XAS studies of metal speciation in hydrothermal fluids

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# Table of Contents

Abstract.......................................................................................................................... v

Declaration...................................................................................................................... vii

Acknowledgements........................................................................................................ ix

List of publications........................................................................................................ xi

Chapter 1 ....................................................................................................................... 1
  1.1 Metal speciation and hydrothermal ore deposits ...................................................... 3
  1.2 Research objectives .................................................................................................. 6
  1.3 Experimental approaches and advances of XAS technology .................................. 6
  1.4 Thesis organization.................................................................................................. 11
  1.5 References .............................................................................................................. 12

Chapter 2 ....................................................................................................................... 21
  2.1 Introduction ............................................................................................................. 23
  2.2 Instrument description ........................................................................................... 24
    2.2.1 Stainless steel autoclave and internal sample cell .......................................... 26
    2.2.2 Pressure and temperature control ................................................................. 28
    2.2.3 Safety measures ............................................................................................ 29
  2.3 Commissioning and results...................................................................................... 30
  2.4 Conclusions ............................................................................................................. 36
  2.5 References .............................................................................................................. 37

Chapter 3 ....................................................................................................................... 41
  3.1 Introduction ............................................................................................................. 43
  3.2 Method .................................................................................................................... 48
  3.3 Ab initio XANES simulations for solid standards .................................................. 49
    3.3.1 Calculation method: MST vs FDM ................................................................. 50
    3.3.2 Effect of cluster size ...................................................................................... 52
  3.4 Ab initio XANES simulations for aqueous species ................................................. 54
3.4.1 Effect of the self-consistent field (SCF) calculations ...................................... 54
3.4.2 Effect of bond distance .................................................................................... 55
3.4.3 Effect of stoichiometry and distortion ............................................................. 57
3.4.4 Effect of hydrogen ........................................................................................... 60
3.4.5 Contributions of second hydration shell .......................................................... 62
3.5 Conclusions ............................................................................................................. 63
3.6 References .............................................................................................................. 65

Chapter 4........................................................................................................................ 71
4.1 Introduction ............................................................................................................. 75
4.2 Materials and measurements ................................................................................... 76
  4.2.1 Experimental setup .......................................................................................... 77
  4.2.2 XAS measurements ....................................................................................... 77
4.3 Results and data analysis ......................................................................................... 77
  4.3.1 Results of XANES spectroscopy ........................................................................ 77
  4.3.2 EXAFS analysis ................................................................................................. 81
  4.3.3 Density Functional Theory calculations ........................................................ 83
  4.3.4 Ab initio XANES simulation ............................................................................ 83
4.4 Discussion................................................................................................................ 85
  4.4.1 Ni speciation in chloride brines ....................................................................... 85
  4.4.2 Thermodynamic analysis and comparison with previous studies.................... 87
  4.4.3 Comparison to Co chloride complexes ............................................................. 91
4.5 References ............................................................................................................... 92

Chapter 5........................................................................................................................ 95
5.1 Introduction ............................................................................................................. 101
5.2 Materials and methods.......................................................................................... 104
  5.2.1 Experimental samples ..................................................................................... 104
  5.2.2 XAS Measurements ....................................................................................... 106
  5.2.3 EXAFS data analysis ....................................................................................... 108
  5.2.4 Density Functional Theory calculations ........................................................ 108
  5.2.5 Ab initio XANES simulations ........................................................................ 110
5.3 Qualitative analysis of XAS spectra ..................................................................... 110
  5.3.1 Effect of temperature ..................................................................................... 110
  5.3.2 Effect of salinity............................................................................................. 114
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3.3 XANES spectra of bromide solutions</td>
<td>116</td>
</tr>
<tr>
<td>5.4 EXAFS refinements</td>
<td>118</td>
</tr>
<tr>
<td>5.4.1 Mn-Cl solutions</td>
<td>119</td>
</tr>
<tr>
<td>5.4.2 Mn-Br solutions</td>
<td>129</td>
</tr>
<tr>
<td>5.5 DFT calculations</td>
<td>131</td>
</tr>
<tr>
<td>5.6 Ab initio XANES simulations</td>
<td>132</td>
</tr>
<tr>
<td>5.6.1 Simulations for solid standards</td>
<td>132</td>
</tr>
<tr>
<td>5.6.2 Simulations of aqueous complexes</td>
<td>135</td>
</tr>
<tr>
<td>5.7 Discussion: Mn(II) speciation in chloride brines</td>
<td>139</td>
</tr>
<tr>
<td>5.7.1 Nature of Mn(II) chlorocomplexes</td>
<td>139</td>
</tr>
<tr>
<td>5.7.2 Thermodynamic analysis</td>
<td>141</td>
</tr>
<tr>
<td>5.7.3 Comparison with Fe(II) chloride complexing</td>
<td>147</td>
</tr>
<tr>
<td>5.8 Annexes</td>
<td>148</td>
</tr>
<tr>
<td>5.8.1 Single crystal x-ray diffraction for (NEt₄)₂MnCl₄(s)</td>
<td>148</td>
</tr>
<tr>
<td>5.8.2 DFT optimized geometries for Mn(II) complexes</td>
<td>150</td>
</tr>
<tr>
<td>5.8.3 Classical Molecular Dynamics (MD) simulation</td>
<td>155</td>
</tr>
<tr>
<td>5.9 References</td>
<td>158</td>
</tr>
<tr>
<td>Chapter 6</td>
<td>169</td>
</tr>
<tr>
<td>6.1 Ni(II) speciation in hydrothermal brines</td>
<td>171</td>
</tr>
<tr>
<td>6.2 Mn(II) speciation in hydrothermal brines</td>
<td>172</td>
</tr>
<tr>
<td>6.3 Ab initio XANES simulations to explore structure of hydrothermal solutions</td>
<td>173</td>
</tr>
<tr>
<td>6.4 Future work</td>
<td>174</td>
</tr>
<tr>
<td>6.5 References</td>
<td>176</td>
</tr>
<tr>
<td>Appendix A</td>
<td>179</td>
</tr>
<tr>
<td>Appendix B</td>
<td>199</td>
</tr>
<tr>
<td>Appendix C</td>
<td>203</td>
</tr>
<tr>
<td>Appendix D</td>
<td>223</td>
</tr>
</tbody>
</table>
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Abstract

Knowledge of metal speciation and thermodynamic properties underpins our capability to model metal transport and deposition in natural and engineered systems. Using synchrotron-based X-ray Absorption Spectroscopy and high temperature – high pressure experimental techniques, this project aims to elucidate nickel and manganese speciation in hydrothermal chloride solutions, and obtain the thermodynamic properties for predominant species.

*Ab initio* XANES simulation methods were used in this study to provide independent or complementary information about the nature (stoichiometry and geometry) of aqueous complexes. Application of this technique to the calculation of XANES spectra of Mo(VI) complexes in hydrothermal systems confirmed that [MoO₄]²⁻ is stable in neutral and basic solutions over a wide range of temperature and salinity, and chlorinated Mo complexes (e.g., [MoCl₂O₂(H₂O)₂]ₐq, [MoOCl₄]ₐq) exist in strongly acidic solutions. XANES simulations of Te complexes added additional evidence that [Te(OH)₃] and [TeO₃] species predominate in basic and acidic solutions, respectively, and that the deprotonation process to convert [Te(OH)₃] to [TeO₃] is associated with a distance contraction for the Te-O bond.

Ni(II) speciation in hydrothermal brines was investigated over a wide range of temperatures (25-434 °C) and fluid compositions (0-7.68 m Cl⁻) at 400 and 600 bar. Quantitative XAS data interpretation revealed that Ni(II) chloroaqua complexes undergo a structural transition from octahedral at room temperature to distorted tetrahedral at elevated temperatures. Both heating and an increase in salinity promote the stability of tetrahedral complexes relative to octahedral complexes. The NiCl₂(aq) species exists in both octahedral [NiCl₂(H₂O)₄]ₐq and tetrahedral [NiCl₂(H₂O)₂]ₐq forms, with the ratio of octahedral to tetrahedral decreasing at
high temperature (> 200 °C). The highest order Ni chloride complex identified in this work is not the fully chlorinated [NiCl₄]²⁻ but the tri-chloro mono-aqua complex [NiCl₃(H₂O)]⁻, confirmed by both EXAFS analysis and XANES simulations.

A similar coordination change of Mn(II) chloroaqua complexes has been quantitatively identified by analysis of both XANES and EXAFS data collected between 30 to 550 °C at 600 bar, with chlorinity ranging from 0.100 to 10.344 m. Octahedral species predominate at room temperature within the whole salinity range and persist up to ~400 °C in low salinity solutions (mCl < 1 m), and tetrahedral species become significant at temperatures above 300 °C. Compared with Fe(II) chloride complexation, the octahedral to tetrahedral structural transition occurs at higher temperature for Mn(II) complexes. A combination of EXAFS refinements, Density Functional Theory calculations and ab initio XANES simulations confirmed that at elevated temperatures (≥ 400 °C) the highest order chloride complex predominating in highly saline brines (mCl > 3 m, Cl:Mn ratio > 53) is [MnCl₃(H₂O)]⁻ with [MnCl₄]²⁻ being unstable through all T-P-salinity range, while a lower order chlorocomplex, [MnCl₂(H₂O)₂]₉,aq, is the major species in low salinity solutions (mCl < 0.5 m, Cl:Mn ratio < 10). The differences regarding to the stoichiometry and stability of highest order metal chloride complexes identified in this study, [NiCl₃(H₂O)]⁻ and [MnCl₃(H₂O)]⁻, and in previous studies (i.e., [CoCl₃]²⁻ and [FeCl₄]²⁻) may play a role in the fractionation between metals with closely related geochemical properties in hydrothermal systems (e.g., Ni/Co; Mn/Fe).

Overall, the combination of XANES and EXAFS data provided us with a molecular level understanding of Ni and Mn speciation in hydrothermal brines and improved our capability for modeling metal mobility in the Earth’s crust.
Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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I always feel lucky that I made the right decision to come to down under to pursue something I was really interested in 3.5 years ago, because I was introduced to a great project and some great people, although I had a steep learning curve in the beginning of this project, which is far away from what I’ve learnt for my undergraduate study. This PhD experience is a unique journey in my life when it comes to the final stage, and everything in the past three and a half years comes to my mind all together.

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List of publications

Part of the thesis has been published in the following peer-reviewed conference paper and abstract.


The following peer-reviewed journal paper and manuscript are based on this PhD project, and they comprise the main body of this thesis (chapters 4 and 5):


Manganese (II) chloride complexes in hydrothermal fluids: \textit{in situ} XAS study.

(under review for Geochimica Cosmochimica Acta)

The XANES simulation work (chapter 3) of this PhD project contributes to the following peer-reviewed research paper and manuscript:
