleavage. A prominent chert layer, approximately 30 m thick and representing a tuff layer, is present within the sequence. The CSA Siltstone features abundant sedimentary structures e.g. graded beds, load casts, ripple marks, etc. A very strong cleavage, obliterating the bedding, is developed in the immediate vicinity of the orebodies (Scott and Phillips, 1990). Several chloritic shears, containing abundant black Mg-rich chlorite, are developed throughout the deposit. Some of these shears are host to sulphides and talc. The mineralised zones are genetically linked to these shears and occur immediately above them in the hangingwall. The alteration halo is dominated by Fe-rich chlorite (up to 50 m wide zone) followed by a relatively narrow zone of sericite alteration (Scott and Phillips, 1990). A weak to moderate pervasive silicification surrounds the entire mineralising system. The orebody consists of several sub-parallel, vertical to sub-vertical (~70° eastward dipping) massive and sub-massive podiform lenses and zones of strong sulphide veining. These bodies are laterally discontinuous, but continue vertically for over 2 km. The deposit is subdivided into zones of mineralisation according to occurring ore types and changes of metal contents and ratios. A vertical metal zonation is expressed by an increase of copper and decrease of lead and zinc with depth (Lawrie and Hinnman, 1998). Laterally, ore lenses are enriched in Cu in core zones whereas Zn and Pb concentrations increase towards peripheral zones, similarly as observed at the Peak deposit.

![Geological map of the eastern margin of the Cobar Basin showing the locations of important mineral deposits](image-url)
Chapter 3

The Elura Orebody

The Elura Deposit is the largest mineral resource in the Cobar region. It is located at the north-eastern margin of the Cobar Basin in the vicinity of a basement protrusion (figure 3.1). At present, the mineralising system is still open along strike and towards depth and its full dimension is yet to be identified. The current geological model is defined by approximately 2000 diamond drill holes in addition to underground mapping.

Glen (1990) divided the Cobar Basin in a high and a low strain zone, with the Elura deposit located in the latter (figure 3.1). Four major faults define the basin block hosting the deposit (Glen et al., 1994): the Little Tank Fault to the north, the Bundella Fault to the south, the Myrt Fault to the east and the Buckwarroon Fault to the west (figure 3.1).

The geology of the deposit was first described by Schmidt (1980); Adams and Schmidt (1980); Archibald (1983). Since then, further geologists, inter alia Taylor et al. (1984); De Roo (1989a,b); Schmidt (1990); Seccombe (1990); Lawrie and Hinman (1998); Webster and Lutherborrow (1998); David (2008), studied the base metal system. Outcrops in the vicinity of the deposit are sparse, subsequently most of the geology is interpreted based on diamond drill hole data and from underground exposure.

3.1 Geological characteristics*

3.1.1 Host lithology

The orebody is hosted by the CSA Siltstone, a turbiditic sediment sequence which is a member of the Early Devonian Amphitheatre Group (see figure 3.1 and figure 2.10 Schmidt, 1990).

These turbidites consist of interbedded sand-, silt- and mudstone layers in a (A-B)-C-D-E Bouma sequence and show a variety of soft sediment deformational structures such as convolute bedding, slumps, load casts or flame structures. The siltstone beds are pale grey in colour whereas the mudstone layers are dark grey to black. The regularity of this interbedding and the relative amount of sandstone in comparison to the finer grained mud- and siltstone beds changes significantly. The variation of average greywacke content and its maximum bed thickness was calculated based on 6877 logging data points out of 155 diamond drill holes throughout the deposit in the course of this study ( figure 3.2, data supplied by CBH Resources Ltd). The host rock contains a median of 20% sandstone with thicknesses of most of the sandstone

*The following summary on the geological characteristics of the Elura Orebody is based on observations made by the author during employment as geologist at the Endeavor Mine by CBH Resources Ltd between 2006 and 2008 in addition to cited work of other authors. It needs to be stressed, that acquired geological data, e.g. mapping, drill core logs, etc., and improvements made to the geological model during the stated time period has to be understood as a team effort of the entire Geology department of the Endeavor Mine and is not exclusively based on the author’s work.
3. THE ELURA OREBODY

Figure 3.1: Geological map covering the area proximal to the Elura Orebody at the north-eastern margin of the Cobar Basin; map data is from the 1:250 000 Australian National Grid Cobar SH/55-14 map sheet (Brunker, 1969).

beds ranging between 0.5 cm and 15 cm (median 8 cm) but, in places, can become as thick as 3 m. The thickness of the turbiditic host rock sequence is in excess of 1200 m. Nine thin tuff beds with true thicknesses between 1 and up to 20 cm represent the only volcanic rocks identified within the host rock sequence (figure 3.3). They are laterally continuous and used as marker beds. Some zones in the stratigraphic column are significantly calcareous and may also be used as marker beds in the future. According to Schmidt (1990) the unaltered CSA Siltstone is composed of 35-40% quartz, 35-40% muscovite, 10-15% chlorite, 5% albite and 1-5% calcite. Minor constituents are stilpnomelane, pyrite (0.25-0.7%), kerogen-graphite (0.1%), detrital biotite and heavy minerals (Adams and Schmidt, 1980; Taylor et al., 1984). The host rock experienced lowermost green-schist facies metamorphism (Schmidt, 1990).
Brill (1988) investigated crystallographic characteristics of illite and white mica in order to estimate pressure conditions during metamorphism. Results showed a decrease in metamorphic intensity from anchizonal to epizonal in the south near Cobar to anchizonal at the Elura mine. An average metamorphic pressure of 3 kbar was calculated based on silica content of white micas in samples taken near the CSA mine. This pressure indicates a lithostatic load of approximately 11 km and would require the Late Devonian to Early Carboniferous Mulga Downs Group to overlie the Cobar Supergroup sediments in this particular area (Brill, 1988).

The Elura limestone is the deepest known lithology at the deposit. The limestone is commonly developed as a clast-supported foliated breccia that, in places, had been affected by ductile deformation. It is composed of crystalline or recrystallised limestone, crinoid stems, shell and coral fragments, as well as variable quantities of shale. The limestone commonly contains thin stylolites and quartz veins.

David (2000) interpreted the limestone as an in situ part of the shelf sediments of the Kopyje Group and described it as an open platform reef limestone, composed of reef rudstone, boundstone, coquina and bioclastic packstone, according to the classification scheme of Dunham (1962). Leevers (2000) suggested the reef formed above a basement high because silicified CSA had been intersected to the east and the west at greater depths than the top of the limestone complex. Carolan (1999) interpreted the reef sequence as belonging to the Brookong Formation.

A deep drilling exploration program during 2006/07 was designed to test the contact of the limestone for economic mineralisation. Furthermore, it was aimed to investigate the true thickness of the limestone, the nature of the contact to and the type of the underlying rock se-
3. THE ELURA OREBODY

The overall drill hole information density within the limestone is rather limited and neither of these recent, nor any previous diamond drill holes intersecting the limestone ever reached the footwall contact. Despite the deposit being located in the vicinity of the basin margin, the regional correlation of the limestone to the Kopyje Group is uncertain and the exact stratigraphic position within the Cobar Supergroup unknown. The Elura limestone may as well represent an allochtonous mass several kilometres distant to the actual reef complex as part of an olistostrom.

An approximately 100 m thick transitional rock sequence beneath the turbiditic host rocks conformably overlies the limestone. The sequence consists of interbedded fossiliferous, calcareous mud- and siltstone with minor sandy beds. David (2008) interpreted them as distal back-reef lithofacies.

Two very regular interbedded unites are found within the CSA host rock, the so called upper and lower laminated units (ULU and LLU respectively), both approximately 50 m in thickness and characterised by rather sparse and thinly bedded sandstone (~15 wt%). These units were first identified and described by Nicholson et al. (2006), suggesting that they probably truncate the lower sheet-like mineralisation on either side at a depth of ~400 and ~900 m below surface. The southernmost and largest sulphide body penetrates the ULU, however a lateral contraction of the pyrrhotite rich inner ore zone is noticeable. Both, average greywacke contents and its maximum bed thicknesses, feature minima at the approximate depths of the proposed ULU and LLU (figure 3.2).
3.1 Geological characteristics

3.1.2 Ore types and their zoning

The overall geometry of the Elura orebody can be described as sheet-like, characterised by a general NNW orientation and a sub-vertical plunge (see figure 3.17). The mineralisation stretches laterally 850 m along strike and varies in vertical extent from almost 1000 m in the southern parts in the so called main lode area, to 400 to 500 m in northern pods. The sheet itself consists of six grossly concentric to ellipsoidal sub-vertical pipes containing massive and semi-massive sulphide mineralisation (figure 3.5). They are from south to north the main lode (ML) and the five northern pods (z1 to z5). These pipes are 120 m wide in the ML and 30 to 50 m wide in z1 to z5. A smaller and rather narrow lenticular sulphide body, the z6 pod (˜15 by 20 m wide and vertical extent of ˜40 m), represents the currently known northernmost economic mineralisation.

The orebody is discordant to the CSA host rock, the exception being the contacts of the uppermost caps of the mineralisation where they appear to be concordant. A strongly deformed and sheared wall rock zone with increased quartz and carbonate veining envelopes the orebody. Minor occurrences of stratiform mineralisation are predominantly composed of pyrite with rare base metal sulphides and are preferably hosted in sandstone beds.

In decreasing order of abundance, the sulphide mineral paragenesis consists of iron sulphides (median of 55 wt%, ratio of pyrite to pyrrhotite varies between ore types), sphalerite (median of 16 wt%), galena (median of 6.5 wt%), chalcopyrite (median of 0.6 wt%) and arsenopyrite (median of 0.15 wt%). Silver-bearing mineral phases (e.g. freibergite, argento-tetrahedrite, native silver) occur preferably in the uppermost and peripheral mineralised areas as minor constituent. The sulphide mineralogy has been investigated throughout the orebody as part of this thesis in great detail and is described in chapter 4 on page 63.

The gangue mineralogy predominantly consists of carbonates such as siderite and ankerite (Fe : [Fe+Mg+Mn] = 0.76-0.98) and, to a lesser extent, quartz (Schmidt, 1990). Chlorite (Fe : [Fe+Mg+Mn] = 0.81-0.98) and sericite contents are variable and overall rather low. Minor minerals are barite, albite and barian-alkali feldspars.

Quartz occurs mainly cherty in silicified host rock fragments and as post mineralisation quartz veining. Accessory detrital zircon, tourmaline, apatite and kerogen are described by Schmidt (1990).

The different ore types occurring at the Elura deposit were first described by Schmidt (1980). He defined three ore types: (1) Siliceous ore, (2) massive ore and (3) pyrrhotite ore. Later, Webster and Lutherborrow (1998) refined the ore classification and introduced three additional ore categories. Ore classification is now also based on an economic point of view, i.e. on the contained metal as lead-zinc combined grade (wt% Pb+Zn). Economic massive and siliceous ore types contain equal to or more than 10 wt% wt% Pb+Zn and represent the main resource. Massive ore is abbreviated as Po or Py for pyrrhotite and pyrite dominated types. Semi-massive ore is abbreviated analogue as SiPo or SiPy. The breccia vein and stringer style mineralisation, abbreviated as VEIN, contains between 3 and 10 wt% Pb+Zn. Whether economic or not strongly depends on the current
metal prices. Accordingly, the sub-economic weakly mineralised zones contain less than 3 wt% Pb+Zn but either sphalerite or galena must be present in order to be classified as this ore type (abbrev. as MinA).

When comparing pyrrhotite to pyrite dominated ore types the former is characterised by slightly elevated concentration levels of Zn, Cu, Co, and Se, whereas the latter is relatively enriched in As, Ag, Sb, Au, Hg, Mo, Sn and Tl (described in chapter 5 on page 149).

The six currently distinguished ore types used in mine geology at the Elura deposit are modified versions of those defined by Webster and Lutherborrow (1998) and are outlined below:

Massive pyrrhotitic mineralisation (Po)

The massive Po ore type contains in the order of 65 to 95 wt% sulphides with significant content of pyrrhotite which, in places, may also represent the main iron sulphide phase (example shown in figure 3.6). The gangue mineralogy is dominated by siderite. Po commonly occurs in the central core zones of the massive sulphide pipes, however is not restricted to those areas (figure 3.11). Schmidt (1990) argued, that retrograde alteration of primary hexagonal pyrrhotite subsequent to regional metamorphism caused the formation of the magnetic monoclinic pyrrhotite variety. Prolonged retrograde alteration generated abundant marcasite in the upper and minor goethite in particular in peripheral zones. Silver-bearing mineral phases do occur, but not as commonly as in pyrite and the siliceous ore types.

Massive pyritic mineralisation (Py)

The main iron sulphide in the Py ore type is pyrite and/or marcasite. Pyrrhotite is generally absent and only rarely observed as very minor constituent. The ore contains between 55 and 98 wt% sulphides and commonly occurs as an irregular, although concentric halo surrounding the massive pyrrhotite mineralisation (figure 3.11). Major parts of the upper main lode mineralisation consist of the Py ore type also due to the earlier described alteration of pyrrhotite to marcasites. Quartz and siderite are the dominant gangue phases with median concentrations of 4 and 12 wt%, respectively.

Siliceous pyrrhotitic (SiPo) & siliceous pyritic (SiPy) mineralisation

Siliceous ore types occur mostly but not exclusively at the margins of massive Po and Py mineralisation (figure 3.11). They contain highly silicified and variably chloritised wall rock fragments accompanied by increased quartz as gangue phase and quartz veining at variable intensities (figure 3.6). In places, these remnant siltstone clasts are rounded but most commonly are angular in shape and form breccias with sulphides.

Breccia vein and stinger type mineralisation (VEIN)

The VEIN ore type envelopes the siliceous ore and represents the interface to weakly mineralised altered wall rock. The width is highly variable and rather narrow in places below one metre in the mid to upper parts of the orebody but can be up to tens of meters wide, particularly
3.1 Geological characteristics

at depth (figure 3.11). The type of mineralisation is characterised by reticulate sulphide vein-ing, most commonly in a highly fractured and silicified host rock (figure 3.7). The mineral assemblage consist of pyrite-pyrrohotite-sphalerite with variable galena content, which may represent only a minor constituent. Significant chalcopyrite is associated with this ore type particularly at greater depths. Visual discrimination between siliceous and vein style mineralisation can be difficult, hence an arbitrary boundary based on a combined Pb+Zn grade is used.

Mineralised altered host rock (MinA)

MinA represents the outermost sub-economic mineralised halo surrounding the orebody. This ore type is predominantly developed in the lower orebody and weaker or absent in the upper main lode zone. There is associated siderite alteration and silicification at variable intensity. Sulphides, predominantly iron sulphides, sphalerite and minor galena and chalcopyrite, occur either as thin sulphide stringers or disseminations. Sandstone beds are commonly the preferred host for sulphides as they feature higher permeability compared to silt- and mudstone beds. In places, disseminated sphalerite commonly replaces siderite spotting in mudstone rich sequences (figure 3.8). The contact between MinA and VEIN is gradational. A Pb+Zn combined grade is used as distinguishing feature.

The zonation of the different ore types is roughly concentric in the upper main lode mineralisation, however it becomes increasingly complex and more irregular at depth. Figure 3.11 shows the development of ore zonation in plan view at five different depth levels below surface. The contacts between massive Po and Py are commonly gradational. Po ore type occurs almost exclusively in the core zones of the massive sulphide pipes. SiPo and SiPy domains were modelled individually for the geological and resource model in the past. Due to the increased geometrical complexity of those ore types with increasing mining depth, nowadays they are treated similarly and modelled as a single domain. The transition from siliceous ore (SiPy and SiPo) via the VEIN breccia stringer zone to the sub-economic minor mineralised host rock (MinA) is relatively narrow. The transition zone surrounding the massive mineralisation (Po and Py) can be as thin as 10 to 50 cm and up to several tens of metres wide, in particular at depth (figure 3.7). De Roo (1989b) suggested that the peripheral breccia zones (mainly VEIN and to a lesser extent SiPo and SiPy) formed due to wall rock fragments being forced or collapsing into zones of dilation and pressure relaxation.

The massive Py and Po core zones narrow towards north and with increasing depth (figure 3.11). By contrast, the width of the VEIN mineralisation surrounding the massive pipes remains roughly constant with increas-

NOTE:
This figure/table/image has been removed to comply with copyright regulations. It is included in the print copy of the thesis held by the University of Adelaide Library.
3. THE ELURA OREBODY

Figure 3.8: Sphalerite in mudstone rich sequence preferably replacing siderite. Sample image from drill hole NP915A; lower main lode area below 9260RL. Image supplied by CBH Resources Ltd.

ing depth, connecting and enveloping individual mineralised pods. At approximately 950 m below surface (9250m RL), the massive sulphide pipes contract further before they disappear entirely (see plan view section 9300RL in figure 3.11). However, VEIN ore continues to greater depth hosted in hydraulic or hydrothermal breccias (figure 3.9) and extensive reticular vein systems in highly silicified CSA siltstone (figure 3.7). This change in mineralisation style is accompanied by a change in ore mineralogy characterised by a slight increase in quantities of chalcopyrite, the preferred occurrence of pyrrhotite over pyrite and elevated iron content in sphalerite (visually identified – darker in colour). Increased ore hardness due to this strong silicification (figure 3.9) and the greater depth of this mineralised zone causes significantly higher production costs. Hence, cut-off grades strongly depend on the current metal prices. Remnant angular chloritised wall rock fragments in semi-massive ore as well as the mineralised breccia vein zones indicate that fracturing was a major mechanism for the development of zones of increased permeability acting as fluid pathways and as space for ore precipitation (figure 3.9).

Sub-vertical sulphide banding, defined by layers enriched in pyrite, pyrrhotite, galena or sphalerite, is present throughout the orebody. The banding is found in all ore types, best developed in Po and least in siliceous ore type. In peripheral ore zones, it is commonly characterised by a concentric orientation relative to the orebody. A sub-horizontal rather fine sulphide layering was described by Schmidt (1990). This banding is expressed by quartz-siderite fracture filling in pyrite-rich bands. These dilational structures post-date the sulphide mineralisation. De Roo (1989b) linked the sulphide banding to the three deformational events (D2-D4; see table 3.1 and chapter 3 on page 45) causing inhomogeneous intense foliation of the ore. Similarly, Schmidt (1990) explained the compositional layering by a cleavage formation event, either contemporaneously to ore formation or

Figure 3.9: Hydrothermal breccia with minor sulphides (MinA ore type) in strongly silicified host rock. Image width 3cm; sample image from drill hole NP915A; lower main lode area below 9260RL. Image supplied by CBH Resources Ltd.
3.1 Geological characteristics

Figure 3.11: The spatial distribution of different ore types and their zoning. Sections in plan view (downwards) are shown for five depth levels, covering the entire vertical extent of the Elura Orebody. Section depths are visualised in a longitudinal view (looking towards WSW) of the orebody (upper right in figure; red shape is the semi-massive SiPy resource domain). The spatial extent of the different ore types are based on the geological and resource model, supplied by CBH Resource Ltd.
overprinting slightly older mineralisation.

Webster and Lutherborrow (1998) described three types of banding: (a) Discrete sphalerite bands at millimetre-scale alternating with bands enriched in pyrite and pyrrhotite; (b) smears and streaks of sphalerite not as continuous and consistent as type (a) banding; and (c) intense, deformational induced cleavage-style banding at the margins of the orebody. Bands are defined by coarse-grained galena-forming veinlets oriented parallel to the cleavage in wall rocks.

3.1.3 Wall rock alteration

Chlorite, sericite, strong silicification and carbonate alteration in the form of pervasive siderite spotting are the most common alteration features. Siderite alteration occurs predominantly on the eastern side of the deposit as a halo up to a distance of 50 m surrounding the mineralisation. On the western side, the halo of siderite spotting is not as pronounced and, in places, only extends for a few metres (Webster and Lutherborrow, 1998). Siderite spotting also occurs adjacent to sulphide veins as shown in figure 3.12.

The size of siderite spots (< 1 mm-10 mm) increases towards the deposit and they occur preferentially in sandstone beds. The extent of silicification between and enveloping the massive sulphide pipes varies in width and intensity. However, it increases significantly below a depth of approximately 900 m from surface. Silicification can be entirely absent in the upper parts of the orebody. The zone of intense silicification at depth correlates with the changeover
3.1 Geological characteristics

from massive pipe-like to a vein/stringer type mineralisation. Strong pervasive silicification altered the CSA siltstone to an almost cherty rock (figure 3.9 and figure 3.7). Webster and Lutherborrow (1998) identified a close spatial relationship between the density of sulphide veining and the intensity of silicification.

CSA siltstone contains nodules of pyrite and minor euhedral pyrite (figure 3.13), more abundant in sandstone relative to silt- and mudstone beds. The pyrite content increases towards the orebody indicating a genetic link (Schmidt, 1990). Sulphide replacement of wall rock occurred along more permeable sandstone beds several metres distant from the massive sulphide body indicating migration of the metal-bearing fluid outwards into the country rock. Schmidt (1990) described mineralised sandstone beds, containing a sulphide assemblage of pyrite-sphalerite-galena-chalcopyrite-tetrahedrite as far as 150 m distant to the orebody.

Intense chloritisation, ankeritisation, albition and sericitisation in the innermost 20-25 m wide alteration halo has been described by Schmidt (1990). This zone is characterised by elevated concentrations of S, As, Ba, Hg, Pb, Sb and Zn whereas MgO, CaO and Mn are depleted (Taylor et al., 1984). Fresh CSA siltstone proximal to the orebody shows similar chemical signatures compared to remote host rock samples with the exception of elevated Ba and depleted Mn.

A cryptic alteration halo was described by Schmidt (1990) featuring an increased carbonate content and K$_2$O:Al$_2$O$_3$ ratio accompanied by losses of Na$_2$O. He explained the chemical modification with the destruction of chloride, albite and detrital components e.g. biotite and iron-titanium oxides caused by acidic carbon dioxide-rich fluids. Iron and Mg released during alteration led to the replacement of calcite by ankerite and siderite.

Sun et al. (2001) used short-wave infrared reflectance spectra (SWIR), obtained via a portable infrared mineral analyser (PIMA), in order to investigate the alteration halo around the Elura orebody. In this study she identified hydrothermal white mica (sericite), chlorite and carbonates (siderite, ankerite and calcite) up to 80 m distant to the orebody. Albition was not detected via this analytical technique, however, accompanying XRD analyses showed that sodium alteration is rather weak and predominantly occurred during regional metamorphism.

Whitbread and Moore (2004) tried to identify "vectors to ore" caused by alteration via the application of Pearce element ratio and isocon analysis and identified several element trends characterised by concentration increase towards the orebody: (1) elements known to form complexes with sulphur, e.g. Sb, Ag, As, Zn, Cu, Pb, Ni, Cd and possibly Ba, (2) alteration of il- lite to muscovite is reflected by elements incorporated in muscovite, e.g. K, Rb, Cs and possibly Ba, (3) siderite and ankerite contents increase towards the orebody subsequently causing elevated concentrations of CO$_2$ and Mn, (4) increases of La and Ce towards the orebody indicate association to either carbonates or sheet silicates, and (5) Ca and Sr follow the increasing trend, however are depleted immediately proximal to the orebody due to pronounced replacement of Ca and Sr by Fe.

3.1.4 Structural setting

The Elura orebody is highly discordant to the host rock and truncated, as well as intersected by several NNW and NNE trending sub-vertical faults (figure 3.15). These faults define a north-north-westerly oriented transpressional structural high strain corridor, characterised by vertical and an overall dextral strike-slip movement. The corridor narrows in a NNW direction. The most prominent of these faults is the "Western Shear" as the western truncation of the southern parts of the orebody. This fault crosses the sheet of mineralisation, intersecting the orebody between the z1 and z2 ore zones. Very poor ground conditions along this structure caused significant geotechnical issues and subsequent production losses in the past. The host rock is strongly folded and faulted in the vicinity of the orebody up to a distance of 30 m (Schmidt, 1990). The intensity of deformation rapidly de-
3. THE ELURA OREBODY

Figure 3.15: Major structures truncating, intersecting and partly offsetting the Elura deposit; section at 9500RL depth in plan view (downwards). The spatial extent of ore types and locations of faults were modified from the geological and resource model, supplied by CBH Resource Ltd. Faults are based and modelled from rock quality designation (RQD) values from diamond drill hole data.

creases away from the sulphide body, characterised by a much more open folding. Proximal to the orebody, the NNW-trending folds form rather tight anticlines and synclines accompanied, in places, by pronounced quartz veining. S₂ defined by De Roo (1989b) (table 3.1) represents the dominant cleavage and is axially planar to those folds. According to Leevers (2000), folds in the host rock are symmetric on the eastern side of the orebody and asymmetric to the west with westerly-dipping fold hinges. The NNE trending faults intersect the NNW-striking fault corridor and partly offset the orebody (figure 3.15). These faults have similar strike orientation as and are likely sympathetic to the Buckwaroon fault approximately 2 km distant (figure 3.1), interpreted as reactivated transfer fault (Glen et al., 1996). Strong silicification and quartz veining occur along faults that truncate or offset the sulphide body. The orebody comprises pinch-and-swell and boudinage structures which are either developed in dilational sites, along bending faults, or they reflect rheological and competency contrasts between the sulphides and the siliciclastic host lithology, which is, in places, strongly silicified.

De Roo (1989b) studied the southernmost main lode zone (the northern ore bodies were unknown at that time) and described four deformations (D₁ to D₄) and their associated structural elements (table 3.1). He suggested that the main ore-forming event occurred during D₂ with contemporaneous establishment of the alteration halo. The two sulphide rock apophyses, developed in the upper main lode zone, are hosted in core zones of doubly-plunging anticlines. Deformation of the massive sulphide body along ductile shears caused vertical stretching into its present shape accompanied by the development of sub-horizontal dilational structures. Glen (1990) suggested that the Elura mine is localised in an area where early WNW-orientated folds (F₁) were refolded by NE-striking folds (F₂) causing the rotation of F₁.
3.1 Geological characteristics

into the apparent NNW trend. He suggested the doubly plunging $F_2$ folds identified by De Roo (1989b) correspond to these $F_1$ folds.

According to structural studies done by Webster and Lutherborrow (1998) the view that the orebody is hosted within domes of a single doubly-plunging anticline is far too simplistic. They suggest that the anticline may represent an array of *en echelon* anticlines.

David (2008) interpreted the anticline as a fault-propagation fold developed within the NNW-oriented fault corridor due to reactivation of faults during basin inversion. Furthermore he suggested three different strain domains: (1) Negative dilation zone with volume loss within the limestone, partially extending into the overlaying clastic shelf sediments. The domain is characterised by pure shear and ductile deformation. The E-W shortening based on stretching lineations is estimated at approximately -60%. (2) The neutral strain domain is interpreted to occur at the lowermost extents of the main sulphide mineralisation coinciding with the zone of pronounced breccia stringer style mineralisation. Both compressional and extensional textures are described and (3) Most of the mineralisation formed within a zone of positive dilation accompanied by volume increase. It has been suggested that conical-shaped fracture zones developed as a consequence of shockwaves generated due to lateral movement along reversal or normal faults.

3.1.5 Regolith expression

**Surficial weathering**

The Cobar region is now an elevated palaeo-plain that has been exposed to surficial conditions since at least Mesozoic times (McQueen, 2004). Climatic cycles during the Cainozoic, defined by warm humid conditions, were followed by cooler more arid episodes that created deep chemical weathering. Two major and widespread periods of iron fixation occurred during the Early Palaeocene and the Middle Miocene and were identified based on palaeomagnetic dating of ferruginised saprolites (McQueen, 2004).

Three main soil types are found within the greater region around the Elura mine (Gibson et al., 2003). A loamy soil, 30 to 60 cm thick and red to brown in colour, represents the most abundant type and formed from the underlying saprolite in addition to a potential aeolian input. Rare thin stony skeletal soils are only developed above the scarce remnants of Mesozoic sedimentary cover. Clay-rich soil, grey, red and brown in colour and predominantly found on topographic highs, has been described by Gibson.
et al. (2003) as the third soil type.

At the Elura mine, up to 1.5 to 2.0 m thick red top soil covers the weathered bed rock (Reed, 2004; Lorrigan, 2005). This surface layer contains abundant pisoliths of maghemite-bearing iron-rich lag. The host rock is completely oxidised to a depth of approximately 80 m below surface, coinciding with the depth of the current water table (Taylor et al., 1984). Irregular partial weathering is controlled by structures and fracture zones and extents to greater depths up to 135 m. The weathering formed bleached saprolite, white to yellowish in colour, which can contain significant calcrite (Lorrigan, 2005).

The saprolite is composed of quartz, muscovite, K-feldspar, secondary kaolinite, goethite and hematite. Kaolinite and alunite are found marginal to the orebody (5 to 10 m) at even greater depths than complete host rock oxidation. Elemental leaching caused by weathering is reflected in pronounced losses of MgO, CaO, P₂O₅, Mn and Zn, and to a lesser extent of Fe₂O₃, K₂O, Hg and Cu (Taylor et al., 1984). These losses were accompanied by enrichments of SiO₂, Al₂O₃, Ba and Pb relative to unweathered CSA siltstone. Iron oxides commonly occur within the saprolite and are developed near fracture zones or along bedding planes. They form thin Liesegang or thicker bands and are characterised by elevated concentrations of As, Bi, Cu, Pb, Zn, Co, Ni and Mn (Taylor et al., 1984).

The Elura gossan and supergene mineralisation

The gossan was initially exposed on the surface (Schmidt, 1980) and was buried as a consequence of strong ground subsidence caused by stope collapses in 1996. Taylor et al. (1984) was the first to study the gossan and supergene mineralisation in greater detail. The oxidation of the orebody formed a dark brown to red gossan to a depth of approximately 100 m. Total and partial oxidation occurred to a depth of 80 m and 100 m, respectively. However, sulphide oxidation is found in cavities within the orebody to depths greater than 800 m (Reed, 2004). Taylor et al. (1984) distinguished two types of ironstone gossan: (1) In situ direct gossan where the texture of the iron oxides developed varies from sponge-like to massive and (2) Solution-deposited gossan which originated due to precipitation of iron oxides from fluids in open space e.g. open joints or cavities. Acidic iron-rich fluids generated by the weathering of the orebody partially infiltrated the surrounding host rock and lead to local ferruginisation. The contact between gossan and altered host rock is very sharp. The mineral assemblage consists of goethite and hematite as major, quartz, kaolinite and beudantite \( \text{PbFe}_2^3(\text{AsO}_4)(\text{SO}_4)\text{(OH)}_6 \) as minor constituents. The latter mineral phase is responsible for elevated concentration levels of Pb and As in the gossan (Taylor et al., 1984).

A supergene enrichment zone of six metre thickness developed between the gossan and the massive sulphide body (Taylor et al., 1984). The supergene zone is composed of an equally thick sulphide zone above primary sulphide ore and an overlying oxide zone. Later studies showed that the supergene oxide zone is with up to 15 m significantly thicker than previously thought (Scott, 2003).

The supergene sulphide zone comprises primary and secondary pyrite, galena, chalcopyrite, marcasite, digenite, bornite, anglesite and beudantite (Taylor et al., 1984) and is characterised by a vertical zonation form Pb-rich to Cu-rich at its bottom (Scott, 1994). The occurrence of covellite is described by Scott (1994) and cerussite by Scott (2003). A detailed study of the supergene mineralogy by Leverett et al. (2005) unraveled the true complexity of the mineral assemblage and identified at least further 20 phases. The supergene sulphide zone is enriched in Cu, Ag, Ti, Bi, Pb, Hg and As. All element concentrations, except As, are highest at the base of the layer and decrease upwards (Taylor et al., 1984). Ba, Cd, Mo, Sn and Zn are generally depleted. Occurrences of rare oxychloride mineral phases have been reported by Scott (1994). He identified blixite \( \text{Pb}_8\text{O}_5(\text{OH})_2\text{C}_14 \) and mendipite \( \text{Pb}_3\text{Cl}_2\text{O}_2 \), mostly replacing anglesite and to
3.1 Geological characteristics

a lesser extent cerussite. The relatively narrow sulphide zone suggests a rather stable water table over a prolonged time (Taylor et al., 1984).

A distinct band, composed of "blue-black sooty chalcosite", approximately 15 cm in thickness, is developed at the transition to the overlying oxidised zone (Scott, 2003; Lorrigan, 2005). Minor digenite and enargite are also present in this band.

The overlying oxidised zone consists of sulphates, carbonates and arsenates. The zone is predominantly composed of several secondary lead mineral phases, e.g. beudantite, cerussite, mimetite \((\text{Pb}_5(\text{AsO}_4)_3\text{Cl})\), nadorite \((\text{Pb}_3\text{SbO}_2\text{Cl})\), lanarkite \((\text{Pb}_2(\text{SO}_4)\text{O})\), and to a lesser extent of goethite, quartz and barite (Taylor et al., 1984). Scott (2003) and Lorrigan (2005) described a lowermost zone predominantly composed of native silver and cassiterite in addition to the occurrence of hidalgoite \((\text{PbAl}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6)\). This part of the supergene zone is characterised by enrichment of Pb, Ag, As, Ba, Hg, Mo, Sb and Sn.

Near surface geochemical anomalies

The metal dispersion outwards from the orebody is a function of the stability of mineral phases that interacted with surficial fluids. Rather stable secondary Pb mineral phases (e.g. beudantite, mimetite) are common at the Elura deposit. Further lead is to some extent incorporated in resistant arsenates (Leverett et al., 2005). The copper content is rather low and is mostly associated with soluble mineral phases (e.g. malachite). No stable zinc mineral phases formed.

The surface expression of the deposit is generally leached of many elements, except silica which is enriched. Taylor et al. (1984) identified As, Bi, Hg, Pb, and Sb as being important near surface enrichments up to a depth of 6 m. However, these surface anomalies are only developed above the southern main lode zone.

No geochemical surface expression has been observed for the deeper northern pods, located approximately 400 m below surface. These anomalies are strongest developed around 50 to 100 m distant to the orebody. Lead and arsenic represent the most important anomalies for outlining the mineralisation. The more mobile elements copper and zinc show much more diffuse and dispersed low-contrast anomalies. The Zn soil anomaly can be followed for more than 1 km to the south-west (Lorrigan, 2005). Lead is preferably concentrated in coarser soil fractions whereas zinc is anomalous in finer fractions < 63 µm (Scott and Lorrigan, 2009). Zinc concentrations within the weathered profile increase with depth towards the water table whereas copper and arsenic remain relatively constant (Taylor et al., 1984).
3. THE ELURA OREBODY

3.2 The current genetic model for the Elura deposit∗

3.2.1 Chronological overview

The first researcher to describe the regional geology of and to study mineral deposits around Cobar was Andrews (1913, 1915). During the subsequent decades, geological and structural mapping, in addition to ore petrological investigations continued (Lloyd, 1935, 1936; Joklik, 1950; Sullivan, 1951; Thomson, 1953), followed by the first airborne magnetic and radiometric surveys (Spencer, 1961). The first detailed studies of the mineral deposits in Cobar were undertaken by Rayner (1958); Russell and Lewis (1965); Rayner (1969); Kappelle (1970). Since then many other geologists tried to answer questions related to the genesis of the Cobar ore deposits and several genetic models have been proposed: (1) a hydrothermal replacement origin was suggested by Andrews (1913); Sullivan (1951); Mulholland and Rayner (1961); (2) syngenetic sediment-hosted models, some of them involving submarine exhalative origin, were proposed by Brooke (1975); Gilligan and Suppel (1978); Sangster (1979); Marshall et al. (1981); (3) Marshall and Gilligan (1993) suggested a hybrid model involving syngenetic ore formation and deformational epigenetic emplacement; (4) several authors supported an epigenetic hydrothermal replacement origin and syn-deformational ore formation for the Cobar deposits including the Elura, inter alia Schmidt (1980, 1990); Glen (1987); De Roo (1989b); Brill (1988); Hinman and Scott (1990); Scott and Phillips (1990); Perkins et al. (1994).

The main characteristics of the Cobar deposits are best compiled by Lawrie and Hinman (1998); Stegman (2001), highlighting and discussing the deposits’ similarities and differences. Lawrie and Hinman (1998) presented common features of the deposits clearly distinct from other know base metal systems, e.g. SEDimentary-EXhalative, Mississippi-Valley-Type, Irish-style or Broken Hill Type deposits. Some similarities between Cobar deposits and those of Tennant Creek were identified. According to Lawrie and Hinman (1998) the Cobar deposits formed as a consequence of mixing of two contrasting fluids, a basement derived oxidising and a basinal reduced fluid, during basin inversion or shortly after during subsequent relaxation. The loci for fluid focus and for ore precipitation are defined by dilation and fracture induced permeability along major fault and shear zones. Lawrie and Hinman (1998) furthermore precluded the possibility of mixing with a locally derived basinal fluid due to the low permeability of the lithified host rocks.

3.2.2 Contributions to the genetic model for the Elura deposit

On the basis of a detailed structural study of the upper main load zone at the Elura deposit, De Roo (1989b,a) suggested the ellipsoidal sulphide bodies formed predominantly via metasomatism and selective replacement of host sediments within hinge zones of a doubly plunging anticline. Infill of sulphide in fracture dilation did occur but was subordinate during sulphide formation. The anticline developed as a consequence of shortening in a compressional stress regime. Partitioning of deformation led to strain concentration and the development of shears along the limbs of the anticline. These shears acted as fluid pathways and micro-fracturing within the anticline due to vertical elongation created space for precipitation and allowed metal bearing fluids to flux to the site of ore formation. Compressional dissolution caused volume loss and dissolved material from the host rocks. Crack-seal mechanism and repeated influx of overpressured fluids into fracture zones are described as major processes during ore genesis. De Roo (1989a) suggested an early formation of a massive pyrite and silica body followed by further dilation and a second phase of sulphide, silicate and carbonate precipitation, including base metal sulphides. Schmidt (1990) discussed both, a replacement and a syngenetic origin. Considering

∗ With reference to other deposits in the Cobar region and the general genetic model for Cobar-style deposits
3.2 The current genetic model for the Elura deposit

the data and conclusions presented by De Roo (1989b,a) he preferred the former. Ore formation as replacement was induced by fluid to wall rock disequilibrium when the ascending metal bearing brine reached a certain level within the stratigraphic column. Temporal and/or spatial variability in fluid characteristics led to the development of the pronounced zonation of the orebody and alteration halo. He suggested furthermore that the different ore types at the Elura deposit had formed contemporaneous by replacement, progressively advancing upwards within the mineralising system. The pyrrhotite-dominated core zones reflect advanced replacement stages whereas peripheral siliceous ore represents are remnant early and immature stage.

Webster and Lutherborrow (1998) scrutinised the theory of a single anticline hosting the Elura orebody postulated by De Roo (1989b). Based on structural data obtained from oriented core intersecting the NNW-striking fold axis the authors concluded, that the simplistic view of the northern pods being hosted in domes within a doubly plunging anticline is difficult to confirm. Apart from a narrow zone of intense deformation and cleavage at the immediate orebody margin, they observed rather uniform structural settings for the orebody as well as for the surrounding country rock. Upon this observation the authors challenged the syn-deformational replacement origin and suggested the possibility of ore formation prior to deformation. They suggested that competency and rheology contrasts between host rocks and sulphides focussed strain and movement during later deformation represented in the earlier described intensely deformed marginal zone. Furthermore, the authors speculated that stratigraphic deeper sequences of CSA siltstone represent sources for base metals whereas gold and copper mineralisation in the Cobar deposits is linked to strongly faulted basin margins. The more distant Elura deposit compared to the other copper and gold dominated deposits, therefore contains only very minor levels of copper and almost no gold (Webster and Lutherborrow, 1998).

David (2008) proposed a genetic model that implies an early mineralisation in semi-lithified sediments during basin formation followed by deformation and modification during basin inversion. The author argued, that an epigenetic origin, as proposed by several authors (inter alia De Roo (1989b,a); Schmidt (1990); Lawrie and Hinman (1998); Stegman (2001), is unlikely due to: (a) the lithified nature of the host rock sequence characterised by low permeability, and (b) seismic pumping through lithified rock would create large zones of hydrothermal brecciation, which do not exist at Elura.

3.2.3 Age, metal source and physiochemical fluid characteristics

Radiogenic isotopes

The age of the Cobar Supergroup sediments, the host rocks for all of the Cobar deposits, is poorly constrained to the latest Silurian to Early Devonian based on paleontological chronology (Stegman, 2001). On the basis of $^{40}$Ar-$^{39}$Ar whole rock dating Glen et al. (1992) estimated the peak cleavage formation event during basin inversion had occurred between 395-400 Ma.

Pb-Pb isotopic data of sulphides available in literature (Pogson and Hilyard, 1981; Gulson, 1984; Carr et al., 1995; Sun, 2000; David, 2005), is very similar for all mineral deposits in the Cobar Basin. Due to their minor lead signature variations, Carr et al. (1995) proposed an isotopically uniform metal source or magmatic and hydrothermal processes causing homogenisation (Stegman, 2001). A recent study by Mernagh (2007) confirmed previous Pb isotope data. Isotopic ratios compiled from several sources range between 18.108-18.157 for $^{206}$Pb/$^{204}$Pb, 15.614-15.672 for $^{207}$Pb/$^{204}$Pb and 38.232-38.450 for $^{208}$Pb/$^{204}$Pb (David, 2008). Two lead sources are indicated by lead isotope signatures according to Lawrie and Hinman (1998), a basement and a basin component. Compared to Au-Cu deposits, those which are Pb-Zn dominated are characterised by a slightly more radiogenic lead signature, interpreted to reflect a predominance of a basi-
nal metal source. A basement source is proposed for Au-Cu deposits. Jiang et al. (2000) speculated that an initial lead accumulation had been facilitated by older granitic intrusion into the basement and was later remobilised by hydrothermal systems and released into the basin sequence. Sun (2000); Sun and Seccombe (2000) suggested a ternary mixing scenario for ore lead sourced from I- and S-type granites as well as from the Devonian Cobar Supergroup sediments. The difference in lead signature could also reflect an increasing age of the Cobar deposits from North to South as suggested by Stegman (2001).

David (2005) modelled a plombochronological formation age of 411 Ma for the Elura deposit based on the Lachlan Orogen growth curve from Carr et al. (1995). David (2008) noticed significant differences in lead isotope signatures (see figure 14, page 440 in David, 2008): (a) the lower main mineralisation (below level 6) is characterised by a rather uniform isotopic composition, (b) only one sulphide sample from the limestone mineralisation as the lowest part of the Elura system was analysed. This sample is significantly more radiogenic, expressed by an elevated $^{208}\text{Pb}/^{204}\text{Pb}$ ratio whereas the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are the lowest values observed, and (c) samples from the upper main mineralisation (above level 6) feature a linear trend originating near the cluster defined by (a) and a decrease in all three isotope ratios approaching $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of (b). The author explained these differences via variations in lead source mixing and concluded that initially the upper part of the mineralisation was formed via an undiluted mantle-derived fluid enriched in metals. Subsequently the lower part of the mineralisation formed from a mixed fluid, characterised by a basal fluid component and the initial fluid.

Based on recent data from the Elura Mine, Mernagh (2007) calculated a model age ranging between 440 Ma and 410 Ma years and identified at least four Pb isotope fractionation trends. These ages coincides with granite intrusion ages within the basement, estimated at 440 Ma to 415 Ma (Pogson and Hil-loyd, 1981). Mernagh (2007) suggested that $^{206}\text{Pb}/^{204}\text{Pb}$ signatures indicate an interaction with the Cambro-Ordovician sediments of the Girilambone Group.

The strontium isotope signature of sphalerite, siderite, ankerite and calcite was investigated by Sun (2000). Sphalerite and siderite, as mineral phases representing the ore-forming fluid, contain minor Sr (2.5-45.4 ppm) at high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.75501-0.83947). The highest Sr content was observed in calcite from veins and limestone (260.3-550.9 ppm) with substantially lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70936-0.72547). Variations of Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in alteration carbonates were interpreted to represent mixing of a hydrothermal and a marine sedimentary strontium source.

Sun (2000); Sun et al. (2000) dated sericite contained in massive sulphide samples within the Elura orebody via $^{40}\text{Ar}/^{39}\text{Ar}$ and identified two events at 385-389 Ma and 376-379 Ma. The former age resulted from cleavage-parallel sericite and was interpreted as reflecting a major deformational event, challenging the basin inversion age suggested by Glen et al. (1992); Perkins et al. (1994). The younger age range was suggested to represent the hydrothermal ore forming event, subsequent to peak metamorphic condition during continuing basin inversion.

Stable isotopes

Sulphur isotope studies on sulphide minerals form the Elura deposit have previously been performed by Sun (1983); Seccombe (1990); Sun (2000); David (2005); Mernagh (2007). The observed $\delta^{34}\text{S}$ enrichment sequence, i.e. pyrite $>$ sphalerite $\approx$ pyrrhotite $>$ chalcopyrite $>$ galena, indicates precipitation conditions near equilibrium (Ohmoto and Goldhaber, 1997). Those sulphide phases yielded $\delta^{34}\text{S}$ values between 4.7 and 12.6% with a mean of 8.1% (Seccombe, 1990). Seccombe (1990) calculated an average isotopic ore formation temperature of 275 °C based on sphalerite-galena pairs, and interpreted this temperature as a minimum value.
due to potential isotopic re-equilibration below peak metamorphic conditions. Isotope data suggests a mixed sulphur source from early Devonian Cobar Supergroup sediments and underlying Ordovician metasediments of the Girilambone Group (Seccombe, 1990).

Sun (2000) observed similar $\delta^{34}$S values for ore sulphides, but in a slightly narrower range (4.7 to 12.6‰, mean of 8.1‰). Distinctly heavier sulphur isotope signatures were identified for syngenetic disseminated and framboidal pyrite contained in the CSA host rock ranging between 9.5 and 20.1‰ (mean of 13.9‰). Sun (2000) suggested these $\delta^{34}$S values reflect seawater sulphate reduction as sulphur source. Isotopic temperatures calculated based on sphalerite-galena and pyrite-pyrrhotite pairs range between 220 and 449 °C. She concluded that the sulphur for ore formation was sourced from host rocks and a deeper crustal source. Stratigraphic horizons within the sedimentary basin fill that contain syngenetic and diagenetic pyrite, in places, up to significant quantities, has been observed at several localities (Stegman, 2001). Therefore, locally-derived sulphur seems highly likely as important source during ore formation.

The significant spread of sulphur isotopes in addition to relatively high values at Elura compared to other Cobar deposits which are characterised by rather low and uniform values, may indicate a significant proportion of sulphur being sourced from syngenetic/diagenetic pyrite from the host rocks. Jiang and Seccombe (2000) observed increases of $\delta^{34}$S and temperature values in the early sulphide paragenesis before dropping back to initial values and suggested these variations are responsible for the spread of $\delta^{34}$S signatures.

Investigation of carbon isotope signatures of calcite, ankerite and siderite led to a similar conclusion as for the sulphur isotopes (Sun, 2000). The $\delta^{13}$C variations are proposed to reflect mixing of a low $\delta^{13}$C component sourced from carbonaceous metasediments with a higher $\delta^{13}$C component from the underlying limestone and calcareous host rock sequences.

Hydrogen and oxygen isotope analyses were undertaken on chlorite, sericite and fluid inclusions hosted by quartz and sphalerite by Sun (2000); Jiang et al. (2000). Chlorite samples associated with early pre-base metal mineralisation exhibits isotopic signatures of a metamorphic fluid. The fluid linked to main base metal formation is characterised by a clear shift in isotopic composition towards lower $\delta^{18}$O values. Sun (2000); Sun and Seccombe (2000); Jiang et al. (2000) concluded that: (a) the ore forming fluid is of meteoric origin that circulated deeply with in basin and basement, thereby modifying its initial signature, (b) the isotopic data indicates limited fluid-rock interactions at high fluid fluxing rates without any magmatic contribution to the hydrothermal system, and (c) the data showed that two contrasting fluids were present at different paragenetic stages and therefore times, hence precluding a fluid mixing scenario as a mechanism for ore precipitation.

**Fluid inclusion studies**

Seccombe (1990) was the first to study fluid inclusion hosted in quartz at the Elura deposit. Inclusions had been visually recognised by Schmidt (1980). Analysed quartz grains were either intergrown with sulphide minerals or sourced from quartz veins in the wall rock. Two-phase, liquid-rich primary fluid inclusions of H2O-CO2-CH4 type were identified characterised by higher CH4/CO2 ratios in ore samples indicating reducing condition during ore formation. Neither N2 nor H2S were detected. The uncorrected homogenisation temperature ($T_h$) of fluid inclusions in massive and siliceous ore samples yielded two populations ranging between 150 to 231 °C (mean 188 °C) and 298 to 354 °C (mean 320 °C). Fluid inclusions hosted by quartz from extensional veins in wall rock are characterised by $T_h$ between 170 and 225 °C (mean 190 °C). Seccombe (1990) argued that due to missing high temperature mineral assemblages and results based on sulphur isotope thermometry, a pressure correction of the higher temperature fluid would insignificantly elevate the temperature and therefore is unnecessary. However, he suggested the need of pressure corrections for the lower temperature fluid in the
order of 110 to 150 °C. This would result in a $T_h$ raise to approximately 260 to 380 °C, temperatures similar to the other fluid population.

Seccombe (1990) concluded that the orebody is of metamorphic origin and formed as a consequence of host rock replacement accompanied by significant mass loss, in line with the suggested origin of De Roo (1989a). Chloride complexing in a CH$_4$ bearing fluid was suggested as mechanism for metal transport.

Lawrie and Hinman (1998) presented six stages of sulphide and alteration mineral parageneses and corresponding fluid inclusion data.

- **Stage (1)**
  
  carbonate + silicification + chlorite; no fluid inclusion data;

- **Stage (2)**
  
  crack-seal and breccia quartz veins + carbonate; H$_2$O + n-alkanes $T_h$ ranging between 120 and 160 °C;

- **Stage (3)**
  
  framboidal pyrite + quartz; H$_2$O + CH$_4$ + C$_2$H$_6$ + CO$_2$ $T_h$ < 220 °C (type 1 fluid); H$_2$O + Ca (type 2 fluid);

- **Stage (4)**
  
  quartz + pyrite + arsenopyrite + sphalerite; no fluid inclusion data;

- **Stage (5)**
  
  sphalerite + galena + pyrrhotite $\pm$ pyrite-serecte-chlorite-dolomite; H$_2$O + CH$_4$ + CO$_2$, $T_h$ 220-270 °C, max. NaCl$_{equiv}$ 13 wt%;

- **Stage (6)**
  
  argentian-tetra-hedrite + tennantite + enargite + chalcopyrite + galena + pyrite + Ba-feldspar + chlorite + albite; H$_2$O + CH$_4$ + CO$_2$, $T_h$ 330-380 °C, max. NaCl$_{equiv}$ 6 wt%.

Lawrie et al. (1999) studied fluid inclusions hosted in quartz and sphalerite via Raman Spectroscopy and thermal decrepitation mass spectrometry (TD-MS) in order to investigate the nature of hydrocarbon species. Samples of pre-mineralisation quartz veins and syn-mineralisation breccia veins were analysed. The fluid inclusions yielded $T_h$ of 110-230 °C and low to moderate salinities (2-5 wt% NaCl$_{equiv}$). Raman spectra of long chain n-alkanes were identified in pre-mineralising fluid inclusions whereas those of syn-mineralisation fluid inclusions are characterised by peaks for CO$_2$ and CH$_4$. Pyrobitumen occurs in inclusions in the vicinity of the main mineralisation and is interpreted to represent in situ thermal degradation of a hydrocarbon bearing fluids. TD-MS results showed that predominantly n-alkanes and minor H$_2$O, CO$_2$ and N$_2$ are released at lower temperatures, shifting to H$_2$O, CO$_2$ and N$_2$ towards higher temperatures. According to Lawrie et al. (1999) the results are supportive to the fluid-mixing model suggested by Lawrie and Hinman (1998). A positive correlation between increasing methane concentration and higher temperature and salinities was observed. Lawrie et al. (1999) concluded that: (a) the abundance of hydrocarbons in fluid inclusions precludes a local source from host rocks and rather suggests a basin wide maturation of organics, (b) the occurrences of various hydrocarbon species suggests their generation at different temperature and therefore different depths within the basin, and (c) potentially important mechanism for ore genesis are either organic complexing of zinc at low temperatures as metal transport and/or mixing of cooler hydrocarbon-rich fluid with a hotter zinc-rich fluid.

Sun (2000); Sun and Seccombe (2000) investigated fluid inclusions in quartz, carbonate and sphalerite hosted in massive and vein-style ore samples as well as from unmineralised quartz veins. Although using different mineral paragenetic stages as defined by Lawrie and Hinman (1998), a significant temperature increase was observed in stage 2 fluids with $T_h$ and salinities ranging between 268 to 374 °C (mean 318 °C) and 2.2 to
4.2 wt% NaCl$_{\text{equiv}}$ (mean 3.2 wt% NaCl$_{\text{equiv}}$), respectively. In stage 4, temperature conditions dropped to lower levels (mean $T_h$ 180 °C and mean 4.0 wt% NaCl$_{\text{equiv}}$), slightly increasing in stage 5 (mean $T_h$ 209 °C and mean 4.6 wt% NaCl$_{\text{equiv}}$) before reaching maxima in both, temperature and salinity, in stage 6. The last stage is characterised by $T_h$ between 130 and as high as 423 °C (mean 265 °C) and salinities between 2.2 and as high as 63.4 wt% NaCl$_{\text{equiv}}$ (mean 16.1 wt% NaCl$_{\text{equiv}}$). Sun and Seccombe (2000) suggested the mineralising hydrothermal system ramped up twice, once during peak metamorphism resulting in pyrite-dominated mineralisation (stage 1 to 3), and during a second later phase as the main ore forming event (stage 4 to 6). Fluid inclusions related to pre-mineralisation quartz veining are marked by a Na$^+$$>$ K$^+$$>$ Ca$^{2+}$$>$ Cl$^-$ $>$ Mg$^{2+}$ $>$ F$^-$ $\pm$ hydrocarbons (CH$_4$/CO between 0.27 and 1.58) chemical signature, whereas fluid inclusions associated with the main mineralising event shift to a composition characterised by Mg$^{2+}$$>$ Ca$^{2+}$$>$ Na$^+$$>$ Cl$^-$ $+$ F$^-$ $+$ K$^+$ $\pm$ hydrocarbons, characterised by increased CH$_4$ levels (CH$_4$/CO between 1.05 and 8.16). Calculated log $f_o_2$ values range between -58.69 and -28.27 and are more reducing than ore fluids at the Peak Mine (Sun and Seccombe, 2000). Sun (2000) argued that because of low and high temperature fluids occurring exclusively in different paragenetic stages, the two fluid mixing model proposed by Lawrie and Hinman (1998) and Lawrie et al. (1999) couldn’t be substantiated. She suggested ore formation was supported by decrease in temperature, rise in pH and an oxygen fugacity gradient characterised by an inward directed decrease towards the core zones of the massive mineralisation. High salinities of fluids are related to significant concentrations of Ca$^{2+}$ and Mg$^{2+}$. The enrichment of those elements (subsequently incorporated in siderite and ankerite) was established via alteration of calcite and dolomite contained in the host rock sequence. Jiang et al. (2000) also studied inclusions of the ore-forming fluid in sphalerite and identified moderate to high salinities ranging between 5 and 41.7 wt% NaCl$_{\text{equiv}}$ and $T_h$ between 200 and 343 °C. Fluids trapped in sphalerite are weakly acidic to alkaline (pH 5.72 to 7.51) and are enriched in F$^-$, Cl$^-$ and CH$_4$ relative to those contained in inclusions hosted by quartz.
3.3 Research objectives and methodology

At the Elura Mine, three different metal concentrates are produced in its mineral processing facility: zinc concentrate as the main product, lead-silver concentrate as secondary product and copper concentrate as by-product. In the past, the metal recoveries during the mineral processing stage at the Elura Mine were and still are fluctuating as a function of ore from different locations throughout the orebody being mined and mixed before differential froth flotation.

The tertiary zinc-lead-copper flotation process is a complex and highly sensitive mineral separation technique. The flotation recovery rate and the quality of the mineral concentrates are strongly affected by changes in whole rock geochemistry, ore mineralogy and mineral chemistry, in addition to the textural characteristics (e.g. grain size, grain shape, intergrowth, inclusions, ex-solutions, etc.) of the massive sulphide ore. Apart from regular metallurgical test work on material from the flotation feed and tailings, only limited studies on geo-metallurgical ore characteristics had been undertaken since production commenced.

The silver recovery (floated as a bonus metal within the lead flotation circuit) never exceeded values above approximately 50%. The 3-dimensional silver grade distribution is very well known and is modelled within the resource block model. However, the silver occurrence e.g. as discrete silver mineral phases, as solid-solution or as impurities in other sulphide phases, is only poorly understood. Consequently, the lack of this knowledge seems likely to represent the explanation for the low silver recovery rates. The copper concentrate represents only a minor by-product. However, due to indicated increases of copper concentrations within the Elura orebody as a function of mining depth, the copper flotation process might become increasingly important in near future.

Apart from the influence of the ore mineralogy for ore to concentrate metal recovery and subsequently directly influencing the mine economics, the mineralogy and more importantly the mineral chemistry and whole rock geochemistry are responsible for the quality of the mineral concentrate. That is, because of: (a) worthless mineral species are separated together with ore minerals, passively lowering the metal recovery rate; (b) penalty elements, for instance bismuth in the lead concentrate, actively lowering the quality and subsequently the value of the mineral concentrate.

Despite the obvious importance of those ore characteristics mentioned above, very little is known about them in general and basically nothing is known about their 3-dimensional spatial variability. This project will investigate the geochemical, mineralogical, mineral chemical and textural zonation of the Elura deposit based on a large set of samples taken throughout the orebody. By filling this gap in knowledge, a significant contribution to a better understanding of the ore forming processes will be made, and will in particular be a great benefit to the ore processing (i.e. milling, screening, flotation, etc.) at the Elura Mine. Furthermore, a detailed study at stope scale is undertaken in order to investigate local spatial changes of ore characteristics in the three dimensions, which have the potential of being significant for the mineral flotation process in respect to concentrate recovery rate and quality.

Although several research and mine geologists have studied and investigated the orebody in the past, the genesis of the Elura orebody remains contentious. Almost as many different genetic models were proposed as scientists had studied the deposit. As shown in the previous section, fundamentally two opposing genetic models have been proposed in the past: (1) a syngenetic, remobilisation model; and (2) an epigenetic syn-deformational model. Recently, David (2008) suggested significant similarities to Irish base metal deposits and proposed a diagenetic model. Therefore, based on a detailed study of the mineralogy, texture, mineral chemistry and geochemistry on a large selection of samples, the ore genesis of the Elura deposit will be investigated in this study.
3.3 Research objectives and methodology

A large set of data (in particular consisting of fluid inclusion, in addition to some stable and radiogenic isotope data) had already been acquired during the last three decades. It is unfortunate that these studies were rarely based on an adequately large sample set, considering the deposit’s large size and its pronounced heterogeneity. According to the previously formulated first research objectives, this study predominantly focuses on the economic proportion of the mineralising system (i.e. massive and semi-massive ore types) and on sulphide mineral phases. It is aimed to answer genesis-related questions by focussing on, for example, different isotopic systems and/or analytical techniques, not utilised in previous studies. However, some investigations, already undertaken in the past (e.g. analyses of fluid inclusion hosted in sphalerite), will be performed in order to confirm the legacy data and/or to improve vertical data resolution over the entire depth extent of the orebody.

The second research objective aims at improving the knowledge of: (a) the temperature and pressure conditions during, and (b) the time of the ore formation and/or emplacement. The integration of mineralogical, geochemical, isotopic and thermodynamic data may even help to gain a better understanding of: (a) the properties of the ore forming fluid(s), and (b) the potential metal sources.

It should be stressed that the entire Cobar Basin represents an enormous accumulation of lead-zinc-silver-copper-gold base metal occurrences. Coeval structurally similar deposits in Cobar region have to be genetically linked. An aim of this study is to fill the knowledge gaps in respect to ore characteristics and the genesis of the Elura deposit. By increasing the understanding of one ore deposit, the genetic model of the entire metallogenic province will be enhanced, directly linking into the improvement of mineral exploration techniques.

The research project was carried out in conjunction with the metallurgical department of the Endeavor Mine. An extensive sampling campaign had been executed for the purpose of a good overall 3-dimensional coverage of the entire orebody (see chapter 3 on page 59). In order to address the problems and questions outlined above, the following aspects and objectives were defined for this research project.

3.3.1 Petrography and texture of the massive sulphide mineralisation

A detailed knowledge about ore characteristics is of great importance for a successful mineral flotation process and for the production of a high quality mineral concentrate. Those characteristics can either directly or indirectly influence the mine production and the mineral recovery rate during the flotation process. Amongst the important petrographic and textural characteristics are: grain size (e.g. influences milling time), shape (e.g. elongated grains potentially inter-grown with different minerals specimen negatively affecting the flotation properties), intergrowths, inclusions, exsolution, sulphide banding, etc. Last but not least, the modal percentage of the sulphide mineral phases is of great importance, in particular the content of pyrrhotite. Pyrrhotite is a highly reactive mineral phase and easily oxidises on ore piles underground and on the run of mine stockpile. This \textit{in situ} oxidation creates consolidated ore (production losses and delays) and sulphuric acid which affects the pH in the flotation circuit and hence lowers mineral recovery rates.

Reflected and transmitted light ore microscopy, followed by particle mineral analysis and field scans via the application of the \textsc{QEMSCAN®} technique had be used to investigate those petrographic and textural characteristics mentioned above.

3.3.2 Mineral chemistry of sulphide ore phases

Similar to petrographic and textural ore characteristics, the mineral chemistry of sulphide phases is very important for the mineral flotation technique. That is because minor changes can result in significantly different mineral flotation characteristics. A profound knowl-
edge of the ore mineral and gangue mineral chemistry is also important for a successful application of the QEMSCAN\textsuperscript{®} technique. The trace element composition of sulphide minerals can furthermore indicate potential metal sources and the composition of ore forming fluids. Chlorite and arsenopyrite geothermometry will be used to further constrain temperature conditions during the mineralising event. Sphalerite geobarometry will help to estimate pressures either of ore formation or deformation.

If penalty elements have been identified via whole rock geochemistry, the knowledge of the mineral chemistry will help to identify the host mineral of those elements and the nature of their occurrence, e.g. as solid solutions, exsolutions, inclusions, or as individual mineral phases. Similar to penalty elements, the host minerals and the occurrence of silver will be determined via mineral chemical investigations.

### 3.3.3 Whole rock geochemistry

#### Major and trace element geochemistry

Major and trace element geochemistry will be used to acquire information about compositional variability of different ore types, the original host sediments and will be used to reconcile geochemistry to mineralogy. The analysis of trace element concentrations will contribute to the classification of the host lithology and will enable the identification of alteration/ore forming processes and potentially the origin of metal bearing fluid and metal source. Furthermore, trace element geochemistry will be used to identify penalty elements (e.g. bismuth) which have the potential of negatively affecting the quality of the mineral concentrate. The distribution of other elements might have an influence on the mineral processing.

#### Rare Earth Element geochemistry

Currently, the epigenetic syn-deformational model represents the genetic model with the highest acceptance within the research community. In this theory, the ore deposition is accompanied by significant replacement of the host sediments. Rare earth elements (REE) are incorporated in minerals like zircon and monazite which are highly refractory. These minerals are known to be not affected by hydrothermal alteration during ore formation and therefore should be preserved within the massive and semi-massive sulphide mineralisation. REE in combination with trace element concentrations and their distribution will be used in order to investigate mechanisms of ore precipitation. In contrast, hydrothermal carbonates (e.g. siderite) are also known to incorporate REEs to some extent, therefore should reflect the REE signature of the ore forming fluid. By comparing REE distribution patterns from unaltered country rock with those from orebody samples, information about the extent of replacement as well as the ratio between replacement and ore precipitation in open spaces (e.g. fractures, cavities) can be determined. REEs might also help to investigate physio-chemical features of the ore forming fluid.

#### Platinum group element geochemistry

A massive sulphide sediment hosted base metal deposit is under "normal" circumstances not a deposit style where someone would expect to find high concentrations of platinum group elements (PGE) and therefore were not investigated at the Elura deposit in the past. However, PGEs are quite mobile under certain conditions such as under an oxidising environment or via transport as chloride complexes (Wood, 2002). As a trial, the analysis of sulphide samples was proposed for this research project (approximately 5 to 7 samples). If PGEs have been identified and are at sufficient concentrations, the following information can be acquired:

(a) Timing of ore formation via Re-Os geochronology

(b) Fluid and metal source based on PGE distribution pattern and Re-Os isotopic signature.
3.3.4 Fluid characteristics and timing of the ore forming event

In the past, the deposits in the Cobar Basin including the Elura deposit were dated based on Pb-Pb and Ar-Ar techniques resulting in a significant age discrepancy for the genesis of the Elura deposit in the order of 35 Ma (based on oldest age defined by David (2005) and youngest age by Sun (2000); Sun et al. (2000). In order to better constrain the age of the mineralising event it is proposed to use isotopic systems previously not applied. Re-Os geochronology, which was successfully used for age determination on several sediment hosted base metal deposits, such as the Century deposit (Keays et al., 2006), the Tennant Creek deposits (McInnes et al., 2008) or the Red Dog deposit (Morelli et al., 2004). Keays et al. (2006) for instance was able to identify a two stage origin of the Century deposit, characterised by an early pre-concentration of ore-forming metals, followed by a later transportation and deposition via basinal brines. Alternatively, Rb-Sr isotopes in sphalerite have the potential to directly date the ore formation event (e.g. Brannon et al. (1992); Nakai et al. (1993); Christensen et al. (1995b,a); Schneider et al. (2003)). This technique is still quite experimental, however, it had been successfully applied on many occasions and accurately determined formation age of sulphide deposits.

Investigations of fluid inclusions hosted in sphalerite will determine fluid temperature, salinity and composition, and will particularly focus on their variability as a function of depth within the mineralising system.

Stable isotope signatures of hydrogen, carbon, oxygen and sulphur of various minerals in the Elura orebody have been studied in the past, some of them quite extensively. Rosman (1972) was the first person to investigate the isotopic and elemental abundances of zinc via thermal ionisation mass spectroscopy. Because of high analytical errors as a consequence of the very minor mass dependant isotope fractionation of zinc, the isotopic system remained unexplored until the late 1990s. Upon invention of the multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), a significantly higher analytical accuracy was made possible. A breakthrough in zinc isotope analytic was achieved by Maréchal et al. (1999) who, for the first time, was able to determine zinc isotope fractionation in nature on various samples, including geological materials. Since then, the stable isotope systematics of zinc gained increasingly more attention. However, the Zn isotope data pool for ore forming systems is still rather small and its isotopic fractionation mechanisms far from well understood. Its use for discrimination between different deposit types and for identification of important genetic mechanisms is therefore limited at this point in time. Nevertheless, as a trial and in order to make an effort to increase the isotopic data available to the research community, zinc isotope signatures of sphalerite are investigated as part of this PhD study.

3.4 Sampling

The main strategy for the sampling campaign was to: (a) achieve a good three dimensional coverage of the entire orebody, (b) take samples over the entire longitudinal and in particular depth extent of the mineralisation, and (c) sample each individual pipe versus depth with high sample density particularly in the main lode zone that represents the largest metal accumulation. Only fresh samples were taken, i.e. that were not affected by supergene processes. The two year life of mine plan from August 2008 was considered during the sampling in order to make direct use of the scientific outcome of this study for potential production and mineral processing related questions or problems. The achieved spatial sample coverage is visualised in figure 3.17.

Due to the pipe-like geometry of the individual massive sulphide bodies, which is rather narrow in several zones within the northern pods in particular having an east-west direction, a detailed sampling of their lateral zonation was not
feasible without significantly increasing the already substantial sample set (figure 3.17). However, the more or less concentric development of different ore types is rather similar for individual pods, although becoming more irregular towards the north. These ore domains are well constrained by the geological and resource model. The exact co-ordinate location of all samples and their geological context is well documented. Therefore, characterisation of different ore types will also give evidence of the nature of ore zonation.

Major difficulties and problems which were encountered during sampling were: (a) core from many diamond drill holes (DDH) is strongly weathered, in particular those containing pyrrhotite-rich ore, (b) several DDH are untraceable, and (c) sampling from underground (U/G) was not always possible because many areas have already been mined, have poor ground conditions, poor ventilation, ground failures or collapses. Subsequently, the ambitious target to sample each individual massive sulphide pipe was not possible. The main lode zone (ML) and the northern pods z1, z3 and z5 were sampled sufficiently over their depth extent (figure 3.17). Samples from other zones of the orebody were taken where possible.

The sample set consists of a total of 131 representative bulk samples from DDH and U/G. DDH composite samples were taken as quarter core over an approximately interval of 1-2 m in order to avoid excessive sample bias. Grab samples of homogeneous ore were taken from
3.4 Sampling

U/G in similar quantities as DDH samples. The equipment at the core storage facility at the Endeavor Operations Pty Ltd mine site and at the Department of Geology and Geophysics at the University of Adelaide were used for sample preparation. Samples were crushed in a jaw crusher to approximately 10-15 mm before being ground to analytical fineness in a chrome-steel swing mill. Samples were quarter split and an aliquot was used for major and trace element, REE and PGE geochemistry, one as spare and one as reference sample. Mineral separates were acquired via hand picking under the binocular microscope from sieve fractions of crushed sample material.

Out of this set of samples, 124 were analysed for whole rock geochemistry of major and trace elements, 34 were analysed for REE, 21 were used to extract sphalerite grains for Zn isotope investigations and 8 samples were used for PGEs and Re-Os dating. Samples for individual sub sets were chosen in order to cover all parts of the orebody and all ore types.

Petrographic samples (222) were taken from the bulk sample set as approximately 4 cm long quarter core or as 4x2x2 cm blocks. Uncovered polished thin-sections (133) were prepared at the Department of Applied Geosciences and Geophysics; chair of Resource Mineralogy; University of Leoben, Austria. A selection was used for microscopy, electron microprobe investigations and QEMScan analyses. Uncovered polished thick-sections for fluid inclusion studies and trace element studies via laser ablation ICP-MS were prepared from 19 samples.

The sampling and sample preparation for the ore characterisation study at stope scale is described in chapter 6 on page 199.
Chapter 4

Ore mineralogy and petrography

Detai\l\ed microscopy was undertaken to describe textural ore characteristics, identify the mineral phases and their grain size variability and to describe the paragenetic and temporal association. Electron microprobe analysis (EMPA) was used to determine the major and minor element composition of major sulphide mineral phases and their compositional variations with respect to different ore types and depth within the orebody (sample locations are shown in figure 4.1). Trace element concentrations, with particular emphasis on penalty elements that have a poor detection limit by EMPA and were determined by LA-ICP-MS.

4.1 Microscopic observations

Macroscopic observations from underground exposures and diamond drill core (DDH) throughout the orebody show significant changes in modal abundance demonstrating the highly heterogeneous nature of the ore. This variability is present on metre scales down to scales in the order of a few millimetres. The most noticeable sulphide texture is a distinct sulphide layering or banding on millimetre to centimetre scale defined by elongated areas enriched in sphalerite and pyrite, others by galena and, if present, pyrrhotite and minor chalcopyrite. Large patches, zones or veins significantly enriched in commonly coarse grained galena (in the order of a few millimetres in diameter) are encountered in several mine areas. Within the stringer vein type mineralisation at depth, sphalerite appears to be darker in colour, chalcopyrite tends to occur in greater abundances and the quantity of pyrrhotite exceeds that of pyrite.

Iron sulphides (i.e. pyrite and pyrrhotite) are the most abundant sulphide mineral phases at the Elura deposit. The presence of pyrrhotite, in addition to the occurrence and quantity of remnant wall rock fragments and quartz are used to define different ore types. Base metal sulphides occur in the following decreasing order of abundance:

Figure 4.1: EMPA sample locations; samples were selected in order to cover the entire depth extent of the orebody, all ore zones and ore types. Longitudinal view towards WSW (°245). Yellow shape is the stringer type ore (VEIN) resource domain.
dance: sphalerite > galena > chalcopyrite.

Iron carbonates and quartz represent the most important non-sulphide gangue (NSG) mineral phases. The former preferably but not exclusively occurs in massive ore types (Po and Py). Quartz gangue is predominantly observed in siliceous semi-massive ore types and massive pyritic ore (SiPy, SiPo and Py). Variable quantities of alkali-feldspar, albite, chlorite and sericite are related to metasomatism of wall rock as an in situ alteration or alteration of fragments embedded within sulphide groundmass.

Selected microphotographs and back scatter electron (BSE) images are presented in the following. Further images are shown in appendix A from page 270 (photomicrographs) and appendix A from page 311 (BSE images).

4.1.1 Sulphide gangue phases

Pyrite

Various pyrite species were observed and grouped according to their genetic nature and timing in respect to base metal mineralisation. Distant to the deposit, the CSA siltstone itself contains euhedral and framboidal syn-genetic/diagenetic pyrite at concentrations ranging between 0.25-0.7 wt% (Taylor et al., 1984). These pyrite varieties were not investigated in the course of this study.

**Colloform, framboidal and cloudy pyrite A** (pre-base metal)

Type A pyrite represents the earliest sulphide mineralisation. Microphotographs are shown in figure 4.2 (image a and b) and figure 4.3 (image a and b). Fine-grained cloudy pyrite is commonly in the order of a few microns in size and forms large euhedral aggregates containing abundant inclusion of NSG. The anhedral colloform pyrite generally forms large dense and rather homogeneous aggregates where grain sizes are oblique. Subordinate framboidal pyrite is observed as isolated grains or incorporated in larger pyrite aggregates of other pyrite varieties. These pyrite aggregates are commonly tectonised, as well as replaced and intruded by base metal sulphides. Intrusion and initiation of replacement by base metal sulphides along grain boundaries are common.

**Cataclastic pyrite B** (pre- to early syn-base metal)

Tectonised pyrite B is sub- to euhedral in shape and commonly strongly corroded at grain margins. Abundant inclusions of base metals, pyrrhotite and minor NSG phases are observed. These mineral phases intrude along fractures and grain boundaries, subsequently replacing pyrite. Grain sizes of pyrite B range between 10 and 500 µm with a visual median of approximately 50 to 100 µm. In places, pyrite B is intergrown with pyrite A forming large aggregates of millimetre size but also occurs as isolated porphyroblasts within a groundmass of pyrrhotite and base metal sulphides. Microphotographs are shown in figure 4.2 (image b and c) and figure 4.3 (image c and d).

**Syn-base metal pyrite C varieties**

Late syn- base metal pyrite C, in places, intimately intergrown with magnetite in a symplectic-like texture, occurs exclusively in assemblages with pyrrhotite (image e in figure 4.3). This pyrite C variety is characterised by grain sizes of approximately 5 to 20 µm and occurs as discrete grains commonly within a groundmass of pyrrhotite or may overgrow as well as replace pyrite B. Magnetite is commonly very fine grained in the order of a few microns. In places, larger grains of approximately 10-20 µm are present. Minor marcasite replacing pyrrhotite may occur in the vicinity of pyrite C.

A second pyrite C variety is found in pyrite dominated ore types. It is anhedral in shape, commonly forms grains between a few microns and up to ~50 µm and contains abundant inclusions of NSG phases and base metal sulphides. If present, pyrite C is commonly overgrowing pyrite A and B (image f in figure 4.3).
4.1 Microscopic observations

*Late recrystallised pyrite D (post-base metal)*

Euhedral pyrite D is entirely inclusion free, characterised by small grain sizes in the order of approximately 5-20 µm and is mostly associated with base metals, predominantly sphalerite. This pyrite type is completely unfractured and commonly overgrows earlier pyrite generations A-C or is associated with NSG (image a, b and f in figure 4.3).

*Pyrrhotite*

Pyrrhotite is the dominant iron sulphide phase in core zones of the Elura orebody. Those massive pyrrhotitic ore zones are commonly surrounded by semi-massive siliceous pyrrhotitic or massive pyritic ore. The occurrence of pyrrhotite is manifold:

(1) The vast majority represents the groundmass of massive and semi-massive siliceous pyrrhotitic ore. It is composed of equant sub- to euhedral grains forming a granular texture. Sizes of those pyrrhotite grains range between 20 to 50 µm and commonly feature 120° triple

---

**Figure 4.2:** Back scatter electron images of pyrite and its replacement: (a) Fine grained galena intruding and replacing colloform pyrite A along grain boundaries and fractures; minor argentian tetrahedrite is intergrown with galena; chalcopyrite occurs interstitial to pyrite (sample DE398; Py ore type; 9775mRL; ML zone). (b) A colloform pyrite A fragment intruded and replaced by sphalerite; pyrite A is partially overgrown by sub- to euhedral pyrite B (sample DE174-1-A; Po ore type; 10082mRL; ML zone). (c) Sphalerite, commonly intergrown with galena, is overgrowing and replacing strongly tectonised pyrite B (sample DE174-1-A; Po ore type; 10082mRL; ML zone). (d) Zone of framboidal and sub- to euhedral pyrite contained in weakly mineralised and altered wall rock. It is uncertain whether these pyrite grains are of hydrothermal or diagenetic origin. Both pyrite varieties are partially replaced by goethite. Minor low-iron sphalerite occurs interstitial to pyrite or within the strongly chloritised wall rock. Abundant iron carbonate is observed interstitial to pyrite (sample NP948-2-A; MinA ore type; 9185mRL; ML zone).
Figure 4.3: Reflected light microphotographs of the four pyrite varieties: (a) Sphalerite vugh filling in and partially replacing colloform pyrite A; tiny recrystallised euhedral pyrite D grains in centre of image; most base metal sulphides are sphalerite (medium grey) and minor occurrence of galena (light grey); arsenopyrite (whitish) is contained in the pyrite ground mass; sample DE007, Py ore type, 9959 mRL, ML zone. (b) Colloform pyrite B (yellow) is partially fractured; very minor occurrences of sphalerite (medium grey) and galena (light grey); locally, euhedral inclusion-free pyrite D overgrows pyrite A; NSG phases are iron carbonate (dark grey) and minor quartz (black), both occurring in vughs of colloform and frambooidal pyrite; sample DE218-2-B, Py ore type, 10076 mRL, ML zone. (c) Typical appearance of sub- to euhedral pyrite B, which is corroded and contains abundant inclusions of pyrrhotite (pink) and base metals; chalcopyrite (yellow), sphalerite (medium grey) and pyrrhotite (pink) occur interstitial to pyrite B; minor galena (light grey); sample NP767-2-B, Po ore type, 9354 mRL, z4 zone. (d) A single euhedral pyrite B grain (light yellow) is hosted by a matrix of sphalerite (medium grey), pyrrhotite (pink) and galena (light grey), which are intergrown in an annealed texture; pyrite B is weakly corroded and contains abundant inclusions of pyrrhotite, galena, minor sphalerite and chalcopyrite (yellow); sample NP549-2-A, Po ore type, 9313 mRL, ML zone. (e) Syn-base metal pyrite C (yellow) intimately intergrown with magnetite (medium grey) and surrounded by pyrrhotite (pink); sample NP767-2-B, Po ore type, 9354 mRL, z4 zone. (f) Compact pyrite (yellow) compound consists of pre-base metal pyrite A and coarser euhedral to subhedral pyrite B; euhedral and inclusion free recrystallised pyrite D is mainly observed within sphalerite (medium grey); minor occurrences of fine grained syn-base metal pyrite C; abundant euhedral to subhedral arsenopyrite (whitish); rare galena (light grey); sample DE007, Py ore type, 9959 mRL, ML zone.
4.1 Microscopic observations

junctons. In places, pyrrhotite appears to be replaced by base metals.

(2) Abundant inclusions of pyrrhotite are predominantly hosted by sphalerite and are commonly aligned along its crystallographic planes. Otherwise, pyrrhotite occurs along fractures in cataclastic pyrite type A and B. Grain sizes vary between a few microns and up to 50 µm. Small grains in sphalerite may represent exsolved grains whereas coarse grains are likely to be either linked to annealing of former tiny exsolved grains or are inclusions caused by contemporaneous mineral growth.

(3) The remaining pyrrhotite is generally intimately intergrown with base metals in a myrmekitic-like texture, clearly indicating contemporaneous growth of base metal phases and pyrrhotite. Grain sizes vary largely and range between a few microns and up to 100 µm.

Marcasite

Marcasite is observed in variable quantities in several samples throughout the entire depth extent of the orebody. In the uppermost parts of the orebody, former massive and semi-massive pyrrhotite-rich ore types are strongly altered, most likely due to supergene descending fluids. Most of this pyrrhotite is completely transformed into marcasite in a typical worm- or lamellae-like texture. A distinct marcasite banding is present in places where pyrrhotite occurred in a layered texture (i.e. pseudomorphous texture, example shown in figure 4.4). Marcasite fills interstitial spaces between pyrite A and B. This is a common texture of unaltered pyrrhotite indicating marcasite formation due to alteration of pyrrhotite. Furthermore, marcasite is preserved as small inclusions in sphalerite shielded from alteration fluids, whereas former pyrrhotite intimately intergrown with galena is completely transformed. With increasing depth, pyrrhotite to marcasite transformation becomes progressively incomplete and rather variable, commonly appearing in a “birds-eye-like” texture. In samples where alteration is minor, marcasite formation is clearly linked to iron carbonate veins and commonly progresses along grain boundaries of iron carbonates. Occasionally, marcasite appears to be associated with the formation of pyrite. It is not clear whether the transformation pyrrhotite > marcasite > pyrite took place or the formation of both phases are genetically unrelated.

Arsenopyrite

Arsenopyrite is present in all paragenic stages, ore types and throughout the entire orebody, but occurs in noticeable larger quantities towards the upper parts of the Elura orebody. Grain sizes vary significantly and range between a few microns and up to as large as 300 µm. Small grains tend to be anhedral in shape whereas larger grains are generally sub- to euhedral. Cataclastic textures are commonly observed. Most arsenopyrite is incorporated in large aggregates of pyrite, intergrown with pyrite A and B, but is also found intergrown with syn-base metal pyrite C. In other places, euhedral arsenopyrite is contained within iron carbonate veins. Some larger sub- to euhedral arsenopyrite grains carry
4. ORE MINERALOGY AND PETROGRAPHY

Figure 4.5: Euhedral zoned arsenopyrite with a homogeneous and corroded core; grain is weakly tectonised and contains abundant inclusions of iron carbonate; sample 500-ML-E-A, SiPy ore type, 9505 mRL, ML zone.

abundant inclusions of pyrite, pyrrhotite, base metal sulphides and siderite. Replacements of preferably large sub- to euhedral arsenopyrite grains by base metal sulphides and pyrrhotite are common. An alternating and rather thin growth zonation parallel to the crystallographic planes is observed in several arsenopyrite grains (figure 4.5). A second zonation pattern, characterised by a more irregular zonation, is overprinting the aforementioned pattern.

4.1.2 Base metal and silver phases

Sphalerite

Sphalerite is the most abundant base metal sulphide in the Elura deposit and is characterised by changes in iron content as indicated by its colour (between light brown-yellowish to dark brown). Low-iron sphalerite is primarily present in the upper parts of the orebody as well as in those of minor mineralised wall rock (MinA). Similar to all other sulphide phases, grain sizes vary largely and are in the order of a few microns and up to approximately 400 \( \mu m \) (figure 4.6). Sphalerite is very impure, containing abundant inclusions of siderite, chalcopyrite, pyrite, pyrrhotite, and occasionally galena. Sphalerite textures are variable, e.g. occurring as bands, elongated lenses, interstitial to pyrite, coarse and well defined crystals or intimately intergrown with pyrrhotite and other base metal sulphides in a myrmekitic-like texture. Commonly, pronounced sphalerite replacements of pyrite in general, and vugh or fracture fillings in pyrite A and pyrite B, respectively, are observed (figure 4.6 and image a in figure 4.3).

Galena

The most pronounced grain size variation of all identified mineral phases is exhibited by galena (figure 4.6). Grains as tiny as a few microns contrast with occurrences of large monomineral aggregates or patches up to tens of centimetres in size. These patches are composed of grains with maximum sizes in the order of a few hundred microns. Grains are strongly deformed in places as indicated by bending of cleavage planes. Galena occurs intimately intergrown with other base metal sulphides and pyrrhotite (figure 4.10), fills fractures in pyrite, or occurs in interstitial spaces of pyrite (figure 4.12). Fine-grained galena (2-10 \( \mu m \)) is present in highly altered wall rock fragments (image (a) in figure 4.14) and occasionally as inclusions in sphalerite.

Chalcopyrite

Apart from tetrahedrite, minor chalcopyrite represents the only copper-bearing mineral phase within the orebody. An increase in its quantity towards greater depths within the deposit is a characteristic feature. Fine grained chalcopyrite predominantly occurs as inclusions in sphalerite. These inclusions are likely to represent exsolutions if present as tiny randomly oriented grains smaller than or in the order of 1 \( \mu m \). Lamellae or elongated grains, predominantly occurring along crystallographic or cleavage planes of sphalerite, associated with pyrrhotite at times, are interpreted as intergrowths or replacements. Roundish droplet-like chalcopyrite grains with sizes ranging between 5 to 10 \( \mu m \) are likely caused by annealing of the aforementioned finer grained varieties. In general, chalcopyrite preferentially occurs in the vicinity of iron carbonates and/or quartz, characteristically
4.1 Microscopic observations

Figure 4.6: Significant grain size variation of sphalerite and galena: Galena occurs either as coarse patches or as thin veinlets intruding pyrite along fractures or grain boundaries (upper image); sample DE008-2, Po ore type, 9993 mRL, ML zone. Fine grained sphalerite is progressively replacing a compound of fine grained pyrite A (lower image); sub- to euhedral pyrite B is only replaced at grain margins; fractured arsenopyrite is intruded by galena (white); sample DE174-1-A, Po ore type, 10082 mRL, ML zone.

indicating an affinity to these NSG phases (image c in figure 4.14). Large patches of chalcopyrite up to 400 µm in size may be present preferably in siliceous ore types (SiPy and SiPo) or in breccia-stringer type ore (VEIN). Intimate intergrowths of chalcopyrite with galena and/or pyrrhotite are common.

Tetrahedrite and native silver

Coarse tetrahedrite with sizes up to approximately 200 µm is almost exclusively associated with galena (figure 4.7). It predominantly occurs in massive and semi-massive pyritic ore (Py and SiPy) in the upper 100-150 m of the main lode zone. The uppermost zones of the northern pods (z1 to z5) are enriched in tetrahedrite associated with galena in a similar manner as observed in the upper main lode zone. However, a significant grain size reduction down to maxima of around 15-20 µm is common in these zones. The preferred association with galena is not observed in the remainder of the orebody where manifold mineral associations and intergrowths are present, e.g. with pyrite, chalcopyrite, galena, siderite and quartz (figure 4.7). These tetrahedrite grains are generally in the order of a few microns and up to approximately 15 µm in size. Occasionally, triple junctions between sphalerite, galena, chalcopyrite and tetrahedrite are present, either indicating contemporaneous mineral growth or recrystallisation. Alteration of tetrahedrite to native silver and chalcopyrite is occasionally observed within samples from the upper ore zones. Dendritic native silver occurs in marginal areas of altered tetrahedrite grains. Whereas internally, silver forms tiny inclusions or is intimately intergrown with tetrahedrite in a reticular-like texture. These intimate intergrowths cause a pronounced grainy appearance in back scatter electron imaging. Other zones in altered tetrahedrite now consist of chalcopyrite. The alteration pattern is diffuse with tetrahedrite progressively transformed to chalcopyrite and/or native silver (see section 4.2.2 from page 93).

4.1.3 Non-sulphide gangue phases and altered wall rock fragments

Iron carbonate is the most abundant non-sulphide gangue mineral phase in pyrrhotitic and in most of pyritic ore. A general increase of quartz gangue is obvious towards peripheral zones, particularly in semi-massive ore (Py and Po). Quartz content in massive pyrrhotitic ore is very low. Changes in colour and refraction of iron carbonates observed in transmitted light indicate variability of their chemistry. The chemical variability of iron carbonate phases was qualitatively determined via energy disper-
Figure 4.7: Occurrences of argentian-tetrahedrite: (a) Coarse tetrahedrite is intergrown with galena and occurs as fracture filling within pyrite; BSE image, sample CAF-1LS-1-1, Py ore type, 10135 mRL, ML zone. (b) Very small tetrahedrite at the interface between galena and quartz; cogenetic mineral paragenesis consisting of sphalerite, chalcopyrite and galena, surrounded by pyrite, quartz and iron carbonate; BSE image, sample CAF-6z3-1-A, SiPy ore type, 9709 mRL, z3 zone. (c) Typical association between galena (light grey) with argentian tetrahedrite (greenish grey) found in the upper and peripheral zones within the orebody. These phases are either intimately intergrown with each other or tetrahedrite replaces galena. Commonly they occur as fracture fillings in pyrite (yellow) and associated with quartz-carbonate veins (dark grey); reflected light microphotographs, sample CAF-1LS-1-1, Py ore type, 10135 mRL, ML zone. (d) Tetrahedrite (greenish grey) associated with chalcopyrite (yellow), which is intergrown and possibly partially replacing pyrrhotite (pink), galena (light grey), sphalerite (medium grey) and tetrahedrite; the initial association of galena and tetrahedrite is still preserved in some places; reflected light microphotographs, sample NP870, Py ore type, 9694 mRL, z5 zone.

Siderite and ankerite were identified as the most common iron carbonate phases.

Quartz commonly shows undulatory extinction and occurs together with iron carbonate interstitial to, and as vugh or fracture filling in sulphides. Veins and stringers composed of quartz and/or iron carbonates are common and characterised by varying thicknesses (i.e. between a few microns and up to several hundreds of microns). Quartz and iron carbonate veins occur throughout the entire paragenetic sequence and the time relationship of different vein-generations is complex.

Wall rock fragments embedded in sulphide groundmass are generally strongly affected by chloritic, sericitic and iron carbonate alteration, and, in places, are highly silicified (image a in figure 4.14). Chlorite and sericite preferably occur in former muddy or silty layers, whereas siderite generally occurs in sand-rich beds, replacing quartz in variably intensities. Base metal and iron sulphides are present within many of these fragments. Those fragments are almost exclusively found in peripheral zones of semi-massive ore types (SiPy and SiPo). Pervasive siderite alteration in the form of siderite porphyroblasts (~0.5 to 8 mm) occur in a halo surrounding the orebody or proximal to sulphide veins (figure 3.12). In minor mineralised wall rock (MinA) proximal to the mineralisa-
4.1 Microscopic observations

Replacement of these porphyroblasts by sphalerite is observed (figure 3.8). Subordinate alkali-feldspar and sodium-rich plagioclase is recognised in altered in situ wall rock or wall rock fragments embedded in sulphide groundmass. Feldspars commonly exhibit numerous tiny inclusions of sericite, calcite and chlorite, as a result of alteration.

Minor goethite occurrences are present in all ore types but have been observed particularly in those of pyritic dominance (figure 4.8). It preferably replaces siderite along grain boundaries and fractures mostly as coarser anhedral radial mineral aggregates (several tens of microns) or thin veinlets in the order of a few microns. Minor sub- to euhedral goethite intergrown with iron carbonate is observed in veins or as interstitial filling between pyrite. Occasionally, tetrahedrite is associated with goethite. Barite is a common, but a minor mineral constituent (figure 4.8). Galena may be partially altered to cerussite in the uppermost parts of the orebody affected by supergene processes (image d in figure 4.8).

Subordinated magnetite is exclusively associated and intimately intergrown with pyrite type C. The co-genetic association between pyrrhotite, pyrite and magnetite is very rare. Magnetite grains are very small (commonly below 10 to 15 µm and may be mixed up with sphalerite and or Fe-hydroxides. In order to ensure correct visual identification, mineral composition of the supposed magnetite shown in figure 4.3 (image e) was determined via electron microprobe analyses (see section 4.2 from page 91).

![Figure 4.8: Various non-sulphide gangue (NSG) phases in reflected (a) and transmitted (b) microphotographs (sample DE398, Py ore type, 9775 mRL, ML zone), as well as in BSE images (images c and d; sample DE306, Py ore type, 9713 mRL, ML zone). Goethite (centre of images a and b, medium grey in RL, reddish in TL, both parallel nicols) is replacing iron carbonate (black). For comparison, low iron sphalerite occurs on the right image margin, featuring almost similar reflectance and colour in RL but shows only weak yellowish colouring in TL. (c) Quartz, iron-carbonates and chlorite are the most common NSG phases. Minor occurrences of goethite and barite are observed, the former partially replacing pyrite. (d) Alteration of galena to cerussite is limited to the uppermost parts of the orebody.](image-url)
4. ORE MINERALOGY AND PETROGRAPHY

4.1.4 Ore type specific characteristics and textures

Massive pyrrhotitic ore (Po)

Significant pyrrhotite quantities and pyrite of all varieties are present in this ore type (typical examples shown in figure 4.10). In mine geology, ore classification is based on visual identification of pyrrhotite and the empirically identified intensity of sample magnetism via hand magnet. Pyrrhotite content in this ore type varies significantly. Classification is not strictly constrained and needs to be understood as diffuse transition from pyritic to pyrrhotitic ore. However, most investigated thin sections of the latter ore type contain at least 5 to 10 wt% pyrrhotite, some in excess of 50 wt%. Pyrrhotite commonly represents the sulphide groundmass or is intimately intergrown with base metal sulphides, in places, in an annealed texture. These tight intergrowths are characteristic for this ore type and may be very fine at grain sizes below 10 µm. In areas of intense sulphide banding, pyrrhotite is either intimately intergrown with galena and/or chalcopyrite, or it forms almost monomineralic layers.

Partial transformation of pyrrhotite to marcasite is present in several samples and observed even in the lowermost part of the ore body at depths of almost up to 1,000 m below surface. In contrast, complete transformation is limited to the uppermost areas in the main lode zone. A spatial relationship between occurrences of symplectic pyrite C with beginning marcasite alteration is indicated in some samples. Furthermore, partial pyrrhotite-marcasite transformation is also present in transitional zones between pyrrhotite and pyrite-dominated ore zones. Pyrite abundances vary, with type B significantly exceeding that of pyrite type A. Pyrite C and D commonly represent minor constituents. Pyrite B is strongly corroded and, in places, features a pronounced cataclastic texture. The grains contain abundant inclusions of, and are intensely replaced by base metal sulphides in addition to pyrrhotite. These mineral phases are present along fractures. Pyrite C is intimately intergrown with magnetite in a symplectic-like texture, present exclusively in samples of massive pyrrhotitic ore.

Sphalerite is commonly medium to dark brown in colour and rather impure due to abundant inclusions comprising NSG (i.e. predominantly iron carbonate), pyrrhotite, minor galena and chalcopyrite. The abundance of inclusions is variable. Chalcopyrite inclusions in sphalerite are more abundant compared to pyrite dominated ore. In samples featuring sulphide banding, layers significantly enriched in sphalerite are observed. Galena is commonly associated with pyrrhotite or occurs interstitial to pyrite and is characterised by a pronounced grain size variability. Chalcopyrite is preferably associated with iron carbonate. Otherwise it occurs as inclusions in sphalerite or interstitial to pyrite. Tetrahedrite is rarely observed microscopically and appears in very small grain size (i.e. 5 to 10 µm).

General features of sulphide banding are defined by layers enriched in: (1) pyrite with pronounced occurrence of galena and/or chalcopyrite in interstitial spaces; (2) galena, pyrrhotite and occasionally chalcopyrite; and (3) inclusion-rich sphalerite. Layers (2) and (3) are either rather continuous or occur as elongated lentoidal bodies, or reminiscent of pinch-and-swell textures. A mylonitic texture is observed in samples featuring intense sulphide banding. This texture is characterised by the occurrence of rounded clasts of sphalerite either isolated in layers composed of pyrrhotite and galena or within sphalerite-rich layers.

Massive pyritic ore (Py)

Pyrite is by far the most dominant iron sulphide mineral species, and represents the major sulphide phase in general (typical examples shown in figure 4.12). Locally, traces of pyrrhotite may be observed. Former pyrrhotite affected by complete transformation to marcasite is observed in samples taken from the uppermost central parts of the main lode zone. These areas are classified as pyritic ore type, although in genetic terms, they would need to be viewed as pyrrhotite-rich ore. Traces of pyrrhotite may
4.1 Microscopic observations

Figure 4.10: Typical examples of massive pyrrhotitic ore and its textural characteristics (reflected light images). (a) Pyrite B (yellow) dominates over pyrite type A and occur in a pyrrhotite (pink) rich zones. In this image, only pyrite B is observed, which is fractured, strongly corroded and contains abundant inclusions of sphalerite (medium grey), chalcopyrite (yellow) and galena (light grey). Pyrrhotite is intimately intergrown with sphalerite. A weak sulphide banding is observed, indicated by the elongated sphalerite rich zone; sample NP776-2, 9334 mRL, z3 zone. (b) Intimate myrmekitic intergrowths of sphalerite (medium grey), galena (light grey) and pyrrhotite (pink); euhedral to subhedral pyrite B is corroded and commonly contains inclusions of base metals; sample NP245-1, 9613 mRL, z4 zone. (c) Weakly developed sulphide banding is defined by elongated grains of galena (light grey) in a matrix consisting of pyrrhotite (pink); rounded clasts of sphalerite (medium grey) without preferred orientation. Minor iron carbonate (medium-dark grey) and quartz (dark grey) as NSG phases; sample NP767-2-A, 9354 mRL, z4 zone.

be preserved in sphalerite. All pyrite types are present with pyrite A and B as the most abundant species, and within those types, pyrite B subordinate to pyrite A. Very fine grained syn-base metal pyrite C is likely to have formed in low quantities, however, microscopic identification and quantification is difficult. Similarly to pyrrhotitic ore, pyrite D is common but occurs in minor quantities. Pyrite A and B are generally intruded and replaced by base metal sulphides, either along fractures or grain boundaries. In places, primary colloform or framboidal textures are preserved.

Grain sizes of base metal sulphides vary and may be rather fine (sub-micron to 10 \( \mu m \)) if occurring in interstitial space between pyrite or in narrow fractures. Most sphalerite is coarser compared to galena. It occurs as bands and lenses at grain sizes in the order of a few to several tens of microns but may be larger than 200 \( \mu m \). The colour of sphalerite is medium to dark brown. A shift to slightly lower iron content compared to sphalerite in Po ore is indicated. Tiny inclusions of chalcopyrite are occasionally present in very minor quantities. Galena is present as large patches in excess of 200 \( \mu m \) but may be as fine as less than one micron in size. Chalcopyrite concentration is generally low but highly variable, absent in most areas but relatively enriched in others. If present it is associated with galena but preferentially occurs in zones rich in NSG (quartz/carbonate...
Figure 4.12: Typical examples of massive pyritic ore and its textural characteristics (reflected light images). (a) Tectonised compounds of pyrite A (yellow) intergrown with abundant sub-to anhedral arsenopyrite (whitish) and intruded as well as replaced by sphalerite (medium grey) and galena (light grey). Both phases are almost perpendicular to each other. Subordinate euhedral to subhedral pyrite B at rather small grain sizes; quartz occurs in minor quantities; sample CAF-1LS-1-1, 10135 mRL, ML zone. (b) Left side of image: zone of tectonised coarse euhedral pyrite B (yellow) in a NSG groundmass predominantly composed of iron carbonate (dark grey) and subordinate quartz (black); minor sphalerite (medium grey) and galena (light grey) occur interstitially to pyrite or intrudes and partially replaces it. Right side of image: zone is predominantly composed of cloudy pyrite A, in places, overgrown by anhedral pyrite C and euhedral pyrite D. Minor occurrences of tectonised subhedral pyrite B, partially replaced by base metal sulphides. Arsenopyrite (whitish) is intergrown with pyrite; sample DE008-3, 9937 mRL, ML zone. (c) Tectonised fragment of rather compact pyrite (light yellow) composed of pyrite type A. Fracture is filled by sphalerite (medium grey), chalcopyrite (yellow) and galena (light grey); ground mass consists of finer grained cloudy pyrite type A and minor sub- to euhedral pyrite type B and D. Base metals occur interstitial to pyrite A and C; minor type D pyrite occurs in sphalerite; abundant arsenopyrite (whitish); quartz (black) as none sulphide gangue (NSG) phase; sample DE007, 9959, mL, ML zone.

veins). Tetrahedrite is most common in pyritic-dominated ore as trace mineral phase. In the upper and peripheral parts of the main lode zone it is almost exclusively associated with galena, exhibiting commonly large grain sizes in the order of 200 µm. In most other zones within the ore body, a significant grain size reduction down to approximately 5-20 µm is observed. Here, tetrahedrite is not necessarily associated with galena but is observed to be intergrown with sphalerite and chalcopyrite. Pyrrhotite may be associated with tetrahedrite in transitional ore zones close to massive pyrrhotitic ore.

Locally-developed sulphide banding is not as pronounced when compared to pyrrhotitic ore. The nature of preferred orientation of layers or lenses enriched in different base metal sulphides is controlled by brittle deformation, whereas sulphide banding in Po ore preferably exhibits ductile features. The brittle nature of pyrite deformation is expressed by an almost perpendicular alignment between sphalerite-rich layers or lenses, and dilational fractures in pyrite filled with galena. Galena appears to be deformed in some areas. Sphalerite rich layers are impure and contain abundant inclusions of pyrite, NSG (predominantly iron carbonate) and minor galena.
Semi-massive siliceous ore (SiPy and SiPo) and breccia-stringer type mineralisation (VEIN)

The main difference between the siliceous semi-massive analogues of the previously outlined massive sulphide ore types are higher quartz content and the occurrence of wall rock fragments. Those fragments are incorporated in the sulphide groundmass and commonly strongly altered and replaced. Ore textures and sulphide pargeneses are similar (figure 4.14).

Base metal sulphides in SiPo ore are commonly intimately intergrown. An- to subhedral quartz and iron carbonate are the most important NSG phases in both ore types. Chalcopyrite preferably occurs within or proximal to NSG. Locally, pyrrhotite is completely transformed to marcasite. These zones are now classified as SiPy but textures are similar to pyrrhotite dominated ore types. Pyrrhotite to marcasite transformation appears to be intensified in siliceous compared to massive pyrrhotitic ore. SiPy is dominated by variably fractured pyrite A and B.

Wall rock fragments are generally strongly altered. Sericite and chlorite are abundant but appear to occur preferably in former mud- and siltstone rich layers. Iron carbonates and base metal sulphides are commonly present in sandstone rich layers, partially to completely replacing quartz. The fragments may be, in places, strongly silicified in particular in semi-massive
ore at greater depths.

The borderline-economic breccia-stringer type mineralisation (VEIN) is characterised by reticular quartz-iron carbonate-sulphide veining hosted by brecciated and strongly altered CSA wall rock. The shell of VEIN surrounding semi-massive and massive ore is rather narrow in most zones of the orebody (see chapter 3 on page 39). At depth below approximately 9300 mRL, the zone becomes more prominent accompanied by pronounced and widespread silicification and iron carbonate alteration. The sulphide stringers contain abundant chalcopyrite in these zones, particularly beneath the massive sulphide pipes.

The prevalence of iron sulphide species and the base metal sulphide content vary between locations. The intensity of alteration generally increases towards zones of intensifying sulphide veining. Proximal to those veins, former CSA siltstone wall rock is entirely replaced by iron carbonates, quartz, sericite and chlorite. Altered wall rock fragments are occasionally observed within these veins and are hosted by a matrix composed of sulphide phases.

Contents of pyrrhotite, chalcopyrite and iron-rich sphalerite are elevated in stinger ore proximal to and below the sub-vertical ore shoots. Further distant to these core zones, iron in sphalerite decrease and pyrrhotite is commonly absent. Similarly, the intensity of wall rock alteration decreases. Chalcopyrite may still occur in relatively large quantities, even rather distant to core zones. Pyrite content is variable but generally low and type B is more abundant than A. Pyrite is strongly corroded and replaced by base metal sulphides and, in places, appears rounded.

4.1.5 Mineral paragenesis

The mineral paragenesis relative to the different pyrite varieties observed during microscopic investigations is described. It is obvious that the sulphide ore body has been modified during deformation. Many sulphide mineral phases, in particular galena, pyrrhotite, and chalcopyrite and to a lesser extent sphalerite, were strongly remobilised. In contrast, pyrite, as a brittle mineral phase, was fractured and, in places, significantly tectonised. Primary mineral intergrowths were lost in many areas as a consequence of deformational induced remobilisation, thus concealing the initial mineral paragenesis. Nevertheless, several observations were made that indicate the sequence of mineral formation and are summarised below. The mineral paragenesis of the Elura deposit is shown in figure 4.15.

- Sphalerite, galena and chalcopyrite are clearly associated and commonly intimately intergrown with pyrrhotite which is by far the most abundant iron sulphide phase during the main stage of base metal formation. Intergrowths of tetrahedrite with galena are common, thus contemporaneous.

- Pre-base metal pyrite A is fine grained, fractured and occurs as colloform, frambooidal and cloudy varieties. Replacement of pyrite A by sphalerite and galena has been observed but no primary intergrowths or mineral associations are present. This pyrite variety clearly formed prior to the main stage of base metal precipitation, most likely from a lower temperature hydrothermal fluid.

- Coarse cataclastic pyrite B is observed within pyrite (Py and SiPy) and, in places, in pyrrhotite dominated ore zones (Po and SiPo). Strong replacement by and inclusions of base metal sulphides and pyrrhotite were observed. Most inclusions appear to be not primary. They are interpreted to represent internal replacements as the metal bearing fluid migrated along abundant fractures and fissures within the cataclastic pyrite B. It needs to be kept in mind that the formation of large ore bodies such as Elura is a consequence of a prolonged and continues process where the hydrothermal system evolves over time, characterised by changes in fluid temperature and chemistry. The formation of pyrite B is interpreted to have occurred in a period when the fluid temperature in-
4.1 Microscopic observations

Increased and when base metal concentrations began to increase. The main stage of base metal formation is dominated by pyrrhotite. Thus, pyrite B formed pre- to early base metal mineralisation.

- Minor pyrite C is overgrowing pyrite A and B in pyrite dominated ore zones. It contains abundant inclusions of base metal sulphides. In pyrrhotite dominated ore, pyrite C is rare and, in places, intimately intergrown with magnetite. This pyrite variety is post pyrite A and B and contemporaneous with base metal precipitation. Due to its low abundance, pyrite C formation is interpreted to have occurred during the latest stages of the main base metal formation event and prior to its cessation. The presence of rare magnetite-pyrite intergrowths closely associated with pyrrhotite indicates a changing fluid chemistry towards higher oxygen fugacity during the very latest stages of ore formation.

- Pyrite D is entirely free of inclusions, unfractured and commonly overgrowths pyrite varieties A and B. Pyrite D formation is interpreted to have occurred after the base metal event during a later fluid influx event accompanied by the recrystallisation of earlier pyrite.

- Meteoric fluids that interacted with sulphides within the shallow supergene zone became acidic and caused transformation of pyrrhotite to marcasite. Partial transformation is observed even within the deepest parts of the orebody. No primary marcasite has been noticed. Minor alteration of tetrahedrite to native silver within primary sulphide mineralisation is also likely to be caused by meteoric fluids that descended from surface along fracture zones.

- Arsenopyrite is associated with pyrite A and B as well as with base metal sulphides. It formed during the early pyrite dominated hydrothermal stage and during the main
4. ORE MINERALOGY AND PETROGRAPHY

base metal formation event.

- Quartz, ankerite and siderite represent the most abundant none-sulphide gangue mineral phases. The early pyrite alteration stage (formation of pyrite A) is dominated by quartz, progressively shifting to ankerite and siderite as the hydrothermal fluid became enriched in base metals. Minor goethite is present in iron carbonate veins in peripheral zones of the orebody.

- Chlorite and sericite are common hydrothermal alteration phases in remnant wall rock fragments within semi-massive ore types. It was not possible to establish a clear timing relative to sulphide formation in the course of this study. Most probably the mineral phases formed during the entire period of hydrothermal activity.
4.2 Electron microprobe analyses

The chemical compositions of major sulphide mineral phases in various ore types were determined using electron microprobe analysis (EMPA). Major sulphide phases were analysed in 44 samples (see figure 4.1 for sample locations). Seven additional samples were chosen in order to increase the data set for analyses of galena. Chlorite composition was determined on 9 samples and used for geothermometric calculations. All samples were polished thin sections with analyses performed at the Department of Applied Geosciences and Geophysics, University of Leoben. The selected samples were from locations throughout the entire orebody in order to establish data coverage of all ore types and ore zones, although primarily focussing on the entire depth extent of the main lode zone (table 4.1; figure 4.1). Samples were also selected from the rather small northernmost z6 pod (2) and from the western mineralisation (2).

EMPA were conducted on a JEOL Superprobe JXA 8200 at 20 kV acceleration voltage and 10 nA probe current for sulphide phases and 15 kV acceleration voltage at the same probe current for chlorite analyses. The achieved minimum, average and maximum lower detection limits are summarised in appendix A on page 332. Analyses are corrected via ZAF and PRZ methods. Standards, peak position and corresponding element concentrations used for calibration are given in table 4.9.

The entire data set of high quality EMPA results, i.e. correct stoichiometry and total element concentration, is presented in appendix A on page 332.

<table>
<thead>
<tr>
<th>Lithology</th>
<th>ML</th>
<th>z1</th>
<th>z2</th>
<th>z3</th>
<th>z4</th>
<th>z5</th>
<th>z6</th>
<th>W-min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Po</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Py</td>
<td>11</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiPo</td>
<td>3</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>SiPy</td>
<td>1</td>
<td>2</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Vein</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>24</td>
<td>7</td>
<td>4</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Number of samples taken from different ore zones and ore types.

4.2.1 Compositional variability of sulphides throughout the Elura orebody

Sphalerite

Macroscopic and microscopic observations indicate significant chemical variability with respect to iron content in solid solution with zinc. Abundant inclusions of several other mineral phases (e.g. chalcopyrite, pyrrhotite, pyrite, NSG, etc.) were encountered, potentially negatively effecting analytical quality. All EMPA results of sphalerite (total of 275) were scrutinised based on totals and stoichiometry, 252 considered as valid (summarised in table 4.2).

Optical identifications were confirmed by EMPA. Iron content in sphalerite significantly varies and ranges between 2.41 and 8.22 wt%. High-iron sphalerite is common in the lower mineralisation whereas sphalerite from the upper part of the ML zone and the vein style mineralisation further distant to the orebody is characterised by less iron substituting for zinc (figure 4.17). The three deepest samples were taken from deepest zones of but peripheral to the orebody, thus feature lower iron content.

Consistently high iron content with a median of approximately 7 wt% is observed in pyrrhotite-dominated ore types (figure 4.16). The chemical composition of sphalerite contained in pyritic ore types as well as those in...
lower grade MinA and VEIN ore strongly varies throughout the entire observed iron concentration range (figure 4.16). The iron content in sphalerite of pyritic massive ore appears bimodal. However, if the entire data set excluding pyrrhotite dominated ore types is considered the bimodal distribution becomes less obvious. Manganese was detected in some samples at very low concentrations close to the detection limit (median 400 ppm). Cadmium concentrations are relatively low (median 1800 ppm) and rather consistent in all different ore types. A weak trend of higher cadmium towards increasing depth is present (figure 4.18).

Mercury and Bi were detected in 33 and 40% of all analyses at concentrations ranging between 0.12 to 0.48 wt% and 0.03 to 0.16 wt%, respectively. Copper was detected at a median concentration of 700 ppm although only 27% of all analyses are above the detection limit. Some Cu may be incorporated in the sphalerite lattice, outliers of high concentrations (maximum 1.46 wt%) are most probably caused by micro-inclusions of chalcopyrite. Indium and Au are detectable in only 7% of analyses, their concentrations are barely above the average detection limit of 163 and 494 ppm, respectively. Nevertheless, the observed maximum concentration of gold is significant at 0.21 wt%. Other elements are detected at concentrations close to the detection limit, with most analyses falling below it.

**Galena**

In late 2008, the first time since mining commenced in 1983, lead concentrate from Elura was significantly enriched in bismuth. Part of
4.2 Electron microprobe analyses

this study focuses on the investigation and identification of the source for Bi. Discrete Bi mineral phases are reported to occur in other deposits in the region.

No potential Bi phases were encountered during microscopic observations. Considering that Bi is enriched in the lead concentrate and the fact that no other Bi mineral phases are identified, the possibility of Bi enrichment in galena seems self-evident. The concentration of Bi in galena, its distribution and spatial variability throughout the orebody was one of the areas investigated.

A total of 441 points were analysed, 407 deemed to be of high analytical quality based on stoichiometry and total element concentrations (table 4.3). Bismuth is above the lower detection limit in 85% of all analyses at a median concentration of 0.28 wt% and as high as 0.85 wt%. A clear enrichment trend of Bi incorporated in galena with increasing depth below surface is present (figure 4.20). The deepest two samples do not fit this trend. These samples are low grade ore (MinA and VEIN) and are not directly part of the massive sulphide orebody. The pronounced variability of Bi concentrations in galena suggests that these concentrations are not artificial, i.e. caused by interference with lead intensity peaks. Galena seems to contain higher levels of Bi in pyrrhotitic-dominated ore types (figure 4.19).

Qualitative wavelength dispersive element mapping indicates that Bi is predominantly evenly distributed within galena as shown (figure 4.22; Sample NP549-1-B, SiPo ore type, 9323 mRL, ML zone). This distribution and the similar atomic radius of Pb and Bi suggest its occurrence as solid solution rather than micro inclusions. However, four tiny areas elevated in Bi are present, each around 1 to 3 µm in size (figure 4.22). These areas coincide with enrichments of either Ag or Sb, suggesting the presence of sulfosalt inclusions or intergrowths. Occurrences of discrete Bi mineral phases were investigated by element mapping of a larger section area of one sample (Sample NP910-2-B, SiPy ore type, 9237 mRL, ML zone). The sample was selected based on whole rock geochemistry that showed high levels of Bi, i.e. 171 ppm. All areas elevated in Bi concentration coincide with galena (figure 4.21). No potential Bi-phases are observed.
4. ORE MINERALOGY AND PETROGRAPHY

<table>
<thead>
<tr>
<th>Sphalerite</th>
<th>Major</th>
<th>Traces and impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 252</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>Fe</td>
</tr>
<tr>
<td>Max [wt%]</td>
<td>64.60</td>
<td>8.22</td>
</tr>
<tr>
<td>Mean [wt%]</td>
<td>60.70</td>
<td>5.76</td>
</tr>
<tr>
<td>Median [wt%]</td>
<td>59.85</td>
<td>6.68</td>
</tr>
<tr>
<td>Min [wt%]</td>
<td>57.12</td>
<td>2.41</td>
</tr>
<tr>
<td>n analysed [%]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>n &gt; LDL [%]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Avg. LDL [ppm]</td>
<td>344</td>
<td>206</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Galena</th>
<th>Major</th>
<th>Traces and impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 407</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>S</td>
</tr>
<tr>
<td>Max [wt%]</td>
<td>87.26</td>
<td>13.93</td>
</tr>
<tr>
<td>Mean [wt%]</td>
<td>86.16</td>
<td>13.36</td>
</tr>
<tr>
<td>Median [wt%]</td>
<td>86.23</td>
<td>13.33</td>
</tr>
<tr>
<td>Min [wt%]</td>
<td>84.32</td>
<td>12.93</td>
</tr>
<tr>
<td>n analysed [%]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>n &gt; LDL [%]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Avg. LDL [ppm]</td>
<td>753</td>
<td>388</td>
</tr>
</tbody>
</table>

Table 4.2: Summary of sphalerite composition determined via EMPA.

Table 4.3: Summary of galena composition determined via EMPA.

Figure 4.21: Search for mineral phases enriched in Bi via WDS element mapping; Sample NP910-2-B (SiPy, 9237 mRL, ML zone); no mineral phases significantly enriched in Bi were identified; minor enrichments of Ag occur in the vicinity of galena and are likely caused by intergrowths with argentian tetrahedrite; concentrations of Bi, Se, Te and Tl are indicated to be elevated in galena.
4.2 Electron microprobe analyses

<table>
<thead>
<tr>
<th>Chalcopyrite Major Traces and impurities</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
<th>Zn</th>
<th>As</th>
<th>Se</th>
<th>Ag</th>
<th>Cd</th>
<th>Bi</th>
<th>Sn</th>
<th>Sb</th>
<th>Te</th>
<th>Au</th>
<th>Hg</th>
<th>Pb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 187</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max [wt%]</td>
<td>35.25</td>
<td>30.95</td>
<td>35.62</td>
<td>0.09</td>
<td>0.10</td>
<td>0.10</td>
<td>2.78</td>
<td>0.20</td>
<td>0.11</td>
<td>0.28</td>
<td>0.06</td>
<td>0.04</td>
<td>0.09</td>
<td>0.11</td>
<td>0.06</td>
<td>0.06</td>
<td>0.21</td>
<td>0.42</td>
<td>0.38</td>
</tr>
<tr>
<td>Mean [wt%]</td>
<td>34.53</td>
<td>29.92</td>
<td>34.78</td>
<td>0.05</td>
<td>0.04</td>
<td>0.03</td>
<td>0.04</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
<td>0.05</td>
<td>0.04</td>
<td>0.04</td>
<td>0.08</td>
<td>0.21</td>
<td>0.14</td>
<td>0.06</td>
</tr>
<tr>
<td>Median [wt%]</td>
<td>34.59</td>
<td>29.88</td>
<td>34.83</td>
<td>0.05</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>0.07</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>Min [wt%]</td>
<td>32.71</td>
<td>28.66</td>
<td>33.91</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
<td>0.11</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>n analysed [%]</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>40</td>
<td>100</td>
<td>83</td>
<td>100</td>
<td>100</td>
<td>83</td>
<td>100</td>
<td>100</td>
<td>40</td>
<td>100</td>
<td>83</td>
<td>83</td>
<td>57</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>n &gt; LDL [%]</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>17</td>
<td>92</td>
<td>20</td>
<td>81</td>
<td>38</td>
<td>10</td>
<td>47</td>
<td>14</td>
<td>11</td>
<td>30</td>
<td>16</td>
<td>4</td>
<td>21</td>
<td>37</td>
<td>47</td>
<td>43</td>
</tr>
<tr>
<td>Avg. LDL [ppm]</td>
<td>324</td>
<td>235</td>
<td>220</td>
<td>312</td>
<td>199</td>
<td>233</td>
<td>340</td>
<td>328</td>
<td>382</td>
<td>280</td>
<td>605</td>
<td>161</td>
<td>341</td>
<td>381</td>
<td>313</td>
<td>451</td>
<td>830</td>
<td>416</td>
<td>361</td>
</tr>
</tbody>
</table>

Table 4.4: Summary of chalcopyrite composition determined via EMPA.

Figure 4.22: Trace element mapping in galena; Sample NP549-1-B (SiPo, 9323 mRL, ML zone); (a) BSE image, (b) reflected light microphotograph and (c) wavelength-dispersive-spectra (WDS) element mapping (c); minor tiny concentration highs of Bi were identified, some of them correspond to Ag and/or Sb and are likely to be caused by micro impurities of argentian tetrahedrite; concentration levels of Cd, Te and Hg are indicated to be homogeneously enriched throughout the galena grain without any apparent zonation; weak enrichments of Cd and Hg as well as depletion of Te coincide with grinding damage of the thin sections’ surface and are artefacts.
4. ORE MINERALOGY AND PETROGRAPHY

Silver, Cd and Sb were at low concentration levels up to approximately 0.2 wt%. Tellurium was detected in 34% of all analyses. Despite the fact that tellurium is an element known to be incorporated in galena at trace levels, the observed median concentration of 0.07 wt% appears rather high. Mercury and In were detected only rarely at median concentrations of 0.07 and 0.03 wt%, respectively. Other element concentrations are erratic and generally very low.

Chalcopyrite

Of the 210 chalcopyrite analyses, 187 were selected based on total element concentration and stoichiometry (table 4.4). Elements incorporated in chalcopyrite at low concentration levels are Co (median conc. 0.04 ppm; \(n > LDL = 92\)%), Zn (median conc. 0.10 ppm; \(n > LDL = 81\)%), Ag (median conc. 0.05 ppm; \(n > LDL = 47\)%), Bi (median conc. 0.06 ppm; \(n > LDL = 43\)%), As (median conc. 0.07 ppm; \(n > LDL = 38\)%), and Sn (median conc. 0.05 ppm; \(n > LDL = 30\)%). Cobalt, the most common trace element, does not show affinities to any particular ore types. Nickel occurs above the detection limit in only 20% of all analyses with a maximum concentration of 0.1 wt%. Significant and rather constant high levels of Hg were present in 37% of all analyses at a median concentration of 0.20 wt%.

Gold levels in chalcopyrite are highly variable. In most cases concentrations are below the detection limit, but may reach rather significant levels with a maximum of 0.21 wt%. Such high Au concentrations are unlikely to be caused by lattice substitution but may be explained by sub-micro inclusions. Despite the erratic occurrence, a clear concentration trend versus depth within the orebody is apparent. This trend is defined by increasing Au concentrations towards the surface (figure 4.24). The number of analyses detecting Au above the detection limit is low. Nevertheless, chalcopyrite in pyritic ore types (Py and SiPy) are likely to contain higher Au levels compared to other ore types (figure 4.26). Other elements (e.g. Pb, Sb, In, Se, Te) were rarely detected at low concentrations, in most cases close to the detection limit.

Figure 4.23: Ternary diagram showing pyrite compositions within the Co-Ni-As system; pyrite type A (red), type B (green) and undifferentiated pyrite analyses (grey).

<table>
<thead>
<tr>
<th>Pyrite</th>
<th>Major</th>
<th>Traces and impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 191</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max [wt%]</td>
<td>47.48 53.92</td>
<td>0.26 0.11 2.14 0.19 0.20 0.16 0.10 1.05 1.86 0.07 0.08 0.04 0.07 0.78 0.13 0.38 0.84</td>
</tr>
<tr>
<td>Mean [wt%]</td>
<td>46.28 53.07</td>
<td>0.08 0.04 0.15 0.06 0.06 0.07 0.07 0.07 0.07 0.17 0.06 0.04 0.04 0.06 0.08 0.05 0.23 0.19</td>
</tr>
<tr>
<td>Median [wt%]</td>
<td>46.30 53.10</td>
<td>0.07 0.04 0.08 0.05 0.06 0.07 0.07 0.08 0.04 0.08 0.06 0.04 0.04 0.04 0.05 0.05 0.04 0.20 0.16</td>
</tr>
<tr>
<td>Min [wt%]</td>
<td>44.47 51.27</td>
<td>0.02 0.02 0.03 0.03 0.03 0.03 0.04 0.03 0.02 0.03 0.04 0.04 0.04 0.03 0.01 0.02 0.11 0.09</td>
</tr>
<tr>
<td>n analysed [%]</td>
<td>100 100</td>
<td>100 79 100 100 79 100 14 100 100 79 100 14 16 100 79 36 100</td>
</tr>
<tr>
<td>n &gt; LDL [%]</td>
<td>100 100</td>
<td>100 79 100 100 79 100 14 100 100 79 100 14 16 100 79 36 100</td>
</tr>
<tr>
<td>Avg. LDL [ppm]</td>
<td>248 240</td>
<td>190 215 343 264 448 390 292 289 301 401 542 153 317 359 293 792 472</td>
</tr>
</tbody>
</table>

Table 4.5: Summary of pyrite composition determined via EMPA.
4.2 Electron microprobe analyses

Iron sulphides, arsenopyrite & magnetite

Pyrite

Four pyrite generations were identified from microscopic investigations. Pyrite types A and C are generally fine grained, very impure or intimately and finely intergrown with other sulphide mineral phases. EMPA results of high quality were difficult to achieve for these pyrite varieties. Pyrite B is coarse grained, commonly intruded and replaced by other sulphide phases. Post-base metal pyrite D was not investigated in detail as part of this study.

No compositional changes related to different pyrite types could be identified (table 4.5) from 191 high quality analyses out of total data set of 265. Most of the rejected 28% of analyses are from impure and fine grained pyrite A.

Figure 4.23 shows the variability of atomic ratios between Co, Ni and As for pyrite type A (red), type B (green) and undifferentiated pyrite analyses (grey). No clustering of type A and B is indicated. Cobalt concentrations were above the lower detection limit (avg. LDL 190 ppm) in all pyrite analyses at a median concentration of 0.07 wt% and as high as 0.26 wt%. Nickel is present at a median concentration of 0.04 wt% based on 27% of analyses above the detection limit. Pyrite of all ore types contain arsenic at rather constant median concentrations ranging between 0.07 and 0.1 wt%. Arsenic levels from pyritic massive ore samples, however, feature a significant greater variability and maximum concentration of 2.14 wt% as shown in figure 4.27.

Silver and Au are observed at median concentrations of 0.05 and 0.06 wt%, respectively.
4. ORE MINERALOGY AND PETROGRAPHY

Figure 4.26: Box and Whisker plot showing the content of gold detected in chalcopyrite of different ore types.

Figure 4.27: Box and Whisker plot showing the content of arsenic detected in pyrite of different ore types.

Figure 4.28: Box and Whisker plot showing the content of silver detected in pyrite of different ore types.

Figure 4.29: Box and Whisker plot showing the content of Bi detected in pyrite of different ore types.

Table 4.6: Summary of pyrrhotite composition determined via EMPA.

<table>
<thead>
<tr>
<th>Pyrrhotite</th>
<th>Major</th>
<th></th>
<th>Traces and impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 142</td>
<td>Fe</td>
<td>S</td>
<td>Co</td>
</tr>
<tr>
<td>Max (wt%)</td>
<td>60.97</td>
<td>42.41</td>
<td>0.17</td>
</tr>
<tr>
<td>Mean (wt%)</td>
<td>59.07</td>
<td>40.48</td>
<td>0.09</td>
</tr>
<tr>
<td>Median (wt%)</td>
<td>58.87</td>
<td>40.67</td>
<td>0.09</td>
</tr>
<tr>
<td>Min (wt%)</td>
<td>57.36</td>
<td>38.56</td>
<td>0.03</td>
</tr>
<tr>
<td>n analysed [%]</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>n &gt; LDL [%]</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Avg. LDL [ppm]</td>
<td>275</td>
<td>222</td>
<td>188</td>
</tr>
</tbody>
</table>
Their erratic concentrations (20% above LDL for Ag and 24% for Au) indicate the occurrence as micro-inclusions. Silver concentrations tend to be slightly elevated in pyrite from siliceous semi-massive ore (SiPo and SiPy) (figure 4.28). A weak Ag enrichment trend towards the surface is present (figure 4.25). Maximum concentrations for Ag and Au were at 0.19 wt% and 0.20 wt%, respectively. Bismuth is detected in almost 60% of all analyses at a median concentration of 0.07 wt%. High Bi concentrations preferably occur in pyrite contained in pyrrhotitic ore types (figure 4.29). Other element concentrations are sporadic and are likely to be caused by micro-inclusions.

**Pyrrhotite**

Pyrrhotite is the main iron sulphide phase associated with base metal sulphides. It is commonly free of inclusions and other impurities but may be intimately intergrown with other sulphide phases. Most of analyses are of good analytical quality with 142 results selected out of a total of 152 (table 4.6). It is beyond the scope of this thesis to study the stoichiometry and crystallography of pyrrhotite at the Elura Mine. Therefore a general overview is given in the following. The calculated median stoichiometry is Fe$_{0.83}$S (n=142) with an Fe-deficiency $x$ equal to 0.17 (average $x=0.16$) (figure 4.30). This deviation is described by Anthony *et al.* (1990) as the maximum Fe-deficiency observed in naturally-occurring pyrrhotite. Although other sources, e.g. Back *et al.* (2008), suggests 0.2 as a maximum. It is known from field observations that pyrrhotite is commonly magnetic, a feature of monoclinic pyrrhotite Fe$_7$S$_8$ ($x=0.125$). Despite the indication of two Fe-deficient populations (figure 4.30), no correlation with depth nor an affinity to particular ore types or ore zones were identified.

Cobalt was identified as the most abundant trace element incorporated in pyrrhotite. All analyses are above the average detection limit of 188 ppm. The median and maximum concentrations are 0.09 and 0.17 wt%, respectively. By contrast, nickel is only present in approximately a quarter of all results at lower concentrations (median 0.03 wt%, maximum 0.07 wt%). A median As concentration of 0.07 wt% is defined by 53% of all analyses above the detection limit (average detection limit 348 ppm).

Gold and Ag were rarely detected at concentrations up to 0.17 and 0.10 wt%, respectively. Due to the erratic nature of their occurrence, these elements are likely to be linked to micro inclusions. Bismuth is more common and present in above 50% of the analyses at a median concentration of 0.07 wt%. The determination of Hg in pyrrhotite showed a concentration range between 0.12 and 0.36 wt%. Some 31% of the analyses are above the average detection limit of 899 ppm.

Elements such as Mn, Se, Cd, Sn, Sb and Te were detected at low concentrations close to the detection limit. The pronounced fluctuating nature of these elements and base metals (i.e. Zn, Pb, Cu) detected in pyrrhotite is indicative of being caused by micro inclusion of base metal sulphides rather than lattice substitution. Neither, correlation trends with depth nor affinities to particular ore types are identified for any of the analysed trace elements.

