Assessing the reliability of detrital zircon in Early-Earth provenance studies

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Abstract

Our understanding of the Early Earth and the processes that have shaped its evolution have spawned predominantly from the geochemical and isotopic signatures of a small number of zircon populations around the world. Studies of trace element distributions, Hf and O isotope systematics as well as mineral inclusion chemistry in detrital zircon are combined with U-Pb chronology in order to constrain source rock characteristics. However, previous research has highlighted the potential for primary isotopic and geochemical signatures to be modified after deposition, enhanced by self-induced radiation damage and crystal-plastic deformation. Further complications arise when an unknown number of source rocks contribute to the detrital sediments, or when the source rocks are absent as is the case for Hadean detrital zircon.

In this thesis, a range of analytical methods are applied to relatively uncharted ancient detrital zircon populations, in addition to a systematic investigation into the behaviour of titanium, rare earth elements, U-Th-Pb, Lu-Hf and O isotopes in a magmatic source-rock analogue to such ancient detrital zircon suites. Three localities are studied: Mt. Alfred, within the Yilgarn Craton of Western Australia (detrital study); the Saglek Block, the western-most extent of the North Atlantic Craton in northern Labrador (detrital study); and a locality south of Isua in southern West Greenland (analogue study).

We have utilised a CAMECA ims 1280 Secondary Ion Mass Spectrometer (SIMS) for its high spatial resolution and small volume sampling, except for the Lu-Hf analyses which were carried out using a Laser Ablation Multicollector Inductively Coupled Plasma Mass Spectrometer (LA-MC-ICP-MS).

The main outcomes of this study are threefold. 1) Heavily discordant, ancient detrital zircon populations require extensive data filtering in order to produce reliable data for age comparison. Further, age estimations of pervasive Pb loss even in metamict detrital zircon may be achieved using intragrain discordia intercept ages. Applying this in a regional sense reveals that detrital zircon from Mt. Alfred, Western Australia have a distinct provenance in comparison to other metasedimentary units of the Youanmi Terrane, and bear resemblance to the Mt. Narryer metasediments of the Narryer Terrane. 2) Detrital zircon from metasedimentary rocks exposed to high grade metamorphism in the Saglek Block, Northern Labrador yield predominantly Mesoarchaean age signatures, along with a minor Eoarchaean aged component. Lu-Hf isotope data from these zircon reveal up to five near-chondritic populations. U-Pb-Hf data from two samples of metapelite (L1407 and L1408) suggest that a previous re-assignment of deposition age for this unit to >3.95 Ga is unsubstantiated, undermining later studies based on that interpretation. 3) Geochemical complexities in zircon from an Eoarchaean metatonalite, taken as a source analogue to ancient detrital zircon, challenge the assumptions and interpretations drawn from detrital zircon studies. Lu-Hf and O isotope systems display mostly homogenous compositions, despite recognised U-Pb disturbance. Petrogenetic trace element proxies such as REE and Ti yield heterogeneous results, even within individual grains. Discerning magmatic signals from detrital zircon populations can therefore, without careful scrutiny, portray artificially complex results and consequently, lead to false interpretations.

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ASSESSING THE RELIABILITY OF DETRITAL ZIRCON IN EARLY-EARTH PROVENANCE STUDIES

Ross Kielman
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Ross Kielman
For my Grandma,
Sandra Hearne
Abstract

Our understanding of the Early Earth and the processes that have shaped its evolution have spawned predominantly from the geochemical and isotopic signatures of a small number of zircon populations around the world. Studies of trace element distributions, Hf and O isotope systematics as well as mineral inclusion chemistry in detrital zircon are combined with U-Pb chronology in order to constrain source rock characteristics. However, previous research has highlighted the potential for primary isotopic and geochemical signatures to be modified after deposition, enhanced by self-induced radiation damage and crystal-plastic deformation. Further complications arise when an unknown number of source rocks contribute to the detrital sediments, or when the source rocks are absent as is the case for Hadean detrital zircon.

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Sammanfattning


I denna avhandling har ett antal analysmetoder tillämpats på relativt outforskade detritiska zirkonpopulationer, tillsammans med systematiska undersökningar av titans, sällsynta jordartselements, U-Th-Pb, Lu-Hf och O-isotopers beteende i en magmatisk ursprungsbergart analog med sådana tidiga detritiska zirkonsviter. Tre lokaler har studerats: Mt. Alfred i Yilgarn-kratonen i västra Australien (detritisk studie); Sagleq Block, den västligaste utlöparen av den nordatlantiska kratonen i norra Labrador (detritisk studie); och en lokal söder om Isua i sydvästra Grönland (jämförelsestudie). Vi har använt oss av en CAMECA ims 1280 jonmikroskop (SIMS) för dess höga rumsliga upplösning och goda förmåga att analysera små provvolymer, med undantag av Lu-Hf analyserna, vilka utfördes med laserablation (Laser Ablation Multicollector Inductively Coupled Mass Spectrometer, LA-MC-ICP-MS).

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List of papers and author contributions

The core of the thesis presented here is composed of the three papers listed below. Paper I is published in Precambrian Research, paper III is accepted in Chemical Geology pending minor revisions and paper II is a manuscript.


III. Kielman, R. B., Whitehouse, M. J., Nemchin, A. A., Kemp A. I. S. (Accepted manuscript, minor revisions pending). A tonalitic analogue to ancient detrital zircon.

**Paper I:** Kielman R. B. carried out zircon imaging, sample preparations, U-Pb isotope analyses, interpreted the data and wrote the manuscript. Nemchin A. A. and Pidgeon R. T. provided the samples and support for data interpretation and manuscript corrections. Whitehouse M. J. and Bellucci J. J. provided support for data interpretation, acquisition and manuscript corrections.

**Paper II:** Kielman R. B. carried out field sampling, sample preparation, zircon imaging, U-Pb and Lu-Hf analyses, interpreted the data and wrote the manuscript. Whitehouse M. J., Dunkley D. and Kusiak M. carried out field sampling and discussion, and support for data interpretation and manuscript corrections. Nemchin A. A. and Salacińska A. provided support for data interpretation and manuscript corrections. Schmitt M. provided support with Lu-Hf analyses, data interpretation and manuscript corrections. Kooijman E. provided support with data interpretation.

**Paper III:** Kielman R. B. carried out sample preparation, zircon imaging, U-Pb, O-OH isotope and REE, Ti trace element analyses, interpreted the data and wrote the manuscript. Whitehouse M. J. provided the samples and support for data interpretation, acquisition and manuscript corrections. Nemchin A. A. provided support for data interpretation and manuscript corrections. Kemp A. I. S. carried out the Lu-Hf analyses and assisted in data interpretation and manuscript corrections.

List of poster and oral presentations

2014 – A New Perspective on the Pb Isotopic Composition of Mars. *In 77th Annual Meeting of the Meteoritical Society (Vol. 1800).*


2016 – A North Atlantic Craton analogue for ancient detrital zircon suites. *In North Atlantic Craton+ meeting 2016.*

2017 – Investigating the reliability of data from ancient detrital zircon populations using a tonalitic source analogue. *Invited presentation at Polish Academy of Sciences, Kraków, Poland.*
1.0 Introduction and aims

Zircon (ZrSiO$_4$) is an accessory mineral common to a wide range of rock types. To date, it is perhaps one of the most versatile minerals used in geochronology as it is highly resistant to both chemical and mechanical erosion, and consequently, can retain primary features relating to its crystallisation environment. U and Th are incorporated within the crystalline lattice during zircon crystallisation, whilst Pb is excluded (Silver & Deutsch 1963). This characteristic allows for the use of three independent radioactive decay systems ($^{238}$U-$^{206}$Pb, $^{235}$U-$^{207}$Pb and $^{232}$Th-$^{208}$Pb) for radiometric dating, within single zircon grains. The result is a geochronometer that is precise for almost the entirety of Earth history and also permits a means for internal data quality assessment by comparing the ages calculated for each decay system.

Trace elements such as Hf, rare earth elements (REE) and Ti are also readily substituted into the zircon structure during crystallisation, recording petrogenetic characteristics at the time of zircon crystallisation. For instance, Ti concentration in zircon is correlated with temperature of the melt from which it formed, at the time of crystallisation (Watson 2005; Ferry & Watson 2007), whilst REE distributions in zircon may provide information regarding the crystallisation of other mineral phases from a melt, thus helping to identify the rocks from which they are sourced (Belousova et al. 2002). Hafnium isotope systematics in zircon can also reflect the composition of its protolith, along with providing a measure of crust-mantle interaction (Thirlwall & Walder 1995; Kemp et al. 2010; Naeraa et al. 2012; Vervoort & Kemp 2016). Though not a trace element, the variations in oxygen isotope composition can indicate the involvement of meteoric and hydrothermal fluids during or prior to crystallisation, as is the case in the recycling of supracrustal material into the mantle (Valley et al. 1998; Wilde et al. 2001; Dhuime et al. 2012). These geochemical characteristics may then be correlated to the U-Th-Pb isotope systematics of the same growth zone to identify the conditions during zircon crystallisation and its relation to the host rock.

