



UNIVERSITY OF THE
WITWATERSRAND,
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**Characterization of Mafic Crustal Xenoliths from the Wyoming Craton, Montana (USA), using
Accessory Mineral Geochronology and Geochemistry with Implications for Lower Crustal Evolution**

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DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

A handwritten signature in black ink, appearing to be 'Yael', written above a horizontal line.

(Signature of candidate)

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Abstract

Lower-middle crustal xenoliths from the Bearpaw Mountains, Montana, USA provide a valuable opportunity to investigate deeper crustal processes along the northern margin of the Wyoming Craton. In this study, combined geochemistry and geochronology on zircon and apatite from a suite of amphibolite and granulite xenoliths are used to constrain the processes of xenolith formation, and the large-scale geological implications for the deeper continental lithosphere in the region.

Whole-rock geochemistry and thermobarometry, combined with U-Pb (SIMS) geochronology were conducted on a single amphibolite and four granulite xenoliths. The xenoliths are hosted within Eocene alkaline volcanic rocks ("minette"). Thermobarometric calculations indicate temperatures and pressures of 642-817 °C and 3.5-7.5 kbar confirming the middle-lower crustal nature of these xenoliths. Mantle-normalised trace element patterns for all xenoliths show a subduction-type signature, with extreme enrichments in large-ion lithophile (LILE) and fluid mobile elements (Cs, Rb, Ba, Pb, Sr) relative to high-field strength elements, together with relative Zr-Hf and Nb-Ta-Ti depletions. SEM-CL imaging of zircons reveals complex internal microstructures characteristic of both magmatic and metamorphic zircon. Magmatic zircon is recognised by weakly preserved oscillatory zoning and high Th/U ratios ($\bar{x} = 1.2$). Metamorphic zircon is present as overgrowths and newly formed grains, and is devoid of internal microstructures together with low Th/U (0.08-0.2). In more complex cases, magmatic zircon is recrystallised in the presence of a melt phase to create a variety convolute internal textures. U-Pb geochronology within magmatic zircon yield dominantly Proterozoic populations between 1834±19 Ma and 1874±8 Ma. Ages within metamorphic domains constrain a slightly younger population between 1772±5 Ma and 1788±4 Ma. A series of dispersed ages within complex magmatic zircon yield dates between 2004±17 and 2534±9 Ma. Proterozoic ages are correlated with lithospheric processes along the cratonic north-western margin (Great Falls Tectonic Zone, Medicine Hat Block and Montana Metasedimentary Terrane), involving arc-related melting and collisional metamorphism. The protolith to xenoliths containing mid-Proterozoic (ca. 1800 Ma) magmatic zircon ages were formed by subduction-induced melting of the overlying mantle wedge. Xenoliths containing older magmatic zircon ages (ca. 2534 Ma) sample protoliths produced by melting of a subduction-related metasomatised mantle in the Late Archaean or earlier. Both Proterozoic and Late Archaean protolith magmas are envisaged as new additions to the Wyoming Craton that resided within middle to lower crustal levels of the continental lithosphere before being subjected to metamorphism and recrystallisation at ca. 1770 Ma.

Trace elements (REE) together with oxygen and hafnium isotopes were obtained using LA-ICP-MS on previously dated and imaged zircon grains. REE in zircon for all xenoliths are steep and positively

sloping without discernible HREE depletion, implying zircon (re)crystallisation in the absence of garnet. Negative Eu anomalies signify concomitant zircon and feldspar crystallisation. Solid-state recrystallisation may be responsible for variations in LREE, Eu and Ce. Xenoliths containing magmatic zircon (1834 ± 19 Ma) with mantle-like $\delta^{18}\text{O}$ (4.4-5.5 ‰) and radiogenic initial ϵ_{Hf} (-2.3 to +3.7) likely formed through crystallisation of melts derived from a mantle source that incorporated minor amounts of subducted sedimentary/supracrustal material. Proterozoic (1874 ± 8 Ma) xenoliths with elevated $\delta^{18}\text{O}$ (6.0-7.0 ‰) and unradiogenic ϵ_{Hf} (-8.2 to -9.6) within magmatic zircon represent melt products of subduction-induced melting and metasomatism in the mantle wedge. Zircons containing non-mantle like $\delta^{18}\text{O}$ (6.4-7.2‰) and unradiogenic ϵ_{Hf} (+1.4 to -17.6) in older (ca. 2534 Ma) xenoliths represent protolith magmas derived from a subduction-metasomatised mantle prior to crystallisation in the Late Archaean or earlier.

U-Pb geochronology and trace element chemistry (LA-ICP-MS), together with major element and halogen geochemistry was then conducted on apatite grains in order to provide insight into lower temperature processes operating within amphibolite and granulite xenoliths. Apatite in all xenoliths are metamorphic and show light rare earth (LREE) enrichments relative to heavy rare earth elements (HREE), negative Eu anomalies and generally high concentrations of trace elements. Halogen compositions are uniform and allow classification of the apatites as fluorapatite. Trace element patterns in metamorphic apatite signify progressive prograde metamorphism in which apatite grains continuously exchanged ions with minerals in the system, and acquired trace element concentrations redistributed by newly forming and previously crystallised metamorphic phases. Specifically, as metamorphic grade increases, the break-down of monazite and crystallisation of metamorphic feldspar resulted in LREE enrichments and Eu depletions in metamorphic apatite respectively. Growth of garnet near the metamorphic peak depleted apatite in HREE. Due to the high metamorphic grade of these rocks, the rock volume is likely to have been in large-scale chemical equilibrium, resulting in uniform apatite trace element and halogen concentrations in each xenolith. Geochronology on granulite xenoliths yield Neoproterozoic to Palaeozoic (ca. 300-500 Ma) lower-intercept ages that are not correlated with known thermal or metasomatic events within the Wyoming Craton that could have induced isotopic resetting at these times. Rather, these young ages are interpreted to represent protracted and slow cooling in the middle to lower crust following a thermal maximum in the mid-Proterozoic (ca. 1770 Ma).

Integration of geochronological and geochemical data on apatite and zircon indicate the formation of new melts added by subduction-induced melting in the Proterozoic (ca. 1800 Ma). These new magmatic additions form the protolith to the xenoliths, and resided at lower to middle portions of the continental lithosphere before being recrystallised to amphibolite/granulite facies during collision-

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1 Introduction: The Lower Continental Crust

An understanding of the continental lithosphere requires an integrated knowledge of both upper and lower portions of Earth's crust. The characteristics of upper continental crust are well constrained due to surface exposure of such rocks in a variety of tectonic settings. Middle to lower crustal lithologies are often not directly accessible and, as such, are not fully understood in terms of age, composition and petrogenesis. It is therefore desirable to study fragments of the lower crust in order to establish geological processes operating at deeper levels, which may have implications for crust formation and tectonic evolution beneath cratonic domains. In this study, a variety of middle-lower crustal fragments ("xenoliths") from the Wyoming Craton in Montana, USA, are characterised using geochronology, thermometry and geochemistry (radiogenic and stable isotopes, major and trace elements) in order to constrain middle-lower crustal petrogenetic processes in the region.

The lower continental crust is generally considered to represent the portion of crust beneath the middle continental crust and above the Mohorovičić Discontinuity (Rudnick, 1992; Rudnick and Gao, 2003). The depth and relative thickness of this layer is defined by seismic data and varies from craton to craton and/or tectonic setting. Since average continental crust is around 40 km thick, the lower crustal portion begins at approximately 23 km depth (Christiansen and Mooney, 1995; Rudnick and Fountain 1995, Rudnick and Gao, 2003).

There are several methods which may enable the investigation of the lower crust. Ideally, one would study a portion of lower continental crust exposed at surface. Such exposures include the well-studied Ivrea-Verbano crustal segment in Northern Italy (Fountain, 1976). Numerous other lower crustal slices are exposed worldwide, such as the Vredefort Dome (Kaapvaal Craton) and Kapuskasing Uplift (Superior Craton) among others (Rudnick and Gao, 2003 and references therein). Alternatively, lower crustal bodies brought to the surface by kimberlitic or alkaline volcanic magmatism (xenoliths) may be considered to better represent lower crust (Rudnick and Presper, 1990; Rudnick, 1992; Ruiz, 1992; Downes, 1993). A drawback to using xenoliths as representatives of lower-middle crust is that they represent minute portions of the wider continental lithosphere. Remote methods of studying lower crust include geophysical methods, such as seismic refraction surveys to estimate P-wave (V_p) velocities of different crustal segments. Lower crust is generally associated with higher V_p 's (>6 km/s) (Rudnick, 1992; Hacker et al., 2015). Finally, heat flux considerations (based on relative abundances of heat producing elements: Th, U, K) can be used to differentiate crustal layers together with their relative thicknesses (Rudnick and Gao, 2003, 2014; Huang et al., 2013; Hacker et al., 2011, 2015).

Based on the averaging of xenolith compositions worldwide, the composition of lower continental crust is generally considered to be mafic ($\text{SiO}_2 < 57\%$), and contains lower proportions of heat

producing elements (Rudnick, 1992; Rudnick and Gao, 2003). On the other hand, using combined P-wave velocity and thermal flux inferences from xenoliths, Hacker et al. (2015) argued that lower crust is not required to be mafic, and suggested that continental crust is composed of a two-layer felsic structure.

The petrogenetic mechanisms controlling the formation of lower crust are varied. A frequently described process of lower crustal petrogenesis is magmatic underplating, which involves the ponding of basaltic melts beneath continental cratons (e.g. Voshage et al., 1990). At convergent margins, subduction-induced melting in the mantle wedge may result in new magmatic additions to the overlying continental lithosphere (Mirnejad and Bell, 2008). Both these mechanisms would imply that the lower crust is predominantly newly formed and younger than the overlying continental crust. Alternatively, existing continental crust may be partially melted, leaving behind a mafic residue that then forms a largely restitic lower crust (Rudnick, 1992). More recent mechanisms of lower crustal evolution have been proposed, which involves the relamination of subducted felsic components together with delamination of mafic crustal portions at convergent margins (Hacker et al., 2011, 2015; Keleman and Behn, 2016). The elucidation of the process(s) that operated at deeper crustal levels requires knowledge of both xenolith compositional characteristics and age data, and is the major focus of this study.

Zircon Geochronology and Geochemistry

U-Pb zircon geochronology is a robust and reliable method for dating crustal xenoliths. Zircons can record complex, multi-episodic tectonic histories involving a variety of magmatic, metamorphic and metasomatic events; the timing of which may be recorded texturally and compositionally within the zircon crystal. Zircons that crystallise directly from a melt are considered to be magmatic/igneous zircon (Pidgeon, 1992; Corfu, 2003). Metamorphic zircons are generally considered to form in the solid-state, but have also been interpreted to form from melts produced by metamorphism (anatexis and partial melting) (Rubatto, 2017). In this study, metamorphic zircon is considered strictly to form in the solid-state. Finally, metasomatic zircon refers to zircon that may have precipitated from a fluid, or was modified post-crystallisation by hydrothermal or metasomatising fluids (Tomaschek et al., 2003; Xia et al., 2010). Apart from this basic classification of zircon, numerous secondary processes can modify the zircon crystal, such as metamorphic overgrowth, dissolution recrystallisation, solid-state recrystallisation and replacement crystallisation among others (Pidgeon, 1992; Vavra et al., 1994, 1996; Corfu et al., 2003, Xia et al., 2009 and references therein). Correct interpretation of zircon petrogenesis requires careful inspection of zircon microtextures (revealed by back-scattered and cathodoluminescence (CL) imaging), together with zircon geochemistry (Th/U, REE) and U-Th-Pb

geochronology. This enables the crystallisation age and subsequent evolution of xenoliths to be inferred from zircon data and, together with whole-rock geochemistry, comprises the first part of this study.

Oxygen isotopes allow for further characterisation of the protolith magma, or source from which protolith melts were derived. Oxygen isotopes in zircon are measured in per mill (‰) relative to a fresh water standard such as V-SMOW (Valley et al., 1994). Oxygen isotopes in zircon forming from melts derived from a unmodified mantle source are characterised by a $\delta^{18}\text{O}$ value of 5.3 ± 0.6 ‰, while sources/melts that incorporated significant supracrustal components are reflected by zircon $\delta^{18}\text{O}$ values of >5.9 ‰ (Valley et al., 2003; 2005). Post-crystallisation metasomatic alteration of zircon grains may also be inferred based on variable oxygen isotopic compositions in zircon domains (Chen et al., 2011; Sheng et al., 2012).

Due to the small atomic radius (2.25-2.30 Å) and identical charge of the Hf^{4+} ion relative to the Zr^{4+} ion, zircon (ZrSiO_4) constitutes one of the primary reservoirs for Hf (Hoskin and Schaltegger, 2003). Measurement of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio in zircon at a specific age (defined by U-Pb zircon geochronology) within a zircon domain allows for the calculation of an epsilon hafnium value (ϵ_{Hf}), which is a measure of the deviation of Hf from the Chondritic Uniform Reservoir (CHUR) at a certain age, and can provide information about the source from which rocks were derived. More specifically, radiogenic Hf compositions (positive ϵ_{Hf}) may indicate derivation of the source melt from the Depleted Mantle (DM), while unradiogenic hafnium (negative ϵ_{Hf}) may imply the presence of older crustal components in the source, or re-melting of existing crust (Kinny and Maas, 2003). Additionally, relative compositions of $^{176}\text{Hf}/^{177}\text{Hf}$ through time can provide insight to processes such as Pb-loss and recrystallisation of zircon (Xia et al., 2009). Both oxygen and hafnium data complement previous geochronology, which aids in the interpretation of lower crustal xenoliths in a geological context, and forms the second part of this study.

Trace elements in zircon, particularly the rare earth elements (REE), provide valuable insight into the (re)crystallisation history of zircon relative to co-existing mineral phases. In general, zircon tends to preferentially incorporate heavier rare earth elements (HREE) over light rare earth elements (LREE) (Hoskin and Schaltegger, 2003). However, if a HREE sequestering phase such as garnet grows concomitantly with zircon, HREE will be depleted in zircon (Rubatto, 2002). Other such minerals that affect REE in zircon include feldspar, which sequesters europium and may result in a recognizable negative Eu anomaly in chondrite-normalised patterns of zircon. Cerium and europium in zircon may also be used to constrain the oxygen fugacity of the host melt (Trail et al., 2011, 2012).

Apatite is an increasingly prominent geochronological and geochemical tool used in a variety of ore-petrology and detrital provenance studies (e.g. Mao et al., 2016; O'Sullivan et al., 2018). Unlike zircon, apatite is ubiquitous in mafic and felsic lithologies (Piccoli and Candela, 2002), and therefore provides massive potential for use in petrochronological studies (Engi, 2017). The trace element compositions of apatite in lower crustal rocks are not commonly reported in existing literature. In this study, REE in apatite from high-grade, mid-lower crustal xenoliths are characterised in order to provide valuable insight into trace element processes operating at deeper crustal levels, but within a lower temperature regime when compared to P-T conditions of zircon growth and recrystallisation. The trace element chemistry of apatite is used to distinguish between magmatic/metamorphic apatite, and provide information regarding crystallisation processes operating in the protolith melt. The reduced closure temperature of apatite (375-550 °C, Schoene and Bowring, 2007; Cochrane et al., 2014) enables uranium-lead geochronology within a lower temperature spectrum in contrast to higher temperature minerals such as zircon (>800 °C, Cherniak and Watson, 2003). A challenging aspect of U-Pb apatite geochronology is the presence of significant and variable non-radiogenic Pb (or common lead, Pb_c) and is accounted for using a Pb_c correction (Chew et al., 2011). The combination of low temperature mineral geochronology and geochemistry of apatite may offer information complementary to what can be gained from whole rock and zircon data alone, and can provide insight into the long term evolution of continental cratons. This forms the final part of this study.

1.1 Aims and objectives of this study

In this study, a suite of xenoliths from the middle-lower continental crust of the Wyoming Craton, Montana, USA are studied using accessory mineral (zircon, apatite) geochronology (U-Pb) and geochemistry (hafnium and oxygen isotopes and REE). The study aims to answer the following questions:

- What is the age of the xenoliths and do these ages constrain specific magmatic/metamorphic events?
- What are the whole-rock compositions of the xenoliths and can they be related to petrogenetic processes in the region?
- Knowing the age and composition of the xenoliths, are they coupled to upper crustal sections? More specifically are the xenoliths representative of existing continental crust or are they new additions to the continental lithosphere?
- What tectonic regime can explain the compositional and geochronological characteristics of these xenoliths (subduction/anatexis/underplating)?

- Do the results agree with previous interpretations of lower crustal processes in the region or are new and/or multiple mechanisms responsible for lower crustal formation and evolution?

Previous lower crustal work within the Wyoming Craton involved investigations of lower crust using remote methods (geophysical surveys). Of the xenolith studies that do exist, most are restricted to U-Pb geochronology, while relatively few lower crustal studies combine U-Pb, Hf, O and REE techniques. In this way, our study should provide a broader insight into lower crustal processes whilst building upon previous studies.

An initial hypothesis may be gleaned from previous literature studies on lower crust in the region and from xenolith localities worldwide.

- Since the majority of lower crustal xenoliths appear mafic, they likely represent new basaltic additions that are younger than predominantly Archaean cratonic crust. Ages obtained from zircons should be related to a convergent margin/continental collisional processes north-west of the Wyoming Craton.
- The tectonic regime in which the protolith melts form is likely a subduction regime, as implied by existing studies in the region and the location of xenoliths along a subduction-related boundary (Great Falls Tectonic Zone). Alternatively, a mechanism of underplating may be operating, as reported beneath numerous ancient continental cratons.

1.2 Structure of this thesis

This dissertation is divided into five chapters. Chapter 1 provides a brief introduction and contextualises the study. Chapter 2 provides a short summary of the geological setting and locality where xenoliths were obtained. Chapters 3, 4 and 5 comprise of manuscripts either published, submitted or intended for submission to peer-reviewed journals. Chapter 6 is a concluding chapter that summarises and synthesises the findings of the respective papers and integrates the conclusions in a large scale geological context.

1.3 Contributions to written works

Chapter 3 comprises the first manuscript: Thakurdin, Y., Bolhar, R., Horváth, P., Rocholl, A., and Collerson, K. 2019a. Characterization of Lower Crustal Xenoliths from the Bearpaw Mountains, Montana (USA), using U-Pb Geochronology, Whole-Rock Geochemistry and Thermobarometry, with Implications for Lower Crustal Processes and Evolution of the Wyoming Craton. This manuscript has been published in *Chemical Geology* (Thakurdin, Y., Bolhar, R., Horváth, P., Rocholl, A., & Collerson, K. (2019). *Characterization of crustal xenoliths from the Bearpaw Mountains, Montana (USA), using U-*

Pb geochronology, whole-rock geochemistry and thermobarometry, with implications for lower crustal processes and evolution of the Wyoming Craton. Chemical Geology, 524, 295-322, <https://doi.org/10.1016/j.chemgeo.2019.05.034>.

Contribution of individual authors are as follows:

Thakurdin, Y - 70 % (produced all sections of the written text of the manuscript, including figures, performed mineral separation on xenoliths, obtained mineral and whole-rock element compositions and U-Pb, Ti and O isotope data on zircons, performed data reduction)

Bolhar, R - 15 % (1st supervisor, provided initial idea and funding for research, edited and corrected previous manuscript drafts)

Horváth, P - 10 % (2nd supervisor, assisted with metamorphic petrology and P-T estimations, edited and corrected previous manuscript drafts, assisted with electron microprobe work)

Rocholl, A - 4 % (assisted with U-Pb analysis on zircon using SIMS)

Collerson, K - 1 % (collected and provided xenolith samples)

Chapter 4 comprises the second manuscript: Thakurdin, Y., Bolhar, R., Horváth, P., Wiedenbeck, M. 2019b. Formation of Lower to Middle Crust of the Wyoming Craton, Montana (USA), Using Evidence from Zircon Hf-O Isotopic and Trace Element Compositions. This manuscript has been published in *Chemical Geology* (Thakurdin, Y., Bolhar, R., Horváth, P., Wiedenbeck, M., & Rocholl, A. (2019). *Formation of lower to middle crust of the Wyoming Craton, Montana (USA), using evidence from zircon Hf-O isotopic and trace element compositions. Chemical Geology, 525, 218-244, <https://doi.org/10.1016/j.chemgeo.2019.07.021>.*

Contribution of individual authors are as follows:

Thakurdin, Y - 70 % (produced all sections of the written text of the manuscript, including figures, obtained Hf and REE compositions on zircon, performed data reduction)

Bolhar, R - 20 % (1st supervisor, provided initial idea and funding for research, edited and corrected previous manuscript drafts)

Horváth, P - 5 % (2nd supervisor, edited and corrected previous manuscript drafts)

Wiedenbeck - 5 % (assisted with oxygen isotope data reduction and edited and corrected previous manuscript drafts)

Chapter 5 comprises the third manuscript: Thakurdin, Y., Bolhar, R., Horváth, P., O'Sullivan, G. Coupled U-Pb Geochronology and Major and Trace Element Geochemistry of Apatite in High-Grade Metamorphic Rocks – A Record of Mid- to Lower Crustal Processes beneath the Wyoming Craton, Montana. This manuscript is in the final stages of preparation with intended submission to *Precambrian Research*.

Thakurdin, Y - 70 % (produced all sections of the written text of the manuscript, including figures, obtained U-Pb and trace element data on apatite, performed data reduction)

Bolhar, R - 20 % (1st supervisor, provided initial idea and funding for research, edited and corrected previous manuscript drafts)

Horváth, P - 5 % (2nd supervisor, edited and corrected previous manuscript drafts)

O'Sullivan - 5 % (provided LA-ICP-MS U-Pb and trace element data on apatite along with data reduction on a portion of samples in this study, edited and corrected previous manuscript drafts)

Conference abstracts pertaining to this thesis are included on Page 145. This includes two conference abstracts (Geocongress, 2018; Goldschmidt, 2018).

1.4 Methods

Electron microprobe (EPMA) analyses were conducted at the University of Johannesburg. Accessory minerals (zircon and apatite) were separated using a standard mineral separation techniques and mounted on epoxy resin. A Panalytical PW2404 X-ray fluorescence spectrometer was used for element analysis at the University of the Witwatersrand. Zircons were imaged using back-scattered (BSE) and cathodoluminescence imaging at the GeoforschungsZentrum (GFZ) in Potsdam, Germany. U-Pb geochronology and oxygen isotope analysis using Secondary-Ion Mass Spectrometry (SIMS) was also performed at the GFZ using the CAMECA 1280-HR SIMS instrument. Following geochronological measurements on zircon using SIMS, REE and Ti in zircon was measured using laser-ablation mass spectrometry (LA-ICP-MS) using a Teledyne Photon Machines G2 laser system coupled to a Thermo iCapQ) at Trinity College in Dublin, Ireland. The mount was repolished for hafnium analysis on previously dated zircon grains using a 193nm ArF RESOLUTION SE excimer laser (Australian Scientific Instruments) coupled to a Nu Plasma II MC-ICPMS (Nu Instruments)) at the University of Johannesburg. U-Pb geochronology and trace element analyses of apatite were also conducted at Trinity College using a (Photon Machines Analyte Exite 193 nm ArF Excimer laser-ablation system with a Helex 2-volume ablation cell, coupled to an Agilent Technologies 7900 LA-ICP-MS instrument. Details of analytical methods, data treatment and instrumental procedures are provided in the methods section of chapters 3, 4 and 5.

2 The Wyoming Craton and Bearpaw Mountains

A synthesised summary of the geological setting is provided here, to avoid repetition with each successive manuscript.

The Wyoming Craton is situated within the state of Montana in the North-Western United States. This Archaean craton is flanked by Proterozoic margins, such as the Great Falls Tectonic Zone (GFTZ, 1700-1900 Ma) to the north, and the Trans-Hudson Orogen (1720-1830 Ma) and Cheyenne Belt (1750-1780 Ma) toward the eastern and southern margins of the craton, respectively (Mogk et al., 1992; Mueller and Frost, 2006). The Farmington Zone and Selway Terrane (1600-2500 Ma) lie along the poorly constrained western margin of the craton (Mueller et al., 2004a, Foster et al., 2006). Regionally associated cratonic blocks adjacent to these collisional zones are the Superior Craton and Hearne-Craton, which form part of the Laurentian supercontinent (Mueller and Frost, 2006). The cratonic interior is categorised into three distinct regions, namely the Beartooth-Bighorn Magmatic Zone (BBMZ), Montana Metasedimentary Terrane (MMT) and Southern Accreted Terranes (SAT) (Chamberlain et al., 2003; Mueller and Frost, 2006). The BBMZ and MMT are related through a unique, elevated Pb isotope signature (high μ), which identifies the craton as extracted, newly formed crust as opposed to an origin involving Archaean terrane collision and amalgamation (Mueller and Frost, 2006). Geophysical studies have shown that the Wyoming Craton is a strong, stable block with a relatively thick mafic crustal root, implying crustal growth through extended magmatic underplating and/or arc volcanism (Snelson et al., 1998; Clowes et al., 2002; Gorman et al., 2002).

The early Archaean history (3000-3600 Ma) of the Wyoming Craton begins with volcanic arc-accretion to form a stable cratonic block. Subsequent amalgamation of the Wyoming, Hearne and Superior cratons resulted in the formation of the supercontinent Laurentia, and is marked by Proterozoic (1800-1900 Ma) collisional zones along the margins of the craton (Chamberlain et al., 2003). Within-craton tectonic activity, including calc-alkaline magmatism, underplating and arc-related magmatic pulses reportedly occurred from the Late to Mesoarchaeon within the Beartooth-Bighorn Magmatic Zone (BBMZ) (Frost et al., 1998; Mueller et al., 2010; Dragovic et al., 2016). Interior tectonic and magmatic activity largely ceased around 2600 Ma (Frost and Fanning, 2006).

Subsequent tectono-thermal events in the region were restricted to marginal zones such as the western margin and GFTZ. Ocean closure between the Medicine Hat Block and Wyoming Craton and associated subduction likely occurred between 1864 and 1867 Ma (Mueller et al., 2002). Subduction was directed northward, with oceanic crustal material being thrust beneath the Medicine Hat Block (Fig. 2.1). This may have resulted in the production of subduction-related melts in the overlying mantle wedge (e.g. Mueller et al., 2002). Following ocean closure, the Medicine Hat Block and northern

Wyoming Craton collided at ca. 1770 Ma. This likely resulted in metamorphism and deformation of existing crust at this time (Mueller et al., 2002, 2004, 2005; Gifford, 2013; Gifford et al., 2014, 2018). As the Wyoming and Medicine Hat tectonic blocks continued to be compressed, the tectonic regime likely shifted to a more transpressional environment, as the Wyoming Craton moved eastward towards the Superior Craton (Dahl et al., 1999; Mueller et al., 2005). The collision of the Wyoming Craton and Medicine Hat Block was broadly coeval with adjacent cratonic collisional activity, including the Hearne-Medicine Hat collision (ca. 1800 Ma) to the north (Vulcan Zone), the Wyoming-Colorado collision (ca. 1600-1800 Ma) to the south and the Wyoming-Superior (ca. 1700-1770 Ma) collision to the east (Trans-Hudson Orogen) (Gifford et al., 2014 and references therein). Following these Proterozoic events, within-craton and marginal activity largely ceased up until the Cretaceous to Eocene (Blackburn et al., 2011, 2012).

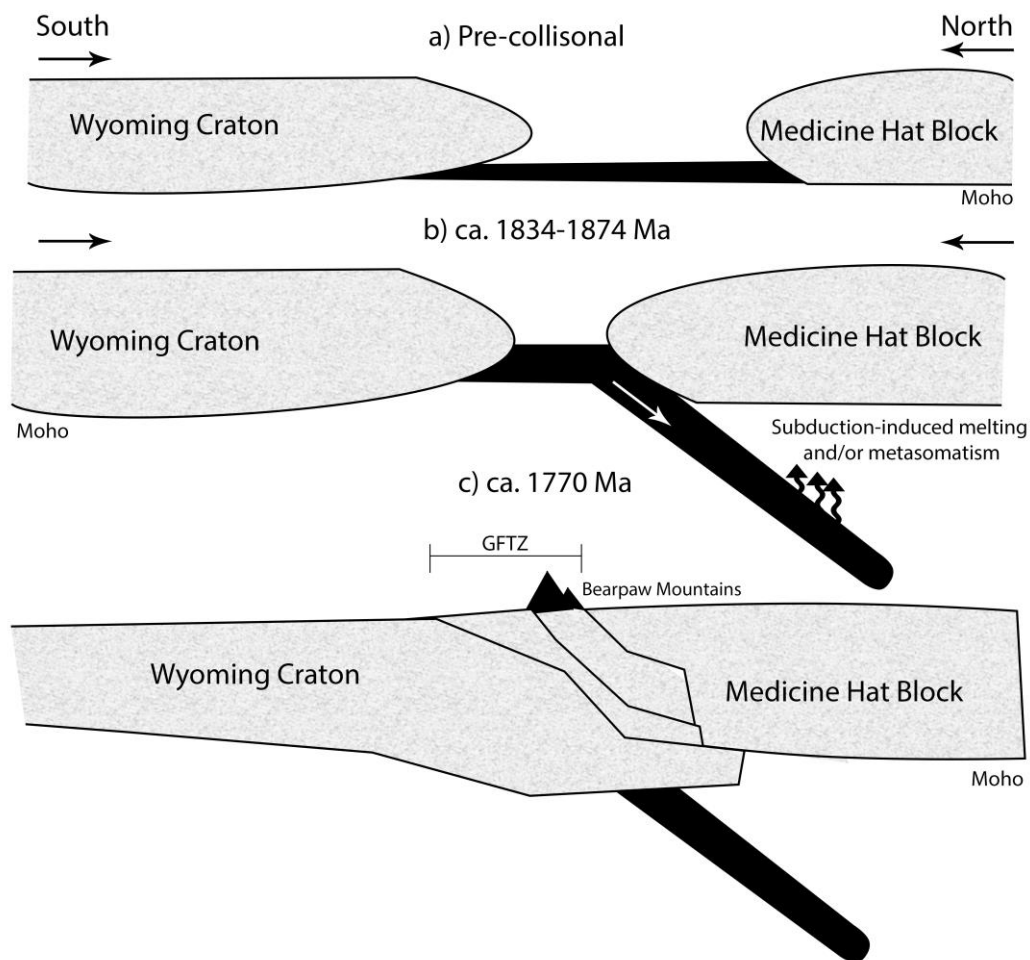


Figure 2.1: Schematic cross-sections for the tectonic evolution of the Wyoming Craton (WC), Medicine Hat Block (MHB) and Great Falls Tectonic Zone (GFTZ). a) Pre-collisional stage preceding Proterozoic subduction between the WC and MHB. Earlier subduction events in the region may have occurred (Wooden and Mueller 1988, Mueller et al., 2010), but are poorly constrained by geochronology in our

xenoliths (See Chapter 3). b) Ocean closure commences at ca. 1860 Ma (Mueller et al., 2002). Subduction is orientated such that material is thrust beneath the MHB. Fluids emanating from the subducting slab result in melting and/or metasomatism of the overlying mantle wedge. c) Following subduction, the WC and MHB collide at ca. 1770 Ma.

Geochronological studies within the GFTZ generally report a narrow range of ages between 1770 and 1860 Ma, which are related to the above-mentioned magmatic and metamorphic activity associated with convergent margin processes (Foster et al., 2006; and references therein). For example, ^{40}Ar - ^{39}Ar ages between 1775 and 1800 Ma were associated with the collision of the Medicine Hat and Wyoming cratons (Holm and Schneider, 2002). U-Pb zircon ages of 1864-1867 Ma from the Little Belt Mountains within the GFTZ were interpreted to represent new material formed from subduction-related ocean closure (Mueller et al., 2002), while a distinct metamorphic monazite age of 1770 Ma was reported for the Tobacco Root and Highland Mountains (Mueller et al., 2004b, 2005), together with granulite facies metamorphic zircons dated at 1760 Ma as a result of collisional tectono-thermal activity. Ages and tectonic domains along the western margin of the craton are not well defined. Collisional tectonics associated with the generation of mafic crust has been suggested to occur during the Late Archaean to Proterozoic (1600-2500 Ma) along the western cratonic boundary (Foster et al., 2006). Similar studies on the western margin constrain both older (2200-2500 Ma) and younger age populations (1860-1910 Ma) (Mueller et al., 2004a).

The Bearpaw Mountain range forms part of the Eocene Alkali Magmatic Province (50-54 Ma) and is located along the northern edge of the Wyoming Craton within the Great Falls Tectonic Zone (GFTZ) (Fig. 2.2a, b). Other nearby mountain ranges associated with extrusive volcanism include the Eagle Buttes (50-52 Ma), Highwood Mountains (50-53 Ma), Sweetgrass Hills (50-54 Ma) and Missouri Breaks Diatremes (47-52 Ma) (Downes et al., 2004; Facer et al., 2009). Major rock types include minettes, latites and phonolites, which entrained mantle and mid- to lower crustal xenoliths (Collerson et al., 1988; Bolhar et al., 2007). Sharp contacts with the host minette imply minor to no interaction of the extrusive lava with the xenolith bodies (Bolhar et al., 2007).

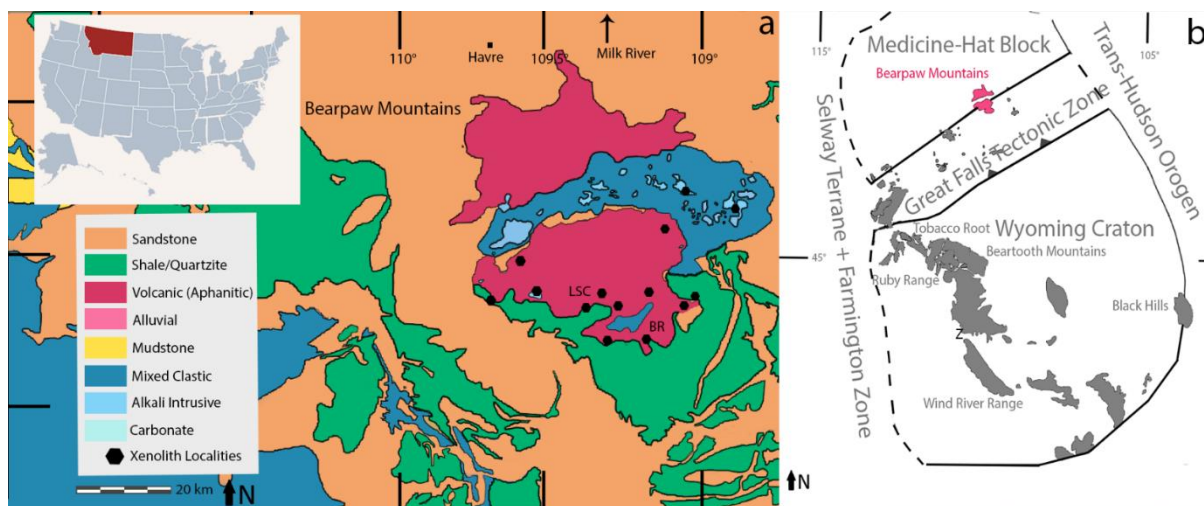


Figure 2.2: Simplified geological map showing xenolith sampling localities within the Bearpaw Mountains (a) and regional geographical context after Foster et al. (2006) (b).

2.1 Potential economic significance

Rare earth elements (REE) are of increasing importance in the electronics and transportation industry, amongst numerous other technological applications. Although chiefly produced and exported by China, the rising demand for REE has led to prospecting worldwide. Within the vicinity of the Wyoming Craton, potential REE-bearing rocks include Precambrian magmatic and metamorphic rocks, and younger alkali intrusive rocks such as those that brought our xenoliths to the surface (Sutherland and Cola, 2016). Exposures of such rocks are present within, and along the margin of the BBMZ. REE-bearing lithologies are distributed amongst regional uplifts such as the Wind River Range, Owl Creek Mountains, Bighorn Mountains and Granite Mountains. Indicator minerals for REE-enrichment include monazite, allanite and epidote among others. Therefore, geochronological classification of metamorphic rocks with ancient, Precambrian origins (and containing REE-enriched minerals) may lend to potential economic significance within the region. Zircon geochronology is ideally suited to dating such rocks and may further constrain regions of economic importance within the Wyoming Craton.

Perhaps of greater significance to lower crustal xenoliths is diamond exploration. U-Pb and Sm-Nd geochronology on accessory minerals extracted from mantle and lower crustal xenoliths may enable elucidation of the age and structure of the lithosphere of the Wyoming Craton. Specifically, a study using Sm-Nd model ages combined with zircon geochronology on basement samples from the Saskatchewan region along the eastern margin (Trans-Hudson Orogen) of the Wyoming Craton was conducted by Collerson et al. (1990). The authors concluded that the mantle lithosphere beneath the Wyoming Craton was sufficiently old (Archaean) and stable enough to allow for diamond formation, and envisaged economic potential of erupted kimberlite pipes in the area. In general, favourable

environments for diamond formation include areas of extreme depth (>100km) (such as beneath thick continental cratons) that have been unaffected by thermal events for an extended period of time (Hausel, 2007). The Wyoming Craton may be one such example due to its thick crustal root (up to 60 km) (Gorman et al., 2002; Mahan et al., 2012) and general tectonic quiescence since the mid-Proterozoic. Indeed, diamond bearing kimberlites have been reported at multiple localities within the Wyoming Craton (e.g. Hausel, 2007). In this study, accessory mineral data (specifically apatite) obtained from our xenoliths imply a slowly cooled, thick continental lithosphere that was unperturbed by thermal activity since ca. 1800 Ma, which may represent favourable conditions for diamond formation.

3 Characterization of Lower Crustal Xenoliths from the Bearpaw Mountains, Montana (USA), using U-Pb Geochronology, Whole-Rock Geochemistry and Thermobarometry, with Implications for Lower Crustal Processes and Evolution of the Wyoming Craton

This chapter contains the contents of a paper entitled: “Characterization of crustal xenoliths from the Bearpaw Mountains, Montana (USA), using U-Pb geochronology, whole-rock geochemistry and thermobarometry, with implications for lower crustal processes and evolution of the Wyoming Craton” by Thakurdin, Y., Bolhar, R., Horváth, P., Rocholl, A. and Collerson, K. and has been published in *Chemical Geology* (Thakurdin et al., 2019a, Volume 524, 295-322, <https://doi.org/10.1016/j.chemgeo.2019.05.034>).

3.1 Abstract

A suite of crustal xenoliths from the Bearpaw Mountains, Montana, USA, was examined using zircon geochronology, whole-rock geochemistry and petrology in order to investigate lower crustal geological processes along the northern margin of the Wyoming Craton. The xenoliths are hosted within Eocene alkaline volcanic rocks (“minette”) and include mafic to intermediate granulites and amphibolites. Whole-rock geochemistry and geothermobarometry indicate igneous protoliths of alkaline to sub-alkaline composition, which recrystallised at lower to middle crustal conditions (642-817 °C and 3.5-7.5 kbar). Mantle-normalised trace element patterns for all xenoliths show a subduction signature, with extreme enrichments in large-ion lithophile (LILE) and fluid mobile elements (Cs, Rb, Ba, Pb, Sr) relative to high-field strength elements, together with relative Zr-Hf and Nb-Ta-Ti depletions. While late-stage modification of the xenolith compositions by the magma host cannot be excluded, simple binary mixing models between the host lava and xenoliths indicate that such a process was insignificant, and implies that the xenoliths preserved their original geochemical signatures. SEM-CL imaging of zircon reveal complex internal structures and indicates the presence of both magmatic and metamorphic zircon. In the simplest cases, magmatic grains are recognised by weakly preserved, altered oscillatory zoning. In more complex magmatic grains, high Th/U ($\bar{x} = 1.2$) zircon appear recrystallised in the presence of a melt phase, resulting in resorbed internal domains and exterior morphology. Metamorphic zircon with low Th/U (0.03-0.8, $\bar{x} = 0.2$) is present as whole grains or rims with uniform domains devoid of recognizable internal microstructures. Zircon U-Pb dating produces a spectrum of dispersed Late Archaean to Early Palaeoproterozoic ages (2000-2534

Ma), including a dominant mid-Proterozoic age population that records both magmatic (1834 ± 19 and 1874 ± 10 Ma) and metamorphic (1772 ± 5 - 1788 ± 4 Ma) events. Proterozoic ages are correlated with lithospheric processes along the cratonic north-western margin (Great Falls Tectonic Zone and Montana Metasedimentary Terrane), involving arc-related melting (at ca. 1834-1874 Ma) and subsequent collisional metamorphism at ca. 1770 Ma. The protolith to xenoliths containing mid-Proterozoic (ca. 1834-1874 Ma) magmatic zircon ages were formed by subduction-induced melting of the overlying mantle wedge. Xenoliths containing older magmatic zircon ages (ca. 2000-2534 Ma) do not produce a significant age population that can be well correlated with the Wyoming Craton/GFTZ, and its protolith was likely produced by melting of a subduction-related metasomatised mantle in the Late Archaean or earlier. Both Proterozoic and Late Archaean protolith magmas are envisaged as new additions to the Wyoming Craton that resided within middle to lower crustal levels of the continental lithosphere before being subjected to collision-related metamorphism and recrystallisation.

3.2 Introduction

Unravelling the evolution of the continental lithosphere requires an integrated knowledge of both structure and composition of upper and lower portions of the Earth's crust. Elusive lower crustal lithologies are restricted to exhumed segments of lower crust, such as exposed granulite terranes, and xenoliths entrained within extrusive lava flows and tuffs (Rudnick, 1992). However, the rarity of lower crustal slices (e.g. Ivrea Zone, Italy) has somewhat restricted our understanding of deeper crustal processes. At many localities, xenoliths are often the only reliable source of information regarding the lower crust. An inherent limitation of using xenolith suites is that they represent minute portions of larger segments of heterogeneous crust. Nevertheless, xenoliths exposed in the Bearpaw Mountains, Montana, USA, provide a rare opportunity to investigate the middle to lower crust, exemplified by the north-west portion of the Wyoming Craton. Previous petrological studies on lower crustal xenoliths in the Bearpaw Mountains (Collerson et al., 1988) reported on the mineralogy and major element geochemistry of the xenoliths, including bulk-rock oxygen data and pressure-temperature estimations, from which a mixed deep crustal and mantle origin was inferred. Geophysical and experimental constraints were used by Rushmer (1993) to characterise the crust-mantle transition using data from the Delegate Pipes (Australia) and the Bearpaw Mountains. Scherer et al. (2000) established mid-Proterozoic (ca. 1700 Ma) Lu-Hf dates on a garnet pyroxenite from the Bearpaw region. Focussing on ultramafic xenoliths, Downes et al. (2004) and Facer et al. (2009) used whole-rock and mineral compositional data to infer fluid-related serpentinization and metasomatism beneath the Bearpaw Mountains. Whole-rock oxygen data for Little Sandy Creek (LSC) xenoliths from the Bearpaw Mountains were compiled by Kempton and Harmon (1992), who proposed equilibration

between mantle and restitic sources in order to account for varying $\delta^{18}\text{O}$ values within lower crustal mafic granulites. Geophysical data, along with U-Pb monazite ages, for Bearpaw Mountain lower crustal xenoliths were compiled by Barnhart et al. (2012) to confirm the residence of mafic granulites with a complex metamorphic history within a deep, high velocity layer extrapolated from studies beneath the Rocky Mountain Region of the Western USA. A two-stage evolution of the lower crust underlying the Wyoming Craton, concurrent with mobile element depletion and compositional reconstitution, was inferred on the basis of Pb isotope systematics from leached feldspars by Bolhar et al. (2007).

Previous studies within the northern Wyoming Craton were restricted largely to mantle xenoliths and seismic data. The study of crustal xenoliths therefore further contributes to the understanding of mid- to lower crustal processes in this area. Questions still remain as to the composition of mid- to lower crust in the region, and whether the timing of formation of deeper crust can be constrained to the Archaean or Proterozoic. Another question is which petrogenetic mechanism(s) (i.e., subduction, underplating and/or crustal reworking?) operated to produce lower to middle crust of the northern Wyoming Craton. Using detailed cathodoluminescence (CL) imaging and U-Pb geochronology on zircon, this study firstly aims to establish an age for middle to lower crust. Secondly, whole-rock major and trace element chemistry, combined with mineral geothermobarometry (including Ti-in-zircon thermometry) are used to establish the depth and compositional characteristics of the xenoliths, which are then integrated with zircon geochronological data to provide insight into the petrogenesis and evolution of mid- to lower crust within this portion of the Wyoming Craton.

3.3 Methods

A total of thirty eight zircon grains were extracted from four granulite (LSC 33, LSC 72, LSC 89 and LSC 105) and one amphibolite xenolith (BR 47). Two additional granulite xenoliths (LSC 36 and LSC 90) and one additional amphibolite xenolith (Z2) were used to provide pressure temperature determinations for the sample suite, but yielded no extractable zircon. Zircons were separated using standard techniques, and subsequently mounted and polished for imaging using cathodoluminescence (CL) and back-scattered electron (BSE) methods. Secondary Ion Mass Spectrometry (SIMS) was employed for U-Pb geochronology. For metamorphic P-T estimations, in-situ mineral compositional analysis was performed on thin sections using an electron microprobe (EPMA).

A Panalytical PW2404 X-ray fluorescence spectrometer was used for element analysis at the University of the Witwatersrand. Major elements were determined using the Norrish Fusion 1 technique using in-house correction procedures, and were fused using Johnson Matthey Spectroflux 105 at 1100 °C. Standard calibrations were made up using synthetic oxide mixtures and international standard rock

samples, as well as in-house controls. Calibration standards included certified reference materials (CRMs): USGS series (USA) and NIM series (South Africa). Standard calibrations used BCR2, NIM-P, NIM-D, W-2, NIM-S, GSP-2, NIM-N, NIM-G, PCC1, BHVO2, AGV2, and G2 DTS1. All standards are used as calibrations for initial runs, after which they are analysed as unknowns. Sample weight used was 0.35 g with flux weight 2.5 g. Raw data was corrected using in-house software (“SuperQ”). Precision is better than, or equal to, 1 % for elements with > 5 wt% abundance, and 5 % for elements with < 5 wt% abundance.

Electron microprobe (EPMA) analyses were conducted at the University of Johannesburg. Si, Al, Ti, Cr, Fe, Mn, Mg, Ca, Na and K (with oxygen calculated by stoichiometry) were analysed within representative silicate phases. All elements were analysed at 15 kV accelerating voltage on their K α lines, except for Ba, where the Ba L α was used. The reference materials for the calibration were fluorite (F), jadeite (Na), olivine (Mg), almandine (Al), diopside (Si), halite (Cl), orthoclase (K), wollastonite (Ca), baryte (Ba), TiO₂ (Ti), Cr₂O₃ (Cr), rhodonite (Mn) and hematite (Fe).

CL and BSE imaging, together with SIMS on zircon grains, was conducted at the GeoforschungsZentrum (GFZ) in Potsdam, Germany. The Potsdam CAMECA 1280-HR SIMS instrument was used for U-Th-Pb dating of zircon grains at high spatial resolution. A spot size of around 15 μ m using a 1-2 nA, ¹⁶O₂⁻ primary ion beam was employed for U-Pb. Analysis time per spot was 20 minutes. Zircon reference material 91500 (²⁰⁶Pb/²³⁸U age: 1062.4 $\pm$ 0.4 Ma; ²⁰⁷Pb/²⁰⁶Pb age: 1065.4 $\pm$ 0.3 Ma; Wiedenbeck et al., 1995) was used for instrumental and data calibration, for which ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb ages of 1062.1 $\pm$ 4.5 Ma and 1068.4 $\pm$ 4.2 Ma were achieved respectively, in excellent accordance with literature values. The data quality was established by co-analysis of zircon reference material Temora-2, from which a ²⁰⁶Pb/²³⁸U age of 420.5 $\pm$ 3.6 Ma was achieved, in excellent accordance with reported literature values for this standard (²⁰⁶Pb/²³⁸U age: 416.78 $\pm$ 0.33 Ma; Black et al., 2004). Positive secondary ions were extracted using a +10 kV potential applied to the sample holder. Each analysis was preceded by a 2 nA pre-sputtering lasting 120 seconds, and employed a 25 μ m raster to remove surface contaminants. Oxygen flooding was used to enhance lead sensitivity. The mass resolution of the instrument was set at M/ Δ M $\approx$ 5400. Data were acquired using an ETP electron multiplier operating in mono-collection mode. A single analysis consisted of 16 cycles of the peak stepping sequence: ⁹⁰Zr₂, ¹⁶O (1 second integration time per cycle: 1s), ⁹²Zr¹⁶O (1s), 200.5 (4s), ⁹⁴Zr¹⁶O (1s), ²⁰⁴Pb (6s), ²⁰⁶Pb (4s), ²⁰⁷Pb (6s), ²⁰⁸Pb (2s), ¹⁷⁷Hf¹⁶O₂ (1s), ²³²Th (2s), ²³⁸U (2s), ²³²Th¹⁶O (2s), ²³⁸U¹⁶O (2s) and ²³⁸U¹⁶O₂ (2s). Data collection employed a series of regularly interspersed analyses of the above mentioned reference materials between multiple analyses (usually four) of the unknown sample grains. Data reduction used the Excel©-based program “NordAge” (Whitehouse M., NORDSIM facility, Stockholm), which established the U-Pb inter-element fractionation against which the unknowns were calibrated by way

of a Pb/UO vs. UO₂/UO systematics. The software package Isoplot (Ludwig, 2012) was used to graphically display the data using the decay constants recommended by the IUGS sub-commission on geochronology (Steiger and Jäger, 1977). A total of 171 spot analyses were obtained for zircon grains. Ages are excluded based on mixed analyses, analyses involving cracks or inclusions, degree of discordance, as well as equivalence parameters for ²⁰⁷Pb/²³⁸U and ²⁰⁶Pb/²³⁸U, in which Isoplot requires a mean squares weighted deviation (MSWD) of less than 3.8 to calculate a concordant age. Ages used for concordia and weighted ²⁰⁷Pb/²⁰⁶Pb averages are shown in bold (Table 3.3, see Appendices). Probabilities of concordance for all samples are >0.001, indicating non-discordant data for age populations.

Ti-in-zircon was analysed in the tCRAGlabs@TCD lab at Trinity College Dublin, Ireland, by LA-Q-ICP-MS. The equipment comprises a Teledyne Photon Machines G2 laser system coupled to a Thermo iCapQ. The laser was fired with a fluence of 2.75J cm⁻² and ablation occurred in ultra-pure He (0.475 l min⁻¹), to which Ar (0.75 l min⁻¹) and N₂ (16 ml min⁻¹) were added to aid aerosol transport and ionisation. Ti was measured first by defining a rectangular raster over the zircon grains using a 15x15 µm² square aperture, a stage travel speed of 40 µm sec⁻¹ and a repetition rate of 40 Hz. White light interferometry was used to determine that the raster removed 1.0 µm² of material. Only ²⁹Si (5 ms) and ⁴⁹Ti (30 ms) were analysed, and the signals were quantified using NIST 610, with a preferred Ti concentration of 434 ppm. NIST 612 and zircon reference materials 91500 and Temora-2 were analysed as quality control standards. The NIST 612 glass reference material yielded an average Ti concentration of 40.62±0.69 ppm (2SE), in good accordance with literature values (44.00±10 ppm, 2SE, Jochum et al., 2005). Zircon standards 91500 and Temora-2 yielded average Ti concentrations of 4.39±0.23 ppm (2SE) and 10.56±0.34 ppm (2SE) respectively, well within reported literature values (91500: 5.20±3.00 ppm, Temora-2: 10.20±7.30 ppm; 2SE; Fu et al., 2008). Because the rasters only removed 1 µm of material, any down-hole element fractionation can be assumed as minimal, avoiding potential Ti over-estimation (see e.g. Kenny et al., 2016). Titanium in zircon (T_{zircon}) temperatures were estimated from: $T(^{\circ}C)_{zircon} = \frac{5080 \pm 30}{(6.01 \pm 0.03) - \log(Ti)} - 273K$ (Watson, 2006).

3.4 Results

3.4.1 Petrography

Granulite sample mineralogy includes plagioclase + clinopyroxene ± orthopyroxene ± garnet ± hornblende ± biotite ± quartz. Amphibolites comprise plagioclase + hornblende ± garnet ± biotite ± quartz. Major minerals (plagioclase, clinopyroxene, orthopyroxene, garnet, hornblende, biotite) are

interpreted as metamorphic phases. Accessory minerals include small (50-250 μm) apatite and zircon grains, while minor rutile and sulphide phases are present in both rock types.

Amphibolite xenoliths (BR 47 and Z2) contain idioblastic hornblende (35-85 modal %), which vary optically from deep green colours in Z2 to paler brown shades in BR 47 (Fig. 3.1a). Xenolith BR 47 displays granoblastic amphibole (0.5-2 mm, 85 modal %) and plagioclase (0.5-1 mm, 15 modal %), with minor proportions of dispersed biotite. Xenolith Z2 contains a larger proportion of plagioclase (0.25-0.5 mm, 35 modal %) with roughly equal amounts of idioblastic hornblende (1-2 mm) and minor quartz (< modal 1 %). Garnet porphyroblasts (0.5-1 mm, 15 modal %) are also observed. Accessory zircon occurs as inclusions within amphibole grains in xenolith BR 47 (Fig. 3.1b).

Granulite xenoliths LSC 36, LSC 90 and LSC 105 are characterised by the predominance of large (0.25 - 3 mm) granoblastic plagioclase grains (35-55 modal %), together with green, subidioblastic clinopyroxene (1-2 mm, 10-35 modal %) and pink garnet (0.5-3 mm, 5-40 modal %). Garnet is commonly surrounded by dark, kelyphytic rims. Minor amounts of quartz (<1 modal %) are also observed in these three xenoliths. Clinopyroxene forms narrow rim-like features around garnet grains together with a similar texture at the plagioclase-garnet interface (Fig. 3.1c). Xenoliths LSC 36 and LSC 90 are the only granulite xenoliths containing biotite, which occurs as large (0.5-2.5 mm), elongated grains intergrown with clinopyroxene, garnet and plagioclase (Fig. 3.1d). Orthopyroxene (10 modal %) is only observed as large (2-3 mm) idioblastic grains in LSC 105. Plagioclase in xenolith LSC 105 is inclusion-rich with notable occurrences of zircon and apatite (Fig. 3.1e,f). Opaque minerals include small (<1 mm) rutile grains distributed non-uniformly throughout the rock, and display exsolution lamellae of magnetite and ilmenite. Xenolith LSC 89 shows a granoblastic polygonal texture, but also a granular microtexture consisting of pyroxene and plagioclase. Xenoliths LSC 33 and LSC 72 also display a granoblastic texture together with much larger plagioclase (5-10 mm, 50-85 modal %) porphyroclasts surrounded by smaller grains of clinopyroxene (10-40 modal %). Weak layering of clinopyroxene and plagioclase is rarely preserved. Granulite xenoliths LSC 33, LSC 72 and LSC 89 appear to be quartz-absent. Garnet is observed as tiny grains (<0.1 mm) within a microcrystalline matrix in LSC 33 and is absent in LSC 72.

3.4.2 Major elements

Whole-rock chemistry (Table 3.1) characterises the rocks as mafic ($\text{SiO}_2 = 47\text{-}53 \text{ wt\%}$) with a single intermediate xenolith (LSC 89, $\text{SiO}_2 = 57 \text{ wt\%}$). Amphibolite xenoliths have lower Al_2O_3 (~12 wt%) with a large range in FeO (7-17 wt%) and MgO (5-12 wt%). Granulite xenoliths have higher Al_2O_3 (13- 25 wt%) along with variable FeO (4-13 wt%) and MgO (2-9 wt%). Alkali contents ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) are lower

in amphibolites (3-4 wt%) compared to granulites (3-7 wt%) (Fig. 3.2a). Mg numbers ($\text{Mg}/\text{Mg}+\text{Fe}^{\text{T}}$) are variable for amphibolite (0.36-0.76) and low for granulite xenoliths (0.48-0.65).

3.4.3 Trace elements

Whole-rock trace element data are presented in Primitive Mantle-normalised multi-element diagrams (Fig. 3.3a) and show variable patterns across all xenoliths. Highly incompatible and mobile elements

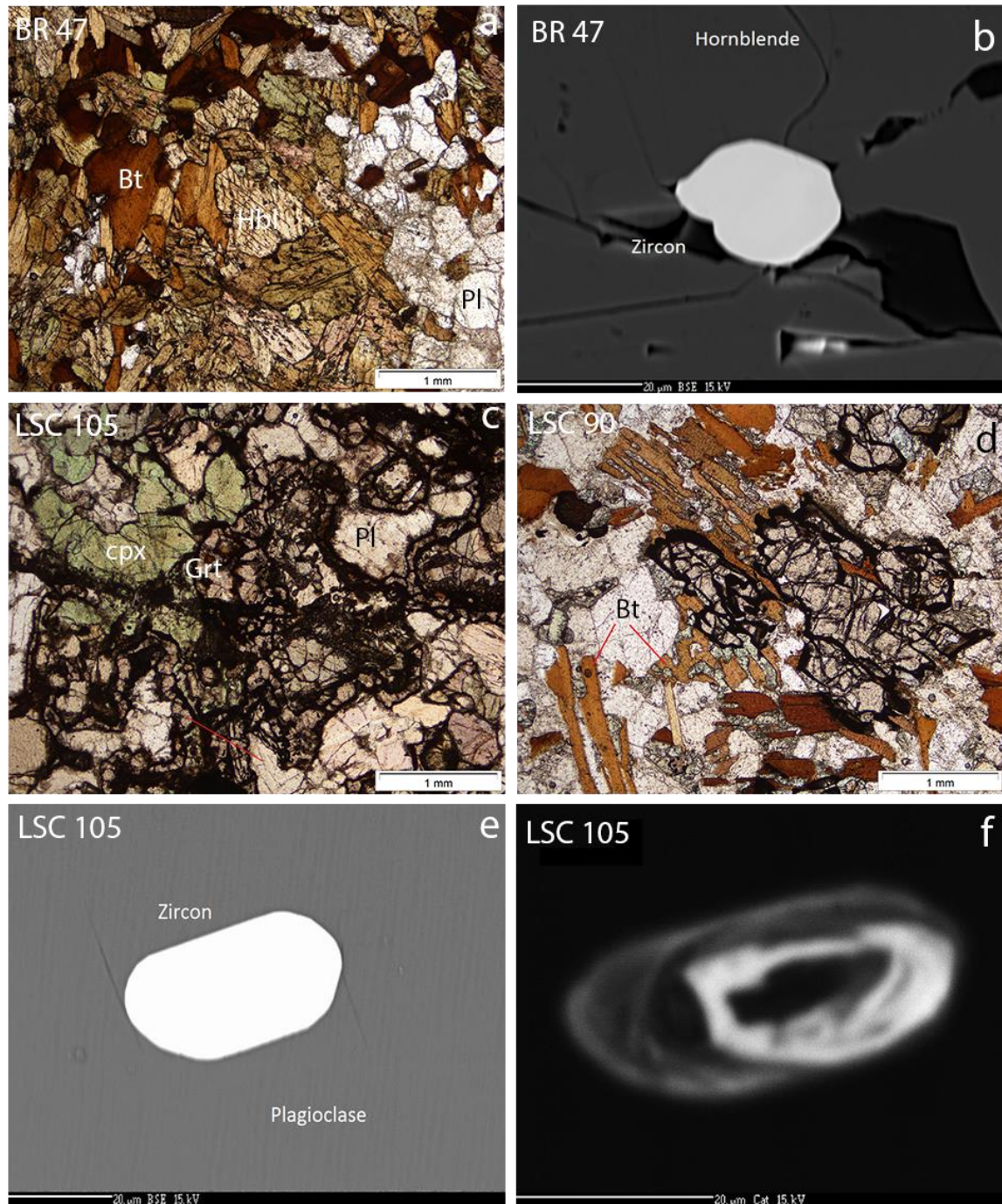


Figure 3.1: Photomicrographs showing mineral phases and textures within xenolith samples BR 47 (amphibolite, a,b) and granulites: LSC 105 (c) and LSC 90 (d). In-situ BSE (b, e) and CL (f) of zircon are also shown (BR 47, LSC 105).

(LILEs), such as Cs (0.7-48 ppm), Rb (18-123 ppm) and Ba (147-2299 ppm) are significantly enriched relative to high-field strength elements (HFSE). Pb (5-11 ppm) and Sr (96-1068 ppm) also show strong positive enrichments. Coupled Nb-Ta and Zr-Hf HFSE depletions are observed, including a negative Ti anomaly for xenoliths LSC 33, LSC 72 and LSC 89. Th (0.07-0.16 ppm) and U (0.04-0.17 ppm) appear depleted in xenoliths LSC 72 and LSC 89. Chondrite-normalised REE patterns are also variable for all xenoliths and display LREE enrichment ($La_N/Yb_N = 1.21-74.38$) relative to HREE (Fig. 3.3b). The xenoliths show a weak negative/absent Eu anomaly ($Eu_N/Eu_N^* = 0.69-1.01$), except for samples LSC 36 and LSC 72, which display moderate to strong positive Eu anomalies ($Eu_N/Eu_N^* = 1.24-2.17$).

	Amphibolite		Granulite					
	Z2	BR 47	LSC 33	LSC 36	LSC 72	LSC 89	LSC 90	LSC 105
SiO ₂	49.99	51.19	52.95	52.99	52.96	56.96	50.58	47.47
TiO ₂	2.05	0.99	0.56	1.48	0.44	1.20	0.89	1.37
Al ₂ O ₃	11.61	12.17	22.60	20.45	25.44	16.23	13.39	13.82
K ₂ O	0.58	1.40	1.22	2.20	0.66	1.87	4.32	1.06
T-Fe ₂ O ₃	18.67	8.14	3.90	9.40	4.12	9.30	10.07	14.42
FeOT	16.972	7.403	3.544	8.545	3.741	8.451	9.151	13.110
MnO	0.25	0.13	0.06	0.16	0.05	0.15	0.16	0.22
MgO	4.72	11.70	2.09	3.94	2.14	4.36	8.67	7.74
CaO	8.83	10.59	10.02	7.28	10.72	7.48	8.04	9.80
Na ₂ O	2.24	2.56	5.08	3.98	4.75	4.39	2.72	2.05
P ₂ O ₅	0.18	0.08	0.20	0.18	<0.001	0.05	0.21	0.13
Total	99.12	98.95	98.68	102.07	101.29	101.98	98.04	96.64
Mg	0.12	0.29	0.05	0.10	0.05	0.11	0.22	0.19
FeT	0.21	0.09	0.04	0.11	0.05	0.10	0.11	0.16
Mg#	0.36	0.76	0.54	0.48	0.53	0.51	0.65	0.54
Na ₂ O+K ₂ O	2.82	3.96	6.30	6.18	5.41	6.26	7.04	3.11
SiO ₂ /Al ₂ O ₃	4.304	4.206	2.343	2.592	2.082	3.510	3.777	3.435
Li	2	4	7	6	5	13	23	6
Be	1	1	1	1	1	2	2	2
Sc	48	42	6	16	9	22	43	41
Ti	11618	6096	2616	6702	3003	2660	7539	9391
TiO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
V	388	270	62	190	102	125	281	323
Cr	81	815	22	220	68	62	222	103
Co	52	46	12	46	17	18	42	57
Ni	44	137	16	86	29	34	87	53
Cu	45	13	13	66	11	10	191	4
Zn	199	108	49	150	47	76	146	150
Ga	21	13	18	29	20	23	20	21
As	1.2	2	3	1.2	1.4	1.2	1.8	2
Rb	18	73	81	82	29	38	123	81
Sr	96	267	734	853	602	1068	998	480
Y	48	14	7	6	7	32	21	28
Zr	151	54	127	17	13	12	48	93
Nb	5	4	3	5	4	4	9	8
Mo	0.8	0.2	0.3	0.5	0.4	0.5	0.8	0.9
Cd	0.1	0.1	0.1	0.1	0.0	0.2	0.1	0.1
Sn	0.1	2	0.6	0.1	0.4	0.1	0.3	0.1
Sb	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.1
Cs	0.7	48	28	2	13	7	5	3
Ba	147	698	954	1969	488	2299	945	1294
La	7	25	42	33	8	22	6	8
Ce	19	57	83	55	17	42	15	21
Pr	3	8	9	5	2	5	2	3
Nd	16	32	33	17	8	22	10	16
Sm	5	6	5	2	2	6	3	5
Eu	2	2	1.4	0.9	1.1	1.4	1.0	1.2
Tb	1.3	0.6	0.4	0.2	0.2	1.0	0.6	0.9
Gd	7	5	3	2	1.4	6	3	6
Dy	8	3	2	1.1	1.3	6	4	5
Ho	2	0.6	0.3	0.2	0.3	1.3	0.8	1.1
Er	5	1.4	0.7	0.7	0.7	3.6	2	3
Tm	0.8	0.2	0.1	0.1	0.1	0.5	0.4	0.4
Yb	5	1.1	0.6	0.8	0.7	3	2	3
Lu	0.8	0.2	0.1	0.1	0.1	0.4	0.3	0.4
Hf	4	2	3	0.4	0.4	0.5	2	3
Ta	0.3	0.3	0.2	0.3	0.2	0.2	0.5	1
W	0.1	0.2	0.2	0.1	0.1	0.0	0.4	0
Tl	0.1	0.4	0.8	1.5	0.3	0.2	1.1	0.2
Pb	7	5	8	6	4	11	10	5
Th	2	2	4	2	0.1	0.2	0.3	4
U	0.5	0.4	0.9	0.3	0.0	0.2	0.5	2.7
LOI	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Th/U	3.4	3.9	4.3	1.6	7.9	0.9	0.5	1.4
Hf/W	28.7	8.2	16.0	5.4	5.2	25.3	4.0	7.2
Nb/Ta	15.3	15.9	17.2	17.4	17.7	24.8	19.6	13.5
Zr/Hf	36.6	34.5	45.8	29.3	39.4	24.6	30.8	35.5
Y/Ho	25.6	24.3	25.3	26.4	25.8	24.6	25.5	25.8
Nb/Y	0.1	0.3	0.4	0.6	0.7	0.1	0.4	0.3
Zr/Y	3.2	3.8	17.5	1.8	2.7	0.4	2.4	3.3
La/Nb	21.0	53.9	89.0	77.3	52.1	34.2	16.0	23.3
(Eu/Eu*) _N	0.8	0.8	1.0	1.2	2.2	0.7	1.0	0.7
(La/Yb) _N	1.2	21.6	74.4	10.9	42.1	7.0	2.5	2.7

Mg# = (MgO/40.3)/(MgO/40.3+Fe₂O₃/80), (Eu/Eu*)_N = Eu/[(Sm*Gd)^{1/2}]

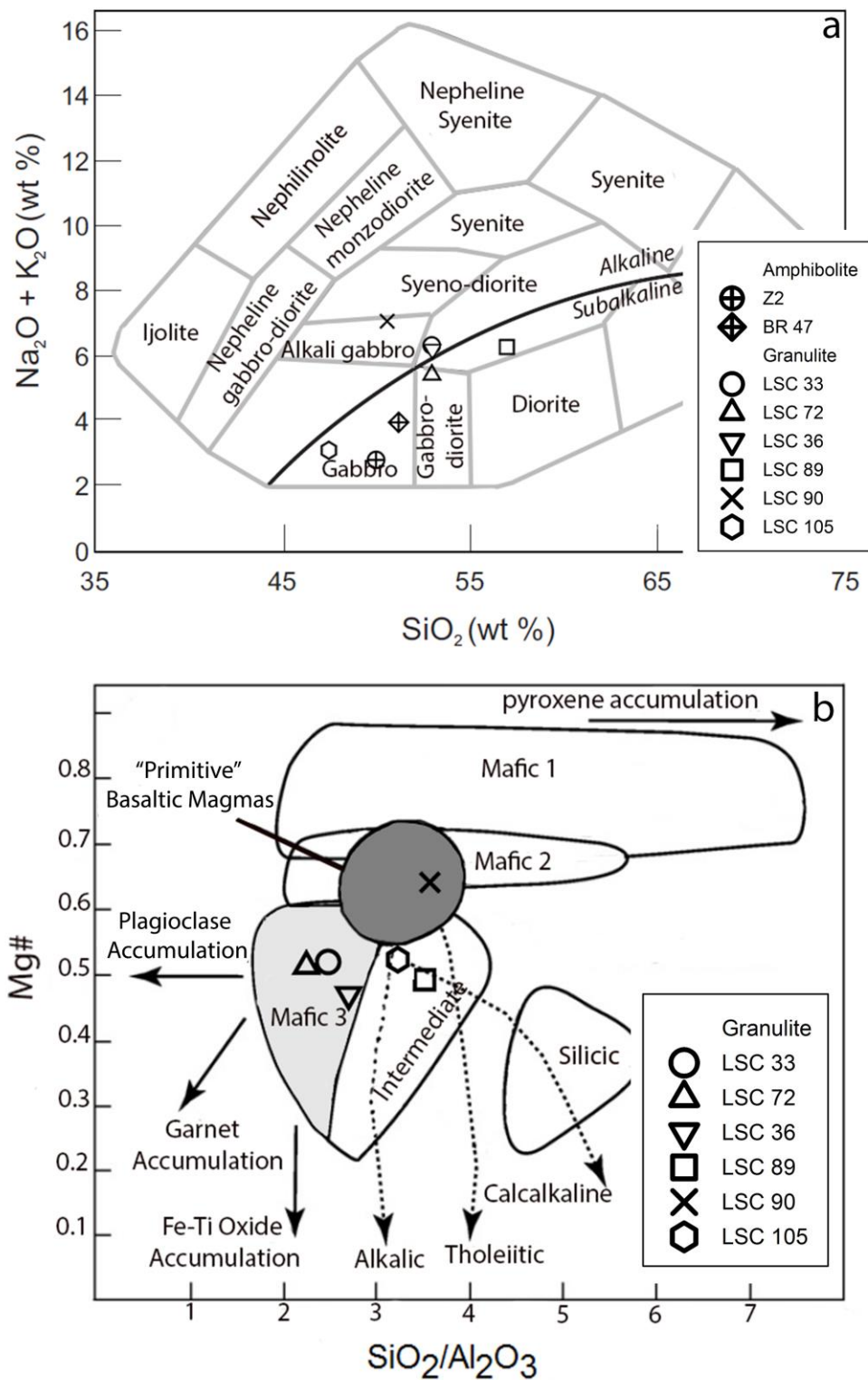


Figure 3.2: (a) Whole-rock classification schemes (SiO₂ versus total alkali (Na₂O + K₂O)) for plutonic samples (Cox et al., 1979; Wilson 1989). (b) Mg# vs. SiO₂/Al₂O₃ (after Kempton and Harmon, 1992). Mafic 1 = cumulates from basaltic melts; Mafic 2 = solidified melts or evolved cumulates, Mafic 3 = cumulates or residues from intermediate igneous rocks.