![Figure 4.30: Box and Whisker plot showing the iron-deficiency range observed in pyrrhotite.](image)
Arsenopyrite occurs in all ore types and forms part of all paragenetic stages. Some arsenopyrite crystals show a well defined zoning in back scatter imaging (Figure 4.34). Qualitative wavelength dispersive (WDS) element mapping was used in order to identify the responsible elements and their distribution. A growth zonation parallel to crystallographic planes is defined by enrichment of Sb and/or Co (Figure 4.33). This pattern is overprinted by a second zonation defined by different ratios of As and S. Most probably, deformation has induced the redistribution of the aforementioned elements. Gold and Ag were identified via energy dispersive spectra analyses and occur as tiny inclusions or fracture fillings in arsenopyrite (Figure 4.34).

The quality of EMPA results (total \( n = 95 \)) was reviewed based on total concentrations and stoichiometry, 11 measurements were rejected (Table 4.7). Figure 4.32 shows the compositional variability of arsenopyrite. WDS element mapping showed that the ratio of As and S is modified during deformation, causing the spread of data points along the constant Fe line. Arsenic to S atomic ratios are below one for most analyses and are rather uniform for all ore types except one. That is, arsenopyrite in massive pyrrhotitic ore (Po) features a weak shift to lower As (Figure 4.31).

Cobalt and Sb are present above the detection limit in 98% of all analyses at concentrations between 0.03 to 2.27 wt% and 0.03 to 5.36 wt%, respectively. Nickel and Cd were rarely detected at low concentrations close to their respective average detection limits of 253 and 453 ppm, respectively. The erratic concentrations of Au and Ag in arsenopyrite suggest presence of micro inclusions as observed during element mapping (Figure 4.33). Gold and Ag were detected at maxima of 0.23 and 0.07 wt%, respectively. Base metals (e.g. Cu, Zn, Pb) are variable and likely either caused by impurities or matrix effects during analysis. Bismuth was detected in 21% of all analyses at generally low values with a median concentration of 0.06 wt%.

![Figure 4.32: The ternary diagram shows the arsenopyrite composition in the Fe-As-S system; the variability in As and S is caused by deformation as shown in figure 4.33.](image-url)
4.2 Electron microprobe analyses

<table>
<thead>
<tr>
<th>Arsenopyrite</th>
<th>Major</th>
<th>Traces and impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 84</td>
<td>Fe</td>
<td>As</td>
</tr>
<tr>
<td>Max [wt%]</td>
<td>35.51</td>
<td>46.65</td>
</tr>
<tr>
<td>Mean [wt%]</td>
<td>33.92</td>
<td>44.29</td>
</tr>
<tr>
<td>Median [wt%]</td>
<td>33.94</td>
<td>44.60</td>
</tr>
<tr>
<td>Min [wt%]</td>
<td>32.23</td>
<td>38.21</td>
</tr>
<tr>
<td>n analysed [%]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>n &gt; LDL [%]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Avg. LDL [ppm]</td>
<td>249</td>
<td>628</td>
</tr>
</tbody>
</table>

Table 4.7: Summary of arsenopyrite composition determined via EMPA.

Figure 4.33: The wave length dispersive spectra (WDS) elemental mapping identified elevated antimony and cobalt concentrations defining the growth zonation whereas the distributions of sulphur and arsenic are responsible for changes in the BSE intensity defining the second zonation pattern.
Figure 4.34: Arsenopyrite zonation is shown of sample NP245-1 (Po, 9613 mRL, z4 zone); (a) reflected light microphotograph, BSE images (b), (c) and (d); (a) Overview of a coarse euhedral arsenopyrite grain (centre of image, light yellow) surrounded by a mineral assemblage consisting of sphalerite (medium grey), galena (light grey), pyrrhotite (pink) and siderite (dark grey) as non sulphide gangue (NSG); (b) The arsenopyrite is characterised by two types of zoning: (1) a growth zonation paralleling crystal faces and (2) a more irregular zonation probably due to deformation; the grain is fractured in places; (c) Close-up of image (b) showing both types of zonation; (d) Minor mineral phases characterised by significantly elevated BSE intensity intrude along fractures; energy dispersive spectra (EDS) identified the occurrence of Ag and minor Au as shown in (e).
4.2 Electron microprobe analyses

*Magnetite*

Subordinate magnetite is exclusively associated and intimately intergrown with pyrite type C. The co-genetic association between pyrrhotite, pyrite and magnetite as shown in figure 4.35 is very rare. Magnetite grains are very small (commonly below 10 to 15 µ) and may be mixed up with sphalerite and/or Fe-hydroxides. EMPA analysis (n = 3; analyses performed on magnetite shown in figure 4.35; analytical results presented in table 4.8) of sample NP767-2-B confirmed that the phase is indeed magnetite, coexisting with pyrite. Both phases are surrounded by pyrrhotite. Magnetite is pure with negligible element concentrations of Mg, V and Cr.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>NP767-2-B</th>
<th>Avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
<td>#2</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>V2O3</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>MnO</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>FeO</td>
<td>93.54</td>
<td>96.70</td>
</tr>
<tr>
<td>NiO</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>93.55</td>
<td>96.74</td>
</tr>
</tbody>
</table>

Calculation based on 32 oxygen atoms

<table>
<thead>
<tr>
<th>Element</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>Avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.000</td>
<td>0.008</td>
<td>0.000</td>
<td>0.003</td>
</tr>
<tr>
<td>Al</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Ti</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>V</td>
<td>0.000</td>
<td>0.005</td>
<td>0.000</td>
<td>0.002</td>
</tr>
<tr>
<td>Cr</td>
<td>0.001</td>
<td>0.000</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Mn</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe2+</td>
<td>8.000</td>
<td>7.992</td>
<td>8.000</td>
<td>7.997</td>
</tr>
<tr>
<td>Fe3+</td>
<td>15.999</td>
<td>15.995</td>
<td>15.999</td>
<td>15.997</td>
</tr>
<tr>
<td>Total</td>
<td>24.000</td>
<td>24.000</td>
<td>24.000</td>
<td>24.000</td>
</tr>
</tbody>
</table>

Table 4.8: Composition of magnetite intergrown with pyrite type C as shown in figure 4.35. Mineral chemistry was determined via EMPA.

Figure 4.35: Magnetite (grey colour) is intimately intergrown with pyrite type C (yellow) and surrounded by pyrrhotite (pinkish phase), representing the sulphide groundmass. Magnetite compositions were determined via EMPA, results presented in table 4.8.
4. ORE MINERALOGY AND PETROGRAPHY

Table 4.9: Standards and conditions for EMPA of sulphide phases; UoFL-IH: in-house standard, Institute for Mineralogy and Petrology, Department of Applied Geosciences and Geophysics, University of Leoben. SPI: multi mineral standard SPI Supplies / Structure Probe, Inc. [http://www.2spi.com/catalog/standards/spiweb/spimin.shtml]
4.2 Electron microprobe analyses

4.2.2 Silver phases – their classification and alteration

Background

Tetrahedrite and tennantite sulfosalts have been described as the most common Ag-bearing mineral phases identified in the Elura orebody (e.g. Lawrie and Hinman, 1998; Taylor et al., 1984; Leverett et al., 2005; David, 2008). These phases are particularly enriched in upper and peripheral mineralised zones within the orebody. The chemical variability of Ag-phases is investigated via EMP as part of this study, mainly focussing on minerals part of the tetrahedrite-tennantite solid-solution series. The standards and peak positions used for calibration are given in Table 4.10.

The solid-solution series is defined by the end members tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) and tennantite (Cu$_{12}$As$_4$S$_{13}$), with Sb and As featuring a complete mutual lattice substitution. Johnson et al. (1986) defined a general formula based on analyses of a large number of natural and synthetic tetrahedrite samples (eq. 4.1). This formula implies a maximum of six Ag atoms per formula unit may be incorporated in the structure. However, tetrahedrite is commonly non-stoichiometric and rarely fits the ideal mineral formula (e.g. Johnson et al., 1988).

Freibergite is a Ag-rich sulfosalt species chemically similar to tetrahedrite. Its status as a discrete mineral phase is, however, still disputed (Moelo et al., 2008). The main characteristic of freibergite is the decrease of S with increasing substitution of Ag for Cu above approximately 4 apfu (Moelo et al., 2008). The general formula is defined in eq. 4.2. The crystal structural formula for maximum Ag content is

$$Ag_6Cu_{4.44}(Fe, Zn)_{1.56}Sb_4S_{12.09}.$$  

Mineral phases that contain less than 4 apfu Ag should be named Ag-rich tetrahedrite rather than freibergite (Moelo et al., 2008).

Argentotetrahedrite is suggested as the Sb-rich analogue to argentotennantite with the ideal formula

$$Ag_{10}(Fe, Zn)_2Sb_4S_{13}.$$  

The phase is currently solely defined based on mineral chemistry. Crystallographic characteristics based on X-ray powder pattern are yet to be determined, subsequently its approval by the International Mineralogical Association as a discrete mineral species is unsettled.

The mineral phase stylotypite with the formula

$$(Ag, Cu, Fe, Zn)_3SbS_3$$

was first described and named by Franz Kobell in 1865 and was accepted as a discrete mineral phase until 1952. Milton and Axelrod (1951) reviewed published data of stylotypite and showed that all samples are either tetrahedrite or a mixture of tetrahedrite with other known mineral phases (e.g. jamesonite). He concluded that stylotypite as an individual mineral species should be discredited.

Analytical results

Throughout most of the orebody, sulfosalts phases occur as small grains, in the order of a few microns, but occur as larger grains towards the uppermost and peripheral areas. Samples from those areas were preferably selected for EMPA. In order to achieve good analytical results, only grains of at least 7 to 10 µm in size were analysed. A total of 97 EMPA analyses of sulfosalt and related alteration phases were undertaken on twelve samples. Five analyses were rejected due to poor analytical quality. Figure 4.36 shows the calculated $Ag/(Ag+Cu)$ and $Zn/(Zn+Fe+Hg+Cd)$ versus $Sb/(Sb+As+Bi+Te)$ ratios. The observed $Sb/(Sb+As+Bi+Te)$ values are rather constant and range between 0.95 and 0.98 with a median of 0.97. The occurrence of tennantite or other arsenic-dominated sulfosalt mineral phases was not verified in the course of this study. The $Ag/(Ag+Cu)$ values vary significantly between 0.20 and 0.60 with a median of 0.35. A weak inverse dependency between Zn and Sb is present. Overall, the $Zn/(Zn+Fe+Hg+Cd)$ ratio ranges between 0.05 and 0.34 with a median of 0.21.

Commonly, the mineral formula for tetrahedrite is calculated based on S equal to 13 apfu.
4. ORE MINERALOGY AND PETROGRAPHY

\[(Cu, Ag)_{6}Cu_{4}(Fe, Zn, Cu, Hg, Cd)_{2}(Sb, As, Bi, Te)_{4}(S, Se)_{13}\]  \hspace{1cm} (4.1)

\[(Ag_{4}+2x, Cu_{2−2x})[(Cu, Ag)_{4}(Fe, Zn)]_{2}\sum_{6}Sb_{4}S_{12−x}\]  \hspace{1cm} (4.2)

with \(0 \leq x \leq 1\)

\[(Ag_{3.20}, Cu_{2.80})_{TRI}^{TET}\sum_{6}Cu_{3.99}^{TET}(Cu_{0.03}, Fe_{1.42}, Zn_{0.58}, Cd_{0.02})_{SM}^{S}\sum_{12.95}S_{12.95}\]  \hspace{1cm} (4.3)

\[(Ag_{3.68}, Cu_{2.32})_{TRI}^{TET}\sum_{6}Cu_{3.98}^{TET}(Cu_{0.01}, Fe_{1.53}, Zn_{0.48}, Cd_{0.02})_{SM}^{S}\sum_{12.51}S_{12.51}\]  \hspace{1cm} (4.4)

\[(Ag_{4.43}, Cu_{1.57})_{TRI}^{TET}\sum_{6}^{10}(Cu_{3.83}, Fe_{1.99}, Zn_{0.27}, Cd_{0.01})S_{SM}^{S}\sum_{12.16}S_{12.16}\]  \hspace{1cm} (4.5)

\[(Ag, Cu, Fe, Zn, Cd)_{1.01}(Sb, As)_{1.07}S_{3.02}\]  \hspace{1cm} (4.6)

\[(Ag_{2.66}, Cu_{3.34})^{TRI}^{SM}Cu_{3.74}S_{6.06}(Cu_{3.74}, Fe_{1.58}, Zn_{0.54}, Cd_{0.00})_{SM}^{S}\sum_{13.86}S_{13.00}\]  \hspace{1cm} (4.7)

\[(Ag, Cu, Fe, Zn, Cd)_{2.87}(Sb, As)_{1.00}S_{13.14}\]  \hspace{1cm} (4.8)

NOTE:
This figure/table/image has been removed to comply with copyright regulations. It is included in the print copy of the thesis held by the University of Adelaide Library.

Table 4.10: Standards and conditions for EMPA of Ag-phases: UofL-IH: in-house standard, Institute for Mineralogy and Petrology, Department of Applied Geosciences and Geophysics, University of Leoben. SPI: multi mineral standard SPI Supplies / Structure Probe, Inc. [http://www.2spi.com/catalog/standards/spiweb/spimin.shtml]

All except four analyses resulted in a stoichiometric misfit for S = 13 apfu due to a deficiency in S. In order to allow these deficiencies to be investigated, formulae are calculated based on total atoms of metals and semimetals equal to 16 apfu (ME + SEM = 16 apfu). Silver-rich tetrahedrite is identified in six samples (abbrev. Ag-Tet, table 4.11). Only one sample contained tetrahedrite close to the ideal mineral formula (first data set abbrev. Ag-Tet*; table 4.11) as defined by Johnson et al. (1986). The mineral formula is calculated based on four analyses (ME + SEM = 16) and shown in eq. 4.3.

The remaining Ag-rich tetrahedrite feature S-deficiencies ranging between 12.01 and 12.83 apfu. The average mineral formula is calculated based on 15 analyses of 5 samples (ME + SEM = 16 apfu) and given in eq. 4.4.
4.2 Electron microprobe analyses

Silver-rich tetrahedrite with excess of 4 apfu Ag is present in three samples (data set 4 to 6 abbrev. Ag-Tet/Frei; table 4.11). These occurrences are defined as freibergite as suggested by Moelo et al. (2008).

Most analyses (51 out of 70) are significantly different to the tetrahedrite stoichiometry (abbrev. Ag-Tet/Styl). The data is summarised in table 4.12. The calculated average mineral formula based on 32 analyses (ME + SEM = 16 apfu), shown in eq. 4.5, indicates a deficiency of semi-metals and excess of metals in the tetrahedral position. Mineral formulae of those 32 analyses are, however, similar to the ideal composition of stylopyrite when calculation is based on total atoms equal to seven as shown in eq. 4.6. Considering stylopyritel is not accepted as a mineral species, the stoichiometric deviation from tetrahedrite is likely to be caused either by submicroscopic intergrowths of other unidentified mineral phases with tetrahedrite or alteration.

Some analyses (n = 19) misfit the tetrahedrite and stylopyrite mineral formulae (abbrev. Ag-Tet/Styl*). Examples are shown in table 4.13, data set 1 and 2. The average composition are calculated based on Me + SEM = 16 apfu and on total atoms equal to seven and given in eq. 4.7 and eq. 4.8, respectively. These phases may represent progressively altered tetrahedrite.

Alteration of Ag-rich tetrahedrite was observed microscopically in several samples (see section 4.1 on page 68). Figure 4.38 shows the result of semi-quantitative wavelength-dispersive spectra (WDS) element mapping, used to investigate element distributions associated with this alteration. Peripheral zones of the former tetrahedrite grain are highly enriched in Ag and depleted in other elements. Antimony is preserved as thin lamellae containing Ag, Hg and minor Zn. The Sb-Ag mineral phase alargentum $Ag_{1-x}Sb_x$ was identified as potential alteration product. Its calculated formula based on total atoms per formula unit equal to 2 is

$$Ag_{1.66}Cd_{0.01}Sb_{0.31}As_{0.01}$$

and shown in (data set 3, table 4.13). Copper in the former tetrahedrite forms Ag-rich chalcopyrite (abbrev. Ag-Tet, data set 4, table 4.13). The average mineral formula calculated based on twelve analyses is

$$Cu_{0.94}Fe_{0.03}Ag_{0.15}S_{1.98}$$

A maximum Ag concentration of 14.50 wt% was detected in Ag-rich chalcopyrite. The rather low amount of Zn contained in tetrahedrite forms minor quantities of sphalerite. The progressive nature of this alteration is displayed by various mineral compositions other than those described above. As an example, two alteration phases high and low in Ag are shown in table 4.13, data set 5 and 6, respectively. The phase enriched in Ag represents the...
transition towards native Ag, whereas that containing less Ag alters towards Ag-rich chalcopyrite. Figure 4.37 shows the $\text{Ag/(Ag+Cu)}$ ratio versus atomic percent sulphur. Most Ag-Tet plot close to 13 apfu S, some are close to 12.5. Ag-Tet/Styl phases feature a pronounced variability in their S content. Alteration phases depart from Ag-Tet and Ag-Tet/Styl compositions towards native Ag via increasing Ag/decreasing S and towards Ag-rich chalcopyrite via increasing S/decreasing Ag.

**Figure 4.37:** Comparison of Ag-phase composition in respect to Ag and S content.
Figure 4.38: Alteration of Ag-rich tetrahedrite; sample NP952-2-B (SiPy, 9688 mRL, z3 zone): (a) BSE image, reflected light microphotograph and (c) WDS element mapping; the element distribution shows the dendritic growth of native Ag; peripheral areas are enriched in Cd; tetrahedrite is not preserved; a thin lamellae features elevated concentrations of Ag, Sb and Hg; Ag-rich chalcopyrite as alteration product is defined by progressive enrichment of Cu and Fe; weakly elevated Bi concentrations coincide with small galena grains.
### Table 4.11: Representative analyses of Ag-rich tetrahedrite (Ag-Tet); Ag-Tet* features nearly ideal stoichiometry as shown in eq. 4.1; Ag-Tet/Frei correspond to stoichiometry given in eq. 4.2; values in round brackets are single standard deviations.

<table>
<thead>
<tr>
<th>Sample Mineral analyses</th>
<th>CAF-1LS-1-1 Ag-Tet</th>
<th>CAF-1LS-1-1 Ag-Tet</th>
<th>DE174-1-A Ag-Tet</th>
<th>775-z1-AI Ag-Tet/Frei</th>
<th>NP919-A Ag-Tet/Frei</th>
<th>DE367-3 Ag-Tet/Frei</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>24.24 (0.24)</td>
<td>24.41 (0.62)</td>
<td>24.39</td>
<td>15.95 (0.13)</td>
<td>19.71 (1.04)</td>
<td>20.17</td>
</tr>
<tr>
<td>Ag</td>
<td>19.29 (0.44)</td>
<td>19.29 (0.96)</td>
<td>18.96</td>
<td>30.87 (0.01)</td>
<td>25.61 (1.32)</td>
<td>25.11</td>
</tr>
<tr>
<td>Fe</td>
<td>4.42 (0.18)</td>
<td>4.52 (0.17)</td>
<td>5.82</td>
<td>4.74 (0.15)</td>
<td>5.25 (0.13)</td>
<td>5.02</td>
</tr>
<tr>
<td>Zn</td>
<td>2.12 (0.09)</td>
<td>2.14 (0.06)</td>
<td>1.00</td>
<td>1.29 (0.06)</td>
<td>1.15 (0.42)</td>
<td>1.37</td>
</tr>
<tr>
<td>Hg</td>
<td>BDL</td>
<td>BDL</td>
<td>0.19</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Cd</td>
<td>0.10 (0.02)</td>
<td>0.09 (0.03)</td>
<td>0.07</td>
<td>0.16 (0.01)</td>
<td>0.10 (0.05)</td>
<td>0.15</td>
</tr>
<tr>
<td>Sb</td>
<td>25.89 (0.18)</td>
<td>26.02 (0.17)</td>
<td>25.75</td>
<td>25.27 (0.03)</td>
<td>25.98 (0.72)</td>
<td>25.99</td>
</tr>
<tr>
<td>As</td>
<td>0.70 (0.11)</td>
<td>0.68 (0.08)</td>
<td>0.45</td>
<td>0.56 (0.01)</td>
<td>0.50 (0.01)</td>
<td>0.52</td>
</tr>
<tr>
<td>Bi</td>
<td>0.04 (0.00)</td>
<td>0.06 (0.01)</td>
<td>0.03</td>
<td>0.05 (0.00)</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Te</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>S</td>
<td>23.22 (0.19)</td>
<td>22.88 (0.21)</td>
<td>22.85</td>
<td>20.92 (0.35)</td>
<td>21.37 (0.16)</td>
<td>21.77</td>
</tr>
<tr>
<td>Se</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Other</td>
<td>0.06 (0.01)</td>
<td>0.03 (0.01)</td>
<td>0.03</td>
<td>0.08 (0.00)</td>
<td>0.00 (0.00)</td>
<td>0.04</td>
</tr>
<tr>
<td>Total</td>
<td>100.01 (0.33)</td>
<td>100.05 (0.21)</td>
<td>99.55</td>
<td>99.81 (0.27)</td>
<td>99.67 (0.01)</td>
<td>100.14</td>
</tr>
</tbody>
</table>

| Σ Metals                | 12.03               | 12.04               | 12.13            | 11.99                  | 12.01             | 12.00               |
| Σ Semimetals            | 3.97                | 3.96                | 3.88             | 4.01                   | 4.00              | 4.00                |
| Σ S & Se                | 12.95               | 12.68               | 12.69            | 12.16 (0.22)           | 12.11 (0.08)      | 12.31               |
| Total                   | 28.95 (0.08)        | 28.68 (0.10)        | 28.69            | 28.16 (0.22)           | 28.11 (0.08)      | 28.31               |
### 4.2 Electron microprobe analyses

Table 4.12: Representative analyses of Ag-rich sulfosalt phases featuring stoichiometry similar to stylotypite (Ag-Tet/Styl); values in round brackets are single standard deviations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>775-z1-A2</th>
<th>DE008-2</th>
<th>NP870</th>
<th>DE174-1-A</th>
<th>DE367-3</th>
<th>NP919-A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag-Tet/Styl</td>
<td>Ag-Tet/Styl</td>
<td>Ag-Tet/Styl</td>
<td>Ag-Tet/Styl</td>
<td>Ag-Tet/Styl</td>
<td>Ag-Tet/Styl</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>8</td>
<td>11</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Cu</td>
<td>15.91 (1.33)</td>
<td>22.05 (0.82)</td>
<td>17.97 (1.17)</td>
<td>24.40 (0.14)</td>
<td>16.48 (1.78)</td>
<td>18.61 (5.25)</td>
</tr>
<tr>
<td>Ag</td>
<td>31.68 (1.66)</td>
<td>21.94 (0.83)</td>
<td>27.67 (1.75)</td>
<td>18.24 (0.93)</td>
<td>29.29 (2.98)</td>
<td>26.76 (7.59)</td>
</tr>
<tr>
<td>Fe</td>
<td>4.87 (0.19)</td>
<td>7.12 (0.46)</td>
<td>6.21 (0.19)</td>
<td>6.55 (0.47)</td>
<td>5.40 (0.11)</td>
<td>5.80 (0.71)</td>
</tr>
<tr>
<td>Zn</td>
<td>1.49 (0.11)</td>
<td>0.54 (0.06)</td>
<td>0.75 (0.18)</td>
<td>0.95 (0.05)</td>
<td>1.36 (0.21)</td>
<td>1.81 (0.12)</td>
</tr>
<tr>
<td>Hg</td>
<td>0.18 (0.03)</td>
<td>0.19 (0.07)</td>
<td>0.22 (0.05)</td>
<td>0.14 (0.01)</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Cd</td>
<td>BDL</td>
<td>0.03 (0.01)</td>
<td>0.05 (0.02)</td>
<td>0.05 (0.01)</td>
<td>0.15 (0.03)</td>
<td>0.06 (0.02)</td>
</tr>
<tr>
<td>Sb</td>
<td>25.04 (0.34)</td>
<td>25.43 (0.3)</td>
<td>25.25 (0.28)</td>
<td>26.44 (0.04)</td>
<td>25.43 (0.51)</td>
<td>24.81 (0.17)</td>
</tr>
<tr>
<td>As</td>
<td>0.73 (0.05)</td>
<td>0.46 (0.08)</td>
<td>0.41 (0.05)</td>
<td>0.44 (0.07)</td>
<td>0.53 (0.12)</td>
<td>0.50 (0.08)</td>
</tr>
<tr>
<td>Bi</td>
<td>0.08 (0.01)</td>
<td>0.03 (0.00)</td>
<td>0.05 (0.02)</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Te</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>S</td>
<td>20.16 (0.49)</td>
<td>22.40 (0.15)</td>
<td>21.53 (0.52)</td>
<td>22.93 (0.26)</td>
<td>21.41 (1.31)</td>
<td>20.77 (0.08)</td>
</tr>
<tr>
<td>Se</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Other</td>
<td>0.05 (0.02)</td>
<td>0.07 (0.04)</td>
<td>0.05 (0.03)</td>
<td>0.07 (0.00)</td>
<td>0.19 (0.22)</td>
<td>0.25 (0.00)</td>
</tr>
<tr>
<td>Total</td>
<td>100.04 (0.39)</td>
<td>100.09 (0.25)</td>
<td>100.01 (0.25)</td>
<td>100.17 (0.49)</td>
<td>99.83 (0.55)</td>
<td>99.70 (0.22)</td>
</tr>
</tbody>
</table>

| Cu       | 1.17 (0.08) | 1.52 (0.05) | 1.28 (0.07) | 1.65 (0.02) | 1.32 (0.32) | 1.19 (0.11) |
| Ag       | 1.37 (0.09) | 0.89 (0.04) | 1.16 (0.09) | 0.73 (0.03) | 1.13 (0.36) | 1.25 (0.14) |
| Fe       | 0.41 (0.02) | 0.56 (0.03) | 0.50 (0.02) | 0.51 (0.04) | 0.44 (0.03) | 0.48 (0.05) |
| Zn       | 0.11 (0.01) | 0.04 (0.00) | 0.05 (0.01) | 0.06 (0.00) | 0.09 (0.01) | 0.13 (0.01) |
| Hg       | 0.00 (0.00) | 0.00 (0.00) | 0.00 (0.00) | 0.00 (0.00) | BDL       | BDL       |
| Cd       | BDL       | BDL       | BDL    | BDL        | BDL      | BDL      |
| Sb       | 0.96 (0.02) | 0.91 (0.01) | 0.94 (0.01) | 0.94 (0.00) | 0.95 (0.02) | 0.94 (0.01) |
| As       | 0.05 (0.00) | 0.03 (0.00) | 0.02 (0.00) | 0.03 (0.00) | 0.03 (0.01) | 0.03 (0.00) |
| Bi       | 0.00 (0.00) | 0.00 (0.00) | 0.00 (0.00) | 0.00 (0.00) | BDL       | BDL       |
| Te       | BDL       | BDL       | BDL    | BDL        | BDL      | BDL      |
| S        | 2.94 (0.03) | 3.06 (0.02) | 3.04 (0.04) | 3.08 (0.02) | 3.03 (0.07) | 2.98 (0.03) |
| Se       | BDL       | BDL       | BDL    | BDL        | BDL      | BDL      |
| Total    | 7.00       | 7.00       | 7.00   | 7.00       | 7.00     | 7.00     |

| % Metals | 3.06 | 3.01 | 2.99 | 2.95 | 2.99 | 3.05 |
| % Semimetals | 1.01 | 0.94 | 0.96 | 0.97 | 0.98 | 0.97 |
| % S & Se | 2.94 | 3.06 | 3.04 | 3.08 | 3.03 | 2.98 |
Table 4.13: Representative analyses of altered Ag-rich sulfosalt phases and alteration products; values in round brackets are single standard deviations.
4.2 Electron microprobe analyses

4.2.3 Chlorite chemistry

Ore mineralogy varies as a function of depth within the sulphide mineralisation at the Elura ore body. This variability is reflected by several element concentration trends caused by changes in modal mineralogy and mineral chemistry. These trends are also observed in whole rock geochemistry (see chapter 5 on page 139). These changes may be linked to vertical temperature gradients within the depositional environment. Chlorite compositions were determined on eight thin-section samples from different depth levels of the orebody. Different chlorite geothermometers were used in order to estimate formation temperatures.

A total of 67 chlorite analyses were performed via EMPA (summarised in table 4.15). Used mineral standards and conditions are shown in table 4.14. The total element concentrations range between 83.37 and 91.56 wt% with a median of 89.39 wt%. These values are consistent with typical chlorite compositions (e.g. Deer et al., 1992). The analyses were checked for Na, K and Ca concentrations (\(\sum\) Na,K,Ca) in order to investigate sub-microscopic intergrowths with other silicates (e.g. muscovite, feldspar or clay mineral phases). The maximum combined atomic percentage of these elements is very low at 0.03 at%, equal to 0.1 wt%. More than 70% of chlorite analyses fall below \(\sum\) Na,K,Ca = 0.01 at% indicating the presence of pure chlorite.

Chlorite compositions vary significantly and are controlled by fluid conditions such as \(f_{O_2}\), pH, temperature, \(F_e/(F_e+Mg)\), and the composition of the host rock (de Caritat et al., 1993). Elements in both octahedral and tetrahedral positions are affected by these compositional variabilities. Chlorite commonly has vacancies (\(\square\)) at the octahedral site typically ranging between -0.1 and 1.1 based on \(O_{20}(OH)_{16}\) (de Caritat et al., 1993). The generalised mineral formula for chlorite is given in eq. 4.9 (Zane and Weiss, 1998).

Chlorite stoichiometry was calculated based on a total of 28 anhydrous oxygen atoms with all Fe assumed to be ferrous. Most calculated compositions feature negative vacancies ranging between -0.44 and 0.14 apfu (table 4.15). Nine chlorite analyses in three samples (table 4.15) are characterised by a total cation occupancy in the octahedral position of less than 12.1 apfu and fall within the commonly observed vacancy range (de Caritat et al., 1993). If vacancies range between 0 and 2 apfu, chlorite is tri-trioctahedral (Zane and Weiss, 1998). The over-occupancy of octahedral coordinated cations is either caused by:

(a) ferric iron not considered during calculation because all Fe is considered as ferrous (de Caritat et al., 1993), or (b) chlorites are sub-microscopically intergrown with other alumino-silicate mineral phases which lack Na, K and Ca (e.g. vermiculite).

Chlorite contains minor Zn at a median concentration of 0.28 wt%, low concentrations of Mn (median of 0.07 wt%) and \(F_e/(F_e+Mg)\) values ranging between 0.75 and 1.00. Classification of chlorite was performed via the scheme defined by Hey (1954). Most chlorite compositions fall within the ripidolite field, some crossing over into the daphnite and the pseudoturtingite fields (figure 4.39). The over occupancy of the octahedral position may be indicative of ferric iron incorporated in the lattice, and thus oxidation. If these chlorite varieties are oxidised they can be classified as thuringite (Hey, 1954).

Chlorite geothermometer

Several different chlorite geothermometers have been proposed in the past. Most of them are empirically determined and based on the temperature dependent changes in aluminium content at the tetrahedral position and octahedral vacancy changes (e.g. Cathelineau and Nieva, 1985; Cathelineau, 1988; Hillier and Velde, 1991). Three groups can be defined according to different approaches.
Table 4.14: Standards and conditions for EMPA of chlorite; UofL-IH: in-house standard, Institute for Mineralogy and Petrology, Department of Applied Geosciences and Geophysics, University of Leoben. SPI: multi-mineral standard SPI Supplies / Structure Probe, Inc. [http://www.2spi.com/catalog/standards/spiweb/spimin.shtml]

Figure 4.39: Chlorite classification after the scheme suggested by Hey (1954); most chlorite compositions fall within the epidolite, some crossing over into the daphnite and the pseudothuringite fields, if these chlorite varieties are oxidised they can be classified as thuringite.
4.2 Electron microprobe analyses

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2) [wt%]</td>
<td>24.96</td>
<td>22.34</td>
<td>22.37</td>
<td>19.34</td>
<td>23.39</td>
<td>22.93</td>
<td>23.36</td>
<td></td>
</tr>
<tr>
<td>Al(_2)O(_3) [wt%]</td>
<td>21.90</td>
<td>19.48</td>
<td>19.64</td>
<td>15.90</td>
<td>18.71</td>
<td>18.58</td>
<td>19.65</td>
<td></td>
</tr>
<tr>
<td>FeO(_{total}) [wt%]</td>
<td>47.19</td>
<td>42.84</td>
<td>43.03</td>
<td>38.40</td>
<td>43.07</td>
<td>44.07</td>
<td>42.36</td>
<td></td>
</tr>
<tr>
<td>MnO [wt%]</td>
<td>0.14</td>
<td>0.07</td>
<td>0.07</td>
<td>0.03</td>
<td>0.07</td>
<td>0.05</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>MgO [wt%]</td>
<td>7.41</td>
<td>4.06</td>
<td>3.89</td>
<td>0.90</td>
<td>3.72</td>
<td>2.70</td>
<td>2.95</td>
<td></td>
</tr>
<tr>
<td>CaO [wt%]</td>
<td>0.08</td>
<td>0.05</td>
<td>0.05</td>
<td>0.03</td>
<td>0.04</td>
<td>0.08</td>
<td>&lt;0.03*</td>
<td></td>
</tr>
<tr>
<td>Na(_2)O [wt%]</td>
<td>0.07</td>
<td>0.06</td>
<td>0.05</td>
<td>0.05</td>
<td>&lt;0.05*</td>
<td>&lt;0.05*</td>
<td>&lt;0.05*</td>
<td></td>
</tr>
<tr>
<td>K(_2)O [wt%]</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>&lt;0.02*</td>
<td>&lt;0.02*</td>
<td>&lt;0.02*</td>
<td></td>
</tr>
<tr>
<td>ZnO [wt%]</td>
<td>2.27</td>
<td>0.52</td>
<td>0.28</td>
<td>0.06</td>
<td>0.14</td>
<td>0.24</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>Total [wt%]</td>
<td>91.56</td>
<td>89.16</td>
<td>89.39</td>
<td>83.37</td>
<td>89.03</td>
<td>88.59</td>
<td>88.45</td>
<td></td>
</tr>
<tr>
<td>Si [apfu]</td>
<td>5.74</td>
<td>5.16</td>
<td>5.14</td>
<td>4.82</td>
<td>5.39</td>
<td>5.36</td>
<td>5.39</td>
<td></td>
</tr>
<tr>
<td>Al(_{total}) [apfu]</td>
<td>5.95</td>
<td>5.30</td>
<td>5.33</td>
<td>4.31</td>
<td>5.08</td>
<td>5.11</td>
<td>5.34</td>
<td></td>
</tr>
<tr>
<td>Al(_{IV}) [apfu]</td>
<td>3.18</td>
<td>2.84</td>
<td>2.86</td>
<td>2.26</td>
<td>2.61</td>
<td>2.64</td>
<td>2.61</td>
<td></td>
</tr>
<tr>
<td>Al(_{VI}) [apfu]</td>
<td>2.85</td>
<td>2.46</td>
<td>2.45</td>
<td>2.05</td>
<td>2.47</td>
<td>2.47</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>Fe [apfu]</td>
<td>10.16</td>
<td>8.28</td>
<td>8.30</td>
<td>7.33</td>
<td>8.30</td>
<td>8.62</td>
<td>8.17</td>
<td></td>
</tr>
<tr>
<td>Mn [apfu]</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Mg [apfu]</td>
<td>2.47</td>
<td>1.35</td>
<td>1.33</td>
<td>0.00</td>
<td>1.28</td>
<td>0.93</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>Ca [apfu]</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Na [apfu]</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>K [apfu]</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Zn [apfu]</td>
<td>0.39</td>
<td>0.08</td>
<td>0.04</td>
<td>0.00</td>
<td>0.02</td>
<td>0.04</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>(\Sigma)(_{VI}) [apfu]</td>
<td>12.44</td>
<td>12.19</td>
<td>12.19</td>
<td>11.86</td>
<td>12.07</td>
<td>12.08</td>
<td>11.94</td>
<td></td>
</tr>
<tr>
<td>Fe/(Fe + Mg)</td>
<td>1.00</td>
<td>0.86</td>
<td>0.86</td>
<td>0.75</td>
<td>0.87</td>
<td>0.90</td>
<td>0.89</td>
<td></td>
</tr>
</tbody>
</table>

GT-1 [°C] | 450 | 395 | 398 | 302 | 358 | 363 | 359 |
GT-2 [°C] | 469 | 384 | 388 | 239 | 326 | 334 | 327 |
GT-3 [°C] | 419 | 383 | 386 | 321 | 359 | 365 | 361 |
GT-4 [°C] | 307 | 271 | 271 | 209 | 246 | 246 | 244 |

Table 4.15: Overview of chlorite composition and representative analyses; geothermometric calculations are given in eq. 4.10 for GT-1, eq. 4.11 for GT-2, eq. 4.12 for GT-3 and eq. 4.13 for GT-4; (*) are average lower detection limits as shown in appendix A on page 332

1. Octahedral vacancy

Cathelineau and Nieva (1985) investigated chlorite compositions from samples in Los Azufres, Mexico and observed a negative correlation between octahedral vacancies (\(\Box_{VI}\)) and temperature. The equation, based on half-cell vacancies, is defined by the regression line given in eq. 4.10.

\[
(R_{x}^{2+}R_{y}^{3+}\Box_{(12-x-y)})_{12}^{[VI]}(Si_{z}R_{8-z}^{3+})_{8}^{[IV]}O_{20}(OH)_{16}
\]  

(4.9)

2. Alumina in the tetrahedral position

During the same study, Cathelineau and Nieva (1985) also noticed a positive linear correlation of Al\(_{IV}\) and temperature and suggested it can be used as geothermometer. This temperature dependency is, when compared to the octahedral vacancy method, better constrained with a corre-
4. ORE MINERALOGY AND PETROGRAPHY

...lation coefficient of 0.946 compared to 0.870. The equation, $Al^{[IV]}$ based on half-cell, is defined by the regression line given in eq. 4.11.

Cathelineau (1988) revisited the estimation of crystallisation temperatures of chlorite based on a larger sample set composed of different lithologies (Los Azufres and Salton Sea). He suggested that the observed temperature-$Al^{[IV]}$ dependency is independent of lithology changes and may therefore be used as general geothermometer in various settings (e.g. hydrothermal, metamorphic or diagenetic). The calculated regression, $Al^{[IV]}$ based on half-cell, is given in eq. 4.12.

Hillier and Velde (1991) investigated compositions of chlorites occurring in early diagenetic to low grade metamorphic lithologies, covering a temperature range between approximately 40 and 330 °C. Similarly to earlier studies, they found a temperature dependency as a function of the $Al^{[IV]}$ content and calculated a best-fit line based on mean compositions (see eq. 4.13; $Al^{[IV]}$ based on full-cell). Their results indicate a systematic temperature overestimation of the geothermometer defined by Cathelineau (1988).

$$T = 2.41 - 116.69 \Box^{[IV]}$$  \hspace{1cm} (4.10)

$$T = 17.54 + 212.31 \ Al^{[IV]}$$  \hspace{1cm} (4.11)

$$T = -61.92 + 321.98 \ Al^{[IV]}$$  \hspace{1cm} (4.12)

$$T = -325.32 + 249.56 \ Al^{[IV]}$$  \hspace{1cm} (4.13)

3. Correction based on $Fe/(Fe+Mg)$ ratio

Kranidiotis and MacLean (1987) suggested that the $Fe/(Fe+Mg)$ ratios of chlorite is positively correlated to the $Al^{[IV]}$ content. They used a modified version of eq. 4.11 defined by Cathelineau and Nieva (1985) and added a correction term in order to account for the increase of $Al^{[IV]}$ caused by increasing iron content in chlorite. The proposed temperature dependency where $Al^{[IV]}$ is based on full-cell, is given in eq. 4.14.

Zang and Fyfe (1995) presented a modified version of the relationship defined by Cathelineau and Nieva (1985) based on similar arguments as suggested by Kranidiotis and MacLean (1987), and proposed eq. 4.15 ($Al^{[IV]}$ based on full-cell).

The geothermometer based on $Al^{[IV]}$ occupation defined by Cathelineau (1988) (eq. 4.12) is a modified and improved version of that defined by Cathelineau and Nieva (1985) (eq. 4.11). Most chlorite compositions feature negative vacancies in the octahedral coordination, subsequently the relationship eq. 4.10 defined by Cathelineau and Nieva (1985) cannot be used. Therefore, chlorite geothermometer defined by Cathelineau (1988) given in eq. 4.12 (abbrev. GT-1), Hillier and Velde (1991) given in eq.
4.2 Electron microprobe analyses

4.13 (abbrev. GT-2), Kranidiotis and MacLean (1987) given in eq. 4.14 (abbrev. GT-3) and Zang and Fyfe (1995) given in eq. 4.15 (abbrev. GT-4) were used to calculate chlorite formation temperatures in the course of this study.

Temperature estimates for the individual geothermometers vary (figure 4.40). Geothermometer GT-1, GT-2 and GT-3 give similar results for individual chlorite analyses with an average standard deviation of 14.9 °C and median values of 398, 388 and 386 °C, respectively. Temperatures calculated via GT-4 are consistently lower with an average difference of 117 °C (σ = 14 °C) and a median of 271 °C.

GT-3 and GT-4 estimates are characterised by the lowest standard deviations of analyses within individual samples at 12.6 and 11.3 °C, respectively, and will therefore be preferred over GT-1 and GT-2. The maximum temperature of GT-3 (419 °C) and the minimum temperature of GT-4 (209 °C) are commensurate with fluid inclusion homogenisation temperatures from earlier studies (see chapter 3 on page 50). The main difference between both GT-3 and GT-4 is the power of the Fe/(Fe+Mg) correction term. Thus, these estimates may represent extreme values. Average values were calculated on the basis of those two GTs, in order to achieve the most likely temperature range of chlorite crystallisation for the entire mineralising system, and to investigate temperature trends versus depth below surface. The temperature estimates range between 314 °C and 343 °C, based on the 25 and 75% percentiles. The median is calculated at 328 °C. These values are within the temperature range proposed for the main base metal precipitating fluid as suggested based on fluid inclusion studies. Consequently, it can be concluded that chlorite geothermometry results give correct temperature estimates.

A systematic temperature change with increasing depth is recorded for samples taken from the lower mineralisation (figure 4.41). Temperature estimates based on chlorite analyses of one sample from the upper mineralisation is at the higher end of the estimated range. A clear drop is observed in the lower mineralisation. Maximum temperature is around 9700 mRL, it then decreases with increasing depth, before increasing again up to maximum temperatures in the lowermost parts of the orebody. This trend roughly correlates with a changing host lithology as described in chapter 3 on page 35. Most chlorite geothermome-

Figure 4.40: Box and Whisker plot comparing temperature estimates of different geothermometers; geothermometric calculations are given in eq. 4.10 for GT-1, eq. 4.11 for GT-2, eq. 4.12 for GT-3 and eq. 4.13 for GT-4.

Figure 4.41: Chlorite temperature variability vs. depth.
4. ORE MINERALOGY AND PETROGRAPHY

ters are empirically based. It is well known that chlorite composition can be sensitive to many factors, not solely to temperature (e.g. de Caritat et al., 1993). Changes in fluid conditions (e.g. $f_O$, pH, temperature) and/or host lithology (e.g. $Fe/Mg$ values) are amongst those factors. Temperature values should always be taken with caution and only used in combination with alternative methods. Some authors even refuse chlorite geothermometry entirely. However, temperature estimates calculated in the course of this study are in agreement with results presented in other studies using different methods, e.g. fluid inclusions studies. The calculated temperature dependency as a function of depth is related to a change in host lithology. This change may reflect either changing crystallisation temperatures, changes in fluid characteristics or is induced by the changing chemical composition of the host lithology.

4.2.4 Application of the sphalerite geobarometer

There is a large literature on sphalerite incorporating Fe in the lattice structure and its dependence on temperature, sulphur fugacity and pressure (e.g. Barton and Toulmin, 1966; Scott and Barnes, 1971; Scott and Kissin, 1973; Hutchison and Scott, 1981). If the activity of FeS ($a_{FeS}$) is buffered by sphalerite coexisting with pyrite and hexagonal pyrrhotite, temperature dependency is negligible at up to approximately 530 °C. Under these circumstances, the Fe content in sphalerite is strongly dependant on the effective pressure during mineral growth, enabling its utilisation for geobarometric calculations.

Microscopic observations and mineral chemical investigations as part of this study clearly showed that: (1) sphalerite and pyrrhotite are co-genetic; (2) pyrite varieties occur throughout the paragenetic sequence and in the wall rock sequence; (3) initial hexagonal pyrrhotite was retrogressed to the monoclinic polymorph; and (4) most of the orebody has been deformed at varying intensities. Pyrrhotite is the most abundant syn-base metal iron sulphide species but pyrite is present within the host rocks and is a major mineral within the orebody. The ore-forming fluid certainly would have interacted with the wall rock during ascent and with pre-enriched pyrite at the site of ore precipitation. Thus it can be assumed that the $a_{FeS}$ of the ore forming fluid is at or close to the pyrrhotite-pyrite buffer assemblage. Therefore, sphalerite was in equilibrium with both iron sulphides at the time of precipitation. However, re-equilibration is highly probable to have occurred during the transformation of hexagonal to monoclinic pyrrhotite. During deformation of the orebody, remobilisation and recrystallisation of sulphides occurred. Ore textures such as sulphide banding clearly indicate disequilibrium of base metal sulphides with iron sulphides. Considering these observations, it is unlikely that the application of the sphalerite geobarometer will result in correct pressure estimates. Nevertheless, an obvious and systematic change of iron content in sphalerite is present throughout the orebody that needs explanation (section 4.2.1 on page 79).

Pressure was calculated via the equation

$$P = 42.30 - \log (mole\% \text{Fe}_{Sph})$$

(Hutchison and Scott, 1981) for sphalerite compositions as described in section 4.2.1 on page 79 (complete sphalerite data set is shown in appendix A section A.4.2). The results range between 6.6 and 23.5 kbar, and are, as expected, far too high as to be plausible. Despite the absolute pressure values being wrong, their relative changes in respect to ore types and depth within the orebody seem significant and are thus discussed in the following.

Figure 4.42 shows pressure estimates and their variations for different ore types. Pyrrhotite dominated ore types (Po and SiPo) show rather uniform values at a combined median of approximately 8.8 kbar. Results for other ore types feature a significant variation with a combined median of 14.9 kbar. The pronounced spread in pressure is mostly caused by sphalerite analyses from the upper apophysis of the orebody in pyritic ore (Py and SiPy), featuring the lowest Fe content of all analyses.
By plotting calculated pressures vs. depth within the orebody, two groups were defined (Figure 4.43). The pressure values for those two groups are approximately 19.1 and 8.9 kbar. The latter value is close to the median of pyrrhotite-rich ore.

Pressure calculations based on the sphalerite geobarometer were unsuccessful and resulted in far too high and meaningless pressure estimates, confirming microscopic observations of ore texture, indicating that sphalerite and pyrrhotite are not in equilibrium with pyrite. The observed variability of iron incorporated in sphalerite may to some extent be controlled by deformational-induced re-crystallisation and subsequent re-equilibration with adjacent iron sulphide phases.

Two iron populations were identified in massive pyritic ore with the high-Fe one featuring similar concentrations as sphalerite in massive pyrrhotic ore (see Figure 4.42; pressure and Fe content in sphalerite feature an inverse relation). Some ore zones now classified as pyritic would need to, in genetic terms, be classified as pyrrhotitic ore. This is because initial pyrrhotite has been altered to marcasite. Such mis-classified ore zones (in genetic terms) may contain high-Fe sphalerite typical for pyrrhotite dominated ore types, causing the two Fe populations. Low Fe-sphalerite may have formed exclusively via replacement of pyrite in zones where pyrrhotite is absent.

But neither the deformational mechanism, nor the mis-classification of ore types sufficiently explains the systematic shift from low-Fe sphalerite in the upper main lode zone to consistent high-Fe sphalerite in lower zones of the orebody (see Figure 4.43; pressure and iron content in sphalerite feature an inverse relation), independent of whether pyrite or pyrrhotite is the prevailing iron sulphide species. The only feasible explanation seems a change in the fluid chemistry that precipitated sphalerite in the first place as the hydrothermal system evolved. The precipitation of significant pyrrhotite from the hydrothermal fluid may have caused a decrease of its FeS activity, subsequently less FeS is available for the incorporation with sphalerite.
4.3 Trace element composition derived from LA-ICP-MS

MAJOR and minor element composition has been investigated via electron microprobe analysis (EMPA) for all important sulphide mineral phases occurring in the Elura orebody. Several significant elemental trends were identified (see section 4.2.1 on page 79). In order to validate these trends and to further investigate trace element concentrations in sphalerite, galena, pyrite and pyrrhotite down to concentration levels not detectable via EMPA, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) was used. It is known from literature, that the above mineral phases are capable of incorporating a diversity of elements (e.g. Blackburn and Schwiendeman, 1977; Foord and Shawe, 1989; Sharp and Buseck, 1993; Huston et al., 1995; Cook et al., 2009; Large et al., 2009; Ye et al., 2011). The elements are either incorporated via stoichiometric or non-stoichiometric lattice substitution or as evenly distributed micro impurities at nanometre scale.

The main focus in the course of this study is to identify the mineral hosts for important smelter penalty elements (e.g. Bi, Hg, As, Mn, etc.), the potential occurrences of unidentified beneficial elements (e.g. In in sphalerite), and to investigate the amount of Ag incorporated in sulphides other than sulfosalts phases, in particular in galena. Where significant element enrichments were identified, an attempt was made to find evidence of the nature and mechanisms of element incorporation. Trace element concentrations as well as their spatial variability throughout the mineralisation may indicate changes in physio-chemical fluid characteristics or metal source.

Investigated samples roughly cover the depth extent of the Elura orebody (figure 4.44). Sample selection focussed primarily on elevated Bi concentrations observed via EMPA or whole rock geochemistry (see section 4.2.1 on page 79 and chapter 5 on page 149). Nine samples were selected for trace element analysis of sphalerite, galena, pyrite and pyrrhotite. Pyrrhotite is present in three of the samples. Galena was analysed in two additional samples. These two samples were selected based on high Bi concentrations identified via whole rock geochemistry. The samples are prepared as uncovered polished thick sections*.

4.3.1 Analytical background

Trace element analyses were carried out using the LA-ICP-MS system at Adelaide Microscopy, University of Adelaide. The instrument setup consists of a high performance New Wave Nd:Yag 213 nm UV laser ablation system attached to an Agilent 7500cs quadrupole ICP-MS.

---

* Sample preparation was carried out at the Department of Applied Geosciences and Geophysics; chair of Resource Mineralogy; University of Leoben, Austria.
MS. A constant laser spot size of 30 µm at a laser repetition rate of 5 Hz was used. The ablated aerosol was carried by a mixture of helium and argon before being directly introduced into the torch. Counts per second intensities (cps) of the following isotopes were monitored:

\[ \begin{align*}
29Na \quad 34S \quad 43Ca \quad 51V \quad 52Cr \quad 55Mn \quad 57Fe \quad 60Ni \quad 65Cu \quad 66Zn \quad 69Ga \quad 75As \quad 82Se \quad 95Mo \quad 107Ag \quad 111Cd \quad 114Cd \quad 115In \quad 118Sn \quad 119Sn \quad 121Sb \quad 123Te \quad 184W \quad 190Ir \quad 197Au \quad 202Hg \quad 205Tl \quad 208Pb \quad 209Bi
\end{align*} \]

A total acquisition time of 99 s was used with a minimum of 30 s for background and approximately 60 s for sample signal, depending on sample homogeneity.

Raw data was processed using the GLITTER data reduction software package of Van Ackerbergh et al. (1999). Element concentrations used for internal standardisation were: Zn for sphalerite, Pb for galena and Fe for pyrite and pyrrhotite. These element concentrations were established using EMPA. For samples not analysed by EMPA, median element concentrations based on all EMP analyses were used for galena, pyrite and pyrrhotite. For two sphalerite samples not analysed by EMPA, the Zn concentration of adjacent samples with known composition was used.

The USGS polymetal sulphide standard MASS-1, formerly described as PS-1 by Wilson et al. (2002), was used for calibration. The time-resolved intensity profiles of MASS-1 standard analyses (n=40) of all certified elements and of those classified as informative are shown in appendix A on page 379. The counts per second intensities feature well-defined plateaus for most elements with the exception of Ba and Au. Table 4.16 shows the calculated average and maximum RSDs of element intensities and the average sample signal to background ratios (Data/Bkg). The observed average RSD values range between 9 and 15% for most elements. RSD of Ba is significantly higher with an average of 90% and a maximum RSD in excess of 400%. Intensities appear rather erratic. Additionally, the Data/Bkg ratio for Ba is relatively low at 23. Barium concentrations are therefore not considered as valid. The elevated RSD values of Cu at an average of 20% are not considered significant due to very high Data/Bkg ratios in excess of 30,000. The isotopes 111Cd and 119Sn feature higher RSDs and lower Data/Bkg ratios compared to 114Cd and 118Sn. Therefore, element concentrations calculated on the basis of the latter isotopes were preferred.

The MASS-1 standard is not certified for Au. The variable appearance of the time-resolved intensity profiles of Au (appendix A on page 379) and the subsequent high RSD values (average 35%, maximum 156%) are indicative for a heterogeneous Au distribution within the MASS-1 standard. Wilson et al. (2002) noticed this problem and linked the heterogeneity to sub-micron sized micro-nuggets. Analytical results for Au are therefore unreliable, un validated and are informative only. RSDs of Cr, Se and Te are acceptable, however their Data/Bkg ratios are rather low. Concentration data of those elements may involve some degree of uncertainty.

<table>
<thead>
<tr>
<th></th>
<th>Mean detection limit [ppm]</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bkg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg.</td>
<td>Max.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>25.6 36.0</td>
<td>9.2</td>
<td>18.7</td>
<td>96</td>
<td>0.15</td>
</tr>
<tr>
<td>Cr</td>
<td>5.6 9.9</td>
<td>9.6</td>
<td>40.5</td>
<td>4.1</td>
<td>1.00</td>
</tr>
<tr>
<td>Mn</td>
<td>6.1 10.7</td>
<td>9.9</td>
<td>14.3</td>
<td>23</td>
<td>0.61</td>
</tr>
<tr>
<td>Fe</td>
<td>29.6 42.6</td>
<td>10.1</td>
<td>46.6</td>
<td>974</td>
<td>15.57</td>
</tr>
<tr>
<td>Co</td>
<td>33.4 46.6</td>
<td>11.1</td>
<td>20.4</td>
<td>158</td>
<td>0.12</td>
</tr>
<tr>
<td>Ni</td>
<td>32.8 48.0</td>
<td>11.4</td>
<td>19.0</td>
<td>48</td>
<td>0.46</td>
</tr>
<tr>
<td>Cu</td>
<td>74.3 275.2</td>
<td>28.0</td>
<td>75.9</td>
<td>33319</td>
<td>0.72</td>
</tr>
<tr>
<td>Zn</td>
<td>52.5 239.3</td>
<td>10.8</td>
<td>39.8</td>
<td>20154</td>
<td>1.54</td>
</tr>
<tr>
<td>Ga</td>
<td>31.2 45.4</td>
<td>11.2</td>
<td>26.9</td>
<td>124</td>
<td>0.15</td>
</tr>
<tr>
<td>As</td>
<td>28.6 37.9</td>
<td>14.9</td>
<td>18.6</td>
<td>24</td>
<td>0.08</td>
</tr>
<tr>
<td>Se</td>
<td>15.7 25.3</td>
<td>13.1</td>
<td>35.8</td>
<td>2</td>
<td>6.41</td>
</tr>
<tr>
<td>Mo</td>
<td>37.0 53.2</td>
<td>12.1</td>
<td>18.9</td>
<td>45</td>
<td>0.48</td>
</tr>
<tr>
<td>Ag</td>
<td>36.6 51.6</td>
<td>12.6</td>
<td>19.6</td>
<td>128</td>
<td>0.14</td>
</tr>
<tr>
<td>Cd</td>
<td>37.4 50.0</td>
<td>13.8</td>
<td>21.2</td>
<td>27</td>
<td>0.80</td>
</tr>
<tr>
<td>Ce</td>
<td>38.8 52.0</td>
<td>12.7</td>
<td>19.9</td>
<td>67</td>
<td>0.32</td>
</tr>
<tr>
<td>La</td>
<td>37.3 55.4</td>
<td>11.4</td>
<td>22.4</td>
<td>375</td>
<td>0.05</td>
</tr>
<tr>
<td>Sm</td>
<td>33.1 54.2</td>
<td>11.8</td>
<td>18.6</td>
<td>76</td>
<td>0.24</td>
</tr>
<tr>
<td>Eu</td>
<td>36.2 51.7</td>
<td>14.2</td>
<td>31.3</td>
<td>35</td>
<td>0.60</td>
</tr>
<tr>
<td>Yb</td>
<td>39.4 59.3</td>
<td>10.8</td>
<td>18.3</td>
<td>134</td>
<td>0.18</td>
</tr>
<tr>
<td>Tc</td>
<td>12.9 18.2</td>
<td>10.0</td>
<td>19.1</td>
<td>3</td>
<td>0.72</td>
</tr>
<tr>
<td>Ba</td>
<td>39.5 55.4</td>
<td>90.1</td>
<td>418.2</td>
<td>23</td>
<td>3.69</td>
</tr>
<tr>
<td>Sr</td>
<td>39.4 48.7</td>
<td>11.8</td>
<td>18.6</td>
<td>43</td>
<td>0.18</td>
</tr>
<tr>
<td>Ca</td>
<td>39.0 52.9</td>
<td>10.4</td>
<td>22.4</td>
<td>288</td>
<td>0.05</td>
</tr>
<tr>
<td>Au</td>
<td>39.0 48.3</td>
<td>35.6</td>
<td>156.3</td>
<td>128</td>
<td>0.17</td>
</tr>
<tr>
<td>Hg</td>
<td>18.1 24.6</td>
<td>10.3</td>
<td>24.2</td>
<td>36</td>
<td>0.31</td>
</tr>
<tr>
<td>Ti</td>
<td>38.7 52.5</td>
<td>10.3</td>
<td>21.3</td>
<td>389</td>
<td>0.04</td>
</tr>
<tr>
<td>Pb</td>
<td>31.2 108.5</td>
<td>12.6</td>
<td>32.8</td>
<td>161</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 4.16: Calculated average and maximum relative standard deviations (RSD) of element intensities for standard analyses, average sample signal to background ratio (Data/Bkg), and resulting average lower detection limit (LDL).
4. ORE MINERALOGY AND PETROGRAPHY

4.3.2 Overview of analytical results

Time-resolved intensity profiles of a total of 156 analyses were scrutinised for potential impurities and 26 LA-ICP-MS analyses rejected due to heavy contamination with other mineral phases. Element concentrations, 1-σ errors and lower detection limits of the remaining data set of 130 analyses in addition to their corresponding time-resolved intensity profiles are given in appendix A on page 379.

Cluster analysis of counts per second intensity data of sphalerite, galena and pyrite was used to investigate trace element affinities to certain mineral phases (see figure 4.45). The elements Sb, Ag, Tl, Sn, Se, Bi and Te are closely related to Pb, thus indicating galena as their host phase. Hg, Cd, In, Ga and Mn are linked to Zn suggesting incorporation in sphalerite. Elements featuring affinities to Fe are Co, Ni, and As, indicative for their association with pyrite, or to potential impurities of arsenopyrite. According to the cluster analysis, Cu appears linked to As and Fe, but its real nature of occurrence is uncertain.

Cluster analysis* of counts per second intensity data of sphalerite, galena and pyrite was used to investigate trace element affinities to certain mineral phases (see figure 4.45). The elements Sb, Ag, Tl, Sn, Se, Bi and Te are closely related to Pb, thus indicating galena as their host phase. Hg, Cd, In, Ga and Mn are linked to Zn suggesting incorporation in sphalerite. Elements featuring affinities to Fe are Co, Ni, and As, indicative for their association with pyrite, or to potential impurities of arsenopyrite. According to the cluster analysis, Cu appears linked to As and Fe, but its real nature of occurrence is uncertain.

Most Cu is likely associated with chalcopyrite. Gold is not clearly linked to any mineral phase, although relative close relation to Fe suggesting pyrite as the most probable host mineral phase.

Several correlations and trends are present for element concentration and counts per second (cps) intensity data and are presented as correlation matrices and as time-resolved intensity profile diagrams in appendix A on page 379. By comparing cps intensity trends of the investigated mineral phases (figure 4.57), potential trace element contaminations caused by microimpurities may be identified, and will be discussed for individual mineral phases in the following.

Vanadium and Cr were consistently detected at low concentrations in the order of a few parts per million in all investigated mineral phases. Due to the insignificance of these elements for this study, their very low concentrations, in addition to the lack of data and studies available in literature, their occurrence is not further discussed.

4.3.3 Trace elements in sphalerite

There is a literature and comprehensive data available on trace elements in sphalerite and this has been comprehensively compiled in Cook et al. (2009). Sphalerite readily incorporates a significant number of elements in solid solution. Undoubtedly, the three most common and best investigated ones are iron, manganese and cadmium. These two elements are incorporated via stoichiometric lattice substitution in the manner:

\[
\text{Cd}^{2+} \rightleftharpoons \text{Zn}^{2+}
\]

or generalised

\[
\text{M}^{2+} \rightleftharpoons \text{Zn}^{2+}
\]

where M is predominantly Mn, Fe, Co and Cd. Minor quantities of Cu may be incorporated via this mechanism and potentially Ni (Cook et al., 2009). Other mono-, di-, tri- and tetravalent

* Spearman’s correlation coefficients are used as attribute distance measure between elements. Cluster analysis is performed after the approach of Ward.
elements are incorporated via different mechanisms. Johan (1988) investigated the distribution of In in sphalerite and suggested generalised formulae to describe coupled lattice substitutions in sphalerite as either:

\[ M^{1+} + M^{3+} \rightleftharpoons Zn^{2+} \]

or

\[ 2M^{1+} + M^{2+} + M^{4+} \rightleftharpoons Zn^{2+} \]

or

\[ (x + 2y)M^{1+} + yM^{2+} + xM^{3+} + yM^{4+} \rightleftharpoons (4 - 4y - 2x)Zn^{2+} \]

where \( M^{1+} \) is Ag or Cu, \( M^{2+} \) is Cu, Fe, Cd, Hg or Zn, \( M^{3+} \) is In, Ga, Fe or Tl, and \( M^{4+} \) is Ge, Sn, Mo or W. The factors \( x \) and \( y \) are the atomic proportions of \( M^{3+} \) and \( M^{4+} \), respectively.

Cook et al. (2009) investigated trace elements in sphalerite of 26 different ore deposit and confirmed that the elements Cd, Co, Ga, Ge, In, Mn, Sn, As and Tl are incorporated in sphalerite in solid solution. The authors suggested that minor lattice substitution for Se, Ag and Au is possible. Other detected elements such as Pb, Sb and Bi are probably linked to micro impurities of other sulphide phases.

Time-resolved intensity profiles of sphalerite analyses consistently feature plateaus for Mn, Cd, In, Ga and Sn (example shown in figure 4.47). Copper may show plateaus but also exhibit irregular and spiky characteristics. The average trace element concentrations calculated on the basis of representative analyses of eight samples are summarised in table 4.17.

Cadmium is a common substitute for Zn in most natural occurring sphalerite with a typical concentration range of 0.1 to 0.5 wt% (Cook et al., 2009), but may reach concentration levels well in excess of 1 wt% (Ye et al., 2011; Cook et al., 2009). Concentrations in sphalerite of this study are within the lower end of the suggested concentration range with a median of 0.13 wt%. Cadmium appears homogeneously distributed within sphalerite, i.e. no zoning is indicated in the time-resolved intensity profiles. Cadmium concentration is relatively elevated in sphalerite contained in samples from deeper parts of the orebody (figure 4.46).