Owing to its resilience, it is possible for a zircon to record several generations of growth. Zircon may survive later reincorporation into magmatic systems, resulting in the “inheritance” of...
older zircon within zircon formed at an earlier time (Hoppe 1959). Similarly, metamorphism of a zircon-bearing rock can lead to the crystallisation of younger zircon rims over pre-existing cores. As such, a single zircon may record a series of magmatic and metamorphic events throughout its history. Moreover, through the erosion of such magmatic and metamorphic rocks, zircon from multiple sources can incorporated into the sedimentary cycle and deposited within sedimentary basins resulting in a snapshot of the exposed crustal rocks at the time of deposition. For example, zircon extracted from meta-sedimentary rocks in the Archaean Nain Province of Northern Labrador yield ages equivalent to magmatic rocks currently exposed in West Greenland (Schiotte et al. 1989, 1992) and represent the transport of sediments at a time when these continents were once contiguous.

The potential age complexity of zircon was initially recognised as a limitation to zircon age dating, as early methods relied of the dissolution of single or multiple grains (Hansmann & Oberli 1991). Therefore particular effort has to be made to ensure sample homogeneity by optical or scanning electron microscopy, otherwise the mixing of two or more genetically distinct zircon components can yield geologically meaningless “average” ages. The advent of microanalytical techniques with micron-scale spatial resolutions such as secondary ion mass spectrometry (SIMS) and laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) now permit the analysis of genetically distinct domains within multi-age component zircon. Additionally, these methods are significantly faster to perform than dissolution methods, as there is very little preparation required prior to analysis. Unfortunately, mixed ages from genetically distinct domains are also possible with SIMS and LA-ICP-MS techniques (Nutman et al. 1993, 1996), though mitigated by cathodoluminescence or back-scatter electron imaging (Whitehouse et al. 1999). This is especially visible in large (>100 000 grain) datasets (Holden et al. 2009). Further, the integrity of the U-Th-Pb geochronometer may be compromised by emission of a α-particles that occurs during $^{235/238}$U and $^{232}$Th decay events (Holland & Gottfried 1955). The lattice defects accumulate through time, so much so that if sufficient time elapses and abundant parent isotopes (U, Th) are
present, the rate of Pb diffusion increases so that even low temperature, near-surface conditions may reset the zircon U-Pb system (Pidgeon et al. 1966, 2013, 2017; Murakami et al. 1991; Geisler et al. 2002). This characteristic self-induced lattice damage is referred to as metamictisation, and can lead to an underestimation of U-Pb ages.

In the case of the Eoarchaean and Hadean where the rock record is sparse or non-existent, detrital zircon may not easily be correlated with their source rocks. As such, aberrant ages caused by mixing or disturbance of the U-Pb system may not be recognised, affecting the conclusions about evolution of the Earth during these time periods. Whilst the disturbance of the U-Th-Pb system within zircon is now better understood (Pidgeon et al. 1966, 2013, 2017; Mezger & Krogstad 1997; Nasdala et al. 1998; Balan et al. 2001; Geisler et al. 2002; Nemchin & Cawood 2005; Guitreau & Blichert-Toft 2014; Whitehouse et al. 2017b), the degree to which other petrogenetic indicators in zircon can be altered by secondary processes is still being explored (Hoskin 2005; Nemchin et al. 2006; Fu et al. 2008; Claesson et al. 2016). It is therefore the aim of this thesis to explore the potential, and limitations of detrital zircon studies, with particular focus on the Archaean and Hadean populations.

1.1 Thesis aims

The objectives of this research project are as follows: 1) to investigate the reliability of detrital zircon populations affected by extensive Pb loss, by providing new zircon geochronological data for a relatively unexplored metasedimentary unit of the Southern Cross Domain, Yilgarn craton. Variation of U-Th-Pb isotopes within both individual zircon grains and the total population distribution can be compared to the existing zircon record. 2) to investigate a suite of Archaean detrital zircon populations that had experienced high grade metamorphism, by providing new zircon geochronology and Lu/Hf data for the supracrustal units of the Saglek Block, North Atlantic Craton. Further, we sought to test validity of several extraordinary claims regarding the origins of life and modern-styled plate tectonics from this locality. 3) to test the reliability of isotopic and geochemical information produced in many detrital zircon studies by investigating
zircon from an ancient magmatic rock, taken as an analogue to the source materials sampled in such ancient metasedimentary rocks. Comparing the observed isotopic and geochemical characteristics of zircon from a single, magmatic sample should help to constrain the limits of detrital zircon studies where source rock context is otherwise removed.

2.0 Methods and analytical techniques

2.1 Sampling techniques and preparation

The procedure of zircon extraction from a sample, along with preparation and analysis can produce bias on the results. Several investigations into the effect of sampling bias have been performed (Sláma & Košler 2012; Košler et al. 2013), and guides made available to unify different approaches (Chisholm et al. 2014). Common approaches for the preparation of detrital zircon for analysis are broadly as follows: After the collection of samples as either loose sediments, sedimentary or metasedimentary rocks, individual minerals are when applicable liberated from the rock sample either by mechanical crushing or more recently by high voltage electrical pulverisation (Takehara et al. 2018), with the aim to reduce grain size to 20-400 µm, as typical for zircon (Chisholm et al. 2014). Large sample quantities may then be sieved and heavy minerals concentrated by hydrodynamic separation methods (e.g. Wilfley table). Smaller sample quantities, or further concentration of zircon in the heavy mineral separate from large samples can be achieved using heavy liquid floatation methods (e.g. tetrabromoethane, methylene iodide, Clerici solution). Removal of weakly paramagnetic heavy mineral fractions by means of Franz magnetic separator has been shown to improve the quality of extracted zircon (Silver 1963), without significantly biasing the end result (Sircombe & Stern 2002).

Zircon are then handpicked from the heavy mineral fraction, identified through morphology, colour and size under a binocular microscope, and then mounted on double-sided tape. The mounts are then set in epoxy resin and polished to expose the zircon grain interiors whilst maintaining a perfectly smooth surface finish, imperative in SIMS analysis (Kita et al. 2009). Finally, the sample
mounts are ultrasonically cleaned, and coated with approximately 30 nm of gold for imaging surveys and SIMS analysis. The gold coat is removed for LA-ICP-MS analysis, as it only hampers navigation during spot programming.

2.2 Cathodoluminescence imaging of zircon

Whilst resistant to many forms of secondary alteration, any given natural zircon may be comprised of a number of discrete growth zones in the form of metamorphic or magmatic overgrowths or recrystallization. Further, sub-solidus age resetting of zircon or episodic Pb loss enhanced by crystalline imperfections can result in isotopic heterogeneity in zircon grains. Thus, in order to accurately delineate crystallization and alteration events by ion-microprobe or LA-ICPMS, adequate documentation of the internal structure for each analyses zircon grain must be performed (Hanchar & Miller 1993; Hanchar & Rudnick 1995; Whitehouse et al. 1999).

Cathodoluminescence (CL) imaging is the most commonly used technique to reveal such growth zones primarily due to the minimal sample preparation requirements and the well-defined variations in zircon chemistry evident. The CL emission is caused by the excitation of electrons in the sample by a high energy source, in this case the electron beam from a Scanning Electron Microscope (SEM), and immediate restoration to the more stable lower energy ground state. This emission may then be measured with a specialised CL-detector. The detectors may be monochromatic, or polychromatic which allows for the capture of separate emission bands and recognition of particular mineral inclusions, and distinction between igneous and metamorphic domains (Koschek 1993; Hanchar & Rudnick 1995). The CL activity in zircon may be governed by a range of variables, though driving force is the presence of CL-active impurity ions (e.g. trivalent rare earth elements), acting as electron “traps” within the zircon structure (Boggs & Krinsley 2006; Timms & Reddy 2009). The emission of CL in zircon can be dampened by high Y and U contents, as well as defects in the crystalline structure caused by radiation damage or crystal-plastic deformation (Hanchar & Miller 1993; Nasdala et al. 2001; Timms & Reddy 2009). As such,
variations in U (and consequently Th) contents may be inferred from variations in CL brightness (Figure 1).

Figure 1. Cathodoluminescence (CL) image and corresponding scanning ion images of ThO, UO$_2$ and $^{207}$Pb/$^{206}$Pb. Brighter CL response is correlated with Th and U oxide concentrations, yet $^{207}$Pb/$^{206}$Pb is mostly unaffected. Note that ThO and UO$_2$ are also distributed along cracks.

Back-scattered electron (BSE) images also reveal zones of distinct chemical composition in zircon, however typically with a lower contrast from that of CL imaging. In cases where particularly U-rich zircon are imaged, the CL response is diminished whilst BSE images remain unaffected and retain structural features. Therefore depending on the composition of the zircon analysed, appropriate imaging techniques must be employed.

2.3 U-Th-Pb isotope system

The U-Th-Pb isotope system is arguably one of the most versatile, robust and widespread tools in geoscience today. Due to the long-lived nature of the U and Th parent isotopes, effective radiometric dating can theoretically be achieved to times earlier than the formation of the Earth
The three parent isotopes of interest $^{238}\text{U}$, $^{235}\text{U}$ and $^{232}\text{Th}$ each decay through a series of alpha and beta fission events to $^{206}\text{Pb}$, $^{207}\text{Pb}$ and $^{208}\text{Pb}$ respectively. $^{204}\text{Pb}$ however, is non-radiogenic and thus may be used in correcting for Pb contamination from other sources. The difference in half-life between the parent isotopes, summarised in Table 1, enables direct comparison of parent-daughter pairs over different timescales, and in the case of U, with identical geochemical behaviours. The accumulation of radiogenic Pb may be expressed as:

1) \[ \frac{^{206}\text{Pb}}{^{204}\text{Pb}} = \left( \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_i + \frac{^{238}\text{U}}{^{204}\text{Pb}} \left( e^{\lambda_{238}t} - 1 \right) \]

2) \[ \frac{^{207}\text{Pb}}{^{204}\text{Pb}} = \left( \frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right)_i + \frac{^{235}\text{U}}{^{204}\text{Pb}} \left( e^{\lambda_{235}t} - 1 \right) \]

3) \[ \frac{^{208}\text{Pb}}{^{204}\text{Pb}} = \left( \frac{^{208}\text{Pb}}{^{204}\text{Pb}} \right)_i + \frac{^{232}\text{Th}}{^{204}\text{Pb}} \left( e^{\lambda_{232}t} - 1 \right) \]

Such that $\left( \frac{^{208}\text{Pb}}{^{204}\text{Pb}} \right)_i$ is the Pb ratio at time of crystallisation and $\lambda_{238}$, $\lambda_{235}$, $\lambda_{232}$ are the decay constants for $^{238}\text{U}$, $^{235}\text{U}$ and $^{232}\text{Th}$ respectively, listed in Table 1 (Steiger & Jäger 1977). Since the ratio of $^{235}\text{U}$ and $^{238}\text{U}$ is found to be constant and similar in terrestrial, lunar and meteoritic systems (137.88, Barnes et al. 1972; Arden 1977; Steiger & Jäger 1977), a fourth equation can be constructed by combining equations 1) and 2), removing the dependence on parent isotope ratios:

4) \[ \frac{^{207}\text{Pb}}{^{206}\text{Pb}} = \frac{^{235}\text{U}}{^{238}\text{U}} \left( e^{\lambda_{235}t} \right) = \frac{1}{137.88} \left( e^{\lambda_{235}t} - 1 \right) \]

Selecting the appropriate equation for age determination is often based on approximate age of the analysis, where ages calculated from equation 1 are more precise <1.2 Ga and ages calculated from equation 4 are more precise >1.2 Ga, for a similar analytical precision on the ratio. Ages from equations 2 and 3 are not often reported due the low natural abundance of $^{235}\text{U}$ and the greater mobility of Th in respect to U, respectively (Ludwig 1998). The monitoring of common Pb (or initial Pb) included either at the time of crystallisation or later is paramount for accurate age determination. The relative abundance of non-radiogenic isotopes may then be approximated using a two-stage Pb evolution model such as that of Stacey & Kramers (1975), or observed directly.
from measurements of cogenetic feldspar (Kamber & Moorbath 1998). Without correction, the inclusion of common Pb will yield an older apparent age.

**Table 1 - U-Th-Pb system parameters (Steiger & Jäger 1977)**

<table>
<thead>
<tr>
<th>Parent – daughter isotope pair</th>
<th>Abundance (%)</th>
<th>Decay mode</th>
<th>Decay constant ($\lambda$, (year$^{-1}$))</th>
<th>Half-life (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$U – $^{206}$Pb</td>
<td>99.2743</td>
<td>$\alpha, \beta$</td>
<td>$1.55125 \times 10^{-10}$</td>
<td>$4.47 \times 10^9$</td>
</tr>
<tr>
<td>$^{235}$U – $^{207}$Pb</td>
<td>0.7200</td>
<td>$\alpha, \beta$</td>
<td>$9.8485 \times 10^{-10}$</td>
<td>$7.07 \times 10^8$</td>
</tr>
<tr>
<td>$^{232}$Th – $^{208}$Pb</td>
<td>100</td>
<td>$\alpha, \beta$</td>
<td>$4.9475 \times 10^{-11}$</td>
<td>$1.4 \times 10^{10}$</td>
</tr>
</tbody>
</table>

Furthermore, the three parent-daughter isotope pairs enable an internal check as to the disturbance of the system. If all parent-daughter pairs were to yield equivalent ages from a single analysis (otherwise known as concordant), it may be assumed that the sample had retained a closed system from crystallisation or the last complete resetting of the U-Th-Pb system. However, varied ages from the three parent-daughter pairs are referred to as discordant, and may reflect partial resetting, Pb loss or age inheritance (Wetherill 1956). To visualise this, the concordia diagram is employed. Concordia diagrams are a powerful tool for the visualisation of U-Th-Pb data, since it carries both age data as well as a graphical representation of discordance. Two variations of the concordia are used, “conventional” which uses $^{206}$Pb/$^{238}$U vs. $^{207}$Pb/$^{235}$U (Wetherill 1956) and “inverse/Tera-Wasserburg”, plotting $^{207}$Pb/$^{206}$Pb against $^{238}$U/$^{206}$Pb (Tera & Wasserburg 1972). The main feature common to both types of concordia diagrams is the concordia curve, which is the locus of the two ages provided by each axes ratio (equations 1 and 2, Figure 2). Data points that plot on this curve are referred to as concordant whereas deviations from the curve signify discordance of the U-Pb system (typically Pb-loss).
Figure 2. Schematic diagram of a conventional concordia plot. Two discordant data points define a discordia, depicting time of crystallisation ($t_C$) and age of last recorded Pb loss ($t_D$) if absolute concordance is assumed. From Guitreau and Blichert-Toft, 2014.

Zircon from detrital sediments often display a series of different age populations, reflecting the various source rock/s from which the sediments eroded from. As such, the interpretations made in detrital zircon geochronology studies are dependent heavily on statistical data analysis. Displaying age distributions by means of probability density plots (PDP) and kernel density estimates (KDE) as shown in Figure 3 are common in detrital studies, and represent different methods of displaying population density from analytical data with variable uncertainties (Vermeesch 2012). Whilst KDE’s have been suggested as a more appropriate means of displaying detrital zircon age distributions, PDP’s are still commonly used as they are easily compared with previously published PDP data, and more so as they are integrated with the widely used data handling software package, Isoplot (Ludwig 2012). Other frequently used statistical methods involve the measurement of dissimilarity between two or more age distributions, by means of parametric and non-parametric hypothesis tests such as the chi-square test or Kolmogorov-Smirnov test, respectively (Vermeesch 2018). These statistical measures are very powerful in the comparison between detrital populations and source rocks that yield “true” ages, however the
variable effect that Pb loss or resetting has on different detrital packages, as well as their sediment sources, likely results in poor correlations without extensive data treatment.

![Figure 3. Comparison of age distribution between probability density plot (PDP) and kernel density estimator (KDE). Histogram with a bin size of 10 Ma is visible behind both KDE and PDP. Data are from sample 409004 of Kielman et al., (submitted).](image)

2.4 Oxygen isotopes

Oxygen is the most abundant chemical element in the Earth’s crust, and the fractionation of its stable isotopes can provide insight to a wide range of geochemical processes. The mass dependant fractionation of its three stable isotopes $^{16}$O, $^{17}$O and $^{18}$O has led to the discovery of methods for meteorite classification (Clayton et al. 1976), hydrosphere interactions (Gat 1996), water-rock interactions (Clayton et al. 1972; Criss & Taylor Jr 1986), paleothermometry (Craig 1965), as well as clues regarding lunar formation (Epstein & Taylor Jr 1970). In most cases, the variation in $^{18}$O/$^{16}$O ratio is reported in $\delta$ (delta) notation which is normalised to standard mean ocean water (SMOW).

Unaltered mantle derived minerals/rocks yield $\delta^{18}$O values of $+5.3 \pm 0.6 \%$ (2σ), which is taken to be the oxygen isotope composition of the mantle (Valley et al. 1998). However, the interaction of igneous rocks with meteoric or hydrothermal waters can cause isotopic exchange between the two sources and consequently alter the $\delta^{18}$O values in the rock. Similarly, the assimilation of country rock during the crystallisation of a magma also enables oxygen isotope contamination (Taylor 1968). Undamaged, pristine zircon is thought to retain the primary $\delta^{18}$O signature of the magma it crystallised from (Peck et al. 2003), though this is known to be
compromised by metamictisation (Bibikova 1984), subsolidus metasomatic alteration (Hoskin 2005; Nemchin et al. 2006) or dissolution-reprecipitation (Geisler et al. 2007). Zircon δ¹⁸O values exceeding that of mantle-like signatures are taken as evidence of oxygen isotope fractionation in the presence of water, such as that expected in the recycling of supracrustal or near-surface low-temperature environments (Valley et al. 1994).

![Figure 4](image_url)

**Figure 4.** Compilation of δ¹⁸O values from various terrestrial and extraterrestrial rock types. Mantle δ¹⁸O value is from Valley et al., 1998. Modified after Allègre (2005).

2.5 Rare earth elements and titanium concentrations in zircon

Rare earth elements, or REE are the elements with atomic numbers from 57 to 71 (lanthanum to lutetium), which all exhibit similar chemical and physical properties. REE measurements have been applied to studies of igneous, sedimentary and metamorphic petrology for a considerable period of time, due to the relative fractionation of these elements during various petrological processes. For instance, negative Eu anomalies are commonly attributed to the crystallisation of plagioclase in a rock, as Eu²⁺ is readily substituted for Ca²⁺ within the plagioclase structure, consequently fractionating Eu relative to other REE within the melt during crystallisation. Patterns
in REE fractionation can therefore be used in the determination of genesis in igneous rocks, partial melting of crustal or mantle materials, fractional crystallisation or sediment provenance tracing (Haskin et al. 1970; Drake & Weill 1975).

Multi-element REE data are often normalised to a common reference standard, such as the CI chondritic meteorites measured from primitive chondritic meteorites. These data may be plotted from low-mass or light REE (LREE) to high-mass or heavy REE (HREE), against relative concentration to the reference standard as shown in Figure 5. Due to the versatility of REE in whole rock samples and the wealth of information that as be derived relating to the source rock genesis, REE patterns in zircon were explored as a method to distinguish different igneous rock types in detrital zircon populations (Heaman et al. 1990; Dabard et al. 1996; Belousova et al. 2002). However, it has been shown that zircon REE are rarely in equilibrium with the melt during crystallisation, exhibiting remarkably similar REE patterns from a variety of different rock types (Hoskin & Ireland 2000). Further, there is evidence to suggest that REE may become mobile within zircon by means of pipe diffusion along lattice dislocation arrays (Piazolo et al. 2016). In spite of this, zircon REE is still in use, though tentatively (e.g. Bell et al., 2016; Liati et al., 2016).

![Figure 5. Chondrite normalized REE patterns (Matsuda diagram) of zircon reference standards Temora-2 (red) and 91500 (black). Note that 91500 is a reference standard for REE abundances.](image)
2.6 Lu-Hf system

Lutetium is widely distributed in the crust, predominately in phosphates, silicates and oxides (Faure & Mensing 2005). It has two naturally occurring isotopes, the stable $^{175}$Lu and the radiogenic $^{176}$Lu which decays via beta emission to the stable isotope $^{176}$Hf, with a half-life of 37.1 Ga (Söderlund et al. 2004). The ionic radii of Lu$^{3+}$ and Hf$^{4+}$ are similar to those of Ca$^{2+}$ and Zr$^{4+}$, respectively. This results in high Lu/Hf ratios from Ca-bearing mineral phases (e.g. garnet, biotite, hornblende) and low Lu/Hf ratios in Zr-bearing mineral phases, such as zircon or baddeleyite. These accessory phases are however relatively abundant in Lu and Hf, with zircon containing concentrations on the order of ~20 and ~15200 ppm respectively. The relative abundance of REE in zircon presents a caveat for the measurement of Lu-Hf isotopes by LA-ICPMS, as $^{176}$Yb is often present as an isobaric mass interference during analysis (Thirlwall & Walder 1995; Woodhead et al. 2004). The generally accepted method for interference correction is performed by calculating the contribution of the interfering $^{176}$Yb from the natural $^{176}$Yb/$^{171}$Yb ratio and correcting for instrumental mass bias by monitoring the $^{173}$Yb/$^{171}$Yb ratio during the run (Woodhead et al. 2004). A similar approach is used for the correction of the isobaric interference of $^{176}$Lu on $^{176}$Hf.

The abundance of $^{176}$Hf, expressed as a ratio of $^{176}$Hf/$^{177}$Hf is dependent on the abundance of the parent isotope $^{176}$Lu and time passed:

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

where $^{176}\text{Hf}/^{177}\text{Hf}$ = ratio at present day within the rock or mineral, $(^{176}\text{Hf}/^{177}\text{Hf})_{i}$ = ratio at the time of crystallisation of the rock or mineral, $^{176}\text{Lu}/^{177}\text{Hf}$ = the ratio at present day within the rock or mineral, $\lambda$ = decay constant of $^{176}$Lu (1.87 x 10$^{-11}$, Söderlund et al., 2004) and $t$ = time passed since crystallisation in Ma.

Hf isotopes in zircon are typically illustrated using the back-calculated $(^{176}\text{Hf}/^{177}\text{Hf})_{t}$ ratio (at the time of crystallisation) vs. time of crystallisation, or as epsilon Hf ($\epsilon$Hf) vs. time of crystallisation (Figure 6). $\epsilon$Hf notation is simply the comparison of $^{176}$Hf/$^{177}$Hf ratio in the mineral
(or rock) at time \( t \) with that of the so-called chondritic uniform reservoir, or CHUR at time \( t \). The comparison may be done at time \( t \) in the following equation:

\[
\varepsilon^t(Hf) = \left[ \frac{(^{176}Hf/^{177}Hf)_{\text{sample}}^t}{(^{176}Hf/^{177}Hf)_{\text{CHUR}}^t} - 1 \right] \times 10^4
\]

The CHUR composition represents an approximation of the primeval \(^{176}Hf/^{177}Hf\) ratio around the time of early planetesimals accretion within the solar nebula, defined by measurements within a series of chondritic and achondritic meteorites (Tatsumoto et al. 1981; Blichert-Toft & Albarède 1997). As masses of juvenile crust are formed from any initial reservoir, said reservoir becomes increasingly depleted through progressive extraction events. The concept of a Depleted Mantle has been demonstrated in oceanic volcanism through geologic time, where incompatible elements such as Lu are removed from the initially CHUR-like mantle. However, there is conflicting evidence to suggest that such a “depleted mantle” was contiguous through the Archean and Hadean eons (Harrison et al. 2005, 2008; Hiess et al. 2009; Kemp et al. 2010).

The keystone to Hf isotope studies, particularly those that investigate the crust-mantle system, is the accurate and correlated assignment of age to the Lu-Hf isotopes analysed. A number of case studies and review papers have provided suggestions regarding this point, as inadequate constraining of crystallisation age to Hf isotopes in zircon may result in artificially depleted or enriched Hf signatures relative to CHUR (Gerdes & Zeh 2006; Kemp et al. 2010; Guitreau & Blichert-Toft 2014; Vervoort & Kemp 2016; Fisher & Vervoort 2018). This is particularly problematic if the zircon grains have been subjected to Pb loss or age resetting, the visible effect of which in \( \varepsilon \text{Hf} \) vs. crystallisation time space results in an array of data from a single Lu-Hf source reservoir along a slope representing a Lu/Hf = 0 evolution. For this reason, it is useful to plot data susceptible to Pb loss or age resetting in \(^{176}Hf/^{177}Hf\) vs. crystallisation time space, since any Pb loss is would then be visible as horizontal age arrays with equal \(^{176}Hf/^{177}Hf\). If present, age inheritance in zircon is expressed similarly to that of Pb loss, only the data array will in most cases appear more juvenile.
Figure 6. Schematic sketch of Hf isotope behaviour in epsilon Hf vs. age space. The schematic depicts the theoretical trajectories of mafic and felsic crust arrays, and the resulting depletion of the residual mantle from a single time of extraction. Lu/Hf evolution curves for felsic crust are based on values from Rudnick and Gao (2003), mafic crust after Nebel et al. (2013) and chondritic uniform reservoir (CHUR) after Bouvier et al. (2008). Modified after Nebel et al. 2014.

2.7 Secondary ion mass spectrometry (SIMS)

The ability for SIMS instruments to precisely analyse very small sample volumes (nanogram scale) from a wide range of solid materials sets it apart from isotope dilution methods (ID-TIMS) and LA-ICPMS instruments (Košler et al. 2002). Sampling diameters for zircon U-Pb analysis are typically between 10-30 µm, whilst sampling depths of only <2 µm (Ireland & Williams 2003). This is of particular importance with regards to complex, polyphase zircon as lateral complexities may be identified using cathodoluminescence imaging, but mapping distinct zones below the polished surface is restrictively expensive and time consuming (Suuronen and Sayab, 2018).

Currently, there exists a wide range of SIMS instruments for different applications, such as the large geometry configurations like the CAMECA IMS 1280 used here, nanoSIMS, ToF-SIMS or Sensitive High-resolution Ion Microprobe (SHRIMP). The fundamental principles of SIMS instrument operation is based on the ionisation of a small volume of sample material via a focused primary beam of positive or negative ions to generate secondary ions from the target, which are then (in the case of the CAMECA IMS 1280) accelerated through various ion lens and deflector assemblies along the flight path, an electrostatic analyser (ESA), a field aperture for elimination of stray ions, as well as a sector magnet to further focus and separate isotopes of interest which
can finally be measured using either analog current-measuring Faraday cups or ion counting electron multiplier detectors. The ESA serves to refocus the secondary ion beam and apply an energy filter to the beam to limit chromatic aberrations (Ireland 2014). A schematic of a CAMECA IMS 1280 SIMS, illustrating the principle components is shown in Figure 7. This instrument is equipped with both mono- and multi-collector analytical arrays, which typically employ a peak-hopping or static mode respectively, though this is highly dependent on the species of interest. Multicollector static mode uses an array of ion-counters to measure multiple masses simultaneously, whereas monocollector peak-hopping mode cycles the magnet between the masses of interest during sputtering of the sample, collecting statistics over a selected number of cycles per analysis.

Figure 7. Schematic diagram of CAMECA IMS 1280 secondary ion mass spectrometer (SIMS). After Ireland, 2014.

Differently charged primary ion beam sources are used to enhance the ionisation yield of the opposite charged ions of interest. The most common primary beam species are $^{133}$Cs$^+$ and $^{16}$O$_2^-$, as these are both highly electropositive and electronegative, respectively. Primary $^{133}$Cs$^+$ ions are produced by thermally ionising metallic Cs at the source, which is commonly used in zircon studies for the analysis of O isotopes. Primary $^{16}$O$_2^-$ ions are produced by ionising the source gas by plasma discharge at the duoplasmatron, which are commonly used in zircon studies for the analysis of
UO⁺, Pb⁺, REE⁺ and Ti⁺ species. Upon collision of the primary ions with the sample surface, secondary ions are produced whilst simultaneously the sputtering site builds a localised charge. In order to balance this charge, the samples are coated in a thin (~30nm) layer of conductive material, typically gold (Figure 8). This is sufficient for the use of a negative primary beam, however further charge compensation is required when using the positive primary ion beam and is achieved by flooding of electrons into the sputtering area by an electron gun.

In order to resolve isotope of different masses, particularly those with isobaric (equal nominal mass) interference with targeted secondary ion species, sufficient mass resolution (M/ΔM) is required. This is a benefit of using large geometry sector field mass spectrometer such as the CAMECA IMS 1280 used in this thesis, since these instruments have large magnets capable of wide turning radii (58.5 cm for CAMECA IMS 1280, 100 cm for SHRIMP) and are often used to resolve individual masses with a mass resolution (M/ΔM) between 3000 and 10 000(Ireland 2014). For instance, in zircon geochronology a mass resolution of 5400 (M/ΔM) is necessary to resolve Pb isotope species from isobaric HfSi⁺ and REEO₂⁺ species. It is important to note that higher mass resolutions (>8000 for CAMECA IMS 1280) typically result in lower secondary ion intensities, and thus a balance must be made for high precision and accuracy.

The accuracy of SIMS analysis is reliant on the use of matrix-matched, chemical and isotopically homogenous reference materials. This is largely due to the various instrument and element specific effects of mass fractionation inherent with secondary ion techniques, and consequently require reference materials to be analysed within an analytical session (Shimizu & Hart 1982; Ireland 2014; Schaltegger et al. 2015). Matching similar crystalline matrices between sample and reference material helps to ensure similar sputtering rates and controls on instrumental mass fractionation. The calibration of sample raw data can be achieved in some cases by simple linear functions from the comparison of reference material raw data and characterised “true” values determined by highly precise methods such as ID-TIMS. For zircon U-Pb geochronology, several Pb/U- and Pb/UO-related calibration schemes were assessed by Jeon and Whitehouse (2015), with
the recommendation of using a simple power law relationship of Pb/UO−UO2/UO for calibration. However, the sampling of zircon with high U concentration, or of considerable age may be challenging, as the high U domains may have become metamict: a low symmetry, glass-like form of zircon that occurs by radiation damage, which enhances the emission of Pb⁺ relative to U⁺ and UO₂⁺ species during SIMS analysis (Murakami et al. 1991; White & Ireland 2012).

The CAMECA IMS 1280 is also capable of mapping chemical and isotopic variations within a 400 µm x 400 µm area of sample material using a scanning ion imaging technique (SII). This is made possible by rastering a small (~500 nm and 2 µm diameter, respective of Cs⁺ or O₂⁻ source) primary beam across the target area, which approximately defines the lateral resolution. SII has been used in zircon studies to explore the possible heterogeneity of elemental Ti and U-Pb isotopes at the nanometer scale (Harrison & Schmitt 2007; Kusiak et al. 2013) and recent developments have allowed for both accurate and precise zircon geochronology (Bellucci et al. 2018).

U-Th-Pb and O isotopes as well as REE and Ti content in zircon for all papers in this thesis were measured using a CAMECA IMS 1280 SIMS ion microprobe, located at the NordSIM facility, Swedish Museum of Natural History, Stockholm.

![Figure 8. Illustration of surface material sputtering. Emission of secondary ions is caused by 16O²⁻ primary ion beam, and gold coat required for local charge dissipation is shown.](image-url)
2.8 Laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS)

Laser-ablation ICP-MS (Inductively Coupled Plasma Mass Spectrometer) is one of the more recent advances in analytical geosciences (Perkins et al. 1993). During analysis, a finite volume of sample material is vaporised by a pulsed laser beam and transported via inert gases (Ar/N₂/He) to the ICPMS. Isotope and elemental analysis by LA-ICP-MS requires very little sample preparation, allows for shorter analysis times than SIMS and offers a wide range of spot sizes (between 5 and 350 µm) that enable the in situ analysis of low concentration isotope species such as for example the Lu-Hf system (Machado & Gauthier 1996; Xu et al. 2004).

Depending on the application, laser systems with different wavelengths are available, however most studies indicate that shorter wavelength are most suitable for LA-ICP-MS as they offer the advantage of less elemental/isotopic fractionation during ablation, lowering matrix effects and allowing for better precision (Guillong et al. 2003). For geological samples the most widely used laser systems are solid state Nd:YAG laser (213 nm), ArF excimer lasers (193 nm) and more recently femtosecond laser systems (Poitrasson & d’Abzac 2017).

All of the above mentioned laser systems can be coupled to different types of ICP-MS instruments, and in special setups, even to several mass spectrometers at the same time (split-stream or LASS-ICP-MS), enabling simultaneous analyses of different isotope systems (e.g. U-Pb and Hf) (Kylander-Clark et al. 2013). Common to all available ICP-MS instruments is the generation of a high temperature (Ar-)plasma source at the front-end of the instrument that ionizes the sample. These ions are then separated, focused and detected in the mass spectrometer. Most elements with mass number between 7 and 238 can be measured with varying limits of detection. Some instruments allow for high resolution modes, in order to separate isotopes from potential isobaric interferences. The most commonly used ICP-MS systems are quadrupole ICP-MS, sector field single collector (SC-)ICP-MS or multicollector (MC-)ICP-MS (Figure 9). Quadrupole and SC-ICP-MS allow for very fast scanning over the entire mass-range and are therefore commonly used to determine elemental concentrations. Sector field ICP-MS typically produce higher
sensitivities and better precision compared to quadrupole ICP-MS. Multicollector ICP-MS on the other hand enables for the simultaneous measurements of a limited mass range (e.g. m/z = 202 through to m/z = 238) using an array of faraday detectors and ion-counters, therefore allowing for the acquisition of high precision isotope ratios.

Figure 9. Schematics of a) quadrupole ICP-MS and a b) double focusing, reverse-geometry, single-collector magnetic sector ICP-MS (Košler & Sylvester, 2003)

LA-(MC- or SC-) ICP-MS is frequently used and often recommended for the U-Pb dating of detrital zircon as precision and accuracy is comparable to that from SIMS U-Pb analyses, whilst also permitting a high sample throughput required for statistical treatment of detrital populations with analysis times down to ~40 seconds/spot (including both ablation and washout time) (Košler et al. 2002, 2013; Gerdes & Zeh 2006; Schaltegger et al. 2015).

A disadvantage of LA-ICP-MS over SIMS for U-Pb dating however is the need for a larger sample volume per analysis, resulting in deeper ablation craters (and opens up to the possibility of mixed ages) and the so called ‘down-hole fractionation’ that describes the process of a variable fractionation between U (or Th) and Pb that can lead to false ages, if not corrected for carefully (e.g. Horn et al. 2000). The precision of a single analysis with LA-ICP-MS is also limited by the external reproducibility of the reference material that is used, which is reflected in the propagated errors for a single analysis. This is especially important for old samples with high Pb concentration that can be measured with extremely good precision using SIMS, which (for $^{207}$Pb/$^{206}$Pb ages) mainly depends on counting statistics and common lead corrections, whilst for LA-ICP-MS is further limited by the external reproducibility of the reference zircon that is being used and yields, at best, a precision of 1-2% for U-Pb ages (Schaltegger et al. 2015).
With regard to in-situ Lu-Hf analyses in zircon, LA-MC-ICP-MS is the method of choice, with only one published study attempting Lu-Hf analysis by SIMS (Kinny et al. 1991). This is predominantly due to the poor Hf ion yields by SIMS techniques. Relevant interfering masses can be monitored during the ablation and appropriate corrections can be applied. Split-stream LA-ICP-MS have allowed for the simultaneous measurement of Lu-Hf with U-Pb (Kylander-Clark et al. 2013). Semi-simultaneous methods of U-Pb and Lu-Hf measurements through magnet-jumping are also possible without the need of two mass spectrometers, providing better correlation between Lu-Hf and U-Pb age (Kemp et al. 2009, 2010). However both approaches require larger spot sizes and/or longer analysis times than usually required for U-Pb analyses resulting in compromised spatial resolution and higher risk of intersecting mixed age domains, inclusions or Pb-loss affected regions during analysis.

3.0 Detrital zircon geochronology

Combining zircon geochronology with petrogenetic indicators (REE, Lu-Hf, O, mineral inclusions), thermometry (Ti-in-zircon) or other geochemical signatures in zircon (e.g. Pu-Xe or Li isotopes, (Turner et al. 2004, 2007; Ushikubo et al. 2008)) can help to constrain the source and environment from which it crystallises. This is particularly valuable when applied to the detrital zircon analysis, which exploits the natural sampling of eroded source material, often driven by surficial aqueous systems and thus covers a wide “snapshot” of exposed crust in any particular sample. This method also permits the sampling of source rocks not currently reachable (e.g. Froude et al. 1983; Yi et al. 2014). As such, the investigation of sedimentary provenance can provide invaluable constraints for tectonic reconstructions.

An assumption to detrital studies is that the analysed selection of detrital grains are representative of the grains from the sampled sedimentary material. Consequently, the proportion and accumulation of different zircon-bearing sediments should be directly related to the path of sediment transport and its intersection with exposed bedrock. However in practice, these
proportions may be biased by a number of factors: 1) source-rock zircon fertility (Moecher & Samson 2006), 2) hydraulic sorting of grain size (Rittenhouse 1943; Garzanti et al. 2009), 3) loss of poorly crystalline (metamict) zircon during transportation (Fedo et al. 2003; Malusà et al. 2013). Distinct and isolated components (such as smaller igneous plutons) may simply be excluded from a fluvial systems path, and thus not represented in the sedimentary basin.

As any particular detrital zircon population may consist of contribution from an unknown number of sediment sources, the number of grains analysed in a sample can have a significant effect on the representation of zircon populations from that sample. Therefore, it is recommended to obtain large (n>117) datasets, so as to ensure the sampling of minor zircon populations with significance of >5% at a 95% level of confidence (Vermeesch 2004). A previous study by Dodson et al. (1988) posed the need for at least 60 grains to be analysed to achieve a similar level of confidence, however this was intended to identify the probability of missing just one minor population, and not any population of >5% significance. It should be noted that simply obtaining a large number of detrital zircon grains is not necessarily sufficient, as these grains may have suffered significant secondary alteration. Obtaining high quality, primary geochronological data in highly altered detrital zircon populations yields more reliable results, which can be achieved by rigorous filtering of data based on concordance, post-analysis examination and intra-grain consistency (Whitehouse et al. 2017b; Kielman et al. 2018). It is further stressed that studies with less than the recommended 117 grains are not inherently false, only that as there is a higher chance of minor populations missing in the distribution of ages. In any case comparisons should avoid placing undue emphasis on absent age peaks (Vermeesch 2004).

In order to effectively use petrogenetic tracers in zircon, it is necessary to ensure that the age is well constrained to the crystallisation event, and likewise to metamorphic events if secondary features are the focus. Crystalline zircon may preserve primary crystallisation signatures through magmatic assimilation, provided that the melt is saturated in Zr (Watson & Harrison 1983; Mezger & Krogstad 1997; Cherniak & Watson 2001; Hanchar & Watson 2003) and even in some cases,
has been demonstrated to survive ultra-high temperature metamorphism (Kooijman et al. 2011). However, with sufficient time and parent isotope concentration, a zircon will become increasingly prone to diffusive Pb loss. Heavily damaged metamict zircon, such as those consistent with alpha dosages >8 \times 10^{15} \alpha\text{-decay events/mg}, may lose all radiogenic Pb to low temperature surface waters (Pidgeon et al. 1966; Murakami et al. 1991; Geisler et al. 2002). The result of this is depicted on U-Pb concordia diagrams as discordance trends between the primary U-Pb isotope signature and that reflecting the U-Pb systematics at the time of radiogenic Pb loss (Figure 2).

Partial or complete re-equilibration of the U-Pb system post-crystallisation will result in partial or complete resetting and, hence, underestimation of the ages compared to the true crystallisation ages. Theoretically an exception to this is modern day Pb loss and the $^{207}\text{Pb}/^{206}\text{Pb}$ age, however $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages will still be strongly affected. As such, modern Pb loss is best depicted in Tera-Wasserburg concordia space, since it results in horizontal discordance trends. The recognition of U-Pb isotopic disturbance is routinely monitored by the degree of discordance displayed by either a single datum, or data array, falling away from the concordia line (Figure 2). A number of detrital zircon studies employ an arbitrary 5-10% discordance filter so as to concentrate primary crystallisation data. Since concordance is improved with larger analytical uncertainties and vice versa, a more consistent approach may be to use the probability of concordance (within $2\sigma$ uncertainty) to avoid unnecessary bias (Ludwig 1998; Spencer et al. 2016). However, it should be noted that concordant data is not synonymous to undisturbed data. The oldest segment of the conventional concordia curve is near horizontal, which diminishes the use of the $^{238}\text{U}-^{206}\text{Pb}$ systematics for age and discordance calculations, and similarly towards the youngest segment, the $^{235}\text{U}-^{207}\text{Pb}$ system diminishes. As such, zircon that records metamorphism shortly (~200 Ma) after crystallisation can yield apparently concordant results within the analytical uncertainties, though disturbed (Figure 10). Examples of this are numerous in ancient detrital zircon studies (Cawood et al. 2003; Whitehouse & Kemp 2010; Kusiak et al. 2013; Kielman et al. 2018).
Apparent U-Pb age discordance can also arise from contamination during preparation and analysis. Whilst U-Pb analysis of zircon by SIMS or laser ablation techniques have circumvented the need for extensive clean-laboratory preparations (otherwise required for ID-TIMS, solution ICP-MS), common Pb contamination may still be introduced from sources such as adhesive tape commonly used in zircon mounting or residual material deposited in cracks (e.g. polishing compound) (Hiess et al. 2008; Guittreau & Blichert-Toft 2014). Further, a similar discordance pattern to that observed after episodic Pb loss can be achieved by the mixed analysis of two chronologically distinct growth zones. Often this is discerned by a marked difference in time resolved Pb/U ratios, however if the interface between the two distinct zones is parallel to the excavating beam then the analysis will yield an undetectable mixture of two age components. This is further complicated with drastically different U and Pb concentrations (or Hf concentrations, when dealing with Lu-Hf data) between the two components, as demonstrated in Figure 11. The effects of a modelled “worst case scenario” using data from Paper II are illustrated in Figure 11 between the mixing of a U- and radiogenic Hf-rich rim (aged 2415 Ma) with a U- poor and relatively unradiogenic Hf core (aged 3321 Ma). This particular model shows that a mixing of only 5% rim material can affect the $^{207}\text{Pb}/^{206}\text{Pb}$ age by ~240 Ma, and a 50% mixing would result in ~800 Ma. The effect of extreme age underestimation with the inclusion of 5% rim material is
diminished when the U concentrations between rim and core are comparable. Moreover, a series of faux εHf arrays could be formed, depending on the degree of mixing.

Figure 11. Results of a model illustrating a field of possible datpoints in εHf vs. age space caused by the mixing of core and rim components with different Pb concentration, age, Hf isotope ratio at different percentage mixing. Core and rim characteristics are taken from natural zircon in detrital zircon study of Paper II. Changes in age and Hf isotope composition serves to alter the area of ‘possible data’, whilst the dissimilarity in Pb concentration between core and rim increases the degree of age over- or underestimation.

Whilst Pb loss is a well-known consequence of later high-grade events or accumulation of radiation damage in ancient zircon, the redistribution of Pb within a zircon grain has been shown to occur in a number of other unique cases. U-Th-Pb heterogeneity within single CL-defined domains has been recognised in zircon extracted from UHT deformed rocks (Kusiak et al. 2013; Whitehouse et al. 2014; Kusiak et al. 2015; Piazolo et al. 2016; Whitehouse et al. 2017a), UHP deformed rocks (Peterman et al. 2016), seismically deformed rocks (Kovaleva & Klötzli 2017) and even Hadean zircon from the Jack Hills (Valley et al. 2014, 2015; Ge et al. 2018). These cases demonstrate the mobilisation of Pb in partially metamict and/or structurally deformed domains, with the effect of forming locally enriched zones of radiogenic Pb, spatially decoupled from U and Th. In the most extreme case, native Pb “nanospheres” are observed (Kusiak et al. 2015; Whitehouse et al. 2017a). U-Pb analysis of these affected domains can result in a variable ages and discordance from single growth zones.
Igneous zircon typically exhibits a characteristic trend in REE distribution, increasing in abundance with greater atomic number (Figure 5), owing to the increasing compatibility of smaller ionic radii REE in zircon. Attempts have been made to form a framework for distinguishing different geological environments from detrital zircon REE compositions (Belousova et al. 1998, 2002), though crustally sourced zircon display very similar traits, discounting this method (Hoskin & Ireland 2000). Moreover, REE in zircon are susceptible to chemical alteration, particularly by metasomatic and metamorphic fluids (Hoskin & Black 2002; Hoskin & Schaltegger 2003; Hoskin 2005). This typically results in a light rare earth element (LREE) enrichment, displayed as flattened chondrite-normalised REE pattern, prevalent along intragrain cracks and fractures where fluids have migrated (Bell et al. 2016). Similar LREE enrichment may occur by contamination of LREE bearing phosphate inclusions in zircon (Cavosie et al. 2006). As such, variations in REE abundance in a detrital zircon population are not effective in identifying distinct source rocks after metamorphism (Rubatto 2002; Whitehouse & Platt 2003).

The widely used single-mineral thermometer for apparent crystallisation temperature, Ti-in-zircon, exploits the substitution of Ti$^{4+}$ with Zr$^{4+}$ and Si$^{4+}$ in the zircon lattice as a function of temperature (Watson 2005; Watson et al. 2006; Ferry & Watson 2007). This thermometer therefore has the unique potential to define source-specific crystallisation temperatures, invaluable to detrital zircon studies where the source rock may no longer exist. One caveat is that this method requires constraint on the TiO$_2$ and SiO$_2$ activities, determined from whole-rock analysis, or estimated from the occurrence of cogenetic Ti- or Si- bearing minerals from the source rock. Without known TiO$_2$ and SiO$_2$ activities (as in all detrital sediments), the calculated temperature may be over or underestimated. Similar to zircon REE, Ti may be anomalously high in cracks or fractures, yielding higher apparent temperatures (Harrison & Schmitt 2007). Further, significant intracrystalline variability of Ti concentration is documented from a large range of zircon in multiple rock types, not systematically linked with core-rim relationships (Fu et al. 2008; Hiess et
The use of Ti-in-zircon crystallisation temperatures in detrital zircon may therefore lead to spurious results, due to the lack of source rock constraints (Fu et al. 2008).

3.1 The utility of detrital zircon in early crustal research

Many conflicting views surround the origin and evolution of the Earth’s early crust. Beyond the 3.94-4.03 Ga aged components of Acasta Gneiss, northwest Canada (Iizuka et al. 2009), isolated populations of detrital zircon grains and inherited xenocrysts are the only remaining fragments of early crust known to date. The Yilgarn Craton of Western Australia contains the best preserved record of these grains, with several metasedimentary units comprised of zircon with apparent ages of crystallisation up to 4.37 Ga (Froude et al. 1983; Compston & Pidgeon 1986; Amelin 1998; Nelson et al. 2000; Wilde et al. 2001; Cavosie et al. 2004; Wyche et al. 2004; Nemchin et al. 2006; Pidgeon & Nemchin 2006; Cavosie et al. 2007; Kielman et al. 2018). A great deal of research has flourished from these localities, and many authors have sought to define the environments from which these zircon had crystallised. However, as these zircon have outlived their original host rock, there are no methods external to the zircon system available to validate the inferences made, with the possible exception of the mineral inclusions. Several authors have employed the use of rigorous filters to ensure the primary nature of ancient zircon data (Nemchin et al. 2006; Whitehouse et al. 2017b; Kielman et al. 2018). Nevertheless, there exists strongly polarised views regarding the composition and evolution of the early crust.

Most mineral inclusions within the Jack Hills zircon are comprised of quartz and muscovite, consistent with crystallisation from a felsic protolith (Froude et al. 1983; Maas et al. 1992; Wilde et al. 2001; Trail et al. 2004; Hopkins et al. 2008). Thermobarometry of these zircon and hosted inclusions yield pressure-temperature estimates consistent with formation from hydrous granitoid magmas, while the inclusion suite indicate large fluctuations in pressure, used to infer the presence of modern-styled tectonics (Harrison et al. 2008; Hopkins et al. 2008, 2010). However, the underlying assumption that these inclusions are primary and thus representative of the protolith is tenuous, since the geochronological and thermobarometric information are readily altered by later
metamorphism by intersecting fractures and metamict domains, common to Hadean and Archaean zircon (Rasmussen et al. 2011). Nevertheless, a recent apatite inclusion study from a selection of Eoarchaean zircon have been argued to yield primary $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, after careful examination that these zircon are free of cracks, and form a single population of Sr isotope ratio distinct from that of the rock matrix (Emo et al. 2018).

Oxygen isotope signatures in Jack Hills zircon have similarly invited the possibility of modern-styled plate tectonics during the Hadean (Mojzsis et al. 2001; Wilde et al. 2001; Valley et al. 2002). In a modern setting, heavy ($\delta^{18}\text{O}$ values >6.5 ‰) oxygen isotope signatures (greater proportion of $^{18}\text{O}$ to $^{16}\text{O}$) in zircon typically reflect the interaction of the source magma with rocks or sediments that formed near the Earth’s surface (Valley et al. 1994). The observation that Jack Hills zircon exhibit similar heavy oxygen isotope signatures naturally led to the implication that similar subduction processes occurred during the Hadean, and further, surface conditions must have been sufficiently temperate to allow for surface water and sedimentation processes (Mojzsis et al. 2001; Wilde et al. 2001; Valley et al. 2002). These heavy $\delta^{18}\text{O}$ values were assumed to by primary, however a reassessment of these zircon by Nemchin et al. (2006) found that the least altered zircon based on CL patterns yield mantle-like oxygen isotope signatures, suggesting that values >6.5 ‰ are related to secondary alteration. Whitehouse et al. (2017b) also noted that zircon with reproducible $\delta^{18}\text{O}$ values are typically within a mantle-like range. Additionally, primary oxygen isotope signatures may be modified by metamorphism without significant disturbance of CL patterns or U-Pb and Hf isotope systematics (Claesson et al. 2016). These observations imply that the heavy oxygen isotope signatures evident in the Jack Hills population may be the result of post-crystallisation alteration.

As detailed in the previous section, the analysis of Hf isotopes in zircon offers the potential to monitor crust-mantle evolution through time, as the initial $^{177}\text{Hf}/^{176}\text{Hf}$ of a source magma can be inferred from a zircon grain if the time of crystallisation is known. Therefore Hf isotopes in the Jack Hills zircon were investigated in order to reveal the crustal dynamics on the early Earth. Since
strongly positive and negative $^{177}\text{Hf}/^{176}\text{Hf}$ values relative to the bulk Earth or chondritic uniform reservoir (CHUR) were observed in zircon from the Jack Hills, this was taken as evidence for an apparent rapid crustal recycling within 100 Ma of Earth’s formation, with broad trends in Hf evolution equivalent to that of modern continental crust (Harrison et al. 2005, 2008; Blichert-Toft & Albarède 2008). However, concurrent analysis of U-Pb age and Hf isotope composition in these zircon by Kemp et al. (2010) display no such heterogeneity, indicating that the $\varepsilon_{\text{Hf}}$ variation of Harrison et al. (2005) and Blichert-Toft & Albarède (2008) is caused by calculating initial $^{177}\text{Hf}/^{176}\text{Hf}$ compositions at times other than that of crystallisation. This is caused by a number of factors, 1) the loss of Pb during metamorphism and low temperature fluid interactions common to the Jack Hills zircon, 2) the larger sample volumes used in LA-ICP-MS Hf analysis in comparison to SIMS U-Pb geochronology, 3) several generations of zircon growth present increasing the probability of mixed sampling (Valley et al. 2006; Guitreau & Blichert-Toft 2014; Vervoort & Kemp 2016). Rather than invoking the operation of plate tectonics during the Hadean, zircon data by Kemp et al. (2010) define a simpler Hf isotope evolution, which imply that the Jack Hills zircon crystallised from a source magma formed by the internal reworking of a mafic protocrust. Further, this is consistent with an observed spread of $^{207}\text{Pb}/^{204}\text{Pb}$ ratios in Eoarchaean metasediments which corroborates U/Pb fractionation during the Hadean, as would be expected from a high $^{238}\text{U}/^{204}\text{Pb}$ (otherwise known as $\mu$) bearing basaltic crust similar to that observed on the Moon (Kamber et al. 2003, 2005).
4.0 Paper I: U-Pb age distribution recorded in zircons from Archean quartzites in the Mt. Alfred area, Yilgarn Craton, Western Australia

The Yilgarn Craton of Western Australia is home to some of the best preserved and oldest fragments of Hadean and Early Archean detrital zircon (Froude et al. 1983; Compston & Pidgeon 1986; Wyche et al. 2004). Most of these zircon populations are restricted to the Narryer Terrane which includes the Jack Hills and Mt. Narryer zircon, however a later discovery broadened the extend of ancient zircon to the Murchinson and Southern Cross domains (Nelson et al. 2000; Nelson 2002a, b). Preliminary reconnaissance in the Mt. Alfred area had also revealed detrital zircon with ages between 3.50 and 4.32 Ga from a well-sorted quartz-sandstone unit just south of the Maynard Hills locality (Nelson 2005). Expanding on this, zircon from five samples collected across a series of metasedimentary ridges were analysed for their U-Pb isotope compositions and compared to other ancient detrital populations around the Yilgarn Craton.

SIMS U-Pb analyses yielded concordant age distributions between 3.11 and 3.92 Ga, and three significant age peaks at approximately 3.64, 3.69 and 3.76 Ga. A large portion of this data are affected by recent Pb loss and produce discordant U-Pb ages. The timing of this recent Pb loss is approximated using eight single-grain discordia, which is thought to have ceased by ~200 Ma, correlated to both the estimated exhumation age of the sediments (Thern et al. 2011) and percolation of low temperature fluids prevalent in the Yilgarn (Pidgeon et al. 2017). The underrepresentation of ages <3.60 Ga in the Mt. Alfred zircon suite separate it from nearby metasedimentary sequences, including that of the Maynard Hills which has been shown to contain a similar proportion of Hadean zircon grains as the Jack Hills. Interestingly, the Mt. Alfred zircon exhibit similar age distributions to that of the Mt. Narryer detrital zircon. The data therefore suggest a shared link between the Youanmi and Narryer Terranes before ~3.60 Ga.
5.0 Paper II: New geochronology of detrital zircon from the Saglek Block, Northern Labrador

The Saglek Block of Northern Labrador is a part of the western-most extent of the North Atlantic Craton. Archean paragneisses outcrop alongside several generations of gneisses, granulites and ultramafic rocks which have been subject to upper amphibolite to granulite facies metamorphism at around 2.8-2.7 Ga (Ryan & Martineau 2012). Previous work has established the presence of several supracrustal units, ranging in depositional age from the Eoarchaean to the Mesoarchaean, potentially equivalent if not older than the oldest exposed supracrustal sequences to date (Nutman et al. 1989; Schiøtte et al. 1989, 1992; Komiya et al. 2015). Recently, these supracrustal units have been the source of two extraordinary claims; the discovery of >3.95 Ga biogenic graphite significantly pushing back the emergence of organic life (Tashiro et al. 2017) and the evidence of modern-styled plate tectonics operating during this time (Komiya et al. 2015). However, earlier studies have highlighted significant age complexity within the supracrustal rocks of the Saglek Block (Schiøtte et al. 1992; Krogh & Kamo 2006). We present U-Pb-Hf detrital zircon data from eight new samples in an attempt to clarify the age of deposition, crustal formation and validity of early lifesigns in these rocks.

Detrital zircon from the investigated samples yield concordant ages from 2.80 – 3.90 Ga, with several samples displaying metamorphic overgrowths as well as neoblastic zircon with ages between 2.80 and 2.50 Ga. All samples are deposited after formation of the prevalent ~3.72 Ga Uivak I TTG gneisses, and are classified as a part of the Upernavik supracrustal sediments. The maximum age of deposition of these sediments suggest two or possibly three deposition events at after ~3.2, 2.8 and tentatively, 2.7 Ga. This is in line with the conclusions of an earlier detrital study of Schiøtte et al. (1992). Similarly aged zircon populations are found within the Archean rocks of southern West Greenland, once contiguous with those of the Saglek Block and may represent the source of the Upernavik sediments.
The St. John’s Harbour samples from our study are collected from the same unit as one sample published in Tashiro et al. (2017), of which has been assigned to the older (>3.95 Ga) Nulliak supracrustal sequence and contains biogenic graphite. Hf isotopes coupled with $^{206}\text{Pb}/^{207}\text{Pb}$ age express some degree of U-Pb disturbance in these zircon, and at least five distinct chondritic $^{176}\text{Hf}/^{177}\text{Hf}$ signatures, similar to that observed in a comprehensive study across West Greenland (Naeraa et al. 2012). Our data suggest that the field relationships used to constrain a relative age by Tashiro et al. (2017) and further, the onset of plate tectonics by Komiya et al. (2015) are potentially unreliable.

6.0 Paper III: A tonalitic analogue to ancient detrital zircon

Over the last four decades, a wealth of data has been accumulated from Hadean and Early Archean detrital zircon. The application of novel analytical techniques and isotopic tracers have produced exciting developments for our understanding of the Early Earth, ranging from crustal dynamics to the emergence of organic life (Froude et al. 1983; Wilde et al. 2001; Kamber et al. 2003; Harrison et al. 2005; Hopkins et al. 2010; Kemp et al. 2010; Bell et al. 2015). However, these studies often highlight the fact that geological processes operating during the Hadean were vastly different to those in operation today. Additionally, the Hadean rock record is absent and therefore zircon surviving from this period cannot be directly compared to their source rocks. In order to test the reliability of zircon to Hadean and potentially any detrital zircon suite where geological context cannot be restored, zircon from a sample of the best preserved Eoarchaean TTG crust from West Greenland are investigated for U-Pb, Lu-Hf, O-isotopes as well as REE and Ti abundances, correlated with internal features visible by cathodoluminescence (CL) imaging.

Zircon grains from the tonalitic sample exhibit oscillatory zoning with a distinct homogeneous overgrowth, consistent with a magmatic origin followed by a singular overprinting event. Several grains contain evidence for older, xenocrystic cores thought this is not always obvious from CL imaging. Despite relatively low U-Th concentrations in the magmatic cores, U-
Pb ages show considerable variation and multiple age modes. Conversely, \(^{176}\text{Hf}/^{177}\text{Hf}\) ratios indicate crystallisation from a single reservoir. Light rare earth elements are enriched within cracks of the zircon grains, while primary chondrite-normalised zircon REE patterns are consistent with zircon from unaltered continental rocks. The enriched LREE signatures were used to filter out anomalous Ti concentrations, resulting in a range of Ti-in-zircon “crystallisation” temperatures of \(~100^\circ\text{C}\) and apparent inverse cooling trends within individual zircon. Since detrital zircon populations commonly consist of multiple source rocks, the geochemical complexities within this simple source-rock analogue exemplifies the need for care when interpreting more complex, ancient detrital zircon populations such as those from the Jack Hills, Western Australia.

7.0 Conclusions and future work

This thesis presents new U-Pb geochronology and Hf-isotope data of zircon from ancient metasedimentary rocks, subject to pervasive recent Pb loss or high-grade metamorphism, as well as investigating the geochronology, trace element, O and Hf isotope behaviour in a potential source analogue to such metasedimentary units. This provides insight into the reliability of data collected from ancient detrital zircon, while also contributing to the understanding of magmatic and metamorphic events in each of the three study localities. In summary, when assuming general stability of zircon from detrital populations, particular care should be taken when interpreting U-Th-Pb isotope systematics, as well as REE and Ti abundances as these are may be considerably altered post- and pre-deposition. Given that such variable geochemical signatures may be evident in a singular source rock, data obtained from detrital zircon that have been removed from the context of their source rocks may lead to spurious results, particularly in the case when source rocks are now extinct.

Attempts to determine the internal consistency of data from zircon grains has helped to provide estimates of primary geochemical data from ancient detrital zircon populations (Kielman et al. 2015; Whitehouse et al. 2017b; Paper III). Since standard imaging techniques may not
necessarily reflect isotopic or geochemical disturbances (Valley et al. 2015; Claesson et al. 2016), other approaches should be considered. Intra-grain consistency may be assessed by placing multiple spot analyses within individual grains, or applying ion imaging techniques (e.g. Kusiak et al. 2013; Kielman et al. 2015; Whitehouse et al. 2017b; Bellucci et al. 2018). Typically, secondary ion imaging techniques yield the best spatial resolution though are hampered by long session times and therefore can be limiting in studies of detrital zircon. Conversely, multiple analyses in individual grains may be acquired relatively quickly, though lack significant spatial resolution. Therefore the application of a linear traverse method along different crystallographic axes (the long c-axis should produce best resolution in growth zones) may provide a faster method to determine intragrain consistency of U-Th-Pb, as well as other isotopic systems within zircon. To date, this method is rarely used in zircon studies. Examples include a recent study by Guitreau et al. (2018) using linear traverses across Hadean-Archaean aged zircon from the Acasta Gneiss Complex to yield multiple discordia lines, and a case study by Claesson et al. (2016) applying closely spaced O isotope spot analyses in Archean aged zircon from the Ukrainian Shield. Applying linear traverses to Ti abundances in zircon should also improve our understanding of the inverse Ti-in-zircon temperatures from core to rim observed in Paper III.

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9.0 References


Ryan, B. & Martineau, Y. 2012. Revised and coloured edition of 1992 map showing the Geology of the Saglek Fiord-Hebron Fiord area, Labrador (NTS 14L/2, 3, 6, 7). Scale, 1, 000.