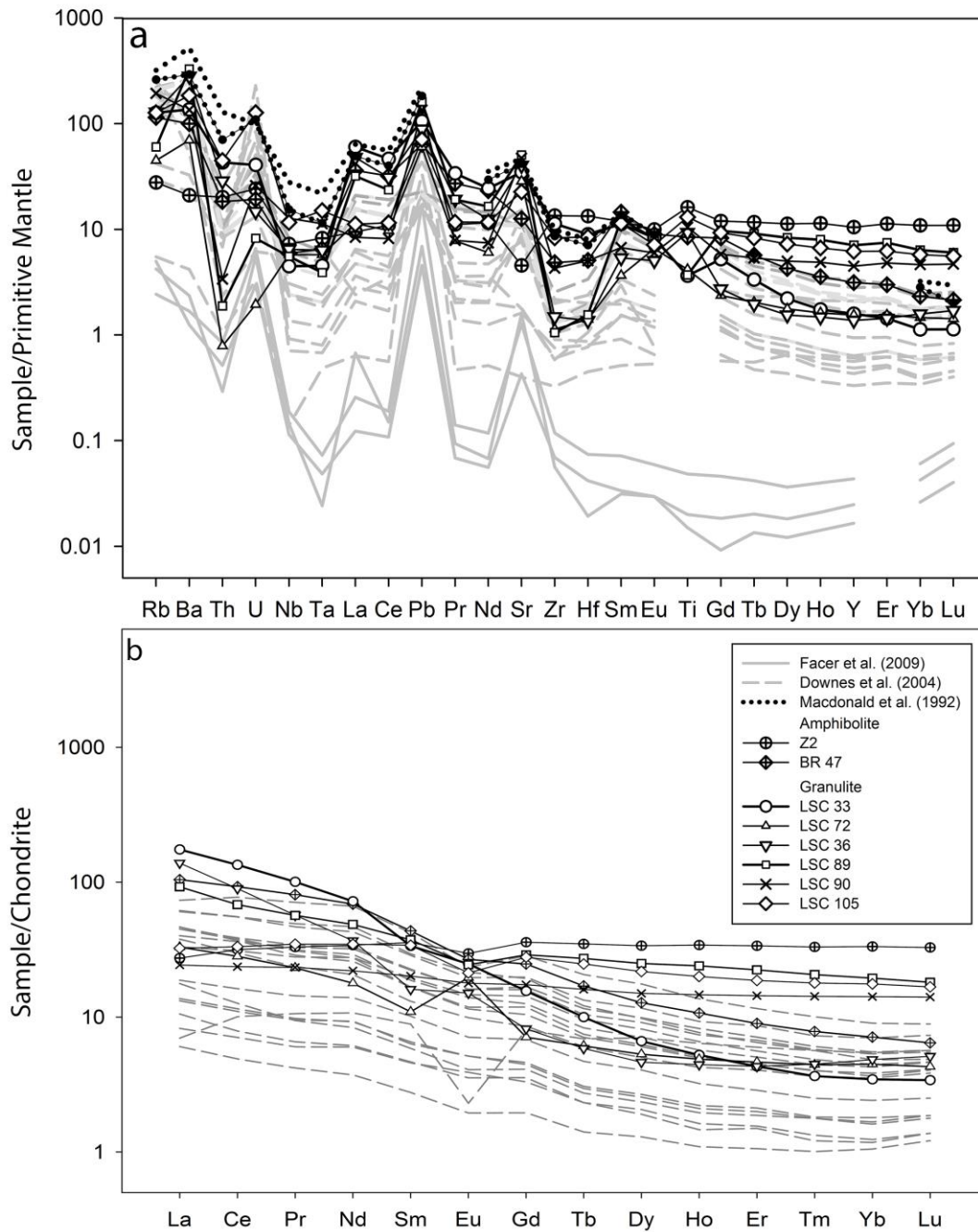


Figure 3.3: Primitive Mantle (PM)-normalised trace element (Sun and McDonough, 1989) and chondrite-normalised REE diagrams (McDonough and Sun and, 1995) showing all xenoliths. Trace element patterns for mantle xenoliths extracted from beneath the Bearpaw Mountains from other studies are also shown (Downes et al., 2004; Facer et al., 2009) together with the host minette trace element pattern of Macdonald et al. (1992).

3.4.4 Mineral chemistry

Garnet

Garnet in granulite xenoliths (LSC 36, LSC 90, and LSC 105) is almandine-rich (50.4-59.5 %), with lesser pyrope (18.8-30.3 %) and grossular (15.9-20.9 %) contents (Fig. 3.4a, Table A1). Spessartine content is low (1.1-1.8 %) in these garnets. The composition of garnet in amphibolite xenolith Z2 is similarly enriched in almandine (55.2-55.6 %), but contains higher grossular (30.1-30.6 %) and spessartine and lower pyrope components compared to the granulite garnets. Garnets in both rock types are homogenous and lack any distinguishable chemical zonation. Mg-numbers ($\text{Mg}/\text{Mg}+\text{Fe}^{2+}$) vary between 0.24 to 0.34 in granulites and 0.09 to 0.11 in amphibolites.

Pyroxene

Although clinopyroxene grains within granulite xenoliths are compositionally homogenous, some variation is observed between separate samples (Fig. 3.4b). Xenoliths LSC 33 contains diopside (enstatite = 32.2-33.6 %, wollastonite = 47.5-48.4 %), while clinopyroxene in xenoliths LSC 72, LSC 89, LSC 90 and LSC 105 is augite (enstatite = 34.9-42.4 % and wollastonite = 36.4-48.3 %). Mg-numbers ($\text{Mg}/\text{Mg}+\text{Fe}^{2+}$) vary between 0.67 and 0.85. Orthopyroxene is only present in LSC 105 and contains negligible end-member variations in enstatite (50.3-52.2 %) and ferrosilite (46.7-48.9 %).

Feldspar

Xenoliths LSC 33 and LSC 72 produce a range in anorthite content in plagioclase between 49 and 57 %, with minimal within-grain zonation and only minor variation between grains. Other xenoliths show considerable inter-sample variation; anorthite content ranges from 34 to 40 % in LSC 36 and from 22 to 25 % in LSC 90, while plagioclase in xenoliths LSC 89 and LSC 105 varies from 60-63 % and 62-78 % anorthite content, respectively. Similar variations hold true for amphibolite xenoliths, in which anorthite content ranges from 49-51 % for BR 47 and 31-32 % for Z2.

Amphibole

Amphibole within BR 47 is classified compositionally as magnesio-hornblende (Leake et al., 1997). TiO_2 and Al_2O_3 vary from (0.8-1.2 wt%) and (7.0-8.4 wt%), respectively. Mg number ($\text{Mg}/\text{Mg}+\text{Fe}^{2+}$) ranges between 0.69 and 0.72. Xenolith Z2 contains ferro-paragasic amphibole with higher TiO_2 (1.3-1.5 %) and Al_2O_3 (11.1-12.1 %) with Mg numbers between 0.38 and 0.39.

Biotite

TiO₂ content in biotite ranges from 3.2 to 5.8 wt% in LSC 36 and LSC 90, accompanied by high Mg numbers (Mg/Mg+Fe²⁺: 0.64-0.82). Fluorine and chlorine contents are higher in LSC 90 (F = 1.6-2.7, Cl = 0.17-0.22 wt%) compared to LSC 36 (F = 0.56-0.70, Cl = 0.07-0.09 wt%).

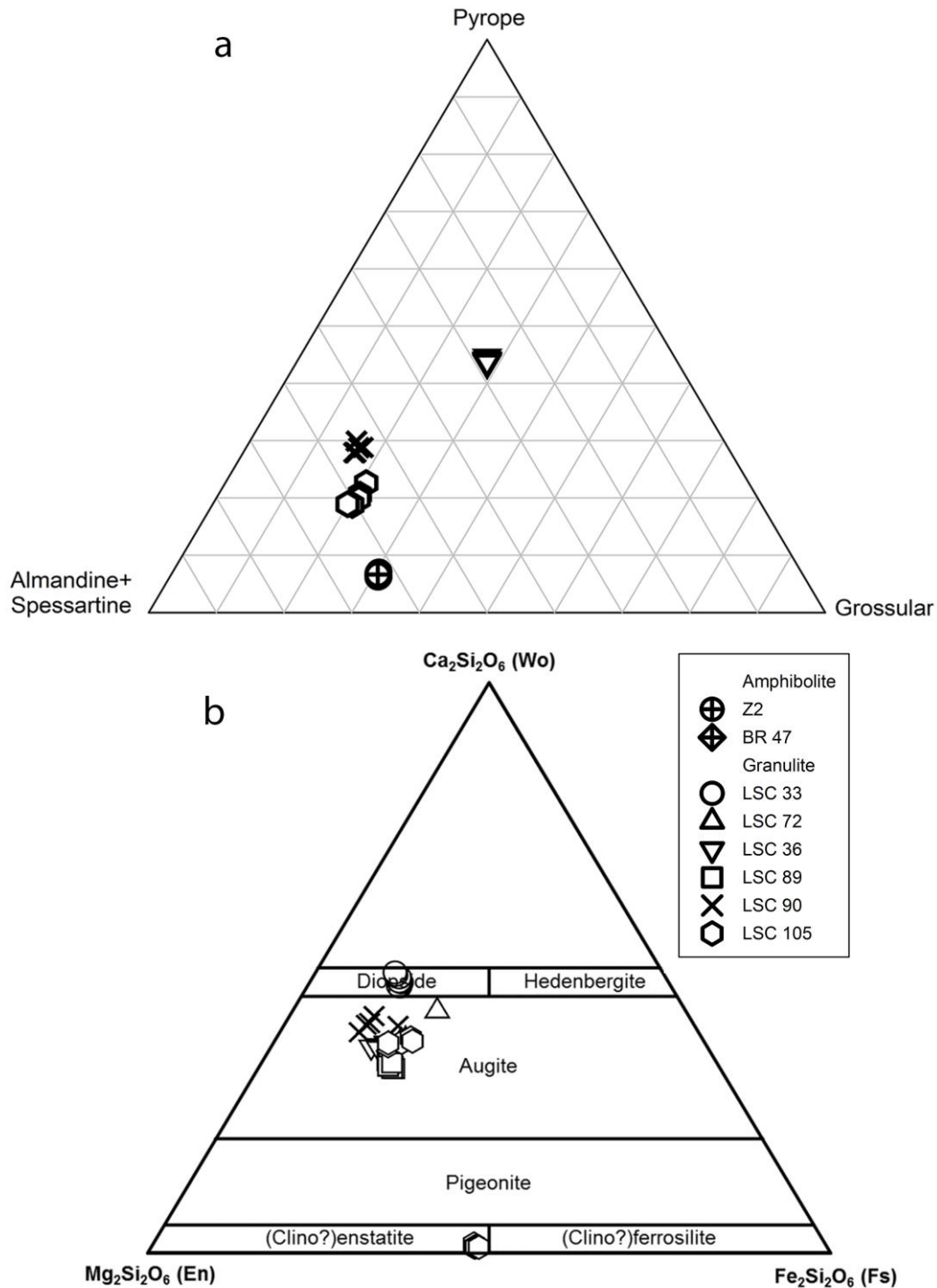


Figure 3.4: (a) Garnet compositions are shown as a function of ternary end-members (Pyr-Grs-Alm+Sps). (b) Pyroxene (Wo-En-Fs) ternary classification diagram (Morimoto, 1988).

3.4.5 Geothermobarometry

In order to quantify equilibrium temperatures and pressures, a variety of mineral geothermometers were applied (Table 3.2). The garnet-clinopyroxene geothermometers (Ellis and Green, 1979) were used for granulite xenoliths (LSC 36, LSC 90, LSC 105), while the garnet-amphibole (Ravna, 2000) and amphibole-plagioclase geothermometers (Blundy and Holland, 1990) were applied to amphibolite xenoliths (BR 47 and Z2). The garnet-amphibole-plagioclase barometer (Kohn and Spear, 1990) was used to calculate pressure for the garnet-bearing amphibolite xenolith (BR 47). The garnet-orthopyroxene thermobarometer (Pattison et al. 2003) was applied to the single orthopyroxene containing xenolith (LSC 105). The Ti-in-biotite thermometer was also used for xenoliths LSC 36 and LSC 90 to estimate temperatures (Henry et al., 2005). The crystallisation temperature of zircon is estimated by measuring the variable uptake of Ti atoms into the zircon structure due to temperature changes (Watson et al., 2006). With consideration of an accompanying Ti-bearing phase (rutile), this method is employed to zircon grains hosted in both amphibolite (BR 47) and granulite xenoliths (LSC 33, LSC 72, LSC 89).

Geothermometric calculations across all xenoliths encompass a temperature range of 642-817 °C. Determinations of pressure were conducted on amphibolite xenolith Z2 (3.5-5.3 kbar) and granulite xenolith LSC 105 (7.4-7.5 kbar). The granulite xenoliths (LSC 36, LSC 89, LSC 90) produce temperatures between 650 and 683 °C at inferred pressures of 7.4 to 7.5 kbar. Amphibolite xenoliths (Z2 and BR 47) equilibrated at temperatures of 642-715 °C for inferred pressures of 3.5-5.3 kbar on amphibolite Z2. Ti-in-biotite thermometry applied to xenoliths LSC 36 and LSC 90 produced slightly higher temperatures of 735-749 °C and 787-817 °C, respectively.

3.4.6 Ti-in-zircon thermometry

The highest abundance of Ti (6-51 ppm) was observed within xenolith BR 47 as determined from 10 analyses of three zircon grains resulting in a temperature range of 692-909 °C (Table A2). A single analysis on LSC 33 (1 grain: 10 ppm Ti) provides a temperature of 737 °C. Six analyses using three grains within LSC 72 produce Ti between 2 and 7 ppm, translating into a temperature variation of 618-712 °C. Twenty-four analyses on seven zircon grains within sample LSC 89 (Ti = 4-15 ppm) yield temperatures from 659-776 °C.

3.4.7 Zircon morphology and CL Imagery

Imaged zircons vary in size from 50 to 350 microns. Only a small proportion of grains display prismatic crystal symmetry. A diversity of sub-angular and sub-rounded zircons with variable aspect ratios (1:2-1:5) are also observed, but with reduced sizes. Back-scattered images (BSE) reveal largely

Table 3.2				
Pressure and temperature calculated from mineral thermobarometry on Bearpaw Mountain xenoliths				
Sample	Rock Type	Temperature(°C)	Pressure (kbar)	Method
LSC 36	Granulite	650-651	x	Garnet-Clinopyroxene Thermometry (Ellis and Green, 1979)
LSC 90	Granulite	667	x	
LSC 105	Granulite	682-683	x	
BR 47	Amphibolite	689-715	x	Amphibole-Plagioclase Thermometry (Blundy and Holland, 1990)
Z2	Amphibolite	642-645	x	Garnet-Amphibole Thermometry (Ravna, 2000)
LSC 105	Granulite	671-683	7.4-7.5	Garnet-Orthopyroxene Thermobarometry (Pattison et al., 2003)
LSC 90	Granulite	787-817	x	Ti-in-Biotite Thermometry (Henry et al., 2005)
LSC 36	Granulite	735-749	x	
Z2	Amphibolite	x	3.5-5.3	Garnet-Amphibole-Plagioclase Barometry (Kohn and Spear, 1990)
BR 47	Amphibolite	692-909	x	Ti-in-zircon Thermometry (Watson et al., 2006)
LSC 33	Granulite	737	x	
LSC 72	Granulite	618-712	x	
LSC 89	Granulite	659-776	x	

homogenous grains lacking visually distinct internal zoning, while mineral inclusions are not observed. Cathodoluminescence (CL) images, on the other hand, show the full extent of zircon complexity, including a variety of discrete and intersecting textural domains (Fig. 3.5a-b).

LSC 72 (Granulite)

Faint oscillatory zoning is observed most clearly in grain 72-5, and to a lesser extent in grain 72-2. This texture is weakly preserved within grain 72-1, albeit with fewer, broadened oscillatory bands. Weak remnants of such zoning are also present within the darker and lighter domains of grain 72-4. Grain 72-3 shows an irregular convolute texture consisting of bright and dark domains. Grain 72-2 displays a relatively large, bright outer rim of varying thickness and less distinct, convolute inner zones of similar shape and proportion. Zircon formation in this sample is explained through initial magmatic crystallisation followed by solid-state recrystallisation. A magmatic origin is consistent with oscillatory zoning (72-1, 72-4, 72-5) (Pidgeon 1992; Corfu, 2003; Zheng et al., 2004). Recrystallisation of grains 72-1 and 72-5 is apparent in the loss of definition of original magmatic zoning (“ghost texture”: Hoskin and Black, 2000) or bleaching of primary oscillatory zoning and enlargement of primary growth zones (Pidgeon, 1992; Vavra et al., 1996). Recrystallisation is also supported by variable Th/U ratios that are mostly greater than 0.1. (Hoskin and Black, 2000). Moreover, absolute Th abundance of these grains are significantly depleted presumably due to the incompatibility of Th⁴⁺ that was preferentially expunged during recrystallisation (1-105 ppm, $\bar{x}$ = 32 ppm, Table 3.3, see Appendices)(Hoskin and

Black, 2000). Grain 72-2 appears to retain faint igneous zoning and “curved, sinusoidal bright outer zones” relative to a darker inner domain resembling a core-rim texture that is a feature indicative of transgressive solid-state recrystallisation (Hoskin and Black, 2000). Grain 72-4 shows a darker island/core with faint remnants of oscillatory zoning, which may again represent relics of original primary zoning.

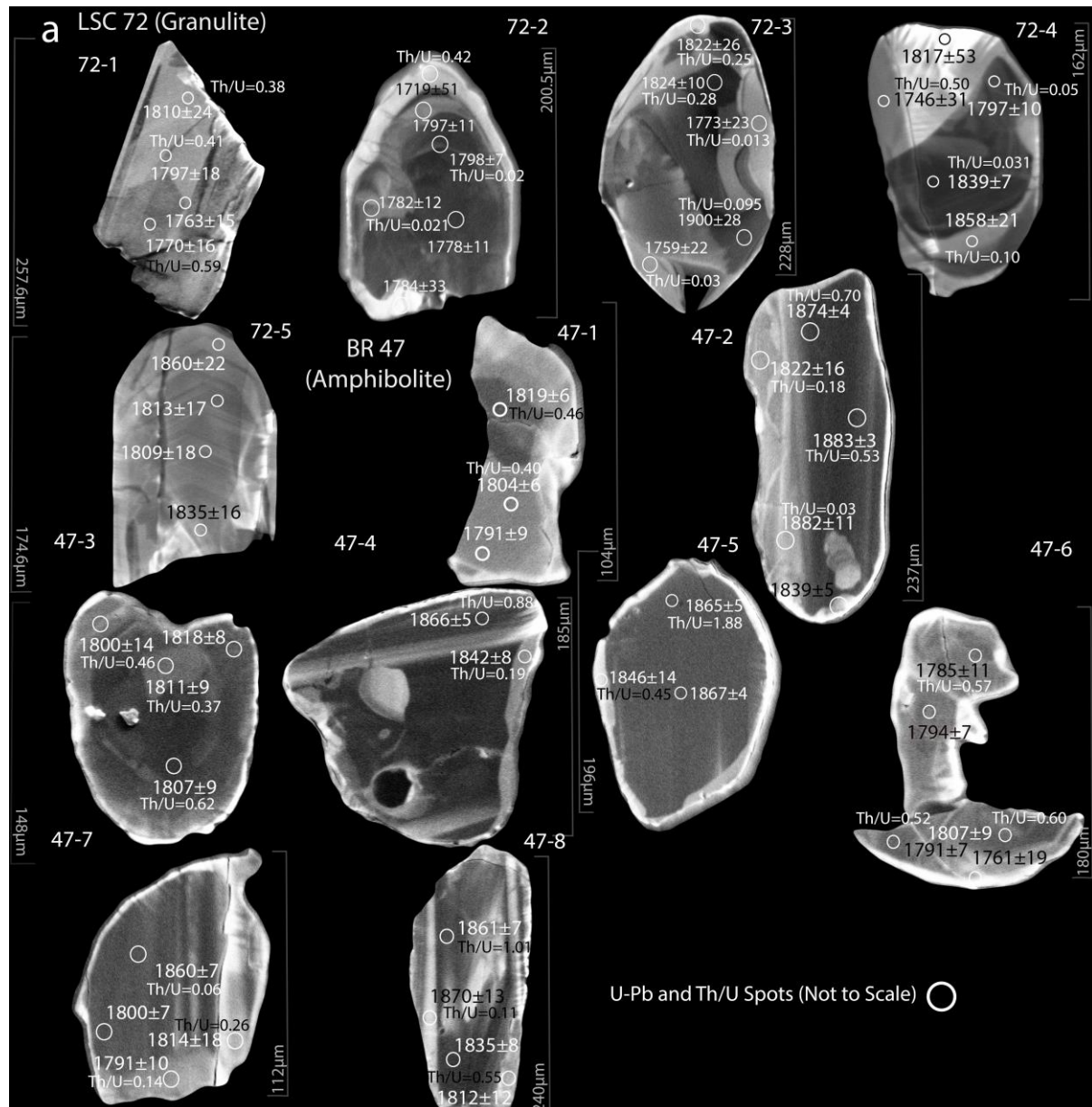


Figure 3.5 (a): Cathodoluminescence (CL) images of zircon in respective xenoliths. LSC 72 and BR 47: weak preservation of magmatic textures. Dates shown are $^{207}\text{Pb}/^{206}\text{Pb}$ ages obtained from spot analysis using SIMS (circles).

BR 47 (Amphibolite)

Zircons in this sample appear to show magmatic zoning and generally elevated Th/U ($\bar{x} = 0.5$, Fig. 3.6a). Grains 47-1, 47-5 and 47-6 display medium grey inner domains that gradually progress into very bright, luminescent outer rims and, based on lack of internal textures, may represent metamorphic zircon. All zircon grains in this sample, apart from 47-1, 47-5, 47-6, retain poorly preserved magmatic zoning as revealed by alternating dark and light banding. Ubiquitous features of all grains are bright, narrow luminescent rims seen at grain boundaries. In some cases these brighter zones clearly truncate original magmatic zoning (47-7) indicating replacement of original textures. Secondary recrystallisation of existing zircon in the presence of melt may have obscured the initial magmatic microstructure. The bright, narrow rims are also a feature of resorption accompanying recrystallisation during final stages of zircon growth (Vavra et al., 1996). The presence of a melt is implied by the presence of rounded external morphologies and embayments.

LSC 89 (Granulite)

Granulite LSC 89 show two zircon types (Type I and Type II) characterised by differing morphology, age and Th/U systematics.

Type I Zircon (Recrystallised Magmatic)

Type I zircon is represented by grains 89-2 to 89-6, 89-8, 89-10, 89-12, 89-12(2), 89-14, 89-15(2), 89-16 and 89-17 (red box, Fig. 3.5b). These zircons all display similar morphological and internal characteristics as well as higher and variable Th/U (0.04-2.2, $\bar{x} = 1.2$) (Fig. 3.6b).

Grains consist of convoluted light and dark domains showing irregular, non-systematic resorbed internal features. Bright discrete zones occur at the apices of some grains (89-3, 89-4, 89-10). Zircon 89-6 consists of a single, poorly resolved darker interior domain surrounded by a faint, irregular banded texture resembling faded magmatic zoning. A brightly luminescent central core feature is enclosed by a complex array of chaotic and diffuse textures in zircon 89-8. Grain 89-10 consists of weak fir-tree, sector and flow zonation. Grains 89-16 and 89-17 also show a darker interior domain surrounded incompletely and non-uniformly by narrow luminescent rims. Homogenous zircons (89-2, 89-14) possess a single grey zone of uniform emittance and high Th/U (0.3-1.7). Morphologically, Type I zircons are characterised by anhedral, rounded and embayed exteriors commonly associated with resorption and magmatic corrosion (Vavra et al., 1994; Vavra et al., 1996; Hoskin and Schaltegger, 2003; Flowerdew et al., 2006; Tichomirowa and Kohler, 2013; O'Brien and Miller, 2014). In some cases, the internal domains appear to follow the exterior morphology of the grain (89-10). Rounded/curved characteristics of zircons within similar xenoliths have been attributed to magmatic corrosion (Bolhar et al., 2007). The internal textures vary from chaotic to completely uniform. Some primary magmatic

features are preserved in grains, however, such as fine-scale, faint oscillatory zoning (89-6), fir tree and flow domains (89-10) and sector zoning (89-17) (Vavra et al., 1996; Vavra et al., 1999; Koreshkova et al., 2009).

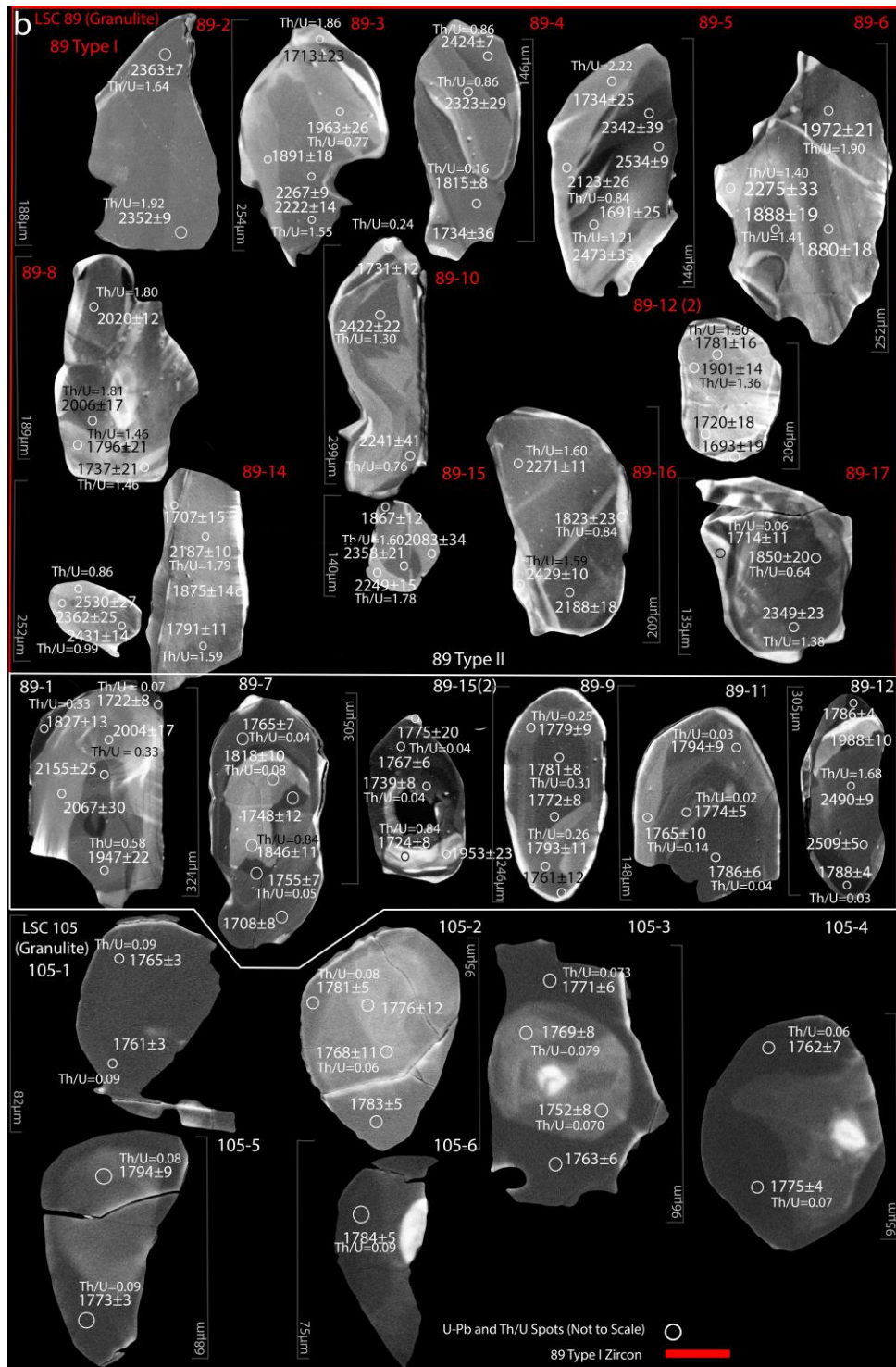


Figure 3.5 (b): Cathodoluminescence (CL) images of zircon in respective xenoliths. LSC 105: homogenous without internal textures, LSC 89: Chaotic, convolute, fir tree, banded and patchy sector zoning. Dates shown are $^{207}\text{Pb}/^{206}\text{Pb}$ ages obtained from spot analysis using SIMS (circles).

These poorly preserved igneous textures, together with high Th/U are therefore interpreted as magmatic grains recrystallised in the presence of a fluid (melt) to create a variety of complex resorbed textures.

Type II Zircon (Metamorphic)

Type II zircon grains are represented by grains 89-9, 89-11 and 89-15 and as dark outer zones on grains 89-1, 89-7 and 89-12 (white box, Fig. 3.5b). Morphologically, these grains are euhedral to subhedral in shape. Th/U is lower (0.03-0.8, $\bar{x} = 0.2$) when compared to Type I zircon (Fig. 3.6b). Absolute Th abundances are also lower ($\bar{x} = 129$ ppm) and less variable than Type I zircons (Table 3.3, see Appendices). Grain 89-7 appears to display a core feature containing weak sector zoning surrounded by a darker, patchy domain. A thin luminescent outer rim is poorly preserved. Grains 89-9 and 89-11 contain a dark central domain surrounded by a faint, poorly preserved, patchy, diffusive corona. Type II grains are clearly distinguishable from the first group of zircons due to the preservation of non-resorbed, prismatic to subhedral/subidiomorphic zircon shapes. Internally they are largely featureless, implying metamorphic zircon growth. These zircons are likely metamorphic grains formed through breakdown of Zr-rich phases (Fraser et al., 1997; Degeling et al., 2001) and/or pre-existing zircon. Although broadly categorised under Type II zircon, three zircons (89-1, 89-7 and 89-12) appear to contain interiors characteristic of Type I magmatic zircon (high Th/U = 0.08-1.7) with metamorphic rims characteristic of Type II zircon (Th/U = 0.03-0.33).

Although Th/U has been demonstrated to be variable in high grade rocks and cannot always distinguish magmatic/metamorphic zircon (Whitehouse and Kamber, 2004; Wan et al., 2011; Rubatto, 2017), in this case it is distinct for Type I (0.04-2.2, $\bar{x} = 1.2$) and Type II (0.03-0.8, $\bar{x} = 0.2$) zircon (Fig. 3.6b). This means that the zircon types grew in different environments of Th/U availability or formed through different (re)crystallisation processes. In our zircons, due to sparse magmatic textures, older zircons (Type I) with higher Th/U, probably grew in a melt while younger zircon (Type II) with lower Th/U formed metamorphically in the solid-state. Since the ages of Type I grains are older and variable within single grains (1700-2500 Ma) and contain high Th/U, a few zircons absent obvious magmatic textures (e.g. 89-2, 89-14), but containing similar variations in age and Th/U, are assumed to be magmatic (Type I) zircon on this basis.

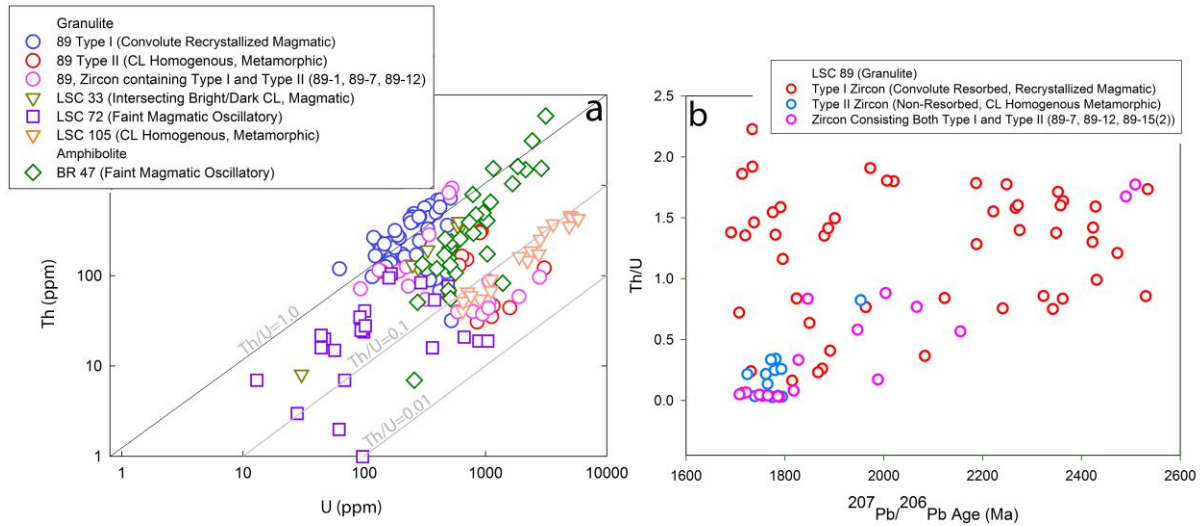


Figure 3.6: U and Th concentrations in zircon for all xenoliths (a) and LSC 89 (b).

LSC 105 (Granulite)

Zircons within this xenolith all display uniform internal and morphological characteristics and consistently low Th/U ($\bar{x} = 0.08$). A number of grains (105-3, 105-4, 105-5, and 105-6) show a relatively homogeneous CL response, with a bright interior relative to a single darker exterior domain. Considering their low Th/U, rounded morphology, small grain size and featureless interior domains, we interpret these grains as newly formed metamorphic zircon that crystallised under granulite facies conditions (Corfu et al., 2003; Wu and Zheng, 2004; Harley et al., 2007; Rubatto, 2017).

LSC 33 (Granulite)

Grain 33 (not shown in Fig. 3.5) shows an irregular, bright central interior domain encompassed by a uniform darker domain. The entire grain is surrounded by a narrow, luminescent rim. Resorbed morphological features and high Th/U ($\bar{x} = 0.5$) are observed suggesting melt crystallisation of zircon combined with dissolution-reprecipitation/recrystallisation mechanisms.

3.4.8 U-Pb geochronology

Thirty eight individual zircons derived from four granulite and one amphibolite xenolith were dated using the SIMS U-Pb method. Zircon U-Pb ages are listed in Table 3.3 (see Appendices) and plotted on Concordia diagrams (Fig. 3.7). All samples with the exception of LSC 33 show concordant to near concordant age groupings. The zircons capture a broad Palaeoproterozoic age distribution encompassing concordant dates from 1707 ± 15 Ma to 2534 ± 9 Ma. The most prominent $^{207}Pb/^{206}Pb$ age grouping across all samples varies between 1707 ± 15 and 1891 ± 19 Ma and comprise 72 % of the

population. Other significant groupings correspond to $^{207}\text{Pb}/^{206}\text{Pb}$ age ranges of 1900 ± 14 - 2534 ± 9 (25 % of population) and 2589 ± 19 - 2907 ± 20 Ma (3 % of population, discordant). Age populations (peaks) are identified from probability density plots and correlated to specific zircon microtextures, from which a weighted mean age and concordia age were calculated.

LSC 72 (Granulite)

Twenty-four individual spots spread across five grains were measured in this xenolith. Two populations may be distinguished on the basis of their optical and age characteristics. Nine spots within bright and dark magmatic zircon domains (72-1, 72-2, 72-3 72-4) define a younger age peak with a concordia age of 1791 ± 5 Ma (MSWD = 2.9) and a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1788 ± 8 Ma (MSWD = 1.1). Seven spots within bright/dark and magmatic oscillatory zircon (72-2, 72-4 and 72-5) constrain an older concordia age of 1838 ± 6 Ma (MSWD = 3.8), together with an identical weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1834 ± 19 Ma (MSWD = 1.4). The age of magmatic crystallisation is therefore taken as 1834 ± 19 Ma since more spots that define this population appear within clearer oscillatory domains, while the younger age distribution (1788 ± 8 Ma) represents a recrystallised population. Two bright rim domains constrain $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 1797 ± 11 (72-2) and 1822 ± 8 Ma (72-3).

BR 47 (Amphibolite)

Thirty-two spots were measured on eight grains in this sample. Once again, two populations may be distinguished on the basis of their optical and age characteristics. Twenty spots within zircon domains (diffuse/homogenous/metamorphic) define a younger peak with a concordia age of 1799 ± 9 Ma (MSWD = 3.1) together with a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1801 ± 7 Ma (MSWD = 2.1) and an older peak (within magmatic domains) with concordia and weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 1874 ± 10 (MSWD = 1.07) and 1874 ± 8 Ma (MSWD = 3.1) respectively. The younger peak (~1800 Ma) contains spots in diffuse/homogenous zircon domains (47-1, 47-3, 47-6), which may record a younger recrystallised/metamorphic age. Therefore the age of magmatic crystallisation in this xenolith is taken as 1874 ± 8 Ma (from the older peak) since these ages occur in clearer magmatic domains (47-2, 47-4, 47-5, 47-7, 47-8). Two bright metamorphic rims yield $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 1842 ± 8 Ma (47-4) and 1846 ± 14 Ma (47-5).

LSC 89 (Granulite)

This xenolith displays a multi-stage history reflecting long-lasting and variable lithospheric evolution. Eighty-seven spots across nineteen grains were analysed for this sample. Three domains may be distinguished on the basis of their optical and age characteristics. Ten spots on generally featureless interior domains within newly formed metamorphic zircon (89-7, 89-9, 89-11) yield a concordia age of 1775 ± 10 Ma (MSWD = 2.5) and a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1773 ± 8 (MSWD = 1.5). Seven spots

for bright rims (89-3, 89-4, 89-8, 89-10, 89-14, 89-15, 89-17) yield a concordia age of 1730 ± 15 Ma (MSWD = 7.4) and a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1722 ± 10 Ma (MSWD = 0.46). Four individual spots on dark metamorphic rims (89-1, 89-12) yield ages of 1722 ± 8 , 1786 ± 4 , 1788 ± 4 and 1827 ± 13 Ma. Ages of metamorphic zircon crystallisation are taken as 1773 ± 8 Ma and 1786 ± 4 - 1788 ± 4 Ma since these ages can be correlated with metamorphic zircon in LSC 105 (1772 ± 5 Ma, see below). The remaining spots fall within convolute and resorbed zircon domains (recrystallised magmatic) and produce a spectrum of concordant to near concordant ages between 1691 ± 25 and 2534 ± 9 Ma (Table 3, Fig. 8c,d) with no identifiable peaks or consistent clusters in distribution from which a concordia or weighted mean age could be calculated.

LSC 105 (Granulite)

Twelve spots within five uniformly dark metamorphic grains constrain a nearly unimodal age distribution yielding a concordia age of 1771 ± 8 Ma (MSWD = 0.29). This age is supported by an identical weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1772 ± 5 Ma (MSWD = 2.6) which is interpreted as the age of metamorphic crystallisation.

LSC 33 (Granulite)

Seven spots within both bright and dark CL imaged domains were measured on a single grain within sample LSC 33 and align along a discordia with an upper and lower intercept of 3231 ± 230 Ma and 1682 ± 130 Ma (MSWD = 3.9), respectively (Fig. 3.7f).

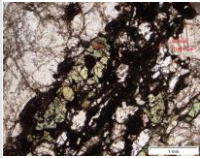
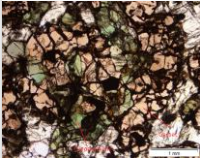
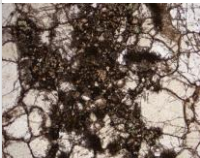
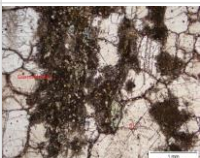
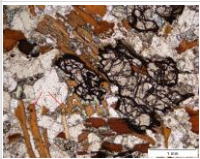
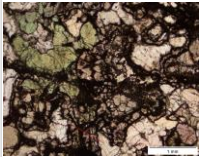
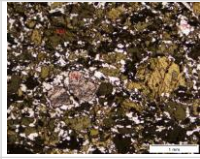
A summary of the above mentioned results is shown below in Table S1.

3.5 Discussion

3.5.1 Thermobarometry

Amphibolite (Z2) and mafic granulite (LSC 105) yield estimated pressures of metamorphic equilibration at 3.5-5.3 kbar and 7.4-7.5 kbar, respectively. This is lower than previous estimates (9-16 kbar) made by Collerson et al. (1988), and overlaps with previous minimum estimates (6-15 kbar: Barnhart et al., 2012) for lower crustal xenoliths from the Bearpaw Mountains locality. Similar conditions (5.8-8.2 kbar) were also estimated by Dragovic et al. (2016) for the Beartooth Mountains, south-east of the Bearpaw Mountain range (Fig. 2.2). Higher pressures (7.4-7.5 kbar) indicate a deeper crustal origin for granulite xenoliths. Generally, temperatures (642-817 °C) across the xenolith suite are consistent with amphibolite to granulite facies conditions. P-T estimations from the Tobacco Root Mountains (MMT) encompass a P-T range (600-750 °C, 5-9 kbar), also similar to our xenoliths and,

importantly, have been attributed to a granulite-facies metamorphic event occurring at 1770 Ma (Cheney et al., 2004; Mueller et al., 2004b; Mueller et al., 2005).

Sample	Lithology	Mineralogy	Photomicrograph	SiO ₂	Mg#	P/T	Zircon Characterisation	Magmatic ²⁰⁷ Pb/ ²⁰⁶ Pb Zircon Ages (Ma)	Metamorphic ²⁰⁷ Pb/ ²⁰⁶ Pb Zircon Ages (Ma)
LSC 33	Granulite	Cpx, Pl, Grt		52.95	0.54	737 °C	Magmatic/Recrystallised Magmatic	3231±230 (Upper ²⁰⁶ Pb/ ²³⁸ U- ²⁰⁷ Pb/ ²⁰⁶ Pb intercept age)	1682±130 (Lower ²⁰⁶ Pb/ ²³⁸ U- ²⁰⁷ Pb/ ²⁰⁶ Pb intercept age)
LSC 36	Granulite	Grt, Cpx, Pl, Bt, Qtz		52.99	0.48	650-749 °C	None	-	-
LSC 72	Granulite	Cpx, Pl		52.96	0.53	618-712 °C	Magmatic/Recrystallised Magmatic	1834±19	1788±8
LSC 89	Granulite	Cpx, Opx, Pl		56.96	0.51	659-776 °C	Recrystallised Magmatic (Type I) and Metamorphic (Type II)	1691±24-2534±9 (Type I)	1773±8-1788±4 (Type II)
LSC 90	Granulite	Grt, Cpx, Pl, Bt, Qtz		50.58	0.65	667-817 °C	None	-	-
LSC 105	Granulite	Cpx, Opx, Pl, Grt, Qtz		47.47	0.54	671-683 °C, 7.4-7.5 kbar	Metamorphic	-	1772±5
Z2	Amphibolite	Grt, Pl, Hbl, Qtz		49.99	0.36	642-645 °C, 3.5-5.3 kbar	None	-	-
BR 47	Amphibolite	Hbl, Pl, Bt		51.19	0.76	689-909 °C	Magmatic/Recrystallised Magmatic	1874±8	1801±7

Grt = garnet Cpx = clinopyroxene Opx = orthopyroxene Bt = biotite Pl = plagioclase, Hbl = hornblende, Qtz = quartz

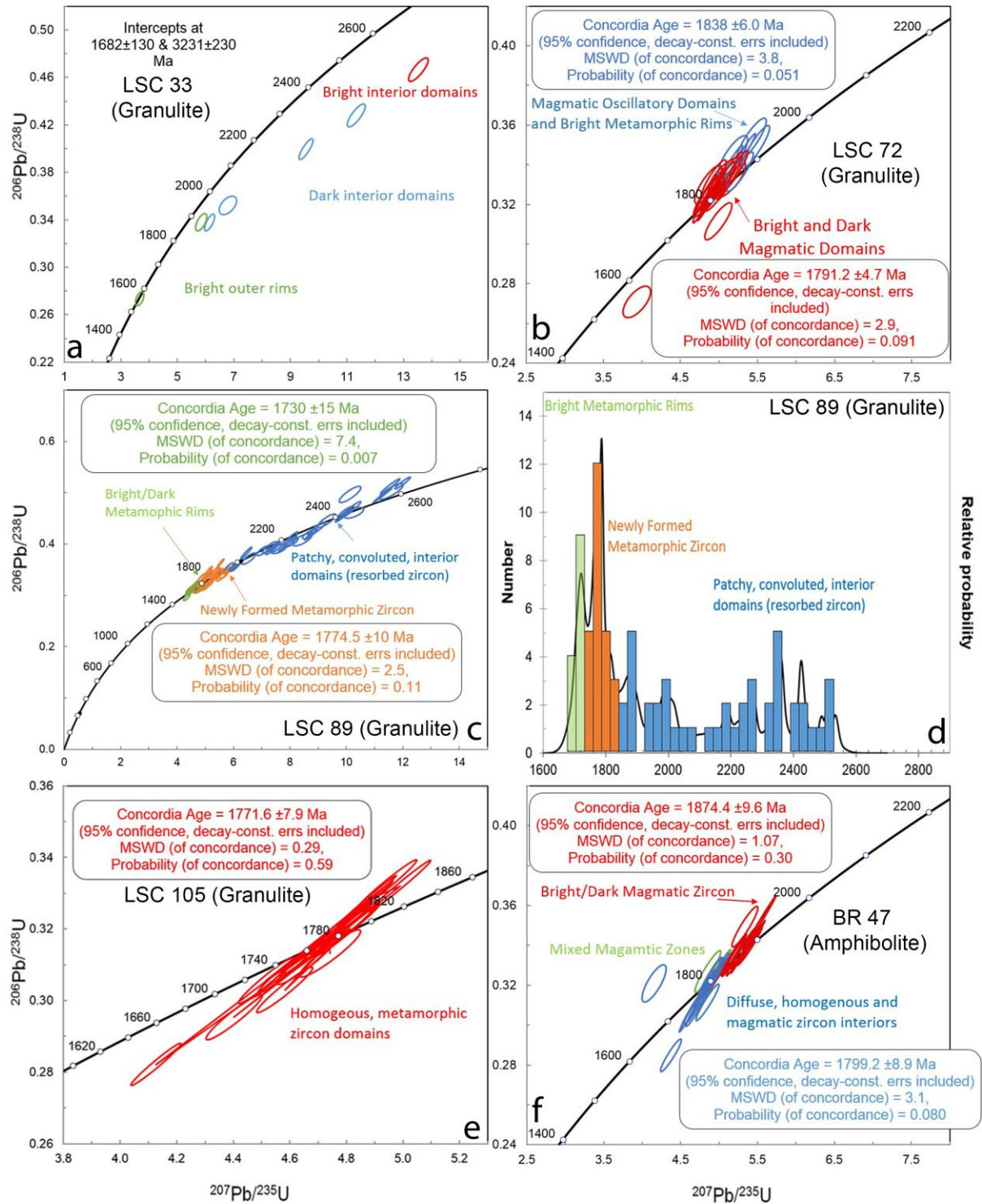


Figure 3.7: Conventional U-Pb concordia and probability density plots for Bearpaw Mountain xenoliths. a: LSC 72 (granulite); b: BR 47 (amphibolite) c and d: LSC 89 (granulite), e: LSC 105 (granulite); f: LSC 33 (granulite). Data point ellipses are 68.3 % conformable.

Given the appearance of Proterozoic metamorphic zircon within granulite xenoliths LSC 105 (1772 ± 5 Ma) and LSC 89 (1733 ± 8 - 1788 ± 4 Ma), together with measured P-T similar to Cheney (2004), we can constrain a granulite facies metamorphic event that occurred at mid-lower crustal levels in the Bearpaw Mountains at this time, or shortly after metamorphic equilibration. Although Scherer et al. (2000) demonstrated slow cooling of granulite xenoliths from the Bearpaw Mountains, the peak metamorphic temperature (assumed by Scherer et al. to be 800 ± 150 °C) was measured at 1707 ± 15 Ma, similar to our equilibration temperatures and metamorphic ages. Therefore maximum and equilibration temperatures should not differ by large amounts during Proterozoic (ca. 1700 Ma) metamorphism. Since no P-T estimates could be obtained for the single Late Archaean xenolith LSC 89 (1691 ± 25 - 2534 ± 9 Ma), there is no evidence to suggest that the lower-middle crust is of this age. Amphibolite xenoliths show lower pressures (3.5-5.3 kbar). Since zircons in amphibolite appear to be igneous and non-inherited, it is likely that these xenoliths formed by crystallisation of juvenile magmas emplaced at shallower levels of the crust prior to the time of metamorphic equilibration. Alternatively, the amphibolite xenolith may represent an existing shallow Archaean/Early Palaeoproterozoic crustal assemblage that was metamorphosed at ca. 1800 Ma. However, the absence of older zircon grains in this sample makes this scenario less likely. Petrographic evidence for retrogression from granulite facies to amphibolite facies is lacking. High Ti-in-zircon temperatures (620-900 °C) are in the same range as mineral thermobarometry values (642-817 °C), testifying to the consistency between datasets. Ti-in-zircon temperatures within granulite xenoliths LSC 72 (618-712 °C, $\bar{x} = 650$ °C) and LSC 89 (659-776 °C, $\bar{x} = 714$ °C) record values that roughly correspond to temperatures obtained through garnet-clinopyroxene (650-683 °C) and garnet-orthopyroxene (671-683 °C) thermometry on granulite xenoliths. No correlation between Ti content and rock type or metamorphic grade is observed, however, thereby limiting useful petrogenetic interpretations, except confirming that metamorphic zircon formed under metamorphic PT conditions. Amphibolite BR 47 contains extreme variations in temperature (6-51 ppm Ti, 692- 909 °C). The highest temperature (909 °C) likely records the zircon crystallisation temperature, while the lowest temperatures (691-692 °C) records re-equilibration at amphibolite facies conditions that correspond to temperatures recorded by amphibole-plagioclase thermometry (689-715 °C) for this xenolith. Ti does not vary coherently with age domains, therefore intermediate temperatures likely resulted from variable degrees of recrystallisation of zircon in the presence of a fluid/melt phase (Ewing et al., 2013; Liu et al., 2015).

3.5.2 Xenolith petrogenesis

Whole-rock major element geochemistry

Using a total alkali-silica (TAS) diagram, Bearpaw xenoliths are classified as originally gabbroic/dioritic in composition with both alkaline and sub-alkaline affinities (Fig. 3.2a). When compared to a global compilation of granulite xenoliths in terms of Mg-number vs. $\text{SiO}_2/\text{Al}_2\text{O}_3$, the samples from our study show compositional characteristics of “Mafic 3” and “Intermediate” xenoliths, with $\text{SiO}_2 < 54\%$ and Mg-number < 0.6 (Kempton and Harmon, 1992) (Fig. 3.2b). These fields represent cumulate xenoliths dominated by feldspar or intermediate igneous rocks following melt extraction. Although feldspar dominates our xenolith assemblage, their recrystallised nature precludes the identification of cumulate textures. A single granulite xenolith (LSC 90) plots within the field of “primitive basalts” suggesting a less evolved protolith. Correlations of major element oxides with Mg-number and SiO_2 , or any other differentiation or mineral accumulation trends, are not observed (Table 3.1). This attests to xenolith heterogeneity due to sampling at different crustal levels and/or the xenoliths not having formed from the same magma batch. The generally low Mg numbers indicates fractionation of igneous precursors rather than immediate derivation from mantle melts (Lai et al., 2011). A first-order petrogenetic assessment therefore suggests non-co-genetic, evolved alkaline/sub-alkaline igneous (perhaps basaltic/gabbroic) precursor melts and/or residues emplaced at different crustal levels, which subsequently recrystallised under granulite to amphibolite facies conditions.

Rare earth elements

Chondrite-normalised enrichments in LREE (Fig. 3.3b) are likely produced by metasomatism (involving fluids), low degrees of partial melting and/or melting of an enriched mantle lithosphere beneath the Wyoming Craton (Dudás et al., 1987; Carlson and Irving, 1994). The REE patterns of the investigated lower crustal xenoliths bear resemblance to compositions of minettes from the Bearpaw Mountains, i.e. to their host rocks (Macdonald et al., 1992; see below), Highwood Mountains (O’Brien et al., 1991), lower crustal xenoliths from Hatcher Mesa, Wyoming (Mirnejad and Bell, 2008), and mantle xenoliths from the Bearpaw Mountains (Downes et al., 2004) attesting to a common geochemical component, which is here tentatively assigned to a subduction-metasomatised mantle beneath the Bearpaw Mountains lithosphere (see below). All xenoliths (apart from LSC 72) display a weak negative Eu anomaly that is not correlated with Mg-number or SiO_2 , implying minimal feldspar fractionation and/or crystallisation from different magma bodies extracted from an enriched mantle. The strong positive Eu anomaly seen within LSC 72 is the result of increased feldspar abundance in this sample (Rudnick, 1992). HREE are flat apart from LSC 33, which shows relative depletion in HREE possibly due to a partial melting in the presence of residual garnet.

Trace element systematics

Trace element patterns observed for Bearpaw Mountain xenoliths closely resemble those of arc-collisional or subduction settings (Pearce, 1983; Saunders et al., 1991). Large-ion lithophile (LILE) element (Cs, Rb, Ba, K, U and Pb) enrichment and depletion of high field strength (HFSE) elements (Nb-Ta, Zr-Hf, Ti) are created when hydrous fluids and/or melts are produced above a subducting slab that enrich the overlying mantle wedge (e.g. Hawkesworth et al., 1994). Enrichment in fluid mobile elements, particularly Rb, Ba and K, and the presence of modal phlogopite in some xenoliths indicates subduction-metasomatism (Downes et al., 2001). Relative Nb-Ta and Zr-Hf negative anomalies are produced through complex mineral-melt or mineral-fluid interactions in the subduction zone. During slab dehydration, less mobile elements (HFSE) are not readily transported in fluids from the subducting slab (Hawkesworth et al., 1994). Mineral retention of Nb and Ta in rutile (Keleman et al., 2003), phlogopites and amphiboles (Ionov and Hoffman, 1995) may contribute to negative Nb-Ta anomalies, while zircon may be partially responsible for Zr-Hf depletions since it hosts considerable concentrations of these elements in subduction zone melts (Rubatto and Hermann, 2003). While negative Nb-Ta and Ti anomalies relative to Primitive Mantle are also indicative of a lithospheric contribution, the Zr-Hf negative anomaly is not always present in continental settings (Rudnick and Fountain, 1995). Convergent-margin trace element signatures may represent an episode of Proterozoic subduction, in which partial melting and metasomatism above the subducting slab is recorded by (ca. 1800 Ma) crystallisation ages in our xenoliths. Alternatively, remelting of a previously enriched mantle lithosphere would show an identical trace element signature, unrelated to convergent margin processes in the Proterozoic. However, a subduction related petrogenesis is implied by the occurrence of our xenoliths within a regional subduction zone, namely the GFTZ, which contains geochronologically-constrained, subduction-related melt generation events that match our zircon ages (ca. 1800 Ma, Mueller et al., 2002, 2005, see below).

Comparison with other mantle xenoliths from the Bearpaw Mountains (Downes et al., 2004; Facer et al. 2009) reveals remarkably similar normalised trace element patterns (negative Nb-Ta, Zr-Hf, positive Pb, Sr and LILE enrichment relative to HFSE) (Fig. 3.3a). This would attest to an enriched mantle source for all xenolith protoliths. Indeed, in the Bearpaw Mountain region, hydrous fluid metasomatism was recognised as a result of subduction and dehydration of the Farallon plate (O'Brien et al., 1991; Downes et al., 2004; Facer et al., 2009) during the Eocene. Geochronological constraints from mantle peridotites and glimmerites corroborate metasomatic and melt enrichment events at 1800 Ma (Carlson and Irving 1994, Eagle Buttes, Highwood Mountains) and 1700-1900 Ma (Rudnick et al., 1999, Highwood Mountains), while a mantle enrichment episode during 1500-1800 Ma was inferred from Nd and Pb isotopic data for alkali igneous rocks from the Crazy Mountains, Montana (Dudás et al., 1987). These mid-Proterozoic enrichment events affected the region from which our xenoliths were

obtained. All above observations strongly point to metasomatic fluid enrichment due to slab dehydration coeval with partial melting at ca. 1800 Ma, as registered by magmatic zircon ages between 1834 and 1874 Ma for our xenoliths (LSC 72, BR 47). Curiously, the oldest xenolith in our suite (2534 ± 9 Ma, LSC 89) post-dates this Proterozoic enrichment event, yet it displays a trace element composition very similar to those observed for the other xenoliths. A possible explanation is that an ancient mantle enrichment event, presumably associated with subduction, occurred during the Late Archaean (Mueller and Wooden, 1988; Gorman et al., 2002; Gifford et al., 2014, 2018). Melting of this metasomatically enriched Late Archaean mantle is not well constrained by the spectrum of older magmatic ages in this xenolith (2000-2534 Ma).

We conclude that major and trace element characteristics of xenoliths suggest subduction-induced melting resulting in the formation igneous (likely basaltic) protoliths in the Proterozoic (1834 ± 19 - 1874 ± 10 Ma). Older subduction-related enrichment events appear possible, as recorded in Late Archaean (2534 ± 9 Ma) xenoliths.

Melt extraction

Due to their similar ionic properties, Nb-Ta, Zr-Hf, Hf-W and Y-Ho pairs rarely fractionate during igneous differentiation from chondritic ratios (Bau, 1996; McDonough and Sun, 1995; Pack et al., 2007; Huang et al., 2011), including partial melting and fractional crystallisation. Deviation from chondritic values, on the other hand, may point to protolith melts enriched in aqueous elements (B, Cl, H₂O, F) due to ligand complexation (Bau et al., 1996). Ratios of Nb/Ta, Zr/Hf and Y/Ho for xenoliths are mostly chondritic (Nb/Ta = 16-19; Zr/Hf $\approx$ 37; Y/Ho $\approx$ 25), with the exception of LSC 89 (Zr/Hf = 25), LSC 33 (Zr/Hf = 46), and LSC 105 (Nb/Ta = 14) (Table 3.1). An enrichment in fluid mobile elements (Cs, Ba, Rb, Sr, Pb, U) is indeed observed within our xenoliths and may point to metasomatic enrichment in sublithospheric portions of the Bearpaw Mountains (Downes et al., 2004; Facer et al., 2009), especially in the case of LSC 89, LSC 33 and LSC 105, which show anomalous HFSE ratios. Alternatively, decoupling of Zr-Hf can occur during high-grade anatexis of mafic rocks in the absence of an aqueous fluid as has been recently demonstrated for pyroxene hornfels metabasalts at the contact to the Sudbury Igneous Complex, with whole rock Zr/Hf ratios as low as 29 (Jørgensen et al., 2017). While partial melting and melt extraction during high-grade metamorphism is consistent with Pb isotope systematics of leached feldspars for the same suite of xenoliths (Bolhar et al., 2007), this process cannot account for enrichment in highly incompatible and mobile elements. Additionally, while anatexis and melt removal from rocks may cause sub-chondritic Zr/Hf in meta-mafic rocks due to preferential removal of Zr by sequestration into newly formed zircon, effects on Nb/Ta (and Y/Ho) may not be sufficient to significantly alter chondritic values. The integration of all available geochemical and isotopic evidence

indicates that portions of the lower and middle crust as represented by xenoliths were either affected by fluid-aided metasomatism or contamination by extraneous sources subsequent to melt extraction. Melt extraction alone cannot be reconciled with significant enrichment of LILE seen in all xenoliths.

3.5.3 Host lava influence on xenolith whole-rock chemistry

Enrichment in major and trace elements may occur as a result of host magma (minette) interaction during Eocene entrainment, masking the original bulk rock and/or protolith melt chemistry of the xenoliths. The effect of the host minette lava on highly incompatible and fluid-mobile elements (Cs, Rb, Ba and Sr and LREE) and generally immobile and major and trace elements (HREE and HFSE) should therefore be tested.

The extent of mixing between the minette host and xenoliths is evaluated using a bulk mixing model (Faure, 1998; Schilling et al., 2005) involving representative samples with lowest LILE (amphibolite Z2) and total REE (granulite LSC 72) from our xenolith suite (“contaminated” endmember), together with an average composition of 14 minettes from the Bearpaw region (Macdonald et al., 1992, Table A3) as the “contaminating” endmember. Both major (K_2O and TiO_2) and trace elements (La, Nd, Rb, Sr) were used to define mixing relationships between the minette host and least contaminated xenoliths (Z2 and LSC 72) (Fig. 3.8a-d). K_2O and TiO_2 were chosen to represent incompatible and mobile versus immobile major oxides, while La, Nd, Rb, Sr were used to represent incompatible and highly mobile versus immobile trace elements. From mixing curves defined for minette and Z2, 25-90 % minette contribution of K_2O/TiO_2 is required to reach xenolith compositions of K_2O/TiO_2 , however, high and variable Sr/Rb (3.7-27.9) and La/Nd (0.4-1.9) result in xenoliths plotting far to the right or above of mixing curves (Fig. 3.8a,b), requiring high (10-75 %) and unrealistic (>100 %) proportions of host minette contributions to reach xenolith Sr/Rb compositions. For mixing curves defined between minette and LSC 72 (Fig. 3.8c,d), generally large amounts of host contamination (25-50 %) are required to match xenolith compositions of Sr/Rb, but highly variable K_2O/TiO_2 (0.3-4.9) and La/Nd (0.4-1.9) produce large scatter that also require high and/or unrealistic contaminant proportions (<1 % or >100 %) to reach Bearpaw xenolith compositions. From bulk mixing calculations, 70 % of admixed host

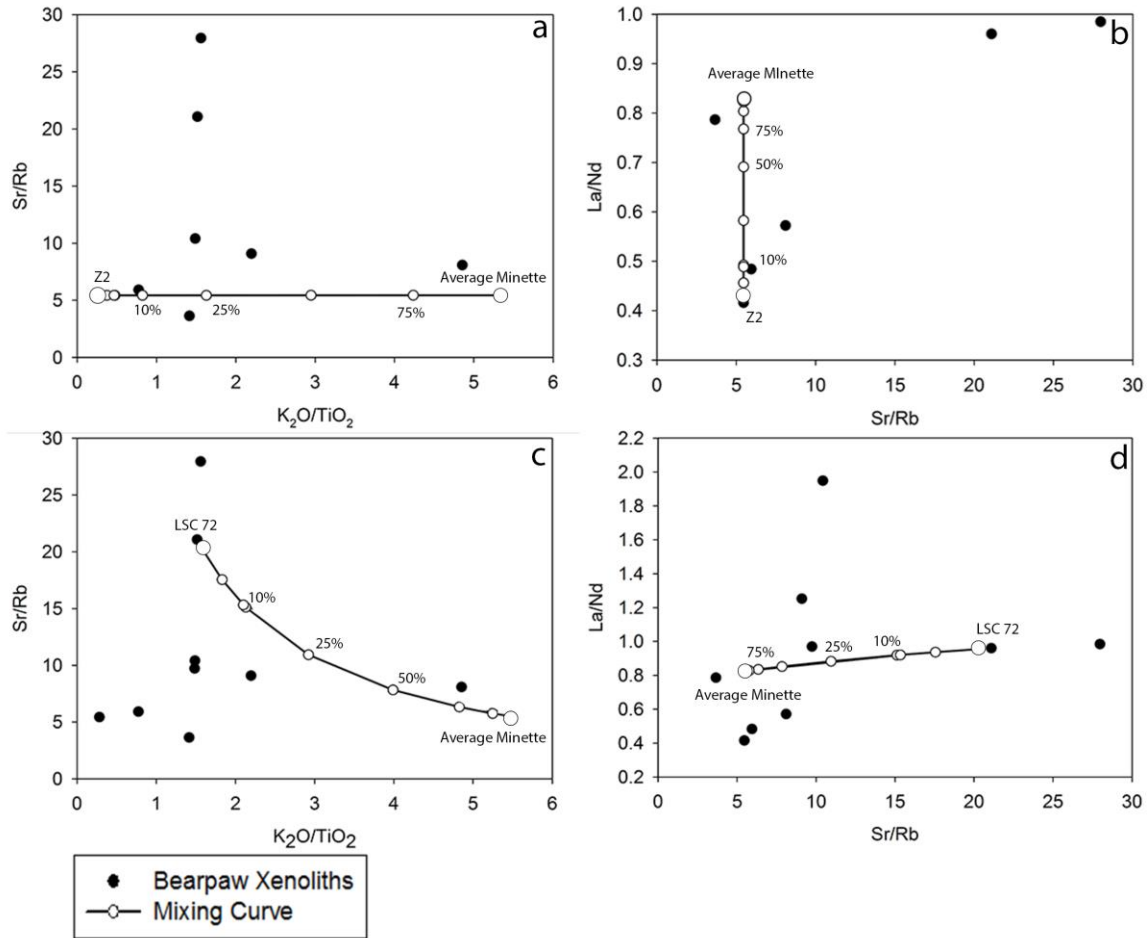


Figure 3.8: Plots of major and trace elements showing simple mixing of amphibolite Z2 (a, b) and granulite LSC 72 (c, d) and minette lava. Scatter in xenolith compositions precludes simple mixing of host basalt (minette) and Bearpaw samples. Percentages indicate proportion of minette contribution. End-member concentration ratios are shown in brackets (Average Minette: $\text{Sr/Rb} = 5.4532$, $\text{K}_2\text{O/TiO}_2 = 5.50$, $\text{La/Nd} = 0.82$, Xenolith Z2: $\text{Sr/Rb} = 5.4509$, $\text{K}_2\text{O/TiO}_2 = 0.30$, $\text{La/Nd} = 0.42$, Xenolith LSC 72: $\text{Sr/Rb} = 20.3$, $\text{K}_2\text{O/TiO}_2 = 1.6$, $\text{La/Nd} = 0.96$).

minette is needed to match average xenoliths compositions of K₂O, while 31-32 % minette contribution is required to reach average xenolith concentrations of TiO₂. Respective amounts of minette contribution for La (4-61 %), Nd (19-46 %), Rb (29-34 %) and Sr (14-70 %) are similarly high in order to reproduce average xenolith abundances of these trace elements. Such high levels of mixing are inconsistent with petrography showing no evidence of host rock infiltration, including sharp contacts between xenoliths and host lithologies (Bolhar et al., 2007). Furthermore, the alkaline host minettes are enriched in immobile and mobile elements (Rb, Cs, Sr, Nd, Nb), at levels comparable to the xenoliths (Macdonald et al., 1992: Rb = 113-233 ppm; Sr = 644-1840 ppm, Cs = 9-54 ppm, Nd = 17-48 ppm, Nb = 5-20 ppm) implying that mixing between these end-members would show negligible changes in compatible and incompatible element concentrations, and that both the host lava and

xenoliths were formed from a similar enriched mantle source. Therefore, while enrichment due to host magma contamination cannot be entirely excluded, simple mixing between Bearpaw xenoliths and host minette magma cannot account for the full spectrum of major and trace element using appropriate end-member compositions for mixing models. Consequently, it is likely that trace element patterns do indeed record a subduction-related signature.

In conclusion, simple binary mixing using whole-rock major and trace element ratios of representative host minette lava and xenolith end-member compositions provide arrays that cannot adequately capture the variability seen in xenolith compositions. Significantly, admixing of minette requires inconsistent quantities for elements with variable petrogenetic properties (mobile versus immobile, incompatible versus compatible). Additionally, petrographic evidence for host rock interaction is lacking. While some host rock contamination cannot be ruled out, other processes (such as subduction-metasomatism) are required to more fully account for the trace element patterns seen in these xenoliths.

3.5.4 Zircon petrogenesis

Of initial concern when interpreting zircon U-Pb ages is whether zircon is co-genetic to the xenolith or inherited from external sources. Features, such as rounded exteriors and inherited cores, which usually suggest a detrital origin, are not observed. Instead, textures described above suggests that all zircon grains are either igneous or metamorphic. In the cases of xenoliths LSC 72, LSC 105 and BR 47, the age distributions are very narrow and almost entirely concordant (1788 ± 8 - 1874 ± 10 Ma), further diminishing a detrital, inherited or entrained origin.

The ages for xenolith LSC 89 define a distinct mid-Proterozoic population (1773 ± 8 - 1788 ± 4 Ma) and a series of dispersed ages between 1700 and 2534 Ma (Fig. 3.7c,d). This spread in ages along concordia represents variations within single grains rather than variation across multiple zircons within the population. Therefore single zircons represent growth during multiple older and younger events and/or secondary recrystallisation processes. The presence of zircon grains containing only younger, mid-Proterozoic ages (1773 ± 8 - 1788 ± 4 Ma) in LSC 89 also does not imply an external origin since similar mid-Proterozoic ages occur as outer rim domains on Late Archaean/Early Palaeoproterozoic (ca. 2000-2534 Ma) grains within the same sample. Therefore metamorphic zircon growth occurred both as entirely new grains (likely through breakdown of Zr-rich phases or pre-existing zircon), and as rims on existing Late Archaean/Early Palaeoproterozoic grains. Both zircon types have a co-genetic, non-inherited origin resulting from one protracted tectono-thermal event at ca. 1700-1800 Ma.

Interaction of Late Archaean magmas with pre-existing (>2500 Ma) crust is plausible, and may result in the presence of detrital/entrained zircon. However, no evidence for Early to Late Archaean zircon grains (2500-3800 Ma) are observed within these xenoliths.

3.5.5 Interpretation of zircon age domains

Metamorphism at lower crustal levels may lead to bleaching and solid-state recrystallisation of original magmatic domains that produce age variation (50-100 Ma) within and between different grains (Hoskin and Black, 2000). This can be observed in grains 72-2, 72-3 and 72-4 where darker interiors (1773 ± 23 - 1900 ± 28 Ma) are slightly older than bright outer exterior domains (1719 ± 51 - 1822 ± 26 Ma). Recrystallisation, likely in the presence of melt, also produced a younger population (1801 ± 7 Ma) within amphibolite BR 47, in addition to older magmatic ages (1874 ± 8 Ma). Mid-Proterozoic metamorphic zircon ages (1772 ± 5 - 1788 ± 4 Ma) are recorded within other xenoliths (LSC 105 and LSC 89), and considering that similar metamorphic ages have been reported for the Bearpaw Mountains elsewhere (1707 ± 15 Ma: Scherer et al., 2000; 1700-1800 Ma: Barnhart et al., 2012), we conclude that a metamorphic event affected the mid-lower crust and overprinted earlier igneous events, now preserved only as faint magmatic textures (LSC 72 and BR 47).

Granulite xenolith LSC 105 also contains mid-Proterozoic (1772 ± 5 Ma) U-Pb ages, however, these zircon grains are clearly metamorphic and ages therefore record metamorphic events.

The spread of Late Archaean/Early Palaeoproterozoic (1690-2534 Ma) U-Pb ages along concordia, the identification of resorbed zircon morphology and large age variations (100-500 Ma) within domains that are not texturally distinct, point to Pb-loss through zircon recrystallisation that artificially spread these ages towards younger values (Pidgeon, 1992; Vavra et al., 1999; O'Brien and Miller, 2014), starting with a cryptic magmatic event at 2534 Ma or earlier. Metamorphic ages obtained from metamorphic domains (whole grains, bright and dark rims) within this xenolith document a mid-Proterozoic (1773 ± 8 - 1788 ± 4 Ma) event. Similar ages are recorded on metamorphic zircon in xenolith LSC 105 (1772 ± 5 Ma) strengthening the validity of this age.

A discordia curve through U-Pb points within LSC 33 points to a much earlier Archaean age (3200 Ma). Although derived from a single grain, this would suggest that Early Archaean ages are preserved in this segment of the crust, if such an inferred upper intercept age can be considered reliable. The lower-intercept is poorly constrained (1682 ± 130 Ma) and contains high errors but broadly correlates with metamorphic zircon ages (ca. 1770 Ma).

3.5.6 Age relationships and implications for the Wyoming Craton lithosphere

Relation to BBMZ and cratonic interior

The central to northern interior (BBMZ) of the Wyoming Craton, including the Beartooth Mountains, Bighorn Mountains, Owl Creek and Wind River Range, record predominantly Archaean ages between 2800 and 3300 Ma (Chamberlain et al., 2003; Frost and Fanning, 2006 and references therein). The Long Lake Magmatic Complex (LLMC) of the Beartooth Mountains records magmatic ages within a narrower range (2670-2690 and 2790-2830 Ma: Mueller et al., 2010; Dragovic et al. 2016). Towards the southern margin of the BBMZ and including the SAT, slightly younger ages (2500-2550 Ma) register arc-related magmatic pulses (Frost et al., 1998, 2000, 2006), also reflected in our oldest concordant zircon spot (2534 ± 9 Ma in grain 89-5). Older tectono-thermal pulses (2630, 2670, 2800 Ma) are not captured in our xenolith set, however. In general, our zircon ages do not directly coincide with ages associated with known events within the BBMZ (Fig. 3.9, Table 3.4). In some cases, single spots correspond to some Late Archaean or Palaeoproterozoic tectonothermal ages, but these spots occur in grains that contain younger Proterozoic ages (1722-1773 Ma) as well. If the BBMZ remained mostly unaffected by tectonism since ca. 2600 Ma (Frost and Fanning, 2006), younger concordant ages (ca. 1700-1800 Ma) within our xenoliths cannot be accounted for by BBMZ processes. Additionally, other interior magmatic provinces have been similarly unaffected since 2500 Ma (Mueller and Frost, 2006). If cratonic stability was reached between 2800 and 3200 Ma (Frost et al., 1998, 2000; Mueller and Frost, 2006), then these xenoliths likely do not sample the original Wyoming cratonic crust. Early Archaean ages are rare in our dataset (single discordant zircon in LSC 33). Derivation of xenoliths from the nearby Medicine Hat Block is unlikely since ages within this block (ca. 2400 to 3300 Ma: Foster et al., 2006; Gifford et al., 2014, 2018) do not correlate well with zircon ages obtained from our xenoliths (ca. 1700-2500 Ma).

Relation to GFTZ and MMT

The Bearpaw Mountains straddle the northern portion of the Great Falls Tectonic Zone (GFTZ) (Fig. 2.2). The extent of the GFTZ is variably delineated by faults, seismics, borehole and aeromagnetic data, therefore, on some maps the Bearpaw suite falls within the GFTZ and intersects the southern tip of the Medicine Hat Block (O'Neill and Lopez, 1985; Davis et al., 1995; Gorman, 2002; Gifford et al., 2014). Geochronological studies within the GFTZ generally report a narrow range of ages between 1770 and 1860 Ma (Foster et al., 2006; and references therein) which match our younger Proterozoic ages (1773-1874 Ma).

