COMBINED NANOSTRUCTURAL AND ISOTOPIC ANALYSIS OF BADELEYITE: NEW HORIZONS IN SOLAR SYSTEM CHRONOLOGY

Lee Francis White

The thesis is submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy of the University of Portsmouth.

School of Earth and Environmental Sciences
University of Portsmouth
January 2017

Advisors
Dr. James R. Darling
Prof. Desmond Moser
Dr. Dean Bullen
Baddeleyite (monoclinic-ZrO$_2$) is an exceptionally common accessory phase in many of the mafic and ultra-mafic rocks prevalent throughout the Solar System. This study presents the first ground-truthing efforts in the development of this robust mineral into a diagnostic indicator, discrete barometer, and precise U-Pb geochronometer of shock metamorphism by combining electron backscatter diffraction and atom probe tomography to generate unique chemical and structural datasets.

Microstructural analysis of variably shocked baddeleyite grains around the Sudbury impact structure (Ontario, Canada) highlights a series of crystallographic structures that can be correlated with discrete variations in formative pressure-temperature conditions. Decompression at high temperatures generates a series of interlocking reversion twinned structures, while quenching forms a quasi-amorphous matrix. These features are comparable to those observed in extra-terrestrial samples, where they can be directly linked with the severity and extent of lead loss and age resetting. This finding facilitates the application of baddeleyite as a shock indicator, barometer (>5 GPa) and chronometer in a wide range of planetary materials.

This structural variability is also observable on the nanometre scale. Analysis of the most highly shocked Sudbury baddeleyite using atom probe tomography reveals planar and curvi-planar fractures, trace element enriched subgrain boundaries, and solid-state diffusion clusters. These micrometre and nanometre scale features encourage localised diffusion of lead, with whole-microtip U-Pb analyses yielding complex partially reset ages. The application of atom probe tomography allows these features to be spatially resolved on the nanometre scale, yielding highly accurate ages for protolith crystallization and impact metamorphism within a single grain. These results have significant implications for the isotopic analysis of baddeleyite-bearing planetary materials, where the mechanisms of U-Pb age resetting have until now been poorly understood.
# TABLE OF CONTENTS

Abstract. . . . . . . . . . . . . . . ii

Table of contents . . . . . . . . . . . . . . iii

Author's declaration . . . . . . . . . . . . . . v

List of figures . . . . . . . . . . . . . . . vi

List of tables . . . . . . . . . . . . . . . ix

Acknowledgements . . . . . . . . . . . . . . x

Research dissemination . . . . . . . . . . . . xi

1 Introduction
  1.1 Interpreting the rock record of Solar System evolution . . 1
  1.2 Baddeleyite as a planetary chronometer . . . . 4
  1.3 Thesis aims & structure . . . . . . . . 7

2 Methodology
  2.1 Fieldwork and sample selection . . . . . . . . 9
  2.2 Scanning electron microscopy imaging and analysis . . 16
  2.3 Atom probe tomography . . . . . . . . 20

3 Developing baddeleyite as a shock indicator and barometer
  3.1 Introduction . . . . . . . . . . . . . . 25
  3.2 Baddeleyite as a widespread and sensitive indicator of meteorite bombardment in planetary crusts . . 26
  3.3 Supplementary materials . . . . . . . . 35

4 Developing baddeleyite as a planetary chronometer
  4.1 Introduction . . . . . . . . . . . . . . 38
  4.2 Atomic-scale age resolution of planetary events . . . 39
  4.3 Supplementary materials . . . . . . . . 46


### 5 Nanostructures and chronostructures in baddeleyite

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>63</td>
</tr>
<tr>
<td>5.2 Chemical nanostructures and chronostructures defined in shock</td>
<td>64</td>
</tr>
<tr>
<td>metamorphosed baddeleyite by atom probe tomography</td>
<td></td>
</tr>
</tbody>
</table>

### 6 Coupling structure and U-Pb geochronology in baddeleyite

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Introduction</td>
<td>85</td>
</tr>
<tr>
<td>6.2 New insights into the shock microstructural evolution of zirconia</td>
<td>86</td>
</tr>
<tr>
<td>and links with U-Pb geochronology</td>
<td></td>
</tr>
<tr>
<td>6.3 Qualifying age resetting by structure</td>
<td>108</td>
</tr>
</tbody>
</table>

### 7 Preservation potential of shocked zircon

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Introduction</td>
<td>110</td>
</tr>
<tr>
<td>7.2 The preservation potential of shocked zircon microstructure</td>
<td>111</td>
</tr>
</tbody>
</table>

### 8 Summary and future directions

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 Radiogenic dating of baddeleyite by atom probe</td>
<td>129</td>
</tr>
<tr>
<td>8.2 Baddeleyite as a shock indicator and barometer</td>
<td>130</td>
</tr>
<tr>
<td>8.3 New horizons in Solar System chronology</td>
<td>132</td>
</tr>
</tbody>
</table>

Bibliography: 134

Appendix I: Ethical review documentation: 144
AUTHORS DECLARATION

Whilst registered as a candidate for the above degree, I have not been registered for any other research award. The results and conclusions embodied in this thesis are the work of the named candidate and have not been submitted for any other academic award.

Word Count; ca. 36,500

Lee F. White
# List of Figures

**Figure 1.1:** BSE images of baddeleyite grains within a range of planetary materials  
**Figure 1.2:** Backscatter diffraction data for highly shocked Martian baddeleyite  
**Figure 2.1:** Over geological map of the Sudbury impact structure  
**Figure 2.2:** Photographs of key field relationships and sampling sites  
**Figure 2.3:** Thin section scans and optical microscopy images for key samples  
**Figure 2.4:** Diffraction pattern generated from crystalline and amorphous baddeleyite  
**Figure 2.5:** Visual workflow of EBSD analytical procedure  
**Figure 2.6:** Visual workflow of microtip preparation for atom probe analysis  
**Figure 2.7:** Sample voltage / time curve generated by atom probe analysis of baddeleyite  
**Figure 2.8:** Sample mass / charge spectrum generated by atom probe analysis of baddeleyite  
**Figure 2.9:** Time of flight event map and 3D reconstruction of analysed microtip  
**Figure 3.1:** Schematic geological map of Sudbury  
**Figure 3.2:** Cross-section of the target rocks underlying the Sudbury igneous complex (SIC), correlating sample locality with baddeleyite microstructures  
**Figure 3.3:** Schematic evolution of zirconia microstructure with increasing proximity to the impact melt sheet  
**Supp. Figure 3.1:** Representative pole figures diagrams for unshocked baddeleyite  
**Supp. Figure 3.2:** Representative pole figure diagrams for minimally shocked baddeleyite  
**Supp. Figure 3.3:** Texture component and pole figures for highly shocked baddeleyite  
**Supp. Figure 3.4:** Additional EBSD data for Sudbury baddeleyite grains  
**Figure 4.1:** Microstructural data for Sudbury m-ZrO2 grain  
**Figure 4.2:** APT data for discrete nanostructural domains preserved within highly shocked baddeleyite
Figure 4.3: $^{206}\text{Pb}/^{238}\text{U}$ APT age data for all eleven microtip specimens subdivided by nano-structural domain 44

Supp. Figure 4.1: 3D atom probe reconstruction of Phalaborwa baddeleyite 48

Supp. Figure 4.2: Back-scatter electron images of four baddeleyite grains 49

Supp. Figure 4.3: Three-dimensional Fe maps of all eleven atom probe microtip specimen 50

Supp. Figure 4.4: Labelled mass-to-charge spectra for bulk microtip #146506 51

Figure 5.1: Full mass-to-charge spectra (< 200 Da) for microtip #R60_147132 68

Figure 5.2: Distribution of individual Zr, Y, Fe and Si atoms within microtip #R60_147132 71

Figure 5.3: 3D model of Fe distribution in microtip #R60_147132 71

Figure 5.4: 2D concentration profiles of Zr, Fe, UO$_2$ and Pb across nanostructures 73

Figure 5.5: 2D distribution of Fe, ZrO$_2$, Pb and UO$_2$ (wavy features) across planar features 79

Figure 5.6: Schematic nanostructural evolution model for highly shocked baddeleyite 83

Figure 6.1: Generalized phase diagram for the ZrO$_2$ system 89

Figure 6.2: Baddeleyite shock microstructural groupings in Shergottite NWA 5298 92

Figure 6.3: Microstructural data for selected baddeleyite grains in unshocked terrestrial igneous rocks 96

Figure 6.4: Microstructural data for selected zirconia grains in NWA 5298 98

Figure 6.5. Microstructural data for selected baddeleyite grains in Lunar breccia NWA 2200, highlighting extensive crystal plastic deformation 100

Figure 6.6: Microstructural data for selected baddeleyite grains in terrestrial diabase JD12SUD14 101

Figure 6.7. Reversion twinning from the tetragonal to monoclinic transformation in zirconia 104

Figure 6.8. Shock microstructural evolution in baddeleyite correlated with U-Pb disturbance 105

Figure 6.9: Nanostructural atomic % versus microtip 108

Figure 6.10: Linking nanostructure with severity of age resetting in zircon 109
Figure 7.1: Overview map of the Sudbury impact structure . . . . 114
Figure 7.2: EBSD maps of zircon feature #277 . . . . 116
Figure 7.3: Optical microscope image of polycrystalline quartz in sample JD12SUD15a 117
Figure 7.4: BSE images of shocked zircon grains within sample JD12SUD15a . 118
Figure 7.5: EBSD maps of shocked zircon (JD12SUD15a) . . . . 118
Figure 7.6: PPL scan of thin section JD12SUD04 . . . . 120
Figure 7.7: BSE grain images for sample JD12SUD04 . . . . 120
Figure 7.8: EBSD data for shocked and sheared zircon grains in sample JD12SUD04 . 121
Figure 7.9: BSE images of highly metamict zircon grains from sample JD12SUD07 . 123
Figure 7.10: EBSD data for metamict zircon grains (JD12SUD07) . . . . 123
Figure 7.11: Schematic cross-section of the Sudbury North Range lithologies correlated with diagnostic shock features . . . . 126
Figure 7.12: Preservation potential of zircon versus other phases . . . . 127
Figure 8.1: Correlation between maskelynite occurrence and planetary escape velocity 130
Figure 8.2: Phase diagram for the ZrO$_2$-SiO$_2$ system . . . . 131
Figure 8.3: A simple workflow approach to dating Solar System materials using U-Pb analysis of baddeleyite . . . . 133
# List of Tables

**Table 1.1:** Shock classification scheme currently applied to chondritic meteorites  
(p. 2)

**Table 1.2:** Overview of baddeleyite ($\text{ZrO}_2$) occurrences within the inner Solar System  
(p. 3)

**Table 2.1:** Overview of the Sudbury, Vredefort and Chicxulub impact structures  
(p. 9)

**Table 2.2:** Overview of samples used during this PhD study  
(p. 12)

**Table 2.3:** Overview of electron backscatter diffraction (EBSD) run conditions  
(p. 18)

**Table 2.4:** Atom probe statistics for all eleven microtip specimens  
(p. 22)

**Supp. Table 3.1:** Overview of electron backscatter diffraction (EBSD) run conditions  
(p. 35)

**Supp. Table 4.1:** Bulk U-Pb data from all eleven microtip specimens  
(p. 52)

**Supp. Table 4.2:** Nanostructurally subdivided U-Pb data from all eleven microtip specimens  
(p. 53)

**Supp. Table 4.3:** Details of analytical parameters and full spectral counts for each microtip specimen  
(p. 54)

**Supp. Table 4.4:** Background corrected ionic counts for baddeleyite microtip specimens used in this study  
(p. 55-58)

**Table 4.5:** MSWD calculations incorporating raw – background uncertainties  
(p. 61)

**Table 4.6:** MSWD calculations incorporating background corrected uncertainties  
(p. 62)

**Table 5.1:** Atom probe tomography data acquisition and run summary  
(p. 67)

**Table 5.2:** Bulk geochemical data for microtip #R60_147132  
(p. 70)

**Table 5.3:** Isolated geochemical data for the larger planar feature  
(p. 72)

**Table 5.4:** Isolated geochemical data for the UO$_2$-enriched clusters  
(p. 74)

**Table 5.5:** U and Pb counts for the bulk, planar feature, curvi-planar feature and UO$_2$-enriched clusters within microtip #R60_147132  
(p. 76)
ACKNOWLEDGMENTS

This study benefited from the input and expertise of a great many people. First and foremost, James Darling is thanked for providing regular “meetings” to offload and discuss, and for providing much appreciated conference, workshop and lab support throughout my time as a PhD student. Desmond Moser is thanked for introducing me to the world of atom probe tomography, and providing support and guidance from the other side of the pond. Many members of the Crustal Evolution Research Group (CERG) at the University of Portsmouth are thanked for their contribution to my development as a scientist and for their help and support as friends, including Craig Storey, Kostas Papapavlou, Joseph Dunlop, Dean Bullen, Emma Hart, Michael Dunk, and Emilie Bruand. Geoff Long is thanked for thin section wizardry, and David Reinhard is thanked for the preparation and analysis of atom probe microtips.

This project was generously funded by an early career researcher grant (University of Portsmouth) and Elspeth Matthews grant (Geological Society of London) awarded to James Darling, a NSERC discovery grant awarded to Desmond Moser, and UK-Canada Foundation and Daniel Pidgeon (Geological Society of London) grants awarded to Lee White. Dissemination of results was supported by travel grants awarded by the Meteoritical Society, Nature Geoscience, the European Mineralogical Union, and the Science Faculty of the University of Portsmouth.

This thesis is dedicated to my wife, Kirstie, for tolerating enough of my rambling that she be considered a baddeleyite expert in her own right.
RESEARCH DISSEMINATION

Publications in review / in preparation


L. F. White et al. Baddeleyite as a widespread and sensitive indicator of bombardment in planetary crusts. Revising manuscript for Geology.

L. F. White et al. Nano-scale element mobility and diffusion in shocked baddeleyite (ZrO₂). In review for AGU Monograph: Nanoscale Geochronology


Conference attendance

Oral presentations

Extra-Terrestrial Materials Meeting, Manchester (UK), November 2016:

“Atomic-scale age resolution of planetary events”

Annual Meeting of the Meteoritical Society, Berlin (Germany), August 2016:

“Atom probe insights into U-Pb age resetting in baddeleyite”

Bridging the Gap III, Freiburg (Germany), September 2015:

“The potential application of baddeleyite (monoclinic-ZrO₂) as a shock indicator”

AGU GAC-MAC Joint Assembly, Montreal (Canada), May 2015:

“Combining atomic scale deformation analysis and U-Pb geochronology of micro-baddeleyite to unravel terrestrial impact structures and bombardment chronology”

UK Planetary Forum Early Career Scientist Meeting, Kent (UK), February 2015:

“Experimental shock deformation of whole-rock samples to ascertain petrologically resolved, impact-analogous deformation of micro-baddeleyite”

Poser presentations

Misasa V Symposium, Misasa (Japan), March 2015:

“Combining nano scale microstructural analysis and U-Pb geochronology of terrestrial micro-baddeleyite to unravel crustal and bombardment chronology”
INTRODUCTION

1.1 INTERPRETING THE ROCK RECORD OF SOLAR SYSTEM EVOLUTION

A great deal of information regarding the formation and evolution of our Solar System is retained in the rock record of solid planetary bodies. Although space missions have returned a small amount of material, most extra-terrestrial geological samples are delivered to Earth directly as meteorites. Subsequent petrological, geochemical and isotopic analysis of these precious rocks has yielded invaluable insight into a wide array of significant issues. For example, radiogenic isotope dating (i.e. U-Pb, Pb-Pb, Ar-Ar, Sm-Nd, Rb-Sr, Lu-Hf) has acted to constrain the timing of Solar System formation and planetary evolution (Papanastassiou & Wasserburg 1971; Compston et al. 1984; Bouvier et al. 2008; Bouvier & Wadhwa 2010), while volatile element abundance and stable isotope analysis (i.e. O, Cl, F, D/H) have greatly aided in assessing the potential extent and composition of water on planetary bodies (McNaughton et al. 1981; Sharp et al. 2010; Greenwood et al. 2011; Barrett et al. 2016). However, meteorites have experienced variable severities of shock metamorphism, a process which involves the mobilisation of cations during high-pressure reworking of the primary magmatic material and disturbance of the isotopic systems incorporated into these studies (Léchuse & Robert 1994; Bouvier et al. 2005; Bogard 2011; Gaffney et al. 2011). This process can yield partial to full disturbance of the primary magmatic signature recorded in the meteorite, greatly confusing chemical records within shocked materials (Nyquist et al. 1979; Nyquist et al. 2001; Swindle et al. 2014; Darling et al. 2016). Constraining the effects of shock metamorphism on the whole-rock, mineralogical and nano-meter scale in planetary materials greatly aids in the interpretation of these geochemical and isotopic data, highlighting the probability that generated data points relate to either primary crystallization or secondary shock disturbance.

There are several well-studied shock indicators that can help characterise the shock state of these precious materials. Larger features, such as shattercones (cm – m scale), are useful in the identification and reconstruction of terrestrial impact structures (Osinski & Ferrière 2016) though are absent within meteoritic samples. On the thin section scale (um – mm), mineralogical features observed through optical microscopy are used to identify and quantify the intensity of shock deformation. Quartz (SiO$_2$) is often implemented as a convincing recorder of impact events (French & Koeberl 2010), where the formation of sub-micron amorphous lamellae, known as planar deformation features (PDF’s), between 10 and 35 GPa (Langenhorst 1994) provide empirical constraints on bulk shock pressures experienced by the sample. Within more mafic meteorites such as ordinary chondrites,
structures within the constituent phases olivine \(((\text{Mg,Fe})_2\text{SiO}_4)\) and plagioclase feldspar \((\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8)\) have yielded a relative shock scheme for application to petrologically-similar materials (Stöffler et al. 1991; Table 1.1). These phases experience fracturing and mosaicism at lower shock pressures (< 20 GPa) before transitioning to ringwoodite (a high pressure polymorph of olivine) and maskelynite (a diaplectic glass of feldspathic composition) at ~23 and ~29 GPa, respectively (Stöffler et al. 1986; Ohtani et al. 2004). Recrystallisation and melting of these phases occurs at the most extreme conditions (~75 GPa; Stoffler et al. 1991).

<table>
<thead>
<tr>
<th>Shock stage</th>
<th>Effects resulting from equilibration peak shock pressure</th>
<th>Shock pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unshocked (S1)</td>
<td>Sharp optical extinction, irregular fractures</td>
<td>&lt;4-5</td>
</tr>
<tr>
<td>Very weakly shocked (S2)</td>
<td>Undulatory extinction, irregular fractures</td>
<td>5-10</td>
</tr>
<tr>
<td>Weakly shocked (S3)</td>
<td>Planar fractures, undulatory extinction, irregular fractures</td>
<td>15-20</td>
</tr>
<tr>
<td>Moderately shocked (S4)</td>
<td>Mosaicism (weak), planar fractures</td>
<td>Undulatory extinction, partially isotropic, planar deformation features</td>
</tr>
<tr>
<td>Strongly shocked (S5)</td>
<td>Mosaicism (strong), planar fractures + planar deformation features</td>
<td>Maskelynite*</td>
</tr>
<tr>
<td>Very strongly shocked (S6)</td>
<td>Solid-state recrystallization and staining, ringwoodite, melting</td>
<td>Shock melted (normal glass)</td>
</tr>
<tr>
<td>Shock melted</td>
<td>Whole rock melting (impact melt rocks and melt breccia)</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Shock classification system currently applied to chondritic meteorites, using the optical properties of olivine and plagioclase. After Stoffler et al. (1991). (*More recent estimates suggest maskelynite forms at lower shock pressures on the order of ~29 GPa; Stöffler et al. 1986; Ohtani et al. 2004).
2010; Cavosie et al. 2015; Reddy et al. 2015). As well as providing a useful insight into the peak shock pressure experienced by the sample, these features can be targeted for small volume isotopic analysis to accurately resolve impact ages (Moser et al. 2011; Cavosie et al. 2015). Importantly, the generation of these features alone does not encourage Pb loss, with the nano-scale structures and deformation pathways instead providing conduits for cation mobilisation during post-impact annealing (Moser et al. 2011).

Although zircon occurs within a wide range of igneous and metamorphic rock types (Hoskin & Black 2000; Haba et al. 2014), the phase is less abundant in more mafic lithologies. While impacts into basaltic target rocks are rare on Earth (perhaps limited to the relatively young 570 ± 47 Ka Lonar crater, India; Jourdan et al. 2011), the prevalence of low-silica lithologies within the inner Solar System (Elkins-Tanton 2012) means that constraining the response of mafic samples to shock metamorphism is vitally important in understanding the formation and evolution of many planetesimals. The robust accessory phase baddeleyite (monoclinic-ZrO$_2$) readily crystallizes from many of these more mafic magmas (Lumpkin 1999), occurring in a range of Martian (Moser et al., 2013; Darling et al., 2016), Lunar (El Goresy et al. 1971) and asteroidal (Bukovansk & Ireland 1992) crustal lithologies (Table 1.2). As a result, the microstructural analysis of these grains may yield important insights into the bombardment histories of mafic samples, though a great deal of groundtruthing work is required to facilitate such applications.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sample</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mars</td>
<td>Shergottite NWA 5298</td>
<td>Darling et al. 2016</td>
</tr>
<tr>
<td></td>
<td>Shergott</td>
<td>Ozawa et al. 2014</td>
</tr>
<tr>
<td></td>
<td>Roberts Massif 04261</td>
<td>Niihara 2011</td>
</tr>
<tr>
<td></td>
<td>Shergottite NWA 3171</td>
<td>Herd et al. 2010</td>
</tr>
<tr>
<td></td>
<td>Zagami</td>
<td>Zhou et al. 2013</td>
</tr>
<tr>
<td></td>
<td>‘Black Beauty’</td>
<td>n/a</td>
</tr>
<tr>
<td>Moon</td>
<td>Lunar KREEP Basalts</td>
<td>El Goresy et al. 1971</td>
</tr>
<tr>
<td></td>
<td>Lunar NWA4485 (KREEP-breccia)</td>
<td>Arai et al. 2010</td>
</tr>
<tr>
<td></td>
<td>Deep Crustal Lunar 76535</td>
<td>Gooley et al. 1974</td>
</tr>
<tr>
<td></td>
<td>Apollo 11, 12 &amp; 14 Material</td>
<td>Andersen &amp; Hinthorne 1972</td>
</tr>
<tr>
<td></td>
<td>Lunar Anorthosite</td>
<td>Lumpkin 1999</td>
</tr>
<tr>
<td></td>
<td>NWA 2200</td>
<td>n/a</td>
</tr>
<tr>
<td>S- and C- type asteroids</td>
<td>Raguli Ordinary Chondrite (H3.8)</td>
<td>Krot et al. 1993</td>
</tr>
<tr>
<td></td>
<td>Ste. Marguerite (H4)</td>
<td>Michel-Levy et al. 1995</td>
</tr>
<tr>
<td></td>
<td>Allende (Carbonaceous, CV3)</td>
<td>El Goresy et al. 1978</td>
</tr>
<tr>
<td>Vesta</td>
<td>Range of Eucrites</td>
<td>Mittlefehlt &amp; Lindstrom 2003</td>
</tr>
<tr>
<td></td>
<td>Camel Donga</td>
<td>n/a</td>
</tr>
</tbody>
</table>

**Table 1.2: Overview of baddeleyite (ZrO$_2$) occurrences within the inner Solar System. Reports with no associated reference represent unpublished baddeleyite grains observed by our research group.**
1.2 BADDELEYITE AS A PLANETARY CHRONOMETER

Although widespread, many baddeleyite grains are tiny (< 20 um), with larger grains (> 100um) generally limited to rare carbonatite and mantle-derived magmas (Kerschhofer et al. 2000; Heaman & LeCheminant 2001; Heaman 2009). Difficulties with the separation and analysis of these grains (Soderlund & Johansson 2002; Chamberlain et al. 2010) has resulted in baddeleyite being generally overlooked, often confined to a simple footnote of its occurrence (i.e. Mittlefehldt & Lindstrom 2003). In many samples this is understandable; within the Allende carbonaceous chondrite, calcium-aluminium rich inclusions (CAI's) host baddeleyite grains as small as ~100nm (Figure 1.1a) which are isotopically unresolvable using modern geochemical and geochronological techniques. Achondritic meteorites have been reported to host larger grains (< 50um), and the in-situ analysis of such materials using laser ablation and secondary ion mass spectroscopy (Ibanez-Mejia et al. 2014; Chamberlain et al. 2010) has recently undergone somewhat of a renaissance. Pb-Pb SIMS dating of grains within NWA 4734, a lunar basalt (Figure 1.1b), has suggested age varies on the intra-grain scale (Wang et al. 2012), while ion probe U-Pb dating of 10-30um sized grains in Zagami (Figure 1.1c,d) has helped to confirm a young age for shergottite crystallisation (Zhou et al. 2013).

As work into these variably shocked meteoritic grains continued, issues regarding the response of the sensitive U-Pb isotopic system to the extreme pressure and temperature (P-T) conditions induced by meteorite impact and ejection events were raised. An experimental study into shock loading and annealing of an artificial baddeleyite-olivine matrix suggested that baddeleyite is a highly robust phase in this regard, unaffected by P-T conditions as extreme as ~59 GPa and ~1300°C (Niihara et al. 2012). These results have been shown to strongly disagree with natural observations of shocked baddeleyite, however, where < 80% of radiogenic lead was reportedly mobilised and lost during and impact (ejection) event (Moser et al. 2013). While this observation can potentially be attributed to numerous issues with the experimental study of Niihara et al (exceptionally large grains (< 200um), highly porous target lithology, etc.), fundamentally experimental shock loading and annealing durations (~µs) will never truly match natural shock profiles (ms - s). The analysis of additional naturally shocked grains will facilitate a better understanding of the isotopic response of baddeleyite to impact metamorphism, acting to either reconcile experimental and natural observations, or explain this variation to better inform future chronological applications. As interest in baddeleyite as a planetary chronometer grows (Moser et al. 2013), accurately defining the isotopic response of the phase to shock-metamorphism will be crucial.
Figure 1.1: Backscatter electron (BSE) images of selected occurrences of baddeleyite within planetary materials. (a) Baddeleyite (ZrO$_2$) in association with refractory materials in calcium-aluminium rich inclusions (CAI’s) within the CV3 carbonaceous chondrite Allende (El Goresy et al. 1978); Larger (< 20μm) grains occur within a large number of mafic achondrites, including lunar basalt NWA4734 (Bdl; b) (Wang et al. 2012) and Martian shergottite Zagami (Badd; c, d) (Zhou et al. 2013). Figures c and d are shown at the same scale (scale bar within figure c). Associated metals (a) and minerals (b, c d) are shown for reference; Ap = apatite; Pyr = pyroxene; Trq = tranquilite; Pl = plagioclase; Ilm = ilmenite; Tmt = titanomagnetite.

Most recently, the coupling of microstructural data from techniques such as EBSD and transmission electron microscopy (TEM), with isotopic age data has begun to resolve complex, partially age-reset grain populations. Within Martian shergottite NWA5298, the variable amorphisation and recrystallisation of individual grains during high pressure shock metamorphism directly correlates with the extent of Pb loss induced by the impact event (Darling et al. 2016). As well as highlighting the wide range of microstructures formed within highly shocked baddeleyite grains (Figure 1.2), this study also suggested that mobilisation and diffusion on the sub-micron scale directly controls the measurable U-Pb age. These sub-micron variations are currently unresolvable even at the length scales of modern laser ablation (~5μm) and secondary ion mass spectrometry (~2μm) techniques (Chamberlain et
al. 2010; Ibanez-Mejia et al. 2014). The sensitive nature of baddeleyite structure and chemistry highlighted by recent studies (Moser et al. 2013; Darling et al. 2016) suggests that such grains can yield discrete information regarding the severity of shock metamorphism, potentially acting to identify and quantify impact events as well as differentiate between crystallisation and impact age data. Detailed groundtruthing work will be required to constrain this unique new tool before application to planetary materials.

Figure 1.2: Backscatter electron (BSE; A&B), cathodoluminescence (CL; C), and electron backscatter diffraction (EBSD; D-F) maps of highly shocked baddeleyite within Martian shergottite NWA 5298. Band contrast (D) and texture component (F) mapping of the grain reveals interlocking amorphous and crystalline domains varying on the sub-micron scale. After Darling et al. (2016), grain #2451.

As links between microstructure and U-Pb age resetting become more well known, understanding the true nature of lead diffusion in this key planetary geochronometer would greatly enhance our interpretation of igneous and impact ages within ex-situ meteoritic samples. Recently, ground-breaking insight into Pb mobility and diffusion in zircon has been gleaned using atom probe tomography, a unique tool capable of generating coupled 3D structural and chemical datasets from ~100nm domains (Valley et al. 2014; Valley et al. 2015; Piazolo et al. 2016; Peterman et al. 2016). The application of this technique to structurally complex baddeleyite grains may generate chemical data of sufficient spatial-resolution to resolve issues of lead diffusion and age resetting, providing a unique insight into the nanoscale mechanisms that constrain the observable U-Pb age at the longer interaction volumes of SIMS (etc.). Such studies have yet to be conducted.
1.3 Thesis Aims & Structure

Given the increasing importance of accessory phases as identifiers, barometers and
chronometers of shock metamorphism, and the relatively untapped potential of baddeleyite
in this regard, this study provides a fantastic opportunity to strengthen the shock
metamorphism toolbox using this widespread geochronometer. Exciting new techniques,
such as electron backscatter diffraction and atom probe tomography, are providing unique
insights into the structure and chemistry of accessory phases such as zircon. The application
of these approaches to baddeleyite will provide the basis for new insights into the structural
and chemical response of the phase to shock metamorphism, acting to ground truth the phase
for application to a wide number of planetary problems. Thus, the principle aims of the thesis
are:

1. To define the full range of shock nanostructures developed within baddeleyite at a
   range of shock-metamorphic conditions.

2. To develop atom probe tomography as a tool for baddeleyite trace element and U-Pb
   isotope analysis, and ascertain the range of structural and chemical data this
   approach can yield.

3. To link shock-induced nanostructure development with U-Pb isotopic resetting to
   enhance future baddeleyite dating of shocked planetary materials

The bulk of this thesis constitutes a total of five papers; four that have either been
revised for publication or are under initial peer review, and one that is in preparation prior to
submission. These highlight the major scientific contributions of this doctoral study and are
included in their entirety in chapters 3 – 7, along with additional discussion where applicable.
A detailed overview of electron beam and atom probe microscopy techniques and
methodology is presented in chapter 2. Finally, a summary and discussion on the future
development and application of these tools is presented in chapter 8.

Chapter 3 presents microstructural data for baddeleyite grains sampled across a
linear transect north of the Sudbury impact structure. As a result, the microstructural
evolution of ZrO₂ can be constrained within a series of pressure-temperature constrained
lithologies in impact proximal and distal localities. This chapter is comprised of the following
paper: White L. F. et al. Baddeleyite as a widespread and sensitive indicator of meteorite
bombardment in planetary crusts. (Manuscript under revision for Geology).

Chapter 4 presents U-Pb atom probe data generated from shocked baddeleyite
sampled from the north range of Sudbury. This study presents the first measurement of U-Pb
ratios by atom probe, the first structural analysis of baddeleyite by atom probe, and the first atom probe study to use eleven microtips to establish statistical variability akin to other analytical methods. The chapter consists of the following paper: White L. F. et al. Atomic-scale age resolution of planetary events. (Manuscript in press with Nature Communications).

Chapter 5 presents an intricate breakdown of the chemistry and structure of a single atom probe microtip from the previous study. This work highlights a wide range of nanoscale shock features that can be correlated with trace element mobility and U-Pb age resetting, providing vital insights into lead loss in this key chronometer. The chapter consists of the following paper: White L. F. et al. Chemical nanostructures and chronostructures defined in shock metamorphosed baddeleyite by atom probe tomography. (In review with AGU Monograph ‘Microstructural Geochronology’).

Chapter 6 is a unique overview of baddeleyite microstructures observed within a wide range of shocked terrestrial and extra-terrestrial materials. These data are correlated with U-Pb measurements to constrain the structural and chemical variability of baddeleyite in impact settings, acting to review the other work presented in this thesis. The chapter includes the following paper: Darling J. R., White L. F. et al. New insights into the shock microstructural evolution of zirconia and links with U-Pb geochronology. (In review with AGU Monograph ‘Microstructural Geochronology’).

Chapter 7 introduces a new report of shock-induced zircon microstructure in the North Range of Sudbury, examining grains sampled across the same linear transect as the baddeleyite-bearing samples reported in chapter 3. The grains are variably shocked and preserved, yielding new insights into the preservation potential of such features in ex-situ grains. The chapter is composed of the following paper: White L. F. et al. The preservation potential of shocked zircon microstructures. (In preparation for Meteoritics and Planetary Science).

By including these five papers, chapters 3, 4, 5, 6 and 7 largely stand alone, and include a detailed introduction and discussion of results. The research for all five papers has been undertaken during my doctoral studies at the University of Portsmouth. Of the five papers presented, I am the primary author of four and second author of the fifth. My contribution to each manuscript is detailed within the introductory segment of the corresponding chapter. The findings of this study as a whole are summarised in chapter 8, along with identified directions for future research.
METHODOLOGY

2.1 FIELDWORK AND SAMPLE SELECTION

2.1.1 Locality selection

Addressing the primary aims of the thesis requires a series of well constrained, highly shocked, baddeleyite bearing samples. Geological context is near impossible to constrain in \textit{ex-situ} meteorite samples, even though such materials record a wide variety of shock metamorphic features (Stoffler et al. 1991). Terrestrial impact structures are more useful in this regard, providing opportunities to ground truth diagnostic shock features within well characterized lithologies in association with an identified impact structure (i.e. Cavosie et al. 2015). On Earth, three large multi-ring impact structures exist in the form of Sudbury, Vredefort and Chicxulub (Table 2.1). Each impact displays many large scale structural similarities, including pseudotachylyte belts, impact breccia deposits and shattercones. They also display similar mineralogical features within the target rocks, most notably planar deformation features in quartz (Grieve et al. 2008). Despite these similarities, the structures vary in terms of target lithology, age, estimated diameter, and extent of preservation.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Location</th>
<th>Age (Ma)</th>
<th>Original diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vredefort, S. Africa</td>
<td>27 30'E, 27 00'S</td>
<td>2023 ± 4</td>
<td>~250 – 300km</td>
</tr>
<tr>
<td>Sudbury, Canada</td>
<td>81 11'W, 46 36'N</td>
<td>1850 ± 3</td>
<td>~250 – 300km</td>
</tr>
<tr>
<td>Chicxulub, Mexico</td>
<td>89 30'W, 21 20'N</td>
<td>65 ± 0.05</td>
<td>~240km</td>
</tr>
</tbody>
</table>

\textit{Table 2.1: Overview of the three largest impact structures on Earth (Vredefort, Sudbury and Chicxulub), taken from Grieve et al. (2008) and references therein.}

At the Vredefort structure, South Africa, the original impact-induced melt sheet has been completely removed by 5 – 10km of erosion since its formation (Therriault et al. 1997). Modelling estimates suggest an original crater diameter on the order of 280 – 300km (Grieve et al. 2008), making the Vredefort structure the largest known impact crater on Earth. The 2.02 Ga impact (Kamo et al. 1996) resulted in the extensive uplift of the Archean to early Proterozoic target rocks in the core of the structure (Therriault et al. 1997; Grieve et al. 2008). Better preserved is the Sudbury impact structure (Ontario, Canada), which boasts the largest and thickest impact melt sheet so far recognized on Earth, preserved largely through tectonic in-folding with Archean and Proterozoic crystalline basement following a meteorite impact at 1.85 Ga (Krogh et al. 1984). Underlying the originally ca. 250 km structure (Spray et al. 2004) to the north is a series of Archaean high-grade metamorphic rocks, principally banded and
migmatitic gneisses of the Levack Complex (2711 ± 7 Ma; Krogh et al. 1984), which host a
number of granitic, tonalitic, granodioritic, mafic and ultra-mafic intrusions (Dressler 1984).
As opposed to the eroded Vredefort and tectonically-deformed Sudbury structures, the
Chicxulub structure, located off the Mexican coast, is almost perfectly preserved. However, the
~65 Ma structure (i.e. Krogh et al. 1993) has been subsequently buried up to 2km of
sediment and is predominately located offshore, limiting sample collection to targeted drilling
projects (i.e. Morgan et al. 2016). The structure itself is a multi-ring basin, with the furthest
peak ring occurring around ~240km from the melt sheet (Morgan et al. 1997). While all three
impacts are hugely exciting sites of scientific interest, the structure at Sudbury has been chosen
as the target for this study for the following reasons:

- The preserved melt sheet allows for shock phenomena to be mapped relative to an
  impact ‘epicenter’, allowing correlation between existing features (such as quartz
  PDF’s and shattercones) and the new microstructural features targeted by this study.
  Given that placing experimental constrains on shock-induced baddeleyite features is
  beyond the scope of this thesis, the constrained isograds inferred from quartz PDF’s
  (~10 GPa) and shattercones (~2 GPa) coupled with robust thermal models for the
  impact target rocks (James et al. 1992) does allow for quantification of the P-T
  conditions experienced by the sampled lithologies.

- The Matachewan dyke swarm represents a baddeleyite-bearing, pre-impact intrusive
  body that outcrops extensively within the North Range of the target rocks. These dykes
  represent a unique opportunity to examine shock conditions in mafic rocks across a
  linear transect radiating outwards from the melt sheet. Aside from greenschist-facies
  metamorphism, the dykes are well preserved, as highlighted by the robust 2473 (± 16)
  Ma U-Pb ages yielded by baddeleyite grains (Heaman 1997). They outcrop allowing for
  a paired sampling strategy to be employed (i.e. one felsic and one mafic sample to be
  collected from each locality). This is exceptionally important for future correlation
  between accessory phase microstructure (baddeleyite, zircon, titanite, apatite, etc.).

- As a primary goal of this thesis is to develop the application of atom probe tomography
to baddeleyite (including potential radiogenic (U-Pb) dating), older grains are
preferred to maximize the abundance of lead and minimize counting statistics
uncertainties on calculated ages. For the Matachewan dyke suite, a protolith age of 2.47
Ga (Heaman 1997), an impact age of 1.85 Ga (Krogh et al. 1984), and measured U
concentrations on the order of 271 – 1822 ppm (Heaman 1997) suggests that U-decay
will have generated substantial counts of Pb for resolution by atom probe.
2.1.2 North Range geology and sample descriptions

The rock units exposed in the North Range of the Sudbury impact structure are generally less deformed than those in the South, though the terrane is still cross-cut by a range of pseudotachylytic breccia and fault systems (Spray et al. 2004). A variety of zircon and baddeleyite-bearing lithologies are present within the terrane, allowing targeted sampling of accessory phase-bearing rock types with predetermined, high resolution U-Pb ages.

The Levack Gneiss Complex, consisting of high-grade (upper amphibolite to granulite facies) metamorphic rocks, constitutes the footwall at the northern margin of the Sudbury Igneous Complex. The suite is predominately composed of tonalitic, granodioritic and dioritic gneisses (Dressler 1984), formed between 2711 – 2645 Ma (Krogh et al. 1984). Peak metamorphism, at 6 – 8 kbar and < 800 °C (James et al. 1992), occurred around ~2645 Ma (Krogh et al. 1984). Magmatic intrusions occur throughout the complex, principally of tonalitic, granodioritic, mafic and ultramafic composition (Card 1994). Further to the north and west, the Cartier granitic batholith underlies both the Sudbury igneous structure and the Levack gneiss complex. This monzogranitic to granodioritic intrusion boasts a bulk enrichment in light rare earth (LREE) elements, U, and Th, and an abundance of zircon which yield a U-Pb age of 2642 ± 1 Ma (Meldrum et al. 1997). Shock features can be observed within 17km of the melt sheet base (Dressler 1984), though they have been widely overprinted in close proximity (~500m) to the igneous complex (Deutsch et al. 1995) by high temperature annealing immediately following the impact event (James et al. 1992).

Outcropping throughout the North Range, the Matachewan dyke swarm represents an estimated ~50,000 km² of basaltic magma intruded within a > 250,000 km² region of North America (Halls & Bates 1990). The Matachewan suite predominately outcrops as north / south striking, ~20m thick dykes of doleritic composition intruded within both the Cartier granite and Levack gneiss complex (Halls & Bates 1990). The dykes contain an abundance of microbaddeleyite grains (< 40 um longest dimension) that yield an average U-Pb emplacement age of 2473 (± 16) Ma (Heaman 1997).

A full and detailed description of the Sudbury melt sheet and South Range lithologies can be found elsewhere (Naldrett et al. 1970; Deutsch et al. 1995; Grieve et al. 1991; Therriault et al. 1997). The scientific content presented in this thesis is principally derived from six felsic and mafic ‘pairs’ sampled from the North Range of Sudbury, yielding twelve distinct samples for accessory phase analysis (Figure 2.1; Table 2.2). Hand samples from all twelve sites were collected during the Summer of 2012, prior to commencement of this study, while further samples, field data and locality images were collected during summer 2016 (Figure 2.2).
Figure 2.1: Overview map of Sudbury geology and sample localities. For reference, the known extent of shattercone and quartz planar deformation feature occurrences are also presented (adapted from Grieve et al. 2008).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distance to melt sheet</th>
<th>UTM E (m)</th>
<th>UTM N (m)</th>
<th>Rock Type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>03</td>
<td>2km</td>
<td>0464642</td>
<td>5164223</td>
<td>Matachewan dyke</td>
<td>Massive, fractured doleritic dyke (Figure 2.2a)</td>
</tr>
<tr>
<td>04</td>
<td>2km</td>
<td>0464642</td>
<td>5164223</td>
<td>Levack gneiss</td>
<td>Pseudotachylyte vein with felsic clasts (Figure 2.2b)</td>
</tr>
<tr>
<td>06</td>
<td>10km</td>
<td>0458468</td>
<td>5169129</td>
<td>Matachewan dyke</td>
<td>~10m wide doleritic dyke crosscutting granitic mass</td>
</tr>
<tr>
<td>07</td>
<td>10km</td>
<td>0458474</td>
<td>5169116</td>
<td>Cartier granite</td>
<td>Coarse grained, fractured granodiorite</td>
</tr>
<tr>
<td>08</td>
<td>400m</td>
<td>0463657</td>
<td>5160917</td>
<td>Matachewan dyke</td>
<td>Medium grained, fractured doleritic dyke in gneiss</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0463627</td>
<td>5160758</td>
<td>Levack gneiss</td>
<td>Gneiss interbedded with coarse granitic layers (Fig. 2.2c)</td>
</tr>
<tr>
<td>10</td>
<td>700m</td>
<td>0462230</td>
<td>5161298</td>
<td>Matachewan dyke</td>
<td>25m wide coarse grained doleritic dyke within gneiss</td>
</tr>
<tr>
<td>11</td>
<td>700m</td>
<td>0462230</td>
<td>5161298</td>
<td>Levack gneiss</td>
<td>Amphibolite facies gneiss, granulite overprint</td>
</tr>
<tr>
<td>12</td>
<td>3km</td>
<td>0460596</td>
<td>5161519</td>
<td>Matachewan dyke</td>
<td>Doleritic dyke within pseudotachylyte belt, interspersed with felsic clasts</td>
</tr>
<tr>
<td>13</td>
<td>3km</td>
<td>0460596</td>
<td>5161519</td>
<td>Carter granite</td>
<td>Massive, coarse grained granite</td>
</tr>
<tr>
<td>14</td>
<td>550m</td>
<td>0465963</td>
<td>5163552</td>
<td>Matachewan dyke</td>
<td>Highly fractured doleritic dyke (Fig. 2.2d) containing shattercones (Fig. 2.2e)</td>
</tr>
<tr>
<td>15a</td>
<td>550m</td>
<td>0465990</td>
<td>5163536</td>
<td>Levack gneiss</td>
<td>Granitic intrusion within Levack gneiss (Fig. 2.2f-h)</td>
</tr>
</tbody>
</table>

Table 2.2: Overview of Sudbury samples selected for this study, including UTM grid references and targeted rock types. All sample ID’s are prefixed by ‘JD12SUD’. Presented coordinates can be located within UTM Zone 17N.
**Figure 2.2:** Field photographs of baddeleyite and zircon bearing samples analysed during this study. The Matachewan dyke swarm outcrops as a massive, fractured, fine grained dolerite throughout the North Range of Sudbury, while the Cartier Granite underlies the Levack gneiss complex further to the north. The granite appears massive and fractured in outcrop scale.
2.1.2.1 Shock features observed in the field

A first-order insight into the shock state of these samples can be gathered in the field, where cross-cutting relationships, pseudotachylyte veins and shattercones can place constraints on the P-T histories experienced by the samples. Within the most proximal samples (JD12SUD14 & JD12SUD15), shattercones within the mafic dyke (Figure 2.2e) provide an empirical > 2 GPa pressure estimate (Osinski & Ferrière 2016). The apex of the observed cone appears to point towards the local interface with the melt sheet (S/SE). Although reported up to ~10km north of the melt sheet (Deutsch et al. 1995; Grieve et al. 1991), convincing shattercones were not observed in association with the other sample localities. Pseudotachylyte bands and veins were commonly observed, varying in thickness from ~3 cm to < 50 m. Finer veins contain predominately local clasts, subsampling the immediately surrounding target rocks (i.e. Figure 2.2b, h), while coarser bands appear to transport entrained clasts further. Pseudotachylyte thickness also appears to control roundness of clasts, with thinner veins preserving sharp inclusions (Figure 2.2h) and thicker bands producing more rounded clasts (Figure 2.2b). Along the dyke - granite contact, localized frictional movement has generated a small pseudotachylyte vein of sheared and mobilized mafic clasts within a felsic belt. Such relationships provide additional insight into the brittle response of the crust during impact events, and further constrain shock pressures to > 6 GPa (Kenkmann et al. 2000).

2.1.2.2 Shock features observed using optical microscopy

Optical microscopy (conducted using a petrological microscope at the University of Portsmouth) reveals further details on the genesis and deformation of the collected samples. The Matachewan dyke swarm is predominately doleritic in composition (plagioclase laths (< 1.5 cm), augite, ± baddeleyite), though has been variably overprinted by greenschist facies metamorphism (chlorite, epidote, actinolite). Feldspar appears crystalline (highlighting an absence of high pressure dialectic maskelynite), though is cloudy in PPL. Planar feature are absent even within the most impact proximal plagioclase, while extinction appears slightly strained in all samples suggesting a maximum shock pressure on the order of ~20 GPa (Stoffler et al. 1991). Augite crystals appear highly cracked and fractured, and contain < 20 um thick planar features shown to crosscut twin lamellae at approximately ~100°. Such structures have been observed in other shocked pyroxene grains (Short 1970), but formative P-T conditions are poorly constrained. Other phases, such as chlorite, show no obvious signs of shock deformation, instead crystallizing during post-impact metamorphism. Although planar deformation features (PDF’s) are known to form in quartz crystals exposed to 10 - 35 GPa of shock loading (Langenhorst 1994; Grieve et al. 1996), the low annealing temperature of quartz means that such features are readily recrystallized during post-shock contact metamorphism (Grieve et al. 2008; Dressler 1984). As a result, quartz-bearing lithologies near to the melt sheet
Methodology

display no convincing PDF's, an effect (annealing of PDF's) which has been reported up to ~500m below the Sudbury impact melt sheet (Grieve et al. 2008). As a result, large (< 4 mm), anhedral quartz crystals display no clear PDF formation, though some subgrains (< 1 mm) appear to preserve highly decorated planar and sub-planar features (i.e. Langenhorst 1994). Outside of this aureole, planar features are observed in impact distal samples within ~10km of the melt sheet (Grieve et al. 2008). Feldspar crystals in felsic samples appear petrologically similar to those within the shocked Matachewan dyke, being cloudy in PPL with strained extinction and an absence of planar deformation features. Actinolite, chlorite and hornblende generally occur as euhedral – subhedral grains within clusters or veins (here inferred to represent points of peak fluid interaction during post-impact metamorphism).

Figure 2.3: Thin section scans and optical microscopy images of impact proximal samples JD12SUD14 & JD12SUD15. For all samples, plane polarized light (PPL) and between cross polarizers (XPL) images are presented. Of note, augite crystals within JD12SUD14 are fractured, while quartz grains within JD12SUD15 appear highly annealed and recrystallized.
2.2 SCANNING ELECTRON MICROSCOPY IMAGING AND ANALYSIS

2.2.1 Thin section preparation

All twelve rock samples were selected for scanning electron microscope (SEM) imaging and electron backscatter diffraction (EBSD) analysis. Polished thin sections were created from each hand sample. Standard thin-section procedures involve progressive polishing steps with diamond suspensions down to 0.3 µm in diameter, but the samples for this project were further polished using a 50 nm alumina suspension with a Buehler Vibromat II vibratory polisher to remove additional surface defects. This process minimizes scatter of the electron beam due to surface interaction and is a critical step for accurate microstructural analysis by EBSD. Sections were imaged using an Epson V550 Photo scanner prior to carbon coating for electron beam imaging and analysis. Samples were carbon coated (< 20 nm thickness) and grounded using copper tape to minimize charging of the sample surface during electron beam interaction.

2.2.2 Micro-baddeleyite grain location

Target zircon and baddeleyite grains were located and imaged using a combination of automated backscatter electron (BSE) and energy-dispersive X-ray spectroscopy (EDS) techniques using the Oxford Instruments INCA and Aztec 'Feature' modules and Oxford X-Max 80 detectors installed on electron microscopes at the University of Portsmouth, UK and the Zircon and Accessory Phase Laboratory (ZAPlab) at the University of Western Ontario, Canada. This method is capable of locating individual zircon and baddeleyite down to ~1 micron in diameter over thin-section scale areas, recording detailed location, morphological and chemical data for each grain. This approach is especially important for preserving the petrological context of grains, such as orientation and host mineralogy, which is lost during traditional separation and mounting of accessory mineral phases.

The 'Feature' module targets individual features based on a grey-scale algorithm defined by the user. Both baddeleyite and zircon grains appear brighter in backscatter imaging as a result of having relatively high mean atomic numbers, increasing the probability of primary electrons being scattered back onto the detector. As a result, brighter features can be isolated within a quickly acquired image (< 20 s) using the INCA or Aztec Feature module, meaning that morphological and chemical data are collected from a limited portion of the section and increasing the speed of data collection. Other bright, high-Z (atomic number) phases, such as Fe-sulphides, are still identified by the software, requiring chemical analysis for differentiation. The chemical segregation of zircon (> 10 wt.% Si; > 30 wt.% Zr) and baddeleyite (< 10 wt.% Si; > 30 wt.% Zr) using EDS techniques further constrains those phases identified by the Feature scan, though more chemically-complex phases, such as zirconolite (CaZrTi₂O₇), may be misidentified during classification. At this point, manual inspection of generated elemental...
spectra allows for greater confidence in feature selection going forward. To aid the relocation of target grains for further imaging, microstructural or isotopic analysis, x-y coordinates of individual zircon and baddeleyite crystals can be superimposed over a BSE montage of the thin section. Here, exported excel data sheets from INCA / Aztec have been imported into QGIS, whereby they are overlain upon a georeferenced image. To ensure accurate mapping of accessory phase occurrences, four anchor points are identified in each thin section. The coordinates of these easily-identified anchor points are recorded during SE imaging and feature scanning and then used as reference points to triangulate feature coordinates in the final, georeferenced backscatter montage.

2.2.3 Scanning electron microscopy (SEM) imaging

Once identified, target zircon and baddeleyite grains were imaged using BSE and secondary electron (SE) techniques to identify features such as fractures and planar features. Grains were imaged using either a Hitachi SU6600 field emission gun SEM (FEG-SEM; ZAPlab) or Zeiss EVO MA10 LaB$_6$-SEM (Portsmouth) using comparable electron beam parameters between the two instruments (15 – 20 kV accelerating voltage, 200 – 500 pA, ~14.5 mm working distance to also match the calibrated interaction distance for EDS chemical analysis). Where possible, cathodoluminescence (CL) was also conducted, though for many smaller grains this technique yielded no additional information. High resolution, high contrast imaging (increased contrast, decreased brightness) was used to better highlight internal variation within each grain. Lower resolution, normal contrast imaging was used to provide information of surrounding phase relationships and to aid future relocation.

2.2.4 Electron backscatter diffraction (EBSD) analysis

Micro- to nano-scale structural analysis was conducted by electron backscatter diffraction (EBSD), using Oxford Instruments Nordlys EBSD detectors mounted on either a Hitachi SU6600 FEG-SEM (ZAPlab) or Zeiss EVO MA10 LaB$_6$-SEM (Portsmouth). Full instrument details can be found in Table 2.3. Diffraction patterns were automatically captured and indexed online by the HKL Channel 5 Flamenco (ZAPlab) or Oxford Instruments Aztec (Portsmouth) software packages. Patterns were acquired every 50 to 200 nm across a manually defined area, often on the order of hundreds of um$^2$ for baddeleyite and mm$^2$ for larger zircon grains. Raw patterns are automatically background-corrected during acquisition, removing ~64 frames of ‘noise’ from each pattern. Zircon diffraction patterns were matched to the lattice parameters defined by Hazen & Finger (1979), while baddeleyite patterns were matched to inorganic crystal structure database (ICSD) card 15,983. Collected pattern maps were exported to HKL Channel 5 software for offline reduction and interpretation. Wild spike reduction was completed on all EBSD datasets, whereby erroneous, mis-indexed pixels are removed from the dataset (set as a zero solution). No other raw data correction was conducted.
Instrumentation

<table>
<thead>
<tr>
<th>Host Institute</th>
<th>Western University</th>
<th>Portsmouth University</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM Model</td>
<td>Hitachi SU6600</td>
<td>Zeiss EVO MA10</td>
</tr>
<tr>
<td>Electron Source</td>
<td>Schottky Field Emission</td>
<td>LaB₆ electron source</td>
</tr>
<tr>
<td>EBSD Detector</td>
<td>Oxford Instruments Nordlys</td>
<td>Oxford Instruments Nordlys-Nano</td>
</tr>
<tr>
<td>EBSD Data Collection Software</td>
<td>HKL Channel 5 Flamenc o</td>
<td>Oxford Instruments AZTEC</td>
</tr>
</tbody>
</table>

SEM settings

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Western University</th>
<th>Portsmouth University</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon coat (&lt;20nm)</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Acc. Voltage (kV)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Working distance (mm)</td>
<td>19</td>
<td>14 to 20</td>
</tr>
<tr>
<td>Probe current (nA)</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>Tilt (°)</td>
<td>70</td>
<td>70</td>
</tr>
</tbody>
</table>

EBSD data collection and processing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Western University</th>
<th>Portsmouth University</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBSP collection time per frame (ms)</td>
<td>80</td>
<td>&lt; 120</td>
</tr>
<tr>
<td>Background (frames)</td>
<td>64</td>
<td>64</td>
</tr>
<tr>
<td>EBSP noise reduction (frames)</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>EBSP noise reduction (binning)</td>
<td>4x4</td>
<td>2x2</td>
</tr>
<tr>
<td>EBSP noise reduction (gain)</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Hough resolution</td>
<td>60</td>
<td>70</td>
</tr>
<tr>
<td>Band detection min/max</td>
<td>4 to 7</td>
<td>10 to 12</td>
</tr>
<tr>
<td>Step size (nm)</td>
<td>50 to 150</td>
<td>80 to 200</td>
</tr>
<tr>
<td>Noise reduction</td>
<td>wildspike only</td>
<td>wildspike only</td>
</tr>
</tbody>
</table>

Table 2.3: Overview of electron backscatter diffraction (EBSD) run conditions.

Each EBSD dataset contains a wealth of information that can be extracted during offline reduction. Band contrast (BC) is a quality factor describing the average intensity of the Kikuchi bands with respect to the overall intensity within the electron backscatter pattern (EBSP). Thus, generated BC maps reflect the strength of diffraction. Plotted in greyscale, the brighter domains reflect well-diffracting crystalline domains (Figure 2.4, while darker grey and black regions highlight weaker diffraction patterns. This often highlights (quasi-) amorphous domains and crystal defects, which is vital when examining highly shocked materials. All Euler maps are colored according to the euler angles, which describe rotation in three crystallographic axes (a, b, c), allowing coloration of EBSD data to best reflect differences in crystal orientation. These maps are often ideal for mapping out randomly oriented granules or misoriented twin planes. Texture component (TC) maps assign a single linear colour scale to display crystallographic misorientation relative to a defined point of reference. Such maps are ideal for highlighting crystal plastic deformation within a single crystal. By following a predefined workflow (Figure 2.5) these maps can be quickly generated (depending on targeted resolution), yielding increasingly important insights into the P-T histories of many accessory phases (i.e. Moser et al. 2011; Darling et al. 2016).
Figure 2.4: Electron backscatter patterns (EBSPs) generated from variably crystalline baddeleyite. Maps are generated at 100nm step size, and refined using 4x4 binning for fast acquisition. Diffraction patterns generated from crystalline (left) and amorphous (right) baddeleyite domains of grain #1700, sample JD12SUD03 (chapter 3).

Figure 2.5: Workflow for scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) analysis, resulting in high-resolution backscatter electron (BSE), secondary electron (SE), band contrast (BC), all euler, and texture component (TC) maps for each grain. This example highlights sample JD12SUD04 (a zircon-bearing pseudotachylite) and zircon grain #414.
2.3 Atom Probe Tomography

Atom probe tomography (APT) is a new (for the Earth Sciences) analytical technique for the acquisition of combined chemical, isotopic and structural data from sub-micron scale domains (Valley et al. 2014; Valley et al. 2015; Piazolo et al. 2016; Peterman et al. 2016; Reddy et al. 2016). Although modern analytical techniques are unable to isotopically resolve nanoscale crystallographic domains in highly shocked baddeleyite (Moser et al. 2013; Darling et al. 2016), the sub-nanometer spatial resolution of APT may yield exciting new insights capable of directly addressing the aims of this study. Therefore, to supplement the array of microstructural (EBSD) data collected during this study we have also conducted APT analysis of the most highly shocked baddeleyite grains from the Sudbury sample set (JD12SUD14). A total of fourteen microtip specimens were created from four ~2 x 10 μm pullouts derived from grains #44755 and #46059. Microtip specimens were prepared using either an FEI Helios or Nova focused ion beam (FIB)-SEM using standard lift-out and mount techniques to produce the desired specimen shape. A series of annular mills with a decreasing inner radius were used to produce needle-shaped specimens with a radius of curvature of less than ~100 nm (Figure 2.6). Typically, each tip will be polished four times using one of two patterns (~200nm tip thickness; ~100nm tip thickness). Full polishing procedures vary between tips and pullouts based on the stability and durability of the material. However, for the baddeleyite analysis presented here two protocols were employed for milling (pattern highlighted in parenthesis):

Mill 1: 0.28 nA, 25 Kx, (1) 0.23 nA, 35 Kx, (1)
Mill 2: 0.28 nA, 25 Kx, (2) 0.23 nA, 35 Kx, (2)
Mill 3: 0.28 nA, 50 Kx, (2) 40 pA, 80 Kx, (2)
Mill 4: 0.28 nA, 80 Kx, (2) 40 pA, 100 Kx, (2)

In this work, the prepared specimens were analyzed with a local electrode atom probe (LEAP) 5000 XR housed at the CAMECA Atom Probe Technology Center, Madison, Wisconsin. Recent advances in atom probe have allowed for electrically insulating materials to be analysed through laser-stimulated ionization (Kelly & Miller 2007), and this approach was implemented here for the study of baddeleyite. The LEAP 5000 XR is more efficient than previous models (~50% ion detection efficiency), while a curved reflectron compensator improves the mass resolution of the atom probe to about ~1000 M/AM, FWHM. During acquisition the specimen was placed under a high electric field and evaporation and ionization of atoms from the surface occur commensurate with a laser pulse (355nm wavelength, 125kHz, 100pJ). The mass to charge ratio of the ions is determined through time-of-flight (ToF) mass spectroscopy, which begins recording ionic flight time with each individual laser pulse. Ion flight paths (~382mm) are terminated on a 2D position-sensitive detector and the spatial
information is reconstructed by projecting the ions back to the spherical end-form of the specimen and considering the sequential order of evaporation. The resultant position (.pos) file contains a full 3D reconstruction of the microtip specimen and a complete mass / charge ratio spectrum, though spectra for individual elements and isotopes must be ranged by eye.

Figure 2.6: Ideal workflow for atom probe tomography (APT) analysis. Following identification and imaging, the grain is isolated using a platinum band. Using a FIB-SEM, a trench is made above and below the target domain, in this case a single baddeleyite crystal. The grain is separated in half to facilitate two separate pullouts, which are each then mounted on a coupon and subdivided into multiple (< 6) microtips. These are individually polished down by operating the FIB-SEM in a circular motion before evaporation for APT analysis.

Tips were cooled to ~50 degrees' kelvin in a high vacuum chamber prior to analysis. Evaporation started between 3 and 5 kV and finishing between 8 and 12 kV, yielding smooth voltage / time curves (Figure 2.7). The exact beginning and end points depend primarily on the
specimen size and shape after FIB milling, and whether the experiment was turned off or was stopped by fracturing of the specimen. Thermal tails are present within the generated mass/charge spectrum, but are generally only visible ~1-3 orders of magnitude down from peak height and so are only visible on the most prominent peaks which have a large signal (Figure 2.8). Of the fourteen tips, three failed early (<100 nm run length) yielding statistically irrelevant datasets restricted to hundreds to thousands of total ionic counts. The remaining eleven tips yielded between $2.3 \times 10^6$ and $3.5 \times 10^7$ background corrected, spectrally ranged ions over the length of the analysis. This represents between 31 and 67% of the total atoms collected during the entirety of the run (averaging ~53% across eleven tips; Table 2.4), yielding a collection efficiency roughly in line with that reported for the LEAP 5000 XR instrument (~50%).

![Figure 2.7: Sample voltage / time curve generated during the APT analysis of highly shocked baddeleyite. Voltage is increased steadily over time to ensure a continued, homogenous evaporation of atoms within the thicker base of the microtip (#145533). To aid the reader a schematic overview of the geometry of an APT instrument is shown (after Valley et al., 2015)](image)

<table>
<thead>
<tr>
<th>Microtip #</th>
<th>Total Ionic Count</th>
<th>Ranged Ions</th>
<th>Ranged Ions (%)</th>
<th>Background Corrected Ranged Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>R60_146506</td>
<td>21,973,219</td>
<td>13,407,632</td>
<td>61</td>
<td>11,344,871</td>
</tr>
<tr>
<td>R60_145533</td>
<td>14,215,013</td>
<td>10,324,166</td>
<td>73</td>
<td>9,223,315</td>
</tr>
<tr>
<td>R60_146475</td>
<td>29,108,763</td>
<td>16,532,292</td>
<td>57</td>
<td>13,977,673</td>
</tr>
<tr>
<td>R60_147132</td>
<td>64,348,159</td>
<td>44,110,385</td>
<td>69</td>
<td>34,429,581</td>
</tr>
<tr>
<td>R60_144153</td>
<td>83,791,461</td>
<td>43,112,812</td>
<td>51</td>
<td>35,271,770</td>
</tr>
<tr>
<td>R60_145547</td>
<td>35,934,177</td>
<td>23,194,486</td>
<td>65</td>
<td>19,259,664</td>
</tr>
<tr>
<td>R60_146995</td>
<td>106,387,272</td>
<td>43,217,828</td>
<td>41</td>
<td>33,402,588</td>
</tr>
<tr>
<td>R60_144108</td>
<td>3,868,269</td>
<td>2,759,954</td>
<td>71</td>
<td>2,331,328</td>
</tr>
<tr>
<td>R60_145519</td>
<td>9,751,559</td>
<td>7,341,701</td>
<td>75</td>
<td>6,502,974</td>
</tr>
<tr>
<td>R60_147129</td>
<td>8,599,402</td>
<td>5,769,975</td>
<td>67</td>
<td>4,923,410</td>
</tr>
<tr>
<td>R60_147070</td>
<td>63,013,496</td>
<td>38,892,134</td>
<td>62</td>
<td>32,300,348</td>
</tr>
</tbody>
</table>

*Table 2.4: Atom probe statistics for the eleven baddeleyite microtip specimen featured within this study.*
Figure 2.8: Sample mass / charge spectrum of the Phalaborwa baddeleyite standard. The spectrum is simpler than that of zircon, owing to the general absence of Si and SiO peaks. As a result, U and Pb can be isolated to allow for radiogenic dating using APT. For reference, an example of ‘peak ranging’ is displayed for Pb (insert), whereby all ionic counts within the dark green field are counted and quantified for compositional and chronological work.

Once collected, the spectrum is manually interpreted to allow for chemical and isotopic quantification (i.e. Figure 2.8). The LEAP instrument measures all atoms using microchannel plate detectors, allowing the uniform measurement of all species up to ~500 Da (daltons). Ranging of the spectra is conducted by eye, constraining and labelling elemental and isotopic peaks of signal which are then background corrected and quantified by the Integrated Visualization and Analysis System (IVAS) software package. Peak location varies very subtly (< 0.1 Da) between spectra, and as such the exact mass/charge location of ranged peaks varies accordingly. In all scenarios, peaks were ranged by eye from baseline to baseline to ensure a reproducible count between microtip spectra. The total ionic counts within this defined range, often on the order of 0.2 – 0.3 Da width (dependent on peak resolution), are defined as the raw counts. This number is uncorrected, combining true signal with potential background interferences. Currently, there are many sources of background interference during atom probe analysis of geological materials, principally regarding the delayed evaporation of ions following laser ablation (confusing the binning algorithm used by time of flight mass spectroscopy) and residual gas retained in the vacuum chamber (Cockeram et al. 2013). Atmospheric gas is a particular concern during APT, given the potential interference of hydroxide phases on true isotopic peaks. Currently, this H interference prevents the accurate measurement of many elemental species as the resolution currently offered by atom probe
prevents discrimination between true and hydroxide peaks. For example, O isotopes ($^{18}$O/$^{16}$O, $^{17}$O/$^{16}$O) are currently beyond the limits of APT, given unconstrained interferences of $^{16}$OH (peaks at ~17 Da) on $^{17}$O and $^{17}$OH (peaks at ~18 Da) on $^{18}$O. This interference on other peaks is poorly constrained, though it is generally accepted that double charged isotopes are more resistant to hydrogen coupling (Heck et al. 2014). A full discussion on isobaric (hydride) interferences can be found in Valley et al. (2015). The severity of these interferences cannot currently be quantified or corrected for, leading to the assignment of fairly significant uncertainties on individual element and isotope measurements (Valley et al. 2014). Presently, IVAS calculates background counts for each ranged peak by extrapolating the surrounding spectrum counts linearly throughout the defined range (Larson et al. 2011). For each individual peak, corrected ionic counts were calculated through the subtraction of background counts from the total (raw) ionic count. Propagation of absolute raw and background counting statistics errors ($\sqrt{\text{counts}}$) allows for estimated uncertainty on the corrected peak. Ion maps produced by IVAS are never background corrected, instead they show all ToF events in a single 3D model. The software cannot differentiate background from signal when assessing these individual ions, only when examining a greater abundance of data points in comparison. As a result, any single datum within the 3D reconstruction may represent background or signal. The reconstructed position of individual ions is accurate to within ~0.3nm (x-y-z) (Figure 2.9). Although the highly shocked baddeleyite grains analysed here were not characterized by EBSD, these highly crystalline grains ran well during laser evaporation. The high diffusivity of baddeleyite aided in maintaining a low temperature during the run, minimizing the presence of thermal tails on peaks and ensuring a clean and reproducible evaporation between microtip specimen. This is particularly important for multiple-tip studies such as that presented here.

Figure 2.9: Example time of flight (ToF) event map, recording the rate of impacts experience by the microchannel plate detector. This map can be coupled with a record of ionic impact order to recreate the three-dimensional distribution of atoms within the original microtip specimen. Each individual datum records its own Da (mass/charge), allowing all ions to be ranged and assigned an element / isotope. This allows for a complete 3D reconstruction of any combination of elements and isotopes present within the material.
DEVELOPING BADDELEYITE AS A SHOCK INDICATOR AND BAROMETER

3.1 INTRODUCTION

Despite its widespread occurrence in mafic planetary crusts (El Goresy et al. 1971; Darling et al. 2016; Moser et al. 2013; Bukovansk & Ireland 1992), baddeleyite has never been used to constrain the shock histories of complex rocks. The establishment of the phase as a new shock indicator and barometer relies on the generation of microstructural data from a range of constrained, highly-shocked samples. To that end, baddeleyite-bearing samples have been collected along a near-linear transect radiating outwards from the Sudbury impact melt sheet. EBSD analysis of these grains reveals a predictable sequence of microstructural evolution which can be correlated to the formation and reversion of the high pressure and temperature ZrO$_2$ polymorphs. Going forward, this discovery will allow for the shock state of mafic samples, both terrestrial and meteoritic, to be better characterised at lower shock pressure conditions (~5 GPa) than other indicators, such as maskelynite (~29 GPa; Stöffler et al. 1986), currently facilitate. The details and results are presented in the following paper, which is included in this chapter:


Samples were collected by J. Darling. EBSD analysis of baddeleyite grains was conducted by L. White, I. Barker and J. Dunlop. Data evaluation and interpretation, together with the preparation of the manuscript, was conducted by L. White, which benefitted from discussion with co-authors. The final manuscript was written by L. White, with input from J. Darling and D. Moser on ideas and wording, and input from I. Barker and J. Dunlop on methods.
3.2 BADDELEYITE AS A WIDESPREAD AND SENSITIVE INDICATOR OF METEORITE BOMBARDMENT IN PLANETARY CRUSTS

White, L. F. 1*, Darling, J. R. 1, Moser, D. 2, Barker, I. 2, Dunlop, J. 1, & Bullen, D. 1

1 School of Earth and Environmental Sciences, University of Portsmouth, Portsmouth
2 Department of Earth Sciences, University of Western Ontario, London, Canada.

The early history of hypervelocity meteorite impacts into planetary crusts is critical to understanding lithosphere evolution and conditions for the transition to habitability. However, conventional indicators of shock metamorphic events on Earth such as quartz (SiO₂) are readily recrystallized during post-impact annealing or tectonic reworking and, like the more retentive phase zircon (ZrSiO₄), are rare in the mafic crusts that dominate the inner planets and asteroids. Baddeleyite (monoclinic ZrO₂) is much more widely distributed throughout the Solar System and boasts a complex but poorly understood array of shock-induced microstructures. Here we show that the ZrO₂ lattice yields a predictable sequence of shock microstructures in the 5 to 20 GPa range, which differ from those in unshocked grains, using a constrained shock gradient on Earth. Localized crystallographic domains undergo high-pressure structural transitions during shock-loading, retrogressing to a quasi-amorphous structure in quenched (impact distal) samples but fully recrystallizing to unique monoclinic-ZrO₂ structures in extensively annealed (impact proximal) material. Our results demonstrate that baddeleyite is a sensitive shock indicator and barometer over a pressure range largely inaccessible with other minerals. This finding opens the door to better quantifying impact intensity and timing in a wide-range of planetary materials, placing important new constraints on Solar System bombardment.

Introduction

Constraining the extent and severity of shock metamorphism in planetary samples is critical when interpreting petrological records of planetary evolution and sensitive isotope ratios (Sm-Nd, Rb-Sr, Pb-Pb, etc.) that are vulnerable to diffusion during shock loading and annealing (Gaffney et al. 2011). Many of the mineral phases currently used in shock classification schemes (Stoffler et al. 1991) require high shock pressures, are readily recrystallized during post-shock metamorphism, or are limited to silica-rich lithologies. Quartz (SiO₂) is scarce in mafic planetary crusts, and impact diagnostic micro-structures are lost during annealing (for example in close proximity to an impact melt sheet (Grieve et al. 2008)). Zircon (ZrSiO₄) has been shown to provide a more robust record of shock histories (Moser et al. 2011; Cavosie et al. 2015), but these valuable grains are also limited to Si-saturated rock types. Maskelynite (diaeplectic plagioclase glass) only occurs at high shock-
pressures (c. 25 GPa; Milton and de Carli, 1963)) and as such is absent from a great deal of lesser shocked materials, only occurring in ~10% of eucrites, ~1% of lunar surface (Apollo) samples, and ~1% (H), ~4% (LL) and ~11% (L) of ordinary chondrites (Rubin 2015). As a result, constraining impact histories in the huge range of low shock pressure, silica-depleted samples is highly challenging.

Baddeleyite (monoclinic-ZrO$_2$) is a more widely occurring accessory phase within a vast array of silica-depleted lithologies throughout the Solar System, including mafic and ultra-mafic terrestrial lithologies (Lumpkin 1999), Martian crustal lithologies (i.e. SNC meteorites; Moser et al., 2013; Darling et al., 2016), Lunar KREEP basalts (El Goresy et al. 1971), asteroidal eucrites (Bukovansk & Ireland 1992) and primitive chondritic meteorites (Michel-Levy et al. 1995). Coupled with a remarkable resilience to tectonic and metamorphic reworking (melting point ~3000°C, Mohs hardness 6.5, resilient to α-decay (Lumpkin 1999)) and robust properties as a U-Pb geochronometer (Heaman 2009; Heaman 1997; Krogh et al. 1984), baddeleyite would provide an ideal crystallographic and isotopic record of planetary-scale events. However, issues regarding the separation, imaging and subsequent analysis of these often tiny (< 20μm) grains have prevented more wide-spread usage (Soderlund & Johansson 2002). Recent work has circumvented these shortcomings through the in-situ analysis of baddeleyite, coupling small-volume isotopic analyses (Chamberlain et al. 2010; Ibanez-Mejia et al. 2014) with microstructural observations to demonstrate its strength as a planetary chronometer (Moser et al. 2013; Darling et al. 2016). Such work has also begun to highlight the wide range of shock-induced structures observable in extra-terrestrial baddeleyite, including amorphisation and granularisation (Darling et al. 2016), suggesting a sensitive and variable crystallographic response to impact events. Further development of these observations into a robust indicator and barometer of impact conditions requires a better understanding of magmatic baddeleyite microstructure to establish an unshocked baseline, a fuller understanding of the evolution of shock microstructures within a constrained impact setting, and insights into the potential mechanisms behind the mineral’s response to shock loading and annealing. Here we document the microstructural evolution of baddeleyite within samples from the Sudbury impact structure, Ontario, coupling these observations with known phase transitions in the ZrO$_2$ system to yield a sensitive, diagnostic indicator of shock metamorphism for application to an array of planetary materials.

Sample background and methods

Any unshocked microstructural baseline will need to recognize the extensive array of terrestrial magmatic conditions that can facilitate $m$-ZrO$_2$ crystallization (Lumpkin 1999). To address this, baddeleyite grains from the doleritic 2.47 Ga Matachewan diabase dyke swarm (Heaman 1997), the 2.06 Ga Phalaborwa carbonatite complex (Heaman 2009), and the
gabbroic 1.05 Ga Anna’s Rust Sill (Reimold et al. 2000) have been examined using electron backscattered diffraction (EBSD) techniques. Of these samples, the Matachewan dyke swarm presents a unique opportunity to directly compare the response of baddeleyite to variable shock loading and annealing (Figure 3.1). Intruded within a ~100,000 km² area of metamorphosed rocks of the Archean Superior Province (Ontario), the swarm was locally shock metamorphosed ~600 million years later as a result of the 1.85 Ga Sudbury impact event (Krogh et al. 1984). Unlike other large impact structures, such as Vredefort (South Africa), the impact melt sheet at Sudbury has been preserved. This allows crystallographic shock phenomena to be mapped relative to the interface of the melt sheet with the crater floor, constraining pressure and temperature histories. For example, lower temperature phases such as quartz and feldspar have been recrystallised within ~500 m of the melt sheet (Grieve et al. 2008) as a result of extensive high-temperature contact metamorphism (< 900°C; James et al. 1992). Further north of this aureole, planar deformation features (PDFs) in quartz, indicative of shock pressures in excess of ~10 GPa (Grieve et al. 1996), can be observed up to 6 km from the melt sheet. Shattercones (> 2 GPa) are present within 10 km (Grieve et al. 2008). Lower pressure estimates for baddeleyite-bearing samples collected across a near linear transect radiating outwards from the melt sheet contact can be assessed using these shock features, constraining their microstructural variability and evolution around the impact structure.

Target baddeleyite grains were located using a combination of automated backscatter electron (BSE) and energy-dispersive X-ray spectroscopy (EDS) using the Oxford Instruments INCA and Aztec ‘Feature’ modules and Oxford X-Max 80 detectors installed on electron microscopes at the University of Portsmouth, UK and the Zircon and Accessory Phase Laboratory (ZAPLab) at the University of Western Ontario, Canada. This method is capable of locating baddeleyites down to ca. 1 micron in diameter over thin-section scale areas. Target grains were imaged using BSE and secondary electron (SE) techniques, and micro- to nano-scale structural analysis was conducted by electron backscatter diffraction (EBSD), using either a Hitachi SU6600 field emission gun SEM (FEG-SEM; ZAPLab) or Zeiss EVO MA10 LaB₆-SEM (Portsmouth). Wild spike reduction was completed on all EBSD datasets, although no other form of raw data correction was conducted.
Figure 3.1: Schematic geological map of the Sudbury impact structure highlighting sample localities of variably shocked ZrO$_2$-bearing material. Three samples of the 2.47 Ga Matachewan diabase dyke swarm (Heaman 1997) (JD12SUD14, JD12SUD03 and JD12SUD06) form a roughly linear transect radiating outwards from the north-western extent of the Sudbury impact melt sheet, while unshocked sample MDS001 provides an ideal unshocked sample for comparison. Full details on shattercone and quartz PDF distribution and importance can be found in the text.

Results

In total, thirty baddeleyite grains were examined within three shocked and three unshocked samples. An overview of microstructural variability can be observed in Figure 3.2.

Unshocked Baddeleyite

Unshocked grains display either polysynthetic {110} twinning, a single simple {100} twin, or do not contain twins. These structures appear to correlate with grain size, with the smallest grains (< 130 $\mu$m$^2$) appearing untwinned and the largest (< 600 $\mu$m$^2$) polysynthetically twinned. These observations strongly agree with previous crystallographic analyses of baddeleyite that suggest the majority of grains will display twinning (McCulough & Trueblood 1959). None of these crystals display evidence for crystal plastic deformation, with cumulative misorientations falling within the $\sim$0.5° detection limit of the EBSD technique.

Shocked Baddeleyite

Lightly Shocked Baddeleyite

Sample JD12SUD06 was collected ~8 km from the lower contact of the melt sheet, falling between the currently defined limits for shatter cone and quartz PDF formation (>2
Moderately Shocked Baddeleyite

Sampled approximately 3km from the melt sheet, seven zirconia grains (70 to 161 μm\(^2\)) have been investigated in moderately-shocked sample JD12SUD03. One of these contains an interlocking microstructure, consisting of recrystallized monoclinic subgrains within a crystal plastically deformed (~7°) baddeleyite host. A ~4 μm wide band of amorphous ZrO\(_2\) surrounds the grain. Three grains are largely amorphous at the length scales of EBSD analyses (ca. 80 × 40 nm), hosting an array of randomly oriented granular baddeleyite (0.5-3 μm long) subgrains within a poorly diffracting lattice. Three further grains display domains of preserved igneous baddeleyite twins crosscut by networks of quasi-amorphous veins. Preserved subdomains occur in two distinct orientations that roughly match those displayed by unshocked simple twin relationships (\{100\}) and display little evidence of crystal plastic deformation (< 3°).

Highly Shocked and Annealed Baddeleyite

Seven grains (52 to 333 μm\(^2\)) within the most highly shocked sample (JD12SUD14; ~550m from the melt sheet) display a complete absence of the igneous structures observed in unshocked baddeleyite. Individual grains are composed of a number of interlocking m-ZrO\(_2\) subgrains within a crystal plastically deformed baddeleyite host boasting < 15° of internal deformation. Subgrains are generally undeformed (total of ~2° internal misorientation), and misorientated 85 to 95° about the host structure. Small (<4 μm) regions of poorly diffracting quasi-amorphous material are observed within these grains. Two of the grains display substantial (0.5 to 4 μm wide) zircon rims, while a single baddeleyite is surrounded by both zircon (in contact with quartz) and magnetite (in association with hornblende amphibole). These polycrystalline overgrowths do not affect the preserved baddeleyite structure, appearing randomly orientated in relation to both the host ZrO\(_2\) and other zircon subgrains.
**Figure 3.2:** Cross-section of the target rocks underlying the Sudbury igneous complex (SIC), correlating sample locality with baddeleyite microstructures. The highly variable nature of intra-crystalline zirconia lattice order is shown by band contrast (BC), a factor describing the average intensity of the Kikuchi bands with respect to the overall electron backscatter pattern, and 0 – 120° texture component maps (TC; crystallographic misorientation relative to a reference pixel) highlight twin and subgrain relationships within each grain. Step size 50 to 250 nm step size. Impact-proximal grains (a) display complex reversion mosaics of interlocking monoclinic-ZrO$_2$. The master grain contains ~10° of crystal plastic deformation, while subgrain domains display ~4° of internal misorientation. Domains of poorly diffraacting quasi-amorphous zirconia are also visible within the lattice. Impact-moderate grains (b) display networks of amorphous material crosscutting undeformed monoclinic zirconia, culminating in the almost complete replacement of igneous baddeleyite. Impact-distal (c) grains display predominately magmatic (simple twinned) structures, though a small number host less extensive networks of amorphous material. Crystals within the completely unshocked material located ~160km from the impact melt sheet (d) display simple or no twinning. A representative TC map of Phalaborwa baddeleyite (e) highlights the typical nature of polysynthetic twinning in larger ZrO$_2$ grains.

**Discussion**

**High Pressure-Temperature Phase Response of ZrO$_2$**

The range of shock microstructures observed around the Sudbury impact structure resembles those reported in Martian shergottites, including amorphisation and incipient granularisation in NWA 5298 (Darling et al. 2016). An initial insight into this response can be gained through previous work into the ZrO$_2$ system, which transitions through a series of orthorhombic structures during shock-loading (>5 GPa (Kudoh et al. 1986)), and tetragonal (> 1300°C) and cubic (> 2500°C) structures during annealing (Subbarao et al. 1974). These transformations are facilitated by the re-coordination of the covalent Zr-O bond which
naturally favours the seven-fold symmetry of the monoclinic structure (Kisi & Howard 1998). Thus, unstable polymorphs formed during natural or artificial shock loading and heating will readily revert to the stable monoclinic structure at ambient conditions (Subbarao et al. 1974; Ohtaka et al. 1991), preventing their observation in crystallographic phase analysis. Both the displasive high-P (o-ZrO$_2$) and martensitic high-T (t-ZrO$_2$, c-ZrO$_2$) reactions are known to destroy internal microstructure during prograde heating and loading (Kudoh et al. 1986; Hannink et al. 2000), while reversion to stable m-ZrO$_2$ generates unique interlocking structures. These features are preserved even in completely reverted m-ZrO$_2$ systems (Hannink et al. 2000).

Coupling this experimental knowledge with the range of microstructures observed here in shocked baddeleyite yields an evolutionary model for the zirconia system that could be used to infer P-T conditions in a wide range of mafic planetary materials (Figure 3.3). Above ~5 GPa, subdomains of the igneous baddeleyite grain transition to the orthorhombic structure to offset the pressure differential introduced by the impact event (Kudoh et al. 1986). The percentage of the grain that transitions increases with escalating shock pressures, yielding a greater abundance of o-ZrO$_2$ in closer proximity to the impact structure. Given its inherent instability at ambient conditions, the meta-stable orthorhombic domains readily recrystallize to m-ZrO$_2$ during decompression and heating. In quickly cooled (3 to 8 km from the Sudbury melt sheet) or quenched (impact-ejected Martian crust (Darling et al. 2016; Moser et al. 2013)) samples this regrowth is limited, yielding domains of monoclinic subgrains <100 nm in size that appear amorphous at the length scales of EBSD (Darling et al. 2016). Transmission electron microscopy (TEM) analysis of similar structures in Martian shergottites suggests these domains are crystalline on the 1 to 100 nm scale (Darling et al. 2016). Post-impact heating of these domains will likely encourage further growth of these nano-crystallites, forming a randomly orientated matrix of granular baddeleyite (Darling et al. 2016). O-ZrO$_2$ domains undergoing reversion during high temperature unloading (~550 m from the melt sheet contact) undergo complete monoclinic recrystallization, forming intergrown reversion twins with the deformed baddeleyite host. Pressure and temperature heterogeneities can result in variable o-ZrO$_2$ formation and m-ZrO$_2$ recrystallisation within a single sample (Darling et al. 2016), while the high anisotropy of baddeleyite can yield structural variations between intercepting crystals (JD12SUD06, grain #2962). Despite these inter-sample deviations, whole rock P-T conditions can be inferred by examining a spatially diverse range of baddeleyite grains within a sample.
Figure 3.3: Schematic evolution of zirconia microstructure with increasing proximity to the impact melt sheet, highlighting its ability to identify and partially quantify shock metamorphic events. Primary igneous structures (i.e. simple or polysynthetic twinning) are preserved in their entirety < 5 GPa. Above these pressures, the zirconia system begins transforming to orthorhombic-ZrO$_2$ (Kudoh et al. 1986) ($\alpha$-ZrO$_2$) to offset the pressure differential introduced by the shock event. The relative percentage of the crystal that transitions is governed by the peak pressure experienced by the grains, with highly shocked material (i.e. impact proximal) producing a larger quantity of $\alpha$-ZrO$_2$ than impact distal grains. As $\alpha$-ZrO$_2$ is metastable, the zirconia system will readily revert to monoclinic structures upon decompression. Pressure release at low temperature (quenching) results in quasi-amorphous ZrO$_2$. In close proximity to the impact (~1km), extensive annealing facilitates more comprehensive monoclinic recrystallization, generating complex interlocking mosaics of m-ZrO$_2$. These domains consist of crystal plastically deformed igneous material crosscut by less deformed, recrystallized baddeleyite.

Baddeleyite as a Recorder of Planetary Bombardment

Although trace element variations in mineral chemistry can subtly alter the P-T conditions required to induce the m-ZrO$_2$ to $\alpha$-ZrO$_2$ transition (Hannink et al. 2000), the orthorhombic structure has never been reported below ~5 GPa (Kudoh et al. 1986). As suggested by the high resistance of ZrO$_2$ to $\alpha$-decay (Lumpkin 1999), metamictization (radiation damage of the crystal lattice) has never been observed in natural baddeleyite. As such the presence of quasi-amorphous or reversion twinned zirconia can be interpreted as a definitive indicator of shock. The only potential for microstructural annihilation within shocked baddeleyite comes from the reaction of zirconia with free silica during
metamorphism or hydrothermal alteration, creating a rim of polycrystalline zircon enclosing
(or completely replacing) the original magmatic crystal (Heaman & LeCheminant 1993). However, as observed in the partially over-printed baddeleyite in the variably
metamorphosed Matachewan dyke swarm (Heaman 1997), both shocked and unshocked
microstructures are retained within any preserved ZrO₂ domains despite extensive
greenschist-facies overprinting (Riller 2005). Moreover, these reactions will be largely absent
on crusts without extensive hydrospheres. Coupled with the natural toughening of zirconia
through structural phase changes (and microstructure retained through their retrogression
(Garvie et al. 1975)), unique impact-generated structures are maintained through extensive
reworking and overprinting and potentially through later impact events. This is in stark
contrast to lower temperature minerals (quartz, biotite) and meta-stable glasses
(maskelynite) which readily recrystallise or devitrify during post-shock tectonic reworking,
destroying the subtle features required to confidently assess the peak shock state of the
material (Langenhorst 1994; Stoffler et al. 1991). By circumventing many of these common
issues with mineralogical shock indicators and barometers, the ZrO₂ system appears to be an
exceptionally powerful tool with which to identify and quantify the shock state of both
terrestrial and extra-terrestrial lithologies. As a result, this widely occurring accessory phase
can become an ideal mineralogical shock indicator, barometer and geochronometer with the
ability to fill a clear gap in our knowledge of shock history in a discretized low pressure range
and within more mafic planetary crusts. Coupled with ongoing work to enhance the accuracy
and precision of in-situ baddeleyite U-Pb dating (Moser et al. 2013; Chamberlain et al. 2010;
Darling et al. 2016; Ibanez-Mejia et al. 2014), this rich microstructural record will deliver a
more accurate history of meteorite bombardment and impact events throughout the inner
Solar System.
3.3 SUPPLEMENTARY MATERIALS

<table>
<thead>
<tr>
<th>Instrumentation</th>
<th>Western University</th>
<th>Portsmouth University</th>
</tr>
</thead>
<tbody>
<tr>
<td>Host Institute</td>
<td>Hitachi SU6600 FEG-SEM (Schottky electron source)</td>
<td>Zeiss EVO MA10 (LaB$_6$ electron source)</td>
</tr>
<tr>
<td>EBSD System</td>
<td>HKL Channel 5</td>
<td>Oxford Instruments AZTEC</td>
</tr>
<tr>
<td>EBSD Software</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**SEM settings**
- Carbon coat (<5nm): Yes
- Acc. Voltage (kV): 20
- Working distance (mm): 19
- Probe current (nA): 8
- Tilt (º): 70

**EBSD data collection and processing**
- EBSP collection time per frame (ms): 80, < 120
- Background (frames): 64
- EBSP noise reduction (frames): 7
- EBSP noise reduction (binning): 4x4
- EBSP noise reduction (gain): High
- Hough resolution: 60
- Band detection min/max: 4 to 7, 10 to 12
- Step size (nm): 50 to 150, 100 to 200
- Noise reduction: wildspike only

*Supplementary Table 3.1: Overview of electron backscatter diffraction (EBSD) run conditions.*
Supplementary Figure 3.1: Representative pole figure diagram for a simple twinned, unshocked baddeleyite grain. The twin domains share a \{100\} pole, but display \(~90^\circ\) rotation about \{110\}. Grain mapped at 75nm, yielding 84,105 individual data points.

Supplementary Figure 3.2: Representative pole figure diagrams for minimally shocked baddeleyite from sample JD12SUD06 (~8km from melt sheet). Two intercepting grains (c-axis offset of \(~70^\circ\)) display variable microstructures; one grain appearing sheared, but preserving an igneous simple twin plane \((90^\circ / \{110\})\), while another hosts bands of degraded crystallinity (visible in band contrast). This variability on the \(~\mu m\) scale highlights the importance of anisotropy in baddeleyite, where grain orientation relative to shockwave direction appears to control microstructural evolution.

Supplementary Figure 3.3: Band contrast (BC), texture component (TC) and all euler angle EBSD maps for grain 5099 (sample JD12SUD14), including baddeleyite pole figures colored per euler angle. The master crystal (or host) represents crystal plastically deformed baddeleyite that did not transition to the high-pressure orthorhombic structure, while the more pristine subgrains likely retrogressed to monoclinic-ZrO_2 sometime after the impact event. The simple and polysynthetic twinning observed in unshocked grains (i.e. Supplementary Figure 1) is completely lost.
Supplementary Figure 3.4: Additional EBSD data (band contrast (BC), texture component (TC) and all euler maps) for baddeleyite grains from the Matachewan dyke samples in the North Range of Sudbury. For reference, an all euler map of the polysynthetic twinning observed in the Phalaborwa baddeleyite standard is included.
DEVELOPING BADDELEYITE AS A PLANETARY CHRONOMETER

4.1 INTRODUCTION

As a late forming accessory phase, one of the largest challenges facing the use of baddeleyite as a planetary chronometer revolves around its inherently tiny grain size. Barring a small number of samples containing larger (mm-scale) grains, such as the Phalaborwa carbonatite complex (Heaman 2009) or the Mbuji Mayi kimberlite (Kerschhofer et al. 2000), the majority of grains are < 20μm, making their physical isolation from a bulk rock aggregate incredibly difficult (Soderlund & Johansson 2002). Small-volume in-situ analyses have begun to circumvent this issue (Ibanez-Mejia et al. 2014), though many grains are still fundamentally too small for modern isotopic techniques. Atom probe tomography (APT) offers an opportunity to target sub-micron domains for isotopic (i.e. Pb-Pb, U-Pb) age analysis (Valley et al. 2014), though the potential of this approach to baddeleyite is currently unexplored.

In order to assess the potential of APT as a planetary dating technique for baddeleyite, highly-shocked grains from the well-studied Sudbury impact structure (Ontario, Canada) have been examined. The results of this paper have potentially huge implications for both the planetary and geochronological communities, providing an exciting insight into the response of lead and uranium during impact events while also highlighting the true potential of APT as a geochronological tool for the first time. The details and results are presented in the following paper, which is included in this chapter:


All authors contributed to this work. D.E.M. and J. R. D. designed the initial project. All authors conducted portions of either, or both, the fundamental SEM and APT data collection and processing. L.F.W., D.A.R., and D.E.M. reduced and interpreted the APT data. L.F.W wrote the paper. All authors discussed the results and commented on the manuscript at all stages.
4.2 ATOMIC-SCALE AGE RESOLUTION OF PLANETARY EVENTS

White, L. F.1, Darling, J. R.1, Moser, D.2, Reinhard, D. A.2, Prosa, T. J.3, Bullen, D.1, Olson, D.3, Larson, D. J.3, Lawrence, D.3 & Martin, I.3

1 School of Earth and Environmental Sciences, University of Portsmouth, Portsmouth, UK
2 Department of Earth Sciences, University of Western Ontario, London, Canada.
3 Cameca, Madison, WI 53711, USA

Resolving the timing of crustal processes and meteorite impact events is central to understanding the formation, evolution and habitability of planetary bodies. However, identifying multi-stage events from complex planetary materials is highly challenging at the length scales of current isotopic techniques. Here we show that accurate U-Pb isotopic analysis of nanoscale domains of baddeleyite can be achieved by atom probe tomography (APT). Within individual crystals of highly-shocked baddeleyite from the Sudbury impact structure three discrete nano-structural domains have been isolated, yielding average $^{206}\text{Pb}/^{238}\text{U}$ ages of $2436 \pm 94$ Ma (protolith crystallization) from Homogenous-Fe domains, $1852 \pm 45$ Ma (impact) from Clustered-Fe domains and $1412 \pm 56$ Ma (tectonic metamorphism) from planar and subgrain structures. Baddeleyite is a common phase in terrestrial, Martian, Lunar and asteroidal materials, meaning this atomic-scale approach holds great potential in establishing a more accurate chronology of the formation and evolution of planetary crusts.

INTRODUCTION

Isotopic heterogeneities within meteorite samples caused by shock metamorphism (Nyquist et al., 2001; Moser et al., 2013; Darling et al., 2016) complicate efforts to characterize and date this precious material. This has resulted in conundrums regarding the timing of major planetary events, including the timing of lunar magma ocean crystallization (Borg et al., 2011), Martian volcanism (Moser et al., 2013; Darling et al., 2016) and impact bombardment of the inner Solar System (Abramov & Mojzsis, 2009). Recently, the coupling of isotopic geochronology with microstructural analysis of robust accessory phases has greatly enhanced our ability to date highly shocked samples by crystallographically contextualizing μm-scale geochemical analyses. In zircon (ZrSiO$_4$), crystallographically deformed grains have been targeted in efforts to ascertain impact ages (Cavosie et al., 2015) while more pristine igneous grains are selected to establish timing of primary crystallization (Darling et al., 2016). However, the occurrence of zircon within the Solar System is restricted to rare high silica (granitic) magmas and highly metamorphosed meteorites (Haba et al., 2014). Baddeleyite (monoclinic-ZrO$_2$) is much more widely occurring, reported from a wide range of terrestrial
mafic and ultra-mafic rock types (Heaman & LeCheminant, 1993) and within Lunar (El Goresy et al., 1971; Arai et al., 2010), Martian (Moser et al., 2013), chondritic (Krot et al., 1993) and asteroidal (HED; Hsu et al., 2013) meteorites. Grains are often small (<20 μm), but develop a range of characteristic microstructures under shock-loading conditions which allow for contextualized dating of target grains (Darling et al., 2016). Although challenging to separate from whole rock aggregates (Söderlund & Johansson, 2002), recent advances of in-situ U-Pb isotope analysis have enabled the dating of this phase using volumes as small as 5x5x1μm (secondary ion mass spectrometry; Chamberlain et al., 2010). However, given that shock microstructures in baddeleyite vary at the μm to sub-μm scale such techniques still homogenize microstructural domains, yielding an array of partially reset ages within highly shocked populations (Darling et al., 2016). Here we use atom probe tomography (APT) to accurately resolve chronological end-members (i.e. protolith crystallization and impact metamorphism) within highly shocked baddeleyite of the Matachewan dyke swarm (Ontario, Canada). This approach has the unique potential to produce coupled isotopic and structural datasets from nanoscale domains (Valley et al. 2014) facilitating direct U-Pb dating of nm-scale features.

RESULTS

Although atom-probe analysis of Pb isotope ratios (207Pb/206Pb) has previously been conducted on zircon (Valley et al., 2014), this study represents the first effort to analyze baddeleyite on the atomic scale. In this regard, reference ZrO₂ grains of the Phalaborwa carbonatite complex, South Africa (Heaman, 2009) have been analyzed under the same conditions as the unknown grain population. Spectral analysis identified the most abundant U-bearing compound as the species ²³⁸U₁⁶O₂²⁺ at 135 Da (mass-to-charge ratio in daltons), though smaller peaks were observed at 270 Da (²³⁸U¹⁴O₂²⁺), 84.66 Da (²³⁸U¹⁶O³⁺), and 127 Da (²³⁸U¹⁴O²⁺). Pb isotopes ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb in the 2+ charge state was ranged and quantified at 103 Da, 103.5 Da, and 104 Da respectively, though counts of ²⁰⁷Pb and ²⁰⁸Pb are below detection limits. This comprehensive analysis of U and Pb isotope systematics is facilitated by the absence of Si within the baddeleyite lattice, limiting a large portion of the isobaric interferences that prevent accurate U measurements in zircon (Valley et al., 2015). Despite being a mineralogical U-Pb reference material (Heaman, 2009), Phalaborwa baddeleyite displays μm-scale uranium variability, including low- and high-U domains and localized zonation (Ibanez-Mejia et al., 2014). Sampling a low-U domain yielded a below-average concentration of U and Pb for this specimen, minimizing counts and resulting in isotopic ratios with large analytical uncertainties. Despite this, the standard microtip yielded a ²⁰⁶Pb/²³⁸U ratio of 0.48 ± 0.09, within uncertainty of small-volume laser ablation analysis (Ibanez-Mejia et al., 2014). All elements, including known minor and trace elements that are incompatible in the ZrO₂ lattice (such as Ti and Fe) are homogeneously distributed
throughout both annealed (400°C for 1 hour) and unannealed microtips (Supplementary Figure 4.1). These observations provide a first order insight into unshocked baddeleyite nano-structure, where heating alone does not encourage a redistribution of incompatible cations.

The studied thin section (JD12SUD14) is from a highly-shocked diabase dyke sampled ~500m beneath the lower northern contact of the Sudbury impact melt sheet. The sample is uniquely well-characterized, with high precision thermal ionization mass spectrometry (TIMS) constraints on the timings of crystallization (2473 ± 16 Ma; Heaman, 1997) and impact shock metamorphism (1850 ± 1 Ma; Krogh et al., 1984), as well as petrologically constrained shock (>10 GPa; Grieve et al., 2008) and post-shock (>850 °C; James et al., 1992) P-T conditions. Baddeleyite is abundant in the sample, with over 100 grains ranging from 15 to 330 µm² found in the exposed surface area (Supplementary Figure. 4.2). Field emission scanning electron microscope (FE-SEM) and electron backscatter diffraction (EBSD) analyses of these grains reveal a range of microstructures, including complex mosaics of interlocking twin domains, partial amorphisation and partial granularization (Figure 4.1). These structures differ greatly from those observed in unshocked grains where simple and polysynthetic twinning is dominant. Two grains (#44755 and #46059) were isolated for APT analyses. The two grains yielded a total of eleven statistically significant atom probe datasets comprising between 2.6 and 35 million total background-corrected ions. The specimens are chemically similar, comprising ~99% Zr and O (bulk compound ZrO₂) with a number of impurities in the form of Hf, Nb, Fe and Y. Other elements, including Ti, Si, Ta, P, Yb, U, Ca, Sc, Mn, Al, Mg and Pb are present in very minor quantities. ²⁰⁶Pb²⁺ produces sharp, well-defined peaks totaling between 269 and 4870 counts in all microtip specimens, and the decomposition of UO and UO₂ peaks yielded between 737 and 15464 total counts of ²³⁸U.

**Figure 4.1: Microstructural data for Sudbury baddeleyite grain showing complex reversion twinning and intensive crystal plastic deformation.** (a) Backscatter electron (BSE) image of grain #8146, displaying a homogenous appearance and absence of planar or curvi-planar features. Electron backscatter diffraction (EBSD) maps (b & c) acquired at 200 nm step size: (b) band contrast (diffraction signal strength) map showing domains and planar features with weak diffraction owing to shock; (c) relative misorientation map of m-ZrO₂ component, highlighting ~90° misorientation between the intensively crystal plastically deformed (<8°) master crystal and relatively undeformed subgrains.
$^{206}\text{Pb}/^{238}\text{U}$ ratios from the bulk tips generate geologically reasonable ages between 2435 ($\pm$ 1075) Ma and 1485 ($\pm$ 313) Ma (Supplementary Table 4.1) albeit with large internal counting statistics errors. Despite this, the bulk ages highlight a partially-resort population yielding ages between crystallization (2.45 Ga; Heaman, 1997) and impact (1.85 Ga; Krogh et al., 1984), although the youngest age (1485 $\pm$ 313 Ma) fails to reflect either of these chronological end-members. Closer inspection of the eleven APT 3D reconstructions reveals three discrete nano-structural domain types, highlighted by variable distribution of incompatible elements (Si, Mg, Al, Yb), most clearly iron (Figure 2): (1) *homogenous-Fe domains* in which all elements are homogeneously distributed throughout the regions, appearing nano-structurally identical to annealed and unannealed microtips of the Phalaborwa baddeleyite standard; (2) *clustered-Fe domains* in which incompatible cations form nano-clusters $\sim$10nm in size that can be clearly isolated by a 2% Fe isosurface and are evenly distributed throughout the domain; (3) *planar and curvi-planar domains* displaying $\sim$10nm nano-clusters enriched in all incompatible elements concentrated along their length. The latter features are either curvi-planar (interpreted as subgrain boundaries) or planar (likely associated with dislocation migration) and are often bound by incompatible-depleted regions within adjacent Clustered-Fe domains. Five datasets are comprised of a single domain type (either Homogenous-Fe or Clustered-Fe), while the remaining datasets contain a mixture of the three defined subdomains (Supplementary Figure 4.3). In these complex tips, nanostructural subdomains were first identified by Fe distribution before segregation using cuboid regions of interest (ROI’s), allowing separate mass-to-charge spectra to be generated for each region and yielding structurally isolated U-Pb ratios and ages.

This approach uniquely facilitates the generation of isotopic ratios from nanostructurally characterized sub-grain domains and hence allows for evaluation of the variability in $^{206}\text{Pb}/^{238}\text{U}$ ages within and between regions with differing nanostructural histories (Supplementary Table 4.2). Homogenous-Fe regions (two full datasets and two subdomains) yield an average $^{206}\text{Pb}/^{238}\text{U}$ age of 2436 $\pm$ 94 Ma (3.9%; 2 SE), within uncertainty of the known age of the diabase protolith. Isolation of the entire Clustered-Fe domains (three full datasets and five subdomains) yield an average $^{206}\text{Pb}/^{238}\text{U}$ age of 1852 $\pm$ 45 Ma (2.4%), which is within uncertainty of the age of the Sudbury impact event. Individual clusters yield low counts of U and Pb which fall below the detection limits of APT. Isolation of four planar and curvi-planar features produces an age of 1412 $\pm$ 56 Ma (4%). This younger age overlaps with the timing of the last significant tectonic event to effect the region, the Chieflakian Orogeny, that resulted in widespread greenschist facies (ca. 350-500 ºC, ca. 2-8 kbar) metamorphism within the study area (Corfu & Easton, 2001). Taking weighted averages of these same datasets yields indistinguishable results, but with very low mean squared weighted deviation (MSWD) values (0.028 – 0.038) that suggest the internal counting statistics errors overestimate the true reproducibility of the measurements.
**Figure 4.2: APT data for discrete nanostructural domains preserved within highly shocked baddeleyite (sample JD12SUD14).** 3D APT reconstruction of three microtip specimens displaying distribution of individual Fe atoms. Three discrete nanostructural domain types are observed, one displaying homogenous distribution of Fe (h-Fe) and the other displaying nano-scale (~10nm) clusters enriched in Fe (c-Fe). These domains are segregated by enriched planar and curvi-planar subgrain boundaries (P). (a) Microtip R60_146475 consists of a single Clustered-Fe domain. The tip yields a bulk $^{206}\text{Pb} / ^{238}\text{U}$ ratio of $0.331 \pm 0.115$ in agreement with age data for the Sudbury impact event. (b) Microtip R60_146506 yields a bulk $^{206}\text{Pb} / ^{238}\text{U}$ ratio of $0.3493 \pm 0.0741$, though this purely represents a homogenization of multiple subdomains. Within this tip, the homogenous-Fe domain yields a $^{206}\text{Pb} / ^{238}\text{U}$ ratio of $0.4776 \pm 0.3015$, the clustered-Fe domain yields a ratio of $0.3525 \pm 0.1154$, and the enriched subgrain boundary yields a significantly lower ratio of $0.2555 \pm 0.0712$. (c) Microtip R60_144153 consists of a single Homogenous-Fe domain, representing the largest single tip within the dataset. The tip yields a $^{206}\text{Pb} / ^{238}\text{U}$ ratio of $0.4297 \pm 0.1697$. 
Figure 4.3: $^{206}\text{Pb}/^{238}\text{U}$ APT age data for all eleven microtip specimens subdivided by nanostructural domain, yielding accurate and precise ages for both crystallization and impact events. These complex tips yield a series of partially to fully reset bulk U-Pb ratios, although separate subdomains are shown here to record both crystallization and impact ages. Amongst the eleven largest microtips, eight domains display clustering of Fe (blue) and yield an average $^{206}\text{Pb} / ^{238}\text{U}$ age of $1852 \pm 45$ Ma (2SE; standard error of the mean), within error of impact age (Krogh et al., 1984). Four display homogenous distribution (green) of Fe and yield an average age of $2436 \pm 94$ Ma, overlapping with the known age for protolith crystallization (Heaman, 1997), while four planar and curvi-planar subgrain boundaries (red) record an average age of $1412 \pm 56$ Ma, in agreement with the youngest orogenic activity in the area (Corfu & Easton, 2001). Darker vertical bars represent bulk microtip analyses, while lighter data represent sub-divided structural domains within a mixed microtip specimen 1σ counting statistic uncertainties).

DISCUSSION

Partially impact age-reset grain populations have typically been inferred to represent variable grain to micron-scale diffusion of radiogenic isotopes during thermal metamorphism of shock-deformed domains (Gaffney et al., 2011), including for baddeleyite. However, our findings show that the development of localized nm-scale structures controls the mobilization potential of Pb in baddeleyite, and results in subdomains that preserve either protolith crystallization or impact-reset $^{206}\text{Pb}/^{238}\text{U}$ ages. These nanostructures probably relate to partial formation of the high-pressure orthorhombic-ZrO$_2$ phase during shock loading (Kudoh et al., 1986). This is known to be a progressive transition above ~5 GPa.
(Kudoh et al., 1986), due to the anisotropic elastic properties of baddeleyite (Ingel & Lewis, 1988). Transformed domains would readily revert to the stable monoclinic structure during melt-sheet induced annealing (> 850°C; James et al., 1992) immediately following impact. It is likely that nano-scale defects induced by these transformations facilitate the migration of Fe into clusters during heating, whilst also facilitating the complete mobilization of Pb from the domain. Preserved igneous $m$-ZrO$_2$ domains would not contain these pathways, preventing the migration of Pb and Fe along dislocation pathways within the lattice and preserving both the homogenous distribution of atoms and the primary U-Pb age. The planar and curvi-planar features observed appear more susceptible to Pb-diffusion during low temperature and pressure (tectonic) metamorphism, suggesting that these operate independently of the host baddeleyite grain. This is in agreement with previous observations that suggest nm-scale planar and linear features undergo continued pipe diffusion of incompatible elements and isotopes below the closure temperature of the crystal (Piazolo et al., 2016). An important implication of the observed nanostructural and isotopic complexity is that larger analytical volumes (Chamberlain et al., 2010; Ibanez-Mejia et al., 2014) will homogenize these domains and yield a mixed age from multiple isotopic reservoirs, which may not have clear geological significance. Despite exposure to high-pressure shock metamorphism (>10 GPa; Grieve et al., 2008) and high-temperature post-shock annealing (> 850°C; James et al., 1992), nm-scale domains in our sample preserve ages for both protolith crystallization (2436 ± 45 Ma) and impact metamorphism (1852 ± 145 Ma) suggesting that such data can be extracted from even the most highly shocked and annealed grain populations. The ability to generate targeted, high precision U-Pb ages with APT yields great promise when examining the tiny (< 3 μm) baddeleyite grains which are reported within many planetary materials (i.e. Lumpkin et al., 1999). Going further, the ability to identify and sub-sample discreet nanostructural subdomains (e.g. Homogenous-Fe versus Clustered-Fe) for isotopic analysis opens new avenues for dating highly deformed materials, including meteoritic samples. This allows for the unambiguous resolution of crystallization and impact ages in highly shocked planetary samples, presenting an exceptional opportunity to constrain timings for major Solar System events.
4.3 SUPPLEMENTARY MATERIALS

Supplementary Methodology

Baddeleyite grains were located in-situ within a single thin section of JD12SUD14 using an automated feature scan of the section coupling a Hitachi SU6600 field emission gun – SEM (FEG-SEM) with an Oxford X-Max Energy-Dispersive Spectroscopy (EDS) detector housed within the Zircon and Accessory Phase Laboratory (ZAPlab) at the University of Western Ontario, Canada. Electron backscatter diffraction (EBSD) analyses were conducted using an Oxford HKL Nordlys detector with step sizes of 150-250 nm (grain size dependent) closely following previously reported instrument conditions (Moser et al., 2011). The only post-analysis noise reduction processing performed was to replace ‘wild-spikes’ (interpreted as isolated, erroneously-indexed pixels) with a zero solution.

Whilst EBSD analyses were ongoing two additional grains were isolated for atom probe tomography. Microtip specimens were prepared using either an FEI Helios or Nova focused ion beam (FIB)-SEM using standard lift-out and mount techniques to produce the desired specimen shape (Miller & Russell, 2007; Miller et al., 2007; Thompson et al., 2007). A series of annular mills with a decreasing inner radius were used to produce needle-shaped specimens with a radius of curvature of less than 100 nm. A total of fourteen microtip specimens were created from four ~2 x 10 μm pullouts derived from grains #44755 and #46059. In this work, the prepared specimens were analyzed with a local electrode atom probe (LEAP) 5000 XR atom probe housed at the CAMECA Atom Probe Technology Center, Madison, Wisconsin. During acquisition the specimen is placed under a high electric field and evaporation and ionization of atoms from the surface occur commensurate with a laser pulse (125kHz, 100pJ). The mass-to-charge ratio of the ions is determined through time-of-flight mass spectroscopy. Ion flight paths (382mm) are terminated on a position-sensitive detector and the spatial information is reconstructed by projecting the ions back to the spherical end-form of the specimen and considering the sequential order of evaporation. Full details of LEAP data acquisition are provided elsewhere (Larson et al., 2012; Kelly & Larson, 2012; Valley et al., 2015).

Of the fourteen tips, three failed early (<100nm run length) yielding statistically irrelevant datasets. The remaining eleven tips yielded between $2.3 \times 10^6$ and $3.5 \times 10^7$ background corrected, spectrally ranged ions over the length of the analysis. Tips ran smoothly, starting evaporation between 3 and 5 kV and finishing between 8 and 12 kV. The exact beginning and end points depend primarily on the specimen size and shape after FIB milling, and whether the experiment was turned off or was stopped by fracturing of the specimen. Background counts are similar between tips, representing between 10 and 22% of
the total (uncorrected) atomic counts. Thermal tails are present, but are generally only visible ~1-3 orders of magnitude down from peak height and so are only visible on the most prominent peaks which have a large signal.

Nanostructural domains were defined visually based on the distribution of Fe within the reconstructed 3D volume. Subdivision of domains yielded a total of 7.6×10⁷ corrected, ranged ions within eight Clustered-Fe domains, a total of 5.2×10⁷ ions within four Homogenous-Fe domains, and 2.5×10⁷ ions within four planar and curvi-planar features. 

²⁰⁶Pb⁺⁺ was measured at 103 Da. U-bearing compound peaks as 135 Da (²³⁸U₁₆O₂⁺), 270 Da (²³⁸U₁₆O₂⁺), 84.66 Da (²³⁸U₁₆O⁺³), and 127 Da (²³⁸U₁₆O⁺²) were decomposed to yield total ²³⁸U counts for all datasets. For each individual peak, corrected ionic counts were calculated through the subtraction of background counts from the total (raw) ionic count. Peak location varied very subtly (< 0.1 Da) between spectra, and such the exact mass/charge location of ranged peaks varies accordingly. In all scenarios, U and Pb peaks were ranged by eye from baseline to baseline to ensure a reproducible count between microtip spectra. Propagation of absolute raw and background counting statistics errors (√counts) allows for estimated uncertainty on the background-corrected peak. Average ages for all subdivided nanostructural domains were calculated by taking the mean ²⁰⁶Pb/²³⁸U age of each tip and/or characterized domain. Presented error bars for average ages (Figure 3) represent 2 standard deviation of the mean (2SE) and include decay constant uncertainties. Mean standard working deviation (MSWD) values were calculated by taking a weighted average of the age population using isoplot (Ludwig, 2001).
Supplementary Figure 4.1: Three-dimensional reconstruction of a single microtip specimen of the Phalaborwa baddeleyite standard. APT reconstruction of a single tip, displaying homogenous distribution of Fe and Zr atoms throughout the specimen. Models display no vertical exaggeration.
**Supplementary Figure 4.2: Back-scatter electron images of four baddeleyite grains from highly shocked Matachewan sample JD12SUD14.** Low (350x) and high (2200 – 5000x) magnification BSE images of baddeleyite grains #46509, #44755, #12122 and #62039. For this study, eleven microtip specimen have been produced from grains #46059 and #44755 for analysis by atom probe tomography.
Supplementary Figure 4.3: Three-dimensional reconstructions of all eleven atom probe microtip specimen incorporated into this study. All images highlight Fe distribution within the dataset and are scaled to match one another. Models display no vertical exaggeration. Each specimen is labeled with its associated microtip number and shorthand notation as to its constituent nanostructural domains. (c-Fe = clustered-Fe; h-Fe = homogenous-Fe; P = planar). In total, the eleven microtip specimen yield eight homogenous-Fe domains, four clustered-Fe domains, and four planar or curviplanar features.
Supplementary Figure 4.4: Labelled mass-to-charge spectra for bulk microtip #146506, with smaller scale images of spectra generated from Homogenous-Fe, Clustered-Fe and planar domains. Major families of species are colored and labelled for reference, while the predominate peaks for $^{206}$Pb (103 Da) and $^{238}$U (135 Da) are highlighted for reference. All spectra are visualized using 0.2nm binning intervals, while all background and signal are displayed up to 200 Da.
Supplementary Table 4.1: Bulk $^{206}\text{Pb}$ and $^{238}\text{U}$ data from eleven microtip specimens extracted from two baddeleyite grains (#44755 and #46059) of the Matachewan dyke swarm, Ontario, Canada. All counts represent background-corrected, ranged ionic counts of $^{206}\text{Pb}$ and $^{238}\text{U}$ within the bulk microtip samples. All reported errors (2σ) have been propagated through from raw and background counting statistics as outlined in Supplementary Methods.

<table>
<thead>
<tr>
<th>Microtip</th>
<th>$^{206}\text{Pb}$</th>
<th>$^{238}\text{U}$</th>
<th>$^{206}\text{Pb}/^{238}\text{U}$</th>
<th>2σ</th>
<th>$^{206}\text{Pb}/^{238}\text{U}$ Age (Ma)</th>
<th>2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>144153</td>
<td>1776</td>
<td>3870</td>
<td>0.4589</td>
<td>0.2026</td>
<td>2435</td>
<td>1075</td>
</tr>
<tr>
<td>147132</td>
<td>2810</td>
<td>6489</td>
<td>0.4324</td>
<td>0.1008</td>
<td>2316</td>
<td>540</td>
</tr>
<tr>
<td>145533</td>
<td>665</td>
<td>1547</td>
<td>0.4297</td>
<td>0.1897</td>
<td>2304</td>
<td>910</td>
</tr>
<tr>
<td>145519</td>
<td>269</td>
<td>737</td>
<td>0.3647</td>
<td>0.2498</td>
<td>2004</td>
<td>1373</td>
</tr>
<tr>
<td>147070</td>
<td>2484</td>
<td>7047</td>
<td>0.3526</td>
<td>0.0837</td>
<td>1947</td>
<td>462</td>
</tr>
<tr>
<td>148506</td>
<td>1483</td>
<td>4246</td>
<td>0.3493</td>
<td>0.0741</td>
<td>1931</td>
<td>409</td>
</tr>
<tr>
<td>145547</td>
<td>3221</td>
<td>9544</td>
<td>0.3375</td>
<td>0.0425</td>
<td>1874</td>
<td>236</td>
</tr>
<tr>
<td>145475</td>
<td>3076</td>
<td>9296</td>
<td>0.3309</td>
<td>0.0405</td>
<td>1843</td>
<td>225</td>
</tr>
<tr>
<td>144108</td>
<td>498</td>
<td>1554</td>
<td>0.3204</td>
<td>0.0856</td>
<td>1792</td>
<td>478</td>
</tr>
<tr>
<td>146995</td>
<td>4870</td>
<td>15464</td>
<td>0.3149</td>
<td>0.0514</td>
<td>1765</td>
<td>288</td>
</tr>
<tr>
<td>147129</td>
<td>950</td>
<td>3666</td>
<td>0.2591</td>
<td>0.0545</td>
<td>1485</td>
<td>313</td>
</tr>
</tbody>
</table>
Supplementary Table 4.2: Nanostructurally subdivided $^{206}$Pb and $^{238}$U data from all eleven microtip specimens. Specimen numbers are followed by shorthand notation as to whether they represent a whole tip (WT) or subdomain (SD) dataset. All reported errors (2σ) have been propagated through from raw and background counting statistics as outlined in Supplementary Methods.

<table>
<thead>
<tr>
<th>Clustered-Fe</th>
<th>$^{206}$Pb</th>
<th>$^{238}$U</th>
<th>$^{206}$Pb/$^{238}$U</th>
<th>2σ</th>
<th>$^{206}$Pb/$^{238}$U Age (Ma)</th>
<th>2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>146506 (SD)</td>
<td>491</td>
<td>1394</td>
<td>0.3525</td>
<td>0.1154</td>
<td>1947</td>
<td>637</td>
</tr>
<tr>
<td>146475 (WT)</td>
<td>3076</td>
<td>9296</td>
<td>0.3309</td>
<td>0.0405</td>
<td>1843</td>
<td>225</td>
</tr>
<tr>
<td>145547 (WT)</td>
<td>3221</td>
<td>9544</td>
<td>0.3375</td>
<td>0.0425</td>
<td>1874</td>
<td>236</td>
</tr>
<tr>
<td>146985 (SD)</td>
<td>1221</td>
<td>3532</td>
<td>0.3456</td>
<td>0.1047</td>
<td>1914</td>
<td>580</td>
</tr>
<tr>
<td>144102 (WT)</td>
<td>498</td>
<td>1554</td>
<td>0.3204</td>
<td>0.0856</td>
<td>1792</td>
<td>478</td>
</tr>
<tr>
<td>145519 (SD)</td>
<td>151</td>
<td>485</td>
<td>0.3112</td>
<td>0.2413</td>
<td>1747</td>
<td>1354</td>
</tr>
<tr>
<td>147129 (SD)</td>
<td>457</td>
<td>1361</td>
<td>0.3355</td>
<td>0.1064</td>
<td>1865</td>
<td>591</td>
</tr>
<tr>
<td>147070 (SD)</td>
<td>2113</td>
<td>6427</td>
<td>0.3287</td>
<td>0.0789</td>
<td>1832</td>
<td>440</td>
</tr>
<tr>
<td>Homogenous-Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>146506 (SD)</td>
<td>365</td>
<td>764</td>
<td>0.4776</td>
<td>0.3015</td>
<td>2517</td>
<td>1589</td>
</tr>
<tr>
<td>145533 (WT)</td>
<td>665</td>
<td>1547</td>
<td>0.4297</td>
<td>0.1697</td>
<td>2304</td>
<td>910</td>
</tr>
<tr>
<td>147132 (SD)</td>
<td>464</td>
<td>985</td>
<td>0.4712</td>
<td>0.2444</td>
<td>2489</td>
<td>1291</td>
</tr>
<tr>
<td>144153 (WT)</td>
<td>1776</td>
<td>3870</td>
<td>0.4589</td>
<td>0.2026</td>
<td>2435</td>
<td>1075</td>
</tr>
<tr>
<td>Planar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>146506 (SD)</td>
<td>452</td>
<td>1768</td>
<td>0.2555</td>
<td>0.0712</td>
<td>1467</td>
<td>409</td>
</tr>
<tr>
<td>147132 (SD)</td>
<td>212</td>
<td>844</td>
<td>0.2514</td>
<td>0.1194</td>
<td>1445</td>
<td>687</td>
</tr>
<tr>
<td>146985 (SD)</td>
<td>2090</td>
<td>8628</td>
<td>0.2422</td>
<td>0.0579</td>
<td>1398</td>
<td>334</td>
</tr>
<tr>
<td>147070 (SD)</td>
<td>159</td>
<td>688</td>
<td>0.2309</td>
<td>0.2454</td>
<td>1339</td>
<td>1424</td>
</tr>
</tbody>
</table>
Supplementary Table 4.3: Details of analytical parameters and full spectral counts for each microtip specimen.
### Supplementary Table 4.4: Background corrected ionic counts for baddeleyite microtip specimens used in this study.

<table>
<thead>
<tr>
<th>Ion Type</th>
<th>R60_146506</th>
<th></th>
<th></th>
<th>R60_145533</th>
<th></th>
<th></th>
<th>R60_146475</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ion Count</td>
<td>2σ</td>
<td>Comp. %</td>
<td>Ion Count</td>
<td>2σ</td>
<td>Comp. %</td>
<td>Ion Count</td>
<td>2σ</td>
<td>Comp. %</td>
</tr>
<tr>
<td>O</td>
<td>751674</td>
<td>1788</td>
<td>6.6257</td>
<td>440726</td>
<td>1353</td>
<td>4.7785</td>
<td>944914</td>
<td>2013</td>
<td>6.7602</td>
</tr>
<tr>
<td>Zr</td>
<td>126991</td>
<td>988</td>
<td>1.1194</td>
<td>77215</td>
<td>743</td>
<td>0.8372</td>
<td>141520</td>
<td>1113</td>
<td>1.0125</td>
</tr>
<tr>
<td>Ti</td>
<td>3452</td>
<td>215</td>
<td>0.0304</td>
<td>2154</td>
<td>146</td>
<td>0.0234</td>
<td>7031</td>
<td>277</td>
<td>0.0503</td>
</tr>
<tr>
<td>Si</td>
<td>7761</td>
<td>221</td>
<td>0.0684</td>
<td>314</td>
<td>89</td>
<td>0.0034</td>
<td>5655</td>
<td>221</td>
<td>0.0405</td>
</tr>
<tr>
<td>O2</td>
<td>3676170</td>
<td>3928</td>
<td>32.4038</td>
<td>2859454</td>
<td>3430</td>
<td>31.0029</td>
<td>4750408</td>
<td>4455</td>
<td>33.9857</td>
</tr>
<tr>
<td>ZrO</td>
<td>6078671</td>
<td>5833</td>
<td>53.5808</td>
<td>533959</td>
<td>5154</td>
<td>57.8322</td>
<td>7075819</td>
<td>6246</td>
<td>50.6223</td>
</tr>
<tr>
<td>ZrO2</td>
<td>412253</td>
<td>1774</td>
<td>3.6338</td>
<td>347547</td>
<td>1485</td>
<td>3.7682</td>
<td>569652</td>
<td>2122</td>
<td>4.0754</td>
</tr>
<tr>
<td>ZrO2H</td>
<td>29410</td>
<td>735</td>
<td>0.2592</td>
<td>15601</td>
<td>534</td>
<td>0.1691</td>
<td>44256</td>
<td>923</td>
<td>0.3166</td>
</tr>
<tr>
<td>HfO</td>
<td>57008</td>
<td>1036</td>
<td>0.5025</td>
<td>40666</td>
<td>795</td>
<td>0.4409</td>
<td>74940</td>
<td>1267</td>
<td>0.5361</td>
</tr>
<tr>
<td>HfO2</td>
<td>7391</td>
<td>665</td>
<td>0.0651</td>
<td>9971</td>
<td>459</td>
<td>0.1081</td>
<td>15548</td>
<td>764</td>
<td>0.1112</td>
</tr>
<tr>
<td>ZrO3</td>
<td>14512</td>
<td>546</td>
<td>0.1279</td>
<td>12622</td>
<td>420</td>
<td>0.1368</td>
<td>18740</td>
<td>672</td>
<td>0.1341</td>
</tr>
<tr>
<td>UO2</td>
<td>3129</td>
<td>244</td>
<td>0.0276</td>
<td>1401</td>
<td>164</td>
<td>0.0152</td>
<td>7127</td>
<td>314</td>
<td>0.0510</td>
</tr>
<tr>
<td>Mg</td>
<td>387</td>
<td>73</td>
<td>0.0034</td>
<td>105</td>
<td>45</td>
<td>0.0011</td>
<td>1032</td>
<td>96</td>
<td>0.0074</td>
</tr>
<tr>
<td>Al</td>
<td>839</td>
<td>97</td>
<td>0.0074</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>741</td>
<td>108</td>
<td>0.0053</td>
</tr>
<tr>
<td>Ca</td>
<td>4262</td>
<td>193</td>
<td>0.0376</td>
<td>202</td>
<td>92</td>
<td>0.0022</td>
<td>3268</td>
<td>208</td>
<td>0.0234</td>
</tr>
<tr>
<td>Fe</td>
<td>38217</td>
<td>426</td>
<td>0.3369</td>
<td>14391</td>
<td>262</td>
<td>0.1560</td>
<td>80201</td>
<td>604</td>
<td>0.5738</td>
</tr>
<tr>
<td>Mn</td>
<td>667</td>
<td>103</td>
<td>0.0059</td>
<td>137</td>
<td>62</td>
<td>0.0015</td>
<td>1158</td>
<td>128</td>
<td>0.0083</td>
</tr>
<tr>
<td>Y</td>
<td>5993</td>
<td>225</td>
<td>0.0528</td>
<td>2953</td>
<td>152</td>
<td>0.0320</td>
<td>11812</td>
<td>291</td>
<td>0.0845</td>
</tr>
<tr>
<td>P</td>
<td>4258</td>
<td>210</td>
<td>0.0375</td>
<td>3342</td>
<td>164</td>
<td>0.0362</td>
<td>8859</td>
<td>264</td>
<td>0.0634</td>
</tr>
<tr>
<td>SiO</td>
<td>3711</td>
<td>194</td>
<td>0.0327</td>
<td>373</td>
<td>105</td>
<td>0.0040</td>
<td>2732</td>
<td>212</td>
<td>0.0195</td>
</tr>
<tr>
<td>La</td>
<td>398</td>
<td>121</td>
<td>0.0035</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
</tr>
<tr>
<td>Ce</td>
<td>773</td>
<td>140</td>
<td>0.0068</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>580</td>
<td>163</td>
<td>0.0041</td>
</tr>
<tr>
<td>YO</td>
<td>5975</td>
<td>218</td>
<td>0.0527</td>
<td>3017</td>
<td>149</td>
<td>0.0327</td>
<td>12527</td>
<td>291</td>
<td>0.0896</td>
</tr>
<tr>
<td>NbO</td>
<td>11069</td>
<td>746</td>
<td>0.0976</td>
<td>4570</td>
<td>650</td>
<td>0.0496</td>
<td>18672</td>
<td>797</td>
<td>0.1336</td>
</tr>
<tr>
<td>SiO2</td>
<td>3809</td>
<td>446</td>
<td>0.0336</td>
<td>456</td>
<td>301</td>
<td>0.0049</td>
<td>2532</td>
<td>533</td>
<td>0.0181</td>
</tr>
<tr>
<td>NbO2</td>
<td>68364</td>
<td>694</td>
<td>0.6026</td>
<td>38789</td>
<td>521</td>
<td>0.4206</td>
<td>124360</td>
<td>901</td>
<td>0.8897</td>
</tr>
<tr>
<td>FeO</td>
<td>5869</td>
<td>366</td>
<td>0.0517</td>
<td>2238</td>
<td>255</td>
<td>0.0243</td>
<td>13245</td>
<td>505</td>
<td>0.0948</td>
</tr>
<tr>
<td>UO</td>
<td>1117</td>
<td>272</td>
<td>0.0098</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>2169</td>
<td>335</td>
<td>0.0155</td>
</tr>
<tr>
<td>Yb</td>
<td>3084</td>
<td>386</td>
<td>0.0272</td>
<td>1505</td>
<td>274</td>
<td>0.0163</td>
<td>6373</td>
<td>501</td>
<td>0.0456</td>
</tr>
<tr>
<td>TiO2</td>
<td>8543</td>
<td>422</td>
<td>0.0753</td>
<td>4847</td>
<td>309</td>
<td>0.0525</td>
<td>17002</td>
<td>568</td>
<td>0.1216</td>
</tr>
<tr>
<td>Ph2O6</td>
<td>1483</td>
<td>183</td>
<td>0.0131</td>
<td>665</td>
<td>131</td>
<td>0.0072</td>
<td>3076</td>
<td>221</td>
<td>0.0220</td>
</tr>
<tr>
<td>Ph2O7</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>263</td>
<td>141</td>
<td>0.0019</td>
</tr>
<tr>
<td>Ph2O8</td>
<td>140</td>
<td>114</td>
<td>0.0012</td>
<td>106</td>
<td>78</td>
<td>0.0011</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
</tr>
<tr>
<td>TaO2</td>
<td>2687</td>
<td>227</td>
<td>0.0237</td>
<td>1982</td>
<td>179</td>
<td>0.0215</td>
<td>4545</td>
<td>276</td>
<td>0.0325</td>
</tr>
<tr>
<td>TaO2H</td>
<td>3982</td>
<td>225</td>
<td>0.0351</td>
<td>1501</td>
<td>180</td>
<td>0.0163</td>
<td>5944</td>
<td>269</td>
<td>0.0425</td>
</tr>
<tr>
<td>Sc</td>
<td>823</td>
<td>109</td>
<td>0.0073</td>
<td>362</td>
<td>68</td>
<td>0.0039</td>
<td>976</td>
<td>128</td>
<td>0.0070</td>
</tr>
<tr>
<td>Ion Type</td>
<td>R60_147132</td>
<td></td>
<td>R60_144153</td>
<td></td>
<td>R60_145547</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>------------</td>
<td>---</td>
<td>------------</td>
<td>---</td>
<td>------------</td>
<td>---</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ion Count</td>
<td>2σ</td>
<td>Comp. %</td>
<td>Ion Count</td>
<td>2σ</td>
<td>Comp. %</td>
<td>Ion Count</td>
<td>2σ</td>
<td>Comp. %</td>
</tr>
<tr>
<td>O</td>
<td>1873747</td>
<td>2822</td>
<td>5.4423</td>
<td>2745077</td>
<td>3469</td>
<td>7.7827</td>
<td>1214470</td>
<td>2257</td>
<td>6.3058</td>
</tr>
<tr>
<td>Zr</td>
<td>237909</td>
<td>1541</td>
<td>0.6910</td>
<td>444330</td>
<td>2042</td>
<td>1.2597</td>
<td>169905</td>
<td>1198</td>
<td>0.8822</td>
</tr>
<tr>
<td>Ti</td>
<td>7023</td>
<td>325</td>
<td>0.0204</td>
<td>3014</td>
<td>447</td>
<td>0.0085</td>
<td>7200</td>
<td>269</td>
<td>0.0374</td>
</tr>
<tr>
<td>Si</td>
<td>6013</td>
<td>259</td>
<td>0.0175</td>
<td>123</td>
<td>329</td>
<td>0.0003</td>
<td>4799</td>
<td>208</td>
<td>0.0249</td>
</tr>
<tr>
<td>O2</td>
<td>12500000</td>
<td>7350</td>
<td>36.3060</td>
<td>11013543</td>
<td>6890</td>
<td>31.2252</td>
<td>6604993</td>
<td>5252</td>
<td>34.2944</td>
</tr>
<tr>
<td>ZrO</td>
<td>17800000</td>
<td>11242</td>
<td>51.6997</td>
<td>19481999</td>
<td>10444</td>
<td>55.2346</td>
<td>9988771</td>
<td>7782</td>
<td>51.8637</td>
</tr>
<tr>
<td>ZrO2</td>
<td>1343877</td>
<td>3169</td>
<td>3.9033</td>
<td>1086745</td>
<td>3275</td>
<td>3.0811</td>
<td>756680</td>
<td>2348</td>
<td>3.9288</td>
</tr>
<tr>
<td>ZrO2H</td>
<td>63585</td>
<td>1107</td>
<td>0.1847</td>
<td>56331</td>
<td>1362</td>
<td>0.1597</td>
<td>51343</td>
<td>925</td>
<td>0.2666</td>
</tr>
<tr>
<td>HfO</td>
<td>117900</td>
<td>1615</td>
<td>0.3424</td>
<td>135822</td>
<td>2290</td>
<td>0.3851</td>
<td>75881</td>
<td>1265</td>
<td>0.3940</td>
</tr>
<tr>
<td>HfO2</td>
<td>77850</td>
<td>962</td>
<td>0.2261</td>
<td>18196</td>
<td>1585</td>
<td>0.0516</td>
<td>14621</td>
<td>775</td>
<td>0.0759</td>
</tr>
<tr>
<td>ZrO3</td>
<td>39464</td>
<td>918</td>
<td>0.1146</td>
<td>40123</td>
<td>1200</td>
<td>0.1138</td>
<td>30479</td>
<td>670</td>
<td>0.1583</td>
</tr>
<tr>
<td>UO2</td>
<td>6292</td>
<td>391</td>
<td>0.0183</td>
<td>884</td>
<td>510</td>
<td>0.0025</td>
<td>8164</td>
<td>322</td>
<td>0.0424</td>
</tr>
<tr>
<td>Mg</td>
<td>454</td>
<td>113</td>
<td>0.0013</td>
<td>438</td>
<td>174</td>
<td>0.0012</td>
<td>827</td>
<td>90</td>
<td>0.0043</td>
</tr>
<tr>
<td>Al</td>
<td>594</td>
<td>129</td>
<td>0.0017</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>543</td>
<td>99</td>
<td>0.0028</td>
</tr>
<tr>
<td>Ca</td>
<td>2038</td>
<td>236</td>
<td>0.0059</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>2620</td>
<td>194</td>
<td>0.0136</td>
</tr>
<tr>
<td>Fe</td>
<td>88380</td>
<td>653</td>
<td>0.2567</td>
<td>40837</td>
<td>577</td>
<td>0.1158</td>
<td>76259</td>
<td>586</td>
<td>0.3959</td>
</tr>
<tr>
<td>Mn</td>
<td>1304</td>
<td>157</td>
<td>0.0038</td>
<td>578</td>
<td>220</td>
<td>0.0016</td>
<td>1125</td>
<td>120</td>
<td>0.0058</td>
</tr>
<tr>
<td>Y</td>
<td>13212</td>
<td>347</td>
<td>0.0384</td>
<td>7381</td>
<td>406</td>
<td>0.0209</td>
<td>14082</td>
<td>304</td>
<td>0.0731</td>
</tr>
<tr>
<td>P</td>
<td>10039</td>
<td>385</td>
<td>0.0292</td>
<td>2827</td>
<td>388</td>
<td>0.0080</td>
<td>10226</td>
<td>307</td>
<td>0.0531</td>
</tr>
<tr>
<td>SiO</td>
<td>3424</td>
<td>252</td>
<td>0.0099</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>1857</td>
<td>197</td>
<td>0.0096</td>
</tr>
<tr>
<td>La</td>
<td>297</td>
<td>194</td>
<td>0.0009</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>332</td>
<td>147</td>
<td>0.0017</td>
</tr>
<tr>
<td>Ce</td>
<td>615</td>
<td>220</td>
<td>0.0018</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>384</td>
<td>173</td>
<td>0.0020</td>
</tr>
<tr>
<td>YO</td>
<td>16921</td>
<td>356</td>
<td>0.0491</td>
<td>6950</td>
<td>366</td>
<td>0.0197</td>
<td>15452</td>
<td>302</td>
<td>0.0802</td>
</tr>
<tr>
<td>NbO</td>
<td>15208</td>
<td>1755</td>
<td>0.0442</td>
<td>25072</td>
<td>1383</td>
<td>0.0711</td>
<td>17138</td>
<td>1132</td>
<td>0.0890</td>
</tr>
<tr>
<td>SiO2</td>
<td>4324</td>
<td>699</td>
<td>0.0126</td>
<td>2217</td>
<td>827</td>
<td>0.0063</td>
<td>2679</td>
<td>542</td>
<td>0.0139</td>
</tr>
<tr>
<td>NbO2</td>
<td>146563</td>
<td>1156</td>
<td>0.4257</td>
<td>122277</td>
<td>1149</td>
<td>0.3467</td>
<td>137333</td>
<td>968</td>
<td>0.7131</td>
</tr>
<tr>
<td>FeO</td>
<td>11684</td>
<td>463</td>
<td>0.0339</td>
<td>6160</td>
<td>721</td>
<td>0.0175</td>
<td>12962</td>
<td>445</td>
<td>0.0673</td>
</tr>
<tr>
<td>UO</td>
<td>207</td>
<td>558</td>
<td>0.0006</td>
<td>2986</td>
<td>533</td>
<td>0.0085</td>
<td>1380</td>
<td>387</td>
<td>0.0072</td>
</tr>
<tr>
<td>Yb</td>
<td>8018</td>
<td>536</td>
<td>0.0233</td>
<td>6740</td>
<td>852</td>
<td>0.0191</td>
<td>6556</td>
<td>461</td>
<td>0.0340</td>
</tr>
<tr>
<td>TiO2</td>
<td>17853</td>
<td>559</td>
<td>0.0519</td>
<td>5624</td>
<td>859</td>
<td>0.0159</td>
<td>18149</td>
<td>513</td>
<td>0.0942</td>
</tr>
<tr>
<td>Pb206</td>
<td>2810</td>
<td>286</td>
<td>0.0082</td>
<td>1776</td>
<td>396</td>
<td>0.0050</td>
<td>3221</td>
<td>221</td>
<td>0.0167</td>
</tr>
<tr>
<td>Pb207</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>259</td>
<td>138</td>
<td>0.0013</td>
</tr>
<tr>
<td>Pb208</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
</tr>
<tr>
<td>TaO2</td>
<td>4144</td>
<td>403</td>
<td>0.0120</td>
<td>6339</td>
<td>474</td>
<td>0.0180</td>
<td>4815</td>
<td>301</td>
<td>0.0250</td>
</tr>
<tr>
<td>TaO2H</td>
<td>6514</td>
<td>388</td>
<td>0.0189</td>
<td>5366</td>
<td>460</td>
<td>0.0152</td>
<td>3263</td>
<td>293</td>
<td>0.0169</td>
</tr>
<tr>
<td>Sc</td>
<td>1318</td>
<td>158</td>
<td>0.0038</td>
<td>1611</td>
<td>235</td>
<td>0.0046</td>
<td>895</td>
<td>120</td>
<td>0.0046</td>
</tr>
</tbody>
</table>

Supplementary Table 4.4: Background corrected ionic counts for baddeleyite microtip specimens used in this study (continued).
### Supplementary Table 4.4: Background corrected ionic counts for baddeleyite microtip specimens used in this study (continued).
<table>
<thead>
<tr>
<th>Ion Type</th>
<th>R60_147129</th>
<th></th>
<th>R60_147070</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ion Count</td>
<td>2σ</td>
<td>Comp. %</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>210238</td>
<td>944</td>
<td>4.2702</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>36699</td>
<td>563</td>
<td>0.7454</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>2033</td>
<td>131</td>
<td>0.0413</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>535</td>
<td>85</td>
<td>0.0109</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>1753949</td>
<td>2698</td>
<td>35.6247</td>
<td></td>
</tr>
<tr>
<td>ZrO2</td>
<td>2530960</td>
<td>3754</td>
<td>51.4066</td>
<td></td>
</tr>
<tr>
<td>ZrO2H</td>
<td>16949</td>
<td>473</td>
<td>0.3442</td>
<td></td>
</tr>
<tr>
<td>HfO</td>
<td>23920</td>
<td>692</td>
<td>0.4858</td>
<td></td>
</tr>
<tr>
<td>HfO2</td>
<td>10512</td>
<td>412</td>
<td>0.2135</td>
<td></td>
</tr>
<tr>
<td>ZrO3</td>
<td>9611</td>
<td>394</td>
<td>0.1952</td>
<td></td>
</tr>
<tr>
<td>UO2</td>
<td>3119</td>
<td>185</td>
<td>0.0634</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>137</td>
<td>43</td>
<td>0.0028</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>102</td>
<td>44</td>
<td>0.0021</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>312</td>
<td>83</td>
<td>0.0063</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>17567</td>
<td>280</td>
<td>0.3568</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>200</td>
<td>55</td>
<td>0.0041</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>3663</td>
<td>152</td>
<td>0.0744</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>3158</td>
<td>147</td>
<td>0.0641</td>
<td></td>
</tr>
<tr>
<td>SiO</td>
<td>401</td>
<td>93</td>
<td>0.0081</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td></td>
</tr>
<tr>
<td>YO</td>
<td>4174</td>
<td>161</td>
<td>0.0848</td>
<td></td>
</tr>
<tr>
<td>NbO</td>
<td>4679</td>
<td>502</td>
<td>0.0950</td>
<td></td>
</tr>
<tr>
<td>SiO2</td>
<td>672</td>
<td>263</td>
<td>0.0137</td>
<td></td>
</tr>
<tr>
<td>NbO2</td>
<td>36883</td>
<td>498</td>
<td>0.7491</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>3369</td>
<td>252</td>
<td>0.0684</td>
<td></td>
</tr>
<tr>
<td>UO</td>
<td>547</td>
<td>214</td>
<td>0.0111</td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>2394</td>
<td>283</td>
<td>0.0486</td>
<td></td>
</tr>
<tr>
<td>TiO2</td>
<td>6793</td>
<td>316</td>
<td>0.1380</td>
<td></td>
</tr>
<tr>
<td>Pb206</td>
<td>950</td>
<td>136</td>
<td>0.0193</td>
<td></td>
</tr>
<tr>
<td>Pb207</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td></td>
</tr>
<tr>
<td>Pb208</td>
<td>bdt</td>
<td>bdt</td>
<td>bdt</td>
<td></td>
</tr>
<tr>
<td>TaO2</td>
<td>1147</td>
<td>172</td>
<td>0.0233</td>
<td></td>
</tr>
<tr>
<td>TaO2H</td>
<td>1543</td>
<td>157</td>
<td>0.0313</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>287</td>
<td>60</td>
<td>0.0058</td>
<td></td>
</tr>
</tbody>
</table>

Supplementary Table 4.4: Background corrected ionic counts for baddeleyite microtip specimens used in this study (continued).
4.4 Refining Atom Probe Tomography as a Geochronological Tool

One of the major outcomes of this study is presented in this chapter, whereby the first multi-microtip application of atom probe tomography as a U-Pb dating tool provides an exciting insight into the potential of this new technique in the fields of Earth and planetary science. Within the paper (White et al., 2017) large internal uncertainties are assigned to each $^{206}\text{Pb} / ^{238}\text{U}$ ratio, producing individual 2σ errors on the order of 12 – 106%. This large uncertainty reflects the ‘worst case scenario’ approach currently championed by CAMECA instruments (David Reinhard & Ty Prosa, pers. comm) and adopted by external atom probe researchers (Valley et al. 2014; Reddy et al. 2016; Peterman et al. 2016). In the case of the dataset presented here, $^{206}\text{Pb}^{++}$ was measured at 103 Da. U-bearing compound peaks as 135 Da ($^{238}\text{U}^{16}\text{O}_{2}^{2+}$), 270 Da ($^{238}\text{U}^{16}\text{O}_{2}^{3+}$), 84.66 Da ($^{238}\text{U}^{16}\text{O}^{3+}$), and 127 Da ($^{238}\text{U}^{16}\text{O}^{2+}$) were decomposed to yield total $^{238}\text{U}$ counts for all datasets. For each individual peak, corrected ionic counts were calculated through the subtraction of background counts from the total (raw) ionic count. Propagation of absolute raw and background counting statistics errors ($\sqrt{\text{counts}}$) allow for estimation of uncertainty on the background-corrected peak. This yields the final error on $^{206}\text{Pb}$ measurement as it is derived from a single peak. As $^{238}\text{U}$ represents the combination of UO and UO$_2$ peaks, individual uncertainties on each peak must be extrapolated through. Once individual errors for $^{206}\text{Pb}$ and $^{238}\text{U}$ have been calculated, isotopic errors can be extrapolated in quadrature to yield an estimated error for the final $^{206}\text{Pb}/^{238}\text{U}$ ratio.

Although statistically logical, this approach yields largely inflated internal uncertainties that we interpret to be overestimated; by assigning such large counting statistics errors to these peaks individual fluctuations in accuracy between datasets are completely masked. In addition, even large (∼1 Ga) age variations cannot be adequately resolved using this method. Given the unique, multi-tip nature of the presented dataset, the reproducibility of U-Pb ratios (and ages) between individual microtip tip specimen can be assessed to better inform such calculations. To this end, mean square weighted deviation (MSWD) values were calculated by taking a weighted average of the age population (along with associated errors) using the Isoplot plugin for Microsoft Excel (Ludwig, 2001). This quality check allows for the comparison of external scatter with assigned internal uncertainties, with an MSWD value of 1 the idealized target. Values falling below this threshold (< 1) suggest individual data point uncertainties are overestimated, while values > 1 indicate that the data are spread beyond the internal errors, suggesting that either the internal uncertainties are underestimated or there is statistically significant variation within the data. Using the currently-accepted approach to APT error propagation yields extremely low MSWD values of 0.038, 0.03 and 0.028 for the structurally subdivided domains (Table 4.5). This suggests that internal
uncertainties are massively overestimated. This presents a key problem when interpreting geochronological data, as discrete end members that could be resolved by atom probe are instead lost within the substantial error bars.

A first-order insight into the level of precision APT data are capable of can be gained by manually assigning individual U-Pb ages a set 2σ% error and examining the resultant MSWD value. Taking each grouping of data (Clustered-Fe, Homogenous-Fe and planar) and assigning a 2σ% uncertainty between 1% and 10% allows for MSWD values to be calculated across an achievable range of error. To generate an MSWD of ~1 from the structurally subdivided domains examined in this study, each individual U-Pb age needs to be assigned an internal uncertainty between 7% and 8.2% 2σ. With the current approach to error calculation and propagation yielding internal errors between 12 and 106%, clearly a new approach must be developed to assign realistic internal uncertainties that better reflect the external reproducibility of the APT U-Pb approach.

This new approach to APT error could feasibly be derived by propagating through counting statistics uncertainties on the final corrected ionic counts. With this model, background uncertainties would be acknowledged by assessing the reproducibility of the spectrum surrounding the ranged peak instead of taking counting statistics on the background related ionic counts within the mass/charge range. Background levels are largely stable during APT analyses (i.e. Larson et al. 2011), so this variability will likely be minimal across the narrow peaks selected for U-Pb analysis (< 0.4 Da). This may vary between models of the LEAP instrument where yield and efficiency differ during acquisition.

A first order insight into the viability of this approach can be generated by reevaluating uncertainties on the multi tip dataset presented in this chapter. Generating uncertainties through the propagation of counting statistics errors on individual background corrected peaks (i.e. ignoring the raw and background counts for each analysis) yields MSWD values of between 0.61 and 0.87, suggesting a more realistic assessment of internal uncertainties (Table 4.6). Furthermore, 2.1 – 4.1% 2σ uncertainties on the mean U-Pb ages are comparable to those generated by taking a standard error measurement across the dataset (2.4 – 4% 2SE), further constraining the statistical viability of the proposed method. Going forward, taking the counting statistics uncertainty on the background corrected counts in tandem with a measure of background reproducibility, and not peak intensity, will allow individual ages to be used more confidently in isolation.
Table 4.5. Background corrected ionic counts for $^{206}$Pb and $^{238}$U highlighting $2\sigma$ uncertainty values calculated through the raw peak and background propagation method. This approach assigns large internal errors to each isotopic species, and hence generates seemingly overestimated uncertainties on the calculated U-Pb ages. This is represented by the extremely low MSWD values between 0.028 and 0.038 for each structurally subdivided dataset.

<table>
<thead>
<tr>
<th>Tip #</th>
<th>Pb206</th>
<th>2σ</th>
<th>U238</th>
<th>2σ</th>
<th>Pb206/U238</th>
<th>2σ</th>
<th>Pb206/U238 Age (Ma)</th>
<th>2σ</th>
<th>Mean</th>
<th>2σ</th>
<th>2σ%</th>
<th>MSWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>146506</td>
<td>491</td>
<td>90</td>
<td>1394</td>
<td>378</td>
<td>0.3525</td>
<td>0.1154</td>
<td>1947</td>
<td>637</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>146475</td>
<td>3076</td>
<td>221</td>
<td>9296</td>
<td>919</td>
<td>0.3309</td>
<td>0.0405</td>
<td>1843</td>
<td>225</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>145547</td>
<td>3221</td>
<td>221</td>
<td>9544</td>
<td>1007</td>
<td>0.3375</td>
<td>0.0425</td>
<td>1874</td>
<td>236</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>146995</td>
<td>1221</td>
<td>228</td>
<td>3532</td>
<td>842</td>
<td>0.3456</td>
<td>0.1047</td>
<td>1914</td>
<td>580</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>146506</td>
<td>365</td>
<td>114</td>
<td>764</td>
<td>419</td>
<td>0.4776</td>
<td>0.3015</td>
<td>2517</td>
<td>1589</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>145533</td>
<td>665</td>
<td>131</td>
<td>1547</td>
<td>530</td>
<td>0.4297</td>
<td>0.1697</td>
<td>2304</td>
<td>910</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>147132</td>
<td>464</td>
<td>104</td>
<td>985</td>
<td>461</td>
<td>0.4712</td>
<td>0.2444</td>
<td>2489</td>
<td>1291</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>144153</td>
<td>1776</td>
<td>396</td>
<td>3870</td>
<td>1475</td>
<td>0.4589</td>
<td>0.2026</td>
<td>2435</td>
<td>1075</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>146506</td>
<td>452</td>
<td>85</td>
<td>1768</td>
<td>365</td>
<td>0.2555</td>
<td>0.0712</td>
<td>1467</td>
<td>409</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>147132</td>
<td>212</td>
<td>65</td>
<td>844</td>
<td>307</td>
<td>0.2514</td>
<td>0.1194</td>
<td>1445</td>
<td>687</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>146995</td>
<td>2090</td>
<td>375</td>
<td>8628</td>
<td>1362</td>
<td>0.2422</td>
<td>0.0579</td>
<td>1398</td>
<td>334</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>147070</td>
<td>159</td>
<td>123</td>
<td>688</td>
<td>501</td>
<td>0.2309</td>
<td>0.2454</td>
<td>1339</td>
<td>1424</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.5: Background corrected ionic counts for $^{206}$Pb and $^{238}$U highlighting $2\sigma$ uncertainty values calculated through the raw peak and background propagation method. This approach assigns large internal errors to each isotopic species, and hence generates seemingly overestimated uncertainties on the calculated U-Pb ages. This is represented by the extremely low MSWD values between 0.028 and 0.038 for each structurally subdivided dataset.
Table 4.6. Background corrected ionic counts for $^{206}\text{Pb}$ and $^{238}\text{U}$ highlighting 2σ uncertainty values calculated by taking the counting statistics errors on the corrected Pb and U ionic counts. This approach still appears to overestimate internal uncertainties on individual U-Pb ages, yielding MSWD values below 1 (0.61 – 0.87), but is far more realistic than the previously implemented method (total peak counts extrapolated through with background errors).
NANOSTRUCTURES AND CHRONOSTRUCTURES IN BADDELEYITE

5.1 INTRODUCTION

While recent work has highlighted the importance of baddeleyite as a planetary chronometer (Zhou et al. 2013), little is known about the isotopic response of this phase to shock metamorphism (Darling et al. 2016). Experimental studies suggest the U-Pb system is undisturbed at pressures as high as ~59 GPa (Niihara et al. 2012), but partially age-reset grains from Martian shergottite NWA 5298 suggest Pb loss at lower shock pressures (Moser et al. 2013). Further nanostructural observations at increasingly higher spatial resolutions have yielded new insights into the mobilisation and loss of lead in shock-metamorphosed baddeleyite (see chapter 4), though little focus was given to the nature of the nm-scale structures, such as planar features and clusters, observed within the atom probe dataset.

Here we seek to augment this work by constraining the mechanisms by which lead is mobilised and lost within baddeleyite during shock metamorphism. By further examining the range of nano-scale features highlighted by our previous atom probe study of shocked baddeleyite (chapter 4), chemically distinct nanostructures enriched in either UO$_2$ or incompatible trace elements (Fe, Si, Mg, etc.) can be correlated with the extent of lead loss and age resetting experienced by the domain. The following paper is included in its’ entirety here:

White, L. F., Darling, J. R., Moser, D., Reinhard, D.A., Dunlop, J., Larson, D. J., Lawrence, D. & Martin, I. Chemical nanostructures and chronostructures defined in shock metamorphosed baddeleyite by atom probe tomography. In review with AGU Monograph 'Microstructural Geochronology'.

L. White led the reduction and interpretation of atom probe data, and wrote the manuscript, with scientific input from J. Darling and D. Moser. Acquisition of data was led by D. Reinhard, with the assistance of D. J. Larson, D. Lawrence and I. Martin. L. White reduced all isotopic and chemical data, and interpreted nanoscale structural relationships with input from J. Darling.
5.2 Chemical Nanostructures and Chronostructures Defined in Shock Metamorphosed Baddeleyite by Atom Probe Tomography

White, L. F.1*, Darling, J. R.1, Moser, D.3, Reinhard, D.A.3, Dunlop, J.1, Larson, D. J.3, Lawrence, D.3 & Martin, I.3

1 School of Earth and Environmental Sciences, University of Portsmouth, Portsmouth, UK
2 Department of Earth Sciences, University of Western Ontario, London, Canada.
3 Cameca, Madison, WI 53711, USA

Baddeleyite (ZrO2) is an abundant and robust U-bearing accessory mineral that holds great promise in the dating of mafic planetary crusts. Recent work has highlighted the influence of nanometer scale structures on the mobilization and diffusion of radiogenic isotopes in other geochronometers, complicating the resultant interpretation of their age. Such work has never been conducted for baddeleyite. Here we correlate nanoscale chemical structures including those defined by geochronology elements such as U (‘chronostructures’) in highly shocked baddeleyite using atom probe tomography. This work has revealed pervasive ~10 nm wide curvi-planar features (enriched in Fe, Al, Mg) throughout the specimen, planar features decorated by enriched wave-like forms compositionally similar to the curvi-planar structures, and extensive ~8 nm-wide clustering of U. Chronologically, the 1.850 Ga impact-induced diffusion pathways (planar and curvi-planar structures) facilitate continued Pb loss during later metamorphism, yielding significantly younger ages (1455 ± 300 Ma) than the bulk microtip (2316 ± 105 Ma). Subtraction of this planar U-Pb reservoir from the bulk tip yields an accurate crystallization age of 2436 (± 127) Ma. This visualization of U and Pb mobility in shocked baddeleyite presents new insights into the movement and mechanisms of atomic change in a lattice during shock metamorphism, and is a proof of concept for extracting natural chronologies from microminerals in a relatively non-destructive way.

Introduction

Microstructural characterization of individual mineral grains prior to dating has greatly aided in the interpretation of age data (see summary in Jones et al., this volume; Darling et al., this volume). For baddeleyite (monoclinic-ZrO2; Smith & Newkirk, 1965) this approach has facilitated the identification of igneous and shock-reset ages within a variably shocked grain population (Moser et al. 2013; Darling et al. 2016). Baddeleyite is a common accessory phase within many of these terrestrial (Lumpkin 1999; Heaman & Lecommentant 2001; Heaman &
LeCheminant 1993) and extra-terrestrial (Moser et al. 2013; Ozawa et al. 2014; El Goresy et al. 1971; Krot et al., 1993) mafic lithologies. Boasting robust U-Pb isotope systematics and an inherent resistance to α-decay (Lumpkin 1999), baddeleyite is an ideal geochronometer in rock-types lacking other U-bearing phases such as zircon, titanite or apatite. The majority of grains however are incredibly small (< 50μm), yielding numerous issues when separating individual crystals for isolated chemical analysis (Söderlund & Johansson 2002). Small volume in-situ dating has circumvented this issue (Chamberlain et al. 2010; Ibanez-Mejia et al. 2014), allowing previously neglected micro-baddeleyite grains to be dated and yielding exciting new insights into Solar System chronology (Moser et al. 2013). Given the extensive occurrence of baddeleyite within planetary mafic crusts, the phase holds great potential when resolving issues of planetary formation and evolution if the geochronology methods can be developed for grains that are frequently only several microns long and contain highly complex fracture, amorphisation, granularisation and twin relationships that vary on the ~nm scale (Darling et al. 2016).

Atom probe tomography (APT) is a unique tool capable of examining the atomic-scale distribution of elements and isotopes in three-dimensional space, producing coupled structural and chemical datasets from ~150nm wide crystal domains (Kelly & Miller 2007). This technique has only recently been applied to mineralogical chronometers but is already providing exciting new insights into the correlation between nanoscale structures and cation mobility. APT analyses of Hadean-aged Jack Hills zircon revealed clustering of Pb and Y atoms associated with domains of elevated $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, highlighting heterogeneous age distribution on the ~20nm scale (Valley et al. 2014). More recently, analysis of tectonically deformed zircon of the Archean-aged Napier Complex demonstrated that the mobilization of crystal lattice dislocations provides a pathway to encourage cation diffusion on the nm-scale (Piazolo et al. 2016). Here we conduct APT analysis of a highly shocked baddeleyite grain from a well characterized sample immediately beneath the Sudbury impact melt sheet in an effort to demonstrate the type of age and microstructural information to be found at the atomic scale within this important geochronometer.

**Geological background and sample selection**

The Sudbury impact structure presents a rare opportunity to examine shock effects on solid lithological targets as extensive post impact tilting (Riller 2005) has presented a transect through shocked target rocks, impactites including a 3 km thick melt sheet, and crater filling sediments. This has facilitated a roughly defined pressure gradient for the structure, with the presence of quartz planar deformation features (PDFs) and shattercones defining ~10 and >2 GPa isobars, respectively (Grieve et al. 2008). This is especially useful when examining minerals with a poorly confined shock response, such as baddeleyite.
Underlying the 1.850 Ga impact structure (Krogh et al. 1984) to the north is a series of Archaean high-grade metamorphic rocks, principally banded and migmatitic gneisses of the Levack Complex (2711 ± 7 Ma; Krogh et al. 1984), which host a number of granitic, tonalitic, granodioritic, mafic and ultra-mafic intrusions (Card et al., 1984). One such suite of intrusions, the 2.47 Ga to 2.46 Ga Matachawan diabese dyke swarm (Krogh et al. 1984; Heaman 1997), occur throughout the Canadian shield and are known to host an abundance of \( \text{ZrO}_2 \) grains. Immediately following impact, the North Range was subjected to extensive high-temperature contact metamorphism (1.5-5 kbar; 800-1015\(^\circ\)C) within ca. 2 km of the superheated melt sheet (James et al., 1992), with the complete recrystallisation of quartz and feldspar estimated within ~500 m of the melt sheet (Grieve & Therriault, 2000).

Sampled from a ~15m thick dyke of the Matachawan swarm, JD12SUD14 is from a highly shocked diabase dyke approximately 550m beneath the lower northern contact of the Sudbury impact melt sheet. Following impact at 1.85 Ga, greenschist-facies metamorphism (i.e. Riller 2005) has generated a modal assemblage of Al-rich amphibole, chlorite mica and plagioclase feldspar with interstitial magnetite and ilmenite. The sample was likely exhumed around ~1 Ga (Thompson et al., 1998). Baddeleyite is abundant, with a scanning electron microscopy (SEM) feature scan of a single thin section revealing over 100 grains ranging from 15 to 330 \( \mu \text{m}^2 \) in exposed surface area. Electron backscatter diffraction (EBSD) analysis of these grains (i.e. chapter 3) reveals reversion twinning of the monoclinic lattice presently interpreted to result from the formation and reversion of the high-pressure orthorombic-\( \text{ZrO}_2 \)-structure. The host grain displays heavy crystal plastic deformation on the order of < 10\(^\circ\), while reverted subdomains display minimal (~1.5\(^\circ\)) distortion.

**Atom probe tomography (APT) methodology**

One of the identified baddeleyite grains (#346059) was chosen for further analysis using atom probe tomography (APT). Following backscatter electron (BSE) imaging, the grain was removed as a single 3 x 5 x 30\( \mu \text{m} \) slice using a focused ion beam (FIB) guided by a field-emission gun scanning electron microscope (FEG-SEM). Upon removal from the thin section, segmenting the slice into multiple microtips (approximately six from each pullout) allows for milling into the needle-shaped profile required for analysis. APT analysis was conducted using a local-electrode atom probe (LEAP) 4000X HR instrument located at the CAMECA Atom Probe Technology Center, Madison, Wisconsin. While this LEAP instrument has previously been described in complete detail elsewhere (Kelly & Miller 2007; Larson et al. 2011; Kelly and Larson, 2012; Larson et al., 2013), it should be noted that other instruments differ greatly in the evaporation and analysis of microtip specimens. Full details of analysis protocols and data reduction can be found in Table 5.1. Of the nine microtips created from grain 46059, four went on to produce full atom probe datasets. Tip R60_147132, totaling 68
millions raw (single, multiple and partial) spectrum counts, presents an example of the striking chemical and structural heterogeneity observed in the suite of analyses and has thus been selected as the focus of this manuscript.

Following acquisition, spectra must be individually evaluated as certain peaks can be masked through isobaric interferences, while others represent complex ionized molecules. A range is selected and defined manually within the atom probe spectrum, following which the Integrated Visualization and Analysis System (IVAS) software sums all counts within this range as the raw total. A background correction is applied through the extrapolation of the spectrum surrounding the isolated peak, rejecting the average counts from the raw total to generate a background corrected count. Isolating, classifying and quantifying all observable peaks can assess the composition of the bulk microtip (Figure 5.1). In all cases, uncertainties on compositional peaks are generated by taking the counting statistics errors on the corrected (raw – background) atomic counts.

<table>
<thead>
<tr>
<th>Specimen Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen Name</td>
</tr>
<tr>
<td>Target Material</td>
</tr>
<tr>
<td>Sample Preparation</td>
</tr>
<tr>
<td>Microtip Milling (1st Mill)</td>
</tr>
<tr>
<td>Microtip Milling (4th Mill)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Data Acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument Model</td>
</tr>
<tr>
<td>Laser Wavelength</td>
</tr>
<tr>
<td>Laser Pulse Energy</td>
</tr>
<tr>
<td>Nominal Flight Path (mm)</td>
</tr>
<tr>
<td>Temperature (K)</td>
</tr>
<tr>
<td>Pressure (torr)</td>
</tr>
<tr>
<td>ToF offset, τ₀(ns)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Data Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Software</td>
</tr>
<tr>
<td>Maximum Spectrum Value (Da)</td>
</tr>
<tr>
<td>Spectrum Bin Width (Da)</td>
</tr>
<tr>
<td>Total Spectrum Count</td>
</tr>
<tr>
<td>Total Ranged Ions</td>
</tr>
<tr>
<td>Total Unranged Ions</td>
</tr>
</tbody>
</table>

*Table 5.1. Atom Probe Tomography data acquisition and run summary.*
Figure 5.1: Full mass-to-charge spectra (< 200 Da) for microtip #R60_147132. Prominent peak families are labeled to aid interpretation. Discrete isotopic variations can be observed in the majority of elemental families (ZrO, ZrO₂, ZrO₃, TiO₂, FeO).

Atom probe tomography of shocked baddeleyite

Whole-Microtip Composition

The bulk of the sample constitutes Zr and O atoms and compounds (Zr, O, ZrO, ZrO₂, ZrO₃), which total approximately 99 wt.% of the volume. Impurities in the form of Hf (0.29 at.%), Nb (0.24 at.%), Fe (0.15 at.%), and Y (0.04 at.%) are all present above 0.04 at.%, while other impurities (La, Ti, Si, Ta, P, Yb, U, Ca, Sc, Mn, Al, Mg and Pb) are all below this threshold, yielding between 300 (La) and 25,000 (Ti) total decomposed and corrected atomic counts (Table 5.2). H (0.1 at.%) was also detected. In nearly all APT analyses prominent peaks are observed at 1, 2 and 3 Da (atomic mass unit, reported in daltons). This free hydrogen most likely originates from the vacuum chamber and not from the sample itself (Cockeram et al., 2013), although this is unresolvable at the mass resolution offered by the LEAP (~1000 M/ΔM). Regardless of source, the presence of H often prevents the accurate discrimination of sensitive isotopic ratios. For example, O peaks may be masked through the isobaric interference of hydroxides ¹⁶O⁻¹H and ¹⁷O⁻¹H on raw ¹⁷O (17 Da) and ¹⁸O (18 Da), respectively. Although this hydride interference may affect a number of stable isotope ratios, including C, N, Mg, Si, and Ca (Valley et al. 2015), doubly charged species are generally less susceptible (Heck et al., 2014).
This is best illustrated by examining the abundant Zr peaks within baddeleyite. There are five isotopes of zirconia (\(^{90}\text{Zr}, {91}\text{Zr}, {92}\text{Zr}, {94}\text{Zr}, {96}\text{Zr}\)) each of which can occur in four charge states (\(\text{Zr}^+, \text{Zr}^{2+}, \text{Zr}^{3+}, \text{Zr}^{4+}\)), theoretically yielding mass-to-charge spectra between 22.5 – 24 (4+), 30 – 32 (3+), 45 – 48 (2+), and 90 – 96 (1+) Da. Isolation and correction of these peaks yield variable relative proportions of the five Zr isotopes, suggesting strong isobaric influence on certain peaks. Known abundances of 51.45%, 11.27%, 17.17%, 17.33% and 2.78% for \(^{90}\text{Zr}, {91}\text{Zr}, {92}\text{Zr}, {94}\text{Zr}\) and \(^{96}\text{Zr}\) respectively, closely match those numbers generated here from doubly charged Zr peaks. All other charge states (1+, 3+ and 4+) yield disproportionately high levels of \(^{96}\text{Zr}\), the least abundant Zr isotope. Given a wide variety of incompatible cations within natural baddeleyite (Lumpkin 1999), a large number of elements and compounds can account for this discrepancy.

For example, a pronounced peak at 24 Da likely combines peaks for \(^{96}\text{Zr}^{4+}, {48}\text{Ti}^{2+}\) and \(^{24}\text{Mg}^+\), preventing the unambiguous resolution of the three species. Oxide and hydroxide phases will also complicate peak analysis; for example, any peak for singly charged \(^{96}\text{Zr}^+\) at 96 Da is susceptible to isobaric interference from HfO, potentially yielding the inflated values observed here. Although doubly charged peaks aren’t completely safe from interference (i.e. \(^{48}\text{Ti}^+\) on \(^{96}\text{Zr}^{2+}\); Watson et al., 2006), they appear to be the most robust species when it comes to inferring elemental and isotopic composition. A full discussion on peak selection and element quantification for baddeleyite can be found in Reinhard et al., this volume.

**Chemical nanostructure**

Although Zr and O are homogeneously distributed throughout the tip, the aforementioned impurities display a large degree of spatial heterogeneity or chemical nanostructure. Most striking in this regard is a pair of planar features (< 25nm thickness) observed in the lower portion of the microtip (Figure 5.2). The features are most clearly defined by Fe, Ca, Mn and Si atoms whose enrichment defines the plane. Quantified within a rectangular prism, a region of interest (ROI), this enrichment is most notable in Al (5.9x bulk concentration) and Mg (5.2x), although Si (4.3x), Mn (4.0x), Ca (4.0x), U (2.4x), Fe (2.4x) and Sc (2.3x) are all at least twice as concentrated along the planar feature as in the bulk. All other impurities are slightly concentrated along these features (between 1.1x (Y) and 1.4x (Ti); Table 5.3).

Focusing on these planes reveals nano-scale heterogeneities in the form of wave-like structures enriched in the same elements as the wider planar feature. Spacing of these structures appears to vary across the plane, ranging from ~12 nm in the shortest instance to ~60 nm in the longest (Figure 5.3). This structure is particularly influential in constraining the U-Pb composition of the tip, highlighting a decoupling of the U-Pb isotope systems with
the isolated plane accounting for ~13% of the bulk uranium and only ~7.5% of the total $^{206}\text{Pb}$. Towards the top of the tip, a number of thin (~15nm) curviplanar features are visible in both Si and Fe distribution (Figures 5.2, 5.3). These structures are relatively enriched in Ca (3.3x), Al (~3x), Si (2.54x) and Mn (2.2x), highlighting a similar pattern of enrichment to the larger plane. For example, Mg, Al and Mn are all detectable, and appear enriched relative to the bulk microtip.

<table>
<thead>
<tr>
<th>Ion Type</th>
<th>Decomposed Count</th>
<th>At. %</th>
<th>2σ%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>48300000</td>
<td>70.5714</td>
<td>0.03</td>
</tr>
<tr>
<td>Zr</td>
<td>19500000</td>
<td>28.4916</td>
<td>0.05</td>
</tr>
<tr>
<td>Ti</td>
<td>24877</td>
<td>0.0363</td>
<td>1.27</td>
</tr>
<tr>
<td>Si</td>
<td>13761</td>
<td>0.0201</td>
<td>1.70</td>
</tr>
<tr>
<td>Mg</td>
<td>454</td>
<td>0.0007</td>
<td>9.39</td>
</tr>
<tr>
<td>Al</td>
<td>594</td>
<td>0.0009</td>
<td>8.20</td>
</tr>
<tr>
<td>Ca</td>
<td>2038</td>
<td>0.0030</td>
<td>4.43</td>
</tr>
<tr>
<td>Fe</td>
<td>100064</td>
<td>0.1462</td>
<td>0.63</td>
</tr>
<tr>
<td>Mn</td>
<td>1304</td>
<td>0.0019</td>
<td>5.54</td>
</tr>
<tr>
<td>Y</td>
<td>30133</td>
<td>0.0440</td>
<td>1.15</td>
</tr>
<tr>
<td>P</td>
<td>10039</td>
<td>0.0147</td>
<td>2.00</td>
</tr>
<tr>
<td>La</td>
<td>297</td>
<td>0.0004</td>
<td>11.61</td>
</tr>
<tr>
<td>Ce</td>
<td>615</td>
<td>0.0009</td>
<td>8.06</td>
</tr>
<tr>
<td>Yb</td>
<td>8018</td>
<td>0.0117</td>
<td>2.23</td>
</tr>
<tr>
<td>Sc</td>
<td>1318</td>
<td>0.0019</td>
<td>5.51</td>
</tr>
<tr>
<td>H</td>
<td>70099</td>
<td>0.1024</td>
<td>0.76</td>
</tr>
<tr>
<td>Hf</td>
<td>195750</td>
<td>0.2860</td>
<td>0.45</td>
</tr>
<tr>
<td>U</td>
<td>6499</td>
<td>0.0095</td>
<td>2.48</td>
</tr>
<tr>
<td>Nb</td>
<td>161771</td>
<td>0.2364</td>
<td>0.50</td>
</tr>
<tr>
<td>Ta</td>
<td>10658</td>
<td>0.0156</td>
<td>1.94</td>
</tr>
<tr>
<td>Pb</td>
<td>3020</td>
<td>0.00441254</td>
<td>3.64</td>
</tr>
<tr>
<td><strong>Sum</strong></td>
<td><strong>68441308</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.2.** Bulk geochemical data for microtip #R60_147132 represented as decomposed, background corrected counts. 2 sigma uncertainties (2σ) are calculated using the counting statistics uncertainty on the background corrected counts for each element and compound before propagation through to the decomposed atomic %.
Figure 5.2: Distribution of individual Zr, Y, Fe and Si atoms within microtip R60_147132. Zr and Y appear homogenously distributed throughout the tip, while larger incompatible cations highlight planar features and clusters. The rectangular box in Si distribution highlights the planar feature segregate by ROI for isolated geochemical analysis (see text).

Figure 5.3: 3D distribution of Fe atoms within microtip R60_147132 highlighted by a 1% isosurface. For reference, 2D cross-sections through the X-axis (b) and Y-axis (c) are presented, while a tilted cross-sectional view of the large planar feature defined in Figure 5.2 in presented in d, highlighting isosurface distribution (left) and raw Fe data points (right).
### Table 5.3

<table>
<thead>
<tr>
<th>Ion Type</th>
<th>Planar</th>
<th>At. %</th>
<th>2σ%</th>
<th>Enrichment Factor (vs. Bulk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>2570834</td>
<td>70.46</td>
<td>0.12</td>
<td>1.00</td>
</tr>
<tr>
<td>Zr</td>
<td>1025963</td>
<td>28.12</td>
<td>0.20</td>
<td>0.99</td>
</tr>
<tr>
<td>Ti</td>
<td>1907</td>
<td>0.052</td>
<td>4.58</td>
<td>1.44</td>
</tr>
<tr>
<td>Si</td>
<td>3177</td>
<td>0.087</td>
<td>3.55</td>
<td>4.33</td>
</tr>
<tr>
<td>Mg</td>
<td>124</td>
<td>0.003</td>
<td>17.93</td>
<td>5.15</td>
</tr>
<tr>
<td>Al</td>
<td>187</td>
<td>0.005</td>
<td>14.62</td>
<td>5.91</td>
</tr>
<tr>
<td>Ca</td>
<td>437</td>
<td>0.012</td>
<td>9.56</td>
<td>4.03</td>
</tr>
<tr>
<td>Fe</td>
<td>12732</td>
<td>0.349</td>
<td>1.77</td>
<td>2.39</td>
</tr>
<tr>
<td>Mn</td>
<td>281</td>
<td>0.008</td>
<td>11.92</td>
<td>4.05</td>
</tr>
<tr>
<td>Y</td>
<td>1777</td>
<td>0.049</td>
<td>4.74</td>
<td>1.11</td>
</tr>
<tr>
<td>P</td>
<td>641</td>
<td>0.018</td>
<td>7.90</td>
<td>1.20</td>
</tr>
<tr>
<td>La</td>
<td>49</td>
<td>0.001</td>
<td>28.58</td>
<td>3.10</td>
</tr>
<tr>
<td>Ce</td>
<td>83</td>
<td>0.002</td>
<td>21.98</td>
<td>2.52</td>
</tr>
<tr>
<td>Yb</td>
<td>481</td>
<td>0.013</td>
<td>9.12</td>
<td>1.13</td>
</tr>
<tr>
<td>Sc</td>
<td>158</td>
<td>0.004</td>
<td>15.89</td>
<td>2.26</td>
</tr>
<tr>
<td>H</td>
<td>4725</td>
<td>0.129</td>
<td>2.91</td>
<td>1.26</td>
</tr>
<tr>
<td>Hf</td>
<td>12756</td>
<td>0.349</td>
<td>1.77</td>
<td>1.22</td>
</tr>
<tr>
<td>U</td>
<td>844</td>
<td>0.023</td>
<td>6.88</td>
<td>2.44</td>
</tr>
<tr>
<td>Nb</td>
<td>10315</td>
<td>0.282</td>
<td>1.97</td>
<td>1.20</td>
</tr>
<tr>
<td>Ta</td>
<td>752</td>
<td>0.020</td>
<td>7.29</td>
<td>1.32</td>
</tr>
<tr>
<td>Pb</td>
<td>280</td>
<td>0.008</td>
<td>11.95</td>
<td>1.74</td>
</tr>
<tr>
<td><strong>Sum</strong></td>
<td><strong>3648505</strong></td>
<td><strong>100</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.3.** Geochemical data generated from the region of interest (ROI) isolating the upper planar feature in microtip #R60_147132, represented as decomposed, background corrected counts. 2 sigma uncertainties (2σ) are calculated using the counting statistics uncertainty on the background corrected counts for each atom and compound before propagation through to the decomposed atomic weight %.

A large number (> 100) of small (5 – 8 nm) UO$_2$ enriched clusters can be also observed throughout the tip (Figure 5.4a). Predominately enriched in U (~9x bulk composition), smaller enrichments in Ta, Yb, Ti, Fe, Ca and Pb are also observed (Table 5.4). Other species, such as Mg, La, Sc and Al, fall below detection threshold, yielding between 0 and 5 raw ionic counts within the single defined cluster. It is notable that the enrichment factors of U and Pb differ greatly (~9x versus 2.2x), although minimal counts of Pb (2 background corrected counts of $^{206}$Pb, no counts of $^{207}$Pb, and 3 counts of Pb$^{208}$) yield statistically irrelevant datasets when taking into account substantial (~100% 2s) counting statistics uncertainties, falling below detection threshold.
Figure 5.4: (A) Fe atoms (1.2% isosurface) highlight a range of planar and curviplanar features within the tip. (B) SiO atoms and SiO (0.7% isosurface) atoms. Of note, Si highlights both the curviplanar, and the lower planar features. (C) 3D distribution of UO$_2$ (1% isosurface) and sum Pb (Pb$^{206}$, Pb$^{207}$ and Pb$^{208}$) atoms. UO$_2$ appears heterogeneously distributed (forming ~10nm clusters) while Pb is homogenous throughout. Planar features are not observed in U-Pb space. For reference, 1D concentration profiles (highlighting selected species) through the highlighted red ROI is presented for each structure.
Table 5.4: Geochemical data generated from the region of interest (ROI) isolating the small UO$_2$-enriched cluster highlighted in microtip #R60_147132 (Figure 5.4), represented as decomposed, background corrected counts. 2 sigma uncertainties (2σ) are calculated using the counting statistics uncertainty on the background corrected counts for each atom and compound before propagation through to the decomposed atomic %.

Uranium – lead isotopic analysis

U-Pb analysis of whole (bulk) microtip

Geologically meaningful Pb-Pb geochronology was not possible from this dataset. Peaks for doubly charged $^{206}$Pb, $^{207}$Pb and $^{208}$Pb would occur at 103, 103.5 and 104 Da, respectively. Singly ionized Pb is not detected between 204 and 208 Da. Peaks for $^{207}$Pb and $^{208}$Pb are minimal, providing 89 ± 19 (all error reported as 2σ) and 122 ± 22 counts and remaining within background of the sample. $^{206}$Pb provides a sharp, well-defined peak totaling 2810 ± 106 counts. An estimated 3-7% of the $^{207}$Pb peak likely comprises $^{206}$PbH, though this may be as low as ~1% (Valley et al., 2015). Ignoring the potentially minor influence of hydride species yields a $^{207}$Pb/$^{206}$Pb ratio of 0.0315, falling well below the
expected ratios of 0.15826 to 0.16048 (Heaman, 1997) and yielding a nonsensical U-Pb age (~1010 ± 252 Ma). Low levels of Si within natural baddeleyite prevent SiO$_2$ ion interference of the $^{208}$Pb$^{++}$ peak at 104 Da, although minimal counts (coupled with an absence of thorium) prevent Th-Pb dating. Doubly charged $^{204}$Pb, expected to peak at ~102 Da, is unresolvable (falling below detection limit), preventing isolated Pb (i.e. $^{206}$Pb/$^{204}$Pb vs. $^{207}$Pb/$^{204}$Pb) isochron work. Concatenating data from multiple microtips to better resolve isotopic peaks from background could overcome this limitation.

The application of $^{206}$Pb/$^{238}$U chronometry shows more promise. Uranium, calculated through the decomposition of UO peaks (at 84.7 and 127 Da) and UO$_2$ peaks (at 135 and 270.1 Da), totals 6499 ± 161 counts. As all isolated U peaks correlate with $^{238}$U, no correction for $^{235}$U is required. However, assuming a natural $^{238}$U/$^{235}$U ratio of 137.82 (Hiess et al., 2012), a total of ~47 counts of $^{235}$U would also be present within the specimen, though associated $^{235}$U, $^{235}$UO and $^{235}$UO$_2$ peaks fall below background within the mass-to-charge spectra. The calculated $^{206}$Pb/$^{238}$U ratio of 0.4324 (± 0.0195) provides an age of 2316 ± 105 Ma, below the crystallization age for the dyke swarm (2473 Ma; Heaman, 1997). However, partial age resetting of the bulk tip may have occurred, driven by lead loss as a result of the ~1.85 Ga impact event (Krogh et al., 1984) or later Proterozoic regional metamorphism.

**U-Pb analysis of chemical nanostructures**

Isolation by region of interest (ROI) of the upper, ~120nm long decorated plane yields 844 ± 58 counts of $^{238}$U (predicting 6 counts of $^{235}$U) and 212 ± 29 counts of $^{206}$Pb, providing a calculated $^{206}$Pb/$^{238}$U ratio of 0.2514 (± 0.0386) and an age of 1455 ± 300 Ma (Table 5.5). Minimal counts of $^{207}$Pb (48 ± 14) and $^{208}$Pb (21 ± 44) again limit application of other isotope systems, with a calculated $^{207}$Pb/$^{206}$Pb age of 3019 ± 1288 Ma and $^{207}$Pb/$^{235}$U age of 2209 ± 2425 Ma. Separation of the plane-hosted waves is impossible for U-Pb analysis, as minimal (often singular) counts of Pb prohibit any statistically relevant data from individual waves. Despite the larger inherent error associated with analyzing a smaller volume, the younger $^{206}$Pb/$^{238}$U age of 1455 ± 300 Ma suggests the planar feature records a later phase of Pb-loss than the impact itself (1850 Ma; Krogh et al., 1984), most closely matching the age of the Chieflakian orogeny (~1460 Ma; Corfu & Easton, 2001). In the bulk tip, this localized region of Pb-loss can be corrected through the rejection of planar U and Pb counts from the total bulk. By removing this planar influence from the bulk tip, a total of 5655 ± 171 counts of U yield 41 ± 12 counts of $^{235}$U, and 5614 ± 150 counts of $^{238}$U. 2598 ± 110 counts of $^{206}$Pb yield a $^{206}$Pb / $^{238}$U ratio of 0.463 and an associated age of 2452 ± 162 Ma, ~100 million years older than the previously calculated bulk age with comparable error.
Within both the curvi-planar features and smaller UO₂ clusters, ²⁰⁷Pb and ²⁰⁸Pb species fall below detection threshold, yielding singular (or even negative) ionic counts following background correction. In addition, peaks associated with ²³⁵U were not discernible within the atom probe spectra, limiting dating of these structures to the radiogenic ²⁰⁶Pb/²³⁸U ratio. Isolation of the curvi-planar feature yields 190 ± 28 counts of ²³⁸U and 60 ± 16 counts of ²⁰⁶Pb, providing a calculated ²⁰⁶Pb/²³⁸U ratio of 0.318 (± 0.0939) and an age of 1780 (± 526) Ma. Despite the substantial uncertainty (~30% 2σ), this age displays no overlap with the crystallization age of the dyke swarm (2473 Ma; Heaman, 1997), but could reflect either impact (1850 Ma; Krogh et al., 1984) or Chieflakian metamorphism (1460 Ma; Corfu & Easton, 2001). A single isolated UO₂ cluster yields 44 ± 13 counts of ²³⁸U and 2 ± 3 counts of ²⁰⁶Pb, an associated ²⁰⁶Pb/²³⁸U ratio of 0.045 and a calculated age of 287 (± 415) Ma. An internal uncertainty on the order of ~145% 2σ reflects the low concentrations of lead within the domain. However, given a total of 9 raw counts of ²⁰⁶Pb (and an associated background of ~7 counts), it may be that a true count simply falls below detection limit at 103 Da.

<table>
<thead>
<tr>
<th>R60_147132</th>
<th>²³⁸U</th>
<th>²⁰⁶Pb</th>
<th>²⁰⁶/²³⁸</th>
<th>²⁰⁶/²³⁸ Age</th>
<th>2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>6499</td>
<td>2810</td>
<td>0.4324</td>
<td>2316</td>
<td>105</td>
</tr>
<tr>
<td>Plane</td>
<td>844</td>
<td>212</td>
<td>0.2514</td>
<td>1445</td>
<td>222</td>
</tr>
<tr>
<td>Bulk - Plane</td>
<td>5655</td>
<td>2598</td>
<td>0.4594</td>
<td>2436</td>
<td>127</td>
</tr>
<tr>
<td>Small (UO₂ Cluster)</td>
<td>44</td>
<td>2</td>
<td>0.0455</td>
<td>287</td>
<td>415</td>
</tr>
<tr>
<td>Curvi-Planar</td>
<td>190</td>
<td>60</td>
<td>0.3181</td>
<td>1780</td>
<td>526</td>
</tr>
</tbody>
</table>

**Table 5.5:** U and Pb counts for microtip #R60_147132. U and Pb ratios and ages for the bulk tip, the larger (upper) planar feature, the planar-corrected bulk tip, the small UO₂-bearing, and a sample curvi-planar feature are presented.

**Evolution of chemical nanostructures and chronostructures in shocked baddeleyite**

Decorated planar, curvi-planar and clustered features enriched in various elements (including U, Si, Ca and Fe) have not previously been reported for baddeleyite. Neither have the U-Pb ratios been measured at these length-scales. Here we present a first-order interpretation of how these features may have formed and their relationship to metamorphic processes. We discuss the features as belonging to two broad categories; chemical nanostructures (defined by atoms of trace elements) and chronostructures (as geometric domains or features defined by spatial relationships of both U and Pb atoms). In both cases, defects within the baddeleyite crystal lattice appear to be constraining the formation and evolution of these nm-scale structures. Understanding these structures and variations will be of vital importance when interpreting U-Pb ages for heterogeneous (i.e. shocked) materials.
Influence of crystal lattice defects on the formation of nanostructures

Solid crystalline substances are rarely stoichiometric; lattice vacancies, interstitial atoms and the substitution of cations and anions into lattice sites all represent point defects within an imperfect crystal (Langenhorst et al., 2013). Oxygen vacancies are most common within baddeleyite, though the quantity and density of these features increases following transition to high pressure and temperature phases (Fabris et al., 2002). These point defects can migrate when exposed to sufficient pressure and temperature conditions, forming dislocation features and strain fields within the lattice (Cordier, 2013) and encouraging nucleation of secondary precipitate phases which decorate the dislocation line (Amelinckx, 1958). During prolonged annealing, dislocation loops and half-loops can grow in-situ and combine together to form a single, larger defect, relaxing strain in the surrounding lattice (Sun et al., 2004). Such strain fields are commonly associated with regions of highly-concentrated solute atoms pulled in from the surrounding lattice, though the size of these enrichment zones vary based on a number of variables, including lattice diffusion rates and cation size (Cottrell, 1965). This effect has recently been reported in geological materials for the first time (Reddy et al., 2016).

Radiation damage has also been shown to dramatically alter the chemical structure of zircon (ZrSiO₄; Valley et al., 2014). Radiation damage induced networks of degraded crystallinity may act as diffusion pathways for larger cations, such as Pb, to escape the lattice (Ewing et al., 2003). Alternatively, α-decay may encourage the solid state diffusion of cations to grain boundaries or locally stabilized nanoclusters (Valley et al., 2014). However, baddeleyite is highly resistant to α-decay, self-annealing crystal lattice damage induced by high uranium domains (Lumpkin 1999). For a similar reason, the amorphisation of baddeleyite (i.e. metamictisation) has not been reported within igneous crystals; however, recent work has highlighted an abundance of poorly diffracting amorphous domains within highly shocked grains, including in the sample analysed by APT for this study (JD12SUD14; Darling et al., this volume).

Formation of baddeleyite nanostructures and chronostructures

Two types of Fe-enriched features are observed within highly shocked baddeleyite in the form of < 25 nm thick planar and 10 - 15 nm thick curvi-planar features enriched in Si, Al, Mg, Mn, U and Fe (i.e. Figure 5.4a & b) but showing no enrichment in U or Pb. Whilst the level of enrichment varies amongst these features (with Mn appearing absent from the smaller curvi-planar structures), both record a younger-than-crystallization U-Pb age (1445 ± 222 Ma for the planar structure and 1780 ± 526 Ma for the curvi-planar). In contrast, although the U enriched clusters appear to be completely age reset (287 ± 415 Ma), in truth they reflect the mobilization of U and Pb cations within the lattice and as such do not affect the bulk
(crystallization) age of the microtip (2436 ± 127 Ma).

**Formation of decorated planar deformation features**

Planar deformation features (PDF's) are common shock features within a number of mineral phases, including quartz (Grieve et al., 1996) and zircon (Moser et al., 2011). While these structures are often sub-micron, those observed here in baddeleyite are approximately ~25nm thick and contain nano-scale chemical heterogeneities in the form of distinguishable wave patterns defined by largely incompatible elements such as Fe, Mg, Mn, Al, Si and Ca (Figure 5.5). More compatible elements (Zr, O, U, Hf) and more mobile elements (Pb) display no variation along this plane. It is probable that these planes fall along the prevalent (100) cleavage plane of baddeleyite, though the absence of coupled EBSD data for the grain prevents exact correlation.

Given the composition and structure of the waves, we suggest these features formed either during the impact event (*syn-impact*) or during post-shock metamorphism (*post-impact*). In both scenarios, the planar feature itself was likely generated during shock metamorphism. (I) *Syn-impact*: Given the apparent absence of wave structures within unshocked ZrO$_2$ systems, the presence of these waves could potentially be explained by the increased velocity of the formative diffusion pathway. Solute cations (Fe, Mg, etc.) are transported along dislocation planes by becoming entrained in the energy wave. Above a critical velocity, the dislocation and solute become detached (Ruoff et al., 1963), resulting in the deposition of the entrained solute atoms within the lattice dislocation. As shock waves propagate through solid material, natural peaks and troughs of velocity will periodically entrain and deposit incompatible elements, forming stable localized features that retain the deposited cations even through post-impact annealing and diffusion. (II) *Post-impact*: Following formation of the PDF during impact, Si, Mg, Fe, Al and Mn enriched fluids were injected along the plane of weakness, where by a small amount of material was deposited within the plane. Given the absence of Si, Mg and Al within the baddeleyite lattice (Lumpkin et al., 2000), we suggest a post-impact origin for the waves, as it's unlikely mobilization of incompatible elements, even across a ~100nm wide lattice domain, could produce the required number of cations from a baddeleyite source alone. Given the calculated U-Pb age of the plane (1445 ± 222 Ma), it is likely these fluids were introduced during the Chieflakian orogeny (Corfu & Easton, 2001).
**Figure 5.5:** 2D distribution of Fe, ZrO₂, Pb and UO₂ atoms and compounds through the upper and lower planar features defined in Figures 5.2 and 5.3. Isolation of the planes using a rectangular region of interest (ROI) allows for nano-scale heterogeneities to be observed easily. In this case, incompatible elements such as Fe form wave structures across the planes, while compatible atoms and compounds, such as ZrO₂, remain homogenous. The wave structures appear to have minimal effect on the distribution of U-Pb systematics.

*Formation of curvi-planar features*

Curvi-planar structures are observed throughout the sample, though appear most prevalently in the upper ~100nm of the microtip. Towards the base of the tip, these structures appear to be offset by the larger planar features, appearing to ‘phase out’ in close proximity to the plane. It is likely these curvi-planar features reflect fracturing of the baddeleyite crystal immediately during the impact event prior to overprinting by planar structures. The observed trace element enrichment within these domains likely reflects the migration of atoms to these crystal defects during post-impact annealing. Fundamentally, these structures appear to mimic those observed in shock-metamorphosed zircon, which predate certain orientations ([1K2]) of planar feature and display bright cathodoluminescence (CL), suggesting trace element enrichment (Moser et al., 2011). Within the Vredefort zircon, decorated planar and curvi-planar lamella are shown to be enriched in various incompatible elements injected into the crystal by partial melting of the host lithology which are then trapped within amorphous (glassy) domains. Although partial-melt textures are not observed within our thin section (JD12SUD14), it is possible that greenschist-facies metamorphism has masked such features. It is more likely, however, that enriched fluids introduced during greenschist-facies metamorphism would induce a similar response. This process of injection and enrichment would account for the high levels of Si, Ca, Al and Fe within the nanoscale (curvi-) planar features observed here, where leaching of the
plagioclase, clinopyroxene and olivine-bearing doleritic protolith would produce a fluid of suitable composition.

Planar shock features in the mineral zircon are known to increase the surface area of the grain leaving them more vulnerable to non-impact Pb loss events (e.g. Krogh et al., 1984; Moser et al., 2011), and we interpret the planar and curvi-planar features in our sample to have witnessed a similar process. Following the formation of these structures, and the associated redistribution of incompatible cations in the defect-proximal lattice (i.e. Cottrell, 1965), diffusion must have either continued until, or been reactivated around, 1455 (± 300) Ma. Curvi-planar features appear to impact an age generated age of 1780 (± 526) Ma, though the large internal uncertainty may also associate this U-Pb age with that of a younger metamorphic overprint. Pipe diffusion has been commonly observed along single dislocations (Legros et al., 2008) and dislocation arrays (Piazolo et al., 2016), and it’s likely a similar diffusion mechanic explains the localized, continued Pb loss observed here. This process was likely driven further by hydrothermal interaction along planar and curvi-planar structures during greenschist-facies metamorphism. Given estimated temperatures of between 350 and 500°C during this event, diffusion must have occurred below the closure temperature of pristine ZrO₂, which is similar to that of zircon (> 900°C; Lee et al., 1997).

Formation of U-enriched clusters

Smaller (8 – 10 nm) clusters, composed of both incompatible (Fe, Y, Yb, Nb, Ta) and compatible (Zr, O, U, Hf) atoms, occur throughout the microtip specimen. These structures are particularly notable for their high enrichment of uranium relative to the bulk microtip (~9x enrichment) but near absence of lead (2 counts of 206Pb, 0 counts of 207Pb, and 3 counts of 208Pb). Given a total of 44 (± 13) counts of 238U, expected concentrations of 206Pb can be retroactively calculated. Assuming the structures formed during the Chieflakan orogeny (~1460 Ma; Corfu & Easton, 2001) roughly ~11 atoms of 206Pb would have formed. A formation age of ~1850 Ma (i.e. during the Sudbury impact event; Krogh et al., 1984) would yield ~15 atoms of 206Pb. The radioactive decay of crystallization-age structures (2473 Ma; Heaman, 1997) would have generated ~21 206Pb atoms. Instead, a 206Pb / 238U ratio of 0.0455 suggests a formation age of 287 (± 415) Ma. It is likely that, rather than reflecting continued lead loss to the present day, the true counts of Pb are so low that they are simply unresolvable using APT (i.e. falling below detection limit). This interpretation is strengthened by the apparent coupling of U and Pb enrichment observed in a 2D cross-section of the cluster (Figure 5.4c).

Given that U (~0.087nm ionic radius) will readily substitute for Zr⁴⁺ (0.084nm) within the baddeleyite lattice (Shannon, 1976), it is unlikely that these compatible cations will be

80
segregated into clusters and boundary defects immediately during the impact event, instead sitting conformably and homogeneously within the lattice to maintain a balanced charge state. However, given the wide range and scale of planar and curvi-planar features within the sample it is highly likely that sub-nm scale diffusion pathways will allow these atoms to migrate following impact. Given the prolonged post-shock heating experienced by this sample (800-1015 °C; James et al., 1992), we predict that these smaller domains reflect the solid-state diffusion of compatible (U) cations into local defects, forming lattice controlled regions of enrichment.

The absence of many elemental species observed in the planar and curvi-planar features, such as Si, Ca, Mg and Mn, suggest these atoms either migrated more readily through the lattice during post-shock heating (either to the (curvi-) planar features or out of the microtip completely) or were simply absent to begin with. Given the presence of Fe, a largely mobile cation, within the clusters, we assume that other species and compounds were simply absent in the ZrO$_2$ lattice to begin with. This observation strengthens the interpretation of enriched planar and curvi-planar features occurring during metamorphic interaction, rather than during the impact event itself.

**Implications on the U-Pb analysis of shocked geochronometers**

*Nanostructural geochronology*

By producing coupled chemical and structural datasets, atom probe tomography provides a unique opportunity to examine both the absolute and relative timings of structure formation and lead loss. Consideration of the cross-cutting relationships and radiometric U-Pb ages of the planar, curvi-planar and clustered nanostructures observed within microtip #147132 allows a schematic structural history to be generated for baddeleyite (Figure 5.6).

*Impact and post-impact annealing (1850 Ma)*

Curvi-planar features appear to be slightly offset by the larger planes (~5nm displacement), suggesting their formation prior to the planes. Given the assumed presence of sub-nm scale structures to facilitate the migration of U atoms into clusters, we speculate that lattice defects form in roughly size order; sub-nm defects near-instantaneously, ~10nm curviplanar features shortly after, and > 100nm long planar features during the final throws of decompression. Shortly after formation, most likely during impact melt sheet induced annealing, diffusion along these structures will have formed localized depletion zones (Cottrell fields) in immediate contact with planar and curvi-planar features while also encouraging lead loss. This period of prolonged heating likely also encouraged solid state diffusion of U cations into lattice defects, forming the clusters observed here. Neither U nor Pb were lost during this clustering process, instead moving within the bulk crystal and
maintaining a crystallization U-Pb age (2436 ± 127 Ma). At this time the bulk microtip preserved a crystallization age, while planar and curvi-planar features were likely reset to impact age.

*Chieflakian greenschist-facies metamorphism (1460 Ma)*

Fluid-driven greenschist-facies metamorphism (350 - 500°C) alone would be insufficient to reset the U-Pb age of the robust baddeleyite chronometer; however, the presence of shock-generated diffusion pathways facilitates localized Pb loss and age resetting. Fluids enriched in Si, Ca, Mg, Al and Fe by the surrounding dolerite are injected along planar and curvi-planar features, decorating them with an array of incompatible cations and removing radiogenic lead. On the larger planes, decorated waves are formed. The U-enriched clusters, situated in crystalline baddeleyite, are unaffected by this process, preserving a bulk crystallization age within the microtip. Planar and curvi-planar structures are variably reset, yielding U-Pb ages between impact (1780 ± 526 Ma; curvi-planar) and metamorphism (1445 ± 222 Ma). Minimal Cottrell field diffusion likely continued in proximity to the larger planar features, partially diffusing decorated curvi-planar structures that occur close to the plane. However, extensive lead loss did not occur, preserving either a magmatic or metamorphic age signature within the various nanostructures.

*Discerning chemical nanostructures and chronostructures*

Within the U-enriched nanoclusters, neither U nor Pb were lost during the annealing process, instead moving within the bulk crystal and maintaining a crystallization U-Pb age of 2436 (± 127) Ma. The only true loss of lead within the microtip has occurred through the planar and curvi-planar features that record either a variably reset series of ages between impact and metamorphism. Within all structures it appears that the formation of shock-induced defects and dislocations alone is insufficient to reset the U-Pb age. Instead, post-shock annealing or fluid / melt interaction actively encourages diffusion along the shock generated pathways. Along large planar and curvi-planar features this results in the complete loss of radiogenic lead, locally resetting the U-Pb ratio to that of the overprinting event. Smaller defects result in clusters of UO₂ and Pb mobilized from within the lattice, not dissimilar to those reported in annealed (but crucially, unshocked) zircon (Valley et al., 2014). Here we apply the term ‘chemical nanostructure’ to define these clusters, given they directly represent elemental movement within the crystal lattice to predetermined point defects but do not affect the bulk age of the sample. Diffusion pathways, such as the planar and curvi-planar features observed here and elsewhere within tectonically deformed zircon (Piazolo et al., 2016), record a younger age that does affect the grain as a reliable chronometer. Here we coin the term ‘chronostructure’ to highlight the significance of these structures not just on the nanostructure of the atom probe tip but on the age of the grain.
**Figure 5.6:** Schematic nanostructural evolution of highly shocked baddeleyite. For all features, nm-scale diffusion pathways are created by the impact event (1850 Ma; Krogh et al., 1984) before melt-sheet induced annealing facilitates solid diffusion within the grain. Enriched fluids introduced by the ~1450 Ma Chieflakian event (Corfu & Easton, 2001) decorate the (curvi-) planar features and reset the U-Pb age of the diffusion pathways. Clusters remain unaffected by this process, preserving a crystallization U-Pb age within the bulk tip.

**Generation of ‘partially reset’ U-Pb ages**

Within the single atom probe tip presented here (0.08μm diameter, 0.35μm length, ~0.00176μm³ area), a wide range of chronostructures are presented that record radiogenic ages < 1000 Ma younger than the bulk (corrected) microtip. In addition, numerous U-enriched clusters highlight the mobility potential of even relatively compatible atoms within a defect-rich (shocked) crystalline lattice. Recent small volume laser ablation work on baddeleyite has yielded encouraging results in unshocked terrestrial grains, although these new results suggest more care must be taken over shocked, heterogeneous grains. For example, 40 ablation bursts with a 10μm spot (7Hz, ~7 J/cm², 0.05μm/burst excavation rate) generate a total ablated volume on the order of 220μm³(Ibanez-Mejia et al., 2014). Although this is acceptable for homogenous grains, within the Sudbury grain examined here this ‘small volume’ approach would effectively homogenise ~125,000 complex atom probe tips into one dataset. With 110 bursts (600μm³), this is increased to 341,000 domains. In-situ SIMS analysis has also developed to a point that entire 3 x 3 μm baddeleyite grains can be consumed for analysis using a larger spot, although common lead can influence these data (i.e. Chamberlain et al., 2010). Assuming a depth on the order of ~1 μm, a total volume of ~9 μm³ will be integrated into the highest resolution of IN-SIMS analysis. Even on this scale, ~5115 individual atom probe pull-outs would become homogenised into a single data set. Given the increased influence of common lead (i.e. along grain boundaries, etc.), it is unlikely
that an IN-SIMS approach would be able to accurately differentiate crystallization and impact ages from a single baddeleyite crystal, instead yielding complex mixtures of discrete age reservoirs. Given recent observations into the variable age resetting of baddeleyite using SIMS analysis (i.e. Moser et al., 2013; Darling et al., 2016), it is likely that such variability is reflecting the abundance of chronostructures within the grain, as opposed to variable Pb loss within the whole grain driven by diffusion alone. If so, true impact and crystallization ages could be extracted from these complex sample sets with a coupled EBSD/APT approach. This is particularly important for highly valuable and irreplaceable materials, such as Apollo samples of the Lunar surface or rare basaltic achondrites, where destructive analysis of multiple grains is not possible.

Conclusions

Through the application of novel, atomic-scale techniques such as atom probe tomography, nano-scale heterogeneities in both structure and chemistry can be resolved. In the case of highly shocked material, such as the Sudbury baddeleyite, resolving these discrepancies can facilitate the accurate dating of crystallization (or impact) events. Within baddeleyite, shock-induced (curvi-) planar features act as diffusion pathways, mobilizing cations within a localized Cottrell field and resetting the primary igneous age of the grain. The structures appear to be readily reactivated during later-stage heating and metamorphism, inducing further lead loss within the domain. Solid-state diffusion of U and Pb atoms into clusters has not reset the bulk U-Pb age of the microtip. Therefore, we apply the terms ‘chronostructure’ to highlight those features that have isotopic compositions clearly distinct from the bulk radiogenic age, and ‘chemical nanostructure’ for those that do not. Going forward, the application of this technique to highly shocked planetary materials, such as Lunar and Martian meteorites, may act to resolve ongoing issues surrounding the formation age of these planetary bodies. Within baddeleyite, the formation of chemical nanostructures and chronostructures only observable at the nano scale may act to evidence a history of shock, despite thermal overprinting and the associated loss of coarser structures. In both cases, the application of atom probe tomography will greatly enhance our ability to pinpoint and date shocked and unshocked crystallographic domains, facilitating the reconstruction of shock and thermal histories within many precious materials.
COUPLING STRUCTURE AND U-Pb CHRONOLOGY IN BADDELEYITE

6.1 INTRODUCTION

Recent work has revealed that a predictable sequence of microstructural evolution exists within the shocked ZrO$_2$ system (see chapter 3), increasing the importance of baddeleyite as an impact barometer. Previous work highlighted the correlation of many of these structures with the extent of Pb loss on the whole grain scale (Darling et al. 2016), although this variability can be resolved using atom probe tomography (see chapters 4 & 5). These observations yield valuable new insights into the effects of shock metamorphism on the microstructure and U-Pb isotope systematics of baddeleyite.

This chapter acts to review these findings, further constraining the isotopic response of baddeleyite to shock metamorphism using a range of individual grains within shocked terrestrial (Sudbury) and extra-terrestrial (Lunar, Martian) materials. The manuscript represents the culmination of research and discussion carried out throughout the PhD, coupling a wide range of exciting new microstructural baddeleyite data with the established phase response of the ZrO$_2$ system to further constrain the shock response of baddeleyite. Most importantly, U-Pb data can be correlated with the microstructural state of the grain to provide exciting new insights into the isotopic response of this key phase during impact events. The details and results are presented in the following paper:

Darling, J. R., White, L. F., Moser, D., Barker, I., Tait, K. New insights into the shock microstructural evolution of baddeleyite and links with U-Pb geochronology. In review with AGU Monograph 'Microstructural Geochronology'

As second author, I conducted EBSD analysis on the shocked and unshocked terrestrial baddeleyite grains and developed many of the ideas regarding the correlation of microstructure and U-Pb data during this PhD study. As such, I have written large sections of the manuscript to reflect this input. Given my involvement with the development of ideas and drafting of the manuscript I have included it in its entirety within this chapter. This is followed by a discussion on the implications of this paper on the interpretation of shock-reset ages in mineral chronometers.
6.2 NEW INSIGHTS INTO THE SHOCK MICROSTRUCTURAL EVOLUTION OF BADDELEYITE AND LINKS WITH U–Pb GEOCHRONOLOGY

Darling, J. R.¹, White, L. F.¹, Moser, D.², Barker, I.², Tait, K.³

¹School of Earth and Environmental Sciences, University of Portsmouth, Portsmouth, PO1 3QL, UK
²Department of Earth Sciences, University of Western Ontario, London, N6A 5B7, Canada.
³Department of Natural History, Mineralogy, Royal Ontario Museum, Toronto, Ontario M5S 2C6, Canada

Baddeleyite (monoclinic zirconia) is a refractory mineral chronometer of great potential to date planetary processes due to its widespread occurrence in achondrites and robust U–Pb isotopic systematics. However, the understanding of shock-metamorphic effects on baddeleyite geochronology is in its infancy. To address this, here we present new microstructural data, including electron backscatter diffraction (EBSD) analyses, from baddeleyite grains in shock-metamorphosed Martian, Lunar and terrestrial samples. Our results highlight new shock-induced crystallographic phenomena that overprint primary igneous features such as twinning on {100} and {110}. These include extensive crystal plastic deformation, amorphisation, granularization and interlocking twins due to reversion from high pressure and temperature polymorphs, and allow a generalized shock microstructural evolution to be developed. Two factors are identified that control this evolution: the transformation to orthorhombic structure (o-ZrO₂; progressive from ca. 5 GPa upwards), and the temperature during shock-decompression or more prolonged heating. High-degrees of Pb-loss are restricted to grains/domains that have experienced both transformation to o-ZrO₂ and high post-shock temperatures, effects that can be recognized via EBSD analyses. Accordingly, linking microstructural data with in-situ isotopic analysis in baddeleyite can resolve the timing of both endogenic geological processes and impact events from individual shock-metamorphosed samples.

1. Introduction

The accurate dating of geological events recorded by planetary materials is very challenging. Although a wide-range of analytical approaches can produce highly-precise isotope ratio data from meteorites, returned Lunar samples and terrestrial impact structures, the interpretation of resultant dates is often complicated due to the effects of severe compression and heating that occurs during hypervelocity impact events: a fundamental geological process that modifies samples both on planetary bodies and during Earthward
launch. This "shock metamorphism" involves rapid (sub-second) loading to pressures up to many tens of GPa, and results in a wide-range of effects that can modify mineral and whole-rock isotope systems. These include phase transformations, deformation, pathways for chemical exchange, melting and even vaporization amongst constituent mineral phases e.g. (Sharp & de Carli 2006; Langenhorst & Deutsch 2012). Resolving these shock effects is not possible by geochemical methods in isolation (Borg et al. 2015), and hence an increasing number of studies are integrating detailed petrological, micro- to nano-structural, and geochemical analyses in order to improve accuracy in interpreting isotopic dates from shocked materials. The ultimate aim is to resolve both the timing of endogenic geological processes (igneous intrusion, crustal metamorphism etc) and the timing of impact from individual samples.

The dating of uranium-bearing accessory phases using in-situ analytical techniques has great potential to differentiate the timing of endogenic and impact events. This approach is widely considered to be less susceptible to disturbance than mineral separate and whole-rock isotopic dating techniques, which are also influenced by the presence of minor phases (e.g. phosphate inclusions), terrestrial or planetary contamination, or preferential leaching during acid washing (Borg et al. 2015). Considerable recent effort has been placed on understanding the shock metamorphic response of accessory minerals for this reason, with a number of studies combining information on the internal structural response to shock metamorphism with in-situ U-(Th)-Pb geochronology of zircon (Moser et al. 2011; Krogh et al. 1996; Grange et al. 2013; Cavosie et al. 2015; Erickson et al. 2013), monazite (Erickson et al. 2013) and baddeleyite (Moser et al. 2013; Darling et al. 2016). This progress has been made possible by continuing analytical advancements in the ability to characterize the structure of materials at the nano-scale, particularly by electron backscatter diffraction (EBSD: e.g. (Schwartz et al. 2009; Qian et al. 2015)) and transmission electron microscopy (TEM; e.g. (Lee 2010)), as well as improved spatial resolution and precision from in-situ measurement of U-Th-Pb isotopes by secondary ion mass spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). In combination, these approaches offer the potential to elucidate linkages between impact induced deformation microstructures and isotopic disturbance.

Of the U-bearing accessory mineral chronometers, baddeleyite (monoclinic zirconia; \( m\)-ZrO\(_2\)) is by far the most widespread in meteorites, although understanding of how it responds to shock events is in its infancy compared with zircon. In this study, we review recent developments into the response of baddeleyite to shock metamorphism and present new microstructural data for shocked grains in Martian, Lunar and terrestrial samples. The overall aim is to document the shock microstructural evolution for this important phase, and how this process influences U-Pb isotope systematics.
1.1 Baddeleyite as a planetary chronometer

Baddeleyite is a highly valuable tool for the dating of mafic igneous rocks using U-Pb isotope methods (Heaman 2009; Chamberlain et al. 2010; Ibanez-Mejia et al. 2014). It shares many of the desirable properties for dating with its silica-enriched cousin zircon (tetragonal ZrSiO$_4$), which is the benchmark chronometer of geological time on Earth. These include taking up significant quantities of uranium (up to thousands of ppm), largely excluding initial common-lead, and having very low volume diffusion rates for both uranium and lead (Heaman 2009), making it very resistant to lead-loss during crustal and weathering processes. In contrast to zircon, baddeleyite occurs in silica-undersaturated lithologies that do not typically crystallize zircon or other minerals suitable for dating. This fact has led to a diverse range of applications of baddeleyite geochronology in Earth science, including the dating of dyke swarms, volcanic rocks and layered intrusions (Kumar et al. 2014; Rioux et al. 2010; Wu et al. 2015; Schmitt et al. 2010; Heaman 2009; Chamberlain et al. 2010; Ibanez-Mejia et al. 2014).

It is recognized that baddeleyite has potential to be an excellent chronometer for planetary processes. It is one of the earliest minerals to have formed in the Solar System (e.g. (Hazen et al. 2008)), and has been found as a micro-scale accessory phase in a wide-array of planetary materials (i.e. chapter 2). These include basaltic Martian meteorites (shergottites; (Jiang & Hsu 2012; Niihara 2011; Zhou et al. 2013; Moser et al. 2013)), Lunar meteorites e.g. (Day et al. 2006; Arai et al. 2010; Wang et al. 2012), asteroidal achondrites (Delaney et al. 1984) and ordinary chondrites (Krot et al. 1993). Although relatively common, the small size (typically ≤10–40 um long by a few um wide) of the baddeleyite crystals within these materials has presented a major analytical challenge for geochronology. Recent developments in micro-analytical techniques have opened up tremendous opportunities to date these samples using in-situ approaches to U-Pb isotope ratio measurement by SIMS (Chamberlain et al. 2010; Schmitt et al. 2010)) and LA-ICP-MS (Ibanez-Mejia et al. 2014). For example, a number of studies have presented SIMS U-Pb isotope data for micro-baddeleyite grains in shergottites, including Roberts Massif 04261 (ca. 200 Ma; (Niihara 2011)), Grove Mountains 020090 (192 ± 10 Ma; (Jiang & Hsu 2012)), Northwest Africa 5298 (187 ± 33 Ma, (Moser et al. 2013)), and Zagami (187 ± 6.9 Ma; (Zhou et al. 2013)).

2. Shock metamorphism of baddeleyite – progress and challenges

2.1 Crystal structure and phase relations of baddeleyite (m-ZrO$_2$)

The crystal structure of ZrO$_2$ at a wide range of pressure-temperature conditions is an issue of high importance to the material sciences, largely due to its widespread use in industrial ceramics. Accordingly, a large number of studies have reported phase data for ZrO$_2$,
at conditions ranging from 0 to >100 GPa and 0 to >3000 °C. It is well known that zirconia has a monoclinic symmetry space group \((P2_1/c)\) at pressures below \(\sim 5\) GPa and temperatures below \(\sim 1200\) °C (Smith & Newkirk 1965; McCullough & Trueblood 1959). Terrestrial \(m\)-ZrO\(_2\) also has near-ubiquitous twinning on \{100\} and \{110\}, both of which can be polysynthetic, and less common twin-boundaries on \{001\} and \{011\} (Bischoff & Ruehle 1983; First & Heuer 1993; Wang et al. 1997; Smith & Newkirk 1965). When exposed to high temperature conditions, distortion of this monoclinic structure occurs through a succession of martensitic phase shifts to tetragonal \((t\text{-}ZrO_2; >1200\) °C at ambient pressure\) and cubic \((c\text{-}ZrO_2; >2400\) °C\) forms (Subbarao et al. 1974). High-pressure conditions (above \(\sim 5\) GPa) likewise encourage a reconfiguration of the ZrO\(_2\) lattice, via displasive transformations to a series of orthorhombic and tetragonal structures with increasing pressure (Kudoh et al. 1986; Arashi et al. 1990; Dewhurst & Lowther 1998) (Figure 6.1). These shifts result from the re-coordination of the zircon-oxygen covalent bond, which favors the seven-fold symmetry of the monoclinic form (Kisi & Howard 1998). As such, the high pressure and temperature polymorphs are metastable in experimental studies (Arashi & Ishigame 1982; Kudoh et al. 1986), and have not been observed in nature. This presents problems when examining the \textit{in-situ} micro-structure of crystalline zirconia as any polymorphs generated by geological/impact activity will readily revert to their stable monoclinic coordination, even at ambient conditions (Ohtaka et al. 1991; Subbarao et al. 1974). Although a great deal of work has been conducted on crystallographic structures and twin planes in \(m\)-ZrO\(_2\) generated by quenching of artificially produced high temperature zirconia polymorphs (Hannink et al. 2000), the phase response in natural lithologies (from \(t\text{-}ZrO_2\), \(c\text{-}ZrO_2\) and \(a\text{-}ZrO_2\)) has never been examined.

---

**Figure 6.1.** Generalized phase diagram for ZrO\(_2\). \(m\), monoclinic \((P2_1/c)\); \(o\text{-}i\), orthorhombic \((Pbca)\); \(o\text{-}ii\), orthorhombic \((Pnam)\); \(t\), tetragonal \((P4_2/nmc)\); \(t\text{-}ii\), tetragonal \((P4_2/nmm)\); \(c\), cubic. Modified from data reported in (Leger et al. 1993; Kisi & Howard 1998; Kudoh et al. 1986; Ohtaka et al. 1991; Subbarao et al. 1974; Arashi et al. 1990).
2.2 Experimental shock metamorphism of zirconia

Experimental constraints on the shock-wave properties, or Hugoniot parameters (shock velocity, particle velocity, stress etc.), of zirconia have been determined for sintered polycrystal (Marsh 1980) and twinned baddeleyite \((m\text{-ZrO}_2)\) crystals (Mashimo et al. 1983). Two-stage light gas gun experiments from 5 to 150 GPa provide a number of important constraints on the shock response (Mashimo et al. 1983), including that: (a) baddeleyite is relatively compressible, with a significantly lower bulk modulus (149 GPa) than zircon (227-234 GPa; (Finch & Hanchar 2003); 203 ± 13 GPa, (Morosova et al. 2017)); (b) its shear strength is relatively weak at lower shock pressures; (c) shock induced temperature rises are significantly lower than in zircon, with an estimated increase of <700 K at 50 GPa (Mashimo et al. 1983). Furthermore it has been shown that transitions to high pressure polymorphs in zirconia are gradual up to particle velocities of 2 kms\(^{-1}\) (ca. 70 GPa), as evidenced by a lack of a distinct kink in plots of shock velocity \((U_s)\) versus particle velocity \((U_p)\) (Mashimo et al. 1983). This is consistent with the observation that the elastic behavior during shock-loading and acoustic pulse testing is highly anisotropic (Morosin et al. 1988; Ingel & Lewis 1988). For example, yttria-doped zirconia crystals have minimum Young's modulus \((E)\) directions in \(<111>\) \((E \approx 170\text{ GPa})\) ca. and maximum in \(<100>\) \((E \approx 360\text{ GPa})\) (Ingel & Lewis 1988).

Shock experiments have also been undertaken on baddeleyite powders at shock pressures up to 27 GPa. These experiments demonstrate that the phase undergoes extensive crystal plastic deformation, decreases in crystallite size and increases in residual strain with increasing shock pressure (Hellmann et al. 1983; Morosin et al. 1988). The resultant defects also enhance the reactivity of particles to low temperature recrystallization, including during electron beam imaging (Hellmann et al. 1983).

Experimental shock-loading of natural baddeleyite grains up to 57 GPa by Niihara et al (2012) showed a very restricted range of shock-microstructural responses. These were limited to fracturing, Raman peak shifts of 2-4 cm\(^{-1}\) in grains from higher pressure experiments (34-57 GPa) and an increase of CL emission at higher shock-pressures. These effects were attributed to micro cracking during shock-loading. Importantly, no high pressure \(o\text{-ZrO}_2\) or \(tii\text{-ZrO}_2\) polymorphs were preserved in the experimentally shocked material, reflecting either that the very short pulse durations of experiments do not allow for the transition, or that very rapid reversion to \(m\text{-ZrO}_2\) occurred. Furthermore, these authors undertook post-shock annealing experiments, and found that baddeleyites shocked at 57 GPa and annealed at 1000 °C did not lose radiogenic lead completely. This evidence was used to conclude that shock metamorphism does not significantly affect the U-Pb systematics of baddeleyite, supporting the notion that baddeleyite ages measured in Martian and Lunar meteorites provide robust magmatic crystallization ages (Niihara 2011; Zhou et al. 2013; Wang et al. 2012).
**2.3 Naturally shocked zirconia**

In stark contrast to experimental studies, recent investigations of naturally shocked baddeleyite have shown that shock metamorphism can lead to variable Pb-loss and hence disturbance of the U-Pb system (Moser et al. 2013; Darling et al. 2016). This work has focused upon Martian meteorite NWA 5298, a highly-shocked basaltic shergottite. Moser et al., (2013) demonstrate that baddeleyite grains in the sample have degraded crystallinity due to shock-metamorphism, leading to partial disturbance of U-Pb isotopic dates. These authors measured a spread of $^{206}\text{Pb}/^{238}\text{U}$ dates from baddeleyite grains in a single thin section, ranging from approximately 200 to 20 Ma, and concluded that shock metamorphism caused by the launch event resulted in minor to approximately 80% loss of radiogenic Pb from the target grains.

Detailed electron backscattered diffraction (EBSD) and transmission electron microscope (TEM) analysis of NWA 5298 by Darling et al. (2016) revealed a range of new shock-microstructural phenomena in baddeleyite (Figure 6.2). They found that microstructures are highly variable on spatial scales down to tens of nanometers, with analyzed grains ranging from those that preserve primary (magmatic) twinning and zonation (baddeleyite shock Group 1), to quasi-amorphous ZrO$_2$ (Group 2) and to recrystallized granular domains of $m$-ZrO$_2$ (Group 3). The latter resemble nanocrystalline domains previously reported in a TEM study of shergottite NWA 3171 (Herd et al. 2010). These microto nano-structural states correlate closely with previously measured U-Pb ages of Moser et al. (2013), demonstrating that shock deformation during launch, and consequent heating and melting reactions, led to variable degrees of Pb loss. Furthermore, the authors conclude that the observed microstructural variability can be explained by a systematic microstructural evolution resulting from a single shock-metamorphic cycle (Figure 2). This includes plastic deformation and amorphization of precursor magmatic $m$-ZrO$_2$ caused by shock deformation and phase transformations, followed by recrystallization and zircon-rim growth driven by post-shock heating. Importantly, these findings reveal that the identification of $m$-ZrO$_2$ (and lack of HP polymorphs) is not sufficient to demonstrate a low degree of shock disturbance of target grains. The transformation of $m$-ZrO$_2$ to $o$-ZrO$_2$ occurs at relatively modest pressures (ca. 5 GPa; (Kudoh et al. 1986)), but this polymorph is known to be unquenchable in both static and shock experiments and will readily revert to $m$-ZrO$_2$. However, the recent studies detailed above provide evidence that these transitions result in characteristic internal microstructures that are distinct from the original magmatic grains, and can be identified by techniques such as EBSD. This provides a new framework to interpret the shock-state of baddeleyite grains in planetary materials. However, the findings of Darling et al. (2016) may not reflect the full range of possible shock-microstructures since the observations are based upon a single, highly shocked, sample (>29 GPa; Darling et al., 2016).
### Chemical microstructure (e.g. CL)
- **Baddeleyite shock Group 1**: Smooth SE + BSE. Oscillatory or planar CL textures.
- **Baddeleyite shock Group 2**: Smooth SE + BSE. Oscillatory or planar CL textures.
- **Baddeleyite shock Group 3**: Granular SE + BSE. Patchy or cloudy CL.

### Orientation microstructure (EBSD/STEM)
- **Baddeleyite shock Group 1**: Crystalline, polysynthetic (110) twins. Crystal-plastic deformation (~8°). Degraded crystallinity in some twins.
- **Baddeleyite shock Group 2**: Highly degraded crystallinity, with nanocrystalline structures. Quasi-amorphous at EBSD lengthscales (tens nm).
- **Baddeleyite shock Group 3**: Hundreds of nm to μm scale granular crystallites with no discernable preferred orientation.

---

**Figure 6.2.** Baddeleyite shock microstructural groupings in Shergottite NWA 5298, ranging from preserved polysynthetic twinning (Group 1) to amorphization (Group 2) and granularization (Group 3). Observed chemical microstructures are represented by schematic cathodoluminescence (CL) textures. See text for detailed description. Modified from Darling et al. (2016).

---

### 3. Materials and Methods

#### 3.1 Baddeleyite from the Earth, Moon and Mars

To further investigate the range of shock-microstructures that occur in baddeleyite, we present data from two unshocked terrestrial igneous rocks and thin-sections of three shock-metamorphosed rocks. The shocked samples span a wide-range of shock and post-shock pressure-temperature conditions, and include new analysis of shergottite data reported by Darling et al. (2016) along with new microstructural data collected from Lunar and terrestrial samples.
3.1.1 Unshocked terrestrial igneous rocks

The 2.06 Ga Phalaborwa complex, South Africa, is a composite intrusion of cumulate clinopyroxenites that was emplaced during multiple injections of carbonatite magma (Heaman 2009). Baddeleyite occurs as large (< 3cm longest axis), elongate, euhedral grains in close association with apatite, and is widely distributed between laboratories as a U-Pb isotope reference material (Heaman 2009). Here we report on the microstructure of smaller fragments (ca. 1 mm in longest axis) previously mounted for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS analyses).

The Anna's Rust intrusion from the Kaapvaal Craton, South Africa, consists of a high-Ti gabbro sheet emplaced in the Vredort Dome area (after the Vredefort impact event; Reimold et al. 2000)). The gabbro contains baddeleyite that has been dated by single-crystal U-Pb isotope techniques at 1108.6 ± 1.2 Ma (Hanson et al. 2004), and the studied thin-section contains over twenty baddeleyite grains ranging from 66 to 437μm² exposed surface area.

3.1.2 Martian meteorite Northwest Africa 5298

NWA 5298 is an unbrecciated, evolved basaltic shergottite with a primary phaneritic igneous texture (Irving et al. 2011). Apart from its relatively oxidized state, being close to the QFM buffer, it is chemically similar to other basaltic shergottites including Shergotty, Zagami and Los Angeles (Hui et al. 2011). The meteorite is predominantly comprised of zoned clinopyroxene and shocked plagioclase, along with phosphates, Fe-Ti oxides, silica and mesostasis. It is highly-shocked, and contains a wide and pervasive array of shock-metamorphic features. These include pockets of impact melt up to 3 mm in diameter, highly fractured clinopyroxene grains exhibiting sub-parallel sets of irregularly-spaced fractures, and pervasive transformation of plagioclase to maskelynite or vesicular plagioclase melt (Hui et al. 2011; Darling et al. 2016). Pervasive shock transformation of plagioclase in NWA 5298 (An40-55; (Hui et al. 2011; Darling et al. 2016)) to maskelynite in this sample suggests a bulk shock pressure of at least 29 GPa (Stöffler et al. 1986)

A thin-section of this material, accession number M53387 from the Royal Ontario Museum collection, is currently the best studied sample in the Solar System regarding shock effects on baddeleyite. Over 220 ZrO₂ grains with surface exposure areas greater than 17 μm² have been reported in this thin-section, which occur in several settings: (a) clinopyroxene-maskeleyne grain boundaries, (b) enclosed within maskelynite, (c) enclosed within clinopyroxene and pyrox-ferroite breakdown assemblages, (d) Fe–Ti-oxide-maskeleyne or Fe–Ti-oxide-clinopyroxene grain boundaries, (e) partially or fully enclosed within mesostasis; (f) partially or fully enclosed within impact melt pockets, and (g) a component of polyphase inclusions within phosphates (Darling et al. 2016). These grains have a range of shock-microstructures, including those that preserve primary (magmatic) twinning and
zation (baddeleyite shock Group 1), to quasi-amorphous ZrO₂ (Group 2) and to recrystallized granular domains of m-ZrO₂ (Group 3) (Darling et al. 2016).

3.1.3 Lunar meteorite Northwest Africa (NWA) 2200

NWA 2200 is a polymict glassy impact-melt breccia with chemical and petrological affinity to ferroan anorthosites (Kuehner et al. 2005). The rock consists of a diverse mixture of lithic clasts, mineral fragments, and impact glass spherules within a dark glassy matrix. Lithic and glassy clasts include ferroan anorthositic granulitic breccias, poikiloblastic granulitic breccia, glassy melt breccia and impact glass spherules (Nagaoka et al. 2008).

We have studied a polished thick-section of this meteorite, accession number M53389 from the Royal Ontario Museum, and have identified 35 ZrO₂ grains in the section, with surface exposure areas ranging from 30 to 233 µm². These occur predominantly as isolated mineral fragments within the glassy matrix, and occasionally within sub-millimeter scale lithic clasts. The latter include ZrO₂ grains within clinopyroxene clasts that are tens to hundreds of microns wide and a single grain within a ca. 300 micron wide gabbroic clast (plagioclase and pyroxene).

3.1.4 Diabase from the Sudbury impact structure (JD12SUD14)

Sample JD12SUD14 was collected from a Palaeoproterozoic diabase dyke within the target rocks of the 1.85 Ga Sudbury impact structure, Ontario (Krogh et al. 1982). The sampling location was ca. 550 m from the base of the Sudbury impact melt sheet, within rocks that experienced shock pressures >10 GPa (Dressler 1984) and post-shock temperatures likely over 800ºC (James et al. 1992). The sample retains relict igneous textures, but the main petrological features reflect post-impact greenschist facies metamorphism, with widespread chloritization of amphiboles and pyroxenes. Over 100 ZrO₂ grains have been identified in the section, with surface areas ranging from 15 to 330 µm². These most commonly have bladed, inclusion-free forms in BSE imaging, although some grains have been variably replaced by late-stage zircon growth that is irregular and patchy in appearance.

3.2 Electron microscopy and electron backscattered diffraction methodology

Electron nanobeam analyses were performed at the Zircon and Accessory Phase Laboratory (ZAPLab), University of Western Ontario, using a Hitachi SU6600 FEG-SEM. The sample was vibratory polished (Buehler VibroMet 2) using a 0.05 µm alumina suspension (pH ≅ 7) and carbon coated. ZrO₂ grains were located using an Oxford Instruments X-Max 80 mm² silicon drift detector with INCA Energy software. Automated location utilized the 'Feature' module of INCA Energy, combining BSE intensity and EDS spectrum. Secondary electron (SE), backscatter electron (BSE) and colour cathodoluminescence (CL; Gatan...
ChromaCL detector) imaging of target grains was undertaken according to protocols described by Moser et al. (2011).

EBSD analyses on NWA 2200 and JD12SUD14 were also performed at the ZAPLab, using the same electron microscope coupled with an Oxford Instruments Nordlys EBSD detector. Procedures followed those documented previously (Darling et al. 2016; Moser et al. 2011). The samples were tilted to 70° and a 20 kV, 8.0 nA electron beam was used to generate EBSD "maps", consisting of an orthogonal grid of electron backscatter diffraction patterns (EBSPs) acquired at step-sizes ranging from 50 to 150 nm. The data were processed using HKL Channel 5 software, and the only post-analysis noise reduction processing performed was to replace 'wild-spikes' (interpreted as isolated, erroneously-indexed pixels) with a zero solution.

4. Electron backscattered diffraction (EBSD) data

All regions of zirconia that diffract well index as the monoclinic structure, highlighting an absence of observable t-, c- or o-ZrO₂ at the length scales of our EBSD analyses (ca. 40 nm diameter and 80 nm depth).

4.1 Unshocked terrestrial igneous rocks

All of the analysed grains in the Phalaborwa and Anna’s Rust samples diffract strongly, reflecting their crystalline nature and lack of radiation damage (metamictization), which is consistent with the known high-resistance of ZrO₂ to α-decay (Lumpkin 1999). No resolvable crystal plastic deformation of the grains has been detected, with cumulative misorientations within the ~0.5° angular detection limit of the analytical setup (Moser et al. 2011).

Three crystal fragments of Phalaborwa baddeleyite were analysed (Figure 6.3), and all display polysynthetic twinning across the length of the crystal, with individual twins varying from 2 to 400 μm in thickness. The twin domains have a common {110} orientation and a 90° rotation in {100} compared to the master crystal ({110} twins). Such polysynthetic twinning is very common in magmatic baddeleyite, and has been widely reported from other localities.

Of the three Anna’s Rust gabbro grains chosen for EBSD analysis, two have a simple twin orientated parallel to the c-axis. The twin domain has common {100} and {110} orientations and a 90° rotation in {102} compared to the master crystal, and an angle between {001} planes of ca. 18°. This is consistent with common {100} twinning in baddeleyite, given the structures β angle of 99.23°. The smallest analysed grain (103 μm² in exposed area) is untwinned.
Figure 6.3. Microstructural data for selected baddeleyite grains in unshocked terrestrial igneous rocks, with backscatter electron (BSE) or secondary electron (SE) images of each grain. Texture component maps display cumulative misorientation as a sum of euler angles relative to reference pixels (white crosses), and all have the same scale. Pole figures display poles to crystallographic planes in a lower hemisphere equal-area projection, contoured with a half-width of 10° and cluster size of 5°. EBSD step size is 300 nm (Phalaborwa) and 150 nm (Anna’s Rust).

4.2 Martian meteorite Northwest Africa (NWA) 5298

New analysis of EBSD data presented by Darling et al. (2016) has revealed a number of important additional intra-crystal microstructural features within grains from each of the three shock-microstructural groupings that these authors identified (Figure 2). A key feature of the zirconia grains in this sample is the high spatial variability of intra-crystalline lattice order, expressed by its band contrast (BC), a quality factor describing the average intensity of the Kikuchi bands with respect to the overall intensity within the Electron Backscatter Pattern (EBSP). For each of the grains shown in Figure 6.4, the BC values in some domains are as low as surrounding plagioclase-composition glass (maskelynite or plagioclase melt), reflecting very low order at the length scales of EBSD analysis. The areas of higher BC (brighter) occur in two distinct microstructural states: (a) irregular domains with simple or polysynthetic twinning or (b) sets of granular subgrains without discernible twinning. These microstructural states correspond generally with least and most Pb-loss experienced during a shock event, in this case ejection from Mars. Three examples in this range are described below.

Primary ‘igneous type’ twins are prevalent in grains from Shock Group 1 of Darling et al., (2016), which have the oldest measured $^{206}\text{Pb}/^{238}\text{U}$ ages in the sample. In grain F2451, the highest band contrast domains form a series of bands that all have a similar crystallographic orientation. Where they diffract well enough to be indexed, the domains in between these
bands have cumulative misorientations of either a ∼45° or ∼90° relative to the master crystal (Figure 6.4a). Twin, has a 90. rotation in {100}, {001} and {110}, and 65° in {111}, whereas Twin, has a common {010} with the master crystal and a 65° rotation in {110}, consistent with {010} twins. Other pixels (red on the texture component map; Fig 6.4a) have a {110} twin relationship with the master crystal. Within grain F1983, polysynthetic twinning occurs in grain environments with high band contrast values. These twins have an angle-axis pair of 90° about {110} axis, with other domains consistent with {100} swallowtail twins (Figure 6.4b).

The transition from primary ‘igneous’ twins to overprinting by granular baddeleyite (Shock Group 3; Figure 2) is exhibited by grain F2. The tip of this grain (Domain 1) has lower BC and two distinct crystallographic orientations, reflecting a twin with an angle-axis pair of 90° about {110}. Misorientation maps and the slight asterism of individual twins on pole-figures reflect up to 7° of crystal plastic deformation (CPD) within this twinned domain, that is typical of Shock Group 1. However, it consists mostly of sub-micron scale granular subgrains with no clear preferred orientation (Figure 6.4c; Domain 2). An example of a completed transition to Shock Stage 3 textures is seen in grain F2158. It is completely transformed to submicron domains of m-ZrO$_2$ separated by high angle grain boundaries (Figure 4D). Importantly, the granular domains of F2 and F2158 are seemingly undeformed, with maximum misorientation within individual domains of ∼1°, close to angular detection limits. This, along with the higher degrees of lattice order (BC) within the granular domains, and the fact that these grains have the youngest $^{206}$Pb/$^{238}$U ages in the sample, supports that they are a product of recrystallization.

4.3 Lunar meteorite Northwest Africa (NWA) 2200

The three analyzed zirconia grains are significantly different to any reported in NWA 5298. They tend to diffract well, with band contrast values amongst the highest relative to all phases in the meteorite. A striking feature of these datasets is the prevalence of crystal plastic deformation in all grains.

4.3.1. Grain F5337

This ca. 4 by 8 micron grain has relatively homogeneous BSE and CL texture, but the EBSD dataset shows significant complexity (Figure 6.5). The band contrast (BC) values are generally high, but with curvilinear domains of lower values, including nano-domains with similar BC values to the glassy matrix. There are two striking features within the EBSD dataset, highlighted by the texture component maps and pole figures: twin domains and a high degree of CPD. The principal twin occurs as 1 to 2 micrometers wide domain that is sub-parallel to the long axis of the crystal, and has a common {110} orientation and a 90° rotation
in \{100\} compared to the master crystal; consistent with commonly occurring \{110\} twin planes in baddeleyite. Other smaller domains also have orientations consistent with twinning, such as, a ca. 2 micron wide domain near the bottom of the main grain has common \{100\} planes with the master crystal. The second striking feature is the very high degree of CPD in the grain, with up to 12° of misorientation in single domains relative to a reference pixel in TC maps and significant smearing of maxima on pole figures. This occurs in both twin domains and the master crystal, and explains the curved appearance of the exposed ‘twisted’ twins due to bending of the c-axis of the master grain.

**Figure 6.4.** Microstructural data for selected zirconia grains in Martian shergottite NWA 5298. Data reprocessed from Darling et al (2016), with each grain shown at the same scale. Texture component maps display cumulative misorientation as a sum of euler angles relative to reference pixels (white crosses), and all have the same scale. Pole figures display poles to crystallographic planes in a lower hemisphere equal-area projection, contoured with a half-width of 10° and cluster size of 5°. EBSD step sizes are 100 nm (A, D), 70 nm (B), 50 nm (C).
4.3.2 Grain F15974

Like F5337, this grain has homogeneous BSE and CL textures, but exhibits two types of crystallographic alteration. The largest area of the grain is a single crystal that has experienced pervasive CPD with 15° of cumulative misorientation (Figure 6.5b). One end of the grain has lower values of band contrast, and some nano-scale domains that diffract as poorly as the glassy matrix, reflecting significantly lower degrees of crystallographic order. This variability in BC is matched in euler angle and texture component (TC) maps, revealing a set of domains that contrast with a broadly consistent crystallographic orientation contained within the majority of the grain. However, unlike the granular subgrains in baddeleyite from NWA5298, these domains show ordered point maxima on pole figures. Two of these domains (orange and green in texture component map in Figure 6.5b) are consistent with {100} and {110} twin laws, and have high levels of cumulative misorientation (<8°) that is similar to the majority of the grain (15° cumulative misorientation). In contrast, two domains (reds in texture component map) have much lower degrees of crystal plastic deformation (misorientation <2°) and crystallographic orientations that are entirely distinct from the other domains (no overlapping planes).

4.3.3 Grain F6104

This small, ca. 2 by 3 micron, grain has relatively high band contrast values compared too other baddeleyites in the sample, demonstrating a high degree of crystallographic order. Similar to F5337 and F15974, it shows evidence for significant CPD, with 6° of cumulative misorientation relative to a reference pixel. The grain also has an irregular domain aligned sub-parallel to the c-axis, with aligned {010} and {111}, and 95 to 100° rotation in {001} and {100}. 


**Figure 6.5.** Microstructural data for selected baddeleyite grains in Lunar breccia NWA 2200, highlighting extensive crystal plastic deformation. The pole figures display poles to crystallographic planes in a lower hemisphere equal-area projection, with coloring according to the 100º scale texture component maps. EBSD step sizes are 75 nm (A) and 60 nm (B).

### 4.4 Terrestrial diabase from the Sudbury impact structure (JD12SUD14)

The studied grains from this sample have somewhat patchy BSE textures, with a higher proportion of inclusions and thicker zircon rims than grains from NWA 5298 or NWA 2200. These grains have complex internal microstructures, as revealed by band contrast and texture component maps (Figure 6.6). These bladed grains are comprised of a number of m-ZrO₂ domains with highly variable band contrast (BC) values. In both grain F5099 (Figure 6A) and F11071 (Figure 6.6b), elongated domains of higher BC values are separated by micro- to nano-scale veins with very low BC values. The better-diffracting domains have three distinct sets of microstructural characteristics: (1) a highly deformed master crystal that has undergone extensive crystal plastic deformation (<15º cumulative misorientation) and in some cases preserves twisted {100} twins; (2) subgrains with much lower cumulative misorientation (<2º) that occur at grain margins, and have variable orientations that do not reflect common monoclinic twin laws (e.g. F11071; Figure 6.6b); (3) a series of highly irregular subgrains with low degrees of misorientation (<2º) that occur penetratively throughout the grain. In both F5099 and F11071, the latter penetrative subgrains occur with common {100} and {011} orientations to the master crystal, with 90º rotation in {110} and {001} (Figure 6.6a). As such, these domains represent twins, but their lack of crystal plastic deformation and highly irregular nature indicates a significant difference in origin to twisted primary twins in NWA 5298 and NWA 2200.
5. Diversity of shock microstructures in baddeleyite

Our new data expands the range of known shock microstructures in naturally shocked baddeleyite. No direct observations of high-pressure α-ZrO₂ polymorphs have been made, likely reflecting their instability and rapid reversion to m-ZrO₂ (Subbarao et al. 1974; Ohtaka et al. 1991). However, the studied grains in the shocked samples record several distinct sets of microstructures. Previous studies have demonstrated that these include degraded crystallinity (amorphization) and granularization (Moser et al. 2013; Darling et al. 2016), and our new data reveal extensive crystal plastic deformation and the growth of irregular interlocking twins. Furthermore, the new data provide important insights into the conditions of formation and preservation of these microstructures.

5.1 Crystal plastic deformation

Crystal plastic deformation occurs in baddeleyite from all three samples. Extensively deformed m-ZrO₂ occurs in three categories: (1) grains that preserve simple or polysynthetic twins, such as the three grains in NWA 2200; (2) domains with simple or polysynthetic twinning surrounded by quasi-amorphous zirconia, such as F1983 in NWA 5298; (3) domains...
with simple or polysynthetic twinning surrounded by untwinned \( m \)-ZrO\(_2\) with low degrees of deformation, such as in JD12SUD14. In all cases, the domains with extensive crystal plastic deformation are the only regions to preserve detectable micro-scale twinning, which is near-ubiquitous in magmatic and synthetic \( m \)-ZrO\(_2\) (Smith & Newkirk 1965; Bischoff & Ruehle 1983; First & Heuer 1993).

### 5.2 Amorphisation

Varying degrees of amorphisation are preserved in the analysed grains from all samples. The abundance of zirconia that is quasi-amorphous at the length scales of EBSD analysis (ca. 40 to 80 nm) is highest in NWA 5298, which is the most highly shocked of the studied samples, and lowest in NWA 2200. This is considered a direct response to successive transformation, and reversion of \( \sigma \)-ZrO\(_2\) (>5 GPa), which causes two effects known to promote amorphization: the mobilization of large cations in the zirconia structure, and the severe deformation of nanocrystalline structures (Han et al., 2012). Whilst industrially generated ZrO\(_2\) can be effectively pure, naturally occurring baddeleyite contains a large amount of trace (ppm) to wt.% impurities, including large incompatible cations such as sodium, calcium, potassium, yttrium, lead and rare earth elements (Heaman 2009; Lumpkin 1999).

These elements would be mobilized during the shock event, producing multiple-vacancy complexes and distorting the structure (Wang et al. 2000), but would be unable to diffuse in their entirety in quickly cooled samples, preventing the nucleation of new \( m \)-ZrO\(_2\) subgrains and retaining regions of amorphous zirconia. This mechanism acts to explain the large quantity of quasi-amorphous ZrO\(_2\) observed within Martian meteoritic samples (Moser et al. 2013; Darling et al. 2016), which would have undergone rapid decompression and cooling upon ejection from the planetary surface. It should be noted that TEM analysis of quasi-amorphous domains in NWA 5298 showed that they had a complex lattice structure at length-scales of, at most, a few tens of nanometres, with crystalline domains separated by low angle grain boundaries or transitional zones of weak ordering (Darling et al. 2016).

### 5.3 Granularization

Granular baddeleyite occurs in all three studied samples, and is characterized by nanometer to micrometer scale domains with low degrees of cumulative misorientation and variable crystallographic orientations that do not show evidence of a preferred alignment or relationship with the host master grain. In Lunar breccia NWA 2200, this is limited to localized micro-scale granular domains that occur at the margins of twinned grains and do not show a preferred crystallographic orientation. Near identical microstructures are preserved in grains from terrestrial diabase JD12SUD14. These also have much lower (<2º)
cumulative misorientation than twinned master crystals (<15°), and occur as patchy regions at grain margins with variable crystallographic orientations (e.g. grain F-11071; Figure 6.6b)

These textures are interpreted to result from growth of new m-ZrO₂ crystallites from quasi-amorphous domains during post-shock heating. This process is evidenced by an increase in the size of granular subgrains, from single nanometer to single micrometer scale, in grains exposed to progressively higher post-shock temperatures in NWA 5298, such as those that are adjacent to impact melt pockets (Darling et al. 2016). The granular domains in NWA 5298 also lack a preferred crystallographic orientation, and do not display evidence for significant crystal plastic deformation. The cumulative misorientation of <1° in granular domains contrasts sharply with high degrees of deformation (<8° cumulative misorientation) in adjacent sub-grain domains that contain polysynthetic twinning, which is consistent with a post-shock origin for granularization.

5.4 Interlocking reversion twins

Within terrestrial diabase JD12SUD14, a coherent set of penetrative sub-domains records an additional microstructural feature with a preferred orientation (e.g. F-5099; Figure 6.6a). The sub-domains have common {100} and {011} orientations to the master crystal, with 90° rotation in {110} and {001}, and show low degrees of internal cumulative misorientation. These features strongly resemble interlocking reversion twins that are well known from the transformation of t-ZrO₂ to m-ZrO₂ (Hannink et al. 2000). The t-ZrO₂ to m-ZrO₂ transformation is martensitic, a diffusionless transformation in which kinetics and morphology are dominated by strain energy, and hence does not require the breakdown to an amorphous precursor. The interlocking reversion twins observed in this sample may reflect such diffusionless transformations, but it is not yet clear whether these are from the high temperature t-ZrO₂ polymorph (>1200 °C at ambient pressure (Subbarao et al. 1974), or directly from a high-pressure o-ZrO₂ polymorph during decompression at higher temperatures than in the meteorite samples.
Figure 6.7. Reversion twinning from the tetragonal to monoclinic transformation in zirconia. (a) TEM micrograph of m-ZrO$_2$ particles grown in Mg stabilized t-ZrO$_2$ during cooling; (b) and (c) schematic representations of predicted morphologies in m-ZrO$_2$ particles formed during the transition from t-ZrO$_2$, based upon experimental and theoretical studies (modified from (Hannink et al. 2000)), with preserved precursor m-ZrO$_2$ (m), t-ZrO$_2$ (t) and m-ZrO$_2$ derived from reversion from t-ZrO$_2$ (m$_r$) highlighted; (d) texture component map of crystal plastically deformed grain F5099 from a terrestrial diabase sample and simplified interpretation of the extent of reversion twins (white).

6. Evolution of shock microstructures in zirconia

The transformation from m-ZrO$_2$ to o-ZrO$_2$ is critical to the microstructural response of baddeleyite to shock loading (Figure 6.8). At pressures below this transformation, precursor (magmatic) m-ZrO$_2$ is preserved, which is supported by a number of lines of evidence: (1) the preservation of simple and polysynthetic twins in grains that have experienced lower shock pressures; (2) the extensive crystal plastic deformation of twinned domains; (3) variably degraded crystallinity in twinned domains; and (4) that the grains with these characteristics in NWA 5298 preserve the oldest U-Pb ages.

At higher pressures (>5 GPa; Kudoh et al. 1986; Arashi et al. 1990; Dewhurst & Lowther 1998), displacive transformations to metastable o-ZrO$_2$ phases and subsequent decompression, cause major structural changes within the precursor grain. The transformation to o-ZrO$_2$ is gradual, with many shocked grains retaining evidence for partial transformation. A gradual transformation to o-ZrO$_2$ is directly evidenced by the amorphization of certain twin domains in studied grains (e.g. Figure 6.2, 6.4a), and the preservation of amorphous and undeformed granular domains in amongst crystal plastically deformed m-ZrO$_2$ with preserved twins. Gradual transformations have been directly observed in shock loading experiments using light gas gun apparatus, whereby the m-ZrO$_2$ to o-ZrO$_2$ transitions to high pressure polymorphs are gradual up to shock pressures of ca. 70 GPa (Mashimo et al. 1983). This effect can be explained by the well-characterized anisotropy of physical properties such as acoustic impedance and Young’s modulus in zirconia (Ingel & Lewis 1988; see Section 1.2).
From the studied samples, grains that record complete conversion to $\alpha$-ZrO$_2$, as evidenced by complete amorphisation or granularization, are limited to the highly shocked meteorite NWA 5298. This rock is thought to have experienced a bulk shock pressure in excess of 29 GPa (Hui et al. 2011; Darling et al. 2016), suggesting that the transformation to $\alpha$-ZrO$_2$ in naturally shocked samples is incomplete at pressures lower than ca. 30 GPa (Figure 6). Of course, the process of shock wave propagation in heterogeneous materials has significant complexity, and loading paths and peak shock pressures experienced by individual crystals can vary dramatically. This is due to shock-wave interactions including refraction and reflection at boundaries between minerals of different shock impedance, as well as collisions between refracted shock fronts that can produce localized pressure spikes. As a result, the peak shock pressure and waste heat experienced on the micrometer-scale can vary by a factor of two or more (Sharp & de Carli 2006).

Figure 6.8. Shock microstructural evolution in baddeleyite (left), showing the predicted observable microstructures generated in grains that have experienced different shock metamorphic pressure and temperature conditions. It should be noted that multiple types of these microstructural forms have been observed within individual thin-sections. Also shown (right) is the predicted extent of Pb-diffusion in these different shock-PT scenarios, based upon available U-Pb data from baddeleyite grains with microstructural context [Moser et al., 2013; Darling et al., 2016; White et al, this volume].

The resulting microstructure observed by EBSD or TEM for grains of different loading pathways is strongly influenced by post-shock heating and the degree of new $m$-ZrO$_2$ growth (Figure 8). At low shock pressures (<5 GPa), microstructures are dominated by crystal-plastic deformation and the absence of amorphization precludes recrystallization, even at high post shock temperatures (e.g. twinned domains in JD12SUD14). However, as pressures become
higher and an increasing proportion of the grain transforms to and from $o$-$ZrO_2$, the difference between preserved microstructures has a much greater dependence on post-shock temperature. In rapidly cooled or quenched samples (e.g. many domains in meteorites NWA 5298 and NWA 2200), quasi-amorphous to nano-granular $m$-$ZrO_2$ subdomains are preserved. In contrast, samples that have experienced prolonged high-temperature conditions (e.g. Sudbury impact structure sample JD12SUD14) contain a large proportion of new granular or reversion twin growth. The occurrence of granular grains adjacent to melt pockets in NWA 5298 indicates that timescales on the order of seconds to minutes are sufficient to drive new growth, given predicted cooling rates for impact-melt rich meteorite samples (Shaw & Walton 2013).

The available U-Pb data for baddeleyite grains with detailed microstructural data (Moser et al., 2013, Darling et al., 2016, Chapters 4 & 5), provide insights into the linkage between shock-microstructures and disturbance of the U-Pb system. It is clear that grains with microstructures limited to crystal-plastic deformation (i.e. pressures below $o$-$ZrO_2$ transformation) preserve isotope ratios that are not dramatically effected by Pb-loss [Darling et al., 2016]. This is in line with the high closure-temperature of baddeleyite, which is similar to that of zircon (>900 °C; (Lee et al. 1997)), although no specific studies are available on the effects of plastic deformation on Pb retention in baddeleyite. In contrast, grains that have microstructures resulting from transformation to $o$-$ZrO_2$ record partial to complete Pb-loss during impact events. This observation is consistent with the prediction that large cations, including Pb, will be mobilized by the displasive transformations to orthorhombic structures (Chapters 4 & 5). However, the transformation to $o$-$ZrO_2$ alone does not necessitate major Pb-loss, as shown by the observation that amorphisation of grains in NWA 5298 does not mobilize trace elements that are responsible for cathodoluminescence emission (Figure 6.2), and only minor loss of radiogenic Pb in quasi-amorphous to nano-crystalline grains [Darling et al., 2016]. Temperature appears to be a critical parameter, as shown by more extensive to near complete age-resetting in grains from NWA 5298 and JD12SUD14 that have granular and interlocking reversion twin microstructures. Intriguingly, atom probe data from JD12SUD14 baddeleyite identifies high-degrees of U-Pb isotopic heterogeneity at the nanoscale, with a clear linkage between Pb-loss and nanostructures (Chapter 4). This study reinforces the idea that structural changes and features have a greater control on U-Pb age resetting in baddeleyite than diffusion driven by heating alone. As summarized in Figure 8, shock-loading to >5 GPa and decompression at high-temperatures must therefore be critical to drive high-degrees of Pb diffusion in shock metamorphosed baddeleyite.
7. Conclusions

All of the shock metamorphosed baddeleyite grains studied are preserved as baddeleyite \((m\text{-ZrO}_2)\) or quasi-amorphous \(\text{ZrO}_2\), and while the intragrain microstructures vary dramatically they can be closely linked with the shock pressure and temperature history of the sample. This allows a new, generalized shock microstructural evolution to be defined for this important planetary chronometer (Figure 6.8). This evolution is controlled by the transformation to \(o\text{-ZrO}_2\) (progressive from ca. 5 GPa upwards) and by the temperature during decompression or more prolonged heating, and can be summarized as follows:

- In grains that experience <5 GPa, shock-microstructures are limited to crystal-plastic deformation.

- At shock pressures between 5 GPa and ca. 30 GPa, partial transformation to \(o\text{-ZrO}_2\) polymorphs drive major structural changes that result in amorphisation (low-T decompression), \(m\text{-ZrO}_2\) reversion twins (high-T decompression) or granularization (low-T decompression followed by heating).

- At higher shock pressures, complete transformation to \(o\text{-ZrO}_2\) results in complete replacement of original magmatic baddeleyite.

Importantly, these findings demonstrate that the identification of the monoclinic structure is not sufficient to preclude a complex shock-history for a studied grain, but techniques such as EBSD can resolve baddeleyite microstructures that result from specific shock loading and heating pathways. Further studies that directly link these microstructures with U-Pb isotope data are urgently required, but preliminary data does suggest that high-degrees of Pb-loss are limited to grains/domains that have experienced both transformation to \(o\text{-ZrO}_2\) and high-temperatures. As such there is tremendous potential tool to resolve the timing of both endogenic geological processes and impact events from individual baddeleyite bearing samples.
6.3 QUALIFYING AGE RESETTLENG BY STRUCTURE

Throughout this study, the microstructure and nanostructure of shocked baddeleyite grains has been analysed using both EBSD and APT (Chapters 4 & 5). Age data (U-Pb) has been generated from a subset of these grains, using SIMS for Martian baddeleyite in NWA5298 (Moser et al. 2013; Darling et al. 2016) and APT for terrestrial grains in JD12SUD14 (chapters 4 & 5). Correlating these data have yielded exciting new insights into the isotopic response of baddeleyite during shock metamorphism, allowing for complex, partially age-reset grain populations to be better resolved in planetary materials. Examining these data more closely reveals a linear correlation between the ratio of shocked to unshocked material and the extent of Pb loss and age resetting on the whole grain scale (Figure 6.9). This link, while strongly suggested by previous studies (Darling et al. 2016), is quantified here for the first time. This allows for the more refined targeting of mineralogical targets for U-Pb analysis based on the observable shock state of the grain (see this chapter), preferentially analyzing geochronological end members (i.e. crystallization and impact) as opposed to complex, partially age-reset grain.

![Figure 6.9](image)

**Figure 6.9:** Comparison between the ratio of nanostructurally divided atoms / total atoms with the bulk tip age for all eleven atom probe tips presented in chapter 4. When the whole tip...
constitutes one nanostructural domain (i.e. Homogenous-Fe or Clustered-Fe) the derived U-Pb age falls within uncertainty of a chronological end member (i.e. crystallization or impact).

U-Pb analysis of shocked zircon features such as microtwins has suggested a similar correlation can be drawn within the phase. The generation of these features alone does not disturb the U-Pb ratio of the grain, instead requiring post-impact heating to encourage lead diffusion along generated deformation and twin pathways (Moser et al. 2011). *In-situ* analysis of these features yield partially reset U-Pb ages, interpreted thus far as true domains of partial Pb loss. However, our new approach to age resetting suggests this variability may be derived from subsampling chronological end members; the crystallization-age host grain, and the younger microtwin plane (Figure 6.10). Unlike baddeleyite, impact disturbed domains of zircon appear more susceptible to continued lead loss (i.e. Piazolo et al. 2016), pulling bulk U-Pb analysis towards a modern lead reservoir (-11 ±31 Ma). As a result, only fresh zircon neoblasts grown *in-situ* immediately following an impact event will yield a true age for shock metamorphism (Cavosie et al. 2015). Approaching age-resetting as a function of structure, rather than bulk diffusion of Pb, will allow for a new approach to generating accurate ages for many planetary events.

![Figure 6.10](image_url)

*Figure 6.10:* (A) EBSD texture component map of a shocked zircon grain from the Vredefort impact structure, South Africa. (B) U-Pb ratios generated from numbered ablation spots highlighted in EBSD space. The severity of lead loss appears to correlate with the abundance of impact-reset material subsamples during analysis, with the least disturbed domains (1 and 2) yielding ages more heavily weighted towards crystallization. Modified from (Cavosie et al. 2015).
7: Shocked Zircon Preservation

PRESERVATION POTENTIAL OF SHOCKED ZIRCON

7.1 INTRODUCTION

Zircon develops a number of diagnostic microstructures during shock loading and annealing, and is recognized as providing a robust record of the severity and timing of impact metamorphism (Moser et al. 2011; Cavosie et al. 2015). These microstructures include planar deformation features and microtwin lamella, which are preserved through low temperature sedimentary reworking (Erickson et al. 2013; Thomson et al. 2014; Reddy et al. 2015). However, many of these studies examine zircon grains in detrital deposits, where the zircon record preferentially chronicles ‘hot shock’ (i.e. age reset) grains (Moser et al. 2011). The preservation potential of these microstructures during high-temperature overprinting is poorly constrained. This includes amphibolite to granulite facies crustal metamorphism, such as the metamorphic overprint masking the controversial Maniitsoq structure in Greenland (Garde et al. 2012), as well as contact-metamorphic overprinting at the base of large impact melt sheets.

Such overprinting makes it incredibly challenging to identify ancient Hadean to Archean aged impact structures, even though such features should be common place given the extent of early bombardment in the turbulent inner Solar System (Melosh 1990). Here we examine zircon grains across a linear transect radiating outwards from the Sudbury impact melt sheet, defining the preservation potential of features such as microtwins within a range of petrological settings. This groundtruthing effort will facilitate the identification of shocked and reworked zircon grains within many impact-proximal lithologies, including brecciated pseudotachylite deposits and highly annealed melt-sheet proximal granulites. Going forward, this work will aid the interpretation of many shock metamorphosed Archean and Lunar zircons. The details and results are presented in the following paper, which is included in this chapter:


Samples were collected by J. Darling and L. White. EBSD analysis of zircon grains was conducted by L. White, I. Barker and J. Dunlop. Data evaluation and interpretation, together with the preparation of the manuscript, was conducted by L. White, which benefitted from discussion with co-authors. The final manuscript was written by L. White, with input from J. Darling and D. Moser on ideas and wording, and input from I. Barker and J. Dunlop on methods.
7.2 THE PRESERVATION POTENTIAL OF SHOCKED ZIRCON MICROSTRUCTURES

White, L. F.1*, Darling, J. R.1, Moser, D.2, Barker, I.2 & Dunlop, J.1

1 School of Earth and Environmental Sciences, University of Portsmouth, Portsmouth
2 Department of Earth Sciences, University of Western Ontario, London, Canada.

Many unique mineralogical records of impact events are susceptible to recrystallization during post-impact metamorphism, eliminating the diagnostic evidence most commonly used in crater identification and reconstruction. Refractory accessory phases such as zircon (ZrSiO4) may provide a more robust record, but the survivability of shock-induced microstructures through high-temperature annealing and tectonic reworking is poorly understood. This has been an open consideration in determining whether the early Earth and Lunar zircon records could retain unambiguous evidence for, and timing of, ancient impact events. Here we report on impact-induced crystallographic microstructures within Archean-aged zircon sampled at varying distances beneath the lower contact of the 1.85 Ga Sudbury impact melt sheet (Ontario, Canada). Here we show that zircon retains a collection of shock-induced microstructures (principally microtwin planes) within highly sheared, brecciated and annealed samples. The preservation of such features through extensive deformation and metamorphism addresses a major concern in the application of zircon as an extra-terrestrial geochronometer, where microstructure is used to target potentially age-reset shocked grains. Here we place further empirical constraints on the formation and preservation of these key features, yielding new insights into the shock pressure regime at Sudbury in the process. Going forward, zircon is a uniquely robust and powerful shock-indicator with which to determine ancient terrestrial and Lunar impact records.

INTRODUCTION

Meteorite impacts, and the cratering processes associated with them, played a key role in the formation and subsequent evolution of planetary bodies within the inner Solar System (Marchi et al. 2014). Diagnostic mineralogical evidence of such events is often lost during crustal recycling, erosion and metamorphism (French & Koeberl 2010), complicating efforts to constrain the shock state of many ancient terrestrial and extra-terrestrial lithologies. This is of fundamental importance when dating planetary material as impact-induced metamorphism disturbs the sensitive isotopic systems used in such work (Borg et al. 2005; Gaffney et al. 2011), potentially yielding a complex array of ages anywhere between crystallization and the point of impact (Darling et al. 2016; Moser et al. 2013). Determining whether such data have been derived from either a pristine igneous or highly shocked sample allows for this age variability to be understood (Darling et al. 2016). Recent work has begun to move away from using
traditional shock-indicators to establish bulk pressures, and instead focus directly on the more robust, refractory and unreactive accessory minerals used as geochronological tools (Cavosie et al. 2010; Moser et al. 2011; Cavosie et al. 2015; Darling et al. 2016). As well as assessing a more resilient recorder of shock, this approach allows for the shock-state of individual crystals to be assessed prior to isotopic analysis (Darling et al. 2016) and acknowledging the heterogeneity of shock pressures and temperatures even on the sub-mm scale.

One such mineral, zircon (ZrSiO₄), has a long and diverse history as a high temperature U-Pb geochronometer, including application to impact events which are known to disturb the crystal lattice and induce partial to complete Pb-loss within the grain (Krogh et al. 1984). Such disturbance induces a number of crystallographic shock structures, including the formation of µm-scale twin lamella above ~16 GPa (Moser et al. 2011; Erickson et al. 2016), the development of granular neoblasts during high-temperature annealing (Cavosie et al. 2015), and the formation of the high-pressure ZrSiO₄ polymorph reidite above ~30 GPa (Leroux et al. 1999). At higher temperatures (~1673°C), the dissociation of zircon (ZrSiO₄) to baddeleyite (ZrO₂) and amorphous silica (SiO₂) has recently been observed in highly shocked and annealed crystals (Timms et al. 2016), though such features are restricted to high-temperature ZrSiO₄ alteration (Kaiser et al. 2008). Sufficient temperatures are rarely generated in the Earth’s crust, uniquely generated by impact-induced evaporation and melting of the lithosphere (Timms et al. 2016). These structures are all readily observable using electron backscatter diffraction (EBSD) techniques, which yield a quantified measurement of both crystalinity and crystallographic orientation variation. Preservation of these features within detrital grains around the Vredefort (Cavosie et al. 2010; Cavosie et al. 2015) and Sudbury (Thomson et al. 2014) impact craters, within brecciated deposits (Reddy et al. 2015) and even as inclusions in other accessory phases (Erickson et al. 2016) acts to evidence zircons ability to preserve crystallographic shock structures through low temperature erosion, deposition and diagenesis. While important, such observations provide no insight into the preservation potential of these crystallographic features during the high-temperature annealing that annihilates conventional shock indicators (Dressler 1984; James et al. 1992; Grieve et al. 2008). This lack of knowledge is particularly troublesome in the reconstruction and dating of extraterrestrial shock events as impact-proximal lithologies (i.e. those exposed to the highest shock pressures) are most susceptible to thermal overprinting from the impact-induced, super-heated melt sheet. For example, although many zircon grains (~41%) are predicted to have undergone partial to complete Pb-loss during Hadean-aged bombardment of the crust (Abramov et al. 2013), the limited zircon record from this time suggests an absence of shock-induced microstructures (Wilde et al. 2001). Given the prevalence of crustal mixing and burial during the Hadean (Marchi et al. 2014), highly shocked grains would likely have been highly annealed and brecciated during continued Hadean and Archean aged bombardment (Melosh
1990). If diagnostic shock features cannot survive such reworking the majority of age-reset zircon grains will be masked from targeted U-Pb dating (Abramov et al. 2013; Cavosie et al. 2015), severely hindering ongoing efforts to reconstruct and date extra-terrestrial impact events. Here we report on the first in-situ evaluation of the survivability of zircon shock microstructures in such conditions, using a set of granitoid intrusions and batholiths sampled at varying distances beneath the Sudbury impact melt sheet. Furthermore, we test the common assumption that such features would not survive the more frequent and intense impact activity early in Solar System history (Melosh 1990).

**GEOLOGICAL BACKGROUND & SAMPLE SELECTION**

The Sudbury impact structure contains the largest and thickest impact melt sheet so far recognized on Earth, preserved largely through tectonic in-folding with Archean and Proterozoic crystalline basement following a meteorite impact at 1852 ± 1 Ma (Krogh et al. 1984). Underlying the originally ca. 250 km structure (Spray et al. 2004) to the north is a series of Archaean high-grade metamorphic rocks, principally banded and migmatitic gneisses of the Levack Complex (2711 ± 7 Ma; Dressler 1984; Krogh et al. 1984), which host a number of granitic, tonalitic, granodioritic, mafic and ultra-mafic intrusions (Card 1994). Immediately following impact, the Levack gneisses were subjected to extensive high-temperature contact metamorphism (1.5-5 kbar; 800-1015 °C) within ca. 2 km of the superheated melt sheet (James et al. 1992), with the complete recrystallisation of quartz and feldspar estimated within ~500 m of the melt sheet (Grieve & Therriault 2000). This was followed by burial to a depth of 5-6 km during the Penokean orogeny (Thompson et al. 1998) and regional folding of the crater, resulting in a strong greenschist-facies overprint throughout the region (Riller 2005). These events can all be associated with substantial hydrothermal activity, including within the Levack gneisses (i.e. Molnár et al. 2001). The North Range was likely exhumed ~1 Ga, during the Grenville orogeny (Thompson et al. 1998).

Analysis focused on four polished thin-sections of zircon-bearing granitic rocks in the North Range of Sudbury sampled at varying distances from the preserved impact melt sheet (Figure 1). JD12SUD09 represents the most impact-proximal sample analysed within this study. This zircon-bearing section of the Levack gneiss complex outcrops approximately 400 m north-west of the melt sheet. JD12SUD15a, a granodioritic intrusion within the Levack gneiss complex, was sampled approximately 550 m north of the base of the impact melt sheet. JD12SUD04 is a more complex sample, taken across the margin of a pseudotachylyte vein ~2 km north of the Sudbury igneous complex. The thin section sub-samples the contact between granitic host material and fine grained, glassy mafic matrix. JD12SUD07 represents the most distal sample within the study, outcropping ~10 km from the melt sheet within the Cartier granite batholith. The sample is hydrothermally altered.
**Figure 7.1:** Schematic geological map of the Sudbury impact structure highlighting sample localities of variably shocked zircon-bearing materials. Four felsic samples (JD12SUD09, JD12SUD15a, JD12SUD04 & JD12SUD07) form a roughly linear transect radiating outwards from the north-western extent of the Sudbury impact melt sheet. The extent of planar deformation features and shattercone occurrences are presented for reference (Grieve et al. 2008).

**METHODOLOGY**

Target zircon grains were located using an automated feature-scan of the thin section using a Phillips XL30 cp Scanning Electron Microscope (SEM) coupled with an Oxford X-Max 80 Energy-Dispersive Spectroscopy (EDS) detector housed at the University of Portsmouth, UK. Once identified, target zircon grains were imaged using backscatter electron (BSE) and secondary electron (SE) techniques to identify features such as cracks, fractures and planar features. Grains were imaged using either a Hitachi SU6600 field emission gun SEM (FEG-SEM; ZAPlab) or Zeiss EVO MA10 LaB$_6$-SEM (Portsmouth) using comparable electron beam parameters between the two instruments (15 – 20 kV accelerating voltage, 200 – 500 pA, ~14.5 mm working distance to also match the calibrated interaction distance for EDS chemical analysis). High resolution, high contrast imaging (increased contrast, decreased brightness) was used to better highlight internal variation within each grain. Lower resolution, normal contrast imaging was used to provide information of surrounding phase relationships and to aid future relocation.

Target grains were imaged using backscatter electron (BSE), secondary electron (SE) and cathodoluminescence (CL) techniques, and subsequently electron backscatter diffraction (EBSD) analyses were undertaken using a Hitachi SU6600 field emission gun – SEM (FEG-SEM)
housed within the Zircon and Accessory Phase Laboratory (ZAPlab) at the University of Western Ontario, Canada. EBSD microstructural analysis was conducted using an Oxford HKL Nordlys detector following procedures outlined by Moser et al., 2011, with step sizes of between 150 nm and 1 μm, dependent on grain size. Wild spike reduction was completed on all EBSD datasets, although no other form of raw data correction was conducted.

RESULTS
JD12SU09 (~400m)

This impact-proximal sample of the Levack gneiss complex has undergone extensive greenschist-facies metamorphism, comprised of quartz, plagioclase feldspar, actinolite, chlorite and sulphide phases. Minor hornblende is present within the sample (< 5%). Quartz grains display no planar or curvi-planar features, while all feldspar appear as fine grained, crystalline masses, potentially crystallized from maskelynite. Shock features are not observed in these major rock forming mineral phases, mirroring observations elsewhere around Sudbury (Grieve & Therriault 2000; Grieve et al. 2008). Such (re)crystallization is expected, given extensive post-shock annealing induced by the nearby impact melt sheet (< 1015 °c; James et al. 1992).

Zircon was scarce in the thin section, with an automated scan of the sample yielding five grains larger than 10 μm². BSE and SE imaging of these grains reveals that four grains aligned with c-axes perpendicular to the thin section are largely metamict, with the largest grain (~150 μm²) appearing more robustly crystalline. These subhedral-anhedral grains preserve no visible planar or curvi-planar features. Live diffraction pattern analysis of the metamict grains suggested that only a small percentage of the crystal (< 5%) would be identified and indexed during further mapping. For this reason, EBSD analysis focused on the larger, more crystalline zircon grain (Figure 7.2). The grain produces a strong diffraction pattern, generating a smooth and uniform band contrast map suggesting a high degree of crystallinity. Up to 10° of crystal plastic deformation can be observed across the upper half of the grain. This misorientation is controlled by low-angle (< 2°) subgrain boundaries facilitating rotation of zircon subgrains about the {001} axis, though subgrains themselves display no internal deformation (within the ~0.2° background of the technique). The lower half of the zircon appears polycrystalline (or granoblastic) with rounded elongate or spherical subgrains overprinting the planar features towards the top of the grain. These subgrains display minimal crystal plastic variation (< 1.5°).
Figure 7.2: EBSD maps of zircon feature #277, highlighting band contrast variation (a measure of diffraction quality) and texture component variation (< 10° crystal plastic deformation). A misorientation profile (< 7°) across recrystallized domains highlight the low angle grain boundaries boasted by the sample, while pole figures for the complete indexed dataset show no evidence of microtwin formation (traditionally 75°/(110); Timms et al. 2016).

**JD12SUD15a (~550m)**

The sample is primarily composed of quartz and saussuritized feldspar, with chlorite, actinolite and epidote also occurring in association with small Ti-rich accessory phases (principally titanite). Polycrystalline quartz occurs throughout the sample, with a small number of sub-grains displaying loosely spaced, sub-parallel features (Figure 7.3) though these are exceptionally rare within the sample (~5% of sub grains) and are more typically induced by tectonic deformation (Grieve et al. 1996). Maskelynite has not been observed, with all feldspatic phases appearing crystalline. No unambiguous shock features are visible in the major mineral phases.
Automated SEM mapping of the section revealed 42 individual zircon grains, ranging in exposed surface area between 30 and 920 μm². Crystallographic microstructures most strongly associated with shock effects were observed using BSE, SE and CL imaging within the seven largest (≥ 300 mm²) grains, although the preservation state of these features varies greatly (Figure 7.4). Planar and curvi-planar features have been observed in ~60% of the total zircon population, though grain size does not appear to correlate with the preservation potential of these features. Comprehensive EBSD analyses were undertaken on the four largest grains (Figure 7.5). All grains exhibit crystal plastic deformation, expressed as between 3° and 8° misorientation, whilst also hosting discrete sub-grain domains subdivided by low angle grain boundaries (<6°). Three of the grains (Grain #60, #260 and #141) display shock-induced zircon micro twins, rotated approximately 65° about the <110> axis, which have been variably overprinted and masked by sub grain formation. Decorated planar and curvi-planar features are observed in all grains, consisting of amorphous 'bubbles' between 0.5 and 3μm in size, roughly aligned in straight and gently curving lines.

Grain #60 displays a series of reasonably well-preserved features, including extensive plastic deformation throughout the crystal, and multiple micro twin planes (350 – 400 nm width) rotated 65° about <110>. Peak crystal-plastic deformation of the zircon (~7.5°) can be observed in the southern-most region of the crystal immediately surrounding a substantial (~2 - 5μm) fracture infilled with crystalline SiO₂. Sub-grains (2-8 μm) defined by low angle (<6°) boundaries, are observed across the crystals exposed surface area, including overprinting the observed microtwin planes. These diagnostic features are less well preserved within grain #260, which displays a lesser degree of crystal plastic deformation (<3°) and less well-developed sub-grain boundaries. Three micro-twin planes (<370nm width) in a single orientation are preserved within the grain, occurring as short (2 – 3μm)
**Figure 7.4:** BSE images of shocked zircon grains within sample JD12SUD15a. The largest grain (#141) hosts several clear planar features which occur in ~three crystallographic orientations (white arrows on grain #141). Polishing artifacts are also present in grains #60, #109 and #260, though these appear as wider (> micron) discontinuous features.

**Figure 7.5:** Texture component (TC) EBSD maps for zircon grain #60 (a = 250 nm step size, b = 175nm step size), grain #260 (c = 150nm step size), grain #109 (d = 150nm step size) and grain #141 (e = 150nm step size) For reference, i - ii cross-sectional misorientation profiles of microtwin planes within grains #60 (f), #260 (g) and #141 (h) demonstrate the misorientation of the <350nm thick planes to be approx. 65° to the master crystal. All transects are approximately 3.5um in length.
discontinuous planes. Decorated planar and curvi-planar features, characterized by larger (< 3 μm) amorphous inclusions, can be seen to run the breadth of the crystal, although true planar features are completely absent.

Grain #60 displays a series of reasonably well-preserved features, including extensive plastic deformation throughout the crystal, and multiple micro twin planes (350 – 400 nm width) rotated 65° about <110>. Peak crystal-plastic deformation of the zircon (~7.5°) can be observed in the southern-most region of the crystal immediately surrounding a substantial (~2 – 5 μm) fracture infilled with crystalline SiO₂. Sub-grains (2-8 μm) defined by low angle (<6°) boundaries, are observed across the crystals exposed surface area, including overprinting the observed microtwin planes. These diagnostic features are less well preserved within grain #260, which displays a lesser degree of crystal plastic deformation (< 3°) and less well-developed sub-grain boundaries. Three micro-twin planes (< 370nm width) in a single orientation are preserved within the grain, occurring as short (2 – 3 μm) discontinuous planes. Decorated planar and curvi-planar features, characterized by larger (< 3 μm) amorphous inclusions, can be seen to run the breadth of the crystal, although true planar features are completely absent.

Micro-twin planes are absent within the grain cut perpendicular to its c-axis (#109), whereby the crystallographic orientation likely masks the rotated twin volume. Less crystal-plastic deformation is observed within this grain (0 – 3°), while small (3 – 5 μm) sub grains displaying ~ 6° misorientation relative to the host appear to occur throughout the crystal, but are generally clustered around the exterior of the crystal. A substantial (~18 μm) metamict core does not appear to influence the degree of crystal lattice misorientation, though does host a small number of crystalline zircon subgrains. The best-preserved features can be observed in grain #141, which contains a series of clearly defined micro-twin planes rotated about <110>, in addition to well-preserved sub grains defined by low angle (<7°) crystallographic boundaries. Continuous, decorated planar features can be seen to run throughout the grain, occurring in similar crystallographic orientations to the micro-twin planes.

**JD12SUD04 (~3km)**

Sampled from a ~20m wide pseudotachylyte belt within the Levack gneiss complex, the thin section subsamples two lithologies; a larger (~20 cm) sub-rounded granitic clast and a fine grained to glassy mafic matrix hosting smaller (mm-scale) rounded and sub-angular felsic inclusions (Figure 7.6). A feature scan of the section yielded 172 zircon grains ranging from 71 – 6627μm² in exposed surface area. BSE and SE imaging of the grains reveals a wide range of highly anhedral grain morphologies, including highly granular (#59, #100, #507) and sheared (#503) structures. The severity of deformation correlates with the location of the grain in the
thin section, with highly strained and sheared zircons occurring in the mafic matrix and better preserved (subhedral – euhedral) grains occurring in the larger granitic clast (Figure 7.7). Planar features can be observed in the better-preserved zircon grains, while these planar features likely constrained the granularisation of grains within the pseudotachylyte matrix, propagating the shock wave through the grain.

**Figure 7.6:** Plane polarized light (PPL) scan of thin section JD12SUD04.

**Figure 7.7:** BSE grain images for sample JD12SUD04. A BSE montage of the thin section with labelled grain location is presented for reference, highlighting whether grains are sourced from the larger granitic inclusion or the more reworked mafic matrix.
Figure 7.8: EBSD data (band contrast and all euler maps) for zircon grains from JD12SUD04. A smaller area of grain #503 (A) was mapped at 200 nm (B, C) to highlight regions of interest, and at higher resolution (50 nm; D) to properly constrain microtwin orientation. Twins are orientated 65° about \{110\}, matching structures reported elsewhere in highly shocked zircon (Timms et al. 2016). Grain #414 (E, F) displays subgrain formation (differentiated by low angle grain boundaries) and minor preservation of microtwin planes. Grain #516 (G,H) was mapped in its entirety at 70nm. Despite the highly brecciated nature of the grain, subgrains are shown to preserve microtwin planes orientated 65° about \{110\} (white box in figure H). The preservation of twin planes in both highly sheared and recrystallized zircon within this pseudotachylyte place important new constraints on the preservation of these diagnostic shock indicators.
EBSD analysis was conducted on five grains in total; two within the larger granitic clast (#414 and #503) and three in the pseudotachylyte matrix (#59, #507 and #516). All grains display significant misorientation across their length (< 100°), though this is primarily constrained by the rotation and recrystallization of zircon subgrains and does not reflect crystal plastic deformation within the grain. Despite the extensive deformation of these grains, shock-induced microtwin planes misoriented ~65° about {110} have been preserved within both sheared (#503) and granulated (#516) zircon. Grain #503, hosted within the larger granitic clast, is fairly euhedral in nature, barring a 20um domain which has been sheared and dextrally transported ~60um during formation of the pseudotachylytic breccia. The core of the grain is highly metamict, and a small domain of this material has also been sheared and transported. The glide plane is decorated by 0.5 – 8 um wide granoblasts of random crystallographic orientation with no discernable relationship to the master crystal. Three microtwin planes (all highlighting 65° of rotation about the {110} plane) are preserved in the sheared tail, occurring parallel to the planar features observed in both SEM imaging and band contrast (BC) analysis. Zircon within the fine grained to glassy matrix are highly granulated and deformed. Band contrast mapping of grain #516 highlights a large variation of granule size and structure. Larger (< 20um) subdomains contain abundant cracks and fractures, and roughly match in crystallographic orientation across the grain. Between these domains, smaller (< 2 um) randomly oriented subgrains occur in association with largely amorphous (poorly diffracting) material. All sub-granules display minimal (<1°) crystal plastic deformation. Within one of the larger subgrains (8 um), a fine ~500 nm microtwin plane (65° about {110}, shared {001}) is preserved.

JD12SUD07 (~8km)

Sample JD12SUD07 is a highly altered section of the Cartier granite. Principally composed of quartz and plagioclase feldspar, hydrothermal mobilization of the more robust mineral phases has resulted in the clustering of zircon grains. Titanite, ilmenite and magnetite commonly occur in association with these clusters. Given the occurrence of zircon within the thin section, a feature scan was not conducted. Zircon clusters were instead identified using EDS prior to large-scale EBSD mapping of the whole cluster or grain. In total, 17 large (> 20 um²) zircon were identified and imaged throughout the section (Figure 7.9). The grains all contain zoned, metamict cores, and display generally subhedral morphologies. Zoning and metamictization are most prevalent in c-axis perpendicular crystals (i.e. grains #2 and #8). EBSD analysis was concentrated on a cluster of seven grains within one field of view (features #3 to #6 in SEM imaging). The orientation of the thin section has resulted in the majority of these grains (~70%) being cut perpendicular to the c-axis. These grains boast substantial metamict cores, constituting up to 70% of the total exposed surface area. Individual grains containing no more than 5° of internal misorientation. Radial cracks and fractures
propagate outwards from these cores, presenting themselves as poorly diffracting domains in EBSD maps. No evidence of microtwins or granularisation is observed within this grain population.

**Figure 7.9:** BSE images of zircon grains from sample JD12SUD07. All grains contain zoned, metamict cores. Planar features are absent within these grains.

**Figure 7.10:** EBSD data for zircon grains #3 to #6. Metamict cores are poorly diffracting amorphous domains, surrounded by slightly deformed crystalline zircon. No evidence for shock induced microtwins is present, with the <4 ° of crystal plastic deformation potentially induced by the expansion and contraction of the zoned cores.
DISCUSSION

**Preservation potential of diagnostic shocked microstructures**

By coupling the thermal history of the North Range of Sudbury with experimental and field observations on the recrystallisation and retrogression of common shock indicator phases, timings of crystallographic microstructure annihilation during metamorphism can be constrained. In the most impact-proximal sample (JD12SUD09), the majority of phases (quartz, maskelynite) would have been recrystallised immediately following impact, with thermal modelling of the North Range suggesting the remnant super-heated melt sheet inducing an ultra-high temperature metamorphic overprint in adjacent lithologies (< 1015°C; James et al. 1992). Higher temperature minerals, such as amphibole and biotite, would have retrogressed to chlorite and actinolite during prolonged Penokean-aged greenschist facies metamorphism (Thompson et al. 1998), although it is likely that these ferromagnesian phases would have also recrystallised during melt-sheet induced annealing (Gibson & Reimold 2005), presenting multiple opportunities for the destruction of microstructure. Zircon has also been heavily recrystallized in this sample, destroying any microtwin or reidite lamella but preserving planar subgrain boundaries only observable in EBSD microstructural analysis. These structures are variably overprinted by true recrystallization of the zircon, forming rounded subgrains (neoblasts) across ~50% of the grain.

Within sample JD12SUD15a, plagioclase has been completely recrystallized, while quartz occurs as heavily reworked, anhedral, polycrystalline crystals. Though a small number of these subgrains appear to preserve decorated planar and curvi-planar structures, these cannot be confidently associated with impact metamorphism in isolation (Grieve et al. 1996). Zircon is the only mineral phase in the sample that retains diagnostic crystallographic evidence of the impact event. Amongst the grain population, decorated planar and curvi-planar features, crystal plastic deformation, and microtwin planes have been observed in variable states of preservation. Truly planar features (defined by continuous parallel lamella) such as those observed in Sudbury-derived detrital zircon (Thomson et al. 2014), have been annealed and degraded to form discontinuous decorated features, which are themselves variably preserved on a grain-by-grain basis. Granularisation of zircon, as reported in association with the Vredefort impact structure and interpreted to represent ultra-high temperature post-impact recrystallisation (Moser 1997; Cavosie et al. 2015) is absent, though the observed abundance of subgrains (defined here by low angle (~ 6°) boundaries) likely represents an incipient version of this texture.

Although sampled ~3km beneath the present extent of the impact melt sheet, the highly brecciated and reworked nature of sample JD12SUD04 (zircon-bearing felsic clasts in a pseudotachylyte belt) means that it is hard to constrain the original position of the sample in
relation to the impact (i.e. Thompson & Spray 1996). However, the presence of shock-induced microtwin planes even within these highly sheared and deformed grains speaks highly of the robustness of the features, regardless of original source. Thus, the absence of microtwin planes within the metamorphosed and reworked distal zircon grains (JD12SUD07) indicates that the sample did not experience sufficient shock pressures to induce the structures (> 19 GPa), rather than these features being lost during post-impact metamorphism.

Of the structures observed here only planar micro-twins misoriented ~65° about the <110> axis are truly diagnostic of an impact event. Planar features, curvi-planar features and crystal plastic deformation have also been reported within tectonic settings (Kovaleva et al. 2015), while recrystallisation of zircon (i.e. granularisation) can also occur during magmatic and metamorphic overprinting (Moser 1997; Cavosie et al. 2015). The discovery of microtwins within the melt-sheet proximal (550m) Levack gneisses and the highly brecciated pseudotachylyte (2km) acts to highlight the robustness of these structures through post-impact heating and reworking. Additionally, the formation of zircon microtwins within > 2km of the impact melt sheet, coupled with their destruction within ~500m, places empirical constraints on the formation and preservation of these microstructures at Sudbury.

Reconstruction of the Sudbury Impact Crater

The quantification of peak shock conditions experienced at Sudbury is challenging, as traditional mineralogical shock barometers within the impact-proximal lithologies (< 500 m) have been lost during extensive high-temperature, melt-sheet induced recrystallisation (James et al. 1992; Therriault et al. 2002). Observations on shatter cones, indicative of shock stresses as low as 2 GPa (Osinski & Ferrière 2016), provide a first order insight into the pressure regime experienced by the region. Here, the discovery of in-situ shocked zircon micro-twins in melt sheet proximal North Range lithologies confirms significant shock pressures (> 19 GPa; Timms et al. 2016) within the target rocks of the North Range. This is permissive of a more central role for the North Range during the impact event, and hence a more northern impact center than previously suggested (i.e. Riller 2005), bringing the observed distribution of shock phenomena (quartz PDFs, shatter cones and pseudotachylyte) at Sudbury into better concordance with that of the Vredefort impact structure (Grieve et al. 2008).

By coupling our new zircon microtwin data with the occurrence of diagnostic shock features (such as quartz PDFs and shattercones) around the Sudbury impact structure, further implications on estimated P-T conditions for the North Range target rocks can be extrapolated (Figure 7.11). With shattercones (> 2 GPa) present to within ~10 km of the melt sheet, quartz PDF’s (> 10 GPa) to within ~6.5 km, and zircon microtwin lamella (> 19 GPa) to within ~3 km, a rough pressure gradient of 3 GPa / km can be generated for the area. Extrapolating this
estimated pressure gradient through to the melt sheet base assuming a linear decay of shockwave velocity (Langenhorst & Deutsch 2012) suggests that peak shock pressures greater than 25 GPa were experienced immediately beneath the impact melt sheet.

**Figure 7.11:** Schematic cross-section of the Sudbury North Range lithologies correlated with diagnostic shock features (zircon microtwins, quartz PDF’s and shattercones). Stars represent samples analysed within this study, black bars represent the occurrence of structures confirmed by this study and white bars represent the occurrence of structures inferred from other published sources (see text for details).

**Implications on the ancient terrestrial and extra-terrestrial zircon record**

Shock micro-twinning of zircon has been reported extensively within both the terrestrial and extra-terrestrial rock records (including within ex-situ Apollo Lunar samples, i.e. Timms et al. 2012)), and grains hosting such microstructure have been identified as key targets for dating impact events in the inner Solar System (Moser et al. 2011; Cavosie et al. 2015). Until now, the provenance of such grains has been poorly constrained, hindering our understanding of their formation and post-impact survivability. Detrital grains on Earth provide little geological context, while the erosional removal of the Vredefort melt sheet and fallback deposits limits interpretation of in-situ observations relative to primary crater morphology. Similar challenges exist for interpreting micro-twinned and partly recrystallized grains from Apollo samples of lunar breccia (Grange et al. 2013). The well-preserved melt-crater interface at Sudbury, coupled with the defined P-T history of the North Range, allows us to demonstrate that microtwin textures and incipient granular zircon formation are characteristic of grains located within the crater floor proximal within at least ~550m of the impact melt sheet, and can endure multiple phases of post-shock annealing and metamorphism. Furthermore, zircon has been shown to retain diagnostic microtwin lamella through extreme brecciation and pseudotachylite formation. Going forward, micro twinning in zircon can be applied to the identification and reconstruction of tectonically altered and overprinted impact craters with a
higher degree of confidence that these diagnostic structures are ubiquitously formed across a wide array of impact-induced P-T conditions and are robust enough to survive extensive post-shock annealing and metamorphism (Figure 7.12). This is important in the analysis of zircon-bearing ex-situ Lunar meteorites and in-situ Apollo materials, which are often highly brecciated (Nemchin et al. 2009).

**Figure 7.12:** Schematic preservation potential of zircon microtwins relative to maskelynite, quartz PDFs and zircon PDFs, which are more easily overprinted during tectonic reworking and annealing.

Terrestrially, the preservation of zircon microstructure is important in the identification and dating of Archean and Hadean-aged craters predicted to have formed during heavy bombardment of the early inner Solar System (Melosh, 1989), in-situ evidence of which has been masked during extensive reworking and overprinting of impacted terranes. With models estimating that ~41% of terrestrial zircon would have undergone partial to complete U-Pb age resetting during this period (Abramov et al., 2013), it is assumed that an abundance of shocked zircon microstructures would have been generated to facilitate such variable lead loss. Here we present compelling evidence that such grains have the potential to clearly preserve microtwin planes through multiple phases of impact and tectonically driven metamorphism, suggesting that potentially shocked Hadean and Archaean grains (such as the Jack Hills zircons; Bell and Harrison, 2013) would retain a discrete micro-structural record of any impact history. In future, the rapid identification of robust zircon microtwins and domains of granular zircon using modern EBSD techniques will allow for ancient impact events to be more robustly identified and dated, complimenting efforts by the community to more accurately reconstruct early bombardment histories from terrestrial, meteoritic and human-returned samples.
CONCLUSIONS

Our new microstructural analysis of shocked and annealed zircon grains from the North Range of Sudbury has yielded new constraints on the formation and preservation of diagnostic shock induced features such as granularisation and microtwin formation. Zircon microtwins form within ~2 km of the impact induced melt sheet, but are annealed and lost within 400 m of the contact. Twins are preserved, though discontinuous and partly recrystallized, within 500 m of the igneous body (suggesting high temperature annealing of the feature), and within highly brecciated and sheared zircon sampled 2 km from the melt sheet. Granularisation is restricted to highly annealed zircon within ~400 m of the melt sheet. These new data provide fresh constraints on the pressure regime experienced by the North Range of Sudbury, while also groundtruthing the preservation potential of shocked zircon microstructures for application to ex-situ meteoritic materials and heavily overprinted Hadean and Archean-aged terrestrial impact structures.
SUMMARY AND FUTURE DIRECTIONS

This study has revealed a number of significant findings regarding the potential applications of baddeleyite to the fields of shock metamorphism and planetary chronology. This chapter aims to summarize these findings, and highlight potential avenues for future development and application of the techniques.

8.1 RADIOGENIC DATING OF BADDELEYITE BY ATOM PROBE

Arguably the most important outcome of this study is that radiogenic U-Pb ratios can be measured to a high degree of precision and accuracy in nanoscale volumes of baddeleyite using atom probe tomography. Until now, geochronological applications of atom probe have been limited to Pb-Pb dating of zircon (Valley et al. 2014; Peterman et al. 2016). Although such studies have revealed nano-scale mechanisms of lead mobility and loss within this key mineral chronometer (Piazolo et al. 2016), they also tend to use atom probe in conjunction with more traditional analytical techniques (i.e. LA-ICP-MS, SIMS) to constrain generated ages, and do not attempt to produce a geologically meaningful age using Pb-Pb ages alone (Valley et al. 2014; Peterman et al. 2016). Large internal uncertainties on generated ages also reduce confidence in the technique, whereby the large counting statistics uncertainties introduced through the measurement of tens or hundreds of counts of $^{207}$Pb and $^{208}$Pb introduce > 10% uncertainties on the final age (Valley et al. 2014). Here, these shortcomings are circumvented by examining radiogenic (U-Pb) ratios across a large number of individual baddeleyite microtips, where large internal errors can be ignored in favor of examining the reproducibility across the dataset rather than over-interpreting individual data points. Statistically, this approach mirrors that used by other analytical techniques, such as secondary ion mass spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), which take weighted averages of multiple individual analyses to generate a final high-precision age. This approach has elevated the importance of atom probe tomography within the Earth and planetary sciences by presenting a dating technique boasting reproducibility comparable to SIMS analyses ($\pm 2 \sim 5\%$ uncertainty) from unprecedentedly small (> 100 nm) crystallographic domains.

Furthermore, by measuring both uranium and lead atoms within baddeleyite (facilitated by the absence of silica within the ZrO$_2$ lattice), isolated radiogenic dating is possible. This is a particularly important discovery given the recent insights U-Pb dating of baddeleyite has yielded into the formation and evolution of planetary bodies within the Solar System (Moser et al. 2013). Many complex, shocked grains contain sub-micron scale
crystallographic domains which are unresolvable at the length scales of traditional isotopic analysis (Darling et al. 2016). This new atom probe approach has demonstrated its ability to isotopically resolve these domains, yielding true crystallization and impact ages from partially age-reset bulk crystals. Going forward, the application of this technique to a wide range of planetary materials, including ZrO$_2$-bearing carbonaceous chondrites (El Goresy et al. 1978), will allow for unique radiogenic dating of many planetary materials previously examined using bulk Pb-Pb techniques (Bouvier & Wadhwa 2010). This will also allow for a more robust history of the formation and evolution of planetesimals to be developed.

8.2 BADDELEYITE AS A SHOCK INDICATOR AND BAROMETER

This study has generated an abundance of microstructural data for shocked baddeleyite grains. Constrained by the Sudbury melt sheet, these data show that baddeleyite can be applied as a sensitive and discrete indicator of bombardment in many of the more mafic crusts that predominate the inner Solar System. Importantly, these unique impact-induced microstructures can be generated at shock pressures as low as ~5 GPa, providing a quantified insight into 'lightly' shocked materials that many existing impact indicators and barometers do not test. For example, within planetary materials that contain limited evidence for high shock-pressure metamorphism (such as many Howardite-Eucrite-Diogenite (HED) and Lunar meteorites; Figure 8.1), this approach may greatly aid in constraining shock pressures experienced by the samples, providing exciting new insights into the extent and severity of shock metamorphism throughout the inner Solar System. Furthermore, such constraints are key to accurately interpreting geochronological data derived from the sample, which may reflect the age of igneous crystallization, the age of impact metamorphism, or a partially-reset combination of the two (Bouvier et al. 2005; Moser et al. 2013; Darling et al. 2016).

![Figure 8.1: Correlation between the velocity required to escape the planetary surface (km s$^{-1}$) and the percentage of maskelynite present in the resultant meteorite sample. (After Rubin 2015).](image-url)
Baddeleyite, like all shock indicators, is not without its shortcomings. While abundant in mafic lithologies, the phase has never been reported from silica-enriched (felsic) rock types where Zr is preferentially incorporated into zircon (ZrSiO₄). In addition, interaction with hydrothermal fluids (such as during greenschist-facies metamorphism) can result in the replacement of baddeleyite with zircon, destroying the subtle crystallographic features used here for impact identification and barometry. However, the preservation of diagnostic, impact-induced microstructures (amorphous domains, reversion twinning) even within the variably overprinted Sudbury samples examined here suggest the phase may be more resilient than previously expected. Examination of additional baddeleyite grains from a wider range of terrestrial tectonic settings will greatly constrain the variation in unshocked ZrO₂ microstructures, and further ground truth the potential for baddeleyite to preserve subtle crystallographic features through metamorphism and reworking.

Recent studies have also begun to reveal the importance of the high temperature ZrO₂ polymorphs (tetragonal and cubic structured) in the understanding of the microstructural evolution of shocked zircon (Timms et al. 2016). Although not directly addressed during this study, our developed understanding of the shock-response of baddeleyite and zircon provide new insights into the high temperature dissociation of zircon following an impact event. Importantly, while baddeleyite alone will provide a new avenue to examine the shock state of more mafic materials, the potential for the coupled occurrence of baddeleyite and zircon in many SiO₂-ZrO₂-bearing systems (Figure 8.2), including HED meteorites (Bukovanski & Ireland 1992), will allow for the more discrete unravelling of P-T histories using these accessory phases. Going forward, further investigation into the microstructural evolution of zircon and baddeleyite at high pressure and temperature conditions will further constrain shock P-T histories in almost all planetary materials.

**Figure 8.2:** Phase diagram for the ZrO₂-SiO₂ system. (After Kaiser et al. 2008).
8.3 NEW HORIZONS IN SOLAR SYSTEM CHRONOLOGY

Going forward, the coupled analysis of planetary baddeleyite grains though EBSD and APT techniques will enable radiogenic dating of a wide array of mafic materials, facilitating a more accurate history of Solar System chronology. Using baddeleyite microstructure to interpret the P-T history and shock-state of the grain, and highlight the most suitable analytical approach (SIMS or APT U-Pb) for targeted isotopic analysis will prove exceptionally powerful in this regard (Figure 8.3).

Given the associated cost and time commitments of atom probe tomography, the technique is best suited to highly complex baddeleyite grains hosting microstructures unresolvable at the length scales of SIMS or LA-ICP-MS, though APT can also be used to augment age data generated through these approaches. Structurally complex grains (as revealed by EBSD mapping) can be targeted for nm-scale U-Pb dating in an attempt to define chronological end members which can then yield insight into a partially-reset spread of ages measured from the wider grain population (i.e. Moser et al. 2013; Darling et al. 2016). This approach, when coupled with the many recent breakthroughs in in-situ isotopic analysis of baddeleyite such as single shot inductively coupled plasma mass spectrometry (SS-ICP-MS; Ibanez-Mejia et al. 2014) and in-situ secondary ion mass spectrometry (IN-SIMS; Chamberlain et al. 2010), provides a truly unique approach to radiogenic dating, with the potential to date grains of varying scales (> 100 um to < 200 nm) to a high degree of precision and accuracy.

Future applications of this work will likely focus on the radiometric dating of exceptionally small baddeleyite grains (i.e. ~500nm crystals within carbonaceous chondrites; El Goresy et al. 1978) and the resolution of complex, partially age-reset grain populations (i.e. Martian shergottite NWA 5298; Darling et al. 2016). Further microstructural characterization of baddeleyite grains within a wider range of chondrites and achondrites will act to constrain whole-rock ages (i.e. Ar-Ar, Pb-Pb) and provide new insight into the isotopic response of these key materials to shock events throughout the inner Solar System.

In summary, this work has elevated the importance of baddeleyite (ZrO$_2$) in the identification, barometry and chronometry of shock metamorphic (impact) events, while also generating the first ever radiogenic (U-Pb) ages using atom probe tomography.
Figure 8.3: A simple workflow approach to dating Solar System materials using baddeleyite. Following microstructural characterization of the grains, the best approach for U-Pb dating can be identified. Unshocked (homogenous) grains can be dated using traditional techniques; larger grains can be separated for TIMS analysis (Heaman 1997), while smaller grains can be analysed in-situ using SIMS (Chamberlain et al. 2010). Resolved U-Pb ages can be generated from both tiny (< 5 um) micro-baddeleyite crystals and more complex shocked grains using atom probe tomography.
BIBLIOGRAPHY


Hanson, R. E., J. L. Crowley, S. a Bowring, J. Ramezani, W. a Gose, I. W. D. Dalziel, J. a Pancake, E. K. Seidel,


Langenhorst, F., Harries, D., Pollok, K., 2013. Non-stoichiometry, defects and superstructures in sulphide
and oxide minerals, In: Minerals at the Nanoscale (Eds; Nieto, F & Livi, K. J. T.), 261 – 295.


140


Thompson, K., Lawrence, D.J., Larson, Olson, J. D., Kelly, T. F., Gorman, B., In-Situ Site-Specific Specimen Preparation for Atom Probe Tomography. Ultramicroscopy. 107 (2007) 131–139.


# Research Ethics Review Checklist

Please include this completed form as an appendix to your thesis (see the Postgraduate Research Student Handbook for more information).

<table>
<thead>
<tr>
<th>Postgraduate Research Student (PGRS) Information</th>
<th>Student ID:</th>
<th>457791</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PGRS Name:</strong></td>
<td>Lee Francis White</td>
<td></td>
</tr>
<tr>
<td><strong>Department:</strong></td>
<td>SEES</td>
<td></td>
</tr>
<tr>
<td><strong>First Supervisor:</strong></td>
<td>Dr. James Darling</td>
<td></td>
</tr>
<tr>
<td><strong>Start Date:</strong></td>
<td>01/02/2014</td>
<td></td>
</tr>
<tr>
<td>(or progression date for Prof Doc students)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Study Mode and Route:</strong></td>
<td>Part-time</td>
<td>MPhil</td>
</tr>
<tr>
<td></td>
<td>Full-time</td>
<td>PhD</td>
</tr>
<tr>
<td><strong>Title of Thesis:</strong></td>
<td>New horizons in solar system chronology</td>
<td></td>
</tr>
<tr>
<td><strong>Thesis Word Count:</strong></td>
<td>c. 36,500</td>
<td></td>
</tr>
<tr>
<td>(excluding ancillary data)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

If you are unsure about any of the following, please contact the local representative on your Faculty Ethics Committee for advice. Please note that it is your responsibility to follow the University’s Ethics Policy and any relevant University, academic or professional guidelines in the conduct of your study.

Although the Ethics Committee may have given your study a favourable opinion, the final responsibility for the ethical conduct of this work lies with the researcher(s).

**UKRIO Finished Research Checklist:**

(If you would like to know more about the checklist, please see your Faculty or Departmental Ethics Committee rep or see the online version of the full checklist at: [http://www.ukrio.org/what-we-do/code-of-practice-for-research/](http://www.ukrio.org/what-we-do/code-of-practice-for-research/))

- a) Have all of your research and findings been reported accurately, honestly and within a reasonable time frame?  
  
<table>
<thead>
<tr>
<th>YES</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

- b) Have all contributions to knowledge been acknowledged?  
  
<table>
<thead>
<tr>
<th>YES</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

- c) Have you complied with all agreements relating to intellectual property, publication and authorship?  
  
<table>
<thead>
<tr>
<th>YES</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

- d) Has your research data been retained in a secure and accessible form and will it remain so for the required duration?  
  
<table>
<thead>
<tr>
<th>YES</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

- e) Does your research comply with all legal, ethical, and contractual requirements?  
  
<table>
<thead>
<tr>
<th>YES</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

**Candidate Statement:**

I have considered the ethical dimensions of the above named research project, and have successfully obtained the necessary ethical approval(s).

**Ethical review number(s) from Faculty Ethics Committee (or from NRES/SCREC):**

n/a

If you have not submitted your work for ethical review, and/or you have answered ‘No’ to one or more of questions a) to e), please explain below why this is so:

**Ethical guidance check highlighted no need for formal review (attached certificate of ethics review)**

**Signed (PGRS):**

**Date:**
Certificate of Ethics Review

<table>
<thead>
<tr>
<th>Project Title:</th>
<th>Combined nanostructural and isotopic analysis of baddeleyite: New horizons in solar system chronology</th>
</tr>
</thead>
<tbody>
<tr>
<td>User ID:</td>
<td>599972</td>
</tr>
<tr>
<td>Name:</td>
<td>Lee White</td>
</tr>
<tr>
<td>Application Date:</td>
<td>15/12/2016 19:40:29</td>
</tr>
</tbody>
</table>

You must download your certificate, print a copy and keep it as a record of this review.

It is your responsibility to adhere to the University Ethics Policy and any Department/School or professional guidelines in the conduct of your study including relevant guidelines regarding health and safety of researchers and University Health and Safety Policy.

It is also your responsibility to follow University guidance on Data Protection Policy:

- General guidance for all data protection issues
- University Data Protection Policy

You are reminded that as a University of Portsmouth Researcher you are bound by the UKRIO Code of Practice for Research; any breach of this code could lead to action being taken following the University’s Procedure for the Investigation of Allegations of Misconduct in Research.

Any changes in the answers to the questions reflecting the design, management or conduct of the research over the course of the project must be notified to the Faculty Ethics Committee. **Any changes that affect the answers given in the questionnaire, not reported to the Faculty Ethics Committee, will invalidate this certificate.**

This ethical review should not be used to infer any comment on the academic merits or methodology of the project. If you have not already done so, you are advised to develop a clear protocol/proposal and ensure that it is independently reviewed by peers or others of appropriate standing. A favourable ethical opinion should not be perceived as permission to proceed with the research; there might be other matters of governance which require further consideration including the agreement of any organisation hosting the research.

**GovernanceChecklist**

**A1-BriefDescriptionOfProject:** Analysing the structure and chemistry of the accessory mineral phase baddeleyite within terrestrial rocks to ground truth numerous applications to planetary materials

**A2-Faculty:** Science

**A3-VoluntarilyReferToFEC:** No

**A5-AlreadyExternallyReviewed:** No

**B1-HumanParticipants:** No

**HumanParticipantsDefinition**

**Certificate Code:** 8623-96E5-10C4-C394-96FC-5E26-0355-52C3
B2-HumanParticipantsConfirmation: Yes
C6-SafetyRisksBeyondAssessment: No
D2-PhysicalEcologicalDamage: No
D4-HistoricalOrCulturalDamage: No
E1-ContentiousOrIllegal: No
E2-SociallySensitiveIssues: No
F1-InvolvesAnimals: No
F2-HarmfulToThirdParties: No
G1-ConfirmReadEthicsPolicy: Confirmed
G2-ConfirmReadUKRIOCodeOfPractice: Confirmed
G3-ConfirmReadConcordatToSupportResearchIntegrity: Confirmed
G4-ConfirmedCorrectInformation: Confirmed