Low quantities of Ga, In and Sn are identified at mean concentrations up to 18, 5 and 26 ppm, respectively. A weak negative correlation trend between Cd and Ga concentrations is noticeable. The concentrations of Cd and Ga in these samples confirm this observation with Ga featuring a weak enrichment trend towards the surface (figure 4.46), the converse is shown by Cd. A rather erratic correlation is observed between Sn and In (see diagram A figure 4.57) and may be caused by sub-micron inclusions of other mineral phases such as petrukite \((Cu, Fe, Zn)_{2}(Sn, In)S_4\) or sakuraiite \((Cu, Zn, Fe)_{3}(In, Sn)S_4\). The
Figure 4.47: Example of time-resolved intensity profile of sphalerite (sample 500-ML-N, analysis ID 11-01-06). The profile features plateaus for Fe, Mn, Ca, and Sn. Mercury intensity increases over time indicating zoning. Intensities of Ag, Sb and Pb are caused by micro-impurities.
4.3 Trace element composition derived from LA-ICP-MS

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Overall (n = 22)</th>
<th>350-ML4-475-2ML-2475-12-2-A</th>
<th>475-12-2-A</th>
<th>500-ML-N</th>
<th>5D-ML-N-A</th>
<th>NPT76-1</th>
<th>NP910-2-2-A</th>
<th>NP950-3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max Median Min</td>
<td>(n = 2) (n = 4) (n = 2) (n = 2) (n = 2) (n = 2) (n = 3) (n = 2) (n = 3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>3.70 0.12 0.09</td>
<td>&lt; LDL 0.15 0.25 3.70 0.10 &lt; LDL &lt; LDL &lt; LDL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>3.20 2.12 0.13</td>
<td>&lt; LDL &lt; LDL &lt; LDL &lt; LDL &lt; LDL &lt; LDL &lt; LDL &lt; LDL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>299.94 35.39 3.13</td>
<td>&lt; LDL 112.30 43.72 23.93 30.23 30.03 44.89 10.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>47.03 2.39 0.07</td>
<td>&lt; LDL 0.12 &lt; LDL &lt; LDL &lt; LDL 1.61 &lt; LDL 44.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.99 1.99 1.99</td>
<td>&lt; LDL &lt; LDL &lt; LDL &lt; LDL &lt; LDL 1.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>6355.02 92.66 5.98</td>
<td>1027.25 251.91 31.15 77.08 63.04 2133.03 2897.12 11.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>6355.02 92.66 5.98</td>
<td>1027.25 251.91 31.15 77.08 63.04 2133.03 2897.12 11.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>7.51 6.23 1.51</td>
<td>&lt; LDL 7.51 &lt; LDL 6.23 1.51 &lt; LDL &lt; LDL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>8.20 5.93 3.65</td>
<td>&lt; LDL &lt; LDL &lt; LDL 3.65 &lt; LDL &lt; LDL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>1.95 1.18 0.41</td>
<td>&lt; LDL &lt; LDL &lt; LDL 1.18 &lt; LDL &lt; LDL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>20.81 8.95 0.84</td>
<td>&lt; LDL &lt; LDL &lt; LDL 4.38 &lt; LDL &lt; LDL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>6355.02 92.66 5.98</td>
<td>1027.25 251.91 31.15 77.08 63.04 2133.03 2897.12 11.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>102.90 23.53 2.69</td>
<td>24.81 13.28 36.66 49.30 11.66 20.88 23.53 92.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>4.08 0.14 0.03</td>
<td>0.24 0.26 &lt; LDL &lt; LDL &lt; LDL &lt; LDL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.17: Summary of trace element composition of sphalerite and average element concentrations of selected analyses, not contaminated by micro-impurities of other mineral phases. Elements labeled with # are detected in most analyses.

A more likely explanation, however, is interference between $^{115}$Sn and $^{115}$In isotopes in tin rich samples.

Manganese concentrations are rather low and range between 3 and 300 ppm (median 35 ppm). Zoning in respect to Mn content is indicated by intensity-profiles of some analyses (appendix A on page 379).

Mercury is incorporated at concentration levels between a few parts per million and up to 100 ppm and features an enrichment trend towards the surface (figure 4.46). One sample mis-fits this trend. This stringer ore sample (NP950-3) was taken at some distance almost 200 m below the orebody, thus it may not immediately support or feature trends observed within the main mineralisation. Thallium concentrations are low at a medium of 0.1 and a maximum of 0.6 ppm. The counts per second intensity relationship between Tl and Hg of sphalerite, pyrite and galena is shown in diagram H figure 4.57 and indicate Tl may be, in places, enriched in sphalerite. However, these analyses also feature high Ag (diagram G figure 4.57) and Sb (diagram E figure 4.57) and their concentrations clearly correlate (see correlation matrix in appendix A on page 379). Silver is known to be incorporated in sphalerite as lattice substitute, Sb is not. Results of this study show that Ag, Sb and Tl are present in galena and, in places, detected in pyrite (see further below). Thus, Tl, Ag and Sb if present in sphalerite, are likely caused by micro-inclusions of galena and/or pyrite.

The observed Cu concentrations are highly variable at a median of 93 ppm and as high as 6,355 ppm. Chalcopyrite inclusions in sphalerite are quite abundant (section 4.1 on page 63). These inclusions predominantly occur as elongated grains or lamellae along cleavage or crystallographic planes. High Cu intensities, despite featuring well defined plateaus, may be caused by such inclusions which are orientated sub-parallel to the laser ablation axis. Copper may be incorporated in the sphalerite lattice either via direct substitution for Zn (minor quantities) or coupled substitution (Cook et al., 2009). According to Huston et al. (1995), sphalerite may contain Cu in solid solution to concentrations up to 4,500 ppm. The real amount of Cu incorporated in solid solution is not quantifiable based on results of this study. Copper in sphalerite at Elura is likely caused by both, chalcopyrite impurities and lattice substitution.
4. ORE MINERALOGY AND PETROGRAPHY

Element counts per second intensity diagrams show that elevated concentrations of Se, Ag, Sb and Bi are caused by micro-inclusions of galena or pyrite (diagram C, F and I figure 4.57). Enrichment of Co, Ni or As is caused by impurities of either pyrite or arsenopyrite (diagram D figure 4.57).

The lattice substitution within sphalerite may involve up to three different exchange reactions (see eq. 4.16 to eq. 4.18). No particular element pairs for coupled substitution were identified based on element correlations in this study.

It has been suggested in the literature that the laser ablation process causes a significant element fractionation between Zn and other elements at variable intensities during sphalerite analysis (Cook et al., 2009). Subsequently, a correction of trace element concentrations is needed. Cook et al. (2009) described these element specific correction factors, e.g. 1.50 for Cd and 1.49 for Fe. Comparison of Cd LA-ICP-MS concentrations with those acquired via EMP confirmed that such a systematic error may exist. The calculated concentration ratios (i.e. conc. EMP/conc. LA-ICP-MS) range between 1.1 and 1.5 with an average of 1.35. However, Fe concentrations established by both methods are relatively close at a median concentration ratio of 1.1. Although not similar, the correction factor of 1.49 as suggested by Cook et al. (2009) appears far too high. Due to these inconsistencies, corrections of measured element concentrations were not carried out.

4.3.4 Galena trace element composition

Trace elements incorporated in galena are not as extensively studied as those in sphalerite. Galena and sulfosalt mineral phases exhibit a complex relationship within the \((Ag + Cu) - (Bi + Sb) - Pb\) ternary phase system. The relationship between galena, matildite \(AgBiS_2\) and miargyrite \(AgSbS_2\) is described in several studies (e.g. Foord and Shawe, 1989; Damian et al., 2008; Chutas et al., 2008). The existence of a complete solid solution series between galena and \(\beta-AgBiS_2PbSS\) is still debated. Five intermediate solid solution phases have been identified and are described in the literature (Foord and Shawe, 1989; Damian et al., 2008), i.e.

\[Ag_2PbBi_2S_5,\]

\[Ag_{5.6}Pb_4Bi_{5.6}S_{15.2},\]

\[AgPbBiS_3,\]

\[Ag_2Pb_3Bi_2S_7\]

and

\[Ag_3Pb_7Bi_3S_{13}.\]

Based on thermodynamic experiments, Chutas et al. (2008) proposed a significant immiscibility gap between galena and miargyrite for temperatures below 400 °C with a solubility of \(AgSbS_2\) in galena of 4 mol% and less than 2 mol% at 300 and 200 °C, respectively.

Foord and Shawe (1989) compiled several analyses of galena associated with sulfosalt phases. The reported concentrations of Bi, Ag, Cu and Sb suggests their incorporation as solid solution in galena reaches maximum levels of 12.2 wt%, 9.0 wt%, 13 wt% and 5.4 wt%, respectively. Whether such high values are achievable via lattice substitution or caused by impurities of discrete sulfosalt species is still debated. Several authors suggest that most detected trace elements are the product of such impurities (e.g. Sharp and Buseck, 1993; Reeson et al., 1990; Costagliola et al., 2003).

Elements described to be enriched up to significant concentration levels are Bi, Ag, Te, Se, Sb, Cu, Tl, Zn and potentially Hg, with Bi, Ag and Sb being most abundant (Foord and Shawe, 1989). The latter three elements in addition to Cu are incorporated via charge balanced coupled lattice substitution (e.g. Blackburn and Schwendeman, 1977) defined by the following exchange:

\[(Ag^{1+} \text{ or } Cu^{1+}) + (Bi^{3+} \text{ or } Sb^{3+} \text{ or } As^{3+}) \rightleftharpoons 2 Pb^{2+}\]
4.3 Trace element composition derived from LA-ICP-MS

The mechanisms of Tl, Hg and Zn incorporation are not described in the literature. Thallium incorporation is likely to be established similar to the aforementioned coupled substitution reaction along with Ag and Cu, or with Bi, Sb and As. That is because Tl may feature monovalent or trivalent charge. Divalent Tl does not occur in nature. Zinc and Hg are most probably directly substituted for Pb in solid solution, although Hg, also occurring in monovalent state, may also take part in the coupled substitution reaction along with Ag or Cu. Selenium substitutes for S within the solid solution series with the end-members clausthalite (PbSe). No solid solution series exists between galena and altaite (PbTe).

Several elements consistently feature plateau-like time-resolved intensity profiles in galena (example shown in figure 4.50). Those elements are Se, Ag, Cd, In, Sn, Sb, Te, Tl and Bi. The average trace element concentrations calculated on the basis of representative analyses of eleven samples are summarised in table 4.18.

The most enriched elements are Bi, Sb and Ag. Bismuth concentrations vary significantly and range between 0.05 and 5,645 ppm. A significant increase in Bi concentration is noticed towards deeper parts of the orebody (figure 4.48). Silver and Sb are not quite as variable with concentrations ranging between 332 to 2,339 ppm and 94 to 2,385 ppm, respectively. A converse trend compared to Bi is observed for Sb with decreasing concentrations with depth, whereas Ag appears to be enriched towards the upper and the lower parts of the mineral-

![Figure 4.48](image-url)  
*Figure 4.48: Compositional variability of galena vs. depth. Selenium and tellurium concentrations increase with increasing depth. An inverse trend is observed for antimony and thallium. Silver content is elevated in galena contained in samples from deep as well as shallow parts of the orebody. One sample miss-fits most trends (symbol filled red). This stringer ore sample (NP950-3) was taken at some distance almost 200 m below the orebody, thus it may not immediately support or feature trends observed within the main mineralisation.*
isation (figure 4.48). Other elements are detected at maximum concentrations of 236 ppm for Se (median 40 ppm) and 7 ppb for Te (median 2 ppm). Both elements feature a clear enrichment trend similar to Bi (figure 4.48). Thallium is commonly present at concentrations in the order of 4 ppm (median) but is detected as high as 82 ppm in one sample (CAF-1LS-1-1) from the upper most part of the orebody (figure 4.48). Tin concentrations are low and range between 24 and 115 ppm, following the enrichment trend defined by Bi, Se and Te (figure 4.48). Similar to sphalerite, trace element concentrations of one sample (NP950-3) is not in accord with the observed depth trends. The observed concentrations of this stringer ore sample, however, are well within the variability defined by the entire data set.

Cadmium, although at rather low concentration levels, is commonly detected between 8 and 21 ppm, featuring plateau-like time-resolved intensity profiles. No significant element concentration or counts per second intensity correlations were identified (appendix A on page 379). If sphalerite micro impurities are the cause for elevated Cd concentrations in galena, correlations between Cd and Ga would have to be present (see diagram B figure 4.57). Those correlations are lacking, thus contamination with sphalerite micro-impurities is unlikely. Because interference between $^{114}\text{Sn}$ and $^{114}\text{Cd}$ is possible, an additional isotope, i.e. $^{111}\text{Cd}$, has been monitored. This isotope does not interfere with any other stable isotope. Intensities (cps) of both Cd isotopes feature a very good correlation ($R^2 > 0.95$, $n = 4$, figure 4.49). Thus, interference is not indicated. It is reported in the literature that Cd may occur in galena (e.g. Blackburn and Schwendeman, 1977; Foord and Shawe, 1989; Sharp and Buseck, 1993). Most authors suggest the presence of sub-micron, evenly distributed micro-impurities as the most likely cause for elevated Sn. Foord and Shawe (1989) reported the occurrence of “tellurian canfieldite” ($Ag_8SnS_4Te_2$), Sharp and Buseck (1993) observed inclusions of franckeite ($Pb,Sn)_6Sn_2Sb_2FeS_14$. The former may be the cause for Sn in galena analysed in this study, the latter not, because of the lack of correlation with Fe and Sb. In fact, none of the element concentration or counts per second intensity correlations between Sn and other measured elements is significant (appendix A on page 379). Neither $^{118}\text{Sn}$ nor $^{119}\text{Sn}$, both measured in this study, are affected by any interference with other stable isotopes, i.e. interference is not a feasible cause for elevated Sn in galena. The ionic radius of Sn is with 1.12 Å even closer to Pb as it is to Cd. Bonding characteristics of Pb and Sn, i.e. percentage of ionic bonding with S, are with 36.4% versus 37.0% very similar (Blackburn and Schwendeman, 1977). It appears that incorporation of Sn via lattice substitution is at least up to minor concentrations in a similar way as in sphalerite for Zn.

Tin is consistently present in galena with a median concentration of 52 ppm and as high as 115 ppm. Time-resolved intensity profiles feature well-defined plateaus. Many studies reported Sn detected in galena analyses (e.g. Blackburn and Schwendeman, 1977; Foord and Shawe, 1989; Sharp and Buseck, 1993). Most authors suggest the presence of sub-micron, evenly distributed micro-impurities as the most likely cause for elevated Sn. Foord and Shawe (1989) reported the occurrence of “tellurian canfieldite” ($Ag_8SnS_4Te_2$), Sharp and Buseck (1993) observed inclusions of franckeite ($Pb,Sn)_6Sn_2Sb_2FeS_14$. The former may be the cause for Sn in galena analysed in this study, the latter not, because of the lack of correlation with Fe and Sb. In fact, none of the element concentration or counts per second intensity correlations between Sn and other measured elements is significant (appendix A on page 379). Neither $^{118}\text{Sn}$ nor $^{119}\text{Sn}$, both measured in this study, are affected by any interference with other stable isotopes, i.e. interference is not a feasible cause for elevated Sn in galena. The ionic radius of Sn is with 1.12 Å even closer to Pb as it is to Cd. Bonding characteristics of Pb and Sn, i.e. percentage of ionic bonding with S, are with 36.4% versus 37.0% very similar (Blackburn and Schwendeman, 1977). It appears that incorporation of Sn via lattice substitution is at least up to minor concentrations in a similar way as in sphalerite for Zn.
4.3 Trace element composition derived from LA-ICP-MS

Figure 4.501: Example of time-resolved intensity profile of galena (sample 775-4/12-2-A, analysis ID II-04-06). Profile features plateaus for Se, Ag, Cd, In, Sn, Sb, Te, Tl, and Bi. No zoning is indicated by any of the detected elements.
4. ORE MINERALOGY AND PETROGRAPHY

The coincidental enrichment of Bi, Sb and Ag suggests a common mechanism for their incorporation in galena. Diagram (a) in figure 4.51 shows the compositional variability of galena analyses in the ternary system Ag-Bi-Pb. Most analyses plot on or very close to the suggested galena-matildite solid solution (PbSS – AgBiS2) mixing line. The maximum observed AgBiS2 component is less than 1.25 mole%. A systematic deviation from the mixing line towards higher Bi is observed with increasing AgBiS2 component. A strong correlation of element concentrations between Bi and Te, and a weak for Bi and Se was measured for galena (see correlation matrix in appendix A on page 379). These correlations most likely indicate the occurrence of bismuth minerals of the tetrahedrite group, e.g. annivite (Cu10(Fe, Zn)2(Bi, Sb, As)4S13), and would explain the deviation from the ideal PbSS – AgBiS2 mixing line. Some Se may substitute for S. Samples with a Bi concentration less than 200 ppm do not contain AgBiS2 in solid solution (blue symbols diagram (a) figure 4.51).

These galena analyses are characterised by significant Ag and Sb concentrations and, in places, elevated Tl. Diagram (b) in figure 4.51 shows the compositional variability of galena analyses in the ternary system Ag-Sb-Pb. Low Bi analyses plot on or very close to the suggested galena-miargyrite solid solution (PbSS – AgSbS2) mixing line. The maximum observed AgSbS2 component is less than 1.25 mole%. A
4.3 Trace element composition derived from LA-ICP-MS

4.3.5 Trace elements incorporated in iron sulphides

Pyrite

Trace element data for pyrite in the literature is abundant, although predominantly focussing on the investigation of invisible gold. The following elements are incorporated in pyrite via stoichiometric or non-stoichiometric lattice substitution (e.g. Huston et al., 1995; Large et al., 2009): V, Co, Ni, As, Se, Te, Mo, Au and Tl, with As being the most important. Elevated concentrations of other elements, i.e. Cu, Zn, Ag, Sb, Ba, Pb and Bi, are suggested to be predominantly caused by micro-impurities.

Despite arsenopyrite containing far more invisible Au, most pyrite can incorporate Au at low concentration levels, and due to its abundance, may represent an important significant gold host. Cook and Chryssoulis (1990) noticed a strong correlation between As and Au in pyrite trace element analyses and suggested, coupled substitution as important mechanism. Arsenic within the pyrite structure forms \([\text{AsS}^-]^{3-}\) pairs, causing a charge imbalance, subsequently enabling the incorporation of trivalent ions. A general formula for this coupled substitution reaction is:

\[
\text{Me}^{3+} + [\text{AsS}^-]^{3-} \rightleftharpoons 2\text{Fe}^{2+} + [\text{S}^-]^2
\]

with Me being As, Au, Sb, etc. (Cook and Chryssoulis, 1990).

Chouinard et al. (2005) observed a clear correlation between Ag and Sb, as well as Au and Cu. The authors proposed the coupled substitution reaction in the manner:

\[
\text{Ag}^+ + \text{As}^{3+} \rightleftharpoons 2\text{Fe}^{2+}
\]

and

\[
\text{Cu}^+ + \text{Au}^{3+} \rightleftharpoons 2\text{Fe}^{2+}
\]

Large et al. (2009) suggested that organic processes are important to enrich Au and other elements (i.e. Ni, V, Zn, Pb, Ag, Mo and Se) in diagenetic pyrite. Recrystallisation induced by

---

**Figure 4.51**: Galena composition in the Ag-Bi-Pb and Ag-Sb-Pb ternary systems [at%]. Diagram (a): samples labeled as black circles plot close to the galena-matildite solid solution \((\text{PbSS} - \text{AgBiS}_2)\) mixing line. Blue symbols misfit but plot along the galena-miargyrite solid solution \((\text{PbSS} - \text{AgSbS}_2)\) mixing line in diagram b (black circles).
4. ORE MINERALOGY AND PETROGRAPHY

Figure 4.52: Compositional variability of pyrite vs. depth. Cobalt and nickel feature a poorly defined enrichment trend with increasing depth. One sample miss-fits this trend (see figure 4.46 for further explanation). Silver and gold exhibit inverse characteristics compared to Co and Ni. Very low antimony and thallium concentrations are detected in most pyrite analyses. One sample from the uppermost area of the ML zone (sample CAF-1LS-1-1) is highly enriched in Ag, Sb, Au and Th.

Figure 4.53: Pyrite classification based on cobalt, nickel and arsenic content. Analyses with significant As concentrations in excess of 1000 ppm (sample CAF-1LS-1-1 and NP950-3) consistently feature Co/Ni ratios below 0.1 (red symbols)

metamorphism or hydrothermal fluids leads to the expulsion of those elements, subsequently “cleansing” pyrite.

Trace element determination is complicated for pyrite samples from the Elura orebody (see section 4.1 on page 64). That is because pyrite:

(a) occurs very small grained (<10 µm) and contains abundant impurities (pyrite type A, C and D); (b) is tectonised and intruded by other sulphide phases (pyrite type A and B); and (c) is replaced by base metal sulphides (pyrite type A and B). Only pyrite type B was considered coarse enough for accurate trace element determination. Nevertheless, most analyses are contaminated, caused by inclusions of other sulphide phases, or by the onset of replacement.

The average trace element concentrations of eight samples calculated based on representative analyses, only mildly affected by contamination of other sulphide phases, are summarised in table 4.19. Elements consistently incorporated in pyrite are Co, Ni and As. These elements commonly feature either gradational or well-defined plateau-like time-resolved intensity profiles, the former indicative for zoning (example see figure 4.55). Cobalt and Ni concentrations range between 0.1 to 77 ppm (median 9 ppm) and 1 to 2018 ppm (median 12 ppm), respectively. Nickel is significantly enriched in pyrite from the deepest two samples (NP950-3 and NP910-2-B; figure 4.52), whereas Co is variable. Neither of those two elements shows intensity or concentration correlations with any other monitored element (see correlation matrix in appendix A on page 379). Co/Ni ratios range between less than 0.01 and over 200. Analyses with significant As
4.3 Trace element composition derived from LA-ICP-MS

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Overall (n = 17)</th>
<th>350-ML4-475-12-2-1</th>
<th>500-ML-CAF-1LS-1-1</th>
<th>NP776-1</th>
<th>NP910-2-A</th>
<th>NP950-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>Median</td>
<td>Min</td>
<td>Max</td>
<td>Median</td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>V</td>
<td>1.56</td>
<td>0.15</td>
<td>0.10</td>
<td>1.56</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>Cr</td>
<td>1.57</td>
<td>0.75</td>
<td>0.65</td>
<td>1.57</td>
<td>1.05</td>
<td>0.72</td>
</tr>
<tr>
<td>Mn</td>
<td>2175.83</td>
<td>9.68</td>
<td>0.39</td>
<td>7.45</td>
<td>7.30</td>
<td>12.64</td>
</tr>
<tr>
<td>Ni</td>
<td>77.13</td>
<td>8.86</td>
<td>0.13</td>
<td>13.86</td>
<td>13.27</td>
<td>0.37</td>
</tr>
<tr>
<td>Cu</td>
<td>1.57</td>
<td>0.75</td>
<td>0.65</td>
<td>1.57</td>
<td>1.05</td>
<td>0.65</td>
</tr>
<tr>
<td>Ga</td>
<td>0.22</td>
<td>0.13</td>
<td>0.05</td>
<td>0.22</td>
<td>0.13</td>
<td>0.05</td>
</tr>
<tr>
<td>As</td>
<td>3.50</td>
<td>3.00</td>
<td>3.00</td>
<td>3.50</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Se</td>
<td>40.00</td>
<td>0.91</td>
<td>0.27</td>
<td>40.00</td>
<td>0.91</td>
<td>0.27</td>
</tr>
<tr>
<td>Sn</td>
<td>118.45</td>
<td>0.39</td>
<td>0.15</td>
<td>118.45</td>
<td>0.39</td>
<td>0.15</td>
</tr>
<tr>
<td>Te</td>
<td>7.44</td>
<td>0.44</td>
<td>0.28</td>
<td>7.44</td>
<td>0.44</td>
<td>0.28</td>
</tr>
<tr>
<td>Ir</td>
<td>0.67</td>
<td>0.25</td>
<td>0.05</td>
<td>0.67</td>
<td>0.25</td>
<td>0.05</td>
</tr>
<tr>
<td>Au</td>
<td>41.03</td>
<td>0.38</td>
<td>0.15</td>
<td>41.03</td>
<td>0.38</td>
<td>0.15</td>
</tr>
<tr>
<td>Bi</td>
<td>8.90</td>
<td>0.55</td>
<td>0.16</td>
<td>8.90</td>
<td>0.55</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 4.19: Summary of trace element composition of pyrite and average element concentrations of selected analyses not affected by contamination with micro-impurities or other mineral phases. Elements labeled with # are consistently detected during pyrite analyses.

Concentrations in excess of 1000 ppm (sample CAF-1LS-1-1 and NP950-3) consistently feature Co/Ni ratios below 0.1 (figure 4.53).

Arsenic concentrations vary strongly, range between 0.7 and 8018 ppm with a median of 242 ppm, and correlating with Mn, Hg and Tl (see correlation matrix in appendix A on page 379). The correlations are, however, caused by three analyses of only one sample from the upper most part of the orebody (CAF-1LS-1-1). This sample is enriched in Mn (avg. 1040 ppm), As (avg. 4593 ppm), Ag (avg. 175 ppm), Sb (avg. 513 ppm), Hg (avg. 24 ppm) and Tl (avg. 676 ppm). Time-resolved intensity profiles of manganese are commonly rather irregular and suggest the occurrence of impurities.

Gold is observed at an average concentration of 0.45 ppm in this particular sample (CAF-1LS-1-1), with one analysis yielding 19.74 ppm. Based on concentrations of As and time-resolved intensity profiles, this high Au value was identified to be caused by arsenopyrite intergrowths. The maximum Au concentration detected in pyrite not caused by arsenopyrite impurities is 1.65 ppm (median 0.25 ppm), featuring a relative constant time-resolved intensity as shown in figure 4.54. The correlation between Au and As (figure 4.54) suggests these elements are incorporated via the coupled substitution mechanism suggested by Cook and Chryssoulis (1990); Chouinard et al. (2005). A weak correlation is observed between Au-Sb and Au-Ag (see correlation matrix in appendix A on page 379) and may indicate the presence of aurostibite (AuSb2) and/or electrum micro-inclusions.

The maximum detected silver and antimony concentrations are 350 ppm (median 11 ppm) and 851 ppm (median 17 ppm), respectively. Both phases are significantly enriched in galena. It is highly probable that elevated concentrations of these two elements are caused, at least to some extent, by impurities of galena (diagram I figure 4.57). Nevertheless, time-resolved intensity profiles of some analyses showed enrichment of Ag and Sb in addition to Cu, with very low, almost absent Pb signal (figure 4.55). The correlation of these three elements is indicative for the occurrence of argentian tetrahedrite inclusions in pyrite.

Other elements, in places, observed at significant concentration levels, are Cu, Zn and Pb.
These elements are most probably caused by micro-impurities, i.e., chalcopyrite, sphalerite and galena, as has been suggested by Huston et al. (1995). Plateau-like time-resolved intensity profiles of those elements may be caused by sub-micron inclusions, which had grown as a consequence of pyrite replacement induced by base metal-bearing hydrothermal fluids. Correlations of Zn and Pb with Au and Ag (see correlation matrix in appendix A on page 379) may display a common mechanism for the introduction into pyrite via replacement and subsequent growth of sub-micron impurities. Bismuth correlates with Pb and is caused by impurities of galena.

**Pyrrhotite**

Trace elements in pyrrhotite were determined in three samples. Analyses (total n = 6) show that most elements are not significantly enriched (table 4.20, figure 4.56). Sporadic and very low concentrations of Ni and As close to detection limit are unlikely to be caused by inclusions but may be present as lattice substitutes. Copper, Zn, Ga and Hg are caused by micro-impurities of sphalerite, and those of Ag, Sb, Pb and Bi are caused by galena. Tin is detected at low concentrations in all pyrrhotite analyses but was also measured in galena, sphalerite and pyrite. Whether Sn is incorporated in pyrrhotite via lattice substitution for Fe or is caused by impurities of other mineral phases is unknown. Similar to Sn, Mn was measured in all investigated mineral phases at varying concentrations. In pyrrhotite, Mn is observed at concentrations up to 300 ppm, featuring a median of 35 ppm (table 4.20). Manganese substitutes for Zn in sphalerite. The results of this study suggests that Mn may substitute for Fe in pyrite or pyrrhotite. Ankerite and mangoan-siderite/calcite are important non-sulphide gangue mineral phases. Impurities of those carbonates may cause elevated Mn concentrations.

**Figure 4.54:** Time-resolved intensity profile for gold in pyrite (sample CAF-1LS-1-1, analysis ID I-02-15) features a relative constant time-resolved intensity; detected concentrations are 0.8 ppm V, 1.4 ppm Co, 56.2 ppm Ni, 2834 ppm As, 47.3 ppm Mo and 1.65 ppm Au.

**Table 4.20:** Summary of trace element composition of pyrrhotite and average element concentrations of selected analyses not affected by contamination with micro-impurities. Manganese labeled with (*) is commonly detected at variable concentrations. It may be incorporated in the pyrrhotite lattice or is caused by impurities of mangoan carbonate.
Figure 4.55: Example of time-resolved intensity profile of pyrite (sample NP922A-2-A, analysis ID II-07-09). Cobalt and Ni intensity profiles increase over time and are most likely caused by growth zonation. Very low intensities of Pb may be caused by replacement of pyrite by galena. Profiles of Sb, Ag and Cu are very irregular but correlate, indicating micro-impurities of argentian-tetrahedrite.
Figure 4.56: Example of time-resolved intensity profile of pyrrhotite (sample NP776-1, analysis ID I-03-09). Only Sn is detected at very low intensities.
Figure 4.57: Element intensity (cps) cross-plots. Comparison of intensity trends of the investigated mineral phases allow the identification of potential contaminations caused by micro-impurities.
4.4 Fluid inclusion study in sphalerite

Several scientists have studied fluid inclusions hosted in various mineral phases of Elura orebody, *inter alia* Seccombe (1990); Sun (2000); Sun and Seccombe (2000); Jiang *et al.* (2000). Most studies investigated fluid inclusions trapped in quartz and carbonate phases. Ideally, fluid inclusions, undoubtedly associated with the main stage of base metal sulphide mineralisation, are used to gain information about the temperature conditions during ore formation. Sphalerite is the only sulphide phase hosting fluid inclusions that may be studied due to its translucent nature. Fluid inclusions contained in this particular mineral phase have been investigated in the past but almost exclusively via crush and leach techniques. Temperature estimates were subsequently calculated based on observed fluid composition. Temperature estimates based on homogenisation temperatures observed via micro-thermometry is sparse (i.e. Sun (2000) reported 5 measurements of fluid inclusion in sphalerite in 1 sample). Fluid inclusions hosted by sphalerite were investigated in the course of this study in order to gain additional temperature estimates of ore formation based on micro-thermometry.

Ten samples were selected, covering the entire depth extent of the Elura orebody (see appendix A from page 258 for sample locations), and prepared as polished thick section*. The sections were investigated on a transmitted light microscope equipped with an infrared light source and a video camera sensitive to 1100 nm wavelength.

The identified fluid inclusions are variable in shape, mostly angular to subangular and, in places, rounded. They are relative abundant and generally small with sizes in the order of 5 to 10 µm. Figure 4.58 shows representative examples of fluid inclusions hosted by sphalerite (sample 775z1-A1; z1 ore zone). All inclusions appear to be either single phase, e.g. liquid or gas, or negative inclusions (i.e. empty). The lack of vapour phases eliminates the investigation of homogenisation temperatures via microthermometry. In places, sphalerite contains abundant microfractures potentially intersecting inclusions. Ore microscopy showed that sulphide minerals are commonly affected by deformation (see section 4.1 on page 63). Sphalerite is relative brittle compared to chalcopyrite, galena and pyrrhotite. It is highly likely that both, liquid and gas phases were lost due to

* Sample preparation was undertaken at the Department of Applied Geosciences and Geophysics; chair of Resource Mineralogy; University of Leoben, Austria.

---

Figure 4.58: Images of fluid inclusions hosted by sphalerite (sample 775z1-A1; z1 ore zone). Photos were taken under transmitted infra-red light.
4.4 Fluid inclusion study in sphalerite

The disintegration of their containment as a consequence of deformation. A weak internal black coating is observed on several inclusions.

Laser Raman micro-spectroscopy has been utilised in order to investigate the occurrence of liquid and/or gas phases potentially missed during microscopy, to identify solid phases within inclusions and to study the cause for the observed black coating. Fluid inclusions were analysed with a Jobin Yvon LABRAM confocal-Raman spectrometer at the Department of Applied Geosciences and Geophysics; chair of Resource Mineralogy; University of Leoben, Austria. The system is equipped with a frequency-doubled Nd-YAG laser (100 mW, 532.2 nm). Detection is realised with a Peltier-cooled, slow-scan, CCD matrix-detector.

Fluid inclusion analyses were compared to sphalerite spectra. Figure 4.60 shows Raman spectra of seven sphalerite analyses. Sphalerite features primary characteristic vibrations at around 300 cm\(^{-1}\), with shoulder signals extending to approximately 460 cm\(^{-1}\). Secondary vibrations occur between ~580 and 700 cm\(^{-1}\). The remaining frequency band is free of significant vibrations. A moderate increase in intensity is observed in the upper frequency band caused by fluorescence. Several inclusions contain calcite with a primary characteristic vibration at ~1085 cm\(^{-1}\) (diagram A and C figure 4.61). The occurrence of carbonaceous matter is indicated by signals at approximately ~1330 and ~1600 cm\(^{-1}\) (diagram B and C figure 4.61). No pure graphite, characterised by a single primary characteristic vibration at approximately 1600 cm\(^{-1}\), has been identified. In some inclusions, signals were observed in the upper frequency band above 2750 cm\(^{-1}\) (diagram B figure 4.61). The observed broad vibration peaks stretching from ~2800 to ~3000 cm\(^{-1}\) is characteristic for long chain n-alkanes (Mazur and Fanconi, 1979; Lawrie et al., 1999). Very minor methane may be indicated by a sharp peak at ~2900 cm\(^{-1}\) (Atamas et al., 2004) although longer chain alkanes may feature similar peaks (Atamas et al., 2004). In places, an OH-bond vibration at ~3620 cm\(^{-1}\) has been observed and is most likely caused by minor chlorite or muscovite. No CO\(_2\) (characteristic vibration spectra shown in figure 4.59) or other gas phases, nor NaCl brines (characteristic vibration spectra shown in figure 4.59) or other liquid phases were detected via Raman.

Figure 4.59: Raman spectra of reference materials and showing their primary characteristic vibrations.
Figure 4.61: Raman spectra of fluid inclusions hosted by sphalerite. Diagram A shows characteristic vibrations of calcite, diagram B those of calcite and carbonaceous material. In some inclusions, vibrations similar to n-alkanes were detected (diagram C). Weak signals characteristic for OH-bonds are likely caused by minor chlorite (diagram C). A sharp intensity peak at ~2910 cm$^{-1}$ was observed in one analysis and may indicate minor CH$_4$ (diagram C).
4.5 Zinc isotopes of sphalerite

The history of Zn isotope analytical methods and development of the techniques is briefly described in chapter 3 on page 56. Maréchal et al. (1999) were the first to describe the successful analyses of natural sample material (e.g. silicates, sulphide ores, biological) via MC-ICP-MS. The isotopic fractionation of Zn on chromatographic columns was further studied by Maréchal and Albarede (2002). Fundamentals of the analytical method and general characteristics of Zn isotope chemistry are best compiled and summarised in Albarede (2004).

Samples for Zn isotope analysis (n = 19) as part of a pilot study were selected in order to cover the entire depth extent of the orebody and all ore zones (see figure 4.62). Sphalerite grains, as pure as possible, were handpicked under the binocular from crushed sample material. Due to the large Zn concentration contrast between sphalerite and potential minor impurities of other mineral phases, it is highly unlikely that impurities have an effect on the Zn isotope composition of sphalerite in any way.

4.5.1 Analytical technique

All reagents and solutions were prepared with > 18 MΩ H₂O from a Milli-Q water purification system. All used acids were sub-boiling double distilled (HCl, HNO₃). Approximately 2 mg sample material was dissolved in aqua regia in capped Teflon beakers on a hot plate at 90 °C. Samples were evaporated to dryness upon complete dissolution. In order to ensure complete chlorite-complexation, samples were dissolved in 2 ml on 7 M HCl and evaporated to dryness. Samples were then dissolved in 1 ml of 7 M HCl for chromatography.

Maréchal et al. (1999) noticed the possibility of artificial isotope fractionation during Zn chromatography if 100% of Zn is not eluted from the columns. Elements incompletely separated from Zn may cause significant matrix-induced interferences as highlighted by Mason et al. (2004a). Important spectral interferences may be caused by argides (NaAr⁺, MgAr⁺, AlAr⁺), oxide/hydroxide (TiO⁺, TiOH⁺, VO⁺, VOH⁺, CrO⁺, CrOH⁺) and double-charged species (Ba²⁺, Ce²⁺) (Mason et al., 2004a). Zinc chromatography is a very delicate procedure and if not executed with care will lead to false analyses. The ion-exchange separation and purification of Zn is performed using the strong anion exchange resin AG MP-1 (100-200 µm, Bio-rad®) in 2 ml columns following the methodology described in Chapman et al. (2006).

Subsequent to zinc separation, samples were evaporated to dryness followed by dissolution in 10 ml 0.5 M HNO₃. An aliquot of each sample was analysed via ICP-MS† for Mg, Ca, Fe, Ni, Cu, Zn, and Cd in order to measure the Zn con-

†. Standard quadrupole Inductively Coupled Plasma-Mass Spectrometer, Adelaide Microscopy
\[
\delta^X \text{Zn} = \left[ \frac{\left( \frac{^X \text{Zn}}{^4 \text{Zn}} \right)_{\text{Samp}}}{\frac{1}{2} \left( \frac{^X \text{Zn}}{^4 \text{Zn}} \right)_{\text{StdA}} + \left( \frac{^X \text{Zn}}{^4 \text{Zn}} \right)_{\text{StdB}}} - 1 \right] \times 1000\%
\]  

(4.19)

where \( x = 66 \) and 68, the subscripts Std A and Std B denote the standard analyses prior and after the unknown sample.

centration and to investigate the quality of element separation and purification. The column chromatography delivered pure Zn solutions for all samples. Sample solutions of 2 ml 0.5 M HNO\(_3\) containing 300 ppb Zn were prepared and spiked with the NIST\(^*\) copper standard for inter-element mass bias correction via EEN\(^\dagger\) (Maréchal et al., 1999). Samples were analysed in duplicates on a Thermo Fisher Neptune MC-ICP-MS system at CSIRO, Adelaide. Analyses are normalised to bracketing standards relative to the Lyon-Johnson Matthey Company (JMC) Zn standard via eq. 4.19 (Wilkinson et al., 2005).

For analytical quality assurance and quality control (QAQC) Maréchal et al. (1999); Albared (2004) suggested to verify the mass dependence of isotopic fractionation. Diagram (a) in figure 4.63 shows the uncorrected lognormal isotopic ratios of \(^{68}\text{Zn} / ^{64}\text{Zn} \) versus \(^{66}\text{Zn} / ^{64}\text{Zn} \). Both ratios were normalised to their true isotopic ratios \( R' (0.37441) \) and \( R (0.56502) \), respectively (Maréchal et al., 1999). One analysis significantly deviated from the ideal ratio of 2:1 and has been rejected (shown as red circle). The accepted data defines a correlation coefficient \( R^2 \) of 0.997 and a ratio of 1.97:1. Diagram (b) and (d) in figure 4.63 plots the corrected and normalised values of \( \delta^{68}\text{Zn}_{JMC} \) versus \( \delta^{66}\text{Zn}_{JMC} \) for single analyses and averages including error bars (2\( \sigma \)) for duplicates. Data appears slightly more scattered due to the little spread between data sets. However, isotopic ratios are close to the ideal ratio. A correlation coefficient of 0.9999 and a ratio of 1.95:1 are calculated if standard analyses are considered (see diagram (c) figure 4.63). It is demonstrated that isotopic fractionation is highly mass dependent.

One inorganic Zn standard JMC\(_{LMTG} – 10k\)\(^\ddagger\) and one natural-like reference material IRMM3702\(^\S\) were analysed between samples for QAQC purposes. Analyses of JMC\(_{LMTG} – 10k\) resulted in an average of \( \delta^{60}\text{Zn}_{JMC} \) of \(-9.986 \pm 0.077\%_\circ\) (2\( \sigma \), n=21) compared to \(-10.00 \pm 0.03\%_\circ\) (2\( \sigma \), n=7) established by Sonke et al. (2008). Seven analyses of IRMM3702 gave an average of \( \delta^{66}\text{Zn}_{JMC} \) of 0.308 \pm 0.065\%_\circ (2\( \sigma \), n=4) as defined by Petit et al. (2008). Both standard analyses are well within error.

---


\( ^\ddagger \) Johnson Matthey Company (JMC) inorganic Zn solutions of 10,000 \( \mu \)g g\(^{-1}\)

4.5.2 Results and discussion

An additional single analysis has been rejected due to high analytical error, thus no average and double standard deviation values can be calculated for two samples. Analyses are summarised in table 4.21 and presented as histogram in figure 4.64. The observed $\delta^{66}\text{Zn}_{\text{JMC}}$ values range between 0.220 and 0.450‰ with an average of 0.295 ±0.117‰ (avg. ±2σ, n=19) based on all averaged duplicate analyses. The high 2σ value indicates variability of the isotopic sphalerite composition of different samples and does not represent poor analytical quality. The averaged 2σ value for duplicates (i.e. analytical uncertainty) is significantly lower at 0.031‰. No systematic $\delta^{66}\text{Zn}_{\text{JMC}}$ values are observed in respect to different ore types (see diagram (b) figure 4.64). The spatial variability in $\delta^{66}\text{Zn}_{\text{JMC}}$ is shown in figure 4.65. Two repetitive trends of increasing $\delta^{66}\text{Zn}_{\text{JMC}}$ are inferred for samples from the lower and the upper mineralisation. Both trends appear to be linked to lithological changes of the host rock sequence as described in chapter 3 on page 35.

The fractionation mechanisms affecting the stable isotope system of Zn in geological processes is poorly understood. Very few Zn isotope data of geologically-constrained material is available in the literature in general and, in particular, for sulphide deposits. Some data has been published for chondrites, basaltic rocks, marine sediments (e.g. shale, limestone) and ferromanganese nodules (Albarede, 2004).

Figure 4.63: (a) Plot of $\ln(68\text{Zn}/64\text{Zn})/R'$ vs. $\ln(66\text{Zn}/^{64}\text{Zn})/R$ to verify the mass dependence of isotopic fractionation after Maréchal et al. (1999); with $R' = 0.37441$ and $R = 0.56502$. Analysis define a linear trend with a slope of 1.97. One analysis (red circle) deviates from this trend and was rejected. Corrected and normalised values of $68\text{Zn}_{\text{JMC}}$ versus $66\text{Zn}_{\text{JMC}}$ for single analyses in diagram (b), including standard analyses in diagram (c) and sample averages including error bars (2σ) for duplicates in diagram (d).
4. ORE MINERALOGY AND PETROGRAPHY

Wilkinson et al. (2005) compiled all data available in the literature at this time and suggested a range between 0.2 and 0.3‰ ($\delta^{66}$Zn) for bulk isotopic composition of average continental crust. Based on this compilation, sphalerite composition ranges between -0.3 and +1.3‰, with most values within the interval between -0.1 and +0.4‰.

Wilkinson et al. (2005) studied sphalerite from base metal deposits in the Midland Basin in Ireland and observed $\delta^{66}$Zn values between -0.17 to 0.64 (one outlier 1.33). The authors suggested four mechanisms potentially controlling the significant isotope variation:

(a) variations in the source rock composition,
(b) temperature gradients,
(c) mixing of multiple Zn sources and
(d) kinetic fractionation during rapid precipitation in disequilibrium conditions and accompanied by enrichment of heavy Zn via Rayleigh fractionation.

Wilkinson et al. (2009) studied underlying basement rocks as the potential source for base metals of these deposits and found the Zn isotope signatures ranging between -0.01 and 0.26‰ ($\delta^{66}$Zn). Partial leaching experiments showed that weakly leached source rock produces a metal-bearing fluid enriched in heavier Zn, whereas the fluid from efficiently leached rock would exhibit a signature similar to the source.

Mason et al. (2005) investigated Zn isotopes of sulphides from the Alexandrinka VHMS deposit. Sphalerite-dominated samples yield an overall range of -0.027 and 0.231‰ ($\delta^{66}$Zn). Samples from stockwork feeder zones are consistently low at 0.0 ±0.1‰ ($\delta^{66}$Zn). This isotopic signature is interpreted to represent the initial hydrothermal fluid and agrees with bulk

Figure 4.64: Histogram showing the distribution of zinc isotope composition of sphalerite ($\delta^{66}$Zn$_{JMC}$) as overview in (a) and for individual ore types in (b).

Figure 4.65: Zinc isotope variability vs. depth; error bars are 2σ values. Two weak repetitive trends of increasing $\delta^{66}$Zn$_{JMC}$ are inferred for samples from the lower and the upper mineralisation.
earth composition suggested by other authors (e.g. Maréchal et al., 1999). The authors suggested a syngenetic Zn isotope fractionation is caused either by a temperature controlled fractionation factor or by Rayleigh fractionation.

John et al. (2008) studied Zn isotope composition of venting fluids of modern hydrothermal seafloor systems. The fluids feature an isotopic composition ranging between 0.00 and 1.04‰ ($\delta^{66}$Zn). A negative correlation between $\delta^{66}$Zn with temperature was identified with isotopically lighter higher temperature fluids (>250 °C). Sub-seafloor precipitation of isotopically light sphalerite induced by cooling during ascent is proposed as the cause for isotope fractionation. This observation is confirmed by high (383 °C) and low (203 °C) temperature sphalerite samples characterised by respective low and high $\delta^{66}$Zn.

The $\delta^{66}$Zn$_{JMC}$ values of this study are with an average of 0.295 ±0.117‰ close to bulk isotopic composition of proposed by Wilkinson et al. (2005). Thus, Zn and most probably other base metals were extracted from a crustal source. The minor spread and lack of extremely high $\delta^{66}$Zn$_{JMC}$ values indicate that Zn has been effectively leached from the source reservoir (Wilkinson et al., 2009). A weak but noticeable Zn fractionation as a function of depth below surface is observed and defined by a light $\delta^{66}$Zn$_{JMC}$ signature at depth, becoming progressively heavier towards the surface (figure 4.65). This trend appears repetitive in nature and inferred in the lower part of the orebody as well as in the upper main lode zone. The two mechanisms most excepted by the research community are syngenetic Rayleigh and temperature controlled fractionation. Both are feasible to be causing the observed Zn isotope fractionations at the Elura, where areas of light isotope signature mark major influx zones of the initially unfractonated hydrothermal fluid. As the fluid ascended it got progressively enriched in heavy Zn isotopes via Rayleigh fractionation. Additionally, fluid temperatures may have decreased due to its constant interaction with wall rock or by mixing with a cooler fluid at the site of ore formation, which was expelled from the country rock. The temperature decrease may have aided the isotopic fractionation of Zn.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Type</th>
<th>Sample</th>
<th>Zone</th>
<th>Analysis</th>
<th>Avg. 2 σ</th>
<th>$\delta^{66}$Zn$_{JMC}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAF-1LS-1-1</td>
<td>Py</td>
<td>ML</td>
<td>10135</td>
<td>0.413</td>
<td>0.413 0.031*</td>
<td></td>
</tr>
<tr>
<td>DE002-1</td>
<td>SiPy</td>
<td>ML</td>
<td>9887</td>
<td>0.251</td>
<td>0.251 0.001</td>
<td></td>
</tr>
<tr>
<td>DE008-3</td>
<td>Py</td>
<td>ML</td>
<td>9937</td>
<td>0.330</td>
<td>0.330 0.022</td>
<td></td>
</tr>
<tr>
<td>4D-ML-C2</td>
<td>Py</td>
<td>ML</td>
<td>9889</td>
<td>0.223</td>
<td>0.223 0.005</td>
<td></td>
</tr>
<tr>
<td>665-ML1-2</td>
<td>SiPo</td>
<td>ML</td>
<td>9668</td>
<td>0.282</td>
<td>0.282 0.034</td>
<td></td>
</tr>
<tr>
<td>NP284-1</td>
<td>Py</td>
<td>ML</td>
<td>9449</td>
<td>0.273</td>
<td>0.273 0.029</td>
<td></td>
</tr>
<tr>
<td>NP553-2</td>
<td>Po</td>
<td>ML</td>
<td>9308</td>
<td>0.312</td>
<td>0.312 0.033</td>
<td></td>
</tr>
<tr>
<td>NP948-2</td>
<td>MInA</td>
<td>ML</td>
<td>9185</td>
<td>0.218</td>
<td>0.218 0.004</td>
<td></td>
</tr>
<tr>
<td>775-z1</td>
<td>SiPy</td>
<td>z1</td>
<td>9785</td>
<td>0.433</td>
<td>0.433 0.048</td>
<td></td>
</tr>
<tr>
<td>DE137</td>
<td>Py</td>
<td>z1</td>
<td>9611</td>
<td>0.346</td>
<td>0.346 0.092</td>
<td></td>
</tr>
<tr>
<td>435-z12</td>
<td>Po</td>
<td>z1</td>
<td>9440</td>
<td>0.281</td>
<td>0.281 0.039</td>
<td></td>
</tr>
<tr>
<td>475-z24-E</td>
<td>Po</td>
<td>z2</td>
<td>9481</td>
<td>0.258</td>
<td>0.258 0.000</td>
<td></td>
</tr>
<tr>
<td>CAF-6z3-1</td>
<td>SiPy</td>
<td>z3</td>
<td>9709</td>
<td>0.292</td>
<td>0.292 0.046</td>
<td></td>
</tr>
<tr>
<td>640-z3-W</td>
<td>Py</td>
<td>z3</td>
<td>9640</td>
<td>0.289</td>
<td>0.289 0.016</td>
<td></td>
</tr>
<tr>
<td>NP776-1</td>
<td>Po</td>
<td>z3</td>
<td>9359</td>
<td>0.296</td>
<td>0.296 0.012</td>
<td></td>
</tr>
<tr>
<td>DE164</td>
<td>Py</td>
<td>z4</td>
<td>9735</td>
<td>0.314</td>
<td>0.314 0.031*</td>
<td></td>
</tr>
<tr>
<td>504-z43</td>
<td>SiPy</td>
<td>z4</td>
<td>9504</td>
<td>0.218</td>
<td>0.218 0.030</td>
<td></td>
</tr>
<tr>
<td>650-z51-N</td>
<td>Py</td>
<td>z5</td>
<td>9644</td>
<td>0.240</td>
<td>0.240 0.044</td>
<td></td>
</tr>
<tr>
<td>NP806-1</td>
<td>Po</td>
<td>z6</td>
<td>9529</td>
<td>0.293</td>
<td>0.293 0.067</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.21: Zinc isotope data for accepted analyses; duplicate analyses were rejected for samples CAF-1LS-1-1 and DE164, thus, no standard deviation can be calculated; starred 2σ values for those two sample are average values calculated based on other analyses.
4. ORE MINERALOGY AND PETROGRAPHY

4.6 Summary of findings

The integration of observations made during microscopic and mineral chemical investigations highlighted the pronounced heterogeneity in respect to grain sizes, texture and mineral composition of Elura’s sulphide ore. Sulphide paragenesis is simple, comprising pyrite, pyrrhotite, sphalerite and galena as major, marmacite, chalcopyrite and arsenopyrite as minor, as well as tetrahedrite, native silver and magnetite as trace mineral phases. Grain sizes of the most important sulphide phases, i.e. sphalerite, galena, chalcopyrite and tetrahedrite, vary strongly over a large size range between a few microns and up to several millimetres for sphalerite and galena.

Sphalerite is the most abundant base metal sulphide phase, followed by galena. Chalcopyrite abundance is generally low and variable but slightly enriched towards increasing depth below surface. In pyrrhotite-dominated ore zones, sphalerite and galena are commonly intimately intergrown with pyrrhotite, whereas in pyritic zones they predominantly occur interstitial to and fill fractures or vughs of pyrite, partially replacing it. Replacement of pyrrhotite by base metal sulphide is subordinate. Sphalerite is impure and contains abundant inclusions of sulphide as well as non-sulphide gangue (NSG) phases.

Sphalerite composition varies throughout the orebody. Low iron concentrations with a minimum detected value of 2.41 wt% are observed in sphalerite from the upper main lode ore zone and in peripheral parts of the orebody. Pyrrhotite dominated ore exclusively contains Fe-rich sphalerite containing up to 8.22 wt% Fe.

Microscopic observations of ore texture showed a clear co-genetic relationship between sphalerite and pyrrhotite. In contrast, sphalerite replacement of pyrite is common. Pressure calculations based on the sphalerite geobarometer were unsuccessful and gave meaningless results, confirming microscopic observations of ore textures indicating that sphalerite and pyrrhotite are not in equilibrium with pyrite. The systematic shift from low-Fe sphalerite in the upper main lode zone to consistent high-Fe sphalerite in lower zones of the orebody is independent of whether pyrite or pyrrhotite is the prevailing iron sulphide species. The only feasible explanation seems a change in the chemistry of the mineralising fluid as the hydrothermal system evolved. The precipitation of significant pyrrhotite from the hydrothermal fluid may have caused a decrease of its FeS activity, subsequently less FeS is available for the incorporation with sphalerite.

Manganese, an important smelter penalty element for zinc concentrate, was detected at trace concentration levels (maximum 300 ppm based on LA-ICP-MS) and has no negative effect on the product quality. Cadmium concentrations are relatively low with a maximum detected value of 0.26 wt%. Results of EMPA suggested significant Hg and Bi concentrations in excess of 1000 ppm incorporated in sphalerite. LA-ICP-MS analyses, however, only confirmed Hg in sphalerite but at much lower concentration levels commonly below 100 ppm (median 24 ppm). Other elements detected at low concentrations in solid-solution in sphalerite are Cu (median of 93 ppm) and very minor Ga (maximum of 18 ppm), In (maximum of 5 ppm), and Sn (maximum of 26 ppm).

Investigations of potential fluid inclusions hosted by sphalerite only identified negative, i.e. empty, inclusions. Most, if not all parts of the orebody were affected by deformation. Former fluid inclusions were lost consequently due to deformation and fracturing of sphalerite, allowing fluid and gas phases to escape. Calcite, carbonaceous matter and long chain n-alkanes, identified via laser Raman micro-spectroscopy, are contained in negative inclusions.

Zinc isotope signatures of sphalerite suggest an average continental crust as likely source for Zn and therefore other base metals. The source reservoir was likely effectively leached by a hydrothermal fluid that subsequently inherited its
crustal isotopic signature. The inferred repetitive depth-dependant Zn isotope fractionations in the upper and lower parts of the mineralisation are caused by syngenetic Rayleigh fractionation. Vertical temperature gradients likely aided the fractionation. The fluid evolved from an initial typical crustal signature in major fluid influx zones to heavier signatures as it evolved during its ascent. Additional analyses on a larger sample set are required in order to prove this theory as this trial study is based on a small number of samples.

*Galena* features the most pronounced grain size variability of all sulphide phases, occurring as small as a few microns in size filling interstitial space between pyrite or as several millimetres large patches.

The detailed mineral chemical study of galena was undertaken in order to explain high levels of Bi in lead concentrate. No discrete Bi-mineral phases were microscopically identified in any of the studied ore samples. EMPA showed significant levels of Bi in galena up to 0.85 wt%, evenly distributed within grains. Bismuth concentrations increase with depth below surface. Galena contained in pyrrhotitic ore features slightly higher Bi concentrations compared to other ore types.

Trace element determination via LA-ICP-MS confirmed high levels of Bi in galena (max. 5,645 ppm) and its depth trend, but showed that EMPA is consistently overestimating Bi concentrations. The analytical error is most likely caused by interference of characteristic X-ray Mα peak positions of Bi and Pb. Silver and Sb are both incorporated up to significant concentration levels at maxima of 2,339 and 2,385 ppm, respectively. The former element is enriched in the uppermost as well as lowermost parts of the orebody (mainly in the main lode ore zone), whereas the latter element features a converse enrichment trend compared to Bi. Other elements detected in galena at low concentration levels and incorporated via stochiometric lattice substitution are Se, Te, Cd and Sn. Low levels of Tl are likely caused by nano-impurities of Tl-bearing sulfosalts species.

The coincidental enrichment of Bi and Ag or Ag and Sb is caused by galena-matildite solid solutions in deepest parts of the orebody, and by galena-miargyrite solid solutions in the uppermost zones of the mineralisation, respectively.

*Chalcopyrite* is, apart from tetrahedrite, the only visually identified copper-bearing mineral phase at Elura. It may occur as inclusions and exsolutions in sphalerite, intergrown with other base metal sulphides and, in places, is enriched in zones enriched in iron carbonate and quartz. Low concentrations of Co, Zn, Ag, Bi, As and Sn were detected in chalcopyrite via EMPA.

It has been shown that galena hosts significant Ag in some areas of the orebody. Apart from these zones, *argentian-tetrahedrite* and minor *native silver* were identified as the only silver hosting mineral phases. Occurrences of native silver and coarser grained tetrahedrite (15-200 µm) are limited to the uppermost areas of the orebody. Here, tetrahedrite is commonly associated and intergrown with galena. Throughout most of the mineralisation, tetrahedrite is significantly finer grained and may be characterised by mineral associations with other phases than galena. In places, tetrahedrite is altered to native silver and chalcopyrite.

The detected Ag concentration of all unaltered tetrahedrite grains via EMPA ranges between ~31 and ~19 wt%. Some analyses with Ag concentrations in excess of 31 wt% feature calculated stoichiometries similar to freibergite. Argentian-tetrahedrite is, in places, altered to native silver and Ag-rich chalcopyrite. Stoichiometries calculated on the basis of several analyses showed significant deviation from ideal tetrahedrite composition and reflect intermediate stages of alteration.

Four *pyrite* generations were identified in the course of this study. Colloform, framboidal and cloudy pyrite A formed prior to the base metal mineralisation. It is the most abundant and represents the oldest pyrite variety in the mineralising system. Most of the second cataclastic, sub- to euhedral pyrite B formed prior to the base metal sulphides during a period
when the fluid temperature increased and when base metal concentrations began to increase. Both pyrite varieties were affected by tectonic strain causing intense fracturing and were subsequently intruded and partially replaced by base metal sulphides. Commonly coarse grains of pyrite B feature typical and characteristic cataclastic textures. The base metal mineralisation stage is dominated by pyrrhotite as the main iron sulphide phase with only minor anhedral pyrite C formation. In places, syn-base metal pyrite C is intimately intergrown with magnetite. In peripheral pyritic-dominated ore zones where pyrrhotite is lacking, minor pyrite C is overgrowing earlier pyrite A and B. In these ore zones, however, pyrite precipitation is subordinate. Replacement of pyrite by base metal sulphides prevails. Late, euhedral and fine-grained pyrite D is observed in minor quantities throughout the orebody and formed after the base metal mineralisation stage.

Pyrite A and B compositions were investigated via EMPA but showed no significant differences. Cobalt, Ni and As contents are low at median concentrations of 0.07, 0.04 and 0.08 wt%, respectively. Silver and Au were detected at a maximum concentration of 0.2 wt%, likely caused by micro-inclusions of unidentified phases. Trace element determination via LA-ICP-MS suggests that Co, Ni, As, Sb, Au and Tl are contained in pyrite at low concentration levels. The impure nature of the pyrite types makes it hard to distinguish between elements incorporated in pyrite via lattice substitution from those linked to micro-inclusions.

Pyrrhotite dominates as iron sulphide in core zones of the deposit where it represents the sulphide groundmass. It is clearly co-genetic with base metal sulphides, commonly occurring intimately intergrown in a myrmekitic-like texture. Transformation of pyrrhotite to marcasite is observed in several samples throughout the entire depth extent of the orebody. In places, transformation is complete, but texture typical for pyrrhotitic ore remains. Pyrrhotite compositions were determined via EMPA and LA-ICP-MS. Results showed that pyrrhotite does not contain any element in significant quantities other than Fe and S.

Arsenopyrite occurs in all different ore types and depths but is enriched in the upper and pyritic peripheral parts of the deposit. It is observed in variable grain sizes, shapes and textures. Partial replacements by base metal sulphides may occur. Cobalt and Sb are the only elements consistently detected in EMPA of arsenopyrite. Some grains feature a well-defined growth zonation and a blurred, overprinting, deformational-induced zoning. The former zonation is caused by elevated Co or Sb concentrations, the latter by changes in As/S ratios. Elevated Ag and Au is observed in some analyses and caused by micro-inclusions of electrum.

Iron carbonates (ankerite and siderite) and quartz are the most important non-sulphide gangue phases (NSG). The former preferably occurs in core zones of the orebody, the latter in peripheral zones. Both phases occur interstitial to sulphides or form vein systems of complex time relationships throughout the entire paragenetic sequence. Minor barite is observed. Rare occurrences of magnetite, intimately intergrown with pyrite type C, are observed.

Strongly altered wall rock clasts are embedded in sulphide matrix in the semi-massive peripheral ore zones. Muscovite and chlorite are common alteration phases in silt- and mudstone rich, quartz in sandstone-rich fragments. Minor goethite formed via alteration of pyrite and siderite and preferably occurs in pyritic ore types. Subordinate alkali-feldspar and sodium-rich plagioclase is recognised as an alteration phase.

Compositions of chlorite clearly related to the mineralising event were determined via EMPA. Most chlorite is ripidolite, some pseudothurin-gite and daphnite. If oxidised, they would be classified as thuringite. Chlorite thermometry estimated a temperature range between 314 and 343 °C, similar to temperature conditions proposed for the mineralising fluid in other studies. A significant temperature change over the depth extent of the orebody is observed and may
reflect changing crystallisation temperatures or changes in fluid characteristics. The temperature dependency as a function of depth also appears to be related to changes in the host lithology, thus may be caused by differences of its chemical composition. In this case, the temperature trend would be unrelated to the mineralising event.

\textit{Ore textures} vary between ore types as well as between zones of intense and weak deformation. Base metal sulphides in massive pyritic ore are commonly characterised by a reticular, vein-style texture, where they fill fractures, interstitial space in rather compact but fractured pyrite groundmass, partially replacing it. Texture of pyrrhotitic-dominated ore is significantly different, commonly featuring myrmekitic-like intergrowths of sphalerite, galena, pyrrhotite and chalcopyrite. Pyrrhotite, syn-genetic to base metal sulphides, commonly features 120-degree grain boundaries. Pyrite B porphyroclasts, which are strongly fractured and partially replaced, occur in varying quantities. In zones of high deformation, sphalerite occurs as bands, elongated grains and boudinaged fragments. Ore texture is reminiscent of mylonites in places where strain was focussed into a rather confined zone. Here pyrrhotite and galena reacted strongly ductile and were remodelised into discrete sulphide bands. In contrast, sphalerite reacted brittle, forming sub-rounded clasts. Deformation of galena is shown by its bending cleavage planes. The sulphide body was affected by prolonged deformation commencing during the early hydrothermal stages as shown by the strongly tectonised early pre-base metal pyrite generations (type A and B) and the deformation of base metal sulphides. Remobilisation and re-crystallisation at varying intensities, caused by the deformation, are responsible for the significant grain size variability and heterogeneity of ore from the Elura orebody.
Chapter 5

Geochemical ore characterisation

The Elura deposit contains an estimated pre-mining resource in excess of 50.7 Mt at 8.8 wt% Zn, 5.6 wt% Pb, 107 g/t Ag and 0.2 wt% Cu. Samples from resource diamond drilling are commonly assayed for Zn, Pb, Ag, Cu and Fe and their spatial distribution modelled in the resource block model. Apart from those elements, other trace elements potentially important for mineral processing (e.g. penalty or potential beneficial elements) are not determined. No comprehensive trace element study has been performed on the Elura orebody since its discovery.

A set of 124 samples, taken from locations throughout the deposit and all occurring ore types, were used for major and trace element whole rock geochemistry as shown in figure 5.1 and summarised in table 5.1. Bulk samples were crushed and ground in a chrome steel swing mill to analytical fineness at the Department of Geology and Geophysics, School of Earth and Environmental Sciences at the University of Adelaide. Sample aliquots were analysed for major and trace elements by ALS Laboratory Group, Australia. Geochemical procedures used for different elements are summarised in appendix B on page 480. Smaller sample sub sets were chosen for rare earth element (REE, n = 34, figure 5.2) and platinum group element (PGE, n = 8, figure 5.4) determination, including Re-Os dating. These elements were analysed at the Department for General and Analytical Chemistry at the University of Leoben, Austria.

Table 5.1: Number of samples for different ore types and ore zones.

<table>
<thead>
<tr>
<th>Ore type</th>
<th>ML</th>
<th>z1</th>
<th>z2</th>
<th>z3</th>
<th>z4</th>
<th>z5</th>
<th>z6</th>
<th>W-Min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Po</td>
<td>20</td>
<td>4</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Py</td>
<td>20</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiPo</td>
<td>9</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>SiPy</td>
<td>11</td>
<td>6</td>
<td>-</td>
<td>1</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>VEIN</td>
<td>5</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MinA/ALT</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CSA</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Calculated by the author based on the resource block model January 2008 (abbrev. Res08_jan) and a cut-off grade of 10 wt% Pb-Zn combined grade, supplied by CBH Resources Ltd.
5. GEOCHEMICAL ORE CHARACTERISATION

5.1 Background and methodology

5.1.1 Major and trace element whole rock geochemistry

Major element analyses of ore samples \( (n = 118) \) were used to estimate their modal mineralogy and subsequently to calculate bulk sample density. Density values are reconciled to gravimetric determined ore density data supplied by CBH Resources Ltd. If density estimates are sufficiently accurate, they will be used to calculate relative volume loss/gains during ore formation. Major element composition of unaltered fresh host rock will be used for source rock provenance discrimination and to classify for tectonic settings.

A standard lithium metaborate-tetraborate fusion (ME-XRF12 ALS lab-code) was used for sample digestion. Approximately 0.66 g sample was fused in a lithium metaborate-tetraborate flux at a ratio of 12:22. Lithium nitrate was added as oxidising agent. Melt was poured into platinum mould in order to produce glass disks, which were analysed via XRF spectrometry on a PANalytical AXIOS PW4400 system. Total sulphur and carbon were determined via LECO CS carbon-sulphur analyser using 0.01 to 0.1 g sample material (S-IR08 and C-IR07 ALS lab-codes). Determination of loss-on-ignition (LOI) is meaningless on samples that contain high sulphide quantities. That is because mass changes are predominantly caused by oxidation of sulphides to either oxides (mass loss) or sulphates (mass gain) upon roasting, and therefore would not accurately reflect contents of volatiles (e.g. water, organics, etc.). Samples that contain significant quantities of chloride and sericite and thus water incorporated in crystal lattice (i.e. siliceous semi-massive sulphide samples with high wall rock component) will result in totals below 100%.

A suite of 40 trace elements contained in massive and semi-massive sulphide ore and wall rock samples \( (n = 118 \) and 6, respectively) was determined in order to investigate affinities between trace elements, their concentration variability and their spatial distribution throughout the entire orebody. Elements identified as being highly immobile during hydrothermal alteration and sulphide precipitation, were used to calculate relative mass changes and subsequently volume gains/losses during ore formation. Trace elements enriched in certain sulphide phases up to significant concentration levels (e.g. Ag and Bi in galena; see section 4.3 on page 108) were reconciled to whole rock geochemistry in order to: (a) identify the potential occurrence of other mineral phases, which may incorporate particular elements, and (b) estimate the relative percentage of metals locked up in certain mineral phases.

For most trace element determinations, approximately 0.250 g of sample material was digested via a multi-acid method using perchloric (\( \text{HClO}_4 \)), nitric (\( \text{HNO}_3 \)) and hydrofluoric (HF) acids. The solution was evaporated to near dryness before hydrochloric acid was used for further digestion/leach (ME-MS61 ALS lab-code). Final sample solution was analysed via inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and -mass spectroscopy (ICP-MS). A Varian Vista Radial instrument and a Perkin Elmer ELAN 9000 system were used for ICP-AES and ICP-MS, respectively. Elements incorporated in refractory mineral phases (e.g. Y, Zr, Sn, W, etc) were analysed using an alternative digestion method in samples enriched in silicates in order to ensure complete sample decomposition. Those samples were fused in a lithium metaborate flux followed by dissolution in a mixture of \( \text{HNO}_3 \) and \( \text{HCl} \) acids followed by analysis via ICP-MS. Samples containing high concentrations of zinc, lead or silver were digested according to ME-MS61 but more diluted (ME-OG62 ALS lab-code). Mercury was determined via aqua regia digestion followed by either ICP-AES (ME-ICP41 ALS lab-code) or ICP-MS (ME-MS42 ALS lab-code) according to concentration levels. Gold analysis was by fire assay fusion followed by ICP-AES (Au-ICP21 ALS lab-code).

---

* Summarised after geochemical laboratory procedures ALS Chemex Laboratory group Australia (pers. comm. Steven Finlayson, 2010)
Approximately 30 g sample material was fused in a mixture of several reagents (e.g. lead oxide, sodium carbonate, borax, silica, etc.). The resulting metal bead was digested in a mixture of diluted HNO$_3$ and concentrated HCl by heating in a microwave oven. Diluted sample solution was subsequently analysed via ICP-AES.

Several geological reference materials were used as laboratory standards for quality assurance quality control (i.e. G2000 ALS Laboratory Group; GBM303-1, GBM305-11, GBM306-12, GBM398-4C, GBM904-11, GBM999-5 Geostats Pty Ltd; SARM-3 South African Bureau of Standards; ST321, ST381 Gannet Holdings Pty Ltd). Analytical results were considered as valid based on standard, blank and duplicate analyses.

### 5.1.2 Rare earth element analysis

Rare earth element (REE) concentrations in ore and unaltered fresh wall rock samples were investigated. Their concentrations and distribution pattern were used to classify the host rock (CSA Siltstone) and to investigate REE mobility caused by the hydrothermal mineralising event. REE commonly occur at low concentrations in geological material. Refractory and chemically highly resistant mineral phase, e.g. zircon, tourmaline, are important hosts for REEs. Complete sample dissolution is vital for accurate determination of those elements. Sodium peroxide sintering was used in order to deliver complete sample digestion, following the method described in Meisel et al. (2002). All acids, sample dilutions in addition to rinsing solutions were prepared with purified reverse osmosis water (mQ H$_2$O), delivered via a MilliQ system (Millipore).

Samples were ground to analytical fineness. Approximately 100 mg of sample material was mixed and homogenised with approximately 0.6 g sodium peroxide with a purity of > 95% m/m in glassy carbon crucible. The mixtures were subsequently sintered at 480 °C for 30 min. The crucibles were allowed to cool to room temperature, before mQ H$_2$O was added drop-wise, in order to control the intensity of the dissolution reaction. Hot plates with magnetic moments maintained constant solution agitation and a temperature of 90 °C. Upon cessa-
tion of the reaction, solutions were centrifuged for 5 min at 4000 rpm in order to separate undisolved hydroxides. The residue was dissolved with 3 ml 3 M HCl. Graphite crucibles were rinsed with 2 ml concentrated HCl. All sample solutions were combined in a 100 ml volumetric flask (resulting dilution is 1:1000).

One ml sample aliquots were diluted with 1% m/m HNO₃ up to a volume of 5 ml. As internal standard, 100 µl of a 0.1 µg ml⁻¹ indium/rhenium solution was added to each sample solution (final dilution is 1:5100).

All samples were digested and analysed as duplicates on a HP4500 Agilent Technologies ICP-MS. One blank and one standard solution were analysed after every 5 samples. Penrhyn Slate (OU-6) was used as standard reference material, certified by the International Association of Geoanalysts (Kane, 2004). Most blank solutions yielded elemental concentrations below 10 ppb. All standard analyses (n = 7) featured high reproducibilities with a maximum RSD of 2.9% with most analyses below 1.7%. Comparison of element concentrations of standard analyses with certified standard reference material concentration data showed a significant and consistent overestimation of Ho caused by laboratory wide contamination (pers. comm. Thomas C. Meisel 2009) and subsequently were rejected. Figure 5.3 shows chondrite-normalised standard analyses (black lines, excluding Ho) superimposed to certified values of OU-6 (blue shape defined by uncertainties). Chondrite data from Palme and O’Neill (2004) was used for normalisations in the course of this study. All REEs fall within certified values except Ce, which is slightly lower. Median Ce concentration defined by seven analyses is nevertheless very close to the certified value with 72.8 ppm compared to 77.1 ppm ±2.7. Based on blank and standard analyses, all analytical results were accepted.

5.1.3 Platinum group element determination (incl. rhenium)

Economic platinum group element (PGE) mineralisation is commonly linked to mafic/ultramafic orthomagmatic deposits, e.g. layered mafic-ultramafic intrusions, Alaskan-type alkaline/calc-alkaline intrusions, etc. Smaller occurrences are found in pyroxenite dykes or ophiolites associated with “Schlieren”-type chromitites. Several studies showed that PGEs may be significantly mobile under aqueous hydrothermal conditions (e.g. Wood, 2002). Thus, significant PGE concentrations may occur in hydrothermal base metal mineralisation hosted by a large variety of different rock types, e.g. sedimentary, magmatic or metamorphic (Maier, 2005). For instance, significant PGE concentrations in excess of 1,000 ppm Pd and Pt are reported for the Kupferschiefer in Poland (Kucha and Przyłowicz, 1999; Bechtel et al., 2001).

The Elura deposit has previously been dated based via Pb-Pb (411 Ma David, 2005) and ⁴⁰Ar-³⁹Ar (376-379 Ma Sun, 2000; Sun et al., 2000) techniques, resulting in a significant age discrepancy for the genesis of the sulphide mineralisation (see section 3.2 on page 50). Thus, a further dating technique was sought in order to better constrain the age of the ore-forming event.

Sphalerite has been successfully dated via the Rb-Sr isotope system (e.g. Brannon et al., 1992; Nakai et al., 1993; Christensen et al., 1995a,b; Schneider et al., 2003) and was initially considered as a good option for age determination. However, microscopic observations revealed the pronounced heterogeneity and impurity of sphalerite contained within ore from Elura. Probably the most important and abundant impurity in sphalerite are inclusions of iron-carbonate mineral phases and sericite. The former phases readily incorporate Sr in solid solution and the latter Rb. Such inclusions would certainly have disturbed the highly sensitive Rb-Sr isotope system. Subsequently, its application has been dismissed.

The Re-Os isotopic system is commonly used
for dating mafic/ultramafic rock suites and associated mineral deposits. Despite low PGE concentration levels, several authors were able to use the dating technique for base metal deposits (e.g. Morelli et al., 2004; Keays et al., 2006; McInnes et al., 2008). Trace element geochemistry of this study showed a weak but noticeable correlation between Re and Mo (figure 5.22), suggesting molybdenite as a major mineral host for Re. The whole rock Re concentrations are variable and would cause the spread of Re and Os isotope ratios needed for accurate isochronage determination.

The whole rock massive sulphide samples were digested and analysed following the isotopic-dilation, on-line cation exchange matrix separation procedure described in Meisel et al. (2001, 2003). All acids, sample dilutions in addition to rinsing solutions were prepared with purified reverse osmosis water (mQ H$_2$O), delivered via a MilliQ system (Millipore). Samples were ground to analytical fineness and thoroughly homogenised before an aliquot of 0.5 g was extracted. The sample material was weight into quartz glass tubes and a multi-element PGE spike solution containing $^{99}$Ru, $^{108}$Pd, $^{185}$Re, $^{190}$Os, $^{191}$Ir and $^{198}$Pt was added. The quartz glass vessels were sealed with Teflon® tape and glass lid immediately after adding 2 ml conc. sub-boiled HCl and 5 ml conc. sub-boiled HNO$_3$. In order to avoid excessive reaction of the sample powder with acids, potentially causing losses of volatile phases (i.e. OsO$_4$, RuO$_4$), quartz glass vessels were cooled in iced water. The glass tubes were subsequently pressurised in an autoclave system (high pressure asher HPA-S; Anton Paar – PerkinElmer Instruments, Graz, Austria) under nitrogen atmosphere at a pressure of 100 bar. The samples were dissolved/leached for three hours at a constant temperature of 300 °C and allowed to cool for an additional hour. The sample solutions were decanted into Teflon® beaker. The volatile OsO$_4$ phase was directly sparked into the torch of the quadrupole ICP-MS instrument (HP4500 Agilent Technologies) and Os concentrations determined via isotope dilution. The sample solutions and the undigested sample material was diluted to 50 ml and carefully separated via centrifuge. The supernatant was decanted into Teflon® beaker, put on hot plates, and allowed to evaporate until almost complete

As a trial, a small set of eight whole rock massive sulphide samples was used for the determination of PGE and Re concentrations in addition to the Os isotope ratio ($^{187}$Os/$^{188}$Os), never investigated at the Elura orebody before. The locations of these massive sulphide samples, comprising 4 pyrrhotite- and 4 pyrite-dominated samples are shown in figure 5.4 and were taken from different locations throughout the orebody. If concentrations are sufficiently high, and PGEs detectable, their distributions, fractionations and Os isotope compositions may help to determine fluid characteristics and confine potential metal sources. Re-Os geochronology will be used for age determination. If successful, the date would represent the first time constraint established by directly dating the sulphide mineralisation.
5. GEOCHEMICAL ORE CHARACTERISATION

dryness in order to remove most acids. The residue was leached in 1 ml 0.1 M HCl and the solution cleansed via a syringe filter. The online matrix separation column is realised via a 1 m long PFA (perfluoralkoxyalkan) tube filled with cation-exchange resin Dowex AG50Wx8 (200-400 mesh, Fluka, Switzerland). The sample is loaded and gently forced through the column by a pressure of 2 bar before being introduced into the ICP-MS (see Meisel et al., 2003, for further details).

Sample preparation, acid attack digestion/leach and the ICP-MS analysis including cation exchange column work was performed by the author. The isotope raw counts per second intensity data were processed and element concentration calculated based on isotope dilution by Thomas C. Meisel in 2009 (see Meisel et al., 2001, for further details).
5.2 Major elements, modal mineralogy and density estimation

**Major** element compositions, calculated modal mineralogy and density of all analysed ore samples are shown in appendix section B.2 on page 480 and summarised for different ore types in table 5.2. Most iron is incorporated in sulphides, thus calculated and presented as elemental concentration.

It needs to be stressed, that the calculated modal mineralogy based on chemical data is at best a rough estimation and has to be understood as informative only. Total Zn, Pb, As, Cu and Ba concentrations were directly used to calculate modal percentages of sphalerite, galena, arsenopyrite, chalcopyrite and barite. Average sphalerite composition, i.e. \((\text{Zn}_{0.9}\text{Fe}_{0.1})\text{S}\) as determined via EMPA (see section 4.2.1 on page 79) was used. Total Ca concentration was used to calculate the amount of calcite, the remaining carbon dioxide was assumed to represent the amount of siderite. The overall low manganese and magnesium concentrations were ignored for carbonate calculation. Sodium and K concentrations were used to calculate the amount of albite and orthoclase, respectively. A significant proportion of K is associated with muscovite, but it was not possible to calculate both phases, i.e. orthoclase and muscovite. The remaining Al was used to calculate the amount of chlorite using its average composition as determined via EMPA (see section 4.2.3 on page 101). The remaining Si was calculated as quartz.

Median Zn and Pb concentrations are rather uniform for massive (Po and Py) and semimassive (SiPo and SiPy) ore types at approximately 9.6 to 10.2 wt% and 5.1 to 5.9 wt% (table 5.2). The highest Zn concentration is observed in massive pyrrhotitic ore at 16.4 wt%. In contrast, maximum Pb is observed in massive pyritic ore at 30.30 wt%. Stringer type ore (VEIN) including one minor mineralised (MinA) and one altered wall rock (ALT) sample feature variable Zn and Pb concentrations between 0.2 to 7.7 wt% and 0.1 to 8.1 wt%, respectively. Median Cu concentrations, with the exception of VEIN/MinA/ALT ore types, range between 0.20 and 0.24 wt% for Po, SiPo and SiPy, and are lowest in massive pyritic ore at 0.16 wt%. A weak tendency of higher Cu concentrations is indicated for pyrrhotitic ore types as expressed by higher chalcopyrite content in figure 5.7.

The calculated modal compositions of different ore types are summarised in figure 5.5. Total silicate content progressively increases from approximately 2 wt% (median) for massive, to 13 wt% (median) for semimassive siliceous and up to 63 wt% (median) for VEIN/MinA/ALT ore types (figure 5.7). Inverse quantities are observed for total sulphide and total iron sulphide (Py + Po) content as the most abundant sulphide species (figure 5.7). Massive ore contains around 85 wt% (median), siliceous ore 75 wt% (SiPo) and 69 wt% (SiPy) total sulphides. Iron sulphide content (pyrite + pyrrhotite) are lowest in SiPy ore (median 46 wt%) and range between 54 to 50 wt% (median) for Po, Py and SiPo, not considering VEIN ore. Total carbonate content is highly variable, ranging between 0.39 and 33.65 wt% (overall range) with no significant differences.
5. GEOCHEMICAL ORE CHARACTERISATION

between ore types (figure 5.7). Arsenopyrite content is slightly elevated in pyritic-dominated ore types (figure 5.7) but overall highly variable with a maximum content observed in Py ore at 3.26 wt% (equal to 1.5 wt% As).

Bulk sample densities are calculated based on the estimated modal mineralogy. Mineral densities defined by Anthony et al. (1990) were used for carbonates and most sulphides. Pyrite and pyrrhotite feature densities of 5.0 and 4.6 g cm\(^{-3}\), respectively. Their individual modal abundances cannot be determined based on geochemical data, thus an average density value of 4.8 g cm\(^{-3}\) is used for bulk density calculation. A uniform density value of 2.7 g cm\(^{-3}\) was used for silicate phases.

Calculated densities (\(\rho_{\text{Calc}}\), n = 116) were compared to gravimetrically measured density data (\(\rho_{\text{Meas}}\), n = 1271) supplied by CBH Resources Ltd (figure 5.6). Standard deviation for \(\rho_{\text{Meas}}\) are consistently higher compared to \(\rho_{\text{Calc}}\), reflecting the pronounced heterogeneity of sulphide ore particularly for small sample quantities used in gravimetric determination techniques. Massive ore types (Po and Py) features uniform average \(\rho_{\text{Calc}}\) of 4.7 g cm\(^{-3}\) ± 0.2 (1-\(\sigma\)) compared to \(\rho_{\text{Meas}}\) of 4.4 g cm\(^{-3}\) ± 0.3 (1-\(\sigma\)) and 4.5 g cm\(^{-3}\) ± 0.3 (1-\(\sigma\)) for Po and Py, respectively. Both siliceous ore varieties have \(\rho_{\text{Meas}}\) of 4.0 g cm\(^{-3}\) ± 0.3 1-\(\sigma\). Calculated densities for these ore types are 4.5 g cm\(^{-3}\) ± 0.2 (1-\(\sigma\), SiPo) and 4.3 g cm\(^{-3}\) ± 0.3 (1-\(\sigma\), SiPy).

Stringer type ore (VEIN) is characterised by similar densities at 3.4 g cm\(^{-3}\) ± 0.2 (\(\rho_{\text{Calc}}\), 1-\(\sigma\)) compared to 3.3 g cm\(^{-3}\) ± 0.5 (\(\rho_{\text{Meas}}\), 1-\(\sigma\)). Both density values, \(\rho_{\text{Meas}}\) and \(\rho_{\text{Calc}}\), overlap for all ore types when single standard deviation is considered. The comparison showed that calculated density values are close to measured and sufficiently accurate when considering standard deviations.

![Figure 5.6:](image-url) Comparison of calculated and measured density data of different ore types. Calculated density data is based on modal mineralogy; measured data is based on several gravimetric density studies undertaken by CBH Resources Ltd and compiled by the author.
## 5.2 Major elements, modal mineralogy and density estimation

<table>
<thead>
<tr>
<th>Ore type</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>BaO</th>
<th>P₂O₅</th>
<th>CO₂</th>
<th>S</th>
<th>Fe-total</th>
<th>Zn</th>
<th>Pb</th>
<th>Ag</th>
<th>Cu</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Max</td>
<td>62.1</td>
<td>0.70</td>
<td>16.75</td>
<td>0.83</td>
<td>3.32</td>
<td>5.86</td>
<td>0.54</td>
<td>5.22</td>
<td>1.43</td>
<td>0.23</td>
<td>13.41</td>
<td>49.50</td>
<td>1.24</td>
<td>45.80</td>
<td>30.30</td>
<td>6.45</td>
<td>1060</td>
<td>2.25</td>
</tr>
<tr>
<td>Min</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.15</td>
<td>1.10</td>
<td>4.17</td>
<td>16.40</td>
<td>0.20</td>
<td>0.09</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Med.</td>
<td>1.26</td>
<td>0.03</td>
<td>0.08</td>
<td>0.03</td>
<td>0.12</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>1.10</td>
<td>3.54</td>
<td>4.17</td>
<td>16.40</td>
<td>0.20</td>
<td>0.09</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Avg.</td>
<td>2.04</td>
<td>0.04</td>
<td>0.09</td>
<td>0.04</td>
<td>0.14</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>1.10</td>
<td>3.54</td>
<td>4.17</td>
<td>16.40</td>
<td>0.20</td>
<td>0.09</td>
<td>0.03</td>
<td>0.01</td>
</tr>
</tbody>
</table>

### Table 5.2: Summary of major element composition of different ore types. Concentration data in wt%, values of elements labeled with # are in ppm. Modal mineralogy and density is calculated based on element concentration data. Density data given in gcm⁻³.
Figure 5.7: Box and whisker plots showing compositional variability in respect to different ore types. Modal mineralogy is calculated based on geochemical data.
5.3 Trace element signature - trends and element affinities

Trace element concentrations of individual samples are presented in appendix B on page 486 and are summarised for different ore types in Table 5.3. Despite a large sample set (n = 118), it is not feasible to accurately determine lateral trace element variability of individual ore zones (i.e. ML, z1-z6) due to their pipe-like geometry. Thus, the sampling strategy focused on testing compositional changes versus depth of the entire longitudinal extent of the Elura orebody. If significant concentration trends versus depth were identified, a prediction map could be interpolated for better visualisation. Prior to the interpolation, east and north coordinates of the 3D data set were projected onto a best-fit 2D plane defined by all sample coordinates, oriented along the longitudinal direction of the orebody. Subsequently, those projections were rotated into the N-S orthogonal plane (Figure 5.8).

5.3.1 Inter-element affinities

Cluster analysis was initially used to investigate inter-element affinities (Figure 5.9). Most high field strength elements (abbrev. HFSE; Sc, Ti, Y, Zr, Nb, Hf, Ta, Th), rare earth elements (abbrev. REE; La, Ce), lithophile elements, including some large ion lithophile elements (abbrev. LILE; Li, Be, Rb, Cs), and elements that may be hosted by detrital refractory mineral phases contained in the wall rock are closely associated with each other (i.e. V, Ni, Cr, Sn). Those elements are summarised as group A elements and are clearly related to the influence of wall rock components. The association of Ge to this group of elements suggests wall rock as its source. The close relation between Zn, Cd and Ga is caused by sphalerite, as the most important host of those elements as suggested by mineral chemical investigations (Chapter 4 on page 79 and page 108) and affirmed by the linear correlation trend between Cd and Zn (Figure 5.8).

Figure 5.8: Coordinate transformation for geostatistical modelling. (a) Plan view of sample locations; (b) view towards W. Transformation is performed in order to reduce a 3D data set to 2D. Transformation consists of projection onto a best-fit longitudinal plane followed by rotation into the N-S orthogonal axis.

* Interpolation was performed via standard inverse distance weighted (IDW) method implemented in the ESRI® ArcGIS software package; neighbours to include was set to 20 with a minimum of 10; due to the pronounced pipe-like geometry, an anisotropy factor of 2 at an angle of 0° was applied, with the search ellipsoid defined at 100 m vertical and 50 m lateral; power of weighting was optimised automatically.

† Spearman’s correlation coefficients are used as attribute distance measure between elements. Cluster analysis is performed after the approach of Ward.
 Associations of Zn and Pb with group A elements are artificial. Both elements are highly enriched in all ore types including semi-massive siliceous ore. Wall rock components contained in siliceous ore types are enriched in group A elements and are causing their proximities. Dilution due to the addition of sulphide is amplifying the inter-element associations.

The remaining elements are clearly related to the sulphide mineralisation and are hosted by various sulphide phases. Cluster analysis of those elements is shown in figure 5.10. Hafnium and Zr were included to investigate proximities to wall rock. Elements with close associations are grouped together: As, Sb, Ag, Au, Hg, Tl and Sn as group B; Co, Cu, Cd, In, Bi, Se, and Te as group C. Although some Ga is incorporated in sphalerite, its relative proximity to Hf and Zr suggests wall rock as important source. Figure 5.10 confirms that Ni and Ge are genetically unrelated to the base metal mineralisation. Their respective concentrations are low and range between 0.4-80.7 ppm and 0.07-0.39 ppm. Strontium and Ba are proximal to group B (figure 5.9), most probably caused by barite enriched in Sr. Barite is a common but minor non-sulphide gangue phase (chapter 4 on...

Figure 5.9: Dendrogram showing inter-element affinities based on cluster analysis (Spearman’s correlation coefficients are used as attribute distance measure between elements; cluster analysis is performed after the approach of Ward). Elements labeled in blue are summarised as group A elements and are clearly related to the influence of wall rock components. Proximity of Zn, Cd and Ga is caused by sphalerite as their common host (green). Other elements are linked to the sulphide mineralisation.

Figure 5.10: Grouping of trace elements related to base metal mineralisation. Dendrogram is based on cluster analysis (Spearman’s correlation coefficients are used as attribute distance measure between elements; cluster analysis is performed after the approach of Ward). Element proximities are predominantly caused by their spatial distribution. Elements grouped in orange are enriched towards increasing depth below surface, whereas those labeled in purple feature inverse characteristics. Molybdenum and Re are closely related, indicating molybdenite as their common host. Gallium appears closer to wall rock (defined by immobile elements) than to sulphides.
5.3 Trace element signature - trends and element affinities

Molybdenum, Re and U are closely correlated. Molybdenite is the most important ore for the production of Re. It is well known that Re is readily incorporated in molybdenite via lattice substitution. Association between Mo and Re is, therefore, likely caused by molybdenite. All samples except one feature a weak but noticeable correlation between Re and Mo (figure 5.22). Rhenium concentrations are very low, commonly close to the detection limit of 2 ppb, causing the pronounced scatter of data points. Nevertheless, the trend affirms molybdenite as host for Re as suggested by the cluster analysis. The proximity of U with Mo as observed in cluster analysis (figure 5.9) and the poorly defined element correlation between U and Mo (figure 5.22) may be caused by mineral phases containing both elements, e.g. sedovite (U(MoO$_4$)$_2$).

5.3.2 Trace element concentrations and their spatial distribution

The investigation of spatial element distributions revealed the reason for the observed clustering of group B and C elements. Group B elements tend to be preferably enriched in the upper parts of the orebody. Elements of group C commonly feature converse trends with enrichment towards increasing depth below surface. Gallium, Mo and Re are not clearly related to either group.

Arsenic concentrations range between 12.6 ppm and 1.50 wt% (table 5.3). An overall trend of increasing concentrations towards the surface is observed despite some samples within the lower mineralisation feature elevated As contents (figure 5.18). Pyritic ore types (Py and SiPy) are significantly enriched in As (median of ~0.1-0.5 wt%, table 5.3) compared to other ore types (figure 5.11).

Silver shows enrichments in two zones: (a) in the uppermost areas of mineralised zones and (b) in the lowermost main lode (ML) zone (figure 5.18). The overall detected Ag concentrations range between 1.2 ppm in minor mineralised altered CSA wall rock (MinA) and up to 1.1 wt% in massive pyritic ore. Median Ag concentrations of massive and semi-massive ore types (Po, Py, SiPo and SiPy) are in the order of 44 to 86 ppm (table 5.3). Pyritic ore types are relatively enriched in Ag compared to pyrrhotitic dominated ore (figure 5.11). It is well known from the resource block model that silver is not only enriched towards the surface but also towards peripheral zones of individual near-concentric sulphide pipes (figure 5.14). This enrichment explains the elevated concentrations within deeper parts of the orebody as indicated in figure 5.18. Due to close affinity of Ag to many of the group B elements, it is likely that those elements feature similar characteristics. The concentration increase of silver towards the surface observed in this study is not an effect of supergene enrichment processes as only fresh unaltered samples were analysed.

A well-defined enrichment trend towards the surface is exhibited by antimony (figure 5.18), partially linked to Ag and caused by the occurrence of argentian-tetrahedrite (chapter 4 on page 63). The remaining Sb may occur as antimonite. Concentrations vary between 9.53 ppm and 0.21 wt% (table 5.3) and are commonly higher in pyritic dominated ore types (figure 5.11).

Gold concentrations are highly variable, ranging between 2 ppb in minor mineralised ore and as high as 8.7 ppm in siliceous pyritic ore. No clear trend versus depth below surface is indicated. Figure 5.11 shows Au variability for different ore types. Pyritic ore types are the preferred host for Au at median concentrations between approximately 0.2 to 0.5 ppm, whereas pyrrhotitic ore commonly contains ~0.09 ppm (median).

Mercury and thallium, both important smelter penalty elements, are most enriched in the upper main lode zone but are also enriched in upper parts of the lower mineralisation, in particular in z2 and z3 zones (figure 5.17). Samples from deeper parts of the orebody that are characterised by high Hg and/or Tl concentrations are from peripheral ore zones (SiPo and SiPy ore types), featuring similar enrichment char-
5. GEOCHEMICAL ORE CHARACTERISATION

Tin and molybdenum concentrations are variable throughout the entire orebody, although a very weak enrichment trend towards the surface is indicated for Mo (figure 5.21). Concentrations range between 2.8 to 30.9 ppm for Sn and 0.34 to 24.6 ppm for Mo. Median Sn and Mo concentrations for massive and semi-massive ore types range between 7.4 to 9.7 ppm and 1.73 to 3.95 ppm, respectively. Both elements feature a weak affinity to pyritic ore type (figure 5.11).

Rhenium concentrations are very low and range between 2 to 52 ppb. No affinities to par-
5.3 Trace element signature - trends and element affinities

ticular ore types or spatial trends were observed. The element cross-plot of Re vs Mo features a good correlation trend when considering the fact that detected Re concentrations are close to the detection limit of 2 ppb (figure 5.22). One sample characterised by the highest observed Re concentration miss-fits this trend. This trend, in addition to the close association of both elements in cluster analysis (figure 5.9 and figure 5.10), suggests molybdenite as the most important host mineral for Re.

Trace element investigations of sulphides have shown that sphalerite is the most important sulphide phase incorporating gallium. Observed concentrations via whole rock geochemistry are low and range between 1.71 and 24.00 ppm. The spatial distribution of Ga indicates enrichment towards peripheral zones of the mineralisation. Median concentrations of massive ore types are slightly lower (5.8-6.4 ppm) compared to semi-massive (6.6-7.0) and are highest in stringer ore (10.7). This observation, in addition to the proximity of Ga to Hf and Zr in cluster analysis (figure 5.10), suggests that elevated Ga concentrations are linked to increased wall rock component.

The remaining investigated trace elements feature clear enrichment trends with increasing depth below surface. The most important amongst them is bismuth as a smelter penalty element for lead concentrate. Concentrations are rather low throughout most of the orebody at median concentrations ranging between 0.16 and 3.47 ppm for all ore types. However, significant concentration levels as high as 714 ppm can be detected. A pronounced enrichment trend with increasing depth below surface is observed (figure 5.20). The highest concentrations are limited to the lower parts of the Elura orebody, in particular in the lowermost ML zone. No element affinity to any particular ore type is observed. Selenium and tellurium strongly correlate with each other in addition to Bi (figure 5.22) and feature almost identical spatial distributions as shown in figure 5.20. Concentrations of both elements are rather low with maxima at 45 and 1.88 ppm for Se and Te, respectively.

Cobalt and indium concentrations vary strongly, but feature significant enrichment towards depth (figure 5.19) in a similar manner as to Bi, Se and Te. Although some samples in upper and central ore zones contain elevated Co. Cobalt concentrations range between 0.2 and 288 ppm with a clear affinity to pyrrhotite dominated ore types at higher concentrations (figure 5.12). The maximum Co content is observed in stringer type ore from the lowermost ML zone. Indium concentrations are very low between 5 ppb and 3.2 ppm. Highest enriched samples cluster at the base of the ML zone, similar to Bi, Se and Te.

A very weak enrichment trend with increasing depth is present for cadmium (figure 5.21). Its inverse distance weighted distribution model

Figure 5.12: Box and Whisker plots for trace elements relatively enriched in massive and semi-massive pyrrhotitic ore types (SiPo, Po).
Figure 5.14: Ag silver distribution according to the resource block model. Silver is significantly enriched in the uppermost main lode zone and in some upper areas of the northern ore zones. Enrichment is observed vertically as well as laterally towards peripheral ore zones. (a) Isometric view down and towards WNW; (b and c) Longitudinal sections looking towards WSW, position of sections is shown in left plan view (red line).
5.3 Trace element signature - trends and element affinities

Figure 5.16: Spatial Cu distribution according to the resource block model. Copper is noticeably enriched with increasing depth below surface and commonly elevated in core zones of massive sulphide pipes. A second Cu enrichment is observed in the main lode area, coinciding with lithological changes of the host lithology (chapter 3 on page 35). (a) to (c) Longitudinal sections looking towards WSW, position of sections is shown in left plan view (red line).
appears rather erratic. Nevertheless, the model indicates a pronounced Cd enrichment in the lower ML zone, which is defined by a cluster of several samples high in Cd. Concentrations range between 17 and 446 ppm and are slightly elevated in pyrrhotitic compared to pyritic ore (figure 5.12).

Many of the investigated elements feature spatial enrichment trends. One element exhibits a repetitive enrichment trend with increasing depth. Copper is relative enriched in most samples from the lower mineralisation compared to those from the upper ML zone (figure 5.19). The overall measured Cu concentration range is defined by a minimum of 155 ppm in minor mineralised rock, and a maximum of 0.78 wt% detected in massive pyrrhotitic ore. Median Cu concentrations range between 0.16 wt% and 0.24 wt% in massive and semi-massive ore types. The resource block model (RBM) estimates a pre-mining Cu grade of 0.2 wt% for the entire resource, thus falls well within the range of observed median concentrations of this study. A clear shift to higher concentrations is observed in pyrrhotitic ore (figure 5.12). The lowermost part of the ML zone is
Figure 5.18: Trace element variabilities vs. depth for As, Ag and Sb. Yellow shape is the stringer type ore resource domain. Interpolated element distribution maps are based on standard inverse distance weighted (IDW) method implemented in the ESRI® ArcGIS software package; neighbours to include was set to 20 with a minimum of 10; due to the pronounced pipe-like geometry, an anisotropy factor of 2 at an angle of 0° was applied, with the search ellipsoid defined at 100 m vertical and 50 m lateral; power of weighting was optimised automatically.
Figure 5.19: Trace element variabilities vs. depth for Co, Cu and In. Yellow shape is the stringer type ore resource domain. Interpolated element distribution maps are based on standard inverse distance weighted (IDW) method implemented in the ESRI® ArcGIS software package; neighbours to include was set to 20 with a minimum of 10; due to the pronounced pipe-like geometry, an anisotropy factor of 2 at an angle of 0° was applied, with the search ellipsoid defined at 100 m vertical and 50 m lateral; power of weighting was optimised automatically.
Figure 5.20: Trace element variabilities vs. depth for Se, Te and Bi. Yellow shape is the stringer type ore resource domain. Interpolated element distribution maps are based on standard inverse distance weighted (IDW) method implemented in the ESRI® ArcGIS software package; neighbours to include was set to 20 with a minimum of 10; due to the pronounced pipe-like geometry, an anisotropy factor of 2 at an angle of 0° was applied, with the search ellipsoid defined at 100 m vertical and 50 m lateral; power of weighting was optimised automatically.
5. GEOCHEMICAL ORE CHARACTERISATION

Figure 5.21: Trace element variabilities vs. depth for Mo, Ga and Cd. Yellow shape is the stringer type ore resource domain. Interpolated element distribution maps are based on standard inverse distance weighted (IDW) method implemented in the ESRI® ArcGIS software package; neighbours to include was set to 20 with a minimum of 10; due to the pronounced pipe-like geometry, an anisotropy factor of 2 at an angle of 0° was applied, with the search ellipsoid defined at 100 m vertical and 50 m lateral; power of weighting was optimised automatically.
characterised by the highest Cu accumulation. A second zone of enrichment, although only defined by one sample, is observed at approximately RL 9700 m. At this depth, the positive Cu anomaly coincides with lithological changes of the host lithology (see chapter 3 on page 35). The spatial distribution of Cu is well known from the RBM. Both Cu enrichment zones described above are also visible and confirmed by the RBM. The set of a total of 117 ore samples is certainly rather low if representing the basis for geostatistical modelling. Nevertheless, rather good agreements are met for the estimated inverse distance weighed distribution models of Ag (figure 5.18) and Cu (figure 5.19) when compared with the RBM (figure 5.14 and figure 5.16). This study highlights the fact that no large sample set, large budget or much effort is needed to gain at least a rough overview of trace element distributions, in particular for smelter penalty elements, even for such a large orebody as Elura.

5.3.3 Element cross-plots

Several linear correlation trends were identified in element-element cross-plots (figure 5.22). Most correlations are caused by mutual element enrichment in particular areas within the orebody, e.g. enrichment of Hg and Tl in the uppermost part of the ML zone (figure 5.17). Geochemical characteristics clearly reflect mineralogical and mineral chemical changes.

**Figure 5.22**: Important element cross-plots indicative for major mineralogical changes and/or mutual element enrichment in particular parts of the orebody.
Silver correlates with Sb in most samples, caused by galena-miargyrite solid solution (see chapter 4 on page 108) and by argentian-tetrahedrite (see chapter 4 on page 93) as common silver mineral. One sample features elevated Sb but low Ag concentration, indicating the occurrence of other Sb-bearing mineral phases (figure 5.22). All samples elevated in Bi are characterised by well-correlated Ag and Bi concentrations (figure 5.22), reflecting solid solution of matildite in galena as described in chapter 4 on page 108. Silver-rich samples that lack significant Bi content contain argentian-tetrahedrite, native silver, or reflect solid solution of miargyrite in galena (see above). Thallium and Hg correlation is due to their strong enrichment in the uppermost parts of the ML zone, their host mineral phase is uncertain. In contrast, the correlation between Bi, Se and Te reflects their mutual enrichment in the lowermost parts of the ML zone, predominantly hosted by galena (figure 5.22).

5.3.4 Reconciliation between geochemistry and mineral chemistry for selected elements

Mineral chemical compositions were determined for selected samples as part of this study. Trace element concentrations of sphalerite and galena were used to reconcile mineral chemistry to whole rock geochemistry based on modal mineral composition, calculated from whole rock geochemical data.

Sphalerite is the most important carrier of Cd and In, although In occurs in very minor quantities of up to ~5 ppm (chapter 4 on page 108). The reconciliation plot for Cd (figure 5.24) shows a strong correlation between whole rock geochemistry and mineral chemistry, with an R² of 0.833. The In concentration plot also indicates a good correlation between whole rock geochemistry and mineral chemistry, with an R² of 0.6855.

Figure 5.23: Reconciliation of mineral chemistry to geochemical data for Bi. Bismuth concentrations incorporated in galena were determined via EMPA. Red circles show whole rock concentrations calculated based on mineral chemistry; blue circles are concentrations determined via whole rock geochemistry. Concentrations are plotted vs. depth below surface as reduced levels (RL).

Figure 5.24: Reconciliation of mineral chemistry to geochemical data (Cd, In). Both elements are predominately incorporated in sphalerite at the Elura orebody. Their concentration were determined via LA-ICP-MS. Black dashed lines are ideal 1:1 ratio; solid black lines are estimated linear trend lines; R² is the coefficient of determination.
5.24) shows a rather good agreement between geochemistry and mineral chemistry. The linear trend defined by those samples feature a slope of 0.94 and are consistently deficient by approximately 50 ppm. The deviation from the ideal 1:1 ratio may be caused by the occurrence of Cd-bearing mineral phases other than sphalerite. If only sphalerite carries Cd, this difference would equal to an underestimation of ~300 ppm via LA-ICP-MS when considering an average modal sphalerite content of 16 wt% (table 5.2). Indium concentration correlate but feature a significant deficiency of In calculated based on sphalerite composition (figure 5.24). Other In-bearing mineral phases are the likely cause for this misfit.

Galena has been identified as the most important host mineral for Bi, also incorporating significant quantities of Ag, Se and Te. Reconciliation between Bi concentrations in galena, established via EMPA with whole rock geochemical data, revealed a significant overestimation for EMPA, particularly for lower Bi concentrations (figure 5.23). Only those analyses that are characterised by the highest detected Bi concentrations reconcile close to geochemical data.

Figure 5.25: Reconciliation of mineral chemistry to geochemical data for Ag. Concentration of Ag incorporated in galena was determined via LA-ICP-MS. Sample labeled as red circle in upper diagram contains significant quantities of argentian-tetrahedrite, thus, galena is not a significant Ag carrier. This sample was not considered in the reconciliation shown in the lower diagram. Black dashed lines are ideal 1:1 ratio; solid black lines are estimated linear trend lines; R² is the coefficient of determination.

Figure 5.26: Reconciliation of mineral chemistry to geochemical data (Bi, Se, Te). Bismuth, Se and Te concentrations incorporated in galena were determined via LA-ICP-MS. Black dashed lines are ideal 1:1 ratio; solid black lines are estimated linear trend lines; R² is the coefficient of determination.
The $M_\alpha$ X-ray line was used for Bi determination via wavelength dispersive EMPA, which is in close proximity to the $M_\alpha$ X-ray line of Pb. Peak overlap between Pb and Bi X-ray lines is most probably causing the overestimation of Bi concentrations in galena.

Reconciliation between geochemical data and Bi in galena determined via LA-ICP-MS is close (figure 5.26). Some samples plot on or very close to the 1:1 ratio, concentrations of others are slightly overestimated based on LA-ICP-MS results. The results verify galena as the most important, if not the only Bi-bearing mineral phase. Correlation between Te and Bi is weak, none is observed between Se and Bi (figure 5.26). The poor linear trend and the consistent deficiency of Te based on mineral chemistry is indicative for the occurrence of another Te-bearing phase in addition to galena. The same applies for selenium.

Argentian-tetrahedrite and other sulfosalt species are the most important Ag-carrying mineral phases, in particular in upper areas of the orebody. Trace element determination via LA-ICP-MS showed significant Ag concentrations in galena (chapter 4 on page 108). Reconciliation of those Ag concentrations to geochemical data is shown in figure 5.25. One sample from the uppermost ML zone (CAF-1LS-1-1) is highly enriched in Ag and is not correlated to other samples. Abundant and coarse sulfosalt phases were microscopically identified (see chapter 4 on page 63), thus galena is a subordinate Ag carrier in this particular sample. Reconciliation of the remaining samples from central and deeper parts of the orebody is close. This proximity suggests that substantial if not most of the Ag within the Elura orebody is hosted by galena. Based on the reconciliation of nine samples (excluding CAF-1LS-1-1), on average, approximately 80% of total Ag contained in massive and semi-massive ore is hosted by galena.
### Table 5.3: Summary of trace element composition of different ore types. Concentration data in ppm, data labelled with (*) in wt%.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.2</td>
<td>85.3</td>
<td>0.2</td>
<td>1.8</td>
<td>3.3</td>
<td>13.1</td>
<td>0.2</td>
<td>1.8</td>
<td>3.3</td>
<td>13.1</td>
<td>0.2</td>
<td>1.8</td>
<td>3.3</td>
<td>13.1</td>
<td>0.2</td>
<td>1.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Mo</td>
<td>0.34</td>
<td>24.60</td>
<td>0.51</td>
<td>1.73</td>
<td>3.00</td>
<td>20.50</td>
<td>0.68</td>
<td>3.95</td>
<td>4.93</td>
<td>24.60</td>
<td>0.93</td>
<td>2.94</td>
<td>2.78</td>
<td>5.32</td>
<td>0.34</td>
<td>1.99</td>
<td>3.82</td>
</tr>
<tr>
<td>Nb</td>
<td>0.4</td>
<td>16.6</td>
<td>0.4</td>
<td>0.9</td>
<td>1.1</td>
<td>2.8</td>
<td>0.6</td>
<td>1.1</td>
<td>1.3</td>
<td>2.8</td>
<td>1.1</td>
<td>1.6</td>
<td>2.04</td>
<td>4.4</td>
<td>0.9</td>
<td>1.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Ag</td>
<td>1.2</td>
<td>0.11*</td>
<td>21.5</td>
<td>57.8</td>
<td>72.9</td>
<td>342.0</td>
<td>25.0</td>
<td>86.4</td>
<td>160.4</td>
<td>0.11*</td>
<td>22.0</td>
<td>43.6</td>
<td>58.8</td>
<td>199.0</td>
<td>13.7</td>
<td>88.1</td>
<td>139.2</td>
</tr>
<tr>
<td>Au</td>
<td>0.002</td>
<td>8.700</td>
<td>0.002</td>
<td>0.093</td>
<td>0.250</td>
<td>2.800</td>
<td>0.040</td>
<td>0.483</td>
<td>0.561</td>
<td>1.900</td>
<td>0.035</td>
<td>0.087</td>
<td>0.149</td>
<td>0.629</td>
<td>0.046</td>
<td>0.218</td>
<td>0.844</td>
</tr>
<tr>
<td>Cu</td>
<td>154.5</td>
<td>0.78*</td>
<td>281.0</td>
<td>0.24*</td>
<td>0.27*</td>
<td>0.78*</td>
<td>597.0</td>
<td>0.16*</td>
<td>0.20*</td>
<td>0.58*</td>
<td>879.0</td>
<td>0.21*</td>
<td>0.25*</td>
<td>0.73*</td>
<td>594.0</td>
<td>0.20*</td>
<td>0.23*</td>
</tr>
<tr>
<td>Co</td>
<td>0.2</td>
<td>288.0</td>
<td>0.5</td>
<td>12.0</td>
<td>16.6</td>
<td>56.3</td>
<td>0.2</td>
<td>12.0</td>
<td>16.6</td>
<td>56.3</td>
<td>0.2</td>
<td>12.0</td>
<td>16.6</td>
<td>56.3</td>
<td>0.2</td>
<td>12.0</td>
<td>16.6</td>
</tr>
<tr>
<td>Ga</td>
<td>1.71</td>
<td>24.00</td>
<td>3.14</td>
<td>6.35</td>
<td>7.23</td>
<td>23.70</td>
<td>2.18</td>
<td>5.81</td>
<td>6.77</td>
<td>12.50</td>
<td>1.71</td>
<td>7.03</td>
<td>8.94</td>
<td>24.00</td>
<td>1.71</td>
<td>7.03</td>
<td>8.94</td>
</tr>
<tr>
<td>Re</td>
<td>0.002</td>
<td>0.052</td>
<td>0.002</td>
<td>0.003</td>
<td>0.004</td>
<td>0.010</td>
<td>0.002</td>
<td>0.004</td>
<td>0.007</td>
<td>0.052</td>
<td>0.002</td>
<td>0.002</td>
<td>0.003</td>
<td>0.008</td>
<td>0.002</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>As</td>
<td>12.4</td>
<td>1.29*</td>
<td>12.6</td>
<td>4.11*</td>
<td>10.3*</td>
<td>34.1*</td>
<td>6.87</td>
<td>16.6</td>
<td>24.3</td>
<td>5.79</td>
<td>12.4</td>
<td>14.2</td>
<td>19.1</td>
<td>50.3</td>
<td>10.3*</td>
<td>24.4</td>
<td>5.79</td>
</tr>
<tr>
<td>Sr</td>
<td>0.4</td>
<td>308.0</td>
<td>0.4</td>
<td>1.9</td>
<td>4.1</td>
<td>27.1</td>
<td>1.3</td>
<td>6.6</td>
<td>9.1</td>
<td>34.8</td>
<td>0.6</td>
<td>2.8</td>
<td>3.6</td>
<td>13.4</td>
<td>1.9</td>
<td>6.6</td>
<td>9.1</td>
</tr>
<tr>
<td>Sb</td>
<td>9.53</td>
<td>0.21*</td>
<td>11.60</td>
<td>5.59*</td>
<td>92.12</td>
<td>573.00</td>
<td>28.70</td>
<td>189.00</td>
<td>341.48</td>
<td>0.12*</td>
<td>26.00</td>
<td>62.10</td>
<td>57.70</td>
<td>121.00</td>
<td>28.70</td>
<td>189.00</td>
<td>341.48</td>
</tr>
<tr>
<td>Sn</td>
<td>2.8</td>
<td>30.9</td>
<td>2.8</td>
<td>8.0</td>
<td>8.3</td>
<td>22.0</td>
<td>2.8</td>
<td>8.0</td>
<td>8.3</td>
<td>22.0</td>
<td>2.8</td>
<td>8.0</td>
<td>8.3</td>
<td>22.0</td>
<td>2.8</td>
<td>8.0</td>
<td>8.3</td>
</tr>
<tr>
<td>Sc</td>
<td>0.1</td>
<td>13.9</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>1.0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>1.0</td>
<td>0.1</td>
<td>0.5</td>
<td>0.8</td>
<td>2.6</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Tl</td>
<td>0.17</td>
<td>405.00</td>
<td>0.17</td>
<td>1.26</td>
<td>4.97</td>
<td>57.60</td>
<td>0.19</td>
<td>11.03</td>
<td>37.45</td>
<td>228.00</td>
<td>0.20</td>
<td>0.83</td>
<td>1.61</td>
<td>10.30</td>
<td>0.25</td>
<td>3.24</td>
<td>34.65</td>
</tr>
<tr>
<td>Sr</td>
<td>0.4</td>
<td>308.0</td>
<td>0.4</td>
<td>1.9</td>
<td>4.1</td>
<td>27.1</td>
<td>1.3</td>
<td>6.6</td>
<td>9.1</td>
<td>34.8</td>
<td>0.6</td>
<td>2.8</td>
<td>3.6</td>
<td>13.4</td>
<td>1.9</td>
<td>6.6</td>
<td>9.1</td>
</tr>
<tr>
<td>U</td>
<td>0.1</td>
<td>10.4</td>
<td>0.1</td>
<td>0.8</td>
<td>1.4</td>
<td>6.4</td>
<td>0.2</td>
<td>1.8</td>
<td>2.4</td>
<td>10.4</td>
<td>0.1</td>
<td>0.9</td>
<td>1.6</td>
<td>7.0</td>
<td>0.2</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Ti</td>
<td>1.0</td>
<td>48.0</td>
<td>1.0</td>
<td>3.0</td>
<td>4.5</td>
<td>15.0</td>
<td>1.0</td>
<td>3.0</td>
<td>4.5</td>
<td>15.0</td>
<td>1.0</td>
<td>3.0</td>
<td>4.5</td>
<td>15.0</td>
<td>1.0</td>
<td>3.0</td>
<td>4.5</td>
</tr>
<tr>
<td>V</td>
<td>1.0</td>
<td>48.0</td>
<td>1.0</td>
<td>3.0</td>
<td>4.5</td>
<td>15.0</td>
<td>1.0</td>
<td>3.0</td>
<td>4.5</td>
<td>15.0</td>
<td>1.0</td>
<td>3.0</td>
<td>4.5</td>
<td>15.0</td>
<td>1.0</td>
<td>3.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

---

#### 5.3 Trace element signature - trends and element affinities

- **Po Py SiPo SiPy VEIN/MinA**
- **Overall range**

<table>
<thead>
<tr>
<th>Po</th>
<th>0.4</th>
<th>308.0</th>
<th>0.4</th>
<th>1.9</th>
<th>4.1</th>
<th>27.1</th>
<th>1.3</th>
<th>6.6</th>
<th>9.1</th>
<th>34.8</th>
<th>0.6</th>
<th>2.8</th>
<th>3.6</th>
<th>13.4</th>
<th>1.9</th>
<th>6.6</th>
<th>9.1</th>
<th>34.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py</td>
<td>0.4</td>
<td>308.0</td>
<td>0.4</td>
<td>1.9</td>
<td>4.1</td>
<td>27.1</td>
<td>1.3</td>
<td>6.6</td>
<td>9.1</td>
<td>34.8</td>
<td>0.6</td>
<td>2.8</td>
<td>3.6</td>
<td>13.4</td>
<td>1.9</td>
<td>6.6</td>
<td>9.1</td>
<td>34.8</td>
</tr>
<tr>
<td>SiPo</td>
<td>0.4</td>
<td>308.0</td>
<td>0.4</td>
<td>1.9</td>
<td>4.1</td>
<td>27.1</td>
<td>1.3</td>
<td>6.6</td>
<td>9.1</td>
<td>34.8</td>
<td>0.6</td>
<td>2.8</td>
<td>3.6</td>
<td>13.4</td>
<td>1.9</td>
<td>6.6</td>
<td>9.1</td>
<td>34.8</td>
</tr>
<tr>
<td>SiPy</td>
<td>0.4</td>
<td>308.0</td>
<td>0.4</td>
<td>1.9</td>
<td>4.1</td>
<td>27.1</td>
<td>1.3</td>
<td>6.6</td>
<td>9.1</td>
<td>34.8</td>
<td>0.6</td>
<td>2.8</td>
<td>3.6</td>
<td>13.4</td>
<td>1.9</td>
<td>6.6</td>
<td>9.1</td>
<td>34.8</td>
</tr>
</tbody>
</table>

- **n = 117**
- **n = 40**
5. GEOCHEMICAL ORE CHARACTERISATION

5.4 Host rock classification

The host lithology of the Elura orebody is the CSA Siltstone. The turbiditic rock sequence consists of interbedded sand-, silt- and mudstone beds at varying quantities and thicknesses (see chapter 3 on page 35 further details). Major and trace elements are used to compare the host rocks composition to reservoir data (upper and lower continental crust, marine shale and turbidite), and for discrimination of their sedimentary provenance and tectonic settings.

The major and trace element compositions of fresh unaltered wall rock samples (abbrev. CSA and ALT) are given in table 5.4. Despite relative low S content, the determination of LOI (loss on ignition) was not carried out in order to avoid mass increases because of oxidation. Total element concentrations of CSA samples are close to 100% and range between 96.74 and 98.34%. According to Schmidt (1990), the wall rock (CSA Siltstone) contains 35-40 wt% muscovite and 10-15 wt% chlorite. This modal composition corresponds to total water content (i.e. approximate LOI) of 2.5 to 3.3 wt%, when considering 4 wt% and 11 wt% H₂O for muscovite and chlorite, respectively (water content based on Anthony et al., 1995). This range is close to the observed deficiencies to 100%. Altered wall rock samples have much lower totals due to pronounced chloritisation and sericite alteration and the accompanied addition of water in mineral lattices.

Sulphur content ranges between 0.2 to 0.6 wt% for CSA samples and increases to 1.2 wt% in altered samples. Most S is linked to pyrite, occurring in minor amounts within

---

**Table 5.4: Major (in wt%) and trace element (in ppm, below detection limit abbreviated with BDL) composition of fresh, unaltered (CSA) and altered (ALT) wall rock.**

<table>
<thead>
<tr>
<th>Lithology</th>
<th>Sample ID</th>
<th>CSA</th>
<th>CSA</th>
<th>CSA</th>
<th>CSA</th>
<th>CSA</th>
<th>CSA</th>
<th>NP &amp; BDL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2/3-1</td>
<td>2/3-2</td>
<td>290-1</td>
<td>290-2</td>
<td>560-1</td>
<td>560-2</td>
<td>ALT</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>62.80</td>
<td>63.00</td>
<td>60.90</td>
<td>60.70</td>
<td>65.70</td>
<td>66.70</td>
<td>54.30</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.64</td>
<td>0.64</td>
<td>0.65</td>
<td>0.63</td>
<td>0.62</td>
<td>0.63</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.75</td>
<td>15.85</td>
<td>15.25</td>
<td>15.15</td>
<td>14.60</td>
<td>14.85</td>
<td>16.75</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃eq</td>
<td>4.91</td>
<td>4.95</td>
<td>5.12</td>
<td>5.08</td>
<td>4.63</td>
<td>4.62</td>
<td>5.36</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.06</td>
<td>0.05</td>
<td>0.09</td>
<td>0.09</td>
<td>0.05</td>
<td>0.06</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
<td>0.05</td>
<td>0.09</td>
<td>0.09</td>
<td>0.05</td>
<td>0.06</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.84</td>
<td>0.84</td>
<td>0.19</td>
<td>0.19</td>
<td>0.17</td>
<td>0.14</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>4.02</td>
<td>4.05</td>
<td>4.32</td>
<td>4.33</td>
<td>3.55</td>
<td>3.57</td>
<td>5.22</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>1.31</td>
<td>1.32</td>
<td>3.82</td>
<td>3.82</td>
<td>1.47</td>
<td>1.47</td>
<td>1.62</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.08</td>
<td>0.08</td>
<td>0.10</td>
<td>0.10</td>
<td>0.12</td>
<td>0.12</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.07</td>
<td>0.07</td>
<td>0.06</td>
<td>0.06</td>
<td>0.08</td>
<td>0.07</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.25</td>
<td>0.27</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>4.44</td>
<td>4.44</td>
<td>5.21</td>
<td>5.17</td>
<td>2.93</td>
<td>2.91</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.35</td>
<td>0.35</td>
<td>0.61</td>
<td>0.63</td>
<td>0.22</td>
<td>0.22</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>97.67</td>
<td>98.34</td>
<td>98.24</td>
<td>98.76</td>
<td>96.74</td>
<td>98.14</td>
<td>91.18</td>
<td></td>
</tr>
</tbody>
</table>

---

**Figure 5.27:** Wall rock discrimination of tectonic settings based on major element concentrations after Roser and Korsch (1986). Classification fields are after Rollinson (1993). Fresh unaltered wall rock samples are shown as open black circles, altered sample is shown in green, and marine shale reference data from Yuan-Hui (1991) in red.
5.4 Host rock classification

the wall rock. Despite some Fe being incorporated in pyrite, most Fe is associated with silicates (e.g. chlorite) in a divalent state and therefore reported as FeO\(_{(\text{total})}\). The wall rock is commonly calcareous, in places carbonaceous and rich in degraded organics. Total carbon is reported as CO\(_2\) and ranges between 2.1 and 5.2 wt%.

Roser and Korsch (1986) suggested a discrimination diagram for sandstone-mudstone rock suits for classification according to their tectonic settings (i.e. island-arc, passive and active continental margins) based on K, Na and SiO\(_2\) contents. Most fresh wall rock samples plot near the border between active and passive continental settings (figure 5.27). The altered sample strongly shifts towards the field for passive continental margin. The shift may be expressed by the following discrimination functions:

\[ \text{discrimination function 1-1} = -1.773 \frac{TiO_2}{Al_2O_3} + 0.607 \frac{Al_2O_3}{Al_2O_3} + 0.76 \frac{Fe_3O_3(\text{total})}{Al_2O_3} - 1.5 MgO \] (5.1)

\[ + 0.616 CaO + 0.509 Na_2O - 1.224 K_2O - 9.09 \]

\[ \text{discrimination function 1-2} = 0.445 \frac{TiO_2}{Al_2O_3} + 0.07 \frac{Al_2O_3}{Al_2O_3} - 0.25 \frac{Fe_3O_3(\text{total})}{Al_2O_3} - 1.142 MgO \] (5.2)

\[ + 0.438 CaO + 1.475 Na_2O + 1.426 K_2O - 6.861 \]

\[ \text{discrimination function 2-1} = 30.638 \frac{TiO_2}{Al_2O_3} - 12.541 \frac{Fe_3O_3(\text{total})}{Al_2O_3} + 7.329 \frac{MgO}{Al_2O_3} \] (5.3)

\[ + 12.031 \frac{Na_2O}{Al_2O_3} + 35.402 \frac{K_2O}{Al_2O_3} - 6.382 \]

\[ \text{discrimination function 2-2} = 56.500 \frac{TiO_2}{Al_2O_3} - 10.879 \frac{Fe_3O_3(\text{total})}{Al_2O_3} + 30.875 \frac{MgO}{Al_2O_3} \] (5.4)

\[ - 5.404 \frac{Na_2O}{Al_2O_3} + 11.112 \frac{K_2O}{Al_2O_3} - 3.89 \]

**Figure 5.28:** Wall rock discrimination for source rock provenance based on major element ratios after Roser and Korsch (1988). The discrimination functions are shown in eq. 5.1 to eq. 5.4. Classification fields and functions are after Rollinson (1993). Fresh unaltered wall rock samples are shown as open black circles, altered sample is shown in green, and marine shale reference data from Yuan-Hui (1991) in red.
plained by a de-silicification or dilution of silica accompanied by potassic alteration. Two samples plot in-between, probably caused by beginning alteration.

The major element composition is used to classify the wall rock samples with respect to their source provenance. Roser and Korsch (1988) established two discrimination schemes for sandstone-mudstone rock suits and their provenance signature. These authors formulated four discrimination functions (eq. 5.1 to eq. 5.4) defining x- and y-axis values in two separate diagrams. In discrimination diagram I (figure 5.28), wall rock samples plot near the intersection of all provenance fields but feature a tendency toward intermediate igneous provenance. The samples plot within the latter aforementioned field in the second discrimination scheme close to the boundary to mafic igneous provenance (figure 5.28). The CSA Siltstone is part of the lower Amphitheatre Group sediments, which were sourced from the northwest and west from the Winduck Shelf (composed of storm sediments and littoral sands), and to some extent from granites to the southwest (Glen, 1990). The observed source rock provenance is a combination of diverse lithologies surrounding the Cobar Basin. The proximity to the mafic igneous provenance may reflect the rifting induced origin of the Cobar Basin, accompanied by bi-modal volcanism.

Trace element concentrations of wall rock samples, fresh and altered, were normalised to average continental crust (data after Wedepohl, 1995) and plotted in a multi-element diagram (figure 5.31). The wall rock samples were taken between 100 and 200 m distant to the orebody. Data is compared to marine shale reference data after Yuan-Hui (1991), average upper and lower continental crust after Wedepohl (1995). Most elements are enriched relative to average continental crust at factors between 1-2 and feature similar pattern compared to marine shale reference data. Caesium, Rb, both highly mobile
elements, and Th are stronger enriched at factors of approximately 6, 3 and 2.5, respectively. The relative mobile element strontium is significantly depleted by the factor 0.3.

Whitbread and Moore (2004) investigated the cryptic alteration halo within wall rock around the deposit. They observed enrichment trends of Cs and Rb towards the mineralisation, caused by their incorporation in muscovite. Strontium is significantly depleted proximal to the orebody, caused by its replacement in carbonates by iron. Macroscopically, these samples are not affected by any significant alteration. However, selective trace element enrichment and depletion observed in the course of this study are in agreement with earlier investigations and are caused by subtle mineralogical changes caused by alteration. The results highlight the significant extent of cryptic alteration to distances in excess of 200 m to the orebody.

Bhatia and Crook (1986) proposed tectonic discrimination diagrams for greywackes, which represent a significant component within the host lithology as sandstone beds. All wall rock samples, including the altered sample, closely cluster in the continental island-arc field in the La-Th-Sc discrimination scheme (figure 5.29). The samples are more scattered in the Th-Sc-Zr/10 diagram and crossover from the aforementioned into the active continental margin field. These results are in agreement with those based on the discrimination after Roser and Korsch (1986).

Figure 5.30 shows chondrite normalised REE distribution pattern for unaltered and altered wall rock samples compared to turbidite and marine shale reservoir data (REE pattern based on CSA sample data presented in table 5.6). The observed distribution patterns are very similar to marine shale. The better fit with shale than with turbidite data suggests that REE content in the wall rock sequence is predominantly controlled by REEs contained in silt- and mudstone, sandstone component appears subordinate. This is in agreement with studies by Cullers et al. (1987) that showed that REE patterns in sedimentary rock suits are predominantly controlled by the clay-sized mineral fraction. The good correlation with reference data confirms that REE analyses are valid and that the minor deviation in Ce in standard analyses (figure 5.3) had no significant effect on accuracy.

Figure 5.31: Multi-trace-element diagram comparing wall rock samples to reference data. Data is normalised to average continental crust (Wedepohl, 1995). Upper and lower continental crust reference data after Wedepohl (1995), marine shale data after Yuan-Hui (1991).
5.5 Mass/volume and element gain-loss estimation

Fluids, introduced into and migrating through lithologies, will in almost any circumstance result in its modification, as long as fluid and bulk rock chemical compositions are in disequilibrium. Modifications may occur via metasomatism, mineral replacements and the formation of new mineral species. The subsequent change of bulk rock chemical composition is accompanied by mass and volume changes. Gresens (1967) described composition-volume relationships caused by metasomatism by comparing modal mineralogy as well as whole rock compositions of unaltered and altered samples. The author’s fundamental argument is that some elements are immobile during alteration, e.g. due to their incorporation in highly refractory mineral phases not affected by metasomatic processes. When comparing concentration changes of identified immobile elements, mass and volume changes, accompanying alteration, can be estimated. Grant (1986) revisited Gresens (1967) proposition and formulated a simplified method to describe mass/volume changes during metasomatic processes and called it the isocon diagram, where isocons describe straight lines of equal element concentrations.

5.5.1 The Isocon-method

The principle of the isocon-method is visualised in figure 5.32. Scaled concentrations are used for altered and less- or unaltered reference sample. Scaling is performed as described in Huston (1993) in order to improve the presentation of isocon diagrams. Elements were ordered according to their expected mass changes beginning with those characterised by largest mass gains. Immobile elements were evenly distributed. Subsequently, an integer (n) was assigned to each of the elements (i) and a scaling factor (F) calculated (eq. 5.5). Scaled concentrations of altered samples (C_A^i) and reference sample (C_{Ref}^i) are defined according to eq. 5.6. By inspecting the distribution of scaled concentrations of potential immobile elements (Al, Ti, Y, Zr, Nb, Hf and Ta in this study), a best-fit isocon through the origin may be constructed. According to Grant’s equation (eq. 5.7), which is a rearranged version of Gresens’, the reciprocal slope (k_{iso}) of the isocon is equal to the relative mass change (ΔM) during alteration, because the concentration change (ΔC_i) of immobile elements is 0 (eq. 5.8). An isocon with k_{iso} < 1 reflects mass gain, k_{iso} > 1 mass loss. If density values of altered (ρ^A) and reference sample (ρ_{Ref}) is known, relative volume changes (ΔV; eq. 5.9; Huston, 1993), and assuming isotropic volume change, relative dimensional change (ΔL; eq. 5.10; Huston, 1993) can be calculated. Relative concentration changes for other elements are calculated according to eq. 5.7.
5.5 Mass/volume and element gain-loss estimation

\[ F_i = \frac{n_i}{C_i^{\text{Ref}}} \]  
\[ C_i^{\text{A}} = F_i C_i \text{ and } C_i^{\text{Ref}} = n_i \]  
\[ C_i^{\text{A}} = \frac{M_i^{\text{Ref}}}{M_i^{\text{A}}} \left( C_i^{\text{Ref}} + \Delta C_i \right) \]  

for immobile elements \( \Delta C_i = 0 \) in eq. 5.7, hence

\[ \Delta M = \frac{M_i^{\text{A}}}{M_i^{\text{Ref}}} = \frac{C_i^{\text{Ref}}}{C_i^{\text{A}}} = \frac{1}{k_{\text{iso}}} \]  
\[ \Delta V = 100 \left( \frac{1}{k_{\text{iso}}} \frac{\rho_i^{\text{Ref}}}{\rho_i^{\text{A}}} - 1 \right) \]  
\[ \Delta L = 100 \left( \frac{1}{k_{\text{iso}}} \frac{\rho_i^{\text{Ref}}}{\rho_i^{\text{A}}} - 1 \right)^{\frac{2}{3}} \]

\[ y = 0.0305x - 0.0558 \]  
\[ R^2 = 0.9966 \]

\[ \text{Figure 5.33: Zirconium-hafnium cross-plot. Good correlation is explained by zircon as their common host, and validates complete sample digestion for chemical analysis.} \]

Whitbread and Moore (2004) used the isocon-method to study the cryptic alteration halo surrounding the Elura orebody. They observed increasing mass changes towards the mineralisation between 18 and 88% for sandstone samples, shale samples yielded increases between 1 and 10%. Composite samples, i.e. bulk rock samples composed of interlayered sand-, silt- and mudstone beds, feature a converse trend with decreasing mass changes from 10 to 3%. Immobile elements identified by the authors and used to construct isocons are Y, Zr and Ti for sandstone; Cr, La, Ce, Y, Th, V, Si, P, Al, Ti and Sc for shale; Cr, Y, Nb, Al and Ti for composite samples.

5.5.2 The hypothesis

The current genetic model, widely supported by the research community, is an epigenetic hydrothermal replacement origin (see chapter 3 on page 50). It appears unlikely that a sulphide mass in excess of 50 Mt is formed solely via replacement of a silicic-clastic host rock sequence in the classical sense. It rather needs to be understood as a combination of sulphide precipitation in fracture-induced openings (e.g. dilational jogs, elevated permeability caused by pronounced fracturing along faults, etc.), accompanied by element remobilisation (e.g. desilicification) causing volume loss and thus space for sulphides to precipitate.

The isocon-method is commonly used to study compositional changes and accompanying mass and volume changes induced by alteration processes. Ore formation at the Elura had most probably occurred via multiple fluid events and hence multiple alteration/sulphide precipitation stages. It is not possible to distinguish and separate the initial volume loss caused by alteration and the following mass accretion via sulphide formation.

The major constituent within the turbiditic host rock is undoubtedly silica. The precursory alteration that potentially create sufficient open space for sulphides must therefore effectively remobilise and remove silica from the wall rock. The isocon-method was tried to qualitatively investigate the amount of wall rock contained in different ore types that has been replaced during ore formation via the following hypothesis:

(a) Comparison of immobile element concentrations of unaltered wall rock with different ore types will allow the estimation of total mass/volume changes and element gains/losses via the isocon-method.

(b) The calculated volume changes are used to estimate the amount of wall rock contained in different ore types, when a maximum possible volume change of 700% or by a factor of 8 is considered.

(c) If initial volume loss via alteration was a sig-
5. GEOCHEMICAL ORE CHARACTERISATION

Significant mechanism of generating space for sulphide precipitation, silica has to be highly depleted relative to immobile elements.

5.5.3 Results

Average scaled (eq. 5.6) element concentrations were calculated for different ore types (i.e. altered minor mineralised-MinA/ALT, breccia-stringer type ore-VEIN, semi-massive ore SiPy/SiPo and massive ore Py/Po) and compared to average scaled fresh/unaltered wall rock samples (CSA, n = 6; see section 5.4 on page 166) in isocon diagrams (figure 5.34 to figure 5.37). Elements obviously highly enriched within the base metal mineralisation (i.e. Zn, Pb, Ag, Cu, As, Cd, Sb) were not considered. Sulphur and Fe are included to represent sulphide enrichment. Aluminium, Ti, Nb and Ta were identified as being immobile and were used to construct best-fit isocon lines. Zirconium and Hf, although generally immobile during hydrothermal alteration, feature a rather good cross-correlation (figure 5.33), but did not define isocons. Their good correlation is explained by their common mineral host zircon, and as a highly refractory mineral phase, the correlation indicates complete sample digestion. In turbiditic rock sequences, zircons are predominantly contained in sandy beds in rather low quantities. Sandstone thicknesses and quantities are highly variable throughout the host rock sequence, hence is the amount of zircon. Whitbread and Moore (2004) suggested

Figure 5.34: Scaled isocon diagram for altered and minor mineralised wall rock (lower diagram). Average scaled element concentrations of altered samples are plotted versus fresh/unaltered wall rock samples (CSA, n = 6). Immobile elements used for isocon construction are shown in red. The upper diagram shows element gains or losses relative to CSA reference samples. Other commonly immobile elements are labeled in yellow.
this heterogeneity as the cause for their isocon misfit. Yttrium, consistently depleted, appears mobile. The estimated mass, volume and elemental changes will be described for different ore types in the following, beginning with ALT/MinA as most distant to the mineralisation. Bulk densities used for the calculation of volume changes are shown in figure 5.6 in section 5.2 on page 146 and based on modal composition derived from whole rock geochemistry.

The isocon of ALT/MinA ore types (figure 5.34) yields a $\Delta M$ of +14.1% and a volume increase of the same value due to similar bulk rock densities of CSA, ALT and MinA ($\rho = 3 \text{ g cm}^{-3}$; figure 5.6). The volume change ($\Delta V$) corresponds to a wall rock component of 98% and to an isotropic dimensional change of $\Delta L = +4.5\%$. Elements significantly depleted are Sr, Ca, C and Na, those enriched are S, Fe, Hg, Tl, Mg, Rb, Cs, Ba and W. With the exception of C, the observations are in agreement with results of strongest altered samples studied by Whitbread and Moore (2004). Silica, Be, Sc and Cr plot close to the isocon line suggesting immobility. Silica most likely takes part in alteration mineral reactions although it is retained and conserved in the system at constant concentrations. The observed minor volume increase may reflect dissolution-precipitation reactions during alteration or formation of mineral phases in permeably sandstone beds, not necessarily caused by fracturing.

![Scaled isocon diagram for breccia-stringer type ore](image-url)
5. GEOCHEMICAL ORE CHARACTERISATION

The total sulphide content of the remaining ore types increases progressively towards the core zones of the orebody, with lowest in breccia-stringer ore (VEIN, figure 5.35), via semi-massive ore (SiPy/SiPo, figure 5.36) to the highest in massive ore (Py/Po, figure 5.37). Thus, elements commonly incorporated in sulphides (e.g. Co, Ni, Se, Mo, In, Hg, Tl, Bi) are strongly enriched following the trend of increasing sulphide content. Enrichments of Mn, Mg, and C are caused by the formation of carbonates. Other elements relatively enriched and indicated to be introduced by the mineralising fluid, are Cr, Sr, Ba, W, U and Ga. Sodium, K, Rb and Cs are depleted at variable degrees.

The element featuring significantly different characteristics between ore types is silica. In breccia-stringer and semi-massive ore types, Si is significantly enriched at 197%, whereas it is almost constant (92%) in massive ore. It is known from macroscopic and microscopic observations that wall rock fragments contained in these ore types are highly silicified, thus validated by the concentration increase established via the isocon-method. Significant silica depletion is not observed.

Estimated mass and corresponding volume/dimensional changes increase from $\Delta M = +147\%$, $\Delta V = +125\%$, $\Delta L = +31\%$ for VEIN, to $\Delta M = +899\%$, $\Delta V = +581\%$.

**Figure 5.36:** Scaled isocon diagram for semi-massive ore (lower diagram). Average scaled element concentrations of altered samples are plotted versus fresh/unaltered wall rock samples (CSA, $n=6$). Immobile elements used for isocon construction are shown in red. The upper diagram shows element gains or losses relative to CSA reference samples. Other commonly immobile elements are labeled in yellow.
\( \Delta L = +90\% \) for SiPy/SiPo, to maxima of \( \Delta M = +1652\% \), \( \Delta V = +1018\% \), \( \Delta L = +124\% \) for Py/Po ore types. Volume gains and dimensional expansion in excess of 700 and 100\%, respectively, are not possible. The overestimation is likely caused by analytical errors due to very low element concentration and subsequent inaccurate isocon construction. Thus, \( \Delta V \) and \( \Delta L \) are interpreted as maximum possible values. Wall rock components, calculated based on \( \Delta V \), increase from 82\% (VEIN), via 17\% (SiPy/SiPo) to 0\% for (Po/Py).

The two most important constituents in the CSA wall rock, i.e. Si and Al, are either immobile or enriched. The lack of significant depletion of silica in addition to the substantial volume gains in breccia-stringer and semi-

massive ore types suggests that most sulphide mass precipitated in fracture induced permeability. Minor replacement of wall rock fragments may have occurred. In contrast, results for massive ore indicate that sulphide precipitation took place exclusively at sites of dilation with negligible interaction with the host lithology. It needs to be stressed, that the application of the isocon-method on massive and semi-

massive sulphide ore is at its best a rough estimation only. Concentrations of elements contained in wall rock are very low in massive ore. Despite those low concentrations, the construction of isocon lines, consistently defined by the same group of immobile elements, was possible for all different ore types.

Figure 5.37: Scaled isocon diagram for massive ore (lower diagram). Average scaled element concentrations of altered samples are plotted versus fresh/unaltered wall rock samples (CSA, n=6). Immobile elements used for isocon construction are shown in red. The upper diagram shows element gains or losses relative to CSA reference samples. Other commonly immobile elements are labeled in yellow.
5. GEOCHEMICAL ORE CHARACTERISATION

5.6 Rare earth element signatures of different ore types

Comparison of rare earth element (REE) distribution pattern of unaltered and fresh wall rock samples with different geological reference data showed a good agreement with marine shale (figure 5.30 in section 5.4 on page 168). REEs are generally considered immobile and their distribution patterns commonly not altered by hydrothermal fluids. The exception to this rule are environments of extreme fluid-rock ratios, where the distribution patterns may be modified due to certain degrees of REE mobilisation (Bau, 1991). REE concentrations of different ore types are compared to unaltered wall rock samples in order to investigate potential REE fractionations and alterations of their distribution patterns. Locations of samples chosen for REE analysis are shown in figure 5.2 in section 5.1 on page 141.

The REE concentrations of all analyses are shown in table 5.6 and are summarised for different ore types in table 5.5. The unaltered wall rock samples (n = 3) contain a total REE (ΣREE) of 209 to 216 ppm. Their chondrite normalised distribution pattern (abbrev. REEChon) feature significant enrichment of light REE (abbrev. LREE; La to Pm) and medium REE (abbrev. MREE; i.e. Sm to Ho). REE concentrations data after Palme and O'Neill (2004) was used for chondrite normalisation (see figure 5.39 for average distribution or figure 5.30 in section 5.4 on page 168 for full data set). A strong overall REE fractionation is observed with (La/Yb)N ranging between ~2-4 and ~1-2 (range based on median values table 5.5). Stronger LREE/MREE fractionation is commonly observed in pyritic ore (Py, Po) and their distribution patterns commonly not altered by hydrothermal fluids. The exception to this rule are environments of extreme fluid-rock ratios, where the distribution patterns may be modified due to certain degrees of REE mobilisation (Bau, 1991). REE concentrations of different ore types are compared to unaltered wall rock samples at (La/Yb)N ~13. LREE/MREE are stronger fractionated than MREE/HREE in all ore types with (La/Sm)N and (Gd/Yb)N ranging between ~2-4 and ~1-2 (range based on median values table 5.5, respectively). Stronger LREE/MREE fractionation is commonly observed in pyritic ore types (diagram a in figure 5.38) whereas most samples feature MREE/HREE fractionation similar to wall rock (diagram b in figure 5.38).

In VEIN samples, Eu/Eu* are variable at values close to wall rock (~0.5) and up to 1.6. Most other ore samples feature strong and well-defined positive Eu/Eu* up to 8.8 and a very weak negative Ce anomaly (abbrev. Ce/Ce*; ~0.8-1.0, table 5.5). Anomalous enrichment of La relative to other LREE may cause artificial Ce/Ce* (e.g. Bau and Dulski, 1996; Shields and Stille, 2001). Bau and Dulski (1996) suggested

<table>
<thead>
<tr>
<th>Ore type</th>
<th>Total REE*</th>
<th>(La/Yb)N</th>
<th>(La/Sm)N</th>
<th>(Gd/Yb)N</th>
<th>Eu/Eu*</th>
<th>Ce/Ce*</th>
</tr>
</thead>
<tbody>
<tr>
<td>VEIN</td>
<td>Min 98.398 2.710 1.517 1.091 0.480 0.896</td>
<td>Median 210.318 5.419 2.660 1.501 0.963 0.916</td>
<td>Avg 257.187 6.211 2.659 1.496 0.989 0.916</td>
<td>Max 509.713 11.296 3.799 1.889 0.937 0.930</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiPy</td>
<td>Min 26.835 2.841 1.705 1.324 1.341 0.830</td>
<td>Median 61.093 12.918 3.838 1.942 2.565 0.872</td>
<td>Avg 70.035 18.669 3.717 2.542 3.488 0.876</td>
<td>Max 159.961 59.259 6.151 5.867 6.720 0.930</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiPo</td>
<td>Min 13.656 1.078 0.853 1.003 0.612 0.794</td>
<td>Median 17.676 4.202 2.578 1.381 1.269 0.859</td>
<td>Avg 49.529 4.599 2.295 1.344 2.388 0.855</td>
<td>Max 142.749 8.521 3.792 1.621 7.490 0.917</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Po</td>
<td>Min 5.004 0.400 0.820 0.929 0.194 0.782</td>
<td>Median 19.405 6.163 2.688 1.671 3.794 0.853</td>
<td>Avg 23.854 7.498 2.809 1.788 3.840 0.853</td>
<td>Max 63.905 22.111 5.568 3.595 7.178 0.926</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py</td>
<td>Min 5.536 0.547 0.868 1.178 0.982 0.822</td>
<td>Median 19.882 5.014 2.317 1.666 4.368 0.854</td>
<td>Avg 27.524 5.739 2.095 1.452 4.715 0.854</td>
<td>Max 67.197 11.657 3.237 3.252 8.795 0.887</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.6 Rare earth element signatures of different ore types

to determine the value for Pr/Pr* as

\[
\frac{Pr}{Pr^*} = 2 \frac{Pr_N}{(Ce_N + Nd_N)},
\]

which would have to be greater or equal to 1, if the Ce/Ce* is not artificial. The calculated Pr/Pr* values range between 1.0 and 1.2, suggesting the negative Ce anomalies, despite minor, are real.

Apart from the earlier described positive Eu/Eu* developed in most samples, REE\textit{Chon} patterns of sulphide ore samples are similar to those of wall rock samples (abbrev. CSA; figure 5.39), although strongly diluted in concentrations. Minor differences become more apparent when sample data is normalised to post-Archean Average Australian Shale (PAAS) reference data (abbrev. REE\textit{PAAS}; figure 5.39; data after Nance and Taylor (1976) was used for normalisation). CSA samples are close to PAAS values for most REE with MREE slightly elevated. REE in sulphide ore samples are diluted by factors between ~0.5 (VEIN) and ~0.01 (Py and Po) compared to CSA. HREE distribution is commonly close to that observed in CSA. LREE and MREE in most semi-massive and massive ore types feature either minor enriched or are similar to CSA, although LREE are significantly diluted in some samples. Examples of the most characteristic REE distribution pattern featuring significant differences in REE fractionation are shown in figure 5.40 and summarised in figure 5.41.

In order to interpret whole rock REE geochemical data of sediments, in particular when mineralised, the modal mineralogy and the capability of REE incorporation within the occurring mineral phases must be considered. Pyrite, pyrrhotite, sphalerite, galena, iron carbonates (i.e. siderite, ankerite), calcite, quartz, muscovite and chlorite are the most important mineral constituents in the sulphide ore of the Elura orebody. Quartz and sulphides are known to incorporate at best only trace REE quantities (e.g. Zhao and Jiang, 2007; Rollinson, 1993). These mineral phases therefore have a diluting effect on the REE content of ore samples. Iron carbonates and calcite are asides from quartz the most important NSG phases. Studies that investigated REE contents in carbonates (e.g. Bau and Möller, 1992; Davies \textit{et al.}, 1998) showed that they preferably accommodate the MREEs and, in places, HREEs (figure 5.42), commonly characterised by a relative depletion of LREE. In reducing environments or at elevated temperatures above ~250 °C, most Eu transported via hydrothermal fluids occurs in divalent state. Eu\textit{2+} is readily incorporated in the calcite or iron carbonate crystal lattice Sverjensky (e.g. 1984); Bau (e.g. 1991); Lottermoser (e.g. 1992). Muscovite and chlorite, the most important alteration mineral phases within
Figure 5.39: REE distributions of different ore types. Red dashed lines are average CSA wall rock REE distributions. Data has been normalised to chondrite (upper diagrams; chondrite data after Palme and O’Neill (2004)) and to post-Archean Average Australian Shale (lower diagrams; abbrev. PAAS; normalisation data after Nance and Taylor (1976)).
5.6 Rare earth element signatures of different ore types

wall rock fragments, preferably incorporate the LREEs (Cullers et al., 1975; Laul and Lepel, 1987).

Considering mineralogy, remnant wall rock fragments, if contained in sulphide ore in sufficient quantities, are clearly the main contributors to the observed REE distribution patterns. If wall rock content within ore is low, these inherited patterns may, however, be masked by REE-bearing mineral phases that precipitated during ore formation, i.e. non-sulphide gangue (abbrev. NSG; iron carbonate, quartz). The hydrothermal fluid may either cause further modifications via alteration of wall rock fragments, accompanied by the formation of sericite and/or chlorite, or, if fluid rock ratios are extremely high, by remobilisation of REEs (Bau, 1991).

The pronounced decrease of total REE content observed in different ore types (table 5.5), in addition to the LREE/MREE/HREE fractionation trends (figure 5.38) indicate a decrease of wall rock component. Massive ore samples yield maximum REE depletions in the order of 0.01, suggesting only a minor wall rock content. The consistently observed pronounced Eu anomalies in semi-massive and massive ore imply a rather reducing depositional environment and/or elevated fluid temperatures in excess of 250°C (Sverjensky, 1984). Absent or minor Eu anomalies in breccia-stringer type ore may be caused by insufficient hydrothermal carbonate precipitation or deficient Eu²⁺ transported in the hydrothermal fluid. The latter case would be indicative for a drop in temperature or changing redox state of the mineralising fluid towards higher oxygen fugacities.

Three groups of REE distribution pattern different to wall rock were identified. Representative examples of these patterns are summarised in figure 5.41. The example patterns are based on average REE concentrations, which were normalised to average wall rock composition.

Figure 5.40: Representative examples of distinct REE distribution patterns significantly different to unaltered CSA wall rock. Left diagram: significant depletion of LREE and to some extent of MREE. Middle diagram: REE distributions are rather similar to wall rock, although slightly enriched in MREE. Right diagram: patterns are characterised by LREE/MREE enrichment. Red dashed lines are average CSA wall rock REE distributions. Green lines are average composition for individual patterns, shown in figure 5.41. Data has been normalised to chondrite (upper diagrams; chondrite data after Palme and O’Neill (2004)) and to post-Archian Average Australian Shale (lower diagrams; abbrev. PAAS; normalisation data after Nance and Taylor (1976)).
5. GEOCHEMICAL ORE CHARACTERISATION

Figure 5.41: Three representative examples of distinct REE distribution patterns significantly different from unaltered CSA wall rock. Pattern A (red) features significant depletion of LREE and to some extent of MREE. REE distributions are rather similar to wall rock in pattern B (blue), although slightly enriched in MREE. Pattern C (green) is characterised by significant LREE enrichment. Data has been normalised to average CSA wall rock composition and to Lu (yellow symbol). Data used in this diagram are average compositions shown in figure 5.40 as green lines.

When comparing pattern A and B (figure 5.41 with REE distributions within siderite, ankerite and calcite reference data (figure 5.42), it becomes clear that the REE distributions are solely controlled by carbonates. Siderite features REE pattern significantly diluted in LREE relative to MREE and HREEs. Pattern A can therefore be explained by samples relatively enriched in siderite. On the other hand, REE distributions of calcite and ankerite are relatively flat, but may be moderately enriched in MREE. Patterns of those two mineral phases are similar to pattern B, indicative for samples dominated by ankerite and/or calcite. Pattern C is exclusively observed in pyritic ore types (SiPy and Py). Both ore types commonly contain sericite and chlorite, mineral phases enriched in LREE. Pronounced sericitisation and chloritisation is thus the most probable explanation for pattern C.

The well-defined and strong Eu anomaly in addition to the enrichment of other MREEs and LREE in carbonates, sericite and chlorite implies that the hydrothermal fluid carried significant REEs in solution. As the hydrothermal fluid ascended from deeper parts within the Cobar Basin, REEs were most probable mobilised from the basinal stratigraphy via alteration of relatively unstable mineral phases, such as feldspar and carbonate phases.

This study showed that modifications of REE distribution pattern associated with hydrothermal fluid events at the Elura orebody are exclusively caused by changes in mineralogy. No local REE remobilisation caused by extreme fluid-rock interaction is needed in order to explain pronounced LREE depletion.
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Lithology</th>
<th>Ore type</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
<th>Total REE</th>
<th>(La/Yb)N</th>
<th>(La/Sm)N</th>
<th>(Gd/Yb)N</th>
<th>Eu/Eu*</th>
<th>Po</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBA-3</td>
<td>WEIN</td>
<td>0.47</td>
<td>0.45</td>
<td>0.09</td>
<td>0.29</td>
<td>0.09</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>1.12</td>
<td>0.56</td>
<td>0.28</td>
<td>0.16</td>
<td>0.36</td>
</tr>
<tr>
<td>NBA-4</td>
<td>WEIN</td>
<td>0.59</td>
<td>0.53</td>
<td>0.08</td>
<td>0.26</td>
<td>0.07</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>1.14</td>
<td>0.58</td>
<td>0.30</td>
<td>0.18</td>
</tr>
<tr>
<td>NBA-5</td>
<td>WEIN</td>
<td>0.68</td>
<td>0.61</td>
<td>0.10</td>
<td>0.26</td>
<td>0.08</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>1.16</td>
<td>0.59</td>
<td>0.32</td>
<td>0.19</td>
</tr>
<tr>
<td>NBA-6</td>
<td>WEIN</td>
<td>0.84</td>
<td>0.75</td>
<td>0.11</td>
<td>0.26</td>
<td>0.08</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>1.18</td>
<td>0.60</td>
<td>0.34</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 5.6: REE concentration data. (#) Total REE concentrations are excluding Ho, which was not analysed. Data given in ppm. Normalisation was performed with chondrite composition after Palme and O'Neill (2004).
5. GEOCHEMICAL ORE CHARACTERISATION

5.7 Platinum group elements and the time of ore formation

5.7.1 PGE concentrations and their fractionations

The elements of the platinum group are with increasing order of natural abundances Rh, Ir, Os, Pd, Ru and Pt (based on data of McDonough and Sun, 1995). The PGEs are part of the D-block elements that mostly consists of siderophile elements featuring similar atomic radii. The PGEs and Re have a highly siderophile character and preferably partitioned into Fe-rich melts during the early genetic stages of the primeval earth, as its differentiation commenced. Subsequently, these elements were incorporated into the earths’ core during its formation, responsible for the very low PGE abundances in mantle and crustal lithologies (Faure and Mensing, 2005; McInnes et al., 2008). New chondritic material was added during the late heavy bombardment at approximately 3.9 Ga, causing a re-enrichment of PGEs in the upper mantle. The PGEs are grouped according to their different geochemical behaviour. The Pd-subgroup (PPGE), consisting of Pd, Pt and Rh, features a stronger affinity to sulphide phases than the elements of the Ir-subgroup (i.e. Ir, Os, Ru; abbrev. IPGE). The less chalcophile IPGEs preferably form alloys and are commonly associated with chromites, whereas PPGEs preferably occur in sulphide phases, or as variable separate PPGE phases. PPGE are generally partitioned into the silicate melt, during partial melting of mantle material, thus fractionating from the IPGE that remain preferably in the mantle residue (Barnes et al., 1985).

The analyses of two samples (NP886-2 and 560-MLR-S; figure 5.4) feature high analytical errors. Those results were rejected and are not presented in this study. The results of the remaining 6 samples are shown in table 5.7. The total PGE content ranges between 3.9 and 49.2 ppb with most being contributed by Pt at approximately 90%. Concentrations of IPGEs are rather low and range between 29 and 136 ppt. On average, the concentrations slightly increase from Os (60 ppt) to Ir (69 ppt), to Ru (74 ppt) and Rh (97 ppt). Platinum is the highest enriched PGE with concentrations ranging between 2.5 and 42.1 ppb (avg. 12.5 ppb). Palladium concentrations are significantly low compared to Pt at an average of 0.5 ppb and a maximum of 1.5 ppb.

A clear fractionation between Pt and Pd is shown in figure 5.43. The primitive upper mantle (PUM) normalised PGE distribution pattern (upper diagram in figure 5.43) features a rather flat pattern for the IPGs, which are depleted by a factor of ~0.02 (average PGE composition of n = 6 samples). Rhodium and Pd are with a factor of ~0.1 less depleted than IPGs. Platinum represents the exception of all PGEs, characterised by almost PUM composition. PGE
5.7 Platinum group elements and the time of ore formation

Pattern normalised to average continental crust (lower diagram in figure 5.43) appear similar, also showing the “zig-zag” distribution. However, it becomes obvious, that all PGEs except Pt are close to concentrations of average continental crust, whereas Pt is significantly enriched by a factor of 30 on average, and as high 100 times.

PGEs are mobile under certain hydrothermal condition and potentially in many other environments such as supergene zones (e.g. Hanley, 2005). Complexations with OH-, HS- and/or Cl- are the most important transport mechanisms (e.g. Mountain and Wood, 1988; Wood et al., 1989; Wood, 2002). PGEs are transported by chloride complexes only under relatively acidic and oxidising conditions by highly saline brines. In relatively reducing fluid conditions up to 250 °C, complexation with bisulfide prevails over hydroxide ions. Above 250 °C this circumstance reverses. Furthermore, PPGEs are far more mobile than IPGEs. The distribution patterns normalised to average continental crust features a clear and significant selective enrichment of Pt compared to all other PGEs. An explanation needs to be found that sufficiently explains the fractionation between Rh, Pd and Pt.

Several studies investigated PGE concentrations in marine ferromanganese crust, concretions and nodules (e.g. Halbach et al., 1984; Hein et al., 1988; Halbach et al., 1989; Stueben et al., 1999; Koschinsky et al., 2005). According to Halbach et al. (1989), ferromanganese material can contain about 100 times more Pt compared to the upper continental crust. The fixation and enrichment of Pt is suggested to be established via either co-precipitation of Pt with MnO₂ (Halbach et al., 1989) or by surface adsorption of Pt tetra- and dichloro complexes (Halbach et al., 1989; Koschinsky et al., 2005). The adsorption to the MnO₂ surface of Pd is an order of magnitude lower compared to Pt, despite being chemically very similar (Koschinsky et al., 2005). Palladium is therefore far less enriched and commonly features a pronounced negative fractionation pattern (e.g. figure 13 in Le Suave et al., 1989). This negative Pd anomaly is observed in hydrothermal, hydrogenous and diagenetic MnO₂ formations, but is most prominent in the latter two (Stueben et al., 1999). The metal-bearing mineralising fluid at the Elura orebody migrated through marine turbiditic sediments during its ascent to the site of ore formation. The isolated strong enrichment of Pt, observed in massive sulphide ore, has most probably been caused by a fluid that leached such hydrogenous and diagenetic ferromanganese rich sequences and mobilised Pt as either bisulfide or hydroxide complexes. Consequently, Pt is significantly enriched compared to other PGEs within the Elura Orebody.

<table>
<thead>
<tr>
<th>Sample ID type</th>
<th>PGE</th>
<th>IPGE</th>
<th>PPGE</th>
<th>Pt/PGEtot</th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
<th>Rh</th>
<th>Pt</th>
<th>Pd</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>435-z24-S Py</td>
<td>10.354</td>
<td>0.132</td>
<td>10.221</td>
<td>95.9</td>
<td>0.049</td>
<td>0.039</td>
<td>0.045</td>
<td>0.060</td>
<td>9.933</td>
<td>0.229</td>
<td>3.823</td>
</tr>
<tr>
<td>4D-ML-C2 Py</td>
<td>4.762</td>
<td>0.299</td>
<td>4.463</td>
<td>82.9</td>
<td>0.103</td>
<td>0.113</td>
<td>0.083</td>
<td>0.218</td>
<td>3.946</td>
<td>0.299</td>
<td>7.580</td>
</tr>
<tr>
<td>DE174-1 Po</td>
<td>3.108</td>
<td>0.262</td>
<td>2.847</td>
<td>90.6</td>
<td>0.052</td>
<td>0.136</td>
<td>0.074</td>
<td>0.031</td>
<td>2.816</td>
<td>high RSD</td>
<td>0.802</td>
</tr>
<tr>
<td>NP022-2 Py</td>
<td>43.882</td>
<td>0.232</td>
<td>43.650</td>
<td>95.9</td>
<td>0.073</td>
<td>0.070</td>
<td>0.089</td>
<td>0.133</td>
<td>42.067</td>
<td>1.450</td>
<td>5.352</td>
</tr>
<tr>
<td>NP243 Po</td>
<td>2.746</td>
<td>0.169</td>
<td>2.577</td>
<td>91.1</td>
<td>0.043</td>
<td>0.027</td>
<td>0.098</td>
<td>0.037</td>
<td>2.502</td>
<td>0.038</td>
<td>1.909</td>
</tr>
<tr>
<td>NP724-2 Py</td>
<td>14.421</td>
<td>0.127</td>
<td>14.294</td>
<td>96.8</td>
<td>0.039</td>
<td>0.029</td>
<td>0.059</td>
<td>0.101</td>
<td>13.954</td>
<td>0.239</td>
<td>2.885</td>
</tr>
<tr>
<td>Average</td>
<td>13.287</td>
<td>0.203</td>
<td>13.084</td>
<td>94.3</td>
<td>0.060</td>
<td>0.069</td>
<td>0.074</td>
<td>0.097</td>
<td>12.536</td>
<td>0.451</td>
<td>3.725</td>
</tr>
</tbody>
</table>

Table 5.7: PGE concentration data for massive sulphide ore samples. Data given in ppb. Palladium concentration of sample DE174-1 is not reported because of high analytical error.
5. GEOCHEMICAL ORE CHARACTERISATION

5.7.2 Principals of the Re-Os isotopic system

The natural abundances of rhenium (Z = 75) and osmium (Z = 76) are very low at concentrations of 0.28 and 3.4 ppb, respectively (concentrations of “Bulk Silicate Earth” after McDonough and Sun (1995)). Rhenium has an unstable (187Re) and a stable (185Re) natural occurring isotope, the former decays to 187Os. Osmium has the highest melting point of all PGEs and is the densest element known to humankind because it consists of the optimum number of protons, neutrons and electrons, arranged in the best available symmetry. It has seven stable natural occurring isotopes including five with invariant abundance. They are in decreasing order of abundance (see Table 5.8): 192Os, 190Os, 189Os, 188Os and 184Os. The abundance of the remaining two isotopes 186Os and 187Os is variable in nature because of the radiogenic decay of 190Pt (α-decay) and 187Re (β-decay), respectively.

The composition of the primeval earth was homogeneous before it began to differentiate commencing with the formation of the earth’s core, predominantly composed of Fe, Ni and other highly siderophile elements including the PGEs. Upon cooling, the remaining “outer earth” progressively differentiated resulting in crust formation and accretion. The PGEs that were not concentrated in the earth’s core behaved refractory and remained in the mantle residue during partial melting and magma generation. In contrast, Re, showing similar behaviour to the PPGE, acted incompatible and, therefore, partitioned into and was extracted with the melt. Subsequently, the granitic crust became enriched in Re relative to Os (Faure and Mensing, 2005). This fractionation led to significantly different Re/Os ratios of igneous mafic/ultramafic rocks (Re/Os <0.1) and granitic gneisses of the continental crust (Re/Os >10). Rhenium is chemically similar to Mo and therefore readily incorporated in molybdenite via stoichiometric lattice substitution. Consequently, high levels of Re are commonly found in sulphide ores enriched in molybdenite. Osmium on the other hand, as part of the IPGEs, is commonly associated with chromitites, commonly depleted in Re (e.g. in reef-type deposits, ophiolites).

The Re-Os geochronometer is based on the radioactive decay of 187Re to the stable 187Os isotope by β-emission (eq. 5.11). The 187Re isotope features a half-life of ~41.6 Ga based on the decay constant defined by Smoliar et al. (1996) \( \lambda = 1.666 \times 10^{-11} \text{ y}^{-1} \).

\[
\frac{187}{187}\text{Re} \rightarrow \frac{187}{186}\text{Os} + \beta^- + \bar{\nu} + Q \quad (5.11)
\]

where

- \( \beta^- \) = negatively charged β-particle
- \( \bar{\nu} \) = antineutrino
- \( Q = \text{total decay energy} (0.0025 \text{ MeV}) \)

According to the law of radioactivity, the increase of radiogenic 187Os is a function of the initial 187Os, the present concentration of 187Re and time (eq. 5.12). In the past, isotope concentrations of 187Re and 187Os were normalised to 186Os, which itself is, although only in minuscule amounts, radiogenically produced by the α-decay of the 190Pt. Thus, the stable 188Os isotope has been recommended by Shirey and Walker (1998) to be used for normalisation. If co-genetic samples plot on a well-defined linear regression line in the 187Os/188Os

---

**Table 5.8**: Naturally occurring isotopes of Re and Os; presented data was used for calculations in this study; (*) variable in nature due to radiogenic decay of 187Re and 190Pt. Re and Os isotope abundances after Faure and Mensing (2005) and Shirey and Walker (1998), respectively; isotope mass values after Wapstra et al. (2003); isotopic ratios after Shirey and Walker (1998) and (*) Luck and Allegre (1983).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance [%]</th>
<th>Mass [u]</th>
<th>Isotopic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>185Re</td>
<td>37.40</td>
<td>184.952955</td>
<td></td>
</tr>
<tr>
<td>186Re</td>
<td>62.6</td>
<td>186.955751</td>
<td>185Re/187Re 0.5974441</td>
</tr>
<tr>
<td>187Re</td>
<td>3.08271</td>
<td>187.958382</td>
<td></td>
</tr>
<tr>
<td>188Os</td>
<td>1.21967</td>
<td>188.958447</td>
<td>186Os/188Os 1.98451</td>
</tr>
<tr>
<td>189Os</td>
<td>1.13791</td>
<td>189.955751</td>
<td></td>
</tr>
<tr>
<td>190Os</td>
<td>1.113791</td>
<td>190.953832</td>
<td></td>
</tr>
<tr>
<td>192Os</td>
<td>0.119848</td>
<td>192.954895</td>
<td></td>
</tr>
</tbody>
</table>
5.7 Platinum group elements and the time of ore formation

vs. \(^{187}\text{Re}/^{188}\text{Os}\) space, an isochron may be constructed. The intercept of the isochron with the y-axis defines the initial \(^{187}\text{Os}/^{188}\text{Os}\) value at the time the Re-Os isotopic system closed.

\[
\left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{t=0} = \left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{t} + \left( \frac{^{187}\text{Re}}{^{188}\text{Os}} \right)_{t=0} (e^{\lambda t} - 1)
\]

where

\[\lambda = 1.666 \pm 0.00517 \times 10^{-11} \text{ yr}^{-1}\] (5.12)

\[
\gamma_{\text{Os}}^{\text{CHUR}} = \left[ \frac{\left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{\text{Sample}}}{\left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{\text{CHUR}}} - 1 \right] \times 100\%
\]

where

\[
\left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{\text{CHUR}} = 0.12863 - 0.423 (e^{\lambda t} - 1)
\] (5.14)

Because of the decay of \(^{187}\text{Re}\) to \(^{187}\text{Os}\) and the differences of Re/Os ratios, the crust (high Re/Os) is significantly enriched in the radiogenic \(^{187}\text{Os}\) compared to lithospheric and asthenospheric mantle (low Re/Os) as visualised in figure 5.44. The growth difference of radiogenic \(^{187}\text{Os}\) in various lithologies (i.e. reservoirs) has been studied by many authors (e.g. Meisel et al., 1996; Shen et al., 1996; Shirey and Walker, 1998; Chen et al., 1998; Pearson, 1999). By comparing measured \(^{187}\text{Os}^{188}\text{Os}\) ratios with that of reservoir data (e.g. continental crust, enriched mantel, depleted mantel, etc.; figure 5.46), potential sources of magma/liquid may be deduced. Because radiogenic \(^{187}\text{Os}\) changes in all reservoirs as a function of their Re content and time, the changes are calculated as percentage relative to the chondrite uniform reservoir (CHUR) defined by Chen et al. (1998) at a specific time according to eq. 5.13. The time of formation and the initial \(^{187}\text{Os}^{188}\text{Os}\) value are defined by the Re-Os isochron. The \(^{187}\text{Os}^{188}\text{Os}\) of the CHUR at this time is calculated according to eq. 5.14 (Faure and Mensing, 2005).

Figure 5.44: Diagram showing the isotopic evolution of Os in continental crust relative to CHUR. The continental crust became significantly enriched in radiogenic \(^{187}\text{Os}\) compared to CHUR since it started to form at 2.9 Ga, caused by much higher Re/Os ratios. \(^{187}\text{Os}, {^{188}\text{Os}}\) and Re/Os data after Esser and Turekian (1993); McDonough and Sun (1995); Wedepohl (1995); Chen et al. (1998).
5. GEOCHEMICAL ORE CHARACTERISATION

5.7.3 The isochron age and potential osmium sources

The analytical results of 6 massive sulphide samples are presented in table 5.9. The observed total Re and Os concentrations are 0.802 to 7.580 ppb and 0.039 to 0.103 ppb, respectively. Relative standard deviations (RSD) are below 1.5%. The present day $^{187}\text{Os}/^{188}\text{Os}$ ratios are commonly high and reach maxima in excess of 3.5. The highly radiogenic samples yield present day $\gamma_{\text{Os}}$ values in the order of ~550 to 2800 compared to present CHUR $^{187}\text{Os}/^{188}\text{Os}$ ratios. RSDs of present day $^{187}\text{Os}/^{188}\text{Os}$ ratios are higher, particularly for one sample (NP243) with 12.6% (table 5.9).

All 6 samples define a model 1 (Ludwig, 2003) isochron age of $377.94 \pm 14.98$ Ma ($2\sigma$) with a MSWD of 0.237 and a probability of 0.964 (figure 5.45). The spread of data points is sufficient, although 3 samples cluster at a $^{187}\text{Re}/^{188}\text{Os}$ value of just over 500. Therefore, the isochron may be viewed as being constrained by only 4 points, instead of 6. An initial $^{187}\text{Os}/^{188}\text{Os}$ value of $0.338 \pm 0.092$ ($2\sigma$) is defined by the isochron, yielding an initial $\gamma_{\text{Os}}$ of 168.46, calculated based on time of formation (378 Ma) and the $^{187}\text{Os}/^{188}\text{Os}$ of the CHUR at this time (eq. 5.13 and eq. 5.14). The initial $\gamma_{\text{Os}}$ values for individual samples range between 68 and 186. The percentage of $^{187}\text{Os}$ from total Os ranges between 10 and 33%. The observed present day $\gamma_{\text{Os}}$ values are highly radiogenic. Approximately 97% of all $^{187}\text{Os}$ has been radiogenically formed ($^{187}\text{Os}^r$; table 5.9) since the time the Re-Os isotope system closed, as defined by the isochron age.

Organic matter is a common minor constituent within the host rock of the Elura (Sun et al., 2001) and probably occurs finely dispersed throughout most of the basin fill metasediments. Hydrocarbons have been identified as an important component (fluid inclusion investigation of this study and e.g. Seccombe, 1990; Lawrie et al., 1999) of the mineralising fluid. Interaction of the hydrothermal fluid with organic-rich rock sequences would have created/mobilised hydrocarbons and, as suggested by Selby et al. (2009), most likely became significantly enriched in Re, bound to organic matter, relative to Os. Rhenium is readily incorporated in molybdenite during ore formation that in turn decayed to radiogenic Os, subsequently causing the pronounced radiogenic signature of the Elura Orebody.

Initial $\gamma_{\text{Os}}$ values are commonly used to identify the extent of crustal components involved during the genesis of ultramafic/mafic magmatic ore deposits, i.e. genetically clearly linked to primitive mantle sources (e.g. Stillwater, Bushveld, Pechenga, Sudbury, etc.). Some of these deposits feature significant radiogenic initial $^{187}\text{Os}/^{188}\text{Os}$ composition. The Kamikivi Sill in the Pechenga Complex, for instance, has a $\gamma_{\text{Os}}$ of +251, some parts of the Sudbury Igneous Complex feature $\gamma_{\text{Os}}$ values as high as +814 (Shirey and Walker, 1998). When comparing the initial $\gamma_{\text{Os}}$ of the Elura orebody with reservoir data, it falls within the very lower end of continental crust composition field (figure 5.46). However, $\gamma_{\text{Os}}$ appears rather low when considering the rather radiogenic $\gamma_{\text{Os}}$ values of the aforementioned ultramafic/mafic
5.7 Platinum group elements and the time of ore formation

Lithologies occurring in the Lachlan Fold Belt are of Cambrian to Early Devonian age (see chapter 2 on page 10), relatively young compared to mineralisation that formed at 380 Ma (figure 5.45). The basin is predominantly filled with silici-clastic rock suits, which were sourced from the hinterland. Lithologies within the basin and/or the underlying basement have been suggested as the most likely metal sources for base metal mineralisation in the Cobar region (see chapter 3 on page 50). Osmium and Re are to some extent mobilised by hydrothermal fluids (e.g. Marcantonio et al., 1994; Xiong and Wood, 1999). The mineralising fluid would have inherited the $^{187}\text{Os}/^{188}\text{Os}$ of the rock sequences it interacted with as it had passed through during its ascent. Therefore, the initial $^{187}\text{Os}/^{188}\text{Os}$ or the corresponding $\gamma_{\text{Os}}$ value of the orebody should reflect the Os isotope signature of the source rocks.

The calculation (eq. 5.13 and eq. 5.14) of a theoretical $\gamma_{\text{Os}}$ for an average upper continental crust (data after Saal et al., 1998, Re = 0.4 ppb, Os = 0.05 ppb, $^{187}\text{Os}/^{188}\text{Os} = 1.9256$) relative to CHUR (Chen et al., 1998) at the time of ore formation 380 Ma ago (based on isochron figure 5.45) resulted in a highly positive value of +1190, by far higher than the initial $\gamma_{\text{Os}}$ of +169 of ore from the Elura. The value clearly does not correspond to the relative non-radiogenic Os
composition of the mineralisation, thus precluding old, relatively evolved continental crust as feasible Os source without the contribution of primitive Os.

Re-Os model ages can estimate the time a crustal sample with a given \(^{187}\text{Os}/^{188}\text{Os}\) signature needed to evolve from a primitive mantle source. The modal ages are based on the assumptions that (Faure and Mensing, 2005):

(a) Os was extracted from a single source without being mixed with Os from another reservoir,

(b) the incorporation of Os into the investigated samples occurred without delay approximately contemporaneous with the extraction and

(c) the Os source is sufficiently represented by the CHUR.

Model ages in this study are calculated in order to investigate whether a juvenile crustal source has the potential to deliver the observed rather non-radiogenic initial \(\gamma_{\text{Os}}\) without the need for the contribution from a primitive Os source. Relative young crustal rock sequences of the Lachlan Fold Belt may feature low and relative non-radiogenic \(^{187}\text{Os}/^{188}\text{Os}\) ratios and may represent a feasible source, if calculated model ages are within their age range.

A slightly modified version of the equation proposed by Esser and Turekian (1993) is used for the calculation of model ages shown in eq. 5.15.

CHUR isotope ratios in eq. 5.15 are based on data after Chen et al. (1998), and were calculated for the time of ore formation at 380 Ma (figure 5.45). The minimum/maximum initial \(^{187}\text{Os}/^{188}\text{Os}\) ratios considering the uncertainty as defined by the isochron are used in order to estimate the formation age range for a hypothetical crust as source. Crustal \(^{187}\text{Re}/^{188}\text{Os}\) ratio is based on average upper continental crust composition after Saal et al. (1998); Sun et al. (2003) and the initial \(^{187}\text{Os}/^{188}\text{Os}\) ratio defined by the isochron.

Using Re and Os concentrations of average upper continental crust (data after Saal et al., 1998, Re = 0.4 ppb, Os = 0.05 ppb) resulted in an age range between ~780 and ~540 Ma. The

\[
T_{MA} = \frac{1}{\lambda} \ln \left[ \frac{\left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{\text{Crust}}}{\left( \frac{^{187}\text{Re}}{^{188}\text{Os}} \right)_{\text{Crust}}} - \left( \frac{^{187}\text{Re}}{^{188}\text{Os}} \right)_{\text{CHUR}} \right]^{-1} \left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{\text{CHUR}} + 1 ; \quad \text{with } \left( \frac{^{187}\text{Re}}{^{188}\text{Os}} \right)_{\text{Sample}} = \left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{\text{initial}} = 0.430
\]

(5.15)
5.7 Platinum group elements and the time of ore formation

The youngest estimate may represent the oldest crustal lithologies in the Lachlan Fold Belt. However, the overall age range suggests that Lachlan lithologies are not old enough in order to represent a feasible single crustal source.

Sun et al. (2003) suggested that Re concentrations of the upper continental crust are significantly higher than previously proposed. Based on undegassed arc rocks, the authors estimated the average concentration at approximately 2 ppb. Rhenium concentrations that high would lead to a much quicker accretion of radiogenic \(^{187}\)Os, thus younger ages of formation. The calculation of model ages using Re (2 ppb) and Os (0.05 ppb) concentrations suggested by Sun et al. (2003) and Saal et al. (1998), respectively, resulted in an age range between ~470 and ~416 Ma. This data is well within the estimated age range of crustal rocks occurring within the Lachlan Fold Belt.

The Re-Os isochron age of 378 ±15 Ma, despite featuring a relative high uncertainty, is in agreement with and validates the formation age determined via \(^{40}\)Ar-\(^{39}\)Ar (376-379 Ma; Sun, 2000; Sun et al., 2000) proposed in previous studies. This date of 378 ±15 Ma represents the first age constraint established via directly dating the sulphide mineralisation. Model age calculations showed that juvenile continental crust of the Lachlan Fold Belt has the potential to cause the observed relatively non-radiogenic initial \(\gamma_{\text{Os}}\) value, as long as Re concentration in the crust is close to concentrations suggested by Sun et al. (2003). The results, however, do not preclude a contribution of primitive Os sourced from the mantle.

The investigation of PGEs and the application of the Re-Os isotope geochronometer in the course of this study were based on a very small sample set and utilised a quick, inexpensive but relatively imprecise analytical method. Nevertheless, the results are conclusive and highlight that age determination of whole rock sulphide samples, containing ultra-trace level PGEs, is possible without the need of highly accurate negative thermal ionisation mass spectroscopy (NTIMS). If a more precise age determination is desired, a larger sample set should be used, and NTIMS technique applied.
5.8 Summary of geochemistry and integration of ore petrology

Geochemical ore characterisation showed various differences between massive (Py and Po) and semi-massive (SiPy and SiPo) ore types. Breccia-stringer type ore (VEIN) features significantly different characteristics due to its much higher wall rock component. Based on median concentrations, massive and semi-massive ore contains in the order of 9.6 to 10.2 wt% Zn and 5.1 to 5.9 wt% Pb. The highest Zn concentration (16.4 wt%) was determined in massive pyrrhotitic ore, whereas massive pyritic ore contained maximum Pb (30.3 wt%). The large overall concentration range of Zn (4.6-16.4 wt%) and particularly Pb (1.7-30.3 wt%) concentrations in massive ore reflects the pronounced heterogenic textural and compositional nature of the Elura ore, also observed in petrographic investigations.

Silver and Cu feature inverse affinities to pyritic (Py and SiPy) and pyrrhotitic (Po and SiPo) dominated ore. The former element is commonly enriched in Py and SiPy at a median concentration range of 86 to 88 ppm and a maximum of in excess of 1000 ppm in Py ore. Copper content is slightly elevated in pyrrhotitic ore (0.21-0.24 wt%; median values) compared to pyritic ore (0.16-0.20 wt%). Arsenic concentrations are generally variable but may reach significant concentrations in pyritic ore up to 1.5 wt%.

Total sulphide, silicate and carbonate content are of great importance for mineral processing due to their significantly different hardnesses. High content of hard components, i.e. quartz, increases the milling time, the power consumption and lowers the mass throughput in the mineral processing facility. Ore elevated in sulphides improves mineral processing performance as they are commonly soft mineral phases. Median silicate content of massive ore is low and yields ~2 wt%, increases to a moderate ~13 wt% in semi-massive ore and reaches highest values in VEIN ore which is commonly in excess of 50 wt%. By definition VEIN type ore contains between 3 and 10 wt% Zn-Pb combined grade. If ore of this type is close to the upper limit of the aforementioned concentration range it may likely be economic to mine if metal prices are sufficiently high and if exclusively contained metal (i.e. Zn, Pb, Ag, Cu) is considered. However, it is important to account for the negative effect caused by the significantly increased ore hardness. Its impact on mine economics needs to be carefully assessed in order to accurately determine resource cut-off grades for VEIN ore containing high content of silicates and low total sulphide.

Bulk ore densities calculated based on modal mineral composition are close to those gravimetrically determined. Calculated densities are with 4.7 g cm$^{-3}$ highest for massive ore and slightly lower for semi-massive ore at 4.4 g cm$^{-3}$. Breccia-stringer style ore yields calculated median densities in the order of 3.4 g cm$^{-3}$.

Apart from elements that are obviously enriched in the orebody, e.g. Zn, Pb, Ag and Cu, analysis of inter-element affinities identified Co, As, Se, Mo, Cd, In, Sn, Sb, Te, Re, Au, Hg, Tl and Bi as clearly linked to the base metal mineralisation. Nickel and Ge, despite being elements commonly incorporated in sulphides, are predominantly associated with and caused by wall rock components. Depite sphalerite being a common host mineral for Ga, the element features stronger affinities to wall rock than to the sulphide mineralisation. Most high field strength and large ion lithophile elements are unrelated to the base metal mineralisation. Their elevated concentrations in sulphide ore are caused by incorporated wall rock fragments.

Whole rock trace element geochemistry revealed several clear concentration trends as a function of depth within the mineralising system as well as element cross-correlations. Changes in mineral composition as described in the previous chapter were used to link and reconcile geochemistry to mineralogy.

The identified element cross-correlations are
5.8 Summary of geochemistry and integration of ore petrology

either caused by their common host mineral phase and/or by their common spatial occurrence within the Elura orebody. Cadmium was consistently detected in sphalerite during mineral chemical analyses (EMP and LA-ICP-MS). Good correlation between Cd and Zn concentrations in whole rock geochemistry suggests sphalerite as the most important host mineral phase. Reconciliation with sphalerite mineral chemistry based on calculated modal mineralogy showed a good agreement but some whole rock samples feature an excess of Cd. A poor correlation was observed in the reconciliation of In contained in sphalerite. Trace levels of Cd and In were observed in galena but are too low to account for the deficiency. Minor occurrences of unidentified mineral phases containing either of those elements are the most probable explanation for the mismatch.

Molybdenite readily incorporates Re into its crystal lattice. Correlation between Mo and Re indicates its presence in small quantities and most likely small grain sizes as it was not encountered during microscopic investigations.

A clear correlation is observed between Tl and Hg for the upper observed concentration range, which is exhibited by samples taken from the upper most parts of the orebody. Their common enrichment is caused by pyrite that features elevated Tl and Hg content in those ore zones. A lower Hg background concentration in whole rocks up to ~20 ppm is due to sphalerite.

Argentian-tetrahedrite is the main silver bearing mineral phase in most areas of the orebody. Galena-matildite and galena-miargyrite solid solutions are responsible for strong enrichments of Bi/Ag and Sb/Ag in galena contained in samples from the lowermost and uppermost main lode ore zones, respectively. Good cross-correlations between these element pairs are observed in geochemical data and confirm mineral chemical data, as well as galena as important host mineral for silver, and most probably the only mineral phase containing Bi. Sulphide ore samples enriched in Bi commonly feature elevated Se and Te concentrations, caused by the occurrence of unidentified sulfosalts or by stoichiometric lattic substitution of Se for S. These observations are confirmed by reconciliation between geochemistry with mineral chemistry of galena determined via LA-ICP-MS. Samples that contain minor argentian-tetrahedrite feature a good correlation for Ag. Similarly, Bi and Te concentrations reconcile well. Minor Te may occur in phases other than galena as indicated by a weak excess in geochemical data. Selenium does not correlate as it most probably substitutes for S in several sulphide phases.

In addition to Ag, Cu and As, which have already been mentioned earlier, further elements are preferably enriched in either pyrite (Py and SiPy) or pyrrhotite (Po and SiPo) dominated ore types. Elements that feature affinities to pyritic ore are commonly enriched in peripheral zones of the orebody and particularly in the upper most ore zones, thus feature clear enrichment trends towards the surface. Those elements are Ag and Sb associated with argentian-tetrahedrite. Hg and Tl caused by pyrite enriched in these elements, As due to the preferred occurrence of arsenopyrite in upper ore zones, as well as Mo, Sn and Au. Gold was commonly detected at low concentrations with an overall median range for all different ore types between 0.09 and 0.48 g/t. In places, significant concentrations were encountered in semi-massive pyritic ore up to 8.7 g/t (overall maximum). Copper, Co and Cd are characterised by a moderate enrichment in pyrrhotitic ore compared to pyrite dominated ore varieties.

Inverse trends, i.e. enrichment towards depth, are featured by the three aforementioned elements in addition to In, Se, Te and Bi, which are highest enriched in the lowermost main lode ore zone.

Distinctly different geochemical characteristics where identified for (a) the upper main lode zone and (b) the lower sheet of mineralisation, consisting of the lower main lode zone and the northern ore pod z1 to z5. Indium, Se, Te and Bi are relatively enriched in the latter, almost undetectable in former parts of the orebody. Copper features two major areas of enrichment. Firstly, it tends to be enriched throughout most of the deepest parts of the orebody and, in
place, in pyrrhotitic zones representing the central ore zones of the individual sulphide pipes. A second enrichment is observed at the transition between the aforementioned upper and lower parts of the mineralisation (a and b), coinciding with lithological changes in the host lithology, i.e. the occurrence of the upper laminated unit. This enrichment is reflected by results of this study and confirmed by the resource block model. Antimony is the only element characterised by converse spatial distribution. High concentrations were consistently encountered throughout most of the upper main lode zone, whereas only the uppermost areas of the lower mineralisation showed weak Sb enrichment.

The isochon method was used in order to assess relative element mobility in different ore types and altered wall rock. Based on relative mass changes, volume gain/losses were determined. Elements commonly incorporated in sulphides (e.g. Co, Ni, Se, Mo, In, Hg, Tl, Bi) are strongly enriched as a function of increasing S content. Enrichments of Mn, Mg and C are caused by the formation of carbonates. Other elements suggested to be introduced by the mineralising fluid are Cr, Sr, Ba, W, U and Ga. Alteration proximal to the base metal mineralisation is characterised by a mass gain of S, Fe, Tl, Mg, Rb, Cs, Ba and W and a relative loss of Ca, C, Na, K and Sr.

The assessment of mass/volume changes of different ore types clearly showed that replacement of the host lithology is a minor mechanism during ore formation. Some replacement may have occurred in zones of elevated fluid-rock ratios, i.e. in breccia-stringer type ore and, in places, in semi-massive ore zones. Results for massive ore showed that most of the sulphide mass exclusively precipitated in sites of fracture-induced dilation, accompanied by negligible interaction with the wall rock. The only substantial replacement that occurred during base metal formation is that of pyrite by base metal sulphides in pyritic dominated ore varieties.

Radiogenic age determination via the Re-Os isotope system resulted in an isochron age of $378 \pm 15$ Ma and represents the first age constraint established via directly dating the sulphide mineralisation. The observed relatively non-radiogenic initial $\gamma_{Os}$ value is either caused by juvenile continental crust of the Lachlan Fold Belt as metal source or a contribution of primitive Os from mantle sources.
The CSA Siltstone, as the host rock, is, in places, calcareous and may contain degraded organics. Sulphur concentrations between 0.2 and 0.6 wt% are mostly associated with sedimentary and diagenetic pyrite. Chondrite normalised REE distribution pattern are similar to marine shale reference data. Mud- and siltstone components in the wall rock are predominantly controlling REE concentrations. Multi-trace element distributions normalised to average continental crust are in agreement with observations made on REE and confirm strong similarities to marine shale reference data. Results confirmed the significant extent of cryptic alteration in excess of 200 m mainly defined by enrichments of Cs and Rb towards the mineralisation and accompanied by a depletion of Sr.

Host rock classification in respect to the tectonic setting of sediment deposition suggested an intermediate setting between active and continental margins based on major element concentrations and an active continental to continental island-arc setting based on trace element composition. Discrimination for potential source rock suggested a weak affinity to intermediate igneous provenance.
Chapter 6

Geo-metallurgical ore characterisation study via QEMSCAN®

6.1 Introduction

At the Endeavor Mine, three different metal concentrates are produced in its mineral processing facility: zinc concentrate as the main product, lead concentrate as secondary product and copper concentrate in minor quantities as by-product. In the past, the metal recoveries during the mineral processing stage at the Endeavor mine were and still are fluctuating as a function of ore from different locations throughout the orebody being mined and mixed before differential froth flotation.

The flotation recovery rate and the quality of the mineral concentrates produced are strongly affected by changes in whole rock geochemistry, ore mineralogy and mineral chemistry, in addition to textural characteristics of the massive sulphide ore. Apart from metallurgical test work on material from the flotation feed, process stream and tailings, only a few studies on ore characteristics have been undertaken since the commencement of mining activities at the Elura deposit. Butcher et al. (1998) and Barnfield (1999) investigated ore characteristics of proposed stoping zones, including the 5/5 stope area, however, the study is based on only one sample from the 5/5 stoping zone. Their conclusion was that ore from this zone will be difficult to treat due to: (a) significant quartz content and subsequently low mill throughput rates (b) small grain sizes, in particular of galena (c) overall poor Pb and Zn recovery performance in addition to (d) potentially significant arsenopyrite quantities. Leevers (2001) undertook extensive metallurgy test work on several zones of the Elura Orebody and tried to correlate observed plant performances to different ore types. He concluded that a prediction of plant performance based on geological data is not reliable due to strong small scale variation of ore characteristics including textures and grain sizes of different ore types.

The present study was undertaken in order to better understand the ore characteristics of the 5/5 stope and, furthermore, to test the predictability of how the ore of different 5/5 stope areas will perform during mineral processing. The investigation is based on a bigger sample set than previously used. Bulk as well as in situ ore samples were prepared and presented as polished block particle separates or as uncovered polished thin-section. Initially, whole rock trace element geochemistry, reflected and transmitted light ore microscopy are used to investigate the ore characteristics, followed by the application of QEMSCAN® technique.

In order to investigate the nature of Ag and Bi occurrence, and furthermore, to attempt the characterisation of different ore types throughout the orebody, additional samples were taken and prepared as polished thin-sections.
The following petrographic and textural ore characteristics were proposed of being analysed via QEMSCAN®:

- Grain size distribution of ore and gangue phases (e.g. have a significant influence on the milling time) and their modal percentages,
- Theoretical grade-recovery graphs and concentrate composition,
- Particle liberation and free particle surface area of important sulphide mineral phases,
- Mineral associations of ore phases (none, binary, ternary, etc.; which phases are intergrown with each other),
- Pyrrhotite content (significantly influencing the mineral recovery rate due to oxidation and production of sulphuric acid subsequently changing the pH in the flotation process),
- Identification of Ag-bearing mineral phases and possibly Bi minerals,
- Classification and distribution of low and high iron sphalerite
- Ore textures (e.g. elongated grains potentially intergrown with different minerals negatively affecting the flotation properties), and
- Exsolution and inclusion (identification of type and quantity)

A better understanding of the occurrence of pyrrhotite in different stope parts can be used as a tool to improve the mining schedule (e.g. smaller portions of ore being fired and bogged faster in order to avoid excessive oxidation of pyrrhotite enriched ore, in addition to blending of high and low pyrrhotite ore). By that, the pH decrease caused by pyrrhotite oxidation could be constrained, certainly of great benefit for the mineral flotation process. Furthermore, the Ag recovery, which is floated as a bonus metal within the Pb flotation circuit, never exceeded recoveries above approximately 50%.

The 3-dimensional silver grade distribution is very well known and is modelled within the block model. However, the Ag occurrence (e.g. as discrete Ag mineral phases, as solid-solution or as impurities in other sulphide phases), is only poorly understood. Consequently, the lack of this knowledge seems likely to represent the explanation for the observed low Ag recovery rates.

Ore mineralogy directly influences ore to concentrate metal recovery rates and thus the mine economics. Furthermore, mineralogy, mineral chemistry and whole rock geochemistry are responsible for the quality of the mineral concentrate. This is because (a) worthless mineral species are separated together with ore minerals, lowering the metal content in the concentrate and (b) penalty elements (e.g. Bi in the lead concentrate) reduce the quality and hence the value of the product.

Despite the obvious importance of all those ore characteristics mentioned above, very little is known about them in general and basically nothing is known about their 3-dimensional spatial variability at stope scale. By filling this knowledge gap, a significant contribution to a better understanding of the ore forming processes will be made, and will in particular be of great benefit to the ore processing at the Endeavor Mine.
6.2 Fundamentals of the QEMSCAN® technique

The QEMSCAN® analysis system is a fully automated, non-destructive quantitative evaluation of materials technique that uses a scanning electron microscope (QEM*SEM), developed and initially distributed by Intellection Pty Ltd. The QEM*SEM technique has been developed in the late 1970s by Dr Alan F. Reid, CSIRO, Australia (Creelman et al., 1989). Other attempts in the development of image analysis systems similar to QEM*SEM were undertaken between the late 1970s and early 1980s in England and Canada (Creelman et al., 1989). In 2003, Intellection Pty Ltd. was founded by CSIRO in order to market their product as QEMSCAN®. All QEMSCAN® assets, including software and intellectual property, were purchased by FEI Company in early 2009. QEMSCAN® is widely used in the mining sector in order to investigate various mineralogical and metallurgical ore characteristics applied to exploration, production and mineral processing. Gottlieb et al. (2000) gives a brief overview about fundamental of the QEMSCAN® technique.

The QEMSCAN® system of AMDEL Laboratories in Adelaide has been utilised in the course of this study. The system is based on a Carl Zeiss EVO 50 scanning electron microscope equipped with four Bruker energy dispersive X-ray detectors.

The sample material can either be prepared as polished block, polished uncovered thin-section or as polished particle separates mounted or embedded in epoxy resin. The latter two were used in this study. The detailed sample preparation procedures are described in the following section 6.3 on page 199.

QEMSCAN® uses back scatter intensity (BSE) and energy dispersive X-ray spectra (EDX) for mineral identification. The BSE intensity increases with the atomic number of elements and can therefore be used for fast identification of chemical differences. However, they are not uniquely material specific resulting in overlapping BSE intensities for some materials. Thus, the EDX spectrum, which is a direct qualitative measure for the chemical composition of an unknown material, is used.

Four different modes of measurement can be performed via QEMSCAN® (Intellection Pty Ltd, 2008):

1. The particle mineral analysis (PMA) is a 2-dimensional, pixel-based data acquisition technique. Each measured particle is represented as a compound of pixels and is visualised as a particle image. The pixel size depends on the detail and resolution which should be achieved during analysis. After an area of the sample has been defined for measurement, the area is subdivided into frames. A BSE image scan is conducted on a frame by frame basis prior to the acquisition of the chemical composition via EDX spectrometry. Epoxy resin is characterised by a rather low BSE intensity, resulting in a significant contrast at the margin of particles embedded in resin. This enables a fast identification of the particles and their exact coordinative position within the sample. Subsequently, every individual particle is subdivided on a predefined grid and each pixel is analysed for its individual EDX spectra. This information is assigned to the particular pixel in addition to its spatial coordinative position and BSE intensity value. The grid spacing is chosen according to the desired analytical resolution. Based on the acquired information, each pixel can be identified as a mineral phase and furthermore, the spatial information enables a realignment of the analysed pixels in order to produce an actual image of the analysed particle sample area. This image information can be used in order to investigate the actual mineral intergrowths and textures and can be utilised for the calculation of parameters based on mineral areas such as liberation and locking information.
2. The bulk mineral analysis (BMA) is a one dimensional analysis mode. The particles in a polished sample block are scanned on a line in X direction. The Y direction defines the line spacing and is set to a value in order to each particle being intersected approximately once, hence representing a function of the analysed particle size fraction. This method produces a very large dataset from randomly orientated particles and therefore is statistically highly robust. The lack of the actual particle image is a disadvantage, compared to PMA. However, limited area based information can be arithmetically extrapolated from the data obtained via BMA mode (e.g. phase specific surface area).

3. If certain mineral phases or those occurring in very low quantities are targeted for investigation, the specific minerals or trace minerals search mode (SMS or TMS respectively) are used. Both modes are based on PMA. However, only particles containing the target mineral phase, as defined via a BSE intensity threshold, are analysed.

4. The field scan mode measures the entire area of a sample and is used for thin-section or polished block samples. The resulting image is utilised to study the in situ textural characteristics of any solid sample material.

In order to assign a mineral species to each pixel analysed, a database is required, which contains the entity of all mineral phases potentially occurring in the studied samples. These mineral phases are defined by their BSE intensity and EDX elemental spectral characteristics. This database or list is the so called species identification protocol (SIP). Several SIPs have been developed in the past for various different types of ore deposits or materials investigated. A standard SIP for base metal deposits was utilised and modified by the author in order to meet the observed mineralogy and mineral chemistry of the deposit. An additional database or list is required in order to assign the chemical compositions to the identified mineral species. This list, the so called primary list, has been modified according to the observed chemical compositions of the main sulphide mineral phases during electron microprobe investigations. For viewing, investigation and calculation purposes, the primary list is still too complex and detailed. In order to simplify the list, mineral phases are grouped together and stored as so-called secondary lists.

Depending on the measurement mode used, the following ore or material characteristics can be calculated: modal mineralogy, particle size distribution, grain size distribution, elemental sample composition, phase specific surface area, theoretical grade-recovery graphs, area based particle liberation and free particle surface, mineral associations, iron deportment (i.e. Fe content within concentrate resolved for different mineral phases), or classification of mineral species characterised by changes in their chemical composition such as sphalerite.
6.3 Sampling

6.3.1 The 5/5 Stope

The stope is located in the northern part of the southern upper main lode zone, at approximately 6785 to 6820 Mine North and 9690 to 9785 Mine RL (see figure 6.1; RL is reduced level depth; coordinates are local mine grid). Based on the stope reserve shape and the resource block model from December 2009, the overall tonnage and grade is estimated at about 220,000 t at 8.8 wt% Zn, 5.7 wt% Pb and 101 g/t Ag (data supplied by CBH Resources Ltd). The mining design sub-divides the stope into a total of eleven portions, which can be combined into three major stope parts, i.e. Eastern, Central and Western part (figure 6.2). The resource model is well constrained in this particular part of the ore body with a total of 35 DDHs in the vicinity or intersecting the reserve stope shape. Table 6.3 summarises the tonnage and grade as well as the percentage split of the different ore types for the three stope parts. The eastern part contributes 66% of the total stope resource and is characterised by a significant quantity of massive pyrrhotitic ore as well as siliceous pyritic and pyrrhotitic ore varieties. The smallest tonnage is contributed by the central part with 10% of the total resource. Massive pyritic ore dominates, in addition to rather low quantities of siliceous ore. The remaining 24% are contained in the western stope portion, comprising 69% massive pyritic and 31% siliceous ore.

6.3.2 Sample preparation

Ten bulk samples were taken with the aim to achieve good sample coverage for each of the three stope parts. Thirty-five diamond drill holes have been identified as being viable for sampling, however, only 19 were located at the mine site’s core storage facility. Furthermore, several of those diamond drill holes were either strongly weathered or partially missing. Despite these difficulties, a rather good coverage has been achieved with the exception of the lower portion of the eastern stope part. Figure 6.3 shows the sampled diamond drill holes. Sample data is summarised in table 6.1 including the sampled diamond drill hole depth interval and the relative quantities of ore types within each sample.

The samples for ore characterisation by PMA via QEMSCAN® were taken as quarter core, ground in a Labtech Essa 450 mm hammer mill to 100% passing 2.36 mm, split by Essa rotary sample divider followed by manual riffle split down to the required sample size of approximately 1.5 to 3 kg. Upon sample reception by AMDEL Laboratories in Adelaide (abbrev. AMDEL), the samples were weighted, stage crushed to 100% passing 600 µm and split via rotary micro riffler. The applied stage crush-
6. GEO-METALLURGICAL STUDY VIA QEMSCAN®

Figure 6.2: Ore types within the three different parts of the 5/5 stope parts. Blue shape is massive pyrrhotitic ore, green massive pyritic ore, red is the combined semi-massive pyritic and pyrrhotitic ore domain and pale yellow the VEIN ore shape.

An equal sample portion (1 g sample size) is used as a library sample, for geochemical analysis, XRD and for the preparation of polished particle blocks in three replicates. In order to provide a supporting matrix, to minimise density segregation and to ensure random orientation as well as dispersion of the particles, 1 g graphite (size fraction -53/+38 \( \mu \)m) has been added to each sample. The sample mixture is homogenised and de-agglomerated, before being mounted in epoxy resin.

For the characterisation of in situ ore samples by field scan via QEMSCAN®, a total of fifteen quarter core blocks of approximately 4 cm in length were taken and prepared as uncovered polished thin-sections*. Sample locations are shown in figure 6.1. Out of this sample set seven samples are from within the 5/5 stoping area, the remaining eight samples were taken from the upper and lower parts of the orebody, primarily to investigate the occurrence of Ag and potentially Bi mineral phases. All thin-sections were investigated via transmitted and reflected light microscopy. The mineral chemistry of the major sulphide species has been determined via electron microprobe on fourteen samples. Table 6.2 summarises sample location, ore type, and if sample is sourced from a diamond drill hole, its hole ID, and sampled depth.

Primary sample preparation was performed by the metallurgical team the Endeavor Operations Pty Ltd/CBH Resources Ltd. All subsequent sample preparation was performed at the Department of Applied Geosciences and Geophysics; chair of Resource Mineralogy; University of Leoben, Austria.

Figure 6.3: Bulk sample locations for 5/5 stope ore characterisation study in plan view (upper diagram, viewing downwards) and cross-section (lower diagram, viewing north). Sampled diamond drill hole depth intervals are shown in green, bulk samples shown in blue (DE381 and DE383) were combined to one sample (DE381/3).

* Sample preparation was performed at the Department of Applied Geosciences and Geophysics; chair of Resource Mineralogy; University of Leoben, Austria.
### Table 6.1: Bulk samples for 5/5 stope ore characterisation study. # Samples were combined to DE381/3.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Orebody</th>
<th>Local mine grid [m]</th>
<th>DDH Ore</th>
<th>sample depth type</th>
</tr>
</thead>
<tbody>
<tr>
<td>475-z12-2-A</td>
<td>ML</td>
<td>4477 6915 9482</td>
<td>grab sample</td>
<td>Po</td>
</tr>
<tr>
<td>560-MLR-S</td>
<td>ML</td>
<td>4464 6794 9567</td>
<td>grab sample</td>
<td>Po</td>
</tr>
<tr>
<td>CAF-1LS-1-1</td>
<td>ML</td>
<td>4450 6841 10135</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAF-z3-1-A</td>
<td>ML</td>
<td>4358 7109 9709</td>
<td></td>
<td>SiPy</td>
</tr>
<tr>
<td>DE008-2</td>
<td>ML</td>
<td>4510 6718 9933</td>
<td></td>
<td>Po</td>
</tr>
<tr>
<td>DE306</td>
<td>ML</td>
<td>4440 6792 9713</td>
<td></td>
<td>Py</td>
</tr>
<tr>
<td>DE367-1-A</td>
<td>ML</td>
<td>4460 6787 9783</td>
<td></td>
<td>SiPy</td>
</tr>
<tr>
<td>DE367-3</td>
<td>ML</td>
<td>4458 6801 9725</td>
<td></td>
<td>Py</td>
</tr>
<tr>
<td>DE377</td>
<td>ML</td>
<td>4486 6801 9756</td>
<td></td>
<td>Po</td>
</tr>
<tr>
<td>DE381-1</td>
<td>ML</td>
<td>4508 6790 9784</td>
<td></td>
<td>Po</td>
</tr>
<tr>
<td>DE381-2</td>
<td>ML</td>
<td>4538 6799 9772</td>
<td></td>
<td>SiPo</td>
</tr>
<tr>
<td>DE398</td>
<td>ML</td>
<td>4439 6796 9775</td>
<td></td>
<td>Py</td>
</tr>
<tr>
<td>NP85-1-B</td>
<td>ML</td>
<td>4511 6850 9323</td>
<td></td>
<td>SiPo</td>
</tr>
<tr>
<td>NP80-1</td>
<td>z4</td>
<td>4331 7175 9458</td>
<td></td>
<td>Py</td>
</tr>
</tbody>
</table>

### Table 6.2: Thin-section samples for ore characterisation study.

<table>
<thead>
<tr>
<th>5/5 Stope</th>
<th>Tonnage</th>
<th>Zn</th>
<th>Pb</th>
<th>Ag</th>
<th>Cu</th>
<th>Fe</th>
<th>Po</th>
<th>Py</th>
<th>SiPy/SiPo</th>
<th>VeIN</th>
<th>MnA</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>East</td>
<td>145381</td>
<td>8.8</td>
<td>5.8</td>
<td>53</td>
<td>0.3</td>
<td>30.7</td>
<td>71509</td>
<td>49</td>
<td>14212</td>
<td>10</td>
<td>354</td>
<td>0</td>
</tr>
<tr>
<td>Centre</td>
<td>22188</td>
<td>9.4</td>
<td>5.4</td>
<td>166</td>
<td>0.2</td>
<td>29.6</td>
<td>6210</td>
<td>28</td>
<td>14192</td>
<td>64</td>
<td>1765</td>
<td>8</td>
</tr>
<tr>
<td>West</td>
<td>52369</td>
<td>8.6</td>
<td>5.5</td>
<td>207</td>
<td>0.2</td>
<td>22.6</td>
<td>7</td>
<td>7</td>
<td>36235</td>
<td>69</td>
<td>15949</td>
<td>30</td>
</tr>
<tr>
<td>TOTAL</td>
<td>220137</td>
<td>8.8</td>
<td>5.7</td>
<td>101</td>
<td>0.2</td>
<td>28.6</td>
<td>77726</td>
<td>35</td>
<td>64639</td>
<td>29</td>
<td>77009</td>
<td>35</td>
</tr>
</tbody>
</table>

Table 6.3: Summary of tonnage and grade as well as the percentage split of the different ore types for the three 5/5 stope parts. Data supplied by CBH Resources Ltd.
quent preparation steps and QEMSCAN® analyses were undertaken by AMDEL. The raw data was subsequently processed to reportable data by the author without significant assistance by AMDEL or any other institution or person.

6.4 Investigations prior to QEMSCAN®

For quality assurance-quality control (QAQC) purpose and in order to maximise the accuracy of the mineral identification process, it is important to gain a profound understanding of ore mineralogy and mineral chemistry prior to the application of an automated analysis technique such as QEMSCAN®.

A detailed study of ore mineralogy and mineral chemistry of the major sulphide phases has been undertaken in the course of this thesis (see chapter 4 on page 63 and chapter 4 on page 79, respectively). Transmitted and reflected light microscopy of in situ ore samples indicate substantial variations of mineral associations, grain sizes, textures, and the mineral chemical composition of sphalerite. The microscopic observations made on a representative selection of five thin-sections from samples taken within the 5/5 stoping are qualitatively summarised in the following. Quantitative mineralogical characteristics (e.g. grain size distribution, modal mineralogy, etc.) are discussed in the analytical results (section 6.6 on page 213).

6.4.1 Ore petrology

Sample DE377 (figure 6.4)

Sphalerite may occur as coarse patches or as small grains in the order of 5 µm interstitial to all other major sulphide phases. It is mostly anhedral in shape, fairly dark brown in colour and contains abundant exsolutions and inclusions of chalcopyrite and pyrrhotite. Galena is commonly present as patches larger than ~100-200 µm and in minor quantities as tiny interstitial grains in a similar way to sphalerite. In places, intimate intergrowths of chalcopyrite and inclusions of pyrrhotite are observed. Chalcopyrite is quite abundant, mostly associated with pyrite as interstitial phase or as fracture infill at rather small grain sizes below ~20 µm. Sub- to anhedral pyrrhotite, characterised by a granular texture, represents the major iron sulphide species, forming the sulphide groundmass. Two pyrite generations are present in several samples. Pyrite type-B is mostly euhedral to subhedral in shape, partially replaced by other sulphides and frequently hosting inclusions of all other major sulphide phases. In this sample, however, pyrite-B grains contain only minor inclusions. Pyrrhotite and chalcopyrite frequently intrude this pyrite variety along fractures. The an- to subhedral pyrite type-A may occur as small grains (10-30 µm) but commonly forms large dendritic compounds (>~100 µm). Abundant inclusions of predominantly gangue phases are observed. Arsenopyrite is found in minor quantities. Only siderite is present as gangue mineral phase.

Figure 6.4: Field scan image (BSE and sulphides) for sample DE377; blue is sphalerite, red is galena, orange is chalcopyrite, yellow is pyrite, medium yellow is pyrrhotite, olive green is arsenopyrite and non-sulphide gangue is shown in dark green.
6.4 Investigations prior to QEMSCAN®

Sample DE306 (figure 6.5)

In this sample, sphalerite either occurs small grained (below ~20-30 µm) intimately intergrown with pyrite, or as coarse patches (>~100 µm) that contain significant quantities of siderite, quartz, sericite and chlorite. In contrast to the previous sample, sphalerite is light brown coloured, indicating a decrease in Fe content. Only minor inclusions and exsolution of chalcopyrite are present. Grain sizes of galena strongly vary, at times occurring tightly intergrown with chalcopyrite and sphalerite and frequently interstitial to pyrite. Chalcopyrite is quite abundant and mostly associated and intergrown with galena. Both are anhedral in shape. Pyrite is the dominant sulphide phase, frequently fractured forming a cataclastic texture, and is at times replaced by base metal sulphides. Differentiation between both pyrite types is difficult. However, it appears pyrite type-B overgrows type-A subsequently forming a massive, almost homogeneous groundmass. Pyrrhotite is absent in this sample. The gangue mineralogy consists of quartz and carbonate, chlorite, sericite and barite are present as minor constituents.

Sample DE381-1 (figure 6.6)

This sample is characterised by a strong sulphide banding or layering. Sphalerite occurs in an irregular layered texture, characterised by a pronounced association with pyrrhotite as intimate intergrowths or as interstitial phase. Tiny chalcopyrite exsolution and slightly coarser exsolution and/or inclusions of pyrrhotite are observed. Sphalerite is relatively dark in colour suggesting elevated Fe content. Galena appearance and grain size strongly varies, occurring as coarse homogeneous patches (>~100 µm), or as rather small grains below 10 to 20 µm, intergrown with sphalerite and/or chalcopyrite, or as interstitial phase to pyrrhotite. Fairly abundant chalcopyrite is characterised by a noticeable affinity to pyrite, occurring in the vicinity or interstitial to this particular mineral phase. Only pyrite of type-B has been observed. It hosts inclusions of gangue and all other occurring sulphide phases, and appears partially replaced at times. In some places, pyrite shows cataclastic textures. Only siderite

Figure 6.5: Field scan image (BSE and sulphides) for sample DE306; blue is sphalerite, red is galena, orange is chalcopyrite, yellow is pyrite, medium yellow is pyrrhotite, olive green is arsenopyrite and non-sulphide gangue is shown in dark green.

Figure 6.6: Field scan image (BSE and sulphides) for sample DE381-1; blue is sphalerite, red is galena, orange is chalcopyrite, yellow is pyrite, medium yellow is pyrrhotite, olive green is arsenopyrite and non-sulphide gangue is shown in dark green.
is present as gangue.

**Sample DE381-2 (figure 6.7)**

Sphalerite occurs as medium to coarse grains between ~50 and $>100 \mu m$, tightly intergrown with pyrrhotite in myrmekitic-like textures. Minor exsolutions of chalcopyrite and intergrows of pyrrhotite are present. Overall, relative small quantities of galena are observed. When found, it occurs as coarse patches or interstitial to sphalerite and pyrrhotite and at times associated as well as intergrown with chalcopyrite. Chalcopyrite is present as accessory mineral phase together with pyrite and/or gangue or rarely as tiny inclusions in pyrite type-B. Subhedral pyrrhotite represents the major sulphide constituent, characterised by a granular texture. Both pyrite types are present in this sample. The euhedrally shaped pyrite type-B contains abundant inclusions of galena, pyrrhotite, sphalerite, chalcopyrite and gangue phases. Pyrite type-A occurs rarely in some areas, entirely absent in others. Single grains are rather small (below ~20 $\mu m$), but commonly forms larger aggregates. Minor arsenopyrite is present. The gangue mineralogy predominantly consists of quartz with subordinate siderite, accessory sericite and chlorite. A very weak sulphide layering or banding is observed.

**Sample DE398 (figure 6.8)**

A moderate sulphide layering/banding, manifested mainly due to irregular zones significantly enriched in sphalerite and pyrite, is present. Sphalerite is coarser grained in these irregular bands compared to grains found interstitially to pyrite. Overall grain sizes range between ~20 and $>100 \mu m$. Relative low quantities of galena are present, featuring similar grain sizes as sphalerite. Accessory chalcopyrite occurs mostly as fracture filling within or as replacement of pyrite and, furthermore, it is commonly intergrown with galena. Most pyrite is colloform to spherulitic type-A. Minor pyrite type-B is fractured to a cataclastic texture and commonly intergrown with pyrite type-A.
Tetrahedrite, exclusively associated and intergrown with galena, is present in small quantities. Quartz, siderite and minor goethite comprise the gangue mineral phases.

### 6.4.2 Mineral chemistry

The mineral chemistry of the major sulphide phases were determined via EMP. The results from seven samples taken within the 5/5 stoping area are summarised in the following.

Sphalerite chemistry (table 6.4) is characterised by a significant variation in Fe content, with highest concentrations in the order of 7 wt% in pyrrhotitic ore types and around 3-3.5 wt% in pyrite-dominated ore. Manganese was not detected. Cadmium is reported in only one sample at 0.2 wt%. Most analyses show trace concentrations of Bi, Sb, cobalt, Pb and As.

Bismuth concentrations in galena (table 6.5) are quite variable, ranging between 0.07 and 0.39 wt%, the lower value representing the average lower detection limit. A median concentration of Hg at 700 ppm and trace level concentrations of Sb and Ag are present.

Chalcopyrite analyses showed that elements such as As, Pb, Co, Sb, Ag and Bi are incorporated at rather low concentrations in the order of 500-1000 ppm. Zinc content in chalcopyrite is elevated, most probable due to sphalerite inclusions (table 6.7).

Argentian tetrahedrite has only been observed in one sample (table 6.6). Some analyses of tetrahedrite contain elevated Bi concentrations (600 ppm). Furthermore, trace levels of Pb, Co and Cd are present.

The occurrence of arsenopyrite is variable, not linked to particular ore types. It is present in three samples. Analyses showed varying concentrations of Fe, As and S, which is to some extent controlled by zoning. Most analyses show significant concentrations of Co, Sb and Pb (table 6.9). Silver, Au and Bi are rarely present at very low levels close to the detection limit. Zinc contents are elevated.

---

### Table 6.5: Mineral chemistry of galena for samples taken from the 5/5 stoping zone determined via EMP. Original EMP data is presented in appendix A on page 332.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ore</th>
<th>Pb [wt%]</th>
<th>S [wt%]</th>
<th>Ag [wt%]</th>
<th>Hg [wt%]</th>
<th>Bi [wt%]</th>
<th>Total [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE306</td>
<td>Py</td>
<td>0.04</td>
<td>0.07</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>100.21</td>
</tr>
<tr>
<td>DE367-3</td>
<td>Py</td>
<td>0.06</td>
<td>0.08</td>
<td>0.06</td>
<td>0.04</td>
<td>0.04</td>
<td>100.14</td>
</tr>
<tr>
<td>DE377</td>
<td>Po</td>
<td>0.07</td>
<td>0.09</td>
<td>0.07</td>
<td>0.04</td>
<td>0.04</td>
<td>100.16</td>
</tr>
<tr>
<td>DE381-1</td>
<td>Po</td>
<td>0.08</td>
<td>0.10</td>
<td>0.08</td>
<td>0.05</td>
<td>0.05</td>
<td>100.18</td>
</tr>
<tr>
<td>DE381-2</td>
<td>SiPo</td>
<td>0.09</td>
<td>0.11</td>
<td>0.09</td>
<td>0.06</td>
<td>0.06</td>
<td>100.22</td>
</tr>
<tr>
<td>DE398</td>
<td>Py</td>
<td>0.10</td>
<td>0.12</td>
<td>0.10</td>
<td>0.06</td>
<td>0.06</td>
<td>100.18</td>
</tr>
</tbody>
</table>

**Total no. of analyses = 101**

### Table 6.4: Mineral chemistry of sphalerite for samples taken from the 5/5 stoping zone determined via EMP. Original EMP data is presented in appendix A on page 332.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ore</th>
<th>Pb [wt%]</th>
<th>S [wt%]</th>
<th>As [wt%]</th>
<th>Co [wt%]</th>
<th>Cd [wt%]</th>
<th>Sb [wt%]</th>
<th>Bi [wt%]</th>
<th>Total [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE306</td>
<td>Py</td>
<td>0.08</td>
<td>0.10</td>
<td>0.08</td>
<td>0.06</td>
<td>0.06</td>
<td>100.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE367-3</td>
<td>Py</td>
<td>0.10</td>
<td>0.12</td>
<td>0.10</td>
<td>0.07</td>
<td>0.07</td>
<td>100.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE377</td>
<td>Po</td>
<td>0.11</td>
<td>0.13</td>
<td>0.11</td>
<td>0.08</td>
<td>0.08</td>
<td>100.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE381-1</td>
<td>Po</td>
<td>0.12</td>
<td>0.14</td>
<td>0.12</td>
<td>0.09</td>
<td>0.09</td>
<td>100.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE381-2</td>
<td>SiPo</td>
<td>0.13</td>
<td>0.15</td>
<td>0.13</td>
<td>0.10</td>
<td>0.10</td>
<td>100.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE398</td>
<td>Py</td>
<td>0.14</td>
<td>0.16</td>
<td>0.14</td>
<td>0.11</td>
<td>0.11</td>
<td>100.39</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Total no. of analyses = 101**

---

* The electron microprobe analyses were carried out on a JEOL Superprobe JXA 8200 at Department of Applied Geosciences and Geophysics, Chair of Resource Mineralogy, University of Leoben/Austria.

† The nature of the zoning is described in more detail in chapter 4 page 79.
Pyrite and pyrrhotite are the most abundant sulphide species occurring in the Elura deposit. Pyrrhotite content varies and is highest in the core zones of the orebody, whereas pyrite is present in all different ore types. The mineral chemistry of both pyrite types has been determined (table 6.8 and table 6.10). However, only differences in Cu and Zn concentrations were identified, with both elements elevated in pyrite type II, most likely due to very fine intergrowths or inclusions of sphalerite and/or chalcopyrite. Bismuth and Ag is contained in both types at median values at 600 ppm and as high as 0.13 wt% and 0.18 wt%, respectively. A median value of 0.1 wt% for Co and 0.17 wt% for Pb has been determined. Pyrrhotite is characterised by increased levels of Co and Pb at a median of 0.12 and 0.11 wt%, respectively. Zinc and Bi are rarely detected at low concentrations.

### Table 6.6: Mineral chemistry of argentian-tetrahedrite for samples taken from the 5/5 stoping zone determined via EMP. Original EMP data is presented in appendix A on page 332.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ore</th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>Zn</th>
<th>Ag</th>
<th>As</th>
<th>Sb</th>
<th>S</th>
<th>Pb</th>
<th>Co</th>
<th>Cd</th>
<th>Bi</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE306 Py</td>
<td>7</td>
<td>35.00</td>
<td>29.70</td>
<td>34.87</td>
<td>X</td>
<td>0.06</td>
<td>0.10</td>
<td>0.07</td>
<td>0.03</td>
<td>0.04</td>
<td>0.07</td>
<td>99.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE377 Po</td>
<td>4</td>
<td>45.68</td>
<td>53.10</td>
<td>0.10</td>
<td>0.06</td>
<td>0.39</td>
<td>X</td>
<td>X</td>
<td>0.09</td>
<td>0.06</td>
<td>0.00</td>
<td>99.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE381-1 Po</td>
<td>5</td>
<td>34.82</td>
<td>30.35</td>
<td>34.94</td>
<td>X</td>
<td>0.11</td>
<td>0.05</td>
<td>0.02</td>
<td>0.04</td>
<td>X</td>
<td>100.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE381-2 SiPo</td>
<td>4</td>
<td>34.46</td>
<td>30.38</td>
<td>34.85</td>
<td>X</td>
<td>0.07</td>
<td>0.12</td>
<td>0.06</td>
<td>0.04</td>
<td>0.05</td>
<td>0.04</td>
<td>100.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE398 Py</td>
<td>7</td>
<td>34.69</td>
<td>30.07</td>
<td>35.08</td>
<td>0.07</td>
<td>0.05</td>
<td>0.11</td>
<td>0.07</td>
<td>0.04</td>
<td>X</td>
<td>100.24</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 6.7:** Mineral chemistry of chalcopyrite for samples taken from the 5/5 stoping zone determined via EMP. Original EMP data is presented in appendix A on page 332.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ore</th>
<th>Fe</th>
<th>S</th>
<th>As</th>
<th>Co</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
<th>Sb</th>
<th>Bi</th>
<th>Ag</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE306 Py</td>
<td>4</td>
<td>46.39</td>
<td>53.18</td>
<td>0.10</td>
<td>0.08</td>
<td>0.07</td>
<td>0.23</td>
<td>0.10</td>
<td>0.02</td>
<td>0.06</td>
<td>0.08</td>
<td>100.31</td>
</tr>
<tr>
<td>DE306 Py</td>
<td>5</td>
<td>46.50</td>
<td>53.02</td>
<td>0.11</td>
<td>0.12</td>
<td>0.71</td>
<td>0.19</td>
<td>0.03</td>
<td>0.04</td>
<td>0.07</td>
<td>0.05</td>
<td>100.84</td>
</tr>
<tr>
<td>DE377 Po</td>
<td>4</td>
<td>46.36</td>
<td>53.29</td>
<td>0.05</td>
<td>0.11</td>
<td>0.06</td>
<td>0.16</td>
<td>0.04</td>
<td>X</td>
<td>0.06</td>
<td>0.05</td>
<td>100.18</td>
</tr>
<tr>
<td>DE377 Po</td>
<td>4</td>
<td>46.29</td>
<td>53.20</td>
<td>0.05</td>
<td>0.12</td>
<td>0.55</td>
<td>0.19</td>
<td>0.03</td>
<td>0.06</td>
<td>0.08</td>
<td>100.60</td>
<td></td>
</tr>
<tr>
<td>DE381-1 Po</td>
<td>6</td>
<td>47.08</td>
<td>52.49</td>
<td>0.09</td>
<td>0.10</td>
<td>0.09</td>
<td>0.16</td>
<td>0.03</td>
<td>0.02</td>
<td>0.07</td>
<td>0.04</td>
<td>100.17</td>
</tr>
<tr>
<td>DE381-2 SiPo</td>
<td>5</td>
<td>46.75</td>
<td>52.83</td>
<td>0.06</td>
<td>0.11</td>
<td>0.13</td>
<td>0.15</td>
<td>0.03</td>
<td>0.01</td>
<td>0.09</td>
<td>0.05</td>
<td>100.21</td>
</tr>
<tr>
<td>DE381-2 SiPo</td>
<td>4</td>
<td>46.90</td>
<td>52.50</td>
<td>0.06</td>
<td>0.09</td>
<td>0.08</td>
<td>0.17</td>
<td>0.04</td>
<td>0.03</td>
<td>0.09</td>
<td>0.04</td>
<td>99.92</td>
</tr>
<tr>
<td>DE398 Py</td>
<td>9</td>
<td>46.62</td>
<td>53.07</td>
<td>0.34</td>
<td>0.10</td>
<td>0.05</td>
<td>0.16</td>
<td>0.05</td>
<td>0.03</td>
<td>0.06</td>
<td>0.06</td>
<td>100.54</td>
</tr>
</tbody>
</table>

**Table 6.8:** Mineral chemistry of pyrite for samples taken from the 5/5 stoping zone determined via EMP. Original EMP data is presented in appendix A on page 332.
6.4 Investigations prior to QEMSCAN®

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ore type</th>
<th>Fe [wt%]</th>
<th>As [wt%]</th>
<th>S [wt%]</th>
<th>Zn [wt%]</th>
<th>Pb [wt%]</th>
<th>Co [wt%]</th>
<th>Sb [wt%]</th>
<th>Ag [wt%]</th>
<th>Au [wt%]</th>
<th>Bi [wt%]</th>
<th>Total [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE367-3</td>
<td>Py</td>
<td>34.12</td>
<td>44.26</td>
<td>20.26</td>
<td>0.31</td>
<td>X</td>
<td>0.05</td>
<td>0.42</td>
<td>X</td>
<td>0.09</td>
<td>X</td>
<td>99.51</td>
</tr>
<tr>
<td>DE377</td>
<td>Po</td>
<td>33.95</td>
<td>44.40</td>
<td>20.85</td>
<td>0.08</td>
<td>0.06</td>
<td>0.78</td>
<td>0.10</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>100.29</td>
</tr>
<tr>
<td>DE381-2</td>
<td>SiPo</td>
<td>33.95</td>
<td>43.89</td>
<td>20.06</td>
<td>1.25</td>
<td>0.08</td>
<td>0.14</td>
<td>0.39</td>
<td>X</td>
<td>X</td>
<td>0.03</td>
<td>99.79</td>
</tr>
</tbody>
</table>

Total no. of analyses = 14

Table 6.9: Mineral chemistry of arsenopyrite for samples taken from the 5/5 stoping zone determined via EMP. Original EMP data is presented in appendix A on page 332.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ore type</th>
<th>Fe [wt%]</th>
<th>S [wt%]</th>
<th>Zn [wt%]</th>
<th>As [wt%]</th>
<th>Pb [wt%]</th>
<th>Cu [wt%]</th>
<th>Co [wt%]</th>
<th>Sb [wt%]</th>
<th>Ag [wt%]</th>
<th>Bi [wt%]</th>
<th>Total [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE377</td>
<td>Po</td>
<td>60.17</td>
<td>39.33</td>
<td>0.92</td>
<td>0.04</td>
<td>0.08</td>
<td>0.04</td>
<td>0.12</td>
<td>0.02</td>
<td>0.06</td>
<td>0.10</td>
<td>100.88</td>
</tr>
<tr>
<td>DE381-1</td>
<td>Po</td>
<td>60.16</td>
<td>39.14</td>
<td>0.06</td>
<td>0.04</td>
<td>0.12</td>
<td>0.03</td>
<td>0.12</td>
<td>0.02</td>
<td>0.05</td>
<td>0.07</td>
<td>99.81</td>
</tr>
<tr>
<td>DE381-2</td>
<td>SiPo</td>
<td>60.74</td>
<td>38.97</td>
<td>0.58</td>
<td>0.04</td>
<td>0.11</td>
<td>0.03</td>
<td>0.12</td>
<td>0.02</td>
<td>0.04</td>
<td>0.04</td>
<td>100.69</td>
</tr>
</tbody>
</table>

Total no. of analyses = 22

Table 6.10: Mineral chemistry of pyrrhotite for samples taken from the 5/5 stoping zone determined via EMP. Original EMP data is presented in appendix A on page 332.

6.4.3 Whole rock geochemistry

The major and trace element geochemical signature and variation of the deposit have been investigated as part of this thesis (see chapter 5 from page 139). Three massive ore samples from this data set were taken in the area of the proposed 5/5 stoping area. Only one of those samples is located within the actual stope shape, however, all samples are at least in its vicinity and should therefore give a preliminary overview of the geochemical ore characteristics in this particular zone of the deposit.

The major and trace element concentrations are shown in table 6.11 and table 6.12. The modal mineral composition is calculated based on major element concentrations and are estimates only. The total carbonate (as siderite) and silicate (predominantly quartz) contents are highest in the pyrrhotitic ore with just over 14 and 6 wt%, respectively. Sphalerite content is variable, ranging between 15 and 21 wt%, whereas galena occurs relatively constant at 7 wt%. Chalcopyrite is strongest enriched in massive pyrrhotitic ore. According to the geochemical data, arsenopyrite is present in all samples at concentrations between 1.0 and 1.2 wt%. Barite, albite and muscovite occur as minor constituents below a combined total concentration of 1 wt%. Iron sulphide concentrations range between 54 and 62 wt%.

The occurrence of tetrahedrite is expressed by elevated Sb values ranging between 183 and 326 ppm. Silver concentrations are quite constant at a mean of 140 g/t. Significant Au concentration has been observed in sample DE367-3 at 1.15 g/t and approximately 0.6 g/t in DE367-1 and -2. Important smelter penalty element concentrations of Bi, Hg and Se were determined at mean values of 0.03 ppm, 21 ppm and 3 ppm, respectively. Manganese is an important penalty element in zinc concentrates and therefore is problematic when incorporated in sphalerite. EMP data revealed no elevated Mn concentrations in sphalerite. Therefore, the observed Mn concentration of 0.1-0.2 wt% is not significant, and is likely to be linked to the substitution in carbonates.
Table 6.11: Major element geochemistry of samples proximal to the 5/5 stope. Data presented in wt%, data labelled with # is given in ppm.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>DE367-1</th>
<th>DE367-2</th>
<th>DE367-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6.27</td>
<td>4.84</td>
<td>1.02</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.03</td>
<td>0.09</td>
<td>0.20</td>
</tr>
<tr>
<td>MnO</td>
<td>0.17</td>
<td>0.13</td>
<td>0.24</td>
</tr>
<tr>
<td>MgO</td>
<td>0.15</td>
<td>0.09</td>
<td>0.23</td>
</tr>
<tr>
<td>CaO</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.01</td>
<td>0.05</td>
<td>0.11</td>
</tr>
<tr>
<td>BaO</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.39</td>
<td>3.30</td>
<td>2.56</td>
</tr>
<tr>
<td>S</td>
<td>36.00</td>
<td>41.00</td>
<td>43.90</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;total&lt;/sub&gt;</td>
<td>29.10</td>
<td>29.70</td>
<td>29.40</td>
</tr>
<tr>
<td>Zn</td>
<td>10.10</td>
<td>9.52</td>
<td>8.62</td>
</tr>
<tr>
<td>Ag&lt;sup&gt;+&lt;/sup&gt;</td>
<td>145</td>
<td>141</td>
<td>133</td>
</tr>
<tr>
<td>Cu</td>
<td>0.35</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>As</td>
<td>0.55</td>
<td>0.59</td>
<td>0.45</td>
</tr>
<tr>
<td>Total</td>
<td>93.99</td>
<td>95.92</td>
<td>98.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ore type</th>
<th>Po</th>
<th>Py</th>
<th>Py</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sph</td>
<td>16.4</td>
<td>15.4</td>
<td>21.4</td>
</tr>
<tr>
<td>Gln</td>
<td>6.7</td>
<td>7.4</td>
<td>7.5</td>
</tr>
<tr>
<td>Cpy</td>
<td>1.0</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Apy</td>
<td>1.2</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Sid</td>
<td>14.2</td>
<td>8.7</td>
<td>6.7</td>
</tr>
<tr>
<td>Cal</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Bar</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Qz</td>
<td>6.2</td>
<td>4.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Ab</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Or</td>
<td>0.0</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Chl</td>
<td>0.0</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Py + Po</td>
<td>54.1</td>
<td>61.7</td>
<td>61.7</td>
</tr>
</tbody>
</table>

Table 6.12: Trace element geochemistry of samples proximal to the 5/5 stope (data presented in ppm).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>DE367-1</th>
<th>DE367-2</th>
<th>DE367-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.5</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Be</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Sc</td>
<td>0.1</td>
<td>BDL</td>
<td>0.1</td>
</tr>
<tr>
<td>V</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>90</td>
<td>93</td>
<td>72</td>
</tr>
<tr>
<td>Co</td>
<td>5.2</td>
<td>1.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Ni</td>
<td>0.9</td>
<td>1.3</td>
<td>1</td>
</tr>
<tr>
<td>Ga</td>
<td>7.37</td>
<td>4.09</td>
<td>5.74</td>
</tr>
<tr>
<td>Ge</td>
<td>0.25</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>Se</td>
<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Rb</td>
<td>0.3</td>
<td>1.1</td>
<td>3.2</td>
</tr>
<tr>
<td>Sr</td>
<td>2.9</td>
<td>2</td>
<td>8.6</td>
</tr>
<tr>
<td>Y</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Zr</td>
<td>BDL</td>
<td>BDL</td>
<td>0.5</td>
</tr>
<tr>
<td>Nb</td>
<td>1.3</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td>Mo</td>
<td>1.18</td>
<td>1.99</td>
<td>1.58</td>
</tr>
<tr>
<td>Cd</td>
<td>243</td>
<td>219</td>
<td>295</td>
</tr>
<tr>
<td>In</td>
<td>0.02</td>
<td>0.01</td>
<td>BDL</td>
</tr>
<tr>
<td>Sn</td>
<td>8</td>
<td>8.1</td>
<td>9.6</td>
</tr>
<tr>
<td>Sb</td>
<td>326</td>
<td>281</td>
<td>183</td>
</tr>
<tr>
<td>Te</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Cs</td>
<td>0.18</td>
<td>0.17</td>
<td>0.21</td>
</tr>
<tr>
<td>Ba</td>
<td>90</td>
<td>50</td>
<td>260</td>
</tr>
<tr>
<td>La</td>
<td>0.6</td>
<td>1.4</td>
<td>BDL</td>
</tr>
<tr>
<td>Ce</td>
<td>1.09</td>
<td>1.97</td>
<td>0.33</td>
</tr>
<tr>
<td>Hf</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Ta</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>W</td>
<td>0.6</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Re</td>
<td>BDL</td>
<td>0.002</td>
<td>BDL</td>
</tr>
<tr>
<td>Au</td>
<td>0.636</td>
<td>0.683</td>
<td>1.15</td>
</tr>
<tr>
<td>Hg</td>
<td>15.75</td>
<td>18.6</td>
<td>28</td>
</tr>
<tr>
<td>Tl</td>
<td>13.9</td>
<td>15.15</td>
<td>6.46</td>
</tr>
<tr>
<td>Bi</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Th</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>U</td>
<td>0.6</td>
<td>0.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 6.12: Trace element geochemistry of samples proximal to the 5/5 stope (data presented in ppm).
6.5 QAQC and data processing

Data validation is essential in any analytical procedure. Assay correlation between chemical compositions calculated based on QEMSCAN® results is compared to assay data obtained from standard geochemical analysis. As already described earlier, to each pixel of a particle, a chemical composition is assigned according to its allocated mineral species. If averaged across the entity of particles, a bulk chemical composition of the sample can be calculated. A detailed mineralogical and mineral chemical understanding is necessary in order to achieve a good assay correlation, subsequently indicating a correct mineralogical classification of samples analysed via QEMSCAN®. To ensure total sample dissolution for major element determination, a lithium metaborate fusion followed by analysis via ICP-OS was used. A modified aqua-regia digestion and analysis by ICP-OS and ICP-MS is applied for trace elements. The concentration of total S was determined by the LECO technique. If sample material was unknown, XRD analyses were used to give an approximation of mineral abundances, especially clay minerals. The geochemical analyses used for QAQC were undertaken by AMDEL.

6.5.1 Adjustment of mineral list and pre-processing of raw data

The SIP and the primary lists contain 336 and 79 mineral species definitions, respectively. Both lists were slightly modified by the author according to the observed mineral occurrences and the determined mineral chemistry of sulphide phases analysed via EMP. The lists are too extensive to be incorporated within this thesis. The most important modifications performed are:

1. Sphalerite definitions were modified based on the observed mineral chemistry. In the initial SIP, sphalerite species were far too detailed for the purpose of this study. Sphalerite occurring within the Elura deposit is characterised by very low Mn concentrations (below electron microprobe detection limit) and Fe content ranging between 2.4 and 8.2 wt%. Therefore, three sphalerite categories were defined to account for the variation of Fe content. Manganese has been ignored as very low concentrations were detected during EMP analyses of sphalerite. In the course of this study it is aimed to identify, high and low Fe sphalerite as well as to quantify contained impurities, such as inclusions and alterations.

2. Two new categories were defined for Ag and Bi. These categories have been designed in order to identify any mineral phases containing these elements above the EDS detection limit.

3. In the initial SIP, siderite as one of the most abundant non-sulphide gangue (NSG) mineral phase, was lacking and had to be defined. The subordinate occurrence of goethite, a mineral phase chemically similar to siderite in respect to its EDS spectra, complicated this exercise. However, by adjusting the BSE intensity range for both mineral phases, acceptable results were achieved.

At the interphase of different mineral phases, a composite EDS spectrum and BSE intensity is generated. Similarly, BSE intensity decreases at the margin of particles embedded in epoxy resin. The analysed particles, presented as particle images, need to be visually investigated in order to detect these excessive boundary-phase artefacts or ambiguous identifications during the measurement. If detected, the removal is performed via the boundary phase processor which enables the modification of the measured data according to the context of the pixels.

Although it is tried to avoid particle agglomeration during sample preparation, occasionally they occur. These particles are identified and separated by a further pre-processor, the so-called “touching particle processor”.

209
6.5.2 Assay correlation

A good agreement between chemical data obtained via QEMSCAN® and conventional methods was met (Figure 6.9). Analytical data is presented in section C.1.2 on page 504. The quality of chemical data is commonly described via the double standard deviation corridor $2\sigma$, which corresponds to a maximum deviation of 5.6%. For the QAQC assay correlation of QEMSCAN® data, a deviation of less than 10% is considered as good analytical results by the industry (pers. comm. Kellie Jones 2010). For the elements Fe, S, Pb and Zn, a deviation of less than or equal to 10% has been achieved throughout the entire sample set. Sulphur correlated exceptionally well, indicating accurate sulphide identification. A minor systematic overestimation of Fe is present, which is potentially explained by compositional variation of carbonates, not sufficiently recognised during analysis. Good As assay correlation has been achieved for the first set of seven samples. However, a sudden drop in analytical quality is observed for the remaining three samples with deviations greater than 20% and characterised by a systematic underestimation of the concentrations based on QEMSCAN®. Those samples were lacking any common features, they were taken from different areas within the 5/5 stope (eastern and western stope part) and are of different ore types. Therefore, an analytical error seems the probable explanation. Copper concentrations are in good agreement, with the exception of two samples with deviations greater than 10%. A correct estimation of silica content in massive sulphide samples appears to be problematic. Assay correlations of only four samples resulted in deviations less than 10%; five samples deviate by 10 to 20% and one sample by over 20%. The deviations are scattered along the correlation line not indicating any systematic analytical error.

It needs to be stressed, that the elements affected by the deviations occur at rather low concentrations, i.e. also low quantities of particles containing the corresponding mineral species were analysed and subsequently, an increase of statistical uncertainty is inevitable. Overall, most of the observed element concentrations are well within analytical errors and therefore the results are considered valid.

**Figure 6.9:** QEMSCAN® – chemical assay correlation; all elemental concentrations shown in diagram (a), diagram (b) presents element correlations of lower concentration levels.
6.5.3 Important QAQC particle features

Initially, a visual inspection of the resulting particle images is carried out in order to determine a successful and sufficient data pre-processing, and to investigate potential particle duplications during analysis. Based on statistics, about 15,000 to 20,000 analysed particles are considered to be a representative sample. The particle count for the samples of this study showed, that approximately 70,000-260,000 particles were analysed per sample (appendix section C.1.2, page 504). Only 0.1% of all particles analysed fall within the size fraction +80/-600 µm. The low quantity is considered not representative and therefore, particles larger than 80 µm are only used for textural investigations and filtered out in other calculations. Overall, less than 10 wt% of particles is contained in the particle size fraction of +0/-3 µm. A pixel size of 2 x 2 µm has been used during analysis. Small particles in the order of the pixel size are likely to be affected by misidentification due to boundary effects, and furthermore would not lead to the gain of any mineral association data. In order to improve data management and software performance, these particles were filtered out without significantly modifying the modal mineralogy or other calculated ore characterisation data. However, a basic ore characterisation and classification is performed on the fine particle fraction (see section 6.6.1 on page 213). The remaining particle size fraction +3/-80 µm was characterised by particle counts in excess of 34,000 particles which is more than sufficient in statistical terms. At the mineral processing facility, the actual particle size distribution of the floatation feed is characterised by a P80 (actually P78) of approximately 45 µm with 4 wt% particles above 75 µm (pers. comm. Andrew McCallum, 2010). When comparing the calculated particle size distributions of the selected size fraction +3/-80 µm with the actual floatation feed, a good agreement is observed (figure 6.10).

Particle count as a function of different mineral phases being contained in them is shown in appendix section C.1.2, page 504. Silver bearing mineral phases were found in a very low particle quantity as low as 51 and up to 346 particles. Compared to the total number of analysed particles this count is negligible, subsequently, any calculations based on this particle group need to be scrutinised and used or interpreted in a cautious manner. No Bi-bearing mineral phases were observed during PMA analysis of samples from the 5/5 stope. For detailed and statistically more robust investigations of Ag mineral phases, the earlier described specific minerals or trace minerals search mode would need to be carried out.

6.5.4 Limitations and analytical problems

QEMSCAN® delivers either one (BMA: line scan) or two dimensional (PMA: particle scan, field scan) results. In most cases the particles, which are randomly orientated, embedded in epoxy resin and polished on a planar surface, are characterised by a section exposure smaller than its actual particle cross section. Subsequently, area and size calculations are always characterised by a negative bias as are other particle features such as volume, surface exposure,
etc. However, an automatic stereological correction is applied during these calculations in order to account for this deviation. Rim and boundary effects are identified and aimed to be reduced via pre-processing of the raw data. The magnitude of how these effects are processed is primarily a function of the achievable assay correlation quality and to some degree variable and operator or user controlled.

The initial field scans of thin-sections gave corrupt results due to a defective sample stage. During the field scan measurement, the entire area selected for analysis, was subdivided into frames and scanned individually. Upon completion of the measurement, the frames needed to be stitched back together in order to produce an actual image of the entire sample area analysed. The sample stage is a highly accurate X-Y positioning device, which allows the sample to be moved and positioned under the electron beam during the scanning process. Due to the defective sample stage, some areas of the frames were not analysed, and some analysed more than once. The subsequent stitching process gave unsatisfactory results. Therefore, all samples were reanalysed upon exchange of the defective sample stage in a second field scan procedure in order to obtain reliable results.

Particle duplication has been observed during visual QAQC inspection of the PMA results in six out of a total of ten samples. AMDEL Laboratories was convinced that the duplication is due to corrupt software and occurred during the raw data being transferred from the QEMSCAN® instrument to the storage media. It was recognised by the author, that the duplicated particles are not identical, showing minor differences in the composition and shape. Particle duplication due to software problems was therefore an illogical explanation. Analytical errors seem highly probable and initially, the defect sample stage was thought to have caused the duplication. However, the reanalysis of 4 samples after the sample stage had been exchanged showed reoccurring particle duplications in 2 samples. Finally, AMDEL Laboratories identified the real cause of the problem as being how the measurement setup is chosen. If the measurement is set to “from the centre of the sample block” compared to “starting from the edge”, particle duplication occurred. Despite finding the root cause of this analytical problem, no explanation for the actual reason has been identified or communicated by AMDEL Laboratories. The samples were reanalysed with measurement setup, now “believing” not to cause particle duplication.

It needs to be stressed that visual inspection of particle images in addition to assay correlation are the only QAQC instruments applicable to the QEMSCAN® technique. Therefore, a profound understanding of ore petrology and mineral chemistry prior to the utilisation of this technique is absolutely essential for high quality ore characterisation results.
6.6 QEMSCAN® results from PMA and field scans

All results were calculated utilising the iDiscover software package version 4.3 supplied by FEI to the author. A detailed summary of measurement setup and raw data of the entire data set is given in appendix C, page 494 for particle mineral analysis (PMA) and in appendix C, page 651 for field scans. Results from PMA and field scans are collectively described with reference to individual 5/5 stope parts and/or ore types. Massive sulphide samples (abbrev. Py for pyritic and Po for pyrrhotitic dominated samples) were preferably selected for field scans, therefore the number of samples of semi-massive pyritic (SiPy; n = 2) and pyrrhotitic (SiPo; n = 2) ore is low. Field scan results of SiPy and SiPo are combined to one sample category. Due to the voluminous character of the reported QEMSCAN® data, only selected diagrams are included in this section. All calculated data is comprehensively compiled in appendix C, page 492. Numerous references to the appendix and its sections are not avoidable and are contained in the following description.

6.6.1 General ore characterisation

The modal mineralogy, elemental composition, iron deportment, calculated ESD (equivalent spherical diameter) sizes and mineral associations are presented in this section. These features will give an overview of compositional variability throughout the sample set and the three different stope parts.

In excess of 90 wt% Zn, Pb and Cu is contained in the particle size fraction (abbrev. PS) +3/-80 μm. Silver phases are commonly finer grained. Approximately 30 wt% Ag is contained in the fine PS below 3 μm. Silver phases are not included in the calculation of modal mineralogy and Fe deportment because of their low abundance.

PMA – Particle size fraction +0/-3 μm

Analytical results are shown in appendix section C.1.4, page 510. An east-west trend is observed for modal mineral composition of ore from the 5/5 stope (abbrev. 5/5-ST). Quantities of sphalerite and galena are highest in the eastern (abbrev. 5/5-E), pyrrhotite dominated stope part with approx. 22 and 18 wt%, respectively. The lowest concentrations are contained in ore from the western stope part (abbrev. 5/5-W), which almost exclusively contains pyritic ore. The central stope segment (abbrev. 5/5-C) consists of pyritic and pyrrhotitic ore and features intermediate Pb and Zn concentrations. Chalcopyrite is recognised in all samples but significantly elevated in 5/5-C and 5/5-E. The most important mineral phases hosting Fe are obviously pyrite and pyrrhotite. Iron-rich sphalerite and non-sulphide gangue mineral phases (NSG) are responsible for an Fe deportment of approximately 10 wt% Fe each (calculated percentage of total Fe). Particles falling within the PS +0/-3 μm are highly liberated with ~90 wt% Zn, ~81 wt% Pb, ~93 wt% Cu and 81 wt% Ag contained in particles at a liberation grade above 90% *. Particles featuring liberation grades in excess of 90% are commonly considered as fully liberated.

PMA – Particle size fraction +3/-80 μm

Results are shown in appendix section C.1.4, page 510. Variation of modal ore composition throughout the 5/5-ST is similar for this PS as observed for the fine PS +0/-30 μm but not as pronounced. High pyrrhotite content in the 5/5-E and 5/5-C corresponds to elevated concentrations of sphalerite (max. Zn 10.7 wt%), galena (max. Pb 9.6 wt%) and chalcopyrite (max. Cu 1.0 wt%). Arsenopyrite occurs in all stope parts at rather constant concentrations ranging between 1.1 and 1.3 wt%.

Siderite and other carbonate mineral phases

* Particle liberation was calculated on the basis of area percent, i.e. a particle has a liberation of more than 90% in respect to Pb if more than 90% of the particle’s area consists of galena.
are highest in 5/5-E and 5/5-C, clearly linked to pyrrhotitic ore types, whereas quartz, chlorite and muscovite, the latter two phases combined as phyllosilicates, preferably occur in 5/5-W, which is almost exclusively composed of pyritic ore. When calculating relative contribution of gangue mineral phases, quartz ranges between 48 wt% (5/5-W) and 20 wt% (5/5-C), siderite between 64 wt% (5/5-E) and 34 wt% (5/5-W). Iron carbonates, if occurring in sufficiently high quantities, may contain up to ~10 wt% of total Fe (calculated percentage of total Fe).

Overall, average equivalent spherical diameter (ESD) grain sizes show a progressive decrease from the eastern to the western stope part for most major mineral phases, i.e. sphalerite, galena, chalcopyrite and siderite (figure 6.11). Pyrite occurs at rather constant average grain sizes throughout the 5/5 stope (~13 µm). Minor pyrrhotite may occur in pyritic ore but in small grain sizes as indicated by a significant drop of ESD in 5/5-W down to ~5 µm. No systematic grain size variation is observed for arsenopyrite in respect to different ore types with highest ESDs in 5/5-C (~12 µm) and lowest in 5/5-W (~12 µm). ESDs of all NSG phases except siderite are constant throughout the 5/5-ST with ~17 µm for quartz, ~11 to ~14 µm for siderite and other carbonates, ~6 µm for phyllosilicates (figure 6.12). It needs to be stressed that calculated average ESDs are guidelines for relative grain size variability. Proper mineral phase specific grain size distributions are discussed later (see section 6.6.3).

Prior to the development of 2-dimensional particle mineral analysis techniques, line scans across particle samples were used. Calculation of free surface of a specific mineral phase contained in particles is obviously not directly possible for 1-dimentional data. Thus, the phase specific surface area (PSSA) value has been introduced (see e.g. Williams, 1993; Sutherland, 2007, for further details), where higher PSSA values reflect lower free surface area. Although this parameter is not used today, it has been calculated to allow comparison with older data. PSSA data are shown in appendix section C.1.4, page 510. All sulphides except Ag minerals feature lower free surface area (i.e. higher PSSA) in the 5/5-W, most probably as a consequence of generally smaller grain sizes (indicated by ESD values) and the subsequent poorer liberation. Free surface area of Ag phases is significantly higher in ore from 5/5-W. It is known from microscopic and geochemical studies (see chapter 4 and chapter 5) that argentian tetrahedrite and other Ag phases preferably occur in peripheral parts of the orebody and in those locations as larger grains. The observed increase of free surface area is likely caused by larger grain sizes and consequently improved liberation.

Field scans

Results of QEMSCAN® field scan analyses complement results from PMA and were used to characterise different ore types based on in situ sample material as represented by thin-sections. All data is presented in appendix section C.7, page 653. The analysed massive sulphide thin-
sections contain on average between ~18 wt% (Py) and ~16 wt% (Po) sphalerite, as well as ~6 wt% (Py ore type) and ~11 wt% (Po ore type) galena. Chalcopyrite content is highest at 0.6 wt% in semi-massive ore (SiPy and SiPo) compared to 0.3 wt% in Po and 0.4 wt% in Py. The pyrite to pyrrhotite ratio is approximately 1:1 in massive pyrrhotitic ore. Only 2.2 wt% pyrrhotite was detected in massive pyritic ore. Detection of Ag-bearing mineral phases was limited to massive pyritic ore. Arsenopyrite concentration of 0.7 wt% was determined for both massive ore types, whereas only 0.3 wt% was observed in semi-massive ore. Quantities of NSG phases range between ~7 and 11 wt% in massive ore but are significantly higher in semi-massive ore at an average concentration of 20 wt%.

Sphalerite and galena are commonly coars-est in Po ore. Average grain sizes (ESD) range between 58 (Py) and 68 \(\mu m\) (Po) for sphalerite and 28 (Py) to 50 \(\mu m\) (Po) for galena. Grain sizes of chalcopyrite are consistent and range between 28 and 34 \(\mu m\). Pyrite and pyrrhotite is significantly coarser at ESDs in excess of ~90 \(\mu m\). Pyrrhotite represents a minor constituent in massive pyritic ore and features small grain sizes with an average of ~25 \(\mu m\). According to field scan data, grain sizes of Ag-phases are estimated at 18 (Po) to 33 \(\mu m\) (Py). ESDs of small-grained mineral phases are significantly underestimated based on field scan results because of the lower analytical resolution, which was set to 10x10 \(\mu m\). If a small grain of for instance 5 \(\mu m\) happens to be identified during field scan, the entire 10x10 \(\mu m\) pixel would be assigned to this particular mineral phase. Such a pixel would yield a calculated ESD of approximately 15 \(\mu m\), significantly larger than the true grain size. Only relative grain size changes between different ore types should be used for ore characterisation, in particular for small mineral phases. The results suggest that pyritic ore contains larger Ag-bearing mineral phases when compared to pyrrhotitic ore. This observation is in agreement with microscopic investigations.

Quartz represents the most important non-sulphide gangue (NSG) mineral phase in semi-massive ore and contributes ~69% of total NSG. Siderite and other carbonate phases were observed at ~23% but their contributions are significantly higher in massive ore ranging between ~70% in Py and ~97% in Po. Concentrations of other NSG phases are variable.

Average ESD grain sizes of quartz range between ~60 and 110 \(\mu m\), coarsest in semi-massive ore. Carbonate grain sizes are rather consistent and range between 70 and 80 \(\mu m\). Other NSG phases, i.e. sericite, chlorite, iron-hydroxides, etc., feature ESDs close to the earlier described limit of accurate determination (~15 \(\mu m\)).

**Theoretical grade/recovery diagrams**

Theoretical grade/recovery diagrams were calculated for Zn, Pb and Cu based on the assumption that mineral liberation (calculated based on area percent) is directly linked to mineral recovery without consideration of mineral losses. If only particles characterised by high liberation are recovered, a high concentrate quality would be achieved but at a low metal recovery rate. The liberation value necessary for mineral recovery is step-wise decreased and the composition of the recovered particles calculated, reflecting the composition of the theoretical concentrate. Recoveries and corresponding element concentrations define the grade-recovery graphs (abbrev. GR). The GR diagrams are calculated for different particle size fractions (PS) in order to investigate at which particle sizes liberation decreases, subsequently causing a drop in concentrate quality. All results are shown in appendix section C.1, page 520.

Figure 6.13 shows the GR diagrams for zinc, suggesting a significant decrease in grade/recovery performance for ore sourced from the 5/5-W. The long-term average plant performance for Zn showed recoveries ranging between ~77 and ~82% at concentrate qualities between ~48 and ~52 wt% Zn. Recoveries and grades of the 5/5-W, although performing poorer than the other stope parts, are close to the achieved plant performance. GR graphs for different PS populations indicate that par-
particles above 38 μm are progressively less liberated. For 5/5-W, a drop of liberation is already indicated for PS +20/-38 μm. The theoretical GR suggests that ore from 5/5-C and 5/5-E should result in either significantly better concentrate quality or higher metal recovery than the long-term average plant performance. However, these results reflect ideal plant conditions, not considering unavoidable losses or dilutions caused by e.g. entrainment, over grinding, slimming, etc. Nevertheless, the results clearly highlight that 5/5-W will most probably feature a significantly lower recoverability by approximately 10% compared to the other stope parts.

An even more significant deviation from the long-term average plant performance is observed for lead (figure 6.14). The deviation translates in a difference of ~30 wt% Pb concentrate grade or ~20% Pb recovery when comparing achieved plant performance to the combined 5/5-ST theoretical GR diagram. The 5/5-W will perform poorer than other stope parts. GR graphs for individual PS suggest that particles smaller than 38 μm feature relatively good liberation for 5/5-E and 5/5-C, whereas for 5/5-W liberation is lower and responsible of the overall poorer performance for this particular stope part. Even when considering that these results are theoretical and do not reflect real plant performance as discussed earlier, the differences are significant.

At the Elura’s mineral processing facility, chalcopyrite is initially recovered along with galena in a composite mineral concentrate. Only in a later processing stage both products, i.e. lead and copper concentrate, are separated by campaigned flotation. It needs to be investigated whether dilution with chalcopyrite and its intergrown mineral phases is a possible explanation for the observed deviations between theoretical and real plant performance. In order to calculate a realistic best-case grade recovery scenario, the following amendments to the data set are made:

(a) Coarse particles above 53 μm may be highly liberated because of the near perfect cleavage of galena. Such large particles may only be recovered if the particle residence time within the flotation cells is long enough what they in reality rarely are. In order to avoid an artificial increase in calculated theoretical recoveries, particles larger than 53 μm are ignored in the calculations.

(b) All Pb and Cu contained in the +0/-3 μm PS is considered as a 100% loss to account for sliming and entrainment mechanisms observed in reality.

(c) The target particle size fraction for galena flotation is between +3/-53 μm and used for calculations as the recoverable particle population.

Figure 6.13: Theoretical grade-recovery diagram for Zn compared to achieved long-term plant performance data (range shown in orange; data from pers. comm. Andrew McCallum, 2010).

Figure 6.14: Theoretical grade-recovery diagram for Pb compared to achieved long-term plant performance data (range shown in orange; data from pers. comm. Andrew McCallum, 2010).
(d) Long-term achieved copper recoveries range between 55 and 61% (pers. comm. Andrew McCallum, 2010). The corresponding particle liberations to the achieved recoveries are estimated at ~97%, ~95 and ~92% (calculated as liberation based on area percent) for Cu recoveries of 55, 58 and 61%, respectively (see appendix section C.4.3, page 604). Three GR diagrams are constructed for galena assuming that those particles that feature the three chalcopyrite particle liberation would report to the lead concentrate.

(e) Mineral phase specific area percentage is the commonly used measure for particle liberation. In differential froth flotation, free mineral surface is even a more important parameter. GR graphs are calculated based on area specific liberation and free surface in order to investigate whether significantly different results are achieved.

Figure 6.15 shows the calculated GR graphs for particle liberation (diagram a) and free particle surface (diagram b). Even when considering the dilutional or “polluting” effect of chalcopyrite reporting to the lead concentrate, theoretical data deviates greatly from long-term plant performance. The difference between GR characteristics based on particle liberation and free particle surface is negligible.

Chalcopyrite is a minor constituent in the ore from Elura, the number of particles containing this particular mineral phase is low and calculations may be inaccurate. The calculated theoretical GR diagram for copper (Figure 6.16) indicates a drop in recovery for ore from the 5/5-W. The long-term average plant recoveries for Cu

![Figure 6.16: Theoretical grade-recovery diagram for copper compared to achieved long-term plant performance data (range shown in orange; data from pers. comm. Andrew McCallum, 2010).](image-url)
range between 55 and 61% and correspond to a theoretical concentrate quality between 33 and 34 wt % Cu, close to the maximum possible of 34.6 wt%.

Zinc recoveries and concentrate quality based on ore characterisation showed similar results to actual plant data when minor metal losses and dilution are taken into account. The same applies to Cu. In respect to the 5/5 stope, calculated theoretical data indicate a significant drop in recoverability of ore sourced from the western stope part.

Observed ore characteristics suggest that a significant better grade/recovery performance for galena/lead should be achieved when compared to the long-term mineral processing performance. If Pb losses or significant dilution by other mineral phase are the cause, they are likely far too extensive as to be acceptable by industry standards. Another possible explanation for a potential overestimation of grade and recovery via QEMSCAN® may be the sample preparation technique. It appears feasible that stage crushing may lead to a significantly different mineral/particle liberation compared to the grinding methodology used in the actual mineral processing plant (ball mill). Galena is a soft mineral with three perfect cleavages. Stage crushing may achieve high liberation without the excessive generation of fine material smaller than 5 μm whereas grinding via ball mill may produce significant quantities. Increased amount of fine material may lead to significant metal loss to tailings due to e.g. sliming and/or entrainment. Geometallurgical test work on the actual flotation feed would need to be undertaken in order to assess this issue.

6.6.2 Mineral specific characterisation

Sphalerite composition

Mineral chemical investigations showed significant variations in the Fe content incorporated in sphalerite (see section 4.2.1). These variations may have an effect on sphalerite recoverability and the quality of the zinc concentrate. Compositional characterisation of sphalerite was therefore undertaken as part of the geometallurgical study. The results of PMA and field scans are presented in appendix section C.2.2, page 531 and appendix section C.7.5, page 670, respectively.

Three Fe categories were defined for sphalerite in addition to a category accounting for small impurities and inclusions of other mineral phases, which cause a mixed energy dispersive spectra. These mineral impurities/inclusions commonly comprise iron carbonates (calculated as siderite), chlorite and sericite. Another category was defined in order to calculate the quantity of sphalerite affected by boundary effects (i.e. analytical uncertainty caused by intergrowth of sphalerite with different mineral phases or caused by the interphase between sphalerite and epoxy resin).

Reconciliation between Fe content of sphalerite determined via EMP and QEMSCAN® showed a very good correlation, indicating correct identification of different sphalerite compositions (figure 6.17).

Most of the sphalerite contained in 5/5-E is Fe-rich. A decrease in Fe content is observed from the eastern via central to the western stope part. Mineral chemistry of sphalerite indicated the preferred occurrence of Fe-rich sphalerite in pyrrhotitic ore types (see section 4.2.1). QEMSCAN® PMA results confirm this observation as the 5/5-E contains the highest percentage of pyrrhotitic ore. Less than 1 wt% low Fe sphalerite is contained in massive pyrrhotitic ore according to field scan results.

The quantities of impure and altered sphalerite are in the order of 10-14 wt% based on

![Figure 6.17: Reconciliation of sphalerite composition determined via QEMSCAN®-fieldscan vs mineral chemical composition based on EMP analyses; solid black line is the 1:1 ratio.](image-url)
PMA, and commonly below ~3 wt% according to field scans. Similarly, significantly more sphalerite is assigned to boundary or rim category during PMA (~8 wt%) compared to field scan (<1 wt%). The comparison suggests that most of the impure and altered sphalerite as well as those affected by boundary effects are caused by the interference with the energy dispersive signal emitted by the epoxy resin. Altered and impure sphalerite are preferably linked to pyritic ore types and elevated in the 5/5-W but commonly accounts for only 3 wt% of total sphalerite content. Sphalerite is highly impure and contains abundant inclusions at variable sizes as indicated by the spongy appearance in the particle images appendix section C.2.2, page 531.

Copper-hosting mineral phases

Microscopic observations indicate that chalcopyrite is the only major copper-carrying mineral phase (see section 4.1). A negligible amount of Cu may be contained in tetrahedrite. PMA is used to search for other important copper minerals in addition to chalcopyrite. The results are presented in section C.4.2, page 602.

In excess of 94 wt% of all Cu-containing particles from the 5/5 stope consist of chalcopyrite. Argentian tetrahedrite hosts a noticeable but variable amount of Cu between less than 1 and up to ~9 wt% of total Cu. The combined amount of particles containing covellite, chalcocite, digenite and/or bornite is less than 0.1 wt% and hence negligible. Minor Cu-phases and boundary effect related identifications were combined in a single category and contain only ~ 0.6 wt% of those particles that contain Cu.

The results showed that chalcopyrite is indeed the only important Cu-phase. However, in areas where the chalcopyrite content is low, and tetrahedrite is relatively abundant, lower Cu recoveries may be achieved.

Silver-bearing mineral phases

Analytical results are show in section C.6, page 638 and appendix section C.7.6, page 673 for PMA and field scan, respectively. Ore petrographic investigations suggested that argentian-tetrahedrite and similar phases with slightly different stoichiometry (e.g. freibergite, styloptyte; all referred to as argentian tetrahedrite in the following and abbrev. as Ag-Tet) are the only important discrete mineral phases hosting silver (see section 4.2.2). Because of the fine-grained nature of Ag-Tet, QEMSCAN® results may be inaccurate. Reconciliation between chemical assay data and composition calculated based on QEMSCAN® results are presented in appendix section C.6.1, page 639. Cross-correlation plots suggest a systematic underestimation of concentrations determined via QEMSCAN® by a factor of ~0.7 and ~0.4 for Ag and Sb, respectively (figure 6.18). Silver and Sb correlate to a relatively high degree for both chemical and QEMSCAN® data. The deviation between both data sets is likely a combination of the following causes:

(a) An average Ag-Tet composition as identified via EMP studies (see section 4.2.2) was used for QEMSCAN® analysis, but the mineral chemical compositions of Ag-Tet varies significantly, in particular in respect to Ag, which cannot be accounted for during QEMSCAN®.

(b) Antimony-bearing mineral phases were generously classified, i.e. upon identification
of Ag-Tet, all phases featuring an EDS Sb signature were assigned to Sb-phase category, composed of 100% Sb. Nevertheless, an even greater underestimation compared to Ag was observed. Both, Ag and Sb mineral phases commonly occur at rather small grain sizes. Despite using a high analytical resolution of 2x2 µm during QEMSCAN® PMA, a significant quantity of particles, containing Ag-Sb-phases, is likely to have been either misidentified or simply not identified at all. Furthermore, particle abundances containing Ag- and Sb-phases are overall rather low, consequently, analytical uncertainty is high.

(c) Significant concentration levels of Ag and Sb were observed in galena (see section 4.3). Galena is a major constituent in sulphide ore at Elura. Trace element compositions were not accounted for during QEMSCAN® analysis, thus may substantially contribute to the systematic underestimation of Ag and Sb concentrations.

Microscopic and mineral chemical observations, part of this study, were confirmed by the QEMSCAN® results. Ag-Tet the major Ag-hosting mineral phase in addition to trace amounts of native silver. No As-Ag phases (e.g. tennantite) were observed. Abundance of Ag particles is low and mineral phases commonly feature small grain sizes. Thus, QEMSCAN® results may not be sufficiently accurate.

Search for bismuth-bearing mineral phases

QEMSCAN® field scans of all 15 thin-sections were used to search for potential discrete Bi-mineral phases that had not been identified microscopically. The identification process of Bi-phases was prioritised, i.e. any mineral phase featuring an EDS Bi signature was assigned to the bismuth mineral phase category prior to the assignment of any other mineral phases. Analytical results are shown in appendix section C.7.7, page 675.

Negligible quantities of Bi-phases were identified. Only 7 out of 15 thin-sections contain a total number of 26 Bi grains. An analytical resolution of 10x10 µm was used during field scans. Considering that an approximate area of 10x20 mm is scanned, this is a very detailed resolution. Nevertheless, small grains below approximately 5-10 µm are likely to be misidentified or not identified at all. A significantly higher resolution is used during PMA (2X2 µm). Not a single grain or even pixel featuring an EDS Bi signature was identified in any of the analysed 1.5 million particles from 12 samples analysed via PMA.

QEMSCAN® results do not preclude the occurrence of trace amounts of discrete Bi-mineral phases. However, observations clearly suggest that their quantities are negligible and galena is the only major Bi-carrying mineral phase as suggested by observation made based on mineral chemical compositions determined via EMP and LA-ICP-MS (see section 4.2.1 and section 4.3).

Iron sulphide characterisation

Four major pyrite generations were identified during microscopic studies as part of this work (see section 4.1.1). The early, pre-base metal pyrite type A is commonly anhedral in shape and represents the most abundant pyrite type. It occurs as colloform, frambooidal and cloudy varieties and generally forms larger compounds of individual grains. Pyrite type B also formed prior to base metals but is exclusively euhe- dral to subhedral in shape, although in places strongly corroded and replaced by base metal sulphides. Pyrite type C is contemporaneous with base metal sulphides but occurs in minor quantities. The post-base metal sulphide type D is the fourth identified pyrite variety and is observed in small quantities and small grain sizes. The pyrite generations A and B in addition to pyrrhotite account for most of the iron sulphides, thus, are important in respect to metallurgical problems. Grain size distributions, pyrite/pyrrhotite ratios and the occurrence of pyrite varieties within different ore types were investigated as part of this study. Results of iron-sulphide characterisation are presented in
section C.5, page 630 and section C.7.4, page 667 for PMA and field scans, respectively.

Grain size distributions of pyrite (undifferentiated between type A and B) based on PMA and for individual pyrite varieties (type A and B) based on field scans are discussed in the following section (section 6.6.3). The analyses of pyrrhotite and pyrite are visualised as particle images in appendix section C.5, page 630. The geological model showed that 5/5-E and 5/5-C contains significant quantities of massive pyrrhotitic ore. The resource model does, however, not differentiate between pyritic and pyrrhotitic semi-massive ore. QEMSCAN® analyses are used to calculate the percentage pyrite of total Fe sulphides ($X_{Py} = Py/(Py+Po)$) for individual stope parts. $X_{Py}$ increases from the eastern (0.32), via the central (0.62) to the western stope parts (0.99). Samples from the 5/5-C feature rather variable $X_{Py}$ indicative of the transition from the pyrite-dominated western to pyrrhotitic-dominated eastern ore zones. Field scans showed that massive pyrrhotitic ore contains on average ~47% pyrrhotite of total Fe sulphides, compared to ~3% contained in massive pyritic ore.

Ore microscopy indicated that pyrite type A and pyrrhotite exclude each other and are commonly not present in the same paragenesis. Thus, pyrite type B is the dominant variety associated with pyrrhotite. It was tried to categorise pyrite according to their shape*, in order to allow the calculation of ratios between pyrite type A and B, and to substantiate microscopic observations.

Particle images of the identified pyrite type A and B grains are presented in figure 6.19. It needs to be stressed that the results are at best a rough estimate only. Nevertheless, the images suggest that the identification of both pyrite types delivered acceptable results. The plot $X_{Py-A}$ (percentage of Py-A relative to total iron sulphides) vs. $X_{Po}$ (percentage of Po relative to total iron sulphides) shows a good negative correlation ($R^2 = 0.94$) whereas $X_{Py-B}$ and $X_{Po}$ are uncorrelated (figure 6.20). The QEMSCAN® results confirm microscopic observations and showed that an increase of pyrrhotite is accompanied by proportional decrease of pyrite type-A, whereas pyrite type-B occurs in both pyritic and pyrrhotitic ore types.

* Categorisation was realised via the calculation of grain shape factors with pyrite featuring shape factor > 10 and shape factor < 25 assigned to pyrite type B category.
6. GEO-METALLURGICAL STUDY VIA QEMSCAN®

6.6.3 Grain size distributions

Grain size data and distributions are based on equivalent spherical diameter sizes (ESD) calculated from 2-dimensional particle cross-sections based on PMA or field scan data. It needs to be kept in mind that grain sizes calculated from PMA results do not reflect real in situ grain sizes, because results are based on broken sample material. These grain sizes are nevertheless important for metallurgical problems. In order to gain at least some information about in situ grain size distributions, they are compared to those calculated from field scan results. However, these results do not necessarily reflect in situ grain sizes either, but reflect an estimated combined size distribution of individual mineral grains and larger compounds. Small grains below ~15 µm are not determined correctly because of the lower analytical resolution (10x10 µm pixel size) used during field scans.

Grain size distribution data and diagrams for sphalerite are presented in section C.2.1, page 529 (PMA) and section C.7.8, page 676 (field scan). PMA analyses suggest that ore from the eastern and central part of 5/5-ST contains slightly coarser sphalerite at a P80 of ~38 µm (P80 defined as 80 wt% of all grains of a particular mineral phase are smaller than the given grain size) compared to 5/5-W with a P80 of ~30 µm. The average grain size, defined as P50, yields ~20 µm for 5/5-E and 5/5-C but is ~12-13 µm for 5/5-W. Individual samples from eastern and western stope parts feature rather consistent grain size distributions, whereas those from 5/5-C are slightly different and reflect the transition from pyrrhotite- to pyrite-dominated ore zones. Field scan data showed that sphalerite in massive pyrrhotitic ore is slightly coarser compared to massive pyritic and semi-massive ore. Overall, grain sizes range between ~35 (P10) and ~500 µm (P90).

Galena grain size distributions based on PMA showed similar trends as sphalerite (section C.3.1, page 563 for PMA and section C.7.8, page 676 for field scan). P80 values range between ~30 and 40 µm for all stope parts.
with larger grain sizes observed in 5/5-E (figure 6.21). Average grain sizes (P50) are rather consistent and range between 12 to 14 µm. Individual samples of the three stope parts feature grain size distributions which are not as uniform as those of sphalerite, indicating a pronounced heterogeneity of galena grain sizes. Particle images of galena (appendix section C.3.1, page 563) show the cubic breaking characteristics of galena caused by its perfect cleavages. ESD grain sizes calculated based on field scan results show that galena in massive Py ore is significantly smaller (P50 of 35 µm) compared to massive Po (P50 of 60 µm) and semi-massive ore types (P50 of 80 µm). Approximately 25 wt% galena is smaller than 20 µm. The upper grain sizes (P90) range between ~80 (Py) and 800 µm (Po).

Similar characteristics were observed for chalcopyrite grain size distributions based on PMA results (section C.4.1, page 599 for PMA and section C.7.8, page 676 for field scan). The P80s feature grain sizes just below 38 µm for 5/5-E and 5/5-C but is with ~20 µm significantly lower for 5/5-W. Average grain sizes (P50) are ~15 µm for eastern and central stope parts and ~11 µm in the west. According to field scan results, the different ore types feature rather similar chalcopyrite grain size distributions. However, the quantity of fine mineral grains (<20 µm) is with ~44 wt% (Py) and ~38 wt% (Po) significantly higher in massive compared to semi-massive ore with only ~27 wt%. The sizes of the largest observed grains range between 60 (Py) and 100 µm (SiPy and SiPo).

Grain sizes of pyrite are rather uniform throughout the 5/5-ST with a P80 of ~50 µm and a P50 ranging between ~23 and ~28 µm (section C.5.1, page 631) according to PMA analysis. Pyrite contained in samples from 5/5-W is slightly smaller grained compared to the other stope parts. Field scan results (section C.7.8, page 676) showed that pyrite contained in massive pyritic ore is much coarser compared to pyrrhotite-dominated ore. The large grains or aggregates predominantly consist of pyrite type A and B as described earlier. Pyrite grain sizes range between ~60 (P10) and ~500 µm (P90) in massive pyrrhotitic ore, and between ~80 (P10) and in excess of 1500 µm (P90) in massive pyritic ore. Field scan grain size distribution data for pyrite type A and B are presented in figure 6.22. Grain sizes of pyrite type A are variable. It commonly forms large aggregates (see section 4.1.1) as indicated by a minimum grain size (P10) between 150 and 300 µm. Pyrite type-B tends to by smaller in pyritic ore compared to pyrrhotitic ore with grain sizes ranging between 45 (P10) to 200 µm (P90) and 75 (P10) to 250 µm (P90), respectively.

Only minor pyrrhotite occurs in pyrite-dominated ore and features small grain sizes at a P80 below ~9 µm (PMA, section C.5.2, page 633) or below ~35 µm (field scan, section C.7.8, page 676). The eastern and central stope parts contain significant quantities of pyrrhotitic ore, but pyrrhotite, which is rather coarse at a P80 of ~50 µm. The overall grain size range of pyrrhotite in Po ore is defined by a P10 of ~30 µm and a P90 above 1000 µm. The large values are likely caused by compounds

Figure 6.22: Grain size distributions of pyrite type A and B for different ore types. Data based on field scan results.
of pyrrhotite and do not represent individual pyrrhotite grains.

Silver phases preferably occur in peripheral zones of the orebody (chapter 4 and chapter 5). Those zones are predominantly composed of pyritic massive and semi-massive ore. The number of particles containing Ag phases is lower in the pyrrhotite dominated 5/5-E zone (appendix section C.1.2, page 504). Grain size distributions show that Ag phases are significantly coarser in those peripheral zones (5/5-C and 5/5-W) at P80s ranging between ~7 and ~14 µm (figure 6.24). Most Ag phases observed in samples from the 5/5-E, i.e. in excess of 90 wt%, are smaller than 1 µm. Long-term plant performance data showed that Ag recoveries drop significantly for particles small than 5 µm (figure 6.23). According to grain size distributions, only ore sourced from western and potentially central stope parts will feature good Ag recoveries.

Grain size distributions calculated based on field scan data (section C.7.8, page 676) indicate a significant shift to coarser grains in pyritic ore (~50 wt% Ag-Tet smaller than 20 µm) relative to pyrrhotitic ore (~94 wt% Ag-Tet smaller than 20 µm). It needs to be kept in mind that ESD grain sizes based on field scans are significantly overestimated and should not be regarded as realistic values (see section 6.6.2).

Three out of the four valuable mineral phases at Elura feature rather similar grain size distribution trends in respect to the investigated stope parts. Results show that ore sourced from 5/5-E and 5/5-C contains coarser sphalerite, galena and chalcopyrite than the western stope part. Ore sourced from the latter location will most probably feature relatively worse grade/recovery performance during min-

---

Figure 6.24: Grain size distributions of argentian tetrahedrite for the three 5/5 Stope parts. Data based on PMA.

Figure 6.23: Long-term Ag recoveries for different particle size fractions achieved at the mineral processing plant. Data supplied by CBH Resources Ltd and pers. comm. Andrew McCallum, 2010. Dashed red lines are median recoveries.
eral processing. An inverse characteristic is observed for Ag phases, which are significantly coarser in western and central stoping areas.

### 6.6.4 Particle liberation

Particle liberation is investigated for sphalerite, galena, chalcopyrite and Ag-phases. Results for the latter mineral phase may be unreliable due to its low abundance. Particle liberation is calculated as area percentage (area%) of a particular mineral phase contained in particles, i.e. liberation of 60% for mineral-X implies that 60 area% of a 2-dimensional particle cross-section consists of this particular mineral phase (see particle image as example in appendix section C.2.3, page 534). A liberation grade of 90% is commonly considered as best case and referred to as fully liberated. Particle liberation, as the name implies, can only be calculated based on PMA of broken sample material.

#### Sphalerite

Analytical results for sphalerite are presented in section C.2.3, page 534. Most of the Zn (in excess of 75%) is contained in the particle size fraction (abbrev. PS) below 38 \( \mu \)m. All stope parts contain about the same quantities of Zn. Sphalerite froth flotation at the Elura processing plant is most efficient at particle sizes between ~5 to 20 \( \mu \)m. Coarse particles are subject to a secondary grinding step via wet quartz sand grinding with a P100 of 30 \( \mu \)m. The P80 of the zinc concentrate yields particle sizes between 20 to 25 \( \mu \)m, indicative for the importance of the secondary grinding procedure. The stage crushing technique used for sample preparation in this study may deliver worse particle liberation compared to that achieved via secondary grinding. QEMSCAN® results may underestimate real particle liberation, thus should only be used to assess relative changes between the different stope parts.

Results show that sphalerite in ore from the eastern (5/5-E) and central (5/5-C) stope parts is highly liberated with approximately 67 wt% sphalerite above 90% (figure 6.25). Liberation characteristics of those to stope parts are almost identical. A significant drop by 10% to ~57 wt% sphalerite (fully liberated) is observed for the western, pyrite-dominated stope part (5/5-W). Liberation of individual PS fractions indicate that the target PS (<20 \( \mu \)m) is highly liberated in 5/5-E and 5/5-C but 10% lower in 5/5-W. Within the PS +20/-38 \( \mu \)m, approximately 65-70 wt% in 5/5-E and 5/5-C, but only 40 wt% sphalerite in 5/5-W is fully liberated.

The grain size distribution of unliberated sphalerite (less than 90%) show a significant shift to smaller sizes for ore from the western stope part. If particle sizes are further reduced via secondary grinding down to 20 \( \mu \)m, ~30 wt% of unliberated sphalerite may be recovered in 5/5-W and ~50 wt% in 5/5-E and 5/5-C. The achieved total amount of fully liberated sphalerite after primary and secondary grinding would be in the order of ~70 wt% for 5/5-W, ~85 wt% for 5/5-E and 5/5-C.

The theoretical recovery and zinc concentrate quality was calculated based on real long-term plant performance/recovery data for individual PS and their corresponding particle liberation of this study (see appendix section C.2.3, page 534). Based on this data, the entire 5/5-stope yields a recovery rate of 75 wt% Zn and a theoretical concentrate quality of 57 wt% Zn.
Galena

Galena is not subject to secondary grinding because of the risk of over-grinding and the consequence of metal losses due to entrainment and sliming. Calculations of galena particle liberation are shown in section C.3.2, page 566.

Particle sizes between ~5 and 38 µm are the main target for galena froth flotation at the Elura Mine (figure 6.26). According to QEMSCAN® results, approximately 80 wt% Pb is contained in this target group. A slight decrease of Pb contained in the 5/5-C is observed compared to 5/5-E and 5/5-W. In contrast to sphalerite, galena particle liberation characteristics are similar for ore sourced from the central and western stope parts (figure 6.27). Approximately 10-12 wt% less galena is fully liberated (>90%) for those two stope parts compared to 5/5-E that yields ~53 wt% fully liberated galena. If a Pb recovery rate of 70% is sought to be achieved, particles featuring liberation grades between ~80% (5/5-E) and ~55% (5/5-W) would need to be recovered. Figure 6.29 shows particle images at different galena liberation grades and grouped in three particle size fractions. Liberation is lower for all PS fractions of ore from 5/5-W with the exception of the fine PS +3/-5 µm. As shown in the previous section, ore from 5/5-W is commonly much finer grained compared to the other stope parts. The smaller grain sizes are the most likely explanation for better galena liberation with PS +3/-5 µm. Galena grain size distributions of unliberated particles suggest that a substantial grain size reduction down to 10 µm would be needed in order to achieve a significant increase of liberation for 50 wt% of unliberated galena.

Long-term plant performance data shows that high Pb recovery rates are achieved for PS +5/-38 µm, significantly decreasing for smaller and
larger particles (figure 6.26). Theoretical recovery rates and Pb concentrate qualities are calculated based on achieved real plan performance and calculated liberation data (figure 6.28). Chalcopyrite is included in the calculation as it is initially recovered along with galena. Results suggest an overall recovery rate for galena between 74 and 77%, considering the fine particle size +0/-3 µm as 100% loss or at the long-term recovery rate of 36%, respectively. Calculated copper recoveries range between 57 and 60% and are within the observed long-term achieved copper recoveries range of 55 to 61% (pers. comm. Andrew McCallum, 2010). The theoretical Pb concentrate quality, including particles recovered for copper, yields concentrations of 73 wt% Pb and 2 wt% Cu. The results confirm that significantly higher concentrate qualities should be achieved at the given recovery rates as suggested by the theoretical grade/recovery diagram. Sample preparation may, however, cause unrealistically good particle liberation for galena as already discussed in section 6.6.1.

**Chalcopyrite**

QEMSCAN® results are shown in section C.4.3, page 604. Approximately 75 wt% of total Cu is contained in particles below 38 µm. The relative Cu contribution between stope parts slightly decreases from 5/5-E (42%) to 5/5-C (32%) and 5/5-W (26%). Between 60 and 65 wt% chalcopyrite is contained in fully liberated particles in 5/5-C and 5/5-E, whereas only 50 wt% is fully liberated in 5/5-W. Comparison of achieved long-term plant recovery rates with liberation data suggests that only fully liberated particles are recovered (i.e. liberation between 92 and 97%). Calculated theoretical copper recovery rates based on liberation data has already been discussed along with galena in the previous paragraph. Grain size reduction to 20 µm via secondary grinding may liberated 20 to 30 wt% of the initially unliberated particles containing chalcopyrite.

**Argentian tetrahedrite**

Liberation data for Ag-Tet is presented in section C.6.3, page 644. The pyrite-dominated western part of the 5/5 stope contains most Ag (66%). Particles smaller than 38 µm carry on average ~83 wt%. Only approximately 30 wt% of all particles that contain Ag-Tet are fully liberated (>90%). Despite the significantly coarser grain sizes of Ag-Tet from 5/5-W compared to the other stope parts, liberation is poor. It is not feasible to increase particle liberation for Ag-Tet via grain size reduction because of its fine-grained nature. Silver is recovered along with Pb, representing a beneficial element in the concentrate. Apart from fully liberated particles, Ag-Tet may only be recovered if associated with galena. Mineral associations are investigated as part of this study and described later in the text.

**6.6.5 Free particle surface**

Calculated particle liberation based on area percentage is a common parameter used for geometallurgical ore characterisation. For some mineral separation techniques, in particular for differential froth flotation, the free particle surface of minerals is important as more bubble-mineral interfaces may be formed if free surface is higher. Free surface data is estimated from the 2-dimensional particle cross sections. If area specific liberation of a certain mineral phase is high, its free particle surface will be high as well. However, if liberation is low,
the free particle surface may still be high if the mineral phase preferably occurs at the particle’s rim. Such particles contain low quantities of the valuable mineral phase and, if recovered, may cause dilution and decrease of the mineral concentrate quality. Whether or not this effect has a major effect depends on the ore’s breaking characteristic, thus, its texture defined by shape and sizes of mineral grains as well as the nature of their intergrowths.

Free particle surfaces are investigated as part of this study and compared to particle liberation data in order to assess its effect on mineral processing of ore from Elura. Comparison of QEMSCAN® with long-term plant performance for individual particle size fractions are used to estimate free particle surfaces that are necessary for mineral recovery. Based on this information, theoretical recovery rates and concentration qualities are calculated in a similar way, as it had been done based on particle liberation data.

Calculated free particle surface data for sphalerite is presented in section C.2.4, page 545, for galena in section C.3.3, page 577 and for chalcopyrite in section C.4.4, page 614.

Free particle surface characteristics are commonly similar compared to particle liberation with particles from 5/5-W samples featuring lower free surface than those from 5/5-E. Approximately 75 wt% sphalerite is contained in particles with a free sphalerite surface of 77% in 5/5-E and 5/5-C but only 60% in 5/5-W. Galena in ore from 5/5-E has the highest free surface with 75 wt% contained in particles characterised by a free galena surface in excess of 60%. Free surface of particles from the central and western stope parts are lower with 75 wt% galena contained in particles with a free surface ranging between 40 and 45%. Free particle surface of chalcopyrite is similar to sphalerite with 75 wt% contained in particle characterised by free surfaces of 60% (5/5-E and 5/5-C) and 45% (5/5-W).

Calculated theoretical recovery rates and concentrate qualities are very similar to those calculated based on particle liberation data. The amount of metal contained in concentrates at respective recovery rates are 57 wt% Zn at 74% for zinc concentrate, 72 wt% Pb at 77% for lead concentrate and 2 wt% Cu at 64% for copper contained in lead concentrate. The results sug-
suggest that ore textures and breaking characteristics have no significant effect on free particle surfaces, recovery rates or concentrate quality.

Three recovery case scenarios were calculated based on three particle subpopulations, which were arbitrarily defined via visual inspection of actual particle images of different PS fractions and free particle surfaces (see figure 6.30 for galena, appendix section C.2.4 for sphalerite, or appendix section C.4.4 for chalcopyrite). Theoretical recovery rates and concentrate grades were calculated for each of the recovery cases. Calculations were performed twice, i.e., for an overall particle size fraction PS +3/-80 µm and PS +3/-53 µm. Only the latter will be summarised in the following as it reflects the target particle size range in mineral processing at Elura.

The results for sphalerite, galena and chalcopyrite are presented in appendix section C.2.4, appendix section C.3.3 and appendix section C.4.4, respectively. Zinc recoveries for the three case scenarios are 68% for case I, 76% for case II and 86% for case III. The latter recovery case is closest to the real plant target recovery rate, which commonly lies above 80%. The calculated theoretical concentrate contains approximately 54 wt% Zn. The results suggest that ore from the 5/5 stope will most probably perform within the plant target recovery range and will lead to a concentrate quality above 50 wt% contained zinc.

The calculated lead recoveries for three different particle subpopulations range between 43% (case I) and 78% (case III). Plant target recoveries are between 72 and 76%, thus, case II with a recovery of 71% is close to this range. This particle recovery scenario resulted in a theoretical concentrate that contains an estimated 80 wt% Pb. Even in a more optimistic recovery scenario as defined by case III, the concentrate would still feature high quality with 78 wt% contained Pb.

As copper is recovered along with galena, the calculation of case scenarios does not reflect Cu concentrate qualities. However, they will indi-
cate how extensive the Pb concentrate may be diluted with other mineral phases caused by recovered chalcopyrite-containing particles. The case scenarios yield Cu recovery rates between 66 and 82%. Maximum achieved long-term average Cu recoveries are in the order of 61% (pers. comm. Andrew McCallum 2010). Even though slightly higher, real plant performance are best met by case I. A rather high Cu concentrate quality is defined by the particle subpopulation of this particular recovery case consisting in excess of 98 wt% chalcopyrite. The results suggest that dilution of the Pb concentrate consequently to chalcopyrite recovery is negligible.

Galena and chalcopyrite are separated via Pb rougher and scavenger flotation cells prior to Zn flotation. Sphalerite associated with particles recovered during this processing stage may lead to losses of Zn. Lead and Cu concentrate compositions of the three recovery case scenarios for galena and chalcopyrite were used to estimate such potential metal losses. For cases I to III, Pb concentrate contains between 0.1 to 0.6 wt% Zn and Cu concentrate between 0.1 and 1.1 wt% Zn. The Zn concentration in Pb concentrate is low and does not represent a significant loss. Zinc recovered along with Cu is higher, however, considering the low abundance of chalcopyrite (average Cu concentration in ore is 0.2 wt%), Zn loss is negligible. It needs to be stressed that this is a rough qualitative estimation and does not represent actual mass flows within the processing stream. Real Zn losses may therefore be higher.

6.6.6 Mineral associations and locking

Particle mineral associations were investigated in order to assess mineral intergrowths and locking characteristics of the valuable sulphide phases. Results based on PMA are presented in section C.2.5, page 555 for sphalerite, section C.3.4, page 588 for galena, section C.4.5, page 623 for chalcopyrite and section C.6.4, page 649 for argentian tetrahedrite. Associations were calculated based on mineral area percentage (abbrev. area%). Particles feature a binary mineral association if 95 area% of the particle cross-section consists of two minerals (e.g. Bn: sphalerite-pyrite). Ternary mineral association is defined analogue but allowing the intergrowth of three phases (e.g. Tn: sphalerite-pyrite-pyrrhotite). Remaining unclassified particles, i.e. not assigned to binary or ternary categories, are classified as complex mineral associations, sub-divided into two categories, one containing in excess the other less than 10 wt% of the investigated mineral phase (e.g. sphalerite). Pyrite and pyrrhotite are combined as iron sulphide and treated as one mineral phase in ternary mineral associations.

Only particles characterised by liberation grades of less than 90% (<90 area% of a particular mineral phase) are investigated. It needs to be kept in mind that the results will only estimate the quantity of metal contained in particles of certain mineral association categories. It, however, does not quantify the liberation grade of these particles. For instance, two hypothetical particles may feature a binary association between sphalerite and pyrite (both phases >95 area%, with area% of sphalerite <90). One of those particles may consist of 80 area% sphalerite, equivalent to a liberation grade of 80%, and 17 area% pyrite. Such a particle would feature a relatively high liberation and if recovered would cause minor dilution of the mineral concentrate. A second particle may contain the same phases but with the inverse sphalerite and pyrite area%. This particle, if recovered, would in contrast cause significant dilution due to the high amount of pyrite intergrown with sphalerite. In other words, if 20 wt% sphalerite is contained in binary association with pyrite, 15 wt% may be contained in highly liberated particles. Therefore, important mineral associations that potentially lock-up significant metal should be assessed with the consideration of particle liberation of this particular mineral association category.

Field scan data cannot be used to assess mineral associations via the same approach because it is not based on broken sample material. However, by the determination of relative pixel adjacencies, mineral associations can be esti-
6.6 QEMSCAN® results from PMA and field scans

Transitions between neighbouring mineral phases are calculated via scanning the sample image horizontally. Counts are subsequently normalised to 100% as relative transitions and reflect relative mineral associations.

**Sphalerite**

Based on PMA, binaries with pyrite and pyrrhotite are the most important associations with sphalerite and contain ~13 and ~7 wt% Zn in the respective particle subpopulation. Ternary associations with iron sulphides (pyrite and pyrrhotite) and galena host approximately 4 wt% Zn. Only 2.9 wt% Zn is locked up in complex association (particle with >10 wt% sphalerite). In excess of 40% of those 2.9 wt% Zn contained in the complex association category is caused by intergrowths with iron sulphides. No significant variation is observed between stope parts.

Iron sulphides in binary association with sphalerite contain ~20 wt% Zn. Approximately half of the Zn metal is contained in relatively liberated particles (>60% liberation), causing only limited dilution. Nevertheless, if lower mineral concentrate grade is observed, it is likely a consequence of elevated content of iron sulphides and to a lesser extent galena.

The estimation of mineral associations of sphalerite based on field scan data is in agreement with PMA results with iron sulphides and galena being most important. The results, however, suggest a significantly higher association with non-sulphide gangue phases (NSG) for semi-massive as well as massive pyrrhotitic ore. The difference is explained by good separation of NSG and sulphides during grinding.

**Galena**

Binaries with iron sulphides (pyrite and pyrrhotite) and with sphalerite, as well as ternary associations with iron sulphides and NSG were identified as the most important mineral associations. These categories contain ~28, ~7 and ~4 wt% Pb, respectively. A significant amount of Pb (~13 wt%) is locked up in complex association in particles containing >10 wt% galena. Approximately 80% of this metal is linked to associations with iron sulphides.

Particle liberation data of the binary galena-iron sulphides show that most of the Pb is contained in relatively liberated particles (liberation >60%) with ~17 out of a total of 28 wt%. Particles in complex locking feature lower galena liberation with only ~5 out of a total of 15 wt% Pb contained in relatively liberated particles (liberation >60%). Figure 6.31 shows the four most important mineral associations of galena in particle images. Calculations from field scan data showed similar results but suggests that mineral associations with sphalerite may be higher in pyrrhotite-dominated ore relative to other ore types.

**Chalcopyrite**

Comparison of long-term plan performance with QEMSCAN® data shows that only highly liberated particles containing more than 90 area% chalcopyrite may be recovered. The investigation of mineral associations is thus needless for geometallurgical characterisation as only near-pure chalcopyrite particles are recovered. Microscopic observations indicate an affinity of chalcopyrite to NSG phases. Neither PMA nor field scan confirmed this observation. The most important mineral associations with chalcopyrite are binaries with pyrite (~12 wt% Cu) and sphalerite (~5 wt% Cu), in ternary association with iron sulphides and NSG (~5 wt%), and in complex locking (~9 wt% Cu). Association with pyrite and sphalerite are in turn most important in the complex locking category.
Argentian tetrahedrite

Mineral associations of silver-bearing mineral phases are highly important for mineral processing at Elura, because argentian tetrahedrite (Ag-Tet) is recovered along with galena. As described earlier, Ag-Tet is very fine grained and poorly liberated. If Ag-Tet is preferably associated with other phases than galena, it will be rejected during mineral processing and lost to the tailings.

Due to the low abundance of particles containing Ag-Tet, relative transitions were used to assess mineral associations for PMA and field scan data. PMA results show that only ~12% of the transitions are between Ag-Tet and galena phases. The most important associations are with NSG phases (~46%), sphalerite (~19%) and iron sulphides (~17%). Field scan data give similar results, although indicating that associations between galena and Ag-Tet are slightly higher compared to PMA result. A maximum relative transition of 20% can be observed for massive pyritic ore during field scans.

According to relative transition data, Ag recovery is likely to be poor due to the preferred association of Ag-Tet with mineral phases other than galena.

Figure 6.31: The four most important mineral associations of galena, grouped according to Pb contained in those particles.
Chapter 7

Interpretation and conclusions

Since its discovery, several scientists have studied the Elura orebody and other deposits in the Cobar region. Their findings, conclusions and proposed genetic models are summarised in chapter 3 on page 50. The aim of this study was to investigate geochemical, mineralogical, mineral chemical and textural ore characteristics on a deposit-wide scale based on a sample set covering the entire extent of the orebody and all different ore types. Geometallurgical ore characterisation was undertaken on a smaller scale, i.e. proposed stopping area, in order to test whether a prediction in respect to mineral processing characteristics of ore sourced from different stope parts can be made. Aspects important for ore genesis as well as applied to mineral processing are summarised in the following.

7.1 Aspects to the genesis of the Elura orebody

Elura’s sulphide ore features pronounced heterogeneity in respect to grain sizes, texture and chemical composition. In many areas, the sulphide body was affected by intense deformation, preserved as sulphide banding, grain size reduction and, in places, as mylonitic textures. Sulphide phases behave differently under deformational conditions. Chlorite thermometry is weak as it is well known that chlorite composition can be sensitive to many factors, not solely to temperature. Temperature values should always be taken with caution and only used in combination with alternative methods. Nevertheless, chlorite thermometry estimated a temperature range between 314 and 343 °C, similar to temperature conditions proposed for the mineralising fluid by other studies. Under elevated temperature conditions >300 °C, galena and pyrrhotite are ductile and mobile; chalcopyrite is relative mobile. Sphalerite and pyrite are brittle and are not remobilised (e.g. Marshall and Gilligan, 1993). Ore textures developed consequently to these different mineral characteristics. Sulphide banding is commonly defined by zones enriched in sphalerite and/or pyrite and those enriched in galena, pyrrhotite and chalcopyrite. Rounded clasts of sphalerite may occur in mylonitic zones. Galena and chalcopyrite feature significant grain size variations. Large grains formed due to remobilisation into fracture zones, commonly hosted by pyrite and/or wall rock fragments.

Primary mineral parageneses are preserved in undeformed massive sulphide ore. Intimate, myrmekitic-like intergrowths of sphalerite, galena and pyrrhotite in pyrrhotite-dominated ore zones in central parts of individual sulphide pipes show their cogenetic nature. Pyrite-dominated ore exclusively occurs in peripheral areas of the orebody and is best developed in the upper apophysis of the main lode zone, forming an outer shell enclosing pyrrhotitic ore. In these pyritic zones, base metal sulphides occur interstitial to and fill fractures or vughs of pyrite, partially replacing it. Replacement of pyrrhotite by base metal sulphides is subordinate.
Four pyrite generations were identified in this study. Fine grained sub- to anhedral, colloform, frambooidal and cloudy pyrite A formed in an early, most likely lower temperature stage of an evolving hydrothermal system. Increasing fluid temperatures lead to the formation of coarse sub- to euhedral pyrite B, to some extent caused by the re-crystallisation of pyrite A. Both pyrite varieties formed prior to the base metal mineralisation, which is dominated by pyrrhotite, indicative for a rather reducing hydrothermal fluid and sulphur activities that favour the precipitation of mono-sulphur sulphides. Only minor syn-base metal sulphide pyrite C formed and is, in places, intimately intergrown with co-genetic magnetite. Pyrite D is unrelated to and formed after the base metal mineralising stage. Most of the total pyrite mass contained in the Elura orebody formed prior to base metal sulphides and pyrrhotite. Sphalerite geobarometry was unsuccessful and confirmed disequilibrium between pyrite and sphalerite/pyrrhotite.

Iron-rich sphalerite (overall max. 8.22 wt%) is common in lower and pyrrhotite-dominated parts of the orebody. A shift to lower Fe content (overall min. 2.41 wt%) is present in sphalerite from the upper main lode zone and, in places, in peripheral pyritic zones. The lack of pyrrhotite in those zones, the replacement of pyrite and the lower Fe-content in sphalerite reflect the changing fluid chemistry characterised by a decrease of FeS activity as pyrrhotite precipitated in central ore zones.

None of the investigated samples contained intact fluid inclusions in sphalerite. This observation is not surprising considering that deformation of the orebody has occurred. Sphalerite, a brittle sulphide phase, was micro-fractured allowing fluid and gas phases to escape. The presence of organic matter and long-chain n-alkanes suggest that the mineralising fluid contained hydrocarbons.

The Elura orebody features a pronounced vertical geochemical zonation. Copper and to a lesser extent Cd and Co are preferably contained in pyrrhotite-dominated ore and generally enriched towards increasing depth. Their enrichment is caused by early sulphide precipitation at initially higher fluid temperatures. Elements enriched in the upper and peripheral zones of the mineralisation (e.g. Ag, Sb, Tl, Hg) remained in solution as the fluid temperatures decreased. Subsequently, these elements became enriched in areas distant to the influx zones of the metal-bearing fluid. Protracted and repeated fluid pulses most probably caused internal zone refinement dissolution-reprecipitation processes, similar to that observed for VHMS deposits and amplified the vertical element zonation.

Zinc isotope composition of sphalerite ($\delta^{66}_{\text{Zn}}$, $^0_{\text{JMC}}$ 0.220-0.450‰) suggests average continental crust as metal source and that the source reservoir had been effectively leached by the hydrothermal fluid. Vertical isotope fractionation trends within the orebody are likely caused by syngenetic Rayleigh fractionation, which was most probably aided by vertical temperature gradients. Initial light crustal isotope signatures define two major zones of fluid influx. Both zones, one at the base of the entire orebody and a second at the transition between the lower and upper main lode zones, feature coinciding enrichments in Cu, in agreement with earlier described internal refinement mechanism and fluid temperature gradients. The fluid became heavier in isotopic composition as it evolved and cooled during its ascent to higher levels in the mineralisation.

The occurrence of the second fluid influx zone is explained by temporal differences between the formation of the lower and the upper parts of the mineralisation. The geometry of the orebody itself suggests some differences in the formation of the large southernmost main lode zone and the smaller northern ore zones. Only the former most prominent ore shoot intersects the upper laminated unit, which confines all northern ore zones. The Elura orebody may have developed in two stages. As the basin inversion commenced, dilation was initially focussed along a transpressional fault corridor. Zones of pronounced fracture-induced permeability occurred in sandstone-rich sediment sequences and were restrained by horizons significantly enriched in silt- and mudstone (i.e. the
upper and lower laminated units). The northern ore zones and the preliminary lower main lode formed. A change in the regional stress regime during progressive basin inversion caused the development of major dilation and jogs at the southern end of the orebody. Subsequently, the lower main lode was further enlarged and the upper main lode formed.

Bismuth and Bi-bearing mineral phases are common minor constitutes in ore from southern deposits in the Cobar region, e.g. the New Cobar and the New Occidental deposits. A sulphur-poor, basement-derived hydrothermal fluid has been proposed as metal-carrying media in previous studies. Significantly elevated concentrations of Bi, Se and Te were present only in the lowermost main lode ore zone and reflect a change in fluid chemistry and temperature (Maslennikov et al., 2009).

These element enrichments are most probably caused by an evolving hydrothermal fluid, featuring a decrease in sulphur activity, an increase in oxygen fugacity and temperature over time. The observed close genetic relationship between pyrrhotite, pyrite and magnetite, despite rare, confirms this proposition. The evolving fluid introduced elements such as Bi, Se and Te during the latest stages of hydrothermal activity. This fluid features compositional similarities to the hydrothermal fluid proposed to have formed Cu-Au and Au-dominated deposits south of Cobar (e.g. the New Cobar and the New Occidental).

David (2005, 2008) compiled and presented Pb isotope data of samples taken from the upper (above approx. 9600 RL) and the lower parts of the Elura orebody (figure 106 on page 152 in David, 2005). A well-defined cluster of consistent radiogenic Pb is present within the lower mineralisation. Other samples, most of them sourced from the upper main lode zone, feature a trail of Pb isotope compositions originating from the data cluster towards less radiogenic Pb. Previous studies proposed two contrasting hydrothermal fluids responsible for the genesis of the Cobar deposits: (a) a reducing basinal fluid, responsible for Pb-Zn-dominated deposits. This fluid was proposed to be slightly more radiogenic than (b) an oxidising basement-derived fluid. The latter fluid led to the formation of Cu- and Au-dominated ore systems. It has been shown by this study that the reducing hydrothermal fluid shifted to higher oxygen fugacities during the latest stages of the mineralising event. The changing fluid characteristics suggest an increased proportion of basement-derived, less radiogenic fluid. The less radiogenic Pb signatures are exclusively observed in the upper main lode zone. The changing fluid composition thereby confirms the proposed two stage genetic model with an initial formation of the lower mineralisation and later development of the upper main lode zone.

Changes in rare earth element signatures of different ore types are exclusively controlled by modal mineralogy, i.e. content of muscovite, chlorite and carbonate gangue phases. No local rare earth element remobilisation caused by extreme fluid-rock interaction is needed in order to explain observed characteristics. The pronounced positive Eu anomaly is indicative of a reducing fluid environment and/or temperatures in excess of 250 °C.

Assessment of mass/volume changes and element mobility via the isocon method showed that replacement of the host lithology was a negligible mechanism during ore formation. Sulphides, including pre-base metal sulphide pyrite, exclusively formed in sites of increased dilation and fracture-induced permeability. The only substantial replacement that occurred during base metal formation is that of pyrite.

Concentrations of most platinum group elements are close to average continental crust reservoir data. Platinum is relatively enriched, most probable due to the interaction of the ascending hydrothermal fluid with ferromanganese rich sediment sequences that contain elevated Pt concentrations compared to other platinum group elements.

Radiogenic age determination via the Re-Os isotope system resulted in an isochron age of 378 ±15 Ma, representing the first age constraint established via directly dating sulphides. The observed relatively non-radiogenic initial $\gamma_{Os}$ of ~170 is either caused by juvenile con-
7. INTERPRETATION AND CONCLUSIONS

tinental crust of the Lachlan Fold Belt as metal source or by a contribution of primitive mantle Os.

7.1.1 The modified genetic model for the Elura orebody

The Elura deposit is epigenetic and syn-deformational in nature, as it formed in zones of pronounced fracture-induced permeability in lithified turbiditic sedimentary strata. The ore formation took place at 378 ±15 Ma based on radiogenic Re-Os age determination. Sandstone-rich sequences reacted more brittle during deformation compared to mud- and siltstone-rich zones and were the preferable site for sulphide precipitation. The deposit is therefore at least to some extent lithologically controlled. The rather compact and competent limestone underneath the deposit may have aided the development of dilational zones.

Prior to the introduction of base metal sulphides, a massive pyrite body formed in zones of positive dilation during an early, low temperature stage as the hydrothermal system ramped up. Prolonged fault activity and subsequent fracturing allowed the ascending metal-bearing fluid to influx the earlier formed pyrite body. Decreasing fluid pressure and accompanying adiabatic cooling caused the breakdown of metalliferous complexes and initiated the precipitation of base metal sulphides and pyrrhotite. No evidence of fluid mixing as important mechanism for ore formation was identified in this study.

Repetitive fracturing events caused the accumulation of massive pyrrhotic ore in central core zones, representing major fluid conduits. The brittle character of pyrite caused the formation of reticular micro-fractures in the massive pyrite shell. The mineralising fluid migrated and infiltrated those zones, precipitated base metal sulphides and partially replaced earlier pyrite, causing the formation of pyrite dominated base metal ore.

Microscopic and geochemical investigations in this study showed that replacement of host sediments was a negligible mechanism during the mineralising event. Semi-massive ore formed during early fracturing events with sulphides precipitating and filling interstitial space between wall rock fragments. As fracturing and dilation continued, permeability was created internally of the existing sulphide body. Subsequently, massive sulphide ore without wall rock components formed in central ore zones.

Changing fluid temperatures, internal refinement via dissolution-reprecipitation of earlier formed mineral phases and a changing fluid composition over time caused the pronounced vertical mineralogical and geochemical zonation.

The Elura orebody developed in two separate mineralising events. Initially, lower parts of the mineralisation formed in zones of dilation along a transpressional fault corridor, followed by the formation of the upper and the upgrade of the lower main lode zone.

Upon cessation of the hydrothermal activity, compression continued during basin inversion. The relative ductile character of sulphides compared to lithified turbiditic sediments caused strain to be focussed within the orebody. The sulphide body was subsequently deformed and vertically elongated. Deformational-induced sulphide remobilisation likely upgraded and amplified vertical ore zonation in respect to ore mineralogy and geochemistry.

7.1.2 Differences to previous genetic models and important new aspects

The genetic model presented in this study is similar to epigenetic syn-deformational models proposed for the Elura and other Cobar deposits in previous studies (Schmidt, 1980, 1990; Glen, 1987; Brill, 1988; De Roo, 1989b; Hinman and Scott, 1990; Scott and Phillips, 1990; Perkins et al., 1994). Differences and important new aspects are briefly summarised in the following.

The genesis of the deposit is to some extent lithologically controlled. Mineralisation

* The modified genetic model is based on result of this study and with the consideration of proposed models of other authors presented in chapter 3 on page 50
occurred in two separate mineralising events. Zones of fracture-induced permeability were initially focussed in sediment sequences enriched in sandstone.

De Roo (1989b,a); Schmidt (1990) suggested the orebody formed predominantly via metasomatism and selective replacement of host sediments. Infill of sulphide in fracture-induced dilation was a subordinate mechanism during ore genesis. This study showed that replacement of the host lithology was negligible during ore formation. Sulphides, including pre-base metal sulphide pyrite, formed exclusively in sites of increased dilation and fracture-induced permeability. Prolonged periods of repetitive fracturing, fluid pulses and internal accretion of sulphides led to the concentric development and ore zonation of the Elura orebody.

The most recent genetic model was proposed by David (2008) suggesting an early mineralisation in semi-lithified sediments during basin formation followed by deformation and modification during basin inversion. Mixing of basement and basin derived fluids are an important mechanism in this model. The author argued that an epigenetic origin is unlikely as lithified sediments feature very low permeabilities, thus the mineralising fluid would have exclusively migrated along reactivated faults. Seismic pumping would have created large zones of hydrothermal brecciation, which, according to David (2008), do not exist at Elura. However, this thesis shows that breccia stringer-type mineralisation surrounding the orebody is in fact rather narrow in most upper ore zones, whereas at depth, it is large and forms a zone of pronounced brecciation, vein-style sulphide mineralisation and significant pervasive silicification. This zone was interpreted in this study as major fluid influx zone. The mineralising fluid ascended along reactivated faults and was channelled and focussed into zones of pronounced dilation. Such hydrothermal brecciation is obviously not possible in semi-lithified sediment sequences.

Stein et al. (2001) showed that the Re-Os system is remarkably robust and not disturbed even during intense deformation and high-grade thermal metamorphism. The Re-Os isochron age of $378 \pm 15$ Ma established in this study estimates the ore formation event and was most probably not affected by deformation. This age is in agreement with previous studies by Sun (2000); Sun et al. (2000) that suggested an ore formation age of 376-379 Ma based on $^{40}$Ar-$^{39}$Ar of sericite contained in massive sulphide samples. The Elura orebody is strongly structural controlled and ore textures clearly show that sulphides were fractured and/or remobilised during deformation. Whole rock dating via K-Ar and $^{40}$Ar-$^{39}$Ar suggested that basin inversion and main cleavage development in the Cobar Group sediments occurred at 395 to 400 Ma (Glen et al., 1992), around 20 Ma prior to ore formation. The age of the main cleavage development reflects the climax of the basin inversion. However, its overall duration is unknown. Sun (2000); Sun et al. (2000) identified a second major deformational event proximal to the Elura orebody at 385-389 Ma via $^{40}$Ar-$^{39}$Ar on cleavage-parallel sericite, suggesting that basin inversion and accompanying compression and fault activities continued over a prolonged period of time. Ages of ore genesis and host lithology clearly preclude a syn- but are in favour of an epigenetic, syn-deformational origin.

Ore textures show that the orebody had been to some extent remobilised, elongated and modified by deformation. Peripheral parts of the orebody are dominated by pyritic ore. Several studies including this one (e.g. De Roo, 1989b; Lawrie and Hinman, 1998; Sun, 2000) suggest that a pyritic body formed prior to the introduction of base metal sulphides. The concentric nature of the Elura orebody and its structural framework doesn’t support a syngenetic origin followed by deformational emplacement. Certain sulphide phases are easy to remobilise whereas others aren’t. The brittle nature of the outer pyritic ore shell makes it rather resistive to deformational remobilisation. If the Elura orebody formed in semi-lithified sediments and was subsequently remobilised and emplaced, the coherence between concentric pyrite and pyrrhotite dominated ore zones would have certainly been lost and a vertical mineralogical
zonation likely developed. Mobile phases (i.e. galena, pyrrhotite) would have travelled furthest, whereas pyrite and sphalerite as rather immobile phases would have became enriched in zone proximal to the initial mineralisation. Such a zonation is not present at Elura.

According to Lawrie and Hinman (1998), the Cobar deposits formed as a consequence of mixing of two contrasting fluids: a basement derived oxidising and a basinal reducing fluid. This study confirmed a change in the hydrothermal fluid’s oxygen fugacity, but no evidence has been found that favours fluid mixing as important mechanism for ore genesis. Sun (2000); Sun and Seccombe (2000); Jiang et al. (2000) reached similar conclusions based on hydrogen/oxygen isotope and fluid inclusion studies.

Observations made during this investigation suggest that the reducing hydrothermal fluid evolved temporal, characterised by an increase in its temperature and oxygen fugacity. The latter had a very minor impact on the mineralisation at Elura and represents the latest fluid pulses before the mineralising event ceased. Whether the changing fluid composition is, as suggested by Lawrie and Hinman (1998), caused by fluids sourced from different reservoirs (i.e. basement and basin) remains speculative. The reducing nature of the basinal fluid is caused by abundant organic matter contained within turbidites, particularly in mud- and siltstone beds that also contain syn- and diagenetic pyrite as sulphur source, and potentially as source for Zn, Pb, Cu and Au (Large et al., 2009). Organics were oxidised, thermally matured and converted to hydrocarbons during metamorphism. The presence of hydrocarbons has been verified by this and previous studies (e.g. Seccombe, 1990; Lawrie and Hinman, 1998; Lawrie et al., 1999; Jiang et al., 2000). The resulting reducing metalliferous pore fluids were expelled from those beds during diagenesis and metamorphosis and would have accumulated in sandstone rich sequences, which are characterised by higher permeability. Other parts of the strata within the Cobar Basin, e.g. the Mouramba Group sediments at its base, consist of outwash fans, shallow water clastics and locally of minor felsic volcanic. Such lithologies most probably contain less organics, feature increased permeability and may contain significant quantities of oxidising sulphate phases in evaporate sequences. Hydrothermal fluids that migrated through and interact with such lithologies would have become saline, leach metals, release sulphur due to sulphate reduction and, in doing so, the fluid’s oxygen fugacity would have increased.

It appears feasible that mineralising fluids which formed within the basin but at different stratigraphic positions also featured differences in their physico-chemical conditions (e.g. temperature, composition, pH, oxygen fugacity, etc.). In the case of Elura, as the deposit in highest stratigraphic position of all known deposits in the Cobar region, the hydrothermal mineralising fluid is predominantly sourced from aquifers within the turbiditic sedimentary sequence that contain reducing metalliferous brines. Only during the latest genetic stages, minor basal fluid characterised by elevated oxygen fugacity and increased temperatures ascended from deeper aquifers to the site of ore formation. Deposits that formed in deeper stratigraphic position (e.g. deposits of the Cobar Goldfield) are more proximal to aquifers at depth and thus dominated by hydrothermal fluids that feature elevated oxygen fugacities.
7.2 Important aspects for mineral processing

Zinc and, in particular, Pb recovery rates significantly fluctuated since production began in the early 1980s. Silver recoveries were commonly poor and rarely exceeded 50%. Recently, high concentration levels of Bi were encountered in lead concentrate. Part of this study was to investigate general and geometallurgical ore characteristics and to determine the cause for the mineral processing problems.

The integration of ore petrography and geochemistry highlighted the pronounced heterogeneity in respect to grain sizes, texture, mineral compositions and trace element geochemistry of Elura’s sulphide ore. Sulphide paragenesis is simple, comprising major pyrite, pyrrhotite, sphalerite and galena, minor marmatite, chalcopyrite and arsenopyrite, and trace tetrahedrite (± freibergite), native silver and magnetite. Tennantite was described as Ag-hosting mineral phase in previous publications but was not identified in this study. Silver concentrations in tetrahedrite range between ~19 to ~31 wt%. Some analyses with Ag concentrations in excess of 31 wt% feature stoichiometries similar to freibergite. Chalcopyrite is, apart from tetrahedrite, the only other Cu-bearing phase. Significant quantities of wall rock as fragments, in places strongly silicified and incorporated in sulphide groundmass, occurs in peripheral semi-massive (SiPy and SiPo) and breccia stringer-style (VEIN) ore types. Siderite and to a lesser extent quartz represent the most important non-sulphide gangue phases in massive ore types. Quartz is slightly more abundant in pyrite-dominated massive ore.

Based on median concentrations, massive and semi-massive ore contains in the order of 9.6 to 10.2 wt% Zn and 5.1 to 5.9 wt% Pb. The highest Zn concentration (16.4 wt%) was determined in massive pyrrhotite ore, whereas massive pyritic ore contained maximum Pb (30.3 wt%). The large concentration range of Zn (4.6-16.4 wt%) and in particular of Pb (1.7-30.3 wt%) reflect the heterogenic textural and compositional nature of Elura’s ore.

Pronounced grain size variability of sphalerite and especially galena and the subsequent decreased particle liberation were identified as the main reasons for fluctuating Zn and Pb metal recovery rates. Base metal sulphides in massive pyritic ore are commonly characterised by a reticulated texture, where they fill fractures and interstitial space in compact but fractured pyrite. Sphalerite and galena are generally much finer grained in this ore type compared to massive pyrrhotite ore and rather variable in semi-massive ore types. Galena, however, may occur as coarse patches in excess of 100 µm throughout the deposit and in all different ore types as it was, in places, strongly remobilised by deformational force. Grain sizes of chalcopyrite are as variable as those of galena.

The reasons for poor Ag recoveries are because grain sizes of the identified Ag-phases (i.e. argentian-tetrahedrite and silver) are very small in central pyrrhotite-dominated zones of the Elura orebody with approximately 70 to 98 wt% smaller than 5 µm. Particle liberation will be poor for such small grains and entrainment during flotation significant. In peripheral semi-massive and massive pyrite-dominated areas, grain sizes are larger and reach maxima in the upper most area of the main lode zone up to 200 µm in size.

As Ag-phases report to the lead concentrate and upgrade its value, their associations with other mineral phases are of great importance. Given that grain sizes are small and particle liberation is poor, Ag-phases may still be recovered if intergrown with galena, but rejected to tailings if, for instance, associated with pyrite or non-sulphide gangue phases. Intergrowths with pyrite in pyrite-dominated ore and with non-sulphide gangue, predominantly Fe-carbonates, in pyrrhotite-dominated ore represent by far the most important mineral associations for Ag-phases. Abundant associations with galena are limited to the uppermost parts of the main lode zone and, in places, in the uppermost areas of the northern ore zones.

High Ag concentration levels up to ~2,300 ppm were present in galena from
7. INTERPRETATION AND CONCLUSIONS

the upper- and lowermost areas of the main lode zone, caused by galena-miargyrite and galena-matildite solid solutions, respectively. Galena recovered from those ore zones would benefit Ag recoveries, although having a negative effect on the concentrate quality in the case of galena-matildite due to the significant Bi content.

Alteration of argentian-tetrahedrite to native silver and chalcopyrite is widespread. Intermediate stoichiometric compositions, deviating from ideal tetrahedrite, are common. Little is known about flotation characteristics of Ag-mineral phases in general (Bulatovic, 2007) and presumably even less for those of alteration products. A change of flotation/activation characteristics of altered tetrahedrite may be another cause for low silver recoveries.

Galena was identified as the only important mineral phase containing Bi with a maximum detected concentration of 5,645 ppm and caused by matildite-galena solid solution. High Bi concentrations are limited to lowermost main lode ore zone. Ore sourced from this area will inevitably cause significant Bi concentrations in lead concentrate. The only feasible strategy to control concentrate quality is ore blending.

Manganese concentrations in sphalerite are low (<300 ppm) throughout the deposit. Mercury is another important penalty element for zinc concentrate and was determined at concentrations up to 100 ppm but is generally contained at concentrations in the order of 25 ppm (overall median).

Arsenic is a penalty element for concentrates. Elevated arsenopyrite content in ore may lead to poorer concentrate qualities if not sufficiently depressed during froth flotation. Arsenopyrite features a clear affinity to pyrite-dominated ore with a maximum determined As concentration of 1.5 wt%. Consistently high As concentration were present throughout the upper main lode ore zone. Ore from this part of the mineralisation may cause poor concentrate qualities.

High concentrations of Tl and Hg were present in pyrite from the uppermost main lode ore zone. Insufficient depression of pyrite when ore from those zones is treated will lead to poor concentrate qualities.

Complete transformation of pyrrhotite to marcasite is limited to the uppermost areas of the sulphide mineralisation and caused by descending oxidising surficial water that became acidic upon interaction with sulphides. Minor incomplete transformation is observed even in deepest sections of the orebody. High marcasite content will have a negative impact on mineral concentrate quality as it features a higher floatability than pyrite under certain pH conditions (Bulatovic, 2007). Furthermore, marcasite oxidises more quickly than pyrite, causing the production of sulphuric acid, subsequently affecting the pH within the mineral processing circuit.

The geometallurgical ore characterisation study at stope scale (5/5-Stope) revealed significant differences in composition, grain sizes, liberation, and thus, flotation characteristics between the three investigated stope parts. Compared to the western stope part, sphalerite and galena are coarser grained, feature higher particle liberation and free particle surface in the eastern stope part. Calculated theoretical grade-recovery diagrams suggest that ore from the western stope part will have by approximately 10% lower Zn and Pb recoveries. Whilst calculated theoretical grade-recovery data of Zn is close to long-term average plant performance, a significant deviation was present for Pb. The deviation translates to a lower concentrate grade (~30 wt% Pb) or lower recovery (~20% Pb). Recovery rates and concentrate qualities calculated on the basis of particle liberation and free particle surface confirmed this observation and suggest that a significantly better grade/recovery performance for galena/lead should be achieved. Excessive Pb losses or concentrate dilution with sulphide and non-sulphide gangue phases may be the cause for the observed poor performance. However, the sample preparation technique used in the course of this study may have caused substantially different liberation compared to real plant grinding via semi-autogenous and ball mill. Consequently, concentrate grade and plant recoveries may be overestimated. Geometallurgical test
work on the actual flotation feed would need to be undertaken in order to assess this issue. Most Ag is contained in the western pyrite-dominated ore.

Results showed that, despite individual ore types that feature similar ore characteristics in different locations throughout the deposit, a generalised characterisation is not feasible as Elura’s ore is far too heterogeneous in respect to texture and composition. However, characterisation on smaller scale, i.e. stoping areas, has the potential to identify significant variations in flotation characteristics for ore sourced from different stope parts. This knowledge will enable the prediction of (a) relative recovery rate changes, (b) potential changes in concentrate qualities and (c) changes in mill-throughput as a function of silica and wall rock content. Consequently, predictions of mine economics will be improved and strategies may be setup and implemented in order to maximise the performance of the mineral processing facility. Amongst those strategies are blending of ore sourced from zones of different ore characteristics, screening, optimisation of type and quantity of chemicals used in flotation (frother, collector or depressant) and mill and flotation residue time.

Improvement of Pb recoveries seems problematic for fine grained ore, as a further particle size reduction would be needed in order to liberate fine grained galena. This would cause over-grinding, sliming and significant entrainment, and subsequently even lower lead recovery rates. The cause for the significant deviation between theoretical and long-term plant recovery-grade performance need to be identified in order to assess whether significant improvements in the lead flotation circuit are feasible. Optimisation of the secondary grinding stage of sphalerite may have the potential to improve Zn recoveries for finer grained ore. Good Ag-recoveries can only be expected for ore from the uppermost areas of individual ore zones, where tetrahedrite is coarse and intergrown with galena. Considering the fine grain sizes, the complex mineral associations with phases other than galena and the uncertain flotation characteristics of altered tetrahedrite, a recovery rate in excess of 50% doesn’t seem very probable for ore from most areas within the Elura deposit. Elevated Bi in lead concentrate is easily manageable by blending ore from different source.
References


REFERENCES


REFERENCES

Geochimica et Cosmochimica Acta, 57 (13), 3093–3104.


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