Table 3.4

Summary of published ages for the northern Wyoming Craton and Northern and Western Margins

Reference	Region	Locality	Age (Ma)	Method	Type/Interpretation
Frost and Fanning, 2006 (and references therein)	BBMZ	Beartooth, Owl Creek, Bighorn, Granite Mountains	ca. 2800-3300 Ma	U-Pb zircon	Magmatic Ages
Mogk et al., 1988	BBMZ	Beartooth Mountains	ca. 2560, 2740	U-Pb Zircon, $^{87}\text{Sr}/^{86}\text{Sr}$	Magmatic Ages
Mueller et al., 1996	BBMZ	Beartooth Mountains	ca. 2550, 3250, 3500	U-Pb Zircon	Magmatic and Hydrothermal Ages
Mueller et al. (2010)	BBMZ	Beartooth Mountains	ca. 2790-2830	U-Pb Zircon	Magmatic Ages
Dragovic et al. (2016)	BBMZ	Beartooth Mountains	ca. 2670-2680	Sm-Nd Garnet, U-Pb Monazite	Metamorphic Ages
Dudas et al. (1987)	GFTZ	Crazy Mountains	ca. 1500-1900 Ma	Nd, Pb Isotopes	Mantle Metasomatism
Barnhart et al. (2012)	GFTZ	Bearpaw Mountains	ca. 1700-1800, ca. 2000-2100	U-Pb Monazite	Metamorphic Ages
Scherer et al. (2000)	GFTZ	Bearpaw Mountains	1707±15	U-Pb Zircon	Metamorphic Ages
Davis et al. (1995)	GFTZ	Medicine-Hat Block	ca. 1700-1800	U-Pb Zircon	Magmatic Ages
Davis and Ross (1999)	GFTZ	Medicine-Hat Block	ca. 1700-1820	U-Pb Zircon	Magmatic Ages
Carlson and Irving (1994)	GFTZ	Highwood Mountains	ca. 1800 Ma	U-Pb Monazite	Mantle Metasomatism
Rudnick et al. (1999)	GFTZ	Highwood Mountains	ca. 1700-1900 Ma	U-Pb Zircon	Mantle Metasomatic/Magmatic Ages
Holm and Schneider (2002)	GFTZ	Little Belt Mountains	ca. 1800 Ma	$^{40}\text{Ar}/^{39}\text{Ar}$ Biotite and Hornblende	Metamorphic/Cooling Ages
Mueller et al., 2002	GFTZ	Little Belt Mountains	1864-1867	U-Pb Zircon	Magmatic Ages
Gifford et al. (2014)	GFTZ	Grassrange Diatremes	ca. 1720, 2550	U-Pb Zircon	Magmatic Ages
Gifford et al. (2018)	GFTZ	Little Rocky Mountains	ca. 2400-2500, 2700-2800, 3000-3300	U-Pb zircon	Magmatic and Metamorphic Ages
Mogk (1992), Mueller (1993)	MMT	Madison, Gallatin	ca. 2500-2800, 3000-3400 3300-3700	U-Pb Zircon	Magmatic and Metamorphic Ages
Mueller et al. (2004b)	MMT	Tobacco Root Mountains	ca. 1770, 3800	U-Pb Zircon	Magmatic and Metamorphic Ages
Alcock et al. (2013)	MMT	Ruby Range	ca. 1780-1830	U-Th-Pb Monazite	Metamorphic Ages
Roberts et al. (2002)	MMT	Ruby, Highland, Tobacco Root	ca. 1740-1820, 2470	$^{40}\text{Ar}/^{39}\text{Ar}$ Biotite, $^{207}\text{Pb}/^{206}\text{Pb}$ garnet	Magmatic and Metamorphic Ages
Mueller et al. (2005)	MMT	Tobacco Root Mountains	ca. 1770	U-Pb Zircon, Monazite	Metamorphic Ages
Mueller et al. (2016)	MMT	Tobacco Root, Beaverhead-Tendoy	ca. 1700-1900, 2400-2800, 3200-3500	U-Pb Zircon	Magmatic and Metamorphic Ages
Kellog et al. (2003)	Western Margin	Beaverhead Structure	ca. 2450	U-Pb Zircon	Magmatic Ages
Mueller and Foster (2006), Foster et al., (2006)	Western Margin	Rocky Mountains	ca. 1800	U-Pb Zircon	Magmatic Ages
Mueller et al. (2004a)	Western Margin	Farmington Complex	ca. 1600-1900, 2200-2500	"Geo/Thermochronology"	Magmatic and Metamorphic Ages
This study	GFTZ	Bearpaw Mountains	1707±15-2534±9	U-Pb Zircon	Igneous and Metamorphic Ages

“Thermo-tectonic activity” associated with the collision of the Hearne and Wyoming cratons was constrained between ca. 1800 and 1860 Ma from studies within the Little Belt Mountains of the GFTZ (Holm and Schneider, 2002). Also within the Little Belt Mountains, U-Pb zircon ages between ca. 1864 and 1867 Ma were interpreted to represent new material formed from subduction-related ocean closure between the Wyoming Craton and MHB (Mueller et al., 2002). Based on the similarity in ages for LSC 72 (1834±19 Ma) and BR 47 (1874±8 Ma) to those reported by Mueller et al. (2002), and incompatible trace element patterns indicating subduction-related characteristics (Zr-Hf and Nb-Ta anomalies, see above), it is likely that these two xenoliths formed during oceanic plate subduction described previously in the Little Belt Mountains (albeit farther north within the GFTZ). A continued process of subduction-induced melting with a large range of ages (2420-3210 Ma), not confined to the Proterozoic, was deduced from basement studies in the Little Belt Mountains (Gifford et al., 2018). However, the majority of ages in this study are outside the range of ages identified in our xenoliths.

The Montana Metasedimentary Terrane (MMT) situated along the most north-western segment of the Wyoming Craton is isotopically and lithologically distinct, and records Early to Late Archaean ages (ca. 2600-3700 Ma) (Mogk et al., 1992; Mueller et al., 1993), which bear no resemblance to ages in our xenoliths.

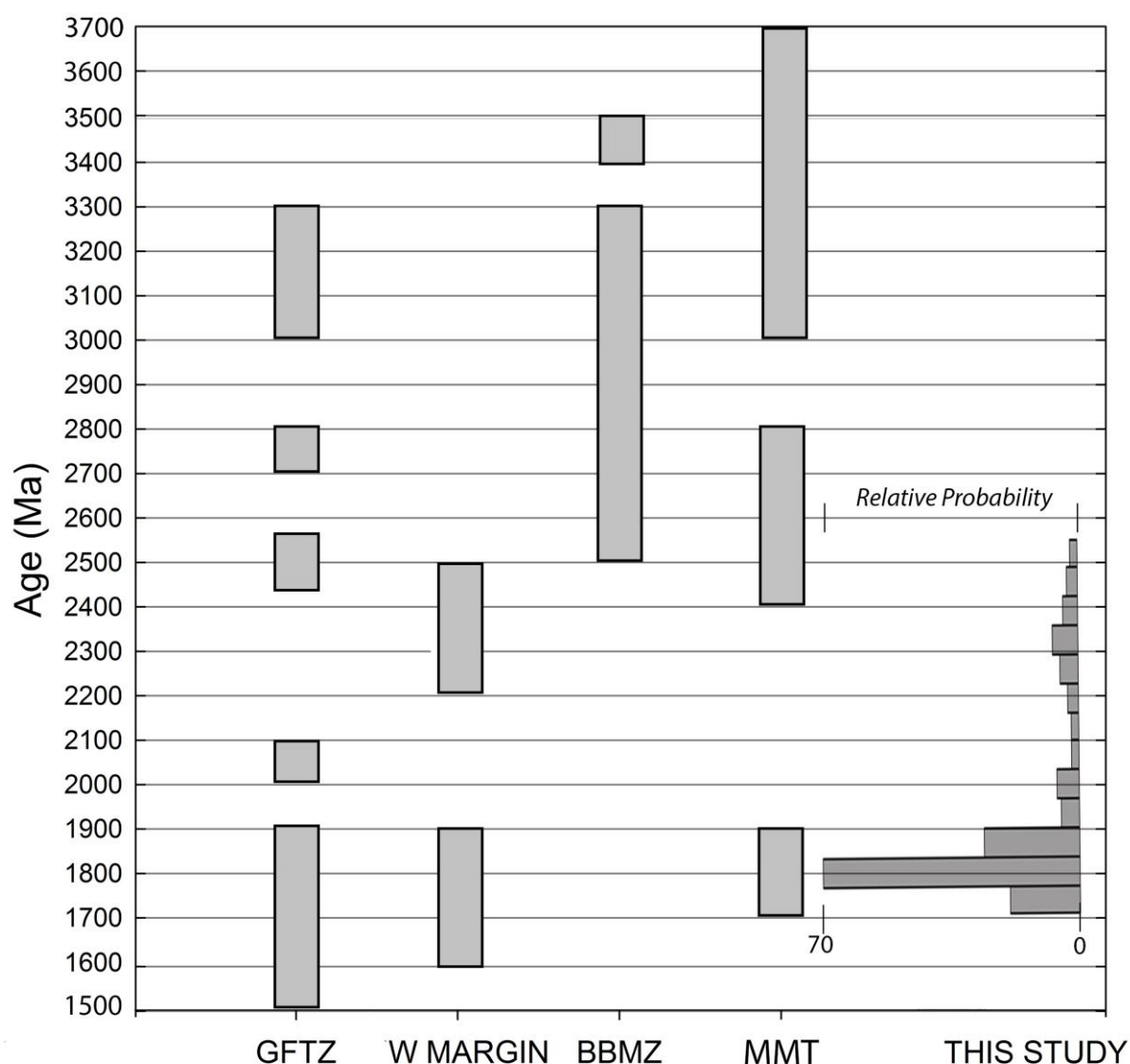


Figure 3.9: Compilation of ages from the Northern Wyoming Craton and adjacent tectonic margin zones (GFTZ and W Margin). GFTZ= Great Falls Tectonic Zone; W Margin = Western Margin; BBMZ = Beartooth-Bighorn Magmatic Zone; MMT = Montana Meta-sedimentary Terrane. References for ages are given in Table 3.4. Probability density plot for $^{207}\text{Pb}/^{206}\text{Pb}$ zircon ages from this study is also shown. Grey bars for other zones represent approximate ranges in age only.

Proterozoic ages (ca. 1770-1820 Ma), however, are recorded within the Ruby Range, Highland and Tobacco Root mountains of the MMT (Roberts et al., 2002; Mueller et al., 2004b; Mueller et al., 2005) and bear similarity to metamorphic ages recorded in LSC 105 (1772 Ma), and LSC 89 (1773-1788 Ma). Various mechanisms can account for younger ca. 1770 Ma ages within the MMT. Collision with a separate arc terrane may have induced tectonic activity with limited magmatism at ca. 1770 Ma (Mueller et al., 2005). Other possible mechanisms include “outward- directed subduction” or metamorphism induced by magmatic underplating (Mueller et al., 2004). A more likely scenario

involves the metamorphic growth of ca. 1770 Ma zircons as a result of metamorphism induced by late-stage collision of the MHB and Wyoming Craton. As mentioned above, oceanic-plate subduction between the Wyoming Craton and Medicine Hat Block occurred at ca. 1860 Ma (Mueller et al., 2002). This subduction initially occurred in a compressional environment and was orientated such that crustal material was subducted beneath the MHB (Fig. 3.10). Following ocean-closure, the Wyoming Craton and MHB collided, possibly resulting in thickening of the crust and associated high-grade metamorphism at ca. 1770 Ma (Mueller et al., 2002; Mueller et al., 2005, Gifford, 2013) (Fig. 3.10). A change in tectonic regime to transpressional likely also occurred within the MMT and GFTZ during this time, as the Wyoming Craton continued to move eastward toward the Superior Craton (Dahl et al., 1999; Mueller et al., 2002; Mueller et al., 2005). Evidence for late-stage continental collision of the MHB with the Wyoming Craton and associated high-grade metamorphism is recorded within 1760-1770 Ma zircon and monazite grains from the Tobacco Root Mountains (Mueller et al., 2005). This late-stage continental collisional activity is likely also responsible for metamorphic zircon growth further northwards within the Bearpaw Mountains (as recorded by ca. 1770 Ma zircon within our xenoliths).

Other ca. 1770 Ma ages within the MMT include metamorphic and post-tectonic cooling ages (ca. 1740-1820 Ma) reported by Roberts et al. (2002) using ^{40}Ar - ^{39}Ar biotite and $^{207}\text{Pb}/^{206}\text{Pb}$ garnet geochronology. A complex temperature-time history involving convergence, thickening, extension and unroofing between ca. 1710 to 1780 was also reported within the Tobacco Root Mountains (Harms et al., 2004). Alcock et al. (2013) also used monazite ages to constrain metamorphism within the Ruby Range at ca. 1780 Ma due to post-collisional delamination, thinning and decompression. Although the Bearpaw xenolith localities lie sufficiently north of the GFTZ to be considered part of the Medicine Hat Block, ages within our xenolith suite (ca. 1700-2500 Ma) are absent a distinct Archaean (ca. 2600-3300 Ma) population commonly associated with the MHB (Foster et al., 2006; Gifford et al., 2014, 2018).

To summarise, existing geochronological studies within the GFTZ and MMT correspond well with our mid-Proterozoic zircon ages. Older Proterozoic ages (1834-1874 Ma) obtained for igneous zircon (LSC 72, BR 47) are associated with subduction-related melt generation events, involving ocean closure between the Wyoming Craton and Medicine Hat Block, while a tightly constrained younger Proterozoic age (1772-1788 Ma: LSC 105, LSC 89) can be assigned to metamorphic events associated with late-stage continental collision between the Wyoming Craton and MHB.

Relation of Older Ages to Western Margin/GFTZ/MMT

Older magmatic ages within granulite LSC 89 (2000-2534 Ma), occurring together with younger Proterozoic ages (ca. 1800 Ma), however, are scarce within the Wyoming Craton and surrounding domains (GFTZ/MMT/MHB/western margin). Gifford (2013) reported metamorphic Proterozoic (1700-1900 Ma) ages from Little Sand Creek xenoliths, and older concordant magmatic ages between 2400 and 2700 Ma within samples from the Missouri Breaks Diatremes, Bearpaw, and Highwood Mountains. Collisional tectonics associated with the generation of mafic crust has been suggested to occur during the Late Archaean to Proterozoic (1600-2500 Ma) along the western margin of the craton (Foster et al., 2006). Roberts et al. (2002) attributed Late Archaean supracrustal ages (2750 Ma), together with Proterozoic ages (2470 Ma and 1780-1820 Ma), to plume activity (Heaman, 1997), the break-up of Kenorland and associated Paleoproterozoic metamorphism. The absence of a distinct population within this range (2000-2500 Ma) in our xenoliths precludes direct comparisons with existing geochronological data in the region. Some form of magmatism, however, must result in initial crystallization of xenolith LSC 89 at 2534 Ma or older. Geochronology is inconsistent with the hypothesis of lower crustal reworking since existing Wyoming Craton/MHB material is largely Archaean in age.

3.5.7 Magmatic additions versus crustal reworking

Various authors have debated the nature of the lower crust beneath the Wyoming Craton and its genesis through crustal reworking and/or magmatic additions during the Archaean and Proterozoic. Crustal growth was inferred through geophysical and/or xenolith studies in the Proterozoic (ca. 1700-1900 Ma) (Davis et al., 1995; Snelson et al. 1998; Davis and Ross, 1999; Mueller et al., 2002, 2004b; Gifford et al., 2014). On the other hand, Proterozoic ages may simply represent crustal reworking and metamorphism at a collisional interface without well-defined magmatic addition (Chamberlain et al., 2003; Barnhart et al., 2012). From the xenolith evidence presented here, new magmatic additions to the crust can be inferred from xenoliths containing mid-Proterozoic (1834 ± 19 - 1874 ± 8 Ma) igneous zircon (LSC 72 and BR 47), probably formed as a result of subduction-related ocean-closure (see above). This finding supports models of Proterozoic underplating and/or arc accretion events involving the generation of new melt beneath the Wyoming Craton at this time. Following ocean-closure, the Wyoming Craton and Medicine Hat Block collided, resulting in ca. 1770 Ma metamorphism that likely recrystallised all xenoliths. The Wyoming craton is largely Mesoarchaeal in age, therefore metamorphism of existing ancient Wyoming Craton material to form granulite xenoliths cannot account for young, largely Proterozoic ages in our xenoliths. Granulite LSC 89 contains variable concordant ages between 2000 and 2534 Ma that do not define a unique population and cannot be readily correlated with existing events within the Wyoming Craton. This lack of correlation suggests

the crystallisation of new magmatic material added to the Wyoming cratonic crust, rather than reworking of existing Archaean crust, that was subsequently metamorphosed to granulite facies during continental collision.

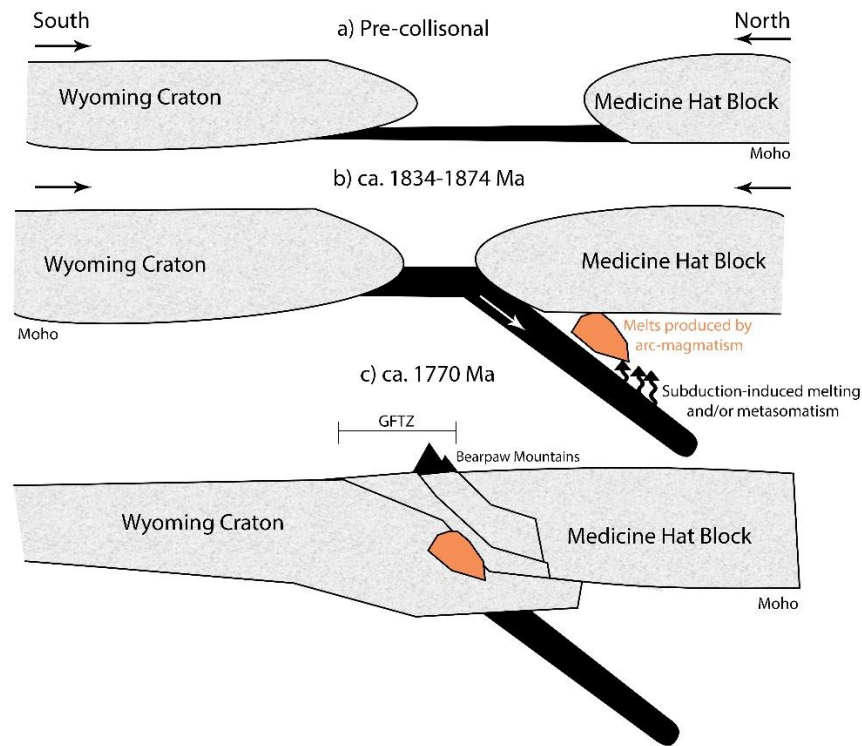


Figure 3.10: Schematic cross-sections for the tectonic evolution of the Wyoming Craton (WC), Medicine Hat Block (MHB) and Great Falls Tectonic Zone (GFTZ). a) Pre-collisional stage preceding Proterozoic subduction between the WC and MHB. b) Ocean closure commences at ca. 1834-1874 Ma. Subduction is orientated such that material is thrust beneath the MHB. Fluids emanating from the subducting slab result in melting and/or metasomatism of the overlying mantle wedge. A similar mechanism of subduction may have operated to create protolith magmas for LSC 33 and LSC 89 in the Late Archaean or earlier. These melts crystallise to form xenolith protoliths. c) Following subduction, the WC and MHB collide at ca. 1770 Ma. Protoliths are subsequently metamorphosed to granulite/amphibolite facies.

3.6 Conclusions

Amphibolite and granulite meta-mafic xenoliths entrained within Eocene lavas of the Bearpaw Mountains, Wyoming Craton, record medium to high temperatures and pressures (642-817 °C and 7.4-7.5 kbar) suggestive of a mid- to lower crustal origin. Major element data indicate alkaline to sub-alkaline igneous basaltic protoliths. Incompatible trace element patterns are characteristic of typical subduction signatures. While late-stage host minette modification cannot be excluded, simple binary mixing models between the host lava and xenolith samples do not fully account for variations in

xenolith chemistry, implying that major and trace elements are still representative of xenolith and/or protolith compositions. SEM-CL imaging of zircon reveals complex internal structures and indicates the presence of both magmatic and metamorphic zircon. Magmatic grains are recognised by weakly preserved, altered oscillatory zoning. In more complex magmatic zircon, high Th/U ($\bar{x} = 1.2$) internal domains appear recrystallised in the presence of a melt phase resulting in resorbed internal domains and exterior morphology. Metamorphic zircon with low Th/U (0.03-0.8, $\bar{x} = 0.2$) is present as whole grains or rims and contain uniform domains devoid of recognizable internal microstructures. Zircon U-Th-Pb isotope dating produces a spectrum of dispersed magmatic Late Archaean to Early Palaeoproterozoic ages (2000-2534 Ma) as well as a dominant mid-Proterozoic population containing both magmatic (1834 $\pm$ 19-1874 $\pm$ 10 Ma) and metamorphic (1772 $\pm$ 5, 1773 $\pm$ 8-1788 $\pm$ 4 Ma) ages. While the spectrum of zircon ages using Bearpaw Mountain xenoliths cannot be correlated with geological events that affected the BBMZ or other Archaean Wyoming sub-provinces, the mid-Proterozoic ages of 1772 $\pm$ 5-1874 $\pm$ 10 Ma are matched by magmatic and metamorphic activity within the GFTZ and MMT. Proterozoic xenoliths (ca. 1834-1874 Ma) record subduction-induced melting resulting in the formation of basaltic protolith magmas that crystallised at lower crustal levels. Younger metamorphic ages (ca. 1772-1778 Ma) are likely related to late-stage continental collisional activity between the Medicine Hat Block and Wyoming Craton. Xenoliths containing zircon with older magmatic ages (up to 2534 Ma) do not define a unique population that can be correlated with events within the Wyoming Craton/GFTZ and its protolith was likely produced by melting of a subduction-related metasomatised mantle in the Late Archaean or earlier. Geochronology is incompatible with reworking of existing Archaean cratonic crust since xenoliths are younger than $\sim$ 2500 Ma, and therefore represent new additions to the middle-lower crust that was metamorphosed shortly afterwards at ca. 1770 Ma. The interpretations provided in this study were limited to whole-rock geochemistry and zircon geochronology. While these techniques are useful in providing an initial characterisation of these rocks, further assessment of the sources of these xenoliths require modern isotopic techniques such as oxygen and hafnium isotopes on zircon. Alternatively, Sm-Nd and/or Rb-Sr isotopic data can be obtained from whole-rock samples. Such isotopic techniques may compliment, or build upon, the petrogenetic mechanisms inferred in this study, and will further contribute to understanding the formation and evolution of lower crust within this region of the northern Wyoming Craton and GFTZ.

4 Formation of Lower to Middle Crust of the Wyoming Craton, Montana (USA), Using Evidence from Zircon Hf-O Isotopic and Trace Element Compositions

This chapter contains the paper entitled: “Formation of Lower to Middle Crust of the Wyoming Craton, Montana (USA), Using Evidence from Zircon Hf-O Isotopic and Trace Element Compositions ” by Thakurdin, Y., Bolhar, R., Horváth, P., and Wiedenbeck, M. and has been published in *Chemical Geology* (Thakurdin et al., 2019b, Volume 525, 218-244, <https://doi.org/10.1016/j.chemgeo.2019.07.021>).

4.1 Abstract

Coupled oxygen-hafnium isotope and trace element geochemical data were obtained using thirty eight previously dated zircon grains extracted from five mafic to intermediate crustal xenoliths of the Wyoming Craton (Montana, USA). Xenoliths include mid- to lower crustal (642-817 °C and 3.5-7.5 kbar) mafic granulites and amphibolites with dominantly mid-Proterozoic (1772-1874 Ma) and minor Paleoproterozoic to Late Archaean (2004-2534 Ma) $^{207}\text{Pb}/^{206}\text{Pb}$ zircon ages. Zircon oxygen isotope data indicate derivation from melts in equilibrium with a mantle source that interacted with limited supracrustal material ($\delta^{18}\text{O} = 4.4\text{-}5.7\text{‰}$), as well as the incorporation of supracrustal fluids or melts into mantle source regions ($\delta^{18}\text{O} = 6.0\text{-}8.1\text{‰}$). The small within-sample isotopic variability suggests that primary zircon did not exchange with isotopically distinct fluids or melts after initial formation. Initial zircon Hf isotopic values are highly variable across all xenoliths ($\epsilon_{\text{Hf}} = +3.7$ to -17.6), consistent with protolith derivation from mantle sources that incorporated evolved, unradiogenic material or were modified by subduction-related fluids. Within a single granulite xenolith, two zircon types are recognised based on CL imagery, Hf isotopes and U-Pb ages (Type I and Type II). Type I magmatic zircons show dispersed ages (ca. 1700-2534 Ma) and unradiogenic initial Hf ($\epsilon_{\text{Hf}} = -17.6$ to -1.5 , $^{176}\text{Hf}/^{177}\text{Hf} = 0.281074\text{-}0.281155$). The spread in ages and initial ϵ_{Hf} , but narrow range in initial $^{176}\text{Hf}/^{177}\text{Hf}$, points to variable Pb-loss in response to dissolution-recrystallisation of pre-existing zircon. Type II metamorphic zircon yields a younger Proterozoic population (ca. 1700-2155 Ma) with more radiogenic initial Hf relative to Type I zircon ($\epsilon_{\text{Hf}} = -7.9$ to $+1.4$, $^{176}\text{Hf}/^{177}\text{Hf} = 0.281427\text{-}0.281578$); this type represents newly grown metamorphic zircon that formed in the solid-state and incorporated Zr and Hf from pre-existing zircon and silicate matrix/metamorphic phases. REE in zircon for all xenoliths are steep and positively sloping without discernible HREE depletion relative to LREE, implying zircon crystallisation/recrystallisation in the absence of garnet. Negative Eu anomalies signify simultaneous

zircon and feldspar crystallisation. Solid-state recrystallisation may lead to variations in LREE, Eu and Ce in certain xenoliths. Xenoliths containing magmatic zircon (1834 ± 19 Ma) with mantle-like $\delta^{18}\text{O}$ (4.4-5.5 ‰) and radiogenic initial ϵ_{Hf} (-2.3 to +3.7) likely formed through crystallisation of melts derived from a mantle source that incorporated minor amounts of subducted sedimentary/supracrustal material. Proterozoic (1874 ± 8 Ma) xenoliths with elevated $\delta^{18}\text{O}$ (6.0-7.0 ‰) and unradiogenic initial ϵ_{Hf} (-8.2 to -9.6) within magmatic zircon represent melt products of subduction-induced melting and metasomatism of the overlying mantle wedge. Older (ca. 2534 Ma) xenoliths containing zircons with high $\delta^{18}\text{O}$ (6.4-7.2 ‰) and unradiogenic ϵ_{Hf} (up to -17.6) represent crystallisation of protolith magmas extracted from a mantle source metasomatised by subduction-derived fluids and melts in the Late Archaean or earlier. Zircon geochronology and isotope systematics within mid-Proterozoic xenoliths support a model of ocean closure and subsequent continental collision between the Medicine Hat Block and Wyoming Craton, resulting in the formation of subduction-related melts at ca. 1834-1874 Ma, followed by ca. 1770 Ma collision-related metamorphism thereafter.

4.2 Introduction

The lower continental crust is an important but largely inaccessible portion of the lithosphere exposed only as exhumed granulite terranes or as fragments brought to the surface by kimberlitic or basaltic volcanism (Rudnick, 1992; Rudnick and Fountain, 1995). The age and composition of the lower crust provides valuable insight into geodynamic processes, such as subduction and magmatic underplating that operated beneath ancient cratons or within adjacent continental marginal zones. The Wyoming Craton stabilised in the Late Archaean or earlier (2800-3200 Ma) (Frost et al., 1998, 2000; Mueller and Frost, 2006) and may possess a crustal thickness of up to 60 km as revealed by seismic studies (Gorman et al., 2002; Mahan et al., 2012). In the Bearpaw Mountains in northern Montana, USA, amphibolite to granulite xenoliths were brought to the surface by alkaline Eocene volcanic activity (Macdonald et al., 1992; Bolhar et al., 2007), and may represent fragments of the middle to lower continental crust of the Wyoming Craton (Collerson et al., 1988; Bolhar et al., 2007).

In a previous study, (Thakurdin et al., 2019a), a representative suite of granulite and amphibolite xenoliths from the Bearpaw Mountains, Montana, USA, was examined both geochronologically and petrologically. Thermobarometric calculations indicate temperatures and pressures of 642-817 °C and 3.5-7.5 kbar, establishing a middle to lower crustal origin. Zircon $^{207}\text{Pb}/^{206}\text{Pb}$ ages define a mid-Proterozoic (1772 ± 5 - 1874 ± 8 Ma) population, in addition to dispersed Late Archaean to Early Palaeoproterozoic ages (2006 ± 17 - 2534 ± 9 Ma). Whole-rock trace element data indicate that all xenoliths carry a subduction-type signature, showing extreme enrichments in large-ion lithophile (LILE) and fluid mobile elements (Cs, Rb, Ba, Pb, Sr) relative to high-field strength elements, together

with relative Zr-Hf and Nb-Ta-Ti depletions. The younger Proterozoic ages (1834 ± 19 - 1874 ± 8 Ma) were obtained from non-inherited, magmatic zircon implying newly formed, subduction-related melts added to lower portions of the crust. Older ages (2006 ± 17 - 2534 ± 9 Ma) within recrystallised magmatic zircon are poorly correlated with tectonic activity or existing ages within the Wyoming Craton, and were also interpreted as newly-formed material formed by melting of a subduction-metasomatised mantle source in the Late Archaean or earlier (Thakurdin et al., 2019a). Slightly younger, internally featureless zircons (1773 ± 8 - 1788 ± 4 Ma) were interpreted to represent a metamorphic event that recrystallised all xenolith protoliths to granulite/amphibolite facies in the mid-Proterozoic. These interpretations, however, were limited to geochronological and bulk-rock geochemical information and cannot provide detailed insight into the mantle source (juvenile versus evolved) or fully differentiate between unique petrogenetic mechanisms (underplating/reworking/subduction).

In this study, hafnium and oxygen isotope determinations supplemented by trace element (REE) analyses on previously dated (and imaged) zircon domains allow for a more rigorous interpretation of xenolith petrogenesis. Hafnium data may enable the identification of the mantle source from which protolith melts were derived (Depleted Mantle/CHUR). Hf isotopes can also constrain whether the source/protolith melt contains components of older, existing crustal material. For example, Gifford et al. (2014, 2018) interpreted unradiogenic ϵ_{Hf} in zircon within gneisses/granites from the Medicine Hat Block and Wyoming Craton as a result of crustal contribution to the source from which these lithologies were derived. Hf in zircon can also provide insight into zircon crystallisation and subsequent modification, which allows for elucidation of larger scale geological processes. For example, ϵ_{Hf} can reveal Pb-loss processes in zircon grains, which may be indicative of long term granulite facies metamorphism (e.g. O'Brien and Miller, 2014) at lower crustal levels. In a similar way, oxygen data can fingerprint the xenolith source as either predominantly mantle-derived ($\delta^{18}\text{O} < 5.6$ ‰), or derived from a source/protolith that contained considerable proportions of older sedimentary material ($\delta^{18}\text{O} > 5.9$ ‰) (Valley et al., 1994, 2003; Kempton and Harmon, 1992). Additionally, sub-mantle $\delta^{18}\text{O}$ (< 4.7 ‰) may indicate interaction of sources with meteoric/hydrothermal fluids or assimilation of $\delta^{18}\text{O}$ -depleted material (Bolhar et al., 2008). Finally, different tectonic processes may be associated with unique O and Hf signatures. Higher O ($\delta^{18}\text{O} > 5.6$ ‰) and unradiogenic (negative) Hf may be produced by melting of a subduction-metasomatised mantle source, while low O ($\delta^{18}\text{O} < 5.6$ ‰) and positive ϵ_{Hf} may be more consistent with protoliths derived from underplated magmas. Therefore, isotopic O and Hf data allow for further interpretation of these xenoliths that cannot be easily recognised using only whole-rock chemistry and zircon geochronology (Chapter 3).

4.3 Methods

Zircons were separated using standard techniques, and subsequently mounted and polished for imaging using cathodoluminescence (CL) and back-scattered electron (BSE) methods. SIMS was employed for U-Pb geochronology (Thakurdin et al., 2019a) and determination of oxygen isotope ratios. Subsequently, LA-MC-ICPMS was employed to measure Hf isotope ratios on spots previously analysed with SIMS. LA-Q-ICP-MS was used to measure REE+Ti concentrations within zircon domains for which U-Pb, O and Hf isotope measurements had been obtained previously. Upon re-polishing, zircon grains for LSC 105 were lost, preventing REE, Ti and Hf isotopic determinations on these grains. Finally, trace elements in silicates was measured using LA-SF-ICPMS.

Ion probe analyses of $\delta^{18}\text{O}$ in zircon grains was carried out at the GeoforschungsZentrum (GFZ) in Potsdam, using a CAMECA SIMS 1280-HR instrument. A ~ 0.5 nA, mass filtered $^{133}\text{Cs}^+$ beam was employed, with a Gaussian density distribution focused to a ~ 5 μm diameter on the polished sample surface with a total impact energy of 20 keV. Before data collection, each analysis was preceded by 20 x 20 μm rastered pre-sputter for 80s. Charge compensation was achieved with low-energy, normal incidence electron flooding using a ~ 1.0 μA current. Secondary ions were accelerated by a -10 kV potential applied to the sample holder. The instrument had a field of view of 80 x 80 μm , in conjunction with a 50 V energy band-pass. The mass spectrometer was operated in static multi-collection mode, with the $^{16}\text{O}^-$ signal being collected in the L2' Faraday cup and the $^{18}\text{O}^-$ signal being collected in the H2' Faraday cup; the amplifier system employed thermally stabilised 10^{10} Ω and 10^{11} Ω amplifiers, respectively. Magnetic field drift on the mass spectrometer was effectively eliminated by use of a NMR-controlled feedback loop. The mass resolution of the instrument was determined to be $M/\Delta M \approx 1900$, which is effectively full transmission for the tool and fully suffices to eliminate both the $^{16}\text{O}^1\text{H}_2$ and the $^{16}\text{O}^2\text{H}$ isobaric interferences from mass ^{18}O . A single analysis consisted of 20 scans of 4s each, resulting in a total data collection time of 80s per analysis, or ~ 3 minutes per point when including the pre-sputter process. This analytical design resulted in a count rate of $\sim 2.4 \times 10^9$ ions per second on mass ^{16}O . A total of 104 analyses were determined for this study in addition to 16 analyses on the 91500 calibration material and 7 analyses on Temora 2 quality control material. The 24 determinations of $^{18}\text{O}^-/^{16}\text{O}^-$ conducted on the 91500 reference material yielded an analytical repeatability of 0.11 ‰ (1sd). We used an absolute value of $^{18}\text{O}/^{16}\text{O} = 0.00204494$ for the 91500 reference material, derived from the value of $\delta^{18}\text{O} = 9.86$ reported for 91500 zircon (Wiedenbeck *et al.*, 2004) in conjunction with a zero-point value of $^{18}\text{O}/^{16}\text{O} \equiv 0.002024971$ for the $\delta^{18}\text{O}$ scale (Baertschi, 1976). In this way we could determine an overall instrumental mass fractionation for the measured/true value of 0.99288 for the 8.5 hour data collection session. Applying this mass fractionation value, we calculated a mean $\delta^{18}\text{O}$ mean value of 7.98 ± 0.18 ‰ (1sd) for the Temora 2 quality control material, which is in good agreement with the published value of 8.20 ± 0.03 ‰ for the material (Black et al., 2004). Our mean

value is slightly lowered by averaging of all analyses on Temora-2, however, most individual analyses fall within error of the reported value of 8.20 ± 0.03 ‰ (Black et al., 2004, Table B4).

The mount was repolished for LA-MC-ICP-MS hafnium isotope ratio analysis on zircon grains at the University of Johannesburg. A 193nm ArF RESolution SE excimer laser (Australian Scientific Instruments) was coupled to a Nu Plasma II MC-ICPMS (Nu Instruments). A plasma RF power of 1300 W was applied. Plasma fluid flow settings include coolant gas flow (13.0 l/min), auxiliary gas flow (0.88 l/min), nebuliser gas flow (0.8 l/min) and laser He gas flow (0.25 l/min). A spot size of 25 μm was used to analyse multiple spots on zircon grains. Other laser parameters include: beam energy (4.5 mJ), attenuation (50 %), repetition rate (7 Hz), fluence (6.4 J/cm^2), blank signal time (25s) and ablation signal time (70s). ^{171}Yb and ^{173}Yb were used to calculate Yb mass fractionation and also used to correct for Lu mass fractionation; ^{179}Hf and ^{177}Hf were used to calculate Hf mass fractionation, while ^{171}Yb was used to calculate and correct for the ^{174}Yb interference on ^{174}Hf as well as for the ^{176}Yb interference on ^{176}Hf ; ^{175}Lu was used to correct for the ^{176}Lu interference on ^{176}Hf . Background signals were collected prior to ablation, and subtracted from the signal. Secondary standards were measured at regular intervals and treated as unknowns to evaluate the accuracy of the measurements. Zircon reference materials include 91500 and Temora 2 (primary) along with Mud Tank, Plešovice and LV11 (secondary) (Woodhead and Hergt, 2005; Heinon et al., 2010; Cecil et al., 2011). Weighted mean $^{176}\text{Hf}/^{177}\text{Hf}$ values for 91500 (0.282301 ± 0.000034 , 1SE, MSWD = 3.9) and Temora-2 (0.282699 ± 0.000013 , 1SE, MSWD = 1.5) show good agreement with published mean $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.282315 ± 0.000013 (1SE) and 0.282684 ± 0.000011 (1SE) respectively (Cecil et al., 2011). Weighted mean $^{176}\text{Hf}/^{177}\text{Hf}$ values for Mud Tank (0.282515 ± 0.000026 , 1SE, MSWD = 2.3) and Plešovice (0.282489 ± 0.000013 , 1SE, MSWD = 2.2) are also well correlated with reported mean $^{176}\text{Hf}/^{177}\text{Hf}$ values (Mud Tank: 0.282508 ± 0.000006 , Plešovice: 0.282476 ± 0.000011 , 1SE) from Cecil et al. (2011) and similar mean values (Mud Tank: 0.282507 ± 0.000006 , 2SE) from Woodhead et al. (2005). Finally, weighted mean $^{176}\text{Hf}/^{177}\text{Hf}$ values obtained from LV 11 ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282897 \pm 0.000016$, 1SE, MSWD = 1.4) generally agree with reported mean values ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282830 \pm 0.000028$, 2SD) from Heinonen et al. (2010).

REE concentrations in zircon were analysed at the tCRAGlabs@TCD lab, Trinity College Dublin, Ireland, by LA-Q-ICP-MS. The equipment comprises a Teledyne Photon Machines G2 laser system coupled to a Thermo iCapQ. The laser was fired with a fluence of 2.75 J cm^{-2} and ablation occurred in ultra-pure He (0.475 l/min), to which Ar (0.75 l/min) and N_2 (16 ml/min) were added to aid aerosol transport and ionisation. The REE were analysed using a $45 \times 45 \mu\text{m}^2$ square aperture by firing 200 shots at 10 Hz. This produced a pit of 15 μm depth, implying that each pulse removed 75 nm of material. Silicon was used as the internal standard, and analyte dwell times were adjusted according to the expected low LREE concentrations to yield a full duty cycle of 300 ms. The signals were quantified with analysis of NIST

610 and NIST 612 glass (Gao et al., 2002), while zircon reference materials 91500 (Yuan et al., 2004) and Temora 2 (Yuan et al., 2008) served as quality control standards, with measured REE concentrations well within accepted literature values (Table B7).

Trace elemental analysis on silicate phases was carried out at the Earthlab at the University of the Witwatersrand, employing an Australian Scientific Instruments (ASI) Resonetics Resolution 193 nm ArF excimer (SE 155) system coupled to a Thermo Scientific Fisher sector-field ICPMS (Element XR). Measurements were performed in low resolution and electrostatic scanning (E-scan) modes. Data were acquired by single spot analysis (40 μm), using a laser repetition rate of 8 Hz and a fluence of 2.5 Jcm^{-2} . Total signal acquisition time was 65s to allow data processing and preparation for the next analysis, comprising 15s of pre- and post-ablation (gas blank) and 15s of ablation measurements. Laser sampling took place in a SE155 dual-volume ablation cell (Laurin Technic, Canberra, Australia) using a mixed He-Ar atmosphere and a small volume of N_2 to enhance signal stability and sensitivity. The following gas flows were applied: He (300-400 ml/min), Ar (800-1200 ml/min) and N_2 (2-4 ml/min), respectively. Synthetic glass NIST 612 (Jochum et al., 2011) served for calibration, while NIST 610 and 614 as well as USGS natural glasses BHVO2, BCR-2 and BIR-2 (Gao et al., 2002) were analysed as unknowns to evaluate accuracy and precision. The LA-ICPMS system was tuned during line scans using NIST 612 glass for maximum sensitivity for ^6Li , ^{115}In and ^{238}U , while maintaining oxide levels (ThO^+/Th) $<0.5\%$. For internal standardization, the isotopes ^{43}Ca or ^{29}Si were used. Typically, two analyses of the primary calibration standard were obtained at the beginning and end of an experiment, and 10-20 analyses of unknowns were followed by analyses of one primary calibration standard and two to four analyses of the secondary standards for quality control purposes. Prior to each spot analysis, surface material was removed using 2 laser pulses. The following masses were measured (40 scans per peak): ^{29}Si , ^{43}Ca , ^{45}Sc , ^{47}Ti , ^{51}V , ^{53}Cr , ^{59}Co , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{174}Yb , ^{175}Lu , ^{178}Hf , ^{181}Ta , ^{208}Pb , ^{232}Th , ^{238}U . All isotopes were measured in pulse counting mode, except for ^{238}U (analog mode). A summary of instrument settings is provided in Table B6. Data reduction was performed using the Iolite extension to the software Igor Pro (Paton et al., 2010, 2011).

4.4 Results

4.4.1 O and Hf isotope systematics

Values for $\delta^{18}\text{O}$ in zircon range from 4.4 to 8.1 ‰ across all samples (Table 4.1, Table B1: see Appendices; Fig. 4.2). The within-sample variability in $\delta^{18}\text{O}$ is considerably smaller, with differences of less than 1.1 ‰ between zircon grains. Homogeneity is also observable within individual grains with small variations between core and rim or across individual domains ($<0.7\%$) (Fig. 4.1). Samples LSC

33 and LSC 72 (granulite) possess the lowest $\delta^{18}\text{O}$ values (4.4-5.7 ‰), while sample LSC 105 (granulite) shows the highest values (7.4-8.1 ‰) (Fig. 4.1A-B and Fig. 4.2). Initial ϵ_{Hf} and $^{176}\text{Hf}/^{177}\text{Hf}$ was calculated for zircon domains using $^{207}\text{Pb}/^{206}\text{Pb}$ ages associated with concordant $^{206}\text{Pb}/^{238}\text{U}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ dates. Values of initial ϵ_{Hf} in all samples produce a broad spectrum from -17.6 to +3.7. The majority of samples show negative ϵ_{Hf} numbers and significant inter-sample variability (Fig. 4.3A). Here we provide a brief summary of the results from each of our five analysed xenoliths:

4.1.1. BR 47 (Amphibolite)

Twenty-five oxygen analyses were conducted on a total of eight zircon grains. These reveal $\delta^{18}\text{O}$ between 6.0 and 7.0 ‰ ($\bar{x}$ = 6.5 ‰). Individual zircon domains show variation of less than 0.7 ‰; no systematic variation is observed between CL light and dark domains. Four hafnium spots on three separate grains yield initial ϵ_{Hf} values between -8.2 and -9.6 calculated using $^{207}\text{Pb}/^{206}\text{Pb}$ ages between 1818 ± 8 and 1866 ± 5 Ma. Intra-grain variation is present within a single zircon (initial ϵ_{Hf} = -8.2 and -8.8, grain 47-4).

4.1.2. LSC 72 (Granulite)

Sixteen oxygen analyses were conducted on a total of four zircon grains and show a small range in $\delta^{18}\text{O}$ from 4.4 to 5.5 ‰ ($\bar{x}$ = 4.9 ‰). Intra-grain variation is observed only in grain 72-4 (4.6-5.1 ‰), while remaining grains record variations in $\delta^{18}\text{O}$ of less than 0.5 ‰. Nine analyses on four grains yield initial ϵ_{Hf} between -2.3 to +3.7 (calculated using $^{207}\text{Pb}/^{206}\text{Pb}$ ages between 1759 ± 22 and 1810 ± 24 Ma) together with a mid-Proterozoic range in modelled T_{DM} (2104-2447 Ma) (Fig. 4.3C).

4.1.3. LSC 89 (Granulite)

Thirty-six oxygen analyses conducted on twelve grains (89-1 to 89-12) produce $\delta^{18}\text{O}$ values from 6.4 to 7.2 ‰ ($\bar{x}$ = 6.8 ‰). Minor variation (<0.4 ‰) is seen within zircon grains; however, this feature does not correlate consistently with zircon internal textures such as bright/dark, core/rim or other individual CL domains. Twenty-nine analyses on a total of fourteen zircon grains yield initial ϵ_{Hf} values ranging from -17.6 to +1.4 (calculated using $^{207}\text{Pb}/^{206}\text{Pb}$ ages between 1708 ± 8 and 2473 ± 35 Ma). Large intra-grain variation in ϵ_{Hf} (>5 epsilon units) is recorded within grains 89-6, 89-7 and 89-15. Two distinct trends in initial ϵ_{Hf} versus time space (Fig. 4.3A) can be discerned within this sample, involving a more radiogenic (Type II, ϵ_{Hf} = -7.9 to +1.4, 1708-2155 Ma) and a less radiogenic trend (Type I, ϵ_{Hf} = -17.6 to -1.5, 1720-2473 Ma).

4.1.4. LSC 105 (Granulite)

Fourteen analyses on a total of five zircon grains yield the highest $\delta^{18}\text{O}$ values of 7.4-8.1 ‰ ($\bar{x}$ = 7.6 ‰) observed in this study. Intra- and inter-grain variability is small and the grains are texturally homogeneous.

4.1.5. LSC 33 (Granulite)

Five oxygen analyses on a single grain within sample LSC 33 (not shown in Fig. 4.1) produce $\delta^{18}\text{O}$ from 5.3 to 5.7 ‰ ($\bar{x}$ = 5.4 ‰). ϵ_{Hf} is not calculated due to the discordancy of $^{206}\text{Pb}/^{238}\text{U}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ ages in this sample. Two hafnium spots constrain initial $^{176}\text{Hf}/^{177}\text{Hf}$ between 0.280670 and 0.280710 and are not shown in Fig. 4.3.

4.4.2 Trace elements in zircon

REE abundances were quantified for zircon within amphibolite (BR 47) and granulite xenoliths (LSC 33, LSC 72, and LSC 89) (Table B2). All patterns show steep positively sloping REE patterns ($\text{La}_\text{N}/\text{Yb}_\text{N}$ = 0.00008-0.0009) (Fig. 4.4A-D). Anomalies for europium and cerium are quantified using equations $\text{Eu}_\text{N}/\text{Eu}_\text{N}^* = \frac{\text{Eu}_\text{N}}{\sqrt{\text{Sm}_\text{N} \times \text{Gd}_\text{N}}}$ and $\text{Ce}_\text{N}/\text{Ce}_\text{N}^* = \frac{\text{Ce}_\text{N}}{\sqrt{\text{La}_\text{N} \times \text{Pr}_\text{N}}}$. Pronounced negative Eu anomalies are observed for LSC 89 (Eu/Eu^* = 0.08-0.2), while remaining samples display a range in europium anomalies (Eu/Eu^* = 0.3-2.2). Ce anomalies are strongly positive and variable (Ce/Ce^* = 2-125) across all samples. Variability in Eu/Ce anomalies and normalised trace element concentrations are observed in grains within each sample, most notably in LSC 72 (Fig. 4.4B, Fig. 4.5A-D).

Table S2: Summary of, U-Pb, Th/U, Hf and Oxygen Data For Bearpaw Xenoliths

Sample	Rock Type	CL Texture	$^{207}\text{Pb}/^{206}\text{Pb}$ U-Pb Ages (Ma)	$\delta^{18}\text{O}$ (‰)	$^{176}\text{Hf}/^{177}\text{Hf}$	ϵ_{Hf}	Th/U
LSC 33	Granulite	Magmatic	1575-2907	5.3- 5.7	0.280670- 0.280710	-	0.3-0.7
LSC 72	Granulite	Magmatic	1719-1900	4.4- 5.5	0.281583- 0.281744	-2.3 to +3.7	0.01- 0.6
LSC 89	Granulite	Magmatic and Metamorphic	1691-2534	6.4- 7.2	0.281074- 0.281744	-17.6 to +1.4	0.03- 2.2
LSC 105	Granulite	Metamorphic	1733-1796	7.4- 8.1	-	-	0.06- 0.1
BR 47	Amphibolite	Magmatic	1761-1883	6.0- 7.0	0.281345- 0.281379	-8.2 to - 9.6	0.03- 1.9

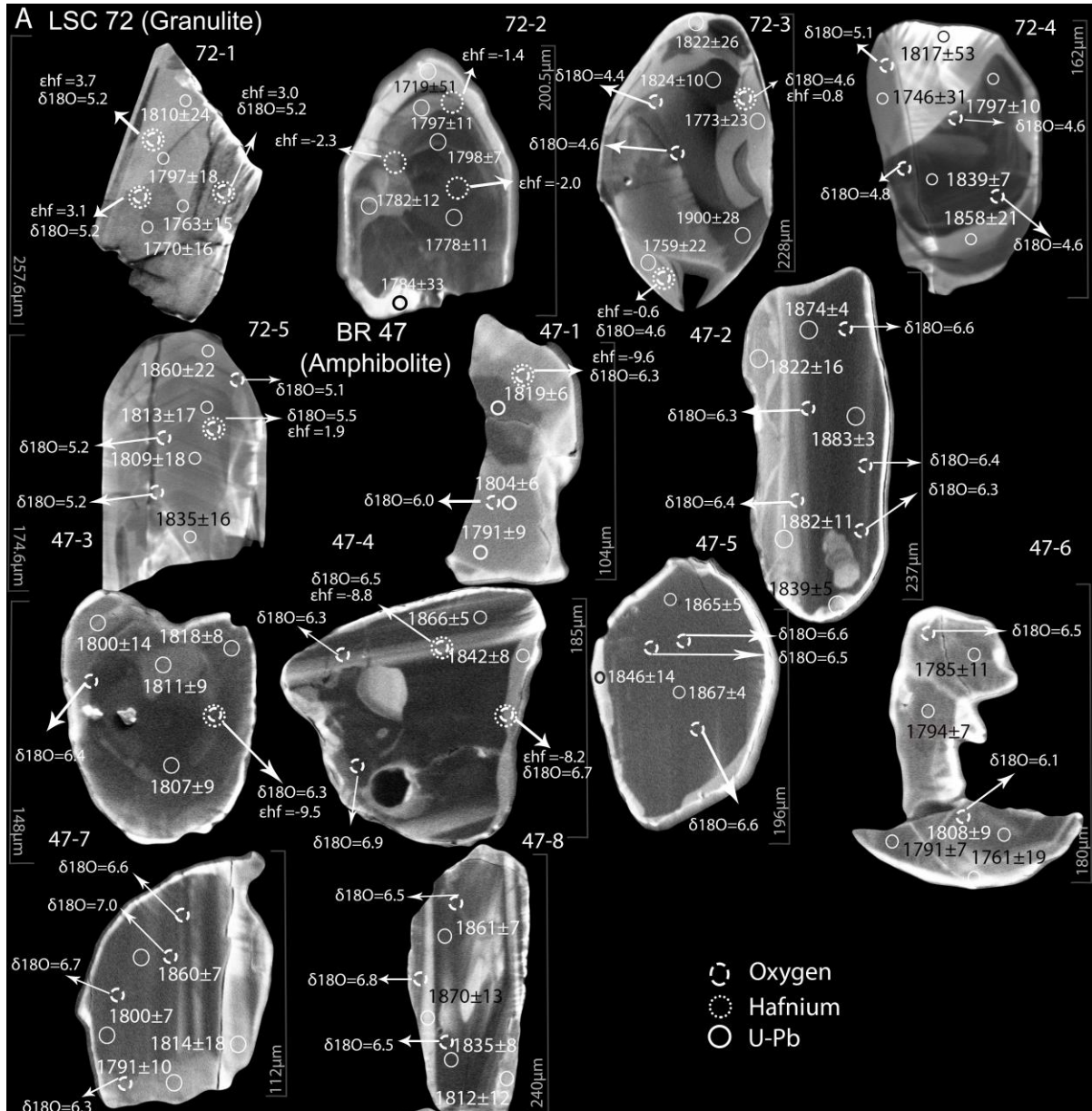


Figure 4.1A: Cathodoluminescence (CL) images of zircon in respective xenoliths. LSC 72 and BR 47: weak preservation of magmatic textures. Dates shown are $^{207}\text{Pb}/^{206}\text{Pb}$ ages obtained from spot analysis using SIMS (circles). ϵ_{Hf} (stippled circles) obtained from LA-ICPMS and $\delta^{18}\text{O}$ (dashed circles) from SIMS are also shown.

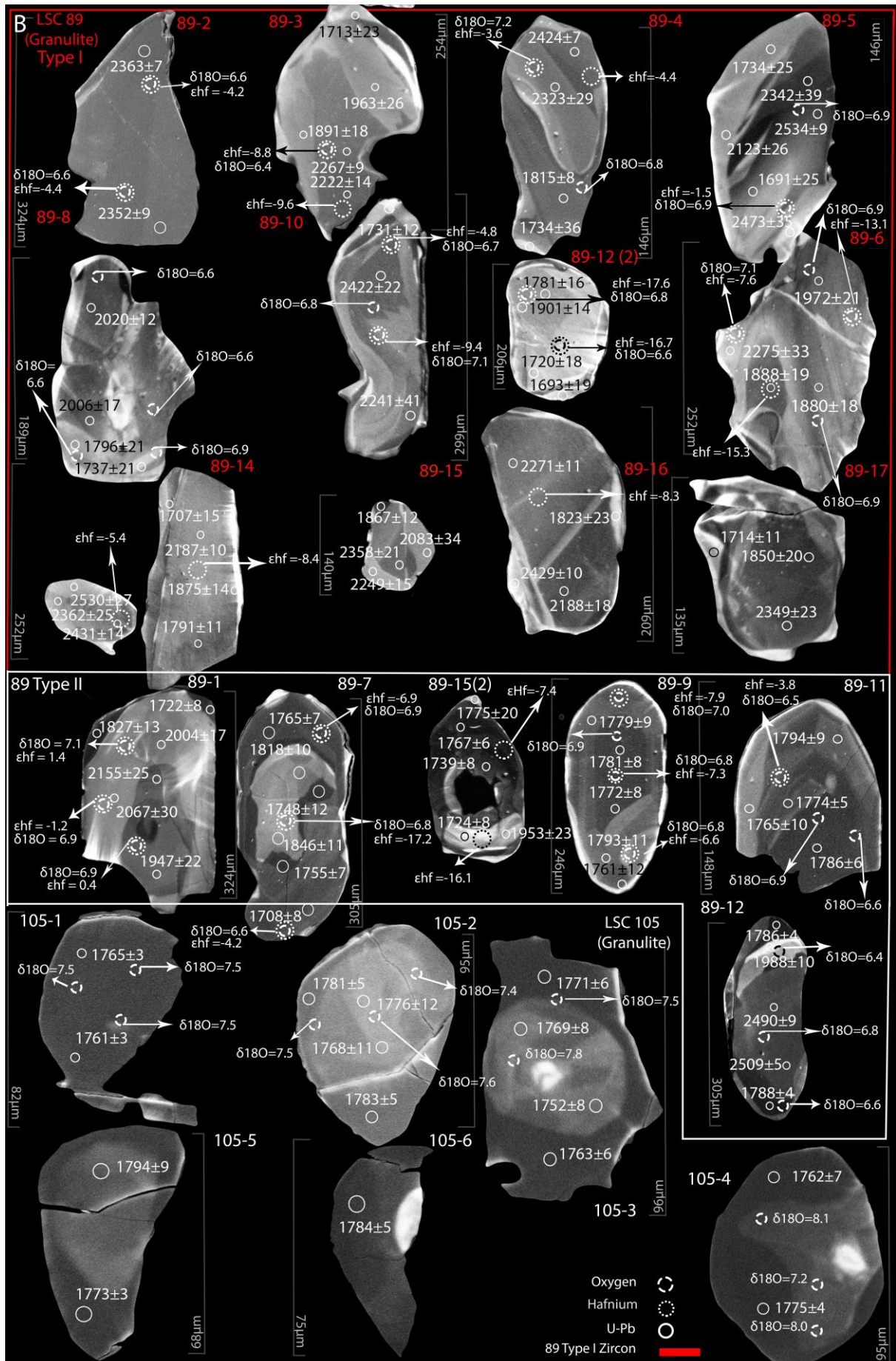


Figure 4.1B: Cathodoluminescence (CL) images of zircon in respective xenoliths. LSC 105: homogenous without internal textures, LSC 89: Chaotic, convolute recrystallised textures. Dates shown are $^{207}\text{Pb}/^{206}\text{Pb}$ ages obtained from spot analysis using SIMS (circles). ϵ_{Hf} (stippled circles) obtained from LA-ICPMS and $\delta^{18}\text{O}$ (dashed circles) from SIMS are also shown. For sample LSC 89, red sample numbers indicate Type II metamorphic zircon, while white numbers indicate Type I recrystallised magmatic zircon.

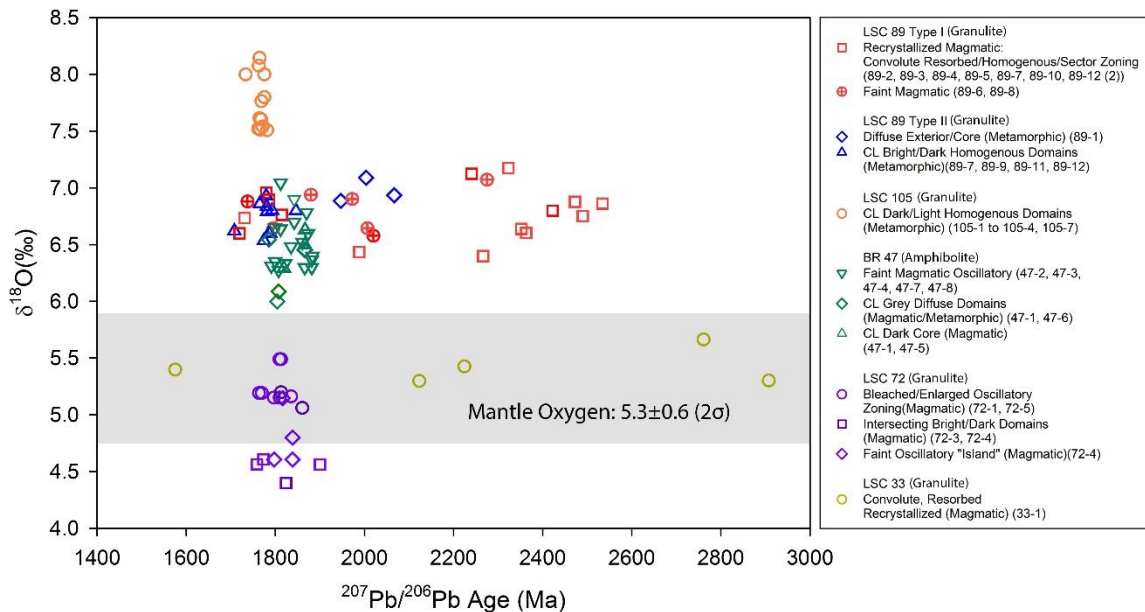


Figure 4.2: Zircon oxygen isotope for xenoliths. Delta-notation ($\delta^{18}\text{O}_{\text{zircon}}$) relative to V-SMOW, and range of mantle values (5.3 ± 0.6 , 2σ) from Valley et al. (2005). For SIMS analyses obtained in this study, 1σ errors range between 0.1 and 0.3 ‰.

4.4.3 Trace elements in silicates

Trace elements in silicates were measured in order to evaluate possible Hf and HREE rich minerals that may contribute to Hf in zircon (particularly metamorphic zircon within xenolith LSC 89) and possible controls on zircon REE patterns. Trace element compositions for silicate phases are shown in Fig. 4.6 A-D and Table B3. Garnet within granulite xenolith LSC 33 shows HREE (Gd-Lu) enrichment relative to LREE (La-Sm) contents as well as relative Zr-Hf-Ti depletions. Clinopyroxene from granulite LSC 72, LSC 89 and LSC 105 is enriched in both LREE and HREE relative to MREE, with particularly notable enrichments in Nd, Sm, Gd and Dy together with Zr, Hf, Ti and Tb depletions. Some variation between clinopyroxene grains is observed, most notably in Ti and Ta.

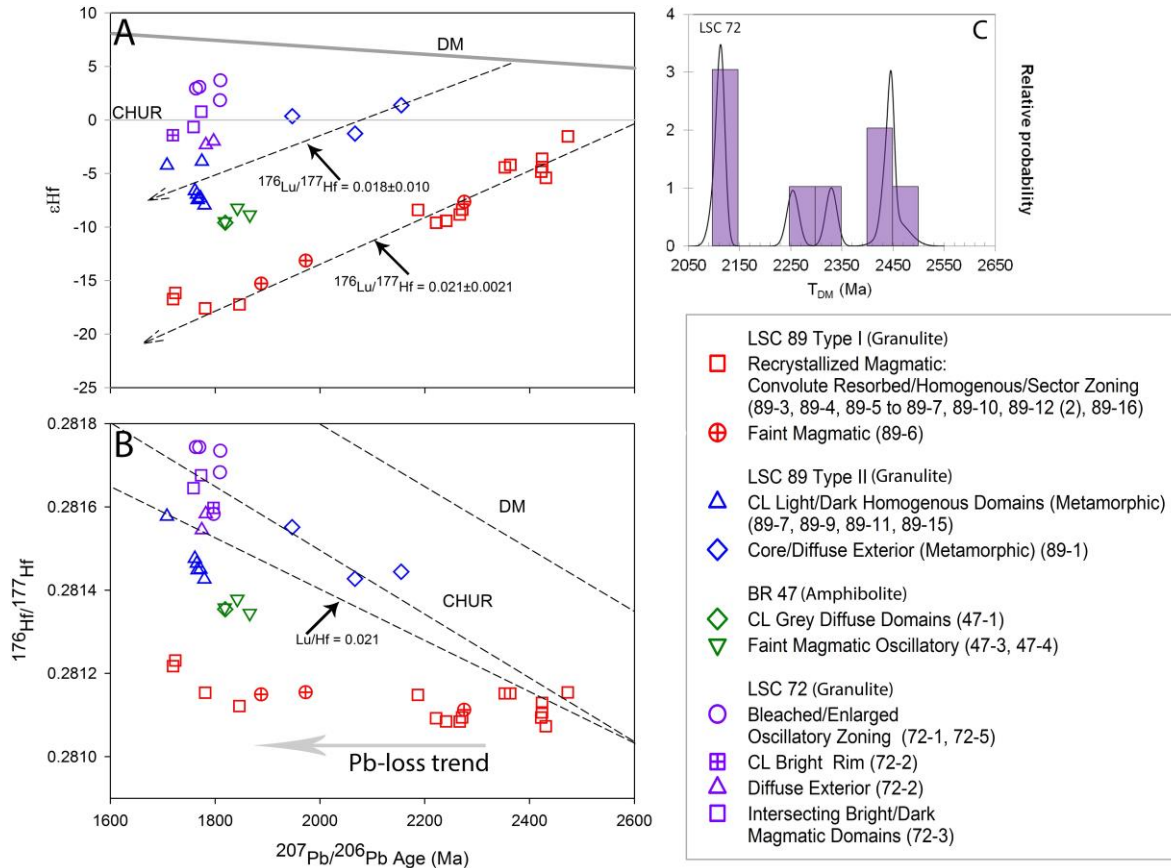


Figure 4.3: ϵ_{Hf} (t) versus $^{207}\text{Pb}/^{206}\text{Pb}$ zircon ages (A) and $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ zircon ages (B) in respective domains. DM: Depleted Mantle, CHUR: Chondritic Uniform Reservoir. Epsilon hafnium (ϵ_{Hf}) was calculated using $^{207}\text{Pb}/^{206}\text{Pb}$ ages associated with concordant $^{206}\text{Pb}/^{238}\text{U}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ dates (Table 4.1, 4.2, 4.3, see Appendices), CHUR parameters of Bouvier et al. (2008): $^{176}\text{Hf}/^{177}\text{Hf} = 0.282785$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0336$, and a decay constant of $\text{Lu}^{176}\lambda = 1.867 \times 10^{-11}$ (Scherer et al., 2001; Soderlund et al., 2004). The 1SE errors for epsilon hafnium values are internal uncertainties for measured $^{176}\text{Hf}/^{177}\text{Hf}$ only, and represent minimum uncertainties that do not account for ages and $^{176}\text{Lu}/^{177}\text{Hf}$ (Bauer et al., 2017). Measured $^{176}\text{Lu}/^{177}\text{Hf}$ ratios were regressed using lines and errors calculated by Isoplot (Ludwig et al., 2001), no points were excluded from calculations. Two-stage Hf (T_{DM}) ages were calculated for xenoliths that show mantle-like O only (LSC 72: $\delta^{18}\text{O} = 4.4$ - 5.5 ‰, $\epsilon_{\text{Hf}} = -2.3$ to $+3.7$), using present-day DM values of $^{176}\text{Hf}/^{177}\text{Hf} = 0.283238$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.03976$ (Vervoort et al., 2015). An average middle/lower crustal Lu/Hf ratio of 0.015 (Griffin et al., 2002) was used together with above mentioned DM parameters.

Orthopyroxene from granulite xenoliths LSC 89 and LSC 105 is notably HREE enriched relative to the LREEs, with large variations in La, Ce, Pr and Nd. Trace element concentrations within orthopyroxene are generally less than 20 ppm, apart from Ti, V, Cr and Co concentrations which range from 78 to 614 ppm. Finally, amphibole from xenolith BR 47 appears to contain similar abundances of LREEs and HREEs with relative depletions in Zr, Hf, Ti and Tb. Lu/Hf for clinopyroxene and orthopyroxene range

from 0.1-1.1 and 0.1-8.5 respectively. Garnet is Lu rich ($\text{Lu}/\text{Hf} = 0.6\text{-}5.3$), while amphibole contains the lowest Lu concentrations ($\text{Lu}/\text{Hf}=0.1\text{-}0.6$).

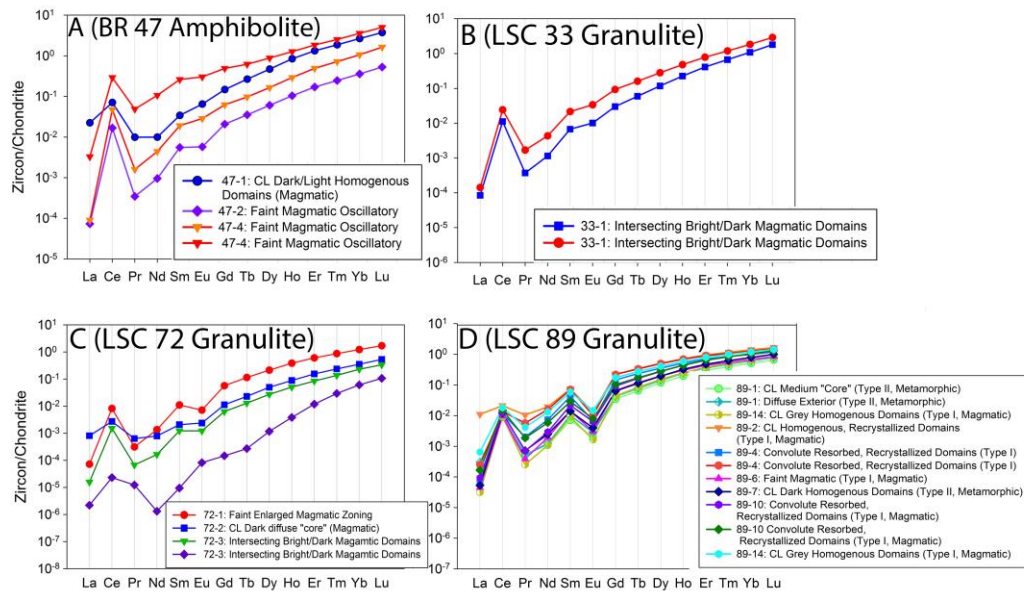


Figure 4.4: REE patterns for zircon domains (A-D). Patterns are normalised using C1 chondrite parameters (Anders and Grevesse, 1989).

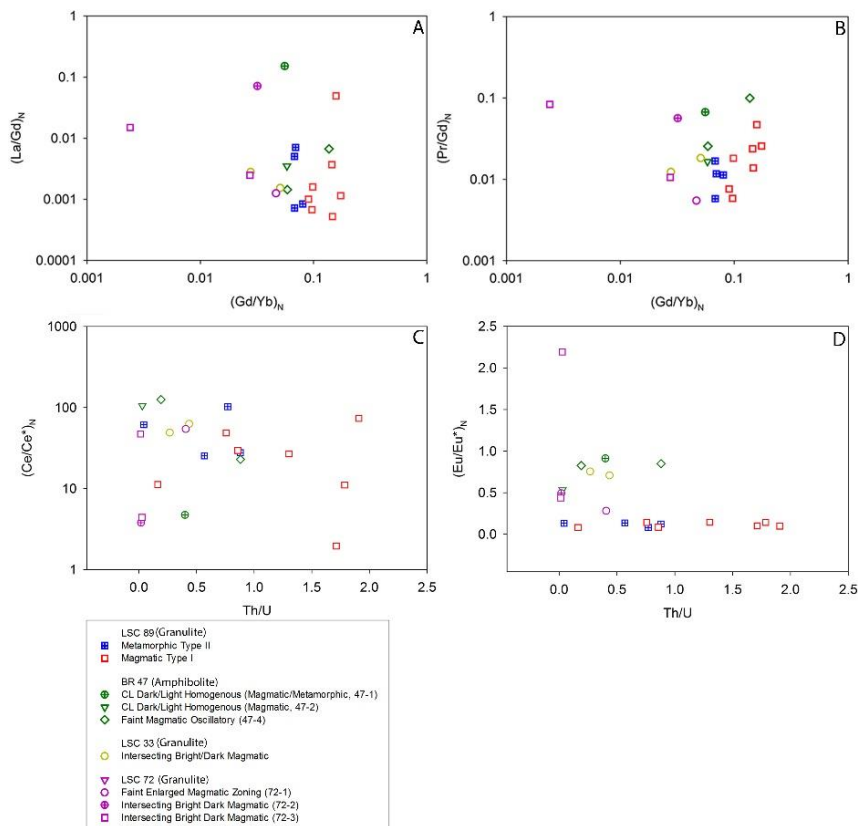


Figure 4.5: LREE ($(La/Gd)_N$) and MREE ($(Pr/Gd)_N$) are plotted against HREE ($(Gd/Yb)_N$) (A-B). Europium anomalies ($(Eu/Eu^*)_N$) and cerium anomalies ($(Ce/Ce^*)_N$) are plotted against Th/U in zircon (C-D). Plots are normalised using C1 chondrite parameters (Anders and Grevesse, 1989).

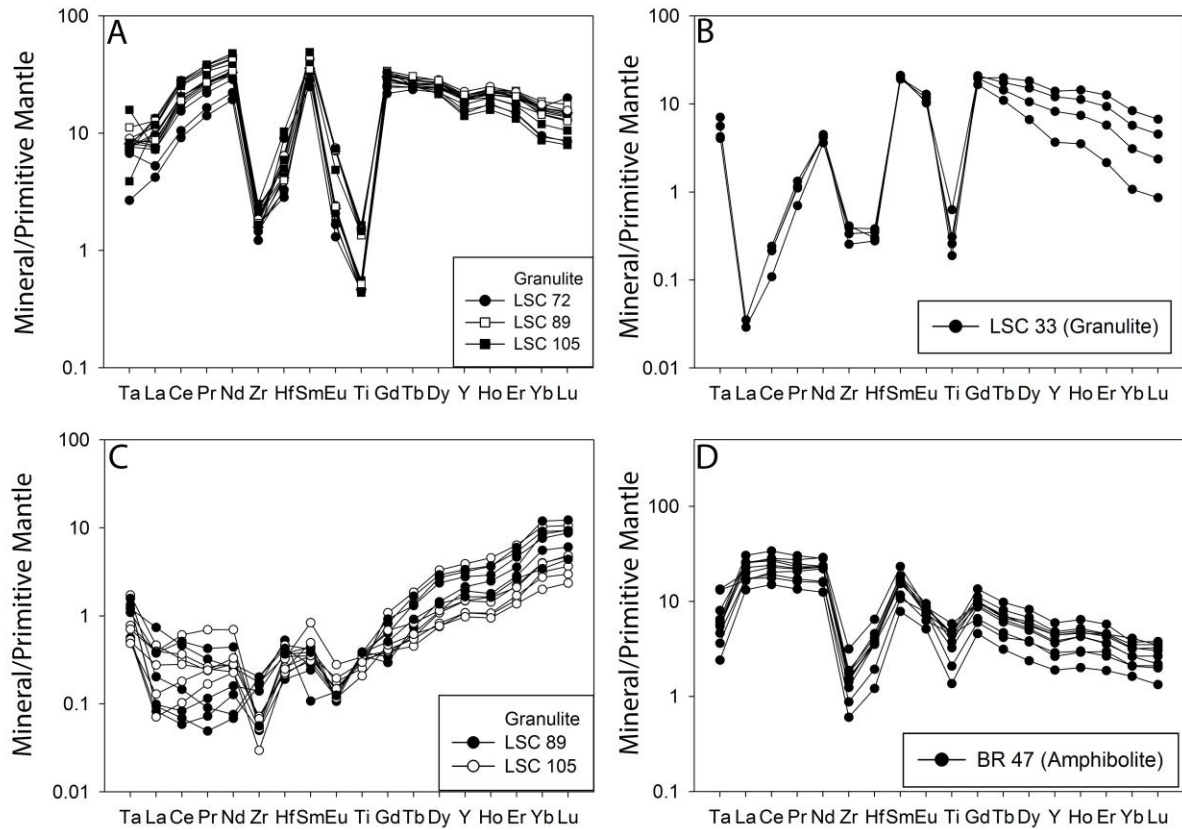


Figure 4.6: Trace element compositions for rock forming minerals from granulite and amphibolite xenoliths: (a) clinopyroxene, (b) garnet, (c) orthopyroxene, (d) amphibole. Normalization using Primitive Mantle parameters (McDonough and Sun, 1989).

4.5 Discussion

4.5.1 Zircon growth mechanisms – evidence from microstructures and geochemistry

A summary of magmatic and metamorphic zircon ages, along with P-T estimates (including Ti-in-zircon) obtained in the previous study (Thakurdin et al., 2019a) is summarised in Table 4.4.

LSC 72: Magmatic Zircon Growth and Solid-State Recrystallisation

Zircon geochronology for this sample defines magmatic population at 1834 ± 19 Ma (Thakurdin et al., 2019a). Cathodoluminescence imaging reveals oscillatory zoning within zircons that is best interpreted

as being of igneous origin, but was subsequently recrystallised (Fig. 4.1A). The weak oscillatory texture (best seen in 72-5, and but also visible in 72-1 and 72-4) is the strongest indication for a magmatic origin (Pidgeon 1992; Corfu, 2003; Zheng et al., 2004).

Sample	Lithology	Mineralogy	SiO ₂	Mg#	P/T	Magmatic ²⁰⁷ Pb/ ²⁰⁶ Pb Zircon Ages (Ma)	Metamorphic ²⁰⁷ Pb/ ²⁰⁶ Pb Zircon Ages (Ma)
LSC 33	Granulite	Cpx, Pl, Grt	52.95	0.54	737°C	1682±130-3231±230	1682±130
LSC 72	Granulite	Cpx, Pl	52.96	0.53	618-712°C	1834±19	1788±8
LSC 89	Granulite	Cpx, Opx, Pl	56.96	0.51	659-776°C	1691±24-2534±9	1773±8-1788±4
LSC 105	Granulite	Cpx, Opx, Pl, Grt, Qtz	47.47	0.54	671-688°C, 7.4-7.5 kbar	-	1772±5
BR 47	Amphibolite	Hbl, Pl, Bt, Qtz	51.19	0.76	689-909°C, 3.5-5.3 kbar	1874±8	1801±7

Grt = garnet Cpx = clinopyroxene Opx = orthopyroxene Bt = biotite Pl = plagioclase, Hbl = hornblende, Qtz = quartz

Broadening of original growth zones (72-1), sinusoidal growth zones (72-2), bleached oscillatory zoning and “ghost textures” (72-5) also imply solid-state recrystallisation (Pidgeon, 1992; Vavra et al., 1996; Hoskin and Black, 2000), that may result in younger ages in certain domains. Textures indicative of fluid-mineral interaction, such as the presence of micro-inclusions and porous/spongy and skeletal textures, are absent (Tomaschek et al., 2003). Importantly, $\delta^{18}\text{O}$ would show variability across zircon domains in response to interaction with hydrous fluids. However, the observed variation in $\delta^{18}\text{O}$ (4.4-5.5 ‰) is both small and not domain-controlled within single grains.

BR 47 and LSC 33: Recrystallisation of Magmatic Zircon

A Proterozoic magmatic population (1874±8 Ma) is defined by multiple magmatic grains within amphibolite BR 47. All zircon grains in BR 47, with the exception of 47-1, 47-5 and 47-6, show poorly preserved magmatic zoning as revealed by alternating CL dark and light banding, suggesting that the majority of grains are igneous. Poor preservation, and in some cases replacement of magmatic textures, together with resorbed external morphology, implies secondary recrystallisation of these zircons in the presence of a melt phase that may induce partial resetting of ages in certain domains. Hf isotope ratios and oxygen isotopes within BR 47 are relatively uniform implying co-genetic crystallisation, consistent with age conformity (Fig. 4.2, 4.3B). In zircon that appears to have been recrystallised, the Hf isotopic composition remained unaffected since it was inherited from previously formed zircon. Grain 33-1 (not shown in Fig. 4.1) likely also represents a resorbed magmatic zircon with convolute internal textures (Thakurdi et al., 2019a) defining a range in discordant ages with an upper and lower intercept of 3231±230 Ma and 1682±130 Ma respectively.

LSC 89

Zircons from this xenolith are classified into Type I and Type II, based on a combination of morphology, internal textures, U-Pb ages, and Hf isotope characteristics. Two grains (89-7, 89-12) probably represent special cases where Type I zircon has been overgrown by Type II zircon.

Type I Zircon: Recrystallisation of Magmatic Zircon

Type I zircon is represented by grains 89-2 to 89-6, 89-8, 89-10, 89-12(2), 89-14, 89-15, 89-16 and 89-17 (red box, Fig. 4.1B). In general, Type I zircon shows highly variable ages (1691 ± 24 - 2534 ± 9 Ma) with $^{176}\text{Hf}/^{177}\text{Hf}$ lying along a distinct, less radiogenic trend when compared to other zircon in the sample (Fig. 4.3B). Morphologically, these zircons are characterised by anhedral, rounded and embayed exteriors commonly associated with resorption/magmatic corrosion. The internal textures vary from chaotic to completely uniform. Some primary magmatic features are preserved, such as fine-scale, faint oscillatory zoning (89-6), fir tree and flow domains (89-10) and sector zoning (89-17) (Vavra et al., 1996; Vavra et al., 1999; Koreshkova, 2009). These poorly preserved igneous textures, together with high Th/U (0.04-2.2, $\bar{x} = 1.2$, Table 4.1, 4.2, 4.3: see Appendices) were interpreted as magmatic grains recrystallised in the presence of a fluid (melt) resulting in a variety of complex resorption textures (Thakurdin et al., 2019a).

The spread in $^{207}\text{Pb}/^{206}\text{Pb}$ ages in Type I zircon can be explained by dissolution-recrystallisation of zircon that results in variable Pb-loss. Pb is not fully re-incorporated into recrystallised zircon, or is partly retained within the primary magmatic structure, such that ages are dispersed along concordia (Flowers et al., 2010). This results in large age variations within single grains such as 89-5 (1734 ± 26 - 2534 ± 9 Ma) within domains that are not visually distinct in CL. Although Pb-loss in zircon often shows up as analyses falling below the concordia curve, this does not presume that concordant/near-concordant ages (observed in LSC 89) are free of similar Pb-loss processes (Vervoort and Kemp, 2016). Concordant mid-Proterozoic ages (ca. 1770 Ma) in Type I zircon grains appear to partially correlate with the metamorphic event recorded in Type II zircons (1773 ± 8 - 1788 ± 4 Ma) and metamorphic zircons within LSC 105 (1772 ± 5 Ma). In some cases these ages occur in distinct domains (white tips: 89-3, 89-4, 89-10, 89-16, 89-17), while in other grains the occurrence ca. 1700 Ma ages do not appear to be domain controlled and occur in a variety of convoluted domains (eg: 89-5, 89-8, 89-12 (2), 89-14). However, since the white tips are very small, the possibility of mixed analyses resulting in artificially young ages seems likely, and most certainly occurs in grains without texturally distinct zircon domains (Kemp et al., 2009; Vervoort and Kemp, 2016). Therefore, as a result of Pb-loss and mixed analyses, ages between ca. 2500 and 1700 Ma within Type I grains are problematic to interpret in the context of geological events.

Additional evidence for variable Pb-loss is provided by the Hf isotope data. Hafnium isotopes do not fractionate through the process of dissolution-recrystallisation (Hoskin and Schaltegger, 2003; Xia et al., 2009). If ages between 1700 Ma to 2534 Ma represented meaningful geological events, Hf isotopic ratios would be expected to vary with time since additional Hf would be incorporated from the matrix

and bulk-rock (Zheng et al., 2005; Sláma et al., 2007), a scenario which is precluded by uniform Hf observed within Type I zircon (Fig. 4.3B). The observation of highly variable ϵ_{Hf} (-1.5 to -17.6) in Type I zircon are therefore artefacts of variable Pb-loss. Other mechanisms of lead loss, such as volume diffusion in closed zircon, is unlikely to produce the range in ages (1700-2534 Ma) observed within our zircon population, and is not deemed to be significant in crustal rocks (Kooijman et al., 2011). Moreover, had uniform thermal diffusion operated within these grains, one would expect progressively decreasing ages from the core of the grain towards the rim, a relationship which is not observed in Type I grains (Flowers et al., 2010). Pb-loss due to metamictization is not recognised since a positive correlation between U and age is observed (Table 4.3, see Appendices). Moreover, zircons do not appear optically damaged and show good luminosity in CL - characteristics of non-metamict zircon (Vavra et al., 1999; Flowers et al., 2010).

Variable Pb-loss likely occurred as a result of melting during high temperature metamorphism resulting in dissolution-recrystallisation of zircon, as has been reported for many other granulite facies rocks (Kröner et al., 1994; Flowers et al., 2010; Siebel et al., 2012; O'Brien and Miller, 2014). Partial melting of the host rock, coupled with dissolution-recrystallisation, is supported by corroded/resorbed zircon shapes and internal textures (Fig. 4.1) (Flowerdew et al., 2006; Tichomirowa and Kohler, 2013). Indeed, Bolhar et al. (2007) suggested partial melting for this group of xenoliths, but direct evidence of such melt was obliterated by subsequent granulite-facies metamorphism.

In summary, combined geochemical characteristics point to similar formation mechanisms for Type I zircon grains, despite inconsistent CL micro-textures. Based on external morphology and sparse magmatic internal textures, it is argued that these zircons formed originally in an igneous protolith and were subsequently affected by recrystallisation accompanied by partial/variable Pb-loss. A dissolution-recrystallisation mechanism can account for the resorbed, embayed shapes of these zircon grains as well as chaotic internal textures. Whatever the recrystallisation mechanism, it resulted in variable resetting of U-Pb while $^{176}\text{Hf}/^{177}\text{Hf}$ remained relatively constant.

89-Type II zircon: Metamorphic Zircon

A smaller grouping of zircon grains are represented by grains 89-1, 89-9, 89-11, 89-15 (2) and as outer domains in 89-7 and 89-12. These grains are clearly distinguishable from Type I zircons on the basis of non-resorbed/subidiomorphic zircon shapes. For grains 89-9, 89-11 and 89-15, $^{207}\text{Pb}/^{206}\text{Pb}$ ages conform to a Proterozoic distribution (1708 ± 8 - 1827 ± 13 Ma) with a single anomalous age at 1953 ± 23 Ma. Th/U is generally lower (0.02-0.3, $\bar{x} = 0.14$) when compared to Type I zircon (Table 4.1, 4.3, see Appendices). Based on the general lack of complex internal textures, homogenous interiors, generally low CL emittance, and ages coinciding with granulite facies metamorphism at ca. 1772 ± 5 Ma (LSC 105),

these zircons are interpreted to be of metamorphic origin (Thakurdin et al., 2019a), having crystallised in the solid-state. Grain LSC 89-1 shows a resorbed CL-grey central domain (1947 ± 22 Ma, $\epsilon_{\text{Hf}} = +0.4$) surrounded by a lighter shaded domain (2066 ± 17 - 2155 ± 25 Ma, $\epsilon_{\text{Hf}} = -0.8$ to -1.2). Thin, dark, outer domains at grain corners yield younger ages (1827 ± 13 ; 1722 ± 8 Ma). Although ages in 89-1 are slightly older than other metamorphic zircons, the Hf characteristics are similar to that of Type II zircon, and together with its similar morphology is considered a Type II grain. ϵ_{Hf} for Type II zircons define a separate trend between $+1.4$ to -7.9 , corresponding to a more radiogenic trend in $^{176}\text{Hf}/^{177}\text{Hf}$ space as compared to Type I zircon (Fig. 4.3A-B). Newly formed and recrystallised metamorphic zircon would have incorporated less unradiogenic Hf from matrix and silicate phases of the host rock, resulting in a more radiogenic trend relative to Type II zircon (Zheng et al., 2005; Zhao et al., 2015; Rubatto, 2017, see below).

Type I and Type II Preserved in Single Zircons (89-7, 89-12)

Zircon 89-7 displays a resorbed core feature with weak magmatic sector zoning surrounded by a darker, patchy to uniform domain. A thin luminescent outer rim is preserved. $^{207}\text{Pb}/^{206}\text{Pb}$ ages within the core vary from 1818 ± 10 to 1846 ± 11 Ma and contains Hf isotopic compositions characteristic of Type I zircon ($\epsilon_{\text{Hf}} = -17.2$). Outer domains yield slightly younger ages from 1708 ± 8 - 1765 ± 7 Ma, with a considerably more radiogenic Hf isotope composition characteristic of Type II zircon ($\epsilon_{\text{Hf}} = -4.2$ to -6.9). Our interpretation is that initial magmatic zircon (Type I) with slightly older ages was overgrown by newly formed metamorphic zircon of younger age (Type II) in this grain. A similar scenario is observed within grain 89-12, in which Late Archaean interiors (Type I, 2490 ± 9 - 2509 ± 5 Ma) are surrounded by Proterozoic (1786 ± 4 - 1788 ± 4 Ma) metamorphic overgrowths representing Type II zircon. Finally, grain 89-15(2) shows euhedral morphology, internally featureless domains and a narrow range of ages (1739 ± 9 - 1775 ± 20 Ma), together with radiogenic Hf ($\epsilon_{\text{Hf}} = -7.4$) characteristic of Type II zircon. However, this grain also contains a CL bright domain (1953 Ma) with unradiogenic ϵ_{Hf} (-16.1) similar to that of Type I zircon.

LSC 105: Metamorphic Zircon Growth

All grains in this sample show a relatively homogeneous CL response, small grain size and low Th/U consistent with metamorphic growth (Thakurdin et al., 2019a). A unimodal age population (1772 ± 5 Ma, MSWD = 2.6, $n = 12$), together with consistently high oxygen compositions and negligible textural variation, suggests that zircon within this xenolith grew during a single metamorphic event.

4.5.2 Oxygen isotopes in zircon

The involvement of supracrustal components in melts produce elevated $\delta^{18}\text{O}$ (V-SMOW) values of up to 10 ‰ in melt-precipitated zircon, while mantle-derived melts crystallise zircon within a restricted range (5.3 ± 0.6 ‰; 2 SE; Valley, 2003). Amphibolite (BR 47) and granulite xenoliths (LSC 89 and LSC 105) record elevated zircon oxygen isotope ratios (6.0-8.1 ‰), suggesting that zircon-forming melts carry a record of metasomatism of sub-continental lithospheric mantle by subduction-derived fluids prior to magma generation and zircon crystallisation. Xenoliths LSC 33 (5.3-5.7 ‰) and LSC 72 (4.4-5.5 ‰) preserve notably lower $\delta^{18}\text{O}$ values, consistent with mantle-derivation. The zircons themselves are not metasomatic due to the absence of a “spongy texture” (Corfu, 2003; Tomaschek et al., 2003; Geisler et al., 2007).

Ages and $\delta^{18}\text{O}$ are not correlated (Fig. 4.2). As mentioned above, the within sample variability of $\delta^{18}\text{O}$ in xenoliths is small, with differences of less than 1.1‰ between zircon grains. Minor variability in $\delta^{18}\text{O}$ between zircons within each xenolith may be attributed to small isotopic heterogeneities within the melt or mantle source from which protolith magmas were derived. The small intra-grain $\delta^{18}\text{O}$ variability across discrete growth zones (<0.7 ‰) indicates that zircons were not subject to post-crystallization alteration by isotopically distinct metamorphic/hydrothermal fluids. The absence of certain zircon structures (porous/spongy/skeletal) furthermore argues against hydrous fluid alteration. The dissolution-recrystallization process previously described for zircon (Type I zircon, LSC 89) allows for the redistribution of Pb (owing to its mobile behaviour) and other incompatible trace elements, while primary $\delta^{18}\text{O}$ are retained. Recrystallized Type I zircon thus inherited $\delta^{18}\text{O}$ from pre-existing zircon domains (Martin et al., 2008). In summary, external factors did not influence oxygen isotopes therefore zircon $\delta^{18}\text{O}$ systematics reflect the mantle source from which igneous protoliths were derived.

It is notable that a few oxygen isotopic compositions ($\delta^{18}\text{O} = 4.4\text{-}4.6$ ‰) in xenolith LSC 72 lie slightly below the mantle range ($\delta^{18}\text{O} = 5.3 \pm 0.6$ ‰). From other studies, oxygen signatures falling below mantle ranges indicate interaction of the protolith with a low $\delta^{18}\text{O}$ reservoir, such as meteoric water ($\delta^{18}\text{O} = -6$ ‰) or seawater ($\delta^{18}\text{O} = 0$ ‰). Interaction of the protolith magma with seawater ($\delta^{18}\text{O} = 0$ ‰) in the subduction zone may variably lower $\delta^{18}\text{O}$ in the zircon forming melt, resulting in mantle and sub-mantle zircon $\delta^{18}\text{O}$ values within xenolith LSC 72. This scenario is consistent with a subduction-related petrogenesis envisioned for this xenolith (see below). Alternatively, the protolith was hydrothermally altered at shallow levels prior to subduction (Zheng et al., 2001; Wei et al., 2002). Post-crystallisation metasomatic and fluid alteration effects have been reported to lower $\delta^{18}\text{O}$ in zircon to below mantle levels (Chen et al., 2011; Sheng et al., 2012; Rubatto and Angiboust, 2015) but these processes can be ruled out for our samples based on minor/absent internal oxygen variations in zircon.

4.5.3 Rare earth elements in zircon

Grains 47-2, 72-1 and a single domain within 72-3 (green, Fig. 4.4B) show LREE depletions relative to the HREEs, positive cerium ($Ce_N/Ce_N^* = 47.3-105.4$) and negative europium anomalies ($Eu_N/Eu_N^* = 0.28-0.54$) typical of magmatic zircon (Fig. 4.4A-B). All grains within LSC 89 (apart from grain 89-2, see below) show similar igneous patterns with distinct negative Eu anomalies ($Eu_N/Eu_N^* = 0.08-0.15$). Knowledge of rare earth elemental abundances in zircon and other co-existing igneous and metamorphic minerals can be used to constrain the relative timing of zircon growth (Schaltegger et al., 1999). Specifically, concomitant crystallisation of zircon with HREE-compatible phases, such as garnet, can produce HREE depleted patterns in zircon (Rubatto, 2002; Whitehouse and Platt, 2003). Relative HREE deficiencies are not observed for zircon within any of our xenoliths, including one sample (LSC 33) containing garnet with high HREE abundances ($\Sigma HREE = 18-269$ ppm) (Fig. 4.4D). This would suggest that zircon crystallisation took place before peak-metamorphic phase transformation in xenolith LSC 33. Within other xenoliths, co-existing HREE enriched phases such as clinopyroxene ($\Sigma HREE = 32-88$ ppm) and to a lesser extent amphibole ($\Sigma HREE = 7-24$ ppm) also do not appear to have affected the heavy rare earth element budget in zircon. Simultaneous crystallisation of LREE-enriched phases, such as clinopyroxene ($\Sigma LREE = 50-155$ ppm) and amphibole ($\Sigma LREE = 60-136$ ppm) may lower LREE within zircon (Rubatto et al., 2009). However, LREE concentrations appear variable and may also be controlled by post-crystallisation effects (e.g. recrystallisation, see below).

Europium (Eu) and cerium (Ce) are redox-sensitive rare earth elements that are primarily controlled by feldspar fractionation (Hoskin et al., 2000) and oxygen fugacity respectively (Trail et al., 2011, 2012). In addition to oxidising/reducing conditions, positive cerium anomalies in zircon can be explained by the size and charge preference of Ce^{4+} in the zircon structure (Hoskin and Schaltegger, 2003). The prominent europium anomaly seen in LSC 89, and to a lesser extent in other xenoliths, can be attributed to the presence of a europium fractionating phase such as feldspar. Negative Eu anomalies may also suggest zircon formation from a melt crystallizing in a reducing environment, even in the absence of feldspar, but this is likely not the case for our xenoliths, which are feldspar rich. (Trail et al., 2012). Since magmatic zircon crystallised during a single event in each xenolith, the variation in Ce and Eu anomalies observed in single xenoliths cannot be ascribed to changing oxidation conditions in an evolving melt. These variations must be caused by post-crystallisation processes (recrystallisation/inclusions, see below) that alters the concentrations of neighbouring LREE and subsequently the measured Ce/Ce^* (Trail et al., 2012). Additionally, the lack of correlation between Eu/Eu^* and Ce/Ce^* suggest control on Eu and Ce independent of oxygen fugacity (Table B2). As described by Schulz et al. (2006) incorporation of Th^{4+} for $Eu^{2/3+}$ may account for negative europium anomalies in zircon as opposed to feldspar fractionation or oxygen fugacity. However, the non-

correlation of Th/U with Eu/Eu* (Fig. 4.5C) again suggests that these substitution processes are not controlling europium anomalies. Within LSC 33 (Fig. 4.5C), LREE and HREE are quite similar implying minimal redistribution of REE, however, the xenolith contains a notably weak negative Eu anomaly ($\text{Eu}_\text{N}/\text{Eu}_\text{N}^* = 0.71\text{-}0.76$), despite the whole-rock containing significant proportions of feldspar (70 modal %). An explanation for such a weakly negative Eu anomaly may include zircon crystallisation before plagioclase, or in equilibrium with metamorphic plagioclase which contains significantly reduced Eu (Gregory, 2009; Rubatto et al., 2009).

Two domains within grain 47-4, and a single domain within grain 72-3 (purple, Fig. 4.4B), show variable cerium ($\text{Ce}_\text{N}/\text{Ce}_\text{N}^* = 4.4\text{-}126$) and significantly smaller or positive europium anomalies ($\text{Eu}_\text{N}/\text{Eu}_\text{N}^* = 0.8\text{-}2.2$) than magmatic grains (Fig. 4.4A-B, 4.5C-D). LREE ($\text{La}_\text{N}/\text{Gd}_\text{N} = 0.001\text{-}0.015$) also appear variably enriched/depleted relative to igneous zircon grains 72-1 and 47-2 ($\text{La}_\text{N}/\text{Sm}_\text{N} = 0.001\text{-}0.004$) (Fig. 4.5A). While broadly similar to magmatic zircon, some mechanism/process must explain the REE variation within the same xenolith. Based on textures, all zircon grains within these two samples (47 and 72) were classified as igneous zircon with some post-crystallisation modification, likely solid-state recrystallisation (LSC 72) or melt-assisted dissolution-recrystallisation (BR 47). Zircons that have undergone solid-state recrystallisation have been shown to possess similar REE characteristics such as reduced/absent Eu anomalies and variable Ce and LREEs (Hoskin and Black, 2000, Whitehouse and Kamber, 2003). Textural evidence for this process within xenolith LSC 72 includes truncated, faded/bleached magmatic zoning together with generally low and variable Th/U (0.01-0.3) in grain 72-3. Additionally, the LREE abundance is the most variable in xenolith LSC 72, possibly attesting to mobilization of light-rare earths during recrystallisation (Hoskin and Black, 2000). Within xenolith BR 47, altered igneous textures, together with variable LREE (Fig. 4.5A) and Th/U (0.2-0.8), suggest similar processes of solid-state recrystallisation occurred in some grains (47-4). From studies of magmatic zircons within the Amîtsoq gneiss in Greenland, grains lacking Eu anomalies and containing variable LREE were interpreted as having undergone a similar process of solid-state recrystallisation (Whitehouse and Kamber, 2003). Similarly, based on internal textures, zircons within lower crustal granulites from the Udachnaya kimberlite pipe were interpreted to have undergone solid-state recrystallisation, resulting in a purging of trace elements, and thus lowered REE abundances and smaller Eu/Eu* anomalies (Koreshkova et al., 2009).

The tighter grouping of REE within LSC 89 (Fig. 4.4D) attests to similarity in LREE and HREE abundances within this xenolith, apart from a single, extremely La-enriched grain (89-2). This uniformity in REEs suggests that the process of melt-assisted dissolution-recrystallisation envisioned for magmatic zircons in this sample does not result in a substantial redistribution of the REEs, and likely inherits such trace elements from previously formed zircon. Similar observations were made by Martin et al. (2008),

in which zircon retains REE, structural elements (weak magmatic zoning) and uniform oxygen compositions (as observed in this xenolith) after undergoing dissolution-recrystallisation of zircon. This is despite complete or partial resetting of ages within the same zircon grains (Martin et al., 2008). Metamorphic zircons (Type II) within LSC 89 are REE depleted ($\Sigma\text{LREE}+\text{MREE} = 14\text{-}23$ ppm; $\Sigma\text{HREE} = 198\text{-}315$ ppm) relative to magmatic Type I zircons ($\Sigma\text{LREE}+\text{MREE} = 22\text{-}81$ ppm; $\Sigma\text{HREE} = 286\text{-}629$ ppm); this observation can be explained by the expulsion of incompatible ions from the zircon lattice during metamorphic zircon crystallisation (Hoskin and Schaltegger, 2003)

Grains 47-1, 47-4, 72-2 and 89-2 show enriched LREE (particularly La) and lowered Ce anomalies diagnostic of “hydrothermal” zircon (Hoskin, 2005) (Fig. 4.4A-B,D, Fig. 4.5A). However, interaction of zircon with a hydrothermal fluid is precluded based on the absence of “murky-brown featureless interiors” or “porous textures” that optically define hydrothermal zircon (Tomaschek et al., 2003). Furthermore, uniform $\delta^{18}\text{O}$ within these zircon grains precludes hydrothermal fluid exchange subsequent to zircon crystallisation. Alternative explanations for such enrichments in LREE include evolution of a melt with progressively increasing LREE (Xia et al., 2010), mineral inclusions, disequilibrium crystallisation of metamict zircon (Whitehouse and Kamber, 2002) and interaction of zircon with metamorphic fluids formed from dehydration reactions (Xia et al., 2010). U-Pb age data suggest that the magmatic zircons crystallised during a single event. Therefore it is unlikely that progressively younger LREE enriched zircons formed from an evolved melt. Zircons grains are likely not metamict based on high luminescence in CL, and therefore cannot result in LREE enrichment via disequilibrium crystallisation. Additionally, La/Gd and Th/U (a proxy for zircon damage; (Whitehouse and Kamber, 2002) are not correlated. Supercritical fluids may be formed via dehydration reactions, whereby hydrous minerals (biotite, muscovite, hornblende) break down due to increased pressure-temperature conditions. Since such a fluid is enriched in LREEs and LILEs and is unlikely to affect the $\delta^{18}\text{O}$ signature (Xia et al., 2010), this mechanism provides a process of fluid alteration in deep granulite lithologies that may result in the elevated LREE contents observed in some zircons (Xia et al., 2010). However, in this scenario, zircons would be texturally distinct and display a “spongy texture” analogous to that of hydrothermal zircon (e.g., Xia et al., 2010). This scenario can be excluded on a textural basis. Sampling of sub-micron scale mineral inclusions could conceivably result in enriched LREE contents in zircon, similar to that expected for hydrothermal zircon (Whitehouse and Kamber, 2002; Schulz et al., 2006; Zhong et al., 2018). Such inclusions include monazite, allanite or apatite and are not visible on the scales of zircon grains (50-250 μm) shown in BSE and CL images (Zhong et al., 2018). A lack of correlation of LREE and Th (Table B2) preclude sampling of monazite/allanite, however, other such inclusions (eg: apatite) may have been ablated by laser spots. Finally, variations in LREE are most apparent with respect to La. Lanthanum is highly variable in zircon (especially at low

concentrations) and may not be truly diagnostic of LREE enrichment. Additionally, since La lies directly next to Ce, increased La concentrations lowers the magnitude of the Ce anomaly and produces the observed variations in Ce/Ce* in these grains.

The chemical composition of the zircon forming melt has been estimated using the mean or median REE compositions in zircon and empirically determined melt-zircon partition co-efficients determined by Chapman et al. (2016) (Fig. 4.7, see caption for details). For xenoliths BR 47, and LSC 72, the estimated bulk-rock composition ($La_N/Sm_N = 5.1-7.3$, $Gd_N/Yb_N = 2.1-3.5$) show patterns similar to that of the measured bulk-rock compositions ($La_N/Sm_N = 2.92-3.02$, $Gd_N/Yb_N = 1.2-1.6$), although some elements (e.g., Eu and Ce) do not correlate well. The similarity between the REE patterns predicted using REE in zircon and those actually measured in bulk-rock samples for these two xenoliths may indicate that zircon formed from a single melt whose composition is recorded, at least in part, by the whole-rock. This interpretation rules out metamorphic crystallisation (for xenoliths LSC 72 and BR 47), since metamorphic zircon would have incorporated REE from fluids and/or break-down of metamorphic phases resulting in dissimilar REEs between the zircon forming melt and the modern day whole-rock. Within xenoliths BR 47 and LSC 89, the europium anomalies are similar in both the zircon and bulk samples, implying a bulk-rock control over Eu in zircon. However, within LSC 72 and LSC 33 slightly positive Eu anomalies for measured whole rock compositions differ from the predicted values. Therefore, elements such as europium and cerium are not well addressed by this model, likely to due to effects arising from their complex oxidation and multi-valence states (Chapman et al., 2016). Within both LSC 33 and LSC 89, measured bulk-rock REE patterns ($La_N/Yb_N = 4.8-50.5$) are not well matched by the predicted patterns ($La_N/Yb_N = 14.4-142.5$). For garnet-bearing xenolith LSC 33, the lower measured bulk-rock HREE ($Gd_N/Yb_N = 4.5$) is lower than what is predicted ($Gd_N/Yb_N = 2.2$), implying zircon crystallised before garnet, and was thus not affected by heavy rare earth element depletion. Another possible explanation is that fluid/melt extraction for these two samples, inferred from the of Pb-isotope ratios in these xenoliths (Bolhar et al., 2007), occurred at some point, resulting in differing zircon-melt partition co-efficients in the protolith melt as compared to the whole-rock.

In summary, a small number of grains display REE characteristics typical of igneous zircon. Textural and geochemical (Th/U) information indicate a process of solid-state recrystallisation resulting in variable LREE, Eu and Ce in certain grains. Metamorphic zircons in a single xenolith (LSC 89) are REE depleted relative to magmatic zircons in the same sample, presumably due to the expulsion of such elements during metamorphic crystallisation. The composition of the zircon forming magma, inferred from published melt-zircon partition coefficients, indicate that in some cases zircon formed from melts represented by bulk-rock compositions. Our data also indicated that effects of fluid/melt extraction

may result in differences between the predicted and measured trace element patterns in other whole-rock samples.

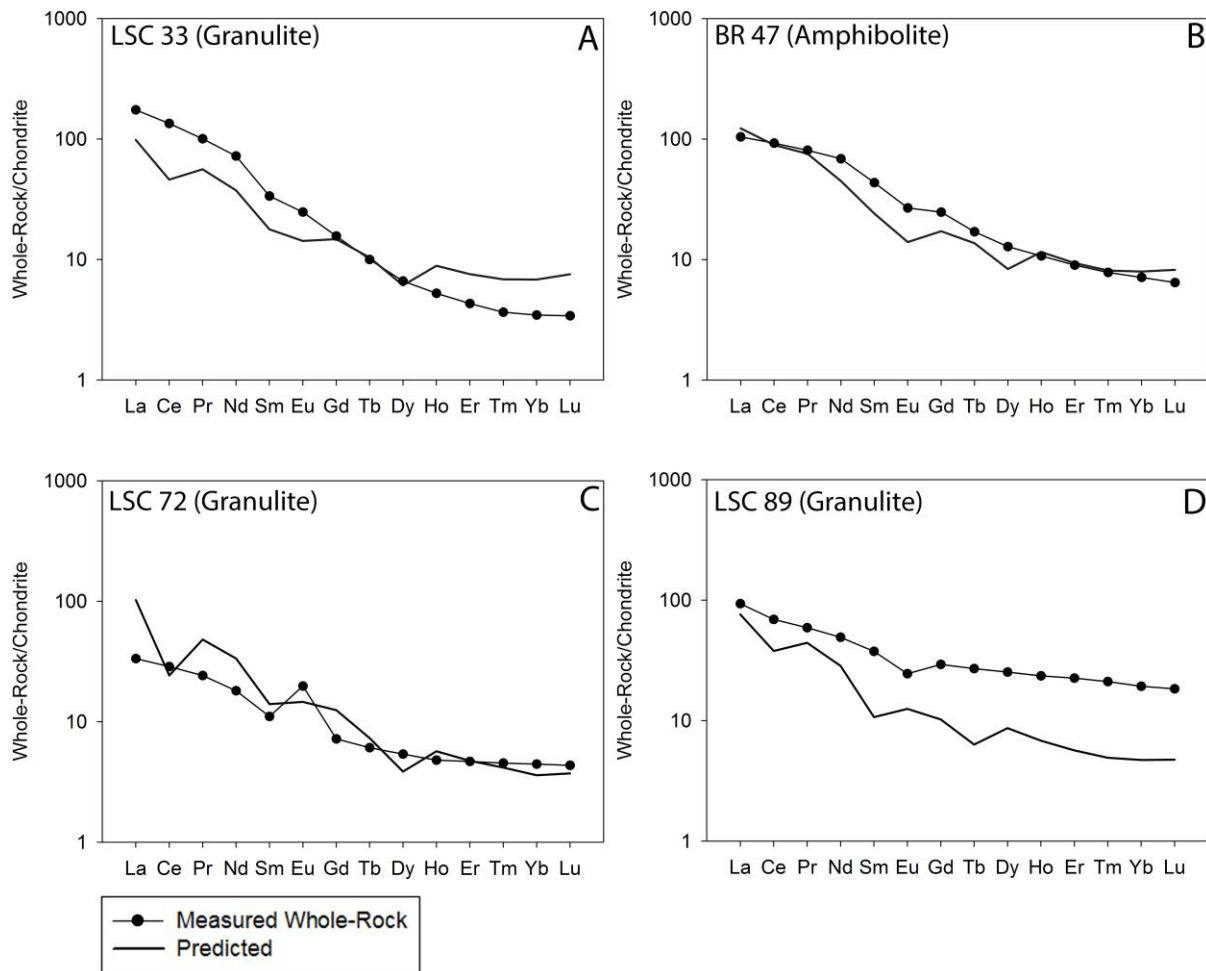


Figure 4.7: Predicted whole-rock REE patterns using trace element concentrations in zircon (grey) are plotted alongside measured REE patterns for the same whole-rocks (black). Predicted patterns are calculated using empirically determined zircon-melt partition co-efficients for the REE (Chapman et al., 2016), and median/mean REE abundances in zircon. For zircons which show relatively uniform REE (LSC 33 and LSC 89), the median value of REE in zircon was used. For zircons that show variability in REE patterns (BR 47 and LSC 72) the mean value of REE concentrations in zircons were used in predicted calculations. Only magmatic zircons were used to calculate average/median REE concentrations. Both predicted and measured REE patterns normalised relative to C1 chondrite parameters (Anders and Grevesse, 1989).

4.5.4 Hafnium isotopes in zircon

LSC 72 and BR 47

Assuming that zircons crystallised from the same melt reservoir over a period of time, a linear array in ϵ_{Hf} versus time space (e.g. Fig. 4.3A, LSC 89, see discussion below) may provide an estimation of $^{176}\text{Lu}/^{177}\text{Hf}$ in the source (Amelin et al., 1999). In the case of xenoliths LSC 72 ($\epsilon_{\text{Hf}} = -2.3$ to $+3.7$) and BR 47 ($\epsilon_{\text{Hf}} = -8.2$ to -9.6) the restricted data range does not translate into sufficiently well-defined linear evolutionary arrays (Fig. 4.3A). Since the Hf isotopic compositions for both samples do not overlap, zircons from individual xenoliths were derived from protolith magmas that were isotopically distinct.

Within xenolith LSC 72, initial ϵ_{Hf} shows a range in values from $+3.7$ to -2.3 (1SE uncertainties of 0.4-0.6 epsilon units), while O isotopic values show a range between 4.4 and 5.5 ‰. The range in ϵ_{Hf} well below Depleted Mantle (DM) in this xenolith indicate derivation from an enriched mantle source that incorporated small amounts of older, subduction-derived sediment/supracrustal material, which dominated the incompatible element (Hf) budget, but was not present in sufficient amounts to shift $\delta^{18}\text{O}$ away from mantle-like values. Mixing between CHUR and DM reservoirs is also possible (Yang et al., 2007; Jiang and Guo, 2010), but difficult to ascertain, given the lack of spread in data for LSC 72.

Xenolith BR 47 shows ϵ_{Hf} values clustering well below CHUR. Binary mixing between supracrustal and mantle sources seems less likely given the restricted range in Hf. Considering that O isotopic values are elevated relative to mantle, a mechanism of subduction involving slab-derived fluid/melts that metasomatised the mantle source appears the most plausible mechanism to explain both unradiogenic Hf and elevated O systematics (see below) with restricted compositional ranges.

LSC 89

Two distinct trends in ϵ_{Hf} and $^{176}\text{Hf}/^{177}\text{Hf}$ versus time space (Fig. 4.3A,B) are separated by approximately 10 ϵ units, comprising unradiogenic (Type I) and more radiogenic values (Type II). The presence of two separate evolution curves within the same xenolith suggests zircon growth within environments that were isolated over a prolonged period of time giving rise to distinct Type I and Type II zircons. Importantly, $^{176}\text{Hf}/^{177}\text{Hf}$ remains uniform through time for either trend defined by Type I or Type II zircon (Fig. 4.3B). Since Type I zircon represents initial magmatic growth and subsequent dissolution-recrystallisation, this trend supports the notion that hafnium isotopes do not fractionate significantly in zircon undergoing such mineralogical reconstitution (Zheng et al., 2005; Xia et al., 2009), but inherits Hf signatures from older zircon domains. Type I grains from LSC 89 falls along an array that can be regressed back to DM with Lu/Hf of 0.021 ± 0.0021 similar to mafic crust (Fig. 4.3A) (Pietranik et al., 2008). However, $^{176}\text{Hf}/^{177}\text{Hf}$ conversely remains constant with time and does not plot on an evolution curve using $^{176}\text{Lu}/^{177}\text{Hf}$ of 0.021 (Fig. 4.3B). This observation is a manifestation of Pb-loss due to dissolution-recrystallisation of Type I zircon, and precludes elucidation of the source reservoir using regressed $^{176}\text{Lu}/^{177}\text{Hf}$ since age is not reliably linked to hafnium compositions. Regression of ϵ_{Hf} in Type

II zircon back to DM shows a sub-parallel curve in ϵ_{Hf} vs time space ($^{176}\text{Lu}/^{177}\text{Hf} = 0.018 \pm 0.010$) compared to Type I zircon. However, since Type II zircon formed metamorphically, and incorporated Lu/Hf from the matrix/silicate phases, these grains are unlikely to be representative of Lu/Hf in the source melt.

The observation of elevated $^{176}\text{Hf}/^{177}\text{Hf}$ in metamorphic zircon (Type II) relative to magmatic zircon (Type I) can be explained by the incorporation of Hf from pre-existing zircon and the matrix and/or metamorphic phases. Since $^{176}\text{Lu}/^{177}\text{Hf}$ is very low in zircons (0.000014-0.004, this study), negligible changes in $^{176}\text{Hf}/^{177}\text{Hf}$ are expected to occur over time. However, Lu/Hf in the bulk rock (Lu/Hf = 0.13, LSC 89) and matrix phases is considerably higher, and will more rapidly evolve to more radiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ through time (Rubatto, 2017). Therefore, newly formed metamorphic zircon that equilibrates with matrix material will contain higher $^{176}\text{Hf}/^{177}\text{Hf}$ than previously formed igneous zircon. Additionally, break-down or recrystallisation of high $^{176}\text{Hf}/^{177}\text{Hf}$ metamorphic phases concomitant with Type II zircon growth will release $^{176}\text{Hf}/^{177}\text{Hf}$ that can be incorporated into newly formed metamorphic zircon (Rubatto, 2017). Such metamorphic phases within LSC 89 include orthopyroxene (Lu/Hf = 0.9-8.5) and clinopyroxene (Lu/Hf = 0.1-1.1) (Table B3) and may conceivably act as sources of Hf for newly crystallised metamorphic zircon. Therefore, Type II metamorphic zircon formed in equilibrium with the bulk-rock/matrix (and possibly recrystallizing metamorphic phases) thereby incorporating more radiogenic Hf from these sources (Zheng et al., 2005; Rubatto, 2017). Given the resorbed shapes of Type I grains in this xenolith (Fig. 4.1, Type I), this process occurred through melting and partial dissolution of zircon, which distributed Lu/Hf and Zr into the matrix. Upon recrystallisation of the rock, the combination of Hf from the matrix, high Lu/Hf metamorphic phases and previously formed magmatic zircon is incorporated into newly formed Type II zircon. This scenario is similar to that of Gerdes and Zeh (2009) in which partial anatexis redistributes Hf into matrix phases which is then taken up by newly formed metamorphic zircon.

4.5.5 Xenolith petrogenesis and implications for the Wyoming Craton – an O and Hf isotopic perspective

LSC 33 and LSC 72 (Granulite)

Granulite LSC 72 contains a narrow range in initial ϵ_{Hf} values above and below CHUR (-2.3 to +3.7) and generally mantle-like oxygen (4.4-5.5 ‰) signatures. Although oxygen signatures and a mafic xenolith composition indicate a mantle source for the protolith magma, initial ϵ_{Hf} is lower than Depleted Mantle (DM) (~8) at 1800 Ma (Vervoort et al., 2015) for LSC 72 (1834 ± 19 Ma), which suggests the involvement of an older supracrustal/sedimentary component. A mechanism which may explain these isotopic signatures is subduction, in which small proportions of downgoing sediment contaminate the

mantle source, resulting in lower ϵ_{Hf} . In this scenario, it is envisioned that the volume of subducted sediment was not large enough to significantly shift oxygen to higher values expected for sources containing significant supracrustal components ($\delta^{18}\text{O} > 6\text{‰}$). As mentioned above, interaction of the protolith with a low $\delta^{18}\text{O}$ component, such as seawater ($\delta^{18}\text{O} = 0\text{‰}$) may also contribute to oxygen isotopic values as low as 4.4 ‰, and further supports a subduction model in which seawater can enter the source region. Additionally, a subduction-related whole-rock trace element signature (enriched LILE and relative Nb-Ta, Zr-Hf negative anomalies) was suggested for this xenolith (Thakurdin et al., 2019a). Finally, U-Pb ages within LSC 72 (1834 ± 19 Ma) coincide with ages of arc-magmatism in the Little Belt Mountains within the GFTZ (1864-1867 Ma: Mueller et al., 2002). It is likely that similar arc-related activity generated protolith magmas for xenolith LSC 72 further north within the GFTZ, during ocean closure between the Wyoming Craton and Medicine Hat Block.

For xenolith LSC 33, mantle-like oxygen ($\delta^{18}\text{O} = 5.3\text{-}5.7\text{‰}$) and arc-related whole-rock trace element patterns imply subduction-related melting of a mantle source in the Early Archaean (as defined by the upper concordia intercept age of 3231 ± 230 Ma for this xenolith). As described for xenolith LSC 72, it is likely that this mantle source did not interact with significant supracrustal components during subduction. Although the upper concordia intercept date for LSC 33 is poorly defined (3231 ± 230 Ma), this older Archaean age is consistent with more unradiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ compositions in this sample, and broadly coincides with Archaean (ca. 3000-3500 Ma) subduction-related activity reported by Mueller and Wooden (2012) in the northern Wyoming Craton. In summary, the integration of O and Hf isotopic data, together with whole-rock chemistry and U-Pb geochronology, suggest a subduction-related petrogenesis for these two xenoliths, consistent with previous studies.

Xenolith 89 (Granulite)

The absence of older (>3000 Ma) zircon, or any inherited zircon, precludes granulite-facies metamorphism of existing ancient crust as a formation process for zircon within this xenolith. Hafnium ($^{176}\text{Hf}/^{177}\text{Hf}$) and oxygen isotope ratios do not vary significantly with time when each zircon type (Type I and II) are considered separately, suggesting that exchange of the protolith with other reservoirs did not occur during the time period of magmatic zircon (re)crystallisation. Instead, isotope compositions reflect mantle source characteristics. Values of $^{176}\text{Hf}/^{177}\text{Hf}$ plot below CHUR for Late Archaean Type I magmatic zircon, indicating that the protolith may represent a reworked source that contained ancient crustal material as implied by $\delta^{18}\text{O} > 5.6\text{‰}$. However, crustal reworking would likely result in a range in ϵ_{Hf} between the mantle and crustal reservoir(s), which is here attributed to Pb-loss as opposed to variable source mixing. Metasomatism of the mantle wedge via subduction-derived fluids and melts would have produced an enriched mantle source with unradiogenic hafnium and elevated

oxygen isotope signatures (eg: Gagnevin et al., 2011). Arc-like trace element signatures for these xenoliths, containing elevated LILE and coupled depleted HFSE anomalies, further suggest subduction related processes producing metasomatised mantle (Thakurdin et al., 2019a). Similar models involving an enriched mantle source were proposed to have occurred beneath the Wyoming Craton, with the enrichment attributed to metasomatism and subduction of continental detritus in the Early to Late Archaean (Mueller and Wooden, 1988; Wooden and Mueller, 1988). Other models involving an enriched mantle source have been proposed for the Wyoming Craton (BBMZ), with the enrichment attributed to metasomatism of the mantle wedge by fluids released from a downgoing subducting slab (Mueller et al., 2010). Subduction-related signatures were also reported within ca. 2400-3300 lithologies from the Grassrange Diatremes and Little Rocky Mountains (Gifford et al. 2014, 2018). Similarly, whole rock trace element systematics of Early Archaean rocks from the Tobacco Root Mountains were attributed to metasomatism and alkali volcanism, and were interpreted within the context of a collisional arc setting, further attesting to the existence of a subduction-related, ancient enriched mantle in some regions of the Wyoming Craton (Mogk et al., 2004). Melting of this enriched source occurred in the Late Archaean or earlier, as implied by the oldest igneous zircon age (2534 Ma) in this xenolith. A younger (1773 ± 8 - 1788 ± 4 Ma) Proterozoic metamorphic event is represented by new metamorphic zircon growth, either as new grains or outer metamorphic domains, and likely transformed the xenolith under granulite facies conditions.

Xenoliths BR 47 (amphibolite) and LSC 105 (granulite)

A Proterozoic (1874 ± 8 Ma) magmatic zircon population for amphibolite BR 47 excludes metamorphism of older existing crust in the petrogenesis this xenolith. Conversely, xenolith LSC 105 contains only Proterozoic (1772 ± 5 Ma) metamorphic zircon, and therefore no inferences can be made regarding the timing of initial xenolith crystallisation. Zircon oxygen isotopic compositions are elevated (6.0-8.1 ‰) relative to mantle values, while ϵ_{Hf} for xenolith BR 47 values plot well below CHUR and DM (-8.2 to -9.6). Hafnium and oxygen do not vary significantly within individual xenoliths, and coupled with the consistent and narrow age range, suggests mantle extraction occurred during a single event in the Proterozoic with little interaction with other reservoirs prior to zircon crystallisation. Hafnium data plotting below CHUR implies that the mantle source for these xenoliths was non-juvenile. A mechanism of subduction-induced metasomatism produced the elevated oxygen and unradiogenic hafnium in the mantle source coeval with magma generation. The presence of such an enriched Proterozoic (1500-1900 Ma) mantle has been previously suggested in northern Wyoming Craton (Dudás et al., 1987), while mid-Proterozoic (1700-1900 Ma) fluid-related subduction-metasomatism has been reported in the Highwood Mountains (Rudnick et al., 1999). Mid-Proterozoic (ca. 1800 Ma) subduction-related magmatism within the Bearpaw mountains and GFTZ has also been inferred based

on previous geochronological studies in the region, and likely resulted in melting and formation of igneous zircon within xenolith BR 47, and metamorphic zircon within LSC 105 shortly afterward (Holm and Schneider, 2002; Roberts et al., 2002; Mueller et al., 2002, 2005; Foster et al., 2006; Barnhart et al., 2012; Gifford et al., 2014). In summary, Hf-O systematics in this xenolith indicate a non-juvenile mantle source that was melted and metasomatically enriched by subduction-related processes during the mid-Proterozoic.

4.5.6 Geodynamic Implications

Hf and O isotope systematics indicate that our xenoliths formed through crystallisation of magmas derived from mantle sources variably modified by subduction-related processes. New magma was generated via subduction-induced melting involving convergence and ocean closure between the Medicine Hat Block and Wyoming Craton during the Proterozoic (ca. 1800 Ma, Fig. 4.8), and is consistent with arc-related trace element systematics in xenoliths (specifically xenolith BR 47) and proposed ages (1800-1900 Ma, BR 47) of subduction (Mueller et al., 2002, 2005; Thakurdin et al., 2019a). The location of xenoliths within the GFTZ supports the notion that this zone represents a subduction-related suture (Mueller et al., 2002, 2005).

4.5.7 Comparison with other Hf-O studies in the Wyoming Craton/GFTZ

Hafnium isotopes may provide clues as to subduction-related mechanisms operating in the region. In this context, ancient (ca. 3000-4000 Ma) detrital zircons from the northern Wyoming Craton (Beartooth Mountains) were found with initial ϵ_{Hf} values between 0 and -9 (Mueller and Wooden, 2012). Lower $^{176}\text{Lu}/^{177}\text{Hf}$ (<0.1) in zircons was interpreted to represent plume-related magmatism in a relatively dry environment, while the onset of subduction in a hydrous environment was associated with higher $^{176}\text{Lu}/^{177}\text{Hf}$ (>0.2). A direct comparison of age/isotopic data with our xenoliths is not possible as ages do not overlap (apart from partial overlap with the 3231 ± 230 Ma upper concordia intercept age defined by zircons within xenolith LSC 33), however, subduction-related processes reported by Mueller and Wooden (2012) show similarities to arc-related petrogenetic processes inferred for our xenoliths. Subduction-related processes also appear to be recorded in xenoliths within the Grassrange diatremes of the Great Falls Tectonic Zone (Gifford et al., 2014). In that case, calculated ϵ_{Hf} range between -20.2 to +2.3. Incorporation of crustal components into protolith sources in a subduction-related environment was used to explain the range in ϵ_{Hf} . The older ages (ca. 2550 Ma) recorded in the study of Gifford et al. (2014) suggest contribution from, or involvement of, the Medicine Hat Block while younger ages (ca. 1800 Ma) represent newly formed, arc-related crust. Other GFTZ studies in the Little Belt Mountains reported approximate zircon ϵ_{Hf} values between -15 and +5 within older gneisses, amphibolites and metasediments (ca. 2400-3300 Ma) that largely pre-date our

xenoliths (Gifford et al., 2018), but also infer convergent margin petrogenetic mechanisms operating in the region. In summary, zircon Hf studies in the region show similarity to Bearpaw xenoliths in that they encompass varying ϵ_{Hf} , consistent with subduction-related magmatism.

Few zircon oxygen isotopic data are available for the Wyoming Craton. Whole-rock oxygen isotopes for lower crustal xenoliths in the Bearpaw Mountains were obtained by Collerson et al. (1988) and Kempton and Harmon (1992) and document a largely supracrustal signature ($\delta^{18}\text{O} = 6.6\text{--}8.6\text{‰}$) matching the isotopic range observed within LSC 89 and BR 47, but lack the low mantle-like oxygen observed within LSC 72 and LSC 33. The absence of lower ($\delta^{18}\text{O} < 5.6\text{‰}$) oxygen isotope signatures in these studies may imply that whole-rock $\delta^{18}\text{O}$ is more susceptible to modification by supracrustal components (Kempton and Harmon, 1992). It is also possible that zircons with mantle-like oxygen isotope signatures in this region have not yet been sampled.

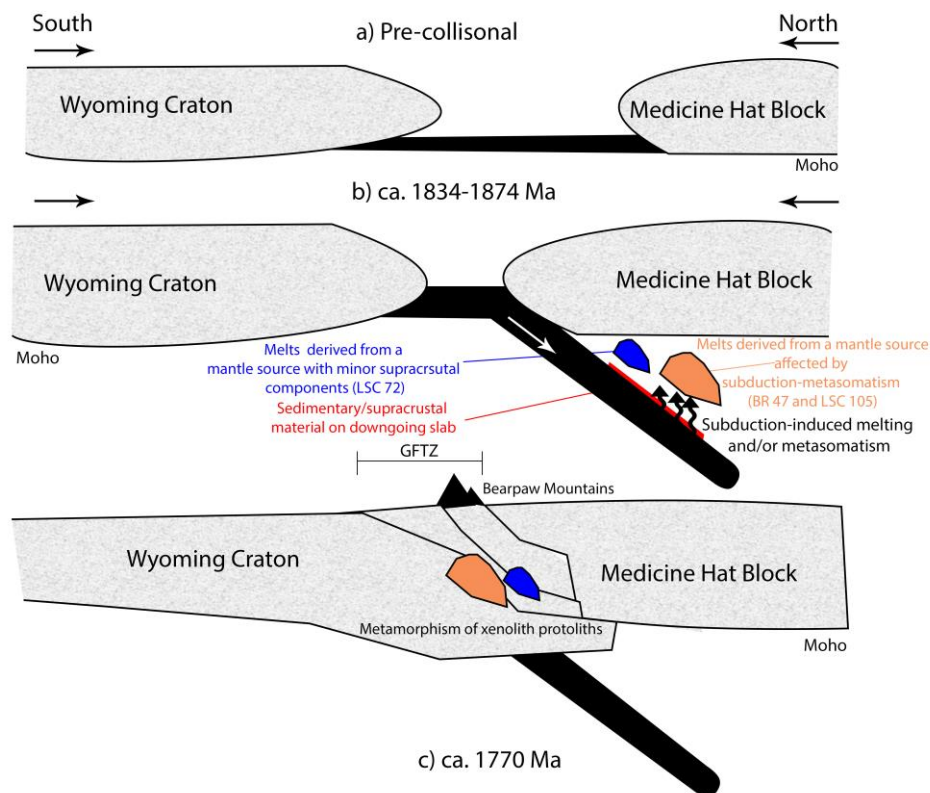


Figure 4.8: Schematic cross-sections for the tectonic evolution of the Wyoming Craton (WC) and Great Falls Tectonic Zone (GFTZ). a) Pre-collisional stage preceding Proterozoic subduction between the WC and Medicine Hat Block (MHB). b) Ocean closure commences at ca. 1834-1874 Ma. Subduction is orientated such that material is thrust beneath the MHB. Fluids emanating from the subducting slab result in melting and/or metasomatism of the overlying mantle wedge. Melting of subduction-metasomatised mantle results in the formation of protolith magmas for xenoliths BR 47 and LSC 105. A similar mechanism of subduction-metasomatism may have operated to create

protolith magmas for LSC 89 in the Late Archaean or earlier. Melting of a mantle source that incorporated minimal amounts of subducted sediment, and was not strongly metasomatised, resulted in the formation of protolith magmas for LSC 72. Melting of a mantle source similar to that of LSC 72 may have produced protolith magmas for xenolith LSC 33 in the Archaean (ca. 3000-3500 Ma). These melts crystallised to form protoliths to xenoliths. c) Following subduction, the WC and MHB collide at ca. 1770 Ma. Protoliths are subsequently metamorphosed to granulite/amphibolite facies.

4.6 Conclusions

Oxygen and hafnium isotope systematics, combined with geochronological and REE data, are used to characterise the nature of zircon grains within compositionally varied mafic to intermediate ($\text{SiO}_2 = 47\text{--}57\%$) granulite and amphibolite xenoliths from the Bearpaw Mountains, Montana, USA. Zircon grains within Proterozoic xenoliths (BR47 and LSC 72) contain uniform O and Hf isotopic compositions. Zircons within a single Late Archaean to Early Paleoproterozoic granulite xenolith (LSC 89) show two zircon types (Type I and Type II). Type I zircons are magmatic and yield older and more variable ages as well as lower initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios that are aligned along a less radiogenic trend. Type II zircons are metamorphic and contain a restricted Proterozoic age distribution, with initial $^{176}\text{Hf}/^{177}\text{Hf}$ lying along a distinct, more radiogenic trend relative to Type I zircon due to the incorporation of additional Hf from the matrix and/or metamorphic silicate phases. Both trends show relatively constant initial $^{176}\text{Hf}/^{177}\text{Hf}$ with time when each trend is considered individually. In rare cases, zircon grains within LSC 89 do not conform to either type and may represent a combination of both. Partial/variable lead loss in zircon via melt-assisted dissolution-recrystallisation within LSC 89 may explain internal age variation and resorption textures as well as highly negative initial ϵ_{Hf} in this xenolith, while the initial $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratios remained unaffected. Uniform O isotopic compositions within grains rules out fluid interaction or alteration during zircon crystallisation/recrystallisation. Zircon REE patterns for all xenoliths are steep and positively sloping with no HREE depletions, despite the presence of garnet (LSC 33). This implies zircon crystallisation before metamorphism in xenolith LSC 33. Other HREE-enriched metamorphic phases appear not to have affected zircon REE characteristics. A negative Eu anomaly in most grains from all xenoliths suggests crystallisation of zircon concomitant with feldspar. LREE together with Eu and Ce anomalies may be variably affected by solid-state recrystallisation. $\delta^{18}\text{O}$ values within LSC 33 and LSC 72 are generally of mantle affinity (4.4–5.7 ‰), therefore protolith melts were derived from a mantle source (initial ϵ_{Hf} in zircon of -2.3 to +3.7) that incorporated minimal amounts of subduction-derived sediment and were likely not strongly metasomatised by slab-derived fluids. Reduced $\delta^{18}\text{O}$ relative to mantle may indicate the interaction of the protolith magma with a

lower $\delta^{18}\text{O}$ reservoir such as seawater. Proterozoic xenoliths (1874 ± 8 Ma, BR 47) with elevated zircon $\delta^{18}\text{O}$ (6.0-7.0 ‰) and unradiogenic initial ϵ_{Hf} (-8.2 to -9.6) represent melt products of subduction-induced melting and metasomatism in the mantle wedge. Older xenolith protolith melts (ca. 2534 Ma, LSC 89), with high $\delta^{18}\text{O}$ (6.4-7.2 ‰) and unradiogenic initial ϵ_{Hf} (up to -17.6), probably originated from mantle sources that experienced subduction-related metasomatism in the Late Archaean or earlier. Based on a suite of representative xenoliths, portions of the lithosphere of the Wyoming Craton were formed through subduction-derived melting and metasomatism during the Proterozoic (1834 ± 19 to 1874 ± 8 Ma), and re-melting of mantle sources in the Late Archaean (2534 ± 9 Ma or older). For mid-Proterozoic xenoliths, a subduction-related petrogenesis is consistent with ocean closure between the Medicine Hat Block and Wyoming Craton at ca. 1834-1874 Ma, followed by ca. 1770 Ma collision-related metamorphism thereafter.

The extent of the lower to middle crust beneath the Wyoming Craton and GFTZ is likely heterogeneous in terms of composition and age (e.g. Mueller et al., 2010; Gifford et al., 2018). Deciphering the mechanisms by which this crustal segment formed and evolved requires further assessment of Proterozoic and Archaean lower crustal samples. The combination of Hf and O isotopes in assessing these processes is essential in differentiating petrogenetic mechanisms, and should be further applied to zircon within temporally and compositionally diverse lower crustal xenoliths. Coupled with new and existing lower crustal data from adjacent blocks (e.g. Medicine Hat Block, Superior Craton, Hearne Craton) a more complete lower to middle crustal geological history can be elucidated for this region of the Laurentian Supercontinent.

5 Coupled U-Pb Geochronology and Major and Trace Element Geochemistry of Apatite in High-Grade Metamorphic Rocks – A Record of Mid- to Lower Crustal Processes beneath the Wyoming Craton, Montana

This section contains the paper entitled “Coupled U-Pb Geochronology and Major and Trace Element Geochemistry of Apatite in High-Grade Metamorphic Rocks – A Record of Mid- to Lower Crustal Processes beneath the Wyoming Craton, Montana” by Thakurdin, Y., Bolhar, R., O’Sullivan, G. and Horváth, P. This manuscript is in the final stages of preparation with intended submission to *Precambrian Research*.

5.1 Abstract

Apatite is a near-ubiquitous accessory mineral with a crystal structure capable of incorporating a variety of trace elements and radiogenic isotopes. This enables apatite to function as a tracer of petrogenetic processes and geo-thermochronological histories within a diverse range of lithologies, including mid- to lower crustal xenoliths. Increasingly more studies use detrital apatite as a provenance tool, complementing zircon and other accessory minerals. However, the trace element systematics of apatite from mid- to lower crust is lacking in the existing literature. In this study, rare earth element (REE) characteristics of apatite from one amphibolite and four granulite xenoliths from the Bearpaw Mountains, Montana (USA) are presented in order to develop insight into apatite trace element processes operating at mid- to lower crustal levels. Apatite in all xenoliths is metamorphic and shows light rare earth (LREE) enrichments relative to heavy rare earth elements (HREE), negative Eu anomalies and generally high concentrations of trace elements. Halogen compositions are uniform and allow classification of the apatites as fluorapatite. Trace element patterns in metamorphic apatite signify progressive prograde metamorphism in which apatite grains continuously exchanged ions with minerals in the system, and acquired trace element concentrations redistributed by newly forming and previously crystallised metamorphic phases. Specifically, as metamorphic grade increases, the break-down of monazite and crystallisation of metamorphic feldspar results in LREE enrichments and Eu depletions in metamorphic apatite respectively. Growth of garnet near the metamorphic peak depletes apatite in HREE. Due to the high metamorphic grade of these rocks, the rock volume is likely to have been in chemical equilibrium, resulting in uniform apatite trace element and halogen concentrations in each xenolith. Grain shapes are euhedral to subhedral and show homogenous internal structure in back-scattered electron (BSE) and cathodoluminescence (CL) images. U-Pb LA-ICP-MS geochronology within apatite on granulite xenoliths yield Neoproterozoic to Palaeozoic (ca.

300-500 Ma) lower-intercept ages on Tera-Wasserburg plots, while a single amphibolite sample records a mid-Proterozoic lower-intercept age (ca. 1600 Ma). Factors complicating U-Pb geochronology in these apatites include low concentrations of uranium and generally high common lead to radiogenic lead ratios. Neoproterozoic to Palaeozoic lower-intercept dates are not correlated with known thermal or metasomatic events within the Wyoming Craton that could have caused isotopic resetting at these times. Rather, these young ages are interpreted to represent protracted slow cooling in the mid- to lower crust following a thermal maximum in the mid-Proterozoic (ca. 1770 Ma), induced by the collision of the Medicine Hat Block and Wyoming Cratons along the boundary of the Great Falls Tectonic Zone (GFTZ).

5.2 Introduction

The near-ubiquitous occurrence of apatite in most rock types (e.g. Piccoli and Candela, 2002) provides a potential tool for monitoring petrological and temporal processes operating at different crustal levels. Development of dating methods and further characterization of apatite trace element chemistry has resulted in an increasing number of studies utilising apatite as a geo(thermo)chronometer (Chew et al., 2015), and as a chemical fingerprint in ore-petrology (Treloar and Colley, 1996; Belousova et al., 2002; Mao et al., 2016) and sedimentary provenance studies (O'Sullivan et al., 2018; Gillespie et al., 2018).

The formation and abundance of apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$) is chiefly governed by the inability of the major rock-forming minerals to incorporate significant P (Piccoli and Candela, 2002). As a result, apatite crystallises in wide variety of lithologies, including mafic rocks that are often devoid of other U-Pb geochronometers, such as zircon (e.g. Tang et al., 2012). REE are incorporated into the apatite crystal structure via coupled substitution reactions into the A-site (Ca-site) of the apatite lattice (e.g. $\text{REE}^{3+} + \text{Na}^+ = 2\text{Ca}^{2+}$) (Pan and Fleet, 2002). Large-ion lithophile (LILE) elements, such as Rb, Cs, Ba and high field strength elements (HFSE), such as Zr and Hf, are incompatible in the apatite structure (Prowatke and Klemme, 2006). The chemistry of apatite relative to its host magma has been previously investigated in igneous rocks (Bea, 1996; Sha and Chappell, 1999; Hsieh et al., 2008; Chu et al., 2009). The concentrations of halogens, Sr, Mn and REE in apatite correlates with the extent of differentiation and crustal-contamination of the host melt. On the other hand, the composition of apatite with regard to isovalent cations and trace elements may be controlled by petrological factors, such as co-existing mineral phases that sequester similar elements (Sha and Chappell, 1999; Belousova et al., 2002). Trace elements compositions in detrital apatite are particularly useful in determining source rock compositions (O'Sullivan et al., 2018). Moreover, using trace elements, it is possible to distinguish magmatic from metamorphic apatite (Henrichs et al., 2018).

Despite its enormous potential for petrological and detrital provenance studies, apatite U-Pb geochronology is complicated by high common lead (Pb_c) concentrations and thus typically requires a Pb_c correction. Application of such correction methods (e.g. ^{207}Pb -correction) has enabled relatively precise and accurate U-Pb dating of apatite from a variety of rock types (Chew et al., 2011; Wohlgemuth-Ueberwasser et al., 2017).

Previous U-Pb zircon dating for the Bearpaw Mountain (Montana, USA) xenolith suite yielded Late Archaean to Palaeoproterozoic ages between 1834 ± 19 and 2534 ± 9 Ma (Thakurdin et al., 2019a). Other high temperature, accessory mineral geochronological studies in the region (U-Pb zircon and monazite) also yield mid-Proterozoic ages (1770-1860 Ma), which are correlated with continental collision and ocean closure along the Great Falls Tectonic Zone (GFTZ) (Mueller et al., 2002, 2005; Roberts et al., 2002, Alcock et al., 2013; Gifford et al., 2014). Ages from low-temperature geochronometers are sparse in this region, however. Proterozoic (1775-1800 Ma) Ar-Ar dates measured within biotite and hornblende from the Little Belt Mountains indicate rapid cooling (Holm and Schneider, 2002). Blackburn et al. (2011, 2012) utilised lower crustal xenoliths from the Sweetgrass Hills and Medicine Hat Block to distinguish between reheating events and slow-cooling mechanisms having affected rutile and titanite grains in rocks along the northern edge of the Wyoming Craton.

5.2.1 Apatite in the lower continental crust

The characterization of apatite from lower crustal lithologies is still relatively scarce, largely due to the preferred utilization of more traditional accessory minerals, such as zircon, monazite, titanite and rutile. Additionally, lower crustal segments are rarely exposed and provide limited opportunities for extensive study.

Bea and Montero (1999) analysed apatite within metapelitic and mafic granulites along a prograde metamorphic sequence within the Ivrea-Verbano Zone of Northern Italy, which represents a traverse across exhumed lower and middle continental crust. REE profiles of apatite showed progressive depletion in HREE with increasing metamorphic grade, attributed to garnet crystallisation in granulite-facies rocks. Apatite Th/U ratios decreased precipitously in high-grade rocks, which was attributed by the authors to melt or fluid extraction.

In the Bergen Arcs, Norway, co-existing apatite, monazite and epidote within retrogressed granulite and amphibolite grade, lower to middle crustal rocks (mangerite and jotunite) were investigated with respect to their REE compositions (Janots et al., 2018). Two populations of apatite were observed in this study, the first population being REE (especially LREE) enriched relative to the second population

of apatite with lower overall REE and LREE. The authors proposed that earlier formed LREE-rich apatite reacted with metasomatic fluids during a granulite facies metamorphic event, resulting in the precipitation of the second LREE poor apatite population. Apatite grains occurring as inclusions within major minerals preserved pre-metasomatic trace element characteristics, demonstrating the effect of grain shielding in preventing trace element redistribution in open-system environments.

Henrichs et al. (2018) investigated apatite with metabasic and metapelitic compositions from a variety of metamorphic rocks. The analysed samples included rocks from low to high metamorphic grades, and showed significant trends linked to peak metamorphic conditions achieved by the samples. In low to medium grade rocks (greenschist and amphibolite), apatite is characterised by very low REE (especially LREE) concentrations, depletion in U and Th, and relatively high concentrations of Pb and Sr. In samples mapped by SEM-EDX and LA-Q-ICPMS, REE and actinides (including Th and U) were mainly hosted by epidote. As a result of high Pb concentrations and low U concentrations, the low and medium grade samples could not be dated using the U-Pb method. However, Henrichs et al. (2018) also analysed several higher-grade orthogneisses and paragneisses from the Peruvian Andes and Paros, Greece. In these samples, apatite was relatively enriched in REEs, and showed concentrations almost indistinguishable from that of apatite crystallised in melts with a large crustal component (e.g. S-type granitoids analysed by Hsieh et al., 2008), apart from the absence of significant Eu-anomalies and extremely low Th/U ratios. Unlike the lower grade samples, the high grade samples analysed by Henrichs et al. (2018) were U-rich and Pb_c poor, and thus provided relatively precise U-Pb ages.

The lower closure temperature (375-550 °C, Schoene and Bowring, 2007; Cochrane et al., 2014) of apatite allows for the interpretation of temperature-time paths when combined with traditionally higher temperature (>600 °C) minerals, such as zircon, titanite and monazite. Such temperature-time paths can be used to elucidate the evolution of lower and upper continental segments by estimating the timing of burial, exhumation and unroofing (Blackburn et al., 2011, 2012; Seymour et al., 2016; Smye et al., 2018). For example, thermal perturbations resulting in partial resetting of rutile, apatite and sphene thermochronometers within granulite facies lower crustal xenoliths allowed for reconstruction of the temperature-time history of the Kaapvaal Craton and off-craton marginal domains in southern Africa (Schmitz and Bowring, 2003). 2σ

In this study, apatite U-Pb geochronology and trace element geochemistry (Th, U, REE) are investigated within a representative suite of mid- to lower crustal amphibolite and granulite xenoliths. Geochronological data on apatite provide information about the lower temperature history of these xenoliths. Combined with high temperature U-Pb analyses on zircon (Chapter 3), this could enable the elucidation of the thermal and geodynamic history of the lower crust in this region. The controls on

U-Pb systematics and trace elements within apatite is also investigated, and is particularly useful since the geochronological and geochemical characteristics of high-grade, lower crustal apatite is scarcely documented in current literature.

5.3 Methods

Apatite grains were obtained from four mafic granulite xenoliths (LSC 33, LSC 72, LSC 75, LSC 89) and one amphibolite xenolith (BR 47). Apatite grains were extracted from xenoliths using standard mineral separation procedures after which they were epoxy-mounted and polished. Back-scattered electron (BSE) and cathodoluminescence (CL) images of apatite were taken using the CAMECA SX-50 electron-microprobe (EPMA) at the University of the Witwatersrand. Once images had been obtained, quantitative EPMA analysis on thin-sections and mounted separates was conducted on all apatite crystals with a minimum of two spots per grain. All elements (Ca, P, Sr, F, Cl, OH) were analysed at a 15 kV accelerating voltage and beam current of 20 nA.

For U-Pb and trace element analyses on apatite, data were acquired using a Photon Machines Analyte Exite 193 nm ArF Excimer laser-ablation system with a Helex 2-volume ablation cell, coupled to an Agilent Technologies 7900 mass spectrometer at Trinity College Dublin in Ireland. Carrier gas (0.4 l/min He) was split between the large exterior sample chamber and the small interior volume wherein the sample is ablated. A small volume of N₂ (ca. 8 ml/min) was also fed into the sample-gas mixture via an in-house signal smoothing device to enhance signal sensitivity and to reduce oxide formation, along with 0.7 l/min Ar nebulizer gas. ²⁰²Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th and ²³⁸U were acquired for U-Pb analyses; all trace elements and U-Pb isotopes were collected in the same analytical session. ⁴³Ca was utilised for internal standardization of element concentrations for apatite. All apatite analyses were acquired using a 47 µm laser spot, a 5 Hz laser repetition rate and a fluence of 3.9 J/cm². For U-Pb dating, the Madagascar natural mineral standard (473.5±0.7 Ma; Thomson et al., 2012) was used as the primary reference material, and the McClure Mountain apatite (523.51±2.09 Ma; Schoene and Bowring, 2006) and Durango apatite (31.44±0.18 Ma; McDowell et al., 2005) were used as secondary standards and processed as unknowns. Madagascar (474±11 Ma, MSWD = 0.40), McClure Mountain (514±13 Ma, MSWD = 0.63) and Durango (30±3 Ma, MSWD = 1.5) apatite standards measured in this study all produce weighted mean ages well within error of the above mentioned ages within reference materials. For trace elements, NIST612 standard glass (Gao et al., 2002) was used as the primary reference material, with Durango apatite used as the secondary trace element standard (Chew et al., 2016). Trace elements measured in standards also produce concentrations within error of reported reference values (Table C2). U-Pb and trace element data was reduced using Iolite software (Paton et al., 2011) in conjunction with VizualAge (Petrus and Kamber, 2012) and VisualAge_UcomPbine (Chew

et al., 2014), which allows for ^{207}Pb common lead corrections in both standards and unknowns. Initial $^{207}\text{Pb}/^{206}\text{Pb}$ (an approximation of ^{207}Pb -based common lead) was estimated using Pb isotope ratios obtained from leached feldspar for each xenolith (Bolhar et al., 2007), together with estimations of initial $^{207}\text{Pb}/^{206}\text{Pb}$ from the evolution curves of Stacey and Kramers (1975) and Kramers and Tolstikhin (1997).

5.4 Results

5.4.1 Petrography and imaging of apatite

The petrography of xenoliths BR 47, LSC 33, LSC 72 and LSC 89 was provided in detail previously (Thakurdin et al., 2019a), so only a brief summary is reported here.

LSC 33 (Granulite)

Plagioclase (70 modal %) and clinopyroxene (10 modal %) dominates this sample, together with minor garnet crystals within a microcrystalline matrix. Accessory rutile (<1 modal %) is dispersed throughout the assemblage. Apatite is not abundant (<1 modal %) and occurs as inclusions within plagioclase grains, at the interface between clinopyroxene and plagioclase, and rarely as inclusions within clinopyroxene crystals. Grains show a well-developed, prismatic shape and vary in size from 100 to 150 microns measured parallel to the c-axis (Fig. 5.1a, b). BSE imaging shows homogenous grains devoid of mineral inclusions and internal structures.

LSC 72 and LSC 75 (Granulite)

Mineral abundances of plagioclase and clinopyroxene within these two xenoliths vary from 55-85 modal % and 10-40 modal %, respectively. In thin-section, apatite (<0.5 modal %) appears included within plagioclase grains as small (100-125 μm) crystals together with zircon. Grain edges are slightly curved, but the majority of apatite show euhedral to subhedral crystal symmetry. In BSE, apatite is homogenous and devoid of mineral inclusions (Fig. 5.1c, d). Abundant pitting and fractures are observable within grain interiors in these samples.

LSC 89 (Granulite)

This xenolith consists predominantly of plagioclase (85 modal %) and clinopyroxene (15 modal %), with minor sulphides and opaque phases (<1 modal %). Abundant apatite (~1 modal %) appears as euhedral or stubby subhedral grains within plagioclase. Grain sizes are slightly more variable in this xenolith (100-150 μm) and contain rare elongated grains up to 200 μm (Fig. 5.1e-f). In BSE, the grains show homogenous interiors with very rare instances of bright inclusions, along with interior pitting and cracks that cut across the short axis of grains.

LSC 93 (Granulite)

Plagioclase (55 modal %), clinopyroxene (5 modal %) and garnet (45 modal %) make up the major minerals in this sample. These compositions vary within discrete bands to create a layered texture. Other accessory minerals include abundant (1-2 modal %) coarse rutile grains. Apatite grains (<1 modal %) occur as euhedral to subhedral crystals within plagioclase, and very rarely as inclusions within clinopyroxene. Grain sizes are small and vary from 50-100 μm , although some larger grains are also present (150 μm) (Fig. 5.1g). In BSE, grain interiors are homogenous, albeit highly pitted and cracked. Exterior grain morphology shows slight resorption in a few grains, however, the majority have straight boundaries and euhedral shapes.

BR 47 (Amphibolite)

This sample consists of hornblende (85 modal %), minor biotite and plagioclase (15 modal %). Accessory brown/red rutile (<1 %) is rare in this xenolith. Apatite (<1 modal %) occurs as well-defined, euhedral grains within hornblende crystals. Grain sizes are small and encompass a narrow range between 100 and 125 μm measured parallel to the c-axis (Fig. 5.1h). In BSE, the grains appear homogenous, although interiors show abundant pitting and cracks. Bright mineral inclusions are rare to absent in most grains.

5.4.2 Major Element and Halogen Chemistry

Major and trace element geochemistry for these xenoliths are listed in Table 5.1. Average major oxides (Ca, P) and halogens (F, Cl, OH) within apatite are listed in Table 5.2 and illustrated on ternary plots (Fig. 5.2a, b). All grains are classified compositionally as fluorapatite (F = 3.5-4 wt%) with only minor chlorine abundances (Cl = 0.02-0.60 wt%) and contain no OH (Table C1). Halogen ternaries bear similarity to apatite from amphibolite and granulite facies rocks (Spear and Pyle, 2002). The consistency of Ca (51-54 wt%) and P (39-42 wt%) are indicative of uniformity in oxide compositions both within grains and between samples.

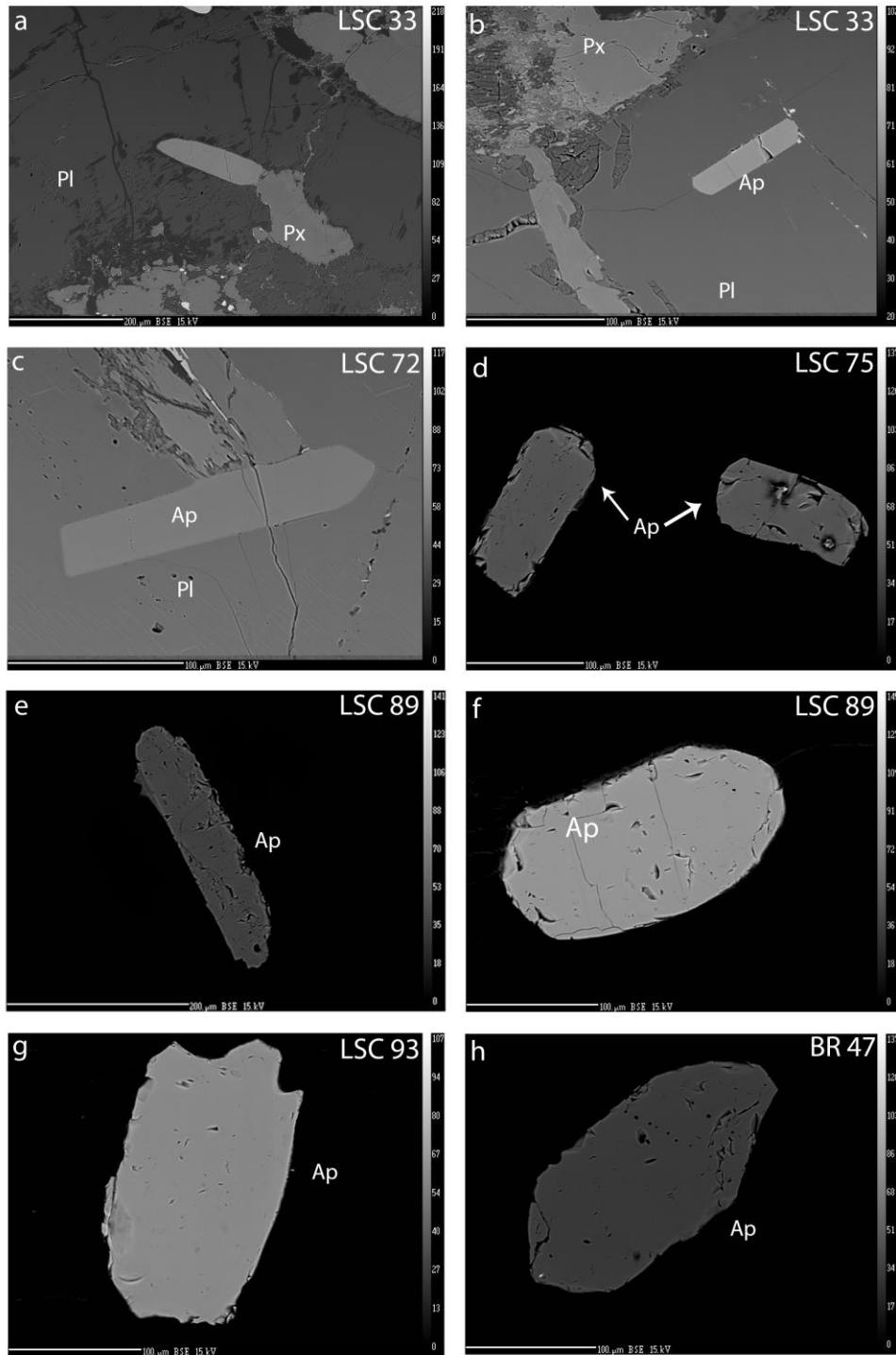


Figure 5.1: Back-scattered electron (BSE) images of apatite in situ within granulite xenoliths LSC 33 (a-b) and LSC 72 (c). Separated BSE images of apatite from granulite LSC 75 (d), LSC 89 (e-f), and LSC 93 (g) and amphibolite BR 47 (h) are also shown. Grains are euhedral prismatic (a-c) or stubby (d,f) and have uniform emittance. Internal microstructures and mineral inclusions are absent. Ap = apatite, Px = pyroxene, Pl = plagioclase.

5.4.3 U-Pb geochronology and trace element chemistry of apatite

Various methods enable for correction of generally high common lead (or initial $^{207}\text{Pb}/^{206}\text{Pb}$) in apatite. A frequently used procedure is to assume an initial Pb ($^{207}\text{Pb}/^{206}\text{Pb}$) composition from an existing terrestrial Pb-evolution model (e.g. Stacey and Kramers, 1975) at a measured crystallisation age for the rock (assuming apatite is igneous and is an early crystallizing phase). Alternatively, common lead can be estimated from a co-crystallizing igneous phase, such as feldspar, which incorporates low levels of radiogenic Pb and no uranium (Schoene and Bowring, 2007; Chew et al., 2011). In some cases, a population of co-genetic apatite grains with differing common and radiogenic Pb compositions may lie along an unanchored discordia curve with low MSWD's, such that an initial $^{207}\text{Pb}/^{206}\text{Pb}$ correction is not required (e.g. Henrichs et al., 2018). Thomson et al. (2012) and Schoene and Bowring (2006) noted that the effectiveness of correcting through the Stacey and Kramers (1975) model (or any Pb evolution curve) decreases with increasing proportions of common lead in apatite. Therefore, initial $^{207}\text{Pb}/^{206}\text{Pb}$ deduced using Pb isotopes from leached feldspars (Bolhar et al., 2007) is applied, in addition to estimates of initial lead from Pb evolution models of Stacey and Kramers (1975) (SK75: $^{207}\text{Pb}/^{206}\text{Pb} = 0.9972$) and Kramers and Tolstikhin (1997) (KT97: $^{207}\text{Pb}/^{206}\text{Pb} = 0.9012$) at 1880 Ma. The age of xenoliths is taken from the most common, concordant magmatic population age (1880 Ma) derived from zircon geochronology on these samples (Thakurdin et al., 2019a). Initial $^{207}\text{Pb}/^{206}\text{Pb}$ measured in leached feldspars for each xenolith are given in Table 5.2. Although CL imagery does not reveal core-rim micro-textures, multiple spots on apatite grains were analysed within central and marginal domains and are referred to as “cores” and “rims” respectively. Europium (Eu/Eu^*)_N and cerium (Ce/Ce^*)_N anomalies are quantified using equations $\frac{\text{Eu}}{\sqrt{\text{Sm} \times \text{Gd}}}$ and $\frac{\text{Ce}}{\sqrt{(2\text{Pr} - 1\text{Nd})}}$ where Eu^* and Ce^* are $(\sqrt{\text{Sm} \times \text{Gd}})$ and $(\sqrt{2\text{Pr} - 1\text{Nd}})$ respectively. Ce is calculated by extrapolation using Pr and Nd to avoid potential overestimation of cerium due to variable La concentrations (Bolhar et al., 2004).

LSC 33 (Granulite)

Fourteen spots on eight apatite grains were measured in this sample. An unanchored discordia curve through seven core domains yields a lower-intercept age of 434 ± 170 Ma (MSWD = 6.9) on a Tera-Wasserburg (TW) plot (Fig. 5.3a). An unanchored discordia curve through rim domains produces a similar but highly imprecise age of 426 ± 350 Ma (MSWD = 21). Anchoring using estimations of initial $^{207}\text{Pb}/^{206}\text{Pb}$ through core domains yields ages of 439 ± 110 Ma (MSWD = 7.6) (SK75), 388 ± 94 Ma (MSWD = 5.8) (KT 97) and 376 ± 96 Ma (MSWD = 6.1) (feldspar). The highest precision lower-intercept age is obtained from the unanchored regression (through core domains), although utilising feldspar and/or Pb evolution curves for estimations of common lead results in similar ages that overlap within errors. Chondrite-normalised patterns in this xenolith are generally uniform in terms of LREE ($\text{La}_N/\text{Sm}_N = 0.9$ -

2.8) but contain highly variable and depleted HREE ($Gd_N/Yb_N = 3.6-216.7$) (Fig. 5.3b). A ubiquitous negative Eu anomaly ($Eu_N/Eu_N^* = 0.3-0.8$) is observed. U (0.2-8 ppm, $\bar{x} = 2.4$ ppm) and Th (8.6-15.8 ppm, $\bar{x} = 1.1$ ppm) contents are low in this xenolith.

LSC 72 (Granulite)

Nineteen spots within ten apatite grains produce a scatter in ages that cannot be regressed to a lower-intercept date (Fig. 5.3c). Unanchored discordia curves through exclusively core or rim domains do not increase the precision of regressions in this sample. Additionally, no statistically meaningful regressions through core/rim domains using initial $^{207}Pb/^{206}Pb$ derived from Pb evolution models or leached feldspar Pb isotopes could be obtained. Apatite within this xenolith shows uniform trace element patterns with LREE enriched relative to HREE ($La_N/Yb_N = 15.3-49.4$), together with a moderate to strong negative Eu anomaly ($Eu_N/Eu_N^* = 0.3-0.5$) (Fig. 5.3d). U (2.7-10.0 ppm, $\bar{x} = 5.5$ ppm) and Th (6.8-36.3 ppm, $\bar{x} = 1.4$ ppm) concentrations are low and variable in this sample.

LSC 75 (Granulite)

Thirty-nine spots on twenty-six core and rim domains were analysed (Fig. 5.3e). This xenolith contains extremely high $^{207}Pb/^{206}Pb$ (>1) in all domains, the result being that discordia curves anchored for initial lead, either from Pb models or feldspar, cannot be regressed through these data points. An unanchored regression through both domains yields a lower-intercept age of 837 ± 120 Ma with large scatter (MSWD = 99) and is considered as a spurious or mixed age without geological significance. Trace element patterns for apatite grains are uniform (Fig. 5.3f), with LREE enrichment relative to HREE ($La_N/Yb_N = 0.4-36.5$) and a pronounced negative Eu anomaly ($Eu_N/Eu_N^* = 0.1-0.3$). U (0.3-9.5 ppm, $\bar{x} = 2.7$ ppm) and Th (0.02-12.2 ppm, $\bar{x} = 1.07$ ppm) concentrations are extremely low in this xenolith.

LSC 89 (Granulite)

Four spots (two rim domains and two core domains) on three grains (with one grain excluded) produces an unanchored TW lower-intercept age of 565 ± 79 Ma (MSWD = 1.03) (Fig. 5.3g). Lower-intercept ages of 578 ± 67 Ma (MSWD = 1.05) (SK75), 425 ± 240 Ma (MSWD = 4.5) (KT97) and 397 ± 270 Ma (MSWD = 5.7) (feldspar) yield less precise regressions through both core and rim domains, therefore the unanchored discordia is assumed to best represent the age of apatite in this sample. Low MSWD's may be the result of few analysed spots on these samples, therefore lower intercept ages are only tentatively assumed to be geologically significant. Chondrite-normalised trace element patterns are variable (Fig. 5.3h). Two grains are HREE enriched relative to LREE ($La_N/Yb_N = 0.1-0.2$), while the remaining apatite is LREE enriched relative to HREE ($La_N/Yb_N = 1.5-2.0$). A negative Eu

anomaly is observed within all grains ($Eu_N/Eu_N^* = 0.1-0.3$), and Th (0.03-3.4 ppm, $\bar{x} = 3.2$ ppm) and U (1.27-7.4 ppm, $\bar{x} = 4.2$) concentrations are generally very low.

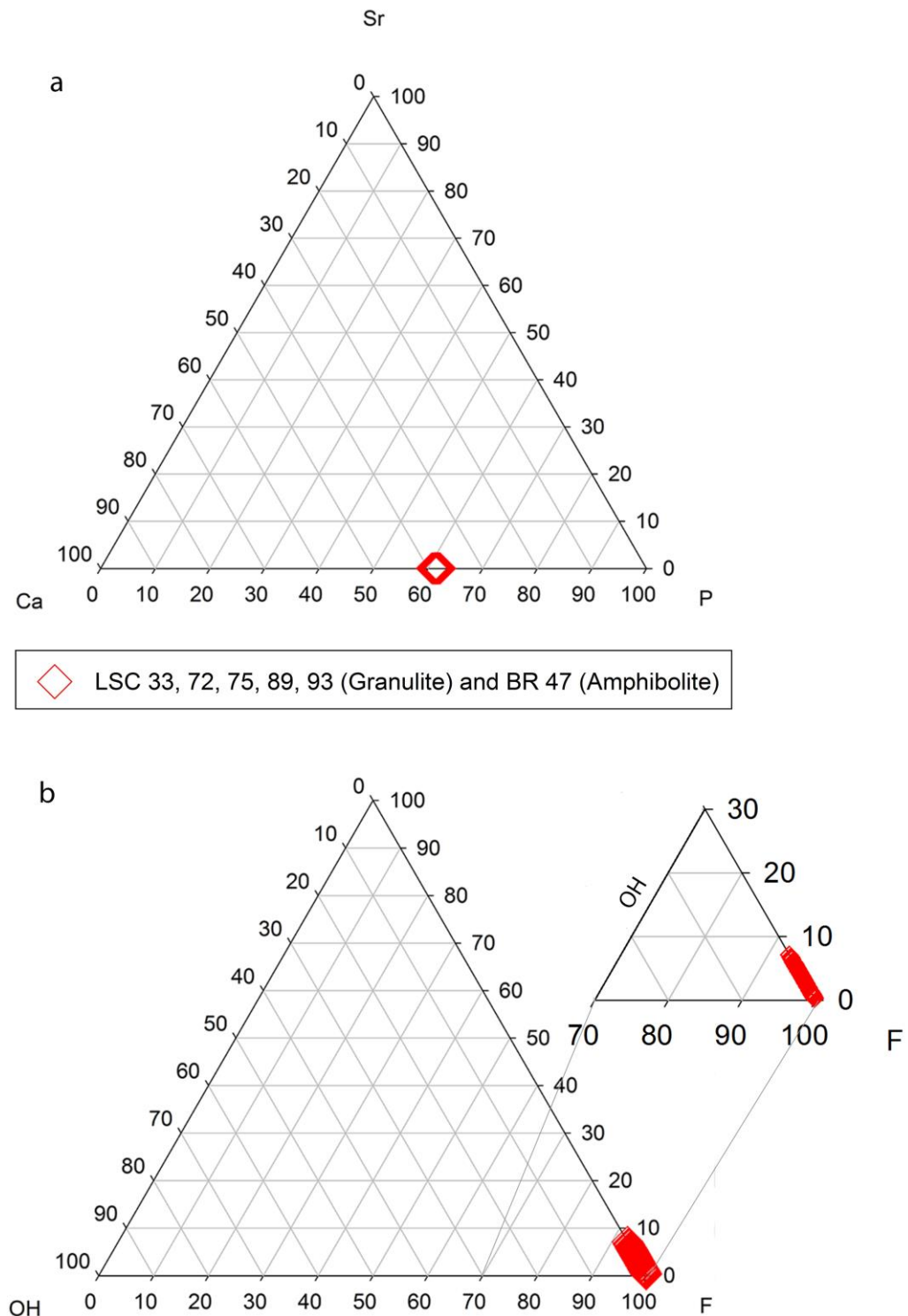


Figure 5.2: Normalised apatite compositions showing primary cations (a) and halogens (b).

Table 5.1: Major (wt%) and trace-element abundances for amphibolite and granulite xenoliths from the Bearpaw Mountains

	Amphibolite	Granulite	Granulite	Granulite	Granulite	Granulite
	BR 47	LSC 33	LSC 72	LSC 75	LSC 89	LSC 93
SiO ₂	51.19	52.95	52.96	52.40	56.96	55.77
TiO ₂	0.99	2.09	0.44	0.06	1.20	0.40
Al ₂ O ₃	12.17	22.60	25.44	28.17	16.23	19.86
K ₂ O	1.40	1.22	0.66	2.27	1.87	0.89
T-Fe ₂ O ₃	8.14	3.90	4.12	3.08	9.30	9.43
MnO	0.13	0.06	0.05	0.05	0.15	0.15
MgO	11.70	2.09	2.14	3.17	4.36	6.31
CaO	10.59	10.02	10.72	11.52	7.48	6.58
Na ₂ O	2.56	5.08	4.75	3.51	4.39	4.86
P ₂ O ₅	0.08	0.20	<0.001	<0.001	0.05	0.05
<i>Total</i>	98.95	100.22	101.29	104.22	101.98	104.28
Li	4	7	5	5	13	8
Be	1	1	1	1	2	1
Sc	42	6	9	3	22	19
Ti	6096	2616	3003	285	2660	1558
TiO	0.00	0.00	0.00	0.00	0.00	0.00
V	270	62	102	16	125	107
Cr	815	22	68	14	62	109
Co	46	12	17	14	18	38
Ni	137	16	29	42	34	67
Cu	13	13	11	7	10	25
Zn	108	49	47	36	76	142
Ga	13	18	20	18	23	15
As	2	3	1	0.5	1	1
Rb	73	81	29	80	38	29
Sr	267	734	602	1332	1068	444
Y	14	7	7	1	32	8
Zr	54	127	13	9	12	22
Nb	4	3	4	1	4	1
Mo	0.2	0.3	0.4	0.3	0.5	0.2
Cd	0.1	0.1	0.0	0.0	0.2	0.1
Sn	2	1	0.4	0.2	0.1	0.1
Sb	0.0	0.1	0.0	0.0	0.0	0.0
Cs	48	28	13	5	7	44
Ba	698	954	488	1034	2299	334
La	25	42	8	5	22	4
Ce	57	83	17	10	42	8
Pr	8	9	2	1	5	1
Nd	32	33	8	3	22	5
Sm	6	5	2	0.4	6	1
Eu	2	1	1	0.5	1	1
Tb	0.6	0.4	0.2	0.0	1	0.2
Gd	5	3	1	0.2	6	1
Dy	3	2	1	0.1	6	1
Ho	0.6	0.3	0.3	0.0	1	0.3
Er	1.4	1	1	0.1	4	1
Tm	0.2	0.1	0.1	0.0	1	0.1
Yb	1	1	1	0.1	3	1
Lu	0.2	0.1	0.1	0.0	0.4	0.2
Hf	2	3	0.4	0.2	0.5	1
Ta	0.3	0.2	0.2	0.0	0.2	0.0
W	0.2	0.2	0.1	0.1	0.0	0.1
Tl	0.4	1	0.3	0.4	0.2	0.4
Pb	5	8	4	8	11	4
Th	2	4	0.1	0.2	0.2	0.03
U	0.4	1	0.04	0.1	0.2	0.04
LOI	0.0	0.0	0.0	0.0	0.0	0.0
(La/Yb) _N	14.7	50.5	7.4	42.1	4.8	2.5
(La/Sm) _N	2.4	5.2	3.0	8.5	2.5	2.1
(Gd/Yb) _N	3.5	954.5	1.6	2.2	1.5	0.9
(Eu/Eu*) _N	0.8	1.1	2.2	4.7	0.7	1.5
(Ce/Ce*) _N	1.0	1.0	1.0	1.0	0.9	1.0

Table 5.2: Average Majors and Halogens in Apatite from Amphibolite and Granulite Xenoliths and Pb Isotope Compositions from Leached Feldspars

	BR 47	LSC 33	LSC 72	LSC 75	LSC 89	LSC 93
	Amphibolite	Granulite	Granulite	Granulite	Granulite	Granulite
CaO	52.61	54.49	52.50	54.10	50.78	52.76
SrO	0.05	0.00	0.02	0.01	0.02	0.02
P ₂ O ₅	41.46	39.62	41.68	39.25	40.37	41.83
F	4.09	3.84	4.09	3.66	3.98	4.09
Cl	0.28	0.26	0.10	0.21	0.40	0.08
OH	0.00	0.00	0.00	0.00	0.00	0.00
Feldspar						
²⁰⁷ Pb/ ²⁰⁴ Pb	15.501	15.571	15.407	15.303	15.477	14.742
²⁰⁶ Pb/ ²⁰⁴ Pb	17.49	17.785	16.056	16.466	17.49	14.605
Calculated Initial ²⁰⁷ Pb/ ²⁰⁶ Pb	0.8863	0.8751	0.9596	0.9294	0.8849	1.0094

LSC 93 (Granulite)

A discordia curve through six core domains produces an unanchored lower-intercept age of 531±130 (MSWD = 13) (Fig. 5.3i). Despite large uncertainty, this age is broadly consistent with ca. 500 Ma apatite ages from xenoliths LSC 33 and LSC 89. Anchored discordia curves through core domains produce lower-intercept of ages of 582±38 Ma (MSWD = 13)(SK75) and 510±42 Ma (MSWD = 13)(KT97), while an anchored regression using initial ²⁰⁷Pb/²⁰⁶Pb derived from Pb in feldspar yields a similar lower-intercept age of 590±39 Ma (MSWD = 13). Trace element patterns are dispersed (La_N/Yb_N = 1.2-886.8) (Fig. 5.3j). As with LSC 33, notable HREE depletion is observed in most grains (Gd_N/Yb_N = 2.9-137.9). LREE are also variable with the majority of apatites being LREE enriched (La_N/Sm_N = 0.3-4.1), while Eu anomalies are negative (Eu_N/Eu_N* = 0.1-0.9). Th (0.2-10.4, $\bar{x}$ = 9.7 ppm) is somewhat enriched relative to other granulites, while U is depleted and variable (2.0-14.5 ppm, $\bar{x}$ = 2.2 ppm).

BR 47 (Amphibolite)

A discordia curve through six spots within core domains produces a lower-intercept age of 1663±47 Ma (MSWD = 20) when anchored for common lead using the Stacey and Kramers (1975) Pb evolution model (Fig. 5.3k). This mid-Proterozoic age is broadly consistent with magmatic U-Pb zircon ages (1874±8 Ma) from the same xenolith, and metamorphic zircon ages (1772±5 Ma) from granulite xenoliths (Thakur et al., 2019a). Initial ²⁰⁷Pb/²⁰⁶Pb derived from the evolution model of Kramers and Tolstikhin (1997) yields a lower-intercept age of 1619±45 (MSWD = 19), while initial ²⁰⁷Pb/²⁰⁶Pb derived from feldspar yields a lower-intercept age of 1607±49 (MSWD = 19). The ratios of initial lead do not vary considerably, resulting in similar (ca. 1600 Ma) lower-intercept ages that overlap within errors. Apatite grains within amphibolite are uniformly enriched in LREE over HREE (La_N/Yb_N = 3.4-92.3). HREE are slightly depleted (Gd_N/Yb_N = 3.5-7.5) in all grains while a small negative Eu anomaly (Eu_N/Eu_N* =

0.6-0.8) is observed (Fig. 5.3I). Th (0.94-151 ppm, $\bar{x}$ = 93.6 ppm) and U (2.2-49 ppm, $\bar{x}$ = 28.5 ppm) are enriched compared to granulite xenoliths.

5.5 Discussion

5.5.1 Magmatic versus metamorphic apatite

A first-order determination of magmatic versus metamorphic crystallisation can be made using apatite morphology and internal structures. Apatite in all samples generally appear as prismatic, euhedral grains suggestive of growth in a melt (Corfu and Stone, 1998; Piccoli and Candela, 2002; Kirkland et al., 2017). Apatite morphology may not be diagnostic, however, since dissolution and reprecipitation of apatite may result in recrystallised grains with a euhedral morphology similar to that of igneous grains (Harlov, 2015). Internal microstructures (such as oscillatory and sector zoning) are also indicative of igneous crystallisation (e.g. Zirner et al., 2015) but no such features are observed in BSE images. The low cathodoluminescence of these grains (likely due to low concentrations of Th and U) results in dark, uniform domains.

Trace element patterns can also be used to distinguish between magmatic and metamorphic apatite. Igneous apatite is typically LREE enriched and contains a pronounced negative Eu anomaly together with high abundances of rare earth elements (O'Sullivan et al., 2018). Metamorphic apatite compositions are generally more variable, and differ according to rock type and metamorphic grade (Bingen et al., 1996; Bea and Montero, 1999; Abdullin et al., 2016; Henrichs et al., 2018). Low to medium grade metamorphic apatite contains lower Th, LREE and overall REE abundances when compared to magmatic apatite. The depletion of LREE is attributed to the growth of co-existing epidote that sequesters these elements preferentially over apatite (Henrichs et al., 2018). In contrast, high-grade metamorphic apatite has been demonstrated to possess trace element compositions almost indistinguishable from that of igneous apatite found in granitic lithologies (e.g. Henrichs et al., 2018). Trace element patterns of igneous apatite from granitic rocks (Sha and Chappell, 1999; Belousova, 2002; Hsieh et al., 2008) as well as metamorphic apatite from high grade lithologies (stromalites: Bea and Montero, 1999; orthogneiss and paragneiss: Henrichs et al., 2018) are plotted alongside apatite compositions from Bearpaw xenoliths (Fig. 5.3, b-l), in order to compare and evaluate magmatic/metamorphic REE characteristics in these apatites relative to apatite in various host rocks from known literature.

Xenoliths LSC 72 and LSC 75

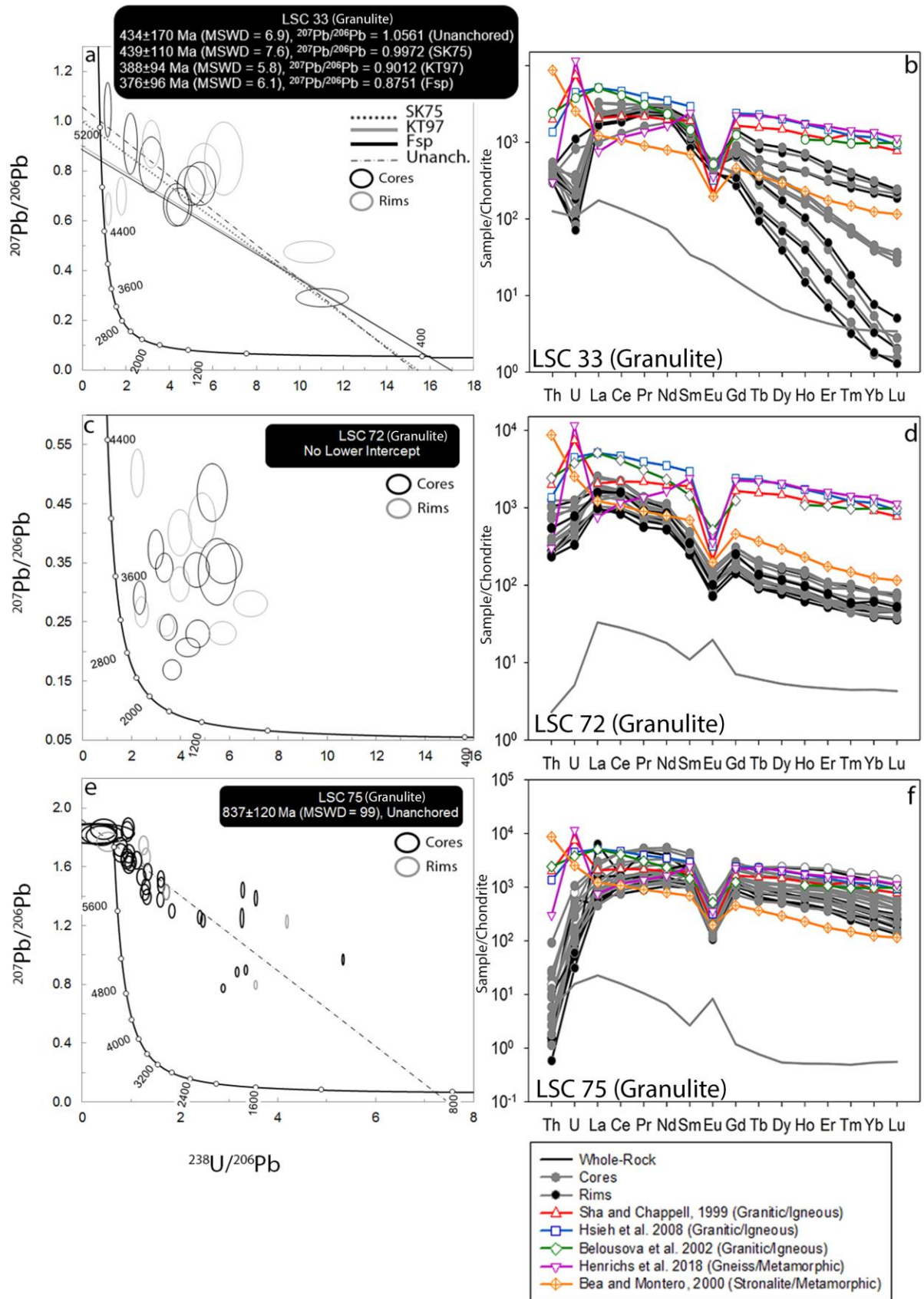
Within these two xenoliths, LREE enrichments relative to HREE, together with a strong negative Eu anomaly bear similarity to igneous apatite patterns from granitic lithologies (Sha and Chappell, 1999;

Belousova et al., 2002; Hsieh et al., 2008) (Fig. 5.3d-f). LSC 72 appears somewhat depleted in REE, but shows a similar overall pattern to apatite within granitic rocks.

Although apatite compositions appear similar to granitic igneous apatite, it has been demonstrated that melt-precipitated apatite is not stable under high-grade metamorphic conditions. More specifically, Nutman (2007) demonstrated using textural characteristics and grain size that apatite undergoes dissolution-recrystallisation and regrowth as metamorphism progresses from greenschist to granulite facies conditions. Additionally, since REE diffusion in apatite begins at approximately 650 °C (Cherniak, 2000), it is unlikely that apatite will keep original igneous trace element compositions under conditions of high-grade metamorphism. Halogens (F, Cl, OH) are also considered to be mobile to temperatures as low as 400 °C (Brenan, 1993) and therefore also cannot retain original igneous abundances at high pressures and temperatures. Therefore, since our xenoliths are of amphibolite to granulite facies (642-817 °C, 3.5-7.5 kbar), an alternate mechanism for explaining seemingly igneous trace elements and constant halogen compositions in our apatite grains is required.

Since the xenolith suite is metamorphic, recrystallisation and consumption of mineral phases during progressive metamorphism may be responsible for trace element compositions observed in apatite grains. To begin, apatite crystallises from a melt and acquires a trace element composition controlled by the protolith magma. Shortly after initial apatite crystallisation, the onset of metamorphism destabilises apatite grains, which allows apatite to exchange ions between co-existing and newly forming phases in the system. Co-existing minerals may also become unstable/break down as metamorphism progresses, releasing elements that may be incorporated into apatite.

However, some mechanism is required to explain how apatite can exchange ions/elements/atoms with other phases in the system during metamorphism. Continuous exchange of atoms between apatite and co-existing/newly forming phases may be enabled by repeated dissolution-reprecipitation of apatite in a metamorphic fluid as metamorphism progresses. Alternatively, a diffusion process operates, in which elements are exchanged between components within the system in the solid-state. Either process is possible, however, since the metamorphic transition of rocks from the igneous protolith to amphibolite-granulite facies may have involved multiple dehydration reactions, it is likely that metamorphic fluids were present, and allowed for continuous dissolution and reprecipitation of apatite during progressive metamorphism. Regardless of which mechanism operates, apatite cannot retain its original igneous composition (ie: its trace element composition is reset) (Bingen et al., 1996).



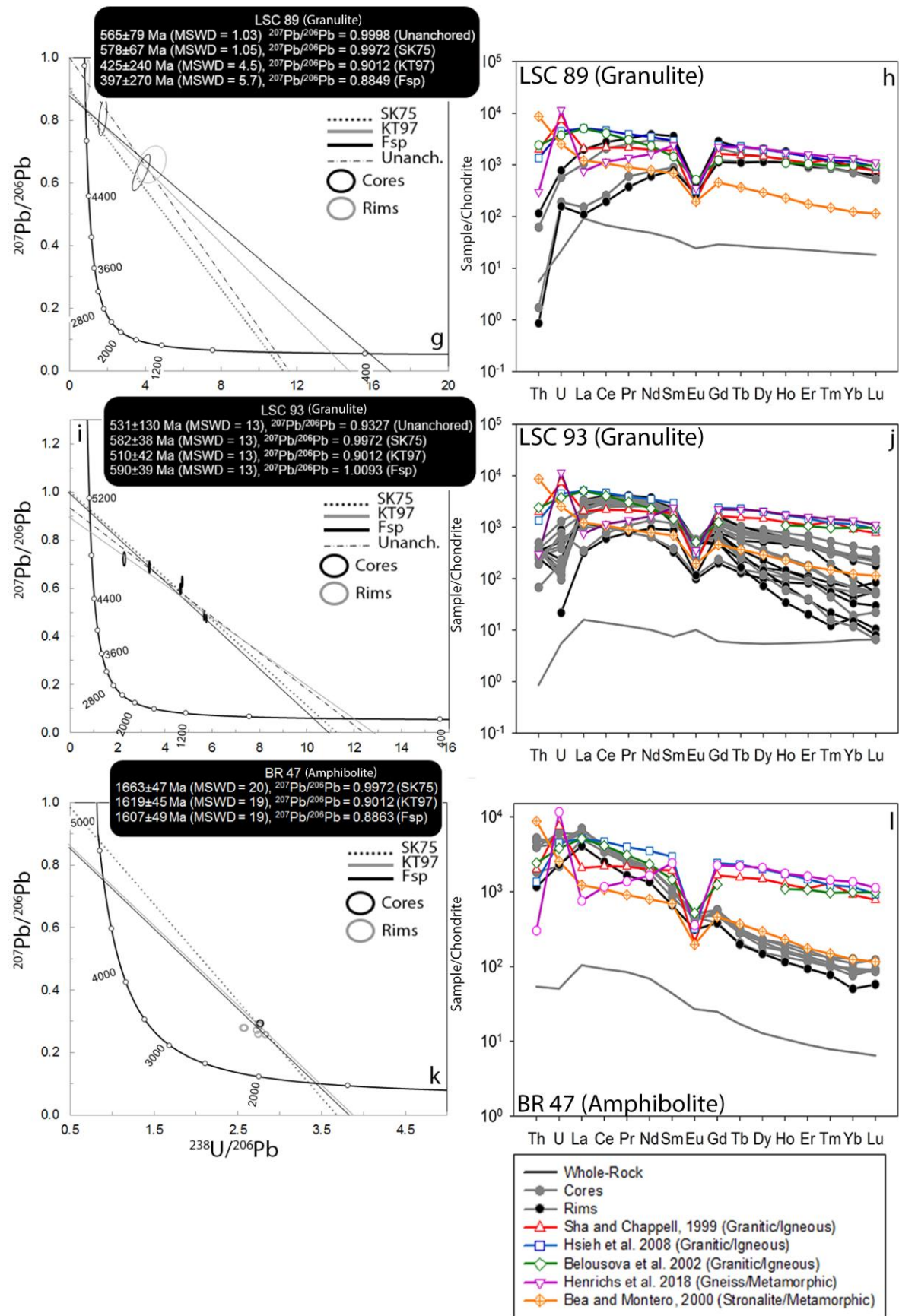


Figure 5.3: Tera-Wasserburg Concordia plots for granulite LSC 33 (a), LSC 72 (c), LSC 75 (e), LSC 89 (g), LSC 93 (i) and amphibolite BR 47 (k). Discordia curves regressed through data points using initial $^{207}\text{Pb}/^{206}\text{Pb}$ inferred from Pb evolution models: Stacey and Kramers (1975) (SK75) and Kramers and Tolstikhin (1997) (KT97), and calculated from feldspar (Fsp) for each xenolith. Chondrite-normalised trace element patterns of apatites and whole-rocks (grey/black patterns) for granulite LSC 33 (b), LSC 72 (d), LSC 75 (f), LSC 89 (h), LSC 93 (j) and amphibolite BR 47 (l). Igneous apatite chondrite-normalised patterns from I-Type and S-Type granites (Sha and Chappell, 1999; Belousova et al., 2002; Hsieh et al., 2008), and a representative metamorphic apatite from stromalite (Bea and Montero, 1999) and high-grade orthogneiss and paragneiss (Henrichs et al., 2018) are shown for comparison. Chondritic values are normalised using C1-chondrite (McDonough and Sun 1995).

In the course of increasing pressure-temperature conditions, new LREE metamorphic phases such as monazite and/or allanite become stable. Nearing granulite facies conditions, however, monazite and/or allanite begin to break down, releasing LREE into the system that is then taken up by apatite. In this way, apatite becomes increasingly LREE enriched with increasing metamorphic grade. The negative Eu anomaly in apatite can be explained by metamorphic feldspar crystallisation in equilibrium with apatite. As temperature increases, feldspar becomes enriched in Ca^{2+} , which readily substitutes for Eu^{2+} . Therefore, as feldspar becomes more Ca-rich at higher temperatures, it sequesters increasing concentrations of Eu, resulting in progressively lower negative Eu anomalies in apatite. Additionally, as metamorphism progresses the breakdown of biotite releases F, resulting in an increasing stability of fluorapatite at higher temperatures (Bingen et al., 1996). Finally, once metamorphism is complete, and monazite has been consumed, LREE are incorporated into apatite (now stable and fully recrystallised). This recrystallised and/or re-equilibrated apatite is referred to as metamorphic apatite. Since metamorphic apatite is the only remaining accessory mineral that can incorporate the lighter rare earth elements in these rocks, most of LREE are sequestered into this phase. At this point, metamorphic apatite has gained LREE and lost Eu such that it is indistinguishable from igneous apatite patterns of Sha and Chappell (1999), Belousova et al. (2002) and Hsieh et al. (2008) (Fig. 5.3b-l). Such a process may explain the depleted “igneous” trace element patterns observed in xenoliths LSC 72 and LSC 75. It is also notable that metamorphic apatite from high-grade stromalites (Bea and Montero, 1999) and paragneisses and orthogneisses (Henrichs et al., 2018) show similar patterns to metamorphic apatite from the Bearpaw Mountains (Fig. 5.3b-l), and attests to similar processes of apatite formation.

Since a process of continuous dissolution-reprecipitation/diffusion of apatite is required to explain the formation of metamorphic apatite in granulite xenoliths, some mechanism must account for the almost constant halogen compositions and nearly uniform trace element patterns in these apatites. During low-grade metamorphism, the chemical composition of the rock body is unlikely to be homogeneously equilibrated, therefore apatite trace element and halogen concentrations are variable

due to differing environments in which apatite forms (Nutman, 2007; Henrichs et al., 2018). During high grade-grade metamorphism, however, the rock volume is likely to have been in chemical equilibrium, resulting in uniform halogen and trace element chemistry throughout the system. This results in metamorphic apatite containing similar REE and halogen concentrations with negligible intra-sample variability. Apatites showing uniform trace element patterns that previously underwent dissolution-recrystallisation as a result of progressive metamorphism was reported by Nutman (2007). Additionally, high grade metamorphic apatites in prograde metamorphic sequences show similarly uniform trace element patterns, attributed to large scale chemical equilibrium of apatite in metamorphic rocks (Bingen et al., 1996; Bea and Montero, 1999). Once metamorphism is complete, the trace element patterns and halogen compositions are locked into newly recrystallised metamorphic apatite. The uniform trace elements in metamorphic apatite imply that no fluid-aided /metasomatic events (that would modify trace element patterns) occurred after metamorphic apatite had stabilised.

With regards to halogen compositions, apatites in our xenoliths are all fluorapatite. Fluorine is heavily partitioned into apatite in metamorphic rocks, presumably due to halogen exchange with minerals such as biotite (Harlov, 2015). It has also been shown experimentally that fluorine preferentially incorporates into apatite at high temperatures (Dong, 2005). Increasing F abundances stabilises the apatite crystal structure and thus results in stable fluorapatite formation at high-grade metamorphic conditions. Once granulite facies metamorphism is complete and cooling commences, the halogen composition in apatite will be retained, even in the case of protracted slow cooling (see below), provided the initial cooling rate is rapid and no post-metamorphic, externally derived fluids interact with the apatite crystal (Brenan, 1993). Therefore it is likely that our xenoliths contain metamorphic fluorapatite which supports the above mentioned process of metamorphic apatite crystallisation. The constant halogen composition of these apatites further suggests that ions were equilibrated throughout the system, and did not interact with externally derived fluids post-metamorphic apatite crystallisation.

A similar scenario was observed within apatite in orthogneiss from the Sveconorwegian province in southwest Norway, in which apatite grains became increasingly REE enriched with metamorphic grade due to release of M-REE, Th-LREE and F via the breakdown of hornblende, biotite, monazite and allanite (Bingen et al., 1996). Increasing REE enrichment in metamorphic apatite with metamorphic grade was also reported by Bea and Montero et al. (1999) within metapelites of the Kinzigite Formation from the Ivrea-Verbano Zone in Italy (see “stronalite” Fig. 5.3b-l). Within metapelitic rocks from the Cooma Complex (SE Australia), apatite was also interpreted to grow and recrystallise during progressive metamorphism from greenschist to granulite facies (Nutman, 2007). Finally, high-grade

paragneisses and orthogneisses from Paros, Greece and the Peruvian Andes, that underwent dissolution-precipitation during anatexis, show similar LREE enriched “igneous” apatite trace element patterns (see “gneiss”, Fig. 5.3b-l; Henrichs et al., 2018).

LSC 33 and LSC 93

Xenoliths LSC 33 and LSC 93 are garnet containing as evidenced by depleted HREE compositions in apatites (Fig. 5.3b,j) and petrographic observations. Although HREE appear variably depleted on normalised trace element plots, absolute concentrations of HREE ($\Sigma\text{HREE} = 47\text{--}729$ ppm) are depleted relative to granitic igneous apatite grains ($\Sigma\text{HREE} = 501\text{--}5078$ ppm), suggesting a single population of HREE depleted metamorphic apatite grains. In LSC 72 and LSC 75 originally igneous apatite is continually dissolved and reprecipitated and equilibrates with newly forming LREE rich and Eu fractionating phases during progressive metamorphism (see above). However, at the peak of metamorphism, garnet is now forming which preferentially sequesters the heavy rare earth elements. This results in the observed HREE depletions in apatite within these two xenoliths. Garnet bearing influence on apatite trace element concentrations with increasing metamorphic grade was likewise reported by Bea and Montero (1999).

Xenolith LSC 89

Two grains within this sample are extremely Th-LREE enriched suggestive of inclusion sampling in this grain (likely monazite). The remaining two apatite spots are LREE depleted relative to HREE. A similar scenario of apatite dissolution-recrystallisation and re-equilibration due to high grade-metamorphism (described above) likely occurs. However, in this case, it is likely that Th-LREE were retained by monazite/allanite, observed as inclusions in some grains, resulting in LREE depletions in apatite.

Amphibolite BR 47

Apatites in amphibolite show uniform, LREE enriched patterns relative to HREE suggestive of re-equilibrated metamorphic apatite formed during progressive metamorphism (described above). A weak Eu anomaly is consistent with apatite in equilibrium with less Ca-rich metamorphic feldspar that retains Eu at lower metamorphic grades. Garnet is absent in this xenolith therefore slight HREE depletions are likely due to sequestration of heavy rare earths by co-existing amphibole (Chu et al., 2009) which is moderately HREE rich in this xenolith ($\Sigma\text{HREE} = 7\text{--}24$ ppm, Table B3).

Total concentrations and variations in LREE (La-Sm) and HREE (Gd-Lu) abundances in apatite from Bearpaw xenoliths, granites (Sha and Chappell, 1999; Hsieh et al., 2008) and high grade stronalites and gneisses (Bea and Montero, 1999; Henrichs et al., 2018) are shown in Fig. 5.4a-b. LREE in apatites from Bearpaw Mountain xenoliths are variably enriched ($\text{La}_N/\text{Sm}_N = 0.12\text{--}8.34$, $\Sigma\text{LREE} = 574\text{--}8525$ ppm),

similar to igneous granitic apatite ($\text{La}_\text{N}/\text{Sm}_\text{N} = 0.21\text{-}10.55$, $\Sigma\text{LREE} = 1180\text{-}10020$ ppm) (Fig 5.4a). Heavy rare earth elements ($\Sigma\text{HREE} = 47\text{-}2150$ ppm) in Bearpaw apatites appear less enriched relative to the majority of granitic apatite ($\Sigma\text{HREE} = 501\text{-}8658$ ppm), although overlap exists at $\Sigma\text{HREE} = 500\text{-}2000$ ppm. Notably, heavier rare earth elements appear more variable within Bearpaw apatites ($\text{Gd}_\text{N}/\text{Yb}_\text{N} = 1.55\text{-}216.73$) compared to granitic apatite ($\text{Gd}_\text{N}/\text{Yb}_\text{N} = 1.02\text{-}4.99$), especially within xenoliths LSC 33 and LSC 93, due to HREE sequestration by garnet in these two xenoliths. Metamorphic apatite from gneisses ($\text{La}_\text{N}/\text{Sm}_\text{N} = 0.22\text{-}0.41$, $\Sigma\text{LREE} = 1368\text{-}3544$ ppm) and stronalites ($\text{La}_\text{N}/\text{Sm}_\text{N} = 2.42\text{-}3.90$, $\Sigma\text{LREE} = 1355\text{-}1665$ ppm) are slightly less LREE enriched compared to our xenoliths, although overlap exists at the 2000-4000 ppm level. HREE in stronalites ($\text{Gd}_\text{N}/\text{Yb}_\text{N} = 4.23\text{-}6.22$, $\Sigma\text{HREE} = 127\text{-}325$ ppm) and gneisses ($\text{Gd}_\text{N}/\text{Yb}_\text{N} = 1.02\text{-}3.58$, $\Sigma\text{HREE} = 1025\text{-}3038$ ppm) are similarly depleted when compared to apatite in Bearpaw xenoliths ($\text{Gd}_\text{N}/\text{Yb}_\text{N} = 1.55\text{-}7.54$, $\Sigma\text{HREE} = 47\text{-}2150$ ppm), apart from xenoliths LSC 33 and LSC 93 which have highly variable normalised heavy rare earths ($\text{Gd}_\text{N}/\text{Yb}_\text{N} = 2.94\text{-}216.73$) due to garnet control of HREE. The similarity of apatite trace element abundances in Bearpaw xenoliths to granitic apatite is indicative of a process of LREE and HREE enrichment resulting in metamorphic apatite that mimics trace element characteristics of igneous apatite. Moreover, the general similarity in LREE and HREE concentration of metamorphic apatite from the Bearpaw Mountains with metamorphic apatite from stronalites (Bea and Montero, 1999) and gneisses (Henrichs et al., 2018) (which underwent similar processes of metamorphic apatite crystallisation) supports the formation of metamorphic apatite through mechanisms described above. A notable feature of apatite in our xenoliths is the depletion of Th and U, also observed in metamorphic gneiss (Henrichs et al., 2018) (Fig. 5.4c).

In summary, apatite trace element patterns are LREE enriched relative to HREE with strong negative anomalies in most cases. These characteristics are typical of high grade metamorphic apatite that has exchanged trace elements with pre-existing and recrystallised metamorphic phases during progressive metamorphism. Breakdown and dissolution of monazite/allanite releases LREE that is incorporated into apatite. Co-existing metamorphic feldspar results in Eu depletions in apatite, while garnet formation at high temperatures results in HREE depleted apatite patterns in two xenoliths.

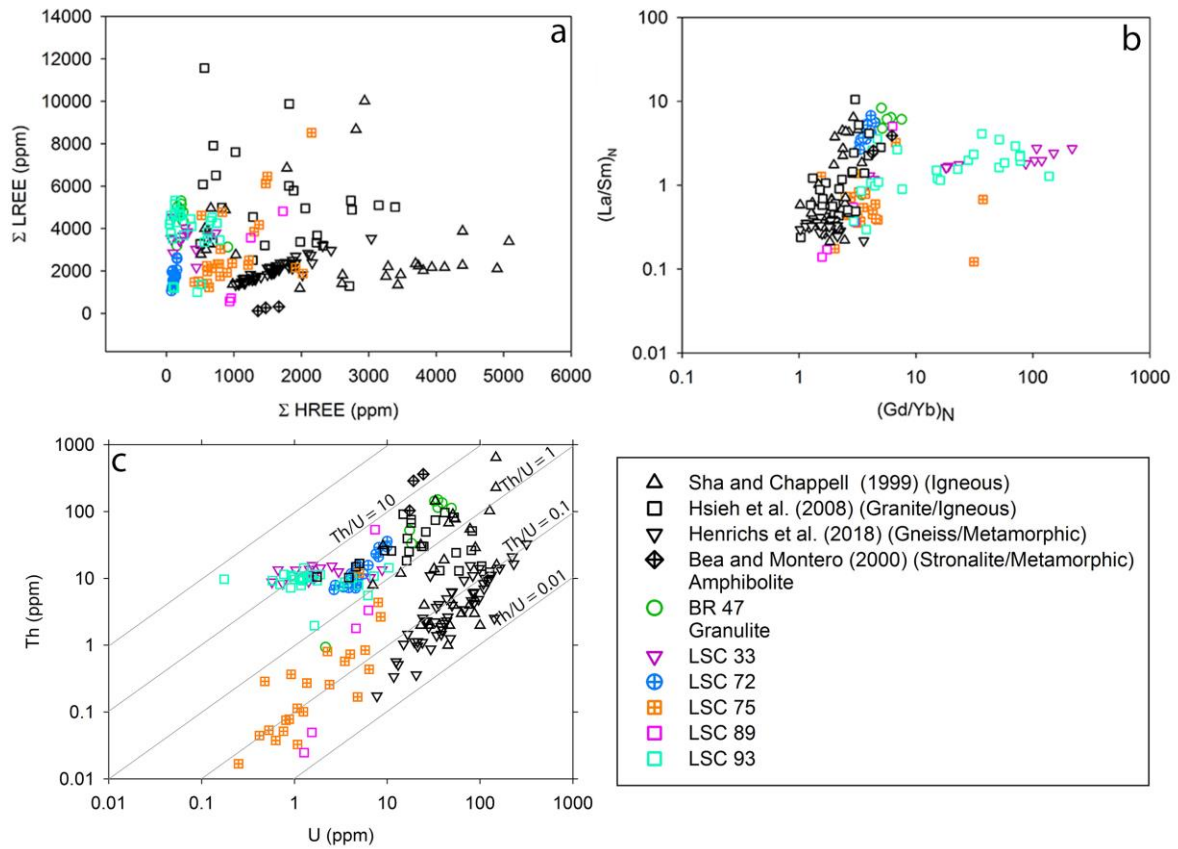


Figure 5.4: Sum of LREE (La-Sm) against HREE (Gd-Lu)(a), variation in LREE (La/Sm)_N and HREE (Gd/Yb)_N (b), and Th/U (c) for Bearpaw xenoliths (this study, BR 47, LSC 33, LSC 72, LSC 75, LSC 89, LSC 93), igneous granitic apatite (Sha and Chappell, 1999; Hsieh et al., 2008) and metamorphic apatite from stronalites (Bea and Montero, 1999) and high grade orthogneiss and paragneiss (Henrichs et al., 2018).

5.5.2 Whole-rock and mineral controls on apatite compositions

Relative and absolute trace element concentrations in apatite are generally controlled by the presence and abundance of accessory phases, such as apatite, monazite, xenotime, sphene and zircon (Bea, 1996; Belousova., 2002). The apatite structure allows for preferential substitution of certain elements such as REE, Th, U, Sr and Mn (Sha and Chappell, 1999; Spear and Pyle, 2002). The concentrations of these elements depends on the whole-rock composition, which governs the order of crystallisation of minerals with respect to apatite, and also controls what the competing REE and actinide hosts will be during crystallisation (e.g. Sha and Chappell., 1999; Piccoli and Candela, 2002). Whole-rock trace element abundances are plotted alongside apatite trace element compositions in order to evaluate similarities and possible host rock controls on such distributions (Fig. 5.3b-l).

As mentioned above, xenoliths LSC 33 and LSC 93 show HREE depletion ($Gd_N/Yb_N = 3-216$) due to heavy rare earth sequestration by garnet in equilibrium with apatite in the system. It is notable that these apatite grains show depleted HREE, whereas magmatic zircon grains in one garnet-bearing xenolith

(LSC 33) show no HREE depletion (Thakurdin et al., 2019b). Therefore, magmatic zircon and metamorphic apatite crystallisation are decoupled from each other, likely as a result of metamorphic apatite and garnet growth occurring post-igneous zircon crystallisation.

Abundances of LREE in apatite are controlled mainly by co-crystallizing, LREE-enriched phases such as monazite, allanite, epidote and xenotime (Sha and Chappell, 1999; Spear and Pyle, 2002). These phases are neither observed as whole grains within the mineral assemblage or as inclusions within apatite (apart from xenolith LSC 89), suggesting that they were consumed during high-grade metamorphism, upon which LREE were incorporated to apatite (Bingen et al., 1996). Two grains within xenolith LSC 89 appear LREE depleted relative to HREE, probably as a result of apatite crystallisation in equilibrium with a LREE enriched phase. This phase may include monazite which is present as an inclusion within grain 89_4 (Th = 54 ppm, Table 5.4, see Appendices).

Concentrations of Th and U for whole-rocks (Th = 0.3-4.0 ppm, U = 0.04-0.4 ppm) and apatite grains (Th = 0.02-36, $\bar{x}$ = 10 ppm, U = 0.02-10 ppm, $\bar{x}$ = 3 ppm) are low for granulite xenoliths. It is possible that other accessory minerals such as zircon (U = 13-3047 ppm, $\bar{x}$ = 418 ppm, Th = 1-914 ppm, $\bar{x}$ = 198 ppm, Thakurdin et al., 2019a) may be controlling the uranium and thorium budget in granulite xenoliths (Bingen et al., 1996), resulting in depleted concentrations of such elements in apatite. Contrastingly, apatite in amphibolite xenolith BR 47 contains relatively high concentrations of Th (34-151 ppm, $\bar{x}$ = 94 ppm) and U (2-49 ppm, $\bar{x}$ = 25 ppm) but contains low whole-rock Th and U abundances (Th = 1.6 ppm, U = 0.4 ppm). Higher concentrations of thorium and uranium in amphibolite apatite may reflect crystallisation of apatite in a melt prior to high Th and U sequestering phases such as zircon (U = 259-3135 ppm, $\bar{x}$ = 986 ppm, Th = 7-5888 ppm, $\bar{x}$ = 689 ppm, Thakurdin et al., 2019a) as suggested by Hsieh et al. (2008) and Tang et al. (2012). Alternatively, low Th and U may simply be a function of low concentration of such elements in the host rock/melt, and at the time of apatite (re)crystallisation.

Cerium does not show a significant positive/negative anomaly in apatite within both granulite and amphibolite xenoliths ($Ce_N/Ce_N^* = 0.33-3.24$, $\bar{x} = 1.26$) (Table 5.4, see Appendices). Within amphibolite BR 47 and granulite LSC 89, apatite shows a negative Eu anomaly ($Eu_N/Eu_N^* = 0.2-0.8$) which is likewise reflected in the bulk rock ($Eu_N/Eu_N^* = 0.7-0.8$). Granulite xenoliths LSC 75 and LSC 93, however, show positive whole-rock Eu anomalies ($Eu_N/Eu_N^* = 1.5-4.7$) contrasted with negative Eu anomalies ($Eu_N/Eu_N^* = 0.1-0.9$) in apatite. The mismatch in Eu anomaly between apatite and whole-rocks suggest that Eu in apatite is influenced by scavenging of this element by other fractionating phases, such as feldspar (Belousova et al., 2002). Epidote may influence the Eu anomaly to a certain extent (Bea et al., 1996), but this phase is not observed in any xenoliths. Since our apatite grains are metamorphic, Eu sequestration takes place during metamorphic feldspar crystallisation in equilibrium with apatite.

HREE depleted ($Gd_N/Yb_N = 18.1-216.7$, $\bar{x} = 87.4$) grains within xenoliths LSC 33 and LSC 93 show less negative Eu anomalies ($Eu/Eu^* = 0.45-1.44$) (Table 5.4, see Appendices) relative to other granulite xenoliths. This weaker negative Eu anomaly may occur as a direct result of HREE depletion in apatite that affects the neighbouring trace elements (Gd) and thus the steepness of the pre-existing Eu anomaly. Another possible factor influencing Eu and Ce anomalies is the oxygen fugacity of the melt from which apatite crystallised. Cerium enters apatite in single a valence state (3+) due to its smaller ionic radius, regardless of oxidising/reducing conditions, and is therefore a poor indicator of oxygen fugacity (Cao et al., 2012). With regards to europium, apatite preferentially incorporates Eu^{3+} over Eu^{2+} due to its smaller ionic radius. At low oxygen fugacities, Eu^{2+}/Eu^{3+} is high, resulting in lower availability of the 3+ ion and thus a highly negative Eu anomaly in apatite. Therefore, low (steeply negative) Eu anomalies indicate a protolith melt existing within a reducing environment, as compared to melts forming within an oxidizing environment with a more positive Eu/Eu^* (Cao et al., 2012). Since whole-rocks and apatite show conflicting Eu anomalies, it is likely that feldspar fractionation is controlling europium concentrations rather than oxidizing/reducing conditions of the host melt.

In summary, apatite chemical compositions are predominantly controlled by co-existing accessory minerals and metamorphic phases. Specifically, light rare earth elements are enriched in apatite due to the incorporation of LREE released from the break-down and consumption of monazite/allanite in the system during high grade metamorphism. Uranium and thorium concentrations in apatite are possibly controlled by competing U/Th-rich phases such as zircon in the melt phase. Apatite grains showing negative Eu anomalies are controlled by metamorphic feldspar growth. In two xenoliths, variable HREE depletions in apatite are controlled by the presence of garnet in the system during high temperature metamorphism.

5.5.3 Factors affecting apatite U-Pb geochronology

Low Th and U concentrations necessarily result in low concentrations of radiogenic lead. All granulite xenoliths are characterised by low U and Th while amphibolite (BR 47) is comparatively enriched in Th and U relative to granulite xenoliths (Fig. 5.4c). The proportion of non-radiogenic lead (or common lead, Pb_c , measured as “f206”, Table 5.3, see Appendices) also influences measured ages since Pb_c is significant in these apatite grains. Other factors influencing apatite U-Pb geochronology include mixtures of ages from differing grain sizes resulting in non-uniform populations within a single xenolith (Cochrane et al., 2014). Grain size is not well correlated with age in these samples, however (Table 5.3, see Appendices), presumably due to small size variations between grains or the relatively few number of U-Pb determinations on grains within each sample

Within xenoliths LSC 33 and LSC 93, large uncertainties in calculated lower intercept ages on Tera-Wasserburg plots are likely the result of low to moderate U (0.18-8 ppm, $\bar{x}$ = 2.4 ppm) and Th (8.6-15.8 ppm, $\bar{x}$ = 1.14 ppm) concentrations, and a narrow spread in $^{238}\text{U}/^{206}\text{Pb}$ ratios. The proportion of common lead in these grains is also high and variable (f_{206} = 0.29-0.98). Within both LSC 33 and LSC 93, a large number of analyses do not produce usable apatite ages which may be attributed to sampling of these low U, high Pb_c metamorphic domains. The mechanism of low U in metamorphic apatite is not well understood. Perhaps U is redistributed by recrystallisation of igneous domains to form metamorphic apatite, resulting in the expulsion of Th and U from the crystal lattice. Alternatively, metamorphic apatite grows together with a strongly fractionating U-bearing phase (zircon). Newly formed metamorphic apatite from other studies have been observed to be Th and U deficient, resulting in undateable metamorphic domains (Henrichs et al., 2018).

Although apatite within xenolith LSC 72 contains the lowest proportion of common lead (f_{206} = 0.09-0.50) and slightly higher U than other granulite xenoliths (2.7-10.0 ppm, $\bar{x}$ = 5.5 ppm), U-Pb isotopic data are dispersed on the Tera-Wasserburg diagram (Fig. 5.3c). Once metamorphic apatite had fully stabilised, dissolution-recrystallisation or metasomatism by externally derived fluids did not occur as evidenced by uniform trace element patterns and halogen compositions. Therefore, poorly constrained ages cannot be attributed to fluid-aided dissolution effects occurring post-metamorphic apatite crystallisation that would redistribute U and Pb together with the trace elements (especially U-Th-LREE) (Barfod et al., 2005; Harlov et al., 2007; Kirkland et al., 2018). However, some process must account for variable U and Pb contents, resulting in dispersion of ages. Variable mineral armouring leading to differing U and Pb concentrations in apatite (Dahl et al., 1997; Janots et al., 2018) is considered unlikely given the almost ubiquitous appearance of apatite as inclusions in feldspar. Other possible redistribution mechanisms include diffusion of U and Pb during thermal resetting and/or slow cooling, or ingress of externally derived common lead (see below).

Within xenolith LSC 75, uranium is extremely low in apatite (0.02-12.2 ppm, $\bar{x}$ = 1.07 ppm), and the proportion of common lead is near 100 % in most cases (f_{206} = 1) resulting in unusable ages. The significant U depletion and dispersion of measured U/Pb cannot result from externally derived fluid-aided dissolution-reprecipitation and/or recrystallisation occurring post-metamorphic apatite crystallisation as indicated by relatively uniform REE and halogen concentrations. U and Pb variations, and largely unradiogenic Pb, are most likely host rock controlled or redistributed by thermal effects (slow cooling/resetting, see below).

Within xenolith LSC 89, U in apatite is moderate to low relative to other granulites (1.27-7.4 ppm, $\bar{x}$ = 4.2 ppm), while the proportion of common lead is variable (f_{206} = 0.39-0.96). Variable LREE

enrichment occurs due to sampling of mineral inclusions (see above). A statistically meaningful chord (MSWD = 1.03) in $^{238}\text{U}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ space is observed, suggesting that U and Pb were not redistributed by secondary recrystallisation/alteration mechanisms. It must be noted, however, that this chord is regressed through relatively few data points.

Amphibolite BR 47 contains the highest U concentrations (2-49 ppm, $\bar{x}$ = 25 ppm) in apatite among all studied xenoliths, together with low proportions of common lead (f_{206} = 0.26-0.31). Thorium (0.9-151 ppm, $\bar{x}$ = 94 ppm) is also enriched relative to apatite from granulite xenoliths. As a result of elevated U and Th, U-Pb data constrain a reasonable Proterozoic age (1663 ± 47 Ma, MSWD = 20) (despite some scatter) that is broadly correlated with magmatic zircon ages from this xenolith (1874 ± 8 Ma) and metamorphic zircon ages from granulite xenoliths (1772 ± 5 - 1788 ± 4 Ma). Trace element patterns are uniform and show minor intra-variation, suggesting little to no re-organization of U and Pb in apatite grains induced by secondary alteration mechanisms occurring post-metamorphic apatite crystallisation.

Common lead in apatite calculated using feldspar compositions ($^{207}\text{Pb}/^{206}\text{Pb}$ = 0.8751-1.0093) or inferred from terrestrial evolution curves ($^{207}\text{Pb}/^{206}\text{Pb}$ = 0.9012-0.9972) is often distinct from unanchored common Pb (0.9327-1.0561) inferred from upper intercepts on Tera-Wasserburg plots (Fig. 5.3a-k). As proposed by Kirkland et al. (2017), this disparity may reflect ingress of common Pb into mineral grains during thermal re-equilibration. Such a Pb-gain mechanism will lead to differing initial lead compared to that predicted by evolutionary models, and will produce poorly constrained mixing lines in $^{238}\text{U}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ space. Pb_c ingress may have occurred in apatite within xenoliths LSC 72 and LSC 75, which contain varying common lead proportions and display scattered ages that cannot be regressed to a lower-intercept on a TW plot. Common Pb in these two xenoliths may be sourced from neighbouring minerals or the host rock at the time of thermal equilibration.

In summary, a general correlation exists between low uranium concentrations in apatite and poorly constrained U-Pb ages, in agreement with previous studies of apatite from metamorphic rocks (Chew et al., 2014; Henrichs et al., 2018; O'Sullivan et al., 2018). Variable incorporation of common lead in apatite probably further induced dispersion of $^{235}\text{U}/^{207}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. Uniform trace element patterns preclude redistribution of Pb and U by secondary fluid alteration and/or recrystallisation processes occurring post-metamorphic apatite growth. Imprecise ages may be further explained by thermal effects (resetting and/or slow cooling, see below).

5.5.4 Age resetting, cooling and re-equilibration

Due to the relatively low closure temperature of the U-Pb system in apatite, measured ages will be significantly younger than those recorded by higher temperature minerals in slowly cooled rocks (e.g. 375-550 °C in apatite versus 1000 °C in zircon: Cherniak, 2000; Schoene and Bowring, 2007; Cochrane et al., 2014). In simple cases, this closure temperature is defined by uniform volume diffusion over time, which is in turn dependent on grain size and temperature (Dodson, 1973; Schoene and Bowring, 2007). Zircon tends to record peak metamorphism or primary igneous ages and is less prone to thermal resetting. In certain cases apatite ages are seen to correlate with zircon ages, but this would imply that the closure temperature of apatite was significantly high and cooled very rapidly to attain closed-system behaviour (Oosthuyzen and Burger, 1973). Since apatite ages (300-500 Ma) differ considerably from zircon ages (1700-2500 Ma) (Table 5.5) in our xenoliths, the processes in generating younger ages in apatite (slow cooling or thermal/isotopic resetting) require assessment.

Resetting

Resetting of the U-Pb system in apatite implies open-system behaviour that cannot be described by uniform volume diffusion processes in apatite grains. Mechanisms of open-system behaviour include recrystallisation and/or fluid-induced dissolution-reprecipitation mechanisms that accelerate Pb diffusion, redistribute radiogenic Pb or induce Pb-loss, resulting in variable measured ages (Watson et al., 1985; Barfod et al., 2005; Nutman et al., 2007; Schoene and Bowring., 2007). Alternatively, a thermal event such as metamorphism or crustal anatexis may induce rapid diffusion of Pb within apatite and, if cooled rapidly, would re-equilibrate to the timing of that thermal event (Corfu and Stone, 1998; Kirkland et al., 2017).

From magmatic zircon data for these samples, xenoliths crystallised between 1834 and 1874 Ma resulting in igneous apatite and zircon growth. A granulite facies metamorphic event (related to regional convergent margin activity) occurred shortly afterward at ca. 1772 ± 5 Ma (Thakurdin et al., 2019a). This high temperature metamorphic event must have resulted in re-equilibration of originally igneous apatite to form metamorphic apatite at a similar time (ca. 1770 Ma). However, U-Pb ages in metamorphic apatite record much younger ages between 300 and 500 Ma. Subsequent resetting/partial resetting via a fluid-induced metasomatic event, resulting in variable radiogenic lead loss and redistribution of Pb in metamorphic apatite could plausibly result in young, Neoproterozoic to Palaeozoic ages observed these grains. However, fluid-induced dissolution-reprecipitation mechanisms occurring post-metamorphic apatite crystallisation is unlikely, since trace element patterns (described above) are relatively uniform and show minor variation in LREE and Th. Additionally, once metamorphic apatite has formed, the stabilised granulite host is generally an anhydrous lithology, precluding fluid-induced, post-crystallisation modification.

Alternatively, thermal resetting after metamorphic apatite crystallisation may have partially re-equilibrated radiogenic Pb in metamorphic apatite resulting in young lower-intercept ages (300-500 Ma). REE profiles would not show significant changes with thermal re-equilibration due to the lower temperatures of Pb diffusion compared to that of the REE (Cherniak, 2000; Kirkland et al., 2018). However, no thermal or geological events, that would have provided the heat for thermal resetting, are reported during the Neoproterozoic to Palaeozoic in the region of the Wyoming Craton.

In summary, overall similar trace element patterns among apatites within individual xenoliths are inconsistent with fluid-induced recrystallisation and resetting occurring post-metamorphic apatite crystallisation that would induce younger (ca. 300-500 Ma) lower-intercept ages. While a thermal peak in the mid-Proterozoic (ca. 1770 Ma) may have reset the apatite chronometer, simple thermal resetting at this time cannot adequately explain young Palaeozoic to Neoproterozoic apatite ages in these xenoliths.

Slow versus rapid cooling

Since metamorphic apatite (300-500 Ma) and zircon (ca. 1770 Ma) from granulite xenoliths record considerably dissimilar ages, a rapid cooling scenario for granulite xenoliths seems unlikely. Apatite within amphibolite xenolith BR 47 yields a lower-intercept apatite age of 1663 ± 47 Ma that is slightly younger than the crystallisation age of this xenolith (1874 ± 8 Ma), and broadly correlates with 1770 Ma metamorphic zircon ages in granulite xenoliths. It is possible that rapidly cooled metamorphic apatite grains in this xenolith record a similar age of metamorphism (ca. 1770 Ma). This is consistent with shallower metamorphic equilibration conditions (3.5-5.3 kbar) for amphibolite xenoliths, which may enable relatively faster cooling to occur compared to deeper lying (7.4-7.5 kbar) granulite xenoliths.

An alternate mechanism to explain decoupling between zircon and apatite ages is slow cooling, whereby thermally activated volume diffusion controls Pb isotope systematics. Slow cooling over geological timescales is plausible during protracted residence within a high temperature and pressure environment, such as the middle to lower crust. Pressure-temperature estimates (642-817 °C, 7.4-7.5 kbar) for granulite xenoliths confirm the residence of these samples within deeper regions of the crust (Thakurdi et al., 2019a). Following initial apatite growth at ca. 1834-1874 Ma (due to subduction-related melt generation events), the xenoliths were affected by a granulite facies metamorphic event during continental collision at ca. 1770 Ma (see Fig. 5.5 below). Originally igneous apatite then re-equilibrated to form metamorphic apatite. Following the metamorphic peak, granulite facies xenoliths (LSC 33, LSC 89, LSC 93) experienced slow cooling at depth, in which Pb slowly diffuses out of apatite grains. The point at which the apatites eventually reach their closure temperature (and Pb diffusion

stops) is represented by the lower-intercept age on the Tera-Wasserburg plot (ca. 300-500 Ma). Slow cooling is probably enabled by long term exhumation of xenoliths towards shallower crustal levels.

Table 5.5: Summary of U-Pb Apatite and Zircon Ages for Bearpaw Xenoliths

Sample	Rock Type	Number Analyses	$^{207}\text{Pb}/^{206}\text{Pb}$ Zircon Populations	Number Analyses	Apatite Ages
BR 47	Amphibolite	32	1834±19-1874±8 Ma (Magmatic)	8	1663±47 Ma (Lower intercept age, unanchored)
LSC 33	Granulite	7	1682±130 (Lower Intercept)- 3231±230 (Upper Intercept) (Magmatic)	14	434±170 (Lower intercept age (unanchored), 1826±342 Ma (Spot age)
LSC 72	Granulite	24	1834±19 Ma (Magmatic)	19	1909±185 and 1913±178 Ma (Spot ages)
LSC 75	Granulite	X	X	39	No lower intercept
LSC 89	Granulite	81	1773±8-1788±4 Ma (Metamorphic), 1690±24- 2534±9 Ma (Recrystallised Magmatic)	5	565±79, (Lower intercept age, unanchored)
LSC 93	Granulite	X	X	39	531±130 Ma (Lower intercept age, unanchored)

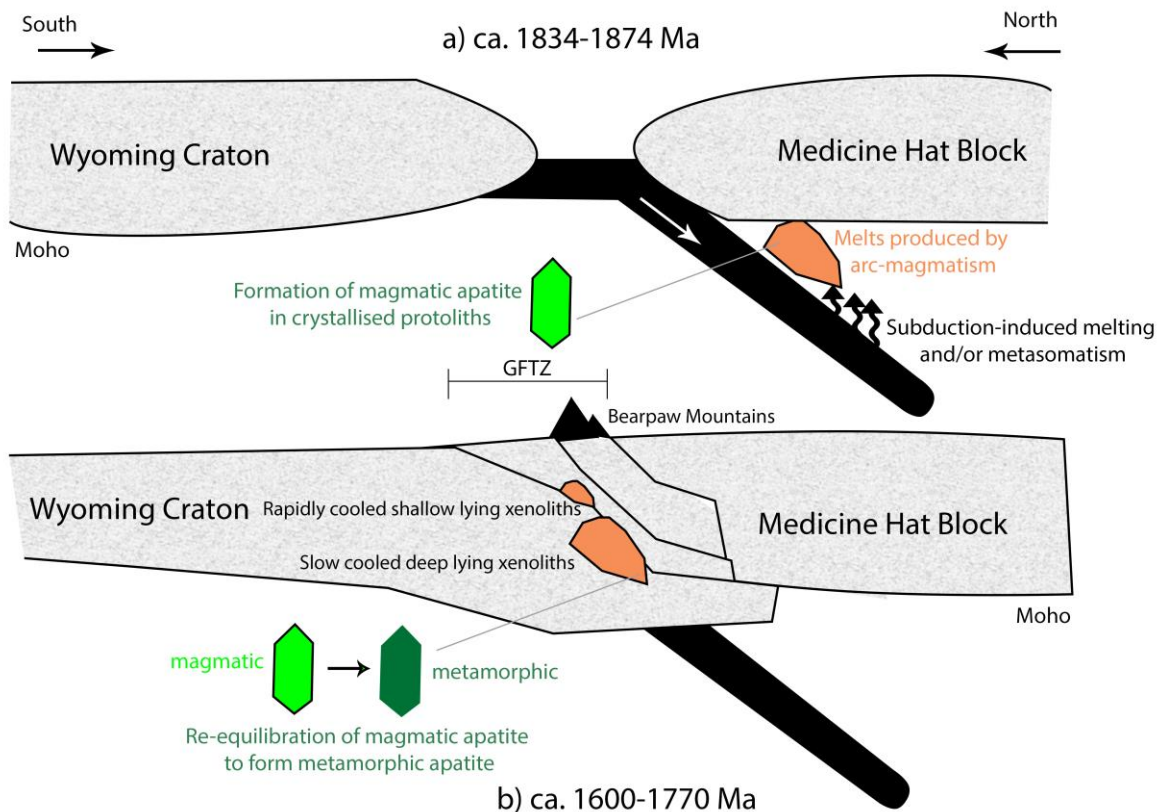


Figure 5.5: Schematic cross-sections showing the tectonic evolution of the Wyoming Craton (WC), Medicine Hat Block (MHB) and Great Falls Tectonic Zone (GFTZ). a) Subduction occurs at ca. 1834-1874 Ma resulting in melting of the overlying mantle wedge. Melts crystallise to form xenolith protoliths

along with magmatic apatite. b) Continental-collision occurs between the WC and MHB resulting in high temperature metamorphism between ca. 1600 and 1770 Ma. Originally magmatic apatite re-equilibrates to form metamorphic apatite. Deeper lying granulite xenoliths are slowly cooled while shallow lying amphibolite xenoliths are rapidly cooled.

From literature studies involving lower crustal samples, slow cooling via volume diffusion in apatite has been recorded to occur over geological timescales (Schoene and Bowring, 2007; Cochrane et al., 2014). More importantly, from studies beneath the Wyoming Craton (GFTZ and Medicine Hat Block), Blackburn et al., (2011, 2012) showed conclusively that volume diffusion and slow cooling, following a thermal peak in the mid-Proterozoic (ca. 1800 Ma), was sufficient to explain the range in young lower-intercept ages (500-800 Ma) in rutile grains, and discounted reheating and resetting of rutile due to the lack of Neoproterozoic to Palaeozoic thermal events in the region. U-Pb chronometry of apatites from xenoliths in this study thus confirms slow cooling within lower crustal sections of the Wyoming Craton as mineral systems with similar closure temperatures (400-600 °C) yield similar lower-intercept ages (500-800 Ma in rutile, 300-500 Ma in apatite). Slow cooling over such an extended period likely results in extensive redistribution of U and Pb resulting in imprecise lower-intercept ages. These results are also consistent with modelled geothermal gradients, inferred from lower crustal xenoliths in the region (Blackburn et al., 2012). Proterozoic (ca. 1800–1900 Ma) geothermal gradients are high, preventing closure of low temperature chronometers such as rutile and apatite at depth. This initially steep geothermal gradient presumably represents increased thermal activity due to convergence and ocean closure between the Medicine Hat Block and Wyoming Cratons at ca. 1800 Ma and subsequent continental collision at ca. 1770 Ma (Mueller et al., 2002, 2005). Subsequent post-orogenic cooling from ca. 1700 onwards, lowers the geothermal gradient considerably (approaching that of a steady state geotherm) and results in slow cooling at deeper crustal levels until the Eocene (Blackburn et al., 2011, 2012).

5.5.5 Relation of apatite and zircon ages

No young zircon ages within the age range defined by xenolith apatites (300-500 Ma) are reported from existing studies within the Wyoming Craton or the adjacent Medicine Hat Block and GFTZ. Apatite and zircon ages from Bearpaw xenoliths in this study are summarised in Table 5.5. Within xenolith LSC 72, two individual apatite spots (1909 ± 185 and 1913 ± 178 Ma) broadly correlate with magmatic U-Pb zircon ages in this xenolith (1834 ± 19 Ma). Similarly, within xenolith LSC 33, a single Proterozoic age of 1826 ± 342 Ma is correlated to magmatic U-Pb zircon ages for this xenolith suite (1834 ± 19 - 1874 ± 8 Ma). This attests to apatite crystallisation in the Proterozoic, followed by metamorphism and slow cooling described above that eventually results in younger Neoproterozoic

to Palaeozoic ages. In our xenoliths, a thermal peak occurred at 1770 Ma, when metamorphic apatite formed, after which it slowly cooled until ca. 300-500 Ma. Within xenolith BR 47, a broad correlation between metamorphic zircon (1772 ± 5 - 1788 ± 4 Ma) and apatite ages (1663 ± 47) is observed, with younger apatite ages potentially representing a rapidly cooled xenolith at a shallower crustal depths.

5.5.6 Implications for lower crust

From zircon data, a thermal maximum likely occurred in the mid-Proterozoic (1772 ± 5 Ma) during granulite facies metamorphism, shortly after magmatic zircon crystallisation at ca. 1834-1874 Ma. Shallow lying samples (3.5-5.3 kbar) are rapidly cooled as represented by ca. 1600 Ma ages in amphibolite xenolith BR 47. Rutile cooling ages beneath the Wyoming Craton and GFTZ (Blackburn et al., 2011, 2012) provide evidence for slow cooling over a period of >1000 Ma, from the time of metamorphism at ca. 1770 Ma up until the Palaeozoic. Such a slow cooling model may be applied to structurally deeper granulite xenoliths (642-817 °C, 7.4-7.5kbar), which show very young apatite ages (300-500 Ma).

5.5.7 Geodynamic implications for the Wyoming Craton

Magmatic zircons record initial crystallisation of these xenoliths in the mid-Proterozoic (ca. 1834-1874 Ma) (Thakurdin et al., 2019a). The protolith to these xenoliths were likely formed through melting induced by convergence and ocean closure between the Medicine Hat Block and Wyoming Cratons along a subduction-related boundary (GFTZ) (Mueller et al., 2002, 2005). Continental collision between the Medicine Hat Block and Wyoming Craton occurred between ca. 1600-1800 Ma (see Fig. 5.5) as recorded by metamorphic zircon ages (1772 ± 5 - 1788 ± 4 Ma), metamorphic apatite ages in amphibolite BR 47 (ca. 1600 Ma) and Ar-Ar ages from low temperature mineral studies (hornblende and biotite) in the region (1775-1800 Ma: Holm and Schneider, 2002). As mentioned above, this metamorphic event likely represents the thermal peak in the region. Once collision-related tectonothermal activity had ceased, slow cooling (up till a minimum age of 300-500 Ma defined by our lower-intercept ages) occurred within deeper levels of the crust. The final event of Eocene entrainment is not recorded in apatite, and suggests that host magma enclosement did not re-equilibrate Pb or trace elements in these xenoliths. Notably, since lower-intercept ages can be explained by slow cooling since the mid-Proterozoic, no significant thermal events occurred between the period 1770 Ma and ca. 55 Ma in this region of the Wyoming Craton. This implies a generally thick, stable continental root established after mid-Proterozoic continental collision that prevented deeper-seated thermal perturbations from affecting the crust, and an extensive continental cover that retained xenoliths at deeper crustal levels and prevented rapid cooling (Blackburn et al., 2012).

5.6 Conclusions

Apatite grains extracted from four granulite xenoliths and one amphibolite xenolith were studied using imaging, trace element and halogen compositions as well as U-Pb geochronology. Apatite grains are small (100-150 μm), generally euhedral to subhedral crystals and largely embodied within rock-forming metamorphic phases. Cathodoluminescence (CL) and back-scattered electron imaging (BSE) show uniform domains without inclusions and discernible internal microstructures. Major (Ca, P) and halogen (F, Cl, OH) chemistry are suggestive of fluorapatite compositions. Trace element compositions of apatite are uniformly LREE enriched relative to HREE and relatively depleted in Eu, resembling reported high-grade metamorphic apatite. Trace element patterns in metamorphic apatite were obtained through progressive prograde metamorphism in which ions were continuously exchanged between components in the system. This process begins with apatite crystallisation from a melt at ca. 1834-1874 Ma. At the onset of metamorphism at ca. 1772 ± 5 Ma, apatite continuously exchanges elements between co-existing and newly forming phases as metamorphism progresses. Specifically, the break-down of monazite and crystallisation of metamorphic feldspar results in LREE enrichments and Eu depletions in apatite respectively. In two xenoliths (LSC 33 and LSC 93) garnet also begins to grow at high temperatures and produces relative HREE depletions in apatite grains. Due to the high metamorphic grade of these rocks, the rock volume is likely to have been in large-scale chemical equilibrium, resulting in uniform apatite trace element and halogen concentrations in each xenolith. Following stable metamorphic apatite crystallisation, apatite was not subsequently altered by dissolution-reprecipitation and retained its uniform trace element patterns and halogen concentrations. U-Pb geochronology yield young Neoproterozoic to Palaeozoic ages (ca. 300-500 Ma) that are suggestive of slow cooling at lower crustal levels for an extended period (>1000 Ma). A single amphibolite xenolith yields a mid-Proterozoic (1663 ± 47 Ma) age that may represent rapid cooling of metamorphic apatite at shallower crustal levels. Geodynamically, the studied section of mid- to lower crust beneath the Wyoming Craton experienced a thermal peak during the mid-Proterozoic collision of the Wyoming Craton and Medicine Hat Block, followed by a period of cratonic stability between the Proterozoic and Eocene, which was enabled by the presence of a thick continental cover and deep lithospheric root and that is unaffected by minor thermo-tectonic events in the region. The limited study of lower temperature minerals (apatite, rutile) in the lower crust may present an opportunity for future study of such phases using modern techniques such as fission-track and/or U-Th/He dating. The integration of new, lower temperature mineral information with existing geochronological data may allow for the construction of temperature-time paths, which may more accurately constrain the thermal history of the Wyoming Craton. The trace element data for lower crustal apatites presented here can be used to compare or contrast apatite petrogenesis in similar geological settings elsewhere.

The refinement in the understanding of apatite trace element systematics is useful since, unlike traditional minerals such as zircon, apatite is almost ubiquitous in all rock types.

6 Summary of lower crustal processes beneath the Wyoming Craton

The lower crust is an enigmatic and often poorly sampled segment of the cratonic lithosphere. Investigation of the lower crust is restricted to exhumed granulite terranes or xenoliths brought to the surface by alkaline or kimberlitic volcanism. Since granulite terranes representative of the lower crust are uncommon, xenoliths are often the only reliable carriers of deeper crustal signatures. It is therefore desirable to study these xenoliths as they provide rare-insight into lower crustal evolutionary processes.

Eight middle-lower crustal xenoliths extracted from the Bearpaw Mountains, Montana, USA were examined using both whole-rock chemistry and zircon geochronology. Xenoliths include amphibolites and mafic granulites formed from alkaline/sub-alkaline igneous (likely basaltic) precursor melts. The xenoliths were hosted within alkaline minnette lavas brought to the surface during Eocene volcanism. Mineral geothermobarometry yield temperature-pressure estimates of 642-817 °C and 7.4-7.5 kbar, confirming a middle-lower crustal residence for these xenolith bodies. Mantle-normalised trace element patterns plots show a subduction signature with extreme enrichments in large-ion lithophile (LILE) and fluid mobile elements (Cs, Rb, Ba, Pb, Sr) relative to high-field strength elements, together with relative Zr-Hf and Nb-Ta-Ti depletions. Based on mixing calculations between the minnette host and the xenolith bodies, contamination of xenoliths by the alkaline host lava is deemed unlikely, therefore the xenoliths retained their original geochemical signatures. Zircon grains were extracted from four granulite and a single amphibolite xenolith. The majority of xenoliths contain magmatic zircon as defined by internal cathodoluminescence textures (oscillatory zoning) and high Th/U ratios (> 1.0). Two xenoliths contain metamorphic zircons which are conversely devoid of internal microstructures and contain low Th/U (< 0.2). Magmatic zircon yield ages between 1834 and 1874 Ma and represent subduction-induced melting of the overlying mantle wedge to produce protolith magmas to these xenoliths. These subduction-related ages are correlated to known magmatic events in the region (ca. 1860 Ma) and represent convergence and ocean closure between the Medicine Hat Block and Wyoming Craton along the Great Falls Tectonic Zone (GFTZ). A single granulite xenolith contains a spectrum of dispersed magmatic ages between 2000 and 2534 Ma. These ages do not produce a statistically significant population that can be correlated to known events within the Wyoming Craton or the adjacent GFTZ and probably represent melting of previously enriched mantle in Late Archaean or earlier. The subduction-related geochemical signature within this older Late Archaean xenolith may indicate an earlier subduction-event in the region. Since ages for all xenoliths are generally younger than existing Archaean to Late Archaean (> 2600 Ma) cratonic crust in the region,

these xenoliths are envisioned as new additions to the Wyoming Craton lithosphere. Metamorphic zircon populations from xenoliths constrain ca. 1770 Ma ages, slightly younger than magmatic zircon ages. These ages likely represent continent collision between the Medicine Hat Block and Wyoming Craton resulting in metamorphism that recrystallised all xenoliths to amphibolite/granulite facies. Zircons from the same amphibolite and granulite xenoliths were then examined using rare earth elements (REE), and hafnium and oxygen isotopes in order to provide a more rigorous interpretation of xenolith sources and petrogenesis. Rare earth elements are steeply positively sloping, do not show HREE depletion, and contain negative Eu anomalies. In general, REE indicate zircon growth together with feldspar before peak metamorphic phase transformation and the crystallisation of garnet. Two xenoliths contained magmatic zircons with high/radiogenic ϵ_{Hf} -2.3 to +3.7 and low, mantle-like oxygen signatures ($\delta^{18}\text{O} = 4.6\text{--}5.7\text{ ‰}$) consistent with a derivation from a mantle source with minimal supracrustal components. Xenoliths with magmatic ages between 1874 and 2534 Ma containing unradiogenic ϵ_{Hf} (-8.2 to -17.6) together with elevated oxygen isotopes relative to mantle values ($\delta^{18}\text{O} = 6.4\text{--}7.2\text{ ‰}$) are indicative of a process of melting of a subduction-metasomatised source. Hf and O data corroborate the petrogenesis of xenoliths in a subduction setting followed by collision-related metamorphism thereafter.

Finally, apatite grains provide insight into lower-medium temperature (350–550 °C) processes operating in these xenoliths. Additionally, the trace element characteristics of apatite within lower crustal lithologies was also investigated in order to add to a particularly scarce repository on rare earth elements within high-grade apatite. Apatite in all xenoliths are metamorphic and show light rare earth (LREE) enrichments relative to heavy rare earth elements (HREE), negative Eu anomalies and generally high concentrations of trace elements. Halogen compositions are uniform and allow classification as fluorapatite. Trace element patterns in metamorphic apatite signify progressive prograde metamorphism in which apatite grains continuously exchanged ions with minerals in the system, and acquired trace element concentrations redistributed by newly forming and previously crystallised metamorphic phases. In particular, break-down of monazite and crystallisation of metamorphic feldspar results in LREE enrichments and Eu depletions in metamorphic apatite respectively. Growth of garnet near the metamorphic peak depletes certain apatite grains in HREE. Such a scenario is supported by granulite/amphibolite mineralogy as well as pressure-temperature determinations (642–817 °C and 3.5–7.5 kbar) on these xenoliths that indicate amphibolite/granulite facies conditions. U-Pb geochronology produces lower-intercept ages between 300 and 500 Ma. Since these ages are decoupled from largely Proterozoic (ca. 1800–2500 Ma) U-Pb ages obtained from zircon from the same xenoliths, a mechanism of slow cooling likely resulted in younger Palaeozoic apatite ages. In this scenario, apatite originally crystallised during the Proterozoic (ca. 1860 Ma) and underwent high

temperature granulite facies metamorphism and recrystallisation at approximately 1770 Ma. From 1770 Ma onwards apatite slowly cooled as xenoliths were exhumed from lower crustal levels. The point at which apatite reached its closure temperature is recorded by the lower intercept on Tera-Wasserburg plots (ca. 300-500 Ma). A slow cooling mechanism was enabled by the high pressure-temperature conditions of xenoliths prevalent in the lower crust over a protracted period of time (>1000 Ma in our xenoliths). Shallower lying xenoliths (amphibolite) likely experienced more rapid cooling as recorded by lower-intercept ages that broadly correlate with that of Proterozoic metamorphic zircon (ca. 1770 Ma). The geodynamic history of the Wyoming craton began with convergence and ocean closure between the Medicine Hat Block and Wyoming Craton in the Proterozoic, resulting in initial apatite (and zircon) growth. Following metamorphism and recrystallisation of apatite, no significant magmatic or metamorphic events subsequently occurred within the Wyoming Craton during the period of 1770 Ma to 55 Ma. This implies a deep mafic root and thick continental cover that remained unaffected by minor thermo-tectonic events in the region. The results of all three studies are summarised in Figure 6.1.

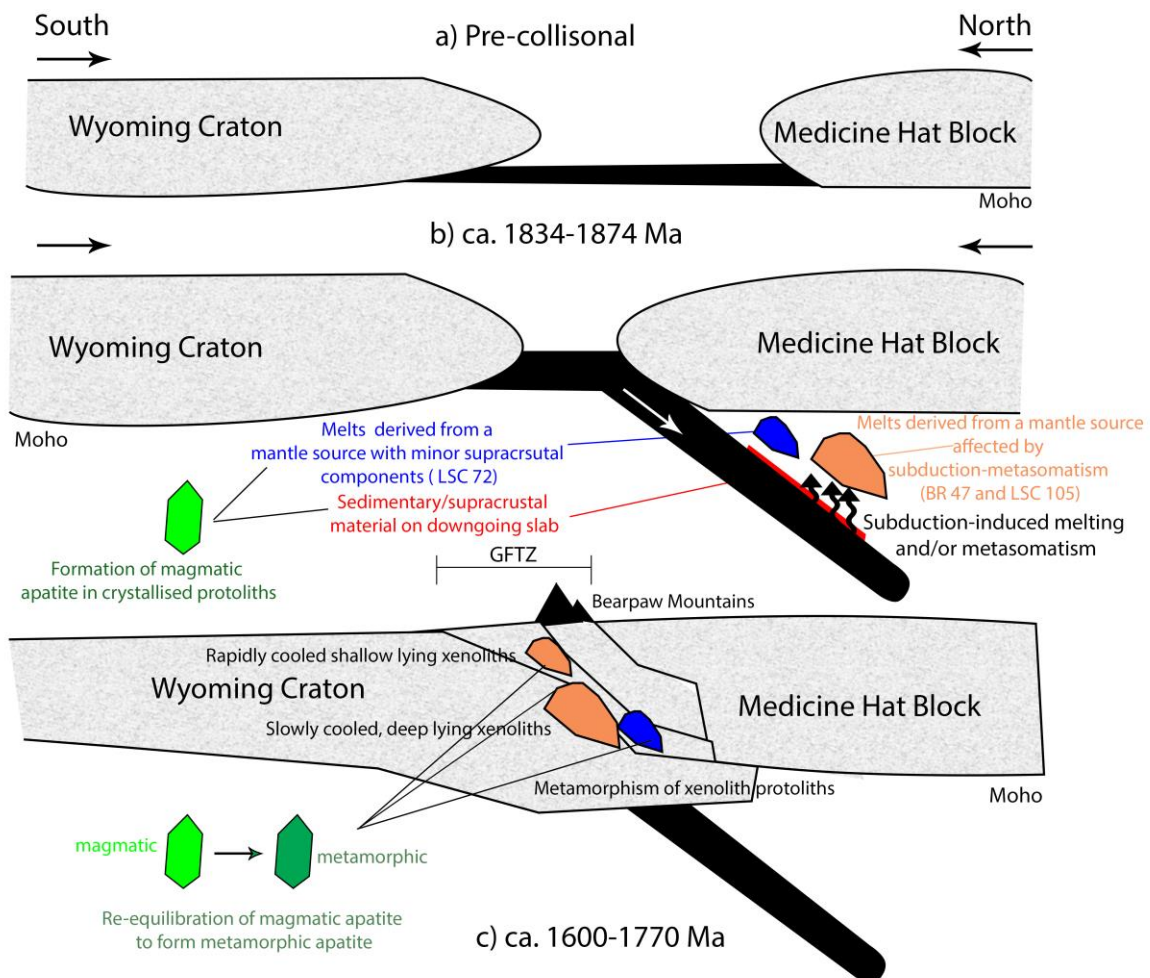


Figure 6.1: Schematic cross-sections for the tectonic evolution of the Wyoming Craton (WC), Medicine Hat Block (MHB) and Great Falls Tectonic Zone (GFTZ). a) Pre-collisional stage preceding Proterozoic subduction between the WC and MHB. b) Ocean closure commences at ca. 1834-1874 Ma. Subduction is orientated such that material is thrust beneath the MHB. Fluids emanating from the subducting slab result in melting and/or metasomatism of the overlying mantle wedge. Melting of subduction-metasomatised mantle results in the formation of protolith magmas for xenoliths LSC 105 and BR 47. A similar mechanism of subduction-metasomatism may have operated to create protolith magmas for LSC 89 in the Late Archaean or earlier. Melting of a mantle source that incorporated minimal amounts of subducted sediment, and was not strongly metasomatised, results in the formation of protolith magmas for LSC 72. Melting of a mantle source similar to that of LSC 72 may have produced protolith magmas for xenolith LSC 33 in the Archaean (ca. 3000-3500 Ma). Melts crystallise to form xenolith protoliths along with magmatic apatite. c) Following subduction, the WC and MHB collide at ca. 1770 Ma. Protoliths are subsequently metamorphosed to granulite/amphibolite facies. Originally magmatic apatite re-equilibrates to form metamorphic apatite. Deeper lying granulite xenoliths are slowly cooled while shallow lying amphibolite xenoliths are rapidly cooled.

Conclusions

In accordance with the aims of the study:

- The ages of the xenoliths are largely Proterozoic 1834-1874, with subordinate Late Archaean to Palaeoproterozoic ages of 2000-2534 Ma. This implies a younger, largely Proterozoic lower-middle crust compared to existing overlying Archaean crust of the Wyoming Craton.
- Whole-rock compositions are consistent with a basaltic precursor and, together with zircon geochronology and geochemistry, suggest new magmatic additions to the Wyoming Craton continental lithosphere in the Proterozoic (ca. 1800 Ma) and possibly Late Archaean (ca. 2500 Ma).
- Juvenile lithospheric material was added during subduction in the region and may have contributed to the largely mafic root underlying the Wyoming Craton/GFTZ, in agreement with previous studies.

In summary therefore, geochronology and geochemistry of zircons and apatite, extracted from amphibolite and granulite xenoliths from the Wyoming Craton, Montana, USA indicate addition of new melts to the continental lithosphere during the Proterozoic (ca. 1800 Ma) and possibly Late Archaean (ca. 2500 Ma). These melts were formed by both subduction-related processes. The melts resided within deeper portions of the continental lithosphere before collision-related metamorphism

at ca. 1770 Ma recrystallised all xenoliths to amphibolite/granulite facies. Following this metamorphic event, the region remained unaffected by significant thermo-tectonic events up until the Eocene, when xenoliths were exhumed by alkaline magmas.

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Conference Abstracts

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Characterization of Lower Crustal Xenoliths From the Wyoming Craton, Montana (USA), Using Accessory Mineral Chemistry and Geochronology with Implications For Lower Crustal Evolution

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The Bearpaw Mountains in north-western Montana comprise Eocene intrusive and volcanic rocks that contain entrained middle to lower crustal xenolith bodies spatially associated with the Wyoming Craton. Xenoliths include mafic granulites and amphibolites along with meta-basic cumulate rocks. Mineral geothermobarometry provides P-T estimates between 524-796 °C and 3.5-8.48 kbar. Detailed cathodoluminescence (CL) imaging of zircon reveal complex internal structures within both metamorphic and magmatic grains resulting from recrystallisation of original domains. U-Pb geochronology on zircon and apatite produce a spectrum of dispersed Late Archaean to Mid-Proterozoic Ages (2.0-2.53 Ga) together with a dominant younger Palaeoproterozoic age population (1.70-1.85 Ga). Zircon oxygen ($\delta^{18}\text{O} = 4.4\text{-}8.2\text{‰}$) and hafnium ($\epsilon_{\text{Hf}} = -20.6$ to $+3.7$) isotope data record both mantle and crustal signatures, and together with trace element information show a complex multi-stage crystallisation history. At least one metamorphic event is inferred between 1.70-1.85 Ga resulting from tectonic activity associated with the Great Falls Tectonic Zone (GFTZ). The xenoliths represent metamorphosed Late Archaean crustal rocks together with juvenile Proterozoic protolith magmas that crystallised at lower crustal levels.

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xenoliths represent metamorphosed Late Archaean crustal rocks together with juvenile Proterozoic protolith magmas that crystallised at lower crustal levels. This implies a complex cratonic history involving compositionally and temporally heterogeneous crustal components.

Appendices

Table 3.3: Summary of U-th-Pb for Bearpaw Xenoliths

Table 4.1: Age, Oxygen, Hafnium and Th/U Data and Internal Textures for Respective U-Pb Spots for zircon in Bearpaw xenoliths

Table 4.2: Summary of U-Th-Pb in Zircon for Bearpaw Xenoliths

Table 4.3: Hf Isotope Analyses for Zircon From Bearpaw Xenoliths

Table 5.3: LA-ICP-MS U-Pb Analyses on Apatite Grains from Amphibolite and Granulite Xenoliths and Apatite Standards

Table 5.4: Trace Element Analyses on Apatite Using LA-ICP-MS

Other Supplementary Data:

Chapter 3

Silicate major mineral compositions (Table A1)

Ti-in-zircon (Table A2)

Host minette Compositions (Table A3)

Quality control data (U-Pb in zircon) (Table A4)

Chapter 4

Oxygen isotopes in zircon (Table B1)

REE in zircon (Table B2)

Silicate trace element compositions (Table B3)

Quality control data (oxygen in zircon) (Table B4)

Quality control data (hafnium in zircon) (Table B5)

Summary of LA-SF-ICPMS instrumental conditions (Table B6)

Quality Control Data, REE in NIST Glasses and Zircon Standards (Table B7)

Chapter 5

Major elements in apatite (Table C1)

Trace Elements in Standards NIST 612 and Durango Apatite in This Study Compared to Reported Values (Table C2)

Sample	Spot #	²⁰⁷ Pb/ ²³⁵ U	±1σ (%)	²⁰⁶ Pb/ ²³⁸ U	±1σ (%)	²⁰⁸ Pb/ ²³² Th	±1σ (%)	²⁰⁷ Pb/ ²⁰⁶ Pb	±1σ (%)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb Age	±1σ (%)	²⁰⁷ Pb/ ²³⁵ U Age	±1σ (%)	²⁰⁶ Pb/ ²³⁸ U Age	±1σ (%)	[U] ppm	[Th] ppm	[Pb] ppm
LSC 33 (Granulite)	33-1*1	13.5261	2.14	0.4667	1.73	0.14	6.27	0.21022	1.26	59571	2907	20	2717	20	2469	35	334	194	215
	33-1*2	6.1366	2.37	0.3375	1.71	0.10	6.22	0.13186	1.64	25951	2123	29	1995	21	1875	28	641	366	283
	33-1*3	11.3368	2.28	0.4278	1.83	0.12	6.28	0.19220	1.37	151525	2761	22	2551	22	2296	35	593	351	345
	33-1*4	5.8464	2.74	0.3378	1.73	0.10	6.23	0.12551	2.12	33109	2036	37	1953	24	1876	28	279	121	118
	33-1*5	3.6723	3.38	0.2734	1.72	0.08	10.93	0.09741	2.91	2160	1575	54	1565	27	1558	24	30	8	10
	33-1*6	9.5429	2.13	0.3995	1.78	0.11	6.30	0.17323	1.17	40002	2589	19	2392	20	2167	33	250	131	132
	33-1*7	6.7873	3.63	0.3522	1.84	0.10	6.26	0.13976	3.13	420038	2224	53	2084	33	1945	31	605	398	284
LSC 72 (granulite)	72-1*1	4.8384	2.54	0.3254	2.41	0.09	5.45	0.10783	0.80	66739	1763	15	1792	22	1816	38	167	105	70
	72-1*2	4.8643	2.58	0.3260	2.42	0.09	5.43	0.10821	0.89	49462	1770	16	1796	22	1819	38	160	95	67
	72-1*3	4.9317	2.62	0.3256	2.41	0.10	5.57	0.10984	1.02	78774	1797	18	1808	22	1817	38	101	41	41
	72-1*4	4.9767	2.76	0.3263	2.42	0.09	5.70	0.11062	1.32	27759	1810	24	1815	24	1820	38	92	35	37
	72-2*1	3.9328	3.70	0.2709	2.39	0.07	7.40	0.11120	2.26	2304	1719	51	1621	30	1546	33	47	20	15
	72-2*2	4.8685	2.43	0.3213	2.40	0.09	5.94	0.10991	0.40	>10 ⁶	1798	7	1797	21	1796	38	880	19	316
	72-2*3	5.1488	2.47	0.3400	2.39	0.09	5.65	0.10985	0.62	135183	1797	11	1844	21	1886	39	493	77	193
	72-2*4	4.9289	2.46	0.3288	2.38	0.10	5.85	0.10873	0.61	>10 ⁶	1778	11	1807	21	1832	38	1045	19	383
	72-2*5	4.8149	2.57	0.3205	2.48	0.09	14.78	0.10896	0.66	41654	1782	12	1788	22	1792	39	381	54	140
	72-2*6	5.1810	3.02	0.3445	2.41	0.09	6.21	0.10907	1.81	14111	1784	33	1850	26	1908	40	44	16	18
	72-3*1	4.9355	2.68	0.3328	2.38	0.12	9.76	0.10756	1.23	19455	1759	22	1808	23	1852	38	62	2	23
	72-3*2	4.9932	2.89	0.3114	2.44	0.07	8.09	0.11630	1.55	71752	1900	28	1818	25	1748	37	28	3	10
	72-3*3	4.8312	2.70	0.3231	2.38	0.13	8.58	0.10844	1.27	15599	1773	23	1790	23	1805	38	97	1	35
	72-3*4	5.3140	2.45	0.3457	2.38	0.10	5.38	0.11150	0.55	267866	1824	10	1871	21	1914	40	293	84	121
	72-3*5	5.4211	2.86	0.3529	2.46	0.10	5.78	0.11140	1.45	17800	1822	26	1888	25	1949	42	99	24	41
	72-4*1	4.9142	2.45	0.3244	2.39	0.10	5.69	0.10988	0.56	121774	1797	10	1805	21	1811	38	365	16	133
	72-4*2	5.1020	3.90	0.3332	2.53	0.10	6.74	0.11104	2.97	4208	1817	53	1836	34	1854	41	13	7	5
	72-4*3	4.8611	2.94	0.3300	2.40	0.10	6.13	0.10684	1.70	2782	1746	31	1796	25	1838	39	44	22	18
	72-4*4	5.1394	2.42	0.3316	2.39	0.10	5.57	0.11241	0.41	600957	1839	7	1843	21	1846	38	667	21	248
	72-4*5	5.2715	2.69	0.3366	2.41	0.11	7.35	0.11359	1.19	17502	1858	21	1864	23	1870	39	69	7	27
	72-5*1	5.4739	2.78	0.3490	2.50	0.10	6.15	0.11376	1.21	15160	1860	22	1897	24	1930	42	57	15	23
	72-5*2	5.1441	2.57	0.3367	2.39	0.10	5.62	0.11080	0.95	>10 ⁶	1813	17	1843	22	1871	39	98	26	39
	72-5*3	5.0598	2.57	0.3319	2.39	0.10	5.64	0.11057	0.97	30527	1809	17	1829	22	1847	38	94	25	37
	72-5*4	5.2140	2.61	0.3371	2.45	0.10	5.64	0.11219	0.91	78225	1835	16	1855	22	1873	40	102	28	41
LSC 89 (Granulite)	89-1*1	5.8109	2.70	0.3530	2.38	0.10	5.60	0.11938	1.28	2940	1947	23	1948	24	1949	40	193	113	88
	89-1*2	6.5412	3.00	0.3715	2.45	0.11	5.60	0.12772	1.72	43104	2067	30	2051	27	2036	43	93	72	47
	89-1*3	7.2831	2.90	0.3933	2.50	0.11	5.52	0.13432	1.48	15597	2155	26	2147	26	2138	46	222	126	113
	89-1*4	6.1126	2.57	0.3597	2.38	0.10	5.38	0.12324	0.97	69071	2004	17	1992	23	1981	41	132	116	65
	89-1*5	4.6037	2.43	0.3167	2.40	0.09	5.74	0.10542	0.41	67670	1722	7	1750	21	1774	37	588	40	210
	89-2*1	8.8100	1.52	0.4243	1.42	0.12	1.85	0.15058	0.54	197949	2352	9	2319	14	2280	27	402	688	277
	89-2*2	8.6869	1.51	0.4158	1.45	0.11	1.81	0.15151	0.40	208857	2363	7	2306	14	2242	28	426	698	284
	89-3*1	7.5441	1.68	0.3921	1.45	0.11	1.83	0.13956	0.84	92145	2222	14	2178	15	2132	26	356		

LSC 105 (Granulite)	89-12*7 (2)	4.8259	2.68	0.3324	2.49	0.09	5.43	0.10530	0.98	38422	1720	18	1789	23	1850	40	123	167	61	
	89-12*8 (2)	4.7728	2.57	0.3179	2.40	0.09	5.37	0.10888	0.92	6699	1781	17	1780	22	1780	37	195	265	92	
	89-12*9 (2)	5.4779	2.52	0.3415	2.39	0.10	5.34	0.11635	0.77	24494	1901	14	1897	22	1894	39	188	282	99	
	89-14*1	5.0150	2.46	0.3322	2.38	0.09	5.30	0.10949	0.62	38265	1791	11	1822	21	1849	38	254	403	131	
	89-14*2	5.2725	2.52	0.3334	2.38	0.10	5.68	0.11471	0.80	3866	1875	14	1864	22	1855	39	345	90	137	
	89-14*3	7.4894	2.46	0.3971	2.38	0.11	5.31	0.13679	0.59	27177	2187	10	2172	22	2156	44	238	426	154	
	89-14*4	4.6052	2.52	0.3193	2.39	0.09	5.51	0.10460	0.80	10941	1707	15	1750	21	1786	37	176	127	74	
	89-14*5	10.1938	2.64	0.4689	2.50	0.13	5.42	0.15767	0.85	35236	2431	14	2453	25	2479	52	333	331	223	
	89-14*6	11.5887	2.99	0.5025	2.49	0.14	5.47	0.16725	1.66	23326	2530	28	2572	28	2625	54	164	140	115	
	89-14*7	9.2996	2.84	0.4453	2.41	0.12	5.50	0.15145	1.51	100133	2362	26	2368	26	2375	48	150	126	93	
	89-15*1 (2)	5.5870	2.75	0.3382	2.41	0.09	5.44	0.11981	1.31	13324	1953	23	1914	24	1878	39	137	113	62	
	89-15*2 (2)	4.5266	2.42	0.3111	2.38	0.09	5.50	0.10554	0.44	33202	1724	8	1736	20	1746	37	606	131	220	
	89-15*3 (2)	4.5428	2.43	0.3096	2.38	0.08	6.25	0.10641	0.48	55054	1739	9	1739	20	1739	36	852	31	294	
	89-15*4 (2)	4.8633	2.41	0.3265	2.39	0.09	5.72	0.10804	0.33	55801	1767	6	1796	21	1821	38	1154	47	422	
	89-15*5 (2)	4.7227	2.64	0.3155	2.39	0.09	5.41	0.10855	1.13	2820	1775	20	1771	22	1768	37	146	226	71	
	89-15*6	5.7252	3.17	0.3221	2.47	0.10	7.47	0.12891	1.99	3549	2083	35	1935	28	1800	39	324	119	130	
	89-15*7	8.9501	2.68	0.4298	2.39	0.12	5.35	0.15105	1.22	62106	2358	21	2333	25	2305	46	242	388	166	
	89-15*8	8.0447	2.55	0.4117	2.40	0.12	5.32	0.14173	0.87	11836	2249	15	2236	23	2222	45	179	318	121	
	89-15*9	5.4054	2.48	0.3434	2.38	0.11	5.56	0.11417	0.69	34514	1867	12	1886	21	1903	39	477	111	195	
	89-16*1	4.8161	2.72	0.3134	2.39	0.08	5.63	0.11146	1.30	7473	1823	23	1788	23	1757	37	116	98	49	
	89-16*2	7.3863	2.61	0.3914	2.39	0.11	5.30	0.13685	1.04	22589	2188	18	2159	24	2130	44	391	501	227	
	89-16*3	9.9002	2.46	0.4560	2.38	0.12	5.32	0.15746	0.61	30374	2429	10	2426	23	2422	48	286	456	207	
	89-16*4	8.0117	2.48	0.4046	2.40	0.11	5.31	0.14362	0.62	58822	2271	11	2232	23	2190	45	282	452	180	
	89-17*1	8.6814	2.19	0.4190	1.71	0.12	2.45	0.15027	1.36	143860	2349	23	2305	20	2256	33	420	578	270	
	89-17*2	4.9381	2.62	0.3167	2.39	0.09	5.35	0.11309	1.09	39978	1850	20	1809	22	1774	37	269	171	110	
	89-17*3	4.6248	2.46	0.3195	2.38	0.09	6.71	0.10500	0.62	11292	1714	11	1754	21	1787	37	522	32	187	
	LSC 105 (Granulite)	105-1*1	4.8608	1.73	0.3265	1.72	0.10	6.16	0.10797	0.15	532181	1765	3	1795	15	1822	27	5006	466	1856
		105-1*2	4.8718	1.74	0.3280	1.74	0.10	6.23	0.10773	0.15	700816	1761	3	1797	15	1829	28	5015	440	1865
		105-2*1	4.9891	1.79	0.3320	1.77	0.10	6.18	0.10899	0.25	769391	1783	5	1817	15	1848	29	5105	447	1924
		105-2*2	4.4029	1.85	0.2953	1.75	0.09	6.37	0.10812	0.60	64923	1768	11	1713	15	1668	26	901	55	300
		105-2*3	4.6595	1.85	0.3112	1.73	0.09	6.53	0.10861	0.65	55417	1776	12	1760	16	1746	26	649	41	227
		105-2*4	4.7938	1.82	0.3192	1.80	0.10	6.21	0.10892	0.28	>10 ⁶	1781	5	1784	15	1786	28	2376	188	859
		105-3*1	4.7721	1.74	0.3195	1.71	0.09	6.21	0.10832	0.31	182867	1771	6	1780	15	1787	27	2217	147	799
		105-3*2	4.6843	1.79	0.3141	1.74	0.09	6.34	0.10816	0.42	193862	1769	8	1764	15	1761	27	711	66	253
		105-3*3	4.5162	1.77	0.3056	1.72	0.09	6.45	0.10718	0.43	67822	1752	8	1734	15	1719	26	656	52	227
		105-3*4	4.9421	1.77	0.3323	1.73	0.10	6.20	0.10785	0.34	509113	1763	6	1809	15	1850	28	5813	429	2182
		105-4*1	4.5850	1.77	0.3085	1.72	0.09	6.19	0.10779	0.40	580808	1762	7	1747	15	1733	26	2749	174	955
		105-4*2	4.8089	1.79	0.3213	1.78	0.09	6.20	0.10855	0.19	780651	1775	3	1786	15	1796	28	4909	355	1781
		105-5*1	4.7846	1.79	0.3201	1.78	0.09	6.21	0.10839	0.19	634575	1773	3	1782	15	1790	28	2821	254	1024
		105-5*2	4.5820	1.78	0.3030	1.72	0.09	6.52	0.10969	0.49	121026	1794	9	1746	15	1706	26	1110	91	381
		105-6*1	4.8133	1.76	0.3201	1.74	0.09	6.20	0.10906	0.26	244680	1784	5	1787	15	1790	27	1898	163	688
	105-7*1	4.1268	1.75	0.2822	1.71	0.08	6.33	0.10608	0.36	103384	1733	7	1660	14	1602	24	1110	68	352	
105-7*2	4.7720	1.80	0.3208	1.79	0.09	6.19	0.10790	0.26												

Table 4.1							
Age, Oxygen, Hafnium and Th/U Data and Internal Textures for Respective U-Pb Spots in Zircon From Bearpaw Mountain Xenoliths							
Sample	CL Texture	U-Pb Spot	²⁰⁷ Pb/ ²⁰⁶ Pb Age	δ ¹⁸ O (‰)	¹⁷⁶ Hf/ ¹⁷⁷ Hf	ε _{Hf}	Th/U
LSC 33 (Granulite)	Convolute Bright/Dark (Magmatic)	33-1*1	2907	5.3	0.280670	-8.6	0.58
	Convolute Bright/Dark (Magmatic)	33-1*2	2123	5.3	0.280710	-25.5	0.57
	Convolute Bright/Dark (Magmatic)	33-1*3	2761	5.7			0.59
	Convolute Bright/Dark (Magmatic)	33-1*4	2036				0.44
	Convolute Bright/Dark (Magmatic)	33-1*5	1575	5.4			0.27
	Convolute Bright/Dark (Magmatic)	33-1*6	2589				0.52
	Convolute Bright/Dark (Magmatic)	33-1*7	2224	5.4			0.66
LSC 72 (Granulite)	Faint Enlarged Magmatic Zoning	72-1*1	1763	5.2	0.281744	3.0	0.63
	Faint Enlarged Magmatic Zoning	72-1*2	1770	5.2	0.281744	3.1	0.59
	Faint Enlarged Magmatic Zoning	72-1*3	1797	5.2			0.41
	Faint Enlarged Magmatic Zoning	72-1*4	1810	5.2	0.281735	3.7	0.38
	CL Bright Rim	72-2*1	1719				0.42
	Diffuse Exterior (Magmatic)	72-2*2	1797		0.281598, 0.281583	-2, - 1.4	0.16
	Diffuse Exterior (Magmatic)	72-2*3	1798				0.02
	CL Dark Diffuse "Core"	72-2*4	1778				0.02
	Diffuse Exterior (Magmatic)	72-2*5	1782		0.281584	-2.3	0.14
	Diffuse Exterior (Magmatic)	72-2*6	1784				0.37
	Intersecting Bright/Dark (Magmatic)	72-3*1	1759	4.6	0.281646	-0.6	0.03
	Intersecting Bright/Dark (Magmatic)	72-3*2	1900	4.6			0.10
	Intersecting Bright/Dark (Magmatic)	72-3*3	1773	4.6	0.281676	0.8	0.01
	Intersecting Bright/Dark (Magmatic)	72-3*4	1824	4.4			0.29
	Intersecting Bright/Dark (Magmatic)	72-3*5	1822				0.25
	Faint Oscillatory "Island"	72-4*1	1797	4.6			0.05
	Intersecting Bright/Dark (Magmatic)	72-4*2	1817	5.1			0.59
	Intersecting Bright/Dark (Magmatic)	72-4*3	1746				0.50
	Faint Oscillatory "Island"	72-4*4	1839	4.6, 4.8			0.03
	Intersecting Bright/Dark (Magmatic)	72-4*5	1858				0.10
	Bleached Oscillatory Magmatic	72-5*1	1860	5.1			0.26
	Bleached Oscillatory Magmatic	72-5*2	1813	5.2			0.27
	Bleached Oscillatory Magmatic	72-5*3	1809	5.5	0.281684	1.9	0.27
	Bleached Oscillatory Magmatic	72-5*4	1835	5.2			0.28
LSC 89 (Granulite)	CL Medium "Core" (Metamorphic, Type II)	89-1*1	1947	6.9	0.281552	0.4	0.58
	Diffuse Exterior (Metamorphic, Type II)	89-1*2	2067	6.9	0.281428	-1.2	0.77
	CL Medium "Core" (Metamorphic, Type II)	89-1*3	2155		0.281445	1.4	0.57
	CL Dark Metamorphic Rim (Type II)	89-1*4	1827				0.33
	CL Dark Metamorphic Rim (Type II)	89-1*5	1722				0.07
	Diffuse Exterior (Metamorphic, Type II)	89-1*6	2004	7.1			0.33
	CL Homogenous, Recrystallised (Magmatic) (Type I)	89-2*1	2352	6.6	0.281153	-4.4	1.92
	CL Homogenous, Recrystallised (Magmatic) (Type I)	89-2*2	2363	6.6	0.281152	-4.2	1.64
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-3*1	2222		0.281093	-9.6	1.55
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-3*2	2267	6.4	0.281085	-8.8	1.58
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-3*3	1963				0.77
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-3*4	1891				0.41
	CL Bright Rim (Type I)	89-3*5	1713				1.86
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-4*1	2424		0.2811068, 0.2811295	-4.4, -3.6	1.42
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-4*2	2323	7.2			0.86
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-4*3	1815	6.8			0.16
	CL Bright Rim (Type I)	89-4*4	1734				1.92
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-5*1	2473	6.9	0.281155	-1.5	1.21
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-5*2	1691				1.38
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-5*3	2123				0.84
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-5*4	1734				2.23
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-5*5	2534	6.9			1.74
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-5*6	2342				0.75
	Faint Magmatic (Type I)	89-6*1	1880	6.9			1.35
	Faint Magmatic (Type I)	89-6*2	1888		0.281150	-15.3	1.41
	Faint Magmatic (Type I)	89-6*3	2275	7.1	0.281113	-7.6	1.40
	Faint Magmatic (Type I)	89-6*4	1972	6.9, 6.9	0.281155	-13.1	1.91
	CL Dark Homogenous Metamorphic (Type II)	89-7*1	1708	6.6	0.281578	-4.2	0.05
	CL Dark Homogenous Metamorphic (Type II)	89-7*2	1755				0.04
	CL Light Magmatic Sector (Type I)	89-7*3	1846	6.8	0.281122	-17.2	0.84
	CL Light Magmatic Sector (Type I)	89-7*4	1818				0.08
	CL Dark Homogenous Metamorphic (Type II)	89-7*5	1748				0.05
	CL Dark Homogenous Metamorphic (Type II)	89-7*6	1765	6.9	0.281465	-6.9	0.04
	Convolute Resorbed/Faint Magmatic (Type I)	89-8*1	2020	6.6			1.80
	Convolute Resorbed/Faint Magmatic (Type I)	89-8*2	2006	6.6			1.81
	CL Bright Recrystallised (Type I)	89-8*3	1796	6.6			1.16
	CL Bright Recrystallised (Type I)	89-8*4	1737	6.9			1.46
	CL Homogenous Dark/Light Metamorphic (Type II)	89-9*1	1779	7.0, 6.9	0.281427	-7.9	0.25
	CL Homogenous Dark/Light Metamorphic (Type II)	89-9*2	1781	6.8			0.34
	CL Homogenous Dark/Light Metamorphic (Type II)	89-9*3	1772		0.281450	-7.3	0.34
	CL Homogenous Dark/Light Metamorphic (Type II)	89-9*4	1761		0.281476	-6.6	0.22
	CL Homogenous Dark/Light Metamorphic (Type II)	89-9*5	1793	6.8			0.26
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-10*2	2241	7.1	0.281085	-9.4	0.76
	Convolute Resorbed (Magmatic), Fir Tree (Type I)	89-10*3	2422	6.8	0.281095	-4.8	1.30
	CL Bright Rim (Type I)	89-10*4	1731	6.7			0.24
	CL Homogenous Light/Dark Metamorphic (Type II)	89-11*1	1794				0.03
	CL Homogenous Light/Dark Metamorphic (Type II)	89-11*2	1786	6.9, 6.6			0.04
	CL Homogenous Light/Dark Metamorphic (Type II)	89-11*3	1774	6.5	0.281545	-3.8	0.03
	CL Homogenous Light/Dark Metamorphic (Type II)	89-11*4	1765				0.14
	CL Dark Metamorphic Rim (Type II)	89-12*1	1788	6.6			0.03
	CL Dark Homogenous Magmatic (Type I)	89-12*2	2509				1.77
	CL Dark Homogenous Magmatic (Type I)	89-12*3	2490	6.8			1.68
	CL Bright Homogenous Magmatic (Type I)	89-12*4	1988	6.4			0.17
	CL Dark Metamorphic Rim (Type II)	89-12*5	1786				0.03

	CL Bright Homogenous (Magmatic) (Type I)	89-12(2)*6	1693				0.47
	CL Bright Homogenous (Magmatic) (Type I)	89-12(2)*7	1720	6.6	0.281218	-16.7	1.36
	CL Bright Homogenous (Magmatic) (Type I)	89-12(2)*8	1781	6.8	0.281154	-17.6	1.36
	CL Bright Homogenous (Magmatic) (Type I)	89-12(2)*9	1901				1.50
	CL Grey Homogenous (Magmatic) (Type I)	89-14*1	1791				1.59
	CL Grey Homogenous (Magmatic) (Type I)	89-14*2	1875				0.26
	CL Grey Homogenous (Magmatic) (Type I)	89-14*3	2187		0.281149	-8.4	1.79
	CL Grey Homogenous (Magmatic) (Type I)	89-14*4	1707				0.72
	CL Grey Homogenous (Magmatic) (Type I)	89-14*5	2431		0.281074	-5.4	0.99
	CL Grey Homogenous (Magmatic) (Type I)	89-14*6	2530				0.86
	CL Grey Homogenous (Magmatic) (Type I)	89-14*7	2362				0.84
	CL Bright Homogenous (Type I)	89-15(2)*1	1953				0.82
	CL Bright Homogenous (Type I)	89-15(2)*2	1724		0.281232	-16.1	0.22
	CL Dark Homogenous Metamorphic (Type II)	89-15(2)*3	1739				0.04
	CL Dark Homogenous Metamorphic (Type II)	89-15(2)*4	1767		0.281449	-7.4	0.04
	CL Bright Rim (Type II)	89-15(2)*5	1775				1.55
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-15*6	2083				0.37
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-15*7	2358				1.60
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-15*8	2249				1.78
	Convolute Resorbed, Recrystallised (Magmatic, Type I)	89-15*9	1867				0.23
	CL Bright Rim (Type I)	89-16*1	1823				0.84
	CL Dark Homogenous Magmatic (Type I)	89-16*2	2188				1.28
	CL Bright Rim (Type I)	89-16*3	2429				1.59
	CL Dark Homogenous Magmatic (Type I)	89-16*4	2271		0.281095	-8.3	1.60
	Faint Magmatic Sector (Type I)	89-17*1	2349				1.38
	Faint Magmatic Sector (Type I)	89-17*2	1850				0.64
	CL Bright Rim (Type I)	89-17*4	1714				0.06
LSC 105 (Granulite)	CL Homogenous Light/Dark Metamorphic	105-1*1	1765	7.5, 7.5			0.09
	CL Homogenous Light/Dark Metamorphic	105-1*2	1761	7.5			0.09
	CL Homogenous Light/Dark Metamorphic	105-2*1	1783				0.09
	CL Homogenous Light/Dark Metamorphic	105-2*2	1768	7.6			0.06
	CL Homogenous Light/Dark Metamorphic	105-2*3	1776	7.4			0.06
	CL Homogenous Light/Dark Metamorphic	105-2*4	1781	7.5			0.08
	CL Homogenous Light/Dark Metamorphic	105-3*1	1771	7.5			0.07
	CL Homogenous Light/Dark Metamorphic	105-3*2	1769	7.8			0.09
	CL Homogenous Light/Dark Metamorphic	105-3*3	1752				0.08
	CL Homogenous Light/Dark Metamorphic	105-3*4	1763				0.07
	CL Homogenous Light/Dark Metamorphic	105-4*1	1762	8.1			0.06
	CL Homogenous Light/Dark Metamorphic	105-4*2	1775	7.8, 8.0			0.07
	CL Homogenous Light/Dark Metamorphic	105-5*1	1773				0.09
	CL Homogenous Light/Dark Metamorphic	105-5*2	1794				0.08
	CL Homogenous Light/Dark Metamorphic	105-6*1	1784				0.09
	CL Homogenous Light/Dark Metamorphic	105-7*1	1733	7.6			0.06
	CL Homogenous Light/Dark Metamorphic	105-7*2	1764	8.1			0.10
	CL Homogenous Light/Dark Metamorphic	105-7*3	1764	7.6			0.10
	CL Homogenous Light/Dark Metamorphic	105-7*4	1797				0.08
BR 47(Amphibolite)	CL Grey, Diffuse (Magmatic/Metamorphic)	47-1*1	1804	6.0			0.40
	CL Grey, Diffuse (Magmatic/Metamorphic)	47-1*2	1791				0.40
	CL Dark Core (Magmatic/Metamorphic)	47-1*3	1819	6.3	0.281355	-9.6	0.46
	CL Bright Rim	47-2*2	1839				0.40
	Faint Magmatic Oscillatory	47-2*3	1882	6.4, 6.3			0.03
	Faint Magmatic Oscillatory	47-2*4	1883	6.4			0.54
	Faint Magmatic Oscillatory	47-2*5	1822	6.3			0.19
	Faint Magmatic Oscillatory	47-2*6	1874	6.6			0.70
	Faint Magmatic Oscillatory	47-3*1	1818	6.3	0.281358	-9.5	0.37
	Faint Magmatic Oscillatory	47-3*2	1811				0.31
	Faint Magmatic Oscillatory	47-3*3	1807				0.63
	Faint Magmatic Oscillatory	47-3*4	1800	6.4			0.46
	Faint Magmatic Oscillatory	47-4*1	1842	6.7, 6.9	0.281379	-8.2	0.19
	Faint Magmatic Oscillatory	47-4*2	1866	6.5, 6.3	0.281345	-8.8	0.88
	CL Dark Core	47-5*2	1867	6.6			1.28
	CL Dark Core	47-5*3	1865	6.5, 6.6			1.88
	CL Bright Rim	47-5*4	1846				0.45
	CL Grey, Diffuse (Magmatic/Metamorphic)	47-6*1	1808	6.1			0.60
	CL Grey, Diffuse (Magmatic/Metamorphic)	47-6*2	1761				0.37
	CL Grey, Diffuse (Magmatic/Metamorphic)	47-6*3	1791				0.52
	CL Grey, Diffuse (Magmatic/Metamorphic)	47-6*4	1785	6.5			0.57
	CL Grey, Diffuse (Magmatic/Metamorphic)	47-6*5	1794				0.54
	Faint Magmatic Oscillatory	47-7*1	1812	7.0, 6.6			0.06
	Faint Magmatic Oscillatory	47-7*2	1814				0.26
	Faint Magmatic Oscillatory	47-7*3	1800	6.7			0.17
	Faint Magmatic Oscillatory	47-7*4	1791	6.3			0.14
	Faint Magmatic Oscillatory	47-8*1	1812				0.55
	Faint Magmatic Oscillatory	47-8*2	1835	6.5			1.33
	Faint Magmatic Oscillatory	47-8*3	1870	6.8			0.11
	Faint Magmatic Oscillatory	47-8*4	1861	6.5			1.01

Table 4.2

Summary of U-Th-Pb in Zircon for Bearpaw Xenoliths

Sample	Spot #	²⁰⁷ Pb/ ²³⁵ U	±1σ (%)	²⁰⁶ Pb/ ²³⁸ U	±1σ (%)	²⁰⁸ Pb/ ²³² Th	±1σ (%)	²⁰⁷ Pb/ ²⁰⁶ Pb	±1σ (%)	Discordance (%)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb Age	±1σ (%)	²⁰⁷ Pb/ ²³⁵ U Age	±1σ (%)	²⁰⁶ Pb/ ²³⁸ U Age	±1σ (%)	[U] ppm	[Th] ppm	[Pb] ppm	
LSC 33 (Granulite)	33-1*1	13.5261	2.14	0.4667	1.73	0.14	6.27	0.21022	1.26	-15.1	59571	2907	20	2717	20	2469	35	334	194	215	
	33-1*2	6.1366	2.37	0.3375	1.71	0.10	6.22	0.13186	1.64	-11.7	25951	2123	29	1995	21	1875	28	641	366	283	
	33-1*3	11.3368	2.28	0.4278	1.83	0.12	6.28	0.19220	1.37	-16.9	151525	2761	22	2551	22	2296	35	593	351	345	
	33-1*4	5.8464	2.74	0.3378	1.73	0.10	6.23	0.12551	2.12	-7.8	33109	2036	37	1953	24	1876	28	279	121	118	
	33-1*5	3.6723	3.38	0.2734	1.72	0.08	10.93	0.09741	2.91	-1.1	2160	1575	54	1565	27	1558	24	30	8	10	
	33-1*6	9.5429	2.13	0.3995	1.78	0.11	6.30	0.17323	1.17	-16.3	40002	2589	19	2392	20	2167	33	250	131	132	
	33-1*7	6.7873	3.63	0.3522	1.84	0.10	6.26	0.13976	3.13	-12.5	420038	2224	53	2084	33	1945	31	605	398	284	
LSC 72 (granulite)	72-1*1	4.8384	2.54	0.3254	2.41	0.09	5.45	0.10783	0.80	3.0	66739	1763	15	1792	22	1816	38	167	105	70	
	72-1*2	4.8643	2.58	0.3260	2.42	0.09	5.43	0.10821	0.89	2.8	49462	1770	16	1796	22	1819	38	160	95	67	
	72-1*3	4.9317	2.62	0.3256	2.41	0.10	5.57	0.10984	1.02	1.1	78774	1797	18	1808	22	1817	38	101	41	41	
	72-1*4	4.9767	2.76	0.3263	2.42	0.09	5.70	0.11062	1.32	0.6	27759	1810	24	1815	24	1820	38	92	35	37	
	72-2*1	3.9328	3.70	0.2709	2.39	0.07	7.40	0.11120	2.26	-10.1	2304	1719	51	1621	30	1546	33	47	20	15	
	72-2*2	4.8685	2.43	0.3213	2.40	0.09	5.94	0.10991	0.40	5.0	>10 ⁶	1798	7	1797	21	1796	38	880	19	316	
	72-2*3	5.1488	2.47	0.3400	2.39	0.09	5.65	0.10985	0.62	-0.1	135183	1797	11	1844	21	1886	39	493	77	193	
	72-2*4	4.9289	2.46	0.3288	2.38	0.10	5.85	0.10873	0.61	3.0	>10 ⁶	1778	11	1807	21	1832	38	1045	19	383	
	72-2*5	4.8149	2.57	0.3205	2.48	0.09	14.78	0.10896	0.66	0.6	41654	1782	12	1788	22	1792	39	381	54	140	
	72-2*6	5.1810	3.02	0.3445	2.41	0.09	6.21	0.10907	1.81	7.0	14111	1784	33	1850	26	1908	40	44	16	18	
	72-3*1	4.9355	2.68	0.3328	2.38	0.12	9.76	0.10756	1.23	5.3	19455	1759	22	1808	23	1852	38	62	2	23	
	72-3*2	4.9932	2.89	0.3114	2.44	0.07	8.09	0.11630	1.55	-8.0	71752	1900	28	1818	25	1748	37	28	3	10	
	72-3*3	4.8312	2.70	0.3231	2.38	0.13	8.58	0.10844	1.27	1.8	15599	1773	23	1790	23	1805	38	97	1	35	
	72-3*4	5.3140	2.45	0.3457	2.38	0.10	5.38	0.11150	0.55	4.9	267866	1824	10	1871	21	1914	40	293	84	121	
	72-3*5	5.4211	2.86	0.3529	2.46	0.10	5.78	0.11140	1.45	6.9	17800	1822	26	1888	25	1949	42	99	24	41	
	72-4*1	4.9142	2.45	0.3244	2.39	0.10	5.69	0.10988	0.56	0.8	121774	1797	10	1805	21	1811	38	365	16	133	
	72-4*2	5.1020	3.90	0.3332	2.53	0.10	6.74	0.11104	2.97	2.1	4208	1817	53	1836	34	1854	41	13	7	5	
	72-4*3	4.8611	2.94	0.3300	2.40	0.10	6.13	0.10684	1.70	5.3	2782	1746	31	1796	25	1838	39	44	22	18	
	72-4*4	5.1394	2.42	0.3316	2.39	0.10	5.57	0.11241	0.41	0.4	600957	1839	7	1843	21	1846	38	667	21	248	
	72-4*5	5.2715	2.69	0.3366	2.41	0.11	7.35	0.11359	1.19	0.7	17502	1858	21	1864	23	1870	39	69	7	27	
	72-5*1	5.4739	2.78	0.3490	2.50	0.10	6.15	0.11376	1.21	3.7	15160	1860	22	1897	24	1930	42	57	15	23	
	72-5*2	5.1441	2.57	0.3367	2.39	0.10	5.62	0.11080	0.95	3.2	>10 ⁶	1813	17	1843	22	1871	39	98	26	39	
	72-5*3	5.0598	2.57	0.3319	2.39	0.10	5.64	0.11057	0.97	2.1	30527	1809	17	1829	22	1847	38	94	25	37	
	72-5*4	5.2140	2.61	0.3371	2.45	0.10	5.64	0.11219	0.91	2.0	78225	1835	16	1855	22	1873	40	102	28	41	
	LSC 89 (Granulite)	89-1*1	5.8109	2.70	0.3530	2.38	0.10	5.60	0.11938	1.28	0.1	2940	1947	23	1948	24	1949	40	193	113	88
		89-1*2	6.5412	3.00	0.3715	2.45	0.11	5.60	0.12772	1.72	-1.5	43104	2067	30	2051	27	2036	43	93	72	47
		89-1*3	7.2831	2.90	0.3933	2.50	0.11	5.52	0.13432	1.48	-0.8	15597	2155	26	2147	26	2138	46	222	126	113
		89-1*4	6.1126	2.57	0.3597	2.38	0.10	5.38	0.12324	0.97	3.0	69071	2004	17	1992	23	1981	41	132	116	65
		89-1*5	4.6037	2.43	0.3167	2.40	0.09	5.74	0.10542	0.41	-1.1	67670	1722	7	1750	21	1774	37	588	40	210
		89-2*1	8.8100	1.52	0.4243	1.42	0.12	1.85	0.15058	0.54	-3.1	197949	2352	9	2319	14	2280	27	402	688	277
		89-2*2	8.6869	1.51	0.4158	1.45	0.11	1.81	0.15151	0.40	-5.1	208857	2363	7	2306	14	2242	28	426	698	284
		89-3*1	7.5441	1.68	0.3921	1.45															

LSC 105 (Granulite)	89-14*5	10.1938	2.64	0.4689	2.50	0.13	5.42	0.15767	0.85	2.0	35236	2431	14	2453	25	2479	52	333	331	223
	89-14*6	11.5887	2.99	0.5025	2.49	0.14	5.47	0.16725	1.66	3.7	23326	2530	28	2572	28	2625	54	164	140	115
	89-14*7	9.2996	2.84	0.4453	2.41	0.12	5.50	0.15145	1.51	0.5	100133	2362	26	2368	26	2375	48	150	126	93
	89-15*1 (2)	5.5870	2.75	0.3382	2.41	0.09	5.44	0.11981	1.31	-3.8	13324	1953	23	1914	24	1878	39	137	113	62
	89-15*2 (2)	4.5266	2.42	0.3111	2.38	0.09	5.50	0.10554	0.44	1.3	33202	1724	8	1736	20	1746	37	606	131	220
	89-15*3 (2)	4.5428	2.43	0.3096	2.38	0.08	6.25	0.10641	0.48	0.0	55054	1739	9	1739	20	1739	36	852	31	294
	89-15*4 (2)	4.8633	2.41	0.3265	2.39	0.09	5.72	0.10804	0.33	3.1	55801	1767	6	1796	21	1821	38	1154	47	422
	89-15*5 (2)	4.7227	2.64	0.3155	2.39	0.09	5.41	0.10855	1.13	-0.4	2820	1775	20	1771	22	1768	37	146	226	71
	89-15*6	5.7252	3.17	0.3221	2.47	0.10	7.47	0.12891	1.99	-13.6	3549	2083	35	1935	28	1800	39	324	119	130
	89-15*7	8.9501	2.68	0.4298	2.39	0.12	5.35	0.15105	1.22	-2.3	62106	2358	21	2333	25	2305	46	242	388	166
	89-15*8	8.0447	2.55	0.4117	2.40	0.12	5.32	0.14173	0.87	-1.2	11836	2249	15	2236	23	2222	45	179	318	121
	89-15*9	5.4054	2.48	0.3434	2.38	0.11	5.56	0.11417	0.69	1.9	34514	1867	12	1886	21	1903	39	477	111	195
	89-16*1	4.8161	2.72	0.3134	2.39	0.08	5.63	0.11146	1.30	-3.6	7473	1823	23	1788	23	1757	37	116	98	49
	89-16*2	7.3863	2.61	0.3914	2.39	0.11	5.30	0.13685	1.04	-2.7	22589	2188	18	2159	24	2130	44	391	501	227
	89-16*3	9.9002	2.46	0.4560	2.38	0.12	5.32	0.15746	0.61	-0.3	30374	2429	10	2426	23	2422	48	286	456	207
	89-16*4	8.0117	2.48	0.4046	2.40	0.11	5.31	0.14362	0.62	-3.6	58822	2271	11	2232	23	2190	45	282	452	180
	89-17*1	8.6814	2.19	0.4190	1.71	0.12	2.45	0.15027	1.36	-4.0	143860	2349	23	2305	20	2256	33	420	578	270
	89-17*2	4.9381	2.62	0.3167	2.39	0.09	5.35	0.11309	1.09	-4.1	39978	1850	20	1809	22	1774	37	269	171	110
	89-17*3	4.6248	2.46	0.3195	2.38	0.09	6.71	0.10500	0.62	4.3	11292	1714	11	1754	21	1787	37	522	32	187
	105-1*1	4.8608	1.73	0.3265	1.72	0.10	6.16	0.10797	0.15	3.2	532181	1765	3	1795	15	1822	27	5006	466	1856
	105-1*2	4.8718	1.74	0.3280	1.74	0.10	6.23	0.10773	0.15	3.8	700816	1761	3	1797	15	1829	28	5015	440	1865
	105-2*1	4.9891	1.79	0.3320	1.77	0.10	6.18	0.10899	0.25	3.7	769391	1783	5	1817	15	1848	29	5105	447	1924
	105-2*2	4.4029	1.85	0.2953	1.75	0.09	6.37	0.10812	0.60	-5.6	64923	1768	11	1713	15	1668	26	901	55	300
	105-2*3	4.6595	1.85	0.3112	1.73	0.09	6.53	0.10861	0.65	-1.7	55417	1776	12	1760	16	1746	26	649	41	227
	105-2*4	4.7938	1.82	0.3192	1.80	0.10	6.21	0.10892	0.28	0.2	>10 ⁶	1781	5	1784	15	1786	28	2376	188	859
	105-3*1	4.7721	1.74	0.3195	1.71	0.09	6.21	0.10832	0.31	0.9	182867	1771	6	1780	15	1787	27	2217	147	799
	105-3*2	4.6843	1.79	0.3141	1.74	0.09	6.34	0.10816	0.42	-0.4	193862	1769	8	1764	15	1761	27	711	66	253
	105-3*3	4.5162	1.77	0.3056	1.72	0.09	6.45	0.10718	0.43	-1.9	67822	1752	8	1734	15	1719	26	656	52	227
	105-3*4	4.9421	1.77	0.3323	1.73	0.10	6.20	0.10785	0.34	4.9	509113	1763	6	1809	15	1850	28	5813	429	2182
	105-4*1	4.5850	1.77	0.3085	1.72	0.09	6.19	0.10779	0.40	-1.7	580808	1762	7	1747	15	1733	26	2749	174	955
	105-4*2	4.8089	1.79	0.3213	1.78	0.09	6.20	0.10855	0.19	1.2	780651	1775	3	1786	15	1796	28	4909	355	1781
	105-5*1	4.7846	1.79	0.3201	1.78	0.09	6.21	0.10839	0.19	1.0	634575	1773	3	1782	15	1790	28	2821	254	1024
	105-5*2	4.5820	1.78	0.3030	1.72	0.09	6.52	0.10969	0.49	-4.9	121026	1794	9	1746	15	1706	26	1110	91	381
	105-6*1	4.8133	1.76	0.3201	1.74	0.09	6.20	0.10906	0.26	0.4	244680	1784	5	1787	15	1790	27	1898	163	688
	105-7*1	4.1268	1.75	0.2822	1.71	0.08	6.33	0.10608	0.36	-7.6	103384	1733	7	1660	14	1602	24	1110	68	352
	105-7*2	4.7720	1.80	0.3208	1.79	0.09	6.19	0.10790	0.26	1.7	>10 ⁶	1764	5	1780	15	1793	28	3081	312	1122
	105-7*3	4.7356	1.75	0.3183	1.73	0.09	6.17	0.10791	0.28	1.0	>10 ⁶	1764	5	1774	15	1781	27	3616	375	1308
	105-7*4	4.7421	1.86	0.3132	1.74	0.10	6.78	0.10983	0.66	-2.2	44286	1797	12	1775	16	1756	27	759	60	270
BR 47 (Amphibolite)	47-1*1	4.8154	2.41	0.3166	2.38	0.10	5.30	0.11029	0.33	-1.7	160514	1804	6	1788	20	1773	37	526	210	206
	47-1*2	4.8984	2.43	0.3245	2.39	0.10	5.30	0.10949	0.47	1.1	194434	1791	9	1802	21	1812	38	508	204	204
	47-1*3	4.8588	2.41	0.3169	2.39	0.10	5.27	0.11120	0.33	-2.4	139930	1819	6	1795	20	1775	37	953	440	379
	47-2*1	5.2013	2.45	0.3356	2.43	0.11	5.31	0.11241	0.29	1.5	340631	1839	5	1853	21	1865	40	1029	409	428
	47-2*2	5.3967	2.47	0.3400	2.38	0.12	6.95	0.11512	0.63	0.3	124898	1882	11	1884	21	1887	39	259	7	99
	47-2*3	5.4413	2.40	0.3425	2.39	0.11	5.30	0.11522	0.18	0.8	766835	1883	3	1891	21	1899	39	2885	1549	1276
	47-2*4	4.3735	2.55	0.2848	2.38	0.08	6.70	0.11138	0.90	-11.3	7827	1822	16	1707	21	1615				

Table 4.3													
Hf-Isotope Analyses For Zircon From Bearpaw Xenoliths													
Sample	Hafnium Spot	U-Pb Spot	¹⁷⁶ Hf/ ¹⁷⁷ Hf	1SE	¹⁷⁶ Lu/ ¹⁷⁷ Hf	1SE	¹⁷⁶ Yb/ ¹⁷⁷ Hf	1SE	²⁰⁷ Pb/ ²⁰⁶ Pb Age	Discordance (%)	εHf	±1σ	T _{DM} (Ma)
LSC 33 (Granulite)	33--1	33-1*1	0.280670	0.000015	0.001485	0.000001	0.046477	0.000083	2907	-15.1	-8.6	0.5	
	33--2	33-1*2	0.280710	0.000015	0.001109	0.000010	0.033189	0.000330	2123	-11.7	-25.5	0.5	
LSC 72 (Granulite)	72--1-2	72-1*1	0.281744	0.000013	0.000496	0.000003	0.006222	0.000087	1763	3.0	3.0	0.5	2115
	72--1-2	72-1*2	0.281744	0.000013	0.000496	0.000003	0.008308	0.000090	1770	2.8	3.1	0.5	2111
	72--1-1	72-1*4	0.281735	0.000013	0.000735	0.000001	0.004525	0.000026	1810	0.6	3.7	0.5	2104
	72--2-1	72-2*1	0.281598	0.000015	0.000205	0.000000	0.000452	0.000016	1797	5.0	-1.4	0.5	2406
	72--2-2	72-2*2	0.281583	0.000013	0.000250	0.000005	0.015083	0.000218	1797	5.0	-2.0	0.5	2438
	72--2-2	72-2*4	0.281584	0.000013	0.000250	0.000003	0.015413	0.000119	1782	0.6	-2.3	0.5	2447
	72--3-1	72-3*1	0.281646	0.000013	0.000142	0.000062	0.148795	0.001960	1759	5.3	-0.6	0.5	2329
	72--3-2	72-3*3	0.281676	0.000010	0.000014	0.000005	0.010807	0.000189	1773	1.8	0.8	0.4	2254
	72--5-1	72-5*3	0.281684	0.000016	0.000429	0.000005	0.022589	0.000230	1809	2.1	1.9	0.6	
LSC 89 (Granulite)	89--1	89*1	0.281552	0.000009	0.000200	0.000001	0.015579	0.000027	1947	0.1	0.4	0.3	
	89--2	89*2	0.281428	0.000010	0.000202	0.000002	0.030138	0.000109	2067	-1.5	-1.2	0.4	
	89--2	89*3	0.281445	0.000010	0.000203	0.000001	0.016827	0.000045	2155	-0.8	1.4	0.4	
	89--2-1	89-2*1	0.281153	0.000013	0.000572	0.000004	0.021555	0.000160	2352	-3.1	-4.4	0.4	
	89--2-1	89-2*2	0.281152	0.000012	0.000572	0.000008	0.020940	0.000263	2363	-5.1	-4.2	0.4	
	89--3-1	89-3*1	0.281093	0.000014	0.000269	0.000003	0.019643	0.000083	2222	-4.0	-9.6	0.5	
	89--3-2	89-3*2	0.281085	0.000016	0.000439	0.000004	0.019920	0.000187	2267	-5.9	-8.8	0.6	
	89--4-2	89-4*1	0.281107	0.000013	0.000587	0.000032	0.034776	0.001260	2424	0.8	-4.4	0.5	
	89--4-1	89-4*2	0.281130	0.000010	0.000275	0.000000	0.005797	0.000008	2424	0.8	-3.6	0.4	
	89--5-1	89-5*1	0.281155	0.000016	0.000437	0.000003	0.011378	0.000090	2473	-1.2	-1.5	0.6	
	89--6-2	89-6*2	0.281150	0.000012	0.000387	0.000001	0.007418	0.000034	1888	-2.0	-15.3	0.4	
	89--6-1	89-6*3	0.281113	0.000015	0.000357	0.000002	0.014281	0.000083	2275	-3.8	-7.6	0.5	
	89--6-3	89-6*4	0.281155	0.000012	0.000515	0.000005	0.015594	0.000229	1972	-2.3	-13.1	0.4	
	89--7-3	89-7*1	0.281578	0.000010	0.000221	0.000001	0.020918	0.000078	1708	0.1	-4.2	0.4	
	89--7-2	89-7*3	0.281122	0.000011	0.000305	0.000001	0.017827	0.000087	1846	-2.4	-17.2	0.4	
	89--7-1	89-7*6	0.281465	0.000011	0.000152	0.000005	0.010940	0.000232	1765	1.5	-6.9	0.4	
	89--9-3	89-9*1	0.281427	0.000020	0.000618	0.000004	0.024110	0.000176	1779	-0.2	-7.9	0.7	
	89--9-1	89-9*3	0.281450	0.000013	0.000667	0.000010	0.009914	0.000411	1772	0.4	-7.3	0.4	
	89--9-2	89-9*4	0.281476	0.000026	0.000617	0.000006	0.016925	0.000305	1761	1.8	-6.6	0.9	
	89--10-2	89-10*2	0.281085	0.000013	0.000749	0.000000	0.028862	0.000045	2241	-5.0	-9.4	0.5	
	89--10-3	89-10*4	0.281095	0.000013	0.000433	0.000000	0.007551	0.000015	2422	1.1	-4.8	0.5	
	89--11-1	89-11*3	0.281545	0.000028	0.000982	0.000000	0.007625	0.000022	1774	1.2	-3.8	1.0	
	89--12-2	89-12*7	0.281218	0.000013	0.000218	0.000000	0.009554	0.000025	1720	7.6	-16.7	0.4	
	89--12-1	89-12*8	0.281154	0.000015	0.000459	0.000003	0.028591	0.000062	1781	-0.1	-17.6	0.5	
	89--14-1	89-14*3	0.281149	0.000015	0.000604	0.000006	0.007540	0.000165	2187	-1.4	-8.4	0.5	
	89--14-2	89-14*5	0.281074	0.000011	0.000252	0.000001	0.007594	0.000057	2431	2.0	-5.4	0.4	
	89--15-2	89-15 (2)*2	0.281232	0.000012	0.000201	0.000005	0.005964	0.000232	1724	1.3	-16.1	0.4	
	89--15-1	89-15*4	0.281449	0.000013	0.000215	0.000002	0.024221	0.000148	1767	3.1	-7.4	0.5	
	89--16-1	89-16*4	0.281095	0.000017	0.000708	0.000001	0.009585	0.000031	2271	-3.6	-8.3	0.6	
BR 47 (Amphibolite)	47--1-1	47-1*3	0.281355	0.000015	0.000659	0.000002	0.017944	0.000062	1819	-2.4	-9.6	0.5	
	47--3-1	47-3*1	0.281358	0.000016	0.000315	0.000003	0.008319	0.000126	1818	0.2	-9.5	0.6	
	47--4-2	47-4*1	0.281379	0.000021	0.004094	0.000008	0.026621	0.000302	1842	0.9	-8.2	0.7	
	47--4-1	47-4*2	0.281345	0.000012	0.000470	0.000005	0.016784	0.000167	1866	5	-8.8	0.4	

Table S.3: LA-ICP-MS U-Pb Analyses on Apatite Grains from Amphibolite and Granulite Xenoliths and Apatite Standards

Grain	Type	Grain Size	Core/Rim	²⁰⁷ Pb/ ²³⁵ U	²⁰⁷ Pb/ ²³⁵ U 2σ	²⁰⁶ Pb/ ²³⁸ U	²⁰⁶ Pb/ ²³⁸ U 2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb 2σ	Final Age ²⁰⁶ Pb/ ²³⁸ U	Final Age ²⁰⁶ Pb/ ²³⁸ U 2σ	Final Age ²⁰⁷ Pb/ ²³⁵ U	Final Age ²⁰⁷ Pb/ ²³⁵ U 2σ	Final Age ²⁰⁷ Pb Corrected	Final Age ²⁰⁷ Pb Corrected 2σ	±2σ6
G_NIST612_0				35.5	1.1	0.296	0.024	0.867	0.025	1671	136	3653	113	-91	65	1.00
G_NIST612_1				35.8	1.1	0.289	0.023	0.895	0.025	1637	130	3661	112	-169	66	1.00
G_NIST612_2				35.64	0.97	0.2969	0.024	0.863	0.025	1676	135	3657	100	-79	65	1.00
G_NIST612_3				35.63	0.99	0.3006	0.024	0.847	0.029	1694	135	3656	102	-33	75	1.00
G_NIST612_4				35.44	0.79	0.2876	0.022	0.885	0.023	1630	125	3651	81	-139	60	1.00
G_NIST612_5				35.87	0.91	0.2944	0.023	0.879	0.021	1663	130	3663	93	-125	57	1.00
G_NIST612_6				36.5	1.2	0.2959	0.023	0.884	0.025	1671	130	3680	121	-141	67	1.00
G_NIST612_7				35.4	1.2	0.2889	0.022	0.867	0.027	1636	125	3650	124	-88	68	1.00
G_NIST612_8				37.9	1.3	0.3029	0.024	0.893	0.029	1706	135	3717	128	-172	79	1.00
G_NIST612_9				36.7	1.5	0.297	0.025	0.878	0.023	1676	141	3685	151	-124	62	1.00
G_NIST612_10				36	1.2	0.291	0.024	0.879	0.024	1647	136	3666	122	-123	63	1.00
G_NIST612_11				37.4	1.2	0.302	0.025	0.885	0.031	1701	141	3704	119	-147	83	1.00
A_MAD_0				0.614	0.08	0.0771	0.0063	0.0579	0.0073	479	39	486	63	478	38	0.00
A_MAD_1				0.622	0.088	0.0807	0.0067	0.0568	0.008	500	42	491	69	501	41	0.00
A_MAD_2				0.564	0.083	0.0725	0.0059	0.056	0.0085	451	37	454	67	451	36	0.00
A_MAD_3				0.589	0.096	0.0762	0.0064	0.0567	0.0092	473	40	470	77	473	39	0.00
A_MAD_4				0.604	0.097	0.0773	0.0064	0.0567	0.0094	480	40	480	77	480	39	0.00
A_MAD_5				0.6	0.07	0.0764	0.0062	0.0568	0.0066	475	39	477	56	474	38	0.00
A_MAD_6				0.624	0.075	0.0761	0.0063	0.0596	0.0075	473	39	492	59	471	38	0.00
A_MAD_7				0.602	0.099	0.0757	0.0063	0.0575	0.0095	470	39	479	79	470	39	0.00
A_MAD_8				0.588	0.087	0.0743	0.0061	0.0575	0.0086	462	38	470	69	461	37	0.00
A_MAD_9				0.59	0.1	0.0766	0.0062	0.056	0.01	476	39	471	80	476	38	0.00
A_MAD_10				0.605	0.076	0.0786	0.0067	0.057	0.0078	488	42	480	60	488	41	0.00
A_MAD_11				0.6	0.11	0.0758	0.0062	0.057	0.01	471	39	477	87	471	38	0.00
A_McClure_0				4.06	0.22	0.1143	0.0094	0.259	0.016	698	57	1646	89	532	45	0.25
A_McClure_1				2.36	0.15	0.0949	0.008	0.181	0.012	584	49	1231	78	499	42	0.15
A_McClure_2				6.51	0.32	0.1339	0.011	0.36	0.023	810	67	2047	101	521	48	0.37
A_McClure_3				5.03	0.3	0.1196	0.0097	0.302	0.016	728	59	1824	109	518	43	0.30
A_McClure_4				2.71	0.15	0.1006	0.0085	0.194	0.011	618	52	1331	74	518	44	0.17
A_McClure_5				2.04	0.11	0.0954	0.0077	0.1536	0.009	587	47	1129	61	521	42	0.12
A_McClure_6				2.44	0.14	0.1033	0.0083	0.17	0.011	634	51	1254	72	551	44	0.14
A_McClure_7				2.94	0.18	0.0989	0.0079	0.212	0.013	608	49	1392	85	496	40	0.19
A_McClure_9				1.61	0.11	0.0881	0.0072	0.1288	NAN	544	44	974	67	498	40	0.09
A_McClure_10				1.54	0.11	0.0876	0.0071	0.1246	0.0074	541	44	947	68	498	40	0.08
A_McClure_11				1.87	0.14	0.0937	0.0079	0.144	0.0091	577	49	1071	80	519	43	0.11
									0.01							
Durango_0				0.68	0.17	0.0112	0.0019	0.44	0.076	72	12	527	132	36	9	0.50
Durango_1				0.18	0.044	0.00682	0.00099	0.226	0.068	44	6	168	41	34	6	0.23
Durango_2				0.238	0.049	0.00622	0.00083	0.35	0.1	40	5	217	45	25	6	0.38
Durango_3				0.178	0.049	0.00601	0.001	0.28	0.12	39	6	166	46	27	7	0.30
Durango_4				0.181	0.056	0.00628	0.001	0.31	0.13	40	6	169	52	27	8	0.33
Durango_5				0.278	0.06	0.00674	0.00088	0.343	0.097	43	6	249	54	27	6	0.37
Durango_6				0.249	0.065	0.0079	0.0012	0.268	0.088	51	8	226	59	37	8	0.28
Durango_7				0.278	0.069	0.0077	0.0011	0.32	0.11	49	7	249	62	32	8	0.35
Durango_8				0.28	0.081	0.00694	0.00098	0.36	0.13	45	6	251	73	27	8	0.40
Durango_9				0.195	0.056	0.0069	0.0011	0.239	0.081	44	7	181	52	34	7	0.24
Durango_10				0.23	0.066	0.0068	0.0013	0.262	0.08	44	8	210	60	32	8	0.27
Durango_11				0.23	0.064	0.00585	0.00088	0.32	0.11	38	6	210	58	25	6	0.35
LSC_89_0	Granulite	115	Core	58.2	3.9	0.524	0.05	0.81	0.046	2716	259	4144	278	148	195	0.96
LSC_89_1			Rim	115.1	7.8	0.908	0.088	0.925	0.054	4165	404	4828	327	-1431	556	1.00
LSC_89_2		110	Core	22.2	1.1	0.256	0.025	0.637	0.047	1469	143	3193	158	451	101	0.72
LSC_89_3			Rim/Inclusion	16.6	nan	0.295	nan	0.402	nan	1666	-	2912	-	1067	-	0.39
LSC_89_4			Rim	20.4	1.9	0.224	0.031	0.661	0.048	1303	180	3111	290	345	95	0.75
LSC_72_0	Granulite	105	Core	14.06	0.72	0.3	0.026	0.342	0.02	1691	147	2754	141	1215	109	0.31
LSC_72_1			Rim	30.5	2.4	0.448	0.043	0.502	0.033	2386	229	3503	276	1329	157	0.49
LSC_72_2		115	Core	15.6	1.4	0.416	0.039	0.267	0.021	2242	210	2853	256	1909	185	0.17
LSC_72_3			Rim	10.88	0.73	0.2526	0.021	0.314	0.024	1452	121	2513	169	1071	95	0.28
LSC_72_4		125	Core	10.11	0.71	0.215	0.02	0.338	0.024	1255	117	2445	172	874	87	0.33
LSC_72_5			Rim	11.93	0.77	0.205	0.019	0.422	0.038	1202	111	2599	168	704	85	0.44
LSC_72_6		100	Core	6.73	0.53	0.2127	0.018	0.23	0.019	1243	105	2077	164	1028	88	0.19
LSC_72_7			Rim	5.56	0.33	0.175	0.014	0.231	0.016	1040	83	1910	113	847	68	0.20
LSC_72_8		120	Core	17	1.3	0.335	0.029	0.373	0.027	1863	161	2935	224	1287	123	0.34
LSC_72_9			Rim	14.2	1.1	0.252	0.025	0.401	0.032	1449	144	2763	214	910	104	0.40
LSC_72_10		100	Core	6.65	0.48	0.233	0.022	0.207	0.013	1350	127	2066	149	1162	108	0.15
LSC_72_11			Rim	17.6	1.5	0.431	0.038	0.291	0.023	2310	204	2968	253	1913	178	0.20
LSC_72_12		105	Core	8.31	0.79	0.173	0.018	0.349	0.028	1029	107	2265	215	688	78	0.35
LSC_72_13			Rim	5.67	0.37	0.1458	0.012	0.281	0.018	877	72	1927	126	654	56	0.27
LSC_72_14		100	Core	10	0.68	0.295	0.025	0.244	0.015	1666	141	2435	166	1394	118	0.18
LSC_72_15			Rim	9.3	0.57	0.286	0.024	0.241	0.018	1622	136	2368	145	1357	115	0.18
LSC_72_16		105	Core	12	1.1	0.189	0.018	0.469	0.04	1116	106	2604	239	580	78	0.50
LSC_72_17		110	Core	6.27	0.49	0.274	0.023	0.169	0.014	1561	131	2014	157	1432	119	0.09
LSC_72_18			Rim	8.4	1	0.182	0.021	0.335	0.046	1078	124	2275	271	743	103	0.33
LSC_33_0	Granulite	130	Core	3.54	0.33	0.0907	0.0081	0.291	0.03	560	50	1536	143	401	41	0.29
LSC_33_1			Rim	6.27	0.46	0.096	0.0088	0.475	0.036	591	54	2014	148	286	37	0.53
LSC_33_2		110	Core	53	4.2	0.56	0.057	0.699	0.062	2867	292	4050	321	792	260	0.77
LSC_33_3			Rim	77	7	0.851	0.086	0.648	0.054	3969	401	4424	402	1826	342	0.62
LSC_33_4		110	Core	53.5	4.5	0.454	0.053	0.91	0.1	2413	282	4060	341	-379	403	1.00

LSC_33_5		Rim	121	11	0.866	0.1	1.046	0.09	4021	464	4878	443	-4172	1571	1.00		
LSC_33_6	120	Core	19.5	1.8	0.225	0.024	0.656	0.062	1308	140	3067	283	356	114	0.75		
LSC_33_7		Rim	19.3	1.9	0.179	0.02	0.807	0.085	1062	119	3057	301	46	124	0.96		
LSC_33_8	110	Core	36.1	4.8	0.316	0.046	0.826	0.091	1770	258	3669	488	30	234	0.99		
LSC_33_9		Rim	19.9	1.4	0.2	0.021	0.741	0.065	1175	123	3087	217	169	105	0.87		
LSC_33_10	110	Core	20.5	2	0.232	0.026	0.664	0.07	1345	151	3115	304	353	131	0.76		
LSC_33_11		Rim	38.3	2.9	0.316	0.034	0.908	0.078	1770	190	3728	282	-230	213	1.00		
LSC_33_12	100	Core	18.6	1.5	0.185	0.02	0.749	0.071	1094	118	3021	244	142	106	0.88		
LSC_33_13		Rim	16.3	1.7	0.154	0.017	0.85	0.12	923	102	2895	302	-20	152	1.00		
LSC75_1	Granulite	125	Core	128.6	33	0.6202	0.057	1.4757	0.044	3111	230	4938	260	-2812	370	1.00	
LSC75_2			Rim	237.8	61	1.05	0.098	1.6148	0.048	4614	300	5552	250	-8990	1800	1.00	
LSC75_3		100	Core	251.6	65	1.092	0.1	1.6449	0.049	4741	310	5607	260	-10740	2500	1.00	
LSC75_4		100	Core	37.52	9.6	0.2989	0.027	0.8984	0.027	1686	140	3706	250	110	150	0.90	
LSC75_5			Rim	39.02	10	0.3157	0.029	0.8847	0.027	1768	140	3745	250	147	140	0.89	
LSC75_6		105	Core	31.32	8	0.2821	0.026	0.7967	0.024	1602	130	3528	250	305	97	0.80	
LSC75_7			Rim	179.8	46	0.768	0.072	1.6665	0.05	3662	260	5256	270	-6180	1300	1.00	
LSC75_8		110	Core	196.3	51	0.798	0.078	1.7466	0.052	3737	270	5316	260	-7510	1800	1.00	
LSC75_9		110	Core	129.5	33	0.622	0.058	1.5173	0.046	3110	230	4942	260	-3030	630	1.00	
LSC75_10			Rim	69.14	18	0.4053	0.037	1.2344	0.037	2191	170	4315	260	-875	170	1.00	
LSC75_11		110	Core	72.25	18	0.416	0.038	1.2579	0.038	2242	170	4359	260	-971	180	1.00	
LSC75_12		Rim	160.6	41	0.747	0.07	1.5654	0.047	3593	260	5160	260	-4450	750	1.00		
LSC75_13		Rim	203.9	52	0.899	0.083	1.6447	0.049	4130	290	5401	260	-7240	1400	1.00		
LSC75_14	110	Core	588	150	2.286	0.22	1.8565	0.056	7620	430	6450	270			1.00		
LSC75_15			Rim	25	6.4	0.18751	0.017	0.9693	0.03	1108	92	3302	250	-30	220	0.97	
LSC75_16		105	Core	61.1	16	0.3047	0.028	1.4425	0.044	1711	140	4167	260	-1185	220	1.00	
LSC75_17	105	Core	272.5	70	1.065	0.1	1.8648	0.056	4630	330	5664	290	-10610	2800	1.00		
LSC75_18			Rim	275.9	71	1.088	0.1	1.8411	0.055	4700	330	5672	280	-10420	2900	1.00	
LSC75_19			Rim	52.8	14	0.3062	0.028	1.252	0.054	1721	140	3989	370	-739	780	1.00	
LSC75_20	125	Core	53.13	14	0.2817	0.025	1.387	0.043	1600	130	4046	250	-936	450	1.00		
LSC75_21			Rim	116.6	30	0.626	0.057	1.3764	0.041	3132	230	4837	260	-2188	360	1.00	
LSC75_22		150	Core	95.46	24	0.5455	0.051	1.2999	0.039	2806	210	4639	250	-1486	250	1.00	
LSC75_23			Rim	1050	300	4.26	0.68	1.8276	0.055	9850	450	6878	160			1.00	
LSC75_24	110		Core	224	58	1.013	0.095	1.634	0.05	4498	320	5477	290	-9570	2500	1.00	
LSC75_25	105	Core	631	160	2.597	0.25	1.8122	0.054	8170	440	6517	250			1.00		
LSC75_26	115	Core	964	260	3.89	0.47	1.824	0.055	9630	570	6809	300	-7400	1500	1.00		
LSC75_27	120	Core	236.4	60	1.05	0.098	1.6895	0.051	4607	300	5540	250	-10160	2000	1.00		
LSC75_28	115	Core	446	120	1.891	0.19	1.7702	0.053	6700	390	6139	230	-12800	3100	1.00		
LSC75_29	115	Core	109.7	28	0.5818	0.053	1.428	0.043	2954	220	4777	260	-2282	460	1.00		
LSC75_30	125	Core	38.57	9.8	0.2389	0.021	1.2276	0.037	1381	110	3731	240	-481	120	1.00		
LSC75_31	100	Core	35.16	8.9	0.3471	0.033	0.7743	0.023	1920	160	3643	250	420	130	0.78		
LSC75_32	100	Core	293.1	75	1.29	0.12	1.7362	0.052	5328	330	5761	260	-14010	4800	1.00		
LSC75_33	105	Core	281.9	72	1.275	0.12	1.6952	0.051	5285	340	5719	260	-12610	3500	1.00		
LSC75_34	100	Core	234.4	60	1.091	0.1	1.6613	0.05	4744	310	5539	260	-10640	2400	1.00		
LSC75_35			Rim	136	35	0.7564	0.07	1.3952	0.042	3627	260	4994	260	-2831	600	1.00	
LSC75_36		125	Core	144.3	37	0.7672	0.07	1.4646	0.044	3667	260	5053	250	-3445	510	1.00	
LSC75_37		Rim	142.8	37	0.782	0.074	1.427	0.044	3699	280	5021	270	-3360	690	1.00		
LSC75_38		Rim	684	180	2.91	0.3	1.8217	0.055	8680	500	6582	280	-19430	740	1.00		
LSC75_39	130	Core	161.1	41	0.827	0.076	1.5307	0.046	3878	270	5162	260	-4476	680	1.00		
LSC93_1	Granulite	100	Core	25.87	6.5	0.2992	0.027	0.6879	0.021	1687	130	3341	250	415	160	0.69	
LSC93_2			Core	40	10	0.438	0.042	0.722	0.024	2333	180	3765	270	484	130	0.72	
LSC93_3		50	Core	11.098	2.9	0.17675	0.016	0.4843	0.015	1049	85	2530	240	518	99	0.49	
LSC93_4		50	Core	10.767	2.8	0.17385	0.015	0.4745	0.014	1033	84	2503	240	522	91	0.48	
LSC93_5		75	Core	19.26	5.1	0.21138	0.019	0.628	0.019	1236	100	3054	250	390	86	0.63	
LSC93_6		100	Core	18.7	4.9	0.21472	0.019	0.5977	0.018	1254	100	3026	250	444	85	0.60	
LSC93_7		100	Core	18.73	4.9	0.21425	0.019	0.5976	0.018	1251	100	3027	260	443	93	0.60	
BR47_1	Amphibolite	100	Core	15.61	4	0.3899	0.036	0.27941	0.0083	2123	170	2853	250	1673	180	0.28	
BR47_2		110	Core	15.499	4	0.3876	0.035	0.27912	0.0083	2112	160	2846	250	1664	170	0.28	
BR47_3				Rim	14.35	3.7	0.3668	0.033	0.28892	0.0086	2014	160	2772	240	1596	150	0.29
BR47_4			125	Core	15.033	3.9	0.3629	0.032	0.2579	0.0077	1996	160	2817	250	1535	140	0.26
BR47_5				Rim	14.907	3.8	0.3638	0.033	0.2587	0.0077	2000	160	2809	240	1543	150	0.26
BR47_6		110		Core	15.957	4.1	0.3629	0.032	0.29362	0.0088	1996	160	2874	250	1470	130	0.29
BR47_7		100	Core	12.888	3.3	0.3534	0.033	0.31111	0.0093	1951	150	2671	240	1576	140	0.31	
BR47_8		120	Core	13.301	3.4	0.36461	0.033	0.28619	0.0085	2004	160	2701	250	1622	160	0.29	
BR47_9		100	Core	14.943	3.8	0.3616	0.034	0.27215	0.0081	1990	150	2811	240	1514	130	0.27	

Table 5.4: Trace Element Analyses on Apatite Using LA-ICP-MS

		Th	U	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	ΣLREE	ΣHREE	Eu/Eu*	Ce/Ce*	(La/Sm) _N	(Gd/Yb) _N	(La/Yb) _N	(La/Gd) _N	Th/U
BR_47_1	Amphibolite	151.00	35.00	1658.00	2439.00	819.00	124.20	25.70	76.30	7.45	37.70	7.30	18.80	2.45	12.20	2.27	5230.37	5040.20	164.47	0.80	3.24	8.34	5.06	92.32	18.25	4.31
BR_47_2		0.94	2.16	386.70	1245.00	1188.00	315.00	16.80	333.00	43.80	253.00	48.40	124.00	15.20	78.00	10.40	4057.30	3134.70	905.80	0.16	0.86	0.77	3.45	3.37	0.98	0.44
BR_47_3		145.00	32.30	1594.00	2573.00	993.00	154.60	24.10	108.80	10.09	45.50	8.80	20.40	2.51	14.40	2.12	5551.32	5314.60	212.62	0.57	2.79	6.44	6.11	75.20	12.30	4.49
BR_47_4		116.00	35.00	1409.00	2274.00	950.00	157.00	27.80	114.00	11.00	56.00	10.30	23.60	3.28	20.40	2.80	5059.18	4790.00	241.38	0.63	2.50	5.60	4.52	46.92	10.38	3.31
BR_47_5		113.00	49.00	1372.00	2401.00	987.00	163.20	26.70	94.50	10.24	52.10	8.91	21.90	2.76	13.60	2.13	5156.04	4923.20	206.14	0.66	2.54	5.25	5.62	68.53	12.19	2.31
BR_47_6		136.00	39.00	1555.00	2475.00	976.00	158.20	23.20	106.20	10.42	52.70	8.45	20.40	2.54	15.20	2.23	5405.54	5164.20	218.14	0.55	2.67	6.14	5.65	69.50	12.29	3.49
BR_47_7		53.00	17.40	1203.00	2078.00	933.00	158.00	29.00	113.20	11.56	56.50	11.10	26.50	3.15	17.80	3.02	4643.83	4372.00	242.83	0.66	2.30	4.75	5.15	45.91	8.92	3.05
BR_47_8		33.70	18.30	959.00	1531.00	615.00	98.10	17.60	75.70	7.17	36.40	6.30	15.00	1.91	18.12	1.42	3372.72	3203.10	152.02	0.62	2.64	6.10	7.54	80.23	10.64	1.84
LSC_33_0	Granulite	13.60	8.81	417.00	1180.00	1023.00	201.00	24.20	174.00	21.30	114.00	22.30	56.10	6.28	34.90	4.59	3490.67	3033.00	433.47	0.39	0.83	1.30	4.03	8.12	2.01	1.54
LSC_33_1		10.39	6.56	240.40	795.00	821.00	175.70	22.21	169.20	20.48	121.70	22.77	58.20	7.09	38.20	5.25	2646.50	2181.40	442.89	0.39	0.91	0.85	3.58	4.28	1.19	1.58
LSC_33_2		13.50	1.03	780.00	1960.00	1350.00	177.00	31.30	73.40	4.03	12.11	1.11	1.40	0.11	0.27	0.04	4674.77	4551.00	92.47	0.84	1.01	2.75	216.73	1933.84	8.92	13.11
LSC_33_3		8.55	0.74	608.00	1450.00	1071.00	157.00	24.30	54.10	3.39	9.60	0.81	1.26	0.08	0.29	0.03	3622.87	3529.00	69.57	0.80	0.82	2.42	150.93	1424.24	9.44	11.49
LSC_33_4		13.60	0.67	769.00	1890.00	1420.00	174.00	27.60	81.40	5.21	19.80	2.46	3.47	0.22	0.61	0.07	4684.84	4544.00	113.24	0.71	0.97	2.76	107.96	856.39	7.93	20.36
LSC_33_5		8.92	0.57	395.00	1130.00	990.00	125.00	21.90	67.90	4.64	17.20	2.16	2.94	0.19	0.53	0.05	2975.51	2858.00	95.61	0.72	0.73	1.97	103.65	506.29	4.88	15.57
LSC_33_6		9.10	1.42	493.00	1390.00	1250.00	262.00	22.70	254.00	29.70	180.00	35.10	80.50	8.63	46.70	5.53	4295.86	3633.00	640.16	0.27	0.95	1.18	4.40	7.17	1.63	6.41
LSC_33_7		9.95	1.61	512.00	1420.00	1300.00	295.00	24.50	289.00	34.60	210.00	38.60	91.40	9.88	50.20	5.99	4555.17	3801.00	729.67	0.26	0.76	1.08	4.66	6.93	1.49	6.18
LSC_33_8		12.70	2.99	576.00	1670.00	1140.00	204.00	29.20	179.00	15.40	74.00	11.20	20.40	1.84	6.20	0.67	4194.91	3857.00	308.71	0.47	0.84	1.76	23.36	63.11	2.70	4.25
LSC_33_9		15.50	2.53	623.00	1450.00	1220.00	230.00	28.20	170.00	15.70	77.70	11.76	22.90	1.87	7.26	0.78	4099.17	3763.00	307.97	0.43	0.95	1.69	18.94	58.29	3.08	6.13
LSC_33_10		15.80	1.56	571.00	1380.00	1102.00	181.00	27.30	128.20	10.13	39.10	5.02	7.23	0.36	0.87	0.05	3669.25	3451.00	190.95	0.55	0.99	1.97	119.22	445.86	3.74	10.13
LSC_33_11		13.81	1.45	558.00	1343.00	1104.00	192.70	27.25	132.60	11.10	42.90	5.62	8.79	0.45	1.23	0.13	3664.77	3434.70	202.82	0.52	0.81	1.81	87.22	308.18	3.53	9.52
LSC_33_12		14.50	1.91	570.00	1640.00	1330.00	219.00	27.40	159.00	13.20	61.50	9.33	18.70	1.69	7.14	0.89	4341.85	4043.00	271.45	0.45	0.83	1.63	18.02	54.23	3.01	7.59
LSC_33_13		11.43	1.64	527.00	1520.00	1150.00	202.00	25.40	145.00	13.10	56.50	8.60	18.50	1.58	6.43	0.80	3923.91	3648.00	250.51	0.45	0.87	1.63	18.24	55.68	3.05	6.97
LSC_72_1	Granulite	11.90	4.08	351.00	702.00	362.00	51.80	5.22	42.80	5.37	30.40	5.85	14.20	1.68	9.68	1.39	1675.59	1559.00	111.37	0.34	0.96	4.23	3.58	24.63	6.89	2.92
LSC_72_2		11.41	4.28	397.00	803.00	369.00	53.40	5.45	47.30	5.72	32.50	5.73	13.80	1.70	9.89	1.45	1833.34	1709.80	118.09	0.33	1.22	4.64	3.87	27.27	7.05	2.67
LSC_72_3		8.00	2.75	344.00	574.00	290.00	38.30	4.23	37.30	4.19	24.80	3.94	10.54	1.19	6.81	1.01	1406.11	1312.10	89.78	0.34	1.20	5.61	4.43	34.32	7.74	2.91
LSC_72_4		15.79	4.80	430.00	818.00	402.00	64.10	6.43	56.00	6.71	36.40	6.74	16.78	2.10	10.92	1.54	1951.72	1808.10	137.19	0.33	1.16	4.19	4.15	26.75	6.45	3.29
LSC_72_5		7.90	4.66	216.00	600.00	280.00	41.80	5.84	33.70	3.97	22.90	3.76	10.21	1.33	8.26	1.19	1295.16	1204.00	85.32	0.47	1.20	3.23	3.30	17.76	5.38	1.70
LSC_72_6		7.23	4.56	204.00	570.00	307.00	47.00	6.39	34.40	4.24	23.50	4.62	11.60	1.48	8.58	1.19	1295.00	1199.00	89.61	0.48	1.08	2.71	3.24	16.15	4.98	1.59
LSC_72_7		21.20	8.07	297.00	867.00	420.00	70.00	7.94	54.20	6.61	35.40	6.80	16.50	2.24	13.20	1.71	1899.60	1755.00	136.66	0.39	1.12	2.65	3.32	15.28	4.60	2.63
LSC_72_8		29.90	9.88	401.00	1030.00	450.00	71.20	8.08	60.80	7.39	40.00	7.42	18.90	2.36	13.10	1.88	2225.13	2065.20	151.85	0.37	1.16	3.52	3.75	20.79	5.54	3.03
LSC_72_9		7.49	3.37	250.00	592.00	277.00	37.90	4.55	32.60	3.45	20.70	3.75	10.36	1.22	7.23	1.12	1305.08	1220.10	80.43	0.39	1.28	4.12	3.65	23.49	6.44	2.22
LSC_72_10		7.29	3.85	247.00	610.00	289.00	43.50	5.59	34.10	4.04	24.80	4.41	11.50	1.52	8.21	1.18	1355.85	1260.50	89.76	0.44	1.11	3.55	3.36	20.44	6.08	1.89
LSC_72_11		36.30	9.98	574.00	1310.00	513.00	68.90	9.25	59.60	7.46	42.00	8.32	19.50	2.52	13.50	1.94	2747.99	2583.90	154.84	0.44	1.50	5.20	3.57	28.88	8.09	3.64
LSC_72_12		6.83	2.66	234.00	512.00	240.00	37.00	4.07	28.40	3.29	19.10	3.37	9.41	1.10	6.25	0.89	1151.38	1075.50	71.81	0.38	1.38	3.95	3.68	25.43	6.92	2.57
LSC_72_13		11.70	5.55	346.00	770.00	329.00	45.10	6.40	36.60	4.13	24.30	4.64	11.00	1.41	8.30</											

Table A1: Electron Microprobe Analysis of Representative Minerals from Different Bearpaw Xenolith Types																															
Element	LSC 89 (Granulite)	LSC 90-2	LSC 90-3	LSC 90-4	LSC 90-5	LSC 90-6	LSC 90-7	LSC 90-8	LSC 90-9	LSC 90-10	LSC 90-11	LSC 90-12	LSC 90-13	LSC 90-14	LSC 90-15	LSC 90-16	LSC 90-17	LSC 90-18	LSC 90-19	LSC 90-20	LSC 90-21	LSC 90-22	LSC 90-23	LSC 90-24	LSC 90-25	LSC 90-26	LSC 90-27	LSC 90-28	LSC 90-29		
SiO ₂	59.31	58.89	58.85	58.73	58.87	59.01	59.15	58.86	59.22	59.74	59.35	58.96	59.06	58.97	59.23	57.54	57.88	58.06	57.75	57.72	57.87	57.87	58.12	58.37	57.87	57.87	57.87	57.87	57.87	57.87	
TiO ₂	0.06	0.06	0.10	0.11	0.07	0.08	0.06	0.07	0.08	0.07	0.09	0.07	0.09	0.07	0.08	0.10	0.08	0.11	0.07	0.08	0.10	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	
Al ₂ O ₃	21.72	21.57	21.57	21.54	21.57	21.57	21.55	21.59	21.60	21.55	21.69	21.71	21.76	21.76	21.80	21.80	21.80	21.80	21.80	21.80	21.80	21.80	21.80	21.80	21.80	21.80	21.80	21.80	21.80	21.80	
Cr ₂ O ₃	0.05	0.06	0.00	0.00	0.09	0.08	0.08	0.07	0.02	0.05	0.04	0.09	0.10	0.15	0.05	0.01	0.02	0.00	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
FeO	25.66	25.66	25.66	25.64	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	25.65	
MnO	0.80	0.64	0.66	0.57	0.62	0.71	0.73	0.64	0.60	0.61	0.64	0.55	0.54	0.61	0.52	2.86	3.08	2.91	3.04	3.00	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	
MgO	7.25	7.10	7.23	7.07	7.10	6.95	7.01	7.27	7.28	7.14	7.29	7.35	7.34	7.45	7.62	1.55	1.54	1.79	1.72	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	
CaO	6.55	6.55	6.55	6.55	6.55	6.55	6.55	6.54	6.49	6.75	6.49	6.75	6.49	6.75	6.49	11.14	11.06	11.11	10.95	11.06	11.06	11.06	11.06	11.06	11.06	11.06	11.06	11.06	11.06	11.06	
Na ₂ O	0.01	0.01	0.01	0.00	0.02	0.00	0.02	0.00	0.01	0.01	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
Total	101.22	100.52	100.61	100.32	100.55	100.43	101.08	100.49	101.14	100.92	101.68	100.52	101.11	100.99	100.96	100.17	100.60	100.60	101.25	100.45	100.63	99.76	99.92	100.67	100.18	99.96	99.96	99.96	99.96	99.96	99.96
Si	3.01	3.00	3.01	3.00	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.01	
Ti	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Al ^{IV}	1.96	1.96	1.96	1.94	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	1.96	
Cr	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Fe ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Fe ²⁺	1.66	1.67	1.67	1.65	1.67	1.65	1.64	1.64	1.64	1.67	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.72	1.71	1.74	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	
Mn	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.20	0.21	0.19	0.20	0.20	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	
Mg	0.83	0.82	0.84	0.83	0.83	0.82	0.82	0.81	0.80	0.80	0.87	0.85	0.84	0.84	0.83	0.18	0.18	0.21	0.20	0.20	0.60	0.58	0.58	0.57	0.57	0.57	0.57	0.57	0.57	0.57	
Ca	0.54	0.54	0.54	0.54	0.54	0.54	0.54	0.54	0.53	0.55	0.51	0.51	0.51	0.51	0.51	0.85	0.84	0.84	0.83	0.84	0.87	0.86	0.86	0.85	0.85	0.85	0.85	0.85	0.85	0.85	
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Sum	8.01	8.02	8.05	8.05	8.03	8.02	8.00	7.98	7.97	7.97	8.07	8.02	8.00	8.01	8.02	8.02	8.01	8.02	8.02	8.01	8.02	8.01	8.07	8.01	7.99	7.93	7.93	7.93	7.93	7.93	
Prp (Mg)	27.50	27.22	28.44	28.37	28.31	27.53	27.28	28.83	28.62	28.34	27.72	27.85	28.63	27.91	30.27	6.08	7.01	6.81	6.53	6.53	21.69	20.09	19.60	18.76	18.80	18.80	18.80	18.80	18.80	18.80	
Ann (Fe)	53.26	53.22	51.85	51.76	51.59	51.60	52.86	53.09	54.42	54.03	50.47	54.09	53.09	54.50	55.26	55.12	55.17	55.18	55.18	55.18	52.51	55.19	56.69	56.89	56.92	56.92	56.92	56.92	56.92	56.92	
Prp (Mn)	1.29	1.39	1.46	1.27	1.38	1.56	1.59	1.38	1.29	1.31	1.44	1.32	1.21	1.16	1.13	6.70	6.91	6.48	6.84	6.75	10.04	1.72	1.66	1.59	1.63	1.63	1.63	1.63	1.63	1.63	
Grs (Ca)	17.49	17.51	18.27	17.66	17.63	17.62	17.48	17.42	17.11	16.97	16.61	16.61	16.60	16.38	15.94	30.41	30.56	30.09	30.14	30.11	20.94	20.43	20.89	20.69	20.69	20.69	20.69	20.69	20.69	20.69	
Mgt (Fe ²⁺)	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.34	0.34	0.34	0.34	0.34	0.10	0.10	0.11	0.11	0.10	0.25	0.24	0.25	0.24	0.24	0.24	0.24	0.24	0.24	0.24	

Calcations on basis of 12 oxygens for garnet, 8 oxygens for feldspar, 6 oxygens for pyroxene, 23 oxygens for amphibole, 22 oxygens for biotite

Pyroxene	MC-100(Granulite)	MC-100-2	MC-100-3	MC-100-4	MC-100-5	MC-100-6	MC-100-7	MC-100-8	MC-100-9	MC-100-10	MC-100-11	MC-100-12	MC-100-13	MC-100-14	MC-100-15	MC-100-16	MC-100-17	MC-100-18	MC-100-19	MC-100-20	MC-100-21	MC-100-22	MC-100-23	MC-100-24	MC-100-25	MC-100-26	MC-100-27	MC-100-28	MC-100-29
SiO ₂	52.58	52.49	52.05	52.41	52.67	52.64	52.99	52.98	53.56	53.07	54.20	53.22	53.34	51.83	52.64	51.78	51.72	52.65	52.81	53.04	52.85	50.35	51.63						
TiO ₂	0.27	0.28	0.35	0.32	0.33	0.30	0.31	0.20	0.22	0.28	0.11	0.19	0.14	0.18	0.15	0.26	0.16	0.12	0.04	0.04	0.03	0.41	0.11						
Al ₂ O ₃	1.08	1.55	1.41	1.45	1.20	1.24	1.48	1.07	1.12	0.53	1.29	1.47	1.29	1.10	0.51	1.01	0.51	1.01	1.00	0.95	1.09	4.50	1.60						
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
FeO	7.41	7.77	7.83	8.12	7.58	6.97	6.72	6.86	7.06	7.50	10.76	6.88	8.19	10.76	8.88	10.47	9.69	9.47	10.42	11.31	10.57	12.64	11.24						
MnO	0.00	0.06	0.12	0.12	0.05	0.11	0.05	0.08	0.05	0.10	0.32	0.36	0.31	0.11	0.24	0.05	0.08	0.10	0.09	0.27	0.12	0.27	0.22	0.32					
MgO	12.98	12.78	12.97	12.79	13.03	13.29	13.43	13.40	13.24	14.25	13.58	14.45	11.84	13.32	11.93	12.50	13.05	12.86	13.00	13.07	12.64	14.40	12.71						
CaO	21.95	21.80	21.77	21.84	21.66	22.21	22.29	22.38	22.27	21.80	23.18	21.48	23.56	22.36	23.29	22.71	23.88	23.45	22.76	23.16	22.88	22.39	17.20	20.60					
Na ₂ O	1.42	1.40	1.39	1.39	1.30	1.22	1.25	1.23	1.26	1.10	1.10	1.48	0.82	0.51	0.22	0.54	0.46	0.32	0.27	0.23	0.26	0.22	0.26						
Total	100.28	99.45	99.45	99.99	100.24	100.06	100.08	100.35	99.90	101.21	99.47	100.35	99.96	99.47	100.16	99.79	99.30	100.20	100.45	100.62	100.14	100.09	98.53						
Si	1.93	1.94	1.93	1.94	1.94	1.94	1.95	1.95	1.96	1.96	1.98	1.99	1.97	1.96	1.96	1.96	1.95	1.95	1.97	1.97	1.98	1.98	1.98						
Ti	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
Al	0.07	0.06	0.07	0.06	0.06	0.06	0.05	0.05	0.04	0.04	0.02	0.01	0.01	0.04	0.04	0.05	0.05	0.03	0.03	0.02	0.02	0.12	0.03						
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
Fe	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06							
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
Fe ²⁺	0.16	0.18	0.18	0.18	0.21	0.18	0.17	0.16	0.18	0.19	0.34	0.30	0.15	0.31	0.23	0.23	0.26	0.26	0.39	0.34	0.34	0.33	0.35						
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01							
Mg	0.71	0.71	0.71	0.71	0.70	0.72	0.73	0.74	0.73	0.74	0.77	0.76	0.78	0.67	0.74	0.67	0.70	0.73	0.72	0.73	0.73	0.71	0.68						
Ca	0.06	0.06	0.07	0.06	0.06	0.08	0.08	0.08	0.08	0.07	0.07	0.07	0.08	0.03	0.03	0.03	0.02	0.02	0.04	0.03	0.02	0.04	0.04						
Na	0.10	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04							
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
Sum	1.91	1.92	1.93	1.93	1.92	1.93	1.92	1.93	1.92	1.93	1.92	1.93	1.92	1.93	1.92	1.93	1.92	1.93	1.92	1.93	1.92	1.93							
En	39.31	39.29	38.90	39.15	38.82	39.12	39.97	40.29	40.26	40.10	40.41	38.51	40.79	35.17	38.06	34.90	36.29	37.17	37.17	37.17	36.30	42.38	37.38						
Wo	47.97	47.51	47.43	47.39	47.26	47.93	48.19	48.26	48.05	47.75	47.15	43.79	47.81	47.34	47.84	47.84	47.74	47.79	46.45	44.27	46.22	36.38	43.54						
Fs	12.71	11.48	11.47	11.48	12.96	11.85	11.41	12.76	11.45	12.78	11.40	12.78	11.40	12.78	11.46	11.46	11.46	11.46	11.46	11.46	11.46	11.46	11.46						
Mg ¹⁰⁰ (Fe)	0.01	0.79	0.80	0.80	0.77	0.80	0.81	0.82	0.80	0.79	0.85	0.72	0.84	0.69	0.78	0.70	0.73	0.74	0.71	0.68	0.68	0.76	0.67						

	89_7_seg_5	6	0.9	692
	89_7_seg_6	6	0.6	698
	89_7_seg_7	8	1.0	718
	89_10_seg_1	6	0.7	699
	89_10_seg_2	5	0.5	683
	89_10_seg_3	5	0.8	681
	89_10_seg_4	6	1.2	700
	89-14	4	0.3	659
BR 47	47_1_seg_1	19	2.9	801
	47_1_seg_2	31	6.0	853
	47_1_seg_3	51	16.0	909
	47_1_seg_4	18	2.6	798
	47_2_seg_1	6	0.6	692
	47_2_seg_2	16	6.0	782
	47_2_seg_3	6	0.8	693
	47_4_seg_1	41	4.1	882
	47_4_seg_2	17	1.2	787
	47_4_seg_3	20	2.2	806
LSC 33	33-1	10	0.5	737
LSC 72	72_1_seg_1	3	0.4	654
	72_1_seg_3	3	0.4	643
	72-2_1	7	0.6	712
	72_3_seg_1	2	0.6	618
	72_3_seg_2	2	0.3	620

Table A3

Major and Trace Elements For Minette Host Lavas (Macdonald et al., 1992)

	P62-35A	P62-41	WC92	WC 88	LSC 288	BR1	P56-10	P56-14	P50-26	P56-32	BC3	P48-25	AC4	CDN1	Average
SiO ₂	47.75	47.55	49.80	47.93	53.39	48.11	48.36	50.71	51.77	50.36	49.00	48.92	52.26	47.75	49.55
TiO ₂	0.62	0.62	0.52	0.55	0.48	0.77	0.75	0.90	0.72	0.76	0.96	0.73	0.80	0.82	0.71
Al ₂ O ₃	8.18	8.33	9.52	9.30	11.87	10.25	12.68	11.61	12.48	11.99	11.65	13.18	12.34	8.27	10.83
K ₂ O	3.68	2.97	4.02	4.89	4.47	5.50	1.75	3.49	4.03	3.56	2.64	6.37	4.82	2.82	3.93
T-Fe ₂ O ₃	9.76	9.28	8.80	9.20	7.59	9.55	8.92	9.75	8.92	9.23	10.87	8.73	9.30	9.89	9.27
MnO	0.17	0.16	0.14	0.16	0.12	0.16	0.15	0.17	0.16	0.17	0.18	0.16	0.18	0.16	0.16
MgO	19.64	18.66	17.24	16.65	12.44	12.43	10.17	8.36	8.36	8.18	8.11	8.03	7.39	19.79	12.53
CaO	6.44	6.04	6.06	6.69	5.25	8.38	9.16	8.47	7.57	9.35	9.75	7.47	7.50	5.75	7.42
Na ₂ O	1.70	2.17	1.89	1.37	2.81	1.17	3.73	3.01	2.80	3.04	3.45	2.09	2.44	2.13	2.41
P ₂ O ₅	0.54	0.59	0.42	0.57	0.46	0.80	0.55	0.65	0.52	0.65	0.62	0.71	0.59	0.46	0.58
Total	98.48	96.37	98.41	97.31	98.88	97.12	96.22	97.12	97.33	97.29	97.23	96.39	97.62	97.84	97.40
Cs	9.00	54.00													
Rb	166	204	126	151	150	222	143	126	124	201	113	233	125	136	159
Sr	882	985	644	997	972	1840	694	803	730	754	783	664	713	645	865
Y	15	16	12	14	16	16	18	22	15	19	21	18	22	23	18
Zr	97	111	81	92	122	127	83	126	94	101	112	125	137	158	112
Nb	11	20	5	12	8	16	7	9	8	7	9	8	9	7	10
Ba	2046	3656	1653	2614	1760	2834	2126	2195	1839	2196	2140	3150	2188	1761	2297
La	34	44	19	28	18	36	22	27	23	25	25	19	33	19	27
Ce	71	99	37	74	50	96	43	69	43	49	59	57	73	50	62
Nd	40	48	17	34	26	47	27	37	25	27	31	36	33	23	32
Sm	6.1	6.3													6
Eu	1.5	1.5													2
Tb	0.63	0.66													1
Hf	2.2	2.5													2
Ta	0.47	0.9													1
Pb	13	16	17	11	19	9	15	12	16	18	13	54	17	12	17
Th	6	11	8	3	4	3	5	6	4	6	5	5	8	6	6
U	2.3	2.1													2
K ₂ O/TiO ₂															5.50
Sr/Rb															5.45
La/Nd															0.82

Table A4: Quality Control Data (U-Pb on Temora-2 and 91500 zircon standards)

Sample/spot	²⁰⁷ Pb/ ²³⁵ U	±σ (%)	²⁰⁶ Pb/ ²³⁸ U	±σ (%)	²⁰⁸ Pb/ ²³² Th	±s %	Disc. %	Disc. %	²⁰⁷ Pb/ ²⁰⁶ Pb	±σ	²⁰⁷ Pb/ ²³⁵ U	±σ	²⁰⁶ Pb/ ²³⁸ U	±σ	[U] ppm	[Th] ppm	[Pb] ppm	Th/U calc	Th/U meas
Tem-2@2	0.509	0.07	1.724	0.47	0.023	6.83	-3.8433		432	71.03	418	12.72	416	6.94	97	49	8	0.54	0.51
Tem-2@3	0.531	0.07	1.721	0.62	0.021	6.50	-7.83803		462	47.41	432	9.80	427	7.11	212	132	18	0.57	0.62
Tem-2Thurs@1	0.510	0.07	1.715	0.74	0.021	6.36	-1.95317		425	34.76	418	8.02	417	6.93	322	163	26	0.50	0.51
Tem-2 Thurs@4	0.518	0.07	1.711	0.45	0.022	7.46	-9.26196		459	73.08	424	13.19	418	6.92	79	27	6	0.33	0.34
Tem-2Thurs@6	0.483	0.07	1.718	0.42	0.022	8.02	22.80102		337	81.21	400	13.51	411	6.85	77	30	6	0.51	0.39
Tem-2Thurs@8	0.526	0.07	1.720	0.46	0.020	8.63	-10.0675		467	72.71	429	13.29	422	7.02	122	43	10	0.31	0.35
Tem-2Thurs@10	0.512	0.07	1.723	0.38	0.020	7.19	-0.18514		420	90.87	420	15.69	420	7.00	134	71	11	0.50	0.53
Tem-2Fri@1	0.527	0.07	1.711	0.46	0.019	7.35	-5.10919		449	71.54	430	13.09	427	7.06	121	66	10	0.47	0.54
Tem-2@1	0.529	0.07	1.715	0.50	0.022	6.95	-19.8022		514	63.86	431	12.10	416	6.91	104	49	8	0.40	0.47
Tem-2 Thurs@5	0.542	0.07	1.726	0.64	0.020	6.49	-22.9419	-0.98756	541	44.74	440	9.68	421	7.03	186	115	16	0.46	0.62
Tem-2Thurs@7	0.549	0.07	1.713	0.42	0.020	7.84	-23.5704		550	78.90	444	14.79	424	7.04	126	42	10	0.24	0.34
Tem-2Fri@1bis	0.539	0.07	1.725	0.56	0.022	7.00	1.727361		432	56.05	438	11.04	439	7.32	111	32	9	0.29	0.28
91500 Wed@1	1.856	0.18	1.738	0.74	0.059	6.62	-4.04289		1093	31.04	1066	15.56	1052	16.90	76	24	16	0.34	0.31
91500 Wed@2	1.701	0.17	1.734	0.59	0.051	7.31	7.557383		963	48.07	1009	19.06	1030	16.53	75	23	15	0.32	0.31
91500 Wed@3	1.824	0.18	1.729	0.73	0.057	6.62	-0.32973		1056	31.83	1054	15.56	1053	16.82	75	24	16	0.33	0.31
91500Wed-A@1	1.809	0.17	1.782	0.72	0.056	6.70	-4.34626		1078	34.26	1049	16.35	1035	17.06	76	25	16	0.33	0.32
91500Wed-A@2	1.907	0.18	1.878	0.74	0.055	6.81	-3.79844		1110	33.91	1084	17.09	1071	18.55	76	25	16	0.32	0.32
91500Wed@4	1.787	0.18	1.721	0.68	0.055	6.68	1.31356		1032	37.13	1041	16.63	1045	16.62	81	28	17	0.36	0.34
91500Wed@5	1.814	0.18	1.720	0.68	0.055	6.80	0.193074		1049	36.92	1051	16.69	1051	16.71	82	28	17	0.36	0.34
91500Wed@6	1.891	0.18	1.716	0.66	0.057	6.79	-6.5868		1124	38.88	1078	17.53	1055	16.73	81	28	17	0.34	0.34
91500Wed@7	1.844	0.18	1.713	0.69	0.056	6.73	-2.04106		1075	35.88	1061	16.53	1055	16.69	80	28	17	0.35	0.34
91500Wed@8	1.859	0.18	1.711	0.65	0.057	7.32	1.787776		1055	40.02	1067	17.59	1072	16.92	79	27	17	0.36	0.34
91500Thurs@1	1.839	0.18	1.716	0.64	0.053	6.61	-3.13426		1080	40.97	1059	17.84	1049	16.64	84	30	17	0.34	0.35
91500Thurs@2	1.875	0.18	1.723	0.64	0.054	6.60	-0.35056		1075	40.92	1072	17.97	1071	17.03	84	30	18	0.35	0.35
91500 Thurs@10	1.908	0.18	1.726	0.73	0.058	6.59	-3.41922		1107	31.73	1084	15.82	1072	17.07	83	30	18	0.36	0.35
91500 Thurs@11	1.840	0.18	1.743	0.73	0.054	6.65	0.677724		1055	32.34	1060	15.79	1062	17.09	85	31	18	0.37	0.36
91500 Thurs@13	1.903	0.18	1.875	0.74	0.053	6.73	-6.87689		1130	33.66	1082	17.03	1058	18.33	83	30	18	0.34	0.37
91500 Thurs@14	1.901	0.18	1.727	0.69	0.055	6.67	-4.50366		1112	36.12	1081	16.88	1066	16.99	82	30	18	0.36	0.36
91500Thurs@15	1.905	0.18	1.791	0.71	0.053	6.70	-6.24923		1126	35.35	1083	17.02	1061	17.55	83	31	18	0.35	0.38
91500Thurs@16	1.797	0.18	1.802	0.71	0.052	6.92	-1.18248		1052	35.98	1044	16.78	1040	17.34	84	32	18	0.36	0.38
91500Thurs@17	1.839	0.18	1.716	0.66	0.052	7.00	0.80794		1054	38.50	1059	17.16	1062	16.82	82	30	17	0.36	0.37
91500Thurs@18	1.922	0.18	1.723	0.58	0.052	7.04	-3.4794		1113	47.12	1089	19.91	1077	17.12	82	31	18	0.35	0.38
91500Thurs@19	1.969	0.18	1.724	0.66	0.052	6.83	-3.38651		1128	38.12	1105	17.62	1093	17.36	82	31	18	0.35	0.38
91500Thurs@20	1.911	0.18	1.740	0.63	0.050	6.99	-3.45149		1109	42.06	1085	18.52	1073	17.23	81	32	17	0.35	0.40
91500Thurs@21	1.867	0.17	1.733	0.58	0.050	7.65	-9.12807		1134	47.93	1069	20.02	1038	16.64	82	32	17	0.34	0.39
91500Thurs@22	1.867	0.18	1.795	0.54	0.048	7.18	-2.11043		1084	55.38	1069	22.30	1063	17.60	83	33	18	0.35	0.40
91500Thurs@23	1.892	0.18	1.744	0.60	0.046	7.22	-10.1054		1150	44.97	1078	19.34	1043	16.81	84	34	17	0.32	0.40
91500Fri@1	1.892	0.18	1.711	0.64	0.053	6.67	-3.95631		1105	40.62	1078	17.94	1065	16.82	83	32	18	0.36	0.38
91500Fri@2	1.814	0.18	1.711	0.58	0.051	6.93	3.264616		1030	47.83	1050	19.49	1061	16.75	82	31	17	0.37	0.38
91500Fri@3	1.931	0.19	1.750	0.68	0.051	6.85	1.208986		1084	37.67	1092	17.44	1096	17.67	81	32	18	0.36	0.39
91500Fri@4	1.870	0.18	1.751	0.78	0.058	6.51	4.29311		1043	28.15	1071	14.98	1084	17.50	83	29	18	0.38	0.35
91500Fri@4bis	1.929	0.18	1.738	0.78	0.059	6.50	-1.28486		1100	27.48	1091	14.98	1087	17.41	83	28	18	0.36	0.34
91500Fri@5	1.882	0.18	1.416	0.70	0.054	2.74	-3.1243		1096	28.84	1075	13.55	1065	13.91	82	31	18	0.37	0.37
91500Fri@6	1.870	0.18	1.422	0.71	0.053	2.65	-4.42497		1101	28.13	1071	13.38	1056	13.86	81	30	17	0.35	0.37
91500Fri@7	1.866	0.18	1.428	0.73	0.055	3.12	-0.19719		1070	26.30	1069	12.94	1069	14.07	80	29	17	0.36	0.36
Tem-2Fri@2	0.528	0.07	1.487	0.51	0.021	4.73	-11.6468		475	54.38	430	10.26	422	6.07	98	32	8	0.28	0.32
91500Mon@1	1.785	0.17	2.400	0.77	0.050	5.81	-2.7		1058	39.00	1040	20.40	1032	22.90	84	29	17	0.34	0.35
91500Mon@2	1.840	0.17	2.390	0.82	0.050	5.79	-8		1115	32.40	1060	19.30	1033	22.90	83	29	17	0.33	0.35
91500Mon@3	1.801	0.17	2.390	0.82	0.060	5.79	-4.5		1076	32.60	1046	19.10	1031	22.80	82	28	17	0.35	0.34
91500Mon@4	1.822	0.17	2.390	0.78	0.050	5.83	-4.6		1085	37.50	1053	20.20	1039	23.00	80	27	16	0.33	0.34
91500Mon@5	1.813	0.17	2.490	0.82	0.050	5.94	-5.3		1086	33.90	1050	19.90	1033	23.80	78	27	16	0.33	0.34
91500Mon@6	1.790	0.18	2.400	0.80	0.050	6.24	0.6		1038	36.30	1042	19.80	1044	23.10	78	27	16	0.35	0.34
91500Mon@7	1.799	0.18	2.430	0.79	0.050	6.10	0.8		1040	37.50	1045	20.30	1048	23.60	78	27	16	0.34	0.35
91500Mon@8	1.783	0.17	2.390	0.84	0.050	5.83	-0.1		1040	31.40	1039	18.80	1039	22.90	78	27	16	0.35	0.34
91500Mon@9	1.872	0.18	2.390	0.84	0.050	5.85	-1.4		1081	30.70	1071	19.00	1067	23.60	79	27	17	0.34	0.35
91500Mon@10	1.856	0.18	2.400	0.84	0.050	5.76	1.5		1056	31.00	1066	19.10	1070	23.70	81	29	17	0.36	0.36
91500Mon@11	1.812	0.18	2.420	0.83	0.050	5.73	-0.6		1054	32.40	1050	19.30	1048	23.40	81	29	17	0.36	0.36
91500Mon@13	1.919	0.18	2.420	0.79	0.050	6.00	-5.7		1127	37.10	1088	20.70	1068	23.90	81	30	17	0.34	0.37
91500Mon@14	1.894	0.18	2.390	0.81	0.050	6.00	-1.7		1091	34.80	1079	19.90	1073	23.70	81	30	17	0.36	0.37
91500Mon@15	1.841	0.18	2.400	0.81	0.050	5.89	1.3		1052	34.90	1060	19.70	1064	23.60	79	30	17	0.36	0.38
91500Mon@16	1.855	0.18	2.390	0.82	0.050	6.01	-0.8		1071	33.50	1065	19.50	1063	23.40	79	29	17	0.35	0.37
91500Mon@17	1.898	0.18	2.380	0.82	0.050	5.82	3		1061	32.80	1081	19.50	1090	24.00	80	29	17	0.37	0.37
91500Mon@18	1.907	0.18	2.440	0.76	0.050	5.94	0.6		1079	41.80	1084	21.70	1086	24.40	81	30	18	0.37	0.37
91500Mon@19	1.894	0.18	2.400	0.82	0.050	5.84	-3		1099	33.10	1079	19.60	1069	23.70	81	30	17	0.35	0.37
91500Mon@20	1.867	0.18	2.390	0.81	0.050	5.83	4.9		1038	34.00	1070	19.60	1085	23.90	80	30	17	0.39	0.37
91500Mon@21	2.027	0.19	2.390	0.77	0.0														

Table B1 Oxygen-Isotope Analyses For Zircon From Bearpaw Xenoliths

Sample	Oxygen Sample Spot	¹⁶ O/Coefficient L'2	±σ	¹⁸ O/Coefficient H'2	±σ	¹⁸ O/ ¹⁶ O (H'2/L'2)	±σ	δ ¹⁸ O[‰]
LSC 33 (Granulite)	33-1*1	2496166000	0.086834	5045339	0.0853	0.002021236	0.009014	5.3
	33-1*2	2496731000	0.095225	5046378	0.0924	0.002021195	0.008132	5.3
	33-1*3	2485646000	0.104531	5025807	0.1045	0.002021932	0.008600	5.7
	33-1*4	2503799000	0.098662	5061302	0.0967	0.002021450	0.006742	5.4
	33-1*5	2496627000	0.100179	5046692	0.0992	0.002021405	0.007083	5.4
LSC 72 (Granulite)	72-1*1	2575828000	0.108936	5205334	0.1058	0.002020840	0.006631	5.2
	72-1*2	2558078000	0.114019	5169674	0.1102	0.002020923	0.007255	5.2
	72-1*3	2559722000	0.114204	5172485	0.1123	0.002020722	0.006023	5.2
	72-1*4	2554191000	0.110312	5161364	0.1100	0.002020743	0.005764	5.2
	72-3*1	2563338000	0.087445	5177094	0.0839	0.002019670	0.008348	4.6
	72-3*2	2569490000	0.091867	5189510	0.0920	0.002019666	0.006583	4.6
	72-3*3	2560135000	0.087798	5169971	0.0864	0.002019414	0.007502	4.4
	72-3*4	2554039000	0.069481	5158550	0.0682	0.002019762	0.005504	4.6
	72-4*1	2505107000	0.077067	5062473	0.0785	0.002020861	0.005302	5.1
	72-4*2	2523058000	0.098855	5095982	0.0960	0.002019765	0.008659	4.6
	72-4*3	2514152000	0.110032	5077732	0.1079	0.002019660	0.005001	4.6
	72-4*4	2441959000	0.107793	4932951	0.1065	0.002020080	0.006212	4.8
	72-5*1	2616818000	0.126646	5287659	0.1259	0.002020645	0.006300	5.1
	72-5*2	2630393000	0.133868	5317392	0.1346	0.002021520	0.007551	5.5
	72-5*3	2607967000	0.115560	5270327	0.1154	0.002020856	0.008086	5.2
LSC 89 (Granulite)	72-5*4	2599008000	0.105988	5252816	0.1047	0.002021086	0.007644	5.2
	89-1*1	2284819000	0.063476	4625826	0.0610	0.002024592	0.007831	6.9
	89-1*2	2281690000	0.055402	4619726	0.0522	0.002024695	0.008301	6.9
	89-1*3	2279421000	0.068005	4615851	0.0690	0.002025010	0.006396	7.1
	89-2*1	2298012000	0.074099	4650450	0.0732	0.002023685	0.005864	6.6
	89-2*2	2290945000	0.060470	4637073	0.0612	0.002024087	0.009094	6.6
	89-3*1	2298012000	0.074099	4650450	0.0732	0.002023685	0.005864	6.4
	89-4*2	2290392000	0.067278	4638417	0.0655	0.002025163	0.008141	7.2
	89-4*3	2303362000	0.074796	4662768	0.0753	0.002024331	0.005519	6.8
	89-5*1	2302466000	0.070300	4661451	0.0657	0.002024549	0.006805	6.9
	89-5*2	2305822000	0.072155	4668180	0.0742	0.002024518	0.008910	6.9
	89-6*1	2285460000	0.079860	4627292	0.0808	0.002024666	0.007956	6.9
	89-6*2	2297685000	0.072318	4651886	0.0681	0.002024598	0.010022	6.9
	89-6*3	2289265000	0.060728	4635623	0.0604	0.002024940	0.009108	7.1
	89-6*4	2293265000	0.077489	4642937	0.0773	0.002024597	0.010681	6.9
	89-7*1	2282827000	0.060128	4620441	0.0616	0.002023999	0.008387	6.6
	89-7*2	2285155000	0.067224	4626139	0.0648	0.002024432	0.008736	6.8
	89-7*3	2287151000	0.066222	4630321	0.0691	0.002024492	0.006557	6.9
	89-8*1	2353305000	0.082944	4762774	0.0829	0.002023866	0.008402	6.6
	89-8*2	2358761000	0.081280	4774139	0.0795	0.002024003	0.008571	6.6
	89-8*3	2354034000	0.079408	4764552	0.0778	0.002023995	0.007264	6.6
	89-8*4	2311842000	0.082585	4680291	0.0806	0.002024486	0.010527	6.9
	89-9*1	2309094000	0.071650	4675151	0.0692	0.002024670	0.006609	7.0
	89-9*2	2310278000	0.066668	4676777	0.0675	0.002024336	0.012392	6.8
	89-9*3	2273202000	0.070143	4601774	0.0705	0.002024358	0.007310	6.8
	89-9*4	2260151000	0.074159	4575938	0.0724	0.002024617	0.009311	6.9
	89-10*1	2289877000	0.078362	4635646	0.0802	0.002024408	0.006615	6.8
	89-10*2	2288996000	0.062019	4635295	0.0588	0.002025035	0.007874	7.1
	89-10*3	2263640000	0.068081	4582169	0.0664	0.002024248	0.007276	6.7
	89-11*1	2270831000	0.077903	4597417	0.0782	0.002024552	0.007039	6.9
	89-11*2	2278198000	0.072652	4610674	0.0727	0.002023825	0.009305	6.5
	89-11*3	2282827000	0.060128	4620441	0.0616	0.002023999	0.008387	6.6
	89-12*1	2344175000	0.072613	4744432	0.0690	0.002023925	0.008943	6.6
	89-12*2	2374519000	0.044979	4806275	0.0474	0.002024232	0.005947	6.8
	89-12*3	2316556000	0.054602	4687764	0.0537	0.002023592	0.007225	6.4
	89-12(2)*4	2310260000	0.067155	4676895	0.0644	0.002024403	0.006913	6.8
	89-12(2)*5	2313508000	0.063521	4682262	0.0647	0.002023879	0.007105	6.6
LSC 105 (Granulite)	105-1*1	2278017000	0.070870	4615002	0.0695	0.002025886	0.008056	7.5
	105-1*2	2275642000	0.079283	4610233	0.0826	0.002025903	0.008248	7.5
	105-1*3	2257573000	0.082136	4573647	0.0821	0.002025913	0.008422	7.5
	105-2*1	2289371000	0.052878	4637667	0.0493	0.002025740	0.007715	7.4
	105-2*2	2272963000	0.067928	4605179	0.0654	0.002026069	0.008301	7.6
	105-2*3	2261052000	0.070568	4580610	0.0696	0.002025876	0.009550	7.5
	105-3*1	2271930000	0.080025	4603858	0.0827	0.002026407	0.009700	7.8
	105-3*2	2268984000	0.069742	4596861	0.0685	0.002025956	0.008933	7.5
	105-4*1	2260008000	0.095091	4580866	0.0937	0.002026926	0.006292	8.0
	105-4*2	2263990000	0.074016	4587905	0.0744	0.002026469	0.009301	7.8
	105-4*3	2244034000	0.079545	4548783	0.0829	0.002027056	0.008426	8.1
	105-7*1	2276285000	0.068681	4611915	0.0668	0.002026072	0.006188	7.6
	105-7*2	2250026000	0.083486	4561252	0.0809	0.002027200	0.006439	8.1
	105-7*3	2282223000	0.077959	4624065	0.0761	0.002026124	0.007248	7.6
BR 47 (Amphibolite)	47-1*1	2469603000	0.074797	4996532	0.0748	0.002023213	0.008725	6.3
	47-1*2	2455651000	0.068701	4966845	0.0661	0.002022619	0.007125	6.0
	47-2*1	2489067000	0.095368	5035820	0.0938	0.002023176	0.007705	6.3
	47-2*2	2491437000	0.080326	5041431	0.0783	0.002023504	0.006559	6.4
	47-2*3	2522737000	0.116454	5104441	0.1163	0.002023374	0.009407	6.4
	47-2*4	2521124000	0.075575	5101016	0.0735	0.002023311	0.005739	6.3
	47-2*5	2450350000	0.077766	4959387	0.0742	0.002023952	0.007598	6.6
	47-3*1	2458773000	0.062128	4974583	0.0617	0.002023197	0.006498	6.3
	47-3*2	2405868000	0.070514	4867927	0.0673	0.002023357	0.007279	6.4
	47-4*1	2405299000	0.075136	4868312	0.0738	0.002023995	0.008419	6.7
	47-4*2	2407859000	0.072392	4872512	0.0738	0.002023587	0.005305	6.5
	47-4*3	2406795000	0.097811	4869425	0.0974	0.002023199	0.008377	6.3
	47-4*4	2403919000	0.062074	4866664	0.0634	0.002024470	0.007405	6.9
	47-5*1	2408157000	0.075685	4873951	0.0740	0.002023935	0.011194	6.6
	47-5*2	2381597000	0.082165	4819341	0.0801	0.002023576	0.005819	6.5
	47-5*3	2382596000	0.091068	4822105	0.0886	0.002023888	0.008722	6.6
	47-6*1	2374094000	0.041607	4804628	0.0371	0.002023774	0.009325	6.5
	47-6*2	2377465000	0.082096	4809241	0.0808	0.002022845	0.008807	6.1
	47-7*1	2376104000	0.083628	4811111	0.0804	0.002024791	0.007825	7.0
	47-7*2	2362399000	0.133456	4779858	0.1329	0.002023307	0.005766	6.3
	47-7*3	2362008000	0.084548	4780696	0.0845	0.002023996	0.007313	6.7
	47-7*4	2365786000	0.092455	4788292	0.0929	0.002023975	0.005804	6.6
	47-8*1	2383903000	0.085842	4824212	0.0812	0.002023662	0.008966	6.5
	47-8*2	2378757000	0.078807	4815247	0.0781	0.002024271	0.005292	6.8
	47-8*3	2373135000	0.077434	4802615	0.0755	0.002023744	0.008142	6.5

Table B2: LA-ICPMS Analyses For Trace Elements in Zircon
From Bearpaw Mountain Xenoliths

	Spot/Texture	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	ΣLREE+MREE	ΣHREE
LSC 33 (Granulite)	33_1: Intersecting Bright/Dark (Magmatic)	0.02	6.81	0.03	0.52	1.00	0.57	5.95	2.17	28.65	12.61	65.60	16.25	177.20	43.74	361.12	14.90	346.22
	33_1: Intersecting Bright/Dark (Magmatic)	0.03	14.72	0.15	1.98	3.20	1.91	18.33	5.86	68.50	26.75	125.30	28.85	298.40	70.80	664.78	40.32	624.46
LSC 72 (Granulite)	72-1: Faint Enlarged Magmatic Zoning	0.02	4.98	0.03	0.62	1.64	0.40	11.30	4.17	52.20	21.54	96.90	21.12	200.50	41.74	457.15	18.98	438.17
	72-2: CL Diffuse Exterior (Magmatic)	0.19	1.66	0.06	0.36	0.31	0.14	2.23	0.84	12.17	4.98	24.78	5.78	57.90	13.00	124.39	4.95	119.45
	72-3: Intersecting Bright/Dark Magmatic	0.00	0.93	0.01	0.08	0.18	0.07	1.25	0.47	6.64	2.83	13.50	3.33	37.70	8.22	75.21	2.52	72.69
	72-3: Intersecting Bright/Dark Magmatic	0.00	0.01	0.00	0.00	0.00	0.00	0.03	0.01	0.29	0.22	1.90	0.72	9.99	2.60	15.76	0.05	15.71
LSC 89 (Granulite)	89-1: CL Medium "core" (Metamorphic, Type II)	0.04	5.37	0.05	0.50	1.05	0.11	6.82	2.37	28.78	10.96	47.33	9.71	83.00	16.03	212.12	13.94	198.18
	89-1: Diffuse Exterior (Type II)	0.07	5.98	0.04	0.57	1.50	0.16	8.39	2.86	35.00	13.48	57.60	11.62	99.80	19.23	256.31	16.72	239.59
	89_1-raster (Type II)	0.01	5.60	0.02	0.49	1.34	0.09	8.69	3.08	37.36	13.90	60.70	12.34	105.60	20.67	269.90	16.25	253.65
	89-2: CL Homogenous, Recrystallised (Magmatic, Type I)	2.60	12.80	0.94	8.80	10.99	0.74	44.10	12.46	124.40	40.23	152.40	28.41	230.80	40.55	710.22	80.97	629.25
	89-4: Convolute Resorbed, Recrystallised (Magmatic, Type I)	0.02	7.07	0.18	3.34	6.28	0.39	28.90	8.60	86.60	29.00	112.60	20.70	162.50	29.30	495.48	46.18	449.30
	89-4: Convolute Resorbed, Recrystallised (Magmatic, Type I)	0.06	8.21	0.51	7.24	10.54	0.58	43.70	12.18	121.90	39.00	146.00	26.17	207.70	36.90	660.69	70.84	589.85
	89-6: Faint magmatic (Type I)	0.01	5.90	0.03	0.88	2.10	0.17	13.11	4.37	48.00	17.01	70.30	13.35	112.00	20.88	308.12	22.21	285.91
	89-7: CL Dark Homogenous (Metamorphic, Type II)	0.01	7.33	0.06	1.13	2.06	0.22	12.56	4.13	47.61	18.26	76.00	15.13	129.20	24.61	338.32	23.38	314.94
	89-10: Convolute Resorbed, Recrystallised (Magmatic, Type I)	0.02	7.57	0.06	1.33	3.21	0.36	18.20	6.02	67.50	25.02	102.80	20.36	166.70	31.85	451.00	30.75	420.25
	89-10: Convolute Resorbed, Recrystallised (Magmatic, Type I)	0.04	9.07	0.17	2.68	4.26	0.45	20.35	6.31	68.90	24.46	103.10	20.20	170.90	31.90	462.79	37.02	425.77
	89-14: CL Homogenous (Magmatic, Type I)	0.15	11.06	0.37	5.97	8.70	0.82	34.60	10.01	99.80	32.72	127.20	24.26	196.80	35.17	587.64	61.68	525.96
	47-1: CL Dark/Light Homogenous (Magmatic)	5.30	43.10	0.89	4.54	5.06	3.66	29.20	9.70	115.00	47.20	212.00	45.30	434.00	91.00	1045.95	91.75	954.20
	47-2: Faint Magmatic Oscillatory	0.02	10.18	0.03	0.43	0.82	0.33	4.13	1.29	14.84	5.81	27.29	5.99	58.60	12.93	142.69	15.94	126.75
	47-4: Faint Magmatic Oscillatory	0.02	28.88	0.14	2.01	2.83	1.61	12.32	3.55	40.30	16.37	78.50	17.48	173.30	39.80	417.11	47.81	369.30
	47-4: Faint Magmatic Oscillatory	0.77	176.30	4.37	48.60	38.60	17.07	96.50	22.67	214.90	70.73	293.80	61.10	582.00	122.40	1749.81	382.21	1367.60

Normalised REE Data (Anders and Grevesse, 1988)

Sample	Spot/Texture	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Eu/Eu*) _N	(Ce/Ce*) _N	(La/Gd) _N	(Pr/Gd) _N	(Gd/Yb) _N	Th (ppm)
LSC 33 (Granulite)	33_1: Intersecting Bright/Dark (Magmatic)	0.0001	0.011	0.000	0.001	0.007	0.010	0.03	0.06	0.12	0.23	0.41	0.67	1.09	1.80	0.71	63.17	0.0028	0.0124	0.0278	121
	33_1: Intersecting Bright/Dark (Magmatic)	0.0001	0.024	0.002	0.004	0.022	0.034	0.09	0.16	0.28	0.48	0.79	1.19	1.84	2.91	0.76	49.29	0.0015	0.0183	0.0508	8
LSC 72 (Granulite)	72-1: Faint Enlarged Magmatic Zoning	0.0001	0.008	0.000	0.001	0.011	0.007	0.06	0.11	0.22	0.39	0.61	0.87	1.23	1.72	0.28	54.62	0.0013	0.0055	0.0466	41
	72-2: CL Diffuse Exterior (Magmatic)	0.0008	0.003	0.001	0.001	0.002	0.002	0.01	0.02	0.05	0.09	0.16	0.24	0.36	0.53	0.49	3.81	0.0717	0.0567	0.0318	19
	72-3: Intersecting Bright/Dark Magmatic	0.0000	0.002	0.0001	0.0002	0.001	0.001	0.01	0.01	0.03	0.05	0.08	0.14	0.23	0.34	0.44	47.32	0.0025	0.0106	0.0274	1
	72-3: Intersecting Bright/Dark Magmatic	0.0000	0.0000	0.0000	0.0000	0.000	0.000	0.00	0.00	0.00	0.00	0.01	0.03	0.06	0.11	2.19	4.44	0.0150	0.0837	0.0024	2
LSC 89 (Granulite)	89-1: CL Medium "core" (Metamorphic, Type II)	0.0002	0.009	0.001	0.001	0.007	0.002	0.03	0.07	0.12	0.20	0.30	0.40	0.51	0.66	0.12	27.88	0.0050	0.0168	0.0679	77
	89-1: Diffuse Exterior (Type II)	0.0003	0.010	0.001	0.001	0.010	0.003	0.04	0.08	0.14	0.24	0.36	0.48	0.61	0.79	0.14	25.48	0.0071	0.0117	0.0695	126
	89_1-raster (Type II)	0.0000	0.009	0.000	0.001	0.009	0.002	0.04	0.08	0.15	0.25	0.38	0.51	0.65	0.85	0.08	102.67	0.0007	0.0058	0.0680	72
	89-2: CL Homogenous, Recrystallised (Magmatic, Type I)	0.011	0.021	0.011	0.019	0.075	0.013	0.22	0.34	0.51	0.72	0.96	1.17	1.42	1.67	0.10	1.96	0.0494	0.0470	0.1579	688
	89-4: Convolute Resorbed, Recrystallised (Magmatic, Type I)	0.0001	0.012	0.002	0.007	0.043	0.007	0.15	0.24	0.36	0.52	0.71	0.86	1.00	1.21	0.09	29.61	0.0005	0.0138	0.1470	245
	89-4: Convolute Resorbed, Recrystallised (Magmatic, Type I)	0.0003	0.014	0.006	0.016	0.072	0.010	0.22	0.34	0.50	0.70	0.92	1.08	1.28	1.52	0.08	11.26	0.0011	0.0258	0.1739	68
	89-6: Faint magmatic (Type I)	0.0000	0.010	0.0004	0.002	0.014	0.003	0.07	0.12	0.20	0.31	0.44	0.55	0.69	0.86	0.10	73.75	0.0007	0.0058	0.0968	488
	89-7: CL Dark Homogenous (Metamorphic, Type II)	0.0001	0.012	0.001	0.003	0.014	0.004	0.06	0.11	0.20	0.33	0.48	0.63	0.80	1.01	0.13	61.69	0.0008	0.0113	0.0804	44
	89-10: Convolute Resorbed, Recrystallised (Magmatic, Type I)	0.0001	0.013	0.001	0.003	0.022	0.006	0.09	0.17	0.28	0.45	0.65	0.84	1.03	1.31	0.14	48.86	0.0010	0.0076	0.0902	163
	89-10: Convolute Resorbed, Recrystallised (Magmatic, Type I)	0.0002	0.015	0.002	0.006	0.029	0.008	0.10	0.17	0.28	0.44	0.65	0.83	1.05	1.31	0.15	26.94	0.0016	0.0182	0.0984	443
	89-14: CL Homogenous (Magmatic, Type I)	0.001	0.018	0.004	0.013	0.059	0.015	0.18	0.28	0.41	0.59	0.80	1.00	1.21	1.45	0.14	11.09	0.0037	0.0239	0.1453	426
	47-1: CL Dark/Light Homogenous (Magmatic)	0.023	0.071	0.010	0.010	0.034	0.065	0.15	0.27	0.47	0.85	1.33	1.87	2.67	3.74	0.91	4.76	0.1520	0.0673	0.0556	210
	47-2: Faint Magmatic Oscillatory	0.0001	0.017	0.000	0.001	0.006	0.006	0.02	0.04	0.06	0.10	0.17	0.25	0.36	0.53	0.54	105.38	0.0035	0.0166	0.0583	7
	47-4: Faint Magmatic Oscillatory	0.0001	0.048	0.002	0.004	0.019	0.029	0.06	0.10	0.17	0.29	0.49	0.72	1.07	1.64	0.83	125.75	0.0014	0.0256	0.0588	108
	47-4: Faint Magmatic Oscillatory	0.003	0.292	0.049	0.107	0.262	0.305	0.49	0.62	0.89	1.27	1.85	2.52	3.58	5.04	0.85	23.00	0.0067	0.0999	0.1370	1622

Table B3. LA-CP-MS Trace Element Concentrations of Silicate Phases in Xenoliths

Element		USC89mp1		USC89mp2		USC89mp3		USC89mp4		USC89mp5		USC89mp6		USC89mp7		USC89mp8		USC89mp9		USC89mp10		USC89mp11		USC89mp12		USC89mp13		USC89mp14		USC89mp15		USC89mp16		USC89mp17		USC89mp18		USC89mp19		USC89mp20		USC89mp21		USC89mp22		USC89mp23		USC89mp24		USC89mp25		USC89mp26		USC89mp27		USC89mp28		USC89mp29		USC89mp30		USC89mp31		USC89mp32		USC89mp33		USC89mp34		USC89mp35		USC89mp36		USC89mp37		USC89mp38		USC89mp39		USC89mp40		USC89mp41		USC89mp42		USC89mp43		USC89mp44		USC89mp45		USC89mp46		USC89mp47		USC89mp48		USC89mp49		USC89mp50		USC89mp51		USC89mp52		USC89mp53		USC89mp54		USC89mp55		USC89mp56		USC89mp57		USC89mp58		USC89mp59		USC89mp60		USC89mp61		USC89mp62		USC89mp63		USC89mp64		USC89mp65		USC89mp66		USC89mp67		USC89mp68		USC89mp69		USC89mp70		USC89mp71		USC89mp72		USC89mp73		USC89mp74		USC89mp75		USC89mp76		USC89mp77		USC89mp78		USC89mp79		USC89mp80		USC89mp81		USC89mp82		USC89mp83		USC89mp84		USC89mp85		USC89mp86		USC89mp87		USC89mp88		USC89mp89		USC89mp90		USC89mp91		USC89mp92		USC89mp93		USC89mp94		USC89mp95		USC89mp96		USC89mp97		USC89mp98		USC89mp99		USC89mp100		USC89mp101		USC89mp102		USC89mp103		USC89mp104		USC89mp105		USC89mp106		USC89mp107		USC89mp108		USC89mp109		USC89mp110		USC89mp111		USC89mp112		USC89mp113		USC89mp114		USC89mp115		USC89mp116		USC89mp117		USC89mp118		USC89mp119		USC89mp120		USC89mp121		USC89mp122		USC89mp123		USC89mp124		USC89mp125		USC89mp126		USC89mp127		USC89mp128		USC89mp129		USC89mp130		USC89mp131		USC89mp132		USC89mp133		USC89mp134		USC89mp135		USC89mp136		USC89mp137		USC89mp138		USC89mp139		USC89mp140		USC89mp141		USC89mp142		USC89mp143		USC89mp144		USC89mp145		USC89mp146		USC89mp147		USC89mp148		USC89mp149		USC89mp150		USC89mp151		USC89mp152		USC89mp153		USC89mp154		USC89mp155		USC89mp156		USC89mp157		USC89mp158		USC89mp159		USC89mp160		USC89mp161		USC89mp162		USC89mp163		USC89mp164		USC89mp165		USC89mp166		USC89mp167		USC89mp168		USC89mp169		USC89mp170		USC89mp171		USC89mp172		USC89mp173		USC89mp174		USC89mp175		USC89mp176		USC89mp177		USC89mp178		USC89mp179		USC89mp180		USC89mp181		USC89mp182		USC89mp183		USC89mp184		USC89mp185		USC89mp186		USC89mp187		USC89mp188		USC89mp189		USC89mp190		USC89mp191		USC89mp192		USC89mp193		USC89mp194		USC89mp195		USC89mp196		USC89mp197		USC89mp198		USC89mp199		USC89mp200		USC89mp201		USC89mp202		USC89mp203		USC89mp204		USC89mp205		USC89mp206		USC89mp207		USC89mp208		USC89mp209		USC89mp210		USC89mp211		USC89mp212		USC89mp213		USC89mp214		USC89mp215		USC89mp216		USC89mp217		USC89mp218		USC89mp219		USC89mp220		USC89mp221		USC89mp222		USC89mp223		USC89mp224		USC89mp225		USC89mp226		USC89mp227		USC89mp228		USC89mp229		USC89mp230		USC89mp231		USC89mp232		USC89mp233		USC89mp234		USC89mp235		USC89mp236		USC89mp237		USC89mp238		USC89mp239		USC89mp240		USC89mp241		USC89mp242		USC89mp243		USC89mp244		USC89mp245		USC89mp246		USC89mp247		USC89mp248		USC89mp249		USC89mp250		USC89mp251		USC89mp252		USC89mp253		USC89mp254		USC89mp255		USC89mp256		USC89mp257		USC89mp258		USC89mp259		USC89mp260		USC89mp261		USC89mp262		USC89mp263		USC89mp264		USC89mp265		USC89mp266		USC89mp267		USC89mp268		USC89mp269		USC89mp270		USC89mp271		USC89mp272		USC89mp273		USC89mp274		USC89mp275		USC89mp276		USC89mp277		USC89mp278		USC89mp279		USC89mp280		USC89mp281		USC89mp282		USC89mp283		USC89mp284		USC89mp285		USC89mp286		USC89mp287		USC89mp288		USC89mp289		USC89mp290		USC89mp291		USC89mp292		USC89mp293		USC89mp294		USC89mp295		USC89mp296		USC89mp297		USC89mp298		USC89mp299		USC89mp300		USC89mp301		USC89mp302		USC89mp303		USC89mp304		USC89mp305		USC89mp306		USC89mp307		USC89mp308		USC89mp309		USC89mp310		USC89mp311		USC89mp312		USC89mp313		USC89mp314		USC89mp315		USC89mp316		USC89mp317		USC89mp318		USC89mp319		USC89mp320		USC89mp321		USC89mp322		USC89mp323		USC89mp324		USC89mp325		USC89mp326		USC89mp327		USC89mp328		USC89mp329		USC89mp330		USC89mp331		USC89mp332		USC89mp333		USC89mp334		USC89mp335		USC89mp336		USC89mp337		USC89mp338		USC89mp339		USC89mp340		USC89mp341		USC89mp342		USC89mp343		USC89mp344		USC89mp345		USC89mp346		USC89mp347		USC89mp348		USC89mp349		USC89mp350		USC89mp351		USC89mp352		USC89mp353		USC89mp354		USC89mp355		USC89mp356		USC89mp357		USC89mp358		USC89mp359		USC89mp360		USC89mp361		USC89mp362		USC89mp363		USC89mp364		USC89mp365		USC89mp366		USC89mp367		USC89mp368		USC89mp369		USC89mp370		USC89mp371		USC89mp372		USC89mp373		USC89mp374		USC89mp375		USC89mp376		USC89mp377		USC89mp378		USC89mp379		USC89mp380		USC89mp381		USC89mp382		USC89mp383		USC89mp384		USC89mp385		USC89mp386		USC89mp387		USC89mp388		USC89mp389		USC89mp390		USC89mp391		USC89mp392		USC89mp393		USC89mp394		USC89mp395		USC89mp396		USC89mp397		USC89mp398		USC89mp399		USC89mp400	
Sc	71.00	76.50	66.00	62.80	43.28	34.80	79.40	7.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90	2.40	1.90</																																																																																																																																																																																																																																																																																																																																		

Pv_1H235f	0.3	0.34	0.25	0.13	0.28	0.25	0.16	0.12	0.17	0.29
Nd	32.1	39.3	31	29.9	31.7	38.4	21.96	16.95	21.47	31.4
Nd_1H235f	1.4	1.4	1.3	1.3	2.1	1.4	0.95	0.4	0.83	1.3
Sm	8.23	10.35	7.55	7.53	7.16	8.24	4.76	3.49	5.19	6.84
Sm_1H235f	0.46	0.61	0.42	0.45	0.3	0.37	0.46	0.18	0.38	0.25
Eu	1.27	1.44	1.47	1.228	1.313	1.598	1.29	0.885	1.06	1.43
Eu_1H235f	0.085	0.14	0.16	0.079	0.092	0.098	0.1	0.069	0.16	0.13
Gd	6.68	8.07	5.78	5.85	5.27	5.98	3.6	2.74	3.84	5.45
Gd_1H235f	0.76	0.4	0.35	0.32	0.5	0.47	0.34	0.28	0.38	0.35
Tb	0.876	1.05	0.763	0.773	0.658	0.772	0.452	0.339	0.507	0.697
Tb_1H235f	0.063	0.056	0.063	0.045	0.044	0.051	0.026	0.017	0.032	0.005
Dy	5.01	6.06	4.48	4.25	3.68	4.11	2.44	1.75	2.76	3.83
Dy_1H235f	0.43	0.4	0.3	0.39	0.41	0.37	0.17	0.29	0.28	0.36
Ho	0.833	1.059	0.81	0.793	0.762	0.948	0.331	0.494	0.704	0.704
Ho_1H235f	0.068	0.09	0.053	0.062	0.06	0.076	0.049	0.047	0.061	0.059
Er	2.2	2.77	2.18	2.06	1.72	2.16	1.43	0.9	1.38	1.751
Er_1H235f	0.23	0.19	0.2	0.16	0.19	0.15	0.18	0.19	0.21	0.089
Tm	0.384	0.384	0.384	0.25	0.214	0.265	0.166	0.177	0.23	0.163
Tm_1H235f	0.022	0.03	0.036	0.049	0.03	0.044	0.02	0.016	0.041	0.024
Yb	1.73	1.85	2.07	1.57	1.31	1.57	1.6	1.03	0.94	1.9
Yb_1H235f	0.14	0.15	0.23	0.34	0.1	0.23	0.17	0.077	0.14	0.23
Lu	0.26	0.28	0.258	0.243	0.197	0.224	0.148	0.099	0.156	0.163
Lu_1H235f	0.038	0.038	0.038	0.039	0.026	0.033	0.035	0.014	0.025	0.021
Hf	1.42	2.01	1.09	1.19	1.11	1.28	0.598	0.376	1.09	1.16
Hf_1H235f	0.22	0.13	0.2	0.17	0.24	0.2	0.063	0.08	0.14	0.13
Ta	0.225	0.31	0.153	0.141	0.249	0.266	0.149	0.099	0.191	0.23
Ta_1H235f	0.031	0.051	0.072	0.087	0.023	0.014	0.049	0.013	0.043	0.044
Pb	1.38	1.13	21	1.28	1.14	1.121	0.87	0.719	1.62	1.383
Pb_1H235f	0.22	0.19	21	0.13	0.16	0.061	0.15	0.098	0.23	0.027
Th	0.062	0.085	0.105	0.019	0.11	0.159	0.053	0.032	0.0386	0.088
Th_1H235f	0.016	0.028	0.077	0.015	0.012	0.011	0.016	0.0078	0.016	0.016
U	0.00	0.042	0.094	0.00	0.00	0.0227	0.00	0.00	0.00	0.00
U_1H235f	0.00	0.021	0.071	0.00	0.00	0.0085	0.00	0.00	0.00	0.00
U/Hf	0.17	0.29	0.18	0.23	0.11	0.17	0.56	0.18	0.18	0.16

grt = garnet cpx = clinopyroxene opa = orthopyroxene amph = amphibole

Table B4: Quality control data for oxygen analysis on zircon using Temora-2 and 91500 zircon standards								
	Analysis	¹⁶ O/Coefficient L'2	±σ	¹⁸ O/Coefficient H'2	±σ	¹⁸ O/ ¹⁶ O (H'2/L'2)	±σ	δ ¹⁸ O[‰]
91500@02	2	2680863000	0.132	5443352	0.129	0.002030449	0.006	9.89
91500@03	3	2675760000	0.134	5431793	0.130	0.002030002	0.008	9.67
Tem2@1	4	2671017000	0.125	5413162	0.124	0.00202663	0.007	8.01
91500@04	15	2627419000	0.111	5334439	0.110	0.002030297	0.007	9.80
91500@05	26	2512556000	0.081	5102462	0.078	0.002030786	0.009	10.03
Tem2@2	27	2496498000	0.098	5059830	0.097	0.002026772	0.006	8.02
91500@06	38	2501621000	0.081	5079325	0.081	0.002030414	0.006	9.83
91500@07	49	2393046000	0.098	4858559	0.098	0.002030282	0.007	9.75
Tem2@3	50	2382635000	0.098	4829017	0.097	0.002026755	0.008	7.96
91500@08	61	2382182000	0.087	4837817	0.088	0.002030834	0.007	10.01
91500@09	72	2337980000	0.089	4746755	0.087	0.002030281	0.006	9.73
Tem2@4	73	2328964000	0.084	4719827	0.085	0.002026578	0.009	7.82
91500@10	84	2305712000	0.098	4682893	0.098	0.002030997	0.007	10.06
91500@11	95	2316690000	0.073	4704277	0.073	0.002030603	0.009	9.86
Tem2@5	96	2303787000	0.070	4670399	0.069	0.002027271	0.008	8.11
91500@12	107	2289626000	0.063	4649186	0.060	0.002030545	0.008	9.81
91500@13	118	2268113000	0.067	4605797	0.066	0.002030674	0.008	9.86
Tem2@6	119	2253063000	0.063	4567209	0.062	0.002027111	0.005	7.97
91500@14	127	2264133000	0.074	4597727	0.074	0.002030679	0.010	9.85
91500@15	128	2266139000	0.071	4601441	0.071	0.00203052	0.007	9.78
Tem2@7	129	2255730000	0.055	4572799	0.053	0.002027193	0.007	7.99
91500@16	130	2259893000	0.066	4589261	0.064	0.002030743	0.007	9.88

Table B6: Operating conditions and data acquisition for trace elements in silicates	
ICP-MS	
Instrument	magnetic sector
Manufacturer	Thermo Scientific Instruments
Model	Element XR
RF power [W]	1200-1400
Gas Flows	
Cooling (Ar) [l/min]	16
Auxiliary (Ar) [l/min]	0.9-1.0
Sample (Ar) [l/min]	0.3-0.4
Carrier (He) [l/min]	0.9-1.1
Laser	
Instrument	ArF excimer
Manufacturer	Australian Scientific Instruments
Model	Resolution SE155
Wavelength [nm]	193
Spot size [microns]	30
Repetition Rate [Hz]	8
Laser Fluence [J/cm2]	2.5
Data Acquisition	
Resolution Mode	Low
Protocol	Time-resolved
Scan Mode	E-scan
	29Si, 43Ca, 45Sc, 47Ti, 51V, 53Cr, 59Co, 60Ni, 65Cu, 85Rb, 88Sr, 89Y, 90Zr, 93Nb, 139La, 140Ce, 141Pr, 146Nd, 147Sm, 151Eu, 157Gd, 159Tb, 163Dy, 165Ho, 166Er, 169Tm, 174Yb, 175Lu, 178Hf, 181Ta, 208Pb, 232Th, 238U
Scanned Masses	
Settling Times	0.001
Sample Times	0.0002-0.003
Samples Per Peak	60
Detection Mode	Counting for all isotopes except 238 (analog)
Detector Deadtime [n sec]	18 (check)
Background (gas blank) [sec]	two times 15
Ablation Time [sec]	20
Standards	
Calibration (primary)	NIST612
Internal	43Ca, 29Si
Control (secondary)	NIST610, 614, BHVO-2G, BIR-1G, BCR-2G
Data Reduction	
Software	iolite, in-built into Igor Pro
Data Reduction Scheme(s)	X_Trace_Elements_IS

Table B5: Quality control data for hafnium on zircon analyses using Temora-2 (TEM), Plesovice (Ples), Mud Tank (MT) and LV 11 zircon standards													
		¹⁷⁴ Hf/ ¹⁷⁷ Hf	SE	¹⁷⁶ Hf/ ¹⁷⁷ Hf	SE	¹⁷⁸ Hf/ ¹⁷⁷ Hf	SE	¹⁸⁰ Hf/ ¹⁷⁷ Hf	SE	¹⁷⁶ Lu/ ¹⁷⁷ Hf	SE	¹⁷⁶ Yb/ ¹⁷⁷ Hf	SE
Spot/Analysis													
TRA_Data_8298_91500-8.csv		0.008657	0.000019	0.282265	0.000017	1.467201	0.000020	1.886632	0.000045	0.000374	0.000000	0.013688	0.000016
TRA_Data_8299_91500-9.csv		0.008670	0.000016	0.282282	0.000016	1.467174	0.000019	1.886633	0.000047	0.000386	0.000000	0.014577	0.000018
TRA_Data_8337_91500-10.csv		0.008731	0.000019	0.282328	0.000019	1.467286	0.000021	1.886773	0.000048	0.000379	0.000000	0.013679	0.000019
TRA_Data_8338_91500-11.csv		0.008658	0.000020	0.282339	0.000019	1.467297	0.000022	1.886754	0.000056	0.000380	0.000000	0.013748	0.000016
TRA_Data_8343_91500-12.csv		0.008696	0.000018	0.282319	0.000017	1.467255	0.000021	1.886780	0.000045	0.000386	0.000000	0.014429	0.000014
TRA_Data_8376_91500-13.csv		0.008631	0.000021	0.282255	0.000019	1.467219	0.000023	1.886830	0.000051	0.000378	0.000000	0.013984	0.000019
TRA_Data_8377_91500-14.csv		0.008704	0.000027	0.282361	0.000027	1.467306	0.000026	1.886723	0.000062	0.000400	0.000002	0.014458	0.000044
TRA_Data_8297_TEM2-6.csv		0.008683	0.000012	0.282710	0.000012	1.467261	0.000015	1.886752	0.000032	0.001224	0.000012	0.047022	0.000381
TRA_Data_8317_TEM2-7.csv		0.008673	0.000015	0.282679	0.000014	1.467270	0.000017	1.886710	0.000039	0.000878	0.000008	0.031276	0.000253
TRA_Data_8318_TEM2-8.csv		0.008695	0.000015	0.282715	0.000014	1.467230	0.000017	1.886637	0.000037	0.001128	0.000006	0.038809	0.000267
TRA_Data_8339_TEM2-9.csv		0.008690	0.000019	0.282690	0.000016	1.467244	0.000023	1.886723	0.000053	0.001281	0.000003	0.045342	0.000075
TRA_Data_8340_TEM2-10.csv		0.008699	0.000018	0.282703	0.000015	1.467275	0.000017	1.886727	0.000041	0.001498	0.000002	0.051902	0.000124
TRA_Data_8361_TEM2-11.csv		0.008791	0.000030	0.282678	0.000031	1.467324	0.000026	1.886856	0.000066	0.002343	0.000030	0.087718	0.000635
TRA_Data_8362_TEM2-12.csv		0.008645	0.000017	0.282686	0.000015	1.467285	0.000018	1.886724	0.000039	0.001261	0.000004	0.047173	0.000150
TRA_Data_8372_TEM2-13.csv		0.008697	0.000016	0.282712	0.000016	1.467245	0.000019	1.886687	0.000044	0.001697	0.000016	0.064880	0.000568
TRA_Data_8373_TEM2-14.csv		0.008665	0.000016	0.282673	0.000014	1.467259	0.000018	1.886819	0.000039	0.001331	0.000002	0.047371	0.000141
TRA_Data_8300_MT-15.csv		0.008667	0.000009	0.282529	0.000010	1.467191	0.000014	1.886639	0.000033	0.000036	0.000000	0.001580	0.000011
TRA_Data_8301_MT-16.csv		0.008683	0.000009	0.282525	0.000010	1.467212	0.000014	1.886644	0.000033	0.000035	0.000000	0.001554	0.000013
TRA_Data_8378_MT-17.csv		0.008652	0.000011	0.282500	0.000011	1.467236	0.000015	1.886677	0.000032	0.000029	0.000001	0.001302	0.000025
TRA_Data_8379_MT-18.csv		0.008661	0.000011	0.282497	0.000012	1.467237	0.000014	1.886693	0.000035	0.000032	0.000000	0.001436	0.000021
TRA_Data_8302_Ples-7.csv		0.008646	0.000009	0.282479	0.000010	1.467237	0.000015	1.886653	0.000032	0.000120	0.000001	0.006590	0.000051
TRA_Data_8303_Ples-8.csv		0.008684	0.000010	0.282505	0.000010	1.467245	0.000013	1.886648	0.000033	0.000120	0.000001	0.006660	0.000055
TRA_Data_8315_Ples-9.csv		0.008699	0.000010	0.282510	0.000010	1.467262	0.000014	1.886728	0.000033	0.000113	0.000001	0.006199	0.000051
TRA_Data_8316_Ples-10.csv		0.008661	0.000010	0.282489	0.000010	1.467238	0.000015	1.886663	0.000032	0.000119	0.000001	0.006534	0.000055
TRA_Data_8363_Ples-11.csv		0.008654	0.000010	0.282472	0.000009	1.467299	0.000015	1.886670	0.000032	0.000119	0.000001	0.006647	0.000059
TRA_Data_8364_Ples-12.csv		0.008702	0.000010	0.282500	0.000011	1.467252	0.000015	1.886761	0.000031	0.000121	0.000001	0.006739	0.000062
TRA_Data_8374_Ples-13.csv		0.008672	0.000010	0.282475	0.000011	1.467278	0.000015	1.886730	0.000032	0.000118	0.000001	0.006576	0.000057
TRA_Data_8375_Ples-14.csv		0.008658	0.000011	0.282475	0.000011	1.467223	0.000014	1.886660	0.000030	0.000118	0.000001	0.006561	0.000056
TRA_Data_8313_LV11-1.csv		0.008737	0.000021	0.282889	0.000018	1.467222	0.000017	1.886585	0.000038	0.002891	0.000001	0.167704	0.000107
TRA_Data_8314_LV11-2.csv		0.008695	0.000022	0.282827	0.000019	1.467233	0.000016	1.886722	0.000042	0.002688	0.000003	0.155458	0.000089
TRA_Data_8335_LV11-4.csv		0.008749	0.000022	0.282882	0.000018	1.467187	0.000017	1.886693	0.000040	0.002644	0.000001	0.151449	0.000127
TRA_Data_8336_LV11-4.csv		0.008806	0.000023	0.282926	0.000018	1.467248	0.000019	1.886641	0.000041	0.002842	0.000002	0.161156	0.000058
TRA_Data_8341_LV11-5.csv		0.008707	0.000021	0.282876	0.000019	1.467192	0.000018	1.886646	0.000040	0.002965	0.000001	0.174580	0.000085
TRA_Data_8342_LV11-6.csv		0.008794	0.000022	0.282928	0.000018	1.467270	0.000018	1.886726	0.000039	0.002951	0.000002	0.178541	0.000149
TRA_Data_8359_LV11-7.csv		0.008776	0.000023	0.282902	0.000018	1.467281	0.000018	1.886789	0.000039	0.003139	0.000001	0.185301	0.000191
TRA_Data_8360_LV11-8.csv		0.008767	0.000021	0.282905	0.000018	1.467221	0.000019	1.886675	0.000045	0.002934	0.000002	0.174017	0.000080
TRA_Data_8370_LV11-9.csv		0.008726	0.000022	0.282865	0.000018	1.467268	0.000020	1.886646	0.000043	0.002617	0.000002	0.154354	0.000078
TRA_Data_8371_LV11-10.csv		0.008768	0.000021	0.282900	0.000018	1.467206	0.000018	1.886652	0.000040	0.002493	0.000001	0.146326	0.000214

Table B7: Quality Control Data, REE in NIST Glasses and Zircon Standards

Sample	NIST610-1	2SE	NIST610-2	2SE	NIST610-3	2SE	NIST610-4	2SE	NIST610-5	2SE	NIST610-6	2SE	Reference Value (Gao et al., 2002)	2SE
Y	449.7	7.5	453.6	7.4	441.9	6.7	452.2	8.7	449.2	7.5	457.8	8.6	450	38.0
La	455.6	7.4	458.4	7.2	457.9	7.9	456	6.8	457	8.8	457.3	8.2	457	144.0
Ce	445.1	6.8	451.5	7.9	445.7	7.9	452.8	8.7	444.2	6.2	452.8	8.0	448	34.0
Pr	428.1	7.6	432.5	7.2	428	7.6	429.8	8.0	433.9	9.1	428.3	8.3	430	60.0
Nd	429.5	7.2	433.3	7.7	430.8	7.3	429.2	9.0	429.5	7.5	433.2	7.4	430	76.0
Sm	451.2	8.0	452.7	7.3	446.5	7.1	450.7	8.4	456.1	7.3	448.9	7.7	449	42.0
Eu	456.7	8.6	466.8	9.5	460	10.0	460.4	9.3	462.2	9.2	460.7	7.1	460	104.0
Gd	445.1	8.2	442	8.3	446.6	9.0	444	10.0	442.6	8.0	444.1	7.2	420	42.0
Tb	437.8	7.4	448.2	7.1	442.2	9.4	442.7	7.8	441.7	6.3	444.5	6.3	442	44.0
Dy	427	6.8	428.1	6.1	424.6	7.0	425.4	8.3	427.6	6.4	429.1	8.5	426	36.0
Ho	445.2	6.8	453.3	6.7	449.2	9.1	446.3	8.7	447.6	8.7	452.2	9.4	448	50.0
Er	423.2	8.2	428.6	8.2	427.5	8.5	425.4	8.5	423.9	8.7	427.4	8.8	426	48.0
Tm	417.8	7.9	421.9	7.1	416.3	8.3	424.7	9.2	418.9	9.9	420.4	8.2	420	38.0
Yb	442.3	9.3	449	10.0	442.7	8.9	445.9	9.2	448.9	9.2	442.8	8.2	460	26.0
Lu	431	10.0	439.7	8.0	432	10.0	429.5	9.4	435.8	9.2	438.4	8.6	435	62.0

Sample	NIST612-1	2SE	NIST612-2	2SE	NIST612-3	2SE	NIST612-4	2SE	NIST612-5	2SE	NIST612-6	2SE	Reference Value (Gao et al., 2002)	2SE
Y	35.81	0.93	37.59	0.89	35.7	1.10	37.1	1.20	38.4	1.10	37.51	0.86	38	4.00
La	37.42	0.64	38.36	0.55	36.98	0.59	38.16	0.83	37.81	0.70	38.52	0.51	37	0.80
Ce	38.59	0.72	39.81	0.63	38.15	0.66	39	0.93	38.82	0.69	39.59	0.63	38	0.80
Pr	36.84	0.66	37.96	0.57	36.48	0.69	37.37	0.83	36.9	0.68	37.51	0.57	37	1.80
Nd	34.73	0.90	35.32	0.75	34.03	0.67	34.5	0.77	35.64	0.80	35.48	0.70	35	0.80
Sm	36.92	0.79	37.93	0.69	36.22	0.76	37.89	0.87	37.33	0.74	36.94	0.65	37	0.80
Eu	35.95	0.86	36.4	0.76	34.85	0.82	36.42	0.81	35.89	0.74	36.18	0.58	35	2.00
Gd	36.6	1.10	37.42	0.90	36.54	0.77	37.45	0.95	37.3	1.00	38.23	0.99	36	0.80
Tb	37.03	0.83	37.99	0.74	36.34	0.77	37.33	0.89	36.92	0.65	37.44	0.67	36	6.00
Dy	34.41	0.83	34.38	0.83	33.98	0.90	35.53	0.77	34.35	0.55	34.74	0.73	36	0.80
Ho	37.21	0.78	38.56	0.66	37.06	0.81	38.34	0.89	38.13	0.79	38.68	0.70	38	2.00
Er	34.71	0.80	36.01	0.91	34.02	0.93	35.02	0.95	36	1.10	35.91	0.71	37	1.80
Tm	34.91	0.86	35.57	0.74	34.86	0.74	35.74	0.85	35.73	0.74	36.32	0.87	37	2.00
Yb	36.9	1.10	38.1	0.96	36.56	0.85	37.8	1.10	37.6	1.10	38.6	1.10	40	0.80
Lu	35.78	0.95	36.33	0.97	34.83	0.65	35.58	0.78	35.76	0.81	36.42	0.83	37	0.8

Sample	91500 large-1	2SE	91500 large-2	2SE	91500 large2-1	2SE	91500 large2-2	2SE	Reference Value (Yuan et al., 2004)
Y	114.4	2.80	107.1	3.00	128.2	3.20	126.5	3.70	143
La	0.0037	0.00	0.0017	0.00	0.05	0.04	0.00064	0.00	0.0014
Ce	2.269	0.08	2.196	0.08	2.45	0.08	2.398	0.05	2.504
Pr	0.0128	0.00	0.0099	0.00	0.0139	0.00	0.014	0.00	0.0119
Nd	0.145	0.03	0.148	0.03	0.19	0.03	0.21	0.03	0.215
Sm	0.356	0.05	0.338	0.04	0.37	0.05	0.434	0.05	0.461
Eu	0.185	0.02	0.176	0.02	0.236	0.03	0.228	0.02	0.227
Gd	1.8	0.14	1.74	0.17	2.12	0.14	2.08	0.12	2.54
Tb	0.728	0.04	0.634	0.04	0.798	0.06	0.792	0.03	0.872
Dy	9.21	0.29	8.68	0.36	10.52	0.37	10.28	0.39	12.33
Ho	3.99	0.11	3.69	0.14	4.47	0.17	4.26	0.14	4.77
Er	20.42	0.52	18.88	0.57	22.45	0.72	22.16	0.69	24.1
Tm	5.01	0.22	4.86	0.18	5.75	0.19	5.62	0.19	7.33
Yb	53.4	1.70	50.4	2.00	59.4	1.90	58.3	1.40	83.7
Lu	10.99	0.31	10.61	0.24	12.19	0.35	12.09	0.29	10.74

Sample	temora-3	2SE	temora-4	2SE	temora-5	2SE	temora-6	2SE	temora-7	2SE	temora-8	2SE	Reference Value (Yuan et al., 2008)
Y	1583	32.00	545	12.00	1133	50.00	783	21.00	525	12.00	907	50.00	
La	0.0136	0.00	0.0024	0.00	0.0202	0.00	0.0075	0.00	0.0023	0.00	0.0289	0.01	0.041
Ce	5.4	0.12	3.472	0.09	3.08	0.12	2.77	0.11	4.63	0.12	3.1	0.14	3.09
Pr	0.1139	0.01	0.0517	0.01	0.188	0.01	0.0739	0.01	0.044	0.00	0.148	0.03	0.14
Nd	1.901	0.09	0.837	0.06	2.67	0.15	1.363	0.08	0.697	0.06	2.18	0.34	1.75
Sm	3.95	0.22	1.67	0.13	4.41	0.25	3.1	0.16	1.416	0.09	4	0.40	3.19
Eu	0.862	0.05	0.346	0.03	0.922	0.06	0.723	0.05	0.371	0.02	0.865	0.08	0.71
Gd	25.37	0.63	9.59	0.37	24.4	1.40	17.95	0.57	8.39	0.34	20.8	1.00	16.32
Tb	9.79	0.22	3.5	0.10	8.34	0.41	5.98	0.19	3.07	0.11	6.68	0.28	6.59
Dy	131.5	2.50	42.9	1.20	102.2	4.20	70.2	2.00	38.8	0.71	80.6	3.50	66.49
Ho	56.1	1.10	17.64	0.45	39.5	1.70	26.79	0.78	16.61	0.43	31.5	1.40	32.38
Er	264.4	6.00	85.4	2.10	180.4	7.40	119.6	3.20	83	2.40	142.5	7.40	118.09
Tm	55	1.30	19.51	0.59	37.9	1.50	25.9	0.81	20.04	0.64	30.7	1.40	33.71
Yb	488	11.00	191.2	5.10	343	14.00	232.7	6.70	205.6	7.30	283	13.00	252.89
Lu	100.4	2.1	41.3	1.2	69.4	1.9	47.8	1.2	45.1	0.97	56.1	3.3	52.57

Table C1: Recalculated Cations and Weight Percent Oxides for Individual Apatite Analyses From Granulite And Amphibolite Xenoliths

LSC 33							LSC 75							LSC 89							LSC 93						
Wt% Oxide							Wt% Oxide							F							Wt% Oxide						
F	Cl	CaO	SrO	P ₂ O ₅	Total		F	Cl	CaO	SrO	P ₂ O ₅	Total		F	Cl	CaO	SrO	P ₂ O ₅	Total		F	Cl	CaO	SrO	P ₂ O ₅	Total	
1 / 1 .	3.79	0.23	54.42	0.00	39.80	96.59	1 / 1 .	3.64	0.23	53.93	0.02	38.59	96.41	2 / 1 .	4.22	0.37	52.39	0.02	41.67	98.46	1 / 1 .	4.19	0.07	52.38	0.05	41.68	98.37
2 / 1 .	3.64	0.26	54.40	0.00	39.97	96.68	2 / 1 .	3.53	0.28	52.14	0.01	38.47	94.43	3 / 1 .	4.27	0.06	52.85	0.00	42.34	99.52	2 / 1 .	4.04	0.06	53.00	0.03	41.70	98.83
3 / 1 .	3.80	0.25	54.28	0.00	39.06	95.74	3 / 1 .	3.84	0.12	54.95	0.04	40.07	99.03	4 / 1 .	4.24	0.07	52.80	0.05	42.31	99.47	3 / 1 .	4.04	0.09	53.03	0.02	41.71	98.89

1 / 1 .	3.84	0.25	54.44	0.02	40.76	97.64	4 / 1 .	3.64	0.17	54.65	0.00	39.96	98.43	5 / 1 .	4.17	0.30	53.32	0.00	41.10	98.88	4 / 1 .	4.26	0.07	52.74	0.00	41.74	98.83
5 / 1 .	3.79	0.26	54.39	0.00	39.14	95.92	5 / 1 .	3.33	0.17	45.12	0.01	32.54	81.17	6 / 1 .	4.30	0.35	53.05	0.05	41.74	99.49	5 / 1 .	4.06	0.04	52.68	0.01	41.92	98.71
6 / 1 .	3.70	0.29	54.52	0.01	39.45	96.35	No of Ions	F	Cl	Ca	Sr	P	Total	7 / 1 .	4.16	0.36	51.92	0.00	41.87	98.32	6 / 1 .	4.17	0.06	52.60	0.00	41.70	98.53
7 / 1 .	3.84	0.30	54.97	0.00	39.19	96.62								8 / 1 .	4.10	0.39	52.42	0.00	41.84	98.75	7 / 1 .	4.25	0.37	52.18	0.02	41.68	98.51
No of Ions	F	Cl	Ca	Sr	P	Total	9 / 1 .	4.03	0.44	52.41	0.03	42.06	98.97	8 / 1 .	4.05	0.45	52.53	0.03	42.21	99.26	7 / 1 .	4.09	0.33	51.85	0.00	41.78	98.05
							10 / 1 .	4.13	0.42	52.44	0.00	41.89	98.87	9 / 1 .	4.07	0.32	52.27	0.09	40.94	97.68	10 / 1 .	4.03	0.05	53.33	0.04	41.01	98.46
							11 / 1 .	4.17	0.48	53.17	0.00	41.74	99.56	12 / 1 .	4.11	0.05	53.43	0.08	41.10	98.73	13 / 1 .	4.07	0.15	52.66	0.06	42.21	99.19
							12 / 1 .	4.18	0.60	52.45	0.00	41.98	99.20	13 / 1 .	4.11	0.15	52.66	0.06	42.21	99.19	14 / 1 .	4.11	0.15	52.45	0.05	42.45	99.06
							13 / 1 .	4.11	0.35	52.51	0.01	42.08	99.05	14 / 1 .	4.18	0.60	52.45	0.00	41.98	99.20	15 / 1 .	4.18	0.03	52.78	0.09	41.22	98.29
14 / 1 .	4.06	0.41	52.45	0.01	41.47	98.41	15 / 1 .	4.17	0.48	53.17	0.00	41.74	99.56	16 / 1 .	4.17	0.03	52.78	0.00	41.43	98.31							
15 / 1 .	4.17	0.35	52.92	0.04	41.70	99.17	16 / 1 .	4.17	0.43	52.42	0.02	40.77	97.73	17 / 1 .	4.17	0.04	53.10	0.00	41.93	99.08							
16 / 1 .	4.08	0.43	52.42	0.02	40.77	97.73	17 / 1 .	4.17	0.43	52.42	0.03	42.18	99.17	18 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59							
17 / 1 .	4.08	0.43	52.42	0.02	40.77	97.73	18 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59	19 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59							
18 / 1 .	4.08	0.43	52.42	0.02	40.77	97.73	19 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59	20 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59							
19 / 1 .	4.08	0.43	52.42	0.02	40.77	97.73	20 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59	21 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59							
20 / 1 .	4.13	0.41	52.42	0.03	42.18	99.17	21 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59	22 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59							
21 / 1 .	4.07	0.44	52.64	0.00	41.43	98.59	22 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59	23 / 1 .	4.17	0.44	52.64	0.00	41.43	98.59							
22 / 1 .	4.16	0.46	52.21	0.03	41.77	98.63	23 / 1 .	4.16	0.46	52.21	0.03	41.77	98.63	24 / 1 .	4.16	0.46	52.21	0.03	41.77	98.63							
23 / 1 .	0.00	0.00	0.00	0.00	0.00	0.00	24 / 1 .	0.00	0.00	0.00	0.00	0.00	0.00	25 / 1 .	0.00	0.00	0.00	0.00	0.00	0.00							
24 / 1 .	0.00	0.00	0.00	0.00	0.00	0.00	25 / 1 .	0.00	0.00	0.00	0.00	0.00	0.00	26 / 1 .	0.00	0.00	0.00	0.00	0.00	0.00							
25 / 1 .	4.02	0.52	52.88	0.00	41.91	99.33	26 / 1 .	4.11	0.56	52.57	0.01	41.22	98.46	27 / 1 .	4.11	0.43	52.00	0.03	42.06	98.62							
26 / 1 .	4.11	0.56	52.57	0.01	41.22	98.46	27 / 1 .	4.11	0.43	52.00	0.03	42.06	98.62	28 / 1 .	4.17	0.50	52.10	0.00	42.41	99.18							
27 / 1 .	4.11	0.43	52.00	0.03	42.06	98.62	28 / 1 .	4.17	0.50	52.10	0.00	42.41	99.18	29 / 1 .	4.17	0.44	52.91	0.00	41.33	98.85							
28 / 1 .	4.17	0.50	52.10	0.00	42.41	99.18	29 / 1 .	4.17	0.44	52.91	0.00	41.33	98.85	30 / 1 .	4.08	0.41	53.30	0.00	41.86	99.64							
29 / 1 .	4.17	0.44	52.91	0.00	41.33	98.85	30 / 1 .	4.08	0.41	53.30	0.00	41.86	99.64	31 / 1 .	4.19	0.43	52.60	0.06	42.07	99.35							
30 / 1 .	4.08	0.41	53.30	0.00	41.86	99.64	31 / 1 .	4.19	0.43	52.60	0.06	42.07	99.35	32 / 1 .	4.15	0.47	52.47	0.00	42.38	99.47							
31 / 1 .	4.19	0.43	52.60	0.06	42.07	99.35	32 / 1 .	4.15	0.47	52.47	0.00	42.38	99.47	33 / 1 .	4.05	0.44	53.19	0.00	41.92	99.60							
32 / 1 .	4.15	0.47	52.47	0.00	42.38	99.47	33 / 1 .	4.05	0.44	53.19	0.00	41.92	99.60	34 / 1 .	4.09	0.55	53.09	0.00	41.60	99.33							
33 / 1 .	4.05	0.44	53.19	0.00	41.92	99.60	34 / 1 .	4.09	0.55	53.09	0.00	41.60	99.33	35 / 1 .	4.00	0.42	52.44	0.01	42.24	99.12							
34 / 1 .	4.09	0.55	53.09	0.00	41.60	99.33	35 / 1 .	4.00	0.42	52.44	0.01	42.24	99.12	36 / 1 .	4.12	0.49	52.53	0.00	42.17	99.31							
35 / 1 .	4.00	0.42	52.44	0.01	42.24	99.12	36 / 1 .	4.12	0.49	52.53	0.00	42.17	99.31	37 / 1 .	4.15	0.31	52.77	0.00	42.21	99.45							
36 / 1 .	4.12	0.49	52.53	0.00	42.17	99.31	37 / 1 .	4.15	0.31	52.77	0.00	42.21	99.45	38 / 1 .	4.12	0.38	52.65	0.04	41.82	99.02							
37 / 1 .	4.15	0.31	52.77	0.00	42.21	99.45	38 / 1 .	4.12	0.38	52.65	0.04	41.82	99.02	39 / 1 .	4.12	0.49	52.63	0.03	41.87	99.10							
38 / 1 .	4.12	0.38	52.65	0.04	41.82	99.02	39 / 1 .	4.12	0.49	52.63	0.03	41.87	99.10	40 / 1 .	4.08	0.49	52.84	0.01	42.49	100.03							
39 / 1 .	4.12	0.49	52.63	0.03	41.87	99.10	40 / 1 .	4.08	0.49	52.84	0.01	42.49	100.03	41 / 1 .	4.20	0.49	52.84	0.01	42.49	100.03							
40 / 1 .	4.08	0.49	52.84	0.01	42.49	100.03	41 / 1 .	4.20	0.49	52.84	0.01	42.49	100.03	42 / 1 .	4.13	0.42	53.00	0.07	42.32	99.94							
41 / 1 .	4.20	0.49	52.84	0.01	42.49	100.03	42 / 1 .	4.13	0.42	53.00	0.07	42.32	99.94	43 / 1 .	4.05	0.40	52.66	0.07	41.92	99.09							
42 / 1 .	4.13	0.42	53.00	0.07	42.32	99.94	43 / 1 .	4.05	0.40	52.66	0.07	41.92	99.09	44 / 1 .	4.11	0.35	52.90	0.01	42.25	99.61							
43 / 1 .	4.05	0.40	52.66	0.07	41.92	99.09	44 / 1 .	4.11	0.35	52.90	0.01	42.25	99.61	45 / 1 .	4.16	0.35	52.92	0.02	41.82	99.26							
44 / 1 .	4.11	0.35	52.90	0.01	42.25	99.61	45 / 1 .	4.16	0.35	52.92	0.02	41.82	99.26	46 / 1 .	4.09	0.32	51.85	0.00	41.91	98.18							
45 / 1 .	4.16	0.35	52.92	0.02	41.82	99.26	46 / 1 .	4.09	0.32	51.85	0.00	41.91	98.18	47 / 1 .	4.16	0.41	52.88	0.00	42.19	99.63							
46 / 1 .	4.09	0.32	51.85	0.00	41.91	98.18	47 / 1 .	4.16	0.41	52.88	0.00	42.19	99.63	48 / 1 .	4.16	0.53	52.67	0.03	41.45	98.87							
47 / 1 .	4.16	0.41	52.88	0.00	42.19	99.63	48 / 1 .	4.16	0.53	52.67	0.03	41.45	98.87	49 / 1 .	4.19	0.47	52.51	0.00	41.39	98.50							
48 / 1 .	4.16	0.53	52.67	0.03	41.45	98.87	49 / 1 .	4.19	0.47	52.51	0.00	41.39	98.50	50 / 1 .	4.17	0.43	52.78	0.01	41.69	99.09							
49 / 1 .	4.19	0.47	52.51	0.00	41.39	98.50	50 / 1 .	4.17	0.43	52.78	0.01	41.69	99.09	51 / 1 .	4.17	0.43	52.78	0.01	41.69	99.09							
50 / 1 .	4.17	0.43	52.78	0.01	41.69	99.09	51 / 1 .	4.17	0.43	52.78	0.01	41.69	99.09	52 / 1 .	4.17	0.43	52.79	0.02	41.68	99.09							
51 / 1 .	4.17	0.43	52.78	0.01	41.69	99.09	52 / 1 .	4.17	0.43	52.79	0.02	41.68	99.09	53 / 1 .	4.04	0.41	53.20	0.00	41.53	99.18							
52 / 1 .	4.17	0.43	52.79	0.02	41.68	99.09	53 / 1 .	4.04	0.41	53.20	0.00	41.53	99.18	54 / 1 .	4.22	0.51	52.74	0.02	41.31	98.80							
53 / 1 .	4.04	0.41	53.20	0.00	41.53	99.18	54 / 1 .	4.22	0.51	52.74	0.02	41.31	98.80	55 / 1 .	4.21	0.40	52.86	0.00	41.78	99.25							
54 / 1 .	4.22	0.51	52.74	0.02	41.31	98.80	55 / 1 .	4.21	0.40	52.86	0.00	41.78	99.25	56 / 1 .	4.14	0.47	52.83	0.02	41.48	98.94							
55 / 1 .	4.21	0.40	52.86	0.00	41.78	99.25	56 / 1 .	4.14	0.47	52.83	0.02	41.48	98.94	57 / 1 .	4.16	0.45	52.40	0.05	42.14	99.20							
56 / 1 .	4.14	0.47	52.83	0.02	41.48	98.94	57 / 1 .	4.16	0.45	52.40	0.05	42.14	99.20	58 / 1 .	4.10	0.44	52.68	0.06	42.38	99.66							
57 / 1 .	4.16	0.45	52.40	0.05	42.14	99.20	58 / 1 .	4.10	0.44	52.68	0.06	42.38	99.66	59 / 1 .	4.15	0.39	52.49	0.00	41.94	98.97							
58 / 1 .	4.10	0.44	52.68	0.06	42.38	99.66	59 / 1 .	4.15	0.39	52.49	0.00	41.94	98.97														
59 / 1 .	4.15	0.39	52.49	0.00	41.94	98.97																					
						</																					

23 / 1 .	2.13	0.03	9.29	0.00	5.85	17.14	48 / 1 .	2.14	0.09	9.20	0.00	5.87	17.07	43 / 1 .	2.14	0.01	9.31	0.00	5.85	17.16
24 / 1 .	2.15	0.06	9.35	0.00	5.82	17.17	49 / 1 .	2.15	0.11	9.26	0.00	5.84	17.11	44 / 1 .	2.14	0.01	9.29	0.00	5.85	17.15
25 / 1 .	2.13	0.04	9.22	0.01	5.88	17.10	50 / 1 .	2.19	0.15	9.33	0.00	5.80	17.13	45 / 1 .	2.05	0.01	9.30	0.00	5.87	17.16
26 / 1 .	2.08	0.04	9.14	0.00	5.92	17.06	51 / 1 .	2.17	0.13	9.33	0.00	5.81	17.14	46 / 1 .	2.13	0.02	9.36	0.00	5.83	17.18
27 / 1 .	2.10	0.02	9.25	0.00	5.88	17.13	52 / 1 .	2.17	0.12	9.32	0.00	5.81	17.13	47 / 1 .	2.11	0.02	9.34	0.00	5.84	17.18
28 / 1 .	2.10	0.02	9.28	0.00	5.86	17.15	53 / 1 .	2.17	0.12	9.32	0.00	5.81	17.13	48 / 1 .	2.11	0.01	9.31	0.00	5.85	17.16
29 / 1 .	2.12	0.03	9.32	0.00	5.84	17.16	54 / 1 .	2.11	0.11	9.40	0.00	5.80	17.19	49 / 1 .	2.06	0.02	9.26	0.00	5.88	17.14
30 / 1 .	2.12	0.05	9.29	0.00	5.85	17.14	55 / 1 .	2.21	0.14	9.35	0.00	5.79	17.14	50 / 1 .	2.15	0.02	9.21	0.00	5.88	17.09
31 / 1 .	2.21	0.03	9.26	0.00	5.85	17.11	56 / 1 .	2.19	0.11	9.31	0.01	5.82	17.13	51 / 1 .	2.15	0.01	9.31	0.00	5.85	17.15
32 / 1 .	2.12	0.06	9.19	0.00	5.89	17.08	57 / 1 .	2.16	0.13	9.35	0.01	5.80	17.15	52 / 1 .	2.19	0.01	9.33	0.00	5.83	17.16
33 / 1 .	2.22	0.02	9.34	0.00	5.82	17.15	58 / 1 .	2.16	0.13	9.22	0.00	5.86	17.07	53 / 1 .	2.15	0.01	9.48	0.00	5.78	17.25
34 / 1 .	2.17	0.05	9.34	0.00	5.82	17.16	59 / 1 .	2.12	0.12	9.22	0.00	5.86	17.09	54 / 1 .	2.12	0.01	9.48	0.00	5.78	17.26
35 / 1 .	2.21	0.02	9.36	0.00	5.81	17.17														
36 / 1 .	2.12	0.02	9.35	0.01	5.83	17.18														
37 / 1 .	2.16	0.02	9.50	0.00	5.76	17.26														
38 / 1 .	2.11	0.02	9.50	0.00	5.78	17.27														
39 / 1 .	2.15	0.02	9.41	0.00	5.80	17.21														
40 / 1 .	2.14	0.02	9.34	0.00	5.83	17.17														
41 / 1 .	2.11	0.03	9.42	0.00	5.80	17.23														
42 / 1 .	2.10	0.03	9.49	0.00	5.78	17.27														
43 / 1 .	2.21	0.03	9.21	0.00	5.87	17.08														
44 / 1 .	2.22	0.02	9.22	0.00	5.87	17.08														
45 / 1 .	2.18	0.02	9.28	0.00	5.85	17.13														
46 / 1 .	2.13	0.02	9.31	0.01	5.85	17.16														
47 / 1 .	2.24	0.02	9.30	0.00	5.83	17.13														
48 / 1 .	2.17	0.02	9.22	0.00	5.88	17.09														
49 / 1 .	2.14	0.02	9.23	0.00	5.88	17.10														
50 / 1 .	2.19	0.03	9.34	0.00	5.82	17.16														
51 / 1 .	2.12	0.05	9.44	0.01	5.79	17.23														
52 / 1 .	2.12	0.04	9.41	0.01	5.80	17.21														
53 / 1 .	2.13	0.03	9.36	0.00	5.82	17.18														
54 / 1 .	2.14	0.02	9.42	0.00	5.80	17.22														
cations on basis of 25 O																				

Table C2: Trace Elements in Standards NIST 612 and Durango Apatite in This Study Compared to Reported Values																																											
		NIST 612 (Gao et al., 2002)																				Durango (Chew et al., 2016))	%RSD	Durango																			
		1s	NIST612_1	NIST612_2	NIST612_3	NIST612_4	NIST612_5	NIST612_6	NIST612_7	NIST612_8	NIST612_9	NIST612_10	NIST612_11	NIST612_12	NIST612_13	NIST612_14	NIST612_15	NIST612_16	NIST612_17	NIST612_18	NIST612_19	NIST612_20			Durango_1	Durango_2	Durango_3	Durango_4	Durango_5	Durango_6	Durango_7	Durango_8	Durango_9	Durango_10	Durango_11	Durango_12	Durango_13	Durango_14	Durango_15	Durango_16	Durango_17		
La	37	1	36	36	37	39	35	35	35	35	38	37	35	37	32	31	34	36	38	39	39	38		3720	8	3910	4060	4470	4110	3870	4290	4380	3850	4000	3830	4380	3970	4065	4138	3700	3961	4210	
La_Int2SE			3	3	3	3	4	4	2	2	3	3	3	3	2	2	1	2	2	1	1	3				300	360	370	280	310	370	430	360	290	290	390	340	73	91	540	86	200	
Ce	38	2	39	39	39	39	39	39	39	39	39	39	37	39	33	33	40	40	41	42	40	40		5184	7	4720	4580	5140	5190	4920	6940	6580	4390	4760	4010	4260	4400	4920	4960	4750	4910	5140	
Ce_Int2SE			3	3	4	3	4	3	3	3	3	3	3	3	2	1	7	1	3	3	4	2				340	440	480	440	470	620	530	360	520	420	430	350	150	120	220	140	260	
Pr	37	1	36	36	39	36	39	38	37	37	38	37	39	36	31	32	36	37	40	42	41	40		452	5	482	492	464	488	455	461	478	458	463	477	515	501	390	401	395	389	420	
Pr_Int2SE			3	3	3	3	3	3	3	3	3	3	4	2	2	2	2	2	2	3	4	4				35	43	37	33	40	46	40	31	35	45	51	43	9	16	16	11	20	
Nd	35	1	36	36	36	36	36	36	36	35	37	35	37	35	29	28	34	38	38	39	41	40		1567	8	1680	1690	1680	1850	1570	1590	1640	1490	1530	1570	1650	1660	1312	1280	1279	1262	1296	
Nd_Int2SE			4	3	4	4	3	3	3	3	4	3	3	3	2	3	5	2	4	4	4	4				150	140	180	170	140	150	140	110	100	120	150	150	140	110	100	120		
Sm	37	1	36	38	40	37	40	38	38	39	39	39	38	37	28	30	37	37	40	47	44	42		224	6	232	229	239	227	217	231	238	232	242	227	257	244	194	180	186	161	170	
Sm_Int2SE			3	3	3	3	4	3	3	3	3	4	3	3	4	2	4	4	3	7	5	4				16	15	20	17	19	23	18	20	19	20	24	20	13	16	13	9	10	
Eu	35	1	35	35	35	35	36	35	34	36	35	35	35	35	27	28	33	36	37	40	39	41		19	5	21	21	20	20	19	20	21	20	20	21	20	21	18	20	21	23		
Eu_Int2SE			3	2	2	2	3	3	2	3	3	3	3	3	1	1	1	2	2	5	4	4				1	1	2	2	1	2	2	2	2	2	2	2	3	2	1	2		
Gd	36	1	36	36	37	37	37	37	38	37	37	37	38	34	26	31	34	38	40	45	43	37		189	6	210	204	204	209	184	200	193	186	195	186	193	198	169	159	169	146	153	
Gd_Int2SE			3	3	3	3	3	3	2	3	3	3	3	3	2	1	5	2	5	2	5	4				14	14	16	13	14	16	15	15	16	13	13	15	6	22	8	6	16	
Tb	36	1	36	35	37	36	37	36	35	36	36	36	38	35	26	27	33	38	39	41	41	42		23	5	26	25	25	24	23	24	25	25	24	23	24	25	21	19	19	18	17	
Tb_Int2SE			2	2	2	3	2	2	2	2	2	2	3	3	2	3	1	2	1	2	2	3				2	2	2	2	2	2	2	2	2	2	2	1	4	2	2	2		
Dy	36	1	35	36	38	35	38	37	35	35	38	35	37	36	26	28	32	40	40	43	41	39		136	5	145	150	148	153	129	142	145	146	133	136	131	140	126	115	121	102	98	
Dy_Int2SE			2	3	3	2	3	3	2	3	3	3	3	3	3	2	4	2	5	5	4					9	10	10	11	9	11	10	11	10	10	11	11	10	11	9	11		
Ho	38	1	38	38	37	38	41	39	38	38	38	38	38	37	27	27	35	39	41	46	44	45		27	5	29	28	30	30	26	28	28	27	26	27	29	28	25	22	20	21		
Ho_Int2SE			3	2	2	2	3	3	2	2	3	3	3	3	2	2	1	3	1	4	3	3				2	2	2	2	2	2	2	2	2	2	3	2	3	6	3	2	4	
Er	37	1	37	37	40	38	39	39	37	39	38	38	37	39	28	26	35	39	43	44	45	44		72	5	78	74	83	80	70	75	74	75	77	70	76	78	69	65	62	60	56	
Er_Int2SE			2	3	3	3	3	3	2	2	2	3	2	3	6	3	2	4	2	3	6	5				6	5	6	6	6	6	5	6	5	5	5	6	9	18	10	6	8	
Tm	37	1	38	38	39	38	39	38	37	37	39	38	38	38	27	28	35	39	42	44	44	46		9	5	9	9	10	10	9	9	9	9	9	9	9	9	8	8	9	7	7	
Tm_Int2SE			2	2	3	2	3	2	2	2	2	2	2	2	2	2	1	2	2	1	4	3				1	1	1	1	1	1	1	1	1	1	1	1	1	2	1	1		
Yb	40	1	38	38	42	38	38	39	40	39	40	40	38	39	30	31	36	40	44	46	45	44		48	6	53	51	52	51	4	46	52	51	50	49	49	51	50	42	40	43	39	39
Yb_Int2SE			3	3	3	3	3	3	2	3	3	3	3	2	2	5	3	4	3	4	5	2				3	4	3	4	4	5	4	4	4	4	4	4	10	11	7	8	11	
Lu	37	1	37	37	37	37	38	37	37	37	38	37	37	37	28	28	34	37	39	43	40	45		5	6	6	6	6	6	5	6	6	5	5	5	6	6	6	5	5	6	4	
Lu_Int2SE			2	2	2	2	3	3	2	2	2	2	2	3	3	2	1	3	2	1	4					0	0	0	0	0	1	0	0	0	0	0	1	1	1	2	2	1	1
Th	37	1	37	39	37	38	38	40	38	38	38	38	36	38	28	28	34	40	41	44	42	43		253	8	254	238	257	270	232	253	260	261	256	250	272	273	258	240	238	199	202	
Th_Int2SE			3	3	3	3	3	3	2	3	3	3	2	3	1	1	1	7	1	3	3	4				16	17	18	22	19	21	19	19	20	22	24	23	71	77	70	51	58	
U	37	1	37	37	38	37	39	37	37	39	38	38	38	36	28	28	34	40	41	44	42	43		13	8	14	14	16	16	13	14	14	14	13	13	14	14	14	15	14	14	12	12
U_Int2SE			2	2	2	2	2	2	2	1	2	2	2	2	2	1	1	7	1	3	3	4				1	1	1	1	1	1	1	1	1	1	1	1	5	4	4	3	4	