

ARCHEAN CHEMICAL GEODYNAMICS: FROM PAST PROCESSES TO MODERN ANALOGUES

Inauguraldissertation

zur

Erlangung des Doktorgrades (Dr. rer. nat.) der Mathematisch-Naturwissenschaftlichen Fakultät der Universität zu Köln

> vorgelegt von CHRISTIAN MARIEN aus Borken (Westf.)

> > - Köln, 2023 -

 Gutachter: Gutachter: 	Prof. Dr. Carsten Münker Prof. Dr. Reiner Kleinschrodt
Vorsitzender der Prüfungskommission: Beisitzender:	Prof. Dr. Joachim Saur Dr. Frank Wombacher
Tag der mündlichen Prüfung:	12.01.2024

Für Maike und Mina Theresa.

TABLE OF CONTENTS

Table of contentsI
List of figuresIV
List of tablesVII
I. Abstract
II. Zusammenfassung
III. Introduction
III.1. Early Earth processes
III.1.1. Archean greenstone belts and the emergence of the first continental crust. 11
III.1.2. Earth's mantle depletion and heterogeneities
III.1.3. The first oceans, an anoxic atmosphere and the 'Cradle of Life'
III.2. Geochemical constraints on geological processes
III.2.1. Trace element geochemistry
III.2.2. Radiogenic and stable isotope perspectives on the early Earth's differentiation
III.3. Scope of this thesis
1. Evolution of the Archean mantle con-strained from combined U-Th-Pb, Sm-Nd, and Rb-Sr isotope measurements on primary minerals from Archean mafic-ultramafic
volcanic rocks
1.1. Abstract
1.2. Introduction
1.3. Geological setting and sample selection
1.3.1. Pilbara Craton, Western Australia
1.3.2. Seqi Ultramafic Complex, North Atlantic Craton, SW Greenland

1.3.3. Sample selection	50
1.4. Analytical methods	52
1.4.1. Sample preparation and digestion	52
1.4.2. Chemical separations and MC-ICP-MS measurements	53
1.5. Results	55
1.5.1. ¹⁴⁷ Sm- ¹⁴³ Nd isotope data and Sm-Nd isochrons	55
1.5.2. ⁸⁷ Rb- ⁸⁷ Sr isotope data	62
1.5.3. U-Th-Pb isotope data and Pb-Pb isochrons	64
1.6. Discussion	67
1.6.1. Pilbara Craton, Western Australia	67
1.6.2. Seqi Ultramafic Complex, southern West Greenland	79
1.6.3. Implications for the evolution of the Earth's $^{238}U/^{204}Pb$ (µ-) and $^{232}Th/(\kappa-)$ values through time	²³⁸ U 84
1.7. Conclusions	86
2. Interstitial carbonates in pillowed meta-basaltic rocks from the Pilbara Craton, Western Australia: A vestige of Archean seawater chemistry and seawater-rock interactions	, 89
2.1. Abstract	89
2.2. Introduction	90
2.3. Geological setting and sample description	93
2.4. Analytical methods	98
2.5. Results	100
2.5.1. Major elements and carbonate compositions	100
2.5.2. Trace element and REY _{PAAS} patterns	102
2.5.3. Stable and radiogenic isotopes	104
2.6. Discussion	107
2.6.1. Potential contamination by clastic components	107
2.6.2. Origin of interstitial carbonates from the Pilbara Craton	110
3.7. Conclusions	122
3. Juvenile continental crust evolution in a modern oceanic arc setting: Petrogene Cenozoic felsic plutons in Fiji, SW Pacific	esis of 125
3.1. Abstract	125
3.2. Introduction	126
3.3. Geological setting and sample collection	127
3.4. Analytical methods	133

3.5. Results
3.5.1. Whole rock major and trace element geochemistry
3.5.2. Hf-Nd-Sr-Pb isotope compositions
3.5.3. U/Pb zircon ages144
3.5.4. Zircon geochemistry
3.6. Discussion
3.6.1. Secondary alteration of the plutonic rocks
3.6.2. Geochemical relationships between the felsic plutons and surrounding mafic basement rocks
3.6.3. Geochemical constraints for genesis of the Fijian felsic suites – A comparison with other intra-oceanic felsic rocks
3.6.4. Geochemical modeling of the Yavuna and Colo plutons
3.6.5. Spatial and temporal diversity of felsic magmas in Fiji 160
3.6.6. Are intra-oceanic arcs an important contributor to continental crustal formation?
3.6.7. Comparison to Archean crust formation processes
3.7. Conclusions
V. References
VI. Appendix
Appendix A
Appendix B
Appendix C
VII. Acknowledgements
VIII. Erklärung

LIST OF FIGURES

Introduction

Figure 0.1: Map of spatial distribution of Archean cratons	11
Figure 0.2: Proposed Archean and present-day tectonics of the silicate Earth	12
Figure 0.3: Photos of Archean mafic volcanic rocks	14
Figure 0.4: Active subduction and Archean subcreation tectonics	15
Figure 0.5: The formation of Archean TTGs	17
Figure 0.6: The isotopic 'mantle zoo'	20
Figure 0.7: The Great Oxygenation Event	23
Figure 0.8: Photos of Archean chemical sedimentary rocks	24
Figure 0.9: Incompatibility of trace elements	27
Figure 0.10: Normalized trace element patterns of selected rock types	28
Figure 0.11: Compatibility of radioactive parent-daughter decay systems	30
Figure 0.12: Schematic radiogenic isotope evolution during the Earth's history	31

Chapter 1

Figure 1.1: U-Th-Pb isotope systematics of mantle derived rocks	41
Figure 1.2:Simplified geological map of the Pilbara Craton	43
Figure 1.3:Simplified geological map of SW Greenland	47
Figure 1.4: Detailed map of the Seqi Ultramafic Complex	48
Figure 1.5: Thin section images of mafic rocks from the Pilbara Craton	50
Figure 1.6: Thin section images of ultramafic rocks from SW Greenland	51
Figure 1.7: Elemental separation procedure	54
Figure 1.8: Measured Sm-Nd concentrations and Sm-Nd isochrons	61

Figure 1.9: Measured Rb-Sr concentrations and Rb-Sr isochrons	3
Figure 1.10: Measured U-Th-Pb concentrations and Pb-Pb isochrons65	5
Figure 1.11: Nd-Sr isotope evolution of the Pilbara Craton during the Archean	3
Figure 1.12: U-Th-Pb isotope evolution of the Pilbara Craton during the Archean7	1
Figure 1.13: Calculated μ_1 -, κ_1 -, μ_2 -, and κ_2 -values for mineral separates from the Pilbara	
Craton and the depletion history of the Archean mantle70	5
Figure 1.14: Calculated µPb- and KPb-values for mineral separates from the SUC	2
Figure 1.15: Calculated μ_1 -, κ_1 -, μ_2 -, and κ_2 -values for SUC mineral separates	3
Figure 1.16: U-Th-Pb isotope evolution of the bulk silicate Earth	5

Chapter 2

Figure 2.1: Simplified geological map of the Pilbara Craton	94
Figure 2.2: Photos and thin section images of selected carbonates	97
Figure 2.3: Ternary CaCO ₃ -MgCO ₃ -(FeCO ₃ +MnCO ₃) diagram	101
Figure 2.4: Normalized trace element patterns	103
Figure 2.5: Sm-Nd isochrons	105
Figure 2.6: Isotope variation diagrams	106
Figure 2.7: Variation diagrams for siliciclastic contamination	108
Figure 2.8: Variation diagrams for fluid-rock interaction	112
Figure 2.9: Sr concent and isotope diagrams	114
Figure 2.10: Sr isotope evolution of the Archean seawater	120

Chapter 3

Figure 3.1: Tectonic reconstruction of the Fijian region (SW Pacific)	. 128
Figure 3.2: Simplified geological map of Southern Viti Levu, Fiji	. 130
Figure 3.3: Thin section images of Fijian granitoids	. 132
Figure 3.4: Ternary An-Or-Ab-diagram	. 136
Figure 3.5: Whole rock element variation diagrams	. 139
Figure 3.6: Normalized extended trace element patterns	. 140
Figure 3.7: Whole rock trace element variation diagrams	. 142

Figure 3.8: Pb-Sr-Nd-Hf isotope composition diagrams	143
Figure 3.9: Trace element co-variation diagrams part 1	147
Figure 3.10: Trace elements co-variation diagrams part 2	151
Figure 3.11: Crystallization and anatexis modeling	154
Figure 3.12: Th/Yb vs. Nb/Yb variation diagrams	163

Appendix B

Figure B1: Shale-normalized (Ce/Ce*) _{SN} vs. (Pr/Pr*) _{SN} plot	219
Figure B2: Initial 87 Sr/ 86 Sr vs. stable δ^{18} OvsMow2	220

Appendix C

Figure C1: Cathodoluminescence images of zircons	231
Figure C2: Tera-Wasserburg Concordia plots of SHRIMP-analyzed zircons	232
Figure C3: Chondrite-normalized REE composition of selected zircons	233
Figure C4: Nb/Yb vs. U/Yb diagram of zircons	233
Figure C5: ⁸⁷ Sr/ ⁸⁶ Sr vs. SiO ₂ diagram	234

LIST OF TABLES

Introduction

Table 0.1: Long-lived radionuclides	. 33
-------------------------------------	------

Chapter 1

1 abic 1.1. Then precision trace crement and isotope tata $\dots \dots \dots$

Appendix A

Table A1: Calculations for the Sm-Nd isotope evolution of the mantle
Table A2: U-Th-Pb and Sm-Nd isotope evolution calculation for the primitive mantle
and depleted mantle from the Pilbara Craton
Table A3: U-Th-Pb evolution calculation for the primitive mantle using values from
Maltese and Mezger (2020)
Table A4: U-Th-Pb isotope evolution calculation for the primitive mantle and depleted
mantle from SW Greenland
Table A5: U-Th-Pb isotope evolution calculation of the Earth's mantle

Appendix B

Table B1: Major, minor and trace element for the interstitial carbonates	221
Table B2: High-precision trace element and isotope data	225
Table B3: Mixing calculations	229

Appendix C

Table C1: Major, minor and trace element data for the Fijian plutons	235
Table C2: High-precision trace element and isotope data	242
Table C3: Partition coefficients	247
Table C4: Calculations for fractional crystallization and patial melting	251



Der Herr der Ringe: Die Gefährten (2001) von J.R.R. Tolkien und Peter Jackson

I. ABSTRACT

Since its formation 4.50 billion years ago, the Earth is in a steady differentiation process. Starting with Earth's last big accretion event, the moon forming giant impact led to the formation of a global magma ocean. Cooling led to the initial segregation into Earth's metallic core and the silicate mantle. Further cooling then led to the crystallization of the ultramafic mantle and the first mafic crust formed. Volatile elements, released from the mantle by degassing and additionally added by volatile-rich meteorites after the coremantle differentiation, formed an initial atmosphere as well as oceans. Since this early time, various geodynamic processes influence the development of the respective geological reservoirs, as well as the physicochemical exchange. Some of these processes are still not fully understood and are part of this thesis. In the Archean, higher temperatures of the Earth's mantle led to high melting rates, resulting in the formation of a mafic to ultramafic crust and the successive incompatible element depletion of the upper mantle. These so-called Archean greenstone belts consist primarily of mafic basalts and ultramafic komatiites and cumulates, which are characteristic of the higher temperatures and melting rates in the Archean mantle. In contrast, present-day melting rates of the upper mantle are lower and result in the formation of a much thinner oceanic crust. During the Archean, intra-crustal differentiation of the mafic crust formed the basis for the continental crust formation, which today covers nearly 40 % of the Earth's surface.

This thesis investigates different aspects of the evolution history of the early Earth and compares them with modern, partly better understood processes. In three chapters, major and trace elements as well as radiogenic Pb-Sr-Nd-Hf isotope compositions of mafic and felsic rocks and mineral separates from the Pilbara Craton (Western Australia),

1

from the North Atlantic Craton (SW Greenland) and from Fiji in the Southwest Pacific are characterized in more detail.

In the first chapter, a combined dataset of the radiogenic U/Th-Pb, Rb-Sr, and Sm-Nd isotope compositions of mineral phases of mafic and ultramafic rocks from the Pilbara Craton and the North Atlantic Craton is presented for the first time. Using these isotope systems, it is possible to further understand the depletion history of the Archean mantle. It will be shown that the mafic rocks from the Pilbara Craton can be assigned to two different mantle domains. The first group of pyroxene separates show primitive mantle signatures in both the initial Nd and Pb isotope systems. Since the host rocks are derived from the lower mantle by plume events, the pyroxene separates provide information on the evolution of the U-Th-Pb isotope evolution before it was overprinted by subduction processes in the late Archean. The second group of pyroxene separates show lower initial Pb isotope compositions than the first group. In conjunction with the initial radiogenic Nd isotope compositions, it can be shown that the later host rocks originate from a depleted mantle source. This allows for the first time the isotopic distinction of two Archean mantle domains and the depletion of the upper mantle in the U-Th-Pb system.

In the second chapter, interstitial carbonates of well-preserved Mesoarchean pillow lavas of the Archean Pilbara Craton, Australia, provide new geochemical insights into the composition of Archean seawater and its interaction with basaltic crust. A comprehensive dataset on calcites of major and trace elements, radiogenic ¹⁴⁷Sm-¹⁴³Nd, ⁸⁷Rb-⁸⁷Sr, and stable C-O isotopes was collected and two types of calcites can be distinguished. The first group of interstitial carbonates yield new insights about Archean fluid-rock interactions of boiling seawater with the basaltic host rock. The second type of carbonates, in contrast, exhibit modern seawater-like compositions, but from an anoxic milieu and therefore hints to stratified Archean oceans that are to some degree not buffered by hydrothermal influx. Furthermore, high Sr concentrations and lower initial ⁸⁷Sr/⁸⁶Sr_(i) isotope compositions, suggest an increasing influence of crustal weathering on the composition of Paleoarchean seawater through time, and a progressive decoupling from the Archean mantle.

In the third chapter, this thesis addresses to what extent the Archean TTGs (tonalitic, trondhjemitic, granodioritic suites) petrogenesis differs from that of present-day chemically similar oceanic plagiogranites. In older studies, it is generally assumed that Archean TTGs were formed by melting processes under eclogitic conditions, which

cannot be reached in modern intra-oceanic settings. More recent studies, however, show that under certain conditions TTG formation could have been formed at lower amphibolitic conditions. For this purpose, tonalitic and trondhjemitic plutons from Viti Levu, Fiji, were investigated for their major and trace element compositions. Special emphasis was put on the high-field strength element (HFSE) budget and the Pb-Sr-Nd-Hf isotope compositions. Felsic rocks from Fiji show more than one distinct process is responsible for the formation of the felsic Fijian plutons, but three: fractional crystallization of two different mafic magmas and the partial melting of the mafic crust by so-called 'underplating'. Especially the last process resembles the Archean dehydration melting process that is able to form voluminous felsic plutons in a predominantly mafic crust. Thus, it lays the foundation for new continental crust. However, the trace element composition of the modern felsic plutons from Fiji also show that the p-T conditions, responsible for Archean TTG formations, are not achieved. Thus, although their petrogenesis resemble the ancient process, they are no modern analogues. I. Abstract

II. ZUSAMMENFASSUNG

Die Erde durchläuft seit ihrer Entstehung vor 4.50 Milliarden Jahre einen stetigen Differenzierungsprozess. Zu Beginn kam es zur Segregation vom metallischen Erdkern und silikatischen Erdmantel. Das Abkühlen in der frühen Erdgeschichte führte schnell zur Kristallisation des ultramafischen Erdmantels und es bildete sich eine erste mafische Erdkruste. Volatile Elemente, die bei diesem Prozess durch Entgasung aus dem Erdmantel freigesetzt wurden und auch über Meteoriten zur Erde nach der Kern-Mantel-Differenzierung hinzugefügt wurden, bildeten eine erste Atmosphäre sowie Ozeane. Seit dieser frühen Zeit beeinflussen diverse geodynamische Prozesse die Entwicklung der einzelnen geologischen Reservoire, sowie den physikochemischen Austausch. Manche dieser Prozesse sind zum Teil noch immer nicht ganz verstanden und sind auch Teil dieser Arbeit. Im Archaikum führten höhere Temperaturen im Erdmantel zu hohen Aufschmelzraten, wodurch mehrere 10er km mächtige mafische bis ultramafische Gesteinsformationen entstanden und der obere Erdmantel sukzessive an inkompatiblen Elementen verarmte. Diese sogenannten archaischen Grünsteingürtel bestehen primär aus mafischen Basalten und ultramafischen Komatiiten, die charakteristisch für die höheren Temperaturen und Aufschmelzraten im archaischen Mantle sind. Im Gegensatz dazu sind die heutigen Aufschmelzraten des oberen Erdmantels geringer und resultiert in die Entstehung der wesentlich dünneren ozeanischen Kruste. Während des Archaikums bildete die intrakrustale Differenzierung der mafischen Kruste die Grundlage zur Entstehung der kontinentalen Kruste, die heute knapp 40 % der Erdoberfläche bedeckt.

Diese Arbeit untersucht verschieden Aspekte der Entwicklungsgeschichte der frühen Erde und vergleicht diese unter anderen mit modernen, z.T. besser verstandenen Prozessen. In drei Kapiteln werden Haupt- und Spurenelemente sowie radiogene Sr-Pb-

5

Nd-Hf Isotopenzusammensetzungen an mafischen und felsischen Gesteinen und Mineralseparaten vom Pilbara Kraton (Western Australia), vom Nordatlantischen Kraton (SW Grönland) und von Fidschi im Südwestlichen Pazifik genauer charakterisiert.

Im ersten Kapitel wird zum ersten Mal eine kombinierte Messung der radiogenen U-Th-Pb, Rb-Sr und Sm-Nd Isotopenzusammensetzung an Mineralphasen von mafischen und ultramafischen Gesteinen aus dem Pilbara Kraton und vom Nordatlantischen Kraton vorgestellt. Mit Hilfe dieser Isotopensysteme ist es möglich, die Verarmungsgeschichte des archaischen Erdmantels weiter zu verstehen. Wie gezeigt wird, lassen sich die mafischen Gesteine vom Pilbara Kraton zwei unterschiedlichen Mantelsektionen zuordnen. Die erste Gruppe von Pyroxenseparate zeigt eine primitive Mantelsignatur in der initialen Nd und Pb Isotopenzusammensetzung. Da die Wirtsgesteine durch Plum-Ereignisse aus dem unteren Erdmantel stammen, geben sie Aufschluss über die Entwicklung des U-Th-Pb Isotopensystems bevor es durch Subduktions-Prozesse im späten Archaikum überprägt wurde. Die zweite Gruppe an Pyroxenseparate wiederrum zeigt im Vergleich zur ersten Gruppe eine unradiogenere initiale Pb Isotopenzusammensetzung. In Verbindung mit der initialen radiogenen Nd Isotopie kann gezeigt werden, dass die Wirtsgesteine aus einer verarmten Mantelquelle stammen. Dies macht zum ersten Mal den isotopische Unterscheidung zweier archaischer Mantelquellen und die Verarmung des oberen Mantels im U-Th-Pb System möglich.

Im zweiten Kapitel liefern Karbonate aus den Zwickeln gut erhaltener mesoarchaischer Kissenlaven vom Pilbara Kraton, Western Australia, neue geochemische Erkenntnisse über die Zusammensetzung des archaischen Meerwassers und dessen Wechselwirkung mit der basaltischen Kruste. Für die Calcite wurde ein umfassender Datensatz von Haupt- und Spurenelementen, radiogenen ¹⁴⁷Sm-¹⁴³Nd, ⁸⁷Rb-⁸⁷Sr und stabilen C-O-Isotopen gesammelt, und es lassen sich zwei Generationen von Calciten unterschieden. Die erste Gruppe der Zwickelcalcite liefert neue Erkenntnisse über die Wechselwirkung zwischen dem kochenden Meerwasser und dem frisch eruptierten basaltischen Wirtsgestein im Archaikum. Die zweite Gruppe von Calciten weist dagegen eine, dem modernen Meerwasser ähnliche Zusammensetzung auf, stammt aber aus einem anoxischen Milieu. Daher deutet die Anwesenheit dieser Calcite darauf hin, dass das archaische Meerwasser geschichtet war und zumindest zum Teil nicht durch den hydrothermalen Zufluss gepuffert war. Darüber hinaus deuten hohe Sr Konzentrationen und eine niedrige initiale Sr Isotopenzusammensetzung auf einen sukzessiv zunehmenden Einfluss der Krustenverwitterung auf die Zusammensetzung des archaischen Meerwassers im Mesoarchaikum und auf eine fortschreitende Abkopplung vom archaischen Mantel hin.

Final wird die Frage angegangen, in wie weit sich die Petrogenese von archaischen TTGs (Tonalite, Trondhjemite, Granodiorite) von heutigen, chemisch sehr ähnlichen, Plagiograniten unterscheidet. Hierfür wurden tonalitische und trondhjemitische Plutone von Viti Levu, Fidschi, auf ihre Haupt- und Spurenelementzusammensetzung hin untersucht. Ein besonderer Schwerpunkt wurde hierbei auf die High-Field-Strength-Elemente, kurz HFSE, und die Pb-Sr-Nd-Hf Isotopenzusammensetzung gelegt. In älteren Studien wird allgemein davon ausgegangen, dass die archaischen TTGs durch Aufschmelzprozesse mafischer Kruste unter sehr hohen, eklogitischen Drücken entstanden sind, die heute in der ozeanischen Kruste nicht mehr zu erreichen sind. Neuere Studien zeigen hingegen, dass diese unter auch unter amphibolitischen Bedinungen entstanden sein können. Felsische Gesteine aus dem mittleren Bereich des vulkanischen Bogens zeigt, dass nicht nur einen Prozess für die Entstehung der felsischen Plutone verantwortlich ist, sondern gleich drei: fraktionierte Kristallisation von zwei unterschiedlichen mafischen Magmen und das partielle Aufschmelzen der mafischen Kruste durch sogenannten "Underplating". Vor allem der letzte Prozess ähnelt dem im archaischen Äon und ist in der Lage voluminöse felsische Plutone in einer primär mafischen Kruste entstehen zu lassen und somit die Grundlage für neue kontinentale Kruste zu legen. Die Spurenelementzusammensetzung der modernen Tonalite und Trondhjemite von Fidschi zeigen jedoch auch, dass die p-T-Bedingungen, die für die archaischen TTGs zuständig waren, nicht ganz erreicht werden. Somit ähneln sie zwar den alten Prozessen, sind jedoch nicht gleichzusetzen.

7

II. Zusammenfassung

III. INTRODUCTION

III.1. Early Earth processes

The solar system has an age of about $4,567.2 \pm 0.6$ Ma years (Amelin et al., 2002), which was determined by U-Pb dating on the oldest solar system components: chondrules and Ca-Al-rich inclusions ('CAIs') of carbonaceous chondrites. Within the first few millions years after solar system formation, the subsequent accretion of near-chondritic planetesimals led to the formation of the early Earth (Palme and O'Neill, 2014). Evidence for a complete core-mantle segregation prior to 4.50 Ga is reported by short-lived ¹⁸²Hf-¹⁸²W isotope variations from younger mantle-derived rocks (e.g., Kleine et al., 2002; Rizo et al., 2016; Tusch et al., 2019; 2021). In this process, chalcophile and siderophile elements segregated into the Fe-Ni-alloy core and had been depleted in the remaining silicate mantle or bulk silicate Earth ('BSE') that remained enriched in lithophile elements (McDonough and Sun, 1995; McDonough, 2003). Coupled radiogenic ¹⁴³Nd-¹⁴²Nd variation measurements however propose a complete core segregation already at 4.53 Ga (e.g., Boyet and Carlson, 2006; Caro et al., 2006; Bennett et al., 2007). The Moon formation also falls within the period of Earth's core-mantle segregation. It is generally assumed that a Mars-sized celestial body collided with the proto-Earth in a "Giant Impact" event, finalized the Earth's accretion, and generated an Fe-depleted Moon from the impact's debris disk between 30 - 75 Ma after solar system formation (e.g., Kleine et al., 2002; Wood and Halliday, 2005; Thiemens et al., 2019; Greer et al., 2023).

The first geological epoch of the Earth, the Hadean, describes the period between the Earth-Moon formation and the hypothesized 'late-heavy-bombardment' ('*LHB*'), a short period of increased meteorite impacts, between 4.2 and 3.8 Ga (e.g., Tera et al., 1974;

9

Koeberl, 2003). The term Hadean derives from the Greek word *hádēs*, the god of the underworld, and describes 'hell' or 'the invisible'. It was believed that the Hadean Earth's mantle was generally molten ('*magma ocean*') and no direct geological record is preserved. However, studies on younger sedimentary rocks from the Jack Hills, Western Australia (Froude et al., 1983; Wilde et al., 2001), reveal remnant detrital zircons that point to the existence of an ancient solid protocrust that was formed between 4.4 - 4.3 Ga (Amelin et al., 1999; Harrison et al., 2005; Blichert-Toft and Albarède, 2008). The chemical composition of the Hadean crust, the geodynamic conditions for their formation, and how long it persisted, however, remain enigmatic (Kemp et al., 2010). Some studies assume a basaltic single-plate protocrust that solidified from the global magma ocean (Kamber et al., 2005; Nemchin et al., 2006; Kamber, 2007), whereas others propose voluminous granitic continental crust shaped by modern-style plate tectonics (e.g., Bowring and Housh, 1995; Harrison et al., 2005). One possible reason for the lack of a Hadean.

The Hadean is succeeded by the Archean eon, the time between $\sim 4.0 - 2.5$ Ga, which comprises nearly a third of the Earth's history. The term Archean or Archæan derives from the Greek *arkaios* 'ancient' or *arkhē* 'beginning'. Literally, the Archean is the age of the beginning, since many geodynamic processes find their start here: the formation of the first continental crust, modern plate tectonics, with orogenic and subduction processes, and hence the start of weathering, erosion and the recycling of sedimentary material into the mantle. Finally, the emergence of primitive life is preserved in Archean rocks, such as stromatolites or hot spring deposits (e.g., Glikson et al., 2008; Van Kranendonk et al., 2008; Djokic et al., 2017). Accompanying the occurrence of primitive life, is the biologically oxygenation of the oceans in the Late Archean (Crowe et al., 2013) and ultimately the injection of free oxygen into the atmosphere; first in small 'whiffs' (e.g., Albut et al., 2018) and consequently by the Great Oxygenation Event or '*GOE*' at 2.4 Ga. The beginning of the GOE also marks the end of the Archean and the transition to the Proterozoic (e.g., Holland, 2002; Lyons et al., 2014).

However, the onset and the occurrence of these geological processes are still not clearly understood and controversially discussed. This is mainly because of the limited access to Archean rocks, which cover less than 5 % of the continental surface (Fig. 0.1;



Figure 0.1: Map of spatial distribution of Archean cratons, Proterozoic (2.5 - 0.54 Ga), and Phanerozoic (< 540 Ma) crustal basement (modified after Lee et al., 2011).

Nisbet, 1987; Artemieva, 2006). In addition to this, a large proportion of these Archean rocks experienced extensive deformation, metasomatism, and metamorphism that obscured primary signatures and caused element remobilization. These secondary processes hinder the comparison with modern rocks and thus better-constrained modern geodynamic processes.

The most important geological processes of the Archean and of this thesis are summarized in more detail in the following section.

III.1.1. Archean greenstone belts and the emergence of the first continental crust

Direct evidence of a Hadean crust is scarce. Only a few hundred Hadean detrital zircons in Mesoarchean meta-conglomerates of the Jack Hills metasedimentary belt argue for a possibly solid evolved Hadean crust at 4.3 Ga (Amelin et al., 1999) or even earlier (Wilde et al., 2001; Harrison et al., 2005). However, it is widely believed that, due to higher radioactive decay rates of radioactive short- and long-lived radionuclides, such as 26 Al, 40 K, and 235 U the mantle temperature was about 150 to 200 °C higher (1500 – 1600 °C) than the present Earth's mantle temperature (Fig. 0.2a; e.g., Brown, 2008;



Figure 0.2: Schematic diagrams illustrating the different proposed Archean and present-day tectonics of the silicate Earth (modified after (a) Windley et al., 2021 and (b) Van Kranendonk, 2011). Horizontal plate tectonics during the Archean are highly controversial (see text). In (a) Windley et al. (2021) propose that Archean tectonics were predominantly 'Accretionary orogeny style plate tectonics', the simultaneous formation of juvenile crust at oceanic spreading centers and oceanic arcs, with accretionary orogens forming in subduction zones and gradual rise of continental crust by dehydration melting of the mantle wedge and subducted oceanic crust. In contrast, modern-style tectonics is a combination of horizontal plate tectonics and Wilson Cycle plate tectonics. Crustal growth curves in the inset are from various studies and compiled by Hawkesworth et al. (2020). Total heat flux curve in the right-hand inset from Arevalo et al. (2009) shows the higher heat flow through the Hadean-Archean due to the higher abundances of highly radioactive nuclides (Abbreviation: L = lithosphere; UM = upper mantle; LM = lower mantle; MTZ = mantle-transitionzone (drawn at 410 - 660 km); D" = D"-layer, the core-mantle boundary zone). In (b) Van Kranendonk (2011) rather suggests Archean crust formation over the upwelling hot mantle with a depleted keel of peridotitic subcontinental lithospheric mantle (SCLM) or in areas of downwelling mantle, where the oceanic crust was imbricated and extensively melted and differentiated. In the post-Archean, like in (a) juvenile crust grew via subduction-related arc magmatism and at hot spots. Subcretion of oceanic crust to the base of the continents resulted in SCLM with a mixed peridotitic and eclogitic composition (Van Kranendonk, 2011; Shirey and Richards, 2011).

Arevalo et al., 2009; Herzberg et al., 2010). Especially the ²³⁵U decay accounted for about 50 % of the Hadean radioactive heat production and the only possible associated solid

crust, stable under these condition, would be of High-Mg mafic to ultramafic composition (Kamber, 2007). The generation of voluminous granitic crust by partial melting of a primary basaltic source rock in modern time is commonly associated with modern style plate tectonics, e.g., subduction, and the presence of liquid water (e.g., Arndt, 2013). Even though some studies argue for the operation of comparable Hadean plate tectonics, a stable long-lived mafic protocrust could only endure in the absence of subduction (Galer and Goldstein, 1991; Kamber et al., 2005; Kemp et al., 2010). The accumulation of mafic crust of up to 40 km may have led to intra-crustal melting events and thus could have caused zircon-saturated granitic melts (Kamber et al., 2005). In contrast, e.g., Nemchin et al. (2006) or Bell (2017) do not find any geochemical indications for water-saturated melts and hence low crystallization temperatures. Rather, the lack of heavy Oxygen isotopes in the majority of Hadean zircons promote igneous and intra-crustal origin. However, a general preservation of the Hadean crust is not observed and is either explained by a complete crustal recycling into the mantle or by to the complete destruction of the Hadean crust by the LHB at the end of the Hadean.

Archean rocks are found in areas known as craton (from the Greek kratos for strength) and form the core formations of all existing Archean and Proterozoic continents. These cratons represent the oldest preserved crusts and are commonly surrounded by orogenic belts that consist of younger volcanic and sedimentary rocks with recycled Archean formations (Fig. 0.1). These Archean cratons consist predominantly of two types of rock assemblages that are characteristic for the early Earth: (1) mafic to ultramafic $(\leq 52 \text{ wt.\% SiO}_2)$ volcanic and sedimentary formations commonly referred to as 'greenstone belts' and (2) sodic and highly felsic (≥ 63 wt.% SiO₂) tonalitictrondhjemitic-granodioritic suites or better known as 'Archean TTGs' (Jahn et al., 1981; Moyen and Martin, 2012). The Archean TTGs generally occur as vast plutonic bodies, whereas the greenstone belts are found either as elongated intrusive enclaves within the TTGs or literally surrounding those plutons like 'belts'. Specifically, Archean greenstone belts on the various continents are again dominated by three types of volcanic rocks: tholeiitic basalts, highly depleted boninites, and komatiites (Fig. 0.3). Additional subordinated rock formations include ultramafic cumulates, volcano-sedimentary rocks, chemical rocks, and shales. Many of these greenstone belts show prominent pillow lavas (Fig. 0.3) and immiscibility structures that indicate the presence of oceans and submarine

III. Introduction



Figure 0.3: In (a) diagnostic pillow lava structures with interstitial carbonate-chert fillings from the Theespruit Formation (Barberton Greenstone Belt; South Africa). In (b) komatiite from the Ruth Well Formation (Pilbara Craton, Western Australia) with characteristic spinifex textures (Photos taken by Christian Marien).

rock emplacements. This indication is also supported by preserved greenschist-facies mineral assemblages, which are commonly green in color due to their elevated chlorite contents (e.g., Condie, 1981). Chemical sedimentary rocks within the greenstone belts, for instance, represent records for the conditions and evolution of the Archean hydrosphere, atmosphere (e.g., Schidlowski et al., 1983), and the first microbial life on Earth (Allwood et al., 2006; Hickman, 2008; Djokic et al., 2017). Additionally, hydrothermally altered pillow lavas also provide information for the Archean ocean's composition and the interaction between rocks and fluids (Fig. 0.3a; e.g., Nakamura and Kato, 2002; 2004).

The discovery of greenstone belts led to early comparisons to the present-day oceanic crust and ophiolites. However, in contrast to the modern oceanic crust that exhibits an average thickness of 7 - 8 km, it is assumed that the Archean oceanic crust had a thickness of 20 - 30 km and was formed by higher melting degrees of about 30 % of the ambient mantle (Herzberg et al., 2010). The occurrence of such high melting degree lavas, e.g., komatiites, is almost exclusively restricted to the Archean (e.g., Brévart et al., 1986; Wilson et al., 2003; Puchtel et al., 2016; Barnes and Arndt, 2019). Komatiites represent ultramafic rocks with very high MgO content of > 18 wt.% (Barnes and Arndt, 2019) and probably required extremely high melting temperatures and pressures, still suggesting a comparably high and slowly declining mantle temperature compared to the modern mantle (Green, 1981; Puchtel et al., 2013). The most likely scenario for their formation is an adiabatic decompression melting of an anhydrous and hot mantle diapir (Green,



Figure 0.4: Schematic illustrations of (a) active subduction and (b) Archean subcretion tectonics (after Bèdard, 2018). In (a) active subduction: the thermal slab pull force acting on a stiff oceanic lithosphere is responsible for plate motions and arc magmas are created by dehydration melting of the hydrated, altered oceanic crust in the convecting mantle wedge. In (b) Archean subcretion tectonics occur when the drifting continent pushes against unsubductable thick oceanic crust. Imbricated basaltic lithosphere heat up and melt to create syn-kinematic TTGs. Localized steepening/eclogitization of imbricated segments in the orogenic foreland could trigger focussed mantle upwelling above a zone where seawater-altered basalts dehydrate, creating subordinate arc-like magmatic suites (from Bèdard, 2018).

1975; Arndt et al., 1997; Sossi et al., 2016). The characteristic spinifex textures, elongated olivine and pyroxene crystals, are considered to have been formed by quenching under submarine conditions (Fig. 0.3b; Faure et al., 2006). Thus, in combination with basalts, komatiitic rocks provide information on the physicochemical conditions and geochemical evolution of both the upper and lower Earth's mantle.

The geochemical similarities between the Archean tholeiitic rocks and modern arcrelated rocks (Hart et al., 1970; Gill, 1979; Polat et al., 2002), however, rather led to the general belief for the existence of arc-like geodynamic settings during the Archean (Figs. 0.2a and 0.4a; e.g., Garde, 2007; Polat et al., 2008; Hoffmann et al., 2010; Windley et al., 2021). This conclusion was backed by the occurrence of highly depleted boninites reported for e.g., the Isua Greenstone Belt (e.g., Polat and Hofmann, 2003; Hoffmann et al., 2010), Gadwal Greenstone Belt (Khanna et al., 2014) and for the Pilbara Craton (e.g., Smithies et al., 2005a). High depleted boninites are commonly associated with suprasubduction zones, horizontal tectonics, and island arc volcanism in modern times (e.g., König et al., 2008; 2010; Dilek and Furnes, 2009; 2011; Dilek and Thy, 2009). All together, these observations strengthened the assumption that horizontal tectonics have already been active at 3.85 Ga in case of the Isua Greenstone Belt (Hoffmann et al., 2010; Nutman et al., 2010). However so far, clear structural evidence for operating modernstyle subduction are only verifiable for the Late Archean (< 3.2 Ga; de Wit, 1998; Van Kranendonk et al., 2004; 2007; Smithies et al., 2005a). Some of those studies rather propose periods of 'stagnant lids' with subduction-like structures in older greenstone belts best been explained by episodic mantle-overturn induced continental drift (Figs. 0.2b and 0.4b). This continental drift passively imbricated and subcreted the oceanic crust (see Van Kranendonk, 2011; Bédard, 2018). Furthermore, Shirey and Richardson (2011) report a compositional change of predominantly peridotitic subcontinental lithospheric mantle ('SCLM') prior 3 Ga to a more mixed, eclogitic SCLM that indicate the addition of subducted oceanic crust (Fig. 0.2b). Thus, the onset of modern plate tectonics is still unresolved and a major controversial debate in the scientific community.

This unsolved puzzle has also a high impact on the generation of the second group of Archean rocks: the TTGs. Archean TTGs are the most prominent granitoids in Archean cratons and represent, combined with their following metamorphic products (grey gneisses), up to 90 % of the preserved Archean crust (e.g., Hoffmann et al., 2019). Archean TTGs are highly felsic and their higher sodic nature distinguishes these rocks from post-Archean granitic plutons that are commonly more potassic (e.g., Moyen and Martin, 2012; Martin et al., 2014). They also represent the nucleus for the continental crust and thus the transfer of a predominantly mafic protocrust to an increasingly



Figure 0.5: Different scenarios proposed for the formation of Archean TTGs and possible modern lowpressure analogues, divided by tectonic styles and source rocks (compiled by Hoffmann et al., 2019). The hypothetical scenario "shallow melting (< 10 kbar) of arc basalts" is the topic of Chapter 3.

stabilized evolved continental crust at the end of the Archean (Martin et al., 2005; Hawkesworth et al., 2010; Moyen and Martin, 2012; Hoffmann et al., 2019).

Again, the formation of the Archean TTGs and the geodynamic conditions of Archean continental crust growth is also still debated (Moyen and Martin, 2012). However, it is generally consensus that the primary source for the Archean TTG formation were hydrated mafic rocks under amphibolitic to granulitic conditions (Beard and Lofgren, 1991; Moyen and Martin, 2012; Moyen and Stevens, 2013; Hoffmann et al., 2019). Moyen and Martin (2012) summarized four respective models for the TTG origin: (1) fractional crystallization of arc-like basaltic melts to form tonalites (e.g., Kleinhanns et al., 2003; Hawkesworth et al., 2010; Jagoutz, 2013); (2) partial melting of hydrous metabasalts in a hot subducted slab (Martin, 1986); (3) partial melting of thickened

oceanic crust, oceanic plateaus (Bolhar and Van Kranendonk, 2007; Hoffmann et al., 2011) or oceanic island arcs (Polat, 2012) by magmatic underplating, or (4) a combination of fractional crystallization of incoming melts, partial melting of pre-existing basaltic crust and incorporating of crustal material (Arndt, 2013).

III.1.1.1. Missing modern analogue to juvenile Archean continental crust formation

Today, nearly 40 % of the Earth's surface is covered with continental crust (Hawkesworth et al., 2010). However, the exact timing of the emergence of the first continental crust as well as the formation rates are still controversially discussed (e.g., McCulloch and Bennett, 1994; Wilde et al., 2001; Belousova et al., 2010; Vervoort and Kemp, 2016). Some models propose an early and complete generation of the continental crust by the end of the Archean or even earlier with post-Archean geological processes destroying it again (e.g., Fyfe, 1978; Armstrong, 1981). However, the majority of models assume that 60 - 80 % of the present continental volume was already formed by the end of the Archean (e.g., Taylor and McLennan, 1985; Belousova et al., 2010; Dhuime et al., 2012) and since then, the last 20 - 40 % were formed either by continuous steady-state rates (e.g., Taylor and McLennan, 1985; Belousova et al., 2010) or episodically in so-called super-continental Wilson Cycles (e.g., McCulloch and Bennett, 1994; Condie, 1998; Condie and Shearer, 2017). In general, all models propose a high net growth rate of the continental crust for the Archean and a decrease of crustal growth rates for the period after 3 Ga (Fig. 0.2; Hawkesworth et al., 2010).

Today, only 5 % of the volume of the continental crust is older than 2.5 Ga (Artemieva, 2006) and much of the original crust is thought to have been destroyed and/or reworked by steady weathering, subduction, or metamorphic processes (e.g., Hawkesworth et al., 2010; Dhuime et al., 2018). Thus, the felsic magma composition of the continental crust changed towards more diverse lithologies with a more calc-alkaline peraluminous granitic composition (Martin, 1993; Laurent et al., 2014). Although partial melting of hydrous basaltic rocks is thought to remain the prevalent source for producing intermediate to felsic melts, post-Archean felsic melts often involve significant amounts of continental crustal recycling, either by sedimentary incorporation or by crustal

contamination and assimilation (e.g., Taylor, 1967; Barbarin, 1999; Belousova et al., 2010; Moyen et al., 2017).

However, the term crust formation is denoted to the formation of 'new' continental crust. While TTGs were widespread in the Archean, large volumes of sodic post-Archean granitoids are scarce. In the Earth's more recent history, oceanic plagiogranites were originally inferred to be the most probable modern analogues for Archean TTGs (e.g., Coleman and Peterman, 1975). The term 'oceanic plagiogranite' is thought to be synonym for rock assemblages of tonalitic, trondhjemitic, and (grano)-dioritic composition in the modern oceanic crust. However, plagiogranites that are found in ophiolitic complexes, such as the Troodos Ophiolite (Marien et al., 2019) and the Oman Ophiolite (Rollinson, 2008; 2009) mostly form near spreading ridges at shallow depths within the oceanic crust and seldom exceed 1 vol.%. In this, they rather appear in form of late-stage melt pockets and dikes within the sheeted dikes (Gillis and Coogan, 2002; Rollinson, 2008). Other studies rather promote adakites for a more fitting modern analogue (e.g., Defant and Drummond, 1990; Drummond and Defant, 1990; Condie, 2005; Hastie et al., 2015). Produced by partial melting of subducted oceanic crust and/or oceanic plateaux (e.g., Hastie et al., 2015), these calc-alkaline and mostly felsic volcanics and plutons are reported in many oceanic and continental arcs along the Pacific 'Ring of Fire', with prominent locations, such as the Aleutian oceanic arc, Alaska (Kay et al., 1990; 2019) and Kamchatka, Russia (e.g., Münker et al., 2004), and the Blue Mountains, Jamaica (Hastie et al., 2015; 2016). However, contamination of highly evolved crustal material or hybridization by metasomatized peridotite may have altered the initial melt composition (Castillo, 2006), which were unlikely for the Archean TTG generation (Smithies, 2000). Although there are some candidates for comparable Archean-like processes on modern setting, a plausible modern analogue still needs to be found.

III.1.2. Earth's mantle depletion and heterogeneities

Throughout the whole Earth's history, extensive melting processes and the recycling of crustal components led to a highly heterogeneous composition of the present Earth's mantle (e.g., Zindler and Hart, 1986; Stracke et al., 2005; Stracke and Bourdon, 2009). At modern Mid-ocean ridge margins, the divergent lithospheric plate separation results in the adiabatically upwelling movement of the underlying mantle. Subsequent

decompression melting has led to the continuous depletion of incompatible elements (see III.2.1.) in the upper mantle (first 660 km) and simultaneously to the formation of depleted **m**id-**o**cean ridge **b**asalts ('*MORB*'), which form a large part of the modern oceanic crust (e.g., Johnson et al., 1990; Workman and Hart, 2005). At convergent plate margin, either in an intra-oceanic arc or continental arc setting, the subduction of oceanic slabs result in the formation of arc related volcanism. During the subduction of the oceanic crust, metamorphic processes conduct the continuous release of volatile und fluid mobile elements into the refertilized overlying mantle (e.g., Jakeš and Gill, 1970; Gill, 1981). Independent from any tectonic plate boundaries is the generation of **o**cean **i**sland **b**asalts ('*OIB*'). Unlike MORB and volcanic arc rocks, OIB generation is caused by hot plume-related intraplate volcanism, which tap more enriched lower mantle reservoirs (e.g., Hofmann and White, 1982; Stracke et al., 2005).

Further modern mantle heterogeneities are rooted in extensive temporal melt depletion, the formation and subsequent destruction of oceanic and continental crust as



Figure 0.6: Three-dimensional projection of ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd, and ²⁰⁶Pb/²⁰⁴Pb isotope arrays of different MORB and OIB groups after Hart et al. (1992) (modified by Hofmann, 2003; 2013). Most of the individual arrays appear to deviate from the region labelled as FOZO, which is thought to represent the deep mantle composition (Hart et al., 1992).

well as crustal recycling into the mantle, ultimately all of which producing characteristic isotope compositions (Hofmann, 2003;2013). Hart et al. (1992) and Stracke et al. (2005) summarized the so called 'mantle zoo' (Fig. 0.6), which subdivided be by their can respective radiogenic Pb-Sr-Nd isotope composition into enriched and depleted sources. Enriched mantle-endmembers comprise the 'Enriched Mantle 1' ('EMI'), 'Enriched Mantle 2' ('EM II'), and '*HIMU*' component ('*high-µ*' or high $^{238}U/^{204}Pb$). The EM I is probably contaminated with lower crustal material by or sub-
continental lithospheric delamination (e.g., Hawkesworth et al., 1986; Boyet et al., 2019), EM II is modified by the recycling of continental clastic sediments (e.g., Hawkesworth et al., 1979; Hofmann, 2003) whereas the HIMU mantle endmember requires a contaminant highly enriched in U and its composition is most likely modified by the recycling of altered and subducted oceanic crust (Stracke et al., 2005). On the depleted side, Stracke et al. (2005) mention the '*depleted MORB mantle*' ('DMM'), also variably altered by the other enriched endmembers, and 'Focal Zone' mantle ('FOZO'). It is generally suggested that the FOZO component derives from the lower mantle that experienced a continuous addition of the other enriched endmembers and lies transitional between the all zoo-member (e.g., Hart et al., 1992; Stracke et al., 2005). The last important mantle reservoir is commonly known as '*primitive mantle*' (*PRIMA*), often also called bulk silicate Earth ('BSE'; Sun, 1982; Hofmann, 1988). This reservoir is thought to represent the most primitive and unaltered composition of the early Earth after core-mantle segregation and prior continental crust formation. A chondritic composition with a depletion in siderophile and highly volatile elements is generally assumed as best estimate of the primitive mantle (Palme and O'Neill, 2014).

However, mantle heterogeneities in the Archean remain uncertain and controversial (e.g., Bennett et al., 1993; Moorbath et al., 1997; Hoffmann et al., 2010; Nebel et al., 2014). Whereas the majority of the modern mantle heterogeneity is caused by convergent plate tectonics, the recycling of crustal material and the occurrence of the modern mantle zoo in the Archean seems unlikely, as a hotter mantle most likely prevented this type of horizontal tectonics until the early Mesoarchean (e.g., Shirey and Richardson, 2011; Næraa et al., 2012). Crustal recycling was presumably limited to lower crustal delamination due to their higher density compared to the hot peridotitic upper mantle (e.g., Bédard, 2006; Bédard et al., 2013; Zhang et al., 2013; Johnson et al., 2014).

One of the most crucial and heavily discussed topics are: When did the mantle depletion start and to what degree did it happen? Based on ¹⁴⁷Sm/¹⁴³Nd data on Archean mafic rocks several studies propose the presence of highly depleted mantle reservoir, inferred by ¹⁴⁷Sm/¹⁴³Nd ratios in Archean mafic rocks that mirror a highly depleted mantle reservoir evolving in the early Archean (e.g., Bennett et al., 1993; Bennett, 2003; Hoffmann et al., 2011). Whereas other studies, report only a moderate mantle depletion (Gruau et al., 1987; Arndt et al., 2001) or at least that the mantle depletion did not start

before 3.6 Ga e.g., in case of the Pilbara Craton, W Australia (Nebel et al., 2014; Kemp et al., 2015; Petersson et al., 2019; 2020). Adding up even complexity, Hasenstab et al. (2021) and Tusch et al. (2021) recently rather suggest the presence of distinctive local mantle heterogeneities in the Archean and the coexistence of a upper mantle reservoir, showing a depletion history that stated at 4.2 Ga, and a near-chondritic lower mantle reservoir (Hasenstab et al., 2021) that remained isolated for nearly 1 billion years and retained Hadean pre-LHB-signatures (Tusch et al., 2021).

III.1.3. The first oceans, an anoxic atmosphere and the 'Cradle of Life'

The first geological and stratigraphical evidence for ambient volumes of water on the Earth's surface is found in Eoarchean pillow lavas and marine chemical sediments at 3.85 Ga from the Isua Greenstone Belt, West Greenland (e.g., Nutman et al., 1996; Frei and Rosing, 2001; Polat and Hofmann, 2003). From such rocks, several geological and geochemical indications hint fundamentally different physicochemical conditions in the Archean seawater compared to modern oceans and margin basins. With some exceptions, this includes the general absence of any free oxygen in the Archean oceans prior to the GOE. Consequently, the hydrothermal influx of redox sensitive elements, such as Fe, Si, Mn, or Cr, from a reduced mantle by volcanic activity resulted in a predominantly ferruginous ocean environment (e.g., Bau and Dulski, 1996).

The effect of continental weathering on the Archean seawater, which has a crucial effect on modern ocean's composition, was assumed to become significant by the global emergence of modern plate tectonics at, or slightly before the Archean-Proterozoic boundary at ca. 2.7 - 2.5 Ga. However, more recent studies suggested that the seawater composition changed from a mantle buffered regime to a system that is characterized by the increasing influx of riverine runoff as a result of enhanced continental weathering arising from the local development and emergence of continental crust via modern-style plate tectonics already by the Mesoarchean, at 3.2 Ga (Smithies et al., 2007; Satkoski et al., 2016; 2017; Ravindran et al., 2020; Roerdink et al., 2022; **Chapter 2**).

The increasing continental influence on the Archean seawater is, in part, caused by the increasing level of atmospheric oxygen. During the Archean, free oxygen was mostly at levels > 0.001 vol.% of the present atmosphere (Lyons et al., 2014). The occurrence of the GOE at the end of the Archean has been the primary topic of many studies and has



Figure 0.7: In (a) mass-independent Δ^{33} S isotope variation preserved in chemical sediments during the Earth's history. Throughout the Archean, deviations in the composition of sulfur isotopes were caused by the photochemical reaction of ultraviolet radiation in an oxygen-free atmosphere, whereas in the presence of atmospheric O₂ no such fractionation occurs due to the shielding ozone layer (Johnston et al., 2011). In (b) oxygenation of the atmosphere during the Earth's history (modified after Lyon et al., 2014). Light blue arrows represent so-called 'whiffs' of oxygen between 3.0 and 2.5 Ga. The great oxygenation event (GOE) occurred around 2.4 Ga (Holland, 2002; Lyons et al., 2014). NOE = Neoproterozoic Oxygenation Event.

been investigated with different redox-sensitive proxies. These studies conclude that both the oxygenation of the Archean seawater and atmosphere was not a sudden process, but rather dynamic and in some cases locally. Specifically, **m**ass-independent fractionation ('*MIF*') of strongly redox-sensitive Sulfur and its isotopes¹ at the end of the Archean and throughout the younger Earth's history (Fig. 0.7). The occurrence of MIF Sulfur

¹ Sulfur isotope ratios are usually reported as $\delta^{3x}S$ (3x being either 33, 34, or 36) values where $\delta^{3x}S = [({}^{3x}S/{}^{32}S)_{sample}/({}^{3x}S/{}^{32}S)_{VCDT} - 1] \times 1000$. The terrestrial mass fractionation law is conventionally defined as $\delta^{3x}S = 1000 \times \ln [({}^{3x}S/{}^{32}S)_{sample}/({}^{3x}S/{}^{32}S)_{VCDT} - 1]$ with VCDT (Vienna Canyon Diabolo Troilite reference standard). Deviation from this relationship are commonly termed "mass-independent fractionation (MIF) and are quantified as $\Delta^{33}S = \delta^{33}S - 0.515 \times \delta^{34}S$ (copied from Paris et al., 2014).



Figure 0.8: Representative chemical sediments from the Archean. In (a) wrinkly laminated stromatolites from the "Buick locality" near the North Pole Dome, Pilbara Craton, with barite pseudomorphs. In (b) representative Strelley Pool stromatolites representing the first signs of life on Earth. In (c) interstitial carbonate between submarine pillow lavas. In (d) early Proterozoic laminated cherts and magnetite-rich iron oxides from the banded iron formations from the Hamersley Basin; Karijini National Park; Pilbara (Photos taken by Christian Marien).

signatures bear evidence to photochemical reactions occurring in the early O₂-free Earth's atmosphere, and consequently the absence of an ultraviolet-shielding ozone layer (e.g., Whitehouse et al., 2005). Mass-IF Sulfur signatures have been reported in minerals, such as easily oxidized sulfides (e.g., FeS₂; e.g., Farquhar et al., 2000; Whitehouse et al., 2005) and sulphates (e.g., Ba[SO4]; e.g., Satkoski et al., 2016). The most profound explanation for the rise of free atmospheric oxygen during the Archean-Proterozoic transition is the evolution of cyanobacteria exerting photosynthesis. However, the presence of bacterial life is already reported throughout the Paleo- and Mesoarchean in form of microbial mats, commonly known as stromatolites (Fig. 0.8) with their first verified appearance at ca. 3.45 Ga in the Pilbara Craton, Western Australia (e.g., Van Kranendonk et al., 2003; Allwood et al., 2006; Viehmann et al., 2020). A more controversial evidence for the presence of the microbial life dates back to 3.7 Ga in the Isua Greenstone Belt, West Greenland (Rosing, 1999; Nutman et al., 2010; 2016) .

Alternatively, indirect evidence of photosynthetic microbial life may be the **b**anded **i**ron formations ('*BIF*'), consisting of alternating layers of iron oxides, either magnetite (Fe₃O₄) or hematite (Fe₂O₃) and Fe-poor chert (amorphous SiO₂). Significant amounts of BIFs started to appear at 3.8 Ga in Isua, West Greenland, and the latest findings are reported at 0.7 Ga in the Urucum Region, Brazil and in the Damara Supergroup, Namibia (compiled by Klein, 2005). The majority of the BIFs however precipitated from an anoxic seawater with the voluminous largest units in Western Australia (Hamersley Range) from 2.6 to 2.45 Ga (e.g., Trendall, 1968; 2002; Trendall and Blockley, 1970; Van Kranendonk, 2010) and South Africa (Transvaal Supergroup) between 2.5 and 2.3 Ga (e.g., Klein and Beukes, 1989; Beukes and Klein, 1990; Bau and Dulski, 1996). This might also coincide with the so-called O₂ whiffs in the late Archean (Fig. 0.7b).

III.2. Geochemical constraints on geological processes

III.2.1. Trace element geochemistry

Trace elements (contents of $\leq 10,000$ ppm), such as rare earth elements ('*REE*') or lanthanides, large-ion lithophile elements ('*LILE*'), or high-field-strength elements ('*HFSE*') have contributed enormously in the understanding the Earth's evolution. All these elements exhibit different compatibilities, which describes the partitioning behavior between the solid and liquid phase in geological processes. Consequently, during partial melting processes compatible elements remain in the solid phase, whereas incompatible elements go preferentially into the liquid phase. This partitioning behavior of the elements is expressed via their respective partitioning coefficient² *D*, which can vary considerably, e.g., between different mineral phases or because of charge, changing compositional, temperature, pressure, and redox conditions.

This also results in substantial variations of trace element concentrations in different rocks or minerals spanning several orders of magnitude. Thus, to simplify the comparison, they are commonly presented in normalized form, i.e., relative to well-defined reservoirs, such as CI-chondrite (Sun and McDonough, 1989; McDonough and Sun, 1995), **pri**mitive **mantle** ('*PRIMA*'; Palme and O'Neill, 2014), or **Post-Archean Australian Shale** ('*PAAS*'; Taylor and McLennan, 1985). PRIMA-normalized diagrams, for instance, simplify the comparison of different rocks with each other and with the respective host rocks. The element in these diagrams are sorted by their relative compatibility in rocks, with increasing compatibility to the right. With this, melting and depletion processes, for example, are easy to determine, since incompatible elements are depleted in the residual reservoir and accumulate in the resulting melt. The higher the degree of melting, the stronger the residual depletion. In the melt, however, the relative

$$D_i = \frac{C_i^C}{C_i^L}$$
.

² The ratio of the concentration of trace element *i* in a mineral (C_i^C) relative to the concentration of the same trace element *i* in the liquid/melt (C_i^L) is called partition coefficient (D_i) of a specific mineral where

If $D_i \ll 1$, the element behaves incompatible and is preferentially concentrated in the liquid in partial melting or fractional crystallization processes. Vice versa, if $D_i \gg 1$, the element behaves compatible and remains preferentially in the solid phases in partial melting processes or preferentially crystallizes in fractional crystallization processes.



Figure 0.9: Comparison of PRIMA-normalized trace and major element abundances in the average continental and oceanic crust compared to their respective partition coefficient values (Hofmann, 2013). The residual mantle is depleted in incompatible elements, such as LILE and LREE, and enriched in highly compatible elements, such as Co and Mg, whereas the continental crust is enriched in incompatible and depleted in compatible elements. Mid-ocean ridge basalts, derivates from the depleted mantle, are relatively enriched in incompatible elements, but mimic the total composition of the depleted upper mantle.

concentration difference between highly incompatible and compatible elements decreases with increasing melt percentages.

In geological systems, e.g., the REE (La to Lu) show coherent geochemical behavior for the whole lanthanide series, due to their specific trivalent charge and only small ionic radius differences. The REE are considered as incompatible elements, the degree of incompatibility, however, varies and generally decreases progressively with their increasing atomic number and respective radii from La^{3+} to Lu^{3+} . Thus, the small differences in the compatibility cause the fractionation of the REE in geological processes, such as partial melting, fractional crystallization or precipitation from solutions, and enable the distinction between different mantle and crust reservoirs (Figs. 0.9 - 0.10). Of the REE, only Ce and Eu are highly redox-sensitive. Europium may also occur in a reduced divalent (Eu²⁺) state, whereas Ce may also occur as oxidized tetravalent (Ce⁴⁺) state. Thus, both can be additionally used to track redox-sensitive conditions (Fig. 0.10b).



Figure 0.10: In (a) PRIMA-normalized (Palme and O'Neil, 2014) trace element abundances of representative mantle and magmatic rock groups sorted by their respective compatibility. Depleted mantle (White and Klein, 2014) is depleted in incompatible LILE and LREE, MORB mirrors the general element distribution of the depleted mantle (Salters and Stracke, 2005). Ocean-island basalts (OIB; Sun and McDonough, 1989) and the bulk continental crust (Rudnick and Gao, 2014) are enriched in incompatible elements. In (b) PAAS-normalized (Taylor and McLennan, 1985) REY patterns of shallow to deep Pacific seawater (blue shades; Zhang and Nozaki, 1996) and high-T hydrothermal fluids from the Mid-Atlantic Ridge (Bau and Dulski, 1999). Typical seawater trace element composition is characterized by LREE depletion relative to HREE, exhibit positive La, Gd, and Y anomalies (superchondritic Y/Ho ratios) and strong negative Ce anomalies. Hydrothermal fluids, in contrast, show large positive Eu anomalies, which express the reduced redox conditions.

This redox-sensitive behavior of Ce^{4+} and Eu^{2+} is commonly used for the distinction of aqueous solutions, such as riverine or seawater as well as hydrothermal fluids and their respective precipitation products. Most hydrothermal fluids, for instance, are generated by diverse volcanic or magmatic processes, are acidic, and enriched in incompatible elements (Bau, 1991; 1996; Bau and Dulski, 1996). Under reduced conditions, Ce is predominantly trivalent, whereas Eu is further reduced to a divalent state. This behavior results in a characteristic positive Eu anomaly in chemical sediments derived from Oxygen-free fluids, such as the Archean ocean. In oxidized fluids, such as modern ocean environments, Ce is commonly present as a Ce⁴⁺ species, which lead to the preferential removal from the fluid in precipitation. In addition, in marine environments the dissolved REE concentrations are not controlled by their charge but also by the presence of carbonate complexes (CO^+ and CO_3^{2-}). Heavy REE (*HREE*) form more stable carbonate solution complexes than the light REE (LREE) and remain in solution, whereas the LREE, and especially the Ce⁴⁺ ions, are highly particle reactive. Thus, the LREE are preferentially removed from the solution, causing low residence times for the REE (e.g., Bau, 1999; Alexander et al., 2008; Viehmann et al., 2015).

The LILE include monovalent elements such as Rb⁺, K⁺, and Na⁺ as well as divalent elements, such as Sr²⁺, Ba²⁺, and Pb²⁺. These elements tend to be highly incompatible in magmatic processes (Fig. 0.10) due to their low ionic potential but are also highly soluble in aqueous solutions and mobile during metamorphic and weathering processes. Thus, they tend to be highly concentrated in hydrothermal and aqueous fluids as well as in altered and highly evolved rocks.

As the name implies, HFSE have a particularly high ionic charge compared to other elements. The so-called geochemical twins Hf^{4+} and Zr^{4+} , for example, are tetravalent, whereas Ta^{5+} and Nb^{5+} show pentavalent behaviors. The LIL elements Th and U are sometimes also counted among the HFSE, since they can also exhibit higher valence states. Because of their higher valence states, the HFSE are compatible und immobile in geological processes. This makes them immobile especially in weathering and metamorphic processes.

29

III.2.2. Radiogenic and stable isotope perspectives on the early Earth's differentiation

In addition to trace element concentration, stable and radioactive isotope variations of different elements can also be used to decrypt differentiation processes of the respective Earth's reservoirs that are still unknown or poorly understood. With the use of radioactive decay systems, it is possible to track different magmatic and metamorphic processes, in which parent and daughter nuclides partition either in different reservoirs or to different degrees between the respective reservoirs. Short-lived isotope systems, such as ¹⁴⁶Sm-¹⁴²Nd and ¹⁸²Hf-¹⁸²W, for instance have been used to track down the earliest Earth mantle-crust differentiation processes in the Hadean or hints for the missing late veneer (e.g., O'Neil et al., 2008; Rizo et al., 2019; Tusch et al., 2019; 2021; Hasenstab-Dübeler et al., 2022).

For this study, the long-lived radionuclides are of more importance as they provide tools to analyze the evolution of the early Earth's mantle composition. The ⁸⁷Rb-⁸⁷Sr and the coupled U-Th-Pb systems are the oldest tools for geochronological constraints on rocks and for the continental crust evolution (e.g., Armstrong, 1968; Moorbath, 1977;



Figure 0.11: Crust-mantle differentiation patterns for the respective Rb-Sr. U-Th-Pb, Sm-Nd, and Lu-Hf decay systems (modified after Hofmann, 2013). This diagram illustrates the depletion-enrichment relationships of the parent-daughter pairs, which lead to different isotope evolution curves in continental crust, oceanic crust, and the residual mantle.



Figure 0.12: Schematic isotope evolution diagrams of the continental crust and depleted mantle (inferred by MORB) relative to primitive mantle or the most undifferentiated solar system material: CHUR (chondritic uniform reservoir; DePaolo and Wasserburg, 1976), respectively. In (a) the ⁸⁷Sr/⁸⁶Sr isotope composition vs. time plot shows the radiogenic increase of the ⁸⁷Sr/⁸⁶Sr over time by the radioactive decay of ⁸⁷Rb. Melt extraction and continental crust generation at 3.5 Ga leads to the fractionation of the Rb/Sr ratio of the primitive mantle, resulting in a continental crust with higher Rb/Sr and a depleted mantle with lower Rb/Sr and increasingly deviating 87 Sr/ 86 Sr isotope compositions. In (b) three different μ -values $(^{238}\text{U}/^{204}\text{Pb})$ show the respective calculated Pb isotope composition curves of the silicate Earth over the last 500 Myrs that lead to the hypothetical present-day composition (geochron). Interestingly, both MORB and OIB are generally more radiogenic than calculated (first Pb paradox), suggesting a change of the initial U/Pb ratio. In (c) the ¹⁴³Nd/¹⁴⁴Nd isotope composition and ¹⁷⁶Hf/¹⁷⁷Hf isotope composition vs. time, respectively, shows the inverse fractionation behavior of the parent-daughter pairs, Sm-Nd and Lu-Hf, compared to Rb-Sr in melting processes. This results in a more radiogenic Nd-Hf isotope composition of the depleted mantle (MORB) relative to the primitive mantle and the continental crust deviates to more unradiogenic isotope compositions. In (d) ϵ^{143} Nd and ϵ^{176} Hf vs. time, respectively. For simplicity, Nd and Hf isotope variations of different rocks are expressed in ε -notation³ and normalized to CHUR (Bouvier et al., 2008).

Taylor et al., 1980; McCulloch et al., 1983b; McCulloch and Bennett, 1994). In crustmantle differentiation processes, Rb and U-Th-Pb behave more incompatible than Sr, which lead to more radiogenic Sr-Pb isotope signatures in the corresponding evolving

³ ε-Notation (deviation in parts per 10,000) e.g., for ¹⁴³Nd/¹⁴⁴Nd, where

$$\varepsilon^{143} N d = \left[\frac{\left(\frac{143}{144} N d \right)_{measured}}{\left(\frac{143}{144} N d \right)_{cHUR}} - 1 \right] \times 10,000$$

crust than in the residual mantle (Figs. 0.11 - 0.12a, b). However, briefly thereafter, studies found that e.g., metasomatic processes can easily affect both systems, since in both cases the highly mobile behavior of the elements irreversibly obscures the primary element and isotope compositions (Moorbath et al., 1997). This metasomatic overprint ensures that whole rock analyses are no longer carried out for Archean rocks but therefore commonly used for modern mantle derived rocks that experienced various replenishment events, such as dehydration of subducted slabs (\rightarrow mantle zoo). In addition, with the onset of convergent plate tectonics, a significant fraction of highly radiogenic Sr and Pb is also reintroduced into the mantle over time. In case of Pb, this highly radiogenic Pb signature is found in all modern mantle-derived rocks and referred to as the 'first Pb paradox' (Fig. 0.12b; Allègre, 1969). In order to determine the initial isotope compositions of mantle derived rocks, accordingly, only mineral separates are used, which 'freeze' the original isotope composition by a very low parent/daughter nuclide ratio and show no signs of alteration. In this case, the best-known representative of Pb are e.g., galena (Richards et al., 1981; Richards, 1983; Dupré et al., 1984; Allègre et al., 1986; Dupré and Arndt, 1990) and K-feldspar (Wooden and Mueller, 1988; Kamber et al., 2003; Hartnady et al., 2022), while barites and primary carbonates are commonly used for Sr (e.g., Veizer et al., 1989a; b; Satkoski et al., 2015; Roerdink et al., 2022).

The more robust ¹⁴⁷Sm-¹⁴³Nd and ¹⁷⁶Lu-¹⁷⁶Hf isotope systems behave almost covariant in magmatic processes but reversed to the ⁸⁷Rb-⁸⁷Sr system (Fig. 0.12c-d). Due to its robustness towards metasomatic processes, the Sm-Nd system also became an accepted tracer for the evolution of individual mantle reservoirs, e.g., the primitive and depleted mantle, and especially the Earth's crust (e.g., DePaolo and Wasserburg, 1976; Wasserburg and DePaolo, 1979; Hamilton et al., 1983; Galer and Goldstein, 1991; Bennett et al., 1993; Moorbath et al., 1997). Since the measurement precision has been increased by new methods, the Sm-Nd isotope system has been complemented by the Lu-Hf isotope system (Patchett and Tatsumoto, 1980; Patchett et al., 1982; Blichert-Toft et al., 1997; Weyer et al., 2002). The Lu-Hf even exhibits some advantages relative to the Sm-Nd decay system, as it is more robust in metamorphic processes and the slightly higher ¹⁷⁶Lu decay rate (Table 0.1) leads to isotope variations that are somewhat more pronounced (better resolvable) compared to those of the Sm-Nd system (Blichert-Toft, 2001). In both cases, the parent nuclide is more compatible than the daughter nuclide,

resulting in a more radiogenic composition of the depleted mantle compared to the primitive mantle or the mantle-derived crust.

e			
Parent nuclide	Daughter nuclide	Half-life (years)	Tracer ratio (radiogenic/nonradiogenic)
⁸⁷ Rb	⁸⁷ Sr	$4.88 imes 10^{10}$	⁸⁷ Sr/ ⁸⁶ Sr
¹⁴⁷ Sm	¹⁴³ Nd	1.06×10^{11}	¹⁴³ Nd/ ¹⁴⁴ Nd
¹⁷⁶ Lu	¹⁷⁶ Hf	3.57×10^{10}	¹⁷⁶ Hf/ ¹⁷⁷ Hf
²³² Th	²⁰⁸ Pb	1.401×10^{10}	²⁰⁸ Pb/ ²⁰⁴ Pb
²³⁵ U	²⁰⁷ Pb	$0.738 imes 10^9$	²⁰⁷ Pb/ ²⁰⁴ Pb
²³⁸ U	²⁰⁶ Pb	$4.468 imes 10^9$	²⁰⁶ Pb/ ²⁰⁴ Pb

Table 0.1: Long-lived radionuclides

III.3. Scope of this thesis

The main objectives of this thesis are to extend the understanding of evolution of the Paleo- to Mesoarchean mantle and its interaction with the emerging continental crust. In the next step, this thesis constrains the differences between the generation of the first continental crust and post-Archean continental crust production. Mineral separates and whole rocks from southern West Greenland, Western Australia, and Fiji are used to investigate the following aspects:

- The continuous depletion of the Archean mantle inferred by coupled U-Th-Pb, Rb-Sr, and Sm-Nd isotope compositions on mineral separates of mantlederived mafic and ultramafic rocks.
- The evolution of heterogeneous primitive and depleted mantle domains by continuous mantle melting.
- The onset of modern-like subduction and its influence on the element budget of the Earth's mantle.
- The temporal emergence of exposed continental crust in the Archean and its contribution on the Archean mantle and seawater composition.
- The comparison of Archean to modern intra-crustal differentiation processes that led to the formation of the continental crust.

This thesis is comprised of three chapters, each highlighting different aspects of the Earth's mantle-crust evolution. To do so, different geological archives were sampled, which include predominantly mafic mineral separates of mafic to ultramafic successions from southern West Greenland and Western Australia (**Chapter 1**), interstitial and void-filling carbonates and quartzes of pillowed metabasalts from Western Australia (**Chapter 2**), and felsic rocks from tonalitic to trondhjemitic plutons from Viti Levu, Fiji, an intra-oceanic island arc (**Chapter 3**).

Chapter 1 shows the first isotope dilution analysis of U, Th, and Pb on mafic minerals using MC-ICP-MS. Within this chapter, we present combined ^{238,235}U-²³²Th-^{206,207,208}Pb, ⁸⁷Rb-⁸⁷Sr, and ¹⁴⁷Sm-¹⁴³Nd isotope measurements on fresh mafic minerals, such as olivine, ortho- and clinopyroxene, and amphibole from the Seqi Ultramafic Complex (SUC), southern West Greenland and the Pilbara Craton, Western Australia.

These mineral separates from several formations, ranging from 3.5 - 2.7 Ga, give information about the depletion history of the Archean mantle, evolving from a primitive composition to a more depleted upper mantle section. Our results show that some Paleoarchean mantle-derived mineral phases inherited the primary Pb and Nd isotope compositions of the primitive mantle. In contrast, younger Mesoarchean clinopyroxene separates from the Pilbara Craton preserved comparably low Pb and Sr isotopic values but are more radiogenic in their Nd isotope compositions that are formed by an early upper mantle depletion. In this context, the mineral separates from the Pilbara Craton give valuable information on the early Archean isotopic evolution of the Archean mantle prior any obscuring influences of modern plate tectonics.

Chapter 2 provides new geochemical observations on interpillow calcites from Paleo- to Mesoarchean pillow lavas of the Pilbara Craton in Western Australia. Based on their petrographic description and their main and trace element compositions, two type of interstitial carbonates have been identified. The first type of coarse-grained carbonates (Type I) exhibits elevated Mn and REY (REE + yttrium) concentrations that match the basaltic host rock composition. This data indicate precipitation from boiling seawater trapped between the pillows during the emplacement of the pillow lavas. Comparably low Y/Ho ratios and low δ^{18} O ratios argue for extensive fluid-rock interaction during the calcite precipitation. The second type of carbonates shows lower Mn and REY concentrations. High Sr concentrations, higher Y/Ho ratios, and seawater-like REY patterns argue for the precipitation from ambient seawater and only a small degree of fluid-rock interaction. Almost all investigated carbonates yield well defined Sm-Nd isochron ages, which overlap with previously reported ages for their respective host rocks. This overlap argues for the pristine unspoiled primary geochemical signatures and applicability of Sm-Nd dating for carbonates, if they are undisturbed. Furthermore, new primary Sr isotopes signatures on the Type II carbonates reveal that surface weathering of continental crust already occurred during the early Mesoarchean and that the influence of hydrothermal fluids on the Archean seawater composition is not as dominant as thought before. The manuscript of Chapter 2, entitled "Interstitial carbonates in pillowed metabasaltic rocks from the Pilbara Craton, Western Australia: A vestige of Archean seawater chemistry and seawater-rock interactions" was published in Precambrian Research (https://doi.org/10.1016/-j.precamres.2023.107109).

Finally, **Chapter 3** aims on the process of continental crust formation itself. The biggest portion of today's continental crust formed in the Archean and the central parts consist of tonalites, trondhjemites and granodiorites. However, similar low volume felsic rocks are also found in modern oceanic arcs, such as Fiji. This study provides new geochemical observations and a combined comprehensive major, minor, and trace element data for several tonalitic-trondhjemitic plutons from Fiji. Moreover, this present work also includes high-precision HFSE concentrations, and Pb-Sr-Nd-Hf isotope compositions on the Fijian trondhjemites and new U-Pb zircon ages. The complete record argues for at least three different petrogenetic processes for pluton formation, each linked to different stages of arc maturation. The manuscript of this **Chapter 3**, entitled "Juvenile continental crust evolution in a modern oceanic arc setting: Petrogenesis of Cenozoic felsic plutons in Fiji, SW Pacific", concludes the combined work of Jim Gill and several theses from previous students and co-authors over *50 years*, and is the final chapter of my thesis and published in *Geochimica et Cosmochimica Acta* (<u>https://doi.org/10.1016/j.gca.2021.11.033</u>).

In summary, this thesis contributes (1) new insights for the understanding of the U-Th-Pb isotope evolution of the Archean mantle (**Chapter 1**), (2) an extension of the rock record for investigating the interaction of the lithosphere and hydrosphere (**Chapter 2**), and (3) a better understanding of intra-crustal melting processes in modern oceanic arc systems, which could be the birthplace of new continental crust (**Chapter 3**).

CHAPTER 1

EVOLUTION OF THE ARCHEAN MANTLE CONSTRAINED FROM COMBINED U-TH-PB, SM-ND, AND RB-SR ISOTOPE MEASUREMENTS ON PRIMARY MINERALS FROM ARCHEAN MAFIC-ULTRAMAFIC VOLCANIC ROCKS

1.1. Abstract

New combined U-Th-Pb concentrations and Pb isotope data are reported for primary magmatic and metamorphic mineral separates, such as olivine, ortho- and clinopyroxene, as well as hornblende from various mafic successions from the Pilbara Craton, Western Australia, and from the Seqi Ultramafic Complex, West Greenland that are complemented by Sm, Nd, Rb, and Sr concentration data and Sr and Nd isotope compositions. Based in these data, we perform isotope modeling in order to better understand the Nd and Pb isotope evolution of the Archean mantle. For Pilbara, the initial Pb isotope compositions of Paleoarchean and Mesoarchean samples are nearly identical, whereas initial Nd isotope compositions suggest different mantle domains. Consequently, our data reveal two mantle evolutions trends for Pilbara: (1) Paleoarchean mafic rocks were derived from a primitive mantle domain with chondritic Nd isotopes, elevated μ_1 $(^{238}\text{U}/^{204}\text{Pb})$ of 8.90 - 8.46 and variable high κ_1 $(^{232}\text{Th}/^{238}\text{U})$ of 4.6 - 7.7, and (2) Mesoarchean mafic formations indicate early Archean upper mantle depletion that might have started at ca. 3.8 Ga. Superchondritic Nd isotopes coupled with lower μ_2 between 5.64 – 6.72 and κ_2 of 4.62 – 6.05, indicate successive U depletion of the Archean upper mantle. In addition, the κ_1 and κ_2 of the Archean primitive and depleted mantle overlap and are consistently higher than the measured $\kappa = 3.8$ of the modern mantle, indicating no U recycling through the Archean. In contrast, Neoarchean formations show crustal contamination, inferred by Sr-Nd isotope compositions and hence the onset of modern plate tectonics.

Initial isotope signatures in mafic mineral separates from the Seqi Ultramafic Complex, West Greenland (emplacement age of ca. 3.2 Ga), were reset by a 2.977 Ga retrograde peak-metamorphic event and tonalite emplacement. Initial Pb isotopes of the minerals separates suggest a depleted mantle source for the mafic precursor material and a relatively short crustal residence time of about 200 Myrs.

1.2. Introduction

Our understanding of the terrestrial mantle-crust evolution and the corresponding depletion and re-enrichment processes for the evolving upper mantle stems from shortlived and now extinct decay systems, such as ¹⁸²Hf-¹⁸²W and ¹⁴⁶Sm-¹⁴²Nd (e.g., Boyet and Carlson, 2006; Schneider et al., 2018; Tusch et al., 2019; 2021; Murphy et al., 2021; Hasenstab-Dübeler et al., 2022), and long-lived decay systems such as ¹⁴⁷Sm-¹⁴³Nd, ¹⁷⁶Lu-¹⁷⁶Hf, ¹³⁸La-¹³⁸Ce, ⁸⁷Rb-⁸⁷Sr, and the three decay-chain system consisting of ²³⁸U-²⁰⁶Pb, ²³⁵U-²⁰⁷Pb and ²³²Th-²⁰⁸Pb (e.g., McCulloch and Bennett, 1994; Vervoort et al., 1994; Vervoort and Blichert-Toft, 1999; Kamber et al., 2003; Murphy et al., 2003; Hasenstab et al., 2021). Opposite to Archean crustal rocks, the modern oceanic crust as well as ophiolitic complexes provide us with a nearly complete mafic rock record and give us detailed insights for the evolution of the Phanerozoic mantle and allow us to determine various tectono-magmatic environments (e.g., Jakeš and Gill, 1970; Pearce and Peate, 1985; Zindler and Hart, 1986; Coogan et al., 2003; Pearce, 2008; 2014). However, the abundance of pristine Proterozoic and especially Archean rocks or primary igneous minerals that contain an undisturbed major and trace element inventory, and corresponding isotope data is limited by effects of metamorphism, associated hydrothermal, metasomatic or erosional processes.

Among the long-lived decay systems, the ¹⁴⁷Sm-¹⁴³Nd and ¹⁷⁶Lu-¹⁷⁶Hf decay systems are common tools to determine evolution of mantle depletion, as their parent-daughter pairs are comparatively immobile during metamorphism (e.g., Blichert-Toft et al., 1999; Vervoort and Blichert-Toft, 1999; Rizo et al., 2011). During mantle melting and crustal

differentiation processes, both Sm and Lu are more compatible in the remaining mantle than Nd and Hf, resulting in higher Sm/Nd and Lu/Hf ratios than in the corresponding melt. Thus, the depleted mantle evolves progressively to more radiogenic, superchondritic ¹⁴³Nd/¹⁴⁴Nd and ¹⁷⁶Hf/¹⁷⁷Hf values, whereas the opposing crustal sections evolve to less radiogenic, subchondritic regimes. The ¹³⁸La-¹³⁸Ce systems, which attracts a lot of recent attention for the use of mantle evolution, behaves opposite to ¹⁴⁷Sm-¹⁴³Nd and ¹⁷⁶Lu-¹⁷⁶Hf (e.g., Boyet et al., 2019; Israel et al., 2020; 2023; Hasenstab et al., 2021). During magmatic processes, La is more incompatible compared to Ce, which results in isotopically depleted mantle domain. Consequently, for older metamorphic rocks the recent use of studying the combined Ce-Nd-Hf isotope systems has improved the understanding of the early Earth evolution (e.g., Makishima and Nakamura, 1991; Makishima et al., 1993; Hasenstab et al., 2021).

In contrast to Sm-Nd and Lu-Hf, there are little robust studies for the radiogenic Sr evolution of the Archean mantle, as both Rb and Sr are highly mobile in magmatic processes (e.g., Moorbath et al., 1981; McCulloch et al., 1983; Machado et al., 1986; McCulloch and Bennett, 1994). This system is rather used for the constraining the emergence of the evolved continental crust, as inferred by feldspar; weathering processes, and its effect on the seawater composition, which is for instance recorded by chemical minerals such as carbonates (see **Chapter 2**). However, pioneering works of Hart and Brooks (1977) and Machado et al. (1986) have shown that analyzing primary mafic minerals from Archean mafic to ultramafic rocks might preserve hints on the Sr isotope evolution of the Archean mantle.

One of the most powerful but also complex isotope systems for investigating the mantle-crust evolution are the U-Th-Pb isotope systematics. Especially the utilization of U-Pb system has broadened the understanding regarding the Earth's differentiation history and the investigation of the Earth's age (e.g., Holmes, 1947; Stacey and Kramers, 1975; Vervoort et al., 1994; Kramers and Tolstikhin, 1997; Maltese and Mezger, 2020). In contrast to other traditional radiogenic systems, such as the long-lived Sm-Nd or Rb-Sr systems, the U-Th-Pb system is not only isotopically, but also geochemically more intricate. Both parent elements, U and Th are incompatible in nearly all silicates (e.g., Galer and O'Nions, 1985). Additionally, under oxidizing conditions U is easily remobilized and thus fractionated from Th (e.g., Elliott et al., 1999). Lead in contrast, is

rather chalcophile and siderophile (Oversby and Ringwood, 1971), and is moderately incompatible in mafic reservoirs but compatible in K-feldspar (Kramers and Tolstikhin, 1997). Lead has four naturally occurring stable isotopes, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb. The latter three isotopes however exhibit an increasing radiogenic component produced by three respective decay series of ²³⁸U, ²³⁵U, and ²³²Th. Interestingly, due to their variable geochemical behavior during magmatic processes, difficulties arose in interpreting the uranogenic (produced by ²³⁵U or ²³⁸U decay) and thorogenic (decay of ²³²Th) Pb isotopes occurred from observations of ²⁰⁶Pb/²⁰⁴Pb excess in oceanic basalts, i.e., Mid-ocean ridge basalts (MORB, representing the depleted upper mantle), ocean island basalts (OIB, representing the lower mantle), and marine sediments. The respective crustal and mantle reservoirs are more radiogenic than the expected time-integrated Pb isotope composition that evolved from the primordial Pb in a closed-system (Fig. 1.1; Allègre, 1969; 1987).

This isotopic discrepancy and the radiogenic characteristics of MORB lead to formulating the 'first lead paradox'. Originally, it was expected that MORB exhibit an unradiogenic Pb isotope composition because U behaves more incompatible than Pb during the prolonged depletion history by mantle melting (Hofmann, 1988). Elemental fractionation of the U/Pb ratio by mantle melting was believed to reduce the uranogenic increase of the Pb isotope composition of the depleted mantle. However, all modern mantle derived mafic rocks are more radiogenic than the time-integrated Pb isotope composition for the bulk silicate Earth (BSE; Fig. 1.1). Possible explanations for the first Pb paradox include a possible complementary hidden reservoir that evolved with a lower U/Pb ($\mu = {}^{238}U/{}^{204}Pb$) for compensating the radiogenic increase (e.g., Murphy et al., 2003; Hofmann, 2008), such as the storage of unradiogenic lead in the lower continental crust (Kramers and Tolstikhin, 1997) or protracted uptake of lead by the core (Allègre, 1987; Wood and Halliday, 2005). Alternatively, other studies propose several mechanisms for elemental partitioning of U and Pb, such as preferential recycling of oxidized U into the mantle (e.g., Staudigel et al., 1995), the storage of Pb in mantle sulfides (e.g., Hart and Gaetani, 2006; Burton et al., 2012) or in the crust by hydrothermal processes (e.g., Peucker-Ehrenbrink et al., 1994; Elliott, 2003).

A 'second lead paradox', the so-called 'kappa conundrum' results from observing an offset of the present-day $\kappa = {}^{232}\text{Th}/{}^{238}\text{U}$ ratio of the modern Earth's mantle, which is much lower than the time integrated κ_{Pb} -value as inferred from the ²⁰⁸Pb/²⁰⁴Pb isotope composition (Fig. 1.1c; Elliott et al., 1999) of mantle-derived mafic rocks (e.g., Tatsumoto, 1978; Galer and O'Nions, 1985; Kramers and Tolstikhin, 1997). One possible explanation for the '*kappa conundrum*' is by increasingly recycling oxidized U into the Earth's mantle during the Proterozoic and Phanerozoic (e.g., Kramers and Tolstikhin, 1997; Elliott et al., 1999). Hofmann and White (1982) already proposed that the preferential recycling of U into the mantle is due to the dissolution of U under oxidizing conditions of oxygen-rich atmosphere. Thus, the change in Th/U ratio might be a possible tracer for the interaction of mantle evolution, atmospheric and weathering chemistry and mantle refertilization processes.



Figure 1.1: U-Th-Pb isotope systematics of Mid-ocean ridge basalts (MORB) and ocean-island basalts (OIB) from literature data (after Elliott et al., 1999; compiled data by Stracke et al., 2003). In (a) $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ space with a 4.56 Ga geochon reference line and single-stage growth curves for BSE (bulk silicate Earth) and μ -values ($^{238}U/^{204}Pb$) of 8.0, 8.2, and 8.4. In (b) $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ space with single-stage growth curve of a fixed μ -value of 8.0 and coupled κ -values ($^{232}Th/^{238}U$) of 3.6, 3.8, and 4.0. In (c) Time-integrated κ -values, calculated from Pb isotope compositions (κ_{Pb}) vs. measured κ -values of MORB samples (compiled by Elliott et al., 1999).

For unravelling the Archean mantle evolution of the isotope systems more susceptible to alteration, e.g., Rb-Sr and U-Th-Pb, previous studies were mainly based on leaching of relatively fresh mafic whole rocks for removing radiogenic components (e.g., Smith et al., 1992; Blichert-Toft et al., 1999; Frei et al., 2004; Toulkeridis et al., 2021). By this approach, a robust Pb isotope measurement is possible, but the determination of elemental concentrations or ratios is not achieved, since U and Th are also fractionated from Pb by this process. Alternatively, Sr and Pb data were obtained by analyzing more robust archives, such as barites, sulfides (galena, chalcopyrite; pyrite) or K-feldspar (e.g., Richards et al., 1981; Richards, 1983; Gariépy and Allègre, 1985; Kamber et al., 2003), where U-Th concentrations are low and age correction is only minor. There are several advantages in using such minerals for pinpointing the Sr and Pb isotopic evolution of the Earth's mantle. First, all these minerals maintain the near-initial isotope composition, since both Sr (except for sulfides and feldspar) and Pb are preferentially incorporated, resulting in extremely low Rb/Sr, U/Pb, and Th/Pb ratios. However, the formation of these minerals is often associated with secondary processes, such as seawater-crust interaction or intra-crustal magmatism. Therefore, direct inferences on the mantle evolution are sometimes questionable. A more direct approach is the isotopic measurement of fresh minerals of mafic rocks (e.g., Machado et al., 1986; Carignan et al., 1995). Primary mafic minerals, such as olivine, clino- or orthopyroxene crystallize from mafic melts that are directly linked to the corresponding mantle and, hence, inherit its isotope composition. Unfortunately, in contrast to galena or K-feldspar, fresh mafic minerals are rare, have low Sr and Pb concentrations, and are additionally prone for secondary processes. Therefore, an accurate simultaneous measurement of the isotope compositions as well as the determination of the Rb/Sr, U/Pb, and Th/Pb parent-daughter ratios are essential for the Archean mantle evolution.

In the present study, we extend the work of Hasenstab et al. (2021) and Tusch et al. (2021) for the Pilbara Craton, northern Western Australia, and of Szilas et al. (2018) for the Seqi Ultramafic Complex of the North Atlantic Craton, southern West Greenland in three directions: first we assess the robustness of initial Nd, Sr, and Pb isotope composition of primary mafic minerals, such as clinopyroxene and pyrite for Pilbara, and olivine, orthopyroxene, hornblende, phlogopite, and secondary talc for the Seqi Ultramafic Complex; secondly, we provide age constraints on the different isotope

systems; and finally we determine the initial μ - (²³⁸U/²⁰⁴Pb), ω - (²³²Th/²⁰⁴Pb), and κ -values (²³²Th/²³⁸U) of the corresponding precursor sources of the mafic minerals, providing conclusions on Archean mantle evolution.

1.3. Geological setting and sample selection

1.3.1. Pilbara Craton, Western Australia

The Pilbara Craton in Western Australia comprises the world's best-preserved and least metamorphosed Paleo- to Neoarchean successions of mafic-ultramafic and felsic volcanic rocks and granitic intrusions, with a prolonged volcanic activity from 3.59 – 2.63 Ga (Van Kranendonk et al., 2007; Smithies et al., 2007). Based on geochemical and structural constraints, the Pilbara Craton is subdivided into the East Pilbara Terrane (EPT), the West Pilbara Superterrane (WPT), and the Kuranna Terrane (Fig. 1.2). Here, we will only describe the volcano-sedimentary successions of the EPT and WPT in more detail, because they comprise the sample localities of this study.

The EPT consists of four well characterized volcano-sedimentary groups (Warrawoona, Kelly, Sulphur Springs, and Soanesville groups) that were deposited from 3.53 to 3.1 Ga, forming the Pilbara Supergroup (Van Kranendonk et al., 2007; 2019). The



Figure 1.2: (a) Simplified geological map of the East Pilbara Terrane (EPT) and West Pilbara Superterrane (WPT), modified after Van Kranendonk et al. (2007; 2010). In (b) generalized lithostratigraphy of the EPT and WPT (modified after van Kranendonk, 2006; Hickman, 2012). Colored diamonds (clinopyroxene) and circles (pyrite) refer to sampled mineral separates from the respective formations.



lowermost Warrawoona Group (3.53 - 3.43 Ga) consists of pillow basalts and komatiitic basalts, suggesting a submarine depositional environment. Hickman (1976) subdivided the mafic successions into the lower Talga Talga Subgroup and the overlying Salgash Subgroup, which were separated by felsic volcaniclastic deposits of the Duffer

Formation. Later studies however distinguish between five mafic formations (Table Top Basalt, Double Bar Basalt, North Star Basalt, Mt. Ada Basalt, and Apex Basalt), which alternate with more felsic deposits (Coucal, Duffer, and Panorama formations; Smithies et al., 2007; Van Kranendonk et al., 2007).

The unconformably overlying Kelly Group shows an erosional unconformity to the older Warrawoona Group (Buick et al., 1995; Van Kranendonk, 2006; Hickman, 2012). Immediately overlying the unconformity, the Strelley Pool Formation, which comprises fluvial sandstones and conglomerates, and shallow-water marine sedimentary rocks with stromatolites and microbial mats (Allwood et al., 2006; Hickman, 2008; Van Kranendonk et al., 2002; 2010). The conformably overlying Euro Basalt consists of komatiites and tholeiitic basalts that were erupted at 3.35 Ga, followed by the rhyolitic Wyman Formation (Van Kranendonk et al., 2007).

The unconformably overlying, ca. 3.24 Ga Sulphur Springs Group is comprised of basal sandstones, komatiitic basalts and komatiites and capping felsic volcaniclastic rocks (Buick et al., 2002; Van Kranendonk et al., 2007). The younger, ca. 3.2 Ga old Soanesville Group, which consists of lower clastic sedimentary rocks (siltstones and shales) and the basaltic Honeyeater Formation, was deposited during a period of rifting (Buick et al., 2002; Van Kranendonk et al., 2007; 2010). The volcanic deposition of the Honeyeater Formation was accompanied by ultramafic to mafic sill intrusions of the Dalton Suite (Van Kranendonk, 2002; Hickman, 2012).

While the Warrawoona, Kelly, and Sulphur Springs groups were deposited during three successive mantle plume events involving depleted mantle melting (Smithies et al., 2005b; Van Kranendonk et al., 2007; 2010), the Soanesville Group was deposited during extensional rifting (Van Kranendonk et al., 2010). Conductively transported heat from the plume events, radioactive decay, and storage of intra-crustal magma resulted in softening of the middle crust leading to extensive granitic melting. The upward migration of tonalitic-granitic melts and gravitational collapse of the dense overlying greenstones led to the characteristic dome-and-keel structure of the Pilbara Craton (Collins et al., 1998; Van Kranendonk et al., 2007; 2015; 2019).

The WPT is an amalgamation of three distinct terranes: The Karratha, Regal, and Sholl terranes (Van Kranendonk et al., 2007). The Karratha Terrane, ranging in age from 3.50-3.25 Ga, was likely separated from the EPT during a 3.22 Ga rifting event (Van Kranendonk et al., 2010; Hickman, 2012). The 3.2 Ga old Regal Terrane has been interpreted to represent the rift-related oceanic crust between the separation of the Karratha Terrane and the EPT (Hickman, 2012). The younger Sholl Terrane consists of granitic intrusions and the bimodal Whundo Group (3.12 Ga), which shows arc-like geochemical characteristics that were interpreted as direct evidence for modern-style subduction in a Mesoarchean intra-oceanic arc setting (Van Kranendonk et al., 2007; Hickman, 2012).

In the late Mesoarchean, the post-orogenic deposition of the De Grey Superbasin followed the accretion and erosion of the EPT and WPT (Van Kranendonk, 2006; Hickman, 2012). This Superbasin represents a phase of lithospheric extension and subsidence, and is composed of several distinctive basins that represent either a continental basin, such as the Gorge Creek Basin (ca. 3,020 Ma) in the east, continental arc basins, such as the Whim Creek Basin (ca 3,010 Ma), or rift-related basin, such as the Mallina Basin (2,970 Ma) or Mosquito Creek Basin (2,930 Ma), respectively (Hickman, 2012). The Gorge Creek Basin is primarily composed of metasedimentary rocks, such as metamorphosed sandstones and conglomerates, cherts, banded-iron formations (BIF), and carbonaceous shales, whereas the Whim Creek Basin exhibits mostly arc-related volcanic rocks that contain Th and light rare-earth element (LREE) enrichments (Smithies et al., 2007b; Hickman, 2012). This late phase of tectonic, crustal reworking was accompanied by post-orogenic granite intrusions, the Split Rock Supersuite.

In the Neoarchean, the Pilbara Craton experienced a phase of cratonization and granitoid doming, which lead to the prominent and well-preserved greenstone synclines between granitic domes (Van Kranendonk et al., 2002; Hickman, 2012). At 2.78 Ga, the northern Pilbara Craton experienced extension and rifting. The 2.78 – 2.63 Ga Fortescue Group consists of predominantly LIP-like (Large Igneous Provinces) basaltic volcanic rocks (Mt. Roe Basalt, Hardey, Kylena, and Maddina formations) and finalizes the cratonization process (Van Kranendonk et al., 2002; Hickman, 2012). The Fortescue Group was intruded by north-northeast trending dolerite dikes, the lithosphere-derived and rift-related Black Range Dolerite in the EPT and the Cooya Pooya Dolerite in the WPT (2.77 Ga; Wingate, 1999; Hickman, 2012).

1.3.2. Seqi Ultramafic Complex, North Atlantic Craton, SW Greenland

The North Atlantic Craton in the Nuuk region, SW Greenland, hosts the largest segment of exposed Eoarchean continental crust, which is known as the Itsaq Gneiss Complex and is the best record for Eoarchean crustal evolution (IGC; Nutman et al., 1996). The studied Seqi Ultramafic Complex (SUC) is part of the much younger Mesoarchean Akia Terrane, which is located at Fiskefjord in the northern Nuuk region, adjacent to the IGC (Fig. 1.3). The Akia Terrane was formed during two episodes of crustal growth and reworking at 3.2 Ga and 3.0 Ga (Garde, 1997; Garde et al., 2000), and tectonically merged with the IGC between 2.8 and 2.7 Ga (e.g., Friend and Nutman,



Figure 1.3: Simplified geological map of the Nuuk region with the Seqi Ultramafic Complex (SUC) and several similar complexes along the Fiskefjord marked in bold. The red square outlines the area of the detailed map of the SUC shown in Figure 1.4. Regional mapping based on fieldwork by the Geological Survey of Denmark and Greenland (GEUS) (Szilas et al., 2017).

2005). The majority of the rocks are compositionally felsic and comprise metamorphosed tonalite-trondhjemite-granodiorite suite (TTGs) orthogneisses. Only minor amounts of metavolcanic and metasedimentary units are present in the Akia Terrane. Additional magmatic units comprise anorthositic complexes, layered ultramafic complexes and supracrustal/greenstone belts (Polat et al., 2002; Szilas et al., 2015). However, the geological origin of the Akia Terrane remains controversial. It was originally proposed that the complex geology, with two generations of dioritic and tonalitic section, intercalated with older remnants of supracrustal mafic rocks, was the result of magmatic accretion in a convergent plate-tectonic setting (Garde, 1990; Garde, 1997; Garde et al., 2000; Polat et al., 2015). Alternatively, a giant impact at ~3.0 Ga was suggested for a prolonged period of melting (Scherstén and Garde, 2013; Garde et al., 2014). However, recent studies by Gardiner et al. (2019) and Yakymchuk et al. (2020) rather infer granite and tonalite melting events of thickened mafic crust at various depths without the direct presence of a subduction zone, while Steenfelt et al. (2021) rather argue for a rather short residence time of only 200 Myrs of depleted mafic material.

The Seqi Ultramafic Complex is a chromite-rich and dunite-dominated peridotitic body that and covers an exposure of approximately 0.5 km² (Fig. 1.4; Szilas et al., 2017;



Figure 1.4: Detailed map of the Seqi Ultramafic Complex (modified from Szilas et al., 2017).

Whyatt et al., 2020). The SUB is one of four (along with Ulamertoq, Miaggoq, Amikoq) predominately ultramafic greenstone remnants and layered ultramafic complexes that are intercalated in the Akia Terrane (Garde, 1997; Szilas et al., 2015; 2017). The hosting Akia Terrane was previously dated by U-Pb zircon analyses and their formation age ranges from 3,050 – 2,975 Ma (e.g., Garde, 1997; 2007). Only subsidiary dioritic rocks exhibit older magmatic ages of around 3.2 Ga (Garde, 2007). Co-existing supracrustal metavolcanics have been dated at 3,070 Ma (Garde, 2007). For the SUC, two opposite main sources are discussed for its origin: Scenario (1) describes the SUC as a fragment of a depleted sub-continental lithospheric mantle that experienced large degrees of melt extraction (Bernstein et al., 2007; Szilas et al., 2017). However, the more likely scenario (2) rather interprets this ultramafic enclave as magmatic cumulates formed by olivine accumulation from a highly magnesian melt (Szilas et al., 2017). This origin is supported by chromite and Fo-rich (forsterite-rich) olivine composition, as well as the platinum group element (PGE) budget (Szilas et al., 2017).

The SUC and the complete Akia Terrane experienced retrograde granulite-facies metamorphism with local late-stage granulite to amphibolite-facies metamorphism at 2,995 – 2,975 Ma (Whyatt et al., 2020). The SUC is primarily comprised of depleted dunites, harzburgitic peridotites, and chromitites and the minerals assemblages that include various combinations of olivine, orthopyroxene, metamorphic amphibole (hornblende) and chromite (Szilas et al., 2017). Following the metamorphic event, the dunites of the SUC experienced dehydration and recrystallization. Geochronological data obtained from zircon crystal inclusions in an olivine porphyroblast yielded a ²⁷⁰Pb/²⁰⁶Pb age of $2,963 \pm 1$ Ma, dating the dehydration and recrystallization of the dunites from Seqi (Whyatt et al., 2020). Field observations and geochemical data show that metasomatic zones within the dunites are dominated by talc, antophyllite, and phlogopite, supposedly formed by olivine dissolutions by residual silica-rich fluids from pegmatitic intrusions. Triple oxygen isotope data for these mineral phases and phase relations yield a temperature range of 600 - 700 °C and pressure below 1 GPa for the metasomatic overprinting of the SUC (Whyatt et al., 2020). Zircon ages of the pegmatitic intrusions are $2,940 \pm 5$ Ma, revealing the metasomatic talc generation at the end of the metamorphic event (Whyatt et al., 2020).

1.3.3. Sample selection

For this study, a sample selection of possibly fresh mafic mineral assemblages with few alterations had to be made. In order to obtain a small set of fresh and primary mafic minerals with possibly few alteration, preliminary studies describing the whole rocks, and measurements for the major and minor element, and radiogenic W-Hf-Nd-Ce isotope compositions of the whore rocks were performed on the sample set of the Pilbara Craton (Hasenstab et al., 2021; Tusch et al., 2021). The list of samples for the Pilbara Craton is



Figure 1.5: Representative thin section images (plane polarized light = PPL; crossed polarized light = XPL) of various mafic formations from the Pilbara Craton. In (a) Mt. Ada Basalt, (b) Apex Basalt, (c) Dalton Suite, (d) Honeyeater Basalt cumulate and (e) Honeyeater Basalt volcanic rock; in (f) and (g) volcanic representatives of the Bradley Basalt formation, and (g) a coarse-grained sample of the Cooya Pooya Dolerite are shown. The following mineral abbreviations are used: amphibole (Amph), clinopyroxene (Cpx), epidote (Ep), chlorite (Chl), and titanite (Ttn).

composed of mineral separates from six basalts (Table Top, Mt. Ada, Apex, and Bradley basalts), three pyroxenites (Honeyeater Basalt, Dalton Suite), and a dolerite (Cooya Pooya Dolerite) that show the least traces of alteration and primary magmatic textures for clinopyroxene and sulfide (Fig. 1.5).

The previous study on the SUC by Szilas et al. (2017) report both whole rock major and trace element budget as well as detailed mineral descriptions of olivine, orthopyroxene, and metamorphic hornblende and their elemental composition (Fig. 1.6).



Figure 1.6: Representative thin section images (plane polarized light = PPL; crossed polarized light = XPL) of various lithological unit from the SUC (modified after Szilas et al., 2017). Images (a) and (c) show layered dunites, (b) and (d) represent peridotites, (e) and (f) show homogeneous dunites, whereas in (g) a porphyritic and in (h) a poikilitic dunite are shown. The following mineral abbreviations are used: amphibole (Amph), olivine (Ol), orthopyroxene (Opx), phlogopite (Phl), and spinel (Spl).

For this thesis, the list of mineral separates, comprising of six olivine, five orthopyroxene, three hornblende, two phlogopite, and one talc separates, derive from three layered dunites, two porphyritic dunites, one homogeneous dunite, and one peridotite (Fig. 1.6).

1.4. Analytical methods

1.4.1. Sample preparation and digestion

Based on their mineral descriptions, fifteen rock samples from several formations of the Pilbara Craton (n = 8) and from the Seqi Ultramafic Complex of the North Atlantic Craton (n = 7) were crushed, sieved into several factions of $63 - 125 \mu m$ and $125 - 250 \mu m$, and purified using a magnet separator. Subsequently, 31 mineral separates (25 mg – 4 g per separate) were prepared using binocular lenses. In total there are 14 pure separates for the Pilbara Craton, consisting of 12 clinopyroxene (cpx) and two pyrite (py) separates of the following formations: Table Top Formation (py, n = 1), Mt. Ada Formation (cpx, n = 2; py, n = 1), Apex Basalt Formation (cpx, n = 1), Dalton Suite (cpx, n = 3), Bradley Basalt Formation (cpx, n = 3), and Cooya Pooya Dolerite (cpx, n = 2). For the Seqi Ultramafic Complex of the North Atlantic Craton 17 olivine (ol, n = 6), orthopyroxene (opx, n = 5), hornblende (hbl, n = 3), phlogopite (phl, n = 2), and talc separates (tlc, n = 1) were obtained from seven respective dunitic rock samples.

Mineral factions of 20 mg to 2 g were used for U-Th-Pb, Rb-Sr, and Sm-Nd concentration and isotope composition measurements. The digestion of the mineral separates was modified and carried out after van de Löcht (2019). The mineral samples were weighted in, cleaned in an ultrasonic bath for 5 - 10 minutes with 0.1 M HNO₃, and subsequently cleaned with deionized water. After drying, the samples were weighted again, to calculate weight loss by removing of altered sections. The samples were digested in a table-top digestion procedure using a 6 ml 14 M HNO₃/ 24 M HF (1:1) mixture at 120 °C for 24 h in a pre-cleaned and closed Savillex beaker. Subsequently, the samples were dried down at 110 °C and treated with 2 – 3 droplets (twice) of 14 M HNO₃, followed by subsequent evaporation. For obtaining simultaneous isotope composition and isotope dilution data an aliquot of ca. 10 - 15 % was taken from the dissolved samples and weighted. Additionally, the 10 % aliquot was spiked with a mixed ²³⁵U-²²⁹Th-²⁰⁶Pb and ⁸⁷Rb-⁸⁴Sr mixed isotope tracers and to the 90 % aliquot a ¹⁴⁹Sm/¹⁵⁰Nd mixed tracer

was added. Following this, the sample-tracer mixture was equilibrated for 24 h at 100 °C. After evaporating to dryness, the samples were re-dissolved in 2 ml 0.5 M HBr.

1.4.2. Chemical separations and MC-ICP-MS measurements

For the respective Pb IC and Pb ID purifications, two separate HBr-HCl chemistries (200 μ l BioRad AG 1-X8 (100 – 200 mesh) anion resin) as described by Korkisch and Hazan (1965) were carried out, respectively. To ensure a clean Pb cut, these procedures were repeated (Fig. 1.7). Uranium and Th were purified from the previous residue cut of the 10 % aliquot and subsequently separated using 1.6 ml Eichrom TRU-spec (200 – 400 mesh) + 0.4 ml Eichrom prefilter material following the procedure from Luo et al. (1997). Rubidium, Sr, Sm, and Nd were purified subsequently from the matrix cuts of the Pb purification chemistry using 4 ml BioRad AG 50W-X8 cation resin (200 – 400 mesh) and 1 ml Ln-spec resin (Pin and Santos Zalduegui, 1997), respectively (Fig. 1.7).

Lead-Nd-Sr isotope compositions as well as U, Th, Pb, Sm, Nd, Rb, and Sr concentrations were measured by isotope dilution using the Thermo-Finnigan Neptune MC-ICP-MS at the University of Cologne. Measured Pb isotope compositions were mass bias corrected to a doped NBS 997 Tl standard (e.g., Rehkämper and Mezger, 2000; Kirchenbaur et al., 2012) and are given relative to NBS 981 with ${}^{206}Pb/{}^{204}Pb = 16.9405$, ${}^{207}Pb/{}^{204}Pb = 15.4963$, and ${}^{208}Pb/{}^{204}Pb = 36.7219$ (Abouchami et al., 2000). Repeated analyses of NBS 981 yield mean values of ${}^{206}Pb/{}^{204}Pb = 16.9402 \pm 170$, ${}^{207}Pb/{}^{204}Pb =$ 15.4962 \pm 210, and $^{208}\text{Pb}/^{204}\text{Pb}$ = 36.7135 \pm 270 (n = 65), respectively. For Th concentration measurements, the Th was mass bias corrected with doped NBL (New Brunswick Laboratories) CRM 112A U standard relative to IRM 035 with a ²³⁰Th/²³²Th value of 11.38×10^{-6} . Analyses for U are given relative to NBL CRM 112A ($^{234}U/^{238}U =$ 5.2841×10^{-5}). Initial Pb isotope compositions were calculated using measured U/Pb and Th/Pb ratios, and respective decay constants of $\lambda^{235}U = 9.849 \times 10^{-10} a^{-1}$ and $\lambda^{238}U =$ 1.551×10^{-10} a⁻¹ (Jaffey et al., 1971), and λ^{232} Th = 4.948×10^{-11} a⁻¹ (le Roux and Glendenin, 1963). Values of ⁸⁷Rb/⁸⁵Rb and ⁸⁷Sr/⁸⁶Sr were mass bias corrected using the exponential law and 91 Zr/ 90 Zr = 0.21795 of doped Zr for Rb (Nebel et al., 2005) and 86 Sr/ 88 Sr = 0.1194 for Sr, respectively. Measured Sr isotope compositions are given



Figure 1.7: Separation procedure for enabling the separation of Pb IC, Pb ID, Rb ID, Sr ID, Th ID, and U ID cuts. Red boxes represent tracer element for conducting concentration measurements, green boxes represent the respective ion-exchange resins, and light blue boxes are the matrix cuts that need further processing in additional separation chemistries. Dark blue boxes represent the final element cuts that are designated for measurement.

relative to a ⁸⁷Sr/⁸⁶Sr of 0.710240 for NBS 987, whereas Rb was measured relative to NBS 984 (⁸⁷Rb/⁸⁵Rb = 0.38554). Repeated measurements of NBS 987 resulted in ⁸⁷Sr/⁸⁶Sr = 0.710271 ± 40 (n = 42). Strontium isotope compositions were age-corrected using λ^{87} Rb = 1.42 × 10⁻¹¹ a⁻¹ (Steiger and Jäger, 1977). Measured ¹⁴³Nd/¹⁴⁴Nd were normalized to a ¹⁴⁶Nd/¹⁴⁴Nd of 0.7219 using the exponential law and the results are given relative to LaJolla (¹⁴³Nd/¹⁴⁴Nd = 0.511859), JNdi (¹⁴³Nd/¹⁴⁴Nd = 0.512115), and CologneAMES (¹⁴³Nd/¹⁴⁴Nd = 0.511971). The repeated analyses of the Nd standards yielded for LaJolla were ¹⁴³Nd/¹⁴⁴Nd = 0.511879 ± 10 (n = 2), for JNdi ¹⁴³Nd/¹⁴⁴Nd = 0.512128 ± 40 (n = 13), and for CologneAMES ¹⁴³Nd/¹⁴⁴Nd = 0.511981 ± 51 (n = 16). Samarium was corrected for Nd and Gd interferences and normalized as reported by (Bouvier et al., 2008). For calculation of initial ε^{143} Nd for the samples, a ¹⁴⁷Sm decay

constant of λ^{147} Sm = 6.54 × 10⁻¹¹ a⁻¹ (Lugmair and Marti, 1978) and respective **ch**ondritic **u**niform **r**eservoir values ('*CHUR*') of 0.282785 for ¹⁴⁷Sm/¹⁴⁴Nd_{today} of 0.512630 for ¹⁴³Nd/¹⁴⁴Nd_{today} (Bouvier et al., 2008) were used.

The external precision for the isotope measurements was further assessed by multiple digestions (n = 6) of the certified reference material BCR-2 (see Table 1.1). The external reproducibility for the BCR-2 was < 90 ppm (2.r.s.d.) for 87 Sr/ 86 Sr, < 50 ppm for 143 Nd/ 144 Nd, < 70 ppm for 206 Pb/ 204 Pb, < 170 ppm for 207 Pb/ 204 Pb, and < 300 ppm for 208 Pb/ 204 Pb, respectively. Total procedural blanks during this study were < 220 pg/g for Sr, < 70 pg/g for Rb, <30 pg/g for Pb, < 10 pg/g for Nd, Sm, and Th, and < 5 pg/g for U.

1.5. Results

Measured isotope compositions and element concentrations for the samples from the Pilbara Craton and from the Seqi Ultramafic Complex of the North Atlantic Craton are listed in Table 1.1. Initial isotope compositions were calculated with their respective measured parent/daughter ratios and ages of their respective formations that are reported by Wingate et al. (2009), Hickman (2012), and Szilas et al. (2017).

1.5.1. ¹⁴⁷Sm-¹⁴³Nd isotope data and Sm-Nd isochrons

Age-corrected initial ϵ^{143} Nd_(i) values were normalized to the CHUR value reported by Bouvier et al. (2008) using 147 Sm/ 144 Nd = 0.1960 and 143 Nd/ 144 Nd = 0.512630.

The initial ε^{143} Nd_(i) values of the EPT differ between their respective lithological groups (Fig. 1.8). The pyroxene separates of the Warrawoona Group range in ε^{143} Nd_(i) from -0.1 ± 0.2 to +0.3 ± 0.2 for both Mt. Ada Basalt and Apex Basalt. These data overlap with compositions of their respective host rocks reported by Hasenstab et al. (2021) and Murphy et al. (2021). Only the pyrite separates have a more depleted signature of ε^{143} Nd_(i) = +5.5 ± 0.2 (Table Top Basalt) and ε^{143} Nd_(i) = +4.2 ± 0.2 (Mt. Ada Basalt), respectively. Samarium and Nd concentrations for all separates of the Table Top Fm. and Mt. Ada Basalt range from 1.20 – 1.75 ppm and 3.08 – 5.53 ppm, respectively. Only the Apex Basalt pyroxene exhibits slightly lower concentrations of 0.417 ppm for Sm and 0.910 ppm for Nd. Excluding the pyrite separate, the pyroxene separates and their host rocks yield a Sm-Nd isochron age of 3,431 ± 57 Ma with an initial ε^{143} Nd_(i) of +1.1 (MSWD = 1.3) for the Mt. Ada Basalt (Fig. 1.8b). This age overlaps within error with previously reported age for the Mt. Ada Basalt by U-Pb zircon geochronology

 $(3,469 \pm 3 \text{ Ma}; \text{Hickman}, 2012)$ and Sm-Nd isochron ages $(3,454 \pm 53 \text{ Ma}; \text{Murphy et al.}, 2021)$, respectively. The Sm-Nd isochron of the Apex Basalt however yields an age of $3,340 \pm 130$ Ma with an initial ϵ^{143} Nd_(i) of +1.5 (MSWD = 1.5), which is still within error the accepted U-Pb zircon age of $3,443 \pm 2$ (Fig. 1.8c; Hickman, 2012).

The Sm and Nd concentrations of the Honeyeater Basalt pyroxenes of the Soanesville Group are generally lower than those of the Warrawoona Group. The Sm concentrations range from 0.304 – 0.457 ppm and Nd contents range from 0.677 – 1.07 ppm. The corresponding initial ε^{143} Nd_(i) range from +2.0 to +2.3 (± 0.2 r.s.d.), which overlap with published initial values of +1.9 to 2.3 for the whole rock samples (Hasenstab et al., 2021). The pyroxenes from the associated Dalton suite exhibit similar Sm (0.330 – 0.515 ppm) and Nd (0.680 – 1.09 ppm) concentrations, but lower initial ε^{143} Nd_(i) of +0.4 ± 0.3 to +1.2 ± 0.3. The pyroxene and their host rocks of the Honeyeater Basalt Formation (Soanesville Group) define a ¹⁴⁷Sm/¹⁴⁴Nd vs. ¹⁴³Nd/¹⁴⁴Nd linear regression corresponding to an isochron age of 3,177 ± 128 Ma (MSWD = 0.19) and an initial ε^{143} Nd_(i) value of +2.5, which is indistinguishable from previously published U-Pb zircon ages of 3,180 Ma (Fig. 1.8d; Hickman, 2012). Including the associated Dalton Suite (3,180 Ma; Wingate et al., 2009) pyroxenes, a younger Sm-Nd age of 3,058 ± 58 Ma (MSWD = 1.5) with a ε^{143} Nd_(i) = +2.9 is obtained.

For the West Pilbara Superterrane, the clinopyroxene separates of the Bradley Basalt (Whundo Group) yield elemental concentrations of 1.61 - 2.13 ppm for Sm and 4.28 - 6.35 ppm for Nd. The initial ϵ^{143} Nd_(i) values range from +0.8 to +1.0 (± 0.2 r.s.d.), which are slightly lower than in their host rocks (ϵ^{143} Nd_(i) = +1.7 to +2.0; Hasenstab et al., 2021). All Bradley Basalt samples yield a Sm-Nd isochron age of $3,087 \pm 85$ Ma (MSWD = 1.0) with an initial ϵ^{143} Nd_(i) = +1.7 ± 0.3 (Fig. 1.8e).

Clinopyroxene separates of the 2.75 Ga old Cooya Pooya Dolerite exhibit low Sm and Nd concentrations of 0.573 - 1.20 ppm and 1.49 - 3.16 ppm, respectively. The initial Nd isotope composition plot in a narrow range for ε^{143} Nd_(i) of -2.5 ± 0.2 to -2.6 ± 0.2 . Compared to the Nd isotope composition of the coeval Black Range Dike from the EPT, there is a clear overlap to its ε^{143} Nd_(i) of -2.8 ± 0.2 (Hasenstab et al., 2021). In this, a combined data plot along a linear array corresponding to a Sm-Nd isochron age of 2,802 ± 65 Ma (MSWD = 0.12) and an initial ε^{143} Nd_(i) value of -2.5 (Fig. 1.8.f.)
Sample	Formation	Mineral	Age (Ga)	U (ppm)	Th (ppm)	Pb (ppm)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	$\mu_{mineral}$	Wmineral	κ _{mineral}
East Pilbara Terra	ne, Western Australia											
Pil16-054	Table Top	ру	3.525	0.0748	0.292	55.3	12.0520 ± 23	13.7080 ± 27	32.1234 ± 66	0.0700	0.283	4.05
Pil17-010	Mt. Ada Basalt	срх	3.480	0.116	0.355	0.741	20.8042 ± 22	16.6396 ± 18	41.8095 ± 49	10.8	8.02	3.18
		cpx		0.030	0.0887	0.258	17.8136 ± 33	15.7887 ± 28	38.4982 ± 69	7.44	16.4	3.06
		ру		0.479	1.75	12.8	14.4067 ± 22	14.8228 ± 24	34.8589 ± 59	2.11	34.4	3.79
Pil16-022a	Apex Basalt	срх	3.465	0.0143	0.0464	0.176	15.5527 ± 43	14.8620 ± 34	35.5603 ± 79	4.80	22.8	3.41
Pil16-049	Dalton Suite	срх	3.180	0.00563	0.0161	0.0663	15.4485 ± 33	14.8671 ± 33	35.3986 ± 79	5.02	15.2	3.02
		cpx		0.00857	0.0269	0.107	15.5074 ± 28	14.8869 ± 31	35.4201 ± 84	5.10	15.0	2.94
		cpx		0.00778	0.0237	0.0990	16.1329 ± 23	14.9854 ± 24	35.9934 ± 62	4.91	15.1	3.07
Pil16-052a	Honeyeater Basalt	срх	3.182	0.0102	0.0103	0.226	13.9008 ± 32	14.4319 ± 33	33.0224 ± 81	2.44	2.67	1.09
Pil16-052b		cpx		0.00970	0.0323	0.0995	15.7895 ± 51	14.8889 ± 46	35.4354 ± 87	5.75	20.0	3.47
West Pilbara Supe	rterrane, Western Austr	alia										
Pil16-069	Bradley Basalt	cpx	3.123	0.0220	0.0264	0.266	17.2298 ± 26	15.5139 ± 23	37.5505 ± 56	5.14	6.60	1.28
Pil16-071	-	cpx		0.0292	0.0731	0.333	17.3325 ± 43	15.4999 ± 38	35.9503 ± 83	5.33	13.9	2.61
Pil16-075b	Cooya Pooya	срх	2.775	0.111	0.306	1.10	18.3797 ± 15	15.6971 ± 13	37.8751 ± 33	6.39	18.2	2.85
		cpx		0.0224	0.0275	0.817	16.2583 ± 16	15.3328 ± 14	35.8961 ± 40	1.63	2.14	1.31
North Atlantic Cra	ton, SW Greenland											
186455	Seqi Ultramafic	ol	2.977	0.00631	0.00619	0.0630	14.2921 ± 13	14.3927 ± 17	34.4199 ± 49	5.59	5.85	1.04
186462	Complex	ol		0.00414	0.00174	0.278	12.6777 ± 8	14.0050 ± 9	32.4587 ± 24	0.78	0.37	0.48
186464		ol		0.00648	0.00861	0.0601	16.4926 ± 12	14.8543 ± 18	36.0658 ± 36	6.41	9.00	1.40
186474		ol		0.0178	0.0167	0.250	12.9614 ± 8	14.0869 ± 14	33.3936 ± 41	3.78	3.72	0.98
186476		ol		0.0125	0.0227	0.203	13.9313 ± 11	14.2768 ± 15	33.5250 ± 46	3.35	6.31	1.89
186486		ol		0.00683	0.00262	0.175	13.1740 ± 7	14.1264 ± 11	32.7521 ± 27	2.06	0.85	0.41
186455		opx		0.0106	0.0450	0.141	14.1449 ± 16	14.3654 ± 17	34.7968 ± 45	4.26	18.7	4.39
186464		opx		0.0192	0.0795	0.105	18.1756 ± 18	15.2039 ± 15	38.8669 ± 41	11.6	49.9	4.28
186474		opx		0.0150	0.0658	0.338	12.9164 ± 6	14.0761 ± 8	33.9688 ± 25	2.40	10.9	4.54
186486		opx		0.00557	0.0347	0.147	13.5695 ± 11	14.1864 ± 13	34.2947 ± 35	2.10	13.4	6.42
186487		opx		0.0128	0.0553	0.235	13.1270 ± 7	14.1386 ± 8	33.8688 ± 23	2.97	13.2	4.46
186455		hbl		0.138	0.823	0.567	23.4818 ± 13	16.4020 ± 12	51.0627 ± 46	19.4	119	6.15
186464		hbl		0.436	1.60	0.918	40.4585 ± 24	20.0985 ± 13	66.4312 ± 61	52.6	199	3.79
186487		hbl		0.210	1.51	0.702	30.0315 ± 30	17.8531 ± 19	67.2441 ± 81	30.0	224	7.45
186464		tlc		0.00795	0.0260	0.0587	20.0560 ± 29	15.7098 ± 24	39.5651 ± 57	9.05	30.8	3.41
186474		phl		0.0513	0.618	0.707	12.8402 ± 8	14.0493 ± 11	39.6523 ± 33	4.25	52.8	12.4
186487		phl		0.0135	0.381	0.999	12.8775 ± 14	14.0992 ± 15	35.2993 ± 45	0.758	21.6	28.5
Reference Materia	1											
BCR-2				1.51	5.17	10.5	18.7565 ± 11	15.6249 ± 11	38.7364 ± 11	9.18	32.6	3.55
				1.57	5.40	10.4	18.7565 ± 11	15.6250 ± 11	38.7382 ± 11	9.73	34.5	3.55
				1.67	5.76	10.1	18.7561 ± 8	15.6269 ± 9	38.7388 ± 26	10.6	37.6	3.56
				1.66	5.97	10.4	18.7548 ± 17	15.6257 ± 18	38.7312 ± 59	10.2	38.0	3.71
				1.71	5.90	10.2	18.7554 ± 16	15.6224 ± 14	38.7261 ± 40	10.9	38.5	3.54
				-	-	10.4	18.7564 ± 21	15.6245 ± 24	38.7246 ± 61			
BCR-2	Schuth et al. (2011)	/GeoReM		1.68	5.7	10.6	18.7599	15.6201	38.7298			

isotope measurements on primary minerals from Archean mafic-ultramafic volcanic rocks Evolution of the Archean mantle constrained from combined U-Th-Pb, Sm-Nd, and Rb-Sr

Sample	Formation	Mineral	Age (Ga)	$^{206}Pb/^{204}Pb_{i}$	$^{207}Pb/^{204}Pb_i$	$^{208}Pb/^{204}Pb_i$	μ_1	ω_1	κ_1	μ_2	ω_2	κ_2
East Pilbara Terra	ne, Western Australia											
Pil16-054	Table Top	ру	3.525	12.001	13.692	32.069	8.90	41.0	4.60	-	-	-
Pil17-010	Mt. Ada Basalt	cpx	3.480	13.055	14.297	35.341	-	-	-	-	-	-
		срх		12.492	14.180	34.222	8.85	68.2	7.70			.
		ру		12.891	14.365	33.351	-	-	-	-	-	-
Pil16-022a	Apex Basalt	срх	3.465	12.134	13.838	32.493	8.46	43.2	5.11	-	-	-
Pil16-049	Dalton Suite	cpx	3.180	12.250	14.069	32.814	8.46	43.2	5.11	6.46	39.1	6.0
		cpx		12.260	14.076	32.869	8.46	43.2	5.11	6.51	36.9	5.6
		срх		13.003	14.205	33.422		-	-			
Pil16-052a	Honeyeater Basalt	cpx	3.182	12.340	14.042	32.567	8.46	43.2	5.11	6.72	31.1	4.62
Pil16-052b		cpx		12.119	13.972	32.030	8.46	43.2	5.11	5.64	15.9	2.8
West Pilbara Supe	erterrane, Western Austr	alia										
Pil16-069	Bradley Basalt	cpx	3.123	14.025	14.742	36.447	-	-	-	-	-	-
Pil16-071		срх		14.011	14.700	33.625	-	-	-	-	-	-
Pil16-075b	Cooya Pooya Dol.	cpx	2.775	14.943	15.030	35.193	-	-	-	-	-	-
		cpx		15.377	15.162	35.581	-	-	-	-	-	-
North Atlantic Cra	aton, SW Greenland						μ_{Pb}	ω_{Pb}	κ_{Pb}			
186455	Seqi Ultramafic	ol	2.977	11.015	13.672	33.492	3.07	12.0	3.91			
186462	Complex	ol		12.220	13.904	32.399	0.31	0.00	0.00			
186464		ol		12.732	14.028	34.638	6.82	22.4	3.28			
186474		ol		10.743	13.599	32.803	0.86	5.53	6.43			
186476		ol		11.969	13.845	32.523	2.45	6.35	2.59			
186486		ol		11.963	13.860	32.617	1.18	1.50	1.27			
186455		opx		11.648	13.816	31.832	2.83	14.4	5.07			
186464		opx		11.349	13.703	30.955	9.68	40.0	4.13			
186474		opx		11.512	13.767	32.242	0.725	8.80	12.1			
186486		opx		12.341	13.916	32.161	1.84	11.2	6.09			
186487		opx		11.386	13.756	31.767	1.08	8.50	7.87			
186455		hbl		12.119	13.904	32.139	18.7	116	6.23			
186464		hbl		9.603	13.316	34.787	47.7	214	4.49			
186487		hbl		12.423	13.981	31.760	29.9	218	7.29			
186464		tlc		14.752	14.544	34.673	12.9	44.4	3.44			
186474		phl		10.350	13.502	31.268	0.60	44.9	74.8			
186487		phl		12.433	14.001	31.866	0.65	17.5	27.0			
Reference Materia	d											
Reference Materia BCR-2	J	 		12.433	14.001	51.800	0.03					
BCR-2	Schuth et al. (2011).	/GeoReM										

58

Sample	Formation	Mineral	Age (Ga)	Sm (ppm)	Nd (ppm)	147Sm/144Nd	143Nd/144	Nd (±2σ)	$^{143}Nd/^{144}Nd_{i} \\$	ε ¹⁴³	Ndi
East Pilbara Terran	e, Western Australia										
Pil16-054	Table Top	ру	3.525	1.42	5.53	0.1551	0.511957	±15	0.508334	+5.5	±0.2
Pil17-010	Mt. Ada Basalt	срх	3.480	1.75	4.45	0.2375	0.513581	±8	0.508112	-0.1	±0.2
		cpx		1.20	3.08	0.2351	0.513547	±9	0.508135	+0.3	±0.2
		ру		1.37	5.21	0.1583	0.511975	±31	0.508330	+4.2	±0.2
Pil16-022a	Apex Basalt	срх	3.465	0.417	0.910	0.2774	0.514492	±16	0.508134	-0.1	±0.3
Pil16-049	Dalton Suite	срх	3.180	0.330	0.680	0.2935	0.514739	±13	0.508571	+1.2	±0.3
		cpx		0.515	1.09	0.2847	0.514534	±12	0.508551	+0.8	±0.3
		cpx		0.508	1.06	0.2892	0.514610	±11	0.508532	+0.4	±0.3
Pil16-052a	Honeyeater Basalt	срх	3.182	0.304	0.677	0.2719	0.514325	±10	0.508608	+2.0	±0.2
Pil16-052b		cpx		0.457	1.07	0.2588	0.514066	±10	0.508624	+2.3	±0.2
West Pilbara Super	rterrane, Western Austr	alia									
Pil16-069	Bradley Basalt	срх	3.123	2.13	6.35	0.2023	0.512812	±13	0.508636	+1.0	±0.2
Pil16-071	5	cpx		1.61	4.28	0.2274	0.513319	±17	0.508626	+0.8	±0.2
Pil16-075b	Cooya Pooya Dol.	срх	2.775	1.20	3.16	0.2295	0.513110	±11	0.508907	-2.6	±0.2
	5 5	cpx		0.573	1.49	0.2325	0.513174	±12	0.508915	-2.5	±0.2
North Atlantic Crat	ton, SW Greenland										
186455	Segi Ultramafic	ol	2.977	0.00434	0.0154	0.1703	0.511790	±185	0.508442	-6.6	±0.4
186462	Complex	ol		-	-	-	-		-	-	
186464	1	ol		-	-	-	-		-	-	
186474		ol		0.00225	0.00678	0.2008	0.513618	±232	0.509671	+17.6	± 0.4
186476		ol		0.00110	0.00527	0.1263	0.510231	±154	0.507747	-20.2	± 0.4
186486		ol		-	-	-	-		-	-	
186455		opx		0.00675	0.0279	0.1460	0.511252	±165	0.508382	-7.8	±0.4
186464		opx		0.0305	0.0359	0.5133	0.512012	±119	0.501920	-134.8	±0.4
186474		opx		0.00605	0.0170	0.2152	0.512077	±150	0.507845	-18.3	±0.4
186486		opx		-	-	-	-		-	-	
186487		opx		0.00620	0.0197	0.1907	0.512150	±217	0.508402	-7.4	± 0.4
186455		hbl		1.38	4.91	0.1702	0.512150	±11	0.508805	+0.6	±0.4
186464		hbl		2.68	7.95	0.2037	0.512803	±13	0.508798	+0.4	± 0.4
186487		hbl		1.17	3.66	0.1939	0.512614	±13	0.508802	+0.5	±0.4
186464		tlc		-	-	-	-		-	-	
186474		phl		-	-	-	-		-	-	
186487		phl		-	-	-	-		-	-	
Reference Material											
BCR-2				6.67	29.2	0.1379	0.512645	±13		+0.3	±0.4
				6.63	29.0	0.1384	0.512621	± 14		-0.2	±0.4
				6.67	29.2	0.1381	0.512642	±13		+0.2	±0.4
				6.45	28.2	0.1382	0.512631	±11		+0.0	±0.4
				6.62	28.9	0.1385	0.512615	±11		-0.3	±0.4
BCR-2	GeoReM			6.9	28.7	0.1383	0.512638			+0.2	

Table 1.1: (continued). Measured Sm-Nd concentrations and initial Sm-Nd isotope compositions for mineral separates from the Pilbara Craton and the SUC. isotope measurements on primary minerals from Archean mafic-ultramafic volcanic rocks Evolution of the Archean mantle constrained from combined U-Th-Pb, Sm-Nd, and Rb-Sr

Sample	Formation	Mineral	Age (Ga)	Rb (ppm)	Sr (ppm)	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr (±20	σ)	⁸⁷ Sr/ ⁸⁶ Sr _i
East Pilbara Terrane	, Western Australia								
Pil16-054	Table Top	ру	3.525	1.38	79.6	0.0503	0.715431	±11	0.712845
Pil17-010	Mt. Ada Basalt	срх	3.480	1.35	13.1	0.2981	0.715787	±15	0.700688
		cpx		0.633	9.51	0.1934	0.710124	±10	0.700327
		py		7.59	54.8	0.4013	0.721760	±25	0.701433
Pil16-022a	Apex Basalt	срх	3.465	0.303	25.9	0.0338	0.706957	±17	0.705253
Pil16-049	Dalton Suite	срх	3.180	0.0462	3.88	0.0345	0.704301	±26	0.702706
		cpx		0.0428	3.85	0.0322	0.707027	±27	0.705538
		cpx		0.0443	3.95	0.0325	0.707478	±36	0.705976
Pil16-052a	Honeyeater Basalt	срх	3.182	0.0315	3.12	0.0292	0.709270	±22	0.707919
Pil16-052b	5	cpx		0.129	7.24	0.0516	0.712534	±14	0.710149
Vest Pilbara Supert	errane, Western Austr	alia							
Pil16-069	Bradley Basalt	срх	3.123	0.446	25.6	0.0516	0.705744	±14	0.703405
Pil16-071	-	cpx		1.36	21.1	0.1869	0.710523	±17	0.702049
Pil16-075b	Cooya Pooya Dol.	срх	2.775	1.97	16.7	0.3422	0.719971	±13	0.706216
	<i>, , , , , , , , , ,</i>	cpx		13.5	34.1	1.1580	0.745112	±13	0.698569
North Atlantic Crate	on, SW Greenland	•							
186455	Seqi Ultramafic	ol	2.977	0.0212	0.0854	0.7193	0.736599	±54	0.705540
186462	Complex	ol		0.554	1.81	0.8901	0.743405	±24	0.704969
186464	1	ol		0.0179	0.0979	0.5305	0.753488	±29	0.730580
186474		ol		0.288	0.242	3.5449	1.031347*	±71	0.878277
186476		ol		0.0362	0.164	0.6395	0.755310	±63	0.727699
186486		ol		0.0517	0.0912	1.6484	0.763718	±30	0.692540
186455		opx		0.0482	0.240	0.5815	0.727727	±82	0.702616
186464		opx		0.0421	0.288	0.4240	0.737488	±72	0.719179
186474		opx		1.732	0.439	11.70	0.958088*	±77	0.452902
186486		opx		0.0183	0.116	0.4589	0.744346	±28	0.724529
186487		opx		0.217	0.255	2.5125	0.911426*	±92	0.802936
186455		hbl		0.446	9.17	0.1407	0.710783	±27	0.704706
186464		hbl		1.798	33.1	0.1572	0.711297	±12	0.704507
186487		hbl		1.583	12.2	0.3764	0.734659*	±18	0.718405
186464		tlc		0.353	0.265	3.8976	0.840136	±28	0.671837
186474		phl		-	-	-	-		-
186487		phl		1268	7.76	685.31	5.313063	±65	-24.278337
eference Material									
BCR-2				39.8	317	0.3623	0.705089	±16	-
				40.8	316	0.3729	0.705089	±17	-
				50.9	321	0.4580	0.705018	±11	-
				63.6	319	0.5757	0.705025	±11	-
				50.6	324	0.4513	0.705028	±14	-
BCR-2	GeoReM			48.5	337	0.402	0.705016		

Evolution of the Archean mantle constrained from combined U-Th-Pb, Sm-Nd, and Rb-Sr isotope measurements on primary minerals from Archean mafic-ultramafic volcanic rocks



Figure 1.8: Measured Sm-Nd concentrations (a), isotope compositions and Sm-Nd isochrons (b-f) obtained for the mineral separates and their respective host rocks from different mafic formations of the Pilbara Craton (host rock data from Hasenstab et al., 2021). All regression lines yield ages that generally overlap with the depositional ages of the respective formation within their uncertainty (see main text).

For most of the mineral separates of the SUC of the North Atlantic Craton no reliable Nd isotope measurements were possible. Generally, the Sm and Nd concentrations of all olivine separates (Sm = 1.11 - 4.34 ppb; Nd = 5.27 - 15.4 ppb), orthopyroxene (Sm = 6.05 - 30.5 ppb; Nd = 17.0 - 35.9 ppb), and phlogopite were too



Figure 1.8: (continued). In (g) measured Sm-Nd concentration of the respective mineral separates and their SUC host rocks (Szilas et al., 2017), and in (h) Sm-Nd isochron of the amphibole separates. The isochron regression line overlaps with the surrounding tonalite intrusion age (Szilas et al., 2017).

low for accurate isotope or concentration measurements (Fig. 1.8g). Only for the hornblende separates, precise Sm-Nd concentration and isotope measurements were carried out. The Sm concentrations of the SUC hornblende separates range from 1.17 - 2.68 ppm and for Nd from 3.66 - 7.95 ppm. Age-corrected ε^{143} Nd_(i) values are from +0.4 to +0.6 for hornblende separate from three different samples. The Sm-Nd isochron yields an age of 2,961 ± 133 Ma (MSWD = 0.21), within error of previously reported ages (2,978 ± 8 Ma; Szilas et al., 2017). The initial ε^{143} Nd_(i) range from +0.4 to +0.6 (Fig. 1.8h).

1.5.2. ⁸⁷Rb-⁸⁷Sr isotope data

Compared to the Nd isotope data, the Sr isotope compositions of most Pilbara clinopyroxenes show a highly heterogeneous character. For the EPT, most initial Sr isotope data of the pyroxenes and pyrites are too radiogenic relative to a primitive Archean mantle source. Initial Sr isotope compositions of these samples vary in 87 Sr/ 86 Sr_(i) between 0.705538 and 0.712845. Only clinopyroxene separates from the Mt. Ada Basalt yield age-corrected 87 Sr/ 86 Sr_(i) of 0.700327 to 0.700688. The associated pyrite yielded slightly a higher 87 Sr/ 86 Sr_(i) = 0.701433. Rubidium and Sr concentrations of the EPT pyroxenes range between 0.0315 – 1.35 ppm and 3.12 – 25.9 ppm, respectively. The pyrite sample exhibit higher concentrations for Rb (1.38 – 7.59 ppm) and Sr (54.8 – 79.6 ppm; Fig. 1.9a).

The Bradley Basalt pyroxene exhibit relatively moderate initial 87 Sr/ 86 Sr_(i) of 0.702049 – 0.703405, low Rb concentrations between 0.446 – 1.36 ppm, and elevated Sr



Figure 1.9: Measured Rb-Sr concentrations and isotope compositions obtained for the mineral separates and their respective host rocks from different mafic formations of the Pilbara Craton (a, b; host rock data from Hasenstab et al., 2021), and from the Seqi Ultramafic Complex (c, d; host rock data from Szilas et al., 2017). The variations in the Rb-Sr space show the relative susceptibility to secondary alteration processes for cpx separates from the Pilbara Craton (a) and most minerals separates from the SUC (c). Only a few selected olivine, orthopyroxene, and hornblende separates from the SUC seem to retain their primary Rb/Sr \approx 0.01, which result in (d) a Rb-Sr isochron that also overlaps with the tonalite intrusion age (Szilas et al., 2017).

concentrations between 21.1 - 25.6 ppm. For the Cooya Pooya Dolerite clinopyroxenes initial Sr isotope composition range from 0.698569 - 0.706216. The overcorrection of some initial ⁸⁷Sr/⁸⁶Sr can be best explained by secondary changes of the Rb/Sr ratio. Measured Rb concentrations range from 1.97 - 13.5 ppm whereas Sr contents for the Cooy Pooya Dolerite clinopyroxenes range from 16.7 - 34.1 ppm.

For the SUC dunites, most mineral separates exhibit extremely high 87 Rb/ 86 Sr ratios (1.65 – 685.31) which often result in overcorrected initial 87 Sr/ 86 Sr ratios. This is best explained by incomplete mineral separation of the different phases. As shown in

Table 1.1, the phlogopite separate of sample 186487 exhibits an extremely high Rb/Sr ratio of 163. Neither today's Sr isotope composition nor the initial value yield reasonable values. However, already small amounts of phlogopite contamination in the pyroxene and olivine factions obscure useful results. Only a few mineral separates exhibit robust initial values. Two olivine separates yield initial Sr isotopes values between 0.704969 and 0.705540 with low Rb (0.0212 – 0.554 ppm) and Sr concentrations (0.554 – 1.81 ppm). One pyroxene sample shows a reasonably low ⁸⁷Sr/⁸⁶Sr_(i) value of 0.702616, coupled with Rb = 0.0482 ppm and Sr = 0.240 ppm (Fig. 1.9c). Initial Sr isotopes for two hornblende separates exhibit nearly identical values between 0.704507 and 0.704706, which are regarded as robust. Their Rb concentrations range from 0.446 – 1.798 ppm and Sr is from 9.17 ppm and 33.1 ppm. Using only these mostly undisturbed samples, a Rb-Sr isochron for the SUC yields an age of 3,002 ± 350 Ma (MSWD = 0.5) and an initial Sr isotope composition of 0.70443 (Fig. 1.9d).

1.5.3. U-Th-Pb isotope data and Pb-Pb isochrons

Similar to the Sm-Nd systematics, the clinopyroxene separates from the Pilbara Craton can also subdivided by their U-Th-Pb concentrations and initial Pb isotope compositions. The clinopyroxenes assigned to the older Warrawoona Group have higher U and Th (0.0143 - 0.116 ppm and 0.0464 - 0.355 ppm, respectively), and Pb concentrations range from 0.176 - 0.741 ppm. Consequently, ²³⁸U/²⁰⁴Pb and ²³²Th/²⁰⁴Pb values vary ($\mu_{cpx} = 4.80 - 10.83$; $\omega_{cpx} = 8.02 - 22.76$; $\kappa_{cpx} = 3.06 - 3.41$). The measured 206 Pb/ 204 Pb, 207 Pb/ 204 Pb, and 208 Pb/ 204 Pb range from 17.814 – 20.804, 15.789 – 16.640, and 38.498 - 41.810 for the Mt. Ada Basalt pyroxenes and 15.553, 14.862, and 35.560 for the Apex Basalt pyroxene, respectively (Table 1.1). Corresponding pyrite samples from the Warrawoona Group exhibit varying U-Th-Pb concentrations. The Table Top Basalt pyrite has higher Pb (55.3 ppm) and lower U (0.0748 ppm) and Th concentrations (0.292 ppm), resulting in comparably low μ_{py} (0.07), ω_{py} (0.28), and κ_{py} (4.05), while the Mt. Ada Basalt pyrite has slightly lower Pb (12.8 ppm), but higher U (0.479 ppm) and Th (1.75 ppm) concentrations (Fig. 1.10a-b), resulting in higher μ_{py} (4.80) and ω_{py} (22.76), and lower κ_{py} (3.79), respectively. Accordingly, both pyrite samples exhibit low measured 206 Pb/ 204 Pb (12.052 - 14.407), 207 Pb/ 204 Pb (13.708 - 14.823), and 208 Pb/ 204 Pb (32.123 -34.859). The separates of the Table Top Basalt and of the Mt. Ada Basalt (Warrawoona Group) define a Pb-Pb isochron with an age of $3{,}623 \pm 370$ Ma, which is older than the respective eruption ages of the two formations (Fig1.10c). Only using the Pb isotope data of the Mt. Ada Basalt, the Pb-Pb isochron yield an age of $3,385 \pm 83$ Ma (not shown here; MSWD = 0.15), which overlaps the eruption age of this formation within error.

The clinopyroxene samples of the Dalton Suite and Honeyeater Basalt exhibit generally lower concentrations for U (5.63 – 10.2 ppb), Th (10.3 – 32.3 ppb), and Pb (66.3 – 226 ppb) with corresponding μ_{cpx} of 2.44 – 5.75, ω_{cpx} of 2.67 – 19.97, and κ_{cpx} of 1.09 – 3.47 (Table 1.1). The Dalton Suite pyroxenes yield the following Pb isotope compositions: ²⁰⁶Pb/²⁰⁴Pb = 15.449 – 16.133, ²⁰⁷Pb/²⁰⁴Pb = 14.867 – 14.985, and ²⁰⁸Pb/²⁰⁴Pb = 35.399 – 35.993. The clinopyroxenes from the Honeyeater Basalt yielded values of ²⁰⁶Pb/²⁰⁴Pb (13.901 – 15.790), ²⁰⁷Pb/²⁰⁴Pb (14.432 – 14.889), and ²⁰⁸Pb/²⁰⁴Pb (33.022 – 35.435), that are slightly lower. The Pb-Pb isochron regression line (Fig. 1.10a-



Figure 1.10: Measured U-Pb (a) and U-Th concentrations (b), and selected Pb-Pb isochrons (c) obtained for different mafic minerals and their respective host rocks from the Pilbara Craton (host rocks from Tusch et al., 2021). In (a) and (b) the cpx mineral separates exibit lower U-Th-Pb concentrations than their host rocks. In addition, the cpx separate show smaller U/Pb and U/Th variations than the host rocks, suggesting less post-depositional elemental fractionation and that the U-Th-Pb system is more robust than the Rb-Sr system. Pyrite separates are generally more enriched in Pb than the cpx separates. Only a few separates tend to lower U/Pb and Th/U ratios. In (c) the Pb-Pb isochrons generally overlap with the respective depositional ages of the Warrawoona Group and the Soanesville Group, respectively.





Figure 1.10: (continued). Measured U-Pb (d) and U-Th concentrations (e), and Pb-Pb isochron obtained (f) for mafic mineral separates and their respective host rocks from the SUC (host rock data from Szilas et al., 2017). In (d) and (e) the olivine and orthopyroxene separates exhibit lower and hornblende separates higher U-Th-Pb concentrations than their host rocks. In addition, most olivine, orthopyroxene, phlogopite separates and hbl-free host rocks show huge variations in the U/Pb ratios (d), whereas the Th/U seem to be more robust (e). Only olivine separates tend to higher U concentrations. In (f) Pb-Pb isochon of all olivine, orthopyroxene, and hornblende separate yield a precise age of 2.977 Ga, which matches the previously reported metamorphic age of 2.978 Ga (Szilas et al., 2017).

b) for the Soanesville Group $(3,190 \pm 240 \text{ Ma}; \text{MSWD} = 1.2)$ and for the Honeyeater Basalt separates only $(3,133 \pm 320 \text{ Ma}; n = 2)$ overlap within error with the eruption age of 3,180 Ma (Hickman, 2012).

The clinopyroxene samples from the WPT have comparable U-Th-Pb concentrations but exhibit more radiogenic Pb isotope compositions. The Bradley Basalt clinopyroxene samples have lower U (22.0 – 29.2 ppb), Th (26.4 – 73.1 ppb), and Pb (266 – 333 ppb) concentrations with the corresponding μ_{cpx} of 5.14 – 5.33, ω_{cpx} of 6.60 – 13.9, and κ_{cpx} of 1.28 – 2.61. The Cooya Pooya Dolerite separates have slightly higher concentrations for U (22.4 – 111 ppb), Th (27.5 – 306 ppb), and Pb (0.817 – 1.10 ppm), and μ_{cpx} of 1.63 – 6.39, ω_{cpx} of 2.14 – 12.22, and κ_{cpx} of 1.31 – 2.85, respectively. Their measured Pb isotope

compositions are also more radiogenic with ${}^{206}Pb/{}^{204}Pb = 16.258 - 18.380$, ${}^{207}Pb/{}^{204}Pb = 15.333 - 15.697$, and ${}^{208}Pb/{}^{204}Pb = 35.896 - 37.875$, respectively.

The respective mineral phases of the SUC have highly variable U-Th-Pb concentrations and isotope compositions (Fig. 1.10d-f; Table 1.1). The SUC hornblende samples yield the highest concentrations for U (0.138 - 0.436), Th (0.823 - 1.60 ppm), and Pb (0.567 – 0.918 ppm) and corresponding μ_{hbl} of 19.38 – 52.62, ω_{hbl} of 119.24 – 223.59, and κ_{hbl} of 3.79 – 7.45 (Table 1.1). Consequently, measured Pb isotopes for the hornblende separates are highly radiogenic with high values for ²⁰⁶Pb/²⁰⁴Pb (23.482 – 40.459), 207 Pb/ 204 Pb (16.402 – 20.099), and 208 Pb/ 204 Pb (51.063 – 67.431), respectively. The olivine samples have the lowest U (4.14 - 17.8 ppb), Th (1.74 - 22.7 ppb), and Pb concentrations (60.1 - 278 ppb), followed by the orthopyroxene separates (U = 5.57 - 200019.2 ppb); Th = 34.7 - 79.5 ppb; Pb = 105 - 338 ppb), but both mineral sets generally overlap in their Pb isotope compositions and range in measured ²⁰⁶Pb/²⁰⁴Pb from 12.678 to 18.176, ²⁰⁷Pb/²⁰⁴Pb from 14.005 to 15.204, and ²⁰⁸Pb/²⁰⁴Pb from 32.459 to 38.867, respectively. Phlogopite samples have relatively low U of 5.13 - 13.5 ppb but higher Th (381 - 618 ppb) and Pb (707 - 999 ppb), coupled with low uranogenic ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ (12.840 - 12.878) and 207 Pb/ 204 Pb (14.049 - 14.099), but relatively radiogenic thorogenic ²⁰⁸Pb/²⁰⁴Pb (35.299 – 39.652). Talc exhibits U (7.95 ppb), Th (26.0 ppb), and Pb (58.7 ppb) concentrations that are comparable to the olivine separates, but has higher measured ${}^{206}Pb/{}^{204}Pb = 20.056$, ${}^{207}Pb/{}^{204}Pb = 15.710$, and ${}^{208}Pb/{}^{204}Pb = 39.565$. Due to the wide range of the measured Pb isotopes, the entire set of mineral separates of the Seqi Ultramafic Complex yields a precise Pb-Pb isochron age of $2,977 \pm 18$ Ma (MSWD = 0.3; Fig. 1.10f), which concurs with the previously reported metamorphic age $(2,978 \pm 8 \text{ Ma; Szilas et al., 2017}).$

1.6. Discussion

1.6.1. Pilbara Craton, Western Australia

1.6.1.1. Initial Sr and Nd isotope composition of the mafic volcanic rocks from the Pilbara Craton

The geological history of the Pilbara Craton spans approximately 1 billion years of episodic volcanic activity (Van Kranendonk et al., 2007). In the Paleoarchean, volcanism of several plume-related events resulted in the mafic volcanics of the Table Top, Apex,





Figure 1.11: Neodymium-Sr isotope evolution of the primitive mantle (PRIMA), depleted mantle (DM), continental crust (TTG extraction) and Archean seawater during the Archean. In (a) initial Nd isotope compositions of the cpx separates from the Pilbara Craton can be grouped in three types: Apex and Mt. Ada basalts separates are nearly chondritic/primitive in their composition, suggesting a primitive mantle origin. Clinopyroxene separates from the Bradley and Honeyeater basalts, and Dalton Suite exhibit slightly positive initial ε^{143} Nd ratios, suggesting an origin from a depleted mantle source. Their Nd isotope compositions are generally in line with their respective host rocks (from Hasenstab et al., 2021). In contrast, cpx separates from the Cooya Pooya Dolerite are less radiogenic and are best explained by the assimilation of crustal material. More radiogenic Nd isotope composition of the pyrite separates from the Table Top and Mt. Ada basalts may suggest an isotopic disturbance (Calculations are listed in supplementary Table A1). In (b) plot of initial ⁸⁷Sr/⁸⁶Sr vs. age (Ma) in order to reconstruct the Sr isotope evolution curves of the primitive mantle, the depleted mantle, and Archean seawater (modified after Roerdink et al., 2022; see Chapter 2). One Mt. Ada Basalt cpx sample overlap with its Sr isotope composition with the proposed composition of the primitive mantle at 3.5 - 3.4 Ga, whereas the other mineral separates of this study are slightly more radiogenic, suggesting either seawater overprinting by hydrothermal alteration or postdepositional alterations.

and Mt. Ada basalt formations of the Warrawoona Group. These formations have near chondritic initial ϵ^{176} Hf_(i), ϵ^{143} Nd_(i), and ϵ^{138} Ce_(i) isotopes and, combined with their positive μ^{182} W excesses, recent studies (Hasenstab et al., 2021; Tusch et al., 2021) verified their primitive mantle origin either from lower mantle upwelling in a plume setting (Arndt et al., 2001; Smithies et al., 2005b; Van Kranendonk et al., 2007) or via a mantle overturn (e.g., Bédard, 2018). The initial Nd isotope compositions of the mineral separates overlap with their respective host rocks (Hasenstab et al., 2021) and can be assigned to the three magmatic events of the Paleo- to Mesoarchean Pilbara Craton. The clinopyroxene separates of the Warrawoona Group exhibit chondritic ϵ^{143} Nd_(i) values (Mt. Ada Basalt: ϵ^{143} Nd_(i) = -0.1 ± 0.2 to +0.3 ± 0.2; Apex Basalt: -0.1 ± 0.2), which suggest an origin from a nearly primitive mantle source (Fig. 1.11a). Only the pyrite separates tend to higher ϵ^{143} Nd_(i) values of +5.5 for the Table Top Basalt and +4.2 for Mt.

Evolution of the Archean mantle constrained from combined U-Th-Pb, Sm-Nd, and Rb-Sr isotope measurements on primary minerals from Archean mafic-ultramafic volcanic rocks

Ada Basalt. These higher values can reflect small Sm-Nd decoupling effects of hydrothermal fluids during the precipitation or are because of secondary metamorphic changes. The Mt. Ada pyrite separate, which is generally associated with hydrothermal alteration processes, also exhibits slightly more radiogenic 87 Sr/ 86 Sr_(3.48 Ga) = 0.701433 and perhaps mirrors Archean seawater composition (Fig. 1.11b), which will be further discussed in **Chapter 2**. Most clinopyroxene samples tend to radiogenic 87 Sr/ 86 Sr that are unlikely for the Sr isotopic evolution of the Earth's mantle, but are best explained by secondary alteration or by a Sr-enriched fluid overprint. However, age-corrected Sr isotope compositions of the Mt. Ada Basalt clinopyroxenes range from 87 Sr/ 86 Sr_(3.48 Ga) = 0.700327 – 0.700688, coinciding with previously published data by McCulloch (1994), and reflecting the primary Sr isotope composition of the corresponding primitive mantle source.

Through geologic time, the underlying Paleo- to Mesoarchean mantle of the Pilbara region gradually evolved from an ambient primitive composition to a more depleted source of MORB-like mafic volcanic successions (e.g., Gruau et al., 1987; Arndt et al., 2001; Smithies et al., 2007; Gardiner et al., 2017; Hasenstab et al., 2021). Positive ε^{176} Hf_(i) and ε^{143} Nd_(i) values in some Mesoarchean mafic to ultramafic volcanic rocks require depletion events prior to 3.5 Ga going back to 4.2 Ga (Hasenstab et al., 2021; and references therein). This successive upper mantle depletion is also supported by recently reported negative ε^{138} Ce_(i) values for contamination- and alteration-free mafic rocks from the Soanesville and Whundo groups (Hasenstab et al., 2021). The observed changes in their isotope and trace element compositions is most likely connected to the emergence of modern-style plate tectonics, such as rift-related volcanism and arc-related volcanism in subduction zones (e.g., Smithies et al., 2005a; Van Kranendonk et al., 2007; 2010).

The younger clinopyroxene separates from the Soanesville Group (Honeyeater Basalt), the corresponding Dalton Suite, and Bradley Basalt of the Whundo Group generally have superchondritic Nd isotopes and indicate a depleted mantle (Fig. 1.11a). In contrast, the pyroxene separates from the younger 2.7 Ga Cooya Pooya Dolerite exhibit negative $\varepsilon Nd_{(i)}$ of -2.5 to -2.6, indicating recycling of pre-existing crust (e.g., Arndt et al., 2001; Smithies et al., 2005a; Hasenstab et al., 2021; Tusch et al., 2021). For the Rb-Sr isotope system, only a few mineral separates provide robust information about the primary composition of the Archean mantle. Both clinopyroxene samples of the Bradley

Basalt that are associated with subduction initiation at 3.12 Ga and one Dalton Suite (3.18 Ga) clinopyroxene separate, associated with the preceding rifting event (Fig. 1.11b; Van Kranendonk, 2010) yield initial ⁸⁷Sr/⁸⁶Sr isotopes between 0.702049 and 0.703405. These slightly more radiogenic Sr isotopes can indicate the incorporation of an enriched component in an arc-related setting (e.g., Smithies et al., 2005a; Hasenstab et al., 2021). This enriched component may originate from the remelting of subducting mafic crust. Alternatively, the Sr isotope values might be evidence for the hydrothermal alteration through ambient Archean seawater (${}^{87}Sr/{}^{86}Sr_{(3.12 Ga)} = 0.70137$; **Chapter 2**) during the host rock emplacement.

1.6.1.2. Initial Pb isotope compositions as probes of the Archean mantle?

Determining the initial Pb isotope composition of mafic to ultramafic volcanic rocks from Archean rocks involves some obstacles. Unlike more evolved rocks, such as TTGs and Pb-rich K-feldspar, mafic volcanic rocks primarily contain phases, i.e., olivine or clinopyroxene that are low in Pb, but have higher U/Pb ratios and, hence, substantial increase of common lead with time. Fresh sulfides, i.e., galena and (chalco)-pyrite, are the only Pb-rich phases in mafic successions that may retain initial Pb isotopes but are not necessarily of magmatic origin (e.g., Richards et al., 1981; Dupré and Arndt, 1990).

Two distinct alteration processes can potentially alter the primary Pb isotope signature in mafic volcanic rocks and hence the composition of their igneous minerals: (1) hydrothermal seafloor alteration or metasomatism following rock emplacement, and (2) metamorphic processes (e.g., Dupré and Arndt, 1990). However, extensive influence of metamorphism can be excluded as most of the Pilbara Craton experienced only a minor degree of greenschist facies metamorphism (Van Kranendonk et al., 2003) and the samples of this study have exceptionally well-preserved primary magmatic features and minerals, such as pristine clinopyroxene. Hydrothermal alteration of the investigated samples can also be excluded for the most part, as in this study only the freshest pyroxenes with preserved magmatic textures are investigated.

Using the measured $\mu_{cpx/py}$ and $\omega_{cpx/py}$ (Table 1.1), the age corrected initial Pb isotope compositions of the Warrawoona Group samples range in ${}^{206}Pb/{}^{204}Pb_{(i)}$ from 12.001 to 13.055, in ${}^{207}Pb/{}^{204}Pb_{(i)}$ from 13.692 to 14.365, and in ${}^{208}Pb/{}^{204}Pb_{(i)}$ from 32.069 to 34.222, respectively (Fig. 1.12a-b). Furthermore, the initial uranogenic Pb isotope values of the Warrawoona Group cpx samples overlap with compositions of K-feldspar separates from



Evolution of the Archean mantle constrained from combined U-Th-Pb, Sm-Nd, and Rb-Sr isotope measurements on primary minerals from Archean mafic-ultramafic volcanic rocks

Figure 1.12: Initial Pb-Nd isotope variation diagrams of the clinopyroxene and pyrite separates from the Pilbara Craton compared to published K-feldspar and galena data from Paleo- and Mesoarchean TTGs of the Pilbara Craton (compiled from Hartnady et al., 2022). In (a) solid black curves illustrate the Archean Pb isotope evolution with different μ -values (= 7, 8, 9). The blue curve represents the most likely μ -value ($^{238}U/^{204}Pb = 8.46$) for the mantle source of the Mt. Ada pyroxene sample. In (b) clinopyroxene samples show a bigger range of variation in the initial Pb isotope compositions than published K-feldspar and galena data. Black curves illustrate different κ_1 - and ω_1 -values for a fixed μ_1 -value = 8. In (c) clinopyroxene separates show Nd-Pb isotope variations that distinguishes between primitive and depleted mantle sources. Blue line represents the calculated Pb-Nd isotope evolution of the primitive mantle, whereas the red curve represents the depleted mantle (see 1.6.1.3). Calculations are listed in supplementary Table A2.

Paleoarchean granitic plutons and galena from the Pilbara Craton (Richards et al., 1981; Richards, 1983; Hartnady et al., 2022). Smaller variations between cpx replicates for the Mt. Ada Basalt, and also for the younger Dalton Suite (further below), can be addressed to either incomplete removal of weathering effects via dilute acid cleaning, incorporation of more radiogenic, secondary phases, or variable degrees of contamination by crustal assimilation. The relatively small isotopic differences between the cpx replicates, however, suggest that they have retained their primary composition in U-Th-Pb in an almost completely closed system. Furthermore, it should be emphasized that the U/Th-Pb isotope system in clinopyroxenes is apparently more robust during secondary alteration or weathering events than the Rb-Sr system (Table 1.1). The accompanying pyrite sample from the Mt. Ada Basalt, for example, is slightly more radiogenic in ²⁰⁶Pb and ²⁰⁸Pb than the corresponding Mt. Ada Basalt clinopyroxene samples (Table 1.1). This more radiogenic signal can either be related to a younger hydrothermal origin of the pyrite and rather mirrors the Archean hydrothermal fluid composition than of the mafic host rock or because it was not a closed system by being more susceptible to secondary processes (Tilton and Kwon, 1990). However, both pyrite separates from the Table Top Basalt that nearly retained its initial Pb isotope composition by an extremely low U/Pb ratio and from the Mt. Ada Basalt, which still overlap with published values from galena samples (Fig. 1.12b; compiled by Hartnady et al., 2022).

On the other hand, it is striking that the ${}^{208}\text{Pb}/{}^{204}\text{Pb}_{(i)}$ isotope compositions of the Warrawoona samples are more scattered then data for the coeval granitic plutons and galena (Fig. 1.12b; Richards et al., 1981; Richards, 1983; Hartnady et al., 2022). While both Table Top Basalt and Apex Basalt samples almost agree with the published data in the initial ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ vs. ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ space, the initial values of the Mt. Ada Basalt clinopyroxenes are much higher and assume a higher ω_1 -value, but also a somewhat higher μ_1 . These variable initial Pb isotope compositions can either hint to magmatic source heterogeneities with different Th/U ratios or preferentially elemental assimilation by crustal contamination (see further below).

Interestingly, the initial Pb isotope compositions of the approximately 200 – 300 Myrs younger Honeyeater Basalt and Dalton Suite cpx separates range between the initial Pb isotopes of the Apex Basalt and Mt. Ada Basalt samples, and thus do not overlap with coeval samples of early Mesoarchean granitic plutons or galena (Fig. 1.12a-b; Hartnady et al., 2022). Putting the Pb isotope data into a tectono-magmatic context, the information from existing isotope data need to be evaluated first. There is no evidence for older, Hadean to Eoarchean crust to be present prior the deposition of the volcanic Pilbara Craton successions, e.g., by inherited zircons or detrital zircons (e.g., Kemp et al., 2015). Kemp et al. (2015) reported the occurrence of only three pre-Paleoarchean detrital zircons (3,795 – 3,681 Ma) from several Mesoarchean metasedimentary formations from the WPT and EPT, respectively, but their origins is still unknown. However, certain depletion trends, like superchondritic Hf and Nd isotopes and subchondritic Ce isotopes in younger rocks and inherited zircons are in favor for an early depletion of the mantle source, which started, depending on the source, between 3.5, 3.8, or even 4.2 Ga (e.g., Bennett et al.,

Evolution of the Archean mantle constrained from combined U-Th-Pb, Sm-Nd, and Rb-Sr isotope measurements on primary minerals from Archean mafic-ultramafic volcanic rocks

1993; McCulloch and Bennett, 1994; Kemp et al., 2015; Hasenstab et al., 2021). For this study, it is important to note that, in part, these aforementioned studies also exclude the assimilation of pre-existing Eoarchean crust in mafic formations. Both, the Warrawoona Group formations and the Paleoarchean granitic plutons have nearly identical isotope compositions (Hartnady et al., 2022). These comparable compositions have been explained by the fact that melting of mafic crust and the granite emplacement occurred within a short time interval and did not develop significant changes in the different, mafic and granitic, reservoirs (Hartnady et al., 2022). This is also seen in the Pb isotope compositions of the Warrawoona Group samples and the Paleoarchean granitic plutons, as inferred by initial Pb isotope measurements on K-feldspar and galena (Richards et al., 1981; Richards, 1983; Hartnady et al., 2022), which retained the Pb isotope compositions of their formation time. Hence, direct assimilation of young granitic material with such similar compositions would probably have no direct effect on the mafic Pb compositions (Fig. 1.12a). However, assimilation may result in increased contamination of incompatible elements, such as $U \ge Th > Pb$, Rb > Sr, and light rare earth elements (LREE), also leading to higher µ-values in the mafic rocks. However, this would not lead to a direct change in the interpretation of these samples, since the age correction to primary magmatic signatures remains accurate. In addition, the minerals studied here crystallized relatively early from their mafic precursor melts, resulting in less assimilation compared to the host melt. This can possibly be shown by slight variations in the Nd isotopes of minerals compared to their respective host rocks. Slightly lower initial Nd isotopes in the host rocks could indicate that preferential assimilation of pre-existing felsic crust occurred, which exhibited a slightly more enriched signature than the original mafic melt.

In contrast to the Warrawoona Group, the younger Honeyeater Basalt and Dalton Suite separates differ significantly in their initial Pb but also in more radiogenic Nd isotope compositions from the co-eval granitic plutons (Fig. 1.12c). Less radiogenic Pb isotope compositions, which are more similar to the older Warrawoona Group samples and older granitic K-feldspars of 3.5 - 3.3 Ga Callina, Emu Pool, and Cleland supersuites (Hartnady et al., 2022), could be explained by the assimilation of felsic material that retain their unradiogenic initial Pb isotope signature. However, this would also have a direct impact on the Nd isotope composition of the mafic melts, as the Nd isotope compositions

Evolution of the Archean mantle constrained from combined U-Th-Pb, Sm-Nd, and Rb-Sr isotope measurements on primary minerals from Archean mafic-ultramafic volcanic rocks

in the granitic bodies will have evolved towards strongly subchondritic Nd isotope ratios within 200 – 300 Myrs. There is no such isotopic evidence for this in both fresh magmatic minerals or in the respective host rocks. Small variations in Pb and Nd isotope compositions between replicates only indicate minimal crustal assimilation, however, it should also be noted that the slightly more radiogenic Nd isotopes of the host rocks relative to the respective cpx separates are also explained by minimal magma-mixing of two compositionally different sources (Fig. 1.12c). It should be emphasized again that the negative co-variation between Pb and Nd isotope ratios in the depleted mafic rocks has already been mentioned in previous studies, where they were also interpreted as not indicative for significant crustal assimilation (Vervoort et al., 1994). Thus, clearly different initial Pb-Nd isotope compositions of the Mesoarchean Dalton Suite and Honeyeater Basalt cpx separates rather hint to an origin from a more depleted mantle domain than the older Warrawoona Group separates. This is also in accordance with previous studies on the host rocks (Hasenstab et al., 2021; Tusch et al., 2021).

In contrast to the above-mentioned formations, a different picture can be drawn for the Bradley Basalt Formation and for the Cooya Pooya Dolerite. While the Cooya Pooya Dolerite samples have subchondritic initial Nd isotopes (ϵ^{143} Nd_(i) = -2.5 - -2.6) and relatively radiogenic initial Pb isotope compositions, the Bradley Basalt cpx samples also show more radiogenic Pb compositions, but superchondritic Nd isotope compositions $(\epsilon^{143}Nd_{(i)} = +0.8 - +1.0)$. Although the Bradley Basalt of the Whundo Group may represent an arc-related mafic successions, those highly radiogenic Nd isotopes exclude significant incorporation of older crustal or sedimentary material (Gardiner et al., 2017; Hasenstab et al., 2021). However, the more radiogenic Pb isotope compositions do not preclude the direct assimilation of slightly older, hydrothermally altered mafic crust or dehydration of subducted altered crust, which have a stronger influence on the fluid mobile Pb than Nd (e.g., Pearce and Peate, 1985; Hawkesworth et al., 1993; Elliott, 2003). For the Cooya Pooya Dolerite, and associated volcanic rocks such as the Mt. Roe Basalt, previous studies have already been proven that assimilation of older crustal rocks significantly modified the plume-derived rocks (e.g., Mole et al., 2018; Hasenstab et al., 2021), which also led to more enriched Pb-Sr-Nd isotope compositions.

In conclusion, nearly all Paleo- to Neoarchean mineral separates of the Pilbara Craton retained their primary Nd-Pb isotope compositions and in most cases undisturbed μ_{cpx} ,

 ω_{cpx} , and κ_{cpx} values. The late Meso- and Neoarchean mafic rocks were subsequently modified by crustal recycling, whereas the Paleo- and Mesoarchean rocks from the Warrawoona and Soanesville groups provide direct information about the isotopic evolution of the Archean Earth's mantle.

1.6.1.3. $^{238}\text{U}/^{204}\text{Pb}~(\mu)$ and $^{232}\text{Th}/^{238}\text{U}~(\kappa)$ constraints on the Archean mantle evolution

It is striking that fresh clinopyroxene separates from different mafic successions of the Warrawoona and Soanesville groups, with a temporal difference of about 300 Myrs, have nearly the same initial Pb isotope compositions. Of course, secondary processes may have reset the original compositions of the older rock formations and aligned them with those of the younger ones. However, careful screening during mineral separation and robust isochrons generally argue against this. But assimilation of pre-existing mafic crust cannot be completely ruled out.

According to Kramers and Tolstikhin (1997), the **b**ulk silicate Earth ('*BSE*') exhibits a μ_{BSE} -value between 8.67 – 9.31, while κ_{BSE} ranges between 3.91 – 4.28. Maltese and Mezger (2020) reported the respective values at $\mu_{BSE} = 8.63$ and $\kappa_{BSE} = 4.05$, which is indistinguishable from previous results. Both however calculated for a homogeneous BSE. Kamber et al. (2003), however, reported Pb isotope data for feldspars from Eoarchean volcano-sedimentary rocks in western Greenland, yielding variable high- and low- μ signatures. They suggested either the presence of early mantle heterogeneities or the early Hadean to Eoarchean separation of a high- μ protocrust, enriched in incompatible U, leaving behind a U-depleted low- μ mantle source that eventually delaminated to the mantle-core boundary as a hidden low- μ reservoir (e.g., Kamber et al., 2003) or is still present in subcontinental lithospheric mantle ('*SCLM*'; Zhang et al., 2020). Mantle heterogeneities for the Pilbara Craton are also reported by Tusch et al. (2021) for observed μ^{182} W variations and by Nebel et al. (2014) and Hasenstab et al. (2021) to explain the spread in initial Hf-Nd isotope data.

Based on the nearly chondritic initial Nd isotope compositions of the Warrawoona clinopyroxene samples and the already mentioned plume-related origin, a one-stage model of the Pb isotope evolution for the Archean mantle can be suggested. Assuming an initial Earth's composition that mirrors the Canyon Diabolo Troilite (*CDT*'; Tatsumoto et al., 1973; Blichert-Toft et al., 2010), the least radiogenic samples of the Warrawoona



Figure 1.13: Comparison of the initial Pb isotope compositions of clinopyroxene and pyrite separates from the Pilbara Craton and calculated Pb isotope evolution curves of the primitive mantle (a-b) and depleted mantle (c-d) with the onset of depletion at 3.8 Ga. The blue line in (a) an (b) represents the preferred μ_1 (8.46) and κ_1 -value (= 5.11) for the Archean primitive mantle of the Pilbara Craton. However, variations in κ_1 -value (b) for the respective mafic formations are visible. Calculations in (c-d) suggest that the Honeyeater Basalt and Dalton Suite cpx separates are derived from a 3.8 Ga depleted mantle source with a μ_2 -value = 6.46 and κ_1 -value = 6.05 (green line). Calculations are listed in supplementary Table A2.

Group yield μ_1 -values of 8.90 for Table Top Basalt, μ_1 of 8.46 for Apex Basalt, and μ_1 of 8.85 for Mt. Ada Basalt, respectively (Fig. 1.13; Supplementary Table A3). The μ_1 of the Table Top Basalt must be taken with caution, as it was calculated on a pyritic sample that may have been formed by a secondary alteration process between the erupting mafic melt and the cooling seawater, and other processes may have contributed to subsequent changes. The other two μ_1 -values for the Archean primitive mantle, however, are in a similar range as the μ_{BSE} -values for the BSE mentioned so far (e.g., Kramers and Tolstikhin, 1997). If we use the recent model of Maltese and Mezger (2020), the initial Pb isotopes of the Warrawoona Group are difficult to reproduce. They assume a highly

depleted proto-Earth by Pb sequestration into the Earth's core and a complementary initial high- μ mantle reservoir of ≥ 100 . A giant impact at 69 Ma after solar system formation led to mantle replenishments and resulted in the decrease in U/Pb to the proposed μ_{BSE} of 8.63. If we use this model, a high- μ reservoir would be necessary as a source to create the initial Pb isotopes of the Warrawoona Group (see supplementary Table A3). This assumes, of course, that this source has not been previously depleted. For reasons of simplicity, we prefer the simpler model for this study using a μ_1 -value of 8.46 to 8.85 (Fig. 1.13a).

As mentioned above, both the older Warrawoona Group samples and the younger samples from the Mesoarchean Honeyeater Basalt and Dalton Suite can all be modelled with a one-stage Pb evolution model using the same μ_1 range of 8.46 to 8.85. However, considering the age difference of more than 200 Myrs and the different initial Nd isotope compositions, no one-stage model can be applied to the Mesoarchean samples. It is striking that all samples of the Honeyeater Basalt and Dalton Suite, even those separates that are probably less pure, have consistent initial Pb isotope compositions. In addition, as mentioned in previous studies, the samples of the Mesoarchean Honeyeater Basalt and Dalton Suite show rather depleted signatures and are probably derived from a mantle source that has been depleted for several 100 Myrs (e.g., Smithies et al., 2005a; Hasenstab et al., 2021). This is also supported by their unradiogenic initial Pb and superchondritic Nd isotope compositions. Vervoort et al. (1994) have shown that there is a co-variation between radiogenic Nd isotopes and low Pb isotopes in Archean mantle-derived rocks, which also argues for an early depletion of the upper mantle. As mentioned by Elliott et al. (1999), elements such as U and Th preferentially enter the melt, leaving a residual mantle depleted in U and Th, and hence low- μ environments, respectively. This depleted mantle source accordingly develops a lower uranogenic and thorogenic Pb isotope composition than a primitive mantle domain. Below, we will therefore consider Pb isotope evolution of a more depleted mantle domain and a two-stage model for the Mesoarchean samples.

If we assume that the depletion of the Australian mantle began by ca. 3.7 - 3.8 Ga (Fig. 1.13c-d), we can assume a primitive mantle μ_1 -value of at least 8.46 up to that time. This value corresponds to the μ_1 -value for the Apex Basalt with the most primitive Nd isotope composition. Furthermore, if we consider no gradual depletion of the upper

mantle but an instantaneous depletion, where the μ_2 (= μ_{DUM}) would be between 5.64 – 6.72 for the 3.18 Ga Honeyeater Basalt and 6.46 – 6.51 for the 3.182 Ga Dalton Suite to explain their compositions. Accordingly, we would have tapped here low- μ residual mantle, similar proposed for Greenland several hundred million years earlier (Vervoort et al., 1994). For Pilbara, this means that the continuous depletion of the low- μ_2 upper mantle evolved into an unradiogenic Pb isotope domain, the composition of which resembles those of the ca. 300 Myrs older plume-derived Warrawoona samples, but at the same time evolving towards a superchondritic ϵ^{143} Nd signature with a higher ¹⁴⁷Sm/¹⁴⁴Nd ratio (Fig. 1.12c). Small-scale variations between both nearly contemporaneous Honeyeater Basalt and Dalton Suite can then be explained either by a variable depletion of co-existing domains or variable degrees of crustal assimilation of pre-existing mostly primitive material.

As for thorogenic Pb, in our calculation the samples from the Warrawoona Group show relatively high κ_1 - (Table Top Basalt: $\kappa_1 = 4.60$; Mt. Ada Basalt: $\kappa_1 = 7.70$; Apex Basalt: $\kappa_1 = 5.11$) and ω_1 -values (Table Top Basalt: $\omega_1 = 40.1$; Mt. Ada Basalt: $\omega_1 = 68.2$; Apex Basalt: $\omega_1 = 43.2$), respectively, in order to explain the initial ²⁰⁸Pb/²⁰⁴Pb compositions. These κ_1 -values are higher than those of the present-day mantle (κ_{BSE} = 3.9; $\kappa_{DUM} = 2.5$; Galer and O'Nions, 1985; Elliott et al., 1999). Several studies have already suggested that there has been a successive decline in the mantle's Th/U ratio over the Earth's history (e.g., Allègre et al., 1986; Elliott et al., 1999; Zartman and Richardson, 2005). Since magmatic processes are assumed to have no effect on the Th/U ratio, only secondary processes, such as the subsequent addition of U, can change this ratio. Using both the one-stage Pb evolution model for the Warrawoona samples and the two-stage Pb evolution model for the younger 3.18 Ga samples (Honeyeater Basalt: $\kappa_2 = 2.81 - 4.62$, $\omega_2 = 15.9 - 31.1$; Dalton Suite: $\kappa_2 = 5.66 - 6.05$, $\omega_2 = 36.9 - 39.5$), we find that the initial 208 Pb/ 204 Pb are reproduced by relatively high κ_1 -values that are different to those proposed for the present-day mantle. A striking feature here is the relatively wide range of κ_1 values, between different stratigraphic units. This could reflect either analytical artifacts that make the values appear extremely high or it could also indicate early kinhomogeneities in the Archean primitive mantle. To assess this more precisely, further measurements are necessary. However, it is also noteworthy that the depleted Archean mantle has a higher κ_{DUM} - and correspondingly higher ω_{DUM} -values than the present-day mantle analogues. Consequently, both sets of clinopyroxene samples, from the Archean primitive mantle and depleted mantle, respectively, support the proposed model in which an larger range of κ for the early Earth explains the second lead paradox, the κ -conundrum.

A precise determination of the μ -values for the magmatic source for the Bradley Basalt and Cooya Pooya Dolerite is of less importance here, because these rocks have undergone substantial contamination and likely tap an older subcontinental lithospheric mantle. As already noted by other studies (Smithies et al., 2005a; Van Kranendonk et al., 2010), the onset of modern-like plate tectonics started at around 3.2 Ga for the Pilbara Craton. For the Bradley Basalt Formation of the Whundo Group, a clear arc-related origin is proposed, which is visible here in more radiogenic Pb isotope compositions, hinting to recycling of radiogenic Pb material by subducted altered oceanic crust. No visible change in initial Nd isotopes argues against significant amounts of recycled evolved continental sediments. For the Cooya Pooya Dolerite, it can be assumed that either evolved crustal material was recycled into the subcontinental lithospheric mantle or that the ascending mafic melt directly assimilated crustal material (Mole et al., 2018). This resulted in more unradiogenic initial Nd and the simultaneous increase of the Pb isotope compositions, which hinders the determination of the original mantle composition prior the onset of subduction difficult.

1.6.2. Seqi Ultramafic Complex, southern West Greenland

1.6.2.1. Pb-Pb, Sm-Nd, and Rb-Sr isochrons – Temporal constraints on the metamorphic event at 2,977 Ma

Our data for the Seqi Ultramafic Complex are the first mafic mineral-based Rb-Sr, Sm-Nd and Pb-Pb isochron ages for an ultramafic complex of the Archean North Atlantic Craton. The Pb-Pb isochron for the SUC (Fig. 1.10f) yields an age of $2,977 \pm 16$ Ma (n = 14) and is in good agreement with the previously reported late-tectonic granulite facies metamorphism of the Akia Terrane between 2,997 - 2,975 Ma (e.g., Garde, 1997; 2007; Garde et al., 2014) and also overlaps with the intrusive U-Pb zircon age of the surrounding orthogneiss of $2,977 \pm 8$ Ma (Szilas et al., 2017). Contrary to the accompanying chromitites, no primary signature dating the magmatic emplacement of the dunites has been preserved. For all four ultramafic bodies of the Fiskefjord region of the Akia Terrane, unpublished Re-Os ages suggest a magmatic age of 3.2 Ga (Szilas, personal communication). During the regional thermal event at 3.0 Ga, incompatible and fluid mobile elements such as U, Th, Pb, Rb, and Sr and, to a certain extent, LREE were redistributed (Taylor et al., 1980; Garde, 1990; 1997; 2007) and overprinted the originally depleted SUC dunites (Szilas et al., 2017). This metamorphic age is also supported by the SUC hornblende separates (n = 3), yielding a Sm-Nd isochron age of 2,961 \pm 133 Ma and by the phlogopite free mafic mineral Rb-Sr isochron of 3,002 \pm 350 Ma (n = 5), even though their respective ages might also overlap, within errors, with those of the magmatic SUC emplacement. However, remnants of original magmatic isotopic signatures are unlikely to be preserved.

1.6.2.2. Origin of Rb-Sr, U-Pb, and REE and possible alteration / contamination of the isotopic systems

Obtaining initial isotope compositions for the respective mineral phases of the SUC is hampered by several processes. First of all, Szilas et al. (2017) already endorsed the depleted character of the dunites and harzburgites of the SUC that represent a remnant layered ultramafic complex or magma conduit. The overall low abundances of trace elements are attributed to a near-anhydrous magma derived from a depleted mantle with extremely high degrees of partial melting of up to 40 % (Szilas et al., 2017). However, Szilas et al. (2017) also reported Fe-Mg exchange within mafic minerals phases, which are explained by metamorphic overprinting and obscured primary isotope signatures. This is also shown in the general enrichment of LILE and LREE relative to the more fluid immobile HFSE and HREE in nearly all studied mineral phases (Szilas et al., 2017). Only the metamorphic hornblende separates are nearly evenly enriched in LILE, REE and HFSE, but can be clearly linked to the metamorphic recrystallization of initially magmatic clinopyroxene (Szilas et al., 2017). Hence, nearly all Pb-Sr-Nd isotopic data here rather represent the metamorphic fluid composition than primary magmatic signatures.

However, other secondary processes, such as late-metamorphic, retrograde mineral recrystallization/phase transformations or cross contamination by enriched phases can also obscure isotopic signatures. For the SUC and the Akia Terrane in general, several thermal and metamorphic events are reported that could potentially change the ^{238,235}U/²³²Th-^{206,207,208}Pb, ⁸⁷Rb-⁸⁷Sr, and ¹⁴⁷Sm-¹⁴³Nd isotopic systems to variable degrees. Several younger Late Archean to Proterozoic metamorphic and deformation events, and plutonic events are reported (e.g., Garde, 1997; Friend and Nutman, 2005;

Kirkland et al., 2018; Yakymchuk et al., 2020). For instance, Whyatt et al. (2020) report late-stage metasomatism at 2,940 \pm 5 Ma at the contact zone of the SUC and the surrounding tonalitic-trondhjemitic intrusion that led to talc, antophyllite, and phlogopite formation. However, the robustness of all three isochrons, yielding the 2,977 Ma thermal event (Szilas et al., 2017), consider an overall minor effect of the late-metasomatism on the studied samples and exclude the influence of younger thermal events.

Another cause for altered isotope composition is the potential contamination due to incomplete mineral separation of enriched accessory phases. Minor phases, enriched in specific elements, can potentially modify parent-daughter ratios of isotope systems or even dominate the budget of radiogenic nuclides. Our isotope data and the isochrons for the SUC samples clearly show that in most cases no such cross contamination occurred (Figs. 1.8; 1.10). Only for the Rb-Sr isotope system, the presence of Rb-enriched phlogopite (${}^{87}\text{Rb}/{}^{86}\text{Sr} > 685$) also featuring extremely high ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ as high as 5.3131 potentially changed the Sr isotope composition of some olivine and orthopyroxene separates with their low Sr concentrations (Fig. 1.9c). Significant amounts of the metasomatic phlogopite (see Whyatt et al., 2020) only exist in two samples (186474 and 186487). However, the occurrence of small amounts of disseminated phlogopite as well as cross contamination during the separation cannot be excluded. This led to the later exclusion of those samples for the further discussion of the Rb-Sr system. Interestingly, because of lower or comparably low Pb and REE concentrations, the phlogopite contamination had only minor effects on the U-Th-Pb system and no influence on the Sm-Nd system in hornblende.

1.6.2.3. Multi-stage isotopic evolution model for the SUC

The initial Nd isotope composition of the metamorphic hornblende ranges from ϵ^{143} Nd_(i) from +0.4 to +0.6 for all three separates, making it slightly superchondritic at 2.977 Ga. For the respective mineral phases, the initial ⁸⁷Sr/⁸⁶Sr ratios vary between 0.704507 and 0.705540 for two olivine and two hornblende separates, respectively. One opx separate has slightly lower initial Sr isotopes of 0.702616. It can be inferred that both the highly fragile Rb-Sr and the more robust Sm-Nd isotope system rather represent the metasomatic fluid that any primary magmatic relics.

In contrast to the mafic mineral phases from the Pilbara Craton, the initial Pb isotope compositions for the contemporaneous mineral phases of the SUC do vary significantly among each other. Using the measured $\mu_{mineral}$ and $\omega_{mineral}$, all samples (olivine, orthopyroxene, and hornblende) are thus much less radiogenic than in a calculated one-stage Pb evolution model and the intersection of the Pb-Pb isochron and the



Figure 1.14: In (a) and (b) comparison of measured $\mu_{mineral}$, $\omega_{mineral}$, and $\kappa_{mineral}$ -values and the calculated μ_{Pb} -, ω_{Pb} -, and κ_{Pb} -values for the SUC mineral separates inferred by the measured Pb isotope compositions, suggesting recent U addition as the SUC Pb/Pb age of 2.98 Ga is robust. Calculated μ_{Pb} -, ω_{Pb} -, and κ_{Pb} -values are listed in Table 1.1. In (c-d) ²⁰⁷Pb/²⁰⁴Pb-²⁰⁶Pb/²⁰⁴Pb and in (e-f) ²⁰⁸Pb/²⁰⁴Pb-²⁰⁶Pb/²⁰⁴Pb variations for SUC mineral separates are compared to the Pb-Pb isochron of 2.98 Ga (in c-d; green line) and the 2.98 Ga geochron of a single-stage Pb growth curve for the Earth (c-f; black line) using the Pb isotope composition of the CDT result in a $\mu_1 = 7.19$ and a $\kappa_1 = 4.48$. The Pb-Pb age of 2.98 Ga, however, does not represent the magmatic age of the SUC, but the the tonalite intrusion age and metamorphic overprint (Szilas et al., 2017).

Evolution of the Archean mantle constrained from combined U-Th-Pb, Sm-Nd, and Rb-Sr isotope measurements on primary minerals from Archean mafic-ultramafic volcanic rocks

2.977 Ga geochron (Fig. 1.14a-b). This calculated μ_1 -value of 7.19 (Fig. 1.14c-f) for a one stage Pb evolution model is slightly lower than in previous estimates for the Early Archean mantle in West Greenland with respective values of $\mu_1 = 7.5 - 7.7$ (Taylor et al., 1980; Frei and Rosing, 2001), or the Abitibi Greenstone Belt with a $\mu_1 = 7.62 - 7.92$ (Gariépy and Allègre, 1985; Dupré and Arndt, 1990), respectively. Assuming a one-stage Pb evolution model until 2.977 Ga for the SUC, μ_{Pb} - and κ_{Pb} -values for the respective minerals, calculated from Pb isotopes, show different values that indicate U addition in the measured U/Pb and Th/U ratios (Fig. 1.14a-b). Since reasonable Pb-Pb isochron ages are calculated, a rather recent U addition, probably related to surface weathering processes, can be assumed. The olivine separates are the most affected by the recent U addition. The measured $\mu_{mineral}$ tend to higher values, whereas $\kappa_{mineral}$ are decreased. The least effect on the measured ratios had the U addition to the hornblende separates, as those lie almost entirely on the 1:1 line. For the orthopyroxene separates, some lie on the line, while others deviated to lower $\kappa_{mineral}$ and higher $\mu_{mineral}$ -values.

The age of the precursor material from which the tonalites surrounding the SUC were derived is still debated. Some studies assume a rather mafic crust that was formed between 3.8 and 3.7 Ga (e.g., Gardiner et al., 2019), while a more recent study by Steenfelt et al. (2021) assumes that only 100 - 200 Myrs elapsed between mafic crust emplacement and anataxis. This has already been suggested by Taylor et al. (1980) for alkaline



Figure 1.15: Comparison of the initial Pb isotope compositions of mafic minerals separates from the SUC and calculated best fitting Pb isotope evolution curves of the primitive mantle (blue line) and depleted mantle (red line/area) with the onset of depletion at 4.2 Ga. The blue line in (a) an (b) represents the published μ_1 - (8.64) and κ_1 -value (4.05; Maltese and Mezger, 2020) for the Archean primitive mantle of SW Greenland. Assuming that the initial Pb isotope signatures of the most pristine mineral separates represent the overprint signal of the tonalite source rock, then it was most probable derived from a depleted mantle section exhibiting a μ_2 -value of ca. 6.46. High- μ growth curve (Kamber et al., 2003) is shown for reference. Calculations are listed in supplementary Tables A3 and A4.

Evolution of the Archean mantle constrained from combined U-Th-Pb, Sm-Nd, and Rb-Sr isotope measurements on primary minerals from Archean mafic-ultramafic volcanic rocks

orthogneisses of the Godthåbsfjord on the basis of Pb isotope compositions with given μ_1 -values of 7.5. However, all these studies suggest a rather mafic protolith for the Akia tonalites. In contrast to the Pilbara Craton, depletion of mantle beneath Greenland started at the latest around 4.2 Ga (Bennett et al., 1993; Frei et al., 2004). Therefore, a one-stage Pb evolution model seems unreasonable. Here we suggest a mode comparable to Pilbara, assuming a more primitive μ_1 -value of 8.63 until 4.2 Ga and the following change to a lower $\mu_2 = \mu_{DUM} = 6.6$, reproducing the most robust Pb isotope composition of selected mineral phases of the SUC (Fig. 1.15). The short residence time of the juvenile mafic crust until anataxis occurred, probably did not have a major impact on Pb isotope evolution. Observed variations in the initial Pb isotope compositions (Fig. 1.15) may be caused by the assimilation of pre-exiting crustal material that carried an old, high- μ signature (Kamber et al., 2003), although is no evidence for the presence of older crust in the Akia Terrane (e.g., Steenfelt et al., 2021).

1.6.3. Implications for the evolution of the Earth's $^{238}U/^{204}Pb$ (µ-) and $^{232}Th/^{238}U$ (κ-) values through time

Looking on modern mantle-derived basalts, it is clearly evident that most modern mantle reservoirs, e.g., the depleted upper mantle and deep-rooted hot spots, exhibit highly radiogenic Pb isotope compositions compared to the geochron, which is referred to as the first terrestrial Pb-paradox (Fig. 1.1; e.g., Allègre, 1969; Murphy et al., 2003; Hofmann, 2008).

Assuming the present bulk silicate Earth's (BSE) Pb isotope composition evolved in a closed system with the primordial Pb signature for the CDT (Tatsumoto et al., 1973) and a fixed μ_1 -value of 8.46 and κ_1 -value of 5.1, obtained by the most primitive sample of this study (Apex Basalt clinopyroxene), a one-stage Pb evolution model was calculated for inferring for Pb isotope variation of the primitive mantle (Fig. 1.16). Compared to modern MORB and OIB, the calculated ²⁰⁷Pb/²⁰⁴Pb (Fig. 1.16a) and ²⁰⁸Pb/²⁰⁴Pb (Fig. 1.16b) ratios of the primitive mantle are too radiogenic, whereas the modelled ²⁰⁶Pb/²⁰⁴Pb is too low. Furthermore, if we assume an incipient mantle depletion of the Archean Pilbara Craton at 3.8 Ga, the calculated Pb isotope composition ($\mu_2 = 5.6 - 6.6$; $\kappa_2 = 2.8 - 6.0$) of the inferred depleted mantle reservoir is too low in all three Pb/Pb ratios and does not match comparable modern mantle-derived rocks (data compiled by Stracke





Figure 1.16: Comparison of Pb isotope evolution curves in (a) $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ and (b) $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ isotope space. The initial primitive mantle isotope composition (blue line) is calculated with the values inferred from the Apex Basalt cpx sample. Assuming that the depletion of the upper mantle started at ca. 3.8 Ga for the Pilbara Craton, a shift to lower μ_2 between 5.6 – 6.6 is suggested by the U-Th-Pb isotope systematics of the cpx separates from the Dalton Suite and Honeyeater Basalt. Calculated Pb isotope evolution curves for the Archean depleted mantle however do not reproduce the Pb isotope composition of modern MORB and OIB. Only oxidized U⁶⁺ addition by subducted, altered oceanic crust and/or high- μ component can increase the mantle's μ_3 (~11.2; White, 1993) to recalculate modern MORB isotope signatures. The calculated 208 Pb- 206 Pb variations in (b) suggest no significant change of κ ($\kappa_1 \approx \kappa_2$), but a significant decline to lower κ_3 is required for matching the MORB Pb isotope signatures. Here, only a sudden increase of μ_3 to 11.2 and decrease κ_3 to 2.67 (White, 1993) is calculated. Calculations are listed in supplementary Tables A2 and A5.

et al., 2003). Comparable depleted signatures, however, were found for other Archean mafic formations, such as from mantle-derived rocks of the Abitibi Greenstone Belt (e.g., Dupré and Arndt, 1990; Carignan et al., 1993; 1995; Vervoort et al., 1994) and from the Western Australian Warrawoona Group and the Kambalda Greenstone Belt (Dupré and Arndt, 1990).

By the end of the Archean, a major atmospheric change with the significant rise of free oxygen started at the Archean-Proterozoic boundary at about 2.4 Ga (GOE; e.g., Holland, 2002; Lyons et al., 2014). This also led to a marked change in the continental weathering patterns. Under O₂-free conditions, both U and Th occur in a tetravalent state and react similarly immobile in magmatic, metamorphic, and weathering processes. However, in the presence of free oxygen, U is preferentially dissolved by oxidation into a hexavalent state, washed into the Archean oceans, and ultimately recycled into the depleted mantle via subduction of hydrothermally altered oceanic crust (e.g., Elliott et al., 1999). If we assume that free atmospheric O₂ and the U addition led to an instantaneous increase of μ (= 11.2; White, 1993) and a simultaneous decrease of κ (= 2.67; White, 1993), the present radiogenic Pb isotope composition for OIB and MORB could be modelled using a two- and three-stage approach, respectively (Fig. 1.16). Furthermore,

the shift in uranogenic Pb to higher 206 Pb/ 204 Pb corresponds to 238 U-rich U addition of post-Archean components, as the 238 U/ 235 U ratio gets successively more depleted in 235 U, due to the shorter half-life.

For a better constraint of the Earth's U-Th-Pb systematics, additional measurements on other fresh Archean mafic minerals from several mantle-derived rocks from other cratons are required. Mafic minerals and rocks that are erupted between 3.2 - 2.0 Ga and preferentially free of secondary processes could give more information on the change of both μ and κ of the Earth's mantle and over which timescales the continuous increase of the Pb isotope compositions was achieved during the Proterozoic, the '*boring billion*'.

1.7. Conclusions

The combined ¹⁴⁷Sm-¹⁴³Nd, ⁸⁷Rb-⁸⁷Sr, and ^{238/235}U/²³²Th-^{206/207/208}Pb isotope measurements and parent-daughter element concentrations on fresh Archean mafic mineral separates provide new constraints on the petrogenesis mafic-ultramafic rocks and radiogenic isotopic evolution of the Paleo- to Mesoarchean mantle and continental crust. Complementary to previous published Hf-Nd-Ce data of the host rocks, most clinopyroxene and pyrite separates reveal different mantle sources for mafic formations of the Paleo- to Mesoarchean Pilbara Craton:

- (1) Initial Pb isotopes of clinopyroxene separates from the older 3.5 3.3 Ga Warrawoona Group formations and the ca. 3.2 Ga old Bradley Basalt and Dalton Suite vary in a narrow range for the uranogenic Pb ratios, but can be distinguished into two separate groups by their initial Nd isotope compositions: the older formations are derived from a primitive mantle domain with high μ_1 -values between 8.46 8.90 and chondritic Nd isotope composition, whereas the 3.2 Ga old formations have lower μ_2 -values of 5.64 6.72 and superchondritic Nd isotopes indicating a depleted mantle source that started to diverge at ca. 3.8 Ga.
- (2) Small variations of calculated μ_1 and κ_1 -values of the respective formations (Table Top Basalt: $\mu_1 = 8.9$ and $\kappa_1 = 4.60$; Mt. Ada Basalt: $\mu_1 = 8.85$ and $\kappa_1 = 7.70$; Mt. Ada Basalt: $\mu_1 = 8.46$ and $\kappa_1 = 5.11$) may indicate small heterogeneities in the primitive Archean mantle, whereas the depleted upper mantle shows smaller variations.

(3) With the onset of modern-style plate tectonics, recycling and incorporation of older crustal material subsequently obscured the initial Pb-Nd isotope composition of late Mesoarchean and Neoarchean mantle-derived rocks.

The geochemical signatures for the Seqi Ultramafic Complex, southern West Greenland, reveal the following:

- (1) The Pb-Pb isochron defined by the mafic minerals from the SUC of the North Atlantic Craton yields an age of $2,977 \pm 18$ Ma. This age is in good agreement with previous U-Pb zircon ages of the surrounding Akia Terrane tonalites and dates both the tonalite intrusion and the retrograde metamorphism of the SUC. Selected Sm-Nd (2.960 ± 133 Ma) and Rb-Sr ($3,002 \pm 350$ Ma) isochrons on the same minerals separates confirm the metamorphic event.
- (2) Some olivine and orthopyroxene samples record secondary events as they are contaminated by secondary mineral phases, such as phlogopite. Phlogopite highly enriched in Rb and radiogenic in their Sr isotope compositions disturb the Sr isotope composition of some olivine and orthopyroxene separates but no such effect is observed for the triple Pb isotope systems. Recent U addition has possibly changed 238 U/ 204 Pb ratios ($\mu_{mineral}$) to higher and 232 Th/ 238 U ratios ($\kappa_{mineral}$) to lower values, potentially also affecting isotopic age-correction.
- (3) Robust initial Nd, Sr and Pb isotope compositions of the SUC indicate a multistage mantle-crust evolution for the overprinting precursor source. Initial ε^{143} Nd of +0.4 to +0.6 (± 0.2) and extremely unradiogenic Pb compositions are in favor of partial melting of mafic crust with a depleted mantle signature at ca. 3.0 Ga and pointing towards a continuous depletion of the Archean upper mantle for West Greenland.

In summary, this study shows that fresh mafic mineral separates from Archean mafic rocks have the potential for retaining primary magmatic signatures of their respective mantle source. Here, we could show that the Archean mantle of the Pilbara Craton evolved at least two separate domains, a lower primitive mantle that exhibits primitive μ_1 -values of 8.46 – 8.85, and the upper depleted mantle with distinctively low μ_2 -values of 5.64 – 6.72, respectively. Interestingly, for both the Archean depleted and primitive mantle domain, all calculated κ_1 -values (4.60 – 7.70) and κ_2 -values (4.62 – 6.05) are

Evolution of the Archean mantle constrained from combined U-Th-Pb, Sm-Nd, and Rb-Sr isotope measurements on primary minerals from Archean mafic-ultramafic volcanic rocks

above the compositions of the modern mantle domains ($\kappa_{BSE} = 3.9$ and $\kappa_{DMM} = 2.5$), suggesting no fractionation of Th/U by U mobilization or recycling of subducted material prior to 3.2 Ga.

CHAPTER 2

INTERSTITIAL CARBONATES IN PILLOWED META-BASALTIC ROCKS FROM THE PILBARA CRATON, WESTERN AUSTRALIA: A VESTIGE OF ARCHEAN SEAWATER CHEMISTRY AND SEAWATER-ROCK INTERACTIONS

2.1. Abstract

Calcites hosted in the interpillow void spaces of extremely well preserved, 3.47 – 3.12 Ga pillow lavas of the Archean Pilbara Craton, Australia, provide new geochemical insights into the composition of Archean seawater and its interaction with basaltic crust. We present a comprehensive dataset of major and trace elements, radiogenic ¹⁴⁷Sm-¹⁴³Nd, ⁸⁷Rb-⁸⁷Sr, and stable C-O isotopes for these calcites.

Based on their elemental composition and Post-Archean Australian Shalenormalized rare earth element and yttrium (REY_{PAAS}) patterns, two types of calcites can be distinguished. Type I (n = 9) are coarse-grained calcites with elevated Mn concentrations (478 – 14,790 ppm) and high REY concentrations that match the basaltic host rock compositions. Petrographic textures in combination with geochemical data indicate precipitation from boiling seawater trapped between pillows during basalt eruption. Small light-REY_{PAAS} depletions, only slightly super-chondritic Y/Ho (34.5 – 39.1), and low $\delta^{18}O_{(VSMOW2)}$ (+9.25 to +16.7 ‰) suggest relatively high fluid-rock interactions of boiling seawater with the basaltic host rock. These characteristics are similar to those of interstitial carbonates found in modern mid-ocean ridge basalts. Type II carbonates (n = 6) are fine-grained, low-Mn (13.7 – 420 ppm) calcites that exhibit comparably high Sr concentrations (825 – 2,516 ppm) and anoxic modern seawater-like REY_{PAAS} patterns, strong super-chondritic Y/Ho (39.1 – 55.8) and $\delta^{18}O_{(VSMOW2)}$ values of 9.10 – 13.18 ‰. These features hint to direct calcite precipitation from seawater within the degassing space with little fluid-rock interaction.

Almost all (Type I and Type II) of the calcites investigated here, combined with their respective host rocks, yield well-defined Sm-Nd isochron ages for the Apex (3,466 \pm 23 Ma), Euro (3,365 \pm 43 Ma), Honeyeater (3,187 \pm 33 Ma), and Bradley (3,131 \pm 24 Ma) formations. Only calcites from the Mt. Ada Basalt and their associated host rocks show a ~100 Myrs younger Sm-Nd isochron age (3,361 \pm 22 Ma) compared to the U-Pb zircon age of formation.

Highly radiogenic initial Sr isotope compositions of the high-Mn calcites (Type I) and low Sr concentrations, suggest Sr remobilization for these calcites. In contrast, the low-Mn calcite (Type II) exhibit higher Sr concentrations and lower 87 Sr/ 86 Sr_(i) of 0.7010 – 0.7011 at 3.34 Ga and 0.70137 at 3.12 Ga, suggesting increasing influence of crustal weathering on the composition of Paleoarchean seawater through time, and progressive decoupling from the Archean mantle (87 Sr/ 86 Sr_(i) = 0.7003 – 0.7007).

2.2. Introduction

Marine chemical sedimentary rocks, such as carbonates, barites, banded iron formations (BIFs), and cherts are geological archives that may provide evidence for the primary chemical compositions of the ocean or other fluids from which they precipitated (e.g., hydrothermal, terrestrial influx, etc.; Veizer et al., 1989a, b; Van Kranendonk et al., 2003; 2007; Bolhar and Van Kranendonk, 2007; Johnson et al., 2022). Additionally, elemental and isotope signatures within marine chemical sedimentary rocks record global tectonic and climatic changes, as these parameters vary in response to the interaction of the lithosphere-atmosphere-hydrosphere systems during deposition (e.g., Schier et al., 2018; Viehmann et al., 2020).

The elemental and isotope composition of the oceans is primarily controlled by two major sources: (i) subaerial weathering of the continental crust and associated sedimentary rocks and (ii) submarine, hydrothermal exchange (e.g., Palmer and Edmond, 1989; Allègre et al., 2010). One of the most important and prominent proxies in chemical sedimentary rocks over time is the ⁸⁷Sr/⁸⁶Sr seawater curve (e.g., Shields and Veizer,

2002; Chen et al., 2022). This is because the ⁸⁷Rb-⁸⁷Sr system has a long residence time in the oceans, such that fluctuations in ⁸⁷Sr/⁸⁶Sr, retained in chemical sedimentary rocks, records global changes in the geosphere, i.e., the growth of continental crust (Broecker and Peng, 1982). The control of subaerial silicate and carbonate weathering on ⁸⁷Sr/⁸⁶Sr in modern seawater is about twice as high as that of hydrothermal seafloor alteration (Shields, 2007; Allègre et al., 2010), resulting in a more radiogenic Sr isotope ratio in seawater-derived sediments. In contrast, periods of extensive seafloor spreading increase the influx of mantle-derived, unradiogenic Sr into the oceans and, thus a lower total seawater ⁸⁷Sr/⁸⁶Sr ratio (Veizer et al., 1989a; Shields and Veizer, 2002). In this regard, temporal changes in the ⁸⁷Sr/⁸⁶Sr signature of seawater reveal geodynamic changes, such as the relative proportion of exposed continental crust over oceanic crust over time, or the amalgamation of continental land masses into supercontinents and their dispersal.

Earlier studies have proposed that the Archean seawater composition was entirely buffered by mantle-derived hydrothermal fluids and therefore concluded that the Sr isotope evolution of Archean seawater was indistinguishable from the Archean mantle (e.g., Shields and Veizer, 2002; Shields, 2007; Veizer, 1989; Veizer and Compston, 1976). The effect of continental weathering on the seawater composition was assumed to become significant by the global emergence of modern plate tectonics at, or slightly before the Archean-Proterozoic boundary at ca. 2.7 - 2.5 Ga. However, more recent studies have suggested that the ⁸⁷Sr/⁸⁶Sr composition of the seawater changed from a mantle buffered regime to a system that is characterized by the increasing influx of riverine runoff due to enhanced continental weathering arising from the local development and emergence of continental crust via modern-style plate tectonics already by the Mesoarchean, at 3.2 Ga (Smithies et al., 2007; Satkoski et al., 2016; 2017; Ravindran et al., 2020; Roerdink et al., 2022).

The relatively incomplete geological record of reliable Archean seawater proxies hampers the reconstruction of seawater evolution through deep time. Sedimentary carbonates derived from Archean seawater are relatively scarce and are quite often contaminated by clastic sedimentary material (Webb and Kamber, 2010; Schier et al., 2018; Viehmann et al., 2020). As well, secondary processes such as post-depositional fluid-rock interaction during diagenesis and metamorphic events often lead to alteration of the pristine geochemical inventory of these ancient sedimentary carbonates. Such disturbances of the primary trace element composition of Archean carbonate sedimentary rocks also affect their Sr isotope systematics, which display a broad scatter between unradiogenic marine and radiogenic continental ⁸⁷Sr/⁸⁶Sr endmembers with time (Shields and Veizer, 2002). Within this scatter, the lowest Sr isotope value have generally been assumed to represent the best estimate of the initial seawater composition, although this disregards any possible syn- or post-depositional hydrothermal overprinting (Satkoski et al., 2017). Other chemical sedimentary rocks and/or hydrothermal precipitates, such as cherts and barites, are more resistant to chemical alteration and generally greatly complement the reconstruction of the Archean seawater compositions (e.g., McCulloch, 1994; Satkoski et al., 2016; 2017; Ravindran et al., 2020; Roerdink et al., 2022). However, these proxies may not always represent global seawater compositions and contain a significant hydrothermal input (e.g., Van Kranendonk, 2006; Harris et al., 2009).

A recent study reported the occurrence of interstitial carbonates and calcite veins hosted in pillow lavas from the Cretaceous Troodos Ophiolite Complex (Quandt et al., 2019). Their geochemical record reveals two generations of carbonates that were either formed by extensive fluid-rock interactions before or during deposition of the host lavas or during precipitation of seawater-derived calcite at lower temperatures (Quandt et al., 2019). Interestingly, a comparison of the Sr isotope composition of the Troodos carbonates with the modern Sr isotope seawater curve (McArthur et al., 2001) indicates possible calcite crystallization ages between 92 - 20 Ma, which coincides with the main phases of volcanic activity and uplift of the Troodos ophiolite (Quandt et al., 2019). Studies by Nakamura and Kato (2002; 2004), Yamamoto et al. (2004), and Lindsay et al. (2005) report the presence of interstitial calcites and dolomites in Paleoarchean volcanic rocks from the Pilbara Craton, which may be able to reveal information on primary seawater composition, fluid-rock interaction, and the hydrothermal carbonatization of the Archean oceanic crust.

Rare earth elements and yttrium (REY) in combination with Sm-Nd isotope measurements are commonly used for pure chemical sediments, such as carbonates, BIFs, and cherts for discerning the influxes of continental weathering and mafic crust-derived hydrothermal fluids related to the relatively short residence time of the particle-sensitive REE in seawater (Alexander et al., 2009; Viehmann et al., 2015; Schier et al., 2018). Furthermore, the REY are in contrast to Sr more robust in secondary processes, such as
metamorphism or alteration (e.g., Banner and Hanson, 1990; Viehmann et al., 2016). In this study, we provide REY concentrations to further constrain the origin of the Pilbara calcites and additionally use their Sm-Nd isotope compositions for Sm-Nd isochron dating.

The Pilbara rock record has only been affected by low-grade (prehnite-pumpellyite, lower greenschist, and local amphibolite facies) metamorphic conditions, and it provides a near continuous archive of crustal evolution through the Paleo- and Mesoarchean (Van Kranendonk et al., 2002; 2007; Smithies et al., 2007). We present a comprehensive dataset of major and trace element, stable C-O isotopes, and Sm-Nd and Rb-Sr isotope data for calcites that were found within the interstitial spaces between pillows of submarine basaltic units across a range of the Pilbara stratigraphy. We also performed Sm-Nd dating of 16 interstitial and vesicle carbonates along with their respective host rocks and we expand the Sr isotope record of Archean seawater evolution by exploring the geochemical potential of interstitial and vesicle filling carbonates within the stratigraphy of one of the best-preserved Archean mafic successions on Earth, the Pilbara Craton (Van Kranendonk et al., 2019; Smithies et al., 2019). The major and trace element budgets of the interstitial carbonates reveal insights into the seawater-rock interaction of pillow basalts during the Paleo-Mesoarchean, while stable and radiogenic isotopes are used to evaluate the impact of post-depositional events on the elemental and isotope composition of the carbonates. Using this information, we evaluate the Sr-Nd isotope systematics in interstitial carbonates of the Pilbara Craton, compare them to their respective host rocks (Hasenstab et al., 2021; Tusch et al., 2021) and fresh clinopyroxene separates, and use this to provide key insights into the interplay between mantle, crust, and oceans across the Paleo- to Mesoarchean boundary.

2.3. Geological setting and sample description

The Pilbara Craton in Western Australia comprises the world's best-preserved and least metamorphosed Paleo- to Neoarchean successions of mafic-ultramafic and felsic volcanic rocks, sedimentary rocks, and granitic intrusions, with a prolonged depositional and tectonic history from 3.59 – 2.63 Ga (Van Kranendonk et al., 2007; Smithies et al., 2007). Based on geochemical and structural constraints, the Pilbara Craton has been subdivided into the East Pilbara Terrane (EPT), the West Pilbara Superterrane (WPT), and the Kuranna Terrane (Fig. 2.1; Van Kranendonk et al., 2007). Here, we will describe



Interstitial carbonates in pillowed meta-basaltic rocks from the Pilbara Craton, Western Australia: A vestige of Archean seawater chemistry and seawater-rock interactions



Figure 2.1: (a) Simplified geological map of the East Pilbara Terrane (EPT) and West Pilbara Terrane (WPT), modified after Van Kranendonk et al. (2007, 2010). Red circles show the sample locations. In (b) generalized lithostratigraphy of the East Pilbara Terrane and West Pilbara Superterrane (modified from Van Kranendonk et al., 2006; Hickman et al., 2012). Colored circles and diamonds refer to interstitial Type I carbonates (circles) and void filling Type II carbonates (diamonds) from the Mt. Ada (purple), Apex (green), Euro (red), Honeyeater (yellow), and Bradley Basalt formations (blue), respectively.

the volcano-sedimentary successions of the EPT and WPT in more detail, because they contain the sample localities of this study.

The EPT consists of four well characterized volcano-sedimentary groups (Warrawoona, Kelly, Sulphur Springs, and Soanesville groups) that were deposited from 3.53 to 3.1 Ga, forming the Pilbara Supergroup (Van Kranendonk et al., 2007; 2019). The lowermost Warrawoona Group (3.53 - 3.43 Ga) consists of pillow basalts and komatiitic basalts indicative of a (dominantly) submarine depositional environment. Hickman (1976) subdivided the mafic successions into the lower Talga Talga Subgroup and the overlying Salgash Subgroup, which were separated by felsic volcaniclastic deposits of the Duffer Formation. Later studies however distinguish between five mafic formations (Table Top Basalt, Double Bar Basalt, North Star Basalt, Mt. Ada Basalt, and Apex Basalt), which alternate with more felsic volcanic units (Coucal, Duffer, and Panorama formation; Smithies et al., 2007; Van Kranendonk et al., 2007).

The unconformably overlying Kelly Group shows an erosional unconformity to the older Warrawoona Group (Buick et al., 1995; Van Kranendonk, 2006; Hickman, 2012). Immediately overlying the unconformity, the Strelley Pool Formation comprises fluviatile sandstones and conglomerates, and shallow-water marine sedimentary rocks with stromatolites and microbial mats (Allwood et al., 2006; Hickman, 2008; Van Kranendonk et al., 2002; 2010). The conformably overlying Euro Basalt consists of komatiites and tholeiitic basalts that were erupted at 3.35 Ga, followed by the rhyolitic Wyman Formation (Van Kranendonk et al., 2007).

The unconformably overlying, ca. 3.24 Ga Sulphur Springs Group is comprised of basal sandstones, komatiitic basalts and komatiites and capping felsic volcanic and volcaniclastic rocks (Buick et al., 2002; Van Kranendonk et al., 2007). The younger, also unconformably overlying, ca. 3.2 Ga Soanesville Group consists of lower clastic sedimentary rocks (siltstones and shales) and the basaltic Honeyeater Formation (Buick et al., 2002; Van Kranendonk et al., 2002; Van Kranendonk et al., 2002; Van Kranendonk et al., 2007; Van Kranendonk et al., 2010). Whereas the Warrawoona, Kelly, and Sulphur Springs groups were deposited during three successive mantle plume events involving depleted mantle melting (Smithies et al., 2005b; Van Kranendonk et al., 2007; Van Kranendonk et al., 2007; Van Kranendonk et al., 2010). Conductively transported heat from the plume events, radioactive decay, and storage of intra-crustal

magma resulted in softening of the middle crust leading to extensive granitic melting. The upward migration of granitic melts and gravitational collapse of the dense overlying greenstones led to the characteristic dome-and-keel structure of the Pilbara Craton (Collins et al., 1998; Van Kranendonk et al., 2004; 2007; 2015; 2019).

The WPT is an amalgamation of three distinct terranes: The Karratha, Regal, and Sholl terranes (Van Kranendonk et al., 2007). The Karratha Terrane, ranging in age from 3.50 - 3.25 Ga, was likely separated from the EPT during the 3.2 Ga rifting event recorded on the western margin of the EPT (Van Kranendonk et al., 2010; Hickman, 2012). The 3.2 Ga Regal Terrane has been interpreted to represent the rift-related oceanic crust between the separation of the Karratha Terrane and the EPT (Hickman, 2012). The younger Sholl Terrane consists of granitic intrusions and the bimodal Whundo Group (3.12 Ga), which shows arc-like geochemical characteristics that were interpreted as direct evidence for modern-style subduction in a Mesoarchean intra-oceanic arc setting (Smithies et al., 2005a; Van Kranendonk et al., 2007; Hickman, 2012).

Chemical sedimentary rocks comprise a small part of the Pilbara greenstone belts and generally have been overprinted by secondary hydrothermal fluids (Van Kranendonk, 2006). Therefore, in this study we investigate a distinctive suite of carbonates that are found within the interpillow space and vesicles of six mafic formations of the Pilbara Craton, ranging in age from 3.47 to 3.12 Ga (Fig. 2.2). The pillow basalts that host the carbonate are mostly affected by greenschist-facies metamorphism (Fig. 2.2a), with some containing fresh magmatic minerals, such as clinopyroxene next to the carbonate fillings. Secondary mineral phases include chlorite, quartz, epidote, prehnite-pumpellyite, carbonate, and local actinolite (e.g., Terabayashi et al., 2003; Caruso et al., 2021). Interpillow spaces exhibit an internal mineralization gradation. In some samples the contact surface of the interstitials is covered with secondary phases, such as chlorite and the inner parts are composed of perpendicular acicular to bladed calcite (Fig. 2.3d) with/without additional layers of fibrous and/or crystalline quartz. The samples investigated here are predominantly euhedral, bladed, light pink calcite that may be locally partially silicified. Only one sample shows solid-solution of ankeritic and calcitic composition (13643), whereas another calcitic sample is associated with reddish Fe-Mnhydroxide (Pil16-005), which is probably a later alteration product from Tertiary



Interstitial carbonates in pillowed meta-basaltic rocks from the Pilbara Craton, Western Australia: A vestige of Archean seawater chemistry and seawater-rock interactions

Figure 2.2: Sampling sites of selected interstitial carbonates (High-Mn Type I carbonates; a-c) and corresponding polarized thin section images of corresponding acicular to bladed and coarse calcite (Cc) with co-eval hydrothermal quartz crystals (Qtz) in (d) and (e) – (h) (cross-polarized). In (g) a sharp transition to the mafic host rock with fresh clinopyroxene (Cpx) is visible. Sampling sites of void-filling carbonates (low-Mn Type II carbonates) in degassing structures of mafic rocks are shown in (i) and (j). Panels (k) to (l) show cross-polarized thin sections images of selected carbonates void-filling calcite that are rather fine-grained and accompanied by chlorite (Chl) in (k).

1 cm

Pil17-008b

Pil16-073b

300 µm

Pil16-073t

50 un

weathering. The innermost part of the interstitial fillings contain either coarse-grained calcite, or quartz (Fig. 2.2e-h). The bladed and coarse-grained habit of the calcite and

their partial silicification is interpreted to be due to precipitation from a boiling fluid soon after the host rock emplacement (Pirajno, 1992; Van Kranendonk et al., 2008). The lack of any veins feeding the distinctive, light pink bladed calcites, and their inward, tapering growth textures of the bladed calcites point to their *in situ* and syn-eruptive precipitation.

These bladed pink calcites differ texturally and compositionally from all other carbonates observed in the Pilbara. Stromatolitic carbonate sedimentary rocks consist of ferroan dolomite, whereas metamorphic carbonate, in veins and in some fill spaces in interpillow spaces (i.e. pillow shelves) are ankerite. For example, Yamamoto et al. (2004) reported mostly euhedral dolomitic/ankeritic interstitial carbonates, but these have completely replaced the original calcite. Van Kranendonk et al. (2008) noted the presence of bladed calcite in drill core samples through the ca. 3.48 Ga Dresser Formation of the Warrawoona Group, associated with boiling fluids in a syn-depositional epithermal system.

A second group of mostly fine-grained calcite are found in elongate marginal vesicles near the rims of pillow lavas (Fig. 2.2i-l). Interestingly, this second group is not associated with other secondary phases and is mostly devoid of reaction rims, indicating no visible alteration of the surrounding host rocks. Only one sample is surrounded by chlorite, but the corresponding mafic host rock is still relatively fresh (Fig. 2.2k).

We collected nine samples of coarse-grained carbonates (herein Type I carbonates), one associated sample of quartz, and six fine-grained carbonates (Type II carbonates) from three localities in the EPT and one locality in the WPT (Fig. 2.1a).

2.4. Analytical methods

For mineral composition and major element concentrations, electron microprobe analyses (EMPA) of polished thin sections were performed on a JEOL JXA-8900RL Superprobe at the University of Cologne. Operating conditions were 15 kV accelerating voltage and 20 nA beam current. A set of natural silicate standards (for Si, Mg, Ca, Na, K, Fe, and Mn) and an oxide standard (for Al) was used for the calibration.

For bulk trace element concentration and isotope composition analyses, small, precleaned carbonate chips were hand-picked and finely crushed in an agate mortar. To omit possible dissolution of detrital components, approximately 200 mg of the powdered samples were weighed into centrifuge tubes and leached with 13 ml of suprapure 1 M acetic acid. Afterwards, the tubes were centrifuged and the leached fraction was pipetted into a Savillex beaker and evaporated to incipient dryness at 100 °C. The previous steps were repeated until no carbonate dissolution reaction was visible and the possible residue was subtracted from the original mass and transferred in separate Savillex beakers. Subsequently, 8 ml of 2 % HNO₃ were added to the carbonate samples and evaporated twice at 100 °C. One associated quartz was treated with 6 ml 14 M HNO₃/24 M HF (1:1) for 24 h on a hotplate at 120 °C. Afterwards, the quartz sample was dried down at 120 °C and subsequently treated with 2 ml 14 M HNO₃ and evaporated afterwards.

Trace element analyses of the carbonates and their respective residues were performed using an Agilent 7900 quadrupole ICP-MS at the University of Vienna, Austria. One dolomite reference material (JDo-1) was included in the trace element measurements.

For Sr-Nd isotope analyses at the University of Cologne, Germany, a separate carbonate digestion step (10 - 200 mg) was carried out using the same procedure as above. After the first 2 % HNO₃ dissolution step, the samples were evaporated before adding mixed ⁸⁷Rb-⁸⁴Sr and ¹⁴⁹Sm-¹⁵⁰Nd tracers that were equilibrated with the samples in 6 ml 6 M HCl for 24 h at 120 °C in a closed beaker. The quartz sample and carbonate associated silicic residues were digested as described above and also equilibrated with ⁸⁷Rb-⁸⁴Sr and ¹⁴⁹Sm-¹⁵⁰Nd tracers in 6 M HCl for 24 h at 120 °C in a closed beaker.

For comparison, we additionally separated fresh pyroxene fractions of surrounding host rocks and analyzed their initial Sr-Nd isotope composition. Prior to digestion, ~30 mg pyroxene separates were weighed in and cleaned with cold 0.14N HNO₃ for 15 min, rinsed with deionized water before adding ⁸⁷Rb-⁸⁴Sr and ¹⁴⁹Sm-¹⁵⁰Nd tracers. The pyroxene separates were digested using a 14 M HNO₃/ 24 M HF (1:2) mixture at 120°C in closed Savillex beakers and passed through the separation protocol reported by van de Löcht et al. (2020).

After evaporation, all samples were dissolved in 1.5 ml 2.5 M HCl, centrifuged, and Rb-Sr as well as Sm-Nd were subsequently separated from the matrices using BioRad AG 50W-X8 (200 - 400 mesh) and Eichrom Ln-Spec resin (100 - 200 mesh), respectively, following the method by Pin and Santos Zalduegui (1997).

Neodymium-Sr isotope compositions as well as Sm, Nd, Rb, and Sr concentrations were measured by isotope dilution using the Thermo-Finnigan Neptune MC-ICP-MS at the University of Cologne. All ¹⁴³Nd/¹⁴⁴Nd measurements were mass bias corrected with

¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 and results are reported relative to LaJolla (¹⁴³Nd/¹⁴⁴Nd = 0.511859) and JNdi (¹⁴³Nd/¹⁴⁴Nd = 0.512115). Procedural LaJolla and JNdi values were measured with a ¹⁴³Nd/¹⁴⁴Nd of 0.511868 (n = 1) and 0.512089 ± 14 (2 s.d.; n = 15), respectively. External reproducibility for ¹⁴³Nd/¹⁴⁴Nd measurements was ±40 ppm and ±0.2 % for ¹⁴⁷Sm/¹⁴⁴Nd. Initial ε¹⁴³Nd were calculated using λ^{147} Sm of 6.54 x 10⁻¹² a⁻¹ (Lugmair and Marti, 1978) and CHUR value of Bouvier et al. (2008). Measured ⁸⁷Sr/⁸⁶Sr ratios were mass bias corrected to ⁸⁶Sr/⁸⁸Sr = 0.1194 and ⁸⁷Rb/⁸⁵Rb were mass biased corrected to ⁹¹Zr/⁹⁰Zr = 0.21795 for doped Zr (Nebel et al., 2005), respectively. Strontium and Rb isotope compositions are given relative to NBS 987 (⁸⁷Sr/⁸⁶Sr = 0.710240) and NBS 984 (⁸⁷Rb/⁸⁵Rb = 0.38554). Measurements of the ⁸⁷Sr/⁸⁶Sr ratios of the NBS 987 averaged at 0.710243 ± 37 (2 s.d; n = 28). The external long-term reproducibility is ± 50 ppm and a λ^{87} Rb of 1.42 x 10⁻¹¹ a⁻¹ (Steiger and Jäger, 1977) was used for the age correction.

Procedural blanks were less than 170 pg for Sr, < 70 pg for Rb, and < 10 pg for both Nd and Sm, and are therefore negligible compared to the total analyte.

Oxygen and carbon stable isotope compositions of the carbonates were determined using a Thermo Kiel IV carbonate preparation device coupled to a Finnigan DeltaPlus dual-inlet-MS at the University of Göttingen, Germany. Carbonate samples were digested for 30 minutes in supersaturated orthophosphoric acid at 70 °C (McCrea, 1950) and the produced CO₂ then analyzed for m/z 44, 45, and 46. All values are reported with δ -notation (‰) relative to PDB (PeeDee Belemnite limestone) for $\delta^{13}C_{(PDB)}$ and VSMOW2 for $\delta^{18}O_{(VSMOW2)}$. The typical external reproducibility is ± 0.06 ‰ for $\delta^{13}C$ and ± 0.1 ‰ for $\delta^{18}O$.

2.5. Results

2.5.1. Major elements and carbonate compositions

Measured major and trace element data for the interstitial carbonates and associated host rocks are reported in Supplementary Table B1. Based on their structure and electron microprobe (EMPA) major element analysis, the interstitial carbonates have been divided into two types: Type I carbonates are coarse-grained calcitic-ankeritic interpillow carbonates (Figs. 2.2 - 2.3) with relatively high Mn contents; and Type II fine-grained, low-Mn calcite vesicle fillings (Figs. 2.2 - 2.3). Compositional differences in the major

element compositions between the respective formations of each type are relatively small. Noteworthy compositional distinctions of specific samples are described further below.

The high-Mn carbonates (Type I) of all volcanic formations exhibit CaO concentrations of 30.1 - 59.5 wt.% at variable MgO contents of 0.04 - 17.5 wt.% (Supplementary Table B1). These carbonates are also characterized by relatively low FeO* (0.1 - 4.5 wt.%) and elevated MnO (0.1 - 1.8 wt.%) concentrations. Hence, most Type I carbonates can be classified as calcite (88.2 - 99.6 vol.%), except for one sample that also shows signs of solid-solution with elevated magnesite (~27.5 vol.%) and siderite



Figure 2.3: Classification of carbonates in the CaCO₃-MgCO₃-(FeCO₃+MnCO₃) ternary diagram after Laverne (1993). Shown are interstitial carbonates (circles) and void filling carbonates (diamonds) from the Mt. Ada (purple), Apex (green), Euro (red), Honeyeater (yellow) and Bradley Basalt Formations (blue), respectively, compared to other interstitial carbonates from the Pilbara Craton (Nakamura & Kato, 2002; Yamamoto et al., 2004) and Strelley Pool stromatolitic dolomites (Lindsay et al., 2005; Viehmann et al., 2020). (b) shows a close-up of (a) starting at 75 vol.% CaCO₃. In (c) Mn (ppm) vs. SiO₂ (wt.%) are shown, illustrating the degree of silicification of the interstitial carbonates and void-filling carbonates of this study compared to published interstitial carbonate (Nakamura & Kato, 2002; Yamamoto et al., 2004), Strelley Pool stromatolitic dolomites (Lindsay et al., 2004), Strelley Pool stromatolitic dolomites (Lindsay et al., 2002), mafic host rocks, and shale from the EPT (Tusch et al., 2021).

(~ 10 vol.%) components, resulting in calcitic-ankeritic composition for this sample (Fig. 2.3a, b). Notably, the degree of silicification of Type I carbonates is significantly lower than found in previous studies (Nakamura and Kato, 2002; Yamamoto et al., 2004) and generally increases with increasing ankerite component, from insignificant silicification to SiO₂ concentrations of up to 8.4 wt.% (Fig. 2.3c).

The low-Mn carbonates (Type II) of the Euro Basalt and Bradley Basalt typically show CaO concentrations between 57.1 and 61.1 wt.%. The overall concentrations of MgO, MnO and FeO* (Supplementary Table B1) of these Type II carbonates are below 0.02 wt.%, which indicates pure calcite (99.9 vol.%). Additionally, these Type II carbonates are characterized by the absence of SiO₂, except for sample Pil16-005 from the Euro Basalt that is also coarser than other of the Type II carbonates, exhibits higher MgO (1.1 wt.%), MnO (2.2 wt.%), and FeO* (2.5 wt.%), and shows a small degree of silicification (SiO₂ = 1.1 wt.%). Combined with the results below, this sample (Pil16-005) is regarded as transitional between Type I and Type II carbonates.

2.5.2. Trace element and REY_{PAAS} patterns

High-Mn Type I carbonates typically exhibit low Sr concentrations that are mostly below 110 ppm (except for Pil16-022b with 263 ppm). In contrast, the low-Mn Type II carbonates are characterized by high Sr contents of 825 - 2,516 ppm. Only Pil16-005 shows a transitional composition between the two carbonate types, with variable and lower Sr contents between 123 - 215 ppm that were obtained from multiple digestions. Both carbonate types show very low Rb concentrations (< 0.1 ppm). In contrast, the associated quartz and residues from sample digestion exhibit significant amounts of Rb (0.620 - 3.70 ppm), generally matching the Sr concentrations (0.602 - 4.88 ppm). Both carbonates types also show very low immobile trace element concentrations. Aluminum concentrations range from 23 to 353 ppm, whereas Th and Zr concentrations range from 0.624 - 34.8 ppb and 7.58 - 67.1 ppb, respectively.

The Post-Archean Australian Shale-normalized (PAAS; Taylor and McLennan; 1985) REY_{PAAS} patterns of the high-Mn Type I carbonates show HREE_{PAAS} enrichments relative to the LREE_{PAAS} and generally display small positive Eu_{PAAS} and Y_{PAAS} anomalies (Fig. 2.4 a-d). This also results in positive Eu/Eu*_{PAAS} of 1.27 - 3.11, slightly elevated La_{PAAS} anomalies of 1.20 - 1.97, and superchondritic Y/Ho (34.5 - 39.1). The



0.1

0.01

0.00

0.0001

La Ce Pr Nd Pm Sm

eawater

Eu Gd Tb Dy

Type I carbona

mafic host rock

Er Tm Yb

Но

0.01

0.001

0.0001

La

Type I carbo

Pm Sm Eu Gd Tb

Pr Nd interstitial quartz

mafic host rock

Но Er Tm

Dy Y

Troodos Mn-rich car

Interstitial carbonates in pillowed meta-basaltic rocks from the Pilbara Craton, Western Australia: A vestige of Archean seawater chemistry and seawater-rock interactions



Lu

Figure 2.4: PAAS-normalized REY patterns of the coarse high-Mn interstitial carbonates (Type I) in (a) Mt. Ada Basalt, (b) Apex Basalt, (c) Euro Basalt, and the (d) Honeyeater Basalt, and low-Mn void-filling carbonates (Type II) in (e) Euro Basalt and (f) Bradley Basalt. For comparison, in each segment is also shown shaded fields that illustrate the composition of the respective host rocks (Tusch et al., 2021), while gray fields depict modern shallow seawater multiplied by 10^5 (Zhang and Nozaki, 1996), and hydrothermal fluids multiplied by 10⁴ (Bau & Dulski, 1999). The dark grey field in (c) corresponds to compositions of Mn-rich carbonates hosted in the mafic successions of the Troodos Ophiolite Complex (Quandt et al., 2019). Note the comparable REY_{PAAS} slopes of the void-filling Type II Bradley carbonate (f) and modern seawater, suggest modern seawater-like conditions in some regions of the Archean oceans. PAAS = Post Archean Australian Shale (Taylor and McLennan, 1985).

associated quartz only exhibits ~10 % of the REY concentration relative to the coeval carbonates, but also shows noticeable positive EuPAAS anomaly of 2.43, a LaPAAS anomaly of 1.40, and comparable Y/Ho of 35.7. The samples do not show any positive or negative Ce_{PAAS} anomalies in any of the measured carbonates (Fig. 2.4).

The low-Mn Type II carbonates can be further subdivided by their respective stratigraphic units. The low-Mn carbonates of the Euro Basalt contain only 10 % of the REY concentrations compared to the high-Mn Type I carbonates from the same formation, and show a negative trend from Er to Lu (decreasing HREE). They have comparable La_{PAAS} anomalies of 1.27 - 1.94 (supplementary Fig. B1) and slightly higher Y/Ho ratios (39.1 – 40.8) than their Type I equivalents. Again, only Pil16-005 shows a positive Eu/Eu*_{PAAS} of 1.15. The low-Mn Type II carbonate of the Bradley Basalt exhibits significant HREE_{PAAS} enrichments relative to the LREE_{PAAS}, but the overall REY concentrations are generally two orders of magnitude lower compared to other carbonates in this study. In addition, this sample displays the highest Y/Ho ratios of 55.8, whereas Eu/Eu*_{PAAS} could not be determined, due to a high isobaric Ba interference during the ICP-MS analysis (758 ppm Ba).

2.5.3. Stable and radiogenic isotopes

Stable and radiogenic isotope data are given in Supplementary Table B1. The ¹⁴⁷Sm/¹⁴⁴Nd ratios in the high-Mn carbonates range from 0.1502 to 0.2390. Initial ϵ^{143} Nd_(i) values are +1.0 ± 0.4 for the 3.47 Ga Mt. Ada Basalt and between +0.8 ± 0.4 and +4.7 ± 0.4 for the 3.46 Ga Apex Basalt Formation. Samples from the younger ca. 3.35 Ga Euro Basalt display ϵ^{143} Nd_(i) values that range from +0.9 ± 0.4 in slightly silicified samples and 2.1 ± 0.4 in highly silicified samples (8.4 wt.% SiO₂). The high-Mn Type I carbonate of the ca. 3.18 Ga Honeyeater Basalt exhibits ϵ^{143} Nd_(i) of +1.6 ± 0.4. Using the measured ¹⁴⁷Sm/¹⁴⁴Nd ratios of 0.2017 – 0.2020, the initial ϵ^{143} Nd_(i) of the low-Mn carbonates (Type II) from the Euro Basalt Formation are slightly higher with values between +1.2 ± 0.4 and +1.5 ± 0.4. Due to the low REE concentrations within the low-Mn Type II carbonate of the Bradley Basalt Formation and the limited amount of material, the age corrected ϵ^{143} Nd_(i) of +4.0 has a relatively large uncertainty of ± 2.5 at a measured ¹⁴⁷Sm/¹⁴⁴Nd of 0.1698.

Combined Sm-Nd isochron calculations using pure carbonate fractions (Fig. 2.5) of the respective carbonate samples, their host rocks and pyroxene separates, yield ages of $3,466 \pm 23$ Ma for the Apex Basalt, $3,365 \pm 43$ Ma for the Euro Basalt, $3,187 \pm 33$ Ma for the Honeyeater Basalt, and $3,131 \pm 24$ Ma for the Bradley Basalt, all of which overlap, within error, with the dated depositional ages obtained via U-Pb zircon geochronology (Fig. 2.6b; Van Kranendonk et al., 2002; 2007). These results indicate that there has been



Figure 2.5: Samarium-Nd isochrons of interstitial carbonates, their respective host rocks (open symbols; Hasenstab et al., 2021), and pyroxene separates (black filled symbols) from associated mafic host rocks. Except for the Mt. Ada Basalt Formation, all regression lines yield ages that overlap with the depositional ages of the respective formations within their uncertainty.

only negligible post-depositional disturbance or isotopic resetting in the Sm-Nd system for these rocks during younger thermal events at between 3.1 and 2.7 Ga (Jahn et al., 1981; Minami et al., 1995). Only the Type I carbonates from the Mt. Ada Basalt and their associated host rocks return an age $(3,361 \pm 22 \text{ Ma})$ that is ~100 Ma younger than the age of eruption of the basalt, indicating resetting of the Sm-Nd system, perhaps by local fluid circulation.

Both Type I and Type II carbonates are nearly devoid of Rb, resulting in extremely



low ⁸⁷Rb/⁸⁶Sr values (0.005). Only high-Mn carbonate sample Pil16-004 exhibited an elevated Rb content, resulting in a higher ⁸⁷Rb/⁸⁶Sr of 0.1091. Initial ⁸⁷Sr/⁸⁶Sr isotope compositions of the high-Mn Type I interstitial carbonates are radiogenic and range from 0.701523 - 0.718776, with the silicified carbonates tending towards more radiogenic ratios. Associated quartz and silicic residues exhibit high 87Rb/86Sr ratios of 0.9523 - 3.2832 resulting in overcorrected low initial 87Sr/86Sr ratios of measured ⁸⁷Sr/⁸⁶Sr values between 0.720822 - 0.828457. The low-Mn

Figure 2.6: Isotope variation diagrams of the interstitial carbonates. In (a) Sr vs. initial ⁸⁷Sr/⁸⁶Sr show the differences between high-Mn and low-Mn carbonates. Low-Mn carbonates exhibit high Sr concentrations and retained the original Sr isotope composition of the Archean seawater, whereas the high-Mn carbonates exhibit lower Sr concentrations and their radiogenic Sr isotope compositions are best explained by the radiogenic overprinting of associated quartz. In (b) initial ε^{143} Nd values vs. age (Ma) show the general overlap of the carbonates with the depleted mantle-derived host rocks (brown circles; Hasenstab et al., 2021). Variations of some carbonate samples can be explained by secondary resetting of the Sm-Nd system. In (c) stable Carbon vs. Oxygen isotope compositions of the interstitial carbonates are plotted, showing a general overlap with published interstitial carbonates from the Pilbara Craton, whereas Strelley Pool stromatolitic dolomites tend to higher $\delta^{18}O$, suggesting lower precipitation temperatures from the Archean seawater and δ^{13} C. The shown covariation of δ^{13} C and δ^{18} O can either be caused by the mixture of Archean seawater and hydrothermal fluids that interacted with mantle-derived rocks or carbonate precipitation under non-equilibrated conditions, resulting in isotope fractionation.

Type II vesicle carbonates are characterized by high Sr concentrations coupled with lower ${}^{87}\text{Sr}/{}^{86}\text{Sr}_{(i)}$ values of 0.701030 - 0.701083 ($\emptyset = 0.701066 \pm 57$; n = 10) for the Euro Basalt and 0.701348 ± 16 (n =3) for the Bradley Basalt (Fig. 2.6a). Most low-Mn Type II carbonates show homogenous Sr isotope compositions as confirmed by multiple digestions and measurements. Only the transitional "low-Mn" carbonate (Pil16-005) with the highest Mn concentration exhibits a heterogeneous initial ${}^{87}\text{Sr}/{}^{86}\text{Sr}$, ranging from 0.701050 - 0.702075 (n = 5).

The high-Mn Type I carbonates display $\delta^{18}O_{(VSMOW2)}$ values that range from +9.3 up to +16.7 ‰ and exhibit $\delta^{13}C_{(PDB)}$ values from -1.83 to +0.07. The $\delta^{18}O_{(VSMOW2)}$ values in low-Mn Type II carbonates range from $\delta^{18}O_{(VSMOW2)} = +9.1$ to +13.2, whereas $\delta^{13}C_{(PDB)}$ values range between -0.37 and +1.37 (Fig. 2.6c).

Measured clinopyroxene separates from the basaltic host rocks show initial ϵ^{143} Nd_(i) values that overlap with their bulk host rock compositions that are reported by Hasenstab et al. (2021). The initial Sr isotope composition of these separates are generally radiogenic and range from 0.702049 to 0.710151. Noteworthy, the Mt. Ada Basalt pyroxene separates show ϵ^{143} Nd_(i) of +0.4 ± 0.4 relative to +0.8 ± 0.4 for the bulk host rock (Hasenstab et al., 2021), and they have low initial ⁸⁷Sr/⁸⁶Sr isotope compositions between 0.700341 – 0.700710.

2.6. Discussion

2.6.1. Potential contamination by clastic components

The trace element and isotope inventory of carbonates may potentially be affected by detritus, either occurring during syn-sedimentary co-sedimentation with the carbonate or induced during acid digestion in the laboratory. Some carbonate samples are either accompanied by hydrothermal quartz and/or are partially silicified. Secondary chloride and epidote are observed between some carbonate phases and the respective host rocks but were thoroughly separated from carbonate fractions (Fig. 2.2). However, incomplete removal of other phases such as clay minerals or Fe-hydroxides before and during digestion cannot be ruled out. To avoid obscuring our data by leaching effects of clay minerals or hydroxides during nitric acid or hydrochloric acid digestions, we dissolved our carbonates in a multi-step leaching procedure only using dilute acetic acid and



Interstitial carbonates in pillowed meta-basaltic rocks from the Pilbara Craton, Western Australia: A vestige of Archean seawater chemistry and seawater-rock interactions

Figure 2.7: Plots illustrating the absence of siliciclastic contamination in the carbonates. In (a) measured Mn concentrations by ICP-MS of the carbonates are compared to Mn concentrations measured by electron microprobe, showing generally a positive 1:1 correlation that rules out preferential Mn leaching of associated clay minerals during acetic acid digestion of the carbonates. In (b) a positive correlation of the REE concentrations with increasing Mn is shown for the interstitial carbonates, which cannot be explained by detrital contamination. Low Zr (c) and Sc (d) concentrations without a positive correlation with REE or Mn concentrations also argue against siliciclastic contamination of the interstitial carbonates from our study. Stippled mixing lines in (d) were calculated between high-Mn carbonate with the highest REE concentration and shale (asterisks) and mafic host rock (crosses), respectively, for clastic contamination (10 % increments; data for clastic sediments by Tusch et al., 2021). Note the positive correlation of the interstitial carbonates studied by Yamamoto et al. (2004) who employed a HNO₃ digestion for the carbonates.

Archean shales

Mt. Ada Basalt

examined for remaining clay minerals that could have an effect on the trace element budget prior to interpretation. The subsequent chemical separation of the carbonate components from other phases generally led to the complete dissolution of the samples. However, for four samples of the Type I carbonates, either small residual amounts of quartz or silicified carbonate components were found in the residue. In all cases, the residual mass never exceeded 0.5 % of the original mass. In another sample of Type I carbonate (Pil16-022b) small amounts of red clay were visible but successfully separated by centrifuging. All Type II carbonates were completely dissolved using dilute acetic acid.

Veizer et al., (1989a; b) proposed that increasing Mn concentrations in carbonates are commonly associated with secondary alteration processes, whereas others (Quandt et al., 2019) rather argue for a primary signature resulting from strong fluid-rock interaction and closed-system disequilibrium precipitation. For Archean seawater however, it is generally agreed on that high Mn and Fe concentrations rather show the lack of oxygen prior the great oxidation event (GOE; Holland, 2002) and chemical sediments derived from this seawater inherit these elevated concentrations. In addition, leaching or incomplete removal of clay minerals would further increase the Mn concentration measured in carbonates. To evaluate clay mineral contamination, we plotted Mn concentrations measured by ICP-MS versus in-situ measurements by EMPA (Fig. 2.7a). Most Type I and Type II carbonates plot on a 1:1 line in a Mn (measured by microprobe) vs. Mn (measured by ICP-MS), suggesting no or only small amounts of clay contamination. Only one sample (Pil16-022b; Apex Basalt Formation) of the high-Mn carbonates exhibits significantly higher Mn content if measured by ICP-MS, most likely resulting from co-digestion of clay minerals, whereas the pure carbonate was measured by Microprobe analysis.

The notably high REE concentrations of the high-Mn Type I carbonates relative to seawater (Fig. 2.4) could be explained by significant amounts of siliciclastic or host rock contamination that affected the pristine geochemical signatures of the fluids from which the carbonates precipitated. In Figure 2.7b-d, however, it is clearly shown that contamination of either associated host rock or shale material can be excluded. Both contaminants would increase both REE and refractory elements, such as Zr or Sc, which are enriched in mafic host rocks and also in shales of the Paddy Market Formation (3.19 Ga) or Hardy Formation (2.755 Ga) (data from Tusch et al., 2021) relative to seawater. To confirm the absence of contamination, we calculated mixing lines between a pure Type I carbonate and contemporaneous shales and mafic rocks (Tusch et al., 2021), respectively (Fig. 2.7d; supplementary Table B2). Only the previously reported interstitial carbonates by Nakamura and Kato (2002, 2004), obtained by HNO₃-HClO₄-HF digestion, seem to have experienced some degree of siliciclastic contamination, as those samples lie

on a mixing line, whereas all samples from this study do not follow the calculated mixing lines. Consequently, both types of carbonates analyzed here are generally devoid of significant clastic contamination and are considered to be representative archives for the geochemical proxies that are discussed further below.

2.6.2. Origin of interstitial carbonates from the Pilbara Craton

2.6.2.1. Hydrothermal alteration

The lack of voluminous Archean carbonate deposits is a feature of Archean greenstone belts worldwide (Veizer et al., 1989a; b). Contrary to modern marine carbonates, Archean carbonates are mainly composed of ferroan dolomite, ankerite, and siderite, suggesting a predominantly hydrothermal origin (Nakamura and Kato, 2002) or precipitation from a Fe-Mn-rich ocean. However, Veizer et al., (1989a; b) pointed out that at least some Archean carbonates in greenstone belts precipitated as pure calcite before secondary alteration by hydrothermal fluids led to the recrystallization to ferroan dolomite. Nakamura and Kato (2002) attributed these differences of carbonate precipitation to the following two main reaction mechanisms affecting modern oceanic carbonate precipitation: (i) mantle-derived dissolved bicarbonate ions within the seawater and (ii) riverine influx of cations, such as Ca^{2+} , released from weathering of continental crust. However, in the Archean, the subaerial emergence of continental crust and its impact on seawater chemistry before 2.7 Ga is still debated (e.g., Flament et al., 2013; Roerdink et al., 2022; Satkoski et al., 2016; Viehmann et al., 2014). In contrast, it has been proposed that CO₂ concentrations of the Archean oceans and the corresponding atmosphere were generally higher than today (e.g., Walker, 1985; Kasting, 1987; Shibuya et al., 2012) and that abiotic carbonate precipitation may have occurred as a result of through extensive hydrothermal alteration and carbonatization of porous volcanic rocks at the seafloor by circulating CO₂-rich seawater and rock-released cations (Nakamura and Kato, 2004), although the occurrence of stromatolitic sedimentary dolomites in the Archean shows that this was not the only mechanism of carbonate precipitation (Hofmann et al., 1999; Nutman et al., 2016).

Many of the high-Mn Type I carbonates of this study plot between the pure calcites of Type II and published high Mn-carbonates of Nakamura and Kato (2002) and Yamamoto et al. (2004) (Fig. 2.3 a-b). Interestingly, both groups of carbonates can be found in outcrops of the same unit only several tens of meters apart (Fig. 2.2 b, c, i). The occurrence of both carbonate types in the same area could theoretically arise from local alteration along veins and fault zones, or from a temporal discrepancy between primary precipitation of high-Mn carbonates and secondary precipitation of low-Mn carbonates in vesicles. However, the lack of any veins feeding the carbonate material and the co-occurrence of both types of carbonates argues against post-depositional alteration. Rather, the bladed texture of the Type I carbonates is indicative of direct precipitation from boiling fluids (cf. Pirajno, 1992) that must have been trapped in the pillow spaces as the pillows were being erupted . Furthermore, Dawans and Swart (1988) suggested that the simultaneous formation of high Sr and low Sr carbonates could be due to variable crystal growth rates and fluid flow. This model can be applied to the formation of the Type I and Type II Pilbara carbonates, whereby the fluid-rock interaction time and temperature of fluid boiling within the interpillow spaces varied for the respective carbonate types.

2.6.2.2. Influence of different sources on the trace element budget

From a trace element perspective, the interstitial high-Mn carbonates (Type I) and vesicle filling low-Mn carbonates (Type II) of this study can be further subdivided by their REE and Sr concentrations. Specifically, the high-Mn Type I carbonates exhibit high REE concentrations and low Sr concentrations (≤ 250 ppm), whereas low-Mn Type II carbonates contain lower REE concentrations and higher Sr concentrations. Interestingly, the low-Mn carbonate of the Bradley Basalt Formation has the lowest REE and highest Sr concentrations, whereas the low-Mn carbonates of the Euro Basalt Formation have slightly higher REE concentrations and lower Sr concentrations (Figs. 2.4 and 2.6a).

Throughout all formations, REY_{PAAS} patterns of the high-Mn Type I carbonates are characterized by HREE enrichments relative to the LREE and generally display small positive Eu_{PAAS} and Y_{PAAS} anomalies (Fig. 2.4). The absence of negative Ce_{PAAS} anomalies indicates formation under reducing conditions and no free oxygen, which is characteristic for most Archean chemical sedimentary rocks (e.g., Van Kranendonk et al., 2003; Kamber et al., 2004; Allwood et al., 2010; Schier et al., 2018; Viehmann et al., 2020). However, the elevated REY concentrations in all Type I carbonates are two to three orders of magnitude higher than in other Archean carbonates, such as Strelley Pool Formation stromatolitic dolomites (Van Kranendonk et al., 2003; Allwood et al., 2010;



Interstitial carbonates in pillowed meta-basaltic rocks from the Pilbara Craton, Western Australia: A vestige of Archean seawater chemistry and seawater-rock interactions

Figure 2.8: Plots of (a) Y/Ho vs. ΣREE, (b) Y/Ho vs. Sm/Yb, and (c) Sm/Yb vs. Eu/Sm. The black arrow in (a) shows a mixing line between a stromatolitic dolomite by Allwood et al. (2010), representing Archean seawater composition and mafic host rock (data by Tusch et al., 2021). Elevated Y/Ho ratios in low-Mn carbonates with low REE concentrations are best explained by a dominant influence of seawater on Y/Ho, while decreasing Y/Ho and increasing REE concentrations argue either for clastic contamination or extensive fluid-rock interaction. In (b) Y/Ho vs. Sm/Yb and (c) Sm/Yb vs. Eu/Sm the varying influences of seawater, high-T hydrothermal fluids and fluid-rock interaction are shown. Noteworthy, the high-Mn Type I carbonates from the Pilbara Craton generally overlap in REE composition with the Mn-rich carbonate interstitials of the modern Troodos Ophiolite complex. Furthermore, at least the low-Mn Type II carbonate of the Bradley Basalt Formation, possibly representing Archean seawater composition, also overlap with seawater-derived carbonates of the Troodos Ophiolite (Quandt et al., 2019). Black line with full black circles represents mixing of modern seawater (489 m depth value of Zhang and Nozaki, 1996) with high Y/Ho and low Sm/Yb and Eu/Sm and high-T hydrothermal fluids (BS-13-4/2 of Bau and Dulski, 1999) with lower Y/Ho and higher Sm/Yb and Eu/Sm ratios. It is clearly shown that all interstitial carbonates of both, the Pilbara Craton and the modern Troodos Ophiolite do not lie on the mixing line between seawater and high-T hydrothermal fluids. The REE composition of the carbonates are rather explained by varying proportions of boiling seawater (ACA-9 of Allwood et al., 2010) with fluid-rock interaction (black mixing line with crosses).

Viehmann et al., 2020), and similar to their respective host rocks, suggestive of high fluid-rock interactions (Figs. 2.4, 2.7b).

Yamamoto et al. (2004) proposed a seawater origin for the interstitial carbonates of the Euro Basalt, which is supported by LREE-depleted REY_{PAAS} patterns, combined with positive La_{PAAS} and Y_{PAAS} anomalies (Figs. 2.4, B1). In contrast, Nakamura and Kato

(2002) proposed that the interstitial carbonates precipitated from hydrothermal fluids, similar to other hydrothermal precipitates in the area, including chert and barite. This interpretation is apparently supported by these carbonates having higher LREE concentrations and small positive Eu_{PAAS} anomalies relative to the broadly contemporaneous stromatolitic dolomites of the ca. 3.35 Ga Strelley Pool Formation (Fig. 2.4a-d). The high-Mn Type I carbonates are considered to have formed from a tapped fluid (seawater) that was boiling within the interpillow space of the host basalt (Pirajno, 1992). This is a critical process for the interstitial carbonate formation with regard to other carbonate sediments, such as near-contemporaneous stromatolites that are generally thought to have precipitated in photic zones of rather shallow seawater zones at ambient (i.e.., not boiling) temperatures (Van Kranendonk et al., 2003; Allwood et al., 2020). The Strelley Pool Formation stromatolitic dolomites are shallow water deposits that display modern seawater like REY_{PAAS} patterns, typically with a small dip from the middle to heavy REY_{PAAS} (Fig. 2.4f; Webb and Kamber, 2000; Van Kranendonk et al., 2003; Allwood et al., 2010; Viehmann et al., 2020).

In a first modeling approach, we calculate the mixing between two potential sources of interstitial carbonates: i) modern shallow Archean seawater (Zhang and Nozaki, 1996) and hydrothermal fluids that interacted with mantle-derived magmas (Bau and Dulski, 1999). Figure 2.8 illustrates these mixing calculations, which help to evaluate possible sources for the interstitial carbonates. This approach demonstrates that most Strelley Pool stromatolitic dolomites (Van Kranendonk et al., 2003; Allwood et al., 2006; 2010; Viehmann et al., 2020) precipitated from a predominantly shallow modern seawater-like fluid with minimal hydrothermal fluid influx (less than 1 %: Fig. 2.8a, b).

However, most of the high-Mn Type I carbonates we studied do not fall on a pure two endmember mixing line between seawater and hydrothermal fluids. Instead, a more plausible origin for the trace element budget of the high-Mn carbonate is better explained in a mixing model involving boiling seawater and variable degrees of direct fluid-rock interaction (Fig. 2.8b, c). Recent analogues from the Troodos ophiolite in Cyprus might provide a basis to explain the compositions of the carbonates from the Pilbara Craton. Recently, Quandt et al. (2019) reported several occurrences of Mn-rich carbonates that exhibit oscillatory growth zonations as well as elongated, blocky calcites in the modern Troodos Ophiolite Complex. Quandt et al. (2019) demonstrated that those carbonates were formed by closed system disequilibrium precipitation and exhibit REY_{PAAS} patterns comparable to their host rocks. Similar to Type I carbonates from Pilbara, Mn-rich layers from the Troodos carbonates and blocky calcites are also characterized by decreasing Y/Ho ratios (33 – 48) and the lack of pronounced positive Eu_{PAAS} anomalies, indicating prolonged fluid boiling with comparably longer fluid-rock interaction time. As illustrated in Figure 2.8b and c mixing calculations between Archean seawater (inferred by a Strelley Pool stromatolitic dolomite from Allwood et al., 2010), mafic host rocks (Tusch et al., 2021), and hydrothermal fluids (Bau and Dulski, 1999) can reproduce the full compositional range observed for the high-Mn Type I carbonates. Heated seawater poured into the interpillow space and prolonged fluid-rock interaction led to REY-rich carbonate precipitation. The prolonged fluid-rock interaction and contemporaneous carbonate precipitation is also supported by their coarse-grained and bladed morphology that suggests epithermal growth (Pirajno, 1992; Van Kranendonk et al., 2008). The



absence of positive Eu_{PAAS} anomalies and lower Eu/Sm ratios in the high-Mn Type I carbonates of our study can either be explained by over-correction of possible Ba interferences or by lower

Figure 2.9: In (a) Sr vs. Mn concentrations illustrates the distinction between low-Mn carbonates and high-Mn carbonates (modified after Banner and Hanson, 1990). High Sr concentration in the low-Mn carbonates can be associated with a seawater origin, whereas low Sr and high Mn concentration are generally attributed to secondary diagenesis (Veizer et al., 1989a; b). Here however, the low Sr and high Mn concentrations can also refer to the calcite precipitation from boiling seawater within the interpillow space. Note that one low-Mn carbonate (Pil16-005; Euro Basalt Formation) exhibits Mn concentrations of ~5,000 ppm, which is due to associated Fe-Mn-hydroxides. In (b) ⁸⁷Sr/⁸⁶Sr_{today} vs. 1/Sr shows the influence of coexisting quartz and silicified portions on the Sr isotope compositions of the interstitial calcites. Pure low-Mn Type II calcite exhibit low measured Sr isotope compositions and low 1/Sr ratios, whereas high-Mn Type I calcites exhibit higher 1/Sr ratios, which means lower Sr concentrations, and their higher measured Sr isotope compositions are best explained by highly radiogenic Sr contamination of co-existing Rbrich quartz components.

rates of Eu incorporation due to higher mobility and incompatibility of REE at higher temperatures. Alternatively, the fluid source of the carbonates was below 250 $^{\circ}$ C and circulated only in a microenvironment without much contact to the ambient seawater reservoir that carries a positive Eu_{PAAS} anomaly.

In contrast to the high-Mn Type I carbonates, the low-Mn Type II carbonate of the Bradley Basalt exhibits a subparallel REY_{PAAS} pattern (Fig. 2.4f) and comparable concentrations a to the Strelley Pool stromatolitic dolomites (Van Kranendonk et al., 2003; Allwood et al., 2006; 2010; Viehmann et al., 2020) and a REY_{PAAS} pattern that is comparable to that of modern seawater with the exception of redox-sensitive Eu and Ce (Zhang and Nozaki, 1996), suggesting a predominant origin from Archean seawater and no significant fluid-rock interaction during carbonate precipitation.

The low-Mn vesicle filling carbonates of the Euro Basalt are characterized by REY concentrations transitional between the high-Mn carbonates and the low-Mn carbonate of the Bradley Basalt (Fig. 2.4). This is also visible from lower Y/Ho ratios than found in the low-Mn carbonate of the Bradley Basalt Formation. Using our three-component mixing model, and assuming that the low-Mn carbonate of the Bradley Basalt approximates the seawater composition of the local Archean ocean, already a small fraction (< 1 %) of hydrothermal fluids or fluid-rock interaction can significantly affect the composition of purely seawater-derived carbonates and reproduce the low-Mn carbonate composition in the Euro Basalt.

2.6.2.3. Preservation of primary C, O, Nd, and Sr isotope signatures

In addition to the trace element budget, the isotope composition of chemical sedimentary rocks has the potential of reflecting primary and secondary effects, such as variability in contribution of trace element sources, changes of tectonic regimes, temperature, or late-stage alterations (Shields and Veizer, 2002). The Nd isotope composition of modern marine chemical sediments for example is strongly controlled by regional influxes. In modern oxygenated oceans, REE are highly particle reactive, which results in relatively small marine residence time. Therefore, a globally homogenous Nd isotope signature cannot be achieved over the timescale required for homogeneous mixing in the modern oceans (Broecker and Peng, 1982; Tachikawa et al., 2003). This causes heterogeneous Nd isotope compositions in seawater that primarily represents the regional influx of weathered material. In contrast, the REE residence time in Archean

oceans is not fully understood. Most likely, the influx of REE in the Archean oceans were not limited to continental weathering, but were rather strongly supplied by hydrothermal alteration of the oceanic seafloor due to higher volcanic activity. This scenario is also supported by more radiogenic, mantle-like initial Nd isotope compositions, and selective positive Eu enrichments in marine sedimentary rocks (e.g., Alexander et al., 2009; Kamber and Webb, 2001; Viehmann et al., 2020, 2016, 2015). In case of the Pilbara Craton, initial ε^{143} Nd values for most of the interstitial carbonates do not show significant variations (Fig. 2.6b) and generally overlap with those of the surrounding mafic host rocks (Hasenstab et al., 2021). Therefore, we conclude that the radiogenic Nd isotope values of the interstitial carbonates do reflect local ambient seawater that is primarily controlled by the REY budget of ambient Pilbara rocks in the form of either weathered and eroded emerged landmasses, mafic seafloor weathering via high-temperature, hydrothermal fluids, and/or the interaction of boiling seawater with coexisting mafic rocks in interpillow spaces.

The preservation of primary Sr isotope compositions in Archean carbonates is hampered by the sensitivity of the Rb-Sr system to secondary processes. A major problem is the fluid mobility of Rb and Sr during post-depositional alteration or metamorphism, which often obscures the initial isotope composition, in particular for Archean rocks (e.g., McCulloch, 1994). Leaching during hydrothermal fluid alteration, for instance, leads to re-equilibration with secondary carbonate phases that often exhibit more radiogenic Sr isotope compositions at lower Sr concentrations. In contrast, post-depositional alteration or metamorphism in presence of less radiogenic authigenic minerals can change the lower Sr isotope composition of altered carbonates (Shields and Veizer, 2002). Therefore, to provide a more robust reconstruction of the Archean Sr evolution, previous studies (McCulloch, 1994; Satkoski et al., 2016; Ravindran et al., 2020; Roerdink et al., 2022) have investigated chemical sedimentary rocks that are more resistant to secondary processes such as barites.

Assuming that high Sr concentrations are primary signatures of carbonates, we conclude that the low Sr isotope composition found in the low-Mn Type II carbonates of the Euro Basalt (87 Sr/ 86 Sr_(i) = 0.7010 – 0.7011) and Bradley Basalt (87 Sr/ 86 Sr_(i) = 0.7013) represent the original composition of the precipitating medium, the Archean seawater. Hence, the more radiogenic Type I carbonates found in the Pilbara Craton likely carry a

secondary signature. For example, diagenesis and high fluid-rock ratios can alter the major element compositions to higher Fe, Mn, and Mg, and lower Sr concentrations (Fig. 2.9a), and lead to radiogenic Sr isotope compositions inherited from the fluids or host rocks, respectively (Fig. 2.6a; Siahi et al., 2018). For the Pilbara Craton, several metamorphic overprinting events have been reported (Van Kranendonk et al., 2003; Caruso et al., 2021) that could have potentially altered the elemental distribution and isotope composition of Pilbara Supergroup cherts and carbonates (cf. Minami et al., 1995; Viehmann et al., 2020).

The ⁸⁷Sr/⁸⁶Sr isotope compositions of the high-Mn Type I carbonates from Pilbara (0.701523 to 0.718776), coupled with extremely low Rb/Sr ratios (< 0.001) would support alteration via a secondary process that altered the Sr budget of the high-Mn carbonates to low Sr concentrations and radiogenic isotopes. Only one high-Mn carbonate exhibits a slightly higher Rb/Sr of 0.037 (Pil16-004 from the Euro Basalt). Possible alteration sources are meteoric water, or hydrothermal fluids with a radiogenic Sr isotopic signature. However, extensive meteoric water alteration can be ruled out because these were submarine deposits and because modern meteoric water exhibits both a highly radiogenic Sr isotopic signature and light ¹⁸O/¹⁶O isotope values. In contrast, the high-Mn carbonates do not show a co-variation between theses isotope systems (Fig. B2) and the δ^{18} O values are generally too heavy to account for extensive alteration (Fig. 2.6c). Considering a radiogenic hydrothermal fluid derived from an underlying granitic intrusive body, a successive increase of the Sr isotopic signature is feasible. However, this alteration process is rather regional and should affect all carbonates, at least of the same formations. The occurrence of both highly radiogenic high-Mn Type I carbonates and unradiogenic low-Mn Type II carbonates within tens of meters' distance most likely excludes a granitic source for the Sr isotopes.

The boiling of trapped hot fluids and the high fluid-rock interaction led to the formation of the bladed Type I calcites, followed by the formation of hydrothermal quartz and partial silicification of interstitial carbonates (Figs. 2.2g, 2.3c). With the prolonging fluid-rock interaction and boiling, the initially high Sr concentrations of the pure calcite were remobilized and removed to lower concentration (Fig. 2.9a; < 250 ppm; Banner and Hanson, 1990; Banner, 1995; Yamamoto et al., 2004). The Type II carbonates, which are predominantly found in degassing vugs, rather than in the interpillow space, did not

experience the extensive boiling and fluid-rock interaction and therefore retained their initial seawater-like Sr isotope composition. In contrast, there is a high chance that the high-Mn Type I carbonates obtained a lower, more mantle-like Sr isotope composition as inferred from the clinopyroxene separates (87 Sr/ 86 Sr_(i) = 0.700341 – 0.700710). However, this signal is not preserved within the Type I carbonates. The co-precipitation of interstitial high-Mn Type I carbonates and hydrothermal quartz observed in pillow lavas from the Pilbara Craton is similar to observations from modern hydrothermal systems (Peter and Scott, 1988; Lindsay et al., 2005) that were interpreted to record decreasing hydrothermal activity over a temperature range from ca. 270 to 100 °C. The late stage fluid, i.e., remnants of the trapped boiling Archean seawater, responsible for the quartz formation and silicification of the high-Mn Type I carbonates, was enriched in highly mobile elements such as Li and Rb. The accompanying quartz of Pil17-008d exhibits Li and Rb concentrations of 1.78 ppm and 3.11 ppm, respectively, whereas the pure calcite only has Li and Rb concentrations of 0.144 ppm and 0.0196 – 0.0477 ppm. Thus, higher Rb/Sr ratios in silicified carbonates and coexisting quartz also resulted in very radiogenic Sr isotope compositions on a relatively local scale. Hence, highly radiogenic ⁸⁷Sr/⁸⁶Sr isotope compositions in the high-Mn carbonates can be best explained by silicified Rbrich areas that induced a strong radiogenic ingrowth of ⁸⁷Sr by the decay of ⁸⁷Rb (Fig. 2.9b).

Post-depositional alteration of the Pilbara interstitial carbonates, for what no textural evidence exists from the bladed textures, should also have affected stable isotope systematics. Both types of carbonates exhibit comparable stable ¹⁸O/¹⁶O isotope values, whereas the high-Mn Type I carbonates show a tendency towards slightly lower ¹³C/¹²C values (Fig. 2.6d). Also considering published data for sedimentary carbonates from the Pilbara Craton (Nakamura and Kato, 2004; Lindsay et al., 2005; Shibuya et al., 2012), it appears that most carbonates exhibit δ^{13} C values around $0 \pm 2\%$. This range is comparable to that of modern marine carbonates, thus suggesting that the carbonatization of Archean oceanic crust have been driven by dissolved CO₂ derived from seawater and the atmosphere. Variations in δ^{18} O are either interpreted as a temperature proxy for the precipitation environment (Siahi et al., 2018) or as the result of post-depositional alteration. Carbonates with the highest δ^{18} O values are considered to be best preserved and to reflect seawater composition at lower temperatures (Schidlowski et al., 1983;

Veizer et al., 1989a; b), while increasingly lighter oxygen isotope compositions indicate higher precipitation temperatures of the coexisting fluid. Similar δ^{18} O values in both types of the Pilbara carbonates (high-Mn and low-Mn) indicate a similar temperature range during carbonate precipitation. In case of the interstitial carbonates from the Pilbara Craton, both Lindsay et al. (2005) and Shibuya et al. (2012) proposed calcite precipitation and oceanic crust alteration temperatures between 80 and 270 °C. However, these lower δ^{18} O of the interstitial carbonates, may not necessarily reflect an increase in temperature, but could, however, result from a generally lower δ^{18} O of Archean seawater. Recent studies suggest extensive sequestration of CO₂ into the oceanic crust to be the driving mechanism of lowering global ocean δ^{18} O (Herwartz et al., 2021; Kanzaki and Bindeman, 2022).

A shift towards slightly negative δ^{13} C values has been explained either by metamorphic reworking or diagenesis (Bottinga, 1969; Nakamura and Kato, 2004). Alternatively, degassing of mantle-derived plutonic or volcanic rocks may also lead to a decrease of δ^{13} C (Lindsay et al., 2005). The conceptual assumption of mixing hot, mantlederived fluid (low δ^{13} C and δ^{18} O) and seawater-like fluid (higher δ^{13} C and δ^{18} O), is in line with a positive co-variation observed for carbonate samples from the Pilbara Craton (Fig. 2.6c). The variations, we find between the Type I and Type II carbonates can therefore be best explained by varying degrees of fluid-rock interaction and boiling within the interpillow space. The Type II carbonates possibly precipitated from relatively hot seawater that intercalated through the degassing spaces. This can be inferred by the low δ^{18} O isotopes, whereas the low REY concentrations and δ^{13} C values show typical seawater compositions and argue against extensive fluid-host rock interaction. In contrast, extensive boiling of fluids within the interstitial led to subsequent equilibration with the mafic host rock and hence a decrease to more mantle-like δ^{13} C values and high REY concentrations for the Type I carbonates. The comparable light δ^{18} O values argue for a similar precipitation temperature for both types of carbonates. The possibly decisive distinction is the duration of seawater boiling and the interaction with the host rock.

2.6.3. Strontium isotope constraints on the origin of interstitial carbonates and implications for the global Archean seawater

It is generally assumed that the Sr isotope evolution of Archean seawater is primarily controlled by hydrothermal alteration of mafic oceanic crust (McCulloch, 1994). Thus,

the isotope composition of Archean seawater is strongly correlated with the Sr isotope evolution of the predominantly unradiogenic upper mantle with ⁸⁷Sr/⁸⁶Sr values between 0.7000 and 0.7005 for the Mesoarchean (e.g., Veizer et al., 1989a; b; McCulloch, 1994). The emergence of local, modern day-like plate tectonics at the Archean-Proterozoic boundary is generally believed to have induced a change in the ancient seawater composition.

Recent studies that investigated the Sr isotope composition of different chemical sediments even propose an earlier subaerial exhumation of evolved continental crust that caused a steeper increase in the Sr isotope seawater curve, which may have already started in the Paleoarchean between 3.7 - 3.2 Ga (Satkoski et al., 2016; 2017; Ravindran et al., 2020; Roerdink et al., 2022), and may have led to an early decoupling of more radiogenic



Figure 2.10: Plot of initial 87 Sr/ 86 Sr_(i) vs. Age (Ma) in order to reconstruct the Sr isotope evolution curve of Archean seawater. Extrapolated global Sr isotope evolution trends are taken from Satkoski et al. (2016), Ravindran et al. (2020), and Roerdink et al. (2022). The onset of subaerial crustal weathering is as proposed by Roerdink et al. (2022). Gray circles represent literature values for Archean barites and blue circles represent values for Archean carbonates (Roerdink et al. 2022, and references therein), whereas the brown circles represent the initial Sr isotope composition of the Archean mantle at 3.46 Ga, inferred by pyroxene separates of this study. Low-Mn carbonates (Type II) of the Euro Basalt Formation plot on the line proposed by Roerdink et al. (2022) confirming the increasing subaerial weathering influx into the Paleoarchean seawater, whereas the low-Mn carbonate of the Bradley Basalt Formation plots beneath the line. This might hint for an increasing recycling of mafic crust after 3.2 Ga (Abbreviation: PM = primitive mantle; DM = depleted mantle; CC = continental crust).

seawater Sr relative to the mantle. Early Archean felsic plutons may already have been subaerially exposed by hydrous melting of basaltic succession of thickened oceanic crust (Smithies, 2000; Nagel et al., 2012). More widespread continental crust by the Paleo- and Mesoarchean have been inferred from the detrital zircons record of clastic sediments, e.g., for the Pilbara, Kaapvaal, Dharwar and North Atlantic Cratons (e.g., Van Kranendonk et al., 2003; Dhuime et al., 2012; Næraa et al., 2012; Siahi et al., 2018; Hoffmann et al., 2019).

Comparison of the initial Sr isotope values of interstitial carbonates with contemporary pyroxene separates from the host rocks obtained here, we can demonstrate that the seawater-derived carbonates are slightly more radiogenic in Sr than the ambient mantle at that time. The low-Mn carbonates of the older Euro Basalt Formation follow the same global Sr seawater evolution line as defined by Mesoarchean barites (compiled by Roerdink et al., 2022), suggesting a global homogenous Sr isotope composition, and supporting an earlier onset of continental weathering at ca. 3.7 Ga (Fig. 2.10). Following Roerdink et al. (2022) the progressive increase in marine Sr isotope compositions is caused by the subaerial chemical weathering of exposed continental crust that could have comprised of up to 7 - 12 % of the Earth's surface. Accordingly, isotope constraints on Archean sediments imply shallow seawater conditions that were suitable for phototrophic metabolism at 3.4 Ga (Wacey, 2010; Duda et al., 2016).

Taking previously published Sr isotope data for the Paleo- to Neoarchean into account, Ravindran et al. (2020) proposed a break in the Sr isotope evolution curve by 3.2 Ga (Fig. 2.10). When compared to the Sr evolution models by Satkoski et al. (2016; 2017) and Roerdink et al. (2022) that propose a continuous increase in radiogenic Sr of the seawater with time, most of the Mesoarchean carbonates reported by Ravindran et al. (2020) fall below this proposed evolution line. These carbonates were originally interpreted as precipitates from mantle-buffered seawater (Veizer et al., 1989a; b). In their study, Ravindran et al. (2020) argue for a temporal excursion of the Sr evolution curve towards less radiogenic values during the Mesoarchean, which has been caused by increasing seafloor spreading that was triggered by increasing subduction (Dhuime et al., 2018). In line with the observations by Ravindran et al. (2020), the Sr isotope composition for the low-Mn carbonate of the Bradley Basalt Formation (87 Sr/ 86 Sr = 0.701372) also falls slightly below the proposed curves by Satkoski et al. (2016; 2017) and Roerdink et al.

Interstitial carbonates in pillowed meta-basaltic rocks from the Pilbara Craton, Western Australia: A vestige of Archean seawater chemistry and seawater-rock interactions

al. (2022). This temporal excursion at ca. 3.2 Ga, as recorded by carbonates from the Pilbara Craton, coincides with a change in the tectonic regime and the local initiation of subduction-like plate tectonics in the Pilbara Craton (e.g., Smithies et al., 2007), supporting the model by Ravindran et al. (2020). Alternatively, however, the decline of the Sr evolution curve during the Mesoarchean could simply reflect a smaller continental weathering flux throughout the Paleoarchean than previously proposed.

Although the temporal evolution of the Sr isotope composition of Archean seawater is still highly debated, it is without a doubt that the original mantle-buffered Archean seawater was increasingly modified by erosion of emerging continental crust and sedimentary input via chemical weathering through the Archean. The record of marine chemical sediments that retained the initial composition of Archean seawater however is small and often obscured by secondary processes (e.g., Polat and Hofmann, 2003; Satkoski et al., 2017). Due to their extremely good preservation, vesicle-filling carbonates of mafic pillow successions from the Pilbara Craton presented in this study can help to better constrain the carbonate information on the Sr isotope evolution of the Archean seawater and the respective influences of the mantle and emerging continental crust.

3.7. Conclusions

Major and trace element systematics of interstitial carbonates provide new insights into the Archean seawater compositions and processes active during the fluid-rock interaction of boiling seawater and mafic crust. High-Mn carbonates (Type I) found in mafic succession of the Pilbara Craton plot together with their respective host rocks on Sm-Nd isochrons, linking their precipitation closely to the eruption and carbonatization of the host rocks. The high-Mn carbonates also exhibit relatively radiogenic initial ⁸⁷Sr/⁸⁶Sr_(i) isotopes (0.701523 – 0.718776) with exceptionally low Rb/Sr ratios. Elevated REY concentrations coupled with only slightly super-chondritic Y/Ho ratios of 34.5 – 39.1 suggest long interaction times of boiling seawater with mafic host rocks in an interpillow system rather than simple hydrothermal alteration. The slightly lower δ^{18} O (9.10 – 13.18) than in the near-contemporary shallow marine Strelley Pool stromatolitic dolomites support higher precipitation temperatures, but also exclude extensive alteration by meteoric water that could also explain the radiogenic Sr isotope compositions. More likely, the elevated ⁸⁷Sr/⁸⁶Sr in many of the high-Mn Type I carbonates can be best explained by co-existing Rb-rich phases, such as secondary quartz with a strongly radiogenic ingrowth of ⁸⁷Sr that has been overprinting the Sr isotope composition of primary carbonates.

In contrast, low-Mn (Type II) carbonates, found as vesicle fillings in pillow basalts, reflect comparably low seawater-host rock interaction times, i.e., they preserved typical seawater-like REY_{PAAS} systematics. They also share compositional similarities with the Strelley Pool stromatolitic dolomites suggesting a shallow water regime at the time of precipitation. The initial Sr isotope compositions of the low-Mn Type II vesicle carbonates are exceptionally low $({}^{87}\text{Sr}/{}^{86}\text{Sr}_{(i)} = 0.701049 - 0.701097$ at 3.34 Ga and 0.701372 at 3.12 Ga) consistent with previously published Sr data for barites (Ravindran et al., 2020; Roerdink et al., 2022) and limestones (Satkoski et al., 2017). However, the Type II carbonates are consistently more radiogenic than the coexisting mantle inferred by fresh pyroxene separates (87 Sr/ 86 Sr_(i) = 0.700341 – 0.700710) suggesting a decoupling of the Sr seawater evolution curve from the ambient mantle already by the Paleoarchean. A temporal decline of ⁸⁷Sr/⁸⁶Sr in carbonates from the Pilbara Craton at around 3.2 Ga coincides with the local onset of modern day-like subduction. This observation is in line with the previous suggestion that the decreasing ⁸⁷Sr/⁸⁶Sr isotope composition of the Archean ocean at 3.2 Ga reflects increased buffering of radiogenic Sr influx from continental crustal sources by increasing seafloor spreading, which was triggered by increasing subduction.

In summary, if shown undisturbed by a combination of geochemical proxies, interstitial carbonates provide a valuable archive offering insights into the temporal evolution of Archean seawater and, together with their host rocks, allow for Sm-Nd dating of submarine volcanic deposits.

CHAPTER 3

JUVENILE CONTINENTAL CRUST EVOLUTION IN A MODERN OCEANIC ARC SETTING: PETROGENESIS OF CENOZOIC FELSIC PLUTONS IN FIJI, SW PACIFIC

3.1. Abstract

Viti Levu, Fiji, provides one of the best exposed Phanerozoic analogues for the formation of juvenile continental crust in an intra-oceanic setting. Tonalites and trondhjemites are present in several large $(75 - 150 \text{ km}^2)$ adjacent, mid-Cenozoic plutons. We report major and trace element data including rare-earth element (REE) and highprecision high field strength element (HFSE) compositions, new Hf-Nd-Sr-Pb isotope data, and zircon U/Pb-ages, O-Hf isotopes, and trace elements, from five different plutons. The Eocene Yavuna pluton and the Miocene Colo plutons are mainly composed of tonalites and trondhjemites and represent the exposed middle crust of the former Vitiaz island arc. The plutons can be divided into three suites. One suite is light REE (LREE) depleted with some trace element ratios lower than average normal mid-ocean ridge basalts (N-MORB). A second suite has flat REE patterns similar to local island-arc basalts. Both suites occur near the coast of Viti Levu, include a wide compositional spectrum from gabbro to tonalite, and can be produced mostly by fractional crystallization of mafic precursor melts. The third suite is characterized by LREE-enrichments with higher La_N/Yb_N (2.3 – 4.9), higher Zr/Y (4.3 – 7.1), and lower Nb/Ta (9.6 – 12.4). They occur closer to the center of the island and are bimodal trondhjemite-gabbro intrusions. These characteristics are consistent with formation mostly by partial melting of mafic crust. Trace element modeling shows that the trace element ratios of the third suite can be produced by 10 – 20 % melting of the mafic crust in the presence of residual amphibole, resulting in the retention of the medium rare earth elements (MREE) and diagnostic trace element ratios including low Nb/Ta and high Zr/Y. Geochemical similarities of the LREE-enriched suite to typical "low"-pressure Archean tonalites-trondhjemites-granodiorites (TTGs) imply a common petrogenetic origin and similar mechanisms for the generation of juvenile Archean and modern differentiated crust by partial melting of mafic crust with residual amphibole. In modern oceanic arcs, genetically unrelated felsic plutonic as well as volcanic rocks co-exist, and in this regard, the Fijian plutons accompany major tectonic disruptions to arc processes.

3.2. Introduction

The formation of continental crust is a fundamental process in Earth's history, yet the processes that led to its formation are still uncertain. Hence, understanding the geodynamic settings in which juvenile felsic magmas are produced from mantle-derived basaltic precursors is important (e.g., Hawkesworth and Kemp, 2006). Several studies propose that by the end of the Archean up to 60 % of the present continental crust was already formed (e.g., Taylor and McLennan, 1995; Belousova et al., 2010) and some essential building blocks are the sodic tonalite-trondhjemite-granodiorite series (TTGs; e.g., Moyen and Martin, 2012; Hoffmann et al., 2019 for a review). The geochemical similarities of those Archean TTGs to modern adakites link the formation of juvenile continental crust to convergent oceanic and continental arcs (Defant and Drummond, 1990; Drummond and Defant, 1990).

In contrast, after the onset of modern, post-Archean plate tectonics, continental crust generation experienced a shift in magma composition towards more diverse lithologies, such as calc-alkaline peraluminous granites (e.g., Martin, 1993; Laurent et al., 2014). Although partial melting of mafic rocks is thought to be the prevalent process producing intermediate to felsic melts in the Archean, modern continental crust production in continental arc settings often involves significant continental crustal recycling (e.g., Taylor, 1967; Barbarin, 1999; Belousova et al., 2010; Moyen et al., 2017). Only the formation of oceanic plagiogranites in ophiolites can be regarded as a completely juvenile process, but their geochemical composition differs from Archean TTG and their volume in the oceanic crust is minuscule (Rollinson, 2008; 2009; Marien et al., 2019).

Although TTGs were widespread in the Archean, voluminous modern post-Archean granitoids in an oceanic arc setting are scarce because modern arcs are mostly submarine. However, recent active seismic surveys in the Izu-Ogasawara island arc (Suyehiro et al., 1996; Kodaira et al., 2007) and Tonga (Crawford et al., 2003), passive seismic studies of Fiji (Chen et al., 2019) and the Aleutians (Janiszewski et al., 2013), and interpretation of gravity data for Fiji (Segev et al., 2012), have revealed 20 - 40 km thick crust in these oceanic island arcs, including the presence of a "granitic" middle crustal layer with P-wave velocities of 6.0 - 6.5 km/s. These discoveries indicate that it is possible to produce tens of km-thick intermediate to felsic crust that is geophysically "continental" in an oceanic setting and thus it is indispensable to study modern intra-oceanic arcs.

In this regard, Fiji is exceptional because the main island, Viti Levu, possesses one of the largest exposures of Cenozoic tonalite and trondhjemite plutons of any known oceanic arc, with about 15 plutons ranging in size from 75 to 150 km² (Gill and Stork, 1979). Their discovery in the 19th century led to the inference that Fiji was a stranded continental fragment (e.g., Woolnough, 1903). However, analyses of zircon crystals from one of the plutons found no evidence of pre-Eocene inheritance (Rickard and Williams, 2013). Moreover, the crust is thicker beneath Viti Levu than elsewhere in Fiji or the rest of the Lau-Colville Ridge (Chen et al., 2019). Thus, Viti Levu appears to be an exceptional place to study the maturation of modern oceanic crust towards a continental crustal nucleus, where juvenile felsic melts are generated by melting of a basaltic protolith, fractional crystallization of mafic melts, or both.

In this study, we present new geochemical data for tonalites and trondhjemites from five different plutons, and associated gabbros, diorites, and rhyolites, demonstrating that at least two end-member processes can account for their generation. In particular, high precision data for HFSE combined with REE and Hf-Nd-Sr-Pb isotope ratios provide novel insights into the formation processes and, hence, an unprecedented opportunity to compare modern intra-oceanic trondhjemite generation to Archean TTG formation and modern continental crustal growth.

3.3. Geological setting and sample collection

The Fijian islands are the northernmost part of the Fiji-Tonga-Kermadec arc system in the southwestern Pacific Ocean. From the late Eocene through early Miocene, Fiji was part of the larger Vitiaz arc that included Vanuatu (Fig. 3.1a), and formed from the Juvenile continental crust evolution in a modern oceanic arc setting: Petrogenesis of Cenozoic felsic plutons in Fiji, SW Pacific



westward subduction of the Pacific Plate beneath the Indo-Australian Plate (Hathway, 1994; Schellart et al., 2006). The magmatic products of this older arc constitute the Yavuna Group, largely consisting of pillow basalts and breccias, and other volcaniclastic sediments (Hathway and Colley, 1994) that form the basement of Viti Levu. Metamorphism has affected these units, ranging from zeolite to facies amphibolite (Hathway and Colley, 1994). The Yavuna Group is dominated by diverse volcanic rocks, most with a strong arc-like signature (Colley and Hindle, 1984; Gill, 1987), that were deposited between 34 and 25 Ma (Whelan et al., 1985; Wharton et al., 1994). The diversity includes typical island-arc tholeiites (YV-IAT) with slight LREE-enrichment, and low-Ti early arc tholeiites (YV-EAT) with MORB-like LREE-depletion (Todd et al., 2012). Todd et al. (2012) also reported high-Ti EAT and boninitic rocks, but both are uncommon so that this study does not consider them. All volcanic rocks of the Yavuna Group are

Figure 3.1: Tectonic reconstruction of the Fijian region (SW Pacific) for the Cenozoic based on Hathway (1993) and Schellart et al. (2006). In (a) Fiji is part of the Vitiaz arc at 40 Ma, which is formed by the westward subduction of the Pacific slab. In (b) opening and spreading of the South Fiji Basin (SFB) caused by the eastward roll back of the Pacific slab. In (c) collision of the Melanesian Border Plateau and the Vitiaz arc at 12 Ma caused north-eastward subduction of the northern SFB, followed by the opening of the North Fiji Basin at 12 - 11 Ma and a ca. 135° counter-clockwise rotation of Fiji at 10 Ma. Initiation of the Lau Basin spreading between the Tonga Ridge and Lau Ridge in the east of Fiji at 5Ma. In (d) present tectonic setting of the SW Pacific region.
thought to be products of decompression- and flux-melting during the initial subduction phase. The corresponding mantle source exhibited a "Pacific" isotopic character with only minor additions of slab-derived fluids and melts (Todd et al., 2012). Sediments of the Yavuna Group include foraminiferal limestones that were deposited between the Upper Eocene and Lower Oligocene (Cole, 1960) and crop out in the western part of the studied area (Fig. 3.2).

The South Fiji Basin (SFB) opened during the Oligocene up to early Miocene (34 – 15 Ma; Fig. 3.1b), and at least the initiation of spreading coincided with the cessation of volcanism in Viti Levu for several m.y. (Herzer et al., 2011). Both features are thought to be associated with the roll-back of the Tonga-Kermadec subduction hinge (e.g., Sdrolias et al., 2003).

Volcanism resumed along the Vitiaz arc, including Viti Levu, during the Miocene as the Pacific slab roll-back continued eastward. The Vitiaz arc shifted to the east and a second arc formed along its SFB margin (Hathway, 1994). The corresponding arc volcanism resulted in the deposition of the Wainimala Group, comprising volcanic rocks with both island-arc tholeiitic and back-arc basin tholeiitic compositions. This chemical dichotomy led to different hypotheses for Viti Levu being either obducted SFB ophiolitic crust (Colley and Hindle, 1984) or of island-arc origin (Gill, 1970; 1987). The Wainimala Group crops out widely in the study area (Fig. 3.2a) and is divided into two assemblages (Wharton et al., 1994). The coastal Wainimala "arc" assemblage (WA-A) represents the axis of the main volcanic arc, while the "basin" assemblage (WA-B) is found in the island interior. The latter has been interpreted as from a fore-arc (Hathway, 1994), although it is geochemically more characteristic of a rear-arc. The WA-A and WA-B assemblages roughly correspond to the Mt. Gordon and Matailombau sub-groups, respectively, within the Wainimala Group. The WA-A is exposed in the southern and western portion of Viti Levu and consists of volcaniclastic rudites, lava flows, and minor limestones (Hathway and Colley, 1994; Wharton et al., 1994). The lavas are LREE-depleted tholeiites (Gill, 1970; 1987) that are similar to the Yavuna Group EAT, although the WA-A group shows more slab-fluid additions and their heavy REE (HREE) concentrations are lower. The WA-B assemblage, unconformably above the Yavuna Group, is exposed in the central portion of Viti Levu and composed of re-deposited rudites, and massive lavas and pillow



Figure 3.2: Simplified geological map of Southern Viti Levu, Fiji. The plutonic bodies comprise the Yavuna Stock and the Colo plutons that are subdivided by their major and trace element compositions (Stork, 1984 and this study) into three distinct suites: central LE-suite (red), coastal EE-suite (blue), and coastal LD-suite (green). Sample locations are marked with diamonds (LE-suite), circles (EE-suite), and triangles (LD-suite). Two plutons (#12 and 18) are mainly gabbroic. Because their gabbros are similarly depleted as those in the LD-Type Korolevu pluton and occur along-strike of Korolevu, we infer that the other two plutons also are LD-Type. There are no analyses of the "unidentified" tonalitic pluton (#7 Mavuvu), but it has prominent biotite similar to LE-Type. In (b) the generalized timeline shows important volcanic, plutonic, and tectonic events for Viti Levu, Fiji. Uranium/Pb zircon ages for the suites and detrital zircons are from Todd et al. (2021). Timing of regional events are from Rodda (1994), Hathway (1994), Hathway and Colley (1994), Wharton et al. (1994), and Herzer et al. (2011).

lavas that have a generally more enriched arc tholeiitic composition like the Yavuna IAT (Wharton et al., 1994), which is attributed to small amounts of slab-melt addition.

Subduction of the Pacific slab beneath the western Vitiaz arc halted after its initial collision with the Ontong Java Plateau in the northern Solomon Islands (25 - 20 Ma; Schellart et al., 2006) and the Melanesian Border Plateau north of Fiji (Fig. 3.1; Gill and Whelan, 1989; Schellart et al., 2006). As a result, the subduction zone in the west reversed polarity to a northeast-dipping regime along the South Solomons and New Hebrides trenches in the Late Miocene (Pelletier and Auzende, 1996). This led to the breakup of the Vitiaz arc, a 60° clockwise rotation of the New Hebrides (Schellart et al., 2006) and

back-arc spreading in the North Fiji Basin. Fiji, on the other side, rotated ca. 135° counterclockwise from ≤ 8 to 3 Ma (Taylor et al., 2000, Fig. 3.1c). A subsequent rollback of the Pacific slab led to formation of the Lau Basin and Havre Trough between the active Tonga-Kermadec arc and the remnant Fiji-Lau-Colville arc in the Pliocene (Fig. 3.1d).

Tonalite and trondhjemite plutons are wide spread in Viti Levu and are the subject of this study. Fifteen plutons form cores of broad anticline structures, and intrude the volcanic sequences of the Yavuna and Wainimala groups, which are locally metamorphosed to hornblende-hornfels facies and silicified (Fig. 3.2; Gill and Stork, 1979; Stork, 1984). Each pluton surface exposure ranges from 75 - 150 km² resulting in the largest cumulative exposure of Cenozoic plutons of any oceanic arc. For comparison, the three well-studied plutons on Adak and Kagalaska in the central Aleutians are ~100 km² each (Kay et al., 2019).

The emplacement ages range from 37 Ma to 7 Ma, and they correspond to episodes of Fiji volcanism (Rodda, 1967; Whelan et al., 1985; this study). They are divided by age into the older Yavuna and Momi plutons (37 Ma and 21 Ma) and the Colo (pronounced Tholo) plutons (12 - 7.5 Ma). A phase of orogenic folding occurred from 12.5 to 8 Ma, which coincides with the emplacement of the Colo plutons (Rodda and Lum, 1990). East of the Sovi Fault (Fig. 3.2), the plutons are exposed in a linear NE-SW trend, while in the west they trend NW-SE. Both are interpreted to be the arc axis, which was deformed during the rotation of the Fiji Platform.

The first detailed geochemical descriptions of the Fijian plutonic rocks were given by Gill (1970) and Gill and Stork (1979). Some of the plutons are intruded into and show geochemical similarities to the poorly studied dacites and rhyolites from the Wainimala Group (Gill and Stork, 1979).

Plutons show a wide compositional range including cumulate gabbro, diorite, tonalite, and trondhjemite. Depending on their location, the plutons can be divided into coastal and central groups (Stork, 1984). The coastal plutons are variable in composition and were mapped as combinations of subordinate quartz-free gabbro with a majority quartz-bearing rocks that range from quartz diorite to trondhjemite and tonalite. For example, the large well-sampled Korolevu pluton (Fig. 3.2) includes cumulate olivine gabbronorite, clinopyroxene-hornblende diorite with and without cumulate textures, hornblende quartz diorite, hornblende tonalite, and hornblende trondhjemite. The pluton





is roughly zoned with the more mafic rocks on the eastern and western margins and the more silicic rocks in the center. Other plutons in the coastal group, although less well sampled, show a similar range of compositions; two (Korosiviliou and Wainadoi) are mostly gabbroic with very low concentrations of Ba (10 - 25 ppm) and Zr/Y < 2. Intermediate rocks were mapped as less common than gabbro or tonalite, and most were interpreted as reflecting magma mingling or assimilation (Band, 1968; Rodda, 1976). In general, the more silicic samples from these plutons are poor in K, LILE and LREE, and rich in Y (35 - 60 ppm) and HREE.

The central plutons show a similar range of rock types, and three of the larger ones (Noikoro, Wainqa and Mavuvu) contain abundant intermediate rocks. However, two of the large well-sampled plutons are homogeneously felsic. The older Yavuna Stock is a hornblende trondhjemite, whereas the Wainivalau pluton is compound with a northern biotite-hornblende trondhjemite and a southern hornblende trondhjemite that has geochemical affinities with the coastal group. Other well-sampled central plutons show a wide range of rock types including olivine gabbro or gabbronorite, diorite, quartz diorite, tonalite, and trondhjemite. The more silicic samples from these plutons are mostly medium-K, biotite-hornblende or hornblende trondhjemites, with higher LILE and LREE concentrations, U-shaped REE patterns, and lower Y (< 30 ppm) and HREE concentrations.

Mineralogically, all selected samples contain mostly prismatic subhedral plagioclase (An₁₅₋₆₅) that retains typical twinning and concentric zoning with albite rims (Fig. 3.3) and sometimes myrmekitic texture (Gill and Stork, 1979). Other major phases are anhedral quartz (15 - 50 vol.%) and green hornblende, ± biotite, ± augite in more intermediate samples. Some samples of the central plutons, such as Yavuna and N-Wainivalau contain small amounts of orthoclase. Common accessories are magnetite, ilmenite, sulfides, and apatite. The samples show variable replacement of hornblende and biotite by chlorite and replacement of plagioclase by sericite.

Although we have studied only three plutons in detail, Figure 3.2 assigns other plutons to our tri-partite geochemical classification scheme based on fewer, or XRF-only, analyses per pluton (Todd et al., 2021). In addition, geological maps of Viti Levu distinguish between tonalite and gabbro as mappable pluton rock types. Most plutons are dominantly tonalitic in the sense of being quartz-bearing, but the felsic rocks range modally from quartz-diorite to trondhjemite. In addition, portions of some plutons are mapped as gabbroic and contain plagioclase plus one or more of olivine, orthopyroxene, clinopyroxene, and hornblende. Outcrops are insufficient to generalize whether the relative proportion of mafic, intermediate, and felsic rock differs between our three suites, or how much of their intermediate rocks reflect magma mingling or assimilation.

3.4. Analytical methods

We present new analyses of 21 well-preserved tonalites and trondhjemites, two diorites, and two rhyolites. All samples were cleaned to eliminate visible alteration rims,

veins and heterogeneities before they were crushed in a steel jaw crusher and pulverized in an agate mill. Some samples were prepared with a steel mill, which resulted in elevated Cr and Ni concentrations that we omit. Major element concentrations were determined by XRF at the University of California Santa Cruz (UCSC) and the University of Cologne (Germany). The trace element data are from UCSC in the early 1980s by XRF (Stork, 1984) and in 2011 using the solution ICP-MS methods of Todd et al. (2012), in 2010 from the Washington State University (WSU; Knaack et al., 1994) and from the University of Kiel in 2016 using the solution ICP-MS methods of Garbe-Schönberg (1993). The samples and four certified reference materials (JG-1, BCR-2, BIR, G-2) were digested using the high-pressure acid digestion procedure for felsic samples by Hoffmann et al. (2011) and modified by Marien et al. (2019).

For the high-precision HFSE and Hf-Nd-Sr isotope analyses at the University of Cologne, approximately 100 – 120 mg of the samples (including duplicates) were weighed in pre-cleaned Savillex Teflon beakers. Prior to sample digestion a mixed ¹⁷⁶Lu-¹⁸⁰Hf-⁹⁴Zr-¹⁸⁰Ta isotope tracer was added in order to determine isotope compositions and element abundances on the same aliquot (see Weyer et al., 2002). Additional Hf-Nd-Sr-Pb isotope separations and measurements were carried out at UCSC in 2011 using the methods of Todd et al. (2012).

Separation of Lu and HFSE was performed via the three-column ion exchange chemistry described by Münker et al. (2001) and Weyer et al. (2002). Strontium and Nd were separated by using the matrix cut from the previous separation using BioRad AG 50W-X8 cation resin (200 – 400 mesh) and Eichrom Ln-spec resin (Pin and Santos Zalduegui, 1997). Lead was eluted as described by Ryder et al. (2006).

The total procedural blanks for the PARR bomb digestions were < 300 pg Sr, < 150 pg Pb, < 100 pg Lu, and < 40 pg for both Hf and Nd.

Isotope compositions of Hf-Nd-Sr as well as the Lu, Hf, Zr-Nb and Ta concentrations were determined via isotope dilution using the Thermo-Finnigan Neptune MC-ICP-MS at Cologne/Bonn. Strontium isotope data are given relative to NBS 987 (87 Sr/ 86 Sr = 0.710240) and were normalized to 86 Sr/ 88 Sr = 0.1194. Neodymium isotopes were normalized to 146 Nd/ 144 Nd = 0.7219 and the results are given relative to a 143 Nd/ 144 Nd value of 0.511859 for the La Jolla standard. Measured 176 Hf/ 177 Hf were normalized to 179 Hf/ 177 Hf of 0.7325 and results are given relative to a 176 Hf/ 177 Hf = 0.282160 for the

MünsterAMES standard, which is isotopically identical to JMC 475 (Münker et al., 2001). External long-term reproducibility is ± 50 ppm for Sr and ± 40 ppm for Nd and Hf (all 2 r.s.d.), respectively. Epsilon-¹⁴³Nd and ϵ^{176} Hf are calculated using the CHUR values of 0.512630 for ¹⁴³Nd/¹⁴⁴Nd and 0.282785 for ¹⁷⁶Hf/¹⁷⁷Hf (Bouvier et al., 2008), respectively.

Lead isotope compositions were determined by Tl-doping using MC-ICP-MS at UCSC in static mode. The Pb cuts were doped with NBS 997 Tl for mass bias correction, assuming 203 Tl/ 205 Tl of 0.418911. Results are given relative to NBS 981 with 206 Pb/ 204 Pb = 16.941, 207 Pb/ 204 Pb = 15.496, and 208 Pb/ 204 Pb = 36.722 (Abouchami et al., 2000).

For Ta analyses by isotope dilution, mass bias correction was carried out using doped Re (Weyer et al., 2002). For the analyses of Zr, the measured 94 Zr/ 90 Zr ratios were corrected for mass bias using doped Sr (Weyer et al., 2002). The Nb concentrations were measured as 93 Nb/ 90 Zr relative to standard solutions prepared from AMES metals (see Münker et al. 2001; Weyer et al. 2002).

Zircons were separated from ten tonalites, one gabbro, and one rhyolite at the Japanese National Institute for Polar Research (NIPR), and analyzed at the NIPR, the Australian National University (ANU), and the University of California Santa Barbara (UCSB). They originate from the Yavuna, N-Wainivalau, Korolevu, and Momi plutons, and one Kalaka rhyolite. Splits of four of the zircon separates were also analyzed at UCSB together with zircons from one otherwise unstudied tonalite sample from the Yavuna pluton. In addition, detrital zircons were separated from two river sand samples. One is from the Sigatoka River that drains most of southern Viti Levu where the main plutons are exposed (sample Fij-1). The other sample is from Nagalitala Creek north of its confluence with the Sigatoka River. Nagalitala Creek drains western Viti Levu including its oldest terrane that is intruded by the Yavuna pluton, and the overlying rocks that are intruded by the Momi and other small plutons (sample Fij-2). The zircons were analyzed for their U/Pb ages, Hf and O isotope ratios, and trace element concentrations. NIPR ages are by SHRIMP of polished grain interiors; UCSB ages represent split-stream LA-ICP-MS analyses on polished grain interiors; and ANU ages are by LA-ICP-MS on grain surfaces. Results and analytical methods are given in Todd et al. (2021).

3.5. Results

Based on geochemical differences in major and trace elements and isotope composition, following the classification of Peccerillo and Taylor (1976), and taking the previous study of (Stork, 1984) into account, the Yavuna and Colo plutons can be divided into three suites: 1. a medium-K suite (Fig. 3.4) enriched in LREE relative to the HREE, which are hereafter designated as the LREE-enriched LE-suite; 2. a low-K suite that exhibits flat, evenly enriched REE patterns (EE-suite); and 3. a low-K suite showing LREE-depletion relative to the HREE (LD-suite).



Figure 3.4: (a) Feldspar-normative An-Or-Ab diagram (after Barker and Arth, 1976) for the three suites (\geq 62 wt.% SiO₂) from Viti Levu, Fiji, and additional data of Stork (1984) and Todd et al. (2021). Also shown are oceanic plagiogranites (light grey) and Archean TTGs (dark grey) for comparison (Rollinson, 2014; Marien et al., 2019); (b) K₂O vs. SiO₂ diagram with defined boundary lines by Peccerillo and Taylor (1976). Distinguishing the mostly medium-K LE-suite and the corresponding central Colo plutons (N-Wainivalau, Yavuna, Noikoro and W-Wainqa) of Stork (1984) from the predominantly low-K LD-suite and EE-suite and their respective coastal Colo plutons (Stork, 1984; Todd et al., 2021). Extensive mapping and major element analyses (Stork, 1984) of Yavuna and N-Wainivalau show mostly felsic compositions (see in b), while other medium-K plutons (Noikoro, W-Wainqa) have broader ranges in SiO₂ and generally lower concentrations (<70 wt.% SiO₂). In (c) primitive mantle normalized La_N/Yb_N vs. SiO₂ diagram shows the discrimination of the three suites depending on the La_N/Yb_N ratios: LE-suite (La_N/Yb_N > 2), EE-suite (0.5 < La_N/Yb_N < 2), and LD-suite (La_N/Yb_N < 0.5), respectively.

Using major element analyses, Stork (1984) divided the Colo plutons into coastal low-K and central medium-K felsic rocks (Fig. 3.2a, LD- and LE-suites, respectively). The central group comprises the Yavuna Stock, North Wainivalau, Noikoro, West and Central Wainqa, Wainiyavu and Namoli plutons. In this study, the medium-K LE-suite is mainly represented by samples from the Yavuna Stock and N-Wainivalau, one sample from Noikoro, and one from the Western Stocks, which are usually low-K (Fig. 3.2a). The low-K samples are found in the plutonic bodies of South Wainivalau, Momi, East Wainqa, Vunambua, Wainivau, the Western Stocks, Waimaro, Wainivesi, Korolevu, that cover the range of from mafic to highly felsic samples (Fig. 3.4b). Our focus here is on felsic samples from the S-Wainivalau and Momi plutons, along with one associated rhyolite sample (representing the intermediate-REE suite) and the Korolevu pluton representing the LD-suite.

3.5.1. Whole rock major and trace element geochemistry

Major and trace element data for the plutons are reported in Supplementary Tables C1 and C2, and shown in Figures 3.4-3.7. Major elements are recalculated to 100 wt.% on an anhydrous basis with total Fe as FeO_{total}.

Based on normative compositions calculated from major element contents (Barker and Arth, 1976), most rocks with > 62 wt.% SiO₂ fall in the tonalite and trondhjemite fields (Fig. 3.4a). The LD- and EE-suites extend from the ophiolitic plagiogranite to trondhjemite fields (Fig. 3.4a) on the albite-anorthite-rich side. The LE-suite samples of our study are mostly trondhjemitic with a higher orthoclase content than the other two suites.

Including the results from Stork (1984), the low-K EE-suite ranges from 51.2 - 78.7 wt.% SiO₂. Potassium concentrations are from 0.02 - 1.04 wt.%. Only two samples of the EE-suite have elevated K₂O contents of 1.69 and 1.76 wt.%. Additional Harker variation diagrams for the EE-suite show well defined chemical trends for all major elements (Fig. 3.5).

CI-chondritic-normalized (Palme and O'Neill, 2014) REE patterns for the two EEplutons, S-Wainivalau and Momi, indicate a 30 - 40 x enrichment of all REE (Fig. 3.6a). In both plutons all REE concentrations gradually increase with increasing SiO₂ (Fig. 3.7) except for Eu which decreases (shown as Eu/Eu* in Fig. 3.7c). Small differences between





Figure 3.5: Whole rock major element variation diagrams for the respective suites of the Colo plutons (Stork, 1984; this study) and mafic-intermediate volcanics of the Yavuna Group, enriched island arc tholeiites (YV-IAT) and depleted early arc low-Ti tholeiites (YV-EAT), and Wainimala Group, enriched "basin" assemblage (WA-B) and more depleted "arc" assemblage (WA-A) (Todd et al., 2012; 2021).

the two plutons lie in their LREE budgets. PRIMA-normalized La_N/Yb_N ratios of S-Wainivalau (Fig. 3.4c) are slightly higher (1.33 - 1.93) than for the Momi plutons (1.04 - 1.24), which is due to higher HREE contents in the Momi pluton (Fig. 3.6a). Only the Momi-associated Kalaka rhyolite exhibits a higher La_N/Yb_N of 1.78. The LILE contents of all EE-suite samples are: Rb (0.440 - 6.97 ppm), Sr (41.6 - 436 ppm), Cs (0.0237 - 0.210 ppm), and Ba (28 - 213 ppm). Notably, the EE-suite has positive Zr-Hf and negative Nb-Ta anomalies relative to primitive-mantle (PRIMA, Palme and O'Neill, 2014) and the samples exhibit broadly positive correlations between HFSEs and SiO₂ (e.g., Fig. 3.6b). The EE-suite is especially rich in Zr and Nb with 116 - 280 ppm, and 2.72 - 3.68 ppm, respectively. Zirconium/Hf, Nb/Ta, and Nb/La ratios in the EE-suite are 33.3 - 39.2, 12.7 - 14.9, and 0.25 - 0.45, respectively.

The LD-suite, including data of (Stork, 1984), shows a continuous range in SiO₂ from intermediate (54.83 wt.%) to felsic values (78.96 wt.%). Their K₂O contents are typically < 0.7 wt.%, the only exception being the rhyolite (1.29 wt.%). Generally, their major elements are negatively correlated with SiO₂ except for Na₂O and K₂O (Fig. 3.5). The LD-suite shows more depletion of the LREE compared to the HREE contents (Fig. 3.7a, b) than in normal mid-ocean ridge basalts (N-MORB; Fig. 6c). One intermediate sample exhibits a positive Eu anomaly, but the more felsic ones have mostly negative Eu/Eu* values (Fig. 3.7c). Concentrations of incompatible elements, such as U, Th, and Cs are very low, and Ba contents (50.7 - 118 ppm) increase with increasing SiO₂, while Sr contents (73.0 – 126 ppm) slightly decrease (Fig. 3.7g). A prominent feature of the LDsamples is their extremely low HFSE concentrations. Relative to the EE-suite, the total HFSE concentrations are lower (e.g., Zr = 97.4 - 105 ppm; Nb = 0.618 - 0.861 ppm, Hf = 3.29 - 3.64 ppm; Fig. 3.6d, e) as are the Zr/Hf (28.8 - 29.6) and, except for one sample, Zr/Sm values (20.6 - 24.1), although Nb/Ta ratios are similar (12.9 - 14.0). These low LREE and HFSE concentrations also result in low Nb/La ratios of 0.24 - 0.33. Two SiO₂poor samples of the LD-suite (ST99 and ST107) exhibit even lower Zr (19.4 – 29.1 ppm), Nb (0.310 - 0.430 ppm), and Hf (0.832 - 1.17 ppm) concentrations, resulting in even lower Zr/Hf (23.4 - 24.8) and Zr/Sm (7.9 - 10.4) but slightly higher Nb/Ta ratios of 15.2 to 15.8.



Figure 3.6: CI-normalized REE patterns and PRIMA-normalized (Palme and O'Neill, 2014) extended trace element patterns for the Colo plutons. In (a) and (b), respective patterns for the EE-suite plutons compared to the Wainimala "basin" island arc tholeiitic assemblage (WA-B; Todd et al., 2021); in (c) and (d), LD-suite relative to the Wainimala "arc" tholeiitic assemblage (WA-A; Todd et al., 2021) and N-MORB (White and Klein, 2014); in (e) and (f), respective LE-suite plutons compared to the Yavuna Group island arc tholeiities (YV-IAT), low-Ti tholeiites (YV-EAT; Todd et al., 2012), bulk continental crust (BCC; Rudnick and Gao, 2014), and Archean TTGs, subdivided in "low"-, "medium"-, and "high"-pressure regimes (Moyen and Martin, 2012). Here, it is clearly shown that the HREE budget of the LE-suite generally overlaps with BCC and "low"-pressure TTGs but lack higher LREE concentrations.

The LE-suite has SiO₂ contents between 68.8 - 75.6 wt.% and generally higher K₂O contents relative to the EE- and LD-suites (Fig. 3.4b). However, including the less well studied samples of the other central plutons from Stork (1984), the LE-suite extends down to 59 wt.% for W-Wainqa and 53 wt.% SiO₂ for Noikoro, respectively. In the LE-suite Al₂O₃, TiO₂, FeO_{total}, CaO, and P₂O₅ are negatively correlated with SiO₂ (Fig. 3.5). Compared to the LD- and EE-suites, the TiO₂ and FeO_{total} concentrations of the LE-suite are slightly lower at comparable SiO₂ concentrations, while Al₂O₃ contents are slightly higher (Fig. 3.5e).



Figure 3.7: Whole rock trace element variation diagrams of the LE-, EE-, and LD-suites compared to the mafic Viti Levu basement of the Yavuna Group and Wainimala Group (Todd et al., 2012; 2021). For comparison, XRF data for Zr, Y, Rb, and Sr for additional Colo plutonic rocks by Stork (1984) and Todd et al. (2021) are shown in (d), (g), and (h).

Chondrite- and PRIMA-normalized trace element patterns of the LE-suite show enrichments of the more incompatible LREE and LILE relative to the MREE and HREE, resulting in distinctive HREE-concave patterns (Fig. 3.6e-f). Lanthanum concentrations range from 6.23 to 14.4 ppm and overlap with the EE-suite. In contrast, Yb has lower and less variable concentrations from 1.54 to 2.59 ppm (Fig. 3.7a, b), resulting in higher La_N/Yb_N ratios (Fig. 3.4c). Except for three samples, most Eu/Eu* values range between 0.85 and 0.94, and hence no significant positive or negative Eu anomalies, whereas the LILE contents (Fig. 3.7c), such as Ba (145 – 384 ppm) and Rb (11.7 – 36.3 ppm), are higher than in the other two suites (Fig. 3.7g). Other distinctive features are relatively small positive Zr-Hf anomalies, and strong negative Nb-Ta anomalies. In general, the HFSE concentrations range from 64.9 - 121 ppm for Zr, 1.86 - 3.55 ppm for Hf (Zr/Hf = 29.3 - 35.1; Zr/Sm = 29.9 - 54.3), 1.39 - 2.81 ppm Nb, and 0.110 - 0.285 ppm for Ta, exhibiting remarkably low Nb/Ta (9.5 - 13.2) and Nb/La (0.16 - 0.29). Overall, the LEsuite has HFSE concentrations that are intermediate between those of the EE- and the LDsuites (Fig. 3.7d, e). Our two Yavuna trondhjemites have similar trace element concentrations as the Fij-3 tonalite reported by Sommer et al. (2020) except for not having the low Zr and Hf contents that may reflect incomplete zircon dissolution in their HF-HNO₃ tabletop digestion. To ensure complete zircon digestion, an additional PARR[®]digestion is recommended (Zhao and Zhou, 2008; J Elis Hoffmann et al., 2011).

3.5.2. Hf-Nd-Sr-Pb isotope compositions

New Hf, Nd, Pb, and Sr isotope data were measured for the three different suites (Supplementary table C2). In Figure 3.8, the data are compared to those for the Viti Levu basement (Todd et al., 2012; 2021). Although each pluton has to be evaluated in detail separately, there appear to be general trends. All intermediate and felsic rocks are characterized by radiogenic ε^{143} Nd and ε^{176} Hf ratios. Furthermore, the Pb isotope ratios generally overlap those of fresh mafic volcanics found on Viti Levu (Todd et al., 2012; 2021).

The older Yavuna trondhjemites have more radiogenic Pb isotope ratios, while the younger Wainivalau samples are less radiogenic. The Hf and Nd isotope compositions of

all LE-samples overlap with values for the Fijian basement with ε^{176} Hf between +11.8 and +15.0 and for ε^{143} Nd with +7.1 to +9.2. The ⁸⁷Sr/⁸⁶Sr compositions of the Colo LE-suite are less radiogenic than in the other two suites, with ratios between 0.703157 and 0.703744, whereas the Yavuna pluton exhibits the most radiogenic values (⁸⁷Sr/⁸⁶Sr – 0.703599 – 0.703744) in the LE-suite. Further, in most isotope systems the older Yavuna pluton does not overlap with the younger plutons of the LE-suite, EE-suite or the LD-suite.



Figure 3.8: Pb-Sr-Nd-Hf isotope composition diagrams (modified after Todd et al., 2012) of the respective suites $(\pm 2r)$ compared to the Fijian basement volcanics (Todd et al., 2012; 2021). Indian and Pacific MORB in (b) and (e) from Stracke et al. (2003), the Indian-Pacific Discrimination Line in (b) of Pearce et al. (2007), and the Northern Hemisphere Reference Line (NHRL) of Hart (1984). References for additional pelagic and volcaniclastic sediments are in Todd et al. (2012).

The ε^{176} Hf and ε^{143} Nd of the EE-suite cover a narrower range from +12.6 to +14.1 and +7.3 to +8.5, respectively. Lead isotopes are less radiogenic than in the LE-suite, with lower 206 Pb/ 204 Pb at comparable 208 Pb/ 204 Pb and 207 Pb/ 204 Pb ratios. The Sr isotope compositions range from 0.703219 to 0.703824. The Momi pluton has slightly more radiogenic Sr, Nd, and Hf, and slightly less radiogenic Pb than the S-Wainivalau pluton. Nevertheless, a close relationship between all EE-suite samples and the Wainimala "basin"-assemblage (WA-B) is supported by their isotopic similarities.

The LD-suite differs from the other two suites isotopically. It has the most radiogenic Hf and Nd with ε^{176} Hf and ε^{143} Nd values between +13.7 and +17.4, and +8.8 and +10.0, respectively. Its Pb isotope compositions show only a small range within the values of the other two suites. In addition, the LD-suite extends to the most radiogenic Sr isotope ratios of up to 0.704403 in a dacite/rhyolite sample.

3.5.3. U/Pb zircon ages

Corrected ²⁰⁶Pb/²³⁸U ages for twelve igneous rocks and 47 detrital zircons from this study are given in Todd et al. (2021) and shown in the supplementary Figures C3 – C4. The plutonic zircon ages can be separated into three age populations: 7.9 – 11.7 Ma in southern and central Viti Levu, 21 – 22 Ma for the Momi pluton (EE-suite), and 36 – 37 Ma for the Yavuna pluton (LE-suite). The 8 – 12 and ~36 Ma ages are slightly older than or equal to previous K-Ar biotite and hornblende results for Colo plutons (e.g., Rodda, 1994). Only the 21 – 22 Ma age group has not been identified before. The NIPR and UCSB ages for grain interiors agree within 1 Ma, as do results for most individual plutons by the different labs. In N-Wainivalau, the western trondhjemites (T36 and T44: higher K₂O, La/Yb, Nb/Yb) are ~0.5 Ma older (11.73 ± 0.1 versus 11.28 ± 0.4 Ma) than the less enriched trondhjemites to the east. Due to insufficient zircon, we were unable to date the low-K tonalites of the EE-suite (S-Wainivalau) that form the southern border of the composite pluton.

Three different samples of the Yavuna pluton (LE-suite) gave similar ages of 36.3 ± 0.3 Ma consistent with other zircon results for the pluton (Rickard and Williams, 2013; Sommer et al., 2020) and roughly coeval with the Late Eocene fossil age of the Yavuna Group tholeiitic to boninitic lavas and sedimentary rocks that it intrudes (Todd et al., 2012). It post-dates the ~50 Ma Ar-Ar date of tholeiitic basalts on the Tonga Trench wall (Meffre et al., 2012), and the similar age obtained for zircons in an oxide-gabbro

(47.1 Ma) like those on the eastern edge of the Yavuna pluton (Sommer et al., 2020). The 21 - 22 Ma early Miocene Momi pluton of the EE-suite overlaps the opening of the South Fiji Basin and may be roughly coeval with the Wainimala rocks that it intrudes. Two samples of the Korolevu pluton (LD-suite) in southern Viti Levu gave an age of 9.5 Ma, which may overlap with the initial opening of the North Fiji Basin. One sample from the Western Stocks, with LE-affinity, exhibits an age of 7.9 Ma.

All of the detrital zircons from the Sigatoka River, and 70 % of those from the Naqalitala Creek, have ages within the youngest population of the pluton ages: 9.7 ± 1.0 Ma, with ages down to 7.4 Ma. We take this to be the most robust age range of the most widespread plutonism in Fiji thus far. Two of the detrital zircons from Naqalitala Creek have ages overlapping those of the Yavuna pluton. Four others have ages ranging from 27 - 34 Ma that overlap with the early opening of the South Fiji Basin, but plutons of that age are unknown. As with the detailed study of zircons from the Yavuna pluton by Rickard and Williams (2013), none of our > 200 detrital or plutonic zircons have pre-Eocene cores, unlike some reported from neighboring Vanuatu (Buys et al., 2014).

Drewes (2011) undertook a reconnaissance (U-Th)/He-(ZHe) study of ~25 plutonic and detrital zircons. The zircon He closure (~180°C) ages are 6.6 - 8.0 Ma for the younger group of zircons, post-dating pluton emplacement by 1 - 4 m.y., and corresponding to 1 - 3 km/m.y. uplift rates. This is the first radiometric age constraint on the uplift of the Fiji Platform, and it coincides with the age of the angular unconformity between the Wainimala and Tuva groups versus the overlying Navosa and Nadi groups (Rodda, 1994). The 21 Ma old Momi pluton cooled at about the same time (9.1 ± 1.1 Ma) as the younger ones. Only zircons from the Yavuna pluton gave cooling ages > 15 Ma, indicating an earlier episode of uplift possibly related to the opening of the South Fiji Basin.

3.5.4. Zircon geochemistry

Our zircon trace element and isotope data are given in Todd et al. (2021) and summarized here. The Hf isotope ratios in most zircons overlap those of the plutonic rocks, and yield zero model ages (T_{DM}) if one assumes the arc mantle source of Iizuka et al. (2013). Most detrital zircons have $\delta^{18}O = 4.81 \pm 0.35$ which is a typical mantle value. Consequently, there is no evidence for assimilation of old sialic crust or altered oceanic crust. Therefore, detrital zircons in an oceanic arc faithfully record their plutonic sources,

demonstrate very short crustal residence time for juvenile arc crust, and document that such crust and its mantle source are isotopically coupled.

All of the zircons trace element abundances are typical of igneous zircons (Fig. C3). However, they have distinctive U/HREE ratios (e.g., U/Yb \leq 0.25; Fig. C4) that are lower than in zircons from continental margin arcs but greater than from mid-ocean ridges, especially relative to Nb/Yb (Barth et al., 2017). Those from LD-tonalites have even lower Nb/Yb than mid-ocean ridge zircons, and are amongst the lowest ratios yet reported from any source. The difference in Y and HREE content between the LD- and EE-tonalites versus LE-trondhjemites is also recorded in their zircons.

3.6. Discussion

3.6.1. Secondary alteration of the plutonic rocks

Plutonic and volcanic rocks in intra-oceanic arc settings generally undergo hydrothermal alteration during and shortly after emplacement. Secondary minerals such as chlorite, K-feldspar, quartz, calcite, and epidote are present in the Fijian plutonic rocks and are the result of zeolite to lower greenschist metamorphism (Gill and Stork, 1979). Locally, stronger hydrothermal alterations are associated with massive sulfide and porphyry Cu-Au deposits (Colley and Greenbaum, 1980). Although we selected the optically freshest samples for our analyses, the occasional occurrence of chlorite, epidote, and secondary quartz nevertheless indicates some alteration took place. A positive covariation of the loss of ignition (L.O.I.) and the concentration of fluid mobile elements such as Rb and Ba is a good indicator of secondary alteration (e.g., Fig. 3.9a). In general, none of the suites shows such a correlation suggesting only minor effects of secondary alteration. Only two samples suggest significant effects, both of which are rhyolitic volcanic rocks that are more susceptible to post emplacement alteration that may not reflect magmatic values.

The rather minor influence of alteration is also indicated by the low Sr isotope ratios (Fig. 3.8e). Seawater alteration or hydrous influx would have increased these ratios (Staudigel et al., 1981). Most plutonic samples lie within the range of coeval mafic volcanics, suggesting a similar or lower range of alteration.



Juvenile continental crust evolution in a modern oceanic arc setting: Petrogenesis of Cenozoic felsic plutons in Fiji, SW Pacific

Figure 3.9: Trace element co-variation diagrams. In (a) plot of fluid-mobile Rb vs. loss of ignition (L.O.I.). Positive correlations would suggest Rb addition during hydrothermal alteration. Only two samples from the LD-suite and EE-suite show this correlation. In (b) Ba/Th vs. PRIMA-normalized La_N/Sm_N diagram (modified after Elliott, 2003) shows the modifying influence of subduction components on mafic precursor rocks (Todd et al., 2012; 2021) of the Colo plutons. Fractional crystallization of mafic melts results in the inheritance of the trace element ratios. LE-suite exhibits higher La_N/Sm_N ratios than found in any mafic precursor material. In (c) Nb/La vs. La_N/Sm_N (after John et al., 2003) shows oceanic arc to back-arc origin of the Fijian basement (Todd et al., 2012; 2021) and the Fijian evolution to a continental arc composition. In (d) PRIMA-normalized La_N/Yb_N vs. Nd isotope composition (\pm 2r) shows close relationship of the LD-suite and EE-suite to respective mafic material (Todd et al., 2021) with an increasing slab contribution. LE-suite's higher La_N/Yb_N ratios are not accompanied by less radiogenic Nd. The variable Nd isotope composition at higher La_N/Yb_N rather suggests variable degrees of partial melting of mafic arc crust.

Therefore, we propose only a minor effect of hydrothermal alteration on our samples, and that the major, trace element, and isotope compositions of the three suites are most likely primary features.

3.6.2. Geochemical relationships between the felsic plutons and surrounding mafic basement rocks

The three felsic suites of this study can be distinguished by their different trace element characteristics that we next compare to those of coeval mafic volcanics, possibly tapping similar melt sources. While ratios of trace elements with different compatibility might be modified during fractional crystallization or partial melting, radiogenic isotope compositions are not. Hence, differences in the amount or kind of slab-derived fluids or melts in the tonalites can be distinguished. With respect to the mafic precursors, Viti Levu underwent a short, yet turbulent geological history including two major episodes of arc volcanism: the older Yavuna Group and the younger Wainimala Group. Both include intrusions (Hathway, 1994) and, hence, there is also a temporal constraint on the precursor material for the plutonic rocks and associated volcanics.

Figure 3.6a-d displays CI-normalized REE patterns and PRIMA-normalized extended element patterns of the highly evolved EE-suite and LD-suite compared to contemporaneous mafic rocks of the island-arc tholeiitic Wainimala "basin"-assemblage (WA-B) and Wainimala "arc"-assemblage (WA-A), respectively. The EE-suite has patterns that are roughly parallel to the more enriched "basin" assemblage, and the LDsuite patterns are generally parallel to more depleted tholeiitic "arc" assemblage (WA-A), consistent with close petrogenetic as well as geographic relationships. The low trace element concentrations of the LD-suite are nearly identical to the WA-A group and elements, such as LREE, HFSE, and Sr are consistently lower than in the other plutonic suites and show well-defined trends over the SiO₂ spectrum (Fig. 3.7). In contrast, the EE-suite tonalites have higher REE contents than the mafic WA-B group (Fig. 3.7) and show consistent correlations with SiO₂. Only Sr and Eu tend to lower concentrations (Fig. 3.7c, h) which can be explained by plagioclase fractionation. Both the LD-suite and the mafic WA-A group exhibit similarly low La_N/Sm_N and Nb/La ratios and higher Ba/Th (Fig. 3.9b, c), whereas the EE-suite and the corresponding WA-B group possess slightly higher La_N/Sm_N ratios but lower Ba/Th. In both cases, the low Nb/La ratio is a clear signature for the subduction related oceanic arc environment, and the different La_N/Sm_N ratios reflect different amounts of incompatible elements added by the subducted slab component (e.g., Hawkesworth et al., 1993; John et al., 2003), which were also inherited by the felsic rocks. In Figure 3.9b, the LD-suite has higher Ba/Th ratios that clearly overlap with those of the LREE depleted tholeiites of the YV-EAT and WA-A depleted tholeiites that experienced the most fluid addition to their mantle source (Todd et al., 2012), since Ba is more soluble than Th in hydrous fluids (Elliott, 2003). In contrast, the EE-suite shows lower Ba/Th ratios and somewhat higher La_N/Sm_N ratios, similar to the WA-B assemblage. This may indicate a higher sediment flux into the source of the WA-B relative to the slab fluid that influenced WA-A precursor material, which also leads to less radiogenic Nd isotopes ratios (Fig. 3.9d).

The isotope composition of the felsic suites from Viti Levu can further be used to discern the relationship between felsic and mafic rocks. The Nd, Sr, and Pb isotope ratios of the LD- and EE-suites overlap with those of the WA-A and WA-B groups, respectively (Fig. 3.8). Some LD-samples are isotopically more radiogenic than any mafic rocks of the WA-A group (Fig. 3.8a-d). Considering the young age of about 9 Ma for the LD-suite, their younger mantle sources were even more depleted, or received even less slab fluids, than the Wainimala Group basement which formed between 30 - 13 Ma (Hathway, 1994). Younger and geochemically similar volcanics are not present on Viti Levu (Fig. 3.2b). Additionally, the LD-suite shows a weak positive correlation between 87 Sr/ 86 Sr ratios and SiO₂ content. This either suggests some minor assimilation of seawater-altered materials during differentiation (Fig. C5) or some alteration after formation, as mentioned in 3.6.1. In contrast, no such covariations are visible for the EE- and LE-suites plutons.

Unlike the other two suites, the REE patterns of the LE-suite are not parallel to those of coeval basalts (Fig. 3.6e-f). Higher La_N/Sm_N and La_N/Yb_N ratios combined with increased LILE concentrations (Fig. 3.9a-d) could indicate a higher slab-derived sediment melt contribution, a more complex hydrous mantle wedge-melting scenario, assimilation of older continental material or partial melting of pre-existing mafic crust. However, the more radiogenic Nd isotope composition of the LE-suite relative to mafic rocks with comparably high La_N/Yb_N (Fig. 3.9d) rule out additional sediment flux or assimilation of older continental material.

In a recent study, Sommer et al. (2020) suggested that the LREE-enriched Yavuna Stock originated from water-saturated anatexis of early arc-tholeiitic material (EAT) of the Fijian middle to lower crust. Melting of pre-existing mafic rocks does indeed result in an increase of LILE and LREE inventory of the co-existing melt. However, the Yavuna pluton exhibits the most radiogenic Pb isotopes, which overlap with the YV-IAT (Fig. 3.8; Todd et al., 2012), so we can exclude the YV-EAT as possible precursors for the Yavuna pluton. The younger LE-plutons, N-Wainivalau and Noikoro, are isotopically similar to the younger WA-B island-arc tholeiites and the older YV-island-arc tholeiites (Fig. 3.8a-e), but are isotopically less radiogenic than the Yavuna trondhjemites.

Collectively, isotope and trace element patterns of all felsic plutons can be directly linked to coeval mafic suites in the basement, thus supporting that the felsic plutons tap ambient arc/back-arc basement.

3.6.3. Geochemical constraints for genesis of the Fijian felsic suites – A comparison with other intra-oceanic felsic rocks

Felsic volcanic and plutonic rocks in various oceanic arcs and ophiolites have been studied (e.g., Rollinson, 2009; Tamura et al., 2009; Furnes and Dilek, 2017; Haraguchi et al. 2017; Marien et al., 2019), and different origins have been assigned to these rocks. Most are attributed to fractional crystallization from mafic precursor melts (e.g., Coleman and Peterman, 1975; Allègre and Minster, 1978; Coleman and Donato, 1979). Alternatively, dehydration melting or water-saturated melting of hydrated mafic oceanic crust also has been proposed (e.g., Allègre and Minster, 1978; Beard and Lofgren, 1991; Koepke et al., 2004; 2007). Partial melts of the subducted slab can be the origin of "adakitic" felsic rocks in oceanic and continental arc settings (Defant and Drummond, 1990; Kay et al., 1990; Danyushevsky et al., 2008). Finally, felsic melts can involve mixing in the lower arc crust by, for example, simultaneous **a**ssimilation and **f**ractional **c**rystallization ('**MASH**'; Hildreth and Moorbath, 1988).

Considering the similar geological settings of the former Vitiaz arc and the Izu arc, and the many geochemical similarities between their felsic suites (Fig. 3.10) common petrogenetic processes for their origin can be explored. Rhyolites at or near the Izu volcanic front are similar to Fijian LD- and EE-tonalites, whereas rhyolites in the Izu rear-arc show similarities to Fijian LE-tonalites (Tamura et al., 2009; Haraguchi et al., 2017; Heywood et al., 2020). Nakajima and Arima (1998), Tamura and Tatsumi (2002), and Tamura et al. (2009) proposed partial melting of pre-existing mafic arc crust with variable ages, geochemical compositions, and melting depths for the generation of some of the rhyolites, whereas Haraguchi et al. (2017) and Heywood et al. (2020) argue for a fractional crystallization origin. In both arcs, the REE patterns and La_{N/}Yb_N ratios of the felsic and mafic rocks are similar, suggesting a fractional crystallization process without much amphibole or garnet. In contrast, the diorite-leucogranodioritic plutons of the Central Aleutian arc, that have similar surface areas as the Fijian felsic plutons and overlie ca. 37 km thick crust, have been attributed to extensive amphibole fractionation of a



Juvenile continental crust evolution in a modern oceanic arc setting: Petrogenesis of Cenozoic felsic plutons in Fiji, SW Pacific

Figure 3.10: Trace element co-variation diagrams that compare Fijian tonalites to felsic rocks (≥ 62 wt.% SiO₂) from other intra-oceanic settings, including rhyolites from the Izu arc (DeBari et al., 2021) that are subdivided into volcanic front rhyolites (La_N/Yb_N \leq 0.8), rift related rhyolites, and rear-arc rhyolites $(La_N/Yb_N \ge 2 \text{ only})$; the Aleutian arc (Kay et al., 2019); Kadavu Island adakites, Fiji (Danyushevsky et al., 2008); Troodos plagiogranites (Marien et al., 2019); and Archean TTGs (Defant and Drummond, 1990; Drummond and Defant, 1990). Black arrows indicate mineral fractionation of plagioclase (pl), orthopyroxene (opx), clinopyroxene (cpx), amphibole (amph), garnet (grt), ilmenite (ilm), magnetite (magn), and apatite (ap), respectively, and drive the liquid composition in the direction of the black arrows. Black arrows are calculated with partition coefficients given in Supplementary Table C3a. In (a), PRIMAnormalized La_N/Yb_N vs. Yb_N (Jahn et al., 1981); (b) CI normalized Dy/Dy* (=Dy_{CI}/(La_{CI}^{4/13} x Yb_{CI}^{9/13})) vs. Dy/Yb space (Davidson et al., 2013); (c) Sr/Y vs. Y (ppm) (Drummond and Defant, 1990); and (d) Zr/Y vs. Zr (ppm) (Pearce and Norry, 1979). Notably, the LD-suite overlaps in composition with both plagiogranites from Troodos and volcanic front rhyolites from the Izu arc, and the EE-suite overlaps with the rift-related rhyolites from the Izu arc. The LE-suite shows similarities to the rear-arc rhyolites from the Izu arc, but has a smaller range. Higher La_N/Yb_N, Dy/Yb, Sr/Y, and Zr/Y ratios for the Aleutian plutons (Kay et al., 2019) and adakites from Kadavu Island, Fiji, suggest garnet involvement and extensive amphibole fractionation would result in positive covariations in (b) and (d), which differ from the LE-suite.

hydrous basaltic melt at mid-crustal levels (Kay et al., 2019). Additionally, all Fijian tonalites lack "adakitic" high La_N/Yb_N, Sr/Y, Zr/Y, and Dy/Yb ratios that accompany melting of slab eclogites or thick arc crust.

The LD-suite also shows geochemical similarities to tonalites in ophiolites (Figs. 3.4, 3.10), such as the Troodos Ophiolite Complex (e.g., Marien et al., 2019), which are

largely products of anhydrous fractionation of basaltic melts from depleted mantle sources in an extensional back-arc or fore-arc setting. These suites have extremely low $La_N/Yb_N < 1$, relatively high HREE concentrations, and comparably radiogenic Nd and Hf isotope compositions.

3.6.4. Geochemical modeling of the Yavuna and Colo plutons

The trace element budget of felsic melts is controlled by the composition of the basaltic source and the element partitioning between an evolving melt and residual or crystallizing mineral phases. For example, Brophy (2008) proposed that the relative compatibility of Y and HREE can be used to distinguish between largely anhydrous versus amphibole-rich genetic options. Amphibole-free fractional crystallization would result in a steady increase of all REE with increasing SiO₂, whereas amphibole-rich fractional crystallization, similar to the Aleutian plutons (Kay et al., 2019), leads to constant or even decreasing HREE. However, the volume of felsic melt produced by fractional crystallization is relatively small. Larger volumes of felsic magmas can be formed by partial melting of amphibolitic middle to lower crusts (e.g., Tamura and Tatsumi, 2002; Tani et al., 2015; Haraguchi et al., 2017). Several studies reported that partial melting of amphibole-rich mafic rocks would lead to the preferential retention of the MREE and thus in concave REE patterns and decreasing HREE concentrations (Brophy, 2008; Davidson et al., 2013).

Both main plutons of the LE-suite, Yavuna and N-Wainivalau were mapped as predominantly felsic, whereas most plutons of the LD-suite and EE-suite are more bimodal and some have mafic rims and felsic centers (Stork, 1984). The relative scarcity of intermediate rocks in the LE-suite, apart from obvious products of magma mingling, as well as their trace element patterns make continuous crystal fractionation less likely. Instead, moderate Al₂O₃, CaO and K₂O contents are more consistent with fluid-absent dehydration melting of low-K rocks through the breakdown of amphibole in the mafic crust (Beard and Lofgren, 1991). Melting under water-saturated conditions would stabilize residual amphibole and increase the consumption of plagioclase resulting in higher Al₂O₃ and CaO contents (Beard and Lofgren, 1991).

In contrast, the nearly parallel trace element patterns, the increasing REE concentrations with increasing SiO_2 , and overlapping isotope ratios of the EE- and LD-suites and coeval mafic rocks, suggest that these tonalites could be the products of

extensive fractional crystallization mostly of anhydrous minerals from local mafic parent melts. The formation of felsic plutons by around 80 % fractional crystallization results in a high mafic to felsic rock ratio (e.g., Lee and Bachmann, 2014). This is also consistent with the relatively high ratio of mafic to felsic rocks in some LD-plutons, such as Korolevu.

Alternatively, the MASH model (Hildreth and Moorbath, 1988) suggests that mantlederived basaltic melts assimilate, and mix with melts of lower mafic crust in a process that tends to homogenize felsic outputs. Although variations on this process might explain the different elemental and isotope compositions of the three suites, the geochemical similarities of the three respective suites to mafic volcanic rocks of similar age strongly suggest a close genetic link between them. In addition, the Fijian tonalites are heterogeneous at small spatial and temporal scales, and their zircons have mantle oxygen isotopes. Consequently, although MASH-type processes cannot be excluded, we will explore the extent to which simple genetic links between the mafic and felsic rocks can explain our observations.

To explain the element inventory of the three suites, we modeled the trace element composition of an evolving melt during fractional crystallization of mafic precursor melts to explain the EE- and LD-suites, and we modeled dehydration melting of basaltic source rocks to explain the LE-suite, using equations from Shaw (1970). As an example of dehydration melting, we used the melt-mineral assemblage from Hoffmann et al. (2019) for 0.8 GPa and a temperature range of 655 - 945 °C, which mimics melting of the lower Viti Levu crust. For fractional crystallization, we used experimental melt-mineral assemblages for a hydrous basaltic melt (2 wt.% H₂O) at 400 MPa and 700 MPa from Blatter et al. (2013). We calculated fractional crystallization models at both pressures for the EE-suite, whereas only the 400 MPa model was used for the LD-suite. We applied the mineral-melt partition coefficients published by Bédard (2006), Klemme et al. (2006), Foley (2008), Adam and Green (2006), Nash and Crecraft, (1985), and Bindeman et al. (1998) for olivine, plagioclase, amphibole, clinopyroxene, orthopyroxene, ilmenite, magnetite, and quartz (Supplementary Table C3a). Given by the relatively low but generally decreasing P₂O₅ concentrations (Fig. 3.5h), we added 0.2 wt.% apatite into the fractional crystallization model. Although these models are heuristic, non-unique, and doubtless oversimplified, they illustrate how the two end-member processes can account for the key differences between the suites.

3.6.4.1. Fractional crystallization

For the fractional crystallization modeling of the EE- and LD-suites we used coeval mafic LREE-enriched WA-B samples (68-920 and WA12; Todd et al., 2021), and a mafic depleted WA-A sample (68-48; Todd et al., 2021) as parental melts. The calculations were carried out at pressures of 400 and 700 MPa to simulate up to 90 wt.% fractionation within the "continental-type" middle crust of Viti Levu.

The fractional crystallization model involving an initially anhydrous assemblage of olivine, clinopyroxene, plagioclase, orthopyroxene, and magnetite produces the observed increase of incompatible REE (Ce, Dy, and Yb) and HFSE, such as Zr and Nb (Figs. 3.7a-e and 3.11a, b, d). The trace element enrichments observed in Fig. 3.7a-e are generally consistent with their incompatible behavior (D << 1) during predominant clinopyroxene and plagioclase fractionation, and the relative lack of La_N/Yb_N variation in the LD-suite and the Momi pluton of the EE-suite (Fig. 3.10a) suggests only small compatibility differences between LREE and HREE and thus only minor amphibole fractionation. Furthermore, increasing plagioclase removal after ~50 % fractionation produces the increasingly negative Sr and Eu anomalies observed in the dataset (Figs. 3.7c, 3.11g).

The Dy/Dy*-Dy/Yb (Fig. 3.11c) approach distinguishes between fractionation effects of plagioclase, pyroxene, amphibole and garnet (Davidson et al., 2013). Amphibole fractionation can result in decreasing Dy/Dy* and Dy/Yb, due to the higher

Figure 3.11: Calculated trace element trends to model the effects of fractional crystallization (FC) of a basaltic melt at different pressures and partial melting (PM) of mafic crust. Calculated trace element trend (starting at black symbols) for MORB-like fractional crystallization (green line) and arc basalt fractional crystallization at 400 MPa (blue line) and 700 MPa (purple line, tick marks in 10 % intervals) are from Supplementary Table C4. They are compared to the measured values for the Fijian felsic suites and mafic rocks (Todd et al., 2012; 2021), bulk continental crust (BCC; Rudnick and Gao, 2014) and amphibolitic Archean TTGs. Plots show (a) Ce vs. Yb; (b) Dy vs. Yb; (c) Dy/Dy* vs. Dy/Yb (after Davidson et al., 2013); (d) Zr vs. Yb; (e) Zr/Y vs. Y (Pearce and Norry, 1979); (f) Nb/Ta vs. Zr/Sm; (g) Sr vs. Yb; and (h) Th vs. Yb. The positive correlations in (a), (b), (d), and (h) between incompatible trace elements versus the more compatible Yb for the calculated fractional crystallization trends of olivine (ol), plagioclase (pl), clinopyroxene (cpx), magnetite (magn), apatite (ap), and orthopyroxene (opx) crystallization overlap with the LD- and EE-suites after 80 – 90 % fractionation. Increasing Zr concentrations in the LD- and EE-suite are due to zircon under-saturation, whereas decreasing Sr contents in (g) suggest plagioclase fractionation. In all plots, steeper positive covariations after 70 % fractionation are due to increasing late-stage amphibole fractionation that result in the preferred removal of the MREE-HREE. In contrast, 15 - 20 % partial melting (black line; tick marks in 5 % intervals) in the presence of residual amphibole results in a narrower range of trace element concentrations, resembling the LE-suite. The preferred retention of the MREE by residual amphibole also results in lower Dy/Dy*, Dy/Yb, and Nb/Ta than and higher Zr/Y and Zr/Sm ratios that are different between the LE-suite and respective tholeiitic groups.



Juvenile continental crust evolution in a modern oceanic arc setting: Petrogenesis of Cenozoic felsic plutons in Fiji, SW Pacific

compatibility of MREE in this mineral. Relatively low Dy/Yb ratios in both mafic and felsic rocks from Viti Levu rule out the influence of garnet (Davidson et al., 2013). Plagioclase and clinopyroxene show opposite Dy/Yb fractionation effects that are nearly nullified by their simultaneous crystallization for the LD- and EE-suites. The influence of some amphibole fractionation especially in the highly evolved EE-suite is clearly visible in Figure 3.11c. Here, model calculations show the decrease in Dy/Dy* and Dy/Yb ratios that is driven by late-stage amphibole fractionation with preferential MREE incorporation. Amphibole fractionation in hydrous arc-basalt melts is, however, highly pressure-sensitive (e.g., Blatter et al., 2013). At 400 MPa, early amphibole crystallization is suppressed, whereas clinopyroxene and plagioclase are the predominant crystallizing phases. In this scenario, amphibole stabilizes after ca. 80 % melt fractionation, whereas at higher pressures amphibole fractionation begins earlier and hence has a stronger influence on the REE budget of the resulting melt (Fig. 3.11b, c). The successive removal of the MREE and HREE by amphibole fractionation may explain the slightly lower Dy to Yb concentrations in the S-Wainivalau pluton relative to the Momi pluton.

Alternatively, Davidson et al. (2007) suggested that residual amphibole-rich wall rocks can be assimilated during fractional crystallization, which also would fractionate La_N/Yb_N and Dy/Yb ratios. However, the lack of isotopic changes shows that any amphibole assimilation is from co-genetic rocks. Only the LD-suite shows a slight increase of ${}^{87}Sr/{}^{86}Sr$ isotope ratios that might be consistent with such a process (Fig. C5).

In Figure 3.11e, the Zr/Y ratios of the Viti Levu mafic basement clearly show variations that are correlated with the greater degree of mantle wedge depletion in YV-EAT and WA-A than in YV-IAT and WA-B. In addition, Zr behaves incompatibly until zircon saturation is achieved. Under relatively dry and hot conditions zircon fractionation is suppressed, which results in higher Zr concentrations in evolved melts(Lee and Bachmann, 2014). Relatively dry conditions for the generation of the EE-suite are also supported by the scarcity of zircons in the tonalites. In contrast, amphibole and clinopyroxene fractionation slightly increases Zr/Y ratios (Pearce and Norry, 1979). This effect is clearly seen for both the LD-suite and the EE-suite. Zirconium/Y in the LD-suite overlaps with its mafic precursor (WA-B), and shows its more depleted character (Fig. 3.11e), whereas the EE-suite exhibits slightly increasing Zr/Y ratios with continuing fractionation as indicated by increasing Zr concentrations. The Zr/Y variations of the EE-suite are also solved as indicated by increasing Zr concentrations.

suite at higher Zr can be explained either by varying ratios in the source, or variable amounts of amphibole fractionation due to differing pressure. Increasing amphibole fractionation leads to the preferential removal of Y relative to Zr and therefore to slightly elevated Zr/Y in the remaining melt under higher pressures as seen for the S-Wainivalau rocks. The Momi pluton shows less influence of amphibole fractionation, which is also in agreement with slightly higher HREE concentration resulting in lower La_N/Sm_N, and La_N/Yb_N ratios (Figs. 3.8d, 3.9a-c). Only the associated Kalaka rhyolite shows stronger amphibole fractionation, similar to the younger S-Wainivalau pluton.

In conclusion, both the LD-suite and the EE-suite tonalites are adequately explained by up to 80 % fractionation of contemporaneous basaltic parents, involving mainly plagioclase, clinopyroxene, and magnetite or ilmenite. All three plutons, Korolevu (LDsuite), and Momi and S-Wainivalau (both EE-suite) show varying amounts of late-stage amphibole fractionation, likely indicative of varying crystallization depths.

3.6.4.2. Partial melting of mafic crust

Partial melting of mafic crust is regarded as a possible process for generating tonalitic/trondhjemitic plutons in arc systems (Beard and Lofgren, 1991; Tamura and Tatsumi, 2002; Clemens et al., 2021) We consider the possibility that the LE-suite originated by partial melting of hydrated mafic rocks in the middle to lower crust rather than water-saturated melting as proposed by Sommer et al. (2020) for the Yavuna pluton. Such mafic rocks in the Vitiaz arc would be a heterogeneous mixture of basaltic-andesitic composition of middle Eocene to early Miocene boninites, arc tholeiites, ultramafic cumulates, and MORB rocks that are metamorphosed under amphibolitic conditions and possibly hydrated by hydrothermal alteration. Collins et al. (2020) emphasized the critical role of hydrous fluids migrating from the subducting slab into the mantle wedge, producing hydrous basaltic melts, which rise to the base of the crust or into the crust where they fractionate, exsolve water, and hydrate the mafic crust. This would also initiate hydrous partial melting.

The major and trace element composition of a partial melt depends on whether or not melting occurs in a water-saturated environment. Under water-saturated melting conditions, the breakdown of K-bearing amphibole is hindered and plagioclase is preferentially consumed (Beard and Lofgren, 1991). In this case, high Al₂O₃, CaO, Sr (> 300 ppm), and Eu concentrations, and low K₂O values are expected in the melt, which

is not observed for the LE-suite. Even though we do not exclude the possibility of watersaturated partial melting for the origin of the LE-suite, lower Al₂O₃, CaO, and Sr concentration coupled with K₂O between 1 - 2 wt.% rather suggest the breakdown of more amphibole than plagioclase during partial melting, and hence this is our preferred process for the LE-suite. Additionally, Clemens et al. (2021) proposed that excess water, not trapped by amphibole formation, would be channelized in fractures and transported into the upper crust. Hence, dehydration melting of amphibole-rich precursor material caused by advected heat from intruding mafic magmas would be more reasonable.

We tested this assumption for the LE-suite by modeling melting of basalt compositions known to be present in Viti Levu. For the Yavuna pluton we used an isotopically similar YV-island-arc basalt with 10.4 wt.% MgO (T08-21; Todd et al., 2012). For the younger Colo plutons, the broader range in isotope compositions for the N-Wainivalau pluton and the Noikoro pluton indicates heterogeneous sources, which mostly overlap with the WA-B volcanics. This could be either because partial melting occurred at different depths, or because the crust of Fiji consists of an amalgamation of mafic to intermediate rocks that are the products of 30 Ma of volcanism ranging from boninitic to island-arc tholeiitic composition. As an example, we used the intermediate 69-920 (Todd et al., 2021) as the starting composition in our calculations (see Supplementary Table C4).

Modeling trace element concentrations during dehydration melting in the presence of residual amphibole generates a good fit for the LE-suite at 10 - 20 % melting (Fig. 3.11). There is only a modest enrichment of LREE in the melt, mimicking the concentrations of the EE-suite, but the MREE are preferentially retained in the amphibole-rich residue due to their higher compatibility in amphibole and they show a relatively narrow range of low concentrations (Fig. 3.11a, b) (Bédard, 2006; Tiepolo et al., 2007; Davidson et al., 2013). This is also expressed by the elevated La_N/Yb_N ratios of the LE-suite (Fig. 3.10a), and in the decrease of Dy/Dy* and Dy/Yb (Fig. 3.11c). In contrast to only late-stage amphibole saturation during fractional crystallization, the MREE-retaining behavior of residual amphibole throughout partial melting events leads to lower MREE/HREE ratios than in the fractionation trend for the EE-suite at lower pressures. Similar degrees of La_N/Yb_N and Dy/Yb fractionation by extensive amphibole crystallization are only achieved at higher Yb concentrations, which are not found in Fiji, although they characterize the Aleutians (Kay et al., 2019) where extensive amphibole fractionation occurred in middle to lower sections of the 37 km thick arc crust (Fig. 3.10a, b).

In addition to REE, high-precision HFSE data are a useful tool for assessing mafic precursors and processes involved during the generation of felsic rocks (e.g., Pearce and Norry, 1979; Klemme et al., 2006; Hoffmann et al., 2011; Hoffmann et al., 2014). The HFSE budget of partial melts at 0.8 GPa is strongly controlled by residual low Mg#-amphibole (e.g., Foley et al., 2002; Hoffmann et al., 2011; 2014) and ilmenite (Klemme et al., 2006). Hence, partial melting in their presence would result in greater HFSE depletion than for largely amphibole-free crystal fractionation. This can explain differences in Nb/Ta, Zr/Y, and Zr/Sm ratios between the LE-suite versus the EE-suite (Figs. 3.5d-f, 3.7d-e, 3.11f). Yttrium behaves like the MREE during both fractionation and melting in the presence of amphibole, while Zr is more incompatible. This results in higher Zr/Y ratios in partial melts than in amphibole-free fractional crystallization, and in Zr concentrations that remain between 80 – 120 ppm, due to the relatively low concentrations in the protolith.

Both Nb and Ta are strongly compatible in Ti-Fe-oxides and amphibole. Considering the minor abundance of ilmenite in mafic protoliths, residual amphibole exhibits the strongest Nb-Ta control relative to LILE and LREE (Fig. 3.6f). Additionally, due to the higher compatibility of Nb than Ta in residual low-Mg# amphibole, a shift towards lower Nb/Ta ratios occurs during partial melting and fractional crystallization of amphibole (Foley et al., 2002; Foley, 2008; Qian and Hermann, 2013; Hoffmann et al., 2014). In contrast, residual ilmenite would increase Nb/Ta ratios because of the preferential incorporation of Ta. Melting in the presence of residual amphibole shows a stronger effect on Nb/Ta fractionation, than late stage fractional crystallization (Fig. 3.11f). Indeed, low Nb/Ta ratios are a diagnostic feature of the LE-suite, while Zr/Sm ratios increase (Fig. 3.9c). In our dehydration melting model, the progressive breakdown of the residual amphibole leads to an a slightly increase of the Nb/Ta ratio, as well as Dy/Dy*, Dy/Yb and Zr/Y ratios at low Zr contents, which can be best explained by the diminishing fractionation effect of residual amphibole as the percent of melting increases. Furthermore, the EE-suite shows a similarly narrow range of Zr/Sm but at slightly higher Nb/Ta and requires a different process to account for the higher Zr/Sm ratios than in the LE-suite (Fig. 3.11f). As already mentioned, during fractional crystallization of a hot melt, zircon fractionation is suppressed (Lee and Bachmann, 2014), which also results in increasing Zr/Sm, whereas low percentages of partial melt of amphibole exhibit high Zr/Sm ratios due to the more compatible behavior of Sm relative to Zr that decreases with ongoing partial melting and results in elevated Zr/Sm at lower Zr concentrations.

This model is, of course, over simplified. Some assimilation, mixing, and fractional crystallization doubtless occurs over the hundreds of thousands of years of pluton formation. However, we found that a simple closed system of intra-crustal melting can explain many geochemical features of the LE-suite.

Therefore, we propose that 10 - 20 % dehydration melting of island-arc tholeiitic crust can produce the medium-K trondhjemites of the LE-suite. Because the LE-suite consists of several plutons with ages ranging from the late Eocene to late Miocene, significant amounts of crustal melt were extracted at least twice over 30 million years. The Yavuna Stock trondhjemites are part of the first magmatic/volcanic succession of the Vitiaz arc and slightly predate the initial opening of the SFB in the early Oligocene (34 Ma; Herzer et al., 2011). This back-arc spreading event accompanied the eastward rollback of the Pacific slab and upwelling of hot mantle material. Subsequent renewal of arc activity may have triggered magmatic underplating beneath Viti Levu. The emplacement of the Colo plutons may coincide with the initial rotation of the Fiji Platform (Fig. 3.2b) and opening of the North Fiji Basin (e.g., Hathway, 1993; Stratford and Rodda, 2000; Schellart et al., 2006). Hence, both episodes of significant melting of the Fijian crust can be linked to unusual tectonic events in the history of the arc.

3.6.5. Spatial and temporal diversity of felsic magmas in Fiji

The Fijian felsic plutons have a remarkable diversity for a relatively small area and short length of time. The Colo plutons range from LD- to LE-suites within 70 km, and overlap in age within 3.5 m.y. At least two individual plutons, Wainivalau and Wainqa, include both EE- and LE-facies (Fig. 3.2). We attribute this diversity to the effects of injecting diverse mantle-derived basaltic melts (like the WA-A and WA-B types shown in our figures) into young arc crust. Some of the basaltic melts fractionated under relatively closed-system "dry" conditions, at least up to dacitic/rhyolitic compositions, to become the LD- to EE-tonalitic plutons. The increased mafic magma influx also may have caused 10 - 20 % dehydration melting of the lower to middle crust, producing the

LE-trondhjemitic plutons. Both processes overlap in space and time at a scale commonly found in individual volcanic edifices in island arcs.

Another feature of our study is that we analyzed rhyolites that are coeval with the tonalites and spatially adjacent to them. Volcanics of the Wainimala Group are bimodal (Todd et al., 2021), with abundant felsic lavas and volcaniclastics that are mapped as "quartz-keratophyre" lava lenses up to 20 km long surrounding the plutons. Most of them are low-K and have LREE-depleted to flat REE patterns. This seems consistent with LD-and EE-Type felsic magmas being drier and hotter versus the LE-Type being wetter and cooler, making them less likely to erupt.

The diversity in Fijian tonalitic plutons is similar to that found in rhyolites in the Izu arc (Tamura et al., 2009; Haraguchi et al., 2017; Heywood et al., 2020). The rhyolitic equivalents of our LD- and EE-types are interspersed along, and slightly behind, the Izu volcanic front, whereas the equivalent of our LE-Type is restricted to > 50 km behind the volcanic front. In general, there is more spatial separation between rhyolite types in Izu where, near the volcanic front, they seem to be associated with local differences in crustal thickness (thicker crust for LD-Type, thinner for EE-Type). To our knowledge, our study is the first documentation of such diversity amongst plutonic equivalents. It suggests, not surprisingly, that there is a smaller spatial scale of diversity amongst felsic plutons than of felsic volcanic rocks because the plutons cover a wider range of temperature and water contents than the volcanics. The plutonic diversity is one reason that we appeal to genetic end-members rather than a uniformly homogenizing MASH process.

Finally, we speculate on the tectonic significance of the spatial and temporal distribution of the Colo plutons. Viti Levu is located at the northwestern terminus if the Lau-Colville Ridge, within 100 km of where the Vitiaz arc broke across-strike to become the now-separate Vanuatu and Fiji segments (Fig. 3.1). The age of break-up is uncertain but may have started by ~10 Ma (Schellart et al., 2006), near the inception age of Colo plutonism. The greater thickness of crust beneath Viti Levu than the arc segments farther east and south (Chen et al., 2019), and the uplift during and after plutonism that we discovered, might result from maximum magma focusing, intrusion, and underplating where the arc broke. If so, then the plutonism records the deformation and weakening of the arc prior to the unusual "double-saloon-door tectonics" that accompanied breaking of the arc and opening of the North Fiji Basin (Martin, 2013).

3.6.6. Are intra-oceanic arcs an important contributor to continental crustal formation?

Modern continental crust has an andesitic bulk composition that is rich in incompatible elements and poor in Nb and Ta, combined with an average Nb/Ta below that of MORBs and ocean island basalts (e.g., Barth et al., 2000; Rudnick and Gao, 2014). At least two stages are required for the formation of such crust: the extraction of a dominantly mafic melt from the metasomatized peridotitic mantle; and the differentiation of such material, either by fractional crystallization of the melts or partial melting of the crystallized mafic magmas, with both processes producing mafic cumulates or residues. However, new continental crust is currently primarily produced in continental arc settings, in which the extracted melts are mixed with earlier eroded or weathered continental material (Rudnick, 1995; Taylor and McLennan, 1995; Clift et al., 2009). Such a reworking of older crust in continental arcs is also consistent with their less radiogenic Hf and Nd isotope composition and the Hf isotope record in zircons (e.g., Belousova et al., 2010).

Intra-oceanic arc systems are alternative settings for juvenile continental formation, with reduced influence of crustal recycling. Due to their mostly basaltic bulk compositions, the preservation of oceanic arcs in destructive plate boundaries is problematic. A crucial factor in whether an oceanic arc is completely subducted or accreted to continental margins, is its crustal thickness (e.g., Stern, 2011). Condie and Kröner (2013) suggest that oceanic arcs thinner than 20 km mostly subduct while convergence proceeds, whereas oceanic arcs > 20 km can accrete to continents or are only partly subducted. However, the trace element budget of felsic rocks in oceanic arcs differs significantly from that of similarly evolved rocks in continental arcs. Felsic rocks in oceanic arcs are similar to ophiolitic plagiogranites that are generally poor in highly incompatible elements and enriched in HREE, resulting in low La/Yb, Th/Yb, and Nb/Yb ratios, whereas in continental arcs those ratios are higher because of incorporating recycled material and the thicker crust filtering out more mafic components near at the base of the crust (Fig. 3.12).

Here again, Viti Levu is a special case in terms of oceanic arc maturation. A recent passive seismic receiver function study by Chen et al. (2019) found a crustal thickness of 29 km for Viti Levu, more than the 20 km that is more typical of the rest of the Fiji-Lau

segment. The latter thickness is consistent with an interpretation of regional free-air gravity data (Segev et al., 2012). Both studies infer a 5 to 10 km thick middle crust of quartz-rich rocks like tonalite beneath Viti Levu that are underlain by up to 20 km of more mafic-ultramafic crust.

In Th/Yb vs. Nb/Yb space (Fig. 3.12a, b; Pearce, 2008), the chemical affinity of the Viti Levu felsic plutons lies in the overlapping field between oceanic and continental arcs. All Fijian suites and the respective mafic volcanics generally exhibit an offset from the mantle array to higher Th/Yb ratios relative to Nb/Yb, which is a consequence of their formation in a subduction-related arc setting. The LD-suite is even more depleted than N-MORB in Nb/Yb and the LE-suite is offset the most from the mantle array. Therefore,



we suggest that central Viti Levu has already evolved to compositions indistinguishable from continentallike arcs in some element ratios. Melting of the mafic crust has produced felsic melts in the presence of residual amphibole that preferentially retain Nb and MREE-HREE, leading to continental arc like

Figure 3.12: Th/Yb vs. Nb/Yb (after Pearce, 2008): (a) illustrates the evolution of oceanic to continental arc and the significance of Fijian trondhjemites. The ratios show an increasing interaction of mantle wedge and subducted material for the mafic volcanic rocks from Viti Levu (Todd et al., 2012; 2021) and the related LDand EE-suites within the oceanic arc. The decoupled trace element ratios of each LEsuite pluton, similar to continental arcs, highlight the importance of partial melting in mafic basements and the approach to bulk continental crust composition (Rudnick and Gao, 2014). In (b) the same ratios are compared to ophiolitic Troodos plagiogranites (Marien et al., 2019), the Tanzawa plutonic complex (Kawate and Arima, 1998), the Aleutian plutons (Kay et al., 2019), and the rear-arc rhyolites (RA) of the Izu arc (Haraguchi et al., 2017).

signatures, slightly enriched in incompatible Th, Rb, and Ba (Rudnick, 1995).

Although even the LE-suite has lower Th/Yb and Nb/Yb ratios than bulk continental crust, it is obvious that the Fiji Platform has emerged from oceanic crust to become a more continental arc-like system in places. Similar occurrences of felsic plutonic rocks in oceanic arcs have been reported for the IBM arc and the Tanzawa complex near Mt. Fuji on Honshu, Japan (e.g., Kawate and Arima, 1998; Tamura et al., 2009; Tani et al., 2010; Haraguchi et al., 2017). In both settings, some of the frontal and rear-arc rhyolites and tonalites were interpreted as re-melting products of mafic arc crust and the emergence of andesitic to felsic middle crust in oceanic arcs is an important first step for the growth of new continental crust.

3.6.7. Comparison to Archean crust formation processes

The search for modern analogues that mimic Archean TTG generation is the focus of many studies addressing Archean crustal evolution. Four different models have been proposed for the origin and the growth of Archean continental crust (Moyen et al., 2017): (1) fractional crystallization of arc-like basaltic melts to form tonalites (e.g., Kleinhanns et al., 2003; Hawkesworth et al., 2010; Jagoutz, 2013); (2) partial melting of hydrous metabasalts in a hot subducted slab, also described as the "adakitic model" (Martin, 1986); (3) partial melting in the deeper regions of thickened oceanic crust, oceanic plateaus (Bolhar and Van Kranendonk, 2007; Hoffmann et al., 2011) or oceanic island arcs (Polat, 2012) by magmatic underplating, (4) a combination of fractional crystallization of incoming melts, partial melting of pre-existing basaltic crust and incorporating of crustal material (Arndt, 2013).

In the Earth's more recent history oceanic plagiogranites were originally inferred to be modern analogues for Archean TTGs (e.g., Coleman and Peterman, 1975). However, plagiogranites that are found in ophiolitic complexes, such as the Troodos Ophiolite (Marien et al., 2019) and the Oman Ophiolite (Rollinson, 2008; 2009) mostly form near spreading ridges at shallow depths and differ from Archean TTGs by having LREE depletions and flat HREE patterns. Although these characteristics are similar to those of the LD-suite, the Archean TTGs are generally more potassic, and a more enriched mafic source is required for their formation (Rollinson, 2009; Martin et al., 2014).

A subdivision of Archean TTGs into "low", "medium", and "high"-pressure types has been proposed based on the presence of residual phases such as garnet, amphibole
and rutile that strongly affect the trace element budgets (e.g., Moyen, 2011; Moyen and Martin, 2012). The "medium"- and "high"-pressure TTGs exhibit especially high Sr/Y and La_N/Yb_N ratios (Figs. 3.6e, 3.10a, c) due to the lack of residual plagioclase and the presence of garnet that retain HREE during their generation. The compositional differences hint at the different melting depths of the Archean TTGs (e.g., Martin, 1986; Moyen and Martin, 2012) or indicate accumulation of amphibole during fractional crystallization (Hoffmann et al., 2014; Laurent et al., 2020). Additionally, at higher pressures (> 1.0 GPa) residual or fractionating garnet, amphibole, and rutile exert substantial influence on the HFSE budget, resulting in high Nb/Ta ratios in presence of rutile (> 1.5 GPa), whereas amphibole lowers Nb/Ta, and amphibole and garnet fractionation leads to elevated Zr/Sm ratios (Foley et al., 2002; Foley, 2008). These conditions do not occur in Fiji.

Amongst the Fijian plutons, the LE-suite differs the most from modern oceanic plagiogranites (e.g., Marien et al., 2019) and shows geochemical and petrogenetic similarities to "low"-pressure Archean TTGs (Figs. 3.6e, 3.11c). Both the LE-suite and "low"-pressure TTGs are voluminous felsic plutons that that can be explained by partial melting of mafic arc crust at relatively shallow depths (e.g., Smithies et al., 2009; Johnson et al., 2017). The major element composition of the LE-suite is akin to the Archean TTGs in being trondhjemitic and sharing K₂O concentrations of 0.5 - 2 wt.%, K₂O/Na₂O between 0.3 and 0.6, and about 14 wt.% Al₂O₃ at 70 wt.% SiO₂ (Moyen and Martin, 2012). Furthermore, low Nb/Ta and slightly elevated Zr/Sm ratios are comparable to low-pressure TTGs (Fig. 3.11f) and suggest similar relatively low pressures with amphibolitic residues.

Differences between the Fijian LE-suite and the Archean TTGs are visible in the REE systematics (Fig. 3.10a, c). As mentioned above, partial melting in the presence of residual garnet produces fractionated La_N/Yb_N , high Sr/Y and distinctively low HREE concentrations in Archean TTGs. The LE-suite has even lower La_N/Yb_N and Sr/Y ratios than the "low"-pressure TTGs derived from garnet-free (< 1.0 GPa) amphibolitic regimes (Fig. 3.6e; e.g., Hoffmann et al., 2014). Higher LREE concentrations and hence higher La_N/Yb_N ratios in the "low"-pressure Archean TTGs are simply the result of more LREE-enriched precursors (Rollinson, 2009), which are less commonly produced from the modern depleted mantle. This degree of LREE enrichment in the modern upper mantle

only occurs in plume related systems like Iceland (e.g., Willbold et al., 2009) or in continental and oceanic subduction settings with more slab components or crustal assimilation (e.g., Hastie et al., 2015).

Viti Levu is located in an intra-oceanic subduction system and the LE-suite most likely originates from partial melting of arc basaltic protoliths within the mafic crust. Polat (2012) proposed that some of the Archean TTGs might result by partial melting of arc basalts under amphibolitic to eclogitic conditions in the Archean lower arc crust in subduction zones. Although the crustal thickness at Viti Levu is < 30 km and the arc basaltic basement is less enriched in incompatible elements than its Archean counterparts, the LE-suite is still comparable to the "low"-pressure regimes in the Archean. We therefore propose that the genesis of the LE-suite trondhjemites can be a plausible modern analogue for the generation of some uncommon shallow level Archean TTGs.

3.7. Conclusions

A comprehensive dataset including major- and trace element, high precision HFSE as well as combined Hf-Nd-Sr-Pb isotope data for well-preserved tonalites and trondhjemites and their zircons from the Cenozoic plutons in Viti Levu, Fiji, permit us to infer the following conclusions about the evolution of oceanic arc basement to continental crust:

- (1) Multiple episodic stages of arc volcanism and back-arc spreading processes are responsible for the generation of an evolved "granitic" layer in this oceanic island arc. The Fijian plutons formed a few million years before (Yavuna) or during (Colo) the initial rifting stage of adjacent back-arc basin formation, and are not a steady-state phenomenon.
- (2) Genetically unrelated felsic plutons and volcanic rocks coexist at short spatial and temporal scales. The tonalitic and trondhjemitic plutons can be divided by their geochemical properties into three suites with different petrogenetic origins. Fractional crystallization processes of depleted (WA-A) and enriched (WA-B) island-arc tholeiitic melts are mostly responsible for the low-K LD-suite and EEsuite during the Miocene. Several of these plutons are surrounded by large volumes of felsic lavas that are similar in composition to the plutons. Major and trace element trends and overlapping Pb-Hf-Nd isotope compositions suggest that

both suites and the surrounding mafic volcanics are genetically linked by fractional crystallization. Geochemical trends, such as decreasing Nb/Ta and Dy/Dy* with simultaneous increasing Zr/Y are best explained by early clinopyroxene + plagioclase and late-stage amphibole fractionation.

- (3) Several pulses of dehydration melting of the island-arc tholeiitic crust contributed to the intrusion of medium-K trondhjemites (LE-suite) in the late Eocene and late Miocene. The LE-suite exhibits higher La_N/Yb_N, La_NSm_N, Zr/Y, low Nb/Ta and Dy/Dy* ratios than can be achieved by simple crystal fractionation of typical Fijian mafic precursors on Viti Levu. Instead, geochemical modeling and matching isotope compositions lead to the conclusion that the LE-suite is mostly the product of dehydration melting of Fijian mafic crust.
- (4) There is no evidence of pre-Eocene continental crust in Fiji. No zircons have pre-Eocene cores, their Hf model age is zero, the zircons have mantle-type oxygen isotopes, and they have lower U/Yb ratios than zircons from continental margin arcs.
- (5) Oceanic arc detrital zircons faithfully retain the geochemical characteristics of their plutonic source rocks, and indicate that juvenile felsic arc crust is extracted from the mantle in only a few million years. Uplift of arc plutons can be just as rapid. In the Fijian case, this may be related to tectonic events, such as opening a back-arc basin.
- (6) The formation and evolution of a new continental nucleus is associated with the emergence of tonalites and trondhjemites in oceanic arcs. The "granitic" middle layer supports the stabilization of an oceanic arc and is the result of internal differentiation processes, either by fractional crystallization or dehydration melting or both.
- (7) The LE-suite from Viti Levu is most similar to the "low"-pressure type of Archean TTGs, likely reflecting similarities during generation. Both are most likely generated by partial melting of mafic arc crust at < 1.0 GPa. Precursor material in the Archean TTGs was presumably more enriched in LILE and LREE than modern mantle derived rocks, resulting also in lower concentrations in modern trondhjemites from Viti Levu.</p>

Juvenile continental crust evolution in a modern oceanic arc setting: Petrogenesis of Cenozoic felsic plutons in Fiji, SW Pacific

In conclusion, Fiji is an exceptional Cenozoic example of an evolving oceanic arc system. We suggest that the felsic rocks from Fiji are, therefore, a reasonable modern analogue to Archean processes and those that create continental crust in oceanic island arcs. The geochemical heterogeneity of Fijian plutons within scores of kilometers and a few million years shows the diverse processes of pluton genesis in island arcs and highlights what is still unknown.

V. REFERENCES

- Abouchami W., Galer S. J. G. and Hofmann A. W. (2000) High precision lead isotope systematics of lavas from the Hawaiian Scientific Drilling Project. *Chem. Geol.* 169, 187–209. Available at: https://doi.org/10.1016/S0009-2541(00)00328-4.
- Adam J. and Green T. (2006) Trace element partitioning between mica- and amphibole-bearing garnet lherzolite and hydrous basanitic melt: 1. Experimental results and the investigation of controls on partitioning behaviour. *Contrib. to Mineral. Petrol.* 152, 1–17. Available at: https://doi.org/10.1007/s00410-006-0085-4.
- Albut G., Babechuk M. G., Kleinhanns I. C., Benger M., Beukes N. J., Steinhilber B., Smith A. J. B., Kruger S. J. and Schoenberg R. (2018) Modern rather than Mesoarchaean oxidative weathering responsible for the heavy stable Cr isotopic signatures of the 2.95 Ga old Ijzermijn iron formation (South Africa). *Geochim. Cosmochim. Acta* 228, 157–189. Available at: https://doi.org/10.1016/j.gca.2018.02.034.
- Alexander B. W., Bau M. and Andersson P. (2009) Neodymium isotopes in Archean seawater and implications for the marine Nd cycle in Earth's early oceans. *Earth Planet. Sci. Lett.* 283, 144–155. Available at: https://doi.org/10.1016/j.epsl.2009.04.004.
- Alexander B. W., Bau M., Andersson P. and Dulski P. (2008) Continentally-derived solutes in shallow Archean seawater: Rare earth element and Nd isotope evidence in iron formation from the 2.9 Ga Pongola Supergroup, South Africa. *Geochim. Cosmochim. Acta* 72, 378–394. Available at: https://doi.org/10.1016/j.gca.2007.10.028.
- Allègre C. J. (1969) Comportement de Systemes U-Th-Pb dans le Manteau Superieur et Modele d'evolution de ce Dernier au Cours des Temps Geologiques. *Earth Planet. Sci. Lett.* 5, 261–269. Available at: https://doi.org/10.1016/S0012-821X(68)80050-0.
- Allègre C. J. (1987) Isotope geodynamics. *Earth Planet. Sci. Lett.* **86**, 175–203. Available at: https://doi.org/10.1016/0012-821X(87)90220-2.
- Allègre C. J., Dupré B. and Lewin E. (1986) Thorium/Uranium ratio of the Earth. *Chem. Geol.* **56**, 219–227. Available at: https://doi.org/10.1016/0009-2541(86)90005-7.

- Allègre C. J., Louvat P., Gaillardet J., Meynadier L., Rad S. and Capmas F. (2010) The fundamental role of island arc weathering in the oceanic Sr isotope budget. *Earth Planet. Sci. Lett.* **292**, 51–56. Available at: https://doi.org/10.1016/j.epsl.2010.01.019.
- Allègre C. J. and Minster J. F. (1978) Quantitative models of trace element behavior in magmatic processes. *Earth Planet. Sci. Lett.* 38, 1–25. Available at: https://doi.org/10.1016/0012-821X(78)90123-1.
- Allwood A. C., Kamber B. S., Walter M. R., Burch I. W. and Kanik I. (2010) Trace elements record depositional history of an early Archean stromatolitic carbonate platform. *Chem. Geol.* 270, 148–163. Available at: https://doi.org/10.1016/j.chemgeo.2009.11.013.
- Allwood A. C., Walter M. R., Kamber B. S., Marshall C. P. and Burch I. W. (2006) Stromatolite reef from the early Archaean era of Australia. *Nature* **441**, 714–718. Available at: https://doi.org/10.1038/nature04764.
- Amelin Y., Krot A. N., Hutcheon I. D. and Ulyanov A. A. (2002) Lead isotopic ages of chondrules and calcium-aluminum-rich inclusions. *Science* 297, 1678–1683. Available at: https://doi.org/10.1126/science.1073950.
- Amelin Y., Lee D., Halliday A. N. and Pidgeon R. T. (1999) Nature of the Earth's earliest crust from hafnium isotopes in single detrital zircons. *Nature* **399**, 252–255. Available at: https://doi.org/10.1038/20426.
- Arevalo R., McDonough W. F. and Luong M. (2009) The K/U ratio of the silicate Earth: Insights into mantle composition, structure and thermal evolution. *Earth Planet. Sci. Lett.* **278**, 361–369. Available at: https://doi.org/10.1016/j.epsl.2008.12.023.
- Armstrong R. L. (1968) A model for the evolution of strontium and lead isotopes in a dynamic Earth. *Rev. Geophys.* 6, 175–199. Available at: https://doi.org/10.1029/RG006i002p00175.
- Armstrong R. L. (1981) Radiogenic isotopes: the case for crustal recycling on a nearsteady-state no-continental-growth Earth. *Philos. Trans. R. Soc. London. Ser. A, Math. Phys. Sci.* **301**, 443–472. Available at: https://doi.org/10.1098/rsta.1981.0122.
- Arndt N. T. (2013) Formation and evolution of the continental crust. *Geochemical Perspect.* 2, 405–533. Available at: https://doi.org/10.7185/geochempersp.2.3.
- Arndt N. T., Bruzak G. and Reischmann T. (2001) The oldest continental and oceanic plateaus: Geochemistry of basalts and komatiites of the Pilbara Craton, Australia. *Spec. Pap. Geol. Soc. Am.* **352**, 359–387. Available at: https://doi.org/10.1130/0-8137-2352-3.359.
- Arndt N. T., Kerr A. C. and Tarney J. (1997) Dynamic melting in plume heads: The formation of Gorgona komatiites and basalts. *Earth Planet. Sci. Lett.* 146, 289– 301. Available at: https://doi.org/10.1016/S0012-821X(96)00219-1.

Artemieva I. M. (2006) Global $1^{\circ} \times 1^{\circ}$ thermal model TC1 for the continental

lithosphere: Implications for lithosphere secular evolution. *Tectonophysics* **416**, 245–277. Available at: https://doi.org/10.1016/j.tecto.2005.11.022.

- Band R. B. (1968) Geology of southern Viti Levu and Mbengga. *Geol. Surv. Fiji Bull.* **15**.
- Banner J. L. (1995) Application of the trace element and isotope geochemistry of strontium to studies of carbonate diagenesis. *Sedimentology* **42**, 805–824. Available at: https://doi.org/10.1111/J.1365-3091.1995.TB00410.X.
- Banner J. L. and Hanson G. N. (1990) Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochim. Cosmochim. Acta* 54, 3123–3137. Available at: https://doi.org/10.1016/0016-7037(90)90128-8.
- Barbarin B. (1999) A review of the relationships between granitoid types, their origins and their geodynamic environments. *Lithos* **46**, 605–626. Available at: https://doi.org/10.1016/S0024-4937(98)00085-1.
- Barker F. and Arth J. G. (1976) Generation of trondhjemitic-tonalitic liquids and Archaean bimodal trondhjemitie-basalt suites. *Geology* **4**, 596–600. Available at: https://doi.org/10.1130/0091-7613(1976)4<596:GOTLAA>2.0.CO;2.
- Barnes S. J. and Arndt N. T. (2019) Distribution and geochemistry of komatiites and basalts through the Archean. In *Earth's Oldest Rocks* Elsevier B.V., pp. 103–132. Available at: https://doi.org/10.1016/B978-0-444-63901-1.00006-X.
- Barth A. P., Tani K., Meffre S., Wooden J. L., Coble M. A., Arculus R. J., Ishizuka O. and Shukle J. T. (2017) Generation of silicic melts in the early Izu-Bonin Arc recorded by detrital zircons in proximal arc volcaniclastic rocks from the Philippine Sea. *Geochemistry, Geophys. Geosystems* 18, 3576–3591. Available at: https://doi.org/10.1002/2017GC006948.
- Barth M. G., McDonough W. F. and Rudnick R. L. (2000) Tracking the budget of Nb and Ta in the continental crust. *Chem. Geol.* **165**, 197–213. Available at: https://doi.org/10.1016/S0009-2541(99)00173-4.
- Bau M. (1996) Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: Evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contrib. to Mineral. Petrol.* **123**, 323–333. Available at: https://doi.org/10.1007/s004100050159.
- Bau M. (1991) Rare-earth element mobility during hydrothermal and metamorphic fluid rock interaction and the significance of the oxidation-state of europium. *Chem. Geol.* 93, 219–230. Available at: https://doi.org/10.1016/0009-2541(91)90115-8.
- Bau M. (1999) Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: Experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect. *Geochim. Cosmochim. Acta* 63, 67–77. Available at: https://doi.org/10.1016/S0016-7037(99)00014-9.
- Bau M. and Dulski P. (1999) Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic ridge: Implications for Y and REE behaviour during near-

vent mixing and for the Y/Ho ratio of proterozoic seawater. *Chem. Geol.* **155**, 77–90. Available at: https://doi.org/10.1016/S0009-2541(98)00142-9.

- Bau M. and Dulski P. (1996) Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa. *Precambrian Res.* 79, 37–55. Available at: https://doi.org/10.1016/0301-9268(95)00087-9.
- Beard J. S. and Lofgren G. E. (1991) Dehydration melting and water-saturated melting of basaltic and andesitic greenstones and amphibolites at 1, 3, and 6.9 kb. *J. Petrol.* 32, 365–401. Available at: https://doi.org/10.1093/petrology/32.2.365.
- Bédard J. H. (2006) A catalytic delamination-driven model for coupled genesis of Archaean crust and sub-continental lithospheric mantle. *Geochim. Cosmochim. Acta* **70**, 1188–1214. Available at: https://doi.org/10.1016/j.gca.2005.11.008.
- Bédard J. H. (2018) Stagnant lids and mantle overturns: Implications for Archaean tectonics, magmagenesis, crustal growth, mantle evolution, and the start of plate tectonics. *Geosci. Front.* 9, 19–49. Available at: https://doi.org/10.1016/j.gsf.2017.01.005.
- Bédard J. H., Harris L. B. and Thurston P. C. (2013) The hunting of the snArc. *Precambrian Res.* 229, 20–48. Available at: https://doi.org/10.1016/j.precamres.2012.04.001.
- Bell E. (2017) Petrology: Ancient magma sources revealed. *Nat. Geosci.* **10**, 397–398. Available at: https://doi.org/10.1038/ngeo2955.
- Belousova E. A., Kostitsyn Y. A., Griffin W. L., Begg G. C., O'Reilly S. Y. and Pearson N. J. (2010) The growth of the continental crust: Constraints from zircon Hf-isotope data. *Lithos* 119, 457–466. Available at: https://doi.org/10.1016/j.lithos.2010.07.024.
- Bennett V. C. (2003) 2.13 Compositional evolution of the mantle. In *Treatise on Geochemistry*, Elsevier Ltd., pp. 493–519. Available at: https://doi.org/10.1016/B0-08-043751-6/02013-2.
- Bennett V. C., Brandon A. D. and Nutman A. P. (2007) Coupled ¹⁴²Nd-¹⁴³Nd isotopic evidence for hadean mantle dynamics. *Science* **318**, 1907–1910. Available at: https://doi.org/10.1126/science.1145928.
- Bennett V. C., Nutman A. P. and McCulloch M. T. (1993) Nd isotopic evidence for transient, highly depleted mantle reservoirs in the early history of the Earth. *Earth Planet. Sci. Lett.* **119**, 299–317. Available at: https://doi.org/10.1016/0012-821X(93)90140-5.
- Bernstein S., Kelemen P. B. and Hanghøj K. (2007) Consistent olivine Mg# in cratonic mantle reflects Archean mantle melting to the exhauston of orthopyroxene. *Geology* 35, 459–462. Available at: https://doi.org/10.1130/G23336A.1.
- Beukes N. J. and Klein C. (1990) Geochemistry and sedimentology of a facies transition - from microbanded to granular iron-formation - in the early Proterozoic Transvaal Supergroup, South Africa. *Precambrian Res.* **47**, 99–139. Available at:

https://doi.org/10.1016/0301-9268(90)90033-M.

- Bindeman I. N., Davis A. M. and Drake M. J. (1998) Ion microprobe study of plagioclase-basalt partition experiments at natural concentration levels of trace elements. *Geochim. Cosmochim. Acta* 62, 1175–1193. Available at: https://doi.org/10.1016/S0016-7037(98)00047-7.
- Blatter D. L., Sisson T. W. and Hankins W. Ben (2013) Crystallization of oxidized, moderately hydrous arc basalt at mid- to lower-crustal pressures: Implications for andesite genesis. *Contrib. to Mineral. Petrol.* **166**, 861–886. Available at: https://doi.org/10.1007/s00410-013-0920-3.
- Blichert-Toft J. (2001) On the Lu-Hf isotope geochemistry of silicate rocks. *Geostand*. *Newsl.* **25**, 41–56. Available at: https://doi.org/10.1111/j.1751-908X.2001.tb00786.x.
- Blichert-Toft J. and Albarède F. (2008) Hafnium isotopes in Jack Hills zircons and the formation of the Hadean crust. *Earth Planet. Sci. Lett.* **265**, 686–702. Available at: https://doi.org/10.1016/j.epsl.2007.10.054.
- Blichert-Toft J., Albarède F., Rosing M., Frei R. and Bridgwater D. (1999) The Nd and Hf isotopic evolution of the mantle through the Archean. Results from the Isua supracrustals, West Greenland, and from the Birimian terranes of West Africa. *Geochim. Cosmochim. Acta* 63, 3901–3914. Available at: https://doi.org/10.1016/S0016-7037(99)00183-0.
- Blichert-Toft J., Chauvel C. and Albarede F. (1997) Separation of Hf and Lu for high precision isotope analysis of rock samples by magnetic sector multiple collector ICP-MS. *Contrib. to Mineral. Petrol.* **127**, 248–260. Available at: https://doi.org/10.1007/s004100050278.
- Blichert-Toft J., Zanda B., Ebel D. S. and Albaràde F. (2010) The solar system primordial lead. *Earth Planet. Sci. Lett.* **300**, 152–163. Available at: https://doi.org/10.1016/j.epsl.2010.10.001.
- Bolhar R. and Van Kranendonk M. J. (2007) A non-marine depositional setting for the northern Fortescue Group, Pilbara Craton, inferred from trace element geochemistry of stromatolitic carbonates. *Precambrian Res.* 155, 229–250. Available at: https://doi.org/10.1016/j.precamres.2007.02.002.
- Bottinga Y. (1969) Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite-carbon dioxide-graphite-methane-hydrogen-water vapor. *Geochim. Cosmochim. Acta* **33**, 49–64. Available at: https://doi.org/10.1016/0016-7037(69)90092-1.
- Bouvier A., Vervoort J. D. and Patchett P. J. (2008) The Lu-Hf and Sm-Nd isotopic composition of CHUR: Constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. *Earth Planet. Sci. Lett.* 273, 48–57. Available at: https://doi.org/10.1016/j.epsl.2008.06.010.
- Bowring S. A. and Housh T. (1995) The Earth's early evolution. *Science* **269**, 1535–1540. Available at: https://doi.org/10.1126/science.7667634.

- Boyet M. and Carlson R. W. (2006) A new geochemical model for the Earth's mantle inferred from ¹⁴⁶Sm-¹⁴²Nd systematics. *Earth Planet. Sci. Lett.* **250**, 254–268. Available at: https://doi.org/10.1016/j.epsl.2006.07.046.
- Boyet M., Doucelance R., Israel C., Bonnand P., Auclair D., Suchorski K. and Bosq C. (2019) New constraints on the origin of the EM-1 component revealed by the measurement of the La-Ce isotope systematics in Gough Island lavas. *Geochemistry, Geophys. Geosystems* 20, 2484–2498. Available at: https://doi.org/10.1029/2019GC008228.
- Brévart O., Dupré B. and Allègre C. J. (1986) Lead-lead age of komatiitic lavas and limitations on the structure and evolution of the Precambrian mantle. *Earth Planet. Sci. Lett.* 77, 293–302. Available at: https://doi.org/10.1016/0012-821X(86)90141-X.
- Broecker W. S. and Peng T. H. (1982) *Tracers in the sea*. Palisades, NY: Eldigio Press. Available at: https://doi.org/10.2307/1309641.
- Brophy J. G. (2008) A study of rare earth element (REE)-SiO₂ variations in felsic liquids generated by basalt fractionation and amphibolite melting: A potential test for discriminating between the two different processes. *Contrib. to Mineral. Petrol.* 156, 337–357. Available at: https://doi.org/10.1007/s00410-008-0289-x.
- Brown M. (2008) Characteristic thermal regimes of plate tectonics and their metamorphic imprint throughout earth history: when did earth first adopt a plate tectonics mode of behavior? *Spec. Pap. Geol. Soc. Am.* **440**, 97–128. Available at: https://doi.org/10.1130/2008.2440(05).
- Buick R., Brauhart C. W., Morant P., Thornett J. R., Maniw J. G., Archibald N. J., Doepel M. G., Fletcher I. R., Pickard A. L., Smith J. B., Barley M. E., McNaughton N. J. and Groves D. I. (2002) Geochronology and stratigraphic relationships of the Sulphur Springs Group and Strelley Granite: A temporally distinct igneous province in the archaean Pilbara Craton, Australia. *Precambrian Res.* 114, 87–120. Available at: https://doi.org/10.1016/S0301-9268(01)00221-2.
- Buick R., Thornett J. R., McNaughton N. J., Smith J. B., Barley M. E. and Savage M. (1995) Record of emergent continental crust ~3.5 billion years ago in the Pilbara craton of Australia. *Nature* **375**, 574–577. Available at: https://doi.org/10.1038/375574a0.
- Burton K. W., Cenki-Tok B., Mokadem F., Harvey J., Gannoun A., Alard O. and Parkinson I. J. (2012) Unradiogenic lead in Earth's upper mantle. *Nat. Geosci.* **5**, 570–573. Available at: https://doi.org/10.1038/ngeo1531.
- Buys J., Spandler C., Holm R. J. and Richards S. W. (2014) Remnants of ancient Australia in Vanuatu: Implications for crustal evolution in island arcs and tectonic development of the southwest Pacific. *Geology* **42**, 939–942. Available at: https://doi.org/10.1130/G36155.1.
- Carignan J., Machado N. and Gariepy C. (1993) Pb isotope composition of Ni-Cu-Pb ore deposits in an Archean greenstone belt: Evidence for Proterozoic remobilization in the Pontiac Subprovince of Canada. *Econ. Geol.* **88**, 709–715.

Available at: https://doi.org/10.2113/gsecongeo.88.3.709.

- Carignan J., Machado N. and Gariépy C. (1995) U-Pb isotopic geochemistry of komatiites and pyroxenes from the southern Abitibi greenstone belt, Canada. *Chem. Geol.* **126**, 17–27. Available at: https://doi.org/10.1016/0009-2541(95)00100-8.
- Caro G., Bourdon B., Birck J. L. and Moorbath S. (2006) High-precision ¹⁴²Nd/¹⁴⁴Nd measurements in terrestrial rocks: Constraints on the early differentiation of the Earth's mantle. *Geochim. Cosmochim. Acta* **70**, 164–191. Available at: https://doi.org/10.1016/j.gca.2005.08.015.
- Caruso S., Van Kranendonk M. J., Baumgartner R. J., Fiorentini M. L. and Forster M. A. (2021) The role of magmatic fluids in the ~3.48 Ga Dresser Caldera, Pilbara Craton: New insights from the geochemical investigation of hydrothermal alteration. *Precambrian Res.* 362, 106299. Available at: https://doi.org/10.1016/j.precamres.2021.106299.
- Castillo P. R. (2006) An overview of adakite petrogenesis. *Chinese Sci. Bull.* **51**, 257–268. Available at: https://doi.org/10.1007/s11434-006-0257-7.
- Chen J., Chen Y. J., Wiens D. A., Wei S. S., Zha Y., Julià J. and Cai C. (2019) Crustal and lithospheric structure of inactive volcanic arc terrains in Fiji. *Tectonophysics* **750**, 394–403. Available at: https://doi.org/10.1016/j.tecto.2018.07.014.
- Chen X., Zhou Y. and Shields G. A. (2022) Progress towards an improved Precambrian seawater ⁸⁷Sr/⁸⁶Sr curve. *Earth-Science Rev.* **224**, 103869. Available at: https://doi.org/10.1016/j.earscirev.2021.103869.
- Clemens J. D., Stevens G. and Mayne M. J. (2021) Do arc silicic magmas form by fluid-fluxed melting of older arc crust or fractionation of basaltic magmas? *Contrib. to Mineral. Petrol.* **176**, 1–28. Available at: https://doi.org/10.1007/s00410-021-01800-w.
- Clift P. D., Vannucchi P. and Morgan J. P. (2009) Crustal redistribution, crust-mantle recycling and Phanerozoic evolution of the continental crust. *Earth-Science Rev.* 97, 80–104. Available at: https://doi.org/10.1016/j.earscirev.2009.10.003.
- Cole W. S. (1960) Upper Eocene and Oligocene larger foraminifera from Viti Levu, Fiji. U.S. Geol. Surv. Prof. Pap., 1–7. Available at: https://doi.org/10.3133/pp374A.
- Coleman R. G. and Donato M. M. (1979) Oceanic plagiogranite revisited. In *Developments in Petrology*, Elsevier Scientific Publishing Company, pp. 149–168. Available at: https://doi.org/10.1016/B978-0-444-41765-7.50010-1.
- Coleman R. G. and Peterman Z. E. (1975) Oceanic Plagiogranite. J. Geophys. Res. 80, 1099–1108. Available at: https://doi.org/10.1029/JB080i008p01099.
- Colley H. and Greenbaum D. (1980) The mineral deposits and metallogenesis of the Fiji Platform. *Econ. Geol.* **75**, 807–829. Available at: https://doi.org/10.2113/gsecongeo.75.6.807.
- Colley H. and Hindle W. H. (1984) Volcano-tectonic evolution of Fiji and adjoining

marginal basins. *Geol. Soc. London, Spec. Publ.* **16**, 151–162. Available at: https://doi.org/10.1144/GSL.SP.1984.016.01.11.

- Collins W. J., Van Kranendonk M. J. and Teyssier C. (1998) Partial convective overturn of Archaean crust in the east Pilbara Craton, Western Australia: Driving mechanisms and tectonic implications. *J. Struct. Geol.* **20**, 1405–1424. Available at: https://doi.org/10.1016/S0191-8141(98)00073-X.
- Collins W. J., Murphy J. B., Johnson T. E. and Huang H. Q. (2020) Critical role of water in the formation of continental crust. *Nat. Geosci.* **13**, 331–338. Available at: https://doi.org/10.1038/s41561-020-0573-6.
- Condie K. C. (1981) Archaean greenstone belts. Elsevier B.V, Amsterdam. 434 pp.
- Condie K. C. (1998) Episodic continental growth and supercontinents: A mantle avalanche connection? *Earth Planet. Sci. Lett.* **163**, 97–108. Available at: https://doi.org/10.1016/S0012-821X(98)00178-2.
- Condie K. C. (2005) TTGs and adakites: are they both slab melts? *Lithos* **80**, 33–44. Available at: https://doi.org/10.1016/j.lithos.2003.11.001.
- Condie K. C. and Kröner A. (2013) The building blocks of continental crust: Evidence for a major change in the tectonic setting of continental growth at the end of the Archean. *Gondwana Res.* 23, 394–402. Available at: https://doi.org/10.1016/j.gr.2011.09.011.
- Condie K. C. and Shearer C. K. (2017) Tracking the evolution of mantle sources with incompatible element ratios in stagnant-lid and plate-tectonic planets. *Geochim. Cosmochim. Acta* **213**, 47–62. Available at: https://doi.org/10.1016/j.gca.2017.06.034.
- Coogan L. A., Banks G. J., Gillis K. M., MacLeod C. J. and Pearce J. A. (2003) Hidden melting signatures recorded in the Troodos ophiolite plutonic suite: evidence for widespread generation of depleted melts and intra-crustal melt aggregation. *Contrib. to Mineral. Petrol.* 144, 484–506. Available at: https://doi.org/10.1007/s00410-002-0413-2.
- Crawford W. C., Hildebrand J. A., Dorman L. M., Webb S. C. and Wiens D. A. (2003) Tonga Ridge and Lau Basin crustal structure from seismic refraction data. *J. Geophys. Res. Solid Earth* 108. Available at: https://doi.org/10.1029/2001JB001435.
- Crowe S. A., Døssing L. N., Beukes N. J., Bau M., Kruger S. J., Frei R. and Canfield D.
 E. (2013) Atmospheric oxygenation three billion years ago. *Nature* 501, 535–538.
 Available at: https://doi.org/10.1038/nature12426.
- Danyushevsky L. V., Falloon T. J., Crawford A. J., Tetroeva S. A., Leslie R. L. and Verbeeten A. (2008) High-Mg adakites from Kadavu Island Group, Fiji, southwest Pacific: Evidence for the mantle origin of adakite parental melts. *Geology* 36, 499– 502. Available at: https://doi.org/10.1130/G24349A.1.
- Davidson J., Turner S., Handley H., Macpherson C. and Dosseto A. (2007) Amphibole "sponge" in arc crust? *Geology* **35**, 787–790. Available at:

https://doi.org/10.1130/G23637A.1.

- Davidson J., Turner S. and Plank T. (2013) Dy/Dy*: Variations arising from mantle sources and petrogenetic processes. J. Petrol. 54, 525–537. Available at: https://doi.org/10.1093/petrology/egs076.
- Dawans J. M. and Swart P. K. (1988) Textural and geochemical alternations in Late Cenozoic Bahamian dolomites. *Sedimentology* **35**, 385–403. Available at: https://doi.org/10.1111/j.1365-3091.1988.tb00993.x.
- Defant M. J. and Drummond M. S. (1990) Derivation of some modern arc magmas by melting of young subducted lithosphere. *Nature* **347**, 662–665. Available at: https://doi.org/10.1038/347662a0.
- DePaolo D. J. (1981) Trace element and isotopic effects of combined wallrock assimilation and fractional crystallization. *Earth Planet. Sci. Lett.* **53**, 189–202. Available at: https://doi.org/10.1016/0012-821X(81)90153-9.
- DePaolo D. J. and Wasserburg G. J. (1976) Nd isotopic variations and petrogenetic models. *Geophys. Res. Lett.* **3**, 249–252. Available at: https://doi.org/10.1029/GL003i005p00249.
- Dhuime B., Hawkesworth C. J., Cawood P. A. and Storey C. D. (2012) A change in the geodynamics of continental growth 3 billion years ago. *Science* **335**, 1334–1336. Available at: https://doi.org/10.1126/science.1216066.
- Dhuime B., Hawkesworth C. J., Delavault H. and Cawood P. A. (2018) Rates of generation and destruction of the continental crust: implications for continental growth. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **376**. Available at: https://doi.org/10.1098/rsta.2017.0403.
- Dilek Y. and Furnes H. (2011) Ophiolite genesis and global tectonics: Geochemical and tectonic fingerprinting of ancient oceanic lithosphere. *Bull. Geol. Soc. Am.* **123**, 387–411. Available at: https://doi.org/10.1130/B30446.1.
- Dilek Y. and Furnes H. (2009) Structure and geochemistry of Tethyan ophiolites and their petrogenesis in subduction rollback systems. *Lithos* **113**, 1–20. Available at: https://doi.org/10.1016/j.lithos.2009.04.022.
- Dilek Y. and Thy P. (2009) Island arc tholeiite to boninitic melt evolution of the Cretaceous Kizildag (Turkey) ophiolite: Model for multi-stage early arc-forearc magmatism in Tethyan subduction factories. *Lithos* **113**, 68–87. Available at: https://doi.org/10.1016/j.lithos.2009.05.044.
- Dilles J. H., Kent A. J. R., Wooden J. L., Tosdal R. M., Koleszar A., Lee R. G. and Farmer L. P. (2015) Zircon compositional evidence for sulfur-degassing from oreforming arc magmas. *Econ. Geol.* **110**, 241–251. Available at: https://doi.org/10.2113/econgeo.110.1.241.
- Djokic T., VanKranendonk M. J., Campbel K. A., Walter M. R. and Ward C. R. (2017) Earliest signs of life on land preserved in ca. 3.5 Ga hot spring deposits. *Nat. Commun.* 8, 15263. Available at: https://doi.org/10.1038/ncomms15263.

Drewes E. K. (2011) Geochemistry and petrogenesis of the Colo Plutons: Viti Levu,

Fiji. Master thesis. University of California Santa Cruz.

- Drummond M. S. and Defant M. J. (1990) A model for trondhjemite-tonalite-dacite genesis and crustal growth via slab melting: Archean to modern comparisons. J. Geophys. Res. 95, 21503–21521. Available at: https://doi.org/10.1029/JB095iB13p21503.
- Duda J. P., Van Kranendonk M. J., Thiel V., Ionescu D., Strauss H., Schäfer N. and Reitner J. (2016) A rare glimpse of Paleoarchean life: Geobiology of an exceptionally preserved microbial mat facies from the 3.4 Ga Strelley Pool Formation, Western Australia. *PLoS One* **11**, 1–18. Available at: https://doi.org/10.1371/journal.pone.0147629.
- Dupré B. and Arndt N. T. (1990) Pb isotopic compositions of Archean komatiites and sulfides. *Chem. Geol.* **85**, 35–56. Available at: https://doi.org/10.1016/0009-2541(90)90122-N.
- Dupré B., Chauvel C. and Arndt N. T. (1984) Pb and Nd isotopic study of two archean komatiitic flows from Alexo, Ontario. *Geochim. Cosmochim. Acta* **48**, 1965–1972. Available at: https://doi.org/10.1016/0016-7037(84)90378-8.
- Elliott T. (2003) Tracers of the slab. *Insid. Subduction Fact.* **138**, 23–45. Available at: https://doi.org/10.1029/138GM03.
- Elliott T., Zindler A. and Bourdon B. (1999) Exploring the kappa conundrum: The role of recycling in the lead isotope evolution of the mantle. *Earth Planet. Sci. Lett.* 169, 129–145. Available at: https://doi.org/10.1016/S0012-821X(99)00077-1.
- Farquhar J., Bao H. and Thiemens M. (2000) Atmospheric influence of Earth's earliest sulfur cycle. *Science* 289, 756–758. Available at: https://doi.org/10.1126/science.289.5480.756.
- Faure F., Arndt N. T. and Libourel G. (2006) Formation of spinifex texture in komatiites: An experimental study. *J. Petrol.* **47**, 1591–1610. Available at: https://doi.org/10.1093/petrology/egl021.
- Flament N., Coltice N. and Rey P. F. (2013) The evolution of the ⁸⁷Sr/⁸⁶Sr of marine carbonates does not constrain continental growth. *Precambrian Res.* 229, 177–188. Available at: https://doi.org/10.1016/j.precamres.2011.10.009.
- Foley S. (2008) A trace element perspective on Archean crust formation and on the presence or absence of Archean subduction. *Geol. Soc. Am. Spec. Pap.* **440**, 31–50. Available at: https://doi.org/10.1130/2008.2440(02).
- Foley S. F., Tiepolo M. Y. and Vannucci R. (2002) Growth of early continental crust controlled by melting of amphibolite in subduction zones. *Nature* **417**, 837–840. Available at: https://doi.org/10.1038/nature00799.
- Frei R., Polat A. and Meibom A. (2004) The Hadean upper mantle conundrum: Evidence for source depletion and enrichment from Sm-Nd, Re-Os, and Pb isotopic compositions in 3.71 Gy boninite-like metabasalts from the Isua Supracrustal Belt, Greenland. *Geochim. Cosmochim. Acta* 68, 1645–1660. Available at: https://doi.org/10.1016/j.gca.2003.10.009.

- Frei R. and Rosing M. T. (2001) The least radiogenic terrestrial leads; implications for the early Archean crustal evolution and hydrothermal-metasomatic processes in the Isua Supracrustal Belt (West Greenland). *Chem. Geol.* 181, 47–66. Available at: https://doi.org/10.1016/S0009-2541(01)00263-7.
- Friend C. R. L. and Nutman A. P. (2005) New pieces to the Archaean terrane jigsaw puzzle in the Nuuk region, southern West Greenland: Steps in transforming a simple insight into a complex regional tectonothermal model. J. Geol. Soc. London. 162, 147–162. Available at: https://doi.org/10.1144/0016-764903-161.
- Froude D. O., Ireland T. R., Kinny P. D., Williams I. S., Compston W., Williams I. R. and Myers J. S. (1983) Ion microprobe identification of 4,100-4,200 Myr-old terrestrial zircons. *Nature* **304**, 616–618. Available at: https://doi.org/10.1038/304616a0.
- Furnes H. and Dilek Y. (2017) Geochemical characterization and petrogenesis of intermediate to silicic rocks in ophiolites: A global synthesis. *Earth-Science Rev.* 166, 1–37. Available at: https://doi.org/10.1016/j.earscirev.2017.01.001.
- Fyfe W. S. (1978) The evolution of the earth's crust: Modern plate tectonics to ancient hot spot tectonics? *Chem. Geol.* **23**, 89–114. Available at: https://doi.org/10.1016/0009-2541(78)90068-2.
- Galer S. J. G. and Goldstein S. L. (1991) Early mantle differentiation and its thermal consequences. *Geochim. Cosmochim. Acta* **55**, 227–239. Available at: https://doi.org/10.1016/0016-7037(91)90413-Y.
- Galer S. J. G. and O'Nions R. K. (1985) Residence time of thorium, uranium and lead in the mantle with implications for mantle convection. *Nature* **316**, 778–782. Available at: https://doi.org/10.1038/316778a0.
- Garbe-Schönberg C. (1993) Simultaneous determination of thirty-seven trace elements in twenty-eight international rock standards by ICP-MS. *Geostand. Newsl.* **17**, 81–97. Available at: https://doi.org/10.1111/j.1751-908x.1993.tb00122.x.
- Garde A. A. (2007) A mid-Archaean island arc complex in the eastern Akia terrane, Godthåbsfjord, southern West Greenland. *J. Geol. Soc. London.* **164**, 565–579. Available at: https://doi.org/10.1144/0016-76492005-107.
- Garde A. A. (1997) Accretion and evolution of an Archaean high-grade grey gneissamphibolite complex: the Fiskefjord area, southern West Greenland. In *Geology of Greenland Survey Bulletin* Available at: https://doi.org/10.34194/ggub.v179.5075.
- Garde A. A. (1990) Thermal granulite-facies metamorphism with diffuse retrogression in Archaean orthogneisses, Fiskefjord, southern West Greenland. J. Metamorph. Geol. 8, 663–682. Available at: https://doi.org/10.1111/j.1525-1314.1990.tb00494.x.
- Garde A. A., Dyck B., Esbensen K. H., Johansson L. and Möller C. (2014) The Finnefjeld domain, Maniitsoq structure, West Greenland: Differential rheological features and mechanical homogenisation in response to impacting? *Precambrian Res.* 255, 791–808. Available at: https://doi.org/10.1016/j.precamres.2014.06.022.

- Garde A. A., Friend C. R. L., Nutman A. P. and Marker M. (2000) Rapid maturation and stabilisation of middle Archaean continental crust: The Akia terrane, southern West Greenland. *Bull. Geol. Soc. Denmark* **47**, 1–27. Available at: https://doi.org/10.37570/bgsd-2000-47-01.
- Gardiner N. J., Hickman A. H., Kirkland C. L., Lu Y., Johnson T. and Zhao J. X. (2017) Processes of crust formation in the early Earth imaged through Hf isotopes from the East Pilbara Terrane. *Precambrian Res.* 297, 56–76. Available at: https://doi.org/10.1016/j.precamres.2017.05.004.
- Gardiner N. J., Kirkland C. L., Hollis J., Szilas K., Steenfelt A., Yakymchuk C. and Heide-Jørgensen H. (2019) Building Mesoarchaean crust upon Eoarchaean roots: the Akia Terrane, West Greenland. *Contrib. to Mineral. Petrol.* **174**, 1–19. Available at: https://doi.org/10.1007/s00410-019-1554-x.
- Gariépy C. and Allègre C. J. (1985) The lead isotope geochemistry and geochronology of late-kinematic intrusives from the Abitibi greenstone belt, and the implications for late Archaean crustal evolution. *Geochim. Cosmochim. Acta* **49**, 2371–2383. Available at: https://doi.org/10.1016/0016-7037(85)90237-6.
- Gill J. B. (1987) Early geochemical evolution of an oceanic island arc and backarc: Fiji and the South Fiji Basin. *J. Geol.* **95**, 589–615. Available at: https://doi.org/10.1086/629158.
- Gill J. B. (1970) Geochemistry of Viti Levu, Fiji, and its evolution as an island arc. *Contrib. to Mineral. Petrol.* **27**, 179–203. Available at: https://doi.org/10.1007/BF00385777.
- Gill J. B. (1981) Orogenic Andesites and Plate Tectonics., Springer Verlag. Available at: https://doi.org/10.1007/978-3-642-68012-0.
- Gill J. B. and Stork A. L. (1979) Miocene low-K dacites and trondhjemites of Fiji. *Dev. Petrol.* **6**, 629–649. Available at: https://doi.org/10.1016/B978-0-444-41765-7.50027-7.
- Gill J. B. and Whelan P. (1989) Early rifting of an oceanic island arc (Fiji) produced shoshonitic to tholeiitic basalts. *J. Geophys. Res.* **94**, 4561–4578. Available at: https://doi.org/10.1029/JB094iB04p04561.
- Gill R. C. O. (1979) Comparative petrogenesis of Archaean and modern low-K tholeiites. A critical review of some geochemical aspects. *Phys. Chem. Earth* **11**, 431–447. Available at: https://doi.org/10.1016/0079-1946(79)90042-9.
- Gillis K. M. and Coogan L. A. (2002) Anatectic migmatites from the roof of an ocean ridge magma chamber. *J. Petrol.* **43**, 2075–2095. Available at: https://doi.org/10.1093/petrology/43.11.2075.
- Glikson M., Duck L. J., Golding S. D., Hofmann A., Bolhar R., Webb R., Baiano J. C. F. and Sly L. I. (2008) Microbial remains in some earliest Earth rocks: Comparison with a potential modern analogue. *Precambrian Res.* 164, 187–200. Available at: https://doi.org/10.1016/j.precamres.2008.05.002.

Green D. H. (1975) Genesis of Archean peridotitic magmas and constraints on Archean

geothermal gradients and tectonics. *Geology* **3**, 15–18. Available at: https://doi.org/10.1130/0091-7613(1975)3<15:GOAPMA>2.0.CO;2.

Green D. H. (1981) Petrogenesis of Archaean ultramafic magmas and implications for Archaean tectonics. *Dev. Precambrian Geol.* **4**, 469–489. Available at: https://doi.org/10.1016/S0166-2635(08)70024-0.

Greer J., Zhang B., Isheim D., Seidman D. N., Bouvier A. and Heck P. R. (2023)
4.46 Ga zircons anchor chronology of lunar magma ocean. *Geochemical Perspect. Lett.* 27, 49–53. Available at: https://doi.org/10.1016/0016-7037(69)90092-1.

- Gruau G., Jahn B. M., Glikson A. Y., Davy R., Hickman A. H. and Chauvel C. (1987) Age of the Archean Talga-Talga Subgroup, Pilbara Block, Western Australia, and early evolution of the mantle: new Sm-Nd isotopic evidence. *Earth Planet. Sci. Lett.* 85, 105–116. Available at: https://doi.org/10.1016/0012-821X(87)90025-2.
- Hamilton P. J., O'Nions R. K., Bridgwater D. and Nutman A. (1983) Sm-Nd studies of Archaean metasediments and metavolcanics from West Greenland and their implications for the Earth's early history. *Earth Planet. Sci. Lett.* 62, 263–272. Available at: https://doi.org/10.1016/0012-821X(83)90089-4.
- Haraguchi S., Kimura J.-I., Senda R., Fujinaga K., Nakamura K., Takaya Y. and Ishii T. (2017) Origin of felsic volcanism in the Izu arc intra-arc rift. *Contrib. to Mineral. Petrol.* **172**, 0. Available at: https://doi.org/10.1007/s00410-017-1345-1.
- Harris A. C., White N. C., Jocelyn M., Bull S. W., Line M. A., Robert S., Mernagh T. P. and Tosdal R. M. (2009) Early Archean hot springs above epithermal veins, North Pole, Western Australia: New insights from fluid inclusion microanalysis. *Econ. Geol.* 104, 793–814. Available at: https://doi.org/10.2113/gsecongeo.104.6.793.
- Harrison T. M., Blichert-Toft J., Müller W., Albarede F., Holden P. and Mojzsis S. J. (2005) Heterogeneous Hadean hafnium: Evidence of continental crust at 4.4 to 4.5 Ga. *Science* **310**, 1947–1950. Available at: https://doi.org/10.1126/science.1117926.
- Hart S. R. and Brooks C. (1977) The geochemistry and evolution of early Precambrian mantle. *Contrib. to Mineral. Petrol.* **61**, 109–128. Available at: https://doi.org/10.1007/BF00374362.
- Hart S. R., Brooks C., Krogh T. E., Davis G. L. and Nava D. (1970) Ancient and modern volcanic rocks: A trace element model. *Earth Planet. Sci. Lett.* **10**, 17–28. Available at: https://doi.org/10.1016/0012-821X(70)90060-9.
- Hart S. R. and Gaetani G. A. (2006) Mantle Pb paradoxes: The sulfide solution. *Contrib. to Mineral. Petrol.* **152**, 295–308. Available at: https://doi.org/10.1007/s00410-006-0108-1.
- Hart S. R., Hauri E. H., Oschmann L. A. and Whitehead J. A. (1992) Mantle plumes and entrainment: Isotopic evidence. *Science* **256**, 517–520. Available at: https://doi.org/10.1126/science.256.5056.517.
- Hartnady M. I. H., Kirkland C. L., Smithies R. H., Johnson S. P. and Johnson T. E. (2022) Pb isotope insight into the formation of the Earth's first stable continents.

Earth Planet. Sci. Lett. **578**, 117319. Available at: https://doi.org/10.1016/j.epsl.2021.117319.

- Hasenstab-Dübeler E., Tusch J., Hoffmann J. E., Fischer-Gödde M., Szilas K. and Münker C. (2022) Temporal evolution of ¹⁴²Nd signatures in SW Greenland from high precision MC-ICP-MS measurements. *Chem. Geol.* 614. Available at: https://doi.org/10.1016/j.chemgeo.2022.121141.
- Hasenstab E., Tusch J., Schnabel C., Marien C. S., Van Kranendonk M. J., Smithies R. H., Howard H., Maier W. D. and Münker C. (2021) Evolution of the early to late Archean mantle from Hf-Nd-Ce isotope systematics in basalts and komatiites from the Pilbara Craton. *Earth Planet. Sci. Lett.* 553. Available at: https://doi.org/10.1016/j.epsl.2020.116627.
- Hastie A. R., Fitton J. G., Bromiley G. D., Butler I. B. and Odling N. W. A. (2016) The origin of Earth's first continents and the onset of plate tectonics. *Geology* **44**, 855–858. Available at: https://doi.org/10.1130/G38226.1.
- Hastie A. R., Fitton J. G., Mitchell S. F., Neill I., M. Nowell G. and Millar I. L. (2015) Can fractional crystallization, mixing and assimilation processes be responsible for Jamaican-type adakites? Implications for generating Eoarchaean continental crust. *J. Petrol.* 56, 1251–1284. Available at: https://doi.org/10.1093/petrology/egv029.
- Hathway B. (1994) Sedimentation and volcanism in an Oligocene-Miocene intraoceanic arc and fore-arc, southwestern Viti Levu, Fiji. *J. Geol. Soc. London.* **151**, 499–514. Available at: https://doi.org/10.1144/gsjgs.151.3.0499.
- Hathway B. (1993) The Nadi Basin: Neogene strike-slip faulting and sedimentation in a fragmented arc, western Viti Levu, Fiji. *J. Geol. Soc. London.* **150**, 563–581. Available at: https://doi.org/10.1144/gsjgs.150.3.0563.
- Hathway B. and Colley H. (1994) Eocene to Miocene Geology of Southwest Viti Levu, Fiji. SOPAC Tech. Bull. Geol. Submar. Resour. Tonga-Lau Reg. 8, 153-169.
- Hawkesworth C. J., Dhuime B., Pietranik A. B., Cawood P. A., Kemp A. I. S. and Storey C. D. (2010) The generation and evolution of the continental crust. *J. Geol. Soc. London.* 167, 229–248. Available at: https://doi.org/10.1144/0016-76492009-072.
- Hawkesworth C. J., Gallagher K., Hergt J. M. and McDermott F. (1993) Mantle and slab contributions in arc magmas. *Annu. Rev. Earth Planet. Sci.* **21**, 175–204. Available at: https://doi.org/10.1146/annurev.ea.21.050193.001135.
- Hawkesworth C. J. and Kemp A. I. S. (2006) The differentiation and rates of generation of the continental crust. *Chem. Geol.* **226**, 134–143. Available at: https://doi.org/10.1016/j.chemgeo.2005.09.017.
- Hawkesworth C. J., Mantovani M. S. M., Taylor P. N. and Palacz Z. (1986) Evidence from the Prana of south Brazil for a continental contribution to the Dupal basalts. *Nature* **322**, 356–359. Available at: https://doi.org/10.1038/322356a0.
- Hawkesworth C. J., Norry M. J., Roddick J. C., Baker P. E., Francis P. W. and Thorpe R. S. (1979) ¹⁴³Nd/¹⁴⁴Nd, ⁸⁷Sr/⁸⁶Sr, and incompatible element variations in calc-

alkaline andesites and plateau lavas from South America. *Earth Planet. Sci. Lett.* **42**, 45–57. Available at: https://doi.org/10.1016/0012-821X(79)90189-4.

- Herwartz D., Pack A. and Nagel T. J. (2021) A CO₂ greenhouse efficiently warmed the early Earth and decreased seawater ¹⁸O/¹⁶O before the onset of plate tectonics. *Proc. Natl. Acad. Sci. U. S. A.* **118**. Available at: https://doi.org/10.1073/pnas.2023617118.
- Herzberg C., Condie K. and Korenaga J. (2010) Thermal history of the Earth and its petrological expression. *Earth Planet. Sci. Lett.* **292**, 79–88. Available at: https://doi.org/10.1016/j.epsl.2010.01.022.
- Herzer R. H., Barker D. H. N., Roest W. R. and Mortimer N. (2011) Oligocene-Miocene spreading history of the northern South Fiji Basin and implications for the evolution of the New Zealand plate boundary. *Geochemistry, Geophys. Geosystems* 12, 1–20. Available at: https://doi.org/10.1029/2010GC003291.
- Heywood L. J., DeBari S. M., Gill J. B., Straub S. M., Schindlbeck-Belo J. C., Escobar-Burciaga R. D. and Woodhead J. (2020) Across-arc diversity in rhyolites from an intra-oceanic arc: Evidence from IODP Site U1437, Izu-Bonin Rear Arc, and surrounding Area. *Geochemistry, Geophys. Geosystems* 21, 1–24. Available at: https://doi.org/10.1029/2019GC008353.
- Hickman A. H. (1977) New and revised definitions of rock units in the Warrawoona Group, Pilbara Block. *Dep. Mines Annu. Rep. 1976* **58**, 97.
- Hickman A. H. (2008) Regional review of the 3426–3350 Ma Strelley Pool Formation, Pilbara Craton, Western Australia. *Geol. Surv. West. Aust. Rec.* **15**, 1–27.
- Hickman A. H. (2012) Review of the Pilbara Craton and Fortescue Basin, Western Australia: Crustal evolution providing environments for early life. *Isl. Arc* **21**, 1–31. Available at: https://doi.org/10.1111/j.1440-1738.2011.00783.x.
- Hildreth W. and Moorbath S. (1988) Crustal contributions to arc magmatism in the Andes of Central Chile. *Contrib. to Mineral. Petrol.* **98**, 455–489. Available at: https://doi.org/10.1007/BF00372365.
- Hoffmann J. E., Münker C., Næraa T., Rosing M. T., Herwartz D., Garbe-Schönberg C.-D. and Svahnberg H. (2011) Mechanisms of Archean crust formation inferred from high-precision HFSE systematics in TTGs. *Geochim. Cosmochim. Acta* 75, 4157–4178. Available at: https://doi.org/10.1016/j.gca.2011.04.027.
- Hoffmann J. E., Münker C., Polat A., König S., Mezger K. and Rosing M. T. (2010) Highly depleted Hadean mantle reservoirs in the sources of early Archean arc-like rocks, Isua supracrustal belt, southern West Greenland. *Geochim. Cosmochim. Acta* 74, 7236–7260. Available at: https://doi.org/10.1016/j.gca.2010.09.027.
- Hoffmann J. E., Münker C., Polat A., Rosing M. T. and Schulz T. (2011) The origin of decoupled Hf-Nd isotope compositions in Eoarchean rocks from southern West Greenland. *Geochim. Cosmochim. Acta* 75, 6610–6628. Available at: https://doi.org/10.1016/j.gca.2011.08.018.

Hoffmann J. E., Nagel T. J., Münker C., Næraa T. and Rosing M. T. (2014)

Constraining the process of Eoarchean TTG formation in the Itsaq Gneiss Complex, southern West Greenland. *Earth Planet. Sci. Lett.* **388**, 374–386. Available at: https://doi.org/10.1016/j.epsl.2013.11.050.

- Hoffmann J. E., Zhang C., Moyen J. and Nagel T. J. (2019) The formation of tonalites– trondjhemite–granodiorites in early continental crust. In *Earth's Oldest Rocks* Elsevier B.V., pp. 133–168. Available at: https://doi.org/10.1016/b978-0-444-63901-1.00007-1.
- Hofmann A. W. (1988) Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. *Earth Planet. Sci. Lett.* **90**, 297–314. Available at: https://doi.org/10.1016/0012-821X(88)90132-X.
- Hofmann A. W. (2003) 2.03 Sampling mantle heterogeneity through oceanic basalts: Isotopes and trace elements. *Treatise on Geochemistry*, Elsevier Ltd., pp. 1–44. Available at: https://doi.org/10.1016/B0-08-043751-6/02123-X.
- Hofmann A. W. (2013) 3.3 Sampling mantle heterogeneity through oceanic basalts: Isotopes and trace elements. *Treatise in Geochemistry: Second Edition*, Elsevier Ltd., pp. 67-101. Available at: https://doi.org/10.1016/B978-0-08-095975-7.00203-5.
- Hofmann A. W. (2008) The enduring lead paradox. *Nat. Geosci.* **1**, 812–815. Available at: https://doi.org/10.1038/ngeo372.
- Hofmann A. W. and White W. M. (1982) Mantle plumes from ancient oceanic crust. *Earth Planet. Sci. Lett.* **57**, 421–436. Available at: https://doi.org/10.1016/0012-821X(82)90161-3.
- Hofmann H. J., Grey K., Hickman A. H. and Thorpe R. I. (1999) Origin of 3.45 Ga coniform stromatolites in Warrawoona Group, Western Australia. *Bull. Geol. Soc. Am.* 111, 1256–1262. Available at: https://doi.org/10.1130/0016-7606(1999)111<1256:OOGCSI>2.3.CO;2.
- Holland H. D. (2002) Volcanic gases, black smokers, and the great oxidation event. *Geochim. Cosmochim. Acta* **66**, 3811–3826. Available at: https://doi.org/10.1016/S0016-7037(02)00950-X.
- Holmes A. (1947) An estimate of the age of the Earth. *Nature* **157**, 680–684. Available at: https://doi.org/10.1038/157680a0.
- Iizuka T., Campbell I. H., Allen C. M., Gill J. B., Maruyama S. and Makoka F. (2013) Evolution of the African continental crust as recorded by U-Pb, Lu-Hf and O isotopes in detrital zircons from modern rivers. *Geochim. Cosmochim. Acta* 107, 96–120. Available at: https://doi.org/10.1016/j.gca.2012.12.028.
- Israel C., Boyet M., Doucelance R., Bonnand P., Dhuime B., Ionov D., Moreira H., Jackson M. G. and Golovin A. V. (2023) First Ce-Nd isotope measurements of middle and lower continental crust samples support massive lower crust recycling over Earth's history. *Lithos* 460–461, 107369. Available at: https://doi.org/10.1016/j.lithos.2023.107369.

Israel C., Boyet M., Doucelance R., Bonnand P., Frossard P., Auclair D. and Bouvier A.

(2020) Formation of the Ce-Nd mantle array: Crustal extraction vs. recycling by subduction. *Earth Planet. Sci. Lett.* **530**, 115941. Available at: https://doi.org/10.1016/j.epsl.2019.115941.

- Jaffey A. H., Flynn K. F., Glendenin L. E., Bentley W. C. and Essling A. M. (1971) Precision measurement of half-lives and specific activities of ²³⁵U and ²³⁸U. *Phys. Rev. C* 4, 1889–1906. Available at: https://doi.org/10.1103/PhysRevC.4.1889.
- Jagoutz O. (2013) Were ancient granitoid compositions influenced by contemporaneous atmospheric and hydrosphere oxidation states? *Terra Nov.* **25**, 95–101. Available at: https://doi.org/10.1111/ter.12010.
- Jahn B. M., Glikson A. Y., Peucat J. J. and Hickman A. H. (1981) REE geochemistry and isotopic data of Archean silicic volcanics and granitoids from the Pilbara Block, Western Australia: implications for the early crustal evolution. *Geochim. Cosmochim. Acta* 45, 1633–1652. Available at: https://doi.org/10.1016/S0016-7037(81)80002-6.
- Jakeš P. and Gill J. (1970) Rare earth elements and the island arc tholeiitic series. *Earth Planet. Sci. Lett.* **9**, 17–28. Available at: https://doi.org/10.1016/0012-821X(70)90018-X.
- Janiszewski H. A., Abers G. A., Shillington D. J. and Calkins J. A. (2013) Crustal structure along the Aleutian island arc: New insights from receiver functions constrained by active-source data. *Geochemistry, Geophys. Geosystems* 14, 2977– 2992. Available at: https://doi.org/10.1002/ggge.20211.
- John T., Schenk V., Haase K., Scherer E. and Tembo F. (2003) Evidence for a Neoproterozoic ocean in south-central Africa from mid-ocean-ridge-type geochemical signatures and pressure-temperature estimates of Zambian eclogites. *Geology* **31**, 243–246. Available at: https://doi.org/10.1130/0091-7613(2003)031<0243:EFANOI>2.0.CO;2.
- Johnson C. M., Zheng X. Y., Djokic T., Van Kranendonk M. J., Czaja A. D., Roden E. E. and Beard B. L. (2022) Early Archean biogeochemical iron cycling and nutrient availability: New insights from a 3.5 Ga land-sea transition. *Earth-Science Rev.* 228. Available at: https://doi.org/10.1016/j.earscirev.2022.103992.
- Johnson K. T. M., Dick H. J. B. and Shimizu N. (1990) Melting in the oceanic upper mantle: An Ion Microprobe study of diopsides in abyssal peridotites. J. Geophys. Res. 95, 2661–2678. Available at: https://doi.org/10.1029/JB095iB03p02661.
- Johnson T. E., Brown M., Gardiner N. J., Kirkland C. L. and Smithies R. H. (2017) Earth's first stable continents did not form by subduction. *Nature* **543**, 239–242. Available at: https://doi.org/10.1038/nature21383.
- Johnson T. E., Brown M., Kaus B. J. P. and Vantongeren J. A. (2014) Delamination and recycling of Archaean crust caused by gravitational instabilities. *Nat. Geosci.* **7**, 47–52. Available at: https://doi.org/10.1038/ngeo2019.
- Kamber B. S. (2007) The enigma of the terrestrial protocrust: Evidence for its former existence and the importance of its complete disappearance. *Dev. Precambrian Geol.* 15, 75–89. Available at: https://doi.org/10.1016/S0166-2635(07)15024-6.

- Kamber B. S., Bolhar R. and Webb G. E. (2004) Geochemistry of late Archaean stromatolites from Zimbabwe: Evidence for microbial life in restricted epicontinental seas. *Precambrian Res.* **132**, 379–399. Available at: https://doi.org/10.1016/j.precamres.2004.03.006.
- Kamber B. S., Collerson K. D., Moorbath S. and Whitehouse M. J. (2003) Inheritance of early Archaean Pb-isotope variability from long-lived Hadean protocrust. *Contrib. to Mineral. Petrol.* 145, 25–46. Available at: https://doi.org/10.1007/s00410-002-0429-7.
- Kamber B. S. and Webb G. E. (2001) The geochemistry of late Archaean microbial carbonate: Implications for ocean chemistry and continental erosion history. *Geochim. Cosmochim. Acta* 65, 2509–2525. Available at: https://doi.org/10.1016/S0016-7037(01)00613-5.
- Kamber B. S., Whitehouse M. J., Bolhar R. and Moorbath S. (2005) Volcanic resurfacing and the early terrestrial crust: Zircon U-Pb and REE constraints from the Isua Greenstone Belt, southern West Greenland. *Earth Planet. Sci. Lett.* 240, 276–290. Available at: https://doi.org/10.1016/j.epsl.2005.09.037.
- Kanzaki Y. and Bindeman I. N. (2022) A possibility of ¹⁸O-depleted oceans in the Precambrian inferred from triple oxygen isotope of shales and oceanic crust. *Chem. Geol.* **604**. Available at: https://doi.org/10.1016/j.chemgeo.2022.120944.
- Kasting J. F. (1987) Theoretical constraints on oxygen and carbon dioxide concentrations in the Precambrian atmosphere. *Precambrian Res.* **34**, 205–229. Available at: https://doi.org/10.1016/0301-9268(87)90001-5.
- Kawate S. and Arima M. (1998) Petrogenesis of the Tanzawa plutonic complex, central Japan: Exposed felsic middle crust of the Izu-Bonin-Mariana arc. *Isl. Arc* **7**, 342–358. Available at: https://doi.org/10.1111/j.1440-1738.1998.00194.x.
- Kay S. M., Jicha B. R., Citron G. L., Kay R. W., Tibbetts A. K. and Rivera T. A. (2019) The calc-alkaline Hidden Bay and Kagalaska plutons and the construction of the Central Aleutian oceanic arc crust. *J. Petrol.* **60**, 393–439. Available at: https://doi.org/10.1093/petrology/egy119.
- Kay S. M., Kay R. W., Citron G. P. and Perfit M. R. (1990) Calc-alkaline plutonism in the intra-oceanic Aleutian arc, Alaska. In *Special Paper of the Geological Society of America*, pp. 233–255. Available at: https://doi.org/10.1130/SPE241-p233.
- Kemp A. I. S., Hickman A. H., Kirkland C. L. and Vervoort J. D. (2015) Hf isotopes in detrital and inherited zircons of the Pilbara Craton provide no evidence for Hadean continents. *Precambrian Res.* 261, 112–126. Available at: https://doi.org/10.1016/j.precamres.2015.02.011.
- Kemp A. I. S., Wilde S. A., Hawkesworth C. J., Coath C. D., Nemchin A., Pidgeon R. T., Vervoort J. D. and DuFrane S. A. (2010) Hadean crustal evolution revisited: New constraints from Pb-Hf isotope systematics of the Jack Hills zircons. *Earth Planet. Sci. Lett.* **296**, 45–56. Available at: https://doi.org/10.1016/j.epsl.2010.04.043.

Khanna T. C., Bizimis M., Yogodzinski G. M. and Mallick S. (2014) Hafnium-

neodymium isotope systematics of the 2.7 Ga Gadwal greenstone terrane, Eastern Dharwar craton, India: Implications for the evolution of the Archean depleted mantle. *Geochim. Cosmochim. Acta* **127**, 10–24. Available at: https://doi.org/10.1016/j.gca.2013.11.024.

- Kirchenbaur M., Münker C., Schuth S., Garbe-Schönberg D. and Marchev P. (2012) Tectonomagmatic constraints on the sources of Eastern Mediterranean K-rich lavas. J. Petrol. 53, 27–65. Available at: https://doi.org/10.1093/petrology/egr055.
- Kirkland C. L., Yakymchuk C., Hollis J., Heide-Jørgensen H. and Danišík M. (2018) Mesoarchean exhumation of the Akia terrane and a common Neoarchean tectonothermal history for West Greenland. *Precambrian Res.* **314**, 129–144. Available at: https://doi.org/10.1016/j.precamres.2018.06.004.
- Klein C. (2005) Some Precambrian banded iron-formations (BIFs) from around the world: Their age, geologic setting, mineralogy, metamorphism, geochemistry, and origin. Am. Mineral. 90, 1473–1499. Available at: https://doi.org/10.2138/am.2005.1871.
- Klein C. and Beukes N. J. (1989) Geochemistry and sedimentology of a facies transition from limestone to iron-formation deposition in the Early Proterozoic Transvaal Supergroup, South Africa. *Econ. Geol.* 84, 1733–1774. Available at: https://doi.org/10.2113/gsecongeo.84.7.1733.
- Kleine T., Münker C., Mezger K. and Palme H. (2002) Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf-W chronometry. *Nature* 418, 952–955. Available at: https://doi.org/10.1038/nature00982.
- Kleinhanns I. C., Kramers J. D. and Kamber B. S. (2003) Importance of water for Archaean granitoid petrology: A comparative study of TTG and potassic granitoids from Barberton Mountain Land, South Africa. *Contrib. to Mineral. Petrol.* 145, 377–389. Available at: https://doi.org/10.1007/s00410-003-0459-9.
- Klemme S., Günther D., Hametner K., Prowatke S. and Zack T. (2006) The partitioning of trace elements between ilmenite, ulvospinel, armalcolite and silicate melts with implications for the early differentiation of the moon. *Chem. Geol.* 234, 251–263. Available at: https://doi.org/10.1016/j.chemgeo.2006.05.005.
- Knaack, C. M., Cornelius, S., Hooper P. R. (1994) Trace element analysis of rocks and minerals by ICP–MS: Washington State University. *GeoAnalytical Lab Washingt. State Univ.*
- Kodaira S., Sato T., Takahashi N., Miura S., Tamura T., Tatsumi Y. and Kaneda Y. (2007) New seismological constraints on growth of continental crust in the Izu-Bonin intra-oceanic arc. *Geology* **35**, 1031–1034. Available at: https://doi.org/10.1130/G23901A.1.
- Koeberl C. (2003) The late heavy bombardment in the inner solar system: Is there any connection to Kuiper belt objects? *Earth, Moon Planets* **92**, 79–87. Available at: https://doi.org/10.1023/B:MOON.0000031927.85937.9e.
- Koepke J., Berndt J., Feig S. T. and Holtz F. (2007) The formation of SiO₂-rich melts within the deep oceanic crust by hydrous partial melting of gabbros. *Contrib. to*

Mineral. Petrol. **153**, 67–84. Available at: https://doi.org/10.1007/s00410-006-0135-y.

- Koepke J., Feig S. T., Snow J. and Freise M. (2004) Petrogenesis of oceanic plagiogranites by partial melting of gabbros: an experimental study. *Contrib. to Mineral. Petrol.* 146, 414–432. Available at: https://doi.org/10.1007/s00410-003-0511-9.
- König S., Münker C., Schuth S. and Garbe-Schönberg D. (2008) Mobility of tungsten in subduction zones. *Earth Planet. Sci. Lett.* **274**, 82–92. Available at: https://doi.org/10.1016/j.epsl.2008.07.002.
- König S., Münker C., Schuth S., Luguet A., Hoffmann J. E. and Kuduon J. (2010) Boninites as windows into trace element mobility in subduction zones. *Geochim. Cosmochim. Acta* 74, 684–704. Available at: https://doi.org/10.1016/j.gca.2009.10.011.
- Korkisch J. and Hazan I. (1965) Anion exchange separations in hydrobromic acidorganic solvent media. *Anal. Chem.* **37**, 707–710. Available at: https://doi.org/10.1021/ac60225a020.
- Kramers J. D. and Tolstikhin I. N. (1997) Two terrestrial lead isotope paradoxes, forward transport modelling, core formation and the history of the continental crust. *Chem. Geol.* **139**, 75–110. Available at: https://doi.org/10.1016/S0009-2541(97)00027-2.
- Laurent O., Björnsen J., Wotzlaw J. F., Bretscher S., Pimenta Silva M., Moyen J. F., Ulmer P. and Bachmann O. (2020) Earth's earliest granitoids are crystal-rich magma reservoirs tapped by silicic eruptions. *Nat. Geosci.* **13**, 163–169. Available at: https://doi.org/10.1038/s41561-019-0520-6.
- Laurent O., Martin H., Moyen J. F. and Doucelance R. (2014) The diversity and evolution of late-Archean granitoids: Evidence for the onset of "modern-style" plate tectonics between 3.0 and 2.5 Ga. *Lithos* **205**, 208–235. Available at: https://doi.org/10.1016/j.lithos.2014.06.012.
- Laverne C. (1993) Occurrence of siderite and ankerite in young basalts from the Galápagos Spreading Center (DSDP Holes 506G and 507B). *Chem. Geol.* **106**, 27–46. Available at: https://doi.org/10.1016/0009-2541(93)90164-E.
- Lee C. T. A. and Bachmann O. (2014) How important is the role of crystal fractionation in making intermediate magmas? Insights from Zr and P systematics. *Earth Planet. Sci. Lett.* **393**, 266–274. Available at: https://doi.org/10.1016/j.epsl.2014.02.044.
- Lindsay J. F., Brasier M. D., McLoughlin N., Green O. R., Fogel M., Steele A. and Mertzman S. A. (2005) The problem of deep carbon - An Archean paradox. *Precambrian Res.* 143, 1–22. Available at: https://doi.org/10.1016/j.precamres.2005.09.003.
- van de Löcht J. (2019) Geochemistry and petroglogy of ~3.8 Ga mafic ultramafic enclaves in the Itsaq Gneiss Complex , SW Greenland. PhD-thesis, University of Cologne, Germany.

- van de Löcht J., Hoffmann J. E., Rosing M. T., Sprung P. and Münker C. (2020)
 Preservation of Eoarchean mantle processes in ~3.8 Ga peridotite enclaves in the Itsaq Gneiss Complex, southern West Greenland. *Geochim. Cosmochim. Acta* 280, 1–25. Available at: https://doi.org/10.1016/j.gca.2020.03.043.
- Lugmair G. W. and Marti K. (1978) Lunar initial ¹⁴³Nd/¹⁴⁴Nd: Differential evolution of the lunar crust and mantle. *Earth Planet. Sci. Lett.* **39**, 349–357. Available at: https://doi.org/10.1016/0012-821X(78)90021-3.
- Luo X., Rehkämper M., Lee D. C. and Halliday A. N. (1997) High precision ²³⁰Th/²³²Th and ²³⁴U/²³⁸U measurements using energy-filtered ICP magnetic sector multiple collector mass spectrometry. *Int. J. Mass Spectrom. Ion Process.* **171**, 105–117. Available at: https://doi.org/10.1016/S0168-1176(97)00136-5.
- Lyons T. W., Reinhard C. T. and Planavsky N. J. (2014) The rise of oxygen in Earth's early ocean and atmosphere. *Nature* **506**, 307–315. Available at: https://doi.org/10.1038/nature13068.
- Machado N., Brooks C. and Hart S. R. (1986) Determination of initial ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd in primary minerals from mafic and ultramafic rocks: Experimental procedure and implications for the isotopic characteristics of the Archean mantle under the Abitibi greenstone belt, Canada. *Geochim. Cosmochim. Acta* **50**, 2335–2348. Available at: <u>https://doi.org/10.1016/0016-7037(86)90086-4</u>.
- Makishima A. and Nakamura E. (1991) Precise measurement of cerium isotope composition in rock samples. *Chem. Geol.* **94**, 1–11. Available at: https://doi.org/10.1016/S0009-2541(10)80012-9.
- Makishima A., Nakamura E., Akimoto S.-i., Campbell I. H. and Hill R. I. (1993) New constraints on the ¹³⁸La β -decay constant based on a geochronological study of granites from the Yilgarn Block, Western Australia. *Chem. Geol.* **104**, 293–300. Available at: https://doi.org/10.1016/0009-2541(93)90158-F.
- Maltese A. and Mezger K. (2020) The Pb isotope evolution of Bulk Silicate Earth: Constraints from its accretion and early differentiation history. *Geochim. Cosmochim. Acta* 271, 179–193. Available at: https://doi.org/10.1016/j.gca.2019.12.021.
- Marien C. S., Hoffmann J. E., Garbe-Schönberg C. D. and Münker C. (2019) Petrogenesis of plagiogranites from the Troodos Ophiolite Complex, Cyprus. *Contrib. to Mineral. Petrol.* **174**, 1–24. Available at: https://doi.org/10.1007/s00410-019-1569-3.
- Martin A. K. (2013) Double-saloon-door tectonics in the North Fiji Basin. *Earth Planet. Sci. Lett.* **374**, 191–203. Available at: https://doi.org/10.1016/j.epsl.2013.05.041.
- Martin H. (1986) Effect of steeper Archean geothermal gradient on geochemistry of subduction-zone magmas. *Geology* **14**, 753–756. Available at: https://doi.org/10.1130/0091-7613(1986)14<753:EOSAGG>2.0.CO;2.
- Martin H. (1993) The mechanisms of petrogenesis of the Archaean continental crust-Comparison with modern processes. *Lithos* **30**, 373–388. Available at: https://doi.org/10.1016/0024-4937(93)90046-F.

- Martin H., Moyen J. F., Guitreau M., Blichert-Toft J. and Le Pennec J. L. (2014) Why Archaean TTG cannot be generated by MORB melting in subduction zones. *Lithos* **198–199**, 1–13. Available at: https://doi.org/10.1016/j.lithos.2014.02.017.
- McArthur J. M., Howarth R. J. and Bailey T. R. (2001) Strontium isotope stratigraphy: LOWESS version 3: Best fit to the marine Sr-isotope curve for 0-509 Ma and accompanying look-up table for deriving numerical age. *J. Geol.* **109**, 155–170. Available at: https://doi.org/10.1086/319243.
- McCrea J. M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* **18**, 849–857. Available at: https://doi.org/10.1063/1.1747785.
- McCulloch M. T. (1994) Primitive ⁸⁷Sr/⁸⁶Sr from an Archean barite and conjecture on the Earth's age and origin. *Earth Planet. Sci. Lett.* **126**, 1–13. Available at: https://doi.org/10.1016/0012-821X(94)90238-0.
- McCulloch M. T. and Bennett V. C. (1994) Progressive growth of the Earth's continental crust and depleted mantle: Geochemical constraints. *Geochim. Cosmochim. Acta* **58**, 4717–4738. Available at: https://doi.org/10.1016/0016-7037(94)90203-8.
- McCulloch M. T., Collerson K. D. and Compston W. (1983a) Growth of Archaean crust within the Western Gneiss Terrain, Yilgarn Block, Western Australia. *J. Geol. Soc. Aust.* **30**, 155–160. Available at: https://doi.org/10.1080/00167618308729243.
- McCulloch M. T., Compston W. and Froude D. (1983b) Sm-Nd and Rb-Sr dating of Archaean gneisses, eastern Yilgarn Block, Western Australia. J. Geol. Soc. Aust. 30, 149–153. Available at: https://doi.org/10.1080/00167618308729242.
- McDonough W. F. (2003) 2.15 Compositional model for the Earth's core. *Treatise on Geochemistry*, Elsevier Ltd., pp. 547–568. Available at: https://doi.org/10.1016/B0-08-043751-6/02015-6.
- McDonough W. F. and Sun S.-s. (1995) The composition of the Earth. *Chem. Geol.* **120**, 223–253. Available at: https://doi.org/10.1016/0009-2541(94)00140-4.
- Meffre S., Falloon T. J., Crawford T. J., Hoernle K., Hauff F., Duncan R. A., Bloomer S. H. and Wright D. J. (2012) Basalts erupted along the Tongan fore arc during subduction initiation: Evidence from geochronology of dredged rