



Development of laser ablation collision/reaction cell Lu-Hf geochronology

Alexander Simpson

This thesis is submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy

School of Physical Sciences
Department of Earth Science
The University of Adelaide
Australia

January 2023

Table of Contents:

List of Figures and tables	iii
Signed Statement	v
Acknowledgments	vi
Abstract	1
Thesis Introduction	2
1. Aims and Rationale	2
2. Thesis background	3
3. Thesis Outline	12
Chapter 1: In-situ Lu-Hf geochronology of garnet, apatite and xenotime by LA ICP MS/MS	15
1.1. Chapter 1 Abstract	19
1.2. Chapter 1 Introduction and background	19
1.3. Chapter 1 Sample descriptions	22
1.4. Chapter 1 Methods	25
1.5. Chapter 1 Results	31
1.6. Chapter 1 discussion and interpretation	39
1.7. Chapter 1 conclusions	45
1.8. Chapter 1 Appendix A: Supplementary Figures	47
1.9. Chapter 1 Appendix B: LA-ICP-MS U-Pb method	49
Chapter 2: In situ Lu–Hf geochronology of calcite	51
2.1. Chapter 2 Abstract	54
2.2. Chapter 2 Introduction and background	54
2.3. Chapter 2 Sample descriptions	55
2.4. Chapter 2 Methods	60
2.5. Chapter 2 Results	65
2.6. Chapter 2 discussion and interpretation	68
2.7. Chapter 2 conclusions	71
2.8. Chapter 2 Appendix A: MKED calcite sample description	72
2.9. Chapter 2 appendix B: Mt Elliott andradite U-Pb	74
2.10. Chapter 2 appendix C: large sample images	76
2.11. Chapter 2 appendix D: Table of analytical parameters	82

Chapter 3: Garnet Lu-Hf speed dating: a novel method to rapidly resolve polymetamorphic histories	84
3.1. Chapter 3 abstract	87
3.2. Chapter 3 introduction	87
3.3. Chapter 3 geological background	88
3.4. Chapter 3 sample descriptions	90
3.5. Chapter 3 methods	93
3.6. Chapter 3 results	94
3.7. Chapter 3 discussion	103
3.8. Chapter 3 conclusions	111
3.9. Chapter 3 appendix A: Supplementary figures and tables	113
Chapter 4: In situ apatite and carbonate Lu-Hf dating reveals the timing of Cu mineralisation and remobilisation within an IOCG system (Vulcan prospect, South Australia)	119
4.1. Chapter 4 abstract	122
4.2. Chapter 4 Introduction	122
4.3. Chapter 4 geological background	124
4.4. Chapter 4 Sample descriptions	126
4.5. Chapter 4 Methods	129
4.6. Chapter 4 Results	130
4.7. Chapter 4 discussion	138
4.8. Chapter 4 conclusions	142
4.9. Chapter 4 appendix A. tables of U-Pb and Lu-Hf analytical parameters	143
Chapter 5: Thesis conclusions	146
5.1. Summary of findings	146
5.2. Current issues and future development	146
5.3. Laser ablation Lu-Hf reference materials	147
5.4. Applicable minerals and potential applications	150
5.5. Conclusion	153
Bibliography	154

List of Figures:

Figure 1: LA-ICP-Q-MS/MS reaction cell cartoon	7
Figure 1.1: Down-hole Lu-Hf signals of analysed minerals and reference materials	29
Figure 1.2: Garnet Lu-Hf isochron plots	33
Figure 1.3: Apatite results plots	35
Figure 1.3: Xenotime results plots	36
Figure 1.4: Plot showing measured Lu-Hf age vs expected age for samples analysed in chapter 1	42
Appendix Figure 1.1: Product ion scan showing product masses for ^{176}Lu and ^{176}Hf when reacted with NH_3 gas	47
Appendix Figure 1.2: U-Pb concordia plots for analysed samples	48
Appendix figure 1.3: Plot showing sensitivity vs laser spot diameter	49
Figure 2.1: Mineral maps of analysed samples	56
Figure 2.2: Down-hole plot of time resolved signals	62
Figure 2.3: Calcite Lu-Hf isochron plot	67
Figure 2.4: Lu ppm vs 2σ age uncertainty	70
Appendix figure 2.1: Images of MKED calcite standard	73
Appendix figure 2.2: Weighted average age plots of MKED standard across four analytical sessions	74
Appendix figure 2.3: Andradite U-Pb age plot for sample ME 2	75
Appendix figures 2.1 – 2.6: Enlarged mineral maps and samples images for analysed samples	76
Figure 3.1: Geological map of NW Scotland showing chapter 3 sample locations	89
Figure 3.2: μXRF elemental maps of Ca, Mn, Fe and Y for analysed garnets	96
Figure 3.3. Inverse Lu-Hf isochron plots of analysed samples	103
Figure 3.4. Geological timeline of NW Scotland, comparing analysed garnet Lu-Hf ages with literature data	105
Figure 3.5. Interpretation figure for DR-1 garnet sample	108
Appendix figure 3.1. Photomicrographs of analysed samples	113
Appendix figure 3.2. μXRF elemental maps of Ti, P, Zr for analysed garnets	114
Appendix figure 3.3. Inverse Lu-Hf isochron plots for Hogsbo and BP1 garnet Lu-Hf standards	116
Figure 4.1. Simplified geological map of the Gawler Craton, showing the location of the Vulcan prospect as well as major IOCG mineral deposits	125

Figure 4.2. Simplified geological map showing the location of the Vulcan IOCG prospect relative to Olympic Dam and Carrapateena and psuedo-colour residual gravity image of the Vulcan prospect	126
Figure 4.3. SEM mineral maps and hand sample photos of analysed apatite sample from the Vulcan prospect	131
Figure 4.4. SEM mineral maps and hand sample photos of analysed carbonate sample from the Vulcan prospect	132
Figure 4.5. Apatite U-Pb and Lu-Hf isochron plots for samples from the Vulcan prospect	136
Figure 4.6. Carbonate Lu-Hf isochron plots for samples from the Vulcan prospect	137
Figure 4.7. Time-resolved laser ablation signals showing the presence of Fe inclusions in the apatite trace element data and the associated effects to the Lu-Hf and U-Pb ratios	138
Figure 4.8. Mineral map of sample 017-1210	140
Figure 4.9. Time space plot comparing existing geochronological data for Gawler Craton IOCG deposits with geochronological data from chapter 4	141
Figure 5.1. Long term average Lu-Hf data for Hogsbo and BP-1 garnet standards	148
Figure 5.2. Long term average Lu-Hf data for OD306, Bamble-1, and HR apatite standards	149
Figure 5.3. Long term average Lu-Hf data for MKED C and ME1 calcite standards	150
<u>Tables:</u>	
Table 1.1: Chapter 1 Lu-Hf analytical parameters	25
Table 1.2: Chapter 1 Results summary table	37
Appendix table 1.1: Chapter 1 U-Pb analytical parameters	50
Tale 2.1: Ages and Lu-Hf concentration information for analysed samples	66
Appendix table 2.1: Chapter 2 Lu-Hf analytical parameters	82
Table 3.1. Chapter 3 sample petrology	92
Table 3.2: Summary of Lu-Hf results	99
Table 3.3: comparison between isochron ages calculated with and without zircon inclusions	110
Appendix table 3.1: Chapter 3 Lu-Hf analytical parameters	117
Table 4.1. Chapter 4 sample descriptions and petrology	127
Table 4.2. Summary of geochronological data for samples from the Vulcan prospect	133
Table 4.3. Summary of ages for secondary U-Pb and Lu-Hf reference materials	133
Appendix table 4.1. Analysis and LA-ICP-MS/MS tuning parameters for U-Pb	143
Appendix table 4.2. Representative analysis and LA-ICP-MS/MS tuning parameters for Lu-Hf	144

Signed Statement

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, 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 in my name, 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.

The author acknowledges that copyright of published works contained within the thesis resides with the copyright holder(s) of those works.

I 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 Search and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

I acknowledge the support I have received for my research through the provision of an Australian Government Research Training Program Scholarship.

23/01/2023

Signed:

Date:

Acknowledgements

There are many people that I would like to thank for making my PhD some of the best years of my life. Firstly, without the help and support of my supervisors, Stijn, Martin and Carl, this research would not have happened. Although not an official supervisor, I cannot thank Sarah Gilbert enough, not only for her technical knowledge, without which, my PhD would probably have gone in a different direction, but also her enthusiasm to try new things. Renée Tamblyn was extremely important in the early development, as well as the application of the technique to garnets (and also as a friend!)

There are too many people to thank for their support and friendship, so hopefully I remember them all. Darwin, Morgan, Priya, Georgie, Kam, and Jarred are just a few of the people who have contributed to the many great memories. Memories that include fancy dinners, trips to the zoo, spontaneous camping trips, and drives to Brisbane. More importantly, everyone has made the Mawson building a fantastic place to work. Angus has been a great office mate, and Brad has been a great addition. I would also like to thank the TES coffee machine, sorry if I didn't look after you properly.

Lastly, I would like to thank my parents and brothers, Henrietta, Charlie, Jack and Oscar. They have always been fantastically supportive no matter what I do, and my PhD has been no different; they haven't complained once that I have been at uni for 12 years!

Abstract

The work conducted in this thesis has led to the successful development of a micro-analytical approach to Lu-Hf geochronology. In order to achieve this, the novel method utilises inductively coupled plasma quadrupole tandem mass spectrometry ICP-Q-MS/MS (in this case an Agilent 8900 'QQQ' was used), coupled to a laser ablation system. The use of a reaction gas within the reaction cell of the mass-spectrometer allows for the chemical separation of same-mass isotopes (of different elements). In the case of the Lu-Hf system, NH_3 gas is introduced, which reacts differently with hafnium (Hf) compared to the Heavy Rare Earth Elements (HREEs), including lutetium (Lu) and ytterbium (Yb). In more detail, the chemical reaction between Hf and NH_3 produces a reaction product that is proportional to Hf, which is the radiogenic daughter isotope in the Lu-Hf dating method. The analytical method has been optimised to promote production of this reaction product at a rate of 50 – 60 % of total Hf, allowing for sufficient sensitivity to measure radiogenic Hf isotopes in a range of minerals, including relatively Lu-poor apatite and carbonate minerals. Most importantly, this reaction product can be measured free from isobaric interferences of ^{176}Lu and ^{176}Yb , which forms the backbone and novelty of the developed method. In this work, it is demonstrated that the laser ablation approach allows for accurate *in situ* Lu-Hf ages to be rapidly and efficiently determined for a variety of minerals while maintaining the geological context in which they formed.

Garnets, which are one of the most important metamorphic minerals, have been dated using the laser-ablation approach with precisions up to ~1.5 % (2σ uncertainty, excluding Lu rich garnets from pegmatites). Given that sample preparation is trivial and that a large amount of data (>1000 analyses) can be collected in a single analytical session, this method has the potential to allow for 'terrane scale' age mapping of metamorphism, something that would be prohibitively difficult with previous Lu-Hf geochronological methods. Further, the spatial resolution and age precision are sufficient to distinguish core-rim age differences in polymetamorphic garnets. Consequently, the development of the laser ablation Lu-Hf method allows for a range of new studies focusing on metamorphic garnets to be pursued.

The ability to determine *in situ* Lu-Hf dates of apatite and calcite has also been demonstrated, with uncertainties as low as 0.6% (2σ). Both apatite and carbonate Lu-Hf dating has been applied to ore deposits, demonstrating that this technique has the potential to produce more reliable ages compared to the U-Pb system in these minerals. Consequently, Lu-Hf dating of both apatite and calcite has great potential to be used to determine the age of mineralisation, as both often form with clear petrological relationships with ore minerals.

Several potential matrix-matched reference materials have been identified, with independent constraints on crystallisation ages. Consequently, this thesis has developed LA-ICP-Q-MS/MS Lu-Hf geochronology to the point that it can be applied to solving geological problems.

Introduction

1. Thesis Aims and Rationale

Geochronology is one of the most important tools available to earth and planetary scientists. Broadly, geochronology is a series of systems and techniques that can be used to determine the age of a rock, mineral, sediment, or other material relevant to the earth sciences (Faure and Mensing, 2005). Of the various methods available in the geochronology toolbox, the radioactive decay of one isotope into another (stable) daughter isotope is particularly important for the investigation of processes that occur in deep time. Such methods include the radioactive decay of Uranium and Thorium (^{238}U , ^{235}U and ^{232}Th) to Lead (^{206}Pb , ^{207}Pb , ^{208}Pb , respectively), Lutetium (^{176}Lu) to Hafnium (^{176}Hf), Samarium (^{147}Sm) to Neodymium (^{143}Nd), Rubidium (^{87}Rb) to Strontium (^{87}Sr), Rhenium (^{187}Re) to Osmium (^{187}Os) and Potassium (^{40}K) to argon (^{40}Ar) and calcium (^{40}Ca) (Faure and Mensing, 2005). These dating methods can (collectively) be applied to every type of rock (i.e., all types of igneous, metamorphic, and sedimentary rocks) to provide important information on the timing of processes relating to, for instance, magma emplacement, metamorphism, deformation and economic mineralisation. Radiometric dating based on the alpha decay systems of U-Th-Pb, as well as ^{40}Ar - ^{39}Ar dating (based on beta decay of ^{40}K into ^{40}Ar) has been the mainstay of geochronology for several decades (Faure and Mensing, 2005). Comparatively, the application of other beta decay systems, such as ^{87}Rb - ^{87}Sr , ^{176}Lu - ^{176}Hf , and ^{187}Re - ^{187}Os , has been more limited, as these methods require time-consuming mineral dissolution and chemical separation of parent isotopes from daughter isotopes, severely compromising their efficiency on a large scale (e.g. Blichert-Toft et al., 1997; Bolea-Fernandez et al., 2016a; Faure and Mensing, 2005; Moens et al., 2001; Zack and Hogmalm, 2016). These time consuming methods are necessitated by the fact that the parent and daughter have the same mass, and therefore cannot be distinguished using traditional mass spectrometry (e.g. Moens et al., 2001). However, recent advances in mass spectrometry have opened the possibility for these decay systems to be measured *in situ* using laser ablation technology (e.g. Bolea-Fernandez et al., 2016b; Hogmalm et al., 2019; Hogmalm et al., 2017; Zack and Hogmalm, 2016), which has the potential to allow rapid sample throughput combined with micron-scale spatial resolution. In more detail, laser ablation inductively coupled quadrupole tandem mass spectrometry (LA-ICP-Q-MS/MS) can effectively separate elements of the same mass (Balcaen et al., 2015; Bolea-Fernandez et al., 2016a; Moens et al., 2001; Zack and Hogmalm, 2016). This technique relies on the use of a collision/reaction cell into which a reactive gas is introduced. The aim of this procedure is that the radiogenic daughter isotopes will react with the gas to form multi-element ions (such as oxides, for instance), while the same-mass parent isotopes are unreactive and consequently retain their original mass. Hence, chemical separation of parent from daughter isotopes is conducted *during*, rather than prior to mass spectrometry. While LA-ICP-Q-MS/MS Rb-Sr and Re-Os geochronology have been demonstrated previously (Hogmalm et al., 2019; Zack and Hogmalm, 2016), the possibility of *in situ* Lu-Hf dating had not been fully explored prior to this thesis.

Traditionally, Lu-Hf dating has largely been restricted to the mineral garnet, which is arguably the most important metamorphic mineral (e.g. Baxter et al., 2017; Duchene et al., 1997; Vervoort, 2014). Briefly, traditional methods rely on chemically digesting the mineral of interest, chemically separating the parent and daughter elements, and then separately measuring these elements using a mass spectrometer (Blichert-Toft et al., 1997; Patchett and Tatsumoto, 1981). While this is discussed in much more detail later, the major drawbacks of this method are that it is both time consuming and removes the mineral from the context in which it formed. The ability to rapidly obtain garnet ages with micron-scale spatial resolution has several benefits for the study of

metamorphic rocks, particularly in cases where rocks have undergone multiple episodes of metamorphism. For instance, a garnet may preserve a texturally distinguishable core that formed during one metamorphic event, and a rim that grew during a subsequent event (for a review on metamorphic garnets, see Baxter et al., 2017). In addition, rapid garnet geochronology may allow for the regional metamorphic history of a region to be constrained with relative ease. As well as garnet, other minerals have been shown to incorporate significantly more Lu relative to Hf, making them potential candidates for Lu-Hf dating. Of particular interest are phosphate minerals such as apatite, and carbonate minerals such as calcite (e.g. Barfod et al., 2003; Maas et al., 2022), which occur in a range of geological environments, including mineral deposits and mineralised systems (e.g. Chew et al., 2011; Debruyne et al., 2016; Glorie et al., 2019; Maas et al., 2022; Mao et al., 2016). Mineral systems can often be temporally complex, with multiple generations of metal enrichment, depletion, and/or mobilisation (e.g. Ehrig et al., 2021). Consequently, developing methods to quickly and easily determine the timing of mineralisation events is of great importance to the mineral exploration industry.

The aims of this thesis are, firstly, to develop LA-ICP-MS/MS Lu-Hf dating, and secondly, to demonstrate the method on a range of minerals, such as apatite and calcite that are difficult to analyse using sample digestion techniques. Finally, this research aims to test the Lu-Hf method in real geological contexts, ranging from polymetamorphic terranes to mineral exploration targets.

2. Thesis Background

The following section details the analytical background for traditional solution Lu-Hf, introduces LA-ICP-MS, followed by a discussion on the current state of LA-ICP-Q-MS/MS. Finally, the main minerals that can be dated by Lu-Hf are discussed in the context of (1) the potential advantages and disadvantages of the laser-ablation method and (2) their applications to Earth Science questions. Note that each thesis chapter is either a published manuscript (chapters 1 and 2), a submitted manuscript (chapter 3), or written as a publishable manuscript (chapter 4), with the exception of chapter 5 (the conclusion chapter). Consequently, each chapter has its own background section and there will be some overlap between what is written there and what is written in the following section.

Introduction to Lu-Hf dating

Traditional methods: Advantages and limitations

The ability to measure ^{176}Lu and ^{176}Hf , and therefore use them to calculate ages, was developed over several decades, using a variety of analytical methods (Blichert-Toft et al., 1997; Boudin and Deutsch, 1970; Duchene et al., 1997; Patchett and Tatsumoto, 1981). It was not until the later methods, however, that widely applicable, routine techniques were established, with Blichert-Toft et al. (1997) demonstrating the basis for much of the work that has been conducted since. This method involves isotope dilution and subsequent isotopic measurements conducted using multicollector inductively coupled plasma mass spectrometry. The isotope dilution method involves the chemical separation of Lu, Yb, and Hf via ion exchange columns ('column chemistry' e.g. Blichert-Toft et al., 1997; Patchett and Tatsumoto, 1981). This process then allows for the elements of interest to be separately and sequentially introduced into a mass spectrometer, thereby removing their isobaric interferences *prior* to mass-spectrometry (Faure and Mensing, 2005). Such chemical dissolution techniques remain the gold standard of precision in isotopic measurements, including geochronology. There are, however, several potential issues with these techniques that limit their application to solve certain geological problems. Analytical issues, such as the high ionisation energy

of Hf (Blichert-Toft et al., 1997) and the difficulty in simultaneously maintaining both Lu and Hf in the same solution (after addition of the spike; Blichert-Toft et al., 1997; Connelly, 2006) have been overcome to some degree. For instance, the higher temperatures of inductively coupled plasma (ICP) allow for more efficient ionisation of Hf compared to thermal ionising mass spectrometry (TIMS) (Blichert-Toft et al., 1997). Issues related to sample-spike equilibration can be overcome as well (e.g. by repeatedly heating with acid till no residue remains; Anczkiewicz et al., 2004; Lapen et al., 2004), however such steps are time consuming (relative to laser ablation), and must be carefully conducted to ensure success.

Perhaps the largest limitation, however, is that dissolution-based sampling techniques compromise spatial resolution. This is because aliquot sizes tend to be significantly larger (~200mg for garnet but up to 2g for low Hf minerals e.g. Ibanez-Mejia et al., 2018; Johnson et al., 2018; Maas et al., 2022) than typical laser ablation sample volumes. Even the largest laser beam diameters (up to 256 microns) that were used during this PhD, with ablation depths of ~60 microns, only produce an ablation volume of ~0.000003 cm³ which will equate to much less than 1 mg for even very dense minerals (and is an extreme case; the majority of samples are analysed with a spot size of 120 microns or less). Although dissolution based techniques require significantly fewer aliquots in order to calculate a reliable date (~3 – 6 vs ~50+), the aliquot size may compromise spatial resolution, making it difficult to sample specific regions of a mineral (e.g. crushing a garnet and hand picking fragments; Bird et al., 2013; Vance et al., 1998). There may be aspects of a mineral's growth that make large aliquot sizes, and therefore lack of spatial resolution, undesirable. For instance, if the mineral contains inclusions of another mineral (that contains Lu and/or Hf), then the measured isotopic data may be contaminated, unless inclusions are removed. This is particularly important if the inclusions are of a different age to the host mineral (Scherer et al., 2000b). For instance, zircons, which typically contain wt.% Hf, and have very low Lu/Hf ratios (e.g. Griffin et al., 2002; Thirlwall and Walder, 1995) are commonly included in garnet (Scherer et al., 2000b). Although techniques exist to remove zircon (such as crushing and attempting to select zircon free garnet fragments under binocular microscope or preferential dissolution of garnet over zircon), these techniques tend to minimise zircon inclusions, rather than eliminate them altogether (Connelly, 2006). Another potential issue with the lack of spatial resolution of solution Lu-Hf analysis arises when a given mineral is not age homogenous. For instance, minerals such as garnet can often grow during different events, sometimes separated by millions of years. In the case of garnet, core – rim age differences are relatively common (e.g. Baxter and Scherer, 2013; Cohen et al., 1988; Vance and O'Nions, 1990; Vance et al., 1998). While such age differences can potentially be determined based on both visual inspection of the mineral as well as by mapping chemical zonation, it is often not practically possible to separate out such age zonation for the purposes of solution Lu-Hf analysis. For instance, many studies have relied on hand picking fragments of crushed garnet under binocular microscope and using the colour of the fragments to distinguish cores from rims (e.g. Bird et al., 2018; Bird et al., 2013; Ibanez-Mejia et al., 2018; Johnson et al., 2018; Lagos et al., 2007). Clearly, this method will only work if there is a very distinct colour difference between the core and rim, and it is likely open to user error. Micro-drilling has proven effective at distinguishing cores and rims in large garnets, but is restricted to the Sm-Nd method, as Hf concentrations in garnet are normally too low for individual micro-drilled holes to produce enough material for successful Hf measurement, and drilling will crush inclusions along with the garnet, thereby contaminating the aliquot (e.g. Cheng et al., 2016; Schmidt et al., 2015). Finally, a significant drawback of the solution Lu-Hf method is the time-consuming nature of analysis. While large scale geochronological studies are possible using solution Lu-Hf (Bird et al., 2013), they are considerably more time consuming and expensive relative to laser ablation geochronology (e.g., U-Th-Pb). For instance, laser ablation detrital zircon U-Pb

studies can include thousands of analyses, whereas the largest published dissolution garnet geochronological studies include < 20 ages, with 3 – 6 analyses per age (e.g. Bird et al., 2013; Cawood et al., 2004; Kirkland et al., 2008). Consequently, terrane-scale age mapping, as well as detrital geochronology, are difficult if not impossible using traditional Lu-Hf methodology. While many of the initial drawbacks of solution Lu-Hf analysis have been overcome (and continue to be improved upon), laser ablation analysis is less affected by these mentioned drawbacks.

Introduction to LA-ICP-Q-MS/MS

Laser Ablation basics

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) involves coupling a laser micro-sampling device with an inductively coupled plasma (Gray, 1985; Longerich, 2008; Mokgalaka and Gardea-Torresdey, 2006). In this setup, a laser (typically with a wavelength of 213 or 193 nm for geochronological purposes; Guillon et al., 2003; Košler, 2007; Longerich, 2008), is used to ablate the sample of interest. The aim is to rapidly 'drill' through the sample, to produce an aerosol that can subsequently be introduced into a mass spectrometer, allowing the composition of the sample to be constrained. The laser used in this study utilises a 'two volume' sample cell, in which samples are held in a large cell 'the first volume', with a smaller 'volume' used to target the region of interest (The larger volume can be moved underneath the smaller volume, in order to target different samples). This allows for many samples to be introduced into the laser chamber, while efficiently transporting the material to the ICP and reducing washout time (Müller et al., 2009). The transport to the ICP involves the flow of an inert gas or 'carrier gas' (normally He) that carries the sample to the plasma torch (Arrowsmith and Hughes, 1988; Eggins et al., 1998; Gunther and Koch, 2008). The plasma is formed through electrically heating and ionising argon gas. Once the sample aerosol reaches the plasma, it is (partially) atomized and ionised (Gray, 1985; Longerich, 2008). The resultant ions are accelerated by applying voltages to a series of lenses, with negative voltages used to control the movement of cations (Longerich, 2008). Subsequently, a mass separating device uses electric and/or magnetic fields to filter ions based on mass/charge (m/z) ratios (Longerich, 2008). Although ideally each m/z ratio will be a single isotope of a given element, this will not always be the case (Longerich, 2008). Isotopes can have the same mass (as mentioned above), multiple isotopes can combine to form a product that has the same mass as a third isotope, and if another isotope has double the mass, a doubly charged ion might interfere (for instance, measuring $m/z = 87$ will include $^{87}\text{Rb}^+$, $^{87}\text{Sr}^+$, and $^{174}\text{Yb}^{2+}$, and $m/z 88$ will include, among others, $^{88}\text{Sr}^+$ and $^{44}\text{Ca}^{44}\text{Ca}^+$). Finally, the intensity of the ion beam (i.e. ions per unit time) is converted into an electrical signal by the detector (Longerich, 2008).

Mass separation in ICP-MS is performed using a 'mass analyser', which can be a quadrupole (utilised in this work), sector field (magnet), or a time-of-flight mass analyser. Quadrupole mass analysers, unsurprisingly, consist of four poles (or rods; Hoffman and Stroobant, 2007). The exact mechanism employed by quadrupole mass analysers is complex, and will only briefly be described here. The four poles consist of opposite pairs that are connected to radio frequency (RF) and direct current power supplies respectively (Hoffman and Stroobant, 2007; Longerich, 2008). Ions travelling between the poles will follow a complex oscillating path, with ions of different mass/charge ratio following different paths (Hoffman and Stroobant, 2007). Consequently, the DC and RF supplied to the quadrupole can be adjusted such that the path of an ion of a given mass/charge can reach the detector, but ions of any other mass/charge will follow unstable trajectories and therefore be filtered out (Hoffman and Stroobant, 2007). An advantage of this method is that different mass/charge ratios can be cycled through relatively quickly (in the order of milliseconds), allowing a large mass range to be measured in less than a second (Longerich, 2008; Mokgalaka and Gardea-

Torresdey, 2006). Typical measurements using a quadrupole mass analyser continuously cycle through mass/charge ratios of interest during ablation of the mineral of interest, such that a given isotope (or m/z) is repeatedly measured. The main alternative of the quadrupole are sector field instruments (at least for geochronology; Longerich, 2008), which use a combination of electric and magnetic fields to accelerate ions along a curved path (Hoffman and Stroobant, 2007). The exact trajectory of this curved path will be dictated by the ion's mass/charge ratio, allowing ions to be separated (Hoffman and Stroobant, 2007). Although some sector field instruments can cycle through measurements in a similar way to quadrupoles, their main advantage is simultaneous measurement, which allows greater sensitivity and precision (Longerich, 2008). Simultaneous measurement, however, severely limits the mass range that can be measured, as this is dependent on both the number of detectors and the geometry of the machine (i.e. masses that are significantly different require detectors to be far apart). The latter limitation is an important consideration for the laser-ablation Lu-Hf method, since the mass range between the measured parent and daughter isotope is 82 amu (discussed further below), which is too large for current multi-collector instruments. Consequently, laser ablation *quadrupole* mass spectrometry is potentially the most efficient technique in terms of sample throughput, with the trade-off that it tends to produce the lowest precision when used to measure isotopic ratios (Kořler, 2007).

The laser ablation sampling method can be employed with laser beam diameters of between 5 and 256 microns, but typical diameters for traditional geochronology purposes range between 20 - 100 microns, depending on the mineral analysed (e.g. monazite and zircon tend to require small spots but carbonates require large spots; Chew et al., 2014; Gillespie et al., 2018; Roberts and Walker, 2016). Currently, LA-ICP-MS U-Th-Pb dating, can be applied to a wide variety of minerals from a wide variety of rocks. The technique is quick, with limited sample preparation (compared to its competitors; Kořler, 2007), produces spatially resolved data at a resolution that allows for distinguishing multiple ages from the same hand sample, or even the same mineral, while only damaging the mineral to relatively small extent (Kořler, 2007; Longerich, 2008). Consequently, the development of other geochronological techniques, beyond U-Th-Pb, will similarly allow for rapid and efficient geochronology to be applied to help investigate geological problems, particularly in cases where no (or only a few) U bearing minerals can be found.

Introduction to LA-ICP-Q-MS/MS

LA-ICP-MS currently has the greatest potential to separate isobaric interferences *during* (rather than prior to) analysis (e.g. Bolea-Fernandez et al., 2016a; Moens et al., 2001; Zack and Hogmalm, 2016). In order to achieve this, the use of a reaction cell has been employed (Moens et al., 2001). In this first study, a collision/reaction cell was attached to a single quadrupole mass spectrometer. Therefore, the ions were not filtered before entering the reaction cell, and consequently, polyatomic isobaric interferences formed. LA-ICP-Q-MS/MS uses a reaction cell sandwiched between two mass analysers to overcome this problem.

Previous studies have demonstrated that ICP-Q-MS/MS analysis can eliminate many of the isobaric interferences that have hindered isotope geochronology in the past (early demonstrations include; Bolea-Fernandez et al., 2016b; Zack and Hogmalm, 2016). The initial application was conducted on the Rb-Sr system, in which Sr can be separated from Rb via reaction with O₂ gas (Zack and Hogmalm, 2016), N₂O gas (Hogmalm et al., 2017), SF₆ gas (Hogmalm et al., 2017) or CH₃Cl gas (Bolea-Fernandez et al., 2016a). Of particular interest is the development of laser ablation Rb-Sr *dating*, which, similar to existing laser ablation U-Pb dating, allows for micro-sampling of a mineral, preserving its petrological context (e.g. Zack and Hogmalm, 2016). Demonstration of laser ablation Rb-Sr has led to the development LA-ICP-Q-MS/MS analysis of other beta decay systems, such as Re-Os (Hogmalm et

al., 2019) and K-Ca (Hogmalm et al., 2017). In addition, the use of NH_3 gas has been demonstrated to remove the isobaric interference of ^{204}Hg on ^{204}Pb , thereby allowing accurate measurement of ^{204}Pb during U-Pb dating (Gilbert and Glorie, 2020). Prior to this thesis, the Lu-Hf system remained one of the few beta decay systems, commonly used for geochronology, that lacked a fully developed method for LA-ICP-Q-MS/MS analysis. Previous work, however, had demonstrated that NH_3 may be a useful reaction gas for separating ^{176}Lu and ^{176}Yb from ^{176}Hf (Woods, 2017; Zack and Hogmalm, 2015).

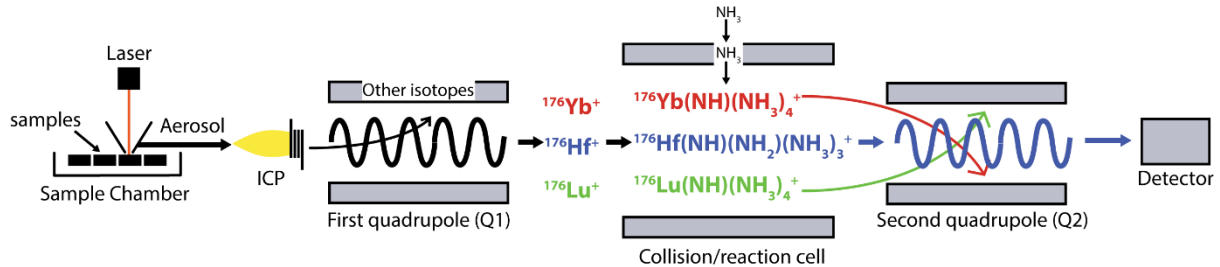


Figure 1: Cartoon showing how LA-ICP-Q-MS/MS separates isobaric interferences. In the example, the first quadrupole mass-analyser (Q1) has been set to only allow ions with mass 176 amu to pass through. In the reaction cell, ^{176}Lu , ^{176}Hf , and ^{176}Yb react with ammonia to form complex product-ions with different masses. The second quadrupole (Q2) can then be set to only allow the mass of the Hf-ammonia complex to pass through (mass-shift +82 in this example), allowing for interference-free measurement of $^{176(+82)}\text{Hf}$. ICP stands for inductively coupled plasma.

Using the Lu-Hf system as an example, ICP-MS/MS utilises a collision/reaction cell sandwiched between two mass separation devices (typically quadrupole mass analysers; Balcaen et al., 2015). The first mass separation device (Q1) is used to allow only the mass/charge of interest to enter the collision/reaction cell (e.g. filtering everything except mass 176/1+ will allow $^{176}\text{Lu}^+$, $^{176}\text{Hf}^+$, and $^{176}\text{Yb}^+$ to enter). Once in the collision/reaction cell, the ions are allowed to react with a gas (such as NH_3 or N_2O), and the reaction products can then be filtered by the second mass analyser (Q2), potentially allowing only the isotope of interest to reach the detector (e.g. Balcaen et al., 2015; Bolea-Fernandez et al., 2016a; Zack and Hogmalm, 2016). In the case of Lu-Hf, Hf reacts with NH_3 in the collision/reaction cell to form $\text{Hf}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$, but Lu and Yb tend to react with one more H, to form $\text{HREE}(\text{NH})(\text{NH}_3)_4^+$. Consequently, Q1 can be set to only allow mass 176 to enter, and Q2 can be set to only allow the mass of $^{176}\text{Hf}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$ to enter (258 amu). As neither Lu nor Yb react significantly to form a product with a mass of 258 amu, they will be filtered at Q2 and only the Hf reaction product will reach the detector. For a full discussion of the analytical details associated with the laser ablation Lu-Hf measurement technique, the reader is referred to chapter 1.

Laser ablation analysis: potential issues

There are a number of issues that must be addressed before laser ablation quadrupole analysis can produce both accurate and geologically meaningful data. One of the potential issues with quadrupole measurements is obtaining sufficient sensitivity and precision to produce geologically useful isotope ratios (and consequently, ages). While this has been clearly demonstrated for U-Th-Pb analysis (and recently for beta decay systems such as Rb-Sr; Hogmalm et al., 2019; Tillberg et al., 2020; Zack and Hogmalm, 2016), it represents a potential hurdle for LA-ICP-Q-MS/MS Lu-Hf analysis. This is because reactions in the collision/reaction cell are unlikely to be 100% efficient (i.e. the reaction between N_2O and Sr^+ to form SrO^+ occurs at a rate of ~85 %; Hogmalm et al., 2017). Further, In contrast to the Rb-Sr system, previous work has indicated that both Lu and Hf are likely to react with NH_3 to form *multiple* reaction products (Koyanagi et al., 2010; Woods, 2017). Consequently, even if reaction efficiency is high, Hf may end up being split between multiple reaction products,

thereby reducing the sensitivity. As such, while developments in ICP-Q-MS/MS geochronology are primarily focussed on reducing or eliminating relevant isobaric interferences, sensitivity can be an important consideration and needs to be carefully evaluated.

Another limitation of the laser-ablation method, of particular relevance to geochronology, is the effect of elemental fractionation at the ablation site and during subsequent aerosol transfer to the ICP (referred to as 'laser induced elemental fractionation' or LIEF; Arrowsmith and Hughes, 1988; Eggins et al., 1998; Gunther and Koch, 2008; Sylvester, 2008). In more detail, LIEF involves elements reaching the ICP at differing rates (Gunther and Koch, 2008). Previous studies have demonstrated that LIEF is controlled in part by elemental volatility (for instance, more volatile elements will reach the ICP faster and in higher abundance relative to more refractory elements; Jackson and Günther, 2003; Sylvester, 2008). However, the effects of elemental volatility can be controlled by the mineral matrix being ablated (Jackson and Günther, 2003; Sylvester, 2008). For instance, studies have demonstrated that LIEF is often dependent on the particle size distribution of the aerosol, with more volatile elements concentrated in smaller particles that more efficiently reach the ICP, and more refractory elements concentrated in larger particles, which are more likely to settle out during transport (e.g. Guillong and Günther, 2002). In U-Pb (and Rb-Sr) the particle size (and consequently LIEF) can change with depth, as larger particles are transferred with decreasing efficiency (e.g. down-hole fractionation; Chew et al., 2011; Gunther and Koch, 2008; Redaa et al., 2020; Wang et al., 2022).

Although Lu and Hf are both refractory elements (Sylvester, 2008), the potential for LIEF of Lu from Hf must be investigated. Importantly, LIEF is thought to be largely mineral matrix dependent, hence the established correction procedure is to analyse a mineral matched (or 'matrix matched') reference material of known and homogenous isotopic composition (Jackson, 2008; Sylvester, 2008). This mineral matched reference material is analysed simultaneously with unknown samples (generally interspaced, so as to correct for instrument drift as well; Jackson, 2008). Homogeneity of the reference material is important so that the measured isotope ratio (for instance $^{176}\text{Lu}/^{177}\text{Hf}$) can be compared to an expected value (determined using an independent analytical method). An alternative method, that does not require an isotopically homogenous reference material, involves first correcting to a homogenous standard that is not matrix matched (to correct for instrument drift and to correct the measured ratios of the radiogenic daughter to a stable (common) isotope, e.g. $^{176}\text{Hf}/^{177}\text{Hf}$, which are not affected by LIEF as they are the same element). This can then be followed by correction to an age homogenous but isotopically heterogeneous reference material (e.g. employed for calcite U-Pb dating; Roberts et al., 2017). In the case of Lu-Hf, this correction can be calculated by the offset between the slope of a traditional isochron (or the x-intercept of an inverse isochron) and a reference slope calculated from the expected age of the reference material. This method is practically beneficial, as it may be difficult to find isotopically homogenous natural minerals to use as reference materials.

Minerals that reject Hf during crystallisation, and have not undergone isotopic disturbance to their Lu-Hf ratios, will produce homogenous $^{176}\text{Lu}/^{176}\text{Hf}$ ratios (defined by their age). Consequently, it may be possible to find isotopically homogenous standards for the minerals apatite and calcite, which tend to reject Hf during crystallisation (e.g. Barfod et al., 2003; Maas et al., 2022). Garnet, however, both incorporates Hf during crystallisation (e.g. Duchene et al., 1997), and tends to be highly zoned in Lu (garnet trace element compositions reviewed in Baxter et al., 2017), making isotopically homogenous natural garnets highly unlikely to occur. Consequently, for garnet Lu-Hf, the alternative correction method (in which an age homogenous, but isotopically heterogeneous standard is used) is likely to be the most realistically viable.

Applicable minerals

Garnet – dating metamorphism

Garnet is a nesosilicate mineral with the formula $X_3Y_2(SiO_4)_3$, with the X site 8-fold coordinated and typically filled by Fe^{2+} , Mg^{2+} , Ca^{2+} , Mn^{2+} , and Y^{2+} and the Y site 6-fold coordinated and generally filled by Al^{3+} . In certain garnet end members the Y site can be filled by other trivalent cations such as Cr or Fe (e.g. andradite and uvarovite; Baxter et al., 2013). Garnets can form in a wide range of rocks types but are characteristic of medium- to high-grade metamorphic rocks, in which they tend to form porphyroblasts (Baxter et al., 2013; Baxter et al., 2017; Duchene et al., 1997). Consequently, garnets are an extremely important mineral for constraining the timing and nature of metamorphism; not only do they occur at many different P-T (pressure-temperature) conditions (typically > 400°C and 0.4 Gpa; Caddick and Kohn, 2013; Spear, 1993), but there has been a huge effort undertaken to understand garnet thermodynamics that allow P-T conditions to be quantified. In addition to its utility as a P-T tool garnet often displays clear genetic relationships with metamorphic mineral assemblages and structural features in rocks due to the large size they commonly grow to (Baxter et al., 2017; Baxter and Scherer, 2013). Further to this, garnets often display many characteristics that can provide important information on the structural character of the metamorphic event in which they formed. A classic example (although sometimes hotly contested e.g. Bell et al., 1992) of this is the 'snowball' inclusion spiral pattern that can occur in garnet interpreted to have rotated due to traction between the garnet and its surrounding matrix during bulk plastic flow (e.g. Passchier et al., 1992; Tracy et al., 1976). Additionally, garnets are often chemically zoned, with this zonation relating to their metamorphic history (Baxter et al., 2017; Spear, 1993). As well as the above, a single garnet can grow during multiple distinct metamorphic events, with new garnet nucleating on the original garnet (e.g. Baxter and Scherer, 2013; Cutts et al., 2010; Vance and O'Nions, 1990). The conditions of a metamorphic event can be used to determine the tectonic regime in which it formed (e.g. high-temperature, low-pressure metamorphism occurs during continental rifting, and high-pressure, low-temperature metamorphism occurs during convergent processes, such as subduction). Consequently, garnet is an extremely important mineral for the investigation of metamorphism and associated tectonic processes.

The importance of garnet as tool for tectonic analysis means constraining the age of garnet is of paramount importance in the study metamorphic rock systems. Dating of garnet has been approached in two ways. The first is indirectly via petrochronology, which attempts to link the timing of accessory mineral growth to the timing of garnet via chemical equilibria arguments (e.g. Rubatto, 2002; Yakymchuk et al., 2017). The second is by dating the garnet itself via REE or U-Pb isotope systematics. Importantly for geochronological purposes, REEs (rare earth elements) can substitute significantly into the X site of garnet (Baxter and Scherer, 2013; Duchene et al., 1997; Vervoort, 2014). This opens the possibility to date garnet using the radioactive decay of ^{147}Sm or ^{176}Lu (both rare earth elements). In addition, garnet tends to strongly reject Pb, meaning the U-Th-Pb system can sometimes be applied (Mezger et al., 1989; Millonig et al., 2020), however this method is often limited by the extremely low U concentrations in typical garnet (e.g. < 1ppm; Millonig et al., 2020). Generally, the U-Th-Pb system is only widely applicable to calcic garnets that do not incorporate Al^{3+} into the Y site (e.g. andradite), which typically form during hydrothermal alteration rather than classical metamorphism (Seman et al., 2017). Consequently, the Sm-Nd and Lu-Hf geochronometers are often employed to determine the age of garnet formation, particularly metamorphic garnet (Baxter and Scherer, 2013). While Sm-Nd can produce high quality garnet ages, there are a number of disadvantages when compared to the Lu-Hf system. Firstly, ^{147}Sm has an nearly an order of magnitude longer half-life (106 Gyr vs 37 Gyr; Söderlund et al., 2004; Villa et al., 2020), making

young samples, in which only limited ^{143}Nd has accumulated, difficult to date. Secondly, as both Sm and Nd are geochemically very similar (i.e. they both tend to form trivalent cations of similar ionic radii), garnet tends to incorporate significant amounts of Nd as well as Sm. Consequently, the low radiogenic and limited variability in Sm-Nd ratios might hinder precise isochron calculations. This contrasts to Lu-Hf, in which the daughter product, Hf, is not a REE, and occurs as tetravalent cations of different ionic radius compared to trivalent Lu. Consequently, Hf is normally not incorporated in the garnet lattice in significant quantities compared to Lu (Baxter and Scherer, 2013). Finally, both empirical and experimental studies have determined that the Sm-Nd system in garnet has a lower closure temperature to volume diffusion than Lu-Hf (Bloch et al., 2015; Scherer et al., 2000a; Smit et al., 2013), making Sm-Nd less likely to faithfully record garnet growth ages, particularly in high-temperature conditions. For instance, garnets of radius $> 1\text{mm}$ are likely to preserve their Lu-Hf systematics at temperatures between 650 and 750°C for typical orogenic system cooling rates, while at these temperatures Sm and Nd are likely to decouple (Bloch et al., 2020).

Garnet tends to incorporate both Lu ($\sim 1 - 100\text{ ppm}$) and Hf ($\sim 1\text{ ppm}$) into its structure, meaning Hf sensitivity may not be a major issue (compared to calcite and apatite; discussed later), however this can also lead to relatively low $^{176}\text{Lu}/^{177}\text{Hf}$ ratios, which may limit precision. Consequently, techniques that maximise the spread $^{176}\text{Lu}/^{177}\text{Hf}$ are important to produce well constrained garnet dates. For instance, elemental imaging of Lu (or a proxy such as another HREE or Y) combined with the small size of a laser beam, can allow for high Lu zones to be targeted, potentially producing much greater $^{176}\text{Lu}/^{177}\text{Hf}$ ratios compared to solution analysis.

Garnet Lu-Hf geochronology has previously required mineral dissolution based methods, which can limit obtained data in terms of quantity and spatial resolution due to the intensive laboratory methods that are required. The ability to obtain rapid, spatial resolved garnet ages open a pathway to both constrain the age of growth zoning in an individual garnet as well as to rapidly constrain the metamorphic history of a terrane.

Apatite

Apatite is a common accessory mineral that forms in a wide variety of rock types. The apatite chemical formula is generally written as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{F}, \text{C})_2$ with a solid solution between end-members in which the anion site consists of OH, F, or Cl (Chew and Spikings, 2015). Apatite forms in many igneous rocks, including mafic igneous rocks that are typically difficult to date (Chew and Spikings, 2015; Larsson and Söderlund, 2005). Additionally, apatite can occur in sedimentary rocks, both as a detrital component (Chew et al., 2011; Gillespie et al., 2018) or as growths during diagenesis (Shemesh, 1990), and is an important constituent of bone material, particularly teeth (e.g. Barfod et al., 2003). Apatite can also form in metamorphic and hydrothermally altered rocks (e.g. Cave et al., 2018; Glorie et al., 2019; Harlov et al., 2005). Furthermore, apatite is common in many mineral deposits, particularly Iron oxide copper gold (IOCG) and similar deposits such as iron oxide apatite (IOA) deposits (e.g. Corriveau et al., 2016; Hunt et al., 2007; Krneta et al., 2017; Mao et al., 2016). Given the wide range of settings in which apatite can form, it is clearly beneficial to be able to determine its age. Apatite is amenable to the U-Pb system, and can produce well constrained ages using this method (Chew et al., 2014; Chew et al., 2011; Oosthuyzen and Burger, 1973). Although apatite U-Pb dating has proven useful in the past, there are some limitations that mean that Lu-Hf ages may be superior in some situations. For instance, the U-Pb system in apatite has a relatively low closure temperature to volume diffusion of Pb (350 – 500°C in typically sized ~ 100 micron crystals; Cherniak et al., 1991; Chew and Spikings, 2015; Cochrane et al., 2014). Therefore, if the apatite has formed at high temperatures, or has been heated to high temperatures after formation, the U-Pb age may not faithfully record apatite formation. In addition, apatite often

incorporates appreciable amounts of Pb during crystallisation (e.g. Chew et al., 2014), which can make U-Pb ages difficult to calculate. For instance, in order to calculate an age, either a series of data points must be measured to determine an isochron, or an assumed initial Pb isotopic composition needs to be used in order to correct the apatite U-Pb age for the Pb incorporated during crystallisation (Chew et al., 2014). Although both methods are demonstrably capable of calculating accurate U-Pb dates for apatite, this is not always the case, consequently alternative geochronological techniques (such as Lu-Hf), would clearly be beneficial.

Similar to garnet, apatite incorporates significant amounts of REEs into its cation sites (Barfod et al., 2003; Chew and Spikings, 2015; Pan and Fleet, 2002). This makes both the Sm-Nd and Lu-Hf methods applicable to apatite. Although the closure temperature of the Sm-Nd system in apatite is likely similar to Lu-Hf (as Lu, Sm, and Nd are geochemically similar), the lack of isotopic variation in Sm-Nd and the longer half-life still hinder application of the system to apatite geochronology (as described above for garnet). Previous studies have demonstrated that laser ablation Sm-Nd isotopic analysis can successfully be applied to apatite crystals (e.g. Fisher et al., 2011; Foster and Vance, 2006), however these tend to be concerned with determining the initial Nd isotopic composition of the apatite, with only relatively recent applications used for geochronology (e.g. Gillespie et al., 2022; Hammerli and Kemp, 2021). The Lu-Hf system holds great promise for dating apatite crystals because it has a relatively high closure to volume diffusion (670 - 700°C; Barfod et al., 2005; Cherniak, 2000) and because apatite tends to strongly reject Hf (Barfod et al., 2003). Previous studies have demonstrated that solution Lu-Hf can successfully be applied to dating apatite crystals (Barfod et al., 2005; Barfod et al., 2003; Larsson and Söderlund, 2005). The technique, however, is limited by the low Hf concentrations of typical apatite, necessitating large quantities of material to be dissolved (e.g. 0.5 g; Barfod et al., 2005), which severely limits application of solution Lu-Hf to apatite. Consequently, in-situ techniques, such as laser ablation, are beneficially because they are both less time consuming, and have a much higher sensitivity relative to sample volume compared to mineral digestion techniques. It should be noted, however, that if no Hf bearing minerals (such as zircon) co-forms with apatite, then apatite may incorporate some common Hf.

Carbonates

Carbonate minerals share some similarities with apatite, in that they form in a wide range of settings, and that current geochronological methods exist but have limitations that make alternative methods, such as Lu-Hf, potentially beneficial. Some of the most common carbonate minerals include calcite, and its common polymorph aragonite (CaCO_3), dolomite (MgCaCO_3), magnesite (MgCO_3) and siderite (FeCO_3). Carbonates can form in a variety of sedimentary rocks (from diagenetic, marine, or meteoric fluids), some igneous rocks, a variety of metamorphic rocks and as a common hydrothermal mineral (Roberts et al., 2020). Carbonates are often visible to the naked eye (as opposed to often microscopic accessory minerals such as apatite), making mineralogical relationships easy to determine. Of particular interest, is the common occurrence of carbonate as vein infill, which can occur in a variety of settings, from upper crustal brittle fracturing to hydrothermal brecciation (e.g. Barker and Cox, 2011; Bons et al., 2012; Debruyne et al., 2016; Maas et al., 2022; Roberts and Walker, 2016). Consequently, if carbonates can be dated, this date can be related to a tectonic process. Furthermore, in a hydrothermal mineral deposit, there may be multiple generations of carbonate veining, with some veins forming in association with economic mineralisation, and others not (e.g. Maas et al., 2022). Consequently, the age of carbonate formation could be used to better understand mineralisation at the deposit scale.

Although carbonates can be dated by solution and laser ablation U-Th-Pb (e.g. Li et al., 2014; Rasbury and Cole, 2009), as well as solution Sm-Nd and Lu-Hf (e.g. Maas et al., 2022; Nie et al., 1999;

Peng et al., 2003), these methods suffer from the same limitations as outlined for apatite, but arguably to a larger degree. For instance, carbonates typically contain lower concentrations of Sm and U compared to apatite (e.g. Belousova et al., 2002; Dawson and Hinton, 2003; Debruyne et al., 2016; Mao et al., 2016; Terakado and Masuda, 1988), requiring larger aliquot sizes for mineral digestion. In addition, it is possible to conduct LA-ICP-MS Sm-Nd dating on apatite (e.g. Hammerli and Kemp, 2021), but this has currently not been demonstrated for carbonate minerals (likely due to sensitivity issues relating to the low Sm and Nd concentrations). The U-Th-Pb closure temperature to volume diffusion has not been fully constrained for carbonates (Roberts et al., 2020) but is thought to be lower than apatite (Cherniak, 1997). Often carbonates incorporate large amounts of Pb during crystallisation, which, coupled with low U concentrations, sometimes precludes the ability to calculate an age (Rasbury and Cole, 2009; Roberts et al., 2020). For instance, carbonates formed from meteoric fluids typically contain high U/Pb ratios, while hydrothermal carbonates from more reduced settings (such as many mineral deposits) often lack U and contain high common Pb (Rasbury and Cole, 2009). Particularly in IOCG mineral deposits, the combination of the relatively high fluid solubility of Pb (Brugger et al., 2016) and the many minerals that will compete for U (e.g. apatite, titanite, monazite; Corriveau et al., 2016) can make U-Pb dating of carbonates difficult.

Similar to apatite, carbonates are expected to incorporate REE including Lu (< 1 - 10 ppm Lu; Elzinga et al., 2002; Terakado and Masuda, 1988; Zhong and Mucci, 1995), but not incorporate appreciable Hf (Maas et al., 2022). Further, unlike Pb, Hf is highly immobile in most hydrothermal fluids (Brugger et al., 2016), meaning Lu-Hf may be more applicable to mineral deposits compared to U-Pb. Currently, a single study has demonstrated that solution Lu-Hf can be applied to carbonates (Maas et al., 2022), indicating that Hf concentrations occur at the ppb to ppt level, at least for carbonates at the Olympic Dam IOCG deposit. Consequently, Maas et al. (2022) used large aliquots (up to 2 g) in order to obtain sufficient sensitivity to detect Hf. Similar to apatite, laser ablation Lu-Hf has the potential to produce straightforward ages (i.e. low common Hf, and potentially higher closure temperature compared to U-Th-Pb), and may be more applicable to mineral deposits, considering that hydrothermal carbonates tend to have high Pb/U ratios (Rasbury and Cole, 2009). The closure temperature of the Lu-Hf system in calcite is, however, poorly understood, with previous work indicating that the effective closure temperature of HREEs in a 100 micron calcite crystal is ~500°C (assuming a cooling rate of 10°C per myr; Cherniak, 1998). We note that calcite crystals can often be much larger than 100 microns, which is expected to increase the effective closure temperature. No data, however, currently exists for Hf diffusion in carbonates. In addition, laboratory experiments such as Cherniak (1998) do not account for the potential Lu partitioning between calcite and surrounding minerals, which is likely to affect closure temperatures in real world situations. As stated, Hf concentrations of calcite can be extremely low (Maas et al., 2022). While LA-ICP-MS analysis, as previously stated, has a better sensitivity/sample volume compared to solution analysis, such low concentrations may pose problems. The most obvious solution is to use large laser beam diameters during analysis, which will increase the amount of sample that reaches the detector for a given time period. Carbonate minerals tend to form large crystals, or masses of smaller crystals, which can allow for extremely large laser ablation spots to be used (i.e. a laser diameter of 257 microns). Consequently, calcite Lu-Hf dating has many benefits for Earth scientists, however laser ablation Lu-Hf has some challenges.

3. Thesis Outline

Chapter 1 details the Laser ablation Lu-Hf method, including demonstration of the technique to a variety of natural minerals. Chapter 2 further develops the method by exploring Lu-Hf dating of

calcite. Chapters 3 and 4 apply the novel analytical methods outlined in chapters 1 and 2 to demonstrate how they can solve geological problems. In more detail, chapter 3 demonstrates the application of garnet Lu-Hf dating to determine the age of polymetamorphic rocks, and chapter 4 explores the use of Lu-Hf dating for determining the age of mineralisation at an IOCG prospect in South Australia. The final (conclusion) chapter summarises the findings and suggests areas that could be developed further as well as potential future applications.

Chapter 1:

Simpson, A., Gilbert, S., Tamblyne, R., Hand, M., Spandler, C., Gillespie, J., Nixon, A., Glorie, S. 2021. In-situ Lu Hf geochronology of garnet, apatite and xenotime by LA ICP MS/MS. *Chemical Geology*, 577. <https://doi.org/10.1016/j.chemgeo.2021.120299>

Chapter 1 is published in *Chemical Geology* (Simpson et al., 2021) and primarily focuses on demonstrating the optimum analytical parameters for laser ablation Lu-Hf dating using LA-ICP-Q-MS/MS. A method is outlined that reduces the interferences of ^{176}Lu and ^{176}Yb on ^{176}Hf to < 0.003%, while measuring 50 – 60 % of total ^{176}Hf . The laser ablation Lu-Hf method is then demonstrated on a variety of materials, including synthetic glass reference materials (NIST SRM 610), for which independently constrained Lu-Hf ratios exist. The method is also demonstrated on a variety of natural minerals (apatite, garnet, and xenotime) including U-Pb reference materials with existing geochronological constraints. Consequently, we demonstrate that laser ablation Lu-Hf can be applied to real world geological problems

Chapter 2:

Simpson, A., Glorie, S., Hand, M., Spandler, C., Gilbert, S., Cave, B. 2022. In situ Lu–Hf geochronology of calcite. *Geochronology*, 4(1): 353-372. <https://doi.org/10.5194/gchron-4-353-2022>

Chapter 2 is published in *Geochronology* (Simpson et al., 2022) and demonstrates that the laser ablation Lu-Hf method can be applied to calcite. One of the main obstacles to applying Lu-Hf dating to calcite is the low Lu and even lower Hf concentrations of typical calcite minerals. In this chapter we use large laser beam diameters to maximise sensitivity and explore the effects that this has on the method. For instance, with such large spot sizes, significantly more material reaches the plasma torch, potentially reducing the efficiency of ionisation. We demonstrate that these effects appear to affect the measured isotopes in the same way, and that if there are slight differences, matrix matched correction procedures are likely to overcome them. Finally, we demonstrate laser ablation Lu-Hf dating to a variety of natural calcite minerals, demonstrating ages that span from 2 to 0.9 Ga (2σ uncertainties between 1.7 and 0.6 %) and agree with expected ages. The samples include (1) hydrothermal calcite from Iron oxide copper gold deposits (IOCG) in the Eastern Fold Belt of Mt Isa, Australia, (2) calcite from the Phalaborwa carbonatite, South Africa, (3) calcite from the Yates Mine, Canada, and (4) a calcite vein that formed in a low-grade metamorphic rock, from Flin Flon, Canada.

Chapter 3:

Chapter 3 explores the application of the laser ablation Lu-Hf method to determining the age of (poly-) metamorphic garnets. This chapter uses garnet samples collected from metapelitic rocks in the Moine supergroup, NW Scotland to demonstrate that laser ablation Lu-Hf is capable of revealing the metamorphic history of a complex polymetamorphic terrane with relative ease. We produce garnet Lu-Hf ages that coincide with all major orogenic events that have been documented in the region (~950 Ma Renlandian Orogeny, the 820 – 730 Ma Knorydian Orogeny, and the 470 – 430 Ma Caledonian Orogeny) and that are in excellent agreement with solution garnet Lu-Hf ages from

the same locations. Following from this, we make a series of recommendations that detail a series of steps that can be used to overcome some of the limitations of laser ablation analysis compared to solution analysis.

Chapter 4:

In chapter 4, we apply laser ablation Lu-Hf dating to the Vulcan IOCG prospect, South Australia to explore the ability of laser ablation Lu-Hf dating to determine the age of mineralisation. We demonstrate that laser ablation Lu-Hf dating can be applied to determine the age of hydrothermal apatite and dolomite. The obtained Lu-Hf ages for the Vulcan IOCG prospect unambiguously reflect the primary mineralisation age (~1600 Ma). Dolomite Lu-Hf dates can preserve primary mineralization ages, but can also be used to date Cu remobilization, opening new opportunities for mineral exploration.

Chapter 5: (conclusion)

Chapter 5 summarises and discusses the findings of this thesis. In addition, a series of recommendations for future improvements and potential applications are made.

Note on supplementary data

In order to make the data used in this thesis easy to access (and to save paper), supplementary datasets are hosted on the internet with their own individual DOI (and not included in this thesis). These datasets are publically available. Relevant DOIs are listed at the start and end of each chapter.

Chapter 1: *In-situ* Lu-Hf geochronology of garnet, apatite and xenotime by LA ICP MS/MS

Published as:

Simpson, A., Gilbert, S., Tamblyn, R., Hand, M., Spandler, C., Gillespie, J., Nixon, A., Glorie, S. 2021. In-situ Lu Hf geochronology of garnet, apatite and xenotime by LA ICP MS/MS. Chemical Geology, 577. <https://doi.org/10.1016/j.chemgeo.2021.120299>

Supplementary data tables can be found at:

U-Pb data set: <https://doi.org/10.25909/21952637.v1>

Lu-Hf data set: <https://doi.org/10.25909/21952640.v1>

Statement of Authorship

Title of Paper	In-situ Lu-Hf geochronology of garnet, apatite and xenotime by LA ICP MS/MS
Publication Status	☒ Published ☐ Accepted for Publication ☐ Submitted for Publication ☐ Unpublished and Unsubmitted work written in manuscript style
Publication Details	Simpson, A., Gilbert, S., Tamblyn, R., Hand, M., Spandler, C., Gillespie, J., Nixon, A., and Glorie, S., 2021, In-situ Lu Hf geochronology of garnet, apatite and xenotime by LA ICP MS/MS: Chemical Geology, v. 577. https://doi.org/10.1016/j.chemgeo.2021.120299

Principal Author

Name of Principal Author (Candidate)	Alexander Simpson		
Contribution to the Paper	conceptualisation, method development, experimentation, data interpretation, manuscript drafting		
Overall percentage (%)	80		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	11/01/2023

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

- i. the candidate's stated contribution to the publication is accurate (as detailed above);
- ii. permission is granted for the candidate to include the publication in the thesis; and
- iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	Sarah Gilbert		
Contribution to the Paper	method development, experimentation, method drafting; manuscript editing		
Signature		Date	11/01/2023

Name of Co-Author	Renee Tamblyn		
Contribution to the Paper	experimentation, method development, providing samples, data interpretation, manuscript editing		
Signature		Date	11/01/2023

Name of Co-Author	Martin Hand		
Contribution to the Paper	conceptualization, data interpretation, supervision, manuscript editing		
Signature		Date	23/01/2023

Name of Co-Author	Carl Spandler		
Contribution to the Paper	providing samples, data interpretation		
Signature		Date	23/01/2023

Name of Co-Author	Jack Gillespie		
Contribution to the Paper	providing samples, data interpretation		
Signature		Date	23/01/2023

Name of Co-Author	Angus Nixon		
Contribution to the Paper	providing samples, experimentation		
Signature		Date	12/01/2023

Name of Co-Author	Stijn Glorie		
Contribution to the Paper	conceptualization, data interpretation, manuscript drafting and editing, primary supervision		
Signature		Date	11/1/23

1.1. Abstract

Lu–Hf geochronology is a powerful method to constrain the temporal evolution of geological systems. Traditional application of this dating method requires time-consuming chemical separation of the parent (^{176}Lu) and daughter (^{176}Hf) isotopes that is commonly accompanied by loss of textural context of the analysed minerals. In contrast, *in-situ* (laser-ablation based) Lu–Hf geochronology offers a number of advantages including rapid analysis with high spatial resolution, as well as control on textural relationships of the analysed mineral. However, laser-ablation based Lu–Hf geochronology has been hindered by isobaric interferences of ^{176}Yb and ^{176}Lu on ^{176}Hf that have effectively masked reliable determination of ^{176}Lu and ^{176}Hf . We present a methodology that resolves these interferences using LA-ICP-MS/MS (laser ablation tandem inductively coupled mass spectrometry) and NH_3 gas to separate Hf from Lu. Both Lu, Yb, and Hf react with NH_3 to form a variety of product ions. By measuring high order reaction products (e.g. $\text{Hf}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$), we demonstrate that ^{176}Hf can be measured interference-free from ^{176}Lu and ^{176}Yb with sufficient sensitivity to yield useful geochronological age data.

The novel *in-situ* Lu–Hf technique has been successfully applied to a variety of Palaeozoic and Precambrian-aged garnet, apatite and xenotime samples, including published reference materials. The resulting age uncertainties are as low as $\sim 0.5\%$ (95% conf. interval). The technique has the potential to obtain spatially-resolved Lu–Hf ages in garnet-bearing samples that would be difficult to obtain by conventional techniques. The method also offers the opportunity for rapid “campaign style” geochronology in complex terrains that record poly-metamorphic histories. In apatite, the expected higher closure temperature of the Lu–Hf system compared to the commonly used U–Pb system allows high-temperature thermal history reconstructions. In addition, Lu–Hf dating of apatite allows dating of samples with low U and high common Pb (e.g. mafic and low-grade metamorphic rocks and ore deposits). Furthermore, apatite tends to incorporate little to no common Hf, allowing single grain ages to be calculated, which opens new doors for detrital provenance studies. *In situ* Lu–Hf dating of xenotime offers an additional avenue to U–Pb dating, and may be particularly beneficial to dating of rare earth element ore deposits that often have complex temporal records of development.

1.2. Introduction

Inductively-coupled plasma mass spectrometry that uses additional collision/reaction cell technology (ICP-MS/MS) is capable of resolving isobaric interferences that previously hindered precise isotope ratio measurement using conventional ICP-MS techniques. When coupled with laser ablation (LA) micro-sampling, this new technology allows for rapid *in-situ* determinations of isotope ratios in solid materials. Previous work has demonstrated the utility of this method when applied to beta decay systems such as ^{87}Rb – ^{87}Sr (e.g. Armistead et al., 2020; Bolea-Fernandez et al., 2016a; Bolea-Fernandez et al., 2016b; Redaa et al., 2020; Tillberg et al., 2017; Tillberg et al., 2020; Zack and Hogmalm, 2016) and ^{187}Re – ^{187}Os (Hogmalm et al., 2019) as well as interference removal for alpha decay systems such as U–Pb (Gilbert and Glorie, 2020). Few studies, however, have applied this technology to the Lu–Hf decay system, with limited successful demonstrations to date (Woods, 2017; Zack and Hogmalm, 2015).

The Lu–Hf decay system, in which ^{176}Lu decays via beta decay to ^{176}Hf with a half-life of ~ 37.12 Ga (Scherer et al., 2001; Söderlund et al., 2004), has been used as a chronometer in a range of geological systems (Vervoort, 2014). Of particular importance is dating metamorphism using garnet Lu–Hf geochronology (e.g. Bird et al., 2013; Duchene et al., 1997; Ibanez-Mejia et al., 2018). Accurate *in-situ* measurement of these isotopes is hindered by isobaric interferences from both ^{176}Lu

and ^{176}Yb on ^{176}Hf (Woods, 2017; Zack and Hogmalm, 2015). Successful analysis of Hf isotopic ratios in zircon (and other minerals with low Lu/Hf ratios) are now routinely conducted *in-situ* by LA-multicollector (MC)-ICP MS (Griffin et al., 2002; Spencer et al., 2020; Thirlwall and Walder, 1995; Woodhead et al., 2004). However, *in-situ* Hf isotopic analysis of zircon relies on Hf concentrations being much greater than Lu concentrations (e.g. $^{176}\text{Lu}/^{177}\text{Hf} < \sim 0.01$) and mathematic corrections for isobaric interferences (Spencer et al., 2020; Thirlwall and Walder, 1995; Woodhead et al., 2004). In contrast, Lu–Hf geochronology on mineral phases with high Lu/Hf ratios (such as garnet) currently requires chemical separation of isotopes in order to obtain accurate results (Vervoort, 2014). Although precise ages can be obtained following chemical separation (Anczkiewicz et al., 2004; Johnson et al., 2018), these techniques can be time consuming and costly, meaning large quantities of data can be difficult to obtain. In addition, the requirement for chemical separation of isotopes hinders the acquisition of spatially-resolved isotopic ratios (Schmidt et al., 2015). Strategies to overcome this, such as micro-drilling, are restricted to large mineral grains (such as garnets), and tend to compromise the spatial resolution of sampling, especially at the μm scale (Schmidt et al., 2015).

In this paper, we present a new technique for *in-situ* Lu–Hf dating using LA-ICP-MS/MS. We describe the methodology in detail and present the first *in-situ* Lu–Hf dates for a series of well-characterized garnet, xenotime and apatite samples, which are compared to published ages obtained via traditional methods. Finally, we explore some applications and discuss methodological limitations and future directions.

1.2.1. LA-ICP-MS/MS technology

LA-ICP-MS/MS uses two quadrupole mass analysers sandwiching a hexapole collision/reaction cell designed to remove mass interferences (Agilent, 2016). The first quadrupole works as a mass filter, whereby a specific mass (e.g. atomic mass 176 for Lu–Hf) is allowed into the hexapole collision/reaction cell. The reaction cell is filled with a gas (e.g. O_2 , SF_6 , NH_3), where flow rate and concentration are optimised such that either only one element reacts, or elements react in different ways, forming product ions of different masses. For example, previous studies have demonstrated that Sr reacts with O_2 and N_2O to form SrO^+ , while Rb does not react (Hogmalm et al., 2017; Redaa et al., 2020; Zack and Hogmalm, 2016). This behaviour has been utilised to allow for accurate determination of $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios.

Isobaric interferences can be resolved for Lu–Hf geochronology using NH_3 , which is a highly reactive gas and often forms multiple high-order reaction products (Woods, 2017). These complex reaction products are slow moving due to their low kinetic energy, which can lead to a decrease in sensitivity. An important feature of the Agilent 8900 ICP-QQQ is the inclusion of axial acceleration in the collision/reaction cell. This setup can modify the axial energy of large and slow moving high-order reaction product ions, thereby increasing sensitivity (Agilent, 2016). Consequently, large cluster-reaction product ions can be used to measure elements even at low concentrations (Woods, 2017), which lies at the foundation of the *in-situ* Lu–Hf development (as explained in detail in the method section, below).

1.2.2. Challenges and opportunities for dating garnet, apatite and xenotime.

It is important to assess the accuracy of new geochronological techniques, such as the one detailed here. Although it may seem preferable to directly compare *in situ* Lu–Hf ages with solution Lu–Hf ages, there are several problems with solution Lu–Hf ages that may affect accuracy. Mixing of age domains in the sample aliquots used for solution Lu–Hf may be problematic, particularly for low Hf

minerals, such as apatite, where a large sample volume is required (~0.5g; Barfod et al., 2005). For example, in hydrothermal systems, multiple fluid events may lead to partial recrystallization of minerals (such as apatite and xenotime). In addition to this, it is often difficult to completely remove Lu- and/or Hf-bearing inclusions from sample aliquots. In cases where inclusions significantly differ in age from analysed samples, meaningless mixing ages may be produced (Scherer et al., 2000). For example, garnet solution Lu–Hf often requires high-pressure digestion, which will also dissolve zircon inclusions (Blichert-Toft et al., 1997; Lagos et al., 2007; Scherer et al., 2000). Zircons contain wt% levels of Hf and are commonly included in metamorphic garnets (Scherer et al., 2000). Due to the different thermodynamic properties of Lu and Hf, sample-spike equilibration can be difficult to achieve, potentially leading to erroneous ages (Blichert-Toft et al., 1997; Lagos et al., 2007). Although there are some solutions that can mitigate these problems (e.g. Lagos et al., 2007), it is important to have external constraints on crystallisation ages in order to compare *in situ* Lu–Hf geochronology. Therefore, samples with geological constraints on crystallisation age and thermal history (e.g. hydrothermal apatites with U–Pb ages that are equivalent to the host rock age) are considered to be better candidates for assessing the accuracy of the technique. Having geological constraints on crystallisation age is also preferable for any *in situ* Lu–Hf reference material.

Garnet ((Fe²⁺, Mn, Mg, Ca)₃(Al, Fe³⁺, Cr)₂(SiO₄)₃) is among the most important of metamorphic minerals, as it forms in a large range of bulk-rock compositions and is extensively used as a petrogenetic recorder of the physical and chemical conditions of metamorphism (Baxter et al., 2017). Garnet has relatively well understood elemental diffusional behaviour, meaning it can also be used to recover thermal histories. Additionally, garnet is a resistant mineral meaning it can preserve records of now largely obliterated tectonic systems (e.g. Smit et al., 2013).

Garnet is potentially amenable to multiple geochronometers such as Sm–Nd, Lu–Hf, and U–Pb (Duchene et al., 1997; Mezger et al., 1989; Smit et al., 2013), although application of the U–Pb system is largely limited to grossular and andradite garnets that are relatively U rich (e.g. Seman et al., 2017). Therefore, the Sm–Nd and Lu–Hf geochronometers are more commonly applied (Vervoort, 2014). The Lu–Hf system has a similar or higher closure temperature than Sm–Nd in garnet (Ibanez-Mejia et al., 2018; Johnson et al., 2018; Scherer et al., 2000; Smit et al., 2013). Hence, Lu–Hf dating is thermally robust in garnet, and garnets can be directly linked to a mineral assemblage and given P – T conditions, making them an excellent mineral for Lu–Hf geochronology (Anczkiewicz et al., 2004; Baxter et al., 2017; Baxter and Scherer, 2013; Smit et al., 2013). Although able to produce highly precise ages, current Lu–Hf geochronology is somewhat limited by the relatively high cost and time requirements associated with traditional techniques based on chemical separation of Lu from Hf.

Apatite (Ca₁₀(PO₄)₆(OH,F,Cl)) is a common minor/accessory mineral of a wide variety of rock types (Chew and Spikings, 2015) and is now routinely analysed for U–Th–Pb geochronology. However, apatite U–Th–Pb dating has a number of challenges. Where U concentrations are low and common Pb concentrations are high (e.g. mafic or low-grade metamorphic rocks), precise U–Pb dating is often not feasible (e.g. Henrichs et al., 2019). Most importantly, apatite has a relatively low closure temperature for the U–Pb system (~350 - 550oC: Cherniak et al., 1991; Chew et al., 2014; Chew and Spikings, 2015; Cochrane et al., 2014), meaning U–Pb ages are highly susceptible to disturbance by post-formation events (e.g. Glorie et al., 2019).

Lu–Hf geochronology has previously been applied to apatite (and other phosphates) from settings such as igneous intrusions (including mafic cumulates; Larsson and Söderlund, 2005), metamorphic rocks (Barfod et al., 2005), animal fossils (Barfod et al., 2002; Barfod et al., 2003) and meteorites (Amelin, 2005). Similar to garnets, all of these published studies used sample digestion and chemical

separation techniques prior to Lu–Hf geochronology. Lutetium and Hf are expected to remain immobile to higher temperatures (~650–700 °C) than U–Pb in apatite, although the closure temperature of the Lu–Hf system is not well constrained (Barfod et al., 2005; Barfod et al., 2003; Cherniak, 2000; Chew and Spikings, 2015).

Xenotime (YPO₄) is often the primary heavy REE host of a large range of rock types formed in a variety of settings (igneous, metamorphic, sedimentary, hydrothermal and diagenetic) (McNaughton and Rasmussen, 2018), and is also an important ore mineral for heavy REE deposits (Nazari-Dehkordi and Spandler, 2019). Xenotime is considered to have a relatively high closure temperature for both the U–Pb and Lu–Hf isotope systems (Cherniak, 2006). The high concentrations of Lu found in xenotime make this an excellent mineral for in-situ LA-ICP-MS/MS Lu–Hf geochronology (e.g. Scherer et al., 2001; Zack and Hogmalm, 2015).

1.3. Sample descriptions.

1.3.1. Garnet samples.

Högsbo Garnet: Garnet grains were sampled from the WNW–ESE trending Högsbo pegmatite in southern Gothenburg (Romer and Smeds, 1996). The mineralogy of the pegmatite is K-feldspar + quartz + cleavelandite + muscovite, with minor garnet, columbite, monazite, beryl, titanite and apatite (Romer and Smeds, 1996). A columbite U–Pb crystallisation age of 1029 ± 1.7 Ma is interpreted to represent emplacement of the pegmatite during the Sveonorwegian Orogeny (Romer and Smeds, 1996). *In-situ* Rb–Sr muscovite dates are consistent with the columbite date, producing ages of ca. 1030–1037 Ma, with uncertainties of ~1.5% (2σ ; Hogmalm et al., 2017). It should be noted, however, that there is no detailed paragenesis that links garnet to columbite, and co-precipitation is currently inferred. Sampled garnets for *in-situ* Lu–Hf dating are up to 4 mm in diameter and are typically intergrown with muscovite. Lutetium concentrations range from 5 – 680 ppm and Hf concentrations ranged from 0.006 – 0.11 ppm.

Usagaran Orogen, Tanzania (T01-40): Garnet grains were sampled from retrogressed eclogites of the Usagaran Orogen of central Tanzania (Brown et al., 2020; Tamblyn et al., 2020a). The mineralogy of the retrogressed eclogites is garnet + diopside + hornblende + plagioclase + quartz and minor rutile + ilmenite + zircon + apatite ± titanite. The Lu–Hf TIMS isochron for sample T01-40 yields an age of 1994 ± 9 Ma (Tamblyn et al., 2020a). The garnet is interpreted to form with zircon, which gives similar U–Pb ages (Tamblyn et al., 2020a). Garnets in T01-40 are up to 1.5 mm in diameter and have prograde zoning, with heavy REE-enriched cores of up to 6 ppm Lu. Hafnium concentrations ranged from 0.015 – 0.45 ppm.

Port Macquarie, Australia (RB10 and RB11): Euhedral garnets, up to 7 mm in diameter, from a block of lawsonite eclogite from the mélange at Port Macquarie in the Southern New England Fold Belt (Australia) were analysed to compare with existing TIMS Lu–Hf geochronology. The eclogite contains the assemblage garnet + lawsonite + omphacite + phengite + quartz + titanite + zircon that formed at pressures of at least 29 kbar and temperatures in excess of approximately 600 °C (Tamblyn et al., 2019). The sampled garnet grains have cores with Lu concentrations of up to 11 ppm, with bell-shaped zoning and thin concentric Lu-enriched (up to 3 ppm) zones throughout the garnet. A published Lu–Hf garnet-whole rock isochron gives an age of 489.7 ± 5.5 Ma (Tamblyn et al., 2019). This sample has a Hf concentration of about 0.001 ppm after zircon inclusions have been accounted for.

Western Gneiss Complex, Norway (WGC-31): Garnets were obtained from metapelitic gneiss on the island of Fjørtoft in the Western Gneiss Complex, Norway. The Fjørtoft metapelite contains an ultra-

high pressure (UHP) diamond-bearing mineral assemblage (Dobrzhinetskaya et al., 1995). The mineral assemblage of the studied sample is garnet + kyanite + biotite + quartz + muscovite + plagioclase + k-feldspar + rutile + zircon + apatite + monazite $\pm$ chlorite $\pm$ sillimanite. A LA-ICP-MS U–Pb age of 386 ± 5 Ma has been obtained from rutile within the gneiss (Zack et al., 2011). SHRIMP and EPMA monazite ages of ca. 408–397 Ma have also been obtained from the locality, as well as an older population of monazites within garnet at ca. 1055 Ma (Terry et al., 2000). Zircon geochronology from this location produced similar ages, with the majority of zircons forming during the Caledonian but additional zircon age populations at $\sim 2.8 - 2.5$ Ma, $1.5 - 1.3$ Ma, $1.1 - 0.9$ Ma and $\sim 0.9 - 0.7$ Ma (Walczak et al., 2019). The garnets show bell-shaped zoning in Lu, with enriched cores (up to 28 ppm Lu; Fig. 1.2G) and flat rims (~ 1 ppm Lu). Hafnium concentrations ranged from 0.17 – 0.55 ppm. These garnets are ~ 1 cm in diameter.

1.3.2 Apatite samples:

The following samples were chosen under two general categories. They either have solution Lu–Hf ages or are constrained by well-characterised emplacement or depositional ages of their host rocks. Therefore these samples can be used to interrogate any analytical age offsets. The second category of samples was chosen to illustrate the power of the Lu–Hf method compared to traditional dating systems.

Otter Lake Apatite from the Yates mine, Otter Lake area, Quebec has been used as a U–Pb reference material for LA-ICP-MS analysis (Chew et al., 2011; Thompson et al., 2016). The Otter Lake area comprises gneisses, skarns and amphibolites (Barfod et al., 2005) that underwent widespread hydrothermal activity associated with upper amphibolite metamorphism during the Grenville Orogeny (Kretz et al., 1999). Although Otter Lake apatite is used as a U–Pb standard, (Thompson et al., 2016) has raised concerns about its suitability as a standard. In contrast to other samples in our study, there is a published Lu–Hf age (1031 ± 6 Ma) for Otter Lake apatite, as well as a published Lu–Hf data for co-genetic titanite, that can be used to correct Lu–Hf data for common Hf (Barfod et al., 2005). This sample contained between 8 and 10 ppm Lu, and between 0.012 and 0.024 ppm Hf.

OD306 apatite is a U–Pb reference material, developed at the University Of Tasmania (Thompson et al., 2016). OD306 is sourced from a hydrothermal apatite vein from the Acropolis Au–Cu prospect in South Australia and has an isotope dilution (ID) MC-ICP-MS U–Pb age of 1597 ± 7.1 Ma (Thompson et al., 2016). The Acropolis Cu – Au prospect is hosted in the 1594.03 ± 0.68 Ma (U–Pb zircon) Gawler Range Volcanics (McPhie et al., 2020). This sample contained between 14 and 21 ppm Lu.

Sample CS5 was taken from the Tabletop Granite in the Pine Creek Orogen, Northern Territory, Australia. The Tabletop Granite comprises part of the Cullen Supersuite batholith; a syn- to post-orogenic granitoid suite emplaced between ca. 1860–1800 Ma (Rasmussen et al., 2006; Stuart-Smith et al., 1993). Emplacement was followed by regional orogenesis and greenschist-facies metamorphism associated with the ca. 1855 Ma Litchfield Event of the Pine Creek Orogeny (Pietsch and Edgoose, 1998; Worden et al., 2008). The Tabletop Granite possesses a major mineralogy of quartz, orthoclase and plagioclase, with significant biotite and minor hornblende content (Stuart-Smith et al., 1993). This sample contained between 22 and 77 ppm Lu.

Mud Tank Apatite from the Mud Tank Carbonatite, situated in the Strangways Ranges, Northern Territory, contains large crystals of both apatite and zircon. Zircon crystallization has been dated at 735 ± 5 Ma (Black and Gulson, 1978). Rb–Sr biotite ages range between ca. 349 – 310 Ma (Haines et al., 2001) indicating overprinting during the (ca. 450 - 300 Ma) Alice Springs Orogeny. The apatite fission track age is 298 ± 23 Ma (Green et al., 2006). Previous geochronology of low U (~ 2 ppm) and

Lu (~ 0.25 ppm) apatite returned an imprecise U–Pb age of 455 ± 51 Ma (Thomson et al., 2012; Yang et al., 2014). Chew et al. (2011) obtained a U–Pb age for apatite from Mud Tank of 349 ± 31 Ma, coincident with the oldest Rb–Sr biotite ages from the area. A cm-scale apatite crystal from Mud Tank carbonatite was sampled for this study. This sample contained between 9 and 12 ppm Lu.

Sample 215 - Ødegårdens Verk apatite is sourced from Ødegårdens Verk, Bamble, Norway, where several generations of apatite occur in scapolitised metagabbro containing apatite-phlogopite veins (Nijland et al., 1993). These include primary igneous apatite in the gabbro and metasomatic chlorapatite in the apatite-phlogopite veins, which are variably replaced by hydroxy-fluor-apatite in albitised zones (Engvik et al., 2009). The apatite used here is a chlorapatite from the apatite-phlogopite veins with 6.04 wt.% Cl. Both scapolitisation and albitisation are thought to have occurred during $\sim 1110 - 1080$ Ma amphibolite-grade metamorphism in response to the Sveconorwegian Orogeny (Bingen et al., 2008; De Haas et al., 2009; Engvik et al., 2017). Poorly constrained U–Pb ages ($1090 - 1084$ Ma) from discordant hydrothermal rutile have been interpreted to constrain fluid alteration at Ødegårdens Verk (Engvik et al., 2011). This sample is from a ~ 5 mm apatite crystal. This sample contained between 27 and 34 ppm Lu.

BC10 apatite is from a vein of coarse-grained apatite (~ 1 cm) from the ‘Inter-Lens’ of the Ernest Henry IOCG deposit, Mt Isa Inlier, Queensland, Australia (Cave et al., 2018). Previous geochronology has constrained the U–Pb age of this sample to 1584 ± 22 Ma, associated with metamorphism during deformation stage D2 of the $1650 - 1500$ Ma Isan Orogeny (Cave et al., 2018). This sample contained between 1 and 4 ppm Lu.

The following two apatite samples were obtained from the Tate Museum, University of Adelaide. Little is known about the exact geological context of these apatite crystals, outside of their general location. They are, however, large hydrothermal/pegmatite apatite crystals (>0.5 cm) that would make potentially useful reference materials.

19589 Harts Range apatite from the Hart Range, Northern Territory has a geological history spanning back to the Proterozoic. Major tectonothermal events occurred from 1800 Ma until the $450 - 300$ Ma Alice Springs Orogeny (Buick et al., 2008; Hand et al., 1999; Mawby et al., 1999). Although this is a museum sample, and no location data exists, the large size (~ 1 cm) of the apatite crystal makes it likely that it was sourced from a pegmatite. Pegmatite ages range between $\sim 450 - 300$ Ma in the Harts Range (Buick et al., 2008), indicating the probable age range for this sample. This sample contained between 24 and 25 ppm Lu.

15836 Wallaroo Mines apatite was sourced from a large (~ 1 cm) hydrothermal apatite from the Moonta-Wallaroo Iron–Oxide–Cu–Au (IOCG) deposit, Gawler Craton, South Australia. Mineralisation is poorly constrained, but Re–Os dates from molybdenite-bearing veins that cross-cut mineralisation provide minimum ages of 1574 ± 6 and 1599 ± 11 Ma (Skirrow et al., 2007). This sample contained between 8 and 14 ppm Lu.

1.3.3. Xenotime samples:

Xenotime reference materials BS-1 (509 ± 0.3 Ma), MG-1 (490 ± 0.3 Ma), and Z6413 (993 ± 1 Ma) (Fletcher et al., 2004; Stern and Rainbird, 2001) were analysed due to their well constrained U–Pb ages. Both BS-1 and MG-1 are hydrothermal crystals samples from Minas Gerais, Brazil (Fletcher et al., 2004). Z6413 is from a granite pegmatite from the Grenville Province, Canada (Fletcher et al., 2004). In addition to the U–Pb xenotime reference materials, a large xenotime crystal (~ 1 cm) of unknown age was analysed. This crystal was sourced from an unknown location in Brazil and has been labelled XST-1. The primary purpose of analysing sample XST-1 is to demonstrate the

application of this technique on xenotime that likely does not have the element and/or isotopic homogeneity associated with LA-ICP-MS reference materials. BS-1 contained 3340 – 3834 ppm Lu, MG-1 contained 854 – 1494 ppm Lu, Z6413 contained 9352 – 9879 ppm Lu, and XST-1 contained 1915 – 2271 ppm Lu.

1.4 Methods.

All samples were mounted in 25 mm diameter epoxy disks. Samples were ground using 800, 1200, and 2500 grit sandpaper and subsequently polished with 3 μ m diamond paste. Prior to Lu–Hf dating, all samples were analysed for their trace element concentrations using traditional LA-ICP-MS techniques, in order to screen for high Lu and Hf crystals. In the same run, samples with unknown U–Pb age were analysed for their relevant U and Pb isotopic ratios. All analyses (both LA-ICP-MS U–Pb and LA-ICP-MS/MS Lu–Hf) were conducted at Adelaide Microscopy at the University of Adelaide.

Details on methods used for LA-ICP-MS U–Pb and trace element analysis can be found in Appendix B

1.4.1 Analytical methodology for Lu–Hf isotope measurement.

The Lu–Hf analyses were conducted using a RESolution 193nm excimer laser ablation system (Applied Spectra) with a S155 sample chamber (Laurin Technic) coupled to an Agilent 8900 ICP-MS/MS. A squid mixing devise (Laurin Technic) was used to smooth the pulses of the laser. Analyses were conducted across 3 sessions. An initial run was used to determine optimal reaction gas flow rates. ICP-MS/MS conditions were first optimised in no-gas mode (with no NH₃ in the reaction cell), to tune for a robust plasma (U/Th = 1.00-1.05) and to minimise oxide interferences (ThO/Th <0.2%). An additional 3.5 mL/min N₂ was added to the carrier gas after the sample chamber to enhance sensitivity (Hu et al., 2008). The ICP-MS/MS lenses were then tuned to maximise sensitivity for Hf reaction products using NH₃ reaction gas

<i>plasma parameters</i>	
<i>RF power</i>	1350 W
<i>Sample Depth</i>	4mm
<i>Ar carrier gas</i>	0.94 L/min
<i>He carrier gas</i>	0.38 L/min
<i>N₂ addition</i>	3.5 mL/min
<i>Lens Parameters</i>	
<i>Extract 1</i>	-1.5 V
<i>Extract 2</i>	-140 V
<i>Omega Bias</i>	-70 V
<i>Omega Lens</i>	8.0 V
<i>Q1 entrance</i>	-45 V
<i>Q1 exit</i>	1.0 V
<i>Cell focus</i>	1.0 V
<i>Cell Entrance</i>	-120 V
<i>Cell Exit</i>	-100 V
<i>Deflect</i>	10.0 V
<i>Plate Bias</i>	-60 V
<i>Q1 parameters</i>	
<i>Q1 bias</i>	-1.0 V
<i>Q1 Prefilter Bias</i>	-10.0 V

Q1 Postfilter Bias	-10.0 V
Cell Parameters	
He flow	1.0 mL/min
10% NH ₃ 90% He gas flow	3 mL/min ('30%' on Agilent 8900 mass flow controller 3)
Octopole bias	-2.0 V
Axial Acceleration	2.0 V
Octopole RF	180 V
Energy Discrimination	-13.0 V
Q2 parameters	
Q2 bias	-15 V
Wait time offset	5ms
Analysis Parameters	
Laser fluence	3 J/cm ²
Laser spot diameter	43 – 120 µm
Laser repetition rate	10 Hz
washout (post cleaning pulse)	30 s
Background	30 s
Analysis time	40 – 50 s
Isotopes measured/dwell times (ms) (runs 1 + 2)	²⁷ Al (5), ⁴³ Ca (5), ⁸⁹ Y (5), ⁹⁰ Zr (5), ¹⁷² Yb (10), ¹⁷²⁺⁸² Yb (30), ¹⁷⁵ Lu (10), ¹⁷⁵⁺¹⁶ Lu (20), ¹⁷⁵⁺⁸² Lu (100), ¹⁷⁶⁺⁸² Hf (100), ¹⁷⁸⁺⁸² Hf (100)
Isotopes measured/dwell times (ms) (runs 3)	²⁷ Al (5), ⁴³ Ca (5), ⁴⁷ Ti (5), ⁸⁹ Y (5), ⁹⁰ Zr (5), ¹⁴⁰ Ce (5), ¹⁷² Yb (10), ¹⁷²⁺⁸² Yb (30), ¹⁷⁵ Lu (10), ¹⁷⁵⁺¹⁶ Lu (20), ¹⁷⁵⁺⁸² Lu (100), ¹⁷⁶⁺⁸² Hf (100), ¹⁷⁸⁺⁸² Hf (100)

Table 1.1: LA-ICP-MS/MS tuning and analysis parameters. We emphasise that some of these parameters (such as ion lens voltages) may vary between lab, and this table should be used as a guide only.

NH₃ was used as the reaction gas, supplied as a mixture of 10% NH₃ in 90% He (all references to the NH₃ reaction gas refer to this NH₃ and He mixture). Unlike other systems dated by LA-ICP-MS/MS (e.g. Rb–Sr and Re–Os) where relatively simple reaction products form (e.g. Sr⁺ → SrO⁺; (Hogmalm et al., 2019; Hogmalm et al., 2017; Zack and Hogmalm, 2016), the reaction between Hf and NH₃ creates many (often complex) reaction products (Woods, 2017). Therefore, it is necessary to determine the best adduct ion to both maximise counts on Hf and to minimise mass interference from Lu and Yb, which also react with NH₃. As demonstrated by Woods (2017), Lu and Yb have a strong tendency to react with one more H than Hf at more complex adduct ions, thereby minimising mass interferences on ¹⁷⁶Hf. Product ion scans were used to monitor expected counts at each adduct ion for a series of gas flow rates. This was conducted separately for both Hf (using zircon reference materials) and Lu (using synthetic Lu doped, Yb and Hf free, glass produced at the University of Adelaide). A flow rate of 3 mL/min was found to maximise production of the +82 Hf reaction product (Hf(NH)(NH₂)(NH₃)₃⁺), while maintaining sufficiently low Yb and Lu +82 (i.e. REE(NH)(NH₂)(NH₃)₃⁺) for mass interference to be negligible. Although the Agilent 8900 cannot measure masses above 270 amu and thus the total reacted/unreacted Hf and Lu cannot be fully calculated, mass +82 accounted for >50% of total measured Hf at 3 mL/min NH₃, whereas mass +82 accounted for ~0.003% of total Lu measured (in the Lu doped glass) (App. Fig. 1.1). This indicates that ¹⁷⁶Lu (+82) interference on ¹⁷⁶Hf (+82) is at most 0.003% of total ¹⁷⁶Lu. ¹⁷²Yb (+82) was only detected in xenotime samples (which contain wt.% Yb). These analyses indicate that production of ¹⁷²Yb (+82) occurs at a rate of ~0.00003% of measured ¹⁷²Yb, and is therefore negligible, even in samples with very high Yb/¹⁷⁶Hf ratios. Given the low production of these interferences, no corrections were necessary for the data presented.

However, in exceptional geological environments, where extremely high Yb/Hf ratios may exist, it is important to monitor and potentially correct for such interferences.

The large cluster ions formed from reactions with NH_3 (e.g. $\text{Hf}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$) have a relatively low kinetic energy. This means that these reaction products require a higher accelerating voltage to efficiently extract them from the reaction cell compared to single element ions. Axial acceleration and cell exit voltages were modified to optimise sensitivity for these large cluster ions (table 1.1).

At initial tuning conditions, isobaric interference on $^{(176+82)}\text{Hf}$ was detected from residual $^{175}\text{Lu}(\text{NH})(\text{NH}_3)_4^+$ (258 amu, equivalent to $^{176+82}\text{Hf}$) ions that had not been fully extracted from the collision/reaction cell after switching Q1 from mass 175 to 176 amu. To eliminate this interference, a 5 ms wait time offset (WTO) was added in order to allow Lu cluster ions to exit the cell before measurement of $^{176}\text{Hf} + 82$. Analysis of the Lu-doped glass indicated that the WTO eliminated the mentioned interference from $^{175}\text{Lu}(\text{NH})(\text{NH}_3)_4^+$ completely.

Laser spots diameters of between 43 and 120 μm were used to analyse various minerals, depending on the Lu and Hf concentrations. Large spot diameters were employed to increase the sensitivity on Hf. Similarly, high laser repetition rates of 10 Hz were used to increase sensitivity.

A limited number of ancillary masses were measured in order to maximise dwell times on low sensitivity isotopes while not increasing the total sampling period such that data quality was affected. Isotopes measured were those necessary for Lu–Hf geochronology as well as a small selection of elements for monitoring inclusions (e.g. Zr for zircon inclusions) and for internal standard normalisation. The following isotopes (mass shifts included in brackets) were measured: ^{27}Al , ^{43}Ca , ^{89}Y , ^{90}Zr , ^{172}Yb , $^{(172+82)}\text{Yb}$, ^{175}Lu , $^{(175+16)}\text{Lu}$, $^{(175+82)}\text{Lu}$, $^{(176+82)}\text{Hf}$, $^{(178+82)}\text{Hf}$. Due to their higher abundance (and in the case of ^{175}Lu , lack of isobaric interferences), ^{175}Lu was monitored as a proxy for ^{176}Lu , and ^{178}Hf was monitored as a proxy for ^{177}Hf . As these are stable isotopes, the present day $^{176}\text{Lu}/^{175}\text{Lu}$ ratio (0.02659) and $^{177}\text{Hf}/^{178}\text{Hf}$ ratio (0.682) (De Bièvre and Taylor, 1993) were used to calculate ^{176}Lu and ^{177}Hf cps.

Lutetium concentrations varied significantly in the minerals analysed in this study, which resulted in Lu being analysed in analogue detector mode (rather than pulse) for high Lu concentrations (with the cross-over between the two modes at approx. 4.5×10^6 cps). To eliminate the additional uncertainty of measuring samples and reference materials in different modes, which is exacerbated when measuring reaction products (Zack and Hogmalm, 2016), the $^{176}\text{Lu}/^{177}\text{Hf}$ reference material (NIST 610 glass) was analysed with two laser spot sizes. A smaller laser spot diameter (43 μm) was used to keep ^{175}Lu in pulse mode. A larger diameter spot (67 μm) was used to measure ^{175}Lu in analogue detection mode. The larger spot size was used to correct minerals where Lu was measured in analogue mode.

1.4.2. Data processing.

Lu–Hf data were reduced using the LADR software package (Norris and Danyushevsky, 2018). LADR was used to calculate background-subtracted ratios and to correct for instrument mass bias and drift for $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. NIST 610 glass was used as the reference material for Lu–Hf analysis (analysed every 20 unknowns), using $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ composition of 0.1379 ± 0.005 and 0.282111 ± 0.000009 respectively, as determined by ID-MC-ICP-MS (Nebel et al., 2009). Additionally, the Lu-doped, Hf- and Yb-free glass was analysed every 20 unknowns in order to monitor mass shifted ^{176}Lu interference on mass 258. As no matrix-matched reference materials are available, unknowns were not corrected for downhole fractionation. Notably, no downhole fractionation was observed in the analysed signals (Fig. 1.1). Signal intervals were selected to avoid

Hf-rich zircon inclusions where applicable. All xenotime samples, as well as garnet sample Hogsbo 1, were corrected to 67 μm NIST 610 analyses with Lu measured in analogue mode. All other samples were corrected to 43 μm NIST 610 analyses with Lu measured in pulse mode.

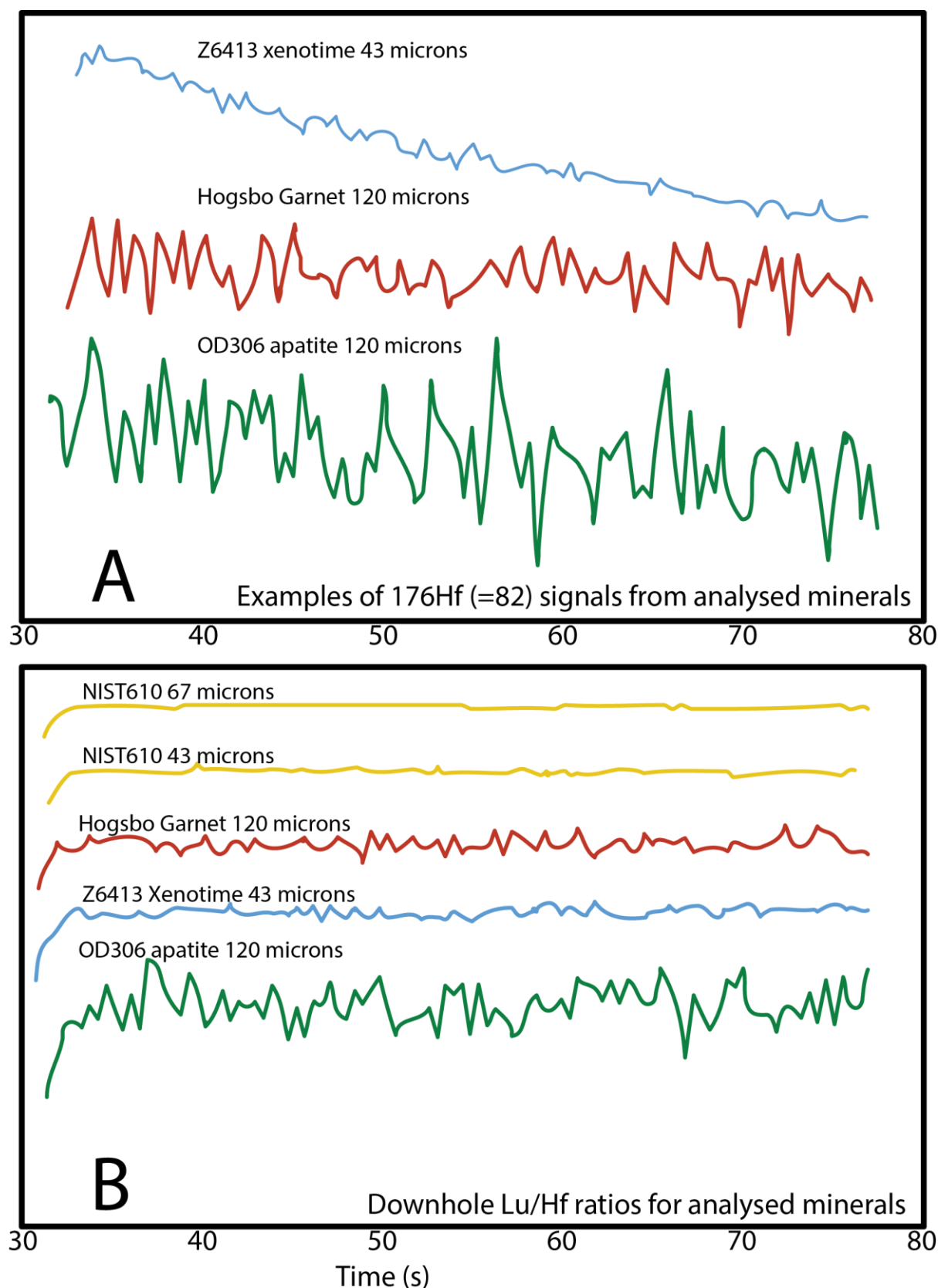


Figure 1.1: Representative ^{176}Hf (+82) (A) and downhole Lu/Hf ratios (B) of analysed minerals and NIST 610 glass. Ratios are ^{175}Lu divided by the most abundant Hf isotope. NIST 610 ratios are $^{175}\text{Lu}/^{178}\text{Hf}$. All other ratios are $^{175}\text{Lu}/^{176}\text{Hf}$. Ratios are arbitrarily spaced for ease of comparison, therefore the y-axis has no scale. Sample analysis begins at ~30 seconds. Each downhole ratio is the average of 5 representative analyses in order to reduce the effects of noise.

Samples with $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between ~ 1 and ~ 10 were anchored to initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios to improve precision. In more detail, Lu–Hf geochronology has the advantage over U–Pb and Rb–Sr geochronology in that $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are relatively invariant over the age of the Earth when compared to $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (DePaolo, 1980; Fisher and Vervoort, 2018; Stacey and Kramers, 1975; Vervoort, 2014). For instance, in normal conditions, crustal Hf isotope ratios are thought to vary from ~ 0.280 – ~ 0.282 in the crust throughout Earth history (Fisher and Vervoort, 2018; Spencer et al., 2020). This means that assumed initial Hf isotope compositions have significantly less impact on the Lu–Hf isochron ages as compared to assumed initial Pb compositions (for instance) in U–Th–Pb systems. This has important bearing on common Hf corrections applied to high Lu/Hf minerals such as apatite and xenotime. An initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282 ± 0.004 was used to cover all likely crustal $^{176}\text{Hf}/^{177}\text{Hf}$ ratios.

In samples with either no common Hf, or with common Hf so low as to not affect the age significantly, ‘single spot ages’ can be calculated from $^{176}\text{Hf}/^{176}\text{Lu}$ ratios by modifying the isochron age equation (Vervoort, 2014) (a $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of ~ 10 is used as a cut-off for the purposes of this study, however more precise data is required to constrain this):

$$\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_m = \left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_c + \left(\frac{^{176}\text{Lu}}{^{177}\text{Hf}}\right)_m (e^{\lambda t} - 1) \quad (1)$$

Where λ = the decay constant of ^{176}Lu , $\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_c$ = the initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of the analysed mineral, and $\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_m$ and $\left(\frac{^{176}\text{Lu}}{^{177}\text{Hf}}\right)_m$ are the measured isotopic ratios. In cases where there is either no common Hf, or $^{176}\text{Hf}_r \gg ^{176}\text{Hf}_c$, $\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_c$ can be approximated to 0, resulting in:

$$\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_m = \left(\frac{^{176}\text{Lu}}{^{177}\text{Hf}}\right)_m (e^{\lambda t} - 1) \quad (2)$$

Which can be simplified and rearranged to solve for time:

$$t = \text{Ln} \left(\left(\frac{^{176}\text{Hf}}{^{176}\text{Lu}} \right)_m + 1 \right) / \lambda \quad (3)$$

Equation 3 can then be used to calculate an age from the $^{176}\text{Hf}_c/^{176}\text{Lu}$ ratio of a single analysis.

Additionally, in cases where common Hf is low but still has a significant impact on the age, the radiogenic common Hf corrected ($^{176}\text{Hf}_r$) values can be calculated and used to determine ages. The following equation is used to calculate $^{176}\text{Hf}_r$. Common Hf corrections are applied to the ^{176}Hf measurements of selected samples after background subtraction and drift correction, but prior to normalisation of $^{176}\text{Hf}/^{176}\text{Lu}$ ratios to NIST 610 glass.

$$^{176}\text{Hf}_r = ^{176}\text{Hf}_m - \left(\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}} \right)_c \times ^{177}\text{Hf}_m \right) \quad (4)$$

Where $^{176}\text{Hf}_r$ = radiogenic ^{176}Hf , $^{176}\text{Hf}_m$ = measured ^{176}Hf , and $^{177}\text{Hf}_m$ = the measured ^{177}Hf .

As ^{178}Hf was measured in this study to monitor common Hf, the $(^{176}\text{Hf}/^{178}\text{Hf})_c$ ratio was used to correct $^{176}\text{Hf}_m$ for common $^{176}\text{Hf}_c$ in place of the $(^{176}\text{Hf}/^{177}\text{Hf})_c$ ratio. Therefore a $^{176}\text{Hf}/^{178}\text{Hf}$ ratio of 0.192 ± 0.002 was used. This was calculated by multiplying a $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282 ± 0.004 (Fisher and Vervoort, 2018) by the stable $^{177}\text{Hf}/^{178}\text{Hf}$ ratio of 0.682 (De Bievre and Taylor, 1993). This ratio is first corrected for mass bias between ^{176}Hf and ^{178}Hf , determined via measurement of NIST 610 glass. After processing in LADR, single spot ages were calculated in excel spreadsheets. ISOPLTR was used

to calculate isochron ages and weighted mean ages (Vermeesch, 2018). The ^{176}Lu decay constant of $0.00001867 \pm 0.00000008 \text{ Myr}^{-1}$ (Söderlund et al., 2004) was used for all age calculations

1.5. Results.

Details on LA-ICP-MS U–Pb and trace element results are presented in supplementary data file 1.2

1.5.1. LA-ICP-MS/MS results.

In the descriptions and figures below, all isochron and weighted average age uncertainties are presented as 95% confidence intervals and uncertainty calculations include overdispersion for samples with MSWD >1. In the current absence of suitable primary reference materials, all presented ages were calculated against NIST 610 glass and are thus uncorrected for any possible matrix-induced Lu–Hf fractionation. The potential influence of matrix-induced fractionation on the age calculations is discussed below. Full data tables are included in supplementary data file 1.1. For easy referencing on all figures, garnet data are highlighted in red, apatite data in green and xenotime data in blue.

1.5.1.1 Garnet Lu–Hf results.

Hogsbo Garnet: Four garnets were analysed from the Hogsbo pegmatite over two analytical sessions. Three of these garnets (Hogsbo 2, 3, and 4) yielded $^{176}\text{Lu}/^{177}\text{Hf}$ ratios that vary between 11 and 480, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 0.5 and 10. Samples Hogsbo 2, 3 and 4 produced consistent data for an isochron regression with an age of $1065 \pm 12 \text{ Ma}$ ($n = 64$, MSWD = 1.5, Fig. 1.2A). One out of sixty-five data points was removed from the regression calculations due to within signal mixing of Lu–Hf domains. When corrected for common Hf (*equ. 4*), the garnets produce a weighted mean Lu–Hf age of $1058 \pm 6.5 \text{ Ma}$ ($n = 61$, MSWD = 1.32, Fig. 1.2C). For the other garnet sample (Hogsbo 1), $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were obtained that vary between 17 and 178, indicating that ^{176}Hf was > ~97% radiogenic for all analyses ($^{176}\text{Lu}/^{177}\text{Hf}$ ratios range between 1730 and 8880). Hence, the $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were sufficiently high to allow the calculation of single ablation spot $^{176}\text{Hf}_r/^{176}\text{Lu}$ ages, using *equation 3* (without requirement for common Hf corrections). The resulting weighted average single ablation spot $^{176}\text{Hf}_r/^{176}\text{Lu}$ age for this garnet was calculated as $1058 \pm 4.5 \text{ Ma}$ ($n = 21$ MSWD = 0.57, Fig. 1.2B). An isochron for Hogsbo 1 garnet produced an age of $1054 \pm 38 \text{ Ma}$ ($n = 21$, MSWD = 0.01, Table 1.2)

Sample T01-40 (Tanzania) was analysed over three analytical sessions, yielding $^{176}\text{Lu}/^{177}\text{Hf}$ ratios that vary between ~0.0001 and 40.4, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 0.26 and 1.9. An isochron regression produced an age of $2046 \pm 61 \text{ Ma}$ ($n = 185$, MSWD = 1.5, Fig. 1.2D). Although some of these data contained zircon inclusions, these data points were not removed from the regression calculation, as the timing of crystallisation of these zircons is within uncertainty of the timing of garnet formation ($^{238}\text{U}/^{206}\text{Pb}$ age of $1994 \pm 9 \text{ Ma}$; Tamblyn et al., 2020a). Therefore, the Hf isotopic composition of the zircons will reflect the initial Hf composition of the garnets (within uncertainty of the technique). However, zircons have been avoided where possible in time integrated signals, in order to favour more radiogenic compositions.

Sample RB10/11 (Port Macquarie) returned $^{176}\text{Lu}/^{177}\text{Hf}$ ratios between 0.02 and 63, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 0.28 and 0.8. An isochron regression produced an age of $482 \pm 23 \text{ Ma}$ ($n = 61$, MSWD = 1.1, Fig. 1.2E). Similar to sample T01-40, some of the analyses are significantly contaminated by zircon micro-inclusions. Textural observations suggest that the zircons grew with the garnets (Tamblyn et al., 2019; Tamblyn et al., 2020b), and, therefore, high Zr analyses have not been removed from the regression calculation. Two data points were removed due to the presence of

(non-zircon) Hf bearing inclusions that were difficult to accurately identify due to the limited masses monitored during analysis.

Sample WGC-31 (Norway) produced $^{176}\text{Lu}/^{177}\text{Hf}$ ratios between 0.12 and 16.7, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 0.285 and 0.61. The resulting isochron regression gave an age of 1060 ± 35 Ma ($n=57$, MSWD = 1, Fig. 1.2G). Three data points were removed due to inconsistent/contaminated signals.

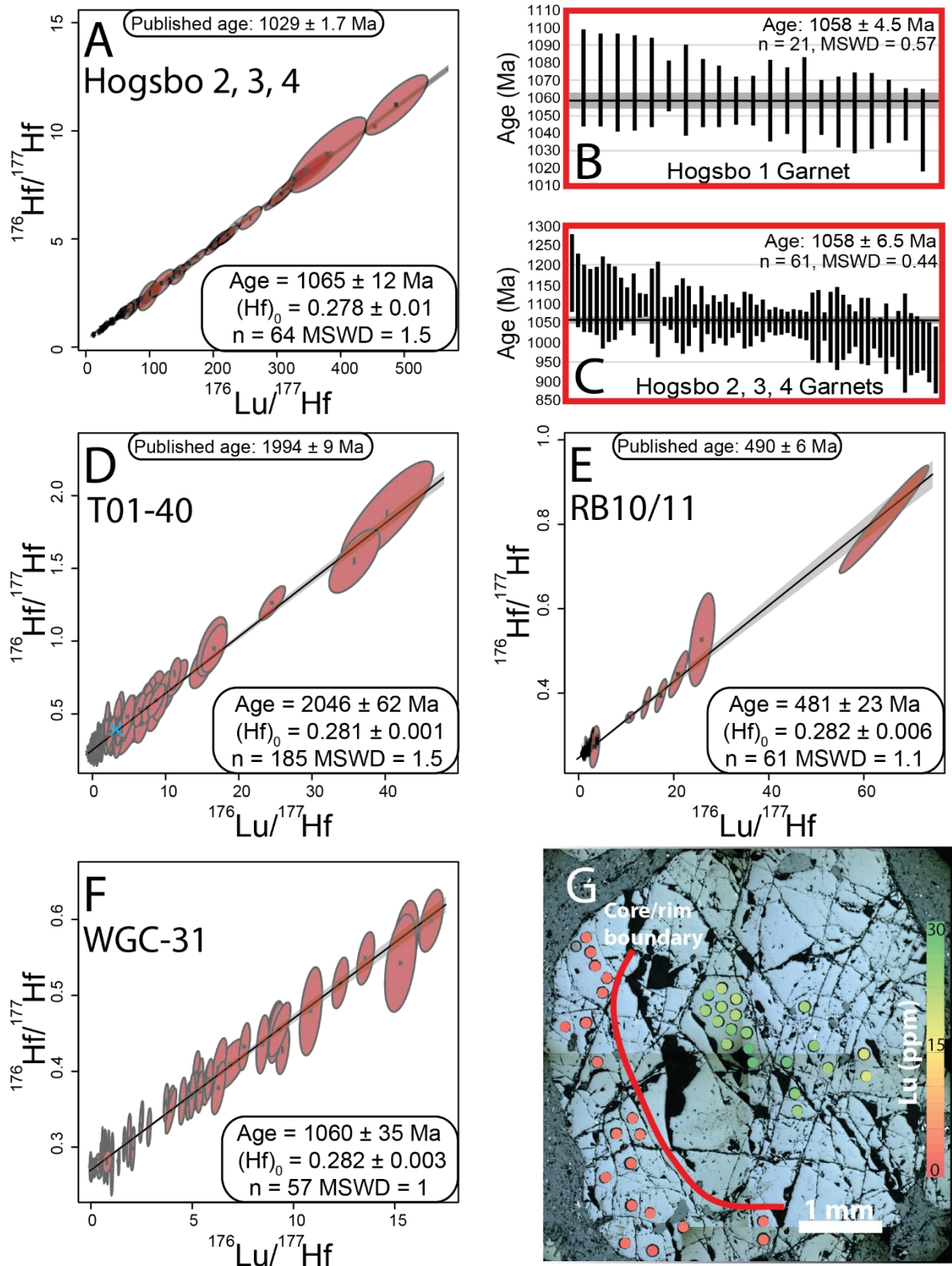


Figure 1.2: Lu-Hf isochron plots and weighted average single spot ages for analysed garnet samples. Ellipses and vertical bars represent 2σ uncertainties. Calculated age uncertainty are 95% confidence intervals. (Hf)₀ is the initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio. A, D, E and F are isochron plots. Blue X on D demonstrates maximum $^{176}\text{Lu}/^{176}\text{Hf}$ ratio obtained for solution Lu-Hf analysis of T01-40 (does not represent uncertainty). B is a weighted average single spot age plot for Hogsbo garnet 1. C is a weighted average common Hf corrected single spot age plot for Hogsbo garnets 2, 3, and 4. Isochrons and weighted averages were calculated using ISOPLOT (Vermeesch, 2018). G shows a reflected light image of sample WGC-31 with ablation spots coloured based on Lu ppm. Red is low and green is high. Data from the rim has not been used in age calculations.

1.5.1.2. Apatite Lu–Hf results.

All apatite samples were analysed with a laser spot size of 120 μm , except for sample CS5, which was analysed using a spot size of 67 μm , as it consists of apatite grains typically smaller than 120 μm . Single spot ages were calculated using *equation 3* and common Hf corrected single spot ages were calculated using *equations 3 and 4*.

Otter Lake Apatite (Quebec) has $^{176}\text{Lu}/^{177}\text{Hf}$ ratios between 49 and 107, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 1.18 and 2.6. The apatite Lu–Hf data was corrected using Otter Lake titanite to constrain the initial $^{176}\text{Hf}/^{177}\text{Hf}$ (0.284663 ± 0.000012) (Barfod et al., 2005). Otter Lake apatite returned a weighted mean common-Hf corrected single spot age of 1053 ± 12 Ma ($n = 40$, MSWD = 1.3, Fig. 1.3A).

OD306 Apatite (South Australia). Analyses contained >97% radiogenic Hf. The apatite produced $^{176}\text{Lu}/^{177}\text{Hf}$ ratios between 94 and 938, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 3.2 and 30. The weighted mean single spot age was 1687 ± 11 Ma ($n = 38$, MSWD = 0.68, Fig. 1.3B). Four analyses were removed due to high common Hf.

Sample CS5 (northern Australia) was analysed with a 67 μm laser spot from grain separates. Although this sample contained variable common Hf as well as zircon inclusions, the total number of analyses was insufficient to calculate a meaningful isochron. CS5 apatite returned $^{176}\text{Lu}/^{177}\text{Hf}$ ratios between 0.001 and 2218, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 0.2 and 82.5. A weighted mean single spot age of common-Hf free analyses was calculated as 1934 ± 30 Ma ($n = 12$, MSWD = 0.55). For this calculation, eight data points had to be removed due to the presence of common Hf. The weighted mean common Hf corrected single spot age was calculated as 1909 ± 23 Ma ($n = 15$, MSWD = 1.1, Fig. 1.3C), which excludes five data points that were removed due to un-correctable common Hf.

Mud Tank DG Apatite (central Australia). Analyses contained >97% radiogenic Hf. The apatite produced $^{176}\text{Lu}/^{177}\text{Hf}$ ratios between 1250 and 4310, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 8.4 and 29.3. The weighted mean single spot age was calculated as 370 ± 5.7 Ma ($n = 35$, MSWD = 0.84, Fig. 1.3D). Five analyses were removed due to high common Hf.

215 Ødegårdens Verk Apatite (Norway). Analyses contained >99% radiogenic Hf. The apatite produced $^{176}\text{Lu}/^{177}\text{Hf}$ ratios between 5720 and 44300, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 121 and 978 although ratios are unreliable (due to ^{177}Hf concentration being too low). The weighted mean single spot age is 1149 ± 7.3 Ma ($n = 39$, MSWD = 1.31, Fig. 1.3E). One data point was removed from the weighted mean calculation due to an anomalous chemistry and $^{176}\text{Lu}/^{177}\text{Hf}$ signal.

BC10 Apatite (Queensland, Australia). Analyses contained >99% radiogenic Hf. BC10 apatite returned $^{176}\text{Lu}/^{177}\text{Hf}$ ratios between 890 and 11400, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 30 and 360 although ratios are unreliable (due to ^{177}Hf concentration being too low). The weighted mean single spot age is 1678 ± 35 Ma ($n = 24$, MSWD = 0.4, Fig. 1.3F). One data point was removed from the weighted mean calculation due to the presence of detected inclusions.

19589 Harts Range Apatite (central Australia). Analyses contained >99% radiogenic Hf. This apatite gave $^{176}\text{Lu}/^{177}\text{Hf}$ ratios between 5990 and 37700, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 40 and 254. These ratios are approximate due to the low counts on ^{177}Hf . The weighted mean single spot age was 361 ± 3.7 Ma ($n = 40$, MSWD = 0.77, Fig. 1.3G). No data points were removed from the age calculation.

15836-Wallaroo Mines Apatite (South Australia). Analyses contained >99% radiogenic Hf. The apatite produced $^{176}\text{Lu}/^{177}\text{Hf}$ ratios between 4740 and 66430, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios between 155 and

2170 although ratios are unreliable (due to ^{177}Hf concentration being too low). The weighted mean single spot age is 1656 ± 12 Ma ($n = 40$, MSWD = 1.28, Fig. 1.3H).

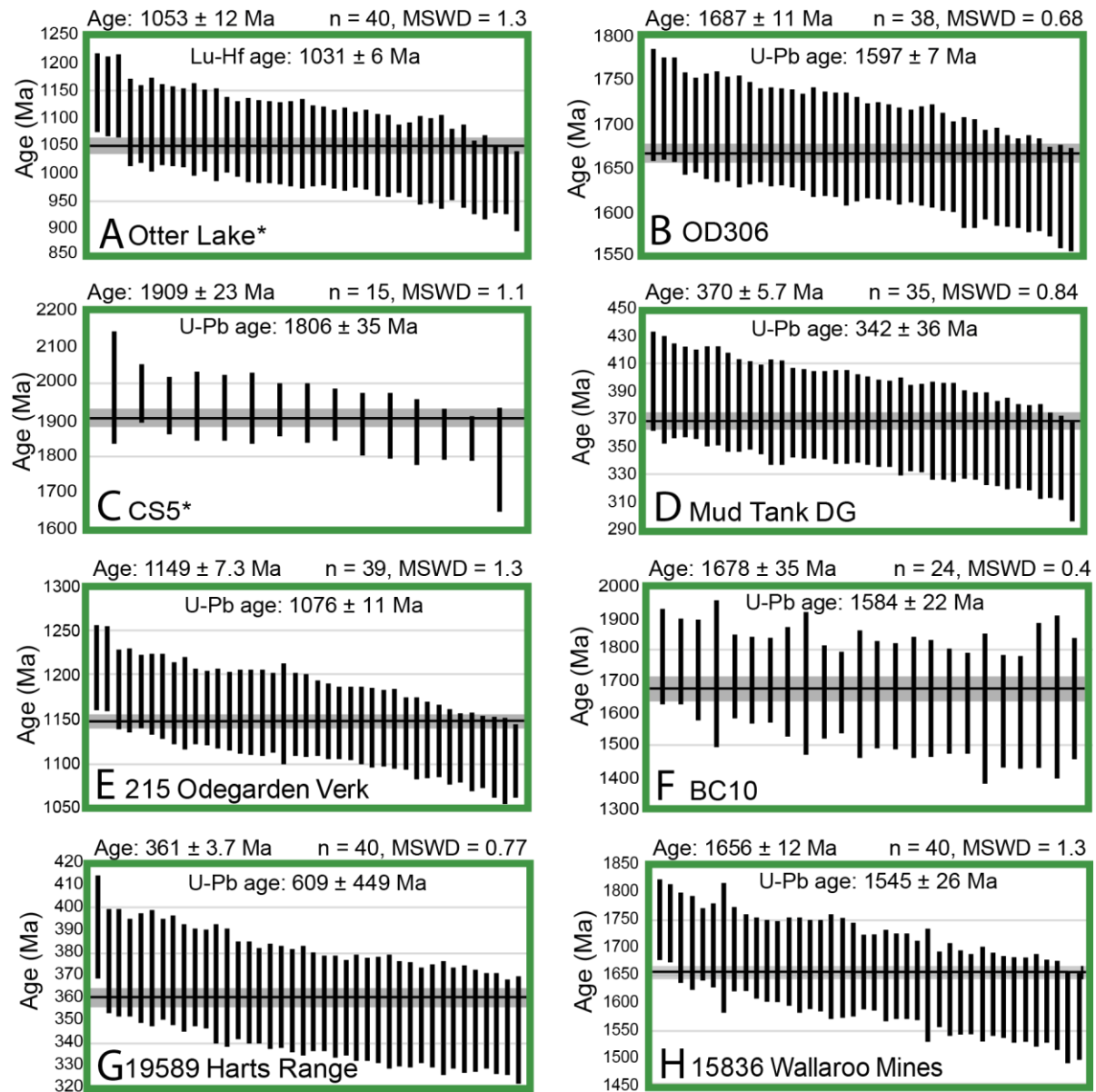


Figure 1.3: Lu–Hf single spot ages for analysed apatite samples. Vertical lines represent 2σ uncertainties. The top left age refers to in-situ Lu–Hf age and the central age refers to expected age. Otter Lake apatite has been corrected using co-genetic titanite (Barfod et al., 2005) to constrain initial $^{176}\text{Hf}/^{177}\text{Hf}$. Ages are weighted averages for all presented data with calculated 95% confidence interval uncertainties. *Denotes samples that have been corrected for common Hf. Single spot ages are calculated using excel spreadsheets. All weighted averages were calculated using ISOPLOT (Vermeesch, 2018).

1.5.1.3. Xenotime Lu–Hf results.

Hafnium corrections and single spot ages have been calculated using equations 3 and 4.

BS-1 Xenotime: Calculated $^{176}\text{Lu}/^{177}\text{Hf}$ ratios ranged from 414 – 842 and calculated $^{176}\text{Hf}/^{177}\text{Hf}$ ratios ranged from 4.3 – 8.5. This sample returned a common-Hf corrected single spot age of 527 ± 2.4 Ma ($n = 22$, MSWD = 0.17, Fig. 1.4A).

MG-1 Xenotime: Calculated $^{176}\text{Lu}/^{177}\text{Hf}$ ratios ranged from 228 – 831 and calculated $^{176}\text{Hf}/^{177}\text{Hf}$ ratios ranged from 2.5 – 8.2. This sample returned a common-Hf corrected single spot age of 515 ± 2.7 Ma ($n = 20$, MSWD = 0.52, Fig. 1.4B).

Z6413 Xenotime: Calculated $^{176}\text{Lu}/^{177}\text{Hf}$ ratios ranged from 64.5 – 92.1 and calculated $^{176}\text{Hf}/^{177}\text{Hf}$ ratios ranged from 1.5 – 2. Z6413 xenotime produced a common-Hf corrected single spot age of 1023 ± 4.7 Ma ($n = 20$, MSWD = 0.21, Fig. 1.4C).

XST-1 Xenotime: Calculated $^{176}\text{Lu}/^{177}\text{Hf}$ ratios ranged from 157 – 1452 and calculated $^{176}\text{Hf}/^{177}\text{Hf}$ ratios ranged from 1.8 – 14.4. XST-1 xenotime produced a common-Hf corrected single spot age of 518 ± 2.3 Ma ($n = 23$, MSWD = 0.54, Fig. 1.4D).

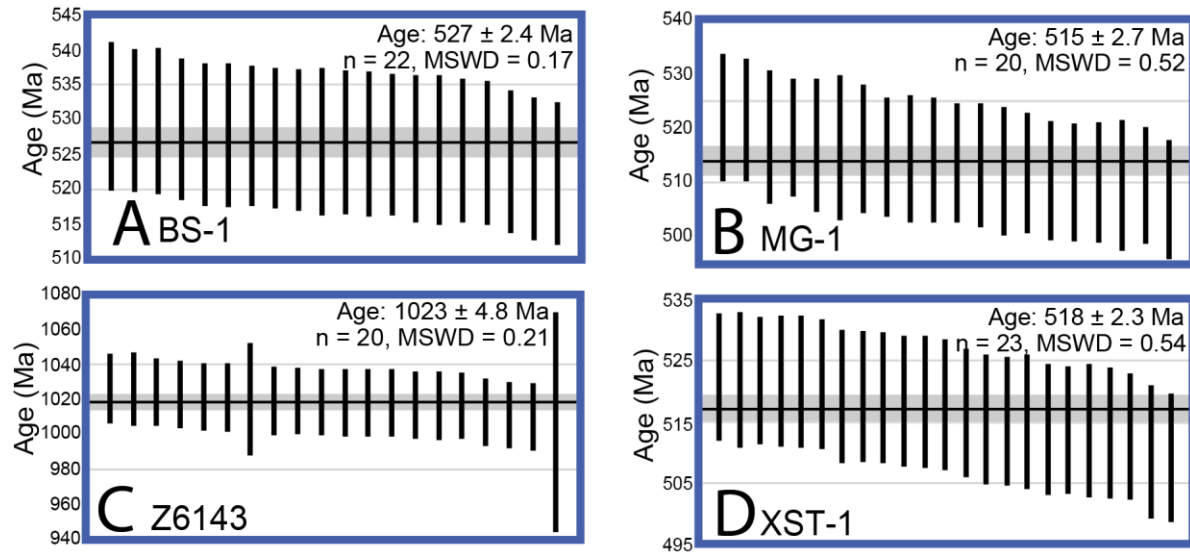


Figure 1.4: Lu-Hf weighted average ages for analysed xenotimes. All weighted average single spot ages have been corrected for common Hf. Vertical lines represent 2σ uncertainties. Calculated age uncertainties are 95% confidence intervals. All data is calculated using ISOPLTR (Vermeesch, 2018).

Sample details							Lu-Hf age				Counts per second values for Hf and potential interferences			
Name	Mineral	Spot size (μm)	Ref spot size (μm)	Age _e (Ma)	2σ Error (Ma)	Dating method	Age (Ma)	95% Conf. Error (Ma)	Age _c /age _e	95% Conf. Error (Ma)	Av. CPS ¹⁷⁶ AlI (+82)	Av. CPS ¹⁷² Yb (+82)	Av. CPS ¹⁷⁵ Lu (+82)	Av. CPS ¹⁷⁸ Hf (+82)
Hogsbo 1	Gnt	120	67	1029	1.7	U-Pb ^b	1058	4.5	1.028	0.005	2010	<5	85	50
Hogsbo others*	Gnt	120	43	1029	1.7	U-Pb ^b	1058	7.5	1.028	0.007	263	<5	10	178
T01-40	Gnt	120	43	1994	9	Lu-Hf ^c	2046 [^]	61	1.026	0.031	490**	<5	<1	2250**
RB11/10	Gnt	120	43	486	11	Lu-Hf ^d	482 [^]	23	0.99	0.053	3100**	<5	1.8	16000**
WGC-31	Gnt	120	43	~400		U-Pb ^e	1060 [^]	35	~2.65	N/A	1200**	<5	5	5600**
				~1050		U-Pb ^e			~1.010	N/A				
Otter Lake*	Ap	120	43	1029	6	Lu-Hf ^f	1053	12	1.020	0.014	156	<5	5	150
				933	12	U-Pb ^g			1.121	0.022				
				1002	7	U-Pb ^h			1.044	0.019				
OD306	Ap	120	43	1597	7	U-Pb ⁱ	1687	11	1.056	0.007	465	<5	12	50
CS5*	Ap	67	43	1806	35	U-Pb ^a	1909	23	1.055	0.023	380	<5	8	32
MT DG	Ap	120	43	342	36	U-Pb ^a	371	6.2	1.059	0.105	60	<5	7	6
215-OV	Ap	120	43	1076	11	U-Pb ^a	1149	7.3	1.068	0.012	350	<5	14	Bdl.
BC10	Ap	120	43	1584	22	U-Pb ⁱ	1678	35	1.059	0.025				
19589-HR	Ap	120	43	609	449	U-Pb ^a	360	3.7	0.591	0.737	122	<5	15	Bdl.
15836-W	Ap	120	43	1545	26	U-Pb ^a	1658	14	1.073	0.019	240	<5	6	Bdl.
Z6413*	Xen	43	67	993	1	U-Pb ^k	1022	5.7	1.029	0.006	18500	38	600	16250
BS-1*	Xen	43	67	509	0.3	U-Pb ^k	527	2.4	1.035	0.005	8100	48	610	2250
MG-1*	Xen	43	67	490	0.3	U-Pb ^k	515	2.7	1.049	0.005	3054	20	240	850

XST-1*	Xen	43	67	495	1.4	U-Pb ^k	518	2.3	1.044	0.005	4860	35	372	1750
--------	-----	----	----	-----	-----	-------------------	-----	-----	-------	-------	------	----	-----	------

Table 1.2: Spot sizes and expected ages for the analysed samples. Expected ages are independently calculated ages; either published ages or U–Pb ages from this study. MT Dg refers to Mud Tank DG apatite. 215-OV refers to apatite sample 215 Ødegårdens Verk. 19589-HR refers to 19589 Harts Range apatite. 15836-W refers to 15836 Wallaroo Mines apatite. Hogsbo ‘others’ refers to Hogsbo garnets 2, 3, and 4. Xen = xenotime, Gnt = garnet, and Ap = apatite. Spot size refers to the LA spot size used to analyse the sample. Reference spot size refers to the laser ablation spot size used to analyse the reference material (NIST SRM 610 glass) for the purpose of calibrating the Lu/Hf ratios. Errors are 95% confidence interval errors unless otherwise indicated. Age_c/Age_e is the calculated in-situ Lu–Hf age divided by the expected age. Errors on Age_c/Age_e are propagated from both calculated ages and expected ages. Age[^] denotes isochron ages. Single spot ages are weighted averages of either common Hf corrected or common Hf free ages. Name denotes common Hf corrected single spot ages. Av. CPS refers to average background subtracted CPS. (+82) refers to the mass increase due to reaction with NH₄; ¹⁷²Yb (+82) and ¹⁷⁵Lu (+82) are used to monitor the ¹⁷⁶Yb and ¹⁷⁶Lu interferences on the ¹⁷⁶Hf measurements. ¹⁷⁶All refers to the combined measurement of ¹⁷⁶Hf, ¹⁷⁶Yb, and ¹⁷⁶Lu, this is >99% ¹⁷⁶Hf in all samples. Minimum detectable CPS values per duty cycle are as follows: ¹⁷⁶All (+82): 10, ¹⁷²Yb (+82): 30, and ¹⁷⁵Lu (+82): 10. Data at less than half minimum CPS is considered unreliable. ** denotes values that are highly variable. References: ^a = U–Pb apatite, this study; supplementary data file 1.2, appendix figure 1.2, ^b = ID TIMS U–Pb columbite; Romer and Smeds (1996), ^c = Lu–Hf garnet; Tamblyn et al. (2020a), ^d = Lu–Hf garnet; Tamblyn et al. (2019), ^e = SHRIMP U–Pb monazite; Terry et al. (2000), ^f = Lu–Hf apatite; Barfod et al. (2005), ^g = LA-ICP-MS U–Pb apatite; Chew et al. (2011), ^h = U–Pb step leaching titanite; Frei et al. (1997), ⁱ = IC-MC-ICP-MS U–Pb apatite; Thompson et al. (2016), ^j = LA-ICP-MS U–Pb apatite; Cave et al. (2018), ^k = IDTIMS U–Pb xenotime; Rasmussen et al. (2006).*

1.6. Interpretations and Discussion.

1.6.1. *In-situ* Lu–Hf age interpretations and comparisons with traditional dating methods.

1.6.1.1. Garnet age interpretations.

The garnet samples were analysed with the *in-situ* Lu–Hf method at a precision of ~3 to 4.8% for isochron ages and ~0.5% for single spot ages. However, single spot ages could only be calculated for one sample (Hogsbo) where sufficient Hf was radiogenic (single spot ages for Hogsbo 1; Fig. 1.2B and Hf-corrected single spot ages for Hogsbo 2, 3, 4; Fig. 1.2C). The obtained uncertainties for the *in-situ* method are ~2 times (Hogsbo 1 and RB11/10) to ~7 times (T01-40) larger compared to those for the reference solution-based Lu–Hf ages (Tamblyn et al., 2020a; Tamblyn et al., 2020b), presenting the primary limitation of the method. However, there are important advantages with the *in-situ* approach, discussed below. Due to the precision on samples with solution Lu–Hf ages (RB10/11 and T01-40) and the lack of direct paragenetic link between the Hogsbo columbite/muscovite ages (~1030 Ma) and the analysed Hogsbo garnets (~1060 Ma), it is difficult to assess the accuracy of the garnet Lu–Hf data.

Samples T01-40 and RB10/11 contain numerous zircon inclusions. Due to the wt.% concentration of Hf in zircons (Thirlwall and Walder, 1995), such inclusions are potentially problematic for *in-situ* Lu–Hf geochronology. In cases where zircon formed cogenetic with garnet, analyses containing substantial zircon inclusions will sit on the same isochron as the garnet analyses. Due to the high Hf content of zircons relative to the Lu content of garnets, these zircon-dominated analyses will contain low $^{176}\text{Lu}/^{177}\text{Hf}$ ratios, meaning any matrix induced elemental fractionation is likely to have no significant effect on the isochron age. These analyses will act as anchors to the Lu–Hf isochron, and we consider these comparable to the use of whole-rock aliquots to anchor Lu–Hf isochrons. Notably, several rutile inclusions were incorporated in the garnets over the course of the analyses, but these do not appear to affect the isotopic ratio measurements.

Despite having reduced precision, the *in-situ* method has a number of advantages over solution-based Lu–Hf garnet dating. A strength of the *in-situ* Lu–Hf technique is that age information is acquired directly, as analyses with low Lu/Hf ratios can be obtained by targeting low Lu domains of garnet (or Hf bearing minerals such as zircon and rutile) allowing for single garnet isochrons (WGC-31 and Hogsbo; Fig. 1.2A and F) or isochrons utilising cogenetic minerals. Micro-scale zonation can easily be lost by traditional Lu–Hf dating techniques, which rely on dissolution of relatively large amounts of material (~70 mg) and often require a separate whole-rock aliquot to form an isochron (e.g. Duchene et al., 1997; Ibanez-Mejia et al., 2018). As an example, solution Lu–Hf data for sample T01-40 has a highest $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of ~3 (Fig. 1.2, D, Tamblyn et al., 2020a), whereas the *in-situ* data from this study has a highest $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of ~40. The *in-situ* approach is useful for instances where the whole-rock may have been subjected to subsequent alteration, veining or metamorphism, which would affect the isotopic composition of the whole-rock aliquot. A potential advantage of the large, spatially-resolved datasets in this study is that they are better suited to interrogation of potential age mixing or contamination when compared to the small datasets (~3-6 analyses, including whole rock) associated with traditional Lu–Hf geochronology (e.g. Anczkiewicz et al., 2004; Smit et al., 2013). Additionally, garnets can grow over a significant period of time (Baxter and Scherer, 2013). Such growth histories must be accounted for when interpreting garnet Lu–Hf data, as this will affect any isochron calculated. Such cases will likely lead to increased scatter in the data points (MSWD >1).

The age obtained from sample WGC-31 (~1060 Ma) is consistent with monazite crystallisation during the Sveconorwegian Orogeny (Terry et al., 2000). Although the monazite data from Terry et al. (2000) was interpreted as detrital, the garnets dated in this study imply that these older dates (1060 - 900 Ma) are a relic of an older metamorphic event. Additionally, The Lu–Hf garnet ages from this study are consistent with the zircon U–Pb age populations from Walczak et al. (2019). These ages are preserved in garnets despite these rocks undergoing temperatures of ~ 800 °C at ultrahigh pressure conditions during the ca. 414 – 397 Ma Caledonian orogeny (Kylander-Clark et al., 2009). Hence, this example highlights an important application for this technique; the ability to quickly resolve the age of garnet growth in poly-metamorphic samples. Importantly, the novel *in-situ* technique has demonstrated that these garnets did not form during Caledonian UHP metamorphism, despite the assumptions of previous studies.

Perhaps the most powerful advantage is the ability to obtain spatially-resolved age data. For garnets with complex growth patterns (e.g. with older cores and younger rims) that have significant age differences (ca. 100 Ma or more) (e.g. Bird et al., 2013; Cutts et al., 2010), *in-situ* dating can provide the required spatial resolution to distinguish these different growth events.

A success of the method is the ability to date young, low- to moderate-temperature eclogitic assemblages, which are notoriously difficult to date using traditional geochronometers. This is demonstrated by our dating of the low-temperature eclogite sample RB10/11 to within uncertainty of the solution/TIMS Lu–Hf age. Although the *in-situ* Lu–Hf age lacks precision, this data can be used to determine in which broad tectonic event these garnets formed. Hence, the *in-situ* technique offers an avenue to quickly and directly constrain the timing of garnet growth in situations where Lu–Hf solution-based analysis may not be available or possible.

A major application for the *in-situ* Lu–Hf method is campaign style garnet geochronology. The ease of analysis associated with this technique allows for potentially >50 individual garnets to be dated across the space of only a few days. In this way entire metamorphic terranes could be targeted to broadly constrain different episodes of metamorphism, following similar approaches using LA-ICP-MS U–Th–Pb geochronology (e.g. Spencer et al., 2013).

1.6.1.2. Apatite age Interpretations.

Although closure temperature differences may play a role in the offset between U–Pb and Lu–Hf ages, OD306 cannot be older than the ca. 1595 Ma emplacement of the Gawler Range Volcanics (McPhie et al., 2020) and CS5 cannot be older than the maximum depositional age of the Tollis Formation in which it intrudes (1865 Ma; Stuart-Smith et al., 1993). Hence we use these two samples as a primary control on the analytical age offset between our *in-situ* Lu–Hf dates and published and or newly-obtained U–Pb ages. The apatite samples were analysed with the *in-situ* Lu–Hf method at a precision of ~1.8 to 2.6% for isochron ages and ~0.5 to 2% for single spot ages. In terms of accuracy, the age offset between published U–Pb dates and *in-situ* Lu–Hf dates for this study varies between ~2% and ~7%.

The primary source of uncertainty on the calculated *in-situ* Lu–Hf ages is the uncertainty on the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio. In apatite, Hf isotopes are often low in abundance, particularly common Hf isotopes (i.e. ^{177}Hf , ^{178}Hf), which leads to a decrease in signal precision in cases where these are close to detection limits. Additionally, $^{176}\text{Hf}/^{177}\text{Hf}$ ratios have significantly less variation compared to $^{176}\text{Lu}/^{177}\text{Hf}$ ratios, which is problematic when analysing young and/or low Lu apatite. These limitations are mitigated where possible by (1) using large spot sizes and (2) calculating single spot ages, which rely only on the $^{176}\text{Hf}/^{176}\text{Lu}$ ratios to calculate an age. Despite these limitations, most of

the analysed samples demonstrate similar or even better precision compared to conventional LA-ICP-MS apatite U–Pb dating (e.g. 215 Ødegårdens Verk, 19589 Harts Range and 15836 Wallaroo Mines, CS5; Table 1.2). Even when Lu concentrations are low (~3 ppm), sample BC10 (Table 1.2) demonstrates that a weighted average single spot age can be calculated with an uncertainty that is comparable to published LA-ICP-MS U–Pb data (Cave et al., 2018). Hence, our study demonstrates that geologically meaningful precision can be obtained from *in-situ* Lu–Hf geochronology, either via isochron regression when common Hf is present, or via single spot ages when common Hf is negligible.

In the case of sample 19589 Harts Range, due to the lack of common Hf, the Lu–Hf age is significantly more precise than the U–Pb age (Fig. 1.3G, Table 1.2). The Lu–Hf age indicates that this apatite formed during the 450–300 Ma Alice Springs Orogeny (Buick et al., 2008; Hand et al., 1999). Similarly, previous U–Pb geochronology of apatite from the Mud Tank carbonatite has returned imprecise ages due to high common Pb (349 ± 31 Ma and 455 ± 55 Ma; Chew et al., 2011; Thomson et al., 2012, respectively). Our calculated Lu–Hf age for Mud Tank DG is within uncertainty to the U–Pb age of Chew et al. (2011) and also agrees with a published Rb–Sr date (Haines et al., 2001). Additionally, the Lu–Hf age for both 19589 Harts Range and Mud Tank DG is significantly more precise than previous dating attempts (Fig. 1.3D).

The main advantage of apatite Lu–Hf dating compared to U–Pb dating is twofold: (1) Lu–Hf dating of apatite is more likely to accurately reflect the crystallisation age due to the higher closure temperature; and (2) U poor and common-Pb rich apatite samples (e.g. apatite from low temperature metamorphic rock or mafic igneous rocks; Henrichs et al., 2019) are likely to produce more precise Lu–Hf ages, when compared to the U–Pb system in apatite (e.g. Mud Tank Apatite, explained above).

Furthermore, apatite is often affected by hydrothermal fluids, leading to isotopic disturbances, new apatite growth, or dissolution-reprecipitation reactions (Cave et al., 2018; Glorie et al., 2019; Harlov et al., 2005; Huang et al., 2015; Kirkland et al., 2018; Krneta et al., 2017; Schoneveld et al., 2015). Such processes can be problematic for accurate dating of common-Pb bearing minerals such as apatite, as ages require a co-genetic suite of analyses (Chew et al., 2014; Tera and Wasserburg, 1972). Particularly in hydrothermal systems, apatite U–Pb data may have greater dispersion due to mixing and/or multiple ages, leading to ambiguity in age interpretations (Kirkland et al., 2018). The *in-situ* Lu–Hf technique has the ability to overcome these difficulties and is more likely to reveal primary age information.

Similarly, while some studies of detrital apatite have been conducted (e.g. Gillespie et al., 2018; Glorie et al., 2020; Mark et al., 2016; O'Sullivan et al., 2018), these are often hindered significantly by the requirement of multiple analyses to calculate a single age. Although common Pb corrections can be applied (e.g. Chew et al., 2014), the significant potential for variation in initial Pb composition, as well as the potentially high % common Pb in a given apatite U–Pb analysis, can make such techniques problematic. The potential to obtain *in-situ* single spot Lu–Hf ages for individual apatite grains opens up new opportunities for detrital apatite studies.

A current limitation of the *in-situ* Lu–Hf technique is the large laser spot size (~120 μm) necessary to accurately measure Hf isotopes. Given the small grain sizes for sample CS5, a smaller laser spot size was used (~67 μm), which is more realistic for traditional analysis of apatite separates. For this sample, the uncertainty on the weighted single spot age is ~1.3%, demonstrating that high precision can be achieved with lower spot sizes, particularly for relatively old samples that have abundant Lu.

1.6.1.3. Xenotime age interpretations.

The xenotime samples were analysed with the *in-situ* Lu–Hf method at a precision of 0.7 to 1% for isochron ages and ~0.4 to 0.6% for single spot ages. The strong agreement between isochron ages and common-Hf corrected ages for these samples indicates that the common-Hf corrections are particularly useful for samples with >80% radiogenic Hf. This is most clearly demonstrated by samples Z6143 (which has the lowest radiogenic Hf) and XST-1 (which has the most precise isochron age) (Fig. 1.3D, Table 1.2).

While U–Pb dating of xenotime is widely seen as a robust and reliable dating method (Rasmussen et al., 2011), *in situ* Lu–Hf dating of xenotime may be an effective alternative geochronometer in the rare cases of hydrothermal xenotime with low U contents (McNaughton and Rasmussen, 2018), or for dating complex xenotime grains with Pb-rich inclusions (e.g., sulfides) that compromise U–Pb dating methods. A promising avenue of future work is to use U–Pb and Lu–Hf dating of xenotime in tandem to more effectively track the timing and conditions of hydrothermal alteration or metamorphism on xenotime-bearing rock samples (e.g. Rasmussen et al., 2011).

1.6.2. Current analytical limitations of the *in-situ* Lu–Hf method.

1.6.2.1. Matrix-induced fractionation and correction strategies.

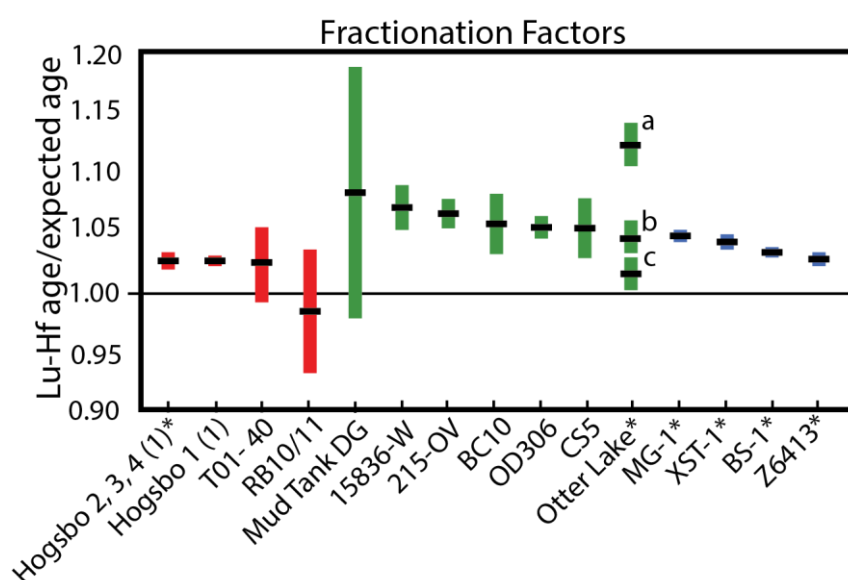


Figure 1.5: Plot showing age offsets between the Lu–Hf ages (this study) and the expected age for analysed samples. Vertical bars are 95% confidence intervals around calculated age offsets (black lines). Name* denotes common Hf corrected samples. Sample 19589 Harts Range has been omitted due to the extremely large uncertainty on the U–Pb age (Table 1.2). ^a denotes Otter Lake apatite in which the expected age is the U–Pb age 933 ± 12 Ma (Chew et al., 2011). ^b denotes Otter Lake apatite in which expected age is the cogenetic titanite U–Pb age of 1002 ± 7 Ma (Frei et al., 1997). ^c denotes Otter Lake apatite in which the expected age is the Lu–Hf age of 1031 ± 6 Ma (Barfod et al., 2005). Analyses were not all analysed with the same laser conditions. Refer to Table 1.2 for details.

Despite the lack of discernible downhole variations in element ratios during our analysis (Fig. 1.1), there is a potential ~2 – 6% offset between *in-situ* Lu–Hf ages and published solution Lu–Hf or U–Pb ages (Fig. 1.5, Table 1.2), when using the non-matrix matched NIST 610 glass as the primary reference material. For the phosphate samples that have a greater age offset compared to the garnets, the age offset might (in part) be associated with the different closure temperature of the Lu–Hf system compared to the U–Pb system. However, as outlined, both OD306 and CS5 apatite samples cannot be older than their host rock ages, which implies that the observed age offset

between expected age and measured Lu–Hf age is most likely due to matrix induced elemental fractionation. OD306 and CS5 suggest that the analytical offset between *in-situ* Lu–Hf age and expected age is ~5 – 6%. The reference age for the other apatite samples is more ambiguous (either imprecise U–Pb date or poor constraints on the age of the host rock), but agrees with the age offset observed for OD306 and CS5. Matrix induced element fractionation can occur without downhole changes in element ratios (Gilbert et al., 2014; Redaa et al., 2020; Sylvester, 2008). In this case, an offset is observed between expected ratios and measured ratios (e.g. Fig. 1.5), which is primarily due to the physical and chemical properties of the analysed material (Sylvester, 2008). Our preliminary results indicate that the measured Lu–Hf ratios may fractionate the least (or not at all) for garnets. If the single outlier (Otter Lake apatite; discussed below) is removed, apatite appears to fractionate the most. Given the lack of significant downhole fractionation (Fig. 1.1), matrix induced Lu–Hf fractionation is easier to constrain and correct for compared to other geochronometers, such as U–Th–Pb and Rb–Sr (Redaa et al., 2020; Sylvester, 2008).

Matrix-induced elemental fractionation effects (Sylvester, 2008) have traditionally limited accurate multi-element isotope ratio measurements by LA-ICP-MS. This generally necessitates ‘matrix matched’ standardisation, in which an isotopically-homogeneous mineral standard that matches the analysed samples is used to correct isotopic ratios. This has been studied in detail for U–Pb dating in zircons (e.g. Marillo-Sialer et al., 2014), apatite (e.g. Thompson et al., 2016) and calcite (e.g. Guillong et al., 2020) and, more recently, for Rb–Sr dating (Armistead et al., 2020; Gorojovsky and Alard, 2020; Li et al., 2020; Redaa et al., 2020; Zack and Hogmalm, 2016). However, isotopically homogeneous natural minerals that are suitable as primary reference materials are difficult to recognise and characterize. An alternative strategy is to use a homogeneous but non-matrix matched primary reference material to correct for instrument drift (e.g. NIST 610 glass), and correct unknowns to a secondary matrix matched mineral of known age (Armistead et al., 2020; Danyushevsky et al., 2011; Li et al., 2020; Redaa et al., 2020). A similar process has been used for U–Pb calcite geochronology (Li et al., 2014; Roberts et al., 2017). In the case of a secondary standard correction, age reproducibility is key, rather than isotopic homogeneity. As both uncertainties on the ‘expected’ age and measured age of secondary standards are propagated to samples during correction, it is important to have precise and accurate constraints on the age of secondary standards.

1.6.2.2. Secondary standard candidates.

Given the well constrained age of the Hogsbo Pegmatite (1029 ± 1.7 Ma) (Romer and Smeds, 1996), the relatively high precision of the *in-situ* Lu–Hf age and the reproducibility of Lu–Hf ratios between different runs, we suggest that the Hogsbo garnets would make a good secondary standard for garnet age corrections. However, it would be preferable to have independent constraints on the garnet Lu–Hf age, as many pegmatites have complex, multistage histories. Furthermore, the lack of a petrological connection between garnet growth and columbite/muscovite growth renders the current reference age somewhat ambiguous.

Several of the analysed apatite samples could be considered candidates for *in-situ* LA-ICP-MS/MS Lu–Hf apatite secondary standards. For apatite sample OD306 (Thompson et al., 2016) both an isochron and a single spot age can be calculated, with relatively high precision (Fig. 1.3B, Table 1.2). The ID-MC-ICP-MS U–Pb age of this sample provides an independent and precise constraint on the crystallisation age (Thompson et al., 2016), although independent constraints on the Lu–Hf age are preferable. Other highly precise candidates include 215 Ødegårdens Verk and 19589 Harts Range (Fig. 1.3; Table 1.2). Since these samples both contain >99% radiogenic Hf, single spot ages are easily calculated that do not rely on the assumptions used in common Hf corrections. If independent

constraints on Lu–Hf ages could be obtained for these samples, they could make appropriate secondary standards for *in-situ* Lu–Hf age determinations in apatite and could be used as primary reference materials for common-Hf free apatite

Otter Lake apatite shows relatively high precision for an isochron age and has a published Lu–Hf age of 1031 ± 6 Ma (Barfod et al., 2005). However, the age offset between the published Lu–Hf age and our *in-situ* Lu–Hf age for Otter Lake Apatite is significantly less compared to the age offsets calculated between U–Pb and *in-situ* Lu–Hf dates for the other analysed samples. This is problematic, given both CS5 and OD306 cannot be older than their U–Pb ages. Hence, Otter Lake apatite does not appear to sufficiently ‘correct’ the Lu–Hf ratios of the other analysed apatites (Table 1.2, Fig. 1.5). Previous analysis has indicated both heterogeneities in U–Pb age, as well as potential matrix-induced element fractionation differences between Otter Lake apatite and other apatite samples (Barfod et al., 2005; Chew et al., 2011; Thompson et al., 2016). Additionally, there is a strong decoupling between the U–Pb age (ca. 913 Ma or ca. 933 Ma) and Lu–Hf age (ca. 1031 Ma; (Barfod et al., 2005). Finally, Otter Lake apatite is thought to have formed at ca. 1000 Ma based on the age of cogenetic titanite which does not agree with either U–Pb or the Lu–Hf age (Barfod et al., 2005). Hence, Barfod et al. (2005) concluded that the isotopic systems in Otter Lake apatite have likely been affected by fluid interactions and may be age zoned. We consider it possible that age domains were mixed during solution Lu–Hf analysis of Otter Lake apatite, and the mineral is therefore not considered a reliable secondary standard for *in situ* Lu–Hf analysis

All analysed xenotime samples could be useful secondary standards for *in-situ* Lu–Hf analysis, given the relatively consistent offset observed between Lu–Hf ages (this study) and U–Pb ages (Fig. 1.5). As samples BS-1, MG-1, and Z6413 have high precision TIMS U–Pb ages, these are the preferred candidates for *in-situ* LA-ICP-MS/MS Lu–Hf secondary standards.

Importantly, at least two secondary standards are required to determine the accuracy of any correction applied to the $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of the analysed samples (e.g. one standard is used to correct the ratios, and another standard is used to check that the correction is accurate).

1.6.2.3. Common Hf corrections.

Generally, common-Hf corrected ^{176}Hf values require precise knowledge of both ^{177}Hf and initial $^{176}\text{Hf}/^{177}\text{Hf}$ (Vervoort, 2014). The results of this study, however, clearly demonstrate the validity of the applied common-Hf corrections, which are based on assumed initial Hf compositions (Table 1.2).

Accuracy can be improved by analysing co-genetic Hf bearing phases to better constrain the $(^{176}\text{Hf}/^{177}\text{Hf})_c$ ratio. Although high Hf minerals (such as zircon) are preferable, even minerals with <100 ppm Hf may be suitable (given detection of sub ppm Hf in apatite). Additionally, as utilised in some common Pb corrections, an iterative approach could be used, in which an initial Hf composition could be refined based on the calculated age. This is likely to be unnecessary for minerals such as apatite and xenotime, given their high $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. It should be mentioned that anchoring to assumed initial $^{176}\text{Hf}/^{177}\text{Hf}$ may not work in situations where anomalous Hf isotopic compositions exist. For instance, remobilisation in a heavy REE rich system may lead to an anomalous initial Hf isotopic composition for subsequently crystallised minerals.

The results of this study suggest that common Hf corrections improve precision for samples with > ~80% radiogenic ^{176}Hf , and that uncorrected single spot ages are valid for samples with >97% radiogenic ^{176}Hf .

1.6.2.4. Sample selection strategies.

As with many geochronometers, success is not guaranteed for every sample analysed. Sample success will likely be a factor of Lu concentration, common Hf content, age and crystal size (which will determine the usable laser spot diameter). All of these factors need to be accounted for when selecting samples. A variety of techniques may be useful when selecting samples for analysis.

Samples can be screened during both sample collection and during sample preparation. During sample collection, techniques such as x-ray fluorescence spectrometry (XRF) may be useful for selecting samples. Although Lu is likely to be low in concentration, and thus difficult to measure without using sensitive techniques such as LA-ICP-MS or sample digestion, Y is expected to correlate with Lu concentrations due to similarities in both ionic radius and valence (Shannon, 1976). As Y is significantly more abundant compared to Lu in the crust (~67 times higher Taylor and McLennan, 1985), Y measurements are likely to be a useful tool for selecting samples. Once samples have been selected, more sensitive techniques, such as LA-ICP-MS may be useful for determining Lu concentrations and potential Lu zonation in minerals. For garnets, techniques capable of producing sub-mineral scale elemental maps (e.g. LA-ICP-MS mapping, Micro XRF; Flude et al., 2018; Raimondo et al., 2017) may be important for determining high and low Lu regions in order to maximise spread on the isochron.

The total concentration of Lu in minerals is likely to be a product of the bulk-rock Lu budget as well as the amount of phases that compete for heavy REEs. For instance, rocks with abundant garnet are likely to dilute the total Lu concentration, as it will be shared between all garnets. It is therefore preferable to sample rocks in which garnet is relatively sparse.

1.7. Conclusions.

1.7.1. Success of the analytical approach.

This paper reports successful *in-situ* Lu–Hf dating using LA-ICP-MS/MS. The presented methodology relies on the measurement of cluster ions that form in a reaction cell where Lu and Hf react differently with NH₃ gas. This approach effectively resolves ¹⁷⁶Yb and ¹⁷⁶Lu isobaric interferences on ¹⁷⁶Hf. For the analysed garnet samples, *in-situ* Lu–Hf dates were calculated at an accuracy of ~97–100% compared to solution-based Lu–Hf studies. Garnet samples with variable common Hf concentrations produced isochron ages at a precision of ~3 to 4.8%. A precision of ~0.5% was achieved for one garnet sample from a REE-rich pegmatite. For the analysed apatite samples, *in-situ* Lu–Hf dates were obtained that correspond within 93 to 98% of associated U–Pb ages. Apatite samples OD306 and CS5 are used to constrain Lu–Hf matrix fractionation between apatite and glass to ~5.5%. The achieved precision for apatite samples with <2% common Hf was ~0.5 to 2%. The xenotime samples were analysed at an accuracy of 95 to 97% compared to U–Pb ages and with a precision below 1%. All analyses were conducted in absence of a matrix-matched primary standard. Given that there appears to be no evidence for down-hole fractionation, a secondary standard correction can be used to correct for the observed age offsets to achieve an accuracy to within 1%. We recommend the Hogsbo garnets as secondary standards for garnet *in-situ* Lu–Hf analysis, OD306 as a secondary standard for apatite *in-situ* Lu–Hf analysis, and BS-1, MG-1, and Z6143 as secondary standards for xenotime *in-situ* Lu–Hf analysis.

1.7.2. Advantages and applications.

There are a number of advantages that make this technique an important new development in geochronology:

1. An important advantage is the ability to quickly and easily obtain large, spatially resolved Lu–Hf geochronology datasets. Compared to the <10 analyses normally obtained during isotope dilution Lu–Hf work, these large datasets are more easily interpretable in terms of isotopic disturbance and age mixing.
2. Minerals can potentially be corrected for common Hf, allowing for single spots ages to be calculated, which significantly improves the precision on Lu–Hf ages and opens doors for detrital studies
3. The ease of analysis associated with *in-situ* Lu–Hf geochronology opens the possibility of “campaign style” dating, in which minerals from an entire tectonic terrane are targeted.
4. Apatite Lu–Hf geochronology is more likely to reveal primary apatite growth ages in thermally disturbed terranes.
5. Xenotime Lu–Hf geochronology has wide applicability to date hydrothermal ore systems including REE deposits, or in cases of low-U xenotime.
6. Additionally, the combination of Lu–Hf (~650 °C), U–Pb (~450 °C), apatite fission track dating (~60 – 120 °C) and apatite U–Th/He dating (Chew and Spikings, 2015) opens up the possibility to easily determine full thermal histories using a single mineral aliquot.

1.7.3. Current Limitations.

Although *in-situ* LA ICP MS/MS Lu–Hf dating shows promise, there are a number of current limitations of the technique and aspects that require further development.

1. Samples need to have sufficient Lu concentrations to be dated with the *in-situ* technique. Although it is difficult to determine exact thresholds, for apatite, we recommend that samples with >8 ppm Lu and ages >500 Ma, are likely suitable. Additionally, Proterozoic (or older) samples with >3 ppm Lu are best. However, the presence of common Hf is likely to increase uncertainties in samples with low Lu concentrations.
2. The low Hf concentrations of many datable minerals means that it is often necessary to use large laser spot diameters (>67 µm and up to 120 µm) in order to achieve useful precision. Hence, samples with large grain sizes are more suitable.
3. For samples with common Hf concentrations >2% (i.e. most garnet), the method relies on calculating isochron ages, which produce relatively high uncertainties. The largest source of uncertainty in most samples is the uncertainty on the $^{176}\text{Hf}/^{177}\text{Hf}$ ratios, as these are the two least abundant isotopes.
4. The demonstrated age offset between *in-situ* Lu–Hf ages and expected ages (Table 1.2, Fig. 1.5) imply that matrix matched standardisation is necessary to obtain accurate results

Future work should prioritise accurate and precise measurement of Lu–Hf ratios and distributions in secondary standards so that corrections for matrix induced elemental fractionations can be made. Isotopically homogenous (primary) reference materials should also be sought to further improve age determinations. Although samples 215 Ødegårdens Verk and 19589 Harts Range would make suitable primary reference materials for common-Hf free apatite (and Hogsbo 1 for garnets), for common-Hf bearing minerals no isotopically homogenous samples are currently known. Going forward, our aim is to accurately and precisely constrain the ages of the Lu–Hf secondary standards presented.

Acknowledgements

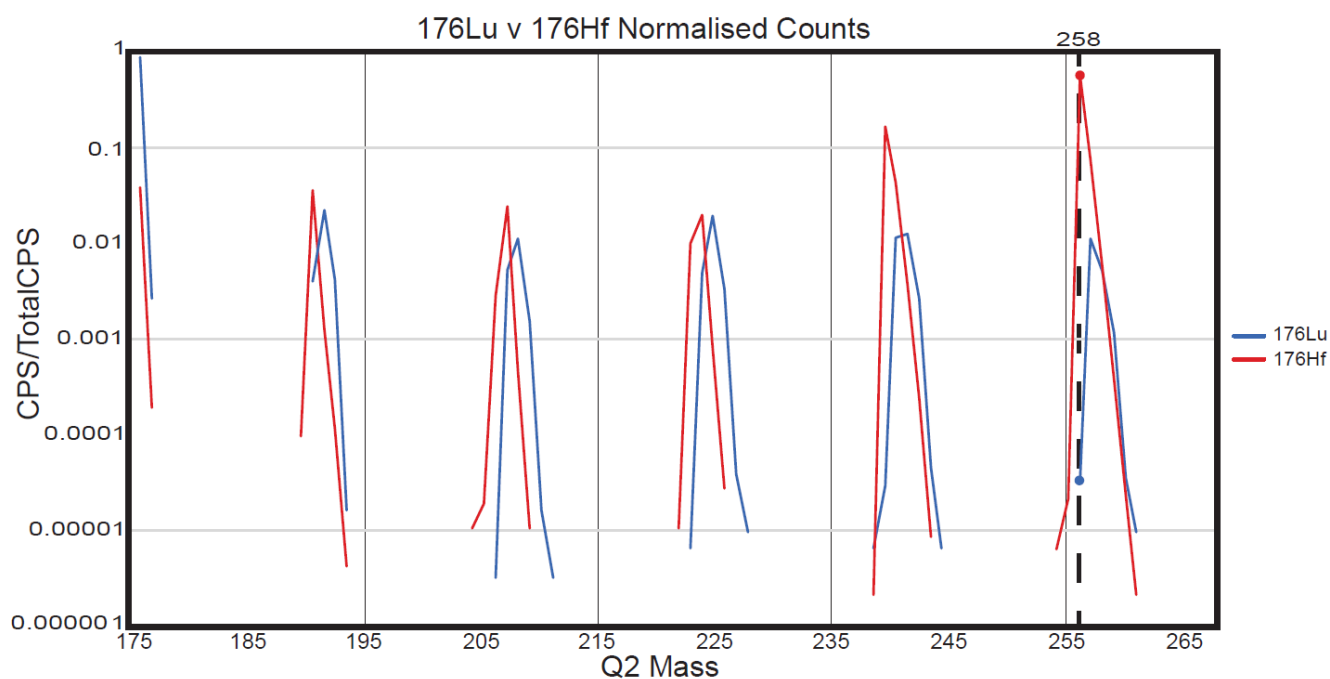
The authors would like to thank the MinEx CRC and the Australian Research Council (ARC DP200101881) for funding this research. Heike Ebendorff-Heidepriem from the Institute for

Photonics and Advanced Sensing (IPAS) is thanked for providing the Lu-doped, Yb- and Hf-free glass for this study. Dr Tony Milnes is acknowledged for providing samples from the Tate Museum at the University of Adelaide. Brad Cave is thanked for providing apatite samples from the Mt Isa district. Professor Balz Kamber is thanked for thorough and efficient handling of the manuscript during review. Dr Thomas Zack and an anonymous reviewer are thanked for constructive feedback during review.

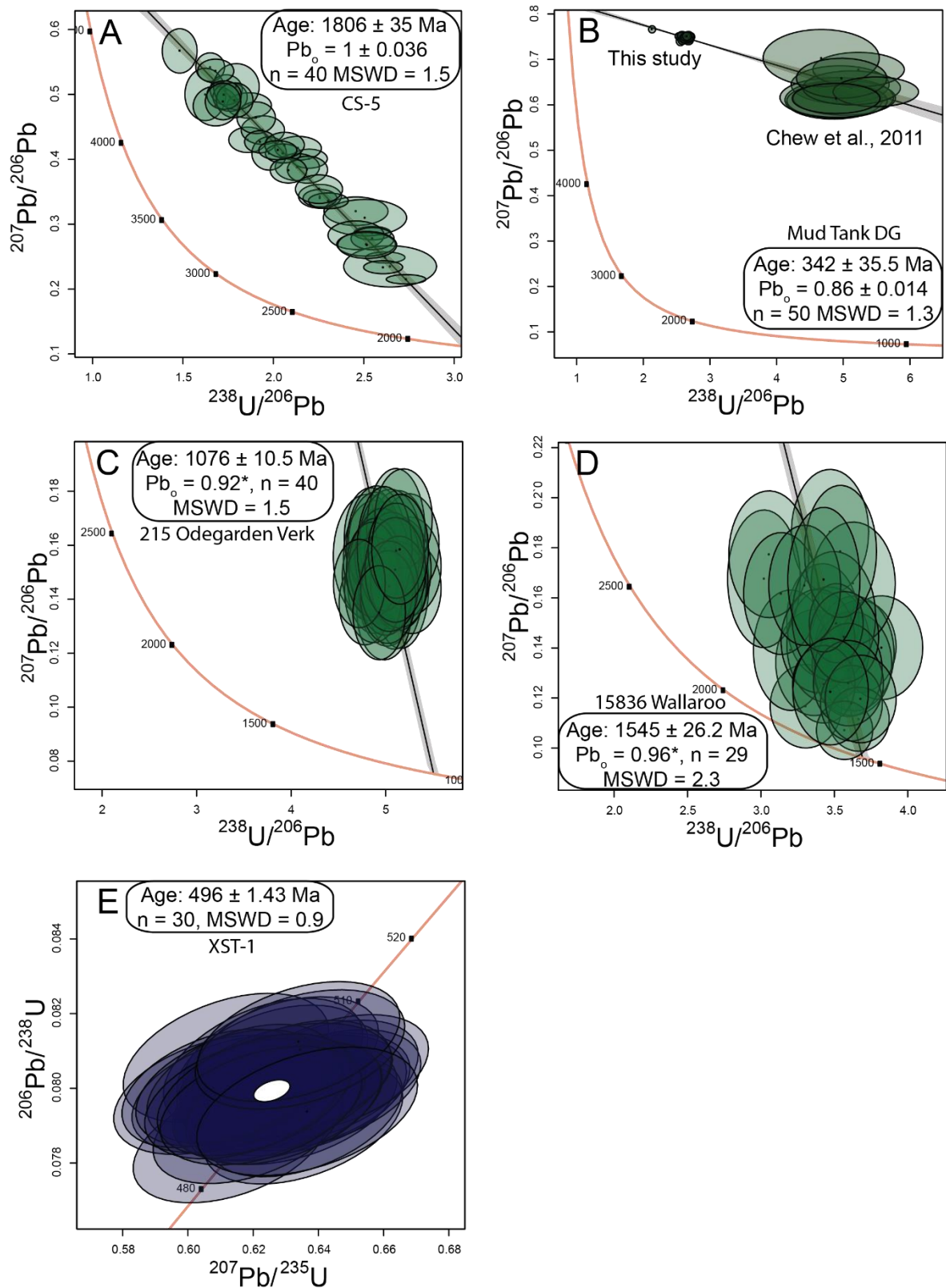
Author Credit Statement

A. Simpson: conceptualisation, method development, experimentation, data interpretation, manuscript drafting; **S. Gilbert:** method development, experimentation, method drafting; manuscript editing; **R. Tamblyn:** experimentation, method development, providing samples, data interpretation, manuscript editing; **M. Hand:** conceptualization, data interpretation, supervision, manuscript editing; **C. Spandler:** providing samples, data interpretation; **J. Gillespie:** providing samples, data interpretation; **Angus Nixon:** providing samples, experimentation; **S. Glorie:** conceptualization, data interpretation, manuscript drafting and editing, primary supervision.

1.8. Chapter 1 Appendix A: supplementary figures:

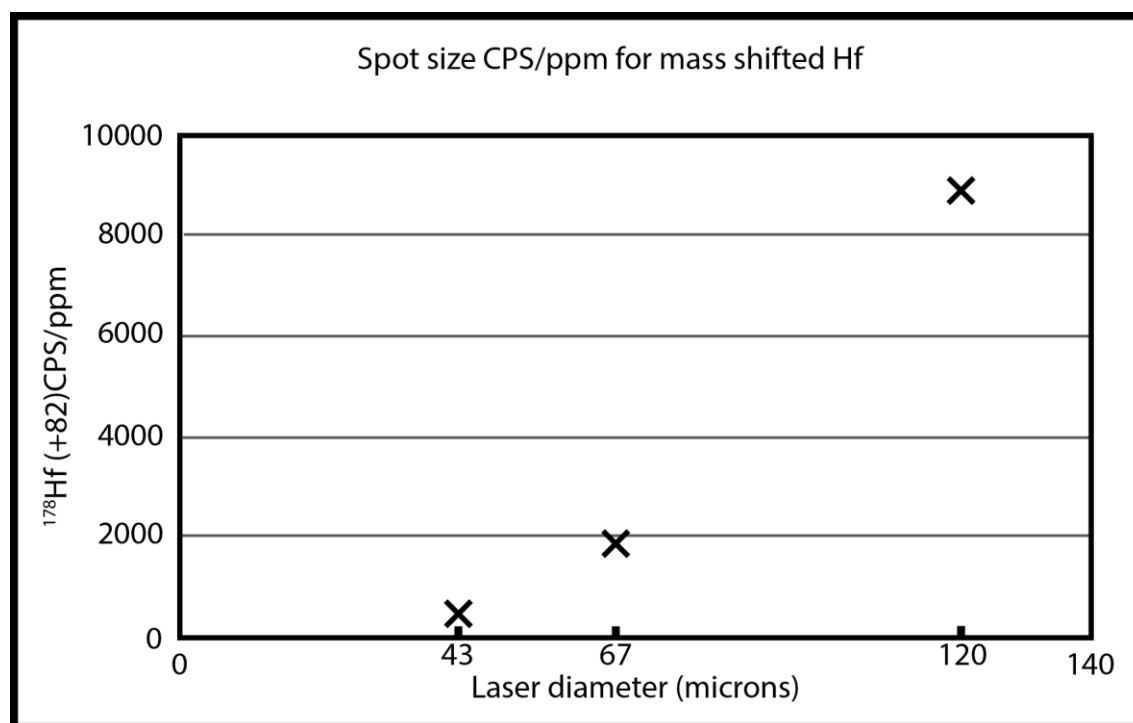


Appendix Figure 1.1: product ion scan showing reaction product masses for ^{176}Lu and ^{176}Hf when reacted with NH_3 . CPS have been normalised to total measured CPS across all masses (separately for each isotope). For each isotope, Q1 mass was set to only allow a single mass though, while Q2 mass (X axis) cycled through all masses up to mass 265. ^{176}Lu data was analysed separately using a Lu doped (and Hf and Yb free) glass. ^{176}Hf was analysed separately using GJ zircon standard.



Appendix figure 1.2: U-Pb concordia plots for analysed samples (apatites are green ellipses, xenotime are purple ellipses). All apatite ages are concordia lower intercept ages. Ellipses represent 2σ uncertainties. Age errors are 95% confidence intervals around the calculated age and include overdispersion where MSWD > 1. For apatite sample Mud Tank DG (B) additional U-Pb data from

Chew et al. (2011) has been added. The uncertainty is slightly higher than Chew et al. (2011) as these data have not been anchored to an initial Pb composition. 215- Ødegårdens Verk (C) isochron has been anchored to the expected initial Pb composition at ~1100 Ma (Stacey and Kramers, 1975). Wallaroo Mines Apatite (D) Tera-Wasserburg concordia plot isochron has been anchored to the expected initial Pb composition at ~1550 Ma (Stacey and Kramers, 1975). Full data tables of individual analyses and trace element compositions can be found in supplementary data file 1.2. Data has been calculated using ISOPLTR (Vermeesch, 2018).



Appendix Figure 1.3: Plot demonstrating the sensitivity changes based on laser spot size used. Data points are pooled averages of samples analysed at different laser ablation spot sizes. Analysis was conducted under the same conditions specified on table 1.1.

1.9: Chapter 1 appendix B: LA-ICP-MS U-Pb method

Analyses were conducted using a RESOLUTION 193nm excimer laser ablation system (Applied Spectra) with a S155 sample chamber (Laurin Technic) coupled with an Agilent 7900x mass spectrometer (ICP MS). A squid mixing devise (Laurin Technic) was used to smooth the pulses of the laser.

LA-ICP-MS trace element and U-Pb analysis used protocols described in Gillespie et al. (2018). MAD apatite (Chew et al., 2014; Thomson et al., 2012) was used as the primary reference material for apatite U-Pb analysis, with 401 apatite (Thompson et al., 2016) and McClure mountain apatite (Chew et al., 2014) used as secondary reference materials. MG-1 xenotime was used as primary reference material for xenotime U-Pb analysis, with BS-1 xenotime used as secondary standard (Stern and Rainbird, 2001). NIST 610 was used as primary reference to correct Pb/Pb ratios for both apatite and xenotime. Trace element concentrations were quantified using NIST610 to correct for instrument drift, with minerals internally normalised to stoichiometric elemental concentrations. Ca was used as internal standard for apatite. For the xenotime sample (XST-1), the Y counts were first normalised to xenotime reference material BS-1 (35.2 wt%; Fletcher et al., 2004), in order to calculate the Y wt%. Following this, Y was used as internal standard to calculate other elemental concentrations. As no major element constraints exist for the analysed garnets, the approximate Al concentration was used as an internal standard.

Comparisons between Hf concentrations from LA ICP MS/MS data and LA ICP MS data revealed that in high REE minerals (such as apatite) with Hf <1ppm, an YbO⁺ interference occurred on 178Hf, leading to overestimation of Hf concentrations. Therefore LA ICP MS Hf apatite data should be treated with caution.

Appendix table 1.1. U-Pb analytical parameters

LASER	
BRAND AND MODEL	RESolution-LR 193nm Excimer Laser System
WAVELENGTH	193nm
SPOT SIZE	30µm
REPETITION RATE	5Hz
ENERGY ATTENUATION	50%T
LASER FLUENCY	4 j/cm ²
ICPMS	
BRAND AND MODEL	Agilent 7900x
FORWARD POWER	1350W
TORCH DEPTH	4.5mm
GAS FLOWS	
PLASMA (AR)	15L/min
AUXILIARY (AR)	1L/min
CARRIER (HE)	07L/min
SAMPLE (AR)	0.88L/min
DATA ACQUISITION PARAMETERS	
DATA ACQUISITION PROTOCOL	Time resolved analysis
SCANNED ISOTOPES (APATITE)	29Si, 35Cl, 43Ca, 44Ca, 51V, 55Mn, 88Sr, 89Y, 90Zr, 139La, 140Ce, 141Pr, 146Nd, 147Sm, 153Eu, 157Gd, 159Tb, 163Dy, 165Ho, 166Er, 169Tm, 172Yb, 175Lu, 178Hf, 202Hg 204Pb, 206Pb, 207Pb, 208Pb, 232Th, 238U
SCANNED ISOTOPES (XENOTIME)	29Si, 43Ca, 89Y, 90Zr, 139La, 140Ce, 141Pr, 146Nd, 147Sm, 153Eu, 157Gd, 159Tb, 163Dy, 165Ho, 166Er, 169Tm, 172Yb, 175Lu, 178Hf, 202Hg 204Pb, 206Pb, 207Pb, 208Pb, 232Th, 238U
DETECTOR MODE	Peak Hopping, Pulse & Analog counting
BACKGROUND COLLECTION	30
ABLATION FOR AGE CALCULATION	30
WASHOUT STANDARDS	20
PRIMARY STANDARDS	NIST610, MAD (apatite) MG-1 (Xenotime)
SECONDARY STANDARDS	401 apatite, McClure apatite, BS-1 Xenotime

Supplementary data tables can be found at:

U-Pb data set: <https://doi.org/10.25909/21952637.v1>

Lu-Hf data set: <https://doi.org/10.25909/21952640.v1>

Chapter 2: *In-situ* Lu – Hf geochronology of calcite

Published as

Simpson, A., Glorie, S., Hand, M., Spandler, C., Gilbert, S., Cave, B. 2022. In situ Lu–Hf geochronology of calcite. *Geochronology*, 4(1): 353-372. <https://doi.org/10.5194/gchron-4-353-2022>

Supplementary data tables can be found at:

<https://doi.org/10.25909/21952646.v1>

Statement of Authorship

Title of Paper	In situ Lu–Hf geochronology of calcite
Publication Status	☒ Published ☐ Accepted for Publication ☐ Submitted for Publication ☐ Unpublished and Unsubmitted work written in manuscript style
Publication Details	Simpson, A., Glorie, S., Hand, M., Spandler, C., Gilbert, S., and Cave, B., 2022, In situ Lu–Hf geochronology of calcite: Geochronology, v. 4, no. 1, p. 353-372. https://doi.org/10.5194/gchron-4-353-2022

Principal Author

Name of Principal Author (Candidate)	Alexander Simpson		
Contribution to the Paper	Conceptualisation, method development, experimentation, and paper drafting		
Overall percentage (%)	80		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	11/01/2023

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

- i. the candidate's stated contribution to the publication is accurate (as detailed above);
- ii. permission is granted for the candidate to include the publication in the thesis; and
- iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	Stijn Glorie
Contribution to the Paper	Conceptualisation, paper drafting, and primary supervision

Signature		Date	11/01/2023
-----------	--	------	------------

Name of Co-Author	Martin Hand		
Contribution to the Paper	Conceptualisation, paper drafting, and secondary supervision		
Signature		Date	23/01/2023

Name of Co-Author	Carl Spandler		
Contribution to the Paper	conceptualisation, sampling, and paper drafting		
Signature		Date	23/01/2023

Name of Co-Author	Sarah Gilbert		
Contribution to the Paper	method development, experimentation, and paper drafting		
Signature		Date	11/01/2023

Name of Co-Author	Bradley Cave		
Contribution to the Paper	Experimentation and paper drafting.		
Signature		Date	23/01/2023

2.1 Abstract.

The ability to constrain the age of calcite formation is of great utility to the Earth Science community, due to the ubiquity of calcite across a wide spectrum of geological systems. Here, we present the first in-situ laser ablation inductively coupled tandem quadrupole mass spectrometry (LA-ICP-MS/MS) Lu–Hf ages for calcite, demonstrating geologically meaningful ages for IOCG and skarn mineralisation, carbonatite intrusion and low grade metamorphism. The analysed samples range in age between ca. 0.9 Ga and ca. 2 Ga with uncertainties between 1.7% and 0.6% obtained from calcite with Lu concentrations as low as ca. 0.5 ppm. The Lu–Hf system in calcite appears to be able to preserve primary precipitation ages over a significant amount of geological time, although further research is required to constrain the closure temperature. The in-situ approach allows calcite to be rapidly dated while maintaining its petrogenetic context with mineralization and other associated mineral processes. Therefore, LA-ICP-MS/MS Lu–Hf dating of calcite can be used to resolve the timing of complex mineral paragenetic sequences that are a feature of many ancient rock systems.

2.2 Introduction

Calcite (CaCO_3) is the main mineral phase of most carbonate sedimentary rocks and their metamorphic equivalents. Calcite is also a common diagenetic phase and is a major component of carbonatites. Calcite is also a common product of hydrothermal alteration and constituent of mineralising systems where it may precipitate from fluids during pre-ore, ore-stage, and post-ore forming processes (Debruyne et al., 2016). The ability to directly date calcite unlocks the possibility to constrain the timing of a vast array of geological processes that can be difficult to date using conventional methods.

Accurate *in-situ* U–Pb geochronology of calcite has been applied to a variety of geological systems (e.g; Li et al., 2014; Ring and Gerdes, 2016; Roberts and Walker, 2016). However, calcite often incorporates significant quantities of Pb during crystallisation (i.e. ‘initial’ or ‘common’ Pb), which can limit the utility of U–Pb geochronology (Rasbury and Cole, 2009). Moreover, Pb is highly fluid mobile (Brugger et al., 2016), so it can be difficult to obtain primary age information with the U–Pb method in hydrothermal or strongly-altered systems (Roberts et al., 2020; Simpson et al., 2021b). Further, given the propensity for calcite to undergo recrystallisation, calcite U–Pb geochronology is rarely applicable to Precambrian systems as the calcite U–Pb system invariably does not remain closed over long timescales (Whitehouse and Russell, 1997).

Alternative dating systems involving the radioisotopic decay of rare earth elements (REE) such as Sm–Nd and Lu–Hf, have previously been applied to calcite (e.g. Barker et al., 2009; Maas et al., 2022; Nie

et al., 1999; Peng et al., 2003), based on the moderate to strong compatibility of REEs in carbonates in many systems (Debruyne et al., 2016; Elzinga et al., 2002; Terakado and Masuda, 1988; Zhong and Mucci, 1995). Although it should be noted that REE compatibility will be dependent on the conditions of calcite formation, and can vary. Importantly for geochronology, experimental evidence indicates that Lu and Hf are highly immobile in many hydrothermal fluids (Brugger et al., 2016; Migdisov et al., 2016), meaning that the Lu–Hf system is potentially during post-formation processes relative to the U–Pb system. However, concentrations of Lu and Hf are generally low (ppm to ppt range) in calcite, necessitating the dissolution of large quantities of material (up to 2g) per sample for conventional Lu–Hf geochronology (Maas et al., 2022). These large quantities significantly reduce the spatial resolution of the technique and have the additional problem of potential contamination from inclusions. Furthermore, age variation is difficult to detect, and bulk samples may produce meaningless average age derived from mixing of age domains. The dissolution process also removes calcite from its petrological context. The recent development of *in-situ* Lu–Hf geochronology of individual minerals by LA-ICP-MS/MS allows for rapid acquisition of spatially resolved data, and has been demonstrated for garnet (Ribeiro et al., 2021; Tamblyn et al., 2021) and apatite (Glorie et al., 2021)

In this study, we present the first *in-situ* Lu–Hf dating of calcite from a variety of geological environments. We demonstrate that *in-situ* calcite Lu–Hf geochronology can produce meaningful ages for complexly deformed and hydrothermally-altered systems, such as mineral deposits, as well as carbonatite intrusions and low grade metamorphism.

2.3. Geological Background of Samples

The analysed samples were selected; (1) to demonstrate that calcite Lu–Hf can date primary calcite formation in carbonatites; (2) to reveal the potential of the method to unravel complex ore systems or later events, and; (3) to characterize large calcite samples that would make suitable reference materials for *in-situ* analysis.

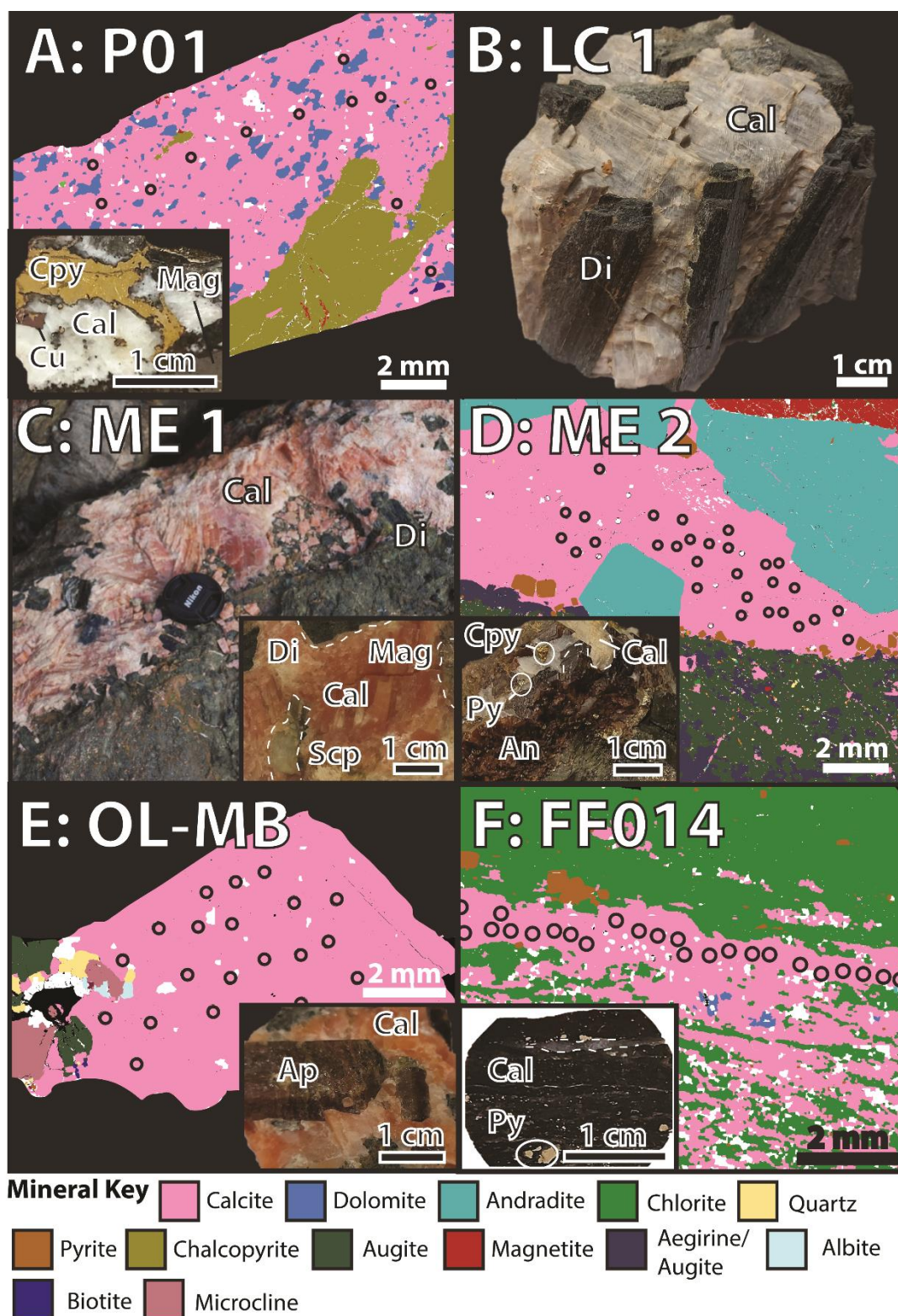


Figure 2.1: A combination of SEM mineral maps (A,C,D,E) and photos of analysed samples. (A) P01 (Phalaborwa Carbonatite) shows calcite in petrogenetic context to chalcopyrite. (B) Photo of LC 1 hand sample. (C) Photo of the ME 1 sample in outcrop, with inset showing the mineralogy of the analysed sample. (D) calcite from ME 2 (Mt Isa) in contact with hematite, pyrrhotite and andradite, with inset showing hand sample (D) OL-MB (Otter Lake), showing analysed calcite with associated minerals, with inset showing relationship between apatite (Ap) and calcite (Cal) in hand sample. (E) FF014 (Flin Flon deposit) shows calcite vein in chlorite matrix with

disseminated pyrite, with inset showing analysed block (dark coloured matrix is composed of chlorite). Black circles represent laser spot locations. Mineral abbreviations: Cal: Calcite, Cpy: chalcopyrite, Py: pyrite, Mag: magnetite, Cu: cubanite, Di: diopside, Scp: scapolite, An: andradite. Larger size sample images are included in appendix C.

2.3.1. Phalaborwa Carbonatite, South Africa

The Phalaborwa Igneous Complex is located ~450 km northeast of Johannesburg, in the Limpopo Province, South Africa. The igneous complex is the result of several distinct pulses of alkaline intrusions that were emplaced into Archean granitic gneiss (Staff, 1976). The Loolekop pipe is located in the centre of the Phalaborwa Igneous Complex and was intruded by two episodes of carbonatite emplaced at the intersection of five major faults and shear zones (Basson et al., 2017; Staff, 1976). The oldest carbonatite is termed the “transgressive banded” carbonatite and has an emplacement age of 2060.0 ± 2.2 Ma (baddeleyite SIMS U-Pb; Wu et al., 2011). This is intruded by a slightly younger carbonatite termed the “banded” carbonatite and has an emplacement age of 2059.8 ± 1.3 Ma (baddeleyite SIMS U-Pb; Wu et al., 2011). The Phalaborwa carbonatite is unique as it is the only known example of a carbonatite containing economic Cu mineralisation (Groves and Vielreicher, 2001). In the banded carbonatite-phoscorite, Cu mineralisation is primarily in the form of bornite inter-grown with valleriite with minor chalcopyrite (Staff, 1976). In the transgressive carbonatite, Cu mineralisation is present as chalcopyrite inter-grown with cubanite and valleriite (Staff, 1976). Cu mineralisation is interpreted to be magmatic-hydrothermal in origin, with Cu leached by high-temperature hydrothermal fluids at depth, precipitating along fractures within the hosting carbonatite (Le Bras et al., 2021). The sample used in this study (P01) is representative of carbonatite hosted Cu-mineralisation from within the Loolekop pipe (Fig. 2.1). The sample is mineralogically composed of chalcopyrite inter-grown with cubanite and pyrrhotite alongside an assemblage of magnetite, dolomite, calcite, biotite, pyroxene and valleriite. As the Phalaborwa carbonatite has a well constrained crystallisation age, it provides an ideal case study to demonstrate the utility of the *in-situ* Lu–Hf method for dating igneous calcite directly associated with Cu mineralisation.

2.3.2. The Eastern Fold Belt, Mt Isa Block, Queensland, Australia

The Eastern Fold Belt of the Mount Isa Domain has experienced multiple episodes of deformation, magmatism, metamorphism, mineralisation and pervasive hydrothermal alteration across the Paleo- to Mesoproterozoic, and hence represents one of the most metasomatized crustal blocks on Earth (Oliver et al., 2008). Hydrothermal calcite is common across the Mount Isa region, in the Mary Kathleen Domain (Oliver et al., 1993) and in many of the IOCG deposit of the Cloncurry District. For this study we have selected calcite samples from the Lime Creek calcite quarry and the Mt Elliott IOCG

deposit for Lu–Hf analysis. The Mt Isa Domain has both regional and deposit level age constraints, making it a good area to demonstrate the technique.

The Lime Creek quarry is one of a number of large calcite pods or veins that are exposed in Mary Kathleen Domain. The Lime Creek quarry is hosted within the ca. 1760 Ma Argylia Formation and lies along the steeply dipping NNW-trending Tribulation-Lime Creek Fault, which offsets regional-scale 'D₂' folds (Marshall, 2003). Breccias along this fault contain clasts of calc-silicate rocks and metadiorite with a matrix consisting of albite-actinolite-diopside-biotite-titanite-apatite that are subsequently overprinted by the undeformed Lime Creek calcite-dominated veins (Marshall, 2003). These veins are extremely coarse-grained with calcite crystals larger than 1 m³, actinolite crystals over 1 m in length, and apatite, biotite, diopside and titanite grains over 20 cm in diameter (Marshall, 2003; Oliver et al., 1993). Based on cross-cutting relationships, it is interpreted that the Lime Creek vein system, and other calcite pods/veins of this style precipitated post-faulting during late-'D₃' deformation (ca. 1550–1500 Ma) of the Isan Orogeny (Giles and Nutman, 2002; Marshall, 2003). This style of veining is common throughout the Mary Kathleen Domain and provides evidence of km-scale fluid transport during late-stage metamorphism (Oliver et al., 1993). Based on C and O isotope analysis of calcite from these veins, they are interpreted to have formed from hydrothermal fluids likely associated with the intrusion of the ca. 1530 to 1500 Ma Williams-Naraku Batholiths (Oliver et al., 1993). Although no direct dating has been completed on the Lime Creek Quarry, titanite from the nearby and cognate Knobby Quarry have produced three titanite U–Pb ages of 1521 ± 5 Ma, 1527 ± 7 Ma, and 1555 ± 5 Ma (Oliver et al., 2004). The sample analysed in this study (LC1) consists of very coarse-grained calcite with coarse-grained diopside collected from a large calcite pod in the Lime Creek Quarry (Fig. 2.1).

Mt Elliott is an IOCG deposit located in the Eastern Fold Belt of the Mount Isa Inlier (Duncan et al., 2011). The deposit is situated within northwest striking splays of the Mount Dore Fault (Duncan et al., 2011; Wang and Williams, 2001), and is hosted within skarn-altered and deformed phyllites and schists (Garrett, 1992; Wang and Williams, 2001). The host rocks were metamorphosed to lower amphibolite facies during the ca. 1600–1580 Ma 'D₂' deformation of the Isan Orogeny (Garrett, 1992; Wang and Williams, 2001). The formation of early albite-hematite (red rock) alteration enhanced brittle fracturing and brecciation of the shale (Garrett, 1992). This was infilled by two stages of open-space skarn development: (1) diopside-magnetite-hematite-calcite-titanite-allanite-phlogopite, and: (2) actinolite-scapolite-magnetite-andradite-calcite-epidote-allanite-chlorite and biotite (Garrett, 1992; Wang and Williams, 2001). Sulphides in the second stage include chalcopyrite, pyrrhotite and pyrite (Garrett, 1992). Although the two skarn assemblages are difficult to distinguish mineralogically, the

second episode is the most widespread and represents the major Cu–Au event (Garrett, 1992; Wang and Williams, 2001). A variety of geochronological techniques have been applied to constrain the age of Cu–Au mineralisation. The earliest phase of skarn development has been dated at 1530 ± 11 Ma (U–Pb titanite; Duncan et al., 2011). The second stage of skarn development associated with Cu–Au mineralisation has been dated at 1513 ± 5 Ma (molybdenite Re–Os; Duncan et al., 2011) and 1510 ± 3 Ma (actinolite Ar–Ar; Wang and Williams, 2001). Two outcrop samples from the Mount Elliot Cu–Au deposit were selected for Lu–Hf geochronology. Mt Elliott 1 (ME 1) consists of coarse-grained pink-coloured calcite that is coeval with the formation of diopside, scapolite and magnetite (Fig. 2.1). Although the paragenesis of this sample is relatively unconstrained, the lack of sulphides may indicate that this sample belongs to the early pre-mineralisation skarn assemblage. Calcite from sample Mt Elliott 2 (ME 2) is coeval with the formation of andradite, pyrite, chalcopyrite, pyrrhotite and magnetite (Fig. 2.1). The close relationship between calcite and chalcopyrite in this sample indicates that it is associated with the main Cu–Au bearing skarn assemblage.

2.3.3. Flin Flon Volcanic Massive Sulphide (VMS) Deposit, Canada

The Flin Flon Greenstone Belt stretches across central Manitoba through to east central Saskatchewan and hosts several world-class Zn–Cu VMS deposits including the Flin Flon, Callinan and 777 deposits (Koo and Mossman, 1975). Zn–Cu mineralisation is interpreted to have formed contemporaneously with deposition of the 1888.9 ± 1.6 Ma Millrock member during the Trans-Hudson Orogeny (Gibson et al., 2012; Koo and Mossman, 1975; Rayner, 2010). The Flin Flon Zn–Cu orebody is recognised to have undergone six distinct deformation events that have affected the shape of the deposit (Lafrance et al., 2016; Schetselaar et al., 2017). ‘D₁’ and ‘D₂’ were associated with the intra-oceanic accretion of the Flin Flon Arc to other volcanic terrains before ca. 1872 Ma (Lafrance et al., 2016). ‘D₃’ occurred from 1847–1842 Ma as a response to the final accretion of the Flin Flon Terrane to the Glennie Terrane, producing west-verging folds within stacked, east dipping thrust sheets of basement and cover rocks bounded by NNW-striking thrust faults (Lafrance et al., 2016). ‘D₄’ resulted from the collision between the Flin Flon and Glennie complex with the Sask Craton and is broadly coeval with the ca. 1840 Ma Phantom Lakes dyke (Gibson et al., 2012; Lafrance et al., 2016). ‘D₅’ deformation produced a penetrative regional cleavage (S₅) that is defined by a continuous chloritic foliation ubiquitous in the volcanic basement rocks (Gibson et al., 2012; Lafrance et al., 2016). EWE–WNW directed compression during ‘D₆’ deformation produced a second regional penetrative cleavage and reactivated a variety of regional-scale faults (Gibson et al., 2012; Lafrance et al., 2016). Regional greenschist to granulite facies metamorphism is associated with D_{5–6} deformation at ca. 1820–1790 Ma (Schneider et al., 2007). The Flin Flon mine horizon was imbricated during ‘D₃’ thrusting with the shape of the ore lenses moulded during ‘D₄’ and ‘D₅’ deformation (Schetselaar et al., 2017). Regional

greenschist to amphibolite grade metamorphism occurred between 1820 – 1790 Ma (U-Pb monazite; Schneider et al., 2007), with rocks in the Flin Flon deposit reaching greenschist facies (Koo and Mossman, 1975). The sample selected for this study is from the hydrothermally altered and sheared footwall of the Flin Flon VMS deposit. This sample is composed of highly foliated chlorite and calcite with disseminated pyrite and residual titanomagnetite. A band of highly foliated calcite was selected for Lu–Hf analysis (sample FF014; Fig. 2.1) to constrain the age of syn-metamorphic shearing of the deposit.

2.3.4. Yates U-Th prospect, Otter Lake Area, Grenville Province, Canada

The Otter Lake area is located in SE Ontario within the Grenville Province. The Grenville Province can be distinguished from surrounding provinces based on various structural, metamorphic and isotopic signatures attributed to the overprinting ca. 1080–980 Ma Grenvillian Orogeny (Rivers, 2015). This orogenic event produced widespread metamorphism from granulite to amphibolite facies (van Breemen and Corriveau, 2005) accompanied by widespread hydrothermal alteration in the Otter Lake area (Kretz et al., 1999). The Yates U-Th prospect is located approximately 100 km northwest of Ottawa, and is renowned for the occurrence of pegmatites that contain large euhedral crystals of apatite set within a matrix of predominantly orange-pink calcite, with diopside, allanite, titanite, fluorite, thorite and phlogopite (Schumann et al., 2019). A wide range of dates have been produced from the Yates mine; including titanite Pb–Pb and U–Pb ages between ca. 1020 and 998 Ma (Frei et al., 1997; Kennedy et al., 2011); apatite Pb–Pb, and U–Pb ages of 913 ± 7 Ma (Barfod et al., 2005), 933 ± 12 Ma and 920 – 850 Ma (Chew et al., 2011; Xiang et al., 2021) respectively, and an apatite Lu–Hf age of 1031 ± 6 Ma (Barfod et al., 2005). In addition, Simpson et al. (2021a) obtained an *in-situ* Lu–Hf apatite age of 1000 ± 11 Ma (when corrected for laser induced elemental fractionation). Importantly, the apatite Lu–Hf and Pb–Pb ages have been obtained from the same large apatite crystal, indicating that the Lu–Hf and U–Pb systems have been decoupled (as opposed to multiple generations of apatite growth). Barfod et al. (2005) argued that late-stage fluid interactions may have affected Pb retentivity in the apatite, as the apatite was unlikely to be above the apatite Pb closure temperature at ca. 913 Ma. Calcite from a specimen containing coarse-grained euhedral apatite with pink calcite, quartz and diopside was selected for calcite Lu–Hf analysis (OL-MB, Fig. 2.1). The apatite is enclosed in the sampled calcite, and is interpreted to have crystallised just prior to the calcite, but during the same hydrothermal event.

2.4. Method

The samples were mounted in 2.5 cm diameter epoxy mounts and screened for Lu concentration by LA-ICP-MS to determine suitability for Lu–Hf analysis. Mineral liberation analysis (MLA) maps were

obtained using a Hitachi SU3800 scanning electron microscope (SEM) to reveal the petrogenetic context of the analysed calcite.

2.4.1 In-Situ Lu-Hf Dating Method

Analysis was conducted at Adelaide Microscopy, The University of Adelaide. Calcite samples were analysed using a RESOLUTION 193 nm laser ablation system (Applied Spectra) with a S155 sample chamber (Laurin Technic). The laser ablation system was coupled to an Agilent 8900 tandem mass spectrometer (ICP-MS/MS). The methodology largely follows that of Simpson et al. (2021a) including an initial instrument tune conducted with no NH₃ in the reaction cell to achieve robust plasma conditions (U/Th = 1.00-1.05) and minimal oxide interferences (ThO/Th <0.2%). A carrier gas of 3.5 mL/min N₂ was added after the sample cell in order to increase sensitivity (Hu et al., 2008). Analytical conditions are included in appendix Table 2.1.

Methods for separation of ¹⁷⁶Hf from ¹⁷⁶Lu and ¹⁷⁶Yb follow that of Simpson et al. (2021a). In more detail, the Agilent 8900x utilises a reaction cell between two quadrupole mass analysers, which can be used to separate isobaric interferences. The first quadrupole is used as a mass filter (e.g., when set to mass 176, only ¹⁷⁶Lu, ¹⁷⁶Yb, and ¹⁷⁶Hf can pass), thereby minimizing potential background interferences and other, unwanted reactions. Following this, a mixture of 10% NH₃ and 90% He is added to the reaction cell (at a rate of 3 mL/min). This mixture is optimized to promote formation of the Hf reaction product Hf((NH)(NH₂)(NH₃)₃)⁺ and the second quadrupole is set to 82 amu higher than the first (e.g., Q1 = 176 amu and Q2 = 258 amu). This method minimizes the equivalent Lu and Yb reaction products (~0.03% for Lu, and below detection for Yb), such that the isobaric interferences on ¹⁷⁶Hf are negligible (Simpson et al., 2021a). Lens voltages were tuned to increase sensitivity on the Hf reaction product (Simpson et al., 2021a). In order to calculate Lu/Hf ratios, ¹⁷⁶Hf (+82) was measured directly, ¹⁷⁵Lu was measured as a proxy for ¹⁷⁶Lu, and ¹⁷⁸Hf (+82) measured as a proxy for ¹⁷⁷Hf (Simpson et al., 2021a). ¹⁷⁶Hf/¹⁷⁶Lu, ¹⁷⁶Lu/¹⁷⁷Hf, and ¹⁷⁶Hf/¹⁷⁷Hf ratios were calculated as part of the normalization to NIST610, as opposed to separately converting measured ¹⁷⁵Lu and ¹⁷⁸Hf into ¹⁷⁶Lu and ¹⁷⁷Hf. In more detail, if we assume that the ¹⁷⁶Lu/¹⁷⁵Lu ratio (or ¹⁷⁷Hf/¹⁷⁸Hf ratio) is identical between NIST SRM 610 and all analysed samples, a correction factor calculated from the % difference between the ¹⁷⁵Lu/¹⁷⁸Hf ratio measured in NIST SRM 610 and the published ¹⁷⁶Lu/¹⁷⁷Hf will correct the unknowns for matrix independent fractionation and differences in isotopic abundance. ⁴³Ca was measured for internal normalization of trace element abundances, and the following isotopes were measured to monitor for inclusions: ²⁷Al, ⁴⁷Ti, ⁸⁹Y, ⁹⁰Zr, ¹⁴⁰Ce, and ¹⁷²Yb.

Lutetium abundances in most calcite samples are low (< 6 ppm), so we employed a large laser diameter of 257 μm , and a repetition rate of 10 Hz to maximize sensitivity. High sensitivity is important in order to either measure common Hf (in this case ^{178}Hf), or demonstrate that ^{176}Hf is sufficiently above detection limits that the effects of common Hf are negligible. Smaller spot sizes could be employed for higher Lu and/or higher Hf samples. An extra 20 seconds delay was added after each interval of sample ablation in order to ensure the washout had reached background levels. NIST SRM 610 glass ($^{176}\text{Lu}/^{177}\text{Hf}$: 0.1379 ± 0.005 , $^{176}\text{Hf}/^{177}\text{Hf}$: 0.282122 ± 0.000009 ; Nebel et al., 2009) was used as the primary reference material and was analyzed using a spot size of 43 μm . The smaller spot size was required to ensure that ^{175}Lu was measured in pulse counting mode (<4 Mcps). Consistent with observations in Simpson et al. (2021a), Lu and Hf showed no measureable down-hole fractionation in the analysed carbonates (fig. 2.2), as such, no down-hole correction was applied to the data.

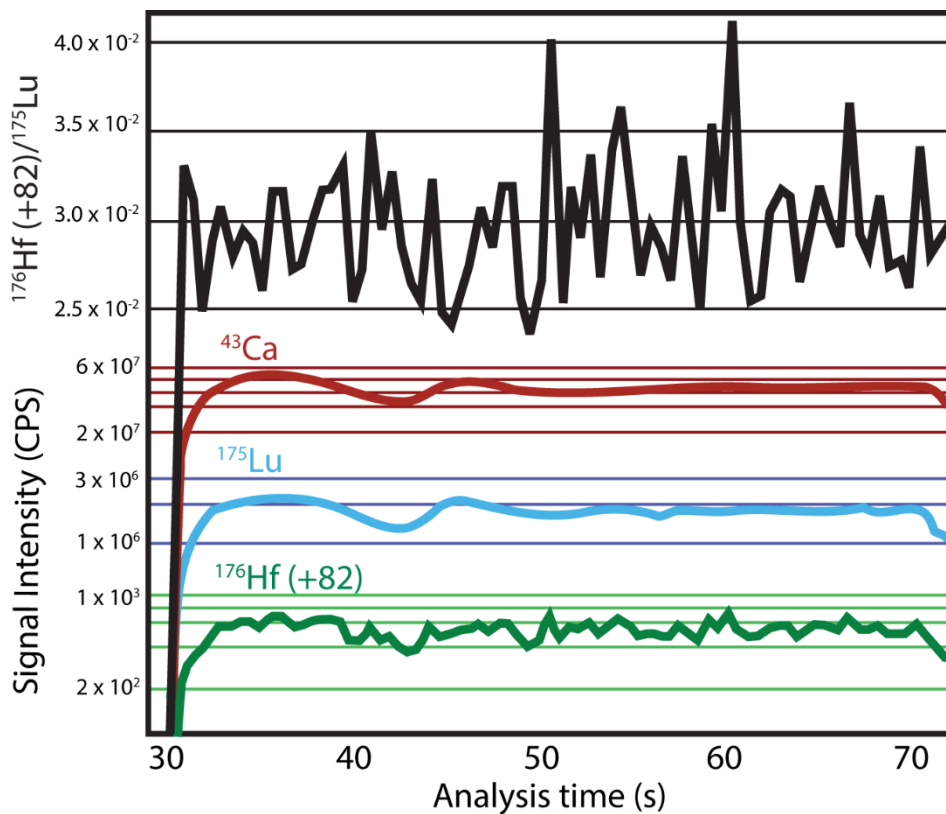


Figure 2.2: Time resolved signals for $^{175}\text{Lu}/(^{176})\text{Hf} (+82)$, ^{43}Ca , ^{175}Lu , and $(^{176})\text{Hf} (+82)$ demonstrating the effects of plasma loading on the signal intensities (i.e. dip in signal intensities at ~10-15s ablation), but not for the $^{176}\text{Hf}/^{175}\text{Lu}$ ratio, which remains constant down-hole. The time resolved intensity of each analyte has been offset in the graph for better comparison, therefore the Y axis scale is not continuous. Green horizontal lines show the scale for $^{176}\text{Hf} (+82)$, blue horizontal lines show the scale for ^{175}Lu , red horizontal lines show the scale for ^{43}Ca ,

and black horizontal lines show the scale for the $^{176}\text{Hf} (+82)/^{175}\text{Lu}$ ratio. Presented data is from an analysis of MKED calcite.

A side effect of the use of large ablation spots is ‘plasma loading’ for which the introduction of a large amount of material reduces the ionizing efficiency of the plasma (Kroslakova and Günther, 2007). Plasma loading was observed in the time resolved signals, with a reduction in signal intensity for all isotopes after ~10 to 15 seconds of ablation. Following this, the signal stabilized after ~18 seconds of ablation (Fig. 2.2). Importantly, this variation in signal intensity was not observed in the calculated time resolved isotope ratios (Fig. 2.2), which means that identical ratios were calculated whether this decrease in signal intensity was included or not in the ratio calculation. Importantly, plasma loading can be affected by sample matrix (Kroslakova and Günther, 2007), especially for minerals containing easily ionized elements such as Ca. This necessitates matrix matched calibration, despite the observed lack of down-hole changes in Lu–Hf ratios (Simpson et al., 2021a).

The large ablation volume caused accumulation of ablated material in the tubing and on the interface cones during the first analytical session, which coincided with a decrease in signal intensity over time. Consequently, session 1 records slightly more signal drift compared to session 2. However, there was no measureable corresponding drift observed in the calculated isotopic ratios, apart from a slight decrease in precision due to the lower sensitivity toward the end of the run. Therefore, we recommend that cones are cleaned prior to analysis, and suggest a maximum session duration of approximately 7 hours when using spot diameters of >200 μm . In addition to this, the accumulated material was sometimes mobilized in later analyses, potentially contaminating data. This was observed by increases in Al during the start of ablation that decayed down to background levels. Importantly, similar Al spikes were not observed during background measurement, indicating contamination due to material remobilized during ablation is likely, hence why the additional 20 seconds of washout did not fix this. This contamination did not generally produce a measurable effect on calculated Lu/Hf ratios. However, we stress that this contamination is important to monitor as Hf concentrations are sometimes in the ppt level. As such we recommend close monitoring of signals, particularly Al concentrations, and the removal of 1-3 seconds of each analysis after signal stabilisation if necessary.

2.4.2. Data Processing

For both LA-ICP-MS and LA-ICP-MS/MS analysis, a stoichiometric Ca concentration of 40.04 wt.% for calcite was used for internal normalization of trace element concentrations. Although the high Ca cps for all analysed samples indicate that they are close to stoichiometric calcite, there may be slight

inaccuracies in calculated element concentrations due to major element substitutions from Mg, Fe, and Mn that are common in carbonates. However, element concentrations were largely used as relative proxies to monitor for inclusions.

Background subtractions, element concentrations and ratio calculations were performed using LADR software (Norris and Danyushevsky, 2018). Where ^{178}Hf was measured above detection limits (~ 2 ppt for ^{178}Hf), common Hf corrections were applied to the data after background subtractions, but prior to normalization to the standard. In more detail, the ^{178}Hf cps measurement for each sampling cycle of the analysis period of each laser spot was used to calculate the common Hf component of the corresponding ^{176}Hf cps measurement, using the following equation:

$$^{176}\text{Hf}_r = ^{176}\text{Hf}_m - \left(\left(\frac{^{176}\text{Hf}}{^{178}\text{Hf}} \right) c \times ^{178}\text{Hf}_m \right)$$

Where $^{176}\text{Hf}_r$ = radiogenic ^{176}Hf , $^{176}\text{Hf}_m$ = measured ^{176}Hf , $^{178}\text{Hf}_m$ = the measured ^{178}Hf and $\left(\frac{^{176}\text{Hf}}{^{178}\text{Hf}} \right) c$ = the initial or ‘common’ $^{176}\text{Hf}/^{178}\text{Hf}$ ratio. These corrections were applied using an assumed initial $^{176}\text{Hf}/^{178}\text{Hf}$ ratio of 0.192 ± 0.004 , which is equivalent to a $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.2816 ± 0.006 . This value is based on the Hf evolution of the crust, with uncertainty that comfortably covers likely natural variation. The uncertainty on the initial $^{176}\text{Hf}/^{178}\text{Hf}$ ratio used for the common Hf corrections has been propagated to the final ages, in order to account for any inaccuracies introduced by value used. However, as most analyses have $<1\%$ common Hf (Table 2.1), any inaccuracy related to the initial $^{176}\text{Hf}/^{178}\text{Hf}$ ratio is negligible compared to the total uncertainty estimates given Hf isotopes do not vary significantly with time (Fisher and Vervoort, 2018; Vervoort, 2014). Such corrections, however, should be used with caution for samples with higher common Hf, although the dataset presented in this study is not sufficient to determine what an appropriate cutoff should be.

Subsequent to this correction, isotopic ratios were corrected using an external reference material bracketing approach (commonly used in LA-ICP-MS geochronology), with primary and secondary reference materials interspaced with unknowns through each analytical session. The data was normalized to NIST SRM 610 glass to correct for drift and matrix independent fractionation. The Lu–Hf isotopic ratios published in Nebel et al. (2009) were used for the NIST610 SRM normalisation. Following this, $^{176}\text{Hf}/^{176}\text{Lu}$, $^{176}\text{Lu}/^{177}\text{Hf}$, and $^{176}\text{Lu}/^{176}\text{Hf}$ ratios were corrected to MKED calcite. Although the age of MKED calcite is currently not independently constrained, calcite is interpreted from textural evidence to have formed with the MKED titanite reference material, and therefore the titanite TIMS U–Pb age was used (1517.32 ± 0.32 Ma; Spandler et al., 2016). Further details are outlined in appendix A. This correction method is similar to that used by Roberts et al. (2017) for calcite U–Pb, where the

observed analytical offset between the measured and expected Lu–Hf ratio in the standard is applied (as a % correction factor) to the ratios of the unknowns. This offset is inferred to be due to a combination of laser induced (matrix-dependent) elemental fractionation and plasma loading. The uncorrected ages for MKED calcite as well as for ME 1 across four analytical sessions are constant within uncertainty, indicating the age offset is a systematic analytical bias that is applicable to the calcite samples of unknown age (Sup. Fig. 2.3). Weighted average ages were calculated using ISOPLOT (Vermeesch, 2018), using the ^{176}Lu decay constant determined by Söderlund et al. (2004); $0.00001867 \pm 0.00000008 \text{ Myr}^{-1}$

Correct handling of uncertainties in geochronology is important in order to draw accurate conclusions about the resulting ages. As per the recommendations for LA-ICP-MS U–Pb uncertainty propagation in Horstwood et al. (2016), uncertainties are categorised as random, in which case they are propagated to individual analyses, or systematic, in which case they are propagated to the final calculated age. As such, the uncertainties associated with the measurement of the primary standard (NIST SRM 610) have been propagated to the uncertainties of individual analyses. The following systematic uncertainties have been propagated to the final ages: Measurement uncertainty on the secondary standard (MKED C), uncertainty on the titanite U–Pb age used as the reference age for MKED C, uncertainties associated with the ^{176}Lu decay constant, the reference $^{176}\text{Hf}/^{177}\text{Hf}$ ratios for NIST SRM 610. Although for completeness it would be good to propagate uncertainty relating to potential differences in $^{175}\text{Lu}/^{176}\text{Lu}$ and $^{177}\text{Hf}/^{178}\text{Hf}$ between NIST SRM 610 and samples (i.e. natural variation in these ratios), currently there appears to be no data on this. These uncertainties are likely to be negligibly small relative to the overall uncertainty estimates for the analyses. The uncertainty associated with the reference $^{176}\text{Lu}/^{177}\text{Hf}$, $^{176}\text{Lu}/^{176}\text{Hf}$, and $^{176}\text{Hf}/^{176}\text{Lu}$ ratios of NIST SRM 610 are not propagated, as the correction factor associated with NIST610 SRM is cancelled during the correction to MKED calcite (as the NIST610 SRM correction factor is applied equally to MKED calcite and the unknowns samples, and thus becomes redundant). Uncertainty relating to long term reproducibility of the standards has not been propagated, as the standard data for all sessions does not show scatter outside of what would be expected from a single population. More data, however, is required to fully constrain this.

2.5. Lu–Hf Results

The analysed calcite generally contain < 1% common Hf, apart from sample P01, which contains up to 13% common Hf in individual analyses (Table 2.1). Consequently, the common Hf corrections are small (or effectively non-existent), and the resultant ages are not significantly affected by the assumed initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio. Corrected and uncorrected data are included in Supplementary data file 2.1. The

inverse isochron and weighted mean single-spot Lu–Hf ages, reported below, are corrected against MKED calcite for matrix-dependant fractionation and common-Hf corrected (where relevant) (Fig. 2.3). For analyses with inclusions, the signals have been cropped to remove inclusions or, in the case of more significant signal disturbances, excluded from age calculations. Inclusions were detected in the following samples: MKED calcite (6), LC1 (1), P01 (19) and FF014 (6). Excluded data points are included in supplementary data file 2.1. Due to the large number of inclusions, P01 was analysed over two sessions. Data is presented as inverse isochrons (Li and Vermeesch, 2021), and as common Hf corrected weighted average ages (Fig. 2.3).

TABLE 2.1: AGES AND LU AND HF CONCENTRATION INFORMATION FOR THE ANALYSED SAMPLES.

Sample	Age	95%	n	Min.	Av %	Max.	Min	Av	Max	Min	av Hf*	Max
	(Ma)	CI		% Hf	Hf	% Hf	Lu	Lu	Lu	Hf*	ppb	Hf
				corr	corr	corr	ppm	ppb	ppb	ppb		ppb
P01	2054	1.5%	36	0%	2.65%	13%	270	505	557	0.03	0.270	1.00
LC 1	1513	1.7%	19	0.16%	0.46%	1.25%	1900	1600	3600	0.011	0.090	0.360
ME 1	1540	0.6%	79	0%	0.28%	2.4%	4300	5325	6300	0.002	0.150	1.80
ME 2	1500	0.9%	29	0.16%	0.58%	3.04%	700	3159	5500	0.002	0.110	0.340
OL-MB	892	1.2%	30	0.16%	0.58%	1.25%	1100	1200	1300	0.003	0.050	0.120
FF014	1807	1.0%	35	0.16%	0.39%	1.3%	616	1020	1170	0.004	0.052	0.210

Note: 95% CI refers to the 95% confidence interval uncertainty on the calculated age. n refers to the number of analyses used for the age calculation. % Hf corr refers to the average % decrease in age due to the common Hf correction. Hf* concentrations have been calculated from ^{178}Hf and assume no radiogenic ingrowth of ^{176}Hf and thus represent the ‘common’ Hf concentration for each sample.

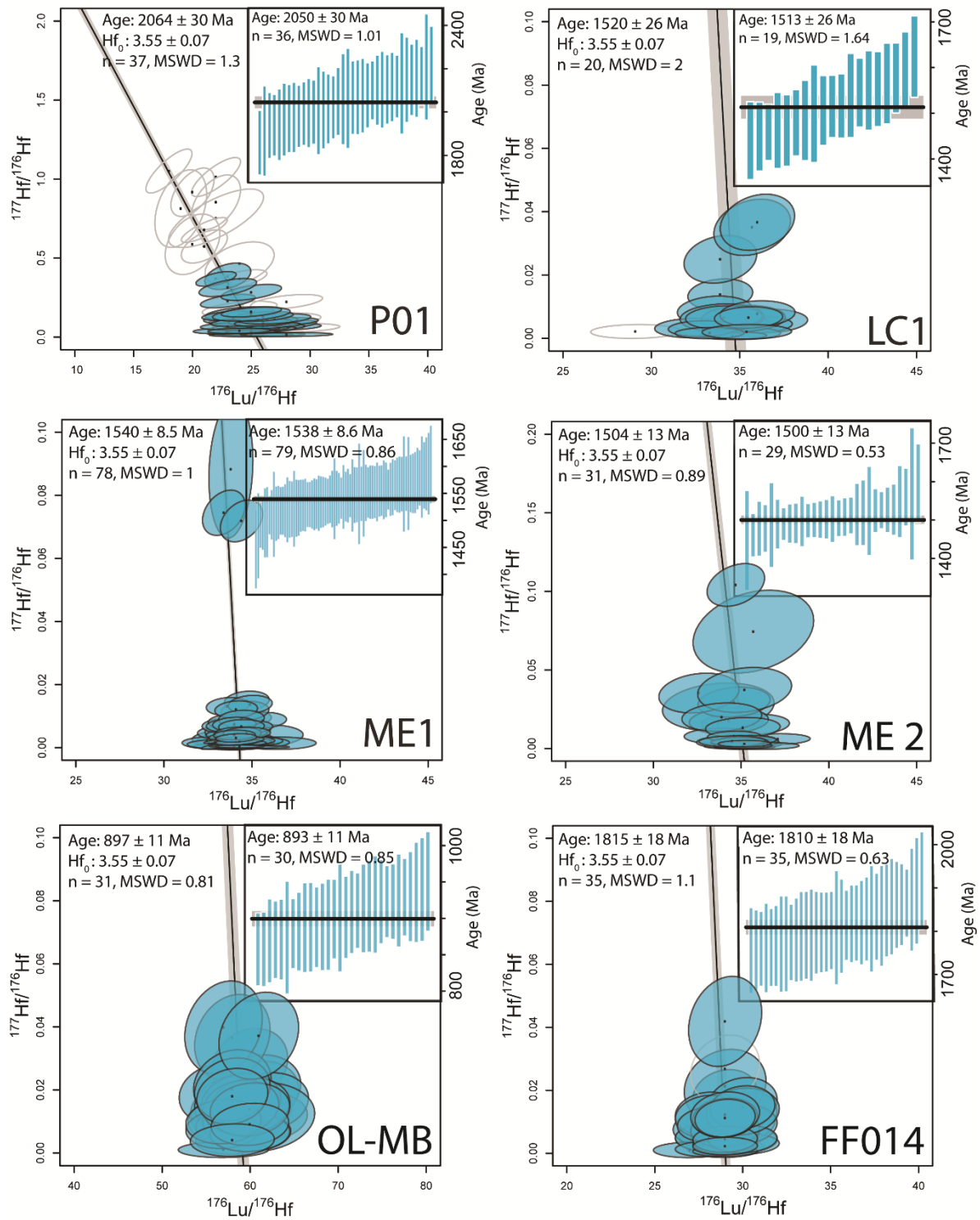


Figure 2.3: Anchored inverse isochron and weighted average 'single spot' ages for analysed samples, corrected for matrix-induced fractionation against MKED1 calcite. Isochrons have been anchored to an initial $^{177}\text{Hf}/^{176}\text{Hf}$ ratio of 3.55 ± 0.07 . Ellipses represent data points and 2σ uncertainty. Weighted average ages are corrected for common-Hf where relevant (see Table 2.1 and text). Blue bars represent 2σ uncertainties. Black lines represent weighted average ages, with grey boxes representing the 95% confidence interval uncertainty.

2.6. Discussion

The Phalaborwa carbonatite sample produced a Hf corrected weighted average Lu-Hf age of 2050 ± 30 Ma (Fig. 2.3), consistent with previous baddeleyite U-Pb SIMS ages (~ 2060 Ma; Wu et al., 2011). Importantly, the consistency between the calcite Lu-Hf age and existing constraints on carbonatite formation demonstrates that calcite Lu-Hf dating can produce primary age information for early Paleoproterozoic calcite. This result also demonstrates that calcite Lu-Hf geochronology is a viable technique to directly date carbonatite magmatism and associated mineralisation, even in the case of old calcite samples with only ~ 0.5 ppm Lu.

The weighted average Lu-Hf ages for samples ME 1 and ME 2 are 1538 ± 9 Ma and 1504 ± 13 Ma, respectively (Fig. 2.3). The ages of these samples are consistent with the paragenetic timing of alteration at Mt Elliott, providing evidence for calcite precipitation during at least two temporally distinct alteration events. Sample ME 1 is from a coarse calcite-diopside-scapolite-magnetite vein that does not contain sulfides (Fig. 2.1), the age is, therefore, consistent with formation prior to the major ~ 1510 Ma Cu-Au mineralisation event (Duncan et al., 2011; Wang and Williams, 2001). In addition, this age overlaps with a titanite U-Pb age from the Mt Elliott deposit (1530 ± 11 Ma; Duncan et al., 2011), and is potentially related to regional Na-Ca alteration between ca. 1555 and ca. 1521 Ma (Oliver et al., 2004). The 1504 ± 13 Ma age obtained from sample ME 2 that has an ore stage paragenesis conforms with the $^{207}\text{Pb}/^{206}\text{Pb}$ age of cogenetic andradite (1507 ± 35 Ma; appendix B), and overlaps with the ca. 1510 Ma main mineralisation event (Duncan et al., 2011; Wang and Williams, 2001). Additionally, data for ME1 was pooled from all four analytical sessions in order to test reproducibility. Similar to the standard (MKED1; appendix A), ME1 does not show excess scatter between sessions (fig. 2.3).

Sample LC1, from the Lime Creek quarry, Eastern Fold Belt, Mt Isa Inlier produced an age of 1513 ± 26 Ma, consistent with published titanite U-Pb ages (1521 ± 5 Ma 1527 ± 7 Ma) from the nearby Knobby Quarry (Oliver et al., 2004). Additionally, this age is consistent with the intrusion of the ca. 1530-1500 Ma Williams-Naraku batholiths, which is interpreted to be the source of the fluids from which the calcite precipitated (Oliver et al., 1993; Page and Sun, 1998). Our results for this sample further demonstrate that calcite Lu-Hf geochronology is an effective technique for constraining the age of calcite mineralisation.

Sample OL-MB from Otter Lake produced a Lu-Hf age of 892 ± 12 Ma (Fig. 2.3). This age is significantly younger than the apatite solution Lu-Hf age of 1030 ± 6 Ma (Barfod et al., 2005) and the *in-situ* apatite

Lu-Hf age of 1000 ± 11 Ma (Simpson et al. 2021), but is similar to the apatite Pb-Pb age of 913 ± 7 Ma (Barfod et al. 2005) and the latest stage of extensional activity on the nearby Bancroft Shear Zone (1045 - 893 Ma, Ar-Ar phlogopite; Cosca et al., 1995). Given the similarity between the ca. 0.9 Ga ages, obtained by different methods, it seems likely that the calcite either grew or records Lu-Hf isotopic resetting during the same event that induced resetting of the apatite Pb-Pb system. The slight difference between the calcite Lu-Hf age (894 ± 12 Ma) and apatite Pb-Pb age (913 ± 7 Ma) may be due to analytical (i.e. mixing of age domains in the solution Pb-Pb age) rather than geological reasons, particularly given an individual crystal of apatite from the Yates mine produced a U-Pb age range of 920-850 Ma (Xiang et al., 2021). The age difference may also be due to underestimation of uncertainties. Large (~3cm) apatite crystals such as the one analysed by Barfod et al. (2005) are expected to have Pb closure temperatures of up to 600 °C (Barfod et al., 2005; Krogstad and Walker, 1994), giving a possible upper limit to Lu-Hf closure in calcite. We note that this is significantly higher than the closure temperature of Ar-Ar in phlogopite (ca. 400 °C), indicating that the Otter Lake area potentially had a different thermal history and/or that isotopic resetting in the apatite and calcite was aided by late fluid interactions, as hypothesised by (Barfod et al., 2005). As such, further work is required to constrain the Lu-Hf closure temperature in calcite.

The *in-situ* Lu-Hf age of 1810 ± 18 Ma for the cleavage-hosted calcite vein from the Flin Flon VMS deposit (FF14; Fig. 2.3), as expected, is younger than the timing of initial mineralisation at the deposit (Koo and Mossman, 1975; Rayner, 2010; Stern et al., 1995). Instead, the age is in excellent agreement with ca. 1820-1790 Ma regional peak greenschist to amphibolite grade metamorphism (Schneider et al., 2007), suggesting the calcite precipitated during metamorphism related to deformation stage 'D₅' or 'D₆', associated with the final collision between the Flin Flon-Glennie Complex and the Sask Craton (Lafrance et al., 2016). This regional event locally reached maximum greenschist-facies metamorphism (Koo and Mossman, 1975), suggesting the calcite grew under low-grade metamorphic conditions. Sample FF014, therefore, demonstrates that calcite Lu-Hf geochronology has the potential to date low grade metamorphism, which has been difficult using traditional dating methods (e.g. Henrichs et al., 2018).

In summary, we demonstrate that *in-situ* Lu-Hf geochronology can produce geologically meaningful ages for calcite from a variety of mineralisation styles (e.g. IOCG, carbonatite, and skarn alteration) as well as greenschist-facies metamorphism. The technique also has great potential to date a range of other geological settings and processes (e.g., chemical sedimentation, carbonation reactions) provided calcite contains sufficient Lu for analysis.

2.6.1. Limitations

The success rate of the *in-situ* Lu–Hf dating approach in calcite is intrinsically related to; (1) the concentration of Lu, and; (2) the ingrowth time for radiogenic Hf (Fig. 2.4). Generally, the method is more suitable for REE-rich calcite typically observed in mineral deposits and carbonatites, and/or for Precambrian samples. In addition, the currently available mass-spectrometers require large laser beam diameters (257 μm) for successful calcite Lu–Hf dating, limiting spatial resolution compared to most laser-ablation dating techniques. We note that for high Lu samples, such as ME 1 (or samples that incorporate common Hf), smaller spot sizes are feasible. Additionally, particularly in hydrothermal settings, calcite often forms large, mm to cm scale crystals, reducing the need for small ablation volumes. While individual calcite crystals in other settings can sometimes be $< 260 \mu\text{m}$, the total amount of calcite is often large enough that aggregates of pure (or close to pure) calcite can be ablated. Caution should be used with such analysis however, as this may affect laser induced fractionation, individual crystals may be of different ages, and there may be micro inclusions of other minerals.

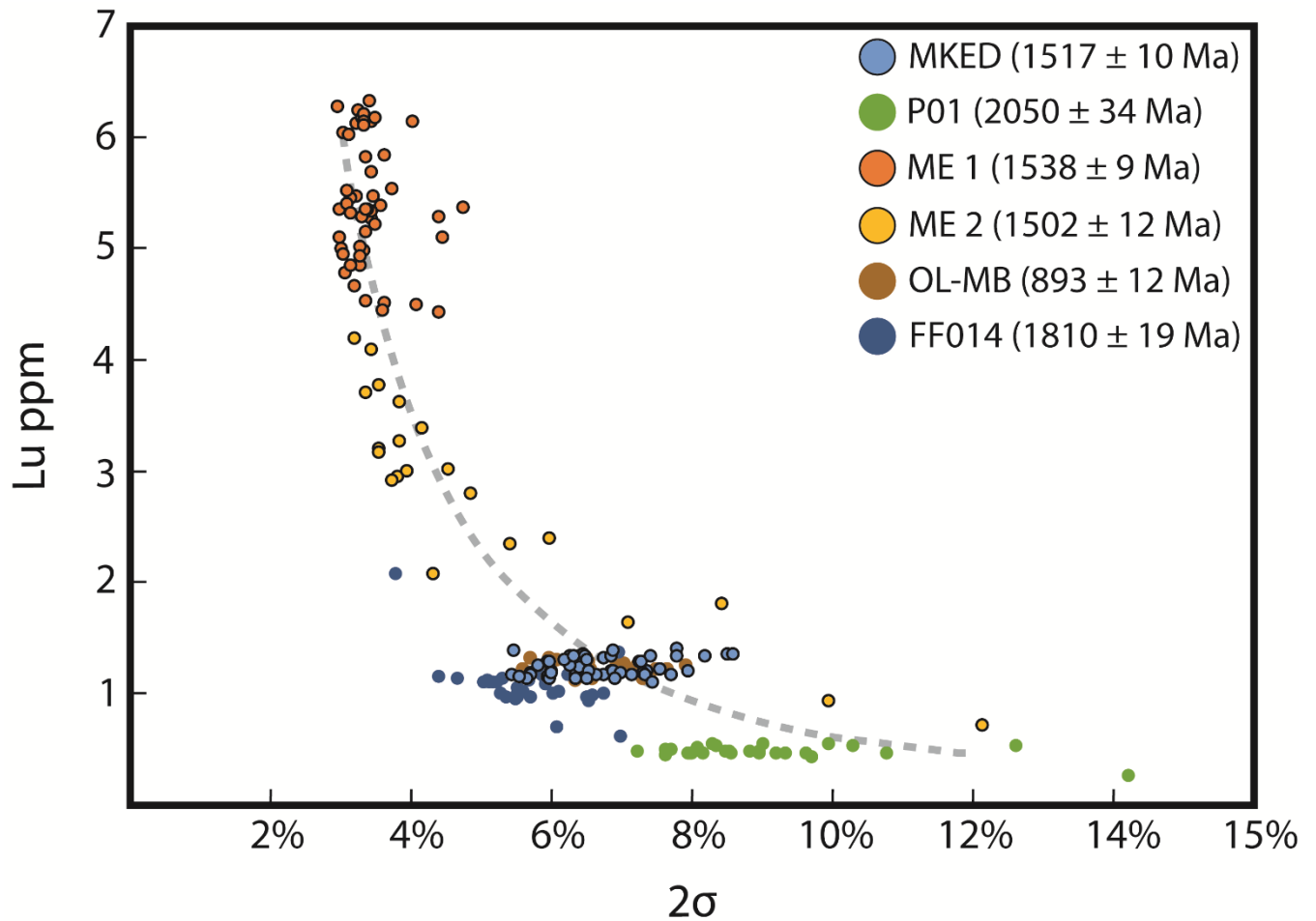


Figure 2.4: Lu ppm vs 2σ uncertainty for each calcite analysis. The grey curve shows a function fitted to the data from samples with ages between 1500 and 1540 Ma (samples ME1, ME2, and MKED, with symbols outlined in

black). Only data points with similar ages were used to construct this guiding curve as the obtained precision is age-dependant. The Lu-Hf ages for older samples (e.g. P01 and FF014) are more precise relative to younger samples for a given Lu concentration (assuming no common Hf). Note: MKED is the calcite Lu-Hf standard used to correct the analysed samples. All data for MKED is included in supplementary data file 2.1.

2.6.2. Advantages of in-situ Lu-Hf dating of calcite compared to other geochronological methods

The Previous dissolution-based Lu-Hf geochronology has produced scattered isochrons, indicative of isotopic disturbances (Maas et al., 2022). While individual data points are significantly less precise than dissolution based methods, the ability to gain spatially resolved data on a much smaller scale (>260 microns), as well as obtain a large number of analyses in a single session can make data interpretation easier (Simpson et al., 2021a). Importantly, trace element data can be obtained simultaneously to interrogate each data point for inclusions or age zonation. Furthermore, calcite Lu-Hf dating can overcome two issues often encountered during U-Pb dating; (1) in contrast to Pb, calcite does not incorporate significant concentrations of common Hf, and; (2) Lu is comparatively resistant to thermal diffusion in calcite (Cherniak, 1997), increasing the likelihood of primary precipitation ages to be preserved. Although it should be acknowledged that fluid mobility and re-crystallisation of the calcite may affect Lu-Hf ages, and are difficult to predict. This opens the possibility that time constraints can be obtained for carbonates from the first three-quarters of Earth history that are generally difficult to date by other methods. Importantly, calcite is commonly associated with ore formation, meaning *in-situ* Lu-Hf dating affords the possibility to directly constrain the age of mineralising events and the temporal evolution of mineral deposit systems.

From our work, we suggest samples ME1 and OL-MB calcite could be developed as primary reference materials due to being (1) common-Hf free, (2) homogenous in age across crystals up ~1cm in size, and (3) available in large quantities. We aim to characterize such reference materials and make them available to the wider geochronology community.

2.7. Conclusions and Future Directions

Calcite is among the most common of rock-forming minerals, meaning that *in-situ* Lu-Hf geochronology of calcite has enormous potential to constrain the age of formation and/or alteration of a range of igneous, sedimentary, metamorphic, and hydrothermal rock systems, including rock-types that are considered very difficult to date (e.g., marbles). This technique has particular application to mineral deposits as it allows for the ability to constrain the age of pre-ore, ore-stage and post-ore events (e.g., Fig. 2.3). Furthermore, given the successful dating of old (~2 Ga) calcite with <1 ppm Lu (e.g., sample P01; Table 2.1), this technique has the potential to date old calcite from a variety of settings with relatively low HREE concentrations. *In-situ* Lu-Hf dating of calcite can be regarded as a

complimentary, and in some cases alternative, technique to carbonate U–Pb dating, where Lu–Hf dating is well suited for older samples, or to obtain primary precipitation ages for systems affected by Pb mobility. Coupling *in-situ* Lu–Hf dating with other isotopic systems (U–Th–Pb, C, O, Sr, Nd) may be particularly powerful for constraining the origin, nature and redox conditions of the fluids or melts from which the calcite precipitated.

Author contributions

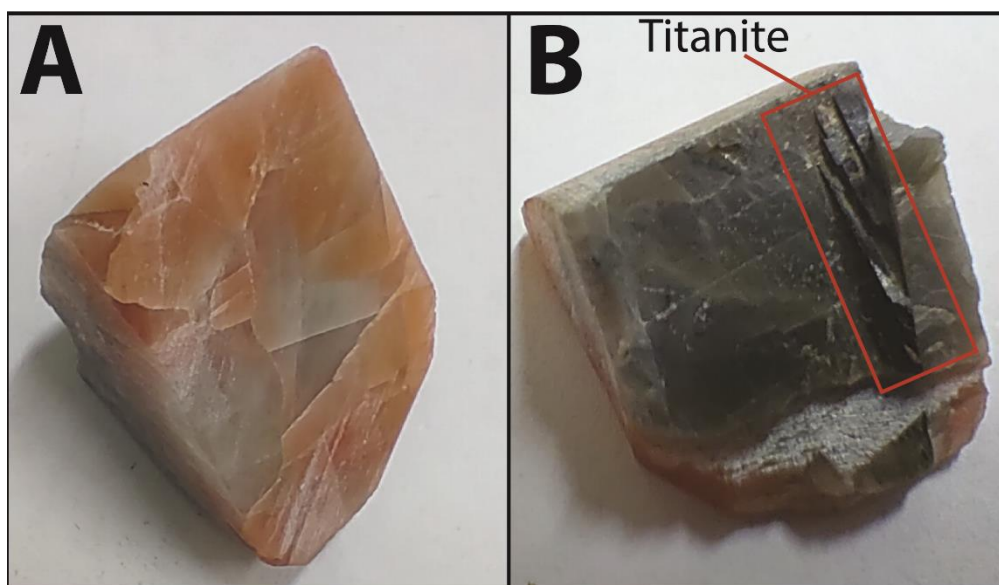
Author contributions: A Simpson (corresponding author): conceptualisation, method development, experimentation, manuscript drafting. S Glorie: conceptualisation, manuscript drafting, primary supervision. M Hand: conceptualisation, manuscript drafting, secondary supervision. C Spandler: Conceptualisation, sampling, manuscript drafting. S Gilbert: Method development, experimentation, manuscript drafting. B Cave. Experimentation, manuscript drafting.

Acknowledgments

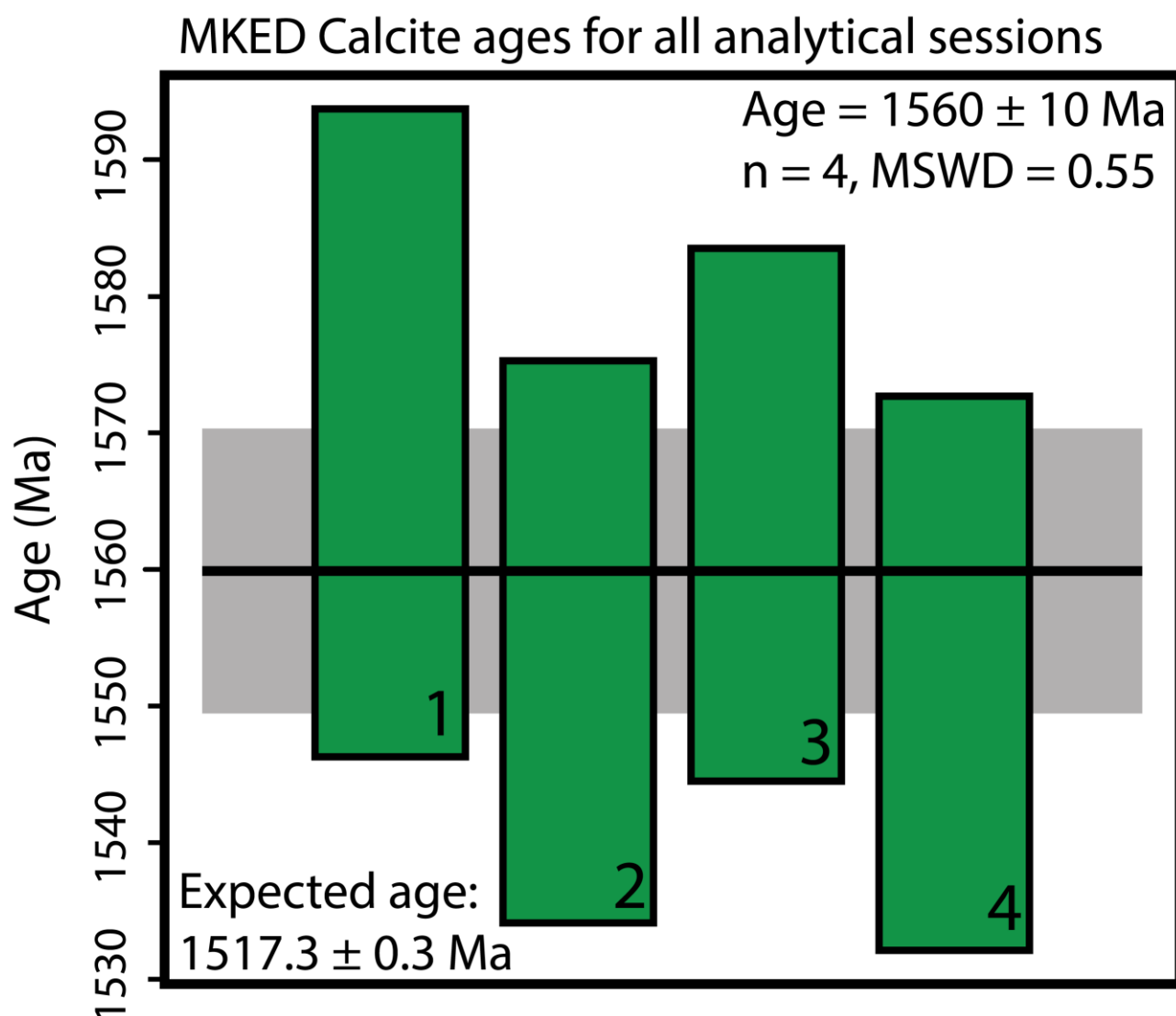
The authors would like to thank the MinEx CRC for funding this research. The initial method development and apatite dating were supported by the Australian Research Council DP200101881. Dr Morgan Blades is thanked for supplying a sample of Otter Lake calcite. Dr Anthony Milnes from the Tate Museum at the University of Adelaide is acknowledged for help during sampling and Aoife McFadden is acknowledged for assistance in operating the SEM at Adelaide Microscopy. Dr Nick Roberts and associate professor Donald Davis are thanked for constructive comments during review.

2.8. Chapter 2 appendix A: MKED calcite sample description

A sample of orange-pink calcite associated with the MKED1 titanite U-Pb standard (1517.3 ± 0.3 Ma, U-Pb TIMS; Spandler et al., 2016) was analysed as a matrix matched secondary standard in order to correct unknown samples for matrix related analytical offsets, such as laser induced elemental fractionation and plasma loading effects. The calcite was sampled from the same drill core from which the titanite standard was taken (full details can be found in Spandler et al., 2016). The sample consists of massive calcite surrounding large (~8cm) euhedral titanite crystals. The titanite is interpreted to have grown in the same fluid as the calcite, but just prior to calcite crystallization. The average age across all 4 analytic sessions is 1560 ± 10 Ma (App. Fig. 2.3), suggesting that matrix fractionation during laser ablation produces ages that are systematically approximately 3% too old



Appendix figure 2.1: images of MKED calcite. A shows calcite chip from where the analysed sample was taken. B shows underside of the same chip, where a large titanite crystal has been removed. Red box shows remnant fragments of titanite.

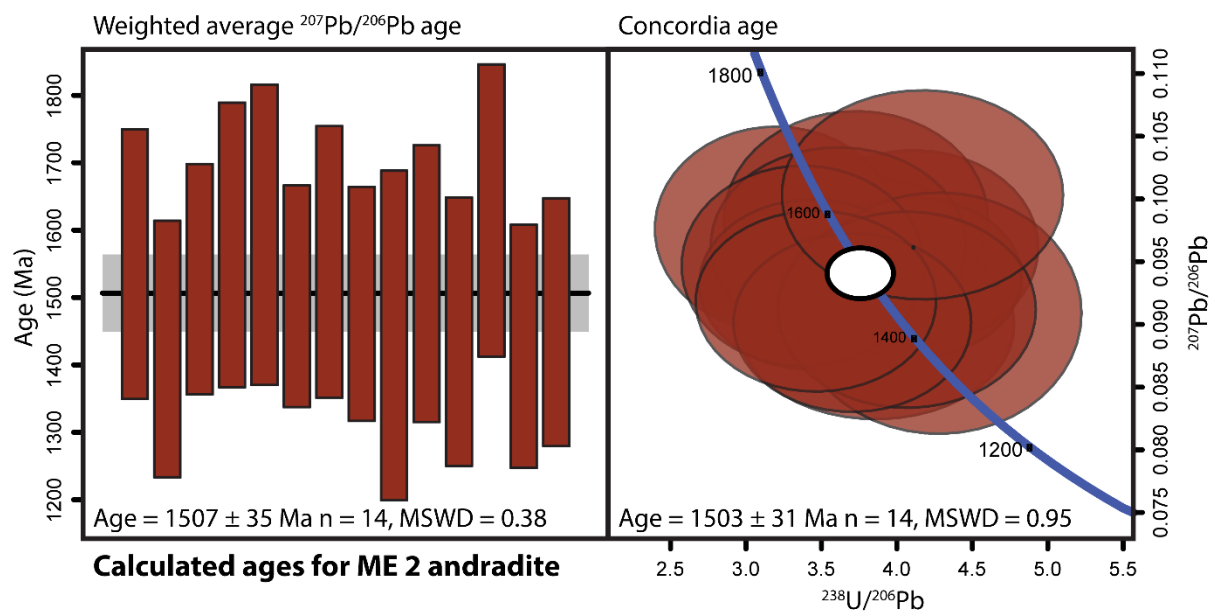


Appendix Figure 2.2: Demonstration of the systematic analytical offset observed for calcite Lu-Hf ages.

Green rectangles are 95% confidence intervals around weighted mean ages for each session, with session number in the bottom right corner of each rectangle. Horizontal black line shows the weighted average age of all analytical sessions, with grey rectangle showing 95% confidence interval uncertainty. The combined weighted average age for all analytical sessions is shown in the top right corner. The expected age is from Spandler et al. (2016). Weighted mean ages were calculated using ISOPLOT (Vermeesch, 2018).

2.9. Chapter 2 appendix B: Mt Elliott Andradite U-Pb data:

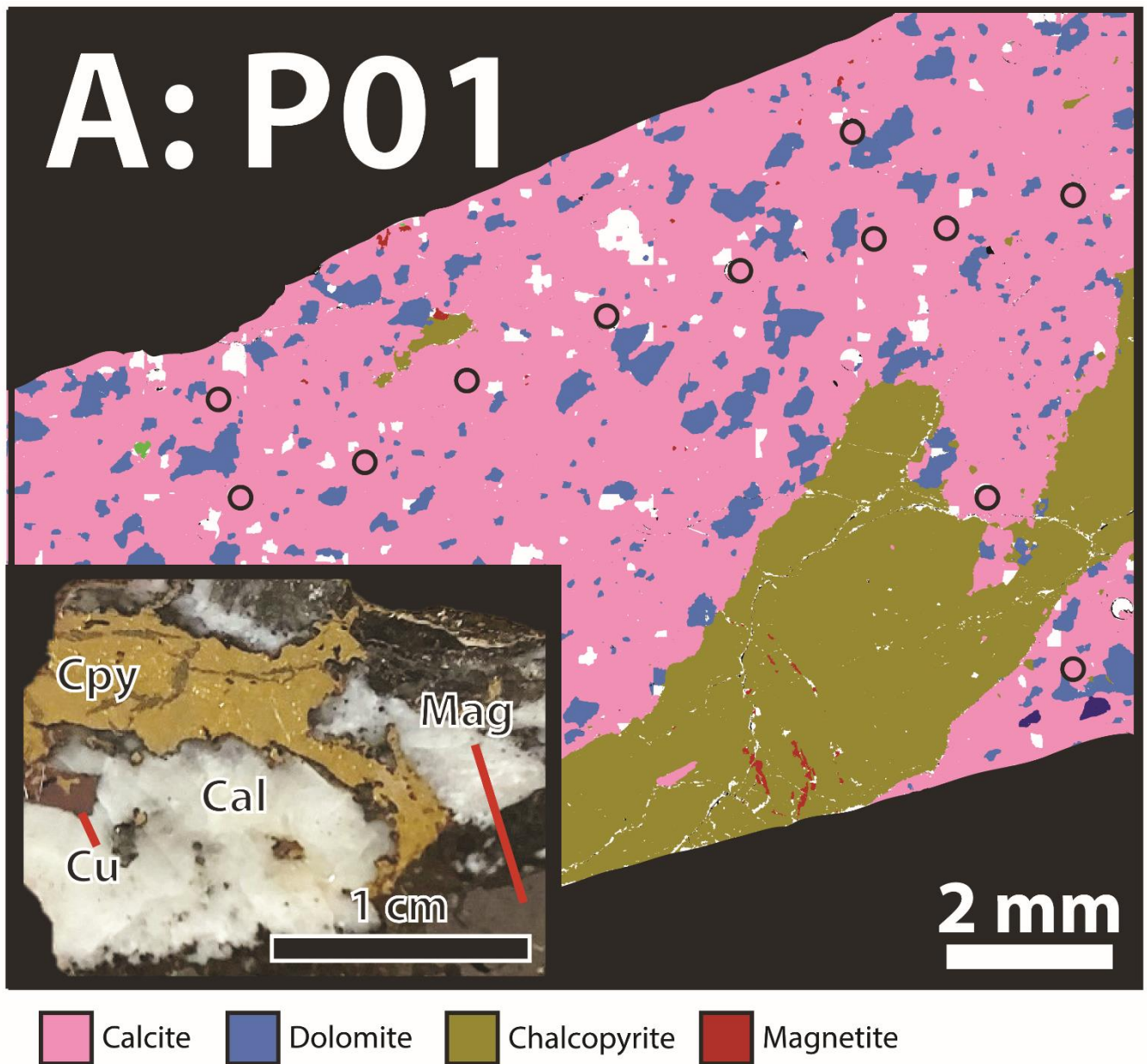
Cogenetic andradite was analysed from the Mt Elliott 2 calcite sample (App. Fig. 2.1). The sample was analysed using the same laser system as used for Lu-Hf analysis, but coupled with an Agilent 7900 quadrupole mass spectrometer. As the University of Adelaide does not currently possess an andradite U-Pb standard, U-Pb and Pb-Pb ratios were corrected to NIST610 SRM, using ratios from (Stern and Amelin, 2003). A large aspect ratio ablation spot (120 microns in diameter, drilling approximately 30 microns deep) was used to minimise the effects of downhole fractionation (Sylvester, 2008) however, it is possible that calculated U-Pb ages are inaccurate due to the lack of matrix matched primary standard. As the data appears to be concordant, however, a weighted average age can be calculated from the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios (App. Fig. 3), which should not be significantly affected by laser induced matrix fractionation. As such, the calculated age is considered accurate within uncertainty.



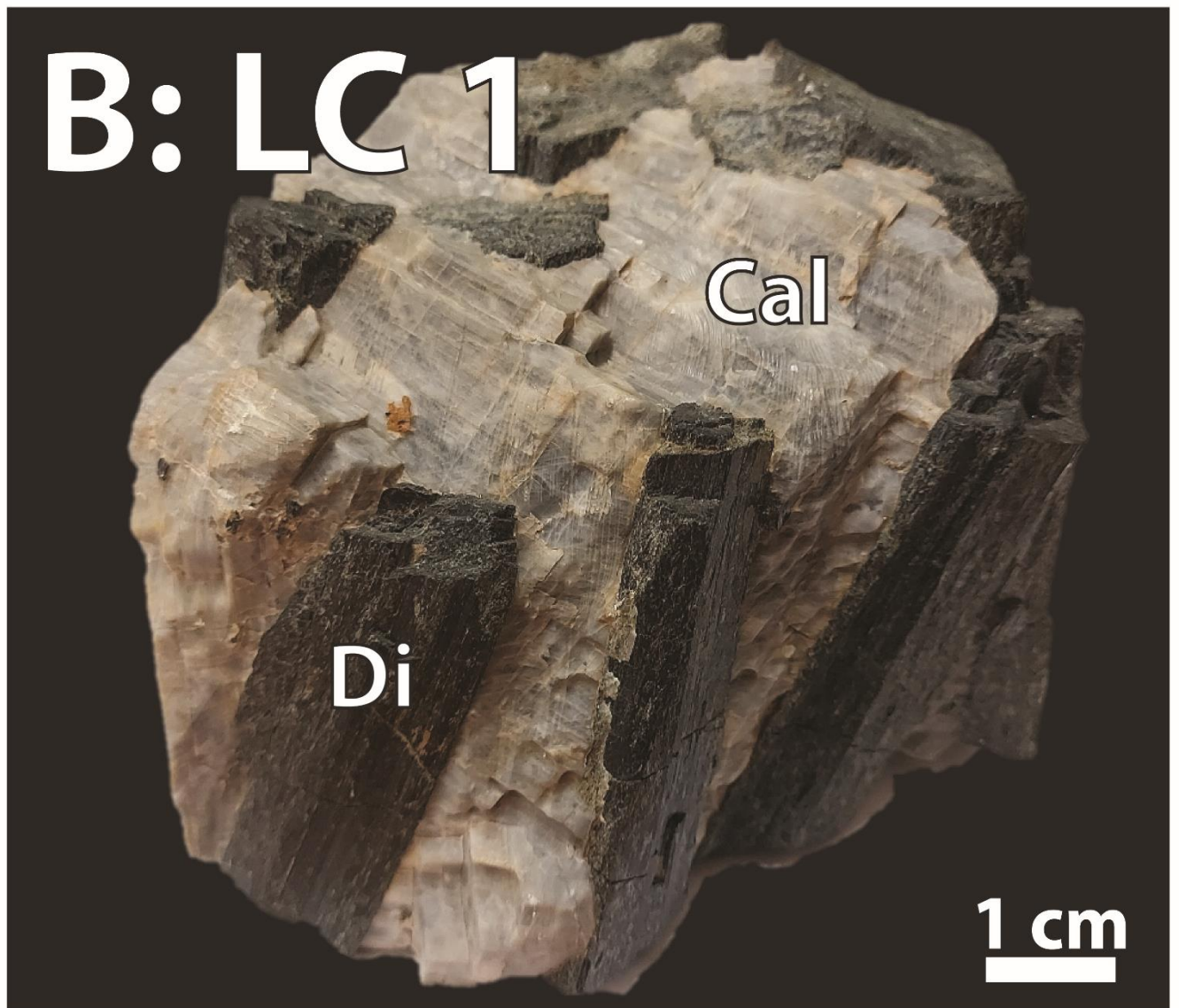
Appendix figure 2.3: U-Pb age of ME 2 andradite. Left panel shows the weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ age and the right panel shows the concordia age on a Tera-Wasserburg concordia plot. For the weighted average, vertical rectangles are 2σ uncertainties around calculated single spot ages, with the black bar showing calculated weighted mean age, and the grey rectangle showing associated 95% confidence interval uncertainty. For the concordia plot, each ellipse shows the 2σ uncertainty around each analysis, with white ellipse representing 95% confidence interval uncertainty around the calculated concordia age. Weighted mean age and concordia age were calculated using ISOPLOT (Vermeesch, P., 2018).

2.10. Chapter 2 appendix C: Large sample images

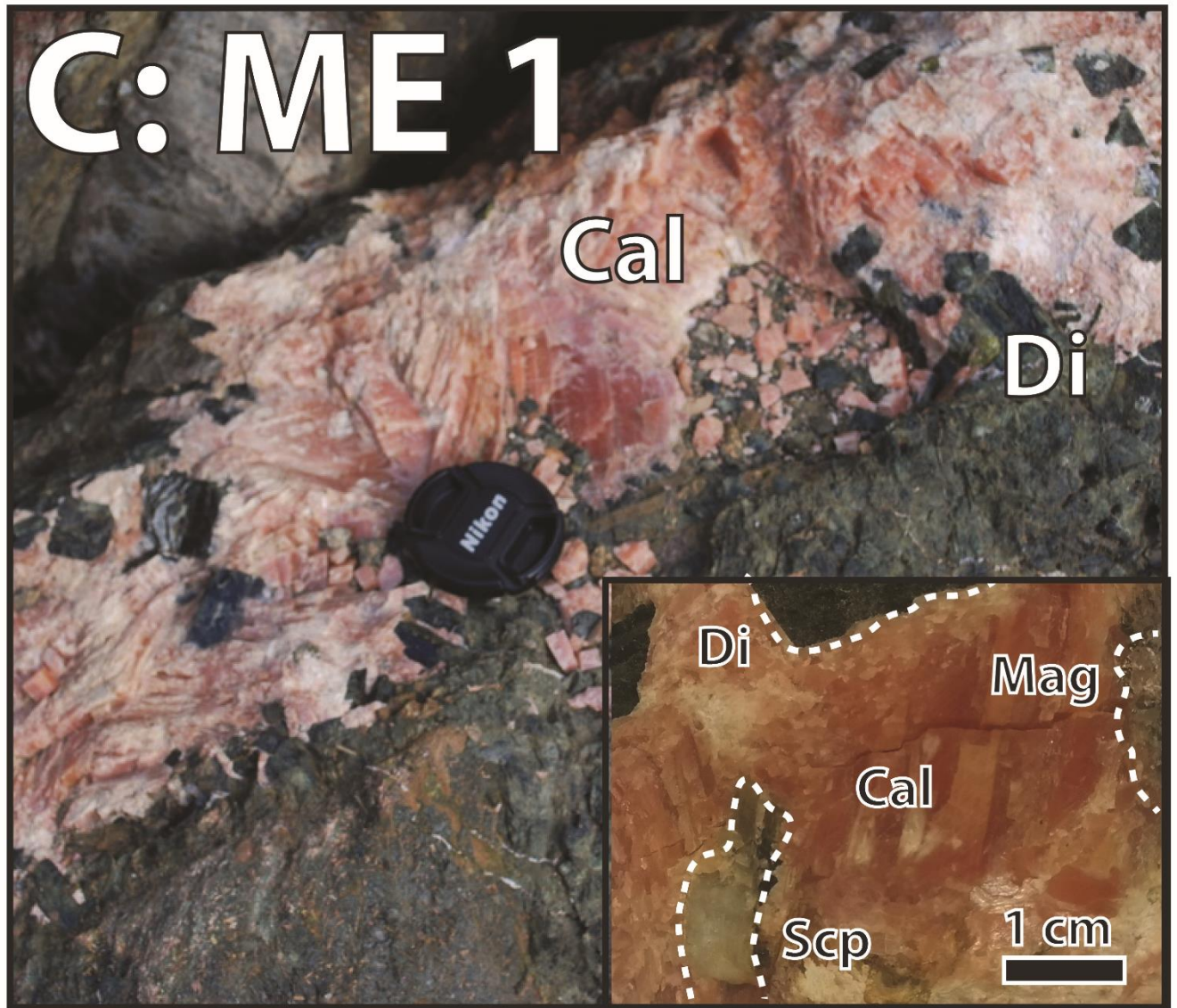
The following are larger versions of the sample images from figure 2.1. Mineral abbreviations are: Cal: Calcite, Cpy: chalcopyrite, Py: pyrite, Mag: magnetite, Cu: cubanite, Di: diopside, Scp: scapolite, An: andradite



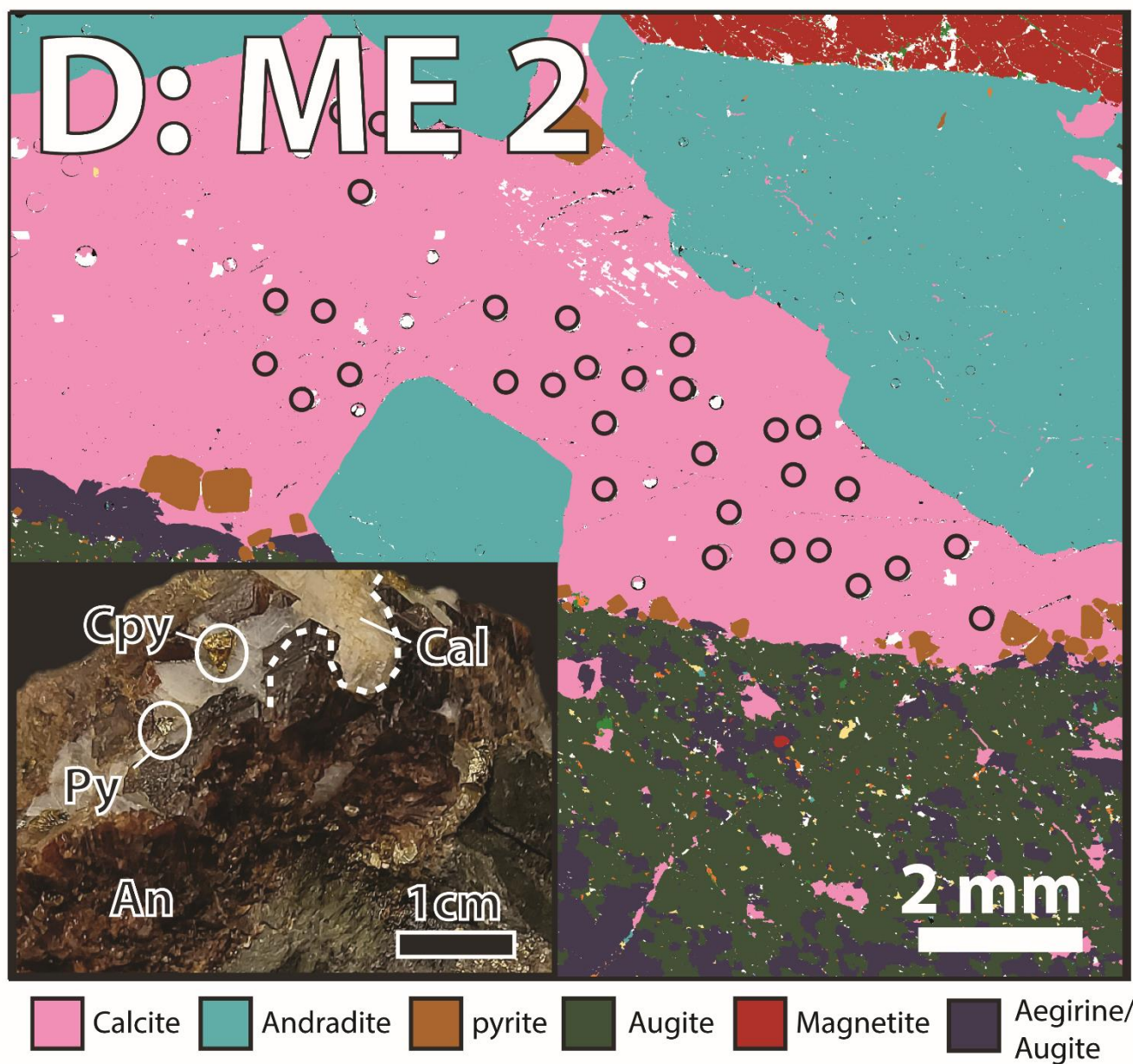
Appendix figure 2.1: Large image of sample P01 from Phalaborwa carbonatite, South Africa. Large image shows SEM mineral map. Inset shows hand sample photo. Cpy: Chalcopyrite, Cu: Cubanite, Cal: calcite, Mag: Magnetite.



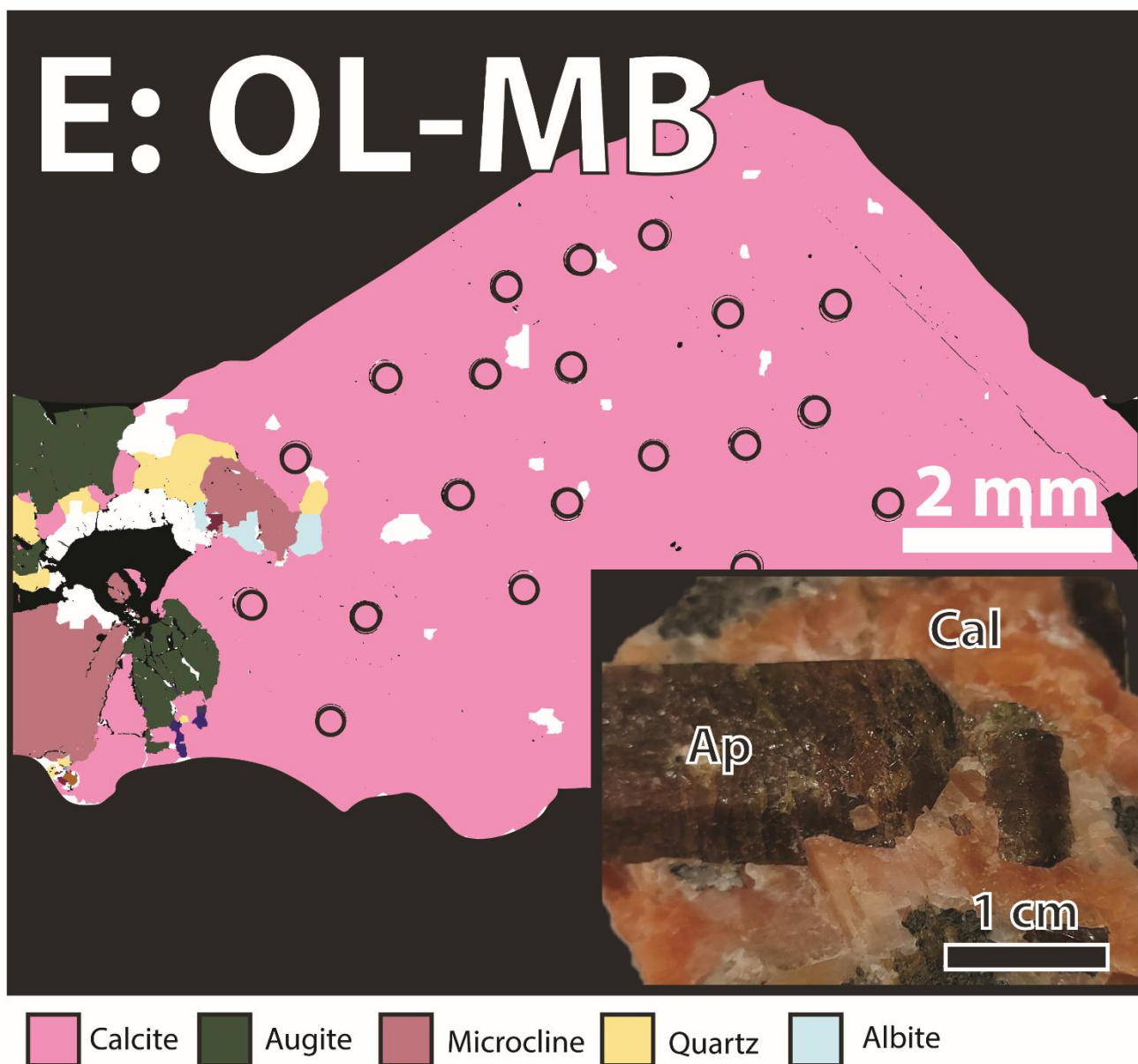
Appendix figure 2.2: Large image of sample LC1 from Lime Creek, Mt Isa region, Australia. Image shows hand sample. Di: diopside, Cal: calcite.



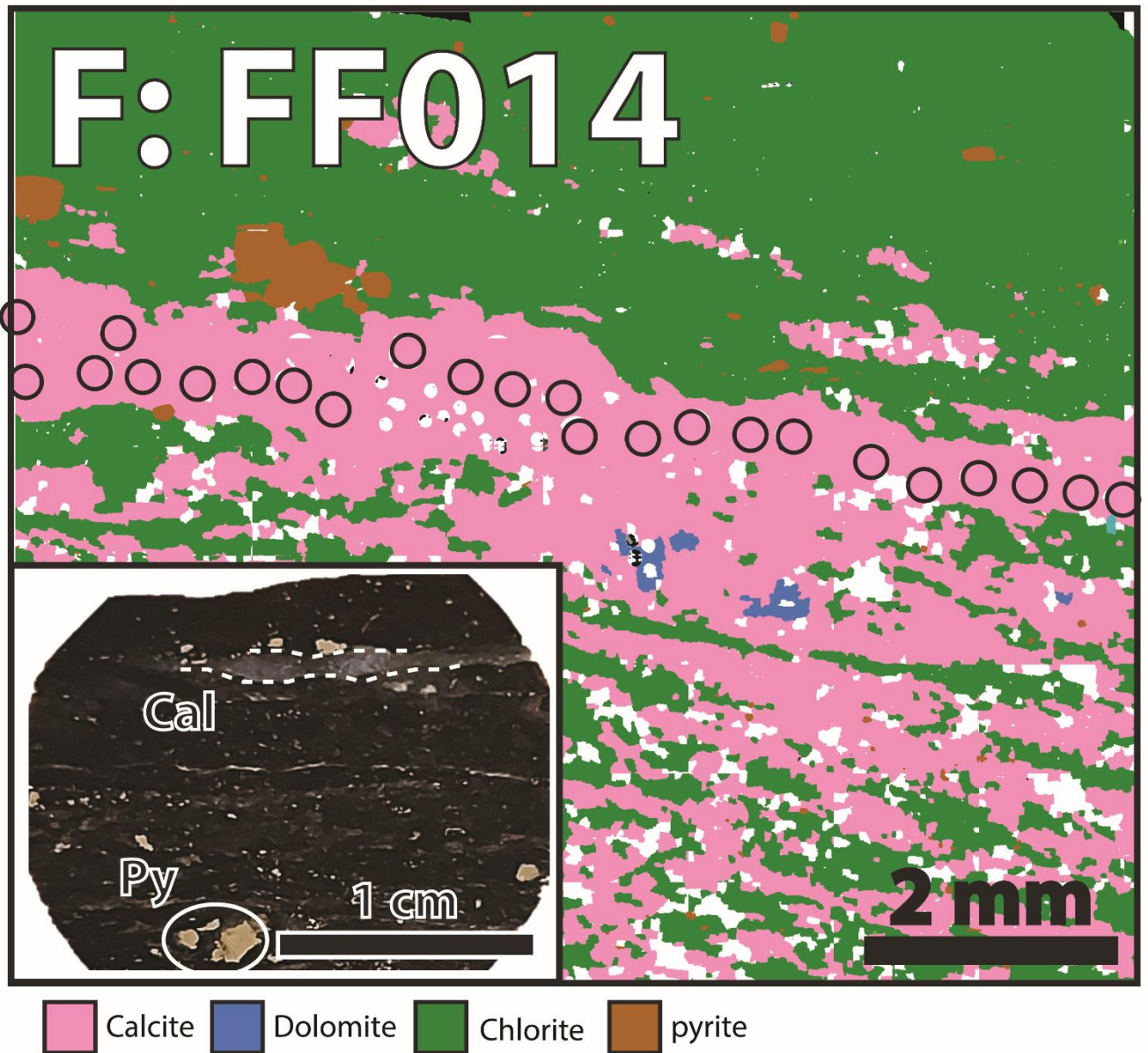
Appendix figure 2.3: Large image of sample ME1 from Mt Elliott, Mt Isa region, Australia. Large images shows sample location and inset shows hand sample. Di: diopside, Scp: scapolite, Cal: calcite, Mag: magnetite



Appendix figure 2.4: Large image of sample ME2 from Mt Elliott, Mt Isa region, Australia. Large images shows SEM mineral map with black circles showing laser spot locations. Inset shows hand sample photo. Cpy: Chalcopyrite, Py: pyrite, Cal: calcite, An: andradite.



Appendix figure 2.5: Large image of sample OL-MB from the Yates mine, Canada. Large images shows SEM mineral map with black circles showing laser spot locations. Inset shows hand sample photo. Ap: apatite, Cal: calcite.



Appendix figure 2.6: Large image of sample FF014 from Flin Flon, Manitoba and Saskatchewan, Canada. Large images shows SEM mineral map with black circles showing laser spot locations. Inset shows hand sample photo. Py: pyrite, Cal: calcite.

2.11. Chapter 2 appendix D: table of analytical parameters

Appendix table 1: analysis and LA-ICP-MS/MS tuning parameters

plasma parameters

<i>RF power</i>	1350 W
<i>Sample Depth</i>	4 mm
<i>Ar carrier gas</i>	0.94 L/min
<i>He carrier gas</i>	0.38 L/min
<i>N₂ addition</i>	3.5 mL/min
<i>Lens Parameters</i>	
<i>Extract 1</i>	-1.5 V
<i>Extract 2</i>	-140 V
<i>Omega Bias</i>	-70 V
<i>Omega Lens</i>	8.0 V
<i>Q1 entrance</i>	-45 V
<i>Q1 exit</i>	1.0 V
<i>Cell focus</i>	1.0 V
<i>Cell Entrance</i>	-120 V
<i>Cell Exit</i>	-100 V
<i>Deflect</i>	10.0 V
<i>Plate Bias</i>	-60 V
<i>Q1 parameters</i>	
<i>Q1 bias</i>	-1.0 V
<i>Q1 Prefilter Bias</i>	-10.0 V
<i>Q1 Postfilter Bias</i>	-10.0 V
<i>Cell Parameters</i>	

<i>He flow</i>	1.0 mL/min
<i>10% HN₃ + 90% He gas flow</i>	3 mL/min
<i>Octopole bias</i>	-2.0 V
<i>Axial Acceleration</i>	2.0 V
<i>Octopole RF</i>	180 V
<i>Energy Discrimination</i>	-13.0 V
Q2 parameters	
<i>Q2 bias</i>	-15 V
<i>Wait time offset</i>	5ms
Analysis Parameters	
<i>Laser wavelength</i>	193 nm
<i>Laser fluence</i>	10 J/cm ²
<i>Laser spot diameter</i>	257 μm (43 μm; NIST610 glass)
<i>Laser repetition rate</i>	10 Hz
<i>washout</i>	30 s (post cleaning pulse) + 20 s (post analysis)
<i>Background</i>	30 s
<i>Analysis time</i>	40 s
<i>Isotopes measured/dwell</i>	²⁷ Al (2), ⁴³ Ca (2), ⁴⁷ Ti (2), ⁸⁹ Y (2), ⁹⁰ Zr (2), ¹⁴⁰ Ce (2), ¹⁷² Yb (10),
<i>times (ms)</i>	¹⁷⁵ Lu (10), ¹⁷⁵⁺⁸² Lu (100), ¹⁷⁶⁺⁸² Hf (150), ¹⁷⁸⁺⁸² Hf (150)

Supplementary data tables can be found at:

<https://doi.org/10.25909/21952646.v1>

Chapter 3: Garnet Lu-Hf speed dating: a novel method to rapidly resolve polymetamorphic histories

Submitted for publication to Gondwana Research as:

Simpson, A., Glorie, S., Hand, M., Spandler, C., Gilbert, S. Garnet Lu-Hf speed dating: a novel method to rapidly resolve polymetamorphic histories.

Supplementary data tables can be found at:

<https://doi.org/10.25909/21952649.v1>

Statement of

Title of Paper	Garnet lu-hf speed dating: a novel method to rapidly resolve polymetamorphic histories
Publication Status	☐ Published ☐ Accepted for Publication ☒ Submitted for Publication ☐ Unpublished and Unsubmitted work written in manuscript style
Publication Details	Simpson, A., Glorie, S., Hand, M., Spandler, C., and Gilbert, S. 2023. Garnet lu-hf speed dating: a novel method to rapidly resolve polymetamorphic histories. In review at Gondwana research

Authorship

Principal Author

Name of Principal Author (Candidate)	Alexander Simpson		
Contribution to the Paper	Conceptualisation, experimentation, and paper drafting		
Overall percentage (%)	80		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	11/01/2023

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

the candidate's stated contribution to the publication is accurate (as detailed above);

permission is granted for the candidate to include the publication in the thesis; and

the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	Stijn Glorie
-------------------	--------------

Contribution to the Paper	Conceptualisation, paper drafting, and primary supervision		
Signature		Date	11/01/2023

Name of Co-Author	Martin Hand		
Contribution to the Paper	Conceptualisation, sampling, paper drafting, and secondary supervision		
Signature		Date	23/01/2023

Name of Co-Author	Carl Spandler		
Contribution to the Paper	Paper drafting and secondary supervision		
Signature		Date	23/01/2023

Name of Co-Author	Sarah Gilbert		
Contribution to the Paper	Experimentation, and paper drafting		
Signature		Date	11/01/2023

3.1. Abstract

Recent advances in laser ablation reaction-cell mass spectrometry have opened the possibility for rapid and efficient Lu-Hf age dating of a variety of minerals. Of particular interest is the important metamorphic mineral, garnet, which is traditionally dated using solution-based Lu-Hf or Sm-Nd methods that are time consuming and often lack micron scale spatial resolution. In this study, we analyse garnets from samples from the 'Moine Supergroup' Scotland with the novel laser ablation inductively coupled quadrupole tandem mass spectrometry (LA-ICP-Q-MS/MS) Lu-Hf dating method, aiming to reveal terrane scale geochronological information in polymetamorphic rocks. We demonstrate that laser ablation Lu-Hf dating of garnet can accurately reveal the timing of different metamorphic events within single multi-growth garnets with precision typically as low as $\sim 1.5\%$ (2σ , including systematic uncertainties). Garnets analysed from our samples produced dates including 957 ± 33 Ma, corresponding to the Renlandian Orogeny, 808 ± 14 Ma, corresponding to the Knoydartian Orogeny, and 471 ± 8 Ma, corresponding to the Caledonian Orogeny; all events which have previously been recorded from this rock suite. Furthermore, laser ablation Lu-Hf dating of garnet can provide insight into micron-scale processes such as Lu diffusion and garnet recrystallization. We recommend a series of sequential protocols, from sample selection through to laser ablation analysis, which should be used to maximize the likelihood of producing well constrained garnet Lu-Hf dates.

3.2. Introduction

Introduction

The ability to determine the timing and nature of metamorphic events is fundamental to resolving the thermal and mechanical evolution of the lithosphere. Garnet growth and its chemical zonation provides foundational information about the nature of metamorphic events and the associated tectonic regimes. Consequently, there has been concerted efforts globally to understand the chemical, mechanical, and thermodynamic behaviour of garnet, and to develop methods to determine garnet ages. Nevertheless, direct dating of garnet is challenging as metamorphic garnets often lack sufficient U for in situ U-Pb dating (Mezger et al., 1989; Millonig et al., 2020), and established methodologies for Sm-Nd and Lu-Hf dating require bulk dissolution techniques (e.g. Duchene et al., 1997; Smit et al., 2013; Thoni, 2003), which are time consuming and limit spatial resolution. Micro-sampling methods can improve spatial resolution but are still efficiency limited by conventional dissolution techniques (Schmidt et al., 2015). While the conventional methods commonly produce high analytical precision, the labour requirement limits their broad application in large and complex orogenic systems. This is particularly important within ancient orogens that have significant temporal range and/or are polymetamorphic, because the number of dates required to resolve complex metamorphic histories can be impractical to achieve with traditional methods.

To overcome the difficulties associated with direct dating of garnet, an approach that has gained considerable popularity is petrochronology (e.g. Rubatto, 2002; Kylander-Clark et al., 2013; Engi et al., 2017). In the context of dating metamorphism, petrochronology uses textural associations and the trace element compositions of accessory minerals such as zircon and titanite to make inferences about their temporal relationships with minerals such as garnet (e.g. Rubatto, 2002; Yakymchuk et al., 2017). Thus, this approach seeks to utilise the efficiency of accessory mineral U-Pb geochronological methods to date garnet (and its coeval assemblage) by proxy. However, a potential limitation of the garnet-by-proxy approach is the assumption of trace element equilibrium behaviour between garnet and accessory minerals. Unfortunately, these potential

equilibrium states are hard to unequivocally demonstrate. Consequently, in many cases, cogenetic relationships between garnet and accessory minerals may not be well constrained. This is further complicated in samples that preserve more than one garnet growth event. For instance, Lihter et al. (2022) dated garnets from metamorphic rocks in the Himalayas, and demonstrate garnet dates of 292-230 Ma, while the majority of accessory monazite and xenotime produce dates of ~15 – 50 Ma. Therefore, rather than attempting to date garnet by accessory mineral proxy, it is clearly better to determine the age of garnet-bearing mineral assemblages by direct dating of garnet.

A recent development that overcomes the logistical barriers of conventional Lu-Hf garnet geochronology is *in situ* Lu-Hf geochronology, which involves the use of laser ablation inductively-coupled tandem quadrupole mass spectrometry (LA-ICP-Q-MS/MS) (Brown et al., 2022; Ribeiro et al., 2021; Simpson et al., 2021; Tamblyn et al., 2021). This method uses a reaction cell sandwiched between two quadrupole mass analysers (i.e. tripe quadrupole or tandem mass spectrometry) to remove the ^{176}Yb and ^{176}Lu interferences on ^{176}Hf (relying on different reactivity between HREEs and Hf when reacted with NH_3 gas; Simpson et al., 2021). Applied to garnet, few recent studies have used the laser ablation Lu-Hf method to constrain the timing of metamorphism in situations where previous geochronology was ambiguous (e.g. Ribeiro et al., 2021 and Brown et al., 2022). For instance, Brown et al., (2022) demonstrated both Proterozoic and early Phanerozoic metamorphism in metasediments that had previously thought to have undergone only early Phanerozoic metamorphism. In addition, Tamblyn et al., (2021) demonstrated the potential for campaign style garnet geochronology and used $\mu\text{-XRF}$ Y maps in order to estimate zones of high HREE (and therefore Lu) which allows for better targeting during laser ablation analysis.

This method has unrivalled potential for large-scale (i.e. campaign-style) garnet-based age mapping because it allows garnet to be rapidly dated, directly from a rock block (Tamblyn et al., 2021) or thin section. Consequently, large age datasets can rapidly be assembled for arguably the most critical mineral used to determine thermobarometric environments in orogenic systems. The derived age data from the LA-ICP-MS/MS method has high spatial resolution and, subject to garnet composition, may have analytical precision to rival conventional Lu-Hf dating.

In this study, we present *in-situ* garnet Lu-Hf dating from Neoproterozoic- and early Palaeozoic-aged metamorphic rocks from the Moine Supergroup, northern Scotland. These metasedimentary rocks have been studied for over a century, with the first systematic description provided by Peach et al., 1907. A variety of geochronological methods, including garnet Lu-Hf and Sm-Nd dating (e.g. Bird et al., 2013; Vance et al., 1999) as well as monazite, zircon, and titanite U-Pb dating (e.g. Friend et al., 1997; Storey et al., 2004; Cawood et al., 2010), has been applied in the region. These studies have revealed multiple metamorphic and igneous events spanning from the Neoproterozoic Renlandian (980 – 910 Ma) and Knoydartian (830 – 725 Ma) Orogenies, till the Palaeozoic Caledonian Orogeny (475 – 425 Ma) (Bird et al., 2013; Cawood et al., 2010; Strachan et al., 2010). Given the significant body of work that exists for the MoGLE rocks and their complex tectonic history, these units provide an excellent natural laboratory to demonstrate the utility of laser ablation Lu-Hf geochronology of garnet.

We show that the laser ablation method effectively illuminates Neoproterozoic-aged metamorphism and later overprinting within the confines of the polymetamorphic Ordovician-Silurian Caledonian orogenic system. We compare LA-ICP-MS/MS generated Lu-Hf garnet dates with conventional Lu-Hf dates to demonstrate the general equivalence of the two approaches for dating garnet. We also assess the effects of inclusions on laser ablation garnet Lu-Hf dates and outline a sequential methodological approach to maximise the success rate of garnet laser ablation garnet Lu-Hf dating.

3.3. Geological Background

This study focuses on a series of Neoproterozoic metasedimentary rocks, previously referred to as the ‘Moine Supergroup,’ located in north-western Scotland (Fig. 1). The rocks consist of the Morar, Glenfinnan, and Loch Eil Groups (oldest to youngest; Holdsworth et al., 1994; Krabbendam et al., 2021; Strachan et al., 2010). The Morar Group is situated within the Moine Nappe, while the other two units form the Sgurr Beag Nappe (Holdsworth et al., 1994). Although these rocks have historically been considered to be stratigraphically continuous, recent evidence points to a difference in depositional age between the Morar Group and the Glen Finnan and Loch Eil Groups (Bird et al., 2018; Krabbendam et al., 2021). In this paper, the term ‘MoGLE rocks’ is used for convenience for the **Morar-Glenfinnan-Loch Eil** successions.

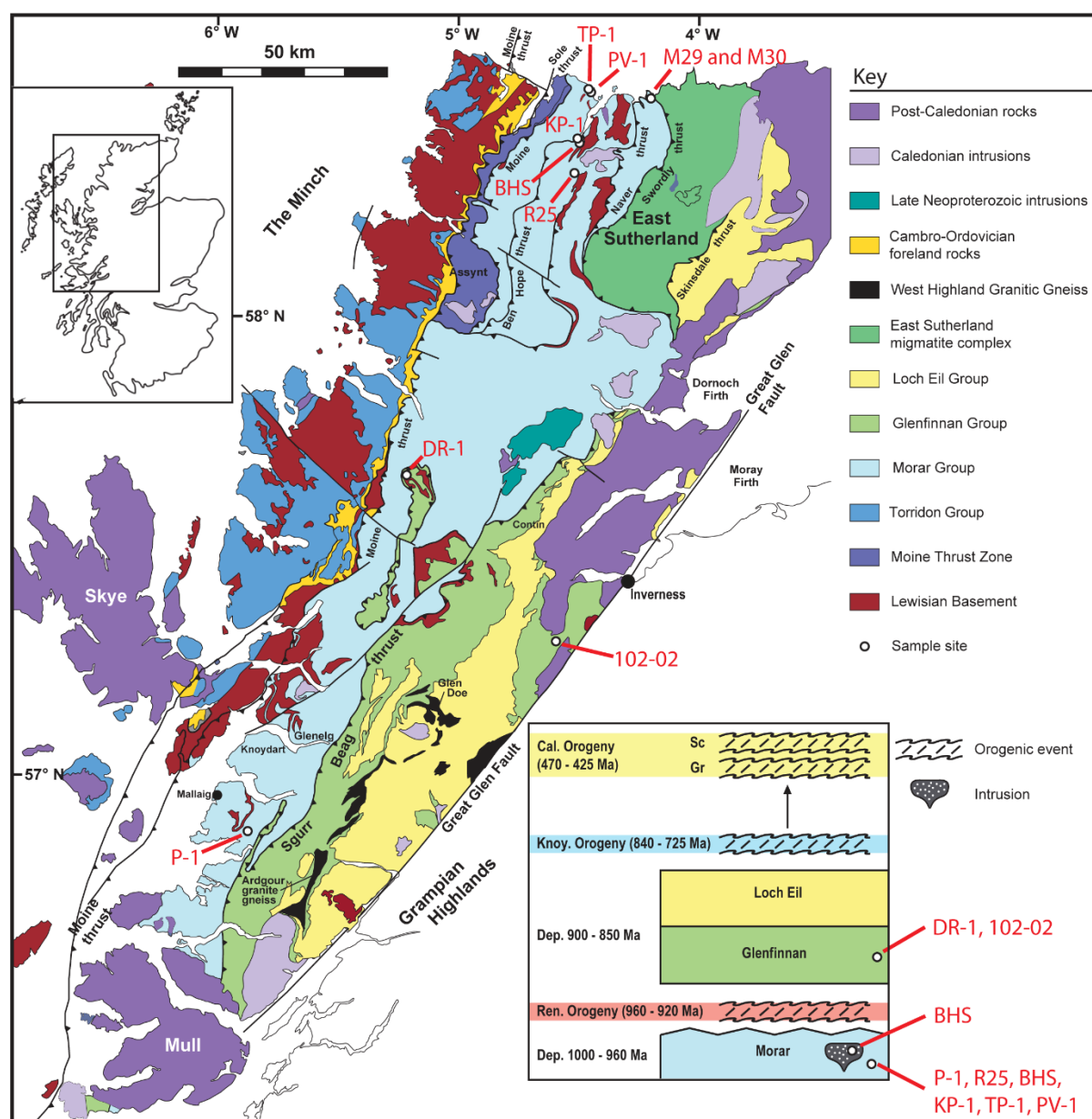


Figure 3.1: Geological map of North West Scotland (based on Cawood et al. (2014), Krabbendam et al. (2021), and Thigpen et al. (2010)) and simplified stratigraphic cartoon of the MoGLE rocks, showing the relative stratigraphic position of analysed samples.

The sedimentary protoliths to the MoGLE rocks (Fig. 1) were deposited between ca. 1000 Ma and 850 Ma, in fluvial to marine settings (Holdsworth et al., 1994; Krabbendam et al., 2021; Strachan et al., 2010), most likely in south eastern Laurentia (Cawood et al., 2014; Strachan et

al., 2010). The Morar Group has recently been reclassified as part of the Wester Ross Supergroup (with the Torridon, Sleat, Tarskavaig, and Iona Groups), while the Glenfinnan and Loch Eil Groups are now classified as part of the Loch Ness Supergroup (located in the Grampian Highlands on the other side of the Great Glen Fault; Krabbendam et al., 2021).

Broadly, the MoGLE rocks are thought to have undergone a series of accretionary orogenic events between ca. 950 Ma until 725 Ma, considered part of the greater Valhalla Orogeny (Bird et al., 2018; Cawood et al., 2010). The earliest documented metamorphism is ca. 950 Ma garnet growth during amphibolite grade metamorphism, inferred to have occurred during the 980 – 910 Ma Renlandian Orogeny (>6-7 kbar, ~600°C; Bird et al., 2018). This episode is only documented in the Morar Group and predates deposition of the Glenfinnan and Loch Eil Groups (Bird et al., 2018). In combination with detrital zircon geochronology (reviewed in Krabbendam et al., 2021), the age of metamorphism in the Morar Group has been used to argue that the Morar group is not stratigraphically continuous with the overlying Glenfinnan Group (Krabbendam et al., 2021). The Renlandian Orogeny was likely followed by a period of extension at ca. 870 Ma, based on the presence of geochemically defined MORB-like metadolerite dykes that formed in association with the ~870 Ma intrusion of the West Highland Granite Gneiss and associated gabbros (Cawood et al., 2014; Friend et al., 1997; Millar, 1999). Evidence from both Sm-Nd dates of metamorphic garnets, and U-Pb dating of pegmatites that formed during high grade metamorphism, has been interpreted to reflect a series of orogenic episodes between ca. 820 – 725 Ma (Cawood et al., 2014; Cutts et al., 2010; Rogers et al., 1998; Vance et al., 1998), and potentially continuing until ca. 670 Ma (Storey et al., 2004). These orogenic episodes are collectively referred to as the Knoydartian Orogeny (Bowes, 1968), although, given the age range and potentially punctuated nature of these events, it may not be appropriate to consider them as a single orogeny (Storey et al., 2004). The ca. 870 Ma extension and the following Knoydartian events are likely related to episodic extension and closure of an intracratonic basin, rather than opening of an oceanic basin (Cawood et al., 2004).

No evidence for significant metamorphism has been documented in typical MoGLE rocks between ca. 670 and 475 Ma, however, previous geochronology indicates that intrusion of granites and granitoids occurred at ca. 600 Ma (Kinny et al., 2003b; Oliver et al., 2008). Similar igneous activity has also been demonstrated in the Dalradian and Appalachians, and is thought to be associated with the opening of the Iapetus Ocean during the break-up of Rodinia (Bingen et al., 1998).

Subsequently, the MoGLE rocks were affected by the ca. 475 – 420 Ma Caledonian Orogeny, which consumed the Iapetus Ocean during collision between Baltica and Laurentia (McKerrow et al., 2000). Within northwest Scotland, this orogenic event can be divided into the ca. 475 – 450 Ma Grampian Orogeny and the ca. 435 – 420 Ma Scandian Orogeny (Strachan et al., 2010). The Grampian Orogeny involved collision between a volcanic arc and western Laurentia (where the MoGLE rocks were situated) and occurred during the early stages of Iapetus closure. The Grampian Orogeny recorded in the MoGLE rock involved two stages: Grampian I occurred between 475 – 460 Ma, and Grampian II at ca. 450 Ma. The timing of these events has been constrained regionally by garnet Lu-Hf and Sm-Nd dating (Bird et al., 2013) and monazite and zircon U-Pb dating (Kinny et al., 1999; Kinny et al., 2003a; Strachan et al., 2020). The Grampian events were followed by the Scandian Orogeny, which involved final closure of the Iapetus Ocean and collision between Baltica and Laurentia between 435 and 420 Ma (Holdsworth et al., 1994; Kinny et al., 2003a; Strachan et al., 2010). The Moine Thrust system developed during the Scandian and transported MoGLE rocks and their Palaeoproterozoic basement westward across a foreland containing Cambrian sequences and underlying Archaean-Palaeoproterozoic basement (Goodenough et al., 2011).

The samples that have been selected include ones containing clear textural evidence for multiple generations of garnet as well samples that show evidence for only one generation of garnet. The aim of selecting samples that show both simple and complex garnet growth is to interrogate what part of the complex tectonic evolution texturally simple garnet records. Where possible, samples have been chosen from locations close to where existing garnet Sm-Nd or Lu-Hf dates or monazite U-Pb dates have been determined. This was done in order to make comparisons between existing geochronology and LA-ICP-Q-MS/MS Lu-Hf garnet dates that delineate the ca. 950 Ma Renlandian Orogeny, (2) the ca. 820 – 725 Ma (820 – 670 Ma) Knoydartain Orogeny and/or (3) the ca. 475 – 420 Ma Caledonian Orogeny.

3.4. Sample descriptions

A total of ten samples have been analysed in this study. 6 samples (R25, P-1, PV-1, TP-1, KP-1 and DR-1) are garnet schist, while samples M30 and M29 (from the Kirtomy Nappe, Betty Hill area, North Sutherland; Fig. 1) and 102-02 (from the Milton area adjacent to the Great Glen Fault; Fig. 1) have gneissic texture in thin section (Fig. S1) and are interpreted to be migmatitic. Sample BHS is from an amphibolite intruded into Morar Group sediments (Fig. 1). Samples contain garnet porphyroblasts between 0.5 to 12 mm in size. In some samples (e.g., PV-1, P-1), garnets are visually multi-stage, with evident colour differences between core and rim in hand sample.

Samples R25, P-1, PV-1, TP-1, KP-1 and DR-1 have pervasive foliation (Fig. S1), given by muscovite and biotite, while samples M29, M30, and 102-02 have gneissic banding (Fig. S1). Most samples show evidence for localised retrograde reaction involving formation of chlorite, or the formation of secondary biotite and plagioclase at the expense of garnet (Fig. S1).

The migmatitic samples are dominated by plagioclase and quartz, and contain a weak foliation defined by biotite. Garnet is mostly irregular in shape with abundant inclusions of quartz and ranges in size between 0.5 and 8 mm. The sample from Milton (102-02) contains two garnet types: (1) coarse-grained, inclusion-rich pale pink garnet within leucosomes and (2) finer-grained red garnet within biotite folia.

A summary of the samples can be found in Table 1 and representative photomicrographs in supplementary file 1, Fig. S1. Table 1 also provides the stratigraphic affinity and existing age data from either the same sample, or a nearby location.

<i>Location</i>	<i>Grid ref (WGS 84, UTM)</i>	<i>Sample number</i>	<i>Unit (Rock type)</i>	<i>Mineralogy (in order of increasing abundance)</i>	<i>Inclusions in garnet</i>	<i>Approximate garnet size (mm)</i>	<i>Retrograde textures</i>	<i>Approximate garnet abundance (%)</i>	<i>Previous age constraints (Ma)</i>
<i>Lochan Dheru</i>	30V 412619 6470942	R25	Morar/Meadie pelite (Metapelite)	Qtz-St-Bi-Mu-Gt-Pl- Ky-Chl	Qtz	1-8	Bi-Ky-Chl replacement of Gt	0.05	950 ± 3
<i>Port Vasgo</i>	30V 415856 6491143	PV-1	Morar (Metapelite)	Mu-Qtz-Gt-Bi-Plag-Chl	Qtz-Ilm in cores, Ru-Graph in overgrowths	2-14	Chl replacement of Gt and Bi. Ilm rimming Ru	0.14	448 ± 7.4*
<i>Polnish</i>	30V 335680 6308864	P-1	Morar/Morar Pelite (Metapelite)	Qtz-Mu-Gt-Bi-Pl-Chl- Ilm-Graph	Qtz-Graph in first generation of Gt, Qtz-Ilm-Bi in second generation Gt	0.5-6	Chl replacement of Gt and Bi.	First generation Gt 5%, second generation Gt 2%	Core: 823 ± 4.6 Rim: 788 ± 4.4
<i>Talmain e</i>	30V 416148 6490200	TP-1	Morar/Talmine Pelite (Metapelite)	Qtz-Mu-Bi-Gt-Chl-Pl	Qtz-Ilm	0.5-4	Chl replacement of Gt and Bi.	0.05	448 ± 7.4
<i>Kinloch</i>	30V 413092 6478836	KP-1	Morar (Metapelite)	Qtz-Pl-Gt-Bi-Cz-Ep- Chl-Mu	Qtz-Ilm-Ep	0.8-5	Ch replacement of Gt	0.09	447.3 ± 1.7*
<i>Kirtomy</i>	30V 433113 6491311	M29	Morar (Quartzofeldspath ic)	Pl-Qtz-Bi-Gt-Hb-Ttn	Qtz-Ilm-Ru	0.8-3.5	Pl-Bi replacement of Gt	0.05	N/A
<i>Kirtomy</i>	30V 433113 6491311	M30	Morar (Quartzofeldspath ic)	Pl-Qtz-Bi-Gt-Ttn-Hb	Qtz-Bi-Ilm-Ru	0.5-2.5	Pl-Bi replacement of Gt	0.04	N/A
<i>Sgurr Breac</i>	30V 374170 6396774	DR-1	Morar (Metapelite)	Bi-Gt-Qtz-Pl-Mu-Ru- Ttn	Qtz-Bi-Ilm-Ru	0.5-12	Bi-Pl replacement of Gt	0.09	N/A
<i>Milton</i>	30V 408721 6358061	102- 02	Glenfinnan (Quartzofeldspath ic)	Pl-Qtz-Gt-Bi-Chl-Ru	Qtz-Ilm in first generation of Gt, Ru-Qtz in second generation Gt	First generation 11, second generation 2	Chl replacement of second generation of Gt	First generation Gt 6%, second	Core 1: 820 – 780 Core 2: 725 ± 6

							generation Gt 4%	Rim: 464 ± 3
Kinloch	30V 413557 6477696	BHS	Ben Hope Sill (Amphibolite)	Hb-Qtz-Gt-Pl-Ilm	Qtz-Ilm-Hb	1.5-4	0.05	447.3 ± 1.7

Table 3.1: Sample locations and petrological information. Previous age constraints are from the following: Plinish; Vance et al., 1998, 102-02; Cutts et al., 2010, R25; Bird et al., 2018, BHS and TP-1; Bird et al., 2013. *KP-1 is from a location close to BHS, and PV is from a location close to TP-1 (Fig. 3.1), and are therefore expected to have similar ages. Mineral abbreviations from Whitney and Evans (2010)

3.5. Methods

3.5.1. Sample preparation

Garnets were selected from hand samples with existing thin sections. Garnet-bearing rock slabs were cut and ground to expose the cores of the garnets as closely as possible prior to mounting. These slabs were mounted in 2.5cm round epoxy resin and polished using standard techniques, as more of these mounts can fit in the laser sample chamber, thus optimising analytical time.

3.5.2. Benchtop XRF mapping

Benchtop μ -XRF mapping of the samples was done using a Bruker M4 Tornado, following protocols outlined in (Tamblyn et al., 2021). In more detail, an accelerating voltage of 50 kV with a beam current of 600 μ A and a beam diameter of 25 μ m was used. Background subtracted maps were produced using M4 software. Mapping was conducted to highlight regions of high Y, which is used as a proxy for Lu because Y contents are typically much higher than Lu (Tamblyn et al., 2022). Garnet domains with higher Y concentrations were targeted for analysis to produce greater spread in Lu/Hf ratios. u-XRF major element maps were also used to monitor sharp changes in the garnet compositions and thus identify possibly different growth zones.

3.5.3. Laser ablation Lu-Hf analysis

Garnet rock blocks were analysed across three analytical sessions following protocols outlined in Simpson et al. (2021) and described below. Samples were analysed using a RESolution 193 nm excimer laser ablation system, coupled to an Agilent 8900 QQQ mass spectrometer (ICP-MS/MS). Laser beam diameters of 43 – 120 μ m were used, with a laser repetition rate of 10 Hz and an energy density of 3.5 J cm⁻². A flow of 4 ml min⁻¹ N₂ gas was added after the sample chamber, but before the ICP in order to increase sensitivity (Hu et al., 2008). Background was measured for 30 s before each analysis, followed by an analysis time of 40 s and a washout of 20 s. A mixture of 10% NH₃ and 90% He was used as the reaction gas, introduced at rate of 3 ml min⁻¹, in order to promote formation of Hf(NH)(NH₂)(NH₃)₃⁺, (a mass shift of +82 amu and reaction rate of 50 – 60%), while the equivalent reaction product forms at a rate of 0.003% for Lu and at a rate of ~0.00003% for Yb (Simpson et al., 2021). The mass spectrometer was first tuned in ‘no gas’ mode to promote a robust plasma and minimise oxide production (U/Th = 1.00 – 1.05, ThO/Th < 0.2%). Following this, ICP-MS/MS parameters were tuned in ‘MS/MS mode’ to maximise sensitivity on the Hf reaction product (while minimising the isobaric interferences). The ¹⁷⁵Lu isotope was used as a proxy for calculating ¹⁷⁶Lu and ¹⁷⁸Hf was used as a proxy for ¹⁷⁷Hf, assuming stable ¹⁷⁵Lu/¹⁷⁶Lu and ¹⁷⁸Hf/¹⁷⁷Hf ratios; for more details see Simpson et al. (2022). The following isotopes were also monitored during analysis to allow detection of incorporated inclusions: ²⁴Mg, ²⁷Al, ⁴³Ca, ⁴⁷Ti, ⁵⁷Fe, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ¹⁴⁰Ce, ¹⁴⁶Nd, ¹⁴⁷Sm and ¹⁷²Yb. Full analytical conditions can be found in supplementary 1, table S1.

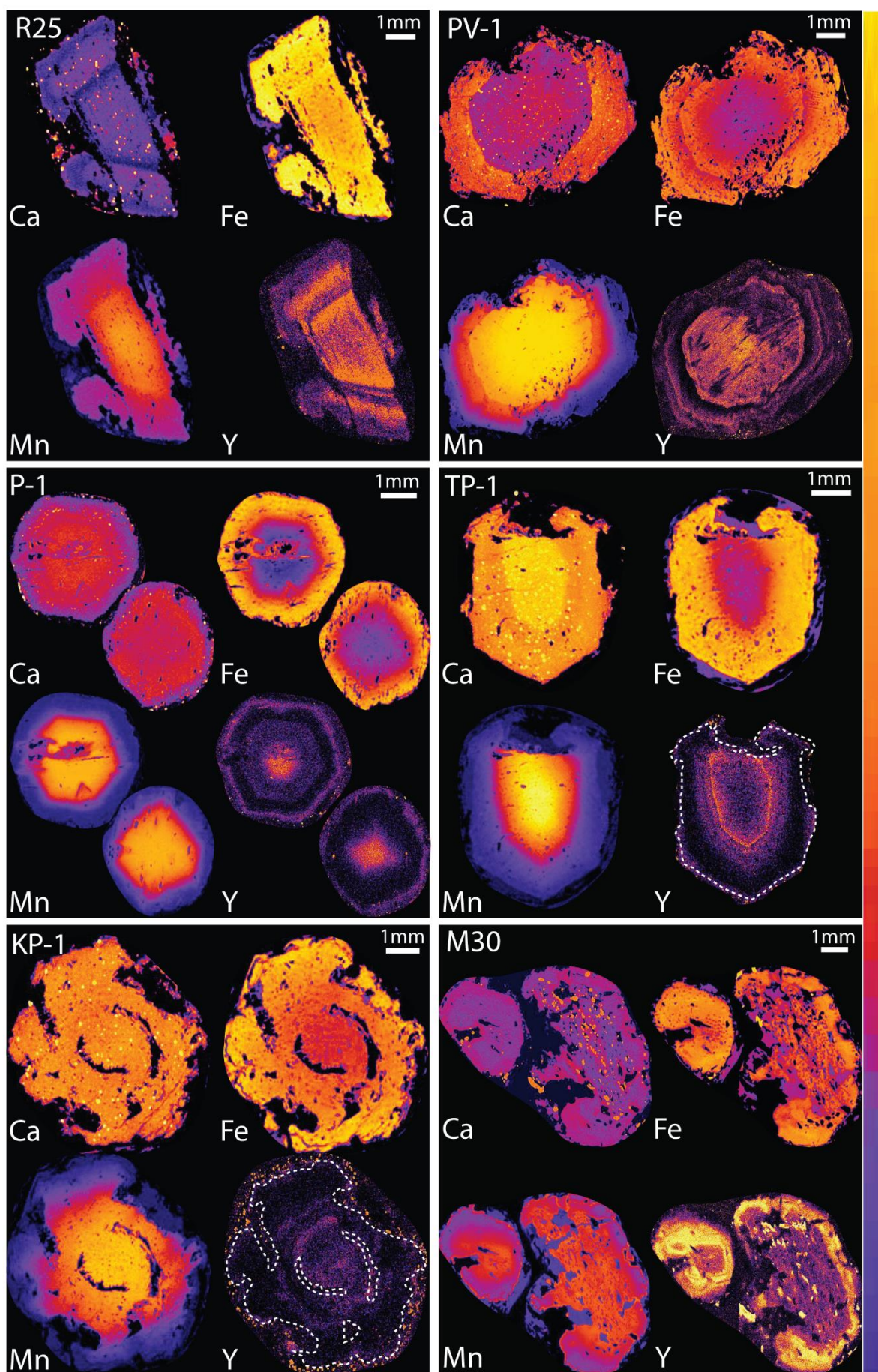
A standard – sample bracketing approach was used to correct for elemental and isotopic fractionation effects, with NIST610 SRM used as the primary reference material to correct for instrument drift and matrix independent fractionation. Lu/Hf ratios for NIST610 can be found in Nebel et al. (2009). Two secondary garnet reference materials were run; Hogsbo garnet (reference age: 1029 ± 1.7 Ma, Columbite U-Pb; Romer and Smeds, 1996) and an in house secondary reference garnet, BP1, which produced dates of 1750 ± 15 Ma, 1757 ± 14 Ma, and 1737 ± 12 Ma (corrected against Hogsbo garnet), consistent with a monazite U-Pb date from the same sample (1745 ± 14 Ma; Lane, 2011). Isochron plots for standards can be found in supplementary file 1, Fig. S3. The Hogsbo secondary reference material was used to correct for laser induced elemental fractionation of Lu relative to Hf. In more detail, data was corrected based on the percentage offset between the measured and expected radiogenic ¹⁷⁶Lu/¹⁷⁶Hf isotope ratio of the Hogsbo garnet, similar to the correction used in Roberts et al. (2017) for

calcite U-Pb dating. The expected radiogenic $^{176}\text{Lu}/^{176}\text{Hf}$ ratio for Hogsbo can be calculated from the expected age (1029 ± 1.7 Ma; Romer and Smeds, 1996), and the measured radiogenic $^{176}\text{Lu}/^{176}\text{Hf}$ ratio is the slope of a traditional isochron, or the x-intercept of an inverse isochron, calculated from un-anchored linear regression through the measured Hogsbo Lu-Hf isotopic data. As this correction was conducted to correct for the effects of laser induced elemental fractionation between Lu and Hf, it was applied only to the $^{176}\text{Lu}/^{176}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios, but not the $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. The LADR software (Norris and Danyushevsky, 2018) was used to process data (background subtractions, instrument drift, fractionation corrections and ratio calculations). Between 60 and 100 ablation spots were collected for most unknowns in order to produce well constrained isochrons (Simpson et al., 2021; Tamblyn et al., 2022), however, due to the small size of the Lu rich cores of sample P-1, only 22 laser spots were used. Isochron regressions were calculated in IsoplotR (Vermeesch, 2018), and include the uncertainty propagated from the ^{176}Lu decay constant ($0.00001867 \pm 0.00000008 \text{ Myr}^{-1}$; Söderlund et al., 2004). Additionally, the uncertainty on the Hogsbo correction factor described above was propagated to the final isochron dates. A discussion of uncertainty propagation for laser ablation Lu-Hf analysis can be found in Simpson et al. (2022).

3.6. Results

3.6.1. Micro-XRF maps

Micro-XRF maps of relative intensities of Ca, Fe, Mn and Y are presented in figure 2. Other elemental maps (P, Ti, and Zr) can be found in supplementary file 1, Fig. S2. We emphasize that the apparent elemental concentrations of inclusions should be treated with caution, as a) high intensity indicates only that the element in question is significantly higher than garnet (but not necessarily a major element), and b) diffraction effects occurring along grain boundaries may lead to false elevated elemental concentrations (e.g. Flude et al., 2017).



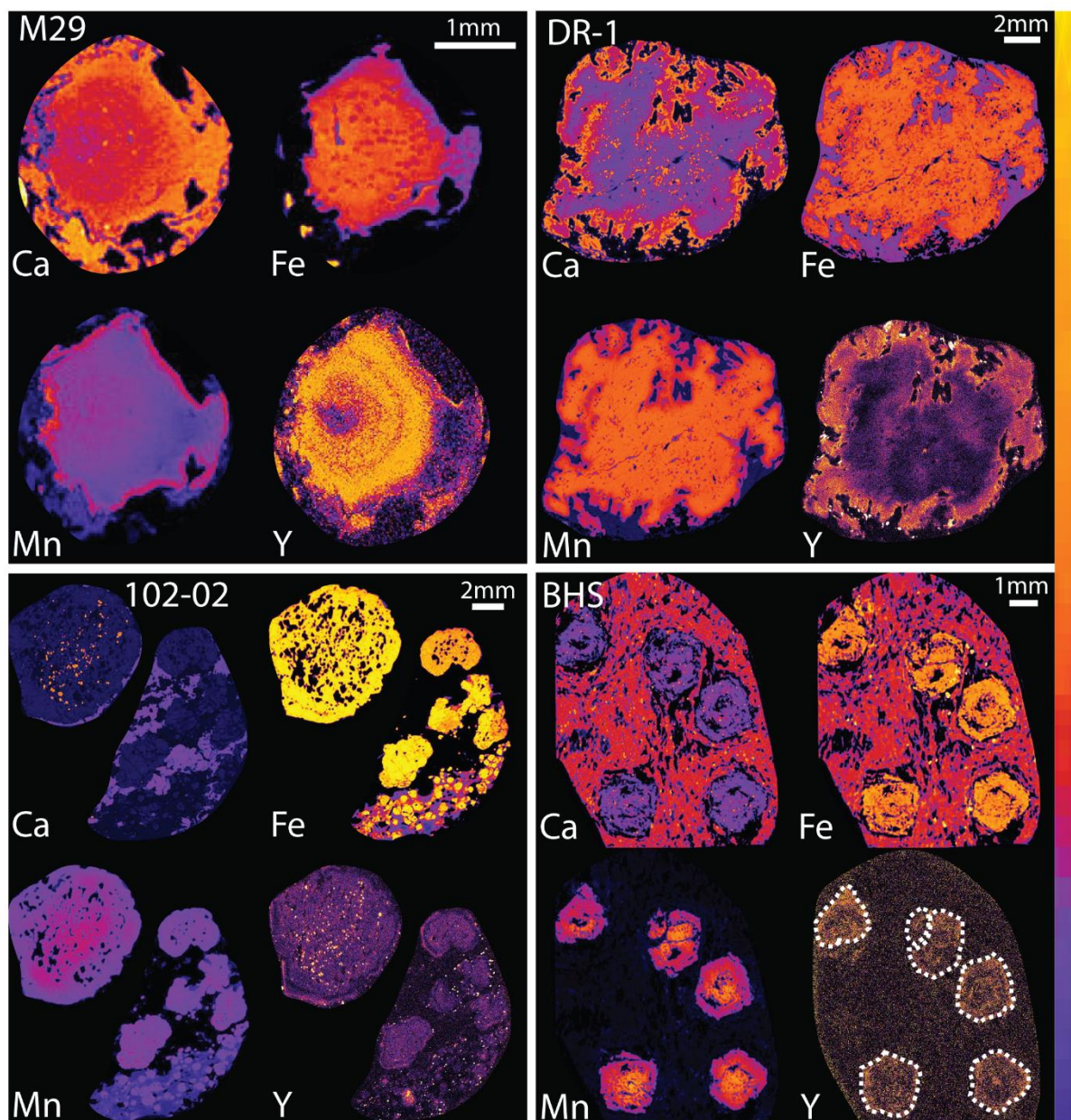


Figure 3.2: μ XRF elemental maps of analysed garnets. The mapped element is labelled in the bottom left corner. The maps show relative concentrations, and are coloured with hotter colours corresponding to high concentrations and cooler colours corresponding to lower concentrations (e.g. yellow = high, red = intermediate, purple = low, and black = below detection). High Ca, low Y inclusions are plagioclase, high Ca, high Y inclusions are apatite. Dotted white outlines have been included in the Y maps for TP-1, KP-1, to show the boundaries of the garnets.

Sample R25

Garnets from sample R25 show a clear distinction between core and rim. This is most evident in Ca where a euhedral core is delineated by a distinct narrow depleted domain. The core is also evident in Fe and Mn, albeit more diffusely expressed. The core shows a diffuse increase in Y from the centre of the garnet to the edge of the core, which is marked by a sharply defined abrupt decrease in Y. The large rim is initially comparatively enriched in Ca, which decreases toward the matrix. Mn and Fe smoothly decrease and increase from the interior to the exterior of the large secondary rim. The inner part of the coarse garnet rim displays diffuse oscillatory-style zoning in Y and progressively becomes Y depleted toward contact with the matrix, with the

exception of small discontinuous patches of Y enrichment. Apatite inclusions are evident by the high Ca contents.

PV-1

The μ -XRF maps of the PV-1 garnet sample show the presence of a well-defined core and rim, consistent with visual observations of the garnet in the hand sample. The core is defined by relatively low Ca contents. The garnet core is weakly zoned in Mn and Fe, which vary inversely. Calcium decreases slightly toward the core-rim boundary. Apatite inclusions are indicated by small bright spots in the Ca map. Yttrium in the garnet core shows a complex pattern. One area of the core shows a region of significant depletion. A series of linear low Y domains define an apparent internal foliation. However, this does not correspond to mineral inclusions. The outer part of the garnet core shows a partial annulus of Y enrichment. In the garnet rim, Fe and Mn vary inversely from interior edge of the rim to the external edge. Calcium shows a subtle decrease. In contrast to the simple compositional patterns exhibited by major elements, Y zonation is concentrated into two concentric partial annuli, and is strongly depleted at the core – rim boundary and again at the outer rim of the garnet (Fig. 2).

P-1

Garnets from the P-1 sample are idioblastic and their core and rim structure is clearly evident optically. The cores have pronounced Mn enrichment, moderate Ca enrichment and Fe depletion relative to the rim. Yttrium is highest in the core, and decreases rapidly toward the edge of the optically distinct core. In the large rim, Y is initially depleted, before increasing near the edge of the garnets (Fig. 2). In one of the garnets, Y enrichment defines near rim annulus that decreases toward to contact with the matrix. In another garnet, the enriched domain is located at the rim contact with the matrix. Ca and P rich inclusions (apatite) are more common toward the rim (Fig. 2).

TP-1

Garnets from TP-1 have a Mn and Fe enriched core, and are relatively homogenous in Ca (Fig. 2 and Fig. S2). Yttrium is moderately enriched in the core, showing patchy zonation, but is barely detectable in the rim. Ca and P rich inclusions are present (apatite).

KP-1

Hypidioblastic garnet grains show a strong enrichment of Mn, a moderate enrichment in Ca, and a depletion in Fe in the core. Bright spots in the Ca map highlight the presence of apatite.

In contrast to the smooth compositional variation shown by the major elements Y is slightly more complex, showing generalised enrichment in the core relative to the rim. However, it is evident there is variably defined oscillatory zoning in the core region of the garnet.

DR-1

The garnet analysed from the DR-1 sample has a uniform concentration of Fe. Similarly, Mn and Ca are also uniform in the garnet interior, but in contrast to Fe show, depletion and enrichment at the rim respectively. Yttrium zonation is patchy in the garnet interior, but shows pronounced enrichment in a wide (1000 - 2000 μ m) annulus at the garnet rim (Fig. 2).

M30

Two garnets were mapped from the M30 sample, one containing abundant biotite and plagioclase inclusions, and the other comparatively inclusion free. In both, Ca is relatively homogenous, with a slight enrichment at the rim (Fig. 2). In the inclusion rich garnet, Fe also appears homogenous, however it is difficult to accurately assess due to the abundance of biotite

inclusions (Fig. 2). In the inclusion poor garnet, there is slight decrease in Fe at the rim that corresponds to Ca enrichment. Manganese is slightly enriched in the cores (Fig. 2) and decreases rimward before increasing again at the very rim forming a continuous enriched domain in inclusion-free garnet and a discontinuous enrichment in inclusion-rich garnet. Yttrium is enriched in the rim relative to the core in inclusion rich garnet (Fig. 2).

M29

Garnets from sample M29 demonstrate subtle changes in major elements, with slight enrichment in Fe and Mn toward the core, and enrichment in Ca toward the rim. Mn shows pronounced enrichment at the garnet rim. Yttrium shows subtle oscillatory-style zonation and in a large region near part of the rim, is significantly depleted. In the apparent core, Y appears depleted.

102-02

102-02 has two distinct types of garnet; (i) large (~11 mm in diameter) idioblastic garnets with abundant quartz inclusions located with quartzofeldspathic domains and (ii) smaller (~2 mm in diameter) idioblastic garnets within biotite folia. The large garnets have very weak zonation in Ca and Fe with slight increases toward the rim corresponding to a decrease in Mn. Yttrium is comparatively homogenous with the exception of a partial rim of enrichment at the garnet rim. Ca and Y delineate abundant apatite inclusions.

The smaller garnets are mostly homogenous with major element compositions that correspond to the rims of the large garnets. The small garnets typically have a tiny Y enriched core with a rapid depletion to the rim. One exception is a high Y enriched small grain evident as a bright area in the sample Y map (Fig. 2).

BHS

The BHS garnets show modest core to rim depletion in Mn. The Mn depletion corresponds to slight enrichment in Fe and depletion in Ca respectively. Yttrium variably displays either diffuse oscillatory-style zonation or enrichment at the rim. Apatite inclusions are marked by small bright spots in Ca.

3.2.2. Garnet Lu-Hf Geochronology

In situ Lu-Hf isotope is presented as inverse isochrons in Fig. 3 and summarised in Table 2. Data is presented as inverse isochrons as highly radiogenic data (with highly correlated errors) can be difficult to visually inspect in traditional isochrons (Li and Vermeesch, 2021). All data point uncertainties are 2σ and resulting date uncertainties are 95% confidence intervals. Uncertainties are increased in cases where MSWDs are greater than expected for a single population (using IsoplotR; Vermeesch, 2018). Garnet Lu-Hf ratios from different growth zones (i.e. core vs rim zones; as evidenced from the maps in Fig. 2) are plotted on separate isochrons. Where no clear multi-growth history is evident in the optical and compositional character of the garnets, core and rim data are grouped together and plotted on the same isochron. Minor zircon inclusions (or other low Lu/Hf minerals detected from the presence of Zr and other ancillary elements) were not filtered from the dataset as they help to define the low radiogenic Lu/Hf end (i.e. upper intercept) of the isochrons. Removal of these inclusions in the down-hole signal did not significantly change the calculated uncertainties. However, large inclusions of REE bearing minerals (such as apatite, monazite or xenotime) were filtered from the data as they can influence calculated dates. We discuss the effects of minerals inclusions during laser ablation Lu-Hf dating in more detail in section 6.4. All calculated isotopic ratios, including data points removed from isochron calculations, as well as trace element concentrations can be found in supplementary file 2.

Table 3.2: summary of geochronological data for the analysed garnets. Garnet radius measurements are given as ranges in situations where more than one garnet was analysed or the radius is not uniform. These values are specifically for the garnets analysed for Lu-Hf, and consequently may differ slightly from the general garnet size estimates in table 3.1. Note that for sample P-1, a separate radius is reported for the core of garnet 1 (of 2 analysed garnets). This is done on the basis of the different Lu-Hf date. Visually the core appears very similar to garnet 2 (Fig. 3.2).

Sample	Approx. grain radius (mm)	session	D a t e (M a)	2 S E	2 S E %	MS WD	n	M i n L u (p p m)	M a x L u (p p m)
BHS	0.5-0.9	28/03/2 022	4	1	4	0.8	1	1	2
			4	9	.	2	0		3
			4		3		4		
102-02 rim + small	N/A	28/03/2 022	4	2	5	1.2	9	N	N
			4	5	.		9	/	/
			7		6			A	A
102-02 rim	0.3-1	28/03/2 022	4	7	1	1.3	4	2	1
			1	9	9		5		1
			3		.				
102-02 small	0.5-1	28/03/2 022	4	2	5	1	5	1	2
			5	6	.		4		8
			0		8				
102-02 core	6-8	28/03/2 022	7	3	4	1.6	9	2	2
			0	0	.		5		1
			1		3				
DR-1 rim	1.5	28/03/2 022	5	1	2	1.4	5	3	3
			4	4	.		2		2
			0		6				
DR-1 core	4	28/03/2 022	8	4	5	1.2	6	2	1
			5	6	.		0		6
			6		4				
M30 rim	0.5-1	28/03/2 022	4	9	1	1.5	6	1	4
			7		.		0		7
			1		9				
M30 core	0.5-2	28/03/2 022	4	8	1	1.3	6	3	3
			7		.		1		4
			8		7				
M29	0.8-1	28/03/2 022	4	1	2	1.2	6	1	4
			7	0	.		9		5
			2		1				
KP-1	1.5-2.8	21/01/2 022	4	1	2	0.8	8	0	8
			6	0	.	2	2	.	2
			6		1			4	
TP-1	1.5-2.2	21/01/2 022	4	2	5	0.6	7	1	1
			6	3	.	2	0		3
			1		0				2

<i>P-1 gnt 1 rim + gnt 2</i>	1.1-1.5	28/03/2 022	8	1	1	0.9	1	0	1
			6	2	.	1	7	.	1
			1		4		3	3	2
<i>P-1 gnt 1 core</i>	0.5	28/03/2 022	8	1	1	1.7	1	9	7
			9	4	.		0		9
			8		6				0
<i>PV-1 rim</i>	1.2	21/01/2 022	5	4	9	0.8	1	0	9
			0	9	.	5	4	.	
			0		8		0	0	
<i>PV-1 core</i>	1.8	21/01/2 022	8	1	1	0.8	8	0	1
			0	4	.	5	0	.	0
			8		7			5	0
<i>R 25 rim</i>	1.5	10/06/2 022	7	2	3	0.6	7	0	1
			7	6	.	3	9	.	2
			6		4			2	
<i>R25 Core</i>	1.5-2	21/01/2 022	9	3	3	0.7	8	3	5
			5	3	.	8	4		9
			7		4				

Sample R25

A single large garnet with textural and compositional evidence for poly stage evolution was analysed from R25 over two sessions (core in session 1, and rim in session 3). The core gives a date of 957 ± 33 Ma (MSWD = 0.78, $n = 84$; Fig. 3.3, table 3.2.) with all of the collected data points included in the isochron calculation.

The rim produced a date of 776 ± 26 Ma (MSWD = 0.63, $n = 79$; Fig. 3.3, table 3.3). Two data points (displayed as open ellipses in Fig. 3.3) are interpreted to have partly incorporated material from the core of the garnet and have been removed from the isochron calculation.

Sample PV-1

A single large garnet displaying a texturally and compositionally distinct core and rim (Fig. 2) was analysed from PV-1 in session 1. A date of 808 ± 14 Ma (MSWD = 0.85, $n = 80$; Fig. 3, table 2) was calculated for the core, with none of the collected data points removed from the isochron calculation.

The rim gives a date of 500 ± 49 Ma (MSWD = 0.86 $n = 139$; Fig. 2, table 2) with one data point of a total of 140 removed from the isochron calculation due to its large $^{177}\text{Hf}/^{176}\text{Hf}$ uncertainty (72%, 2σ), associated with the very low Lu concentration.

Sample P-1

Data was collected from two garnets from the P-1 sample in session 1. The cores of one of these garnets displayed extremely high Lu concentrations (up to ~800 ppm; table. 2), with ^{175}Lu measured in analogue detector mode for many analyses. As accurate pulse-analogue correction factors are difficult to calculate for reaction products (Zack and Hogmalm, 2016), these data points have been excluded from calculated dates. An isochron date of 898 ± 14 Ma (MSWD = 1.7, $n = 10$; Fig. 3, table 2) was calculated using the remaining data points from the Lu-rich core. As some of these data points have >40 times more ^{176}Hf than ^{177}Hf (equating to > 99% radiogenic ^{176}Hf), 'single spot' dates could be calculated (Simpson et al., 2022). The weighted average single spot date is within uncertainty equivalent to the isochron intercept date (901 ± 14 Ma; MSWD =

1.5, $n = 6$; Fig. 3, table 2). We note these extreme $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are exceptional compared to typical metapelitic garnets (e.g. Baxter and Scherer, 2013).

The rest of the data from sample P-1 were pooled to calculate a single isochron. This included data from the rim of the highly Lu enriched garnet, and all the data from a second garnet (which did not display either extremely high $^{176}\text{Hf}/^{177}\text{Hf}$ ratios in its core or evidence of a core-rim age difference). An isochron calculated from the data produced an isochron date of 861 ± 12 Ma (MSWD = 0.91, $n = 173$; Fig. 3, table 2). Two data points were removed from the isochron calculation as they were clear outliers.

Sample TP-1

A single large garnet from the TP-1 sample was analysed in session 1. Similar to the analysed garnet from the Kinloch sample, this garnet did not display evidence for a polyphase history (Fig. 2). Therefore data from both the core and rim have been grouped for the isochron calculation. A date of 462 ± 23 Ma (MSWD = 0.62, $n = 69$; Fig. 3, table 2) was calculated, with a single data point removed due to its large $^{177}\text{Hf}/^{176}\text{Hf}$ uncertainty ($\sim 30\%$ 2σ), associated with a low Lu concentration.

Sample KP-1

A single large garnet from sample KP-1 was analysed in session 1. As the garnet did not display textural or compositional evidence for a multistage history, data from both the core and rim have been used for the isochron calculation. A date of 466 ± 10 Ma (MSWD = 0.81, $n = 81$; Fig. 3, table 2) was calculated, with a single data point removed due to scatter in the down-hole laser signal.

Sample DR-1

A single large garnet displaying textural and composition evidence for partial replacement by biotite was analysed from DR-1 (table 1, Fig. 2) in session 2. Data was collected for the core and the rim (targeting the rim zone that shows evidence for Y enrichment; Figure x). The core produces a date of 856 ± 46 Ma (MSWD = 1.2, $n = 60$; Fig. 3, table 2), with none of the collected data points removed from the isochron calculation.

Lutetium concentrations in the rim range between 3 to 32 ppm. 52 analyses produced a linear array of the data corresponding to an age of 540 ± 14 Ma (MSWD = 1.4, $n = 52$; Fig. 3, table 2) 8 data points that appear to scatter toward the age of the core have been removed. We note that this age should be treated with caution due to potential age mixing (see section 6.3 of the discussion, Fig 3).

Sample M30

Two garnets from sample M30 were analysed in session 2. Compositional images of these garnets suggest a potential core-rim age difference, with the core characterised by lower Y and a significant number of inclusions (mainly quartz, biotite, apatite and rutile), whereas the rim is relatively inclusion free and enriched in Y (Fig. 2). Based on this textural evidence, the data has been divided between core and rim analyses. A date of 478 ± 8 Ma (MSWD = 1.3, $n = 61$; Fig. 3, table 2) is calculated for the cores of the analysed garnets, with a single data point removed due to highly scattered laser signal.

A date of 471 ± 9 Ma (MSWD = 1.3, $n = 60$; Fig. 3, table 2) was calculated for the garnet rim data from sample M30, with none of the collected data points removed from the isochron calculation.

Hence, the core and rim dates are undistinguishable given the analytical resolution of the applied method.

Sample M29

A single large garnet from the M29 sample was analysed in session 2. As this garnet does not display evidence of poly-growth history and data from both the core and rim have been used for the isochron calculation. A date of 472 ± 10 Ma (MSWD = 1.2, $n = 70$; Fig. 3, table 2) was calculated, with none of the collected data points removed from the isochron calculation. Lu concentrations range from 1 to 45 ppm.

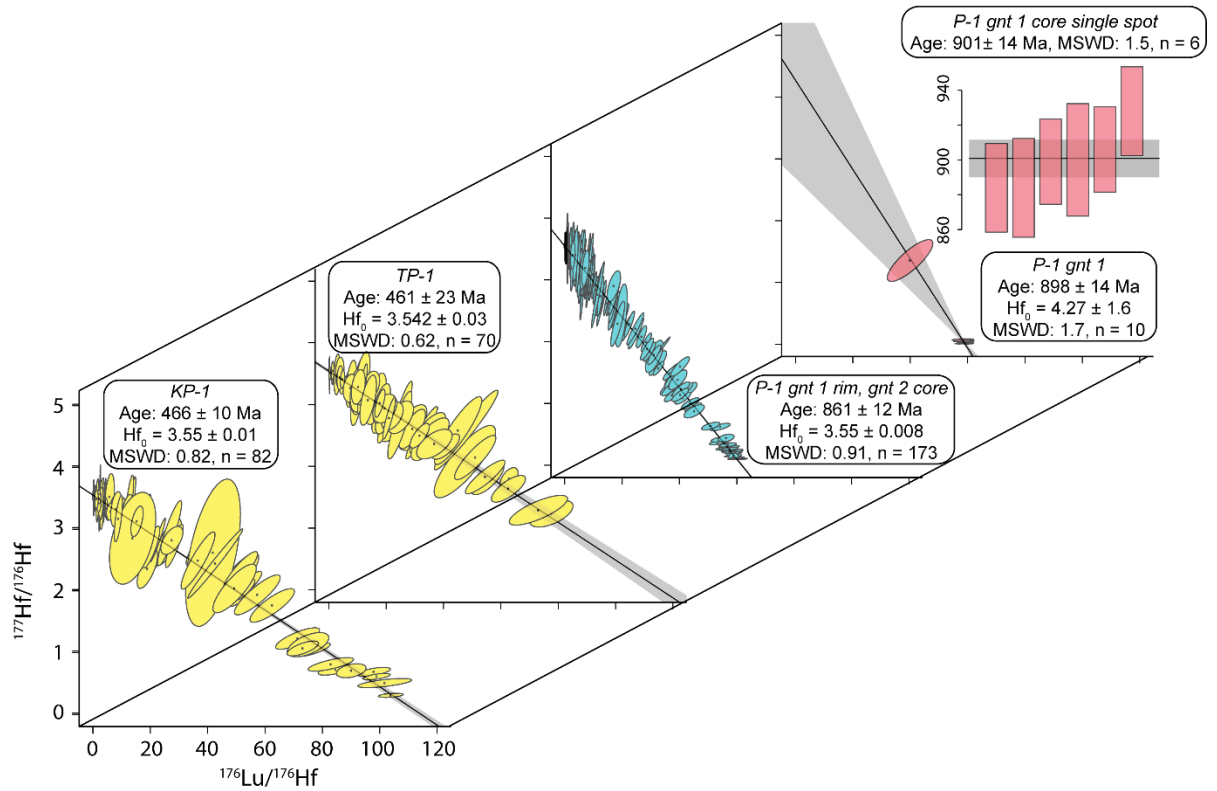
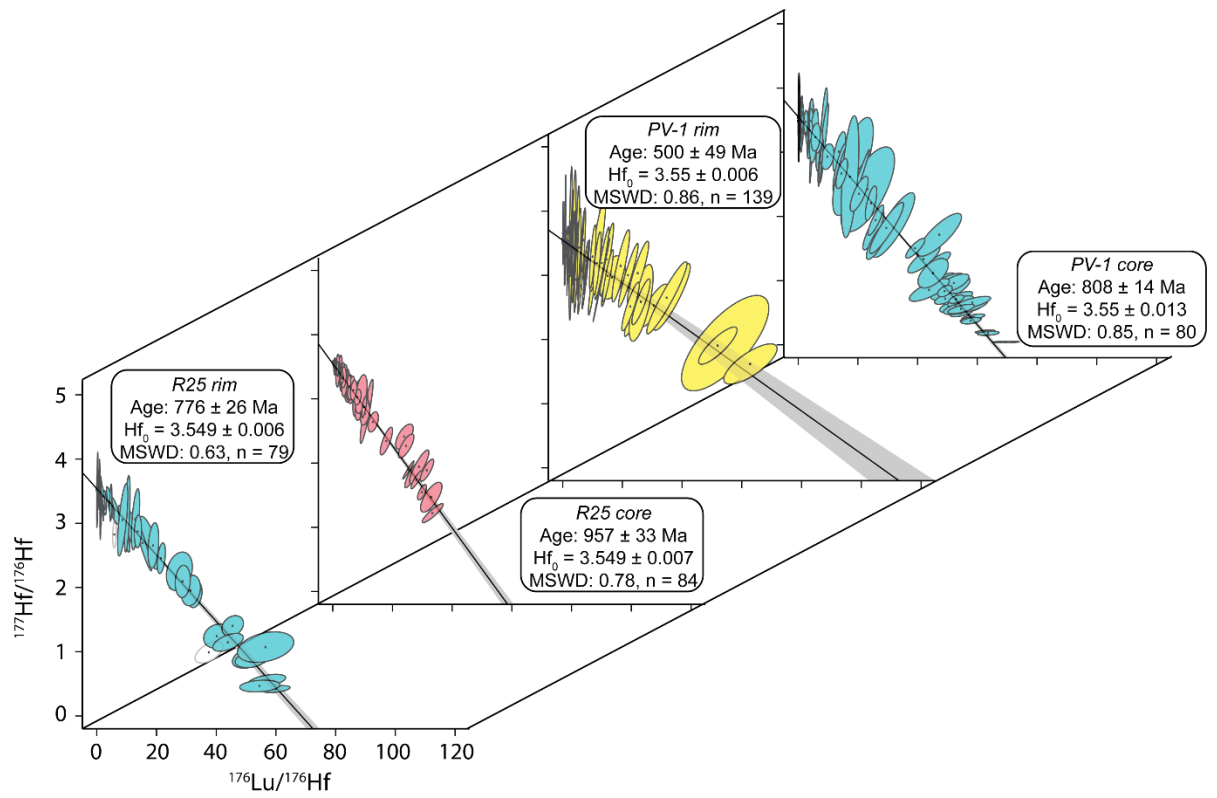
Sample 102-02

Two large garnets and several small garnets from the 102-02 sample were analysed in session 2. Texturally and visually the two garnet types are distinct; Garnet A (quartzfeldspathic domains), and garnet B (phyllosilicate domains). The data has been subgrouped into (1) the cores of the large garnets, (2) the rims of the large garnets, and (3) the small garnets (cores and rims combined). The cores produced a date of 701 ± 30 Ma (MSWD = 1.6, $n = 95$; Fig. 3, table 2), with none of the collected data points removed. The rims give a date of 413 ± 79 Ma (MSWD = 1.3, $n = 45$; table 2), with none of the collected data removed from the isochron calculations.

As the small isochrons plot within uncertainty of the rims of the big garnets (450 ± 26 Ma; table 2), a combined isochron calculated from data from the 102-02 rim and 102-02 small garnets produced a date of 447 ± 25 Ma (MSWD = 1.2, $n = 99$; Fig. 3, table 2).

Sample BHS

Five garnets from sample BHS were analysed in session 2. As there is no evidence for an age difference between garnets, or between cores and rims, data have been combined into the same isochron calculation (Fig. 3). A date of 444 ± 19 Ma (MSWD = 0.89, $n = 104$; Fig. 2, table 3) was calculated, with two data points removed due to highly scattered signals.



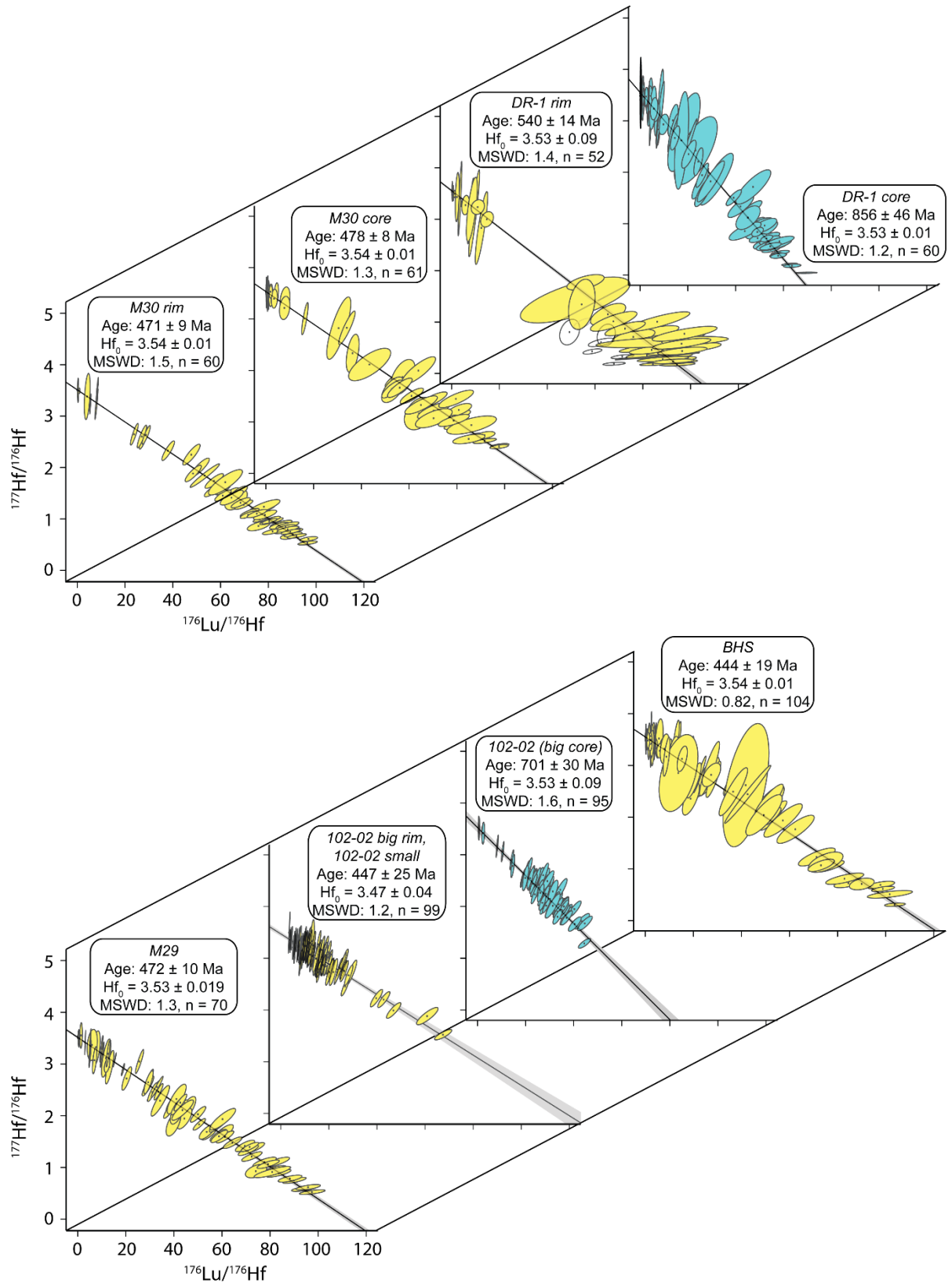


Figure 3.3: Inverse isochron plots of analysed garnet samples. Ellipses are 2σ uncertainties (with vertical bars in weighted average date of P-1 garnet 1 core also showing 2σ uncertainty). Ellipses are coloured based on the orogenic event the corresponding garnet is likely associated with (red = Renlandian, blue Knoydarian, and yellow = Caledonian). Hf_0 refers to the initial $^{177}\text{Hf}/^{176}\text{Hf}$ (Y intercept), which is the inverse of the initial $^{176}\text{Hf}/^{177}\text{Hf}$ of a traditional isochron.

3.7. Discussion

3.7.1. Comparisons with published geochronology

3.7.1.1. In situ garnet Lu-Hf dates reflect the polymetamorphic history of the MoGLE Rocks

Previous geochronological and petrological data indicate that at least three metamorphic events have affected the Moine rocks (Renlandian, Knoydartian, and Caledonian orogenies), inducing metamorphism at a grade that allows garnet growth (Bird et al., 2018; Holdsworth et al., 1994; Strachan et al., 2010). The laser ablation Lu-Hf garnet dates in this study demonstrate good agreement with the previous age constraints on metamorphism within the MoGLE rocks (Fig. 4), with the exception of the P-1 and the rim of DR-1 (Fig. 3; discussed in detail below). The majority of analysed garnets that lack evidence for multiple growth zones produce dates of ca. 470 Ma, consistent with widespread metamorphism during the Grampian stage of the Caledonian orogeny (6.7 kbar, 600 – 700°C; Friend et al., 2000; Baxter et al., 2002; Cutts et al., 2010), similar to previous geochronology from the region (e.g. Bird et al., 2013). Additionally, garnet Lu-Hf dates corresponding to the Renlandian (>6-7 kbar, ~600°C; Bird et al., 2018) and Knoydartian orogenies (P-1 location; ~7.5 kbar, ~650°C; Cutts et al., 2010) have been obtained from the cores of large garnets (Fig. 3, and 4, table 2), demonstrating the power of the *in situ* technique to illuminate the polymetamorphic history of a terrane.

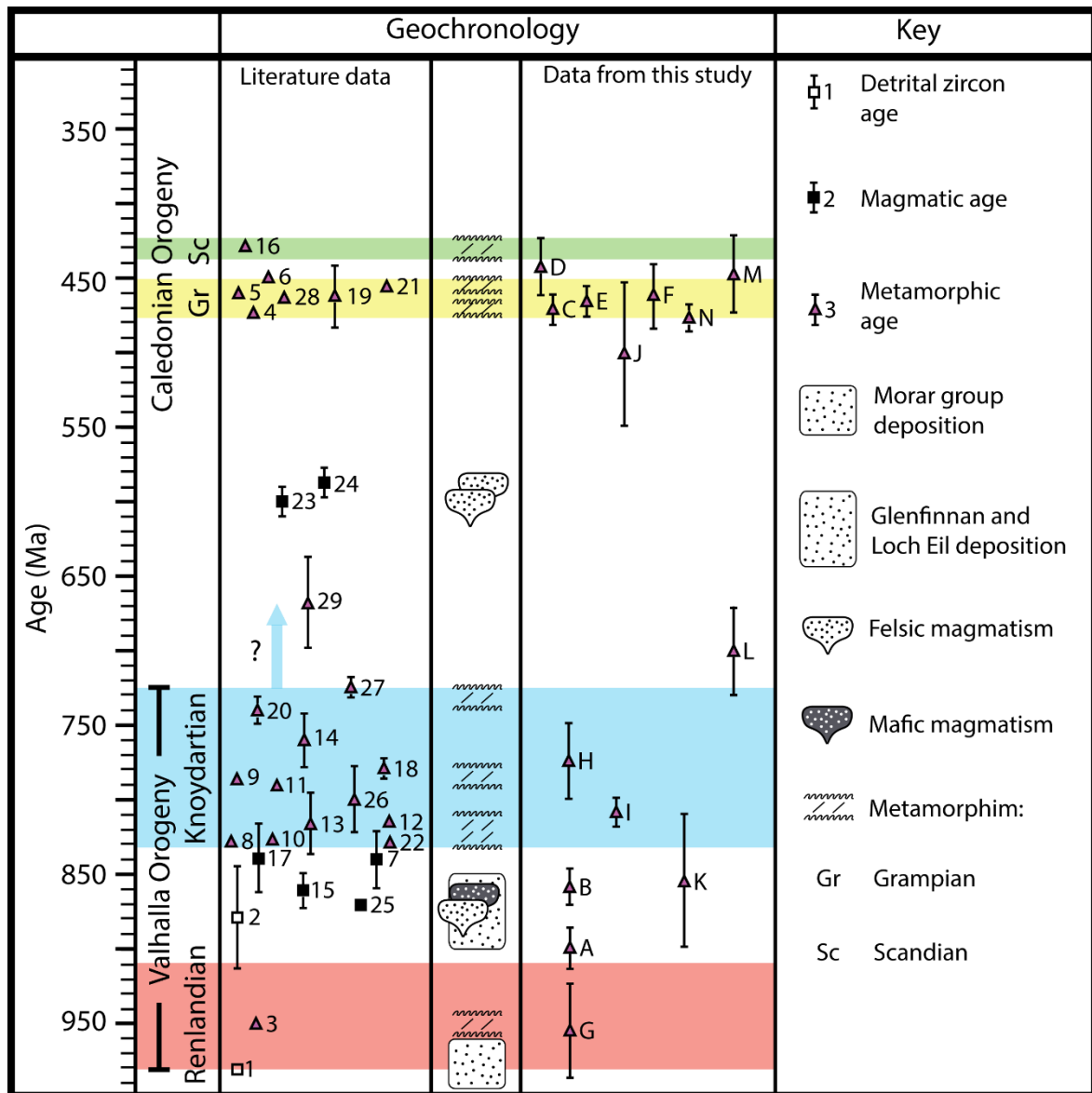


Figure 3.4: Geological timeline for Northwest Scotland comparing literature data (left) to data obtained in this study (right). Orogenic events are shown by coloured bands (Renlandian: red. Knoydartian: blue, Grampian: yellow, Scandian: green). Blue arrow denotes that the Knoydartian Orogeny may extend as late as ca. 670 Ma (Storey et al., 2004). Symbols include uncertainty if uncertainty is larger than the symbol (e.g. box, triangle) used. Numbers for literature data refer to the following: 1: detrital zircon U-Pb (Peters, 2001); 2: detrital zircon U-Pb (Cawood et al., 2004); 3: garnet Lu-Hf (Bird et al., 2018); 4, 5, and 6: garnet Lu-Hf (Bird et al., 2013); 7: zircon U-Pb (Kirkland et al., 2008); 8 and 9: monazite U-Pb (Rogers et al., 1998); 10-14: garnet Sm-Nd (Vance et al., 1998); 15-22: zircon and monazite U-Pb (Cawood et al., 2015); 23 and 24: zircon U-Pb (Kinny et al., 2003b); 25: zircon U-Pb (Millar, 1999); 26, 27, and 28: monazite U-Pb (Cutts et al., 2010); 29: titanite U-Pb (Storey et al., 2003). Numbers for data from this study refer to the following samples: A: P-1 (core); B: P-1 (rest); C: M29; D: BHS; E: KP-1; F: TP-1; G: R25 (ore); H: R25 (rim); I: PV-1 core; J: PV-1 rim; K: DR-1 core; L: 102-02 big (core); M: 102-02 small; N: M30 core. Drum Reid rim has not been included as the date does not have geological significance (see text for discussion) and 102-02 big rim has not been included as the uncertainty is too large.

In cases where previous age constraints exist for samples analysed in this study, the new *in situ* and published conventional Lu-Hf dates are generally in agreement within uncertainty (Fig. 4). For instance, Bird et al. (2013) dated garnets from metapelites and the Ben Hope Sill at Talmine, producing Lu-Hf ages of 448 ± 7.4 (MSWD = 8.3), and 447 ± 1.7 Ma, respectively. Both of these ages overlap with the date obtained from metapelite from Talmine using the *in-situ* garnet Lu-Hf method (TP-1: 462 ± 23 Ma). Further, the Lu-Hf date for the TP-1 metapelite garnet analysed by Bird et al., (2013) produced scattered data (MSWD of 8.3). If this is attributed to a whole-rock

aliquot not in equilibrium with the garnet, then an date of 459 ± 8 Ma can be calculated from the garnet alone (Bird et al., 2013), which is nearly identical to that produced from a sample of the Talmaine pelite in this study. The age obtained by Bird et al (2013) from garnet in the metamorphosed Ben Hope Hill at Talmaine (447 ± 1.7 Ma) is similar to the date obtained in this study (444 ± 19 Ma) from an identical assemblage in the Ben Hope Sill at Kinloch (BHS).

The garnet Lu-Hf date obtained for sample R25 (957 ± 33 Ma; Fig. 3) unambiguously suggests growth during the Renlandian Orogeny (despite a somewhat large uncertainty), providing further evidence that the Morar Group was affected by this event (Bird et al., 2018). Furthermore, Lu-Hf data for the rim of garnet R25 suggests overprinting garnet grew during the Knoydartian Orogeny at ca. 780 Ma. This rim date was not clearly observed in the garnet data by Bird et al. (2018). However, in the study of Bird et al., (2018), there is some scatter in the Lu-Hf rim data, as well as highly scattered (and young) Sm-Nd data (for both garnet core and rim). Hence, the higher spatial resolution of the laser ablation technique allows for more accurate targeting of the garnet rim compared to the technique employed by Bird et al. (2018), which involved crushing garnets, and separating different components (core vs rim) based on the colour of garnet fragments.

3.7.1.2. Differences between Lu-Hf garnet and U-Pb monazite dates

The sample from Milton (102-02) produced different dates from texturally distinct garnet. The cores of large garnets contained within quartzofeldspathic domains give a date of 701 ± 30 Ma. The rims of the garnets in combination with small garnets within biotite folia give a date of 447 ± 25 Ma (Fig. 3). Monazite from this sample has previously been dated by U-Pb, and produced three populations of dates; ca. 825 – 780 Ma, 724 ± 6 Ma, and 462 ± 2 Ma (Cutts et al 2010). The older two populations are associated with monazite grains located in the cores and interiors of the larger garnets, and the youngest population is associated with the monazite grains in the rims of the largest garnets, as well as in the rock matrix (Cutts et al., 2010). These monazite dates were interpreted to correspond to different stages of garnet growth (Cutts et al., 2010). However, the Lu-Hf dates obtained in this study (701 ± 30 Ma for the core, and 450 ± 26 Ma for the rim/smaller garnets) agree within uncertainty with the two younger monazite age populations (724 ± 6 Ma and 462 ± 2 Ma) obtained by Cutts et al., (2010), but not the oldest date (825 – 780 Ma). Given that Lu diffuses more rapidly compared to the relatively immobile Hf (Bloch et al., 2015a) and that peak metamorphic temperatures were lower than the 700°C required for Lu diffusion in 4 mm garnet (Cutts et al., 2010; Block et al., 2015; Bloch et al., 2021), only two likely hypothesis can better explain the missing 825-780 Ma garnet population: One possibility is the oldest population of monazite are relics that predate garnet growth; either from older metamorphism, or detrital monazite. It is also possible some garnets grew between 820 and 780 Ma, but we did not sample such garnets (note, Cutts et al. (2010) only found the 820 – 780 Ma monazite in a single garnet grain). Hence, presently the reasons for the discrepancy between Neoproterozoic monazite and garnet dates in the sample is not clear. However, it is evident the date obtained from the garnet rim, and small garnets in the matrix, are in good agreement with the youngest monazite population.

Unlike the bulk of the samples analysed in this study, the two garnets analysed from sample P-1 (garnet Schist) produced dates (garnet 1 core: $\sim 898 \pm 14$ Ma; garnet 2 core, rim, and garnet 1 rim: 861 ± 12 Ma; Figs. 3, 4) that are not in agreement with previous garnet geochronology from the same location. Vance et al. (1998) obtained Sm-Nd dates of 822.7 ± 4.6 (core) and 788.3 ± 4.4 (rim).

We suggest that the discrepancy between the Sm-Nd derived dates and the Lu-Hf derived dates is most likely due to the differing diffusional responses of the Sm-Nd and Lu-Hf systems during the post-garnet growth thermal history. Diffusion modelling (e.g. Bloch and Ganguly, 2015; Bloch

et al., 2015; Bloch et al., 2020) and empirical geochronological studies (e.g. Smit et al., 2013) have shown the Sm-Nd system in garnet is more susceptible to bulk diffusion modification compared to Lu-Hf, even at conditions below granulite grade. More specifically, however, in rocks belonging to the Morar Group, Bird et al. (2018) showed that Sm-Nd dates are younger than Lu-Hf dates from the same analysed aliquots of garnet. For a sample located close to sample R25 (staurolite-kyanite schist) in this study, Bird et al. (2018) obtained a Lu-Hf age of 950 ± 3 Ma for a garnet core. The corresponding Sm-Nd date is 840 ± 29 Ma. For the garnet rim, Lu-Hf gave a date of 944 ± 7 Ma, which is similarly in sharp contrast to the Sm-Nd date of 705 ± 30 Ma. The grain size, mineral assemblage and metamorphic evolution of the sample analysed by Bird et al. (2018) is quantitatively similar to the P-1 samples analysed by Vance et al. (1998) and in this study (based on P-T modelling of P-1 conducted by Cutts et al., 2010b). Hence, it is apparent that the Sm-Nd system was (at least more substantially) affected by isotopic disturbances after peak garnet growth, and as a consequence, the Lu-Hf system is more appropriate to constrain the age of garnet in complex polymetamorphic terranes.

3.7.2. Lutetium diffusion and its effects on laser ablation Lu-Hf dates

For accurate age date interpretation, it is important to understand the potential effects of isotopic disturbances on geochronological data. For instance, Lu is thought to diffuse faster than Hf in garnet, with the consequence of Lu diffusion being largely controlled by the combination pressure, cooling rate and peak temperature (Bloch et al., 2015). Additionally, significant Lu diffusion is unlikely at temperatures lower than 700 – 800 °C for most garnets at typically orogenic timescales (i.e. a garnet of radius > 1mm would take >1000 Myr for significant modification of Lu-Hf to occur at temperatures of ~700 °C; Bloch and Ganguly, 2015; Bloch et al., 2020). As metamorphic temperatures have not been documented to exceed 700 °C in the MoGLE rocks, we suggest that the garnets analysed in this study are unlikely to have undergone significant volume diffusion of either Lu or Hf.

Only two samples, P-1 (core: 898 ± 14 Ma, rim 861 ± 12 Ma; Fig. 3) and DR-1 (rim: 540 ± 14 ; Fig. 3) produce dates outside the age of expected orogenic events. We consider sample P-1 to be ambiguous, but caution against inferring that the dates produced are either too young or too old due to diffusional decoupling of Lu-Hf. Sample DR-1, however, appears to show mixing of different aged Lu-Hf isotopic compositions (Fig. 5).

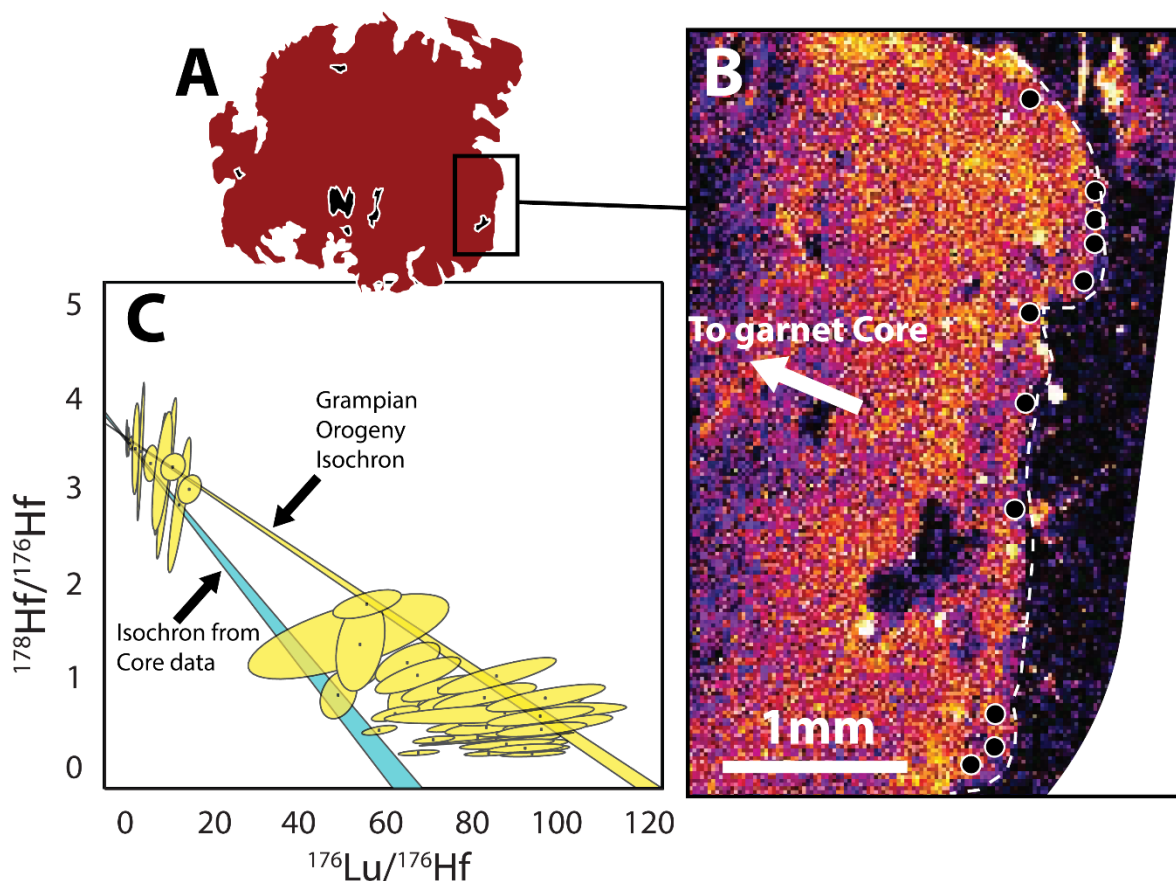


Figure 3.5: DR-1 garnet. **A** shows a cartoon image of the garnet, with red corresponding to garnet and black corresponding to large inclusions/cracks. **B** shows a section of the μ -XRF Y map (red-yellow = high, purple-black = low relative concentration), demonstrating the enrichment in Y toward the rim. Black dots show some laser spot locations. Black rectangle in **A** corresponds to the area of the garnet displayed in **B**. **C** shows all Lu-Hf data (yellow ellipses) for the DR-1 sample, with reference isochron lines for the core age (blue) and the Grampian Orogeny (yellow).

As demonstrated in Figure 5, the rim Lu-Hf data of sample DR-1 is spread between the date of the core and the age of the Caledonian orogeny, indicating that the data may be a mixture between these two events. A purely thermally driven process such as HREE back-diffusion during garnet resorption (e.g. Kelly et al., 2011), as stated above, is unlikely for MoGLE garnets, particularly given DR-1 has a radius of ~ 4 mm, which would limit diffusional decoupling of Lu from Hf (Bloch et al., 2015). What is clear, however, is that the DR-1 garnet edge produces mixed data that is interpreted to indicate some degree of recrystallisation or isotopic resetting during the Caledonian Orogeny (Fig. 5). This demonstrates that within-grain decoupling of Lu from Hf may have a more significant effect on laser ablation Lu-Hf dates compared to dates calculated using conventional bulk sample techniques. We attribute this to the fact that laser ablation analysis samples significantly smaller volumes (individual spot diameter of 100 – 120 μ m, depth of ~ 30 μ m). However, it also demonstrates that the high spatial resolution of the laser ablation Lu-Hf dating technique has the potential to investigate and better understand micron scale diffusion and recrystallisation in garnet.

3.7.3. Poly-metamorphic verse mono-metamorphic garnets side by side.

An intriguing aspect of the garnet dates from the MoGLE rocks is the contrasting records of garnet growth in samples that are located closely together. At Port Vasgo (PV-1), garnets in sampled metapelite interpreted to belong to the Morar Group contain obvious core and rim stages of growth (Fig. 2). The core produced an age of 808 ± 14 Ma, while the rim gives a poorly

defined age that is within uncertainty of the Ordovician Grampian Orogeny (Fig. 3, Fig. 4). In contrast, the nearby (~800 m) sample TP-1 (Fig. 1) has what appears to be a single stage garnet that gives a date of 462 ± 23 Ma (Fig. 3). Similarly in the Kinloch area, sample R25 and KP-1 are both interpreted to come from the Morar Group but have very different records of garnet growth. Sample R25 comes from the Meadie Pelite and contains poly-metamorphic garnets, with the core yielding an age of 957 ± 33 Ma and the rim of 776 ± 26 Ma (Fig. 3). Although separated by several kilometres, sample KP-1 is located along strike, but contains a single stage garnet that gives an age of 466 ± 10 Ma (Fig. 3).

The Morar Group is interpreted to have been deposited between ca. 1000-950 Ma (Krabbendam et al., 2021) and underwent amphibolite-facies metamorphism (at least in part) at ca. 950 Ma (Bird et al., 2018; this study) at P-T conditions of 6-7 kbar and 600 °C (Bird et al., 2018). At these conditions, garnet would have grown in the nearby Kinloch pelite, represented by sample KP-1. However, no Neoproterozoic garnet occurs in the sample. Similarly, the presence of abundant Neoproterozoic garnet in the sampled PV-1 metapelite, but its absence in nearby metapelitic rocks (TP-1), is puzzling.

It is possible that undetected younger stratigraphic units occur within rocks considered to be wholly Morar Group in North Sutherland. However, this is considered unlikely based on the extensive work that has been done in the region (e.g. Bird et al., 2013; Cawood et al., 2004; Holdsworth et al., 1994; Kirkland et al., 2008; Krabbendam et al., 2021; Soper et al., 1998; Strachan et al., 2010). A second possibility is that samples that record Grampian-only ages underwent extensive low-temperature retrogression following Neoproterozoic metamorphism, whereas those that did not undergo significant retrogression preserved Neoproterozoic garnet. Metamorphic terrains commonly undergo hydrous retrogression (Yardley, 2009). This can range from having only minor effects to volumetrically large and wholesale destruction of peak metamorphic assemblages by hydrous low-temperature mineral assemblages (Yardley et al., 2010). Polymetamorphic terrains that have experienced heterogeneous destruction of the original peak assemblages can, in theory, develop complex expressions of polymetamorphism arising from the interference between two or more metamorphic events (e.g. Morrissey et al., 2016). Consequently, if the earliest mineral assemblage is destroyed, an overprinting event will have the appearance of mono-metamorphism, but if the earlier assemblage is preserved, the overprinting event may not be recorded.

In cases where rocks of broadly similar bulk composition look remarkably similar, irrespective of whether they preserve one or more events, the in-situ garnet Lu-Hf dating method can quickly and easily produce dates for many garnets, greatly aiding identification of rocks that effectively record different parts of the polymetamorphic evolution. In the present case, samples such as R25 and PV-1 record Neoproterozoic metamorphism, whereas samples such as TP-1 and KP-1 exclusively record Grampian metamorphism. The LA-ICP-Q-MS/MS garnet Lu-Hf dating method therefore efficiently allows polymetamorphic histories and their associated physical conditions to be unravelled.

3.7.4. Implications of mineral inclusions in garnet for laser ablation Lu-Hf data

Metamorphic garnets commonly incorporate inclusions during crystal growth (e.g. Lagos et al., 2007; Scherer et al., 2000). Lutetium and/or Hf bearing inclusions, such as zircon, titanite, rutile, monazite, xenotime or apatite, may affect calculated garnet Lu-Hf dates, and it is therefore important to be aware of the effect of inclusions on isochron regression calculations. For instance, dominantly Hf bearing inclusions with relatively low Lu such as zircon, titanite or rutile have been documented to affect the accuracy of solution Lu-Hf dates (if the inclusions are derived from a different Hf reservoir to the host garnet), or reduce the precision of the calculated isochron (by decreasing the calculated $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of each aliquot/laser ablation

spot) (Scherer et al., 2000). High Lu/Hf inclusion minerals such as monazite, xenotime and apatite, can also affect the accuracy of the calculated date if they have different Lu-Hf isotope systematics relative to the host garnet (e.g., they crystallised at a different time, or have undergone Lu and/or Hf loss). Scherer et al. (2000) modelled the effect of inclusions on solution garnet Lu-Hf analyses and found that zircons have the largest potential effect on both accuracy and precision of calculated solution Lu-Hf dates. The laser ablation technique produces significantly higher Lu/Hf ratios than typical solution data, so it is important to separately assess the effects of inclusions on laser ablation Lu-Hf data (see table 3, below).

Table 3.3: comparison between isochron dates calculated using filtered (inclusion-free) data, inclusion-free data anchored to extreme initial $^{176}\text{Hf}/^{177}\text{Hf}$ compositions, and the isochron date using all data for reference. Zircon inclusion free data was anchored by adding a data point with Lu-Hf ratios of $^{176}\text{Lu}/^{176}\text{Hf} = 0.00001 \pm 0.000001$, $^{177}\text{Hf}/^{176}\text{Hf} = \text{Anchor} \pm 0.000001$. Extremely high precision was used for the anchor in order to force the isochron through this value, and therefore bias the data as much as possible. The DR-1 rim data were omitted in this exercise due to significant data scatter. Note: uncertainties do not include systematic uncertainties, as correction factor uncertainty and decay constant uncertainty will equally affect all calculations derived from the same set of data points. Consequently, they should not be included when data is compared to itself (but should be included when data is compared to other samples). The initial $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.2860 is an excessively radiogenic value from a depleted and young ultramafic rock (Salters and Zindler, 1995) and the value of 0.2798 is the solar system initial (Iizuka et al., 2015)

Sample	Date (filtered for zircons)	2SE	Date when anchored to $^{176}\text{Hf}/^{177}\text{Hf}$ = 0.2860	Date when anchored to $^{176}\text{Hf}/^{177}\text{Hf}$ = 0.2798	Date (not filtered for zircons)	2SE
PV-1	801	13	806	811	808	11
KP-1	467	11	463	467	465	9
P-1	859	6.1	858	862	861	5.7
rest						
M29	461	11	467	474	472	7.6
M30	480	14	477	481	478	5.7
core						
M30	464	9.4	469	474	471	5.3
rim						
102-02	N/A	N/A	447	510	413	78
Big						
Rim						

To test the effects of zircon inclusions on laser ablation garnet Lu-Hf data, we have calculated dates where all zircon inclusions are removed (by filtering data points in the down-hole signal with Zr above 10 ppm).

Additionally, to demonstrate the possible effects of varying the initial $^{176}\text{Hf}/^{177}\text{Hf}$ of each isochron, we have calculated dates from zircon-free isochrons, anchored to extreme initial $^{176}\text{Hf}/^{177}\text{Hf}$ values; i) 0.2798 (the solar system initial Hf composition; Iizuka et al., 2015), and ii) 0.2860, an excessively radiogenic initial $^{176}\text{Hf}/^{177}\text{Hf}$ that may occur in extreme, restricted, Lu rich reservoirs (i.e. depleted, young ultramafic rocks; Salters and Zindler, 1995).

We emphasize these values have been chosen to demonstrate the *maximum* possible effects of varying the initial $^{176}\text{Hf}/^{177}\text{Hf}$ of each isochron and that these values do not reflect the likely initial values of the samples analysed in this study.

For data obtained in this study, the accuracy of calculated dates does not appear to be significantly affected by the presence of zircon inclusions, with the exception of the common Hf dominated 102-02 Big Rim sample (table 3). Additionally, even if the data is forced through extreme initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios, the dates do not change significantly (table 3). The apparent lack of the affect that both zircons and extreme initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios have on the laser ablation Lu-Hf dates is attributed to; (1) the high number of data points, (2) greater spread toward a more radiogenic, pure garnet composition, and, (3) the generally larger uncertainties for individual analyses by LA-ICPMS derived data compared to solution derived data. Nonetheless, discrete Lu-Hf isotopic datasets that lack high Lu/Hf ratios (such as 102-02 big rim; Fig. 3), are more likely to be significantly affected by zircon inclusions that are not in isotopic equilibrium with the host garnet (table 3). As such, we demonstrate that accurate dates can be calculated from laser ablation spots that include a small to moderate amount of zircon inclusions. Furthermore, zircon inclusions can be used to better define the isochron by providing a low radiogenic anchor in cases where only radiogenic data is obtained.

As garnet is translucent, inclusions below the surface can often be identified prior to the analytical session and avoided during spot analysis. For inclusions inadvertently incorporated into analyses, inspection of down-hole laser ablation signals and calculated trace element concentrations should be used to identify mineral inclusions. For instance, Zr can be used as a proxy for zircon, and Ce as a proxy for LREE-rich inclusions such as apatite or monazite, as, based on our observations, P reacts via charge transfer with NH_3 , and consequently cannot be measured. We suggest that zircons (and other low Lu/Hf minerals) are unlikely to have Zr/Hf ratios lower than the chondritic value of ~ 36 (McDonough and Sun, 1995), although this may not always be the case (for instance, in cases where zircons have formed from highly fractionated magmas, or from hydrothermal fluids). LREE rich inclusions (such as apatite and monazite) are likely to be easily detectable as garnet tends not to incorporate significant concentrations of LREEs (relative to these minerals). HREE rich inclusions, such as xenotime, may potentially effect data, and given the inability to measure P, may also be difficult to detect. Although not measured in this study, the U concentration of garnet may be a good proxy for monitoring xenotime in downhole laser signals, as U is likely to be significantly higher in xenotime compared to metamorphic garnet (generally >100 ppm, and up to several 1000 ppm for xenotime, < 1 ppm for garnet; Fletcher et al., 2004; Millonig et al., 2020). When monitoring U for xenotime, it may be necessary to co-monitor Zr, Ti, Ca and LREEs in order to avoid other U bearing minerals such as zircon, titanite, rutile, apatite or monazite.

We note the relationship described above (in which high Lu/Hf inclusions are more likely to affect laser Lu-Hf data compared to low Lu/Hf inclusions) is the opposite to that observed by Scherer et al. (2000). This is attributed to the enhanced capability of employing the laser ablation technique to better target zones of high Lu/Hf in the analysed garnet, which will produce significantly higher $^{176}\text{Lu}/^{176}\text{Hf}$ ratios, compared to solution Lu-Hf analysis that tend to average various chemical domains of garnet. As discussed above, isochrons constructed using such radiogenic ratios are less likely to be significantly affected by varying the initial $^{176}\text{Hf}/^{177}\text{Hf}$. There are a number of reasons why significantly higher Lu/Hf ratios are produced using laser ablation compared to solution techniques. Firstly, zircon inclusions are difficult to separate from garnet during digestion, meaning solution Lu-Hf data is often contaminated by zircon inclusions (Lagos et al., 2007; Scherer et al., 2000). While techniques exist to preferentially dissolve garnet rather than zircon during sample digestion, these techniques do not necessarily completely remove zircon (e.g. Connelly, 2006; Lagos et al., 2007). Secondly, the laser ablation technique can target high Lu/Hf garnet zones with better accuracy, *and* avoid mixing of high Lu/Hf and low

Lu/Hf zones of garnet (Simpson et al., 2021). For instance, many solution Lu-Hf studies have relied on crushing and hand picking garnet fragments (e.g. Bird et al., 2018; Bird et al., 2013; Ibanez-Mejia et al., 2018; Lagos et al., 2007) and while this technique can be used to minimise zircon inclusions (that are visible under binocular microscope), it may not exclude nano to a few micron-sized inclusions and also will likely mix high Lu garnet zones with low Lu garnet zones. Thus, in summary, the high spatial resolution of the laser ablation method allows for filtering of unavoidable inclusions that might influence the garnet isochron dates, while also enabling the most radiogenic Lu-Hf ratios to be sampled.

3.8. Conclusions and recipe for laser ablation garnet Lu-Hf

While the precision on laser ablation Lu-Hf dates is typically less than that derived from solution-based Lu-Hf geochronology, the laser ablation approach offers enormous efficiency in terms of the number of samples that can be dated, allowing metamorphic age mapping of terrains to be undertaken at an unprecedented scale. In contrast to existing techniques (such as monazite or titanite U-Pb dating), garnet Lu-Hf provides direct constraints on the ages of a major metamorphic mineral, providing more reliable constraints on metamorphism.

Importantly, there are some differences between the treatments of laser ablation data compared to solution Lu-Hf data. For instance, the laser ablation data typically produces more radiogenic Lu-Hf ratios with higher uncertainties compared to solution Lu-Hf. This means that high Hf inclusions, such as zircon tend not to have a significant effect on calculated dates.

In future studies, however, it may be beneficial to combine the rapid data acquisition of laser ablation Lu-Hf with the high precision of solution Lu-Hf. For instance, laser ablation Lu-Hf may not have the necessary precision to distinguish metamorphic events that are close together, whereas solution Lu-Hf may be able to. We also suggest that the laser ablation Lu-Hf method can be used to explore complex metamorphic behaviour, such as different garnet growth histories from rocks along strike from each other, such as exemplified in this contribution/work. Micron scale processes, such as recrystallization and/or diffusion can also be examined, taking advantage of the high spatial resolution of laser ablation analysis.

There are a number of factors that potentially can improve the precision and accuracy of laser-derived Lu-Hf isotopic data from both a sample selection perspective as well as within the applied analytical methodology. Based on our observations, we recommend the following considerations when choosing samples:

Lutetium is thought to partition more readily into garnet in metapelitic rocks compared to metabasic rocks (e.g. Kohn, 2009; Lapen et al., 2003; Skora et al., 2006). Therefore, during primary sample selection, if there are garnet-bearing metasedimentary rocks interlayered with garnet-bearing mafic rocks, metasedimentary lithologies are likely better sampling targets. Garnets from mafic rocks, however, can still produce useful data (e.g. data derived from the Ben Hope Sill garnets in this study (BHS; Fig. 3) produced a meaningful age.

Techniques for imaging of mineral chemistry, (e.g. μ XRF, EPMA, and/or LA-ICP-MS) are important. Firstly, such techniques can be used to determine Lu zonation (or a Lu proxy, such as Y; Tamblyn et al., 2022) to target both high and low Lu zones in garnet to maximise spread along the calculated isochron. Secondly, imaging techniques can also be used to determine both the locations and types of inclusions, which should then be avoided during laser ablation analysis. Inclusions can also be identified using traditional petrographic methods.

Due to the relatively low precision of individual laser ablation Lu-Hf data points, we recommend obtaining a large data set per expected age. In this study we used between 60 and 100 laser ablation spots per age (where possible). However, the optimal number of laser spots is likely to be a function of garnet age, Lu and Hf concentration and Lu and Hf zonation, and consequently

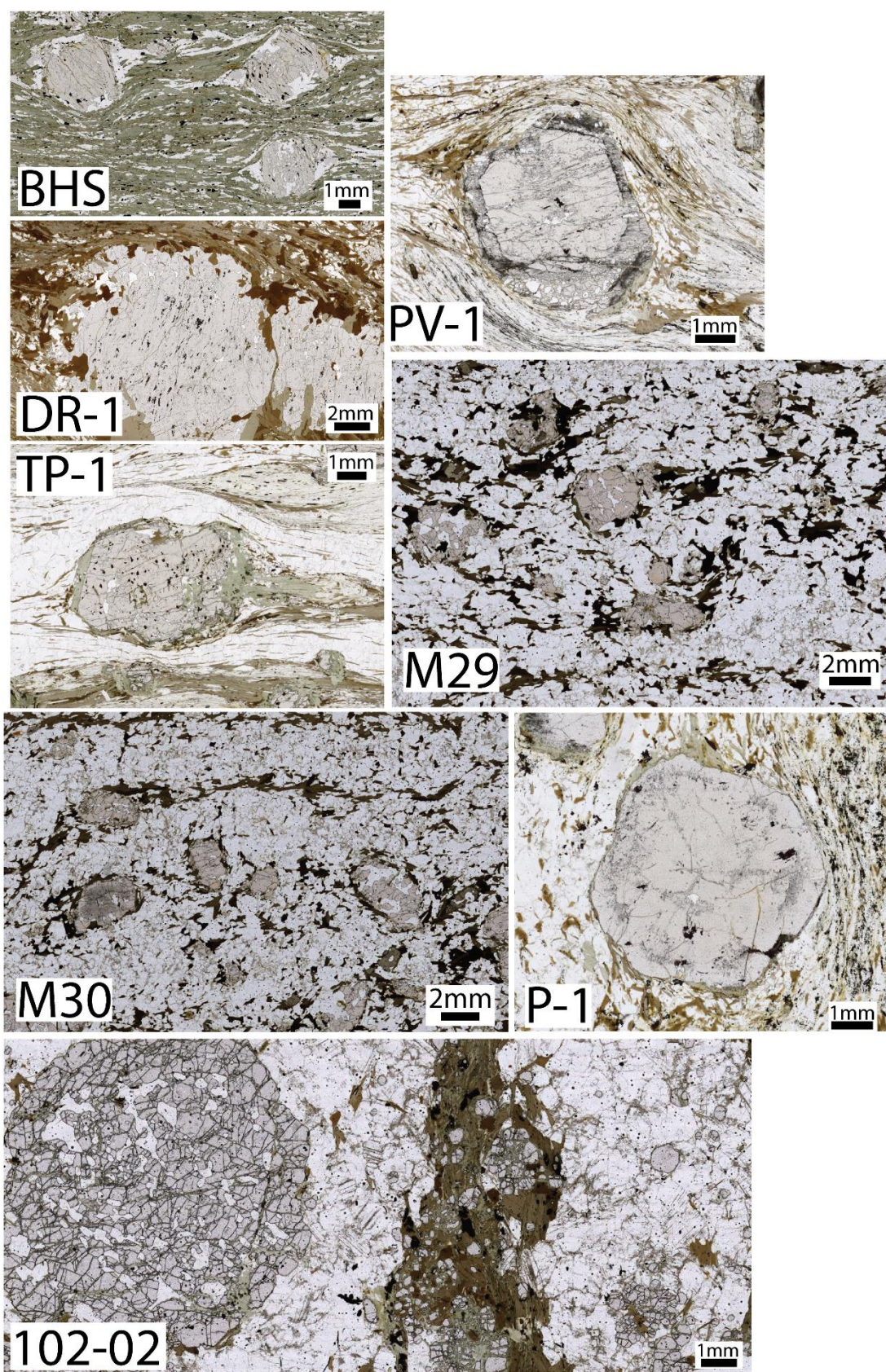
be sample dependent. For instance, an old, single stage garnet with a strongly Lu enriched core is likely to require fewer laser spots than a younger, lower Lu and less zoned garnet. Further, it may be necessary to either select large garnets (> 1 – 2 mm radius) or analyse multiple garnets in order to produce sufficient data for a meaningful date calculation.

Inclusions do not necessarily need to be removed from calculated isochrons, however the potential effects of these inclusions need to be assessed. We recommend the removal of all HREE rich inclusions, as these may bias age calculations. Hf rich inclusions (such as zircon) may not necessarily need to be removed, particularly in cases where the garnet has a significant radiogenic component (refer to section 6.4 for details).

Acknowledgements:

The Authors would like to thank Adelaide Microscopy for help with instrumentation. S. Glorie is supported by an ARC Future Fellowship grant (FT210100906). M. Hand is supported by Australian Research Council grant DP220103037. Rob Strachan is thanked for provide sample R25.

3.9. Chapter 3 appendix A: Supplementary figures and tables.



Appendix figure 3.1: photomicrographs of analysed samples. Presented images are from thin sections made from the same hand sample as rock blocjs that were analysed using μ -XRF and LA-ICP-Q-MS/MS Lu-Hf

Sample descriptions:

BHS: Hornblende (green), quartz (pale) and ilmenite (black), wrapping ~2 mm diameter garnets.

PV-1: Two stage garnet wrapped by quartz, muscovite and biotite foliations.

DR-1 Large (~8mm diameter) hypidioblastic garnet in biotite foliation (brown) with minor quartz (clear). Dark ilmenite inclusions can be seen in the garnet.

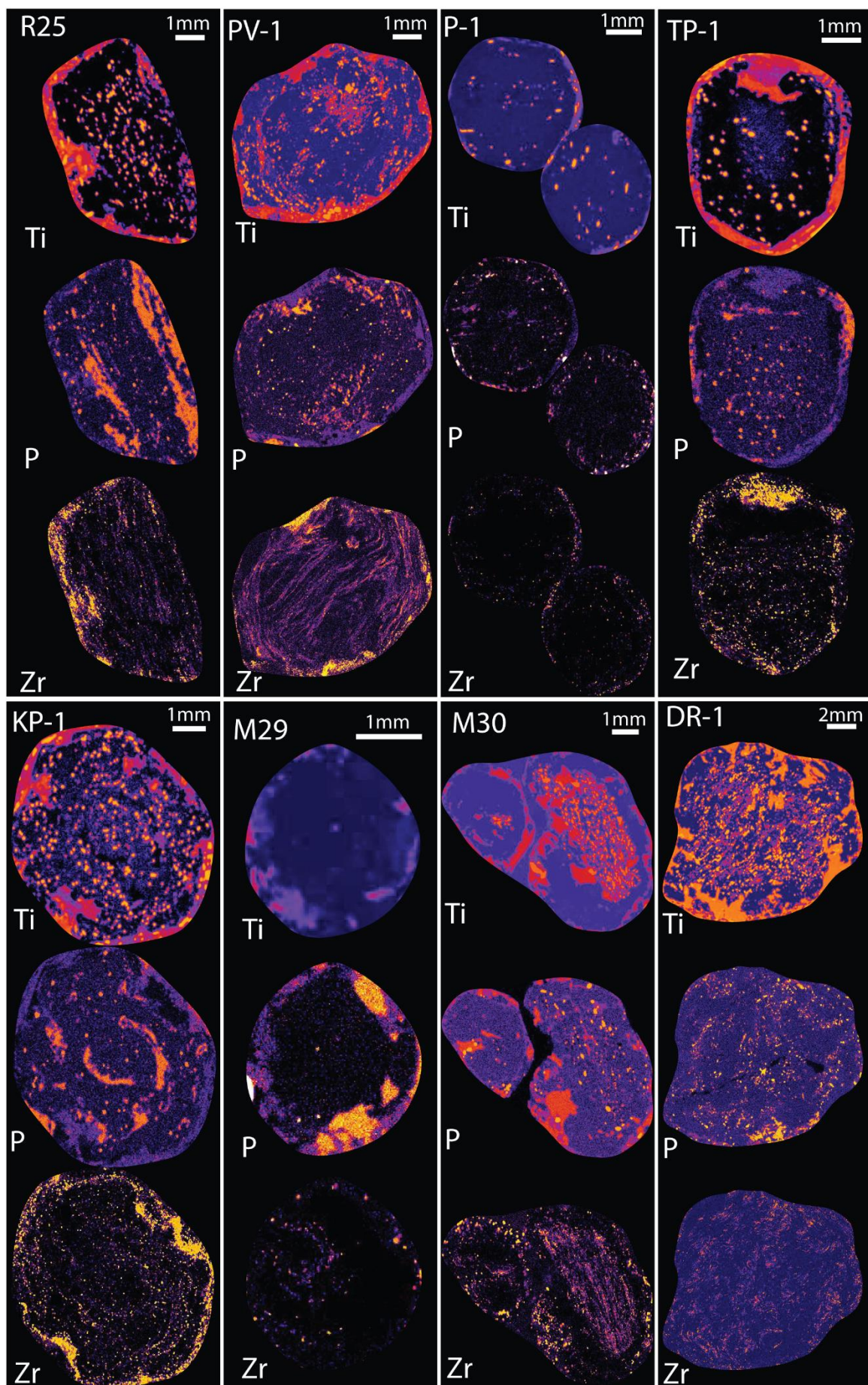
TP-1: Garnet (with dark ilmenite inclusions) wrapped by quartz (clear) and minor muscovite (brown). Chlorite (pale green) can be seen replacing the garnet.

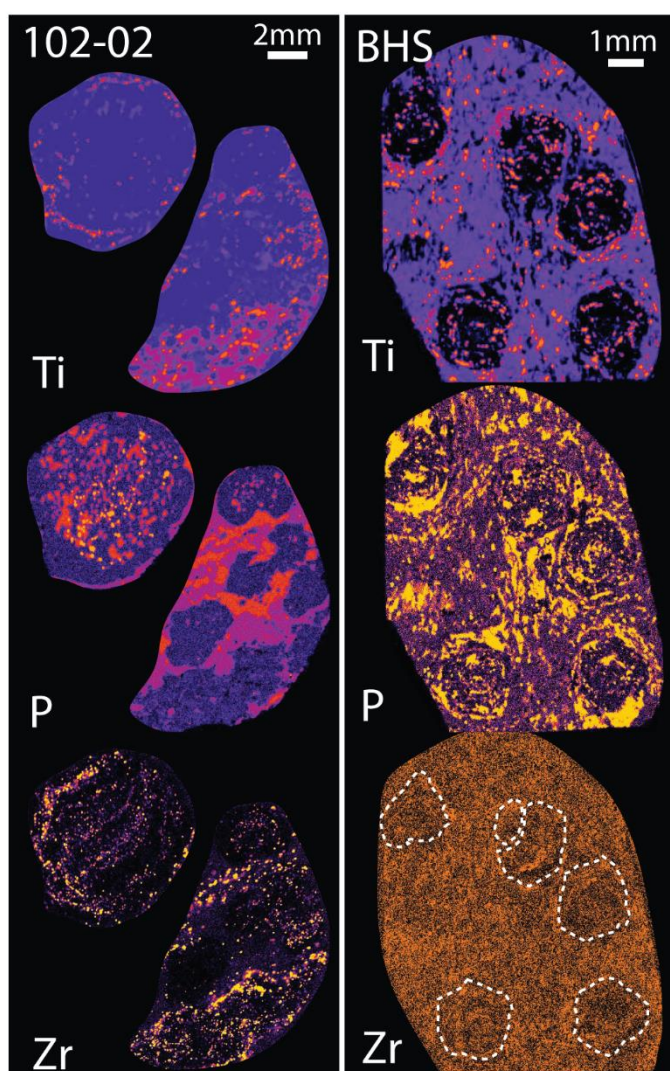
M29: several garnets in quartz and plagioclase, with subtle banding present (distinguished by plagioclase rich bands and minor biotite layers). Pale minerals are quartz and plagioclase (quartz is generally slightly more clear than plagioclase).

M30: Similar to M29; plagioclase rich layers with thin bands of biotite surrounding garnet crystals.

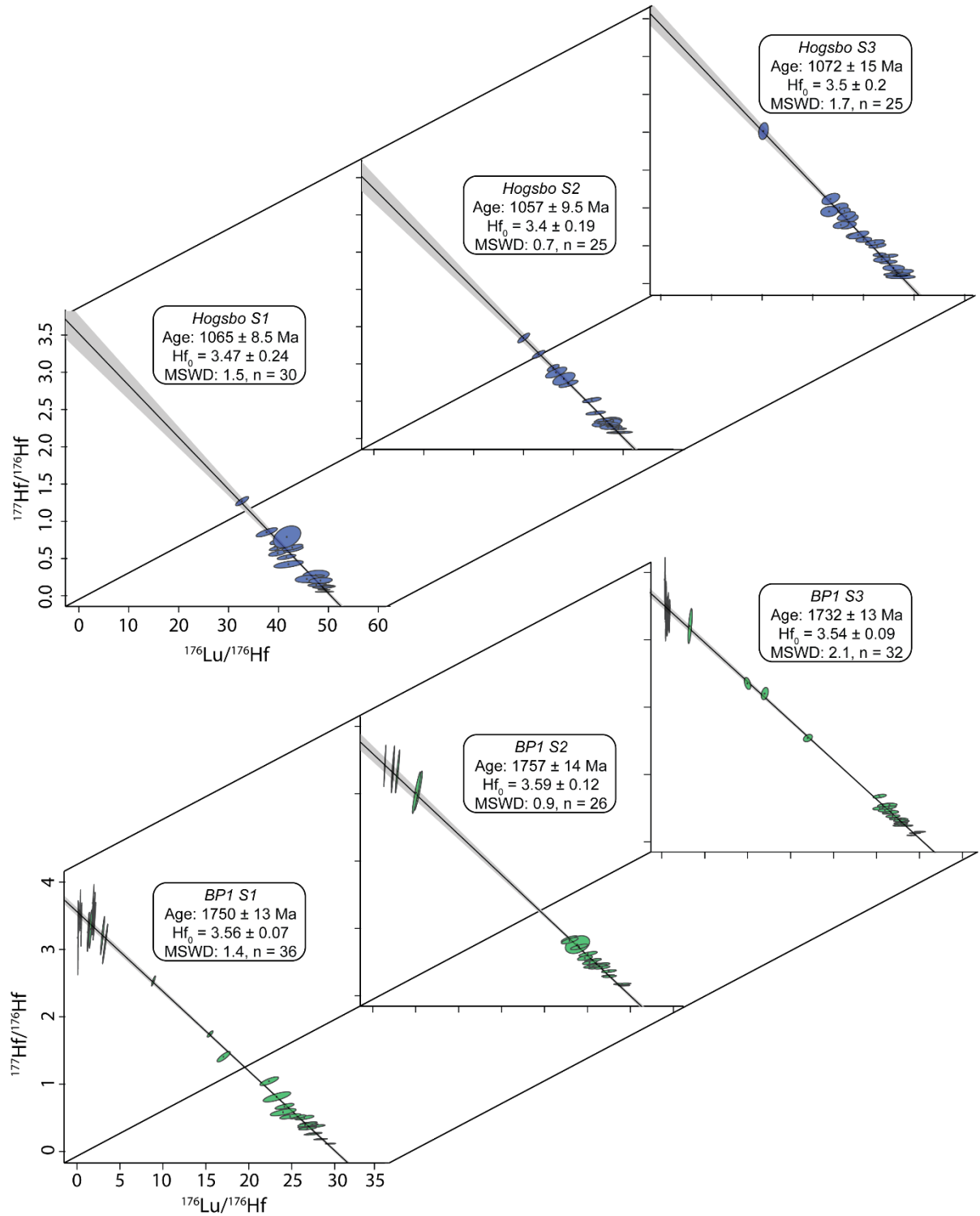
P-1: Garnet surrounded by quartz/muscovite foliations. Dark mineral is ilmenite. Chlorite (pale green) is replacing garnet).

102-02. Garnet in band of quartz and plagioclase (both pale, but plagioclase can be distinguished based on the presence of twinning. A thin, biotite rich layer, has smaller garnet crystals within it. Pale green chlorite can be seen replacing the large garnet, as well as biotite and garnet in the biotite rich layer.





Appendix figure 3.2: extra μ -XRF maps (P, Ti, Zr). The mapped element is labelled in the bottom left corner. The maps show relative concentrations, and are coloured with hotter colours corresponding to high concentrations and cooler colours corresponding to lower concentrations (e.g. yellow = high, red = intermediate, purple = low, and black = below detection).



Appendix figure 3.3: Inverse Isochron plots for analysed garnet standards. Hogsbo garnet data is presented prior to correction to its expected age (1029 ± 1.7 Ma). BP-1 data is presented after correction to Hogsbo. See methods section for details on correction procedure. Ellipses are 2σ uncertainties. Hf_0 refers to the initial $^{177}\text{Hf}/^{176}\text{Hf}$ (Y intercept), which is the inverse of the initial $^{176}\text{Hf}/^{177}\text{Hf}$ of a traditional isochron.

Appendix table 3.1: laser and mass spectrometer analytical parameters

plasma parameters

<i>RF power</i>	1350 W
<i>Sample Depth</i>	4 mm
<i>Ar carrier gas</i>	0.95 L/min
<i>He carrier gas</i>	0.38 L/min
<i>N₂ addition</i>	4 mL/min
Lens Parameters	
<i>Extract 1</i>	-6 V
<i>Extract 2</i>	-140 V
<i>Omega Bias</i>	-70 V
<i>Omega Lens</i>	7.0 V
<i>Q1 entrance</i>	-10 V
<i>Q1 exit</i>	-1.0 V
<i>Cell focus</i>	3.0 V
<i>Cell Entrance</i>	-120 V
<i>Cell Exit</i>	-100 V
<i>Deflect</i>	9 V
<i>Plate Bias</i>	-90 V
Q1 parameters	

<i>Q1 bias</i>	-1.0 V
<i>Q1 Prefilter Bias</i>	-10.0 V
<i>Q1 Postfilter Bias</i>	-10.0 V
<i>Cell Parameters</i>	
<i>He flow</i>	1.0 mL/min
<i>10% HN₃ + 90% He</i>	3 mL/min
<i>gas flow</i>	
<i>Octopole bias</i>	-5.0 V
<i>Axial Acceleration</i>	2.0 V
<i>Octopole RF</i>	180 V
<i>Energy</i>	-15.0 V
<i>Discrimination</i>	
<i>Q2 parameters</i>	
<i>Q2 bias</i>	-15 V
<i>Wait time offset</i>	2ms
<i>Analysis</i>	
<i>Parameters</i>	
<i>Laser wavelength</i>	193 nm
<i>Laser fluence</i>	10 J/cm ²
<i>Laser spot</i>	43 - 120 μm (30 μm; NIST610 glass)
<i>diameter</i>	

<i>Laser repetition rate</i>	10 Hz
<i>washout</i>	30 s (post cleaning pulse) + 20 s (post analysis)
<i>Background</i>	30 s
<i>Analysis time</i>	40 s
<i>Isotopes</i>	^{27}Al (2), ^{24}Mg (2), ^{43}Ca (2), ^{47}Ti (2), ^{57}Fe (2), ^{88}Sr (2), ^{89}Y (2), ^{90}Zr (2), ^{140}Ce (2), ^{146}Nd (2), ^{147}Sm (2), ^{172}Yb (10), ^{175}Lu (10), $^{175+82}\text{Lu}$ (100), $^{176+82}\text{Hf}$ (150), $^{178+82}\text{Hf}$ (150)
<i>measured/dwell times (ms)</i>	

Supplementary data tables can be found at:

<https://doi.org/10.25909/21952649.v1>

Chapter 4: *In situ* apatite and carbonate Lu-Hf dating reveals the timing of Cu mineralisation and remobilisation within an IOCG system (Vulcan prospect, South Australia)

Supplementary data tables can be found at:

<https://doi.org/10.25909/21952655.v1>

<https://doi.org/10.25909/21952658.v1>

Statement of Authorship

Title of Paper	<i>In situ</i> apatite and carbonate Lu-Hf dating reveals the timing of Cu mineralisation and remobilisation within an IOCG system (Vulcan prospect, South Australia)
Publication Status	☐ Published ☐ Accepted for Publication ☐ Submitted for Publication ☒ Unpublished and Unsubmitted work written in manuscript style
Publication Details	N/A

Principal Author

Name of Principal Author (Candidate)	Alexander Simpson		
Contribution to the Paper	Conceptualisation, experimentation, and paper drafting		
Overall percentage (%)	80		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	18/01/2023

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

- i. the candidate's stated contribution to the publication is accurate (as detailed above);
- ii. permission is granted for the candidate to include the publication in the thesis; and
- iii. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	Stijn Glorie
-------------------	--------------

Contribution to the Paper	Conceptualisation, paper drafting, and primary supervision		
Signature		Date	18/01/2023

Name of Co-Author	Martin Hand		
Contribution to the Paper	Conceptualisation, sampling, paper drafting, and secondary supervision		
Signature		Date	23/01/2023

Name of Co-Author	Carl Spandler		
Contribution to the Paper	Paper drafting and secondary supervision		
Signature		Date	23/01/2023

Name of Co-Author	Marija Dimitrieva		
Contribution to the Paper	Sampling, geological interpretation, paper drafting		
Signature		Date	18/01/2023

Name of Co-Author	Greg Swain		
Contribution to the Paper	Sampling, geological interpretation, paper drafting		
Signature		Date	23/01/2023

4.1. Abstract:

Iron-Oxide Copper-Gold (IOCG) deposits can be difficult to accurately date given the general lack of robustly datable minerals that form cogenetic with IOCG mineralisation. The development of laser ablation inductively coupled plasma quadrupole tandem mass spectrometry (LA-ICP-Q-MS/MS) opens new opportunities to accurately and rapidly date a variety of hydrothermal minerals. Here we present *in situ* Lu-Hf and U-Pb age constraints on mineralisation at the Vulcan IOCG prospect in the Olympic copper-gold province, South Australia. We use dating of hydrothermal apatite to demonstrate that mineralisation at Vulcan largely occurred at ca. 1595 Ma, consistent with other deposits in the region, including the world class Olympic Dam deposit. The data indicates, that, while the apatite U-Pb system can record primary apatite growth ages, the Lu-Hf system produces much less ambiguous data. For instance, the apatite U-Pb data was strongly influenced by Pb bearing inclusions, however Hf (or Lu) bearing inclusions were much less significant. In addition, we report the first *in situ* Lu-Hf ages for bastnasite, dolomite, and siderite, and assess their potential for constraining ore deposit geochronology. Although further work is required to fully constrain closure temperature systematics, our data indicate that dolomite Lu-Hf dates can provide primary constraints on the timing of ore mineral crystallisation during brecciation and IOCG mineralisation, and can retain growth ages over an extended time period (~1600 myr). We further reveal the age of texturally late Cu-bearing carbonate veins (~610-570 Ma), illustrating that the carbonate Lu-Hf method provides an ability to directly date Cu remobilisation. This has important implications to mineral exploration, as the transported Cu might now be hosted and concentrated in time-equivalent sedimentary deposits.

4.2. Introduction:

A robust geochronological framework is crucial to develop effective strategies for mineral exploration, particularly in ancient geological terranes with complex evolutionary histories. While magmatism and volcanism in mineralised terranes, can often be precisely dated using zircon U-Pb geochronology, there are a number of reasons why directly dating of hydrothermal mineral assemblages within a deposit can be beneficial. For instance, given the wide variety of potential sources of mineralising fluids and mechanisms for metal precipitation (McCuaig et al., 2010), determining synchronicity between mineral precipitation from a given fluid and a given geological event (e.g. magmatism or fault movement) can be an important step in determining the origins of a deposit. Although other lines of evidence (such as petrology and mineral or whole rock chemistry) can be used to infer the origin of a mineral deposit, this can be complicated if multiple events have affected the region (e.g. multiple magmatic intrusions). Even when mineral deposit genesis is well constrained, this may not tell the full story. For instance, mineral deposits can undergo a variety of post-formation events that may affect their economic potential, such as faulting, erosion, metamorphism, as well as subsequent hydrothermal activity; (e.g. Bastrakov et al., 2007; Duuring et al., 2010; Ehrig et al., 2021; Hall, 2018). Additionally, as the global demand for metals rises, the mineral industry is increasingly searching for economic mineralisation under cover (e.g. Reid, 2019) and within cover sequences (e.g. Leach et al., 2005). It can be challenging to fully understand deeply buried mineral deposits due to the lack of outcrop and reliance on drill core samples. Furthermore, understanding the timing of potential remobilisation events might dictate if exploration efforts should focus more on basement (hypogene) vs sedimentary-hosted (supergene) mineral systems.

Zircon is one of the most commonly dated minerals (Faure and Mensing, 2005), and is capable of providing robust ages on a variety of geological processes, including mineral deposits (e.g. Campbell et al., 2014; Claoue'-Long et al., 1990; Zhai et al., 2022). However, zircon cannot always be relied upon when dating mineral deposits. For instance, it does not always occur in cogenetic context with

ore minerals (e.g. no zircon was identified in any of the samples analysed in this study). This is likely due to zircon only being soluble in limited fluid compositions (e.g. alkaline fluids), and that large scale hydrothermal transport of zirconium is unlikely (Wilke et al., 2012). Consequently, other techniques must be explored in order to better understand mineral deposit formation and subsequent activity. The development and application of novel laser ablation geochronological techniques using reaction-cell mass-spectrometry (e.g. Simpson et al., 2021, 2022) can overcome this issue, as a variety of hydrothermal minerals such as apatite and carbonates, which grow in cogenetic context with ore minerals and/or have the ability to remobilise ore minerals, can now be robustly and directly dated. In contrast to traditional bulk-dissolution approaches (Barfod et al., 2003; Maas et al., 2022) this novel laser-ablation technique has the potential to quickly and efficiently obtain direct, spatially resolved, age constraints for such hydrothermal minerals.

The Olympic Cu-Au Province, in South Australia, hosts a variety of mineral deposits and prospects, the most well known example being the world class Olympic Dam iron oxide copper gold (IOCG) deposit (Hand et al., 2007; Reid, 2019; Skirrow et al., 2007). The Olympic Cu-Au Province is a several hundred kilometres stretch of Proterozoic to Archean crust (Hand et al., 2007; Reid, 2019). IOCG mineralisation is thought to be broadly synchronous with the intrusion of the ~1.59 Ga Hiltaba Suite and its extrusive equivalent, the Gawler Range Volcanics (GRV) (Johnson and Cross, 1995; Reid, 2019; Skirrow et al., 2007; Skirrow et al., 1999). Many of the deposits and prospects of the Olympic Cu-Au Province are buried under cover (Reid, 2019), which can make constraining their nature and origin difficult. Further, recent studies at the Olympic Dam deposit have indicated the presence of multiple reworking events, spanning from original deposit formation at ca. 1.6 Ga to the ca. 500 Ma Delamerian Orogeny (e.g. Ehrig et al., 2021; Maas et al., 2022).

While traditional geochronometers have provided a wealth of data on the regional tectonic history of the Olympic Cu-Au Province, detailed geochronology at the deposit scale is often lacking, and tends to be limited to zircon U-Pb age constraints, which do not necessarily directly relate to mineralisation. The Vulcan prospect, within the Olympic Cu-Au Province, provides a natural laboratory to test novel geochronological methods (such as *in situ* Lu-Hf) and to obtain a detailed geochronological framework for the timing of mineralization and potential ore remobilization. The main advantages of the novel methodology are: (1) very rapid data acquisition with minimal sample preparation, (2) geochronological data is obtained *in situ*, preserving the petrogenetic context; and (3) the ability to date mineral phases that commonly form during alteration/mineralisation (such as apatite and calcite) including minerals that have been proven difficult to robustly date (e.g. calcite; Roberts et al., 2020).

As evidence suggests Olympic Dam has undergone multiple temporally distinct events that may involve 'upgrading' or mobilisation of economic metals (e.g. Ehrig et al., 2021), accurate geochronology is important, particularly if the geochronology can be interpreted within a petrological context. U-Pb dating has been applied to a variety of minerals that can form in hydrothermal systems, such as apatite (Cherry et al., 2018; Chew et al., 2014), titanite (Cherry et al., 2018; Chew et al., 2014; Spandler et al., 2016), Fe-oxides (Ciobanu et al., 2013; Courtney-Davies et al., 2020), monazite (Cave et al., 2022; Cherry et al., 2018), xenotime (Rasmussen et al., 2007) and potentially carbonates (Roberts et al., 2020). There are, however, some complications: Firstly, the most abundant mineral that can be dated in IOCG deposits is often apatite, although Fe-oxides can occasionally be dated (Ciobanu et al., 2013; Corriveau et al., 2016; Courtney-Davies et al., 2020; Skirrow, 2022), but apatite has a relatively low closure temperature to volume diffusion of Pb (~450°C; Cherniak et al., 1991; Cochrane et al., 2014) and is susceptible to resetting during fluid interactions (Harlov et al., 2005). While IOCGs such as Vulcan are thought to form at temperatures

lower than $\sim 450^\circ\text{C}$ (e.g. Corriveau et al., 2016; Skirrow, 2022) post-formational heating and/or recrystallisation may disturb the isotopic U-Pb system in apatite. Secondly, apatite, titanite and carbonates can incorporate Pb into their crystal structure during formation (Chew et al., 2014; Roberts and Walker, 2016). Given Pb is highly mobile in many ore-forming fluids (Brugger et al., 2016), this can make accurate U-Pb ages difficult to calculate due to the large common Pb corrections that are required. Further, traditionally dated minerals will not necessarily occur in every mineral assemblage within a deposit, hence it is beneficial to have access to a wide range of datable minerals in order to best constrain mineralogically diverse domains. Fortunately, new advances in LA-ICP-Q-MS/MS beta decay geochronology have greatly expanded the range of minerals that can be rapidly dated. Consequently, multi-mineral beta decay geochronology may provide an excellent avenue to complement existing U-Pb dating, and may be able to provide more robust ages for hydrothermal processes.

In this paper, we apply in situ Lu-Hf dating, as the Lu-Hf system has been demonstrated to be resistant to isotopic resetting in both apatite and calcite (e.g. Barfod et al., 2005; Gillespie et al., 2022; Glorie et al., 2023; Simpson et al., 2022). Of particular interest is the recent development of calcite Lu-Hf dating, which may be able to overcome many of the issues associated with carbonate U-Pb geochronology in mineral deposits (Maas et al., 2022; Simpson et al., 2022). Hafnium is relatively immobile in many hydrothermal fluids (Brugger et al., 2016), and is strongly rejected during crystallization of common hydrothermal minerals such as apatite (Barfod et al., 2005; Glorie et al., 2021) and carbonates (e.g. calcite, dolomite, and siderite; Maas et al., 2022; Simpson et al., 2022). Hence, the Lu-Hf system may be able to provide more reliable dates for hydrothermal minerals where U-Pb generally seems to fail. Using the Vulcan IOCG prospect as an example, we assess the advantages and limitations of hydrothermal apatite Lu-Hf dating compared to apatite U-Pb dating, as well as explore the potential for laser ablation Lu-Hf dating of other hydrothermal carbonates minerals (dolomite, siderite and bastnasite).

4.3. Geological Background

The Gawler Craton, South Australia, is an approximately 440 000 km² Mesoarchean to Mesoproterozoic rock system (Hand et al., 2007; Reid & Hand, 2012) that hosts the world class IOCG deposit Olympic Dam (Hand et al., 2007; Reid, 2019), as well as other large IOCG deposits (such as Carrapateena and Prominent Hill), and numerous smaller deposits and prospects (e.g. Bastrakov et al., 2007; Skirrow et al., 2007). This system of IOCG mineralisation, defined as the Olympic Cu-Au Province, formed in the eastern part of the Gawler Craton (Fig. 4.1) at ca. 1.59 Ga in temporal association with voluminous extrusive and intrusive felsic-dominated magmatism (e.g. Skirrow et al., 2007).

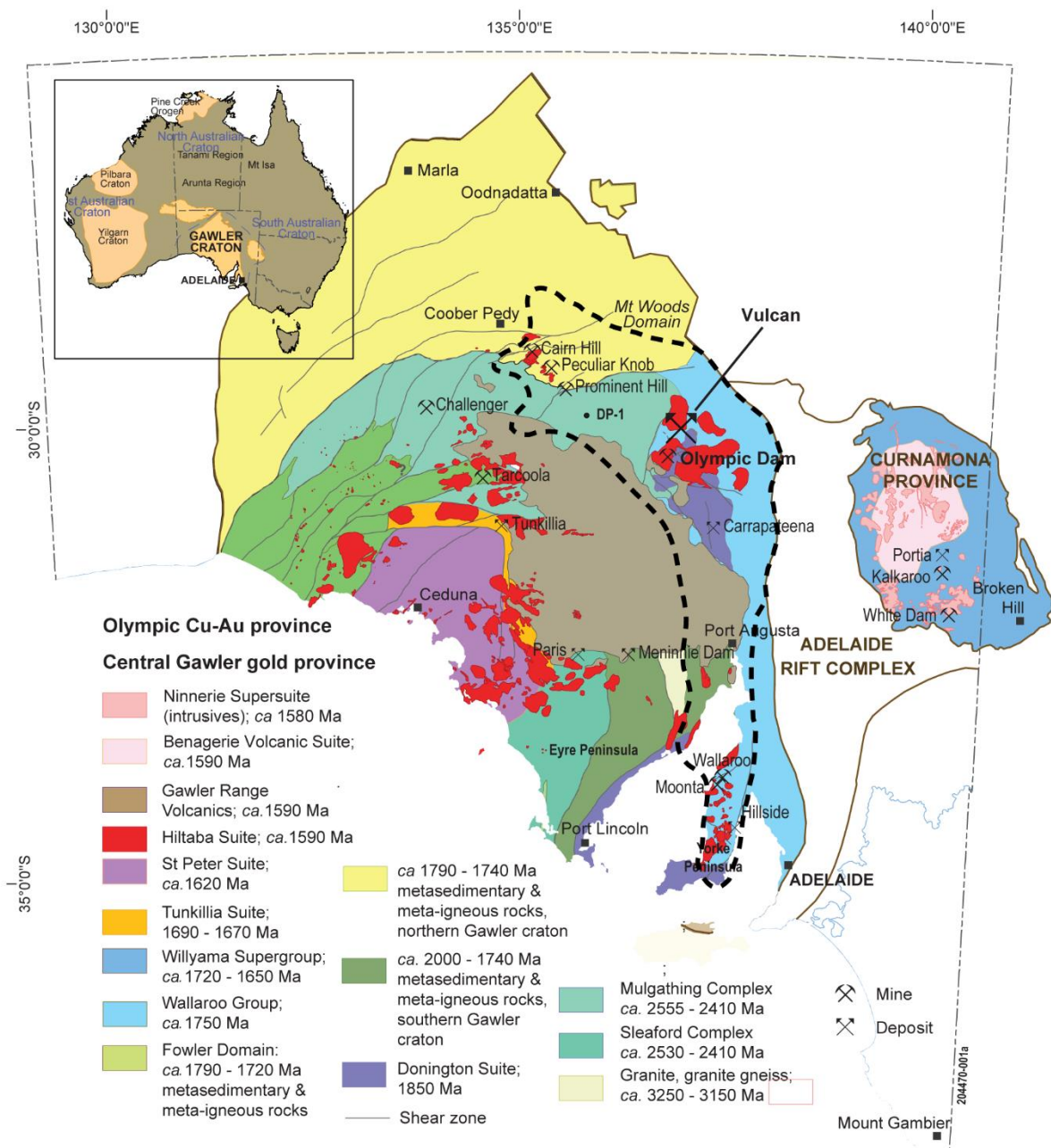


Fig. 4.1: Simplified geological map of the Gawler Craton, showing the location of mineral deposits and prospects (including Vulcan). Inset shows the position of the Gawler Craton in relation to the rest of Australia and Australia's major crustal blocks. From Reid (2019). The dashed line shows the outline of the Olympic Cu-Au Province.

The Vulcan IOCG prospect covers nearly 12 km² and is situated 30 km northeast of the Olympic Dam deposit (Fig. 4.1). Similar to other the IOCG deposits in this region, Vulcan is covered by Neoproterozoic to recent sedimentary units. Copper mineralisation is hosted within hematite dominated brecciated and hematite-altered rocks, with textures and paragenetic evolution similar to other IOCG prospects and deposits in the region (Reeves et al., 1990; Reid et al., 2013). Gravity and magnetic data suggest the alteration system is potentially similar in size to Olympic Dam, but under a significantly thicker blanket of cover sedimentary units (approximately 850m for Vulcan, 350 m for Olympic Dam; Heinson et al., 2018; Reid et al., 2013). The rocks at Vulcan are heavily brecciated and

extensively altered, making identification of the original host rocks difficult. However, regionally, the host rock system consists of ca. 1850 Ma granitic rocks, a sedimentary succession deposited at ca. 1750 Ma, and younger granites that intruded at ca. 1590 Ma (Reid, 2019; Reid et al., 2013). Re-Os dating of molybdenite that formed in association with hematite breccias at Vulcan produced an age of 1586 ± 8 Ma (Reid et al., 2013). Hence, alteration and mineralisation are at least partly contemporaneous with the recognised main ore stage at Olympic Dam (e.g. Cherry et al., 2018; Ciobanu et al., 2013; Johnson and Cross, 1995; McPhie et al., 2011).

Olympic Dam has undergone a complex evolution since formation, responding to many regional tectonic events, such as the ca. 800 Ma break up of Rodinia, and the 515 – 490 Ma Delamarian Orogeny (e.g. Cherry et al., 2018; Ehrig et al., 2021; Huang et al., 2015; Maas et al., 2022). For instance, based on U-Pb dating of uraninite, Pb isotopes in sulphides, and bulk U/Pb ratios, Ehrig et al. (2021) argued that a significant ‘upgrading’ event occurred potentially a billion years after initial mineralisation at Olympic Dam. This event likely involved an influx of U, but may also have been associated with an increase in metals such as Cu. Systematic geochronology focusing on potentially younger mineral assemblages is currently lacking for other Gawler Craton IOCG deposits, although ages of 1450 – 1400 Ma have been recorded for the Acropolis and Oak Dam prospects (Cherry et al., 2018; Davidson et al., 2007). Beyond this, however, the full significance of the spectrum of ages at Olympic Dam for metal endowment and redistribution is not yet completely determined.

Given the limited previous geochronological work at the Vulcan prospect, it remains unclear if the alteration and mineralisation history occurred in a single stage at ca. 1590 Ma as recorded by molybdenite Re-Os (Reid et al., 2013), or is a complex multi-stage system more akin to that recorded at Olympic Dam.

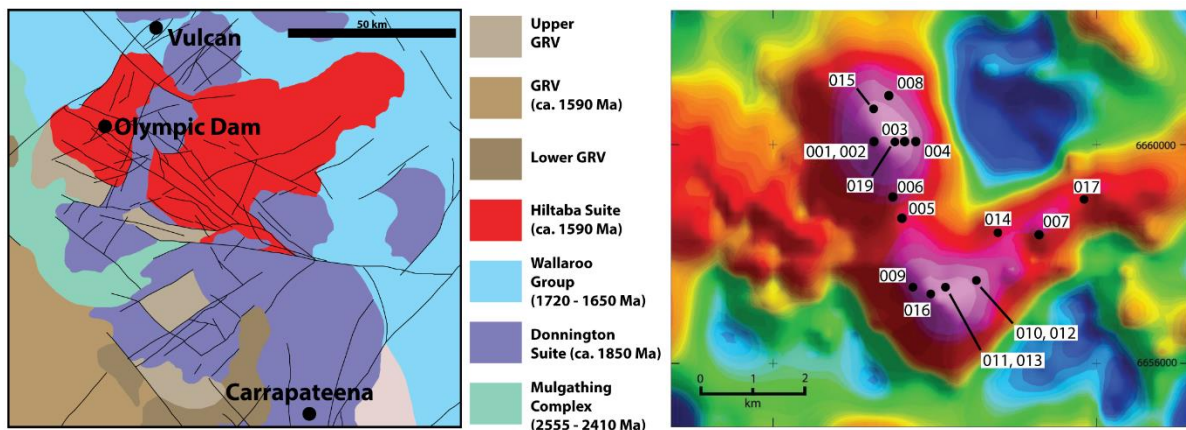


Figure 4.2: Left: geological map showing the location of the Vulcan IOCG prospect relative to Olympic Dam and Carrapateena. Right: Pseudo-colour residual gravity image of the Vulcan IOCG prospect showing the location of drill holes (from Reid et al., 2013). Drill hole names are abbreviated from full names (i.e. VUD019 becomes 019).

4.4. Samples and petrographic descriptions

Hematite breccias at Vulcan consists of fine grained ‘milled’ breccias, as well as massive ‘steely’ hematite breccias. Both breccias have similar mineralogy; hematite with minor to abundant magnetite, pyrite, carbonate minerals (mostly dolomite, siderite and ankerite), as well as minor apatite, chalcopyrite, quartz and chlorite. In some cases, large clasts of steely hematite can be seen within the fine grained breccias (see sample 017-1210, discussed in more detail later). Minor late veins cut across both fine grained breccias and massive steely hematite. These veins tend to consist

of carbonate and occasionally quartz, and often have visible chalcopyrite crystals forming within them.

Samples were collected from three drill cores from the Vulcan prospect (Fig. 4.2). The majority of samples are from drill core VUD019, however a sample from VUD007 (the highest Cu grade drill core) and VUD017 were also collected in order to determine whether the same age was produced across the deposit. VUD019 was chosen because of the abundance of apatite, the presence of bastnasite, and the presence of coarse-grained dolomite-chalcopyrite veins that crosscut the main alteration assemblage. The sample naming scheme refers to the drill core number and the sample interval in meters (e.g. 019-1263 means the sample comes from the 1263-meter interval of VUD019).

Broadly, the drill core consists of highly altered brecciated rocks. Major textures include massive hydrothermal Fe-oxide (both hematite and magnetite) forming in association with siderite and/or dolomite, pyrite, apatite, chlorite, sericite, quartz $\pm$ chalcopyrite (samples 019-1315, 019-1354, and 019-1414; Fig 4.2). The breccias are clast supported, with variable but generally fine-grained matrix minerals. Fragments of hydrothermal Fe-oxide are included in the fine-grained breccia sample 017-1210, indicating that brecciation post-dates hydrothermal Fe-oxide formation. Numerous late, cross cutting veins occur, that appear to post-date brecciation and hydrothermal Fe-oxide formation. Of particular interest are chalcopyrite-bearing dolomite vein.

Table 4.1: summary and petrological descriptions of analysed samples. Mineral abbreviations: Py: pyrite, cpy: chalcopyrite, sph: sphalerite, moly: molybdenite, ser: sericite, qtz: quartz, ba: barite, anh: anhydrite, kspr: K-feldspar, chl: chlorite, hem: hematite, mag: magnetite, sid: siderite, dol: dolomite, bast: bastasite, ap: apatite.

Sample name	Sample description	minerals	Petrographic description	Dating methods
019-1263	Late dol vein with cpy	Dol, cpy	Late cross-cutting dol vein with large euhedral cpy and dol crystals forming in void.	Dol Lu-Hf
019-1315	Massive mag and pyr alteration. Evidence of Cu indicates cpy is present.	Mag, py, ap, sid, cpy, chl	The sample consists of massive Fe-oxide hydrothermal matrix with py, ap, cpy and sid +/- chl. Py occurs in matrix with cpy filling fractures. Ap occurs intergrown with both py and cpy, as well as separate grains within the matrix. The sample is magnetic, indicating that the Fe-oxide is mostly mag. Rare bladed Fe-oxides are present and form around blocky mag crystals.	Ap U-Pb, Ap Lu-Hf
019-1354	Banded hem (compositional layering.) assay data indicates elevated Pd	Hem, sid, chl. Py, ap, cpy	This sample contains matrix of Fe-oxide-sid/chl around py crystals with cpy on edges/cracks. Py can be divided into two textures. The first py texture occurs as a ~1 cm nearly euhedral grain, surrounded by sid. This py grains show cpy forming along fractures and along grain edges. Ap, ch and hem form in association with the surrounding sid. The sid is in turn surrounded by a hem-sid-chl matrix. The second type of py occurs as ragged masses filled with many small ap inclusions, and hosted within hem-sid-chl-ap matrix. Cpy also occurs on its own as a ragged grain within the hem-sid-chl matrix.	Ap U-Pb, Ap Lu-Hf

			Fe-oxides show both bladed and blocky textures, possibly indicating original mag partly converted to hem.	
019-1414	Fe-oxide with disseminated cpy	Hem, sid, cpy, Ap, qtz, dol, chl	The sample consists of ~100 – 200 micron circular features that have hem cores which are surrounded by sid, which are then rimmed by hem. They are further surrounded by cpy with minor ap, qtz, and chl. As both ap and cpy wrap the circular sid-hem features, they are interpreted to be cogenetic. The sample is devoid of py.	Ap Lu-Hf
019-1552	carbonate vein cutting hydrothermal matrix/breccia	Dol, cpy, hem, Ap, chl, py	This sample is a ~2 cm wide dol vein containing cpy. The vein cross cuts typical (of VUD019) 'steely' hem matrix (inferred to be hem-py-ap-sid.)	Dol Lu-Hf
019-1574	Similar to 019-1552	Dol, cpy	Sample contains dol veins (with cpy and reddish qtz) cutting/fracturing 'steely' hem breccia that contains py + cpy.	Dol Lu-Hf
019-1758	Sample contains extremely high LREEs. Breccia clasts surrounded by hydrothermal matrix.	Chl, bast, ser, qtz, cpy, hem, anh, moly, py	The sample consists of a breccia with extensively hydrothermally altered clasts. The matrix is fine-grained bladed bast, ser, and hem with euhedral moly flakes occurring in some sections. Clasts are generally heavily altered to chl with some ser and qtz. A few heavily fractured py grains occur. One sample shows a clast consisting of qtz with anh, cpy, and bladed hem forming in voids. This sample appears to contain no phosphates, and bast is the only carbonate mineral. Fe-oxide is hematite. Texturally, shows large bladed crystals and fractured blocky crystals	Bast Lu-Hf,
017-1210	Hydrothermal breccia.	Dol, sid, hem, py, qtz, Ap, chl, cpy	This sample shows the boundary between coarse breccia, and hydrothermal matrix similar to that observed in VUD019; hem-carb-chl (but with dol instead of sid). The hydrothermal breccia includes both clasts and crystals, and dolomite and siderite form euhedral to subhedral crystals. Based on the hand sample, the hem-dol-chl hydrothermal matrix fragment consists of a large (>2 cm) fragment within the breccia. Ap occurs throughout. Py occurs along the boundary between large hem-dol-chl fragment and coarse breccia. A single clast of cpy is surrounded by qtz was observed. Additionally, the block is cross-cut by a late (but very thin ~ 100 microns wide) dol + cpy vein.	Dol and Sid Lu-Hf

			Fe-oxide in clast supported breccia is a mixture of early magnetite mostly replaced by haematite.	
--	--	--	---	--

4.5. Analytical Methods

4.5.1 Scanning Electron Microscope

The Samples were mounted as 2.5 cm epoxy disks and subsequently imaged using a Hitachi SU38000 scanning electron microscope (SEM). Both backscattered electron imaging and mineral liberation analysis (MLA) were performed. Maps were made with the SEM operating at 20 KeV, and a magnification of 90x.

4.5.2. Laser ablation analysis

All laser ablation analysis was conducted using a RESOLution 193 nm laser system attached to an Agilent 8900x 'QQQ' mass spectrometer. N₂ gas was added after the sample chamber, but before the plasma in order to increase isotopic sensitivities (Hu et al., 2008). In all cases, the ICP was first tuned in 'no gas' mode to demonstrate a robust and consistent plasma (Th/ThO < 0.2%, Th/U 1.00 – 1.05). Following this, tuning was conducted in reaction gas mode for each application. Settings were then optimised and adjusted to demonstrate interferences were removed, and to promote sensitivity on low abundance isotopes (e.g. ¹⁷⁶Hf and ¹⁷⁷Hf for Lu-Hf dating; Simpson et al., 2021). Laser parameters, lens voltages and ICP-MS/MS plasma conditions for all methods are included in appendix A.

All data processing (e.g. background subtractions, drift corrections, ratio normalisations, and trace element abundance calculations) were conducted using LADR software (Norris and Danyushevsky, 2018).

4.5.3 LA-ICP-Q-MS/MS U-Pb dating

LA-ICP-Q-MS/MS U-Pb dating was conducted following the method outlined in (Gilbert and Glorie, 2020), which uses NH₃ gas to eliminate ²⁰⁴Hg, allowing for interference-free measurement of ²⁰⁴Pb. A Laser beam diameter of 43 µm was used, with a fluence of 3.5 J/cm⁻² and repetition rate of 5 Hz. All Pb isotopes were measured 'on mass' and U was measured as UNH⁺ (a mass shift of +15 amu; Gilbert and Glorie, 2020). A sample-standard bracketing approach was used to correct for drift, laser induced and ICP induced fractionation, with MAD apatite (Chew et al., 2014; Thomson et al., 2012) used to calculate the U/Pb ratios (correcting for laser induced elemental fractionation), and NIST610 used to calculate the Pb/Pb ratios (Glorie et al., 2019). ²⁰²Hg was monitored to demonstrate interference-free ²⁰⁴Pb measurements.

4.5.4. LA-ICP-Q-MS/MS Lu-Hf dating

Lu-Hf dating was conducted following protocols in Simpson et al. (2021) and Simpson et al. (2022). For apatite and bastnasite, spot sizes of between 43 and 120 µm were used, with a repetition rate of 10 Hz and fluence of 3.5 J/cm⁻². For dolomite and siderite, a spot size of 257 µm was used, with a repetition rate of 10 Hz and a fluence of 10 J/cm⁻². The Lu-Hf method relies on reacting Yb, Lu and Hf with NH₃ gas. Hf reacts to form multiple reaction products, with gas flows tuned to promote formation of Hf(NH)(NH₂)(NH₃)₃⁺ (+ 82 amu). Both Lu and Yb tend to react with one more H than Hf, with Lu(NH)(NH₂)(NH₃)₃⁺ forming at a rate of 0.003% (relative to Lu on mass) and Yb(NH)(NH₂)(NH₃)₃⁺ forming at a rate of ~0.00003% (relative to Yb on mass). Yb(NH)(NH₂)(NH₃)₃⁺ was not monitored, as

production is not high enough to affect the calculated ratios and it is usually below detection limits unless the mineral contains wt.%. Yb (Simpson et al., 2021). ^{175}Lu was measured as a proxy for ^{176}Lu , and ^{178}Hf was measured as a proxy for ^{177}Hf . Additionally, a small correction (less than 1% for all samples) was applied for the interference of $\text{Lu}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$ on $\text{Hf}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$ (although we note that this correction was not significant for any analysed sample, but is conducted on all samples for consistency). For detailed descriptions of the method, the reader is referred to Simpson et al. (2021) and Simpson et al. (2022).

Data reduction was conducted using LADR software (Norris and Danyushevsky, 2018) with a sample-standard bracketing approach used to calculate isotopic ratios. Data was first corrected to NIST610, and was followed by an external 'secondary standard' correction to the radiogenic $^{176}\text{Lu}/^{176}\text{Hf}$ ratio of OD306 apatite reference material (Thompson et al., 2016). This correction is similar to that used for calcite U-Pb dating (Roberts et al., 2017), and relies on applying a correction factor derived from the percentage offset between the measured and expected radiogenic $^{176}\text{Lu}/^{176}\text{Hf}$ ratios in OD306. The expected ratio is calculated from the age of OD306 (U-Pb, 1597 ± 7.1 Ma; Thompson et al., 2016), and the measured ratio is the calculated intercept on an inverse Lu-Hf isochron. Bamble apatite and HR apatite were run as secondary standards in order to demonstrate reproducibility (Gillespie et al., 2022; Glorie et al., 2023; Simpson et al., 2021). Carbonate samples were analysed using MKED1 calcite and ME1 as standards, with MKED1 as the primary reference, assumed to be the same age as cogenetic titanite (TIMS U-Pb, 1517.3 ± 0.32 ; Simpson et al., 2022; Spandler et al., 2016). ME-1 is from the Mount Elliot IOCG deposit, Queensland, Australia, and is assumed to be the same age as 1530 ± 11 Ma titanite from the deposit (Duncan et al., 2011; Simpson et al., 2022). Calculated dates for standards can be found in Table 4.2 in the results section.

4.6. Results

4.6.1. Mineral Liberation analysis

The following figures display the MLA maps for the analysed samples. Figures include sample photos to give the MLA maps context. For coarse-grained dolomite samples 019-1263 and 019-1574, no MLA map was obtained, as mineralogy is visible to the naked eye. Consequently, for these samples only hand sample photos have been included.

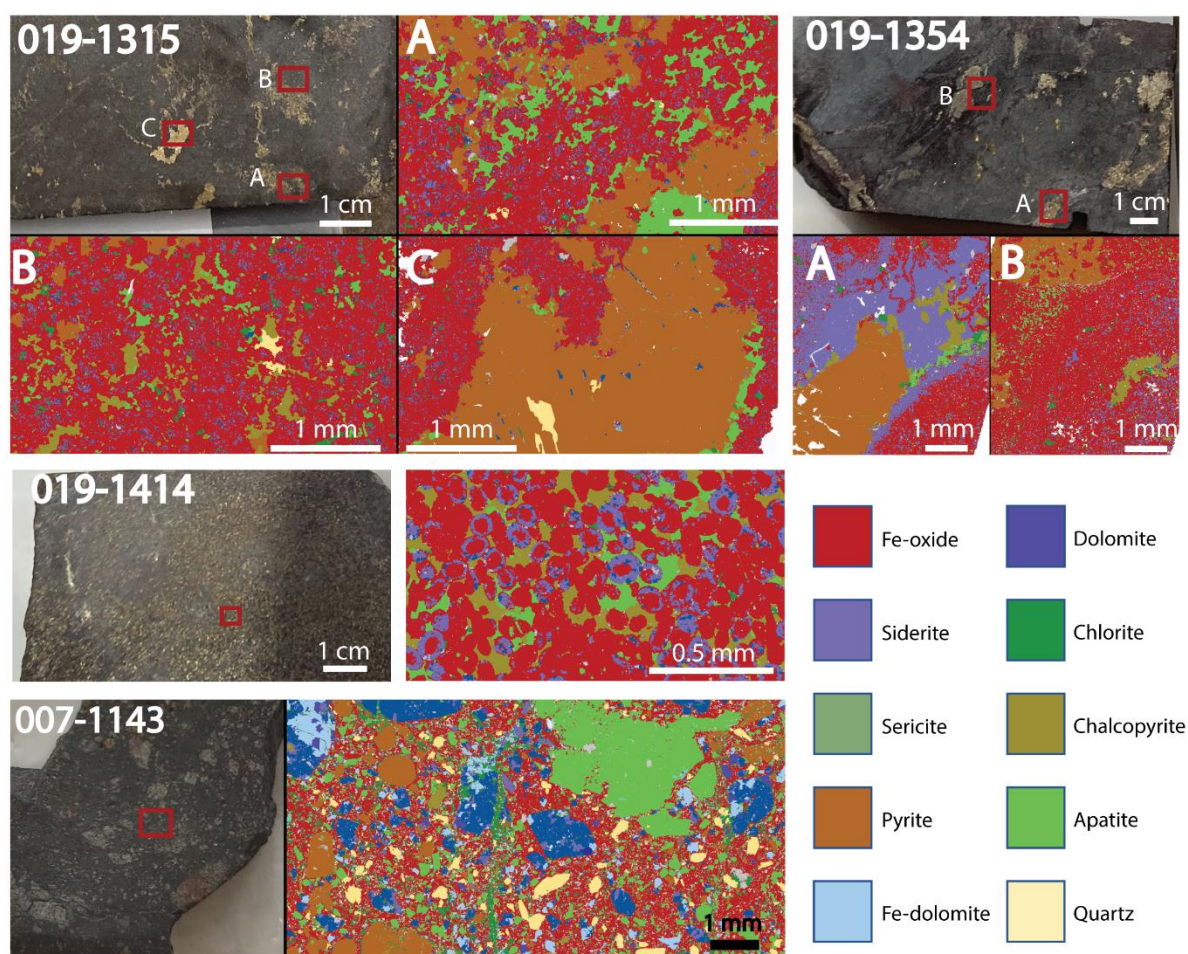


Figure 4.3: SEM mineral maps and hand sample photos showing mineralogy of analysed apatite-bearing samples. Red boxes on the drill core photos correspond to SEM mineral liberation analysis (MLA) maps.

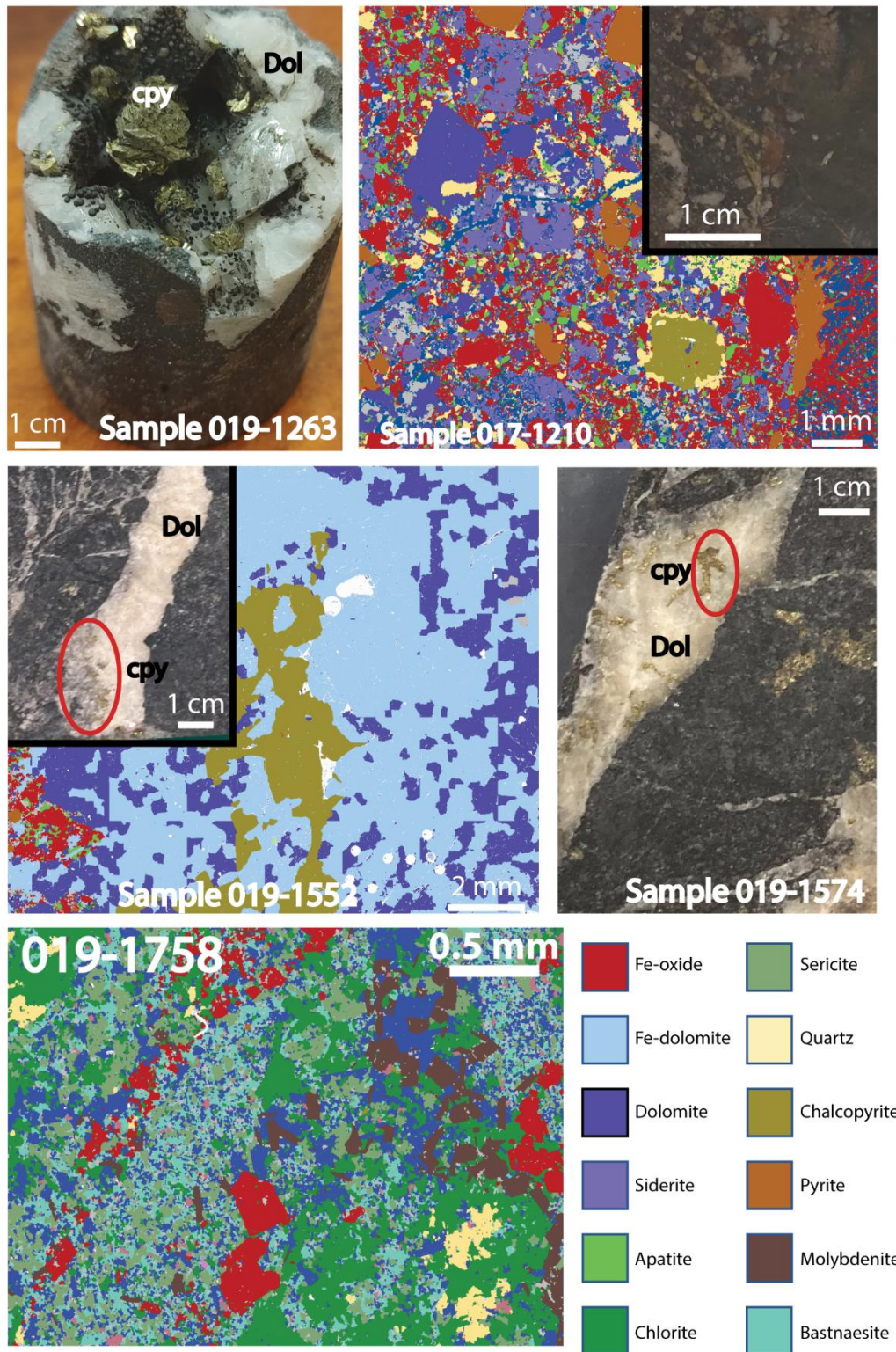


Figure 4.4: Representative examples of carbonate-bearing samples and associated MLA maps. As samples 01901263 and 019-1574 are coarse grained, they were not MLA mapped. Red circles show the area that was mapped for MLA.

4.6.2. Geochronology:

The samples are presented as Tera-Wasserburg concordia plots (U-Pb) or inverse isochrons (Lu-Hf), calculated using IsoplotR (Vermeesch, 2018). Uncertainties are presented as 2σ (Age uncertainties

are expanded to account for data scatter if MSWD is great than expected for a single population; Vermeesch, 2018). Correction factor and decay constant uncertainties are propagated to all Lu-Hf ages. Ages are summarised in table 4.2, and isochrons are displayed in figures 4.5 and 4.6. All analytical data is included in supplementary files 4.1 (U-Pb data) and 4.2 (Lu-Hf data).

Table 4.2: summary of geochronological data obtained from the Vulcan prospect.

<i>Sample</i>	<i>mineral</i>	<i>dating technique</i>	<i>age</i>	<i>2SE</i>	<i>MSWD</i>	<i>Number of analyses</i>
019-1315	apatite	U-Pb	1536	114	0.96	7
019-1315	apatite	Lu-Hf	1577	66	0.82	29
019-1354	apatite	U-Pb	1615	94	0.97	4
019-1354	apatite	Lu-Hf	1631	60	1.1	14
019-1414	apatite	Lu-Hf	1612	57	1	38
007-1143	Apatite	Lu-Hf	1595	32	1	30
019-1263	dolomite	Lu-Hf	560	16	1.2	46
019-1552	dolomite	Lu-Hf	573	18	1.5	29
019-1574	dolomite	Lu-Hf	615	47	0.69	20
019-1758	bastnasite	Lu-Hf	1177	50	0.92	72
017-1210	dolomite	Lu-Hf	1574	39	1.2	22
017-1210	siderite	Lu-Hf	1488	79	1.4	15

Table 4.3: Ages for secondary reference materials. *Denotes that no independent reference age currently exists, and reported reference ages are based on previous analysis using these secondary reference materials (i.e. they demonstrate consistency between analytical sessions).

NAME	MINERAL	METHOD	DATE	AGE	2SE	REFERENCE AGE (MA)	2SE (MA)
401	apatite	U-Pb	20/01/22	525	3	525	7.8
BAMBLE 1	apatite	Lu-Hf	24/01/22	1101	13	ca. 1095*	N/A
HR 1	apatite	Lu-Hf	24/01/22	345	4.5	ca. 343*	N/A
BAMBLE 1	apatite	Lu-Hf	24/03/22	1100	14	ca. 1095*	N/A
HR 1	apatite	Lu-Hf	24/03/22	344	6.7	ca. 343*	N/A
ME1	calcite	Lu-Hf	13/04/22	1544	20	1530	11

ME1	calcite	Lu-Hf	18/04/22	1526	18	1530	11
-----	---------	-------	----------	------	----	------	----

4.6.3. Apatite U-Pb and Lu-Hf

Sample 019-1315

Both U-Pb and Lu-Hf dating was applied to sample 019-1315. Apatite from this sample produced a U-Pb age of 1536 ± 114 Ma, with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ of 0.49 ± 0.16 (MSWD: 0.49, $n = 7$). Of a total of 40 data points, 33 were discarded due to the presence of Pb-bearing inclusions.

The Lu-Hf age of the apatite from this sample is 1577 ± 66 Ma, with an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.282 ± 0.005 (MSWD: 0.82, $n = 29$). No data points were removed.

Sample 019-1354

Both U-Pb and Lu-Hf dating was applied to sample 019-1354. The apatite from this sample produced a U-Pb age of 1615 ± 94 Ma, with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ of 0.89 ± 0.52 (MSWD = 0.97, $n = 4$). Of a total of 81 data points, 77 were discarded due to the presence of Pb bearing inclusions (likely Fe-oxides or sulphides).

The Lu-Hf age for the apatite from this sample is 1631 ± 60 Ma, with an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.278 ± 0.006 (MSWD: 1.1, $n = 14$). No data points were removed.

019-1414

Both U-Pb and Lu-Hf dating was applied to sample 019-1414. The apatite from this sample did not produce a meaningful U-Pb age, as inspection of time-resolved laser ablation signals indicated that all data was contaminated by Fe rich inclusions (hematite, magnetite and/or pyrite)

The Lu-Hf age of the apatite from this sample is 1612 ± 57 Ma, with an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.277 ± 0.008 (MSWD: 1, $n = 38$). ^{178}Hf was below detection for two data points.

007-1143

Both U-Pb and Lu-Hf dating was applied to sample 007-1143. The apatite from this sample did not produce a meaningful U-Pb age, as inspection of time-resolved laser ablation signals indicated that almost all data was contaminated by Fe rich inclusions (hematite, magnetite and/or pyrite). Two data points that contained close to pure apatite (based on down-hole signals) plot close to concordia (Fig. 4.5). However, no age was calculated given two data points is not sufficient for that purpose.

The Lu-Hf age of the apatite from this sample is 1595 ± 32 Ma, with an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.280 ± 0.04 (MSWD = 1, $n = 30$). ^{178}Hf was below detection for two data points.

4.6.4. Carbonate Lu-Hf

019-1263

Late dolomite vein (Fig. 4.6) sample 019-1263 produced a radiogenic Hf composition, close to the x-intercept on an inverse isochron plot. In order to produce a more meaningful isochron, the data was anchored to an initial $^{177}\text{Hf}/^{176}\text{Hf}$ value of 3.55 ± 0.07 (i.e. to force the initial $^{177}\text{Hf}/^{176}\text{Hf}$ to be a realistic value; Simpson et al., 2022). An age of 560 ± 16 Ma (MSWD = 1.3, $n = 45$) was produced for the analysed dolomite. No data points were removed.

019-1552

Similar to sample 019-1263, sample 019-1552 (a late vein; Fig. 4.6) was anchored to an initial $^{177}\text{Hf}/^{176}\text{Hf}$ value of 3.55 ± 0.07 . The resultant inverse isochron produced an age of 573 ± 18 Ma (MSWD = 1.5, n = 28) for the analysed dolomite. No data points were removed.

019-1574

Sample 019-1574, which is also a late vein; Fig. 4.6, contained inclusions with significantly higher Hf than the analysed dolomite. Consequently, rather than anchoring the dolomite Lu-Hf data to an assumed initial $^{177}\text{Hf}/^{176}\text{Hf}$ value, these inclusions were used as an anchor by including the contaminated analyses on the isochron. A resultant age of 615 ± 47 Ma, with an initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio 0.283 ± 0.003 (MSWD = 0.7, n = 20) was produced. No data points were removed.

017-1210

Both siderite and dolomite from sample 017-1210 were analysed using laser ablation Lu-Hf. These are crystals in breccia, not late veins (Fig. 4.6). Similar to sample 019-1574, both the dolomite and siderite isochrons for this sample are anchored to inclusions.

The dolomite from this sample produced an age of 1574 ± 39 Ma, with an initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.284 ± 0.003 (MSWD = 1.2, n = 22). ^{178}Hf was below detection for only one data point.

Siderite from sample 017-1210 produced an age of 1488 ± 79 Ma, with an initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.278 ± 0.008 (MSWD = 1.4, n = 15). One outlier was removed.

019-1758

Bastnaesite from sample 019-1758 produced a date of 1177 ± 50 Ma (MSWD = 0.92, n = 72). No data was removed from the isochron. We note that this data has not been corrected to a matrix matched standard.

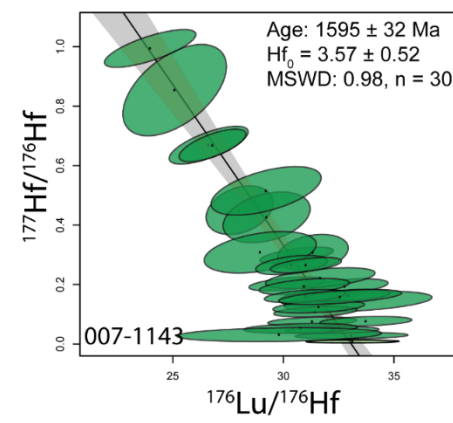
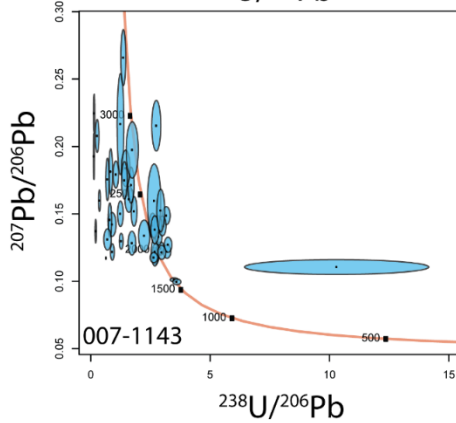
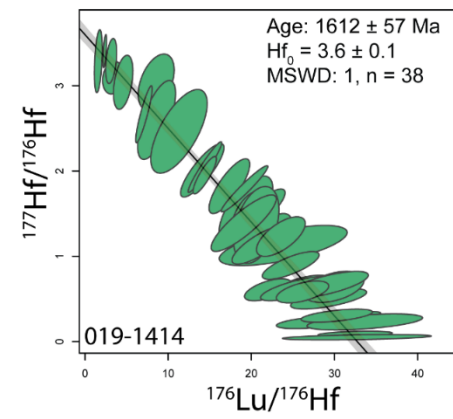
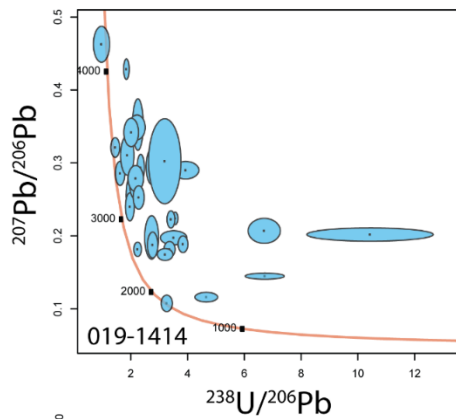
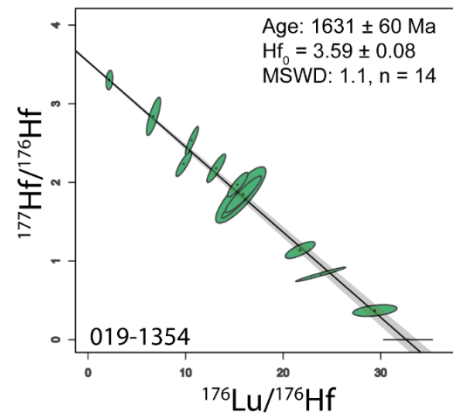
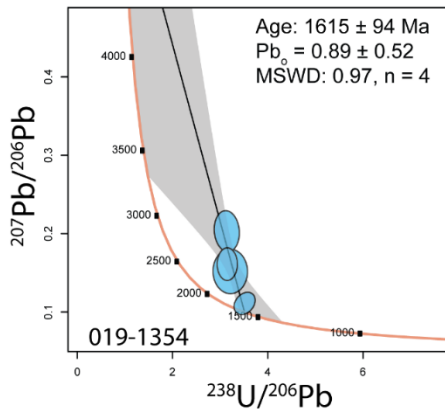
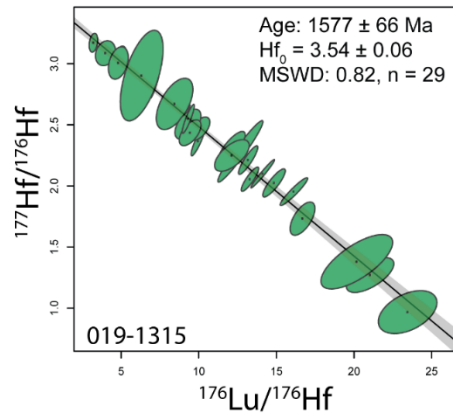
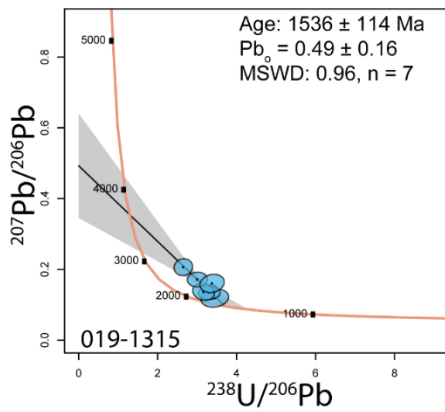


Fig. 4.5. Apatite U-Pb (blue ellipses) and Lu-Hf (green ellipses) isochrons. U-Pb data is presented as Tera-Wasserberg concordia plots, and Lu-Hf data is presented as inverse isochron plots. Sample names are included in the bottom left corner of each plot. Each row shows U-Pb data and Lu-Hf data from the same sample. Ellipses show 2σ uncertainties. Age uncertainties are 2σ . Pb_0 and Hf_0 refer to (respectively) the initial $^{207}Pb/^{206}Pb$ and $^{177}Hf/^{176}Hf$ ratios calculated from each isochron (Y-intercepts).

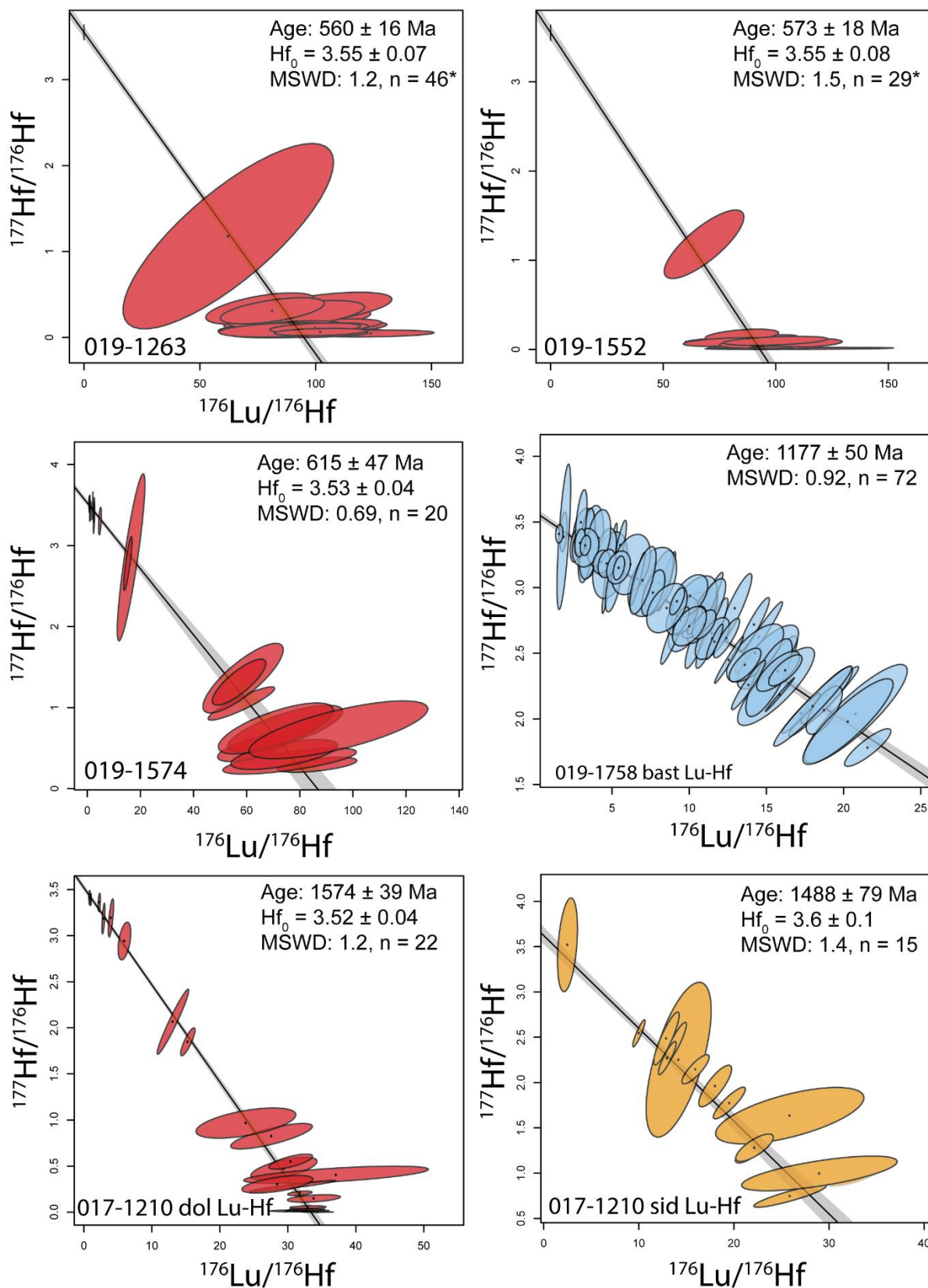


Figure 4.6: Carbonate Lu-Hf inverse isochrons (red = dolomite, orange = siderite). Samples 019-1263 and 019-1552 produced highly clustered data, for which a meaningful regression could not be calculated. To overcome this, the data has been anchored to an initial $^{177}\text{Hf}/^{176}\text{Hf}$ of 3.55 ± 0.07 (designed to cover all likely crustal initial Hf values; see Simpson et al., 2022 for further detail). Sample names are included in the bottom left corner of each plot. Ellipses show 2σ uncertainty around mean values. Age uncertainties are 2σ . Pb_0 and Hf_0 refer to (respectively) the initial $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{177}\text{Hf}/^{176}\text{Hf}$ ratios calculated from each isochron (as Y-intercepts). *denotes that an extra data point has been added in order to anchor the isochron (see text for more details).

4.7. Discussion

4.7.1. Assessment of novel geochronometers

Geochronological data from the Vulcan IOCG system has produced dates for alteration that are generally similar to the ages of primary IOCG mineralisation from across the Olympic Cu-Au Province. This indicates these methods can produce accurate ages that can survive over a significant geological time period.

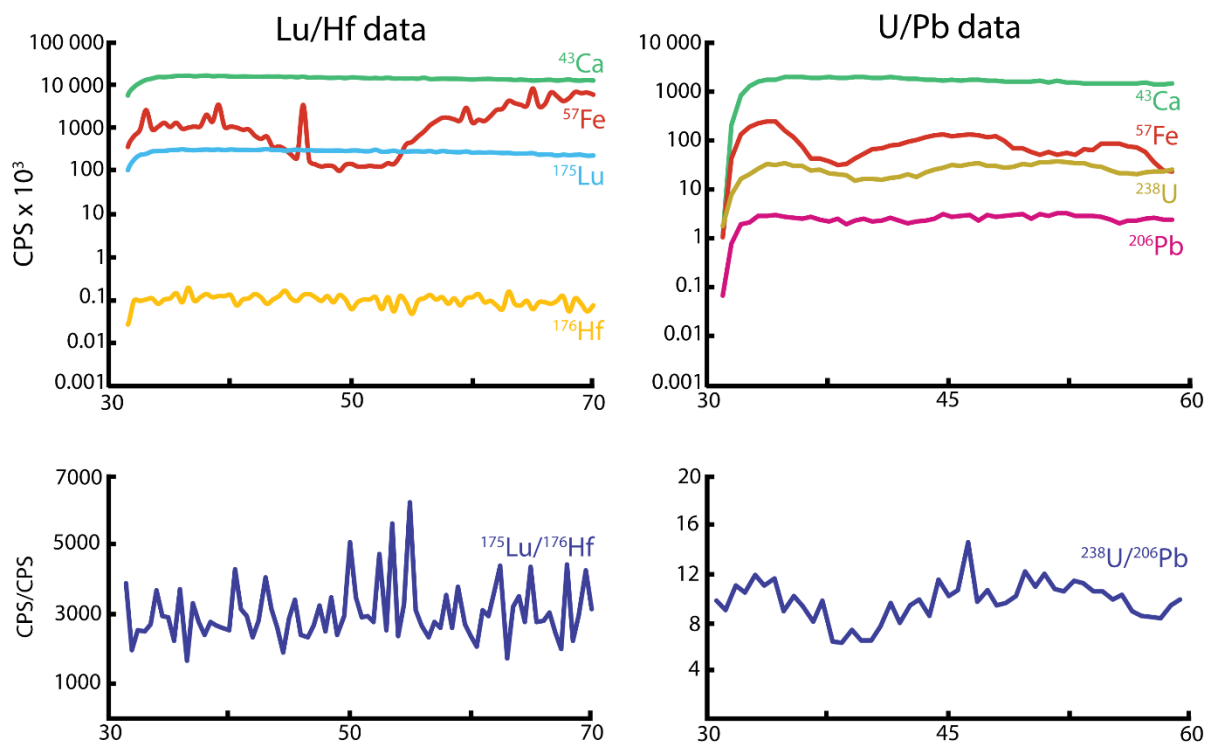


Figure 4.7: Time-resolved laser ablation signals showing the presence of Fe inclusions in the apatite trace element data and the associated effects to the Lu-Hf and U-Pb ratios. The example is based on data from sample 019-1354. Note that $^{175}\text{Lu}/^{176}\text{Hf}$ and $^{238}\text{U}/^{206}\text{Pb}$ are based on raw counts-per-second data, (i.e. the data have not been subjected to any subsequent normalization procedures).

Apatite U-Pb data produced scattered results (fig. 4.5), interpreted to be largely due to significant contamination by various Pb-bearing inclusions (likely Fe-oxides and sulphides). This interpretation is based on the presence of significant and variable Fe in down-hole laser ablation signals (e.g. Fig. 4.7). Scatter may also be caused by minor Pb-loss or minor recrystallisation. Only two out of three analysed apatite samples produced inclusion-free data points, with one sample not producing any pure apatite at all (i.e. 019-1414 and 007-1143 U-Pb data is highly scattered, and all down-hole signals display Pb bearing Fe inclusions; Fig. 4.5, Fig. 4.7, table 4.2). Additionally, of the successful samples, only a small number of data points were deemed usable based on the applied selection criteria discussed above (e.g. 7/40 for 019-1315 and 4/77 for 019-135; Fig. 4.5, table 4.2).

Apatite U-Pb signals that do not show signs of Fe inclusions tend to cluster or form linear arrays in Tera-Wasserburg plots (Fig. 4.5). Conversely, signals in which Fe inclusions tend not to form linear arrays (i.e. they tend not to fall along the linear arrays for pure apatite, and tend not to form their own arrays; Fig. 4.5). A linear array on an isochron plot, such as a Tera-Wasserburg, indicates that data points reflect cogenetic apatite that crystallised with the same initial Pb composition (Tera and Wasserburg, 1972) as is expected for minerals with straightforward crystallisation histories (i.e. no isotopic disturbances). Consequently, we interpret the Pb inclusions to be the source of scatter on the isochron plots. This could be due to a number of reasons, including that the Pb inclusions are not cogenetic with the apatite, that the Pb inclusions formed from a Pb reservoir that is significantly different to the apatite, and that the Pb inclusions have undergone post-formation Pb (and/or U) mobility. We note that these possibilities are not mutually exclusive.

Although the apatite Lu-Hf analyses were contaminated by the same inclusions as the U-Pb data, these inclusions did not contain significant concentrations of either Lu or Hf, and consequently do not appear to have affected the Lu-Hf isotopic ratios, from which the Lu-Hf dates were calculated (fig. 4.5). We attribute this to the following reasons; firstly, Hf is much less mobile than Pb in most hydrothermal fluids (Brugger et al., 2016), meaning Pb is likely much more abundant. Secondly, $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are very unlikely to change significantly with time (crustal values range from ~ 0.280 to 0.283 , with extreme values of ~ 0.286 documented; Fisher and Vervoort, 2018; Izuka et al., 2015; Salters and Zindler, 1995; Vervoort and Patchett, 1996) compared to $^{207}\text{Pb}/^{206}\text{Pb}$, which has expected crustal values ranging from ~ 1.12 to ~ 0.835 (Stacey and Kramers, 1975), but can deviate from this range significantly if the initial Pb is derived from the breakdown of a radiogenic Pb reservoir (e.g. Romer and Wright, 1993). We note that inclusions in the apatite Hf data may have increased the $^{177}\text{Hf}/^{176}\text{Hf}$ ratio slightly, but they appear to not affect the resulting Lu-Hf ages (fig. 4.5). This observation is consistent with the expected lack of significant change in $^{176}\text{Hf}/^{177}\text{Hf}$ ratios with time. While the apatite U-Pb dating undertaken in this study is of limited success, this may not be the case at all mineral deposits. Consequently, we suggest that double-dating of apatite using the Lu-Hf and U-Pb systems can produce more reliable age constraints on apatite crystallisation and its associated mineralisation (e.g. Glorie et al., 2023).

In this study we present the first ever in-situ bastnaesite Lu-Hf geochronology (1177 ± 50 Ma fig. 4.6). It is important to emphasise we do not have a matrix-matched bastnaesite standard for laser ablation Lu-Hf analysis, and consequently the age may not be accurate. The sensitivity of bastnaesite to matrix matching is presently unknown, and therefore it is difficult to interpret the bastnaesite age. However, in our experience, matrix related fractionation is generally less than 6% for laser ablation Lu-Hf (Simpson et al., 2021; Simpson et al., 2022; Tamblyn et al., 2021). Consequently, a better understanding of matrix fractionation in bastnaesite is required to fully understand the age, but any correction is highly unlikely to shift the acquired age by more than $\sim 10\text{-}15\%$. As such, this age may represent a third event that has affected the Vulcan IOCG prospect.

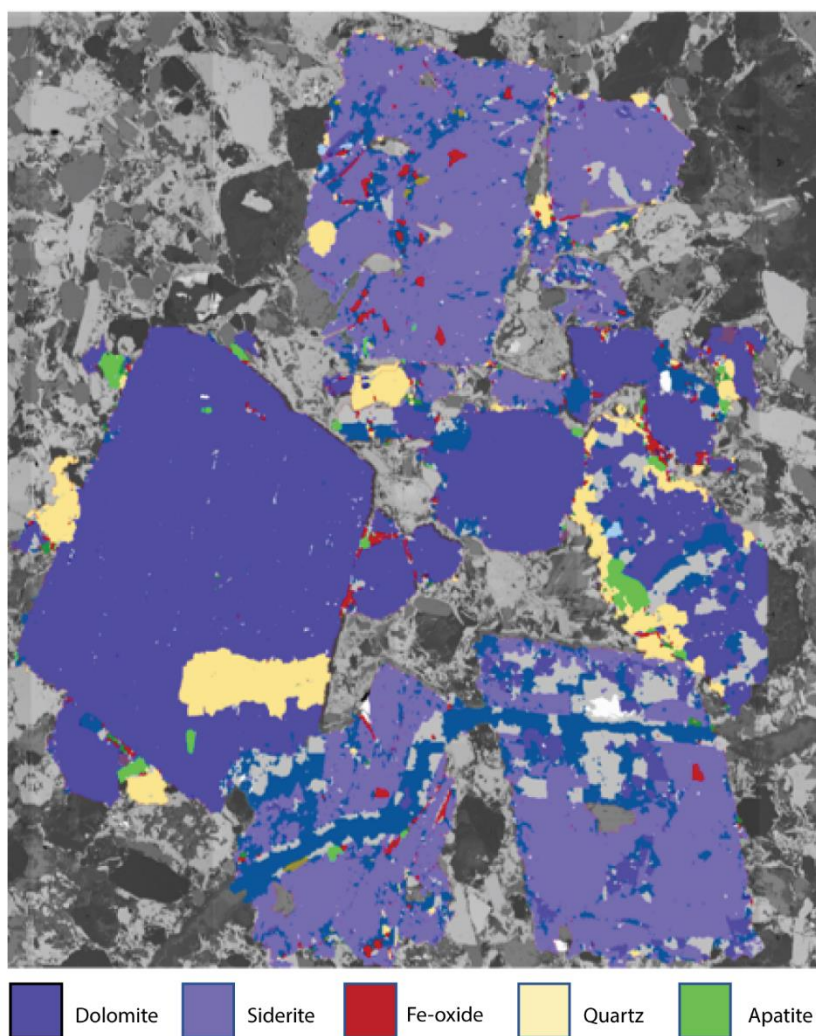


Figure 4.8: MLA image of dolomite and siderite crystals overlaid over BSE image. Dolomite and siderite are euhedral to subhedral, which is interpreted to indicate that they formed in open space, likely early during hydrothermal brecciation.

Dolomite Lu-Hf dating was conducted on dolomite crystals within a breccia (sample 017-1210) as well as late cross-cutting dolomite veins (Fig. 4.4, Fig. 4.8). Dolomite Lu-Hf produced meaningful isochron ages, with the date for the breccia crystals overlapping with ca. 1595 Ma mineralisation, and the late cross-cutting veins dated at ca. 570 Ma (Fig. 4.6). This is the first example of successful laser ablation Lu-Hf dating of dolomite, and demonstrates that dolomite Lu-Hf dating has the potential to be a useful tool for dating mineral deposits. Given that the dolomite Lu-Hf age from sample 017-1210 (1574 ± 39 Ma) agrees with the timing of mineralisation, the applied matrix-correction factor (based on calcite), is likely valid to calculate accurate dolomite Lu-Hf ages. Any offset due to lack of matrix matching is likely to be at least less than uncertainty. Consequently, the ca. 570 Ma dolomite Lu-Hf age is deemed accurate as well from an analytical standpoint. In addition, siderite crystals that formed with the ca. 1574 Ma dolomite produced an age of 1488 ± 77 Ma, i.e. within uncertainty of each other. As the siderite also appears to form euhedral to subhedral crystals within the breccia, it is interpreted to be co-genetic with the dolomite (Fig. 4.8). We emphasize that more data is needed to understand the accuracy of siderite Lu-Hf dating. More generally, successful application of both dolomite and siderite Lu-Hf requires elevated Lu concentrations and/or elevated Hf concentrations in order to produce good quality data, particularly in the case of siderite, which appears to incorporate less Lu than dolomite (e.g. this study and Maas et al., 2022). For instance, the

ca. 570 Ma dolomite has low Lu concentrations (0.5 ppm; sup file 3), however this sample contained sufficient common Hf, to produce ^{176}Hf and ^{177}Hf measurements that are above detection limits.

4.7.2. Implications for Vulcan IOCG system

Broadly, two clear age groups are evident; ca. 1590 Ma and ca. 570 Ma. The majority of samples associated with brecciation and widespread hydrothermal alteration (including all dated apatite) produced ages of ca. 1590 Ma. For instance, sample 019-1414, which has a clear relationship with Cu mineralisation (apatite and chalcopyrite both wrap around Fe-oxides; Fig. 4.3), produced an age of 1612 ± 54 Ma (Fig. 4.5). Consequently the primary stage of IOCG alteration and mineralisation at Vulcan is considered to be ca. 1595 Ma, consistent with both regional constraints and previous Re-Os molybdenite geochronology from the prospect (1586 $\pm$ 8 Ma; Reid et al., 2013). Dolomite from a different drill core (VUD017; sample 017-1210), produced an age of 1574 ± 39 Ma (Fig. 4.6), which overlaps with the interpreted primary mineralisation age for the prospect. This sample consisted of largely euhedral dolomite crystals (Fig. 4.8) that likely formed early during hydrothermal brecciation, and suggest that brecciation at the deposit occurred soon after massive Fe-oxide formation. Consequently, the geochronological evidence suggests that widespread hydrothermal alteration occurred at the Vulcan prospect on a kilometre scale. The ca. 1595 Ma ages produced agree with geochronology from most other IOCG deposits across the Gawler Craton (the notable exception being Oak Dam, based on current data; Fig. 4.9).

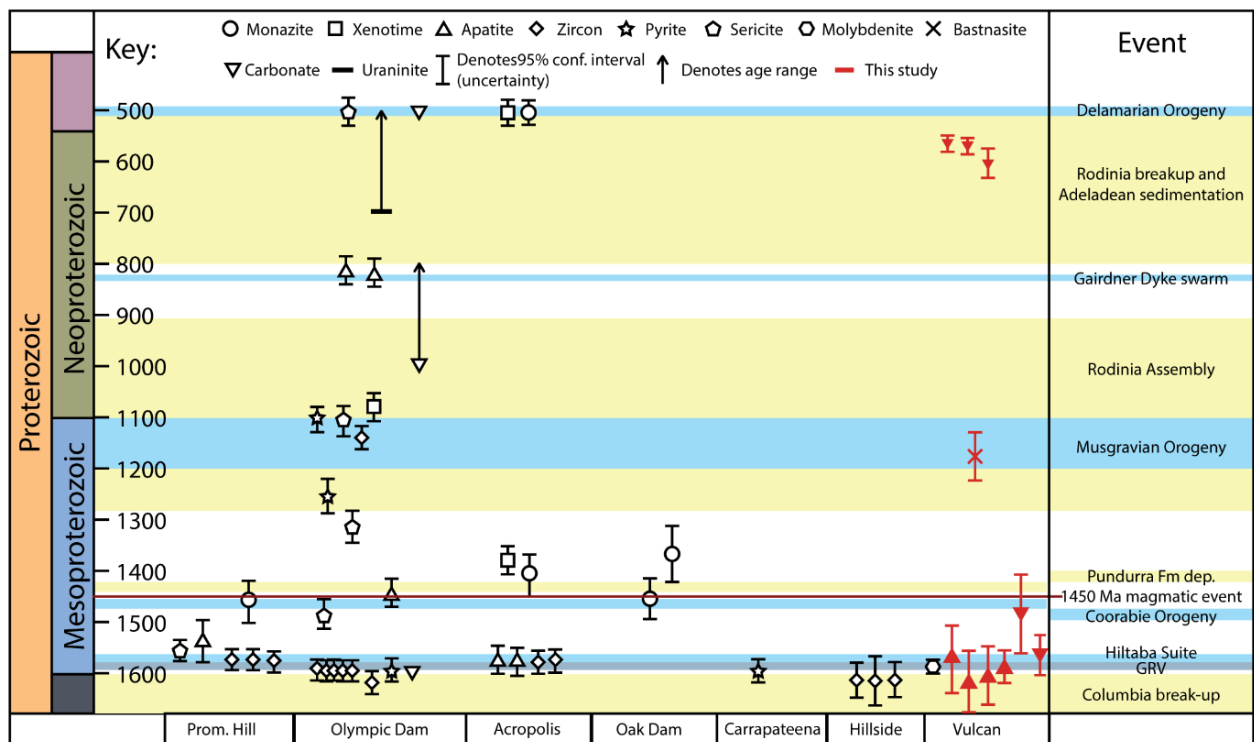


Figure 4.9: Time space plot showing existing geochronology from IOCG mineral deposits and prospects in the Gawler Craton. Age ranges of major tectonic events are included (coloured bands). Red data points are from this study. Literature data: Prominent Hill; (Belperio et al., 2007; Bowden et al., 2017), Olympic dam: (Apukhtina et al., 2017; Cherry et al., 2018; Cherry et al., 2017; Ehrig et al., 2021; Gustafson and Compston, 1979; Huang et al., 2015; Jagodzinski, 2014; Maas et al., 2022; Maas et al., 2011; McInnes et al., 2008; McPhie et al., 2020). Oak Dam: (Davidson et al., 2007). Carrapateena: (Sawyer, 2017). Acropolis: (Cherry et al., 2018; McPhie et al., 2020). Hillside: (Gregory et al., 2011). Vulcan: (Reid, 2019)

The bastnaesite age of 1177 ± 50 is significantly younger than the apatite Lu-Hf dates (Fig. 4.5). The closure temperature to volume diffusion of Lu and Hf is currently unknown for bastnaesite. Consequently, it is unclear whether this date represents a resetting of the Lu-Hf system in bastnaesite or the primary bastnaesite crystallisation age. In the context of southern Australia, the Lu-Hf age derived from bastnaesite corresponds to the 1200 - 1160 Ma Musgravian Orogeny, which is a wide transcontinental orogenic high-temperature system in southern central Australia (Myers et al., 1996). The Musgravian Orogeny tectonically reworked the margins of the Gawler Craton (Hand et al., 2007), and broadly similar ages for REE mineralisation have been produced at Olympic Dam (ca. 1.3 Ga, Fig 4.9; Maas et al., 2011), suggesting that a Musgravian hydrothermal event might have occurred at Vulcan. The bastnaesite age may therefore record a subtle far-field response to the Musgravian Orogeny. Consequently, one possible interpretation is that there may be an episode of REE-rich mobilisation at the Vulcan prospect that is not related to the original (ca. 1590 Ma) mineralisation. However, more data (dating the cogenetic molybdenite, for instance) is needed to validate this bastnaesite age.

The texturally late dolomite-chalcopyrite veins (Fig. 4.4) produced an age of ca. 570 Ma (Fig. 4.6). These veins cross-cut the ~1590 Ma hematite-siderite-chlorite-apatite-sulphide hydrothermal matrix (Fig. 4.4), indicating vein formation post-dates the primary ~1590 Ma Cu mineralisation event. Consequently, the 570 Ma plausibly dates a separate event, in which Cu was mobilised. Importantly, these veins are texturally different to the ca. 1574 Ma dolomite crystals, indicating there may be at least two stages of dolomite formation at Vulcan. Alternatively, the ~570 Ma dolomite age may reflect a resetting or 'closure' age for the Lu-Hf system in dolomite; there is currently insufficient understanding of trace element behaviour in dolomite to assess this possibility further.

There is little evidence for significant tectonism (or magmatism) in the Gawler Craton at ca. 570 Ma, making the nature of the late dolomite age somewhat ambiguous (Hand et al., 2007; Lloyd et al., 2020). However, recent work conducted on uraninite and sulphides from Olympic Dam has suggested the possibility of 'upgrading' of U and potentially Cu between 0.7 and 0.5 Ma (Fig. 4.9; Ehrig et al., 2021). The obtained dolomite vein ages are consistent with this time period (Fig. 4.6, table 4.2). In addition to this, previous Rb-Sr dating of Neoproterozoic shales in the Adelaide Rift Complex has identified 586 ± 30 Ma Rb-Sr resetting, interpreted to be related to basin scale fluid flow, which may have mobilised Cu (Foden et al., 2001). The Adelaide Rift Complex, which overlies the Vulcan prospect, initiated at ca. 830 Ma, and occurred across several stages (Lloyd et al., 2020). 570 Ma was the timing of widespread clastic sedimentation associated with overfill of the Petermann Orogenic foreland (Haines et al., 2001). Consequently, far-field tectonism may have affected the Vulcan deposit, with vein formation possibly related to fault reactivation. In addition, the deposition of the Adelaidean sediments would have insulated the underlying Vulcan Prospect, leading to high heat flow within Mesoproterozoic rocks in the Gawler Craton (McLaren et al., 2003); this heating may have driven fluid flow (e.g. Oliver et al., 2006). The heavily brecciated Vulcan prospect may have had greater permeability relative to the surrounding rocks and overlying rocks, allowing for fluid circulation. Hence, the ~570 Ma Cu-bearing carbonate veins potentially warrant further investigation into the extent to which this 'event' has re-mobilised existing Cu mineralisation or introduced new Cu into the system, or whether Cu was removed from the system and deposited elsewhere.

4.8. Conclusions:

- Our data suggests that widespread hydrothermal alteration and mineralisation in the Vulcan prospect occurred at ca. 1595 Ma, consistent with previous constraints on IOCG mineralisation within the Gawler Craton (ca. 1595 Ma e.g. Skirrow et al., 2007)

- An additional phase, in which dolomite and chalcopyrite were mobilised, may have occurred at ca. 570 Ma, which has implications for Cu mobilisation in South Australia during the Neoproterozoic. However, further work is required to fully understand this age.
- In addition, we demonstrate that apatite U-Pb and Lu-Hf `double-dating` can provide more robust age constraints on mineralisation processes.
- We demonstrate the first ever *in situ* dolomite, siderite and bastnaesite Lu-Hf dates, demonstrating that a range of carbonates have the potential to date mineralisation processes.
- Further work is required to determine accurate closure temperatures, before dolomite (or bastnaesite) Lu-Hf ages can be easily interpreted, however a dolomite age of 1574 ± 39 Ma overlaps with the ca. 1595 Ma main mineralisation stage, suggesting that dolomite Lu-Hf can potentially preserve primary ages.

4.9. Appendix A: Analytical parameters

Appendix table 4.1: Analysis and LA-ICP-MS/MS tuning parameters for U-Pb

plasma parameters	
RF power	1350 W
Sample Depth	4 mm
Ar carrier gas	1 L/min
He carrier gas	0.38 L/min
N ₂ addition	4 mL/min
Lens Parameters	
Extract 1	1 V
Extract 2	-140 V
Omega Bias	-70 V
Omega Lens	7.0 V
Q1 entrance	-10 V
Q1 exit	-1.0 V
Cell focus	-3.0 V
Cell Entrance	-120 V
Cell Exit	-100 V
Deflect	9 V
Plate Bias	-90 V
Q1 parameters	
Q1 bias	-1.0 V
Q1 Prefilter Bias	-10.0 V
Q1 Postfilter Bias	-10.0 V
Cell Parameters	
10% HN ₃ + 90% He gas flow	22 mL/min
Octopole bias	-5.0 V
Axial Acceleration	2.0 V
Octopole RF	180 V
Energy Discrimination	-15.0 V

Q2 parameters	
Q2 bias	-15 V
Analysis Parameters	
Laser wavelength	193 nm
Laser fluence	10 J/cm ²
Laser spot diameter	257 µm (43 µm; NIST610 glass)
Laser repetition rate	10 Hz
washout	30 s (post cleaning pulse) + 20 s (post analysis)
Background	30 s
Analysis time	40 s
Isotopes measured (ms)	²⁴ Mg, ²⁷ Al, ⁴³ Ca, ⁴⁷ Ti, ⁵⁵ Mn, ⁵⁷ Fe, ⁸⁸ Sr, ⁸⁹ Y, ⁹⁰ Zr, ¹³⁹ La, ¹⁴⁹ Ce, ¹⁴¹ Pr, ¹⁴⁶ Nd, ¹⁴⁷ Sm, ¹⁵³ Eu, ¹⁵⁷ Gd, ¹⁵⁹ Tb, ¹⁶³ Dy, ¹⁶⁵ Ho, ¹⁶⁶ Er, ¹⁶⁹ Tm, ¹⁷² Yb, ¹⁷⁵ Lu, ²⁰² Hg, ²⁰⁴ Pb, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²³² Th, ²³⁸ U,

Appendix table 4.2: Representative analysis and LA-ICP-MS/MS tuning parameters for Lu-Hf

plasma parameters	
RF power	1350 W
Sample Depth	4 mm
Ar carrier gas	1 L/min
He carrier gas	0.38 L/min
N ₂ addition	4 mL/min
Lens Parameters	
Extract 1	-2.5 V
Extract 2	-145 V
Omega Bias	-80 V
Omega Lens	7.0 V
Q1 entrance	-10 V
Q1 exit	-1.0 V
Cell focus	-3.0 V
Cell Entrance	-120 V
Cell Exit	-100 V
Deflect	9 V
Plate Bias	-90 V
Q1 parameters	
Q1 bias	-1.0 V
Q1 Prefilter Bias	-10.0 V
Q1 Postfilter Bias	-10.0 V
Cell Parameters	
10% HN ₃ + 90% He gas flow	30 mL/min
Octopole bias	-5.0 V
Axial Acceleration	2.0 V
Octopole RF	180 V

<i>Energy Discrimination</i>	-15.0 V
<i>Q2 parameters</i>	
<i>Q2 bias</i>	-15 V
<i>Analysis Parameters</i>	
<i>Laser wavelength</i>	193 nm
<i>Laser fluence</i>	10 J/cm ²
<i>Laser spot diameter</i>	257 μm (43 μm; NIST610 glass)
<i>Laser repetition rate</i>	10 Hz
<i>washout</i>	30 s (post cleaning pulse) + 20 s (post analysis)
<i>Background</i>	30 s
<i>Analysis time</i>	40 s
<i>Isotopes measured (apatite)</i>	²⁴ Mg, ²⁷ Al, ⁴³ Ca, ⁴⁷ Ti, ⁵⁷ Fe, ⁸⁸ Sr, ⁸⁹ Y, ⁹⁰ Zr, ¹⁴⁰ Ce, ¹⁴⁶ Nd, ¹⁴⁷ Sm, ¹⁷² Yb, ¹⁷⁵ Lu, ¹⁷⁵⁺⁸² Lu, ¹⁷⁶⁺⁸² Hf, ¹⁷⁸⁺⁸² Hf

Supplementary data tables can be found at:

<https://doi.org/10.25909/21952655.v1>

<https://doi.org/10.25909/21952658.v1>

Conclusion

5.1. Summary of findings

The laser ablation Lu-Hf dating method, developed in chapter 1, successfully renders the isobaric interferences of ^{176}Yb and ^{176}Lu on ^{176}Hf negligible. This method uses a mixture of 10 % NH_3 gas and 90 % He, introduced to the reaction cell of the LA-ICP-MS/MS at a rate of 3 mL/min. This gas mixture and flow rate is optimised to promote production of $\text{Hf}((\text{NH})(\text{NH}_2)(\text{NH}_3)_3)^+$ (a reaction rate of 50 – 60%), while minimising the equivalent HREE reaction products (Yb reacts at a rate of < 0.00003%, and Lu reacts at a rate of < 0.003%; Simpson et al., 2021a). In addition to this, the method relies on the use of two key analytical parameters. Firstly, the axial acceleration of the ions is increased in the collision/reaction cell. Further work is required to determine the mechanism behind this, however, an increase in axial acceleration will increase the kinetic energy of the ions, which may increase the efficiency of the reaction with NH_3 . Alternatively, it may be that the large reaction product ions move less efficiently through the reaction cell when using a lower axial acceleration. The second key parameter is the use of a wait time offset (WTO), which is a small delay between each quadrupole changing the mass that it allows through. It was found that without the WTO, a small amount of the previously measured mass was not efficiently leaving the reaction cell, causing interferences. In more detail, Lu reacts to form a product with one more H than the Hf reaction product, creating the interference on $^{176}\text{Hf}((\text{NH})(\text{NH}_2)(\text{NH}_3)_3)^+$ (258 amu) from $^{175}\text{Lu}(\text{NH})(\text{NH}_3)_4^+$. The use of increased axial acceleration and WTO were crucial steps in the development of the analytical method. Laser induced elemental fractionation (LIEF) was found to range between 2 and 6 %, depending on the mineral analysed (described in chapters 1 and 2). With the combination of relatively large laser diameters (67 – 257 micron), high repetition rates (10 Hz) and long dwell times on Hf (100 – 150 ms), the method described in chapter 1 is capable of producing accurate Lu-Hf dates for a wide range of geological samples, including apatite (chapters 1 and 4), garnet (chapters 1 and 3), xenotime (chapter 1), calcite (chapter 2), dolomite (chapter 4) and bastnasite (chapter 4).

5.2. Current issues and future development

Although chapter 1 demonstrated a viable method for LA-ICP-Q-MS/MS Lu-Hf analysis, there are some improvements that can be made, as well as potential for further analytical investigation. The most important limitation, from an analytical perspective, is the sensitivity on Hf measurements, which can make analysis challenging for low Hf minerals (such as apatite and calcite; chapters 1, 2, and 4). The low sensitivity necessitates large laser ablation spot diameters (up to 257 microns for carbonates, which typically contain < 5ppm Lu, and ppb – ppt Hf concentrations) compared to ~30 microns laser beams for apatite U-Th-Pb analysis (e.g. Gillespie et al., 2018; Glorie et al., 2019), and 100 – 120 microns laser beams for calcite U-Pb dating (e.g. Roberts and Walker, 2016; Simpson et al., 2021b). During the method development, a large range of tune settings were tested. Hence, it is unlikely that sensitivity can significantly be enhanced compared to the described method, without the use of new hardware and/or new reaction gases. Analytical parameters, such as spot size, repetition rate, and dwell times have been largely optimised, and increases in these may compromise analysis in other ways. For instance, increasing Hf dwell times may increase sensitivity but may also compromise precision, as this will reduce the total number of measurements per analysis. Increasing the laser repetition rate will increase the depth to which the laser drills, which may increase the chances of incorporating inclusions or Lu-Hf zonation. In the case of carbonates, in which the largest possible laser beam diameter is already used (257 microns), an increase in laser repetition rate may overload the plasma torch, reducing its ionisation efficiency (e.g. Kroslovskaya and

Günther, 2007). Limited effects of plasma-loading have been observed in this work (chapter 3), meaning that further energy increases might compromise effective measurement of isotopic ratios.

While the need to increase the axial acceleration of the ions in the collision/reaction cell and the requirement for the WTO are not in themselves limitations, they prevent application of the laser ablation Lu-Hf technique to instruments that do not have the ability to modify these parameters. The WTO can theoretically be replaced with measurement of a 'dummy' mass between mass 175 (^{175}Lu) and mass 176 (^{176}Hf measurement). For instance, another reaction product of Hf can be measured for 2 ms prior to the quadrupoles switching to measure $^{176}\text{Hf}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$. Unfortunately, axial acceleration is more of an issue, as it is a hardware limitation that will effect some ICP-Q-MS/MS instruments (e.g. the older agilent 8800 QQQ; Agilent, 2016).

Recent work has demonstrated successful laser ablation inductively coupled multi-collector tandem mass spectrometry (LA-ICP-MC-MS/MS) can be used to date minerals via the Rb-Sr system (Bevan et al., 2021; Dauphas et al., 2022). As a multicollector simultaneously measure all masses of interest, they have the potential to achieve significantly higher sensitivity and precision relative to quadrupole instruments (Longerich, 2008). Consequently, it is beneficial for the geological community to develop LA-ICP-MC-MS/MS Lu-Hf dating. Unfortunately, however, this is not possible with the current method. There are two main reasons for this. Firstly, the mass difference between ^{175}Lu and $^{178}\text{Hf}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$ (85 amu) is too large to be handled by the detector array of traditional multicollector instrument (for instance, the pre-commercial ICP-MC-MS/MS cannot measure a mass range of >20 amu; Dauphas et al., 2022). This can potentially be overcome by measuring a Lu reaction product that is closer in mass to the Hf reaction product, however, sensitivity will be strongly compromised given Lu is not as reactive with NH_3 (refer to chapter 1, appendix figure 1.1). An additional, and more serious issue, is that Lu reacts with 1 more H than Hf, meaning that there is a $^{175}\text{Lu}(\text{NH})(\text{NH}_3)_4^+$ interference on $^{176}\text{Hf}(\text{NH})(\text{NH}_2)(\text{NH}_3)_3^+$ (both have masses of 258 amu). Consequently, if isotopes are simultaneously measured, there will be an interference from ^{175}Lu on ^{176}Hf (which is currently mitigated on the quadrupole instrument by the WTO, explained above). Therefore, a new analytical procedure would need to be developed for Lu-Hf analysis to be successful using LA-ICP-MC-MS/MS. This may require the use of alternative (or even mixed) reaction gases.

5.3. Laser ablation Lu-Hf reference materials

Well-characterized matrix-matched standards are an important aspect in the development of any laser ablation geochronological technique, including laser ablation Lu-Hf dating (e.g. Chew et al., 2014; Jackson, 2008; Sylvester, 2008). Several promising candidates have been identified, and work is currently underway to characterise these materials using traditional Lu-Hf analysis. For instance, natural samples of apatite, calcite and garnet have proven useful as secondary standards for LIEF corrections (e.g. Chapters 2, 3, 4 and; Brown et al., 2022; Gillespie et al., 2022; Glorie et al., 2022; Glorie et al., 2021; Glorie et al., 2023; Ribeiro et al., 2021; Tamblyn et al., 2021). Current standards, however, rely on external constraints on their expected age. For instance, the garnet standard, Hogsbo, is reliant on a columbite U-Pb age from the same pegmatite (1029 ± 1.7 Ma; Romer and Smeds, 1996). While chapter 3 demonstrates that Hogsbo can be used to calculate accurate ages, it is desirable to have direct constraints on the Lu-Hf age of the Hogsbo garnet standard in order to improve accuracy. Similarly, the apatite standard, OD306 relies on a U-Pb age (1597 ± 7.1 Ma; Thompson et al., 2016), rather than an independent Lu-Hf age. However, this mineral also has been demonstrated to produce accurate Lu-Hf ages (chapter 4). The ongoing development of multiple standards per mineral will help improve data quality, as they can act as secondary age checks on LIEF corrections. Ideally, any standards that are developed would have independent constraints on Lu-Hf

ratios (determined using solution Lu-Hf methods), are isotopically homogenous (i.e. all data across large crystals produce isochronic results) and occur in a large enough quantity to be shared with other labs. High precision Lu-Hf ratios are important for these reference materials, as the uncertainty on the correction factor must be propagated to the samples (e.g. chapter 2; Horstwood et al., 2016). The potential reference materials demonstrate good between run reproducibility, with all ages plotting within uncertainty (Figs. 5.1, 5.2, and 5.3).

5.3.1. Garnet reference materials

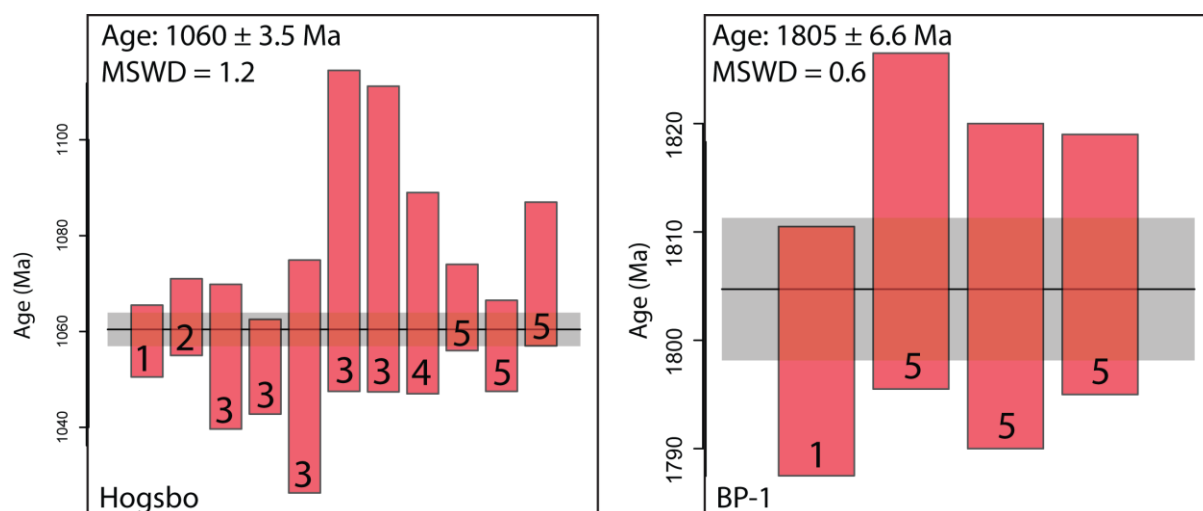


Figure 5.1: long term average ages of potential garnet Lu-Hf standards. Data is presented as a weighted average of ages from chapters in this thesis as well as data from published studies. These plots are designed to demonstrate between session reproducibility, and consequently, data has **not** been corrected for LIEF. 1 refers to chapter 1, 2 refers to Ribeiro et al. (2021), 3 refers to Tamblyn et al. (2021), 4 refers to Brown et al. (2022), and 5 refers to chapter 3.

As stated, Hogsbo garnet can be used a secondary standard to correct for LIEF in garnet samples. Details of this method can be found in chapters 1 and 3. The correction involves using an isochron regression through an age-homogenous, but isotopically heterogenous matrix-matched sample. In this case, the x-intercept of an inverse isochron for the Hogsbo garnet sample is compared to the expected x-intercept (assuming a crystallisation age of ca. 1029 Ma). A correction-based on the measured and expected x-intercept is then applied to the ^{176}Lu - ^{176}Hf ratios of unknown samples. Several studies have used the method outlined in chapter 1 to use garnet Lu-Hf dating to investigate geological problems (e.g. Brown et al., 2022; Ribeiro et al., 2021; Tamblyn et al., 2021).

Garnet sample BP1 is a promising candidate for a secondary standard, and consistently produces ages with uncertainties of < 1 % (when $n > 20$, and data is spread between the core and rim), as well as demonstrating reproducibility across different analytical sessions (Fig. 5.1). This sample currently relies on both regional geochronological constraints, as well as a U-Pb monazite date from the same hand sample (Lane, 2011). Consequently, direct and independent constraints on the Lu-Hf age of the garnet need to be obtained.

Solution Lu-Hf age constraints for Hogsbo and BP1 are being pursued and new potential Lu-Hf standards are being characterised. For new Lu-Hf garnet standards, we recommend finding garnets from HREE-rich pegmatites, as these are likely to incorporate high Lu, and produce more precise dates (for instance, Hogsbo garnet is from a pegmatite). Garnets from metapelitic rocks, in which garnet is relatively sparse (so Lu is concentrated in only a few garnets, rather than diluted across many; chapter 3) may also provide useful standards. Given garnet tends to incorporate a significant

amount of Lu and Hf bearing inclusions (Scherer et al., 2000), it is important to make sure any potential garnet Lu-Hf standard is relatively inclusion free.

5.3.2. Apatite reference materials

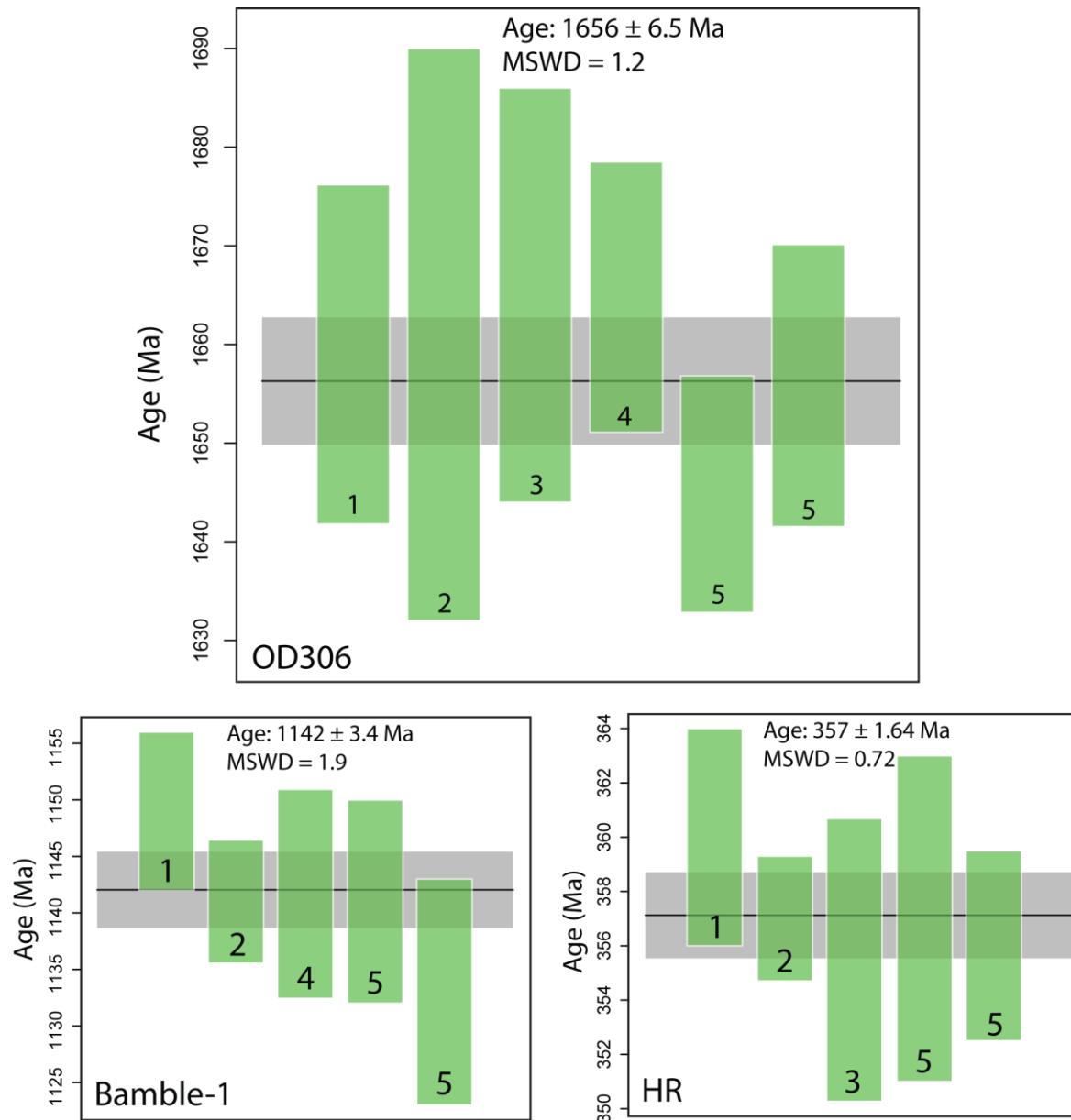


Figure 5.2: long term average ages of potential apatite Lu-Hf standards. Data is presented as a weighted average of ages from chapters in this thesis as well as data from published studies. These plots are designed to demonstrate between session reproducibility, and consequently, data has **not** been corrected for LIEF. 1 refers to chapter 1, 2 refers to Glorie et al. (2021), 3 refers to Glorie et al. (2022), 4 refers to Gillespie et al. (2022) and 5 refers to chapter 4.

Although a series of potential apatite laser ablation Lu-Hf standards were identified in chapter 1, currently only one (OD306) has independent *direct* age constraints (Bamble apatite has regional age constraints, but the hand sample used in this thesis has not been reliably dated by other means). OD306 is capable of producing accurate and reproducible apatite Lu-Hf ages, as demonstrated in chapter 4 and Fig. 5.2. However, OD306 is not isotopically homogenous, whereas some of the other potential standards are. For instance, Bamble-1 (from the same location as 215 from chapter 1, but a

different hand sample), HR-apatite, and Wallaroo mines apatite do not contain significant quantities of common Hf and consequently appear to be isotopically homogenous in $^{176}\text{Lu}/^{176}\text{Hf}$ ratios (chapter 1). If the $^{176}\text{Lu}/^{176}\text{Hf}$ ratio can be constrained for these samples, then they have the potential to correct measured $^{176}\text{Lu}/^{176}\text{Hf}$ ratios in apatite samples, and consequently be used as primary reference materials. Note that the $^{177}\text{Hf}/^{176}\text{Hf}$ ratios can be normalised to homogenous glasses, such as NIST610 SRM, as they are not affected by LIEF. Ages calculated from potential standards provide reproducible ages between analytical sessions (Fig. 5.2), indicating that OD306, bamble-1, and HR would make useful standards for laser ablation Lu-Hf.

5.3.3. Carbonate reference materials

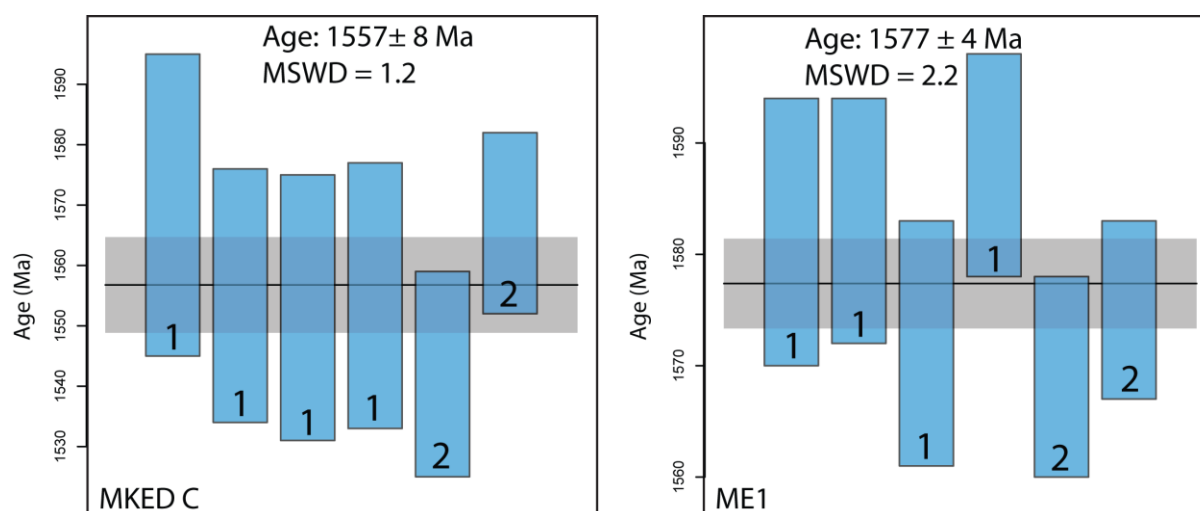


Figure 5.3: long term average ages of potential calcite Lu-Hf standards. Data is presented as a weighted average of ages from chapters in this thesis. These plots are designed to demonstrate between session reproducibility, and consequently, data has **not** been corrected for LIEF. 1 refers to chapter 2 and 2 refers to data from chapter 4.

Similar to apatite, several potential calcite Lu-Hf standards have been identified. MKED-C produces ages with precisions of $\sim 1 - 2\%$ ($n > 20$), and does not appear to contain significant common Hf (see chapter 2). Additionally, MKED-C has an indirect age constraint from co-genetic titanite (1517 ± 0.32 Ma; TIMS U-Pb; Spandler et al., 2016) meaning it can be used to correct laser ablation calcite Lu-Hf data. ME-1 as well as potentially ME-2 and OL-MB all have potential to become laser ablation Lu-Hf reference materials (chapter 2) and solution Lu-Hf constraints on these samples is currently being obtained. Similar to the potential apatite reference materials, these samples are isotopically homogenous in terms of $^{176}\text{Lu}/^{176}\text{Hf}$ ratios. However, no suitable reference materials have been identified for either dolomite or bastnasite. The single bastnasite sample that was dated in this work produced a relatively imprecise Lu-Hf age (1177 ± 50 Ma; chapter 4). Similarly, dolomite samples did not produce ages with high enough precision, or independent ages constraints to be suitable reference materials. We note, however, that given the relatively small offset due to LIEF observed for carbonates ($\sim 3\%$; chapter 2), and the similarities between dolomite and calcite, it may be possible to use calcite reference materials to correct dolomite Lu-Hf ratios. This requires further investigation, however.

5.4. Applicable minerals and potential applications

5.4.1. Laser ablation Garnet Lu-Hf dating

Chapter 1 demonstrated that accurate Lu-Hf ages could be obtained for a variety of garnet samples, including samples from pegmatites, metabasites, and metapelites. Although uncertainties on laser ablation ages for garnets from metabasic and metapelitic rocks were significantly higher than can be obtained using traditional solution Lu-Hf analysis, dates were nonetheless geologically useful. The Hogsbo garnet, on the other hand, produced a relatively precise Lu-Hf age (up to 1058 ± 4.5 Ma: $\sim 0.4\%$ uncertainty, excluding systematic uncertainties; chapter 1). The garnet Lu-Hf method was further developed by Tamblyn et al. (2021) as well as work conducted in chapter 3. These method refinements involve the use of careful sample selection (for instance, targeting rocks with only few garnets, so as not to dilute the Lu concentration), as well as imaging techniques (such as μ -XRF), that allow targeting of high Lu garnet zones. These techniques have been demonstrated to produce garnet Lu-Hf ages from metapelitic rocks with precisions as low as 1.4% (e.g. P-1 garnet; 861 ± 12 Ma; chapter 3), this uncertainty includes reference material and decay constant. Consequently, it is possible to produce laser ablation Lu-Hf dates for metamorphic garnets with a precision that can come close to rivalling dissolution-based Lu-Hf analysis (by collecting >60 data points for an individual garnet age, and targeting regions with high Lu-Hf ratios that are too small to be targeted by solution analysis). We note that this will only be possible for garnets with exceptionally high Lu/Hf ratios, and typical garnet isochron uncertainties are more likely to be 2% or more. Consequently, the method can produce meaningful Lu-Hf ages for garnets and can be used to answer geological questions.

Potential applications of garnet LA-ICP-Q-MS/MS Lu-Hf dating have been explored, demonstrating that the technique has great potential for large scale terrane mapping of metamorphic garnet ages. The ability to quickly and efficiently produce garnet Lu-Hf dates allows for the laser ablation Lu-Hf method to easily determine complex metamorphic histories, provided metamorphic events are sufficiently different in age (ideally $> 4\%$ apart). Further, we demonstrate that the high spatial resolution of laser ablation Lu-Hf dating can resolve multiple metamorphic ages within the same garnet, with several core – rim Lu-Hf age differences demonstrated (e.g. chapter 3, Tamblyn et al., 2021). This is important for investigation of polymetamorphic rocks, as garnets commonly grow new material during subsequent metamorphic events (e.g. Baxter and Scherer, 2013; Vance and O'Nions, 1990). The high spatial resolution also opens the way for investigations of diffusional and resetting processes that effect the Lu-Hf ratios of garnet. For instance, the tendency to form 'bell shaped' Lu zonation profiles, coupled with Lu diffusing faster than Hf at elevated temperatures (Baxter et al., 2017; Bloch et al., 2015) can potentially lead to complex isotopic decoupling between Lu and Hf (i.e. 'isochron rotation'; Bloch and Ganguly, 2015; Bloch et al., 2020). Additionally, Lu can potentially diffuse *into* the garnet, which would lead to excessively high Lu/Hf ratios in the rims of some garnets (e.g. Kelly et al., 2011). As laser ablation Lu-Hf dating has higher spatial resolution compared to traditional dissolution-based techniques, it has the potential to investigate these processes. An additional application is to apply the laser ablation technique to determine the age of detrital garnets, which may be able to provide constraints on the metamorphic history of terranes that cannot easily be sampled directly (e.g. under the Antarctic ice sheet, or in difficult-to-access mountain areas).

5.4.2. Laser ablation apatite Lu-Hf dating

Chapter 1 demonstrated that apatite can be dated with relatively high precision (up to 0.6 % 2SE for Bamble-1/215 apatite). Precision is a function of ingrowth time and Lu concentration and chapter 1 has demonstrated that a precision of $<2\%$ can be obtained for relatively Lu rich Palaeozoic samples (e.g. 343 ± 6 Ma; HR apatite). This work has been followed up with more (e.g. Gillespie et al., 2022; Glorie et al., 2023) demonstrating the closure temperature difference between apatite Lu-Hf and U-

Pb. Apatite appears to incorporate very low Hf concentrations when forming with Hf-bearing minerals, such as zircon, which allows for 'single laser spot' ages to be calculated. However, in cases where no zircon (or other Hf bearing mineral) forms, significant common Hf can be incorporated. This is likely to be the case in mafic rocks as well as some mineral deposits. Chapter 4 demonstrated that apatite Lu-Hf dating, in contrast to U-Pb dating, can produce reliable age constraints on mineralisation. This is due to the Lu-Hf isotopic system generally being more robust to subsequent isotopic disturbances compared to the Pb isotopic system (e.g. Patchett et al., 1982; Stacey and Kramers, 1975; Vervoort, 2014). As significant Pb is often incorporated into apatite (as well as potentially Pb rich inclusions), apatite U-Pb dates can sometimes be complicated, and hence Lu-Hf dating has the ability to date apatites where U-Pb may fail.

There are a variety of potential applications for apatite Lu-Hf dating. For instance, the different closure temperature relative to the U-Pb system may allow for age decoupling to explore thermal histories, particularly in high temperature terranes. Additionally, the ability to obtain single spot Lu-Hf ages, either because the apatite did not incorporate Hf, or because common Hf corrections are relatively straightforward, coupled with U-Pb ages, can allow for robust detrital apatite studies (e.g. Glorie et al., 2021). As demonstrated in chapter 4, apatite laser ablation Lu-Hf can also be used to obtain more straightforward ages for mineralisation processes. If this is coupled with petrological analysis of apatite, then apatite Lu-Hf dating can be used to better understand mineralisation processes (e.g. chapter 4). Potential future applications include dating SiO₂ poor rocks, such as mafic and ultramafic igneous rocks (that often lack zircon), as well as dating extra-terrestrial material (e.g. Glorie et al., 2022).

5.4.3. Laser ablation carbonate Lu-Hf dating

Carbonate Lu-Hf dating was demonstrated in chapters 2 and 4. The technique is capable of producing both precise and accurate ages for Precambrian carbonates (including calcite, dolomite, siderite, and bastnasite). The dated carbonates span from ~2000 to 570 Ma, with uncertainties as low as 0.6 % 2SE.; chapter 2. Although good quality dates were produced, the main limitation of laser ablation carbonate Lu-Hf dating is the large laser ablation spot size required (257 microns), although spot sizes of 170 – 120 microns may be possible for high Lu samples. Laser ablation carbonate Lu-Hf dating appears to be more successful in situations where carbonate U-Pb dating is not feasible (and potentially vice versa). For instance, carbonates at mineral deposits produced the best quality Lu-Hf ages. None of the samples analysed in this thesis could be dated by U-Pb due to high Pb/U ratios. Additionally, although the closure temperature of the Lu-Hf system in carbonates is not currently known, we have produced ages of between 1.5 and 2 Ga from a variety of locations (e.g. Phalaborwa carbonatite, South Africa, Mt Elliott IOCG deposit, Queensland, Australia, Vulcan IOCG deposit, South Australia, Australia, Flin Flon, Canada). This indicates that, at the least, carbonate Lu-Hf ages can be preserved over a significant period of time.

We suggest that the calcite Lu-Hf method can be applied to mineral deposits that have been difficult to obtain ages for in the past. The technique can also be combined with other isotopic systems in carbonates. The following isotopic systems can be preserved in carbonates: Sr isotopes, Nd isotopes, O isotopes and C isotopes to name a few. Additionally, the clumped O isotope thermometer can be used to obtain temperature constraints on carbonate formation (e.g. Eiler, 2011). Finally, the work in this thesis has focused mainly on carbonates from mineral deposits, however carbonates that form in other settings may also be datable using Lu-Hf. For instance, the sample from Flin Flon in Canada, is a calcite vein that formed in association with low grade (greenschist facies) metamorphism, which can be difficult to date (e.g. Henrichs et al., 2019). Consequently, calcite Lu-Hf may be able to provide dates for low grade metamorphism. Additionally, although many sedimentary carbonates

are expected to have relatively low HREE concentrations (e.g. Li et al., 2019; Terakado and Masuda, 1988), it may be possible to apply the laser ablation Lu-Hf technique to carbonates that are sufficiently old to have accumulated measurable radiogenic Hf.

5.5. Conclusion

This thesis has provide a framework to apply LA-ICP-Q-MS/MS Lu-Hf dating to a variety of minerals, opening the way for this technique to be used to solve geological problems. Although there are some outstanding issues, such as the need for high-quality matrix-matched reference materials, the method has been successfully demonstrated in different settings, including regional metamorphic terranes, as well as hydrothermal mineral deposits.

Bibliography

- Agilent, 2016, Agilent 8900 Triple Quadrupole ICP-MS Technical overview: Agilent Technologies.
- Amelin, Y., 2005, Meteorite Phosphates Show Constant ^{176}Lu Decay Rate Since 4557 Million Years Ago: *Science*, v. 310, p. 839-841.
- Anczkiewicz, R., Platt, J. P., Thirlwall, M. F., and Wakabayashi, J., 2004, Franciscan subduction off to a slow start: evidence from high-precision Lu–Hf garnet ages on high grade-blocks: *Earth and Planetary Science Letters*, v. 225, no. 1-2, p. 147-161.
- Apukhtina, O. B., Kamenetsky, V. S., Ehrig, K., Kamenetsky, M. B., Maas, R., Thompson, J., McPhie, J., Ciobanu, C. L., and Cook, N. J., 2017, EARLY, DEEP MAGNETITE-FLUORAPATITE MINERALIZATION AT THE OLYMPIC DAM Cu-U-Au-Ag DEPOSIT, SOUTH AUSTRALIA*: *Economic Geology*, v. 112, no. 6, p. 1531-1542.
- Armistead, S. E., Collins, A. S., Redaa, A., Jepson, G., Gillespie, J., Gilbert, S., Blades, M. L., Foden, J. D., and Razakamanana, T., 2020, Structural evolution and medium-temperature thermochronology of central Madagascar: implications for Gondwana amalgamation: *Journal of the Geological Society*, v. 177, no. 4, p. 784-798.
- Arrowsmith, P., and Hughes, S. K., 1988, Entrainment and Transport of Laser Ablated Plumes for Subsequent Elemental Analysis: *Applied Spectroscopy*, v. 42, no. 7, p. 1231-1239.
- Balcaen, L., Bolea-Fernandez, E., Resano, M., and Vanhaecke, F., 2015, Inductively coupled plasma – Tandem mass spectrometry (ICP-MS/MS): A powerful and universal tool for the interference-free determination of (ultra)trace elements – A tutorial review: *Analytica Chimica Acta*, v. 894, p. 7-19.
- Barfod, G. H., Albarède, F., Knoll, A. H., Xiao, S., Telouk, P., Frei, R., and Baker, J., 2002, New Lu–Hf and Pb–Pb constraints on the earliest animal fossils: *Earth and Planetary Science Letters*, v. 201, p. 203-212.
- Barfod, G. H., Krogstad, E. J., Frei, R., and Albarède, F., 2005, Lu–Hf and PbSL geochronology of apatites from Proterozoic terranes: A first look at Lu–Hf isotopic closure in metamorphic apatite: *Geochimica et Cosmochimica Acta*, v. 69, no. 7, p. 1847-1859.
- Barfod, G. H., Otero, O., and Albarède, F., 2003, Phosphate Lu–Hf geochronology: *Chemical Geology*, v. 200, no. 3-4, p. 241-253.
- Barker, S. L. L., Bennett, V. C., Cox, S. F., Norman, M. D., and Gagan, M. K., 2009, Sm–Nd, Sr, C and O isotope systematics in hydrothermal calcite–fluorite veins: Implications for fluid–rock reaction and geochronology: *Chemical Geology*, v. 268, no. 1-2, p. 58-66.
- Barker, S. L. L., and Cox, S. F., 2011, Oscillatory zoning and trace element incorporation in hydrothermal minerals: insights from calcite growth experiments: *Geofluids*, v. 11, no. 1, p. 48-56.
- Basson, I., Lourens, P., Paetzold, H.-D., Thomas, S., Brazier, R., and Molabe, P., 2017, Structural analysis and 3D modelling of major mineralizing structures at the Phalaborwa copper deposit.: *Ore Geology Reviews*, v. 83, p. 30-42.
- Bastrakov, E. N., Skirrow, R. G., and Davidson, G. J., 2007, Fluid Evolution and Origins of Iron Oxide Cu–Au Prospects in the Olympic Dam District, Gawler Craton, South Australia: *Economic Geology*, v. 102, no. 8, p. 1415-1440.
- Baxter, E. F., Caddick, M. J., and Ague, J. J., 2013, Garnet: Common Mineral, Uncommonly Useful: *Elements*, v. 9, no. 6, p. 415-419.
- Baxter, E. F., Caddick, M. J., and Dragovic, B., 2017, Garnet: A Rock-Forming Mineral Petrochronometer: *Reviews in Mineralogy and Geochemistry*, v. 83, no. 1, p. 469-533.
- Baxter, E. F., and Scherer, E. E., 2013, Garnet Geochronology: Timekeeper of Tectonometamorphic Processes: *Elements*, v. 9, no. 6, p. 433-438.
- Bell, T. H., Johnson, S. E., Davis, B., Forde, A., Hayward, N., and Wilkins, C., 1992, Porphyroblast inclusion-trail orientation data: eppure non son girate*!: *Journal of Metamorphic Geology*, v. 10, no. 3, p. 295-307.

- Belousova, E. A., Griffin, W. L., O'Reilly, S. Y., and Fisher, N. I., 2002, Apatite as an indicator mineral for mineral exploration: trace-element compositions and their relationship to host rock type: *Journal of Geochemical Exploration*, v. 76, no. 1, p. 45-69.
- Belperio, A., Flint, R., and Freeman, H., 2007, Prominent Hill: A Hematite-Dominated, Iron Oxide Copper-Gold System: *Economic Geology*, v. 102, no. 8, p. 1499-1510.
- Bevan, D., Coath, C. D., Lewis, J., Schwieters, J., Lloyd, N., Craig, G., Wehrs, H., and Elliott, T., 2021, In situ Rb–Sr dating by collision cell, multicollection inductively-coupled plasma mass-spectrometry with pre-cell mass-filter, (CC-MC-ICPMS/MS): *Journal of Analytical Atomic Spectrometry*, v. 36, no. 5, p. 917-931.
- Bingen, B., Davis, W. J., Hamilton, M. A., Engvik, A. K., Stein, H. J., Skar, O., and Nordgulen, O., 2008, Geochronology of high-grade metamorphism in the Sveconorwegian belt, S. Norway: U-Pb, Th-Pb and Re-Os data: *Norwegian Journal of Geology*, v. 88, p. 13-42.
- Bingen, B., Demaiffe, D., and Breemen, O. v., 1998, The 616 Ma Old Egersund Basaltic Dike Swarm, SW Norway, and Late Neoproterozoic Opening of the Iapetus Ocean: *The Journal of Geology*, v. 106, no. 5, p. 565-574.
- Bird, A., Cutts, K., Strachan, R., Thirlwall, M. F., and Hand, M., 2018, First evidence of Renlandian (c. 950–940 Ma) orogeny in mainland Scotland: Implications for the status of the Moine Supergroup and circum-North Atlantic correlations: *Precambrian Research*, v. 305, p. 283-294.
- Bird, A. F., Thirlwall, M. F., Strachan, R. A., and Manning, C. J., 2013, Lu–Hf and Sm–Nd dating of metamorphic garnet: evidence for multiple accretion events during the Caledonian orogeny in Scotland: *Journal of the Geological Society*, v. 170, no. 2, p. 301-317.
- Black, L. P., and Gulson, B. L., 1978, The age of the Mud Tank carbonatite, Strangways Range, Northern Territory.: *Journal of Australian Geology and Geophysics*, v. 3, p. 227-232.
- Blichert-Toft, J., Chauvel, C., and Albarède, F., 1997, Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS: *Contributions to Mineralogy and Petrology*, v. 127, p. 248-260.
- Bloch, E., and Ganguly, J., 2015, 176Lu–176Hf geochronology of garnet II: numerical simulations of the development of garnet–whole-rock 176Lu–176Hf isochrons and a new method for constraining the thermal history of metamorphic rocks: *Contributions to Mineralogy and Petrology*, v. 169, no. 2.
- Bloch, E., Ganguly, J., Hervig, R., and Cheng, W., 2015, 176Lu–176Hf geochronology of garnet I: experimental determination of the diffusion kinetics of Lu³⁺ and Hf⁴⁺ in garnet, closure temperatures and geochronological implications: *Contributions to Mineralogy and Petrology*, v. 169, no. 2.
- Bloch, E. M., Jollands, M. C., Devoir, A., Bouvier, A. S., Ibañez-Mejia, M., and Baumgartner, L. P., 2020, Multispecies Diffusion of Yttrium, Rare Earth Elements and Hafnium in Garnet: *Journal of Petrology*, v. 61, no. 7.
- Bolea-Fernandez, E., Balcaen, L., Resano, M., and Vanhaecke, F., 2016a, Tandem ICP-mass spectrometry for Sr isotopic analysis without prior Rb/Sr separation: *Journal of Analytical Atomic Spectrometry*, v. 31, no. 1, p. 303-310.
- Bolea-Fernandez, E., Van Malderen, S. J. M., Balcaen, L., Resano, M., and Vanhaecke, F., 2016b, Laser ablation-tandem ICP-mass spectrometry (LA-ICP-MS/MS) for direct Sr isotopic analysis of solid samples with high Rb/Sr ratios: *Journal of Analytical Atomic Spectrometry*, v. 31, no. 2, p. 464-472.
- Bons, P. D., Elburg, M. A., and Gomez-Rivas, E., 2012, A review of the formation of tectonic veins and their microstructures: *Journal of Structural Geology*, v. 43, p. 33-62.
- Boudin, A., and Deutsch, S., 1970, Geochronology: Recent Development in the Lutetium-176/Hafnium-176 Dating Method: *Science*, v. 168, no. 3936, p. 1219-1220.

- Bowden, B., Fraser, G., Davidson, G. J., Meffre, S., Skirrow, R., Bull, S., and Thompson, J., 2017, Age constraints on the hydrothermal history of the Prominent Hill iron oxide copper-gold deposit, South Australia: *Mineralium Deposita*, v. 52, no. 6, p. 863-881.
- Bowes, D. R., 1968, The absolute time scale and the subdivision of Precambrian rocks in Scotland: *Geologiska Föreningen i Stockholm Förhandlingar*, v. 90, no. 2, p. 175-188.
- Brown, D. A., Simpson, A., Hand, M., Morrissey, L. J., Gilbert, S., Tamblyn, R., and Glorie, S., 2022, Laser-ablation Lu-Hf dating reveals Laurentian garnet in subducted rocks from southern Australia: *Geology*, v. 50, no. 7, p. 837-842.
- Brown, D. A., Tamblyn, R., Hand, M., and Morrissey, L. J., 2020, Thermobarometric constraints on burial and exhumation of 2-billion-year-old eclogites and their metapelitic hosts: *Precambrian Research*, v. 347.
- Brugger, J., Liu, W., Etschmann, B., Mei, Y., Sherman, D. M., and Testemale, D., 2016, A review of the coordination chemistry of hydrothermal systems, or do coordination changes make ore deposits?: *Chemical Geology*, v. 447, p. 219-253.
- Buick, I. S., Storkey, A., and Williams, I. S., 2008, Timing relationships between pegmatite emplacement, metamorphism and deformation during the intra-plate Alice Springs Orogeny, central Australia: *Journal of Metamorphic Geology*, v. 26, no. 9, p. 915-936.
- Caddick, M. J., and Kohn, M. J., 2013, Garnet: Witness to the Evolution of Destructive Plate Boundaries: *Elements*, v. 9, no. 6, p. 427-432.
- Campbell, L. S., Compston, W., Sircombe, K. N., and Wilkinson, C. C., 2014, Zircon from the East Orebody of the Bayan Obo Fe-Nb-REE deposit, China, and SHRIMP ages for carbonatite-related magmatism and REE mineralization events: *Contributions to Mineralogy and Petrology*, v. 168, no. 2, p. 1041.
- Cave, B., Lilly, R., Glorie, S., and Gillespie, J., 2018, Geology, Apatite Geochronology, and Geochemistry of the Ernest Henry Inter-Lens: Implications for a Re-Examined Deposit Model: *Minerals*, v. 8, no. 9.
- Cave, B., Lilly, R., and Rea, P., 2022, IN SITU U-Pb MONAZITE GEOCHRONOLOGY RECORDS MULTIPLE EVENTS AT THE MOUNT ISA Cu ($\pm$ Zn-Pb-Ag) DEPOSIT, NORTHERN AUSTRALIA: *Economic Geology*.
- Cawood, P. A., Nemchin, A. A., Strachan, R. A., Kinny, P. D., and Leowy, S., 2004, Laurentian provenance and an intracratonic tectonic setting for the Moine Supergroup, Scotland, constrained by detrital zircons from the Loch Eil and Glen Urquhart successions: *Journal of the Geological Society*, v. 161, no. 5, p. 861-874.
- Cawood, P. A., Strachan, R., Cutts, K., Kinny, P. D., Hand, M., and Pisarevsky, S., 2010, Neoproterozoic orogeny along the margin of Rodinia: Valhalla orogen, North Atlantic: *Geology*, v. 38, no. 2, p. 99-102.
- Cawood, P. A., Strachan, R. A., Merle, R. E., Millar, I. L., Loewy, S. L., Dalziel, I. W. D., Kinny, P. D., Jourdan, F., Nemchin, A. A., and Connelly, J. N., 2014, Neoproterozoic to early Paleozoic extensional and compressional history of East Laurentian margin sequences: The Moine Supergroup, Scottish Caledonides: *Geological Society of America Bulletin*, v. 127, no. 3-4, p. 349-371.
- Cheng, H., Liu, X. C., Vervoort, J. D., Wilford, D., and Cao, D. D., 2016, Micro-sampling Lu-Hf geochronology reveals episodic garnet growth and multiple high-P metamorphic events: *Journal of Metamorphic Geology*, v. 34, no. 4, p. 363-377.
- Cherniak, D. J., 1997, An experimental study of strontium and lead diffusion in calcite, and implications for carbonate diagenesis and metamorphism: *Geochimica et Cosmochimica Acta*, v. 61, no. 19, p. 4173-4179.
- Cherniak, D. 1998, REE diffusion in calcite: *Earth and Planetary Science Letters*, v. 160, p. 273-287.
- Cherniak, D., 2000, Rare earth element diffusion in apatite: *Geochemistry, Geophysics, Geosystems*, v. 64, no. 22, p. 3871-3885.
- Cherniak, D., 2006, Pb and rare earth element diffusion in xenotime: *Lithos*, v. 88, no. 1-4, p. 1-14.

- Cherniak, D. J., Lanford, W. A., and Ryerson, F. J., 1991, Lead diffusion in apatite and zircon using ion implantation and Rutherford backscattering techniques: *Geochemistry, Geophysics, Geosystems*, v. 55, p. 1663-1673.
- Cherry, A. R., Kamenetsky, V. S., McPhie, J., Thompson, J. M., Ehrig, K., Meffre, S., Kamenetsky, M. B., and Krneta, S., 2018, Tectonothermal events in the Olympic IOCG Province constrained by apatite and REE-phosphate geochronology: *Australian Journal of Earth Sciences*, v. 65, no. 5, p. 643-659.
- Cherry, A. R., McPhie, J., Kamenetsky, V. S., Ehrig, K., Keeling, J. L., Kamenetsky, M. B., Meffre, S., and Apukhtina, O. B., 2017, Linking Olympic Dam and the Cariewerloo Basin: Was a sedimentary basin involved in formation of the world's largest uranium deposit?: *Precambrian Research*, v. 300, p. 168-180.
- Chew, D. M., Petrus, J. A., and Kamber, B. S., 2014, U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb: *Chemical Geology*, v. 363, p. 185-199.
- Chew, D. M., and Spikings, R. A., 2015, Geochronology and Thermochronology Using Apatite: Time and Temperature, Lower Crust to Surface: *Elements*, v. 11, no. 3, p. 189-194.
- Chew, D. M., Sylvester, P. J., and Tubrett, M. N., 2011, U–Pb and Th–Pb dating of apatite by LA–ICPMS: *Chemical Geology*, v. 280, no. 1-2, p. 200-216.
- Ciobanu, C. L., Wade, B. P., Cook, N. J., Schmidt Mumm, A., and Giles, D., 2013, Uranium-bearing hematite from the Olympic Dam Cu–U–Au deposit, South Australia: A geochemical tracer and reconnaissance Pb–Pb geochronometer: *Precambrian Research*, v. 238, p. 129-147.
- Claoue´-Long, J. C., King, R. W., and Kerrich, R., 1990, Archaean hydrothermal zircon in the Abitibi greenstone belt: constraints on the timing of gold mineralisation: *Earth and Planetary Science Letters*, v. 98, no. 1, p. 109-128.
- Cochrane, R., Spikings, R. A., Chew, D., Wotzlaw, J.-F., Chiaradia, M., Tyrrell, S., Schaltegger, U., and Van der Lelij, R., 2014, High temperature (>350°C) thermochronology and mechanisms of Pb loss in apatite: *Geochimica et Cosmochimica Acta*, v. 127, p. 39-56.
- Cohen, A. S., O'Nions, R. K., Siegenthaler, R., and Griffin, W. L., 1988, Chronology of the pressure-temperature history recorded by a granulite terrain: *Contributions to Mineralogy and Petrology*, v. 98, no. 3, p. 303-311.
- Connelly, J. N., 2006, Improved dissolution and chemical separation methods for Lu–Hf garnet chronometry: *Geochemistry, Geophysics, Geosystems*, v. 7, no. 4.
- Corriveau, L., Montreuil, J. F., and Potter, E. G., 2016, Alteration Facies Linkages Among Iron Oxide Copper–Gold, Iron Oxide–Apatite, and Affiliated Deposits in the Great Bear Magmatic Zone, Northwest Territories, Canada*: *Economic Geology*, v. 111, no. 8, p. 2045-2072.
- Cosca, M. A., Essene, E. J., Mezger, K., and van der Pluijm, B. A., 1995, Constraints on the duration of tectonic processes: Protracted extension and deep-crustal rotation in the Grenville orogen: *Geology*, v. 23, no. 4, p. 361-364.
- Courtney-Davies, L., Gilbert, S. E., Ciobanu, C. L., Tapster, S. R., Richardson, M. W., Cook, N. J., Wade, B. P., Verdugo-Ihl, M. R., Ehrig, K., and Condon, D. J., 2020, A Synthetic Haematite Reference Material for LA–ICP–MS U–Pb Geochronology and Application to Iron Oxide–Cu–Au Systems: *Geostandards and Geoanalytical Research*, v. 45, no. 1, p. 143-159.
- Cutts, K. A., Kinny, P. D., Strachan, R. A., Hand, M., Kelsey, D. E., Emery, M., Friend, C. R. L., and Leslie, A. G., 2010, Three metamorphic events recorded in a single garnet: Integrated phase modelling, in situ LA–ICPMS and SIMS geochronology from the Moine Supergroup, NW Scotland: *Journal of Metamorphic Geology*, v. 28, no. 3, p. 249-267.
- Danyushevsky, L., Robinson, P., Gilbert, S., Norman, M., Large, R., McGoldrick, P., and Shelley, M., 2011, Routine quantitative multi-element analysis of sulphide minerals by laser ablation ICP–MS: Standard development and consideration of matrix effects: *Geochemistry: Exploration, Environment, Analysis*, v. 11, no. 1, p. 51-60.
- Dauphas, N., Hopp, T., Craig, G., Zhang, Z. J., Valdes, M. C., Heck, P. R., Charlier, B. L. A., Bell, E. A., Harrison, T. M., Davis, A. M., Dussubieux, L., Williams, P. R., Krawczynski, M. J., Bouman, C.,

- Lloyd, N. S., Tollstrup, D., and Schwieters, J. B., 2022, In situ ^{87}Rb – ^{87}Sr analyses of terrestrial and extraterrestrial samples by LA-MC-ICP-MS/MS with double Wien filter and collision cell technologies: *Journal of Analytical Atomic Spectrometry*, v. 37, no. 11, p. 2420-2441.
- Davidson, G. J., Paterson, H., Meffre, S., and Berry, R. F., 2007, Characteristics and Origin of the Oak Dam East Breccia-Hosted, Iron Oxide Cu-U-(Au) Deposit: Olympic Dam Region, Gawler Craton, South Australia: *Economic Geology*, v. 102, no. 8, p. 1471-1498.
- Dawson, J. B., and Hinton, R. W., 2003, Trace-element content and partitioning in calcite, dolomite and apatite in carbonatite, Phalaborwa, South Africa: *Mineralogical Magazine*, v. 67, no. 5, p. 921-930.
- De Bievre, P., and Taylor, P. D. P., 1993, Table of isotopic composition of the elements: *International Journal of Mass Spectrometry and Ion Processes*, v. 123, p. 149 - 165.
- De Haas, G.-J. L. M., Nijland, T. G., Andersen, T., and Corfu, F., 2009, New constraints on the timing of deposition and metamorphism in the Bamble sector, south Norway: Zircon and titanite U-Pb data from the Nelaug area: *Gff*, v. 124, no. 2, p. 73-78.
- Debruyne, D., Hulsbosch, N., and Muchez, P., 2016, Unraveling rare earth element signatures in hydrothermal carbonate minerals using a source–sink system: *Ore Geology Reviews*, v. 72, p. 232-252.
- DePaolo, D. J., 1980, Crustal growth and mantle evolution: inferences from models of element transport and Nd and Sr isotopes: *Geochimica et Cosmochimica Acta*, v. 44, p. 1185-1196.
- Dobrzhinetskaya, L., Larsen, R. B., Sturt, B. A., Tronnes, R., G, Smith, D. C., Taylor, W. R., and Tatjana, V. P., 1995, Microdiamond in high-grade metamorphic rocks of the Western Gneiss region, Norway: *Geology*, v. 23, no. 7, p. 597-600.
- Duchene, S., Blichert-Toft, J., Luais, B., Télouk, P., Lardeaux, J.-M., and Albarède, F., 1997, The Lu-Hf dating of garnets and the ages of the Alpine high-pressure metamorphism: *Nature*, v. 387, p. 586-589.
- Duncan, R. J., Stein, H. J., Evans, K. A., Hitzman, M. W., Nelson, E. P., and Kirwin, D. J., 2011, A New Geochronological Framework for Mineralization and Alteration in the Selwyn-Mount Dore Corridor, Eastern Fold Belt, Mount Isa Inlier, Australia: Genetic Implications for Iron Oxide Copper-Gold Deposits: *Economic Geology*, v. 106, no. 2, p. 169-192.
- Duuring, P., Bleeker, W., Beresford, S. W., and Hayward, N., 2010, Towards a volcanic–structural balance: relative importance of volcanism, folding, and remobilisation of nickel sulphides at the Perseverance Ni–Cu–(PGE) deposit, Western Australia: *Mineralium Deposita*, v. 45, no. 3, p. 281-311.
- Eggins, S. M., Kinsley, L. P. J., and Shelley, J. M. G., 1998, Deposition and element fractionation processes during atmospheric pressure laser sampling for analysis by ICP-MS: *Applied Surface Science*, v. 127-129, p. 278-286.
- Ehrig, K., Kamenetsky, V. S., McPhie, J., Macmillan, E., Thompson, J., Kamenetsky, M., and Maas, R., 2021, Staged formation of the supergiant Olympic Dam uranium deposit, Australia: *Geology*, v. 49, no. 11, p. 1312-1316.
- Eiler, J. M., 2011, Paleoclimate reconstruction using carbonate clumped isotope thermometry: *Quaternary Science Reviews*, v. 30, no. 25, p. 3575-3588.
- Elzinga, E. J., Reeder, R. J., Withers, S. H., Peale, R. E., Mason, R. A., Beck, K. M., and Hess, W. P., 2002, EXAFS study of rare-earth element coordination in calcite: *Geochimica et Cosmochimica Acta*, v. 66, no. 16, p. 2875-2885.
- Engi, M., Lanari, P., and Kohn, M. J., 2017, Significant Ages—An Introduction to Petrochronology: *Reviews in Mineralogy and Geochemistry*, v. 83, no. 1, p. 1-12.
- Engvik, A. K., Corfu, F., Solli, A., and Austrheim, H., 2017, Sequence and timing of mineral replacement reactions during albitisation in the high-grade Bamble lithotectonic domain, S-Norway: *Precambrian Research*, v. 291, p. 1-16.

- Engvik, A. K., Golla-Schindler, U., Berndt, J., Austrheim, H., and Putnis, A., 2009, Intragranular replacement of chlorapatite by hydroxy-fluor-apatite during metasomatism: *Lithos*, v. 112, no. 3-4, p. 236-246.
- Engvik, A. K., Mezger, K., Wortelkamp, S., Bast, R., Corfu, F., Korneliussen, A., Ihlen, P., Bingen, B., and Austrheim, H., 2011, Metasomatism of gabbro - mineral replacement and element mobilization during the Sveconorwegian metamorphic event: *Journal of Metamorphic Geology*, v. 29, no. 4, p. 399-423.
- Faure, G., and Mensing, T. M., 2005, *Isotopes, principles and applications*, United States, John Wiley & Sons, Inc.
- Fisher, C. M., McFarlane, C. R. M., Hanchar, J. M., Schmitz, M. D., Sylvester, P. J., Lam, R., and Longerich, H. P., 2011, Sm–Nd isotope systematics by laser ablation-multicollector-inductively coupled plasma mass spectrometry: Methods and potential natural and synthetic reference materials: *Chemical Geology*, v. 284, no. 1, p. 1-20.
- Fisher, C. M., and Vervoort, J. D., 2018, Using the magmatic record to constrain the growth of continental crust—The Eoarchean zircon Hf record of Greenland: *Earth and Planetary Science Letters*, v. 488, p. 79-91.
- Fletcher, I. R., McNaughton, N. J., Aleinikoff, J. A., Rasmussen, B., and Kamo, S. L., 2004, Improved calibration procedures and new standards for U–Pb and Th–Pb dating of Phanerozoic xenotime by ion microprobe: *Chemical Geology*, v. 209, no. 3-4, p. 295-314.
- Flude, S., Haschke, M., and Storey, M., 2017, Application of benchtop micro-XRF to geological materials: *Mineralogical Magazine*, v. 81, no. 4, p. 923-948.
- , 2018, Application of benchtop micro-XRF to geological materials: *Mineralogical Magazine*, v. 81, no. 4, p. 923-948.
- Foden, J., Barovich, K., Jane, M., and O'Halloran, G., 2001, Sr-isotopic evidence for Late Neoproterozoic rifting in the Adelaide Geosyncline at 586 Ma: implications for a Cu ore forming fluid flux: *Precambrian Research*, v. 106, no. 3, p. 291-308.
- Foster, G. L., and Vance, D., 2006, In situ Nd isotopic analysis of geological materials by laser ablation MC-ICP-MS: *Journal of Analytical Atomic Spectrometry*, v. 21, no. 3, p. 288-296.
- Frei, R., Villa, I. M., Nagler, T. F., Kramers, J. D., Prybylowicz, W. J., Prozesky, V. M., Hofman, B. A., and Kamber, B. S., 1997, Single mineral dating by the Pb–Pb step leaching method: assessing the mechanisms: *Geochimica et Cosmochimica Acta*, v. 61, no. 2, p. 393-414.
- Friend, C. R. L., Kinny, P. D., Rogers, G., Strachan, R. A., and Paterson, B. A., 1997, U–Pb zircon geochronological evidence for Neoproterozoic events in the Glenfinnan Group (Moine Supergroup): the formation of the Ardour granite gneiss, north-west Scotland: *Contributions to Mineralogy and Petrology*, v. 128, no. 2, p. 101-113.
- Garrett, S. J., 1992, *The Geology and Geochemistry of the Mount Elliott Copper-Gold deposit, Northwest Queensland* [Masters thesis]: University of Tasmania, 139 p.
- Gibson, H. L., Lafrance, B., Pehrsson, S., Dewolfe, M. Y., Gilmore, K., and Simard, R.-L., 2012, *The Volcanological and Structural Evolution of the Paleoproterozoic Flin Flon Mining District: Anatomy of a Giant VMS System*: Geoscience Canada.
- Gilbert, S. E., Danyushevsky, L. V., Goemann, K., and Death, D., 2014, Fractionation of sulphur relative to iron during laser ablation-ICP-MS analyses of sulphide minerals: implications for quantification: *J. Anal. At. Spectrom.*, v. 29, no. 6, p. 1024-1033.
- Gilbert, S. E., and Glorie, S., 2020, Removal of Hg interferences for common Pb correction when dating apatite and titanite by LA-ICP-MS/MS: *Journal of Analytical Atomic Spectrometry*, v. 35, no. 7, p. 1472-1481.
- Giles, D., and Nutman, A. P., 2002, SHRIMP U–Pb monazite dating of 1600–1580 Ma amphibolite facies metamorphism in the southeastern Mt Isa Block, Australia: *Australian Journal of Earth Sciences*, v. 49, no. 3, p. 455-465.

- Gillespie, J., Glorie, S., Khudoley, A., and Collins, A. S., 2018, Detrital apatite U-Pb and trace element analysis as a provenance tool: Insights from the Yenisey Ridge (Siberia): *Lithos*, v. 314-315, p. 140-155.
- Gillespie, J., Kirkland, C. L., Kinny, P. D., Simpson, A., Glorie, S., and Rankenburg, K., 2022, Lu-Hf, Sm-Nd, and U-Pb isotopic coupling and decoupling in apatite: *Geochimica et Cosmochimica Acta*, v. 338, p. 121-135.
- Glorie, S., Burke, T., Hand, M., Simpson, A., Gilbert, S., and Wade, B., 2022, In situ Lu-Hf phosphate geochronology: Progress towards a new tool for space exploration: *Geoscience Frontiers*, v. 13, no. 3, p. 101375.
- Glorie, S., Gillespie, J., Simpson, A., Gilbert, S., Khudoley, A., Priyatkin, N., Hand, M., and Kirkland, C. L., 2021, Detrital apatite Lu-Hf and U-Pb geochronology applied to the southwestern Siberian margin: in review.
- Glorie, S., Hand, M., Mulder, J., Simpson, A., Emo Robert, B., Kamber, B., Fernie, N., Nixon, A., and Gilbert, S., 2023, Robust laser ablation Lu-Hf dating of apatite: an empirical evaluation: *Geological Society, London, Special Publications*, v. 537, no. 1, p. SP537-2022-2205.
- Glorie, S., Jepson, G., Konopelko, D., Mirkamalov, R., Meeuws, F., Gilbert, S., Gillespie, J., Collins, A. S., Xiao, W., Dewaele, S., and De Grave, J., 2019, Thermochronological and geochemical footprints of post-orogenic fluid alteration recorded in apatite: Implications for mineralisation in the Uzbek Tian Shan: *Gondwana Research*, v. 71, p. 1-15.
- Glorie, S., March, S., Nixon, A., Meeuws, F., O'Sullivan, G. J., Chew, D. M., Kirkland, C. L., Konopelko, D., and De Grave, J., 2020, Apatite U-Pb dating and geochemistry of the Kyrgyz South Tian Shan (Central Asia): Establishing an apatite fingerprint for provenance studies: *Geoscience Frontiers*, v. 11, no. 6, p. 2003-2015.
- Goodenough, K. M., Millar, I., Strachan, R. A., Krabbendam, M., and Evans, J. A., 2011, Timing of regional deformation and development of the Moine Thrust Zone in the Scottish Caledonides: constraints from the U-Pb geochronology of alkaline intrusions: *Journal of the Geological Society*, v. 168, no. 1, p. 99-114.
- Gorojovsky, L., and Alard, O., 2020, Optimisation of laser and mass spectrometer parameters for the in situ analysis of Rb/Sr ratios by LA-ICP-MS/MS: *Journal of Analytical Atomic Spectrometry*, v. 35, no. 10, p. 2322-2336.
- Gray, A. L., 1985, Solid sample introduction by laser ablation for inductively coupled plasma source mass spectrometry: *Analyst*, v. 110, no. 5, p. 551-556.
- Green, P. F., Crowhurst, P. V., Duddy, I. R., Japsen, P., and Holford, S. P., 2006, Conflicting (U-Th)/He and fission track ages in apatite: Enhanced He retention, not anomalous annealing behaviour: *Earth and Planetary Science Letters*, v. 250, no. 3-4, p. 407-427.
- Gregory, C. J., Reid, A. J., Say, P., and Teale, G. S., 2011, U-Pb geochronology of hydrothermal allanite and titanite and magmatic zircon from the Hillside Cu-Au deposit, Yorke Peninsula: *PACE Geochronology: Results of Collaborative Geochronology Projects 2009-10 South Australia*, p. 95-126.
- Griffin, W. L., Wang, X., Jackson, S. E., Pearson, N., O'Reilly, S. Y., Xu, X., and Zhou, X., 2002, Zircon chemistry and magma mixing, SE China: In situ analysis of Hf isotopes, Tonglu and Pingtan igneous complexes: *Lithos*, v. 61, p. 237 - 269.
- Groves, D. I., and Vielreicher, N. M., 2001, The Phalaborwa (palabora) carbonatite-hosted magnetite-copper sulfide deposit, South Africa: am emd-member of the iron-oxide-copper-gold-rare earth element deposit group?: *Mineralium Deposita*, v. 36, p. 189-194.
- Guillong, M., and Günther, D., 2002, Effect of particle size distribution on ICP-induced elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry: *Journal of Analytical Atomic Spectrometry*, v. 17, no. 8, p. 831-837.
- Guillong, M., Horn, I., and Günther, D., 2003, A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd:YAG laser for laser ablation ICP-MS: *Journal of Analytical Atomic Spectrometry*, v. 18, no. 10, p. 1224-1230.

- Guillong, M., Wotzlaw, J.-F., Looser, N., and Laurent, O., 2020, Evaluating the reliability of U–Pb laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) carbonate geochronology: matrix issues and a potential calcite validation reference material: *Geochronology*, v. 2, no. 1, p. 155-167.
- Gunther, D., and Koch, J., 2008, Formation of aerosols generated by laser ablation and their impact on elemental fractionation in LA-ICP-MS, *in* Sylvester, P., ed., *Laser Ablation–ICP–MS in the Earth Sciences current practices and outstanding issues*, Volume 40: Vancouver, Mineralogical Association of Canada.
- Gustafson, L., and Compston, W., 1979, Rb-Sr dating of Olympic Dam core samples: Australian National University, Research School of Earth Sciences January, v. 18, p. 1979.
- Haines, P. W., Hand, M., and Sandiford, M., 2001, Palaeozoic synorogenic sedimentation in central and northern Australia: A review of distribution and timing with implications for the evolution of intracontinental orogens.: *Australian Journal of Earth Sciences*, v. 48, no. 6, p. 911-928.
- Hall, J., 2018, The thermochronological evolution of the northern Gawler Craton and northern Adelaide Rift Complex [Doctor of Philosophy: University of Adelaide].
- Hammerli, J., and Kemp, A. I. S., 2021, Combined Hf and Nd isotope microanalysis of co-existing zircon and REE-rich accessory minerals: High resolution insights into crustal processes: *Chemical Geology*, v. 581, p. 120393.
- Hand, M., Mawby, J., Kinny, P., and Foden, J., 1999, U-Pb ages from the Harts Range, central Australia: evidence for early Ordovician extension and constraints on carboniferous metamorphism: *Journal of the Geological Society*, v. 156, p. 715-730.
- Hand, M., Reid, A., and Jagodzinski, L., 2007, Tectonic Framework and Evolution of the Gawler Craton, Southern Australia: *Economic Geology*, v. 102, p. 1377-1395.
- Harlov, D. E., Wirth, R., and Förster, H.-J., 2005, An experimental study of dissolution–reprecipitation in fluorapatite: fluid infiltration and the formation of monazite: *Contributions to Mineralogy and Petrology*, v. 150, no. 3, p. 268-286.
- Heinson, G., Didana, Y., Soeffky, P., Thiel, S., and Wise, T., 2018, The crustal geophysical signature of a world-class magmatic mineral system: *Scientific Reports*, v. 8, no. 1, p. 10608.
- Henrichs, I. A., Chew, D. M., O'Sullivan, G. J., Mark, C., McKenna, C., and Guyett, P., 2019, Trace Element (Mn-Sr-Y-Th-REE) and U-Pb Isotope Systematics of Metapelitic Apatite During Progressive Greenschist- to Amphibolite-Facies Barrovian Metamorphism: *Geochemistry, Geophysics, Geosystems*, v. 20, no. 8, p. 4103-4129.
- Henrichs, I. A., O'Sullivan, G., Chew, D. M., Mark, C., Babechuk, M. G., McKenna, C., and Emo, R., 2018, The trace element and U-Pb systematics of metamorphic apatite: *Chemical Geology*, v. 483, p. 218-238.
- Hoffman, E., and Stroobant, V., 2007, *Mass spectrometry: principles and applications*, United States of America, John Wiley and Sons Ltd.
- Hogmalm, K. J., Dahlgren, I., Fridolfsson, I., and Zack, T., 2019, First in situ Re-Os dating of molybdenite by LA-ICP-MS/MS: *Mineralium Deposita*, v. 54, no. 6, p. 821-828.
- Hogmalm, K. J., Zack, T., Karlsson, A. K. O., Sjöqvist, A. S. L., and Garbe-Schönberg, D., 2017, In situ Rb–Sr and K–Ca dating by LA-ICP-MS/MS: an evaluation of N₂O and SF₆ as reaction gases: *Journal of Analytical Atomic Spectrometry*, v. 32, no. 2, p. 305-313.
- Holdsworth, R. E., Strachan, R. A., Harris, A. L., Gibbons, W., and Harris, A. L., 1994, Precambrian rocks in northern Scotland east of the Moine Thrust: the Moine Supergroup, A revised correlation of Pre-Cambrian rocks in the British Isles, Volume 22, Geological Society of London, p. 0.
- Horstwood, M. S. A., Košler, J., Gehrels, G., Jackson, S. E., McLean, N. M., Paton, C., Pearson, N. J., Sircombe, K., Sylvester, P., Vermeesch, P., Bowring, J. F., Condon, D. J., and Schoene, B., 2016, Community-Derived Standards for LA - ICP - MS U-(Th)-Pb Geochronology –

- Uncertainty Propagation, Age Interpretation and Data Reporting: *Geostandards and Geoanalytical Research*, v. 40, no. 3, p. 311-332.
- Hu, Z., Gao, S., Liu, Y., Hu, S., Chen, H., and Yuan, H., 2008, Signal enhancement in laser ablation ICP-MS by addition of nitrogen in the central channel gas: *Journal of Analytical Atomic Spectrometry*, v. 23, no. 8.
- Huang, Q., Kamenetsky, V. S., McPhie, J., Ehrig, K., Meffre, S., Maas, R., Thompson, J., Kamenetsky, M., Chambefort, I., Apukhtina, O., and Hu, Y., 2015, Neoproterozoic (ca. 820–830 Ma) mafic dykes at Olympic Dam, South Australia: Links with the Gairdner Large Igneous Province: *Precambrian Research*, v. 271, p. 160-172.
- Hunt, J. A., Baker, T., and Thorkelson, D. J., 2007, A Review of Iron Oxide Copper-Gold Deposits, with Focus on the Wernecke Breccias, Yukon, Canada, as an Example of a Non-Magmatic End Member and Implications for IOCG Genesis and Classification: *Exploration and Mining Geology*, v. 16, no. 3 - 4, p. 209-232.
- Ibanez-Mejia, M., Bloch, E. M., and Vervoort, J. D., 2018, Timescales of collisional metamorphism from Sm-Nd, Lu-Hf and U-Pb thermochronology: A case from the Proterozoic Putumayo Orogen of Amazonia: *Geochimica et Cosmochimica Acta*, v. 235, p. 103-126.
- Iizuka, T., Yamaguchi, T., Hibiya, Y., and Amelin, Y., 2015, Meteorite zircon constraints on the bulk Lu-Hf isotope composition and early differentiation of the Earth: *Proc Natl Acad Sci U S A*, v. 112, no. 17, p. 5331-5336.
- Jackson, S. E., 2008, Calibration strategies for elemental analysis by LA-ICP-MS, in Sylvester, P., ed., *Mineralogical Association of Canada Short Course 40*, Vancouver.
- Jackson, S. E., and Günther, D., 2003, The nature and sources of laser induced isotopic fractionation in laser ablation-multicollector-inductively coupled plasma-mass spectrometry: *Journal of Analytical Atomic Spectrometry*, v. 18, no. 3, p. 205-212.
- Jagodzinski, E., 2014, The age of magmatic and hydrothermal zircon at Olympic Dam: AESC-Abstract-Proceedings Newcastle.
- Johnson, J. P., and Cross, K. C., 1995, U-Pb geochronological constraints on the genesis of the Olympic Dam Cu-U-Au-Ag deposit, South Australia: *Economic Geology*, v. 90, no. 5, p. 1046-1063.
- Johnson, T. A., Vervoort, J. D., Ramsey, M. J., Aleinikoff, J. N., and Southworth, S., 2018, Constraints on the timing and duration of orogenic events by combined Lu-Hf and Sm-Nd geochronology: An example from the Grenville orogeny: *Earth and Planetary Science Letters*, v. 501, p. 152-164.
- Kelly, E. D., Carlson, W. D., and Connelly, J. N., 2011, Implications of garnet resorption for the Lu-Hf garnet geochronometer: an example from the contact aureole of the Makhavinekh Lake Pluton, Labrador: *Journal of Metamorphic Geology*, v. 29, no. 8, p. 901-916.
- Kennedy, A. K., Kamo, S. L., Nasdala, L., and Timms, N. E., 2011, GRENVILLE SKARN TITANITE: POTENTIAL REFERENCE MATERIAL FOR SIMS U-Th-Pb ANALYSIS: *The Canadian Mineralogist*, v. 48, no. 6, p. 1423-1443.
- Kinny, P. D., Friend, C. R. L., Strachan, R. A., R., W. G., and Burns, I. M., 1999, U-Pb geochronology of regional migmatites in East Sutherland, Scotland: evidence for crustal melting during the Caledonian orogeny: *Journal of the Geological Society*, v. 156, no. 6.
- Kinny, P. D., Strachan, R. A., Friend, C. R. L., Kocks, H., Rogers, G., and Paterson, B. A., 2003a, U-Pb geochronology of deformed metagranites in central Sutherland, Scotland: evidence for widespread late Silurian metamorphism and ductile deformation of the Moine Supergroup during the Caledonian orogeny: *Journal of the Geological Society*, v. 160, p. 259-269.
- Kinny, P. D., Strachan, R. A., Kocks, H., and Friend, C. R. L., 2003b, U-Pb geochronology of late Neoproterozoic augen granites in the Moine Supergroup, NW Scotland: dating of rift-related, felsic magmatism during supercontinent break-up?: *Journal of the Geological Society*, v. 160, p. 925-934.

- Kirkland, C. L., Strachan, R. A., and Prave, A. R., 2008, Detrital zircon signature of the Moine Supergroup, Scotland: Contrasts and comparisons with other Neoproterozoic successions within the circum-North Atlantic region: *Precambrian Research*, v. 163, no. 3-4, p. 332-350.
- Kirkland, C. L., Yakymchuk, C., Szilas, K., Evans, N., Hollis, J., McDonald, B., and Gardiner, N. J., 2018, Apatite: a U-Pb thermochronometer or geochronometer?: *Lithos*, v. 318-319, p. 143-157.
- Kohn, M. J., 2009, Models of garnet differential geochronology: *Geochimica et Cosmochimica Acta*, v. 73, no. 1, p. 170-182.
- Koo, J., and Mossman, D. J., 1975, Origin and metamorphism of the Flin Flon stratabound Cu-Zn sulfide deposit, Saskatchewan and Manitoba: *Economic Geology*, v. 70, p. 48-62.
- Košler, J., 2007, Laser ablation ICP—MS — a new dating tool in Earth science: *Proceedings of the Geologists' Association*, v. 118, no. 1, p. 19-24.
- Koyanagi, G. K., Cheng, P., and Bohme, D. K., 2010, Gas-Phase Reactions of Atomic Lanthanide Cations with Ammonia: Room-Temperature Kinetics and Periodicity in Reactivity: *The Journal of Physical Chemistry A*, v. 114, no. 1, p. 241-246.
- Krabbendam, M., Strachan, R., and Prave, T., 2021, A new stratigraphic framework for the early Neoproterozoic successions of Scotland: *Journal of the Geological Society*, v. 179, no. 2.
- Kretz, R., Campbell, J. L., Hoffman, E. L., Hartree, R., and Teesdale, W. J., 1999, Approaches to equilibrium in the distribution of trace elements among the principal minerals in a high-grade metamorphic terrane: *Journal of Metamorphic Geology*, v. 8, p. 493-506.
- Krneta, S., Cook, N. J., Ciobanu, C. L., Ehrig, K., and Kontonikas-Charos, A., 2017, The Wirrda Well and Acropolis prospects, Gawler Craton, South Australia: Insights into evolving fluid conditions through apatite chemistry: *Journal of Geochemical Exploration*, v. 181, p. 276-291.
- Krogstad, R., and Walker, R. J., 1994, High closure temperatures of the U-Pb system in large apatites from the Tin Mountain pegmatite, Black Hills South Dakota, USA: *Geochemistry, Geophysics, Geosystems*, v. 58, p. 3845-3853.
- Kroslakova, I., and Günther, D., 2007, Elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry: evidence for mass load induced matrix effects in the ICP during ablation of a silicate glass: *J. Anal. At. Spectrom.*, v. 22, no. 1, p. 51-62.
- Kylander-Clark, A. R. C., Hacker, B. R., Johnson, C. M., Beard, B. L., and Mahlen, N. J., 2009, Slow subduction of a thick ultrahigh-pressure terrane: *Tectonics*, v. 28, no. 2, p. n/a-n/a.
- Lafrance, B., Gibson, H. L., Pehrsson, S., Schetselaar, E., Dewolfe, M. Y., and Lewis, D., 2016, Structural reconstruction of the Flin Flon volcanogenic massive sulfide mining district, Saskatchewan and Manitoba, Canada: *Economic Geology*, v. 111, p. 849-875.
- Lagos, M., Scherer, E. E., Tomaschek, F., Münker, C., Keiter, M., Berndt, J., and Ballhaus, C., 2007, High precision Lu—Hf geochronology of Eocene eclogite-facies rocks from Syros, Cyclades, Greece: *Chemical Geology*, v. 243, no. 1-2, p. 16-35.
- Lane, K., 2011, Metamorphic and geochronological constraints on the evolution of the Kalinjala Shear Zone, Eyre Peninsula [Honours: University of Adelaide].
- Lapen, T. J., Johnson, C. M., Baumgartner, L. P., Mahlen, N. J., Beard, B. L., and Amato, J. M., 2003, Burial rates during prograde metamorphism of an ultra-high-pressure terrane: an example from Lago di Cignana, western Alps, Italy: *Earth and Planetary Science Letters*, v. 215, no. 1, p. 57-72.
- Lapen, T. J., Mahlen, N. J., Johnson, C. M., and Beard, B. L., 2004, High precision Lu and Hf isotope analyses of both spiked and unspiked samples: A new approach: *Geochemistry, Geophysics, Geosystems*, v. 5, no. 1.
- Larsson, D., and Söderlund, U., 2005, Lu—Hf apatite geochronology of mafic cumulates: An example from a Fe—Ti mineralization at Smålands Taberg, southern Sweden: *Chemical Geology*, v. 224, no. 4, p. 201-211.
- Le Bras, L. Y., Bolhar, R., Bybee, G. M., Nex, P. A., Guy, B. M., Moyana, T., and Lourens, P., 2021, Platinum-group and trace elements in Cu-sulfides from the Loolekop pipe, Phalaborwa: implications for ore-forming processes: *Mineralium Deposita*, v. 56, p. 161-177.

- Leach, D. L., Sangster, D. F., Kelley, K. D., Large, R. R., Garven, G., Allen, C. R., Gutzmer, J., and Walters, S., 2005, Sediment-Hosted Lead-Zinc Deposits: A Global Perspective, *in* Hedenquist, J. W., Thompson, J. F. H., Goldfarb, R. J., and Richards, J. P., eds., One Hundredth Anniversary Volume, Society of Economic Geologists, p. 0.
- Li, F., Webb, G. E., Algeo, T. J., Kershaw, S., Lu, C., Oehlert, A. M., Gong, Q., Pourmand, A., and Tan, X., 2019, Modern carbonate ooids preserve ambient aqueous REE signatures: *Chemical Geology*, v. 509, p. 163-177.
- Li, Q., Parrish, R. R., Horstwood, M. S. A., and McArthur, J. M., 2014, U–Pb dating of cements in Mesozoic ammonites: *Chemical Geology*, v. 376, p. 76-83.
- Li, S.-S., Santosh, M., Farkaš, J., Redaa, A., Ganguly, S., Kim, S. W., Zhang, C., Gilbert, S., and Zack, T., 2020, Coupled U-Pb and Rb-Sr laser ablation geochronology trace Archean to Proterozoic crustal evolution in the Dharwar Craton, India: *Precambrian Research*, v. 343.
- Li, Y., and Vermeesch, P., 2021, Short communication: Inverse isochron regression for Re–Os, K–Ca and other chronometers: *Geochronology*, v. 3, no. 2, p. 415-420.
- Lihter, I., Larson, K. P., Smit, M. A., Cottle, J. M., Ashley, K. T., and Shrestha, S., 2022, Decrypting the polymetamorphic record of the Himalaya: *Geology*, v. 50, no. 5, p. 588-592.
- Lloyd, J. C., Blades, M. L., Counts, J. W., Collins, A. S., Amos, K. J., Wade, B. P., Hall, J. W., Hore, S., Ball, A. L., Shahin, S., and Drabsch, M., 2020, Neoproterozoic geochronology and provenance of the Adelaide Superbasin: *Precambrian Research*, v. 350, p. 105849.
- Longerich, H., 2008, Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS); an introduction, *in* Sylvester, P., ed., *Laser Ablation–ICP–MS in the Earth Sciences current practices and outstanding issues*, Volume 40: Vancouver, Mineralogical Association of Canada.
- Maas, R., Apukhtina, O. B., Kamenetsky, V. S., Ehrig, K., Sprung, P., and Münker, C., 2022, Carbonates at the supergiant Olympic Dam Cu–U–Au–Ag deposit, South Australia part 2: Sm–Nd, Lu–Hf and Sr–Pb isotope constraints on the chronology of carbonate deposition: *Ore Geology Reviews*.
- Maas, R., Kamenetsky, V., Ehrig, K., Meffre, S., McPhie, J., and Diemar, G., 2011, Olympic Dam U–Cu–Au deposit, Australia: New age constraints: *Mineralogical Magazine*, v. 75, p. 1375.
- Mao, M., Rukhlov, A. S., Rowins, S. M., Spence, J., and Coogan, L. A., 2016, Apatite Trace Element Compositions: A Robust New Tool for Mineral Exploration*: *Economic Geology*, v. 111, no. 5, p. 1187-1222.
- Marillo-Sialer, E., Woodhead, J., Hergt, J., Greig, A., Guillong, M., Gleadow, A., Evans, N., and Paton, C., 2014, The zircon ‘matrix effect’: evidence for an ablation rate control on the accuracy of U–Pb age determinations by LA-ICP-MS: *J. Anal. At. Spectrom.*, v. 29, no. 6, p. 981-989.
- Mark, C., Cogné, N., and Chew, D., 2016, Tracking exhumation and drainage divide migration of the Western Alps: A test of the apatite U–Pb thermochronometer as a detrital provenance tool: *Geological Society of America Bulletin*, v. 128, no. 9-10, p. 1439-1460.
- Marshall, L., 2003, Brecciation within the Mary Kathleen Group of the Eastern Succession, Mt Isa Block, Australia: Implications of district-scale structural and metasomatic processes for Fe–oxide–Cu–Au mineralisation. [PhD thesis]: James Cook University.
- Mawby, J., Hand, M., and Foden, J., 1999, Sm–Nd evidence for high-grade Ordovician metamorphism in the Arunta Block, central Australia: *Journal of Metamorphic Geology*, v. 17, p. 653-668.
- McCuaig, T. C., Beresford, S., and Hronsky, J., 2010, Translating the mineral systems approach into an effective exploration targeting system: *Ore Geology Reviews*, v. 38, no. 3, p. 128-138.
- McDonough, W. F., and Sun, S. S., 1995, The composition of the Earth: *Chemical Geology*, v. 120, no. 3, p. 223-253.
- McInnes, B. I. A., Keays, R. R., Lambert, D. D., Hellstrom, J., and Allwood, J. S., 2008, Re–Os geochronology and isotope systematics of the Tanami, Tennant Creek and Olympic Dam Cu–Au deposits: *Australian Journal of Earth Sciences*, v. 55, no. 6-7, p. 967-981.

- McKerrow, W. S., Mac Niocaill, C., and Dewey, J. F., 2000, The Caledonian Orogeny redefined: *Journal of the Geological Society*, v. 157, no. 6, p. 1149-1154.
- McLaren, S., Sandiford, M., Hand, M., Neumann, N., Wyborn, L., and Bastrakova, I., 2003, The hot southern continent: heat flow and heat production in Australian Proterozoic terranes, *in* Hillis, R. R., and Müller, R. D., eds., *Evolution and Dynamics of the Australian Plate*, Volume 372, Geological Society of America, p. 0.
- McNaughton, N. J., and Rasmussen, B., 2018, Geochemical characterisation of xenotime formation environments using U-Th: *Chemical Geology*, v. 484, p. 109-119.
- McPhie, J., Ehrig, K. J., Kamenetsky, M. B., Crowley, J. L., and Kamenetsky, V. S., 2020, Geology of the Acropolis prospect, South Australia, constrained by high-precision CA-TIMS ages: *Australian Journal of Earth Sciences*, v. 67, no. 5, p. 699-716.
- McPhie, J., Kamenetsky, V. S., Chambefort, I., Ehrig, K., and Green, N., 2011, Origin of the supergiant Olympic Dam Cu-U-Au-Ag deposit, South Australia: Was a sedimentary basin involved?: *Geology*, v. 39, no. 8, p. 795-798.
- Mezger, K., Hanson, G. N., and Bohlen, S. R., 1989, U-Pb systematics of garnet: dating the growth of garnet in the late Archean Pikwitonei granulite domain at Cauchon and Natawahunan Lakes, Manitoba, Canada: *Contributions to Mineralogy and Petrology*, v. 101, p. 136-148.
- Migdisov, A., Williams-Jones, A. E., Brugger, J., and Caporuscio, F. A., 2016, Hydrothermal transport, deposition, and fractionation of the REE: Experimental data and thermodynamic calculations: *Chemical Geology*, v. 439, p. 13-42.
- Millar, I. L., 1999, Neoproterozoic extensional basic magmatism associated with the West Highland granite gneiss in the Moine Supergroup of NW Scotland: *Journal of the Geological Society*, v. 156, no. 6, p. 1153-1162.
- Millonig, L. J., Albert, R., Gerdes, A., Avigad, D., and Dietsch, C., 2020, Exploring laser ablation U-Pb dating of regional metamorphic garnet – The Straits Schist, Connecticut, USA: *Earth and Planetary Science Letters*, v. 552.
- Moen, L. J., Vanhaecke, F. F., Bandura, D. R., Baranov, V. I., and Tanner, S. D., 2001, Elimination of isobaric interferences in ICP-MS, using ion-molecule reaction chemistry: Rb/Sr age determination of magmatic rocks, a case study: *Journal of Analytical Atomic Spectrometry*, v. 16, no. 9, p. 991-994.
- Mokgalaka, N. S., and Gardea-Torresdey, J. L., 2006, Laser Ablation Inductively Coupled Plasma Mass Spectrometry: Principles and Applications: *Applied Spectroscopy Reviews*, v. 41, no. 2, p. 131-150.
- Morrissey, L. J., Hand, M., Kelsey, D. E., and Wade, B. P., 2016, Cambrian High-temperature Reworking of the Rayner–Eastern Ghats Terrane: Constraints from the Northern Prince Charles Mountains Region, East Antarctica: *Journal of Petrology*, v. 57, no. 1, p. 53-92.
- Müller, W., Shelley, M., Miller, P., and Broude, S., 2009, Initial performance metrics of a new custom-designed ArF excimer LA-ICPMS system coupled to a two-volume laser-ablation cell: *Journal of Analytical Atomic Spectrometry*, v. 24, no. 2, p. 209-214.
- Myers, J. S., Shaw, R. D., and Tyler, I. M., 1996, Tectonic evolution of Proterozoic Australia: *Tectonics*, v. 15, no. 6, p. 1431-1446.
- Nazari-Dehkordi, T., and Spandler, C., 2019, Paragenesis and composition of xenotime-(Y) and florencite-(Ce) from unconformity-related heavy rare earth element mineralization of northern Western Australia: *Mineralogy and Petrology*, v. 113, no. 5, p. 563-581.
- Nebel, O., Morel, M., and Vroon, P., 2009, Isotope Dilution Determinations of Lu, Hf, Zr, Ta and W and Hf Isotope Compositions of NIST SRM 610 and 612 Glass Wafers: *Geostandards and Geoanalytical Research*, v. 33, no. 4, p. 487-499.
- Nie, F. J., Bjørlykke, A., and Nilsen, K. S., 1999, The Origin of the Proterozoic Bidjovagge Gold-Copper Deposit, Finnmark, Northern Norway, as Deduced from Rare Earth Element and Nd Isotopic Evidences on Calcites: *Resource Geology*, v. 49, no. 1, p. 13-25.

- Nijland, T. G., Ben, J., Jansen, H., and Majjer, C., 1993, Halogen geochemistry of fluid during amphibolite-granulite metamorphism as indicated by apatite and hydrous silicates in basic rocks from the Bramble Sector, South Norway: *Lithos*, v. 30, p. 167-189.
- Norris, A., and Danyushevsky, L., 2018, Towards estimating the complete uncertainty budget of quantified results measured by LA-ICP-MS, *Goldschmidt*: Boston, USA.
- O'Sullivan, G. J., Chew, D. M., Morton, A. C., Mark, C., and Henrichs, I. A., 2018, An Integrated Apatite Geochronology and Geochemistry Tool for Sedimentary Provenance Analysis: *Geochemistry, Geophysics, Geosystems*, v. 19, no. 4, p. 1309-1326.
- Oliver, G. J. H., Wilde, S. A., and Wan, Y., 2008a, Geochronology and geodynamics of Scottish granitoids from the late Neoproterozoic break-up of Rodinia to Palaeozoic collision: *Journal of the Geological Society*, v. 165, p. 661-674.
- Oliver, N., Butera, K., Rubenach, M., Marshall, L., Cleverley, J., Mark, G., Tullemans, F., and Esser, D., 2008b, The protracted hydrothermal evolution of the Mount Isa Eastern Succession: A review and tectonic implications: *Precambrian Research*, v. 163, no. 1-2, p. 108-130.
- Oliver, N. H., Cartwright, I., Wall, V. J., and Golding, S. D., 1993, The stable isotope signature of kilometre-scale fracturedominated metamorphic fluid pathways, Mary Kathleen, Australia: *Journal of Metamorphic Geology*, v. 11, no. 5, p. 705-720.
- Oliver, N. H., Cleverley, J. S., Mark, G., Pollard, P. J., Fu, B., Marshall, L. J., Rubenach, M. J., Williams, P. J., and Baker, T., 2004, Modeling the Role of Sodic Alteration in the Genesis of Iron Oxide-Copper-Gold Deposits, Eastern Mount Isa Block, Australia *Economic Geology*, v. 99, no. 6, p. 1145-1176.
- Oliver, N. H. S., McLellan, J. G., Hobbs, B. E., Cleverley, J. S., Ord, A., and Feltrin, L., 2006, 100th Anniversary Special Paper: Numerical Models of Extensional Deformation, Heat Transfer, and Fluid Flow across Basement-Cover Interfaces during Basin-Related Mineralization: *Economic Geology*, v. 101, no. 1, p. 1-31.
- Oosthuyzen, E. J., and Burger, A. J., 1973, The suitability of apatite as an age indicator by the uranium-lead isotope method: *Earth and Planetary Science Letters*, v. 18, no. 1, p. 29-36.
- Page, R. W., and Sun, S. S., 1998, Aspects of geochronology and crustal evolution in the Eastern Fold Belt, Mt Isa Inlier: *Australian Journal of Earth Sciences*, v. 45, no. 3, p. 343-361.
- Pan, Y., and Fleet, M. E., 2002, Compositions of the Apatite-Group Minerals: Substitution Mechanisms and Controlling Factors: *Reviews in Mineralogy and Geochemistry*, v. 48, no. 1, p. 13-49.
- Passchier, C. W., Trouw, R. A. J., Zwart, H. J., and Vissers, R. L. M., 1992, Porphyroblast rotation: eppur si muove*?: *Journal of Metamorphic Geology*, v. 10, no. 3, p. 283-294.
- Patchett, P. J., Kouvo, O., Hedge, C. E., and Tatsumoto, M., 1982, Evolution of continental crust and mantle heterogeneity: evidence from Hf isotopes: *Contributions to Mineralogy and Petrology*, v. 78, p. 279-297.
- Patchett, P. J., and Tatsumoto, M., 1981, A routine high-precision method for Lu-Hf isotope geochemistry and chronology: *Contributions to Mineralogy and Petrology*, v. 75, no. 3, p. 263-267.
- Peach, B. N., Horne, J., Gunn, W., Clough, C. T., Hinxman, L. W., and Teall, J. J. H., 1907, The Geological Structure of the North-west Highlands of Scotland, H.M. Stationery Office, *Memoirs of the Geological Survey of Great Britain*, v. pts. 1-2.
- Peng, J. T., Hu, R. Z., and Burnard, P. G., 2003, Samarium-neodymium isotope systematics of hydrothermal calcites from the Xikuangshan antimony deposit (Hunan, China): the potential of calcite as a geochronometer: *Chemical Geology*, v. 200, no. 1, p. 129-136.
- Peters, D., 2001, A geochemical and geochronological assessment of the Great Glen Fault as a terrane boundary [PhD: Keele University].
- Pietsch, B. A., and Edgoose, C. J., 1998, The stratigraphy, metamorphism and tectonics of the early Proterozoic Litchfield Province and western Pine Creek Geosyncline, Northern Territory: *Precambrian Research*, v. 40-41, p. 565-588.

- Raimondo, T., Payne, J., Wade, B., Lanari, P., Clark, C., and Hand, M., 2017, Trace element mapping by LA-ICP-MS: assessing geochemical mobility in garnet: *Contributions to Mineralogy and Petrology*, v. 172, no. 4.
- Rasbury, E. T., and Cole, J. M., 2009, Directly dating geologic events: U-Pb dating of carbonates: *Reviews of Geophysics*, v. 47, no. 3.
- Rasmussen, B., Fletcher, I. R., and Muhling, J. R., 2011, Response of xenotime to prograde metamorphism: *Contributions to Mineralogy and Petrology*, v. 162, no. 6, p. 1259-1277.
- Rasmussen, B., Fletcher, I. R., Muhling, J. R., Thorne, W. S., and Broadbent, G. C., 2007, Prolonged history of episodic fluid flow in giant hematite ore bodies: Evidence from in situ U-Pb geochronology of hydrothermal xenotime: *Earth and Planetary Science Letters*, v. 258, no. 1, p. 249-259.
- Rasmussen, B., Sheppard, S., and Fletcher, I. R., 2006, Testing ore deposit models using in situ U-Pb geochronology of hydrothermal monazite: Paleoproterozoic gold mineralisation in northern Australia: *Geology*, v. 34, p. 77-80.
- Rayner, N. M., 2010, New U-Pb zircon ages from the Flin Flon Targeted Geoscience Initiative Project 2006-2009: Flin Flon and Hook Lake blocks: Geological Survey of Canada, Current Research, 2010-4, p. 1-12.
- Redaa, A., Farkaš, J., Gilbert, S., Collins, A. S., Wade, B., Löhr, s., Zack, T., and Garbe-Schönberg, D., 2020, Assessment of elemental fractionation and matrix effects during in-situ Rb-Sr dating of phlogopite by LA-ICP-MS/MS: Implications for the accuracy and precision of mineral ages: *Journal of Analytical Atomic Spectrometry*.
- Reeves, J. S., Cross, K. C., and Oreskes, N., 1990, Olympic Dam copper-uranium-gold-silver deposit: *Australasian Institute of Mining and Metallurgy*, v. 14, p. 1009-1035.
- Reid, A., 2019, The Olympic Cu-Au Province, Gawler Craton: A Review of the Lithospheric Architecture, Geodynamic Setting, Alteration Systems, Cover Successions and Prospectivity: *Minerals*, v. 9, no. 6.
- Reid, A., Smith, R. N., Baker, T., Jagodzinski, E. A., Selby, D., Gregory, C. J., and Skirrow, R. G., 2013, Re-Os DATING OF MOLYBDENITE WITHIN HEMATITE BRECCIAS FROM THE VULCAN Cu-Au PROSPECT, OLYMPIC Cu-Au PROVINCE, SOUTH AUSTRALIA: *Economic Geology*, v. 108, no. 4, p. 883-894.
- Ribeiro, B. V., Finch, M. A., Cawood, P. A., Faleiros, F. M., Murphy, T. D., Simpson, A., Glorie, S., Tedeschi, M., Armit, R., and Barrote, V. R., 2021, From microanalysis to supercontinents: insights from the Rio Apa Terrane into the Mesoproterozoic SW Amazonian Craton evolution during Rodinia assembly: *Journal of Metamorphic Geology*, v. 40, no. 4, p. 631- 663.
- Ring, U., and Gerdes, A., 2016, Kinematics of the Alpenrhein-Bodensee graben system in the Central Alps: Oligocene/Miocene transtension due to formation of the Western Alps arc: *Tectonics*, v. 35, no. 6, p. 1367-1391.
- Rivers, T., 2015, Tectonic Setting and Evolution of the Grenville Orogen: An Assessment of Progress Over the Last 40 Years: *Geoscience Canada*, v. 42, no. 1, p. 77-124.
- Roberts, N. M. W., Drost, K., Horstwood, M. S. A., Condon, D. J., Chew, D., Drake, H., Milodowski, A. E., McLean, N. M., Smye, A. J., Walker, R. J., Haslam, R., Hodson, K., Imber, J., Beaudoin, N., and Lee, J. K., 2020, Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) U-Pb carbonate geochronology: strategies, progress, and limitations: *Geochronology*, v. 2, no. 1, p. 33-61.
- Roberts, N. M. W., Rasbury, E. T., Parrish, R. R., Smith, C. J., Horstwood, M. S. A., and Condon, D. J., 2017, A calcite reference material for LA-ICP-MS U-Pb geochronology: *Geochemistry, Geophysics, Geosystems*, v. 18, no. 7, p. 2807-2814.
- Roberts, N. M. W., and Walker, R. J., 2016, U-Pb geochronology of calcite-mineralized faults: Absolute timing of rift-related fault events on the northeast Atlantic margin: *Geology*, v. 44, no. 7, p. 531-534.

- Rogers, G., Hyslop, E. K., Strachan, R. A., Paterson, B. A., and Holdsworth, R. E., 1998, The structural setting and U–Pb geochronology of Knoydartian pegmatites in W Inverness-shire: evidence for Neoproterozoic tectonothermal events in the Moine of NW Scotland: *Journal of the Geological Society*, v. 155, p. 685–696.
- Romer, R. L., and Smeds, S.-A., 1996, U–Pb columbite ages of pegmatites from Sveconorwegian terranes in southwestern Sweden: *Precambrian Research*, v. 76, p. 15–30.
- Romer, R. L., and Wright, J. E., 1993, Lead mobilization during tectonic reactivation of the western Baltic Shield: *Geochimica et Cosmochimica Acta*, v. 57, no. 11, p. 2555–2570.
- Rubatto, D., 2002, Zircon trace element geochemistry: partitioning with garnet and the link between U–Pb ages and metamorphism: *Chemical Geology*, v. 184, no. 1–2, p. 123–138.
- Salters, V. J. M., and Zindler, A., 1995, Extreme $^{176}\text{Hf}/^{177}\text{Hf}$ in the sub-oceanic mantle: *Earth and Planetary Science Letters*, v. 129, no. 1, p. 13–30.
- Sawyer, M., 2017, Carrapateena iron oxide Cu–Au–Ag–U deposit, in Phillips, G. N., ed., *Australian Ore Deposits, Volume 32: Australia*, The Australasian Institute of Mining and Metallurgy, p. 615–620.
- Scherer, E., Cameron, K. L., and Blichert-Toft, J., 2000a, Lu–Hf garnet geochronology: Closure temperature relative to the Sm–Nd system and the effects of trace mineral inclusions: *Geochimica et Cosmochimica Acta*, v. 64, no. 19, p. 3413–3432.
- , 2000b, Lu–Hf garnet geochronology: Closure temperature relative to the Sm–Nd system and the effects of trace mineral inclusions: *Geochimica et Cosmochimica Acta*, v. 64, no. 19, p. 3413–3432.
- Scherer, E., Munker, C., and Mezger, K., 2001, Calibration of the Lutetium–Hafnium Clock: *Science*, v. 293, no. 5530, p. 683–687.
- Schetselaar, E., Ames, D., and Grunsky, E., 2017, Integrated 3D Geological Modeling to Gain Insight in the Effects of Hydrothermal Alteration on Post-Ore Deformation Style and Strain Localization in the Flin Flon Volcanogenic Massive Sulfide Ore System: *Minerals*, v. 8, no. 1.
- Schmidt, A., Pourteau, A., Candan, O., and Oberhänsli, R., 2015, Lu–Hf geochronology on cm-sized garnets using microsampling: New constraints on garnet growth rates and duration of metamorphism during continental collision (Menderes Massif, Turkey): *Earth and Planetary Science Letters*, v. 432, p. 24–35.
- Schneider, D. A., Heizler, M. T., Bickford, M. E., Wortman, G. L., Condie, K. C., and Perilli, S., 2007, Timing constraints of orogeny to cratonization: Thermochronology of the Paleoproterozoic Trans-Hudson orogen, Manitoba and Saskatchewan, Canada: *Precambrian Research*, v. 153, no. 1–2, p. 65–95.
- Schoneveld, L., Spandler, C., and Hussey, K., 2015, Genesis of the central zone of the Nolans Bore rare earth element deposit, Northern Territory, Australia: *Contributions to Mineralogy and Petrology*, v. 170, no. 2.
- Schumann, D., Martin, R. F., Fuchs, S., and de Fourestier, J., 2019, Silicocarbonatitic melt inclusions in fluorapatite from the Yates prospect, Otter Lake, Québec: Evidence of marble anatexis in the central metasedimentary belt of the Grenville Province: *The Canadian Mineralogist*, v. 57, no. 5, p. 583–604.
- Seman, S., Stockli, D. F., and McLean, N. M., 2017, U–Pb geochronology of grossular-andradite garnet: *Chemical Geology*, v. 460, p. 106–116.
- Shannon, R. D., 1976, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides: *Acta Crystallographica A*, v. 32, no. 5, p. 751–767.
- Shemesh, A., 1990, Crystallinity and diagenesis of sedimentary apatites: *Geochimica et Cosmochimica Acta*, v. 54, no. 9, p. 2433–2438.
- Simpson, A., Gilbert, S., Tamblyn, R., Hand, M., Spandler, C., Gillespie, J., Nixon, A., and Glorie, S., 2021a, In-situ Lu Hf geochronology of garnet, apatite and xenotime by LA ICP MS/MS: *Chemical Geology*, v. 577.

- Simpson, A., Glorie, S., Hand, M., Spandler, C., Gilbert, S., and Cave, B., 2022, In situ Lu–Hf geochronology of calcite: *Geochronology*, v. 4, no. 1, p. 353–372.
- Simpson, A., Glorie, S., Morley, C. K., Roberts, N. M. W., Gillespie, J., and Lee, J. K., 2021b, In-situ calcite U–Pb geochronology of hydrothermal veins in Thailand: New constraints on Indosinian and Cenozoic deformation: *Journal of Asian Earth Sciences*, v. 206.
- Skirrow, R., Evgeniy, B. N., Barovich, K., Fraser, G., Creaser, R. A., Fanning, C. M., Raymond, O. L., and Davidson, G. J., 2007, Timing of Iron Oxide Cu–Au–(U) hydrothermal activity and Nd isotope constraints on metal sources in the Gawler Craton, South Australia: *Economic Geology*, v. 102, p. 1441–1470.
- Skirrow, R., Maas, R., and Ashley, P. M., 1999, New age constraints for Cu–Au–(Mo) mineralisation and regional alteration in the Olary–Broken hill region: *AGSO Research Newsletter*, v. 31.
- Skirrow, R. G., 2022, Iron oxide copper–gold (IOCG) deposits – A review (part 1): Settings, mineralogy, ore geochemistry and classification: *Ore Geology Reviews*, v. 140.
- Skora, S., Baumgartner, L. P., Mahlen, N. J., Johnson, C. M., Pilet, S., and Hellebrand, E., 2006, Diffusion-limited REE uptake by eclogite garnets and its consequences for Lu–Hf and Sm–Nd geochronology: *Contributions to Mineralogy and Petrology*, v. 152, no. 6, p. 703–720.
- Smit, M. A., Scherer, E. E., and Mezger, K., 2013, Lu–Hf and Sm–Nd garnet geochronology: Chronometric closure and implications for dating petrological processes: *Earth and Planetary Science Letters*, v. 381, p. 222–233.
- Söderlund, U., Patchett, P. J., Vervoort, J. D., and Isachsen, C. E., 2004, The ^{176}Lu decay constant determined by Lu–Hf and U–Pb isotope systematics of Precambrian mafic intrusions: *Earth and Planetary Science Letters*, v. 219, no. 3–4, p. 311–324.
- Soper, N. J., Harris, A. L., and Strachan, R. A., 1998, Tectonostratigraphy of the Moine Supergroup: a synthesis: *Journal of the Geological Society*, v. 155, no. 1, p. 13–24.
- Spandler, C., Hammerli, J., Sha, P., Hilbert-Wolf, H., Hu, Y., Roberts, E., and Schmitz, M., 2016, MKED1: A new titanite standard for in situ analysis of Sm–Nd isotopes and U–Pb geochronology: *Chemical Geology*, v. 425, p. 110–126.
- Spear, F. S., 1993, *Metamorphic Phase Equilibria and Pressure–Temperature–Time Paths*, Chantilly, VA, Mineralogical Society of America.
- Spencer, C. J., Kirkland, C. L., Roberts, N. M. W., Evans, N. J., and Liebmann, J., 2020, Strategies towards robust interpretations of in situ zircon Lu–Hf isotope analyses: *Geoscience Frontiers*, v. 11, no. 3, p. 843–853.
- Spencer, K. J., Hacker, B. R., Kylander-Clark, A. R. C., Andersen, T. B., Cottle, J. M., Stearns, M. A., Poletti, J. E., and Seward, G. G. E., 2013, Campaign-style titanite U–Pb dating by laser-ablation ICP: Implications for crustal flow, phase transformations and titanite closure: *Chemical Geology*, v. 341, p. 84–101.
- Stacey, J. S., and Kramers, J. D., 1975, Approximation of terrestrial lead isotope evolution by a two-stage model: *Earth and Planetary Science Letters*, v. 26, no. 2, p. 207–221.
- Staff, P. M., 1976, The Geology and the economic deposits of copper, iron, and vermiculite in the Palabora Igneous Complex, A brief review.: *Economic Geology*, v. 71, p. 177–192.
- Stern, R. A., and Rainbird, R. H., 2001, *Advancements in xenotime U–Pb geochronology by ion microprobe*, Goldschmidt: Houston, Texas.
- Stern, R. A., Syme, E. C., Bailes, A. H., and Lucas, S. B., 1995, Paleoproterozoic (1.90–1.86 Ga) arc volcanism in the Flin Flon Belt, Trans-Hudson Orogen, Canada: *Contributions to Mineralogy and Petrology*, no. 119, p. 117–141.
- Storey, C. D., Brewer, T. S., and Parrish, R. R., 2004, Late-Proterozoic tectonics in northwest Scotland: one contractional orogeny or several?: *Precambrian Research*, v. 134, no. 3–4, p. 227–247.
- Strachan, R. A., Alsop, G. I., Ramezani, J., Frazer, R. E., Burns, I. M., and Holdsworth, R. E., 2020, Patterns of Silurian deformation and magmatism during sinistral oblique convergence, northern Scottish Caledonides: *Journal of the Geological Society*, v. 177, no. 5, p. 893–910.

- Strachan, R. A., Holdsworth, R. E., Krabbendam, M., and Alsop, G. I., 2010, The Moine Supergroup of NW Scotland: insights into the analysis of polyorogenic supracrustal sequences: Geological Society, London, Special Publications, v. 335, no. 1, p. 233-254.
- Stuart-Smith, P. G., Needham, R. S., Page, R. W., and Wyborn, L. A. I., 1993, Geology and mineral deposits of the Cullen Mineral Field, Northern Territory: Bureau of Mineral Resources, Australia, v. 220.
- Sylvester, P., 2008, Matrix effects in laser ablation ICP–MS, *in* Sylvester, P., ed., Laser Ablation–ICP–MS in the Earth Sciences current practices and outstanding issues, Volume 40: Vancouver, Mineralogical Association of Canada.
- Tamblyn, R., Brown, D. A., Hand, M., Morrissey, L., Clark, C., and Anczkiewicz, R., 2020a, The 2 Ga eclogites of central Tanzania: directly linking age and metamorphism.: *Lithos*, v. accepted October 2020.
- Tamblyn, R., Hand, M., Kelsey, D., Anczkiewicz, R., and Och, D., 2019, Subduction and accumulation of lawsonite eclogite and garnet blueschist in eastern Australia: *Journal of Metamorphic Geology*, v. 38, no. 2, p. 157-182.
- Tamblyn, R., Hand, M., Morrissey, L., Zack, T., Phillips, G., and Och, D., 2020b, Resubduction of lawsonite eclogite within a serpentinite-filled subduction channel: *Contributions to Mineralogy and Petrology*, v. 175, no. 8.
- Tamblyn, R., Hand, M., Simpson, A., Gilbert, S., Wade, B., and Glorie, S., 2021, In-situ laser ablation Lu–Hf geochronology of garnet across the Western Gneiss Region: Campaign-style dating of metamorphism: *Journal of the Geological Society*, p. jgs2021-2094.
- Taylor, R. S., and McLennan, S. M., 1985, The continental crust: its composition and evolution, United States.
- Tera, F., and Wasserburg, G. J., 1972, U–Th–Pb systematics in three Apollo 14 basalts and the problem of initial Pb in lunar rocks: *Earth and Planetary Science Letters*, v. 14, p. 36-51.
- Terakado, Y., and Masuda, A., 1988, The coprecipitation of rare-earth elements with calcite and aragonite: *Chemical Geology*, v. 69, no. 1, p. 103-110.
- Terry, M. P., Robinson, P., Hamilton, M. A., and Jercinovic, M. J., 2000, Monazite geochronology of UHP and HP metamorphism, deformation, and exhumation, Nordoyane, Western Gneiss Region, Norway: *American Mineralogist*, v. 85, p. 1651-1664.
- Thigpen, J. R., Law, R. D., Lloyd, G. E., Brown, S. J., and Cook, B., 2010, Deformation temperatures, vorticity of flow and strain symmetry in the Loch Eriboll mylonites, NW Scotland: implications for the kinematic and structural evolution of the northernmost Moine Thrust zone, *in* Law, R. D., Butler, R. W. H., Holdsworth, R. E., Krabbendam, M., and Strachan, R. A., eds., *Continental Tectonics and Mountain Building: The Legacy of Peach and Horne*, Volume 335, Geological Society of London, p. 0.
- Thirlwall, M. F., and Walder, A. J., 1995, In situ hafnium isotope ratio analysis of zircon by inductively coupled plasma multicollector mass spectrometry: *chemical Geology (Isotope Geoscience Section)*, v. 122, p. 241 - 247.
- Thompson, J., Meffre, S., Maas, R., Kamenetsky, V., Kamenetsky, M., Goemann, K., Ehrig, K., and Danyushevsky, L., 2016, Matrix effects in Pb/U measurements during LA-ICP-MS analysis of the mineral apatite: *Journal of Analytical Atomic Spectrometry*, v. 31, no. 6, p. 1206-1215.
- Thomson, S. N., Gehrels, G. E., Ruiz, J., and Buchwaldt, R., 2012, Routine low-damage apatite U–Pb dating using laser ablation-multicollector-ICPMS: *Geochemistry, Geophysics, Geosystems*, v. 13, no. 2, p. n/a-n/a.
- Thoni, M., 2003, Sm–Nd isotope systematics in garnet from different lithologies (Eastern Alps): age results, and an evaluation of potential problems for garnet Sm–Nd chronometry [*Chem. Geol.* 185 (2002) 255–281]: *Chemical Geology*, v. 194, no. 4, p. 353-379.
- Tillberg, M., Drake, H., Zack, T., Högmark, J., and Åström, M., 2017, In Situ Rb–Sr Dating of Fine-grained Vein Mineralizations Using LA-ICP-MS: *Procedia Earth and Planetary Science*, v. 17, p. 464-467.

- Tillberg, M., Drake, H., Zack, T., Kooijman, E., Whitehouse, M. J., and Astrom, M. E., 2020, In situ Rb-Sr dating of slickenfibres in deep crystalline basement faults: *Sci Rep*, v. 10, no. 1, p. 562.
- Tracy, R. J., Robinson, P., and Thompson, A. B., 1976, Garnet composition and zoning in the determination of temperature and pressure of metamorphism, central Massachusetts: *American Mineralogist*, v. 61, no. 7-8, p. 762-775.
- van Breemen, O. v., and Corriveau, L., 2005, U-Pb age constraints on arenaceous and volcanic rocks of the Wakeham Group, eastern Grenville Province: *Canadian Journal of Earth Sciences*, v. 42, no. 10, p. 1677-1697.
- Vance, D., and O'Nions, R. K., 1990, Isotopic chronometry of zoned garnets: growth kinetics and metamorphic histories: *Earth and Planetary Science Letters*, v. 97, no. 3, p. 227-240.
- Vance, D., Strachan, R. A., and Jones, K. A., 1998, Extensional versus compressional settings for metamorphism: Garnet chronometry and pressure-temperature-time histories in the Moine Supergroup, northwest Scotland: *Geology*, v. 26, no. 10, p. 927-930.
- Vermeesch, P., 2018, IsoplotR: A free and open toolbox for geochronology: *Geoscience Frontiers*, v. 9, no. 5, p. 1479-1493.
- Vervoort, J., 2014, Lu-Hf Dating: The Lu-Hf Isotope System, *Encyclopedia of Scientific Dating Methods*, p. 1-20.
- Vervoort, J., and Patchett, P. J., 1996, Behavior of hafnium and neodymium isotopes in the crust: constraints from Precambrian crustally derived granites: *Geochimica et Cosmochimica Acta*, v. 60, no. 19, p. 3717-3733.
- Villa, I. M., Holden, N. E., Possolo, A., Ickert, R. B., Hibbert, D. B., and Renne, P. R., 2020, IUPAC-IUGS recommendation on the half-lives of ^{147}Sm and ^{146}Sm : *Geochimica et Cosmochimica Acta*, v. 285, p. 70-77.
- Walczak, K., Cuthbert, S., Kooijman, E., Majka, J., and Smit, M. A., 2019, U-Pb zircon age dating of diamond-bearing gneiss from Fjorftoft reveals repeated burial of the Baltoscandian margin during the Caledonian Orogeny: *Geological Magazine*, v. 156, no. 11, p. 1949-1964.
- Wang, C., Alard, O., Lai, Y.-J., Foley, S. F., Liu, Y., Munnikhuys, J., and Wang, Y., 2022, Advances in in-situ Rb-Sr dating using LA-ICP-MS/MS: applications to igneous rocks of all ages and to the identification of unrecognized metamorphic events: *Chemical Geology*, v. 610, p. 121073.
- Wang, S., and Williams, P. J., 2001, Geochemistry and origin of Proterozoic skarns at the Mount Elliott Cu-Au(-Co-Ni) deposit, Cloncurry district, NW Queensland, Australia: *Mineralium Deposita*, v. 36, p. 109-124.
- Whitehouse, M. J., and Russell, J., 1997, Isotope systematics of Precambrian marbles from the Lewisian complex of northwest Scotland: implications for Pb-Pb dating of metamorphosed carbonates: *Chemical Geology*, v. 136, no. 3-4, p. 295-307.
- Whitney, D. L., and Evans, B. W., 2010, Abbreviations for names of rock-forming minerals: *American Mineralogist*, v. 95, no. 1, p. 185-187.
- Wilke, M., Schmidt, C., Dubrill, J., Appel, K., Borchert, M., Kvashnina, K., and Manning, C. E., 2012, Zircon solubility and zirconium complexation in $\text{H}_2\text{O}+\text{Na}_2\text{O}+\text{SiO}_2\pm\text{Al}_2\text{O}_3$ fluids at high pressure and temperature: *Earth and Planetary Science Letters*, v. 349-350, p. 15-25.
- Woodhead, J., Hergt, J., Shelley, M., Eggins, S., and Kemp, R., 2004, Zircon Hf-isotope analysis with an excimer laser, depth profiling, ablation of complex geometries, and concomitant age estimation: *Chemical Geology*, v. 209, no. 1-2, p. 121-135.
- Woods, G., 2017, Resolution of ^{176}Yb and ^{176}Lu interferences on ^{176}Hf to enable accurate $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratio analysis using La-QQQ with MS/MS: Agilent Technologies.
- Worden, K. E., Carson, C. J., Scrimgeour, I. R., Lally, J., and Doyle, N., 2008, A revised Palaeoproterozoic chronostratigraphy of the Pine Creek Orogen, northern Australia: evidence from SHRIMP U-Pb zircon geochronology: *Precambrian Research*, v. 166, p. 122-144.

- Wu, F.-Y., Yang, Y.-H., Li, Q.-L., Mitchell, R. H., Dawson, J. B., Brandl, G., and Yuhara, M., 2011, In situ determination of U–Pb ages and Sr–Nd–Hf isotopic constraints on the petrogenesis of the Phalaborwa carbonatite Complex, South Africa: *Lithos*, v. 127, no. 1-2, p. 309-322.
- Xiang, D., Zhang, Z., Zack, T., Chew, D., Yang, Y., Wu, L., and Hogmalm, J., 2021, Apatite U-Pb Dating with Common Pb Correction Using LA-ICP-MS/MS: *Geostandards and Geoanalytical Research*, v. 45, no. 4, p. 621-642.
- Yakymchuk, C., Clark, C., and White, R. W., 2017, Phase Relations, Reaction Sequences and Petrochronology: *Reviews in Mineralogy and Geochemistry*, v. 83, no. 1, p. 13-53.
- Yang, Y.-H., Wu, F.-Y., Yang, J.-H., Chew, D. M., Xie, L.-W., Chu, Z.-Y., Zhang, Y.-B., and Huang, C., 2014, Sr and Nd isotopic compositions of apatite reference materials used in U–Th–Pb geochronology: *Chemical Geology*, v. 385, p. 35-55.
- Yardley, B. W. D., 2009, The role of water in the evolution of the continental crust: *Journal of the Geological Society*, v. 166, no. 4, p. 585-600.
- Yardley, B. W. D., Harlov, D. E., and Heinrich, W., 2010, Rates of retrograde metamorphism and their implications for crustal rheology: *Geofluids*, v. 10, no. 1-2, p. 234-240.
- Zack, T., and Hogmalm, J., 2015, In-situ Lu-Hf dating of xenotime by reaction cell isotope separation, *Goldschmidt*: Prague, Czech Republic.
- Zack, T., and Hogmalm, K. J., 2016, Laser ablation Rb/Sr dating by online chemical separation of Rb and Sr in an oxygen-filled reaction cell: *Chemical Geology*, v. 437, p. 120-133.
- Zack, T., Stockli, D. F., Luvizotto, G. L., Barth, M. G., Belousova, E., Wolfe, M. R., and Hinton, R. W., 2011, In situ U–Pb rutile dating by LA-ICP-MS: 208Pb correction and prospects for geological applications: *Contributions to Mineralogy and Petrology*, v. 162, no. 3, p. 515-530.
- Zhai, W., Zhang, E., Zheng, S.-q., Santosh, M., Sun, X.-m., Niu, H.-c., Fu, B., Fu, Y., Li, D.-f., Jiang, Y.-h., Liang, F., Lin, W.-p., Zhao, Y., and Han, S.-y., 2022, Hydrothermal zircon: Characteristics, genesis and metallogenic implications: *Ore Geology Reviews*, v. 149, p. 105111.
- Zhong, S., and Mucci, A., 1995, Partitioning of rare earth elements (REEs) between calcite and seawater solutions at 25°C and 1 atm, and high dissolved REE concentrations: *Geochimica et Cosmochimica Acta*, v. 59, no. 3, p. 443-453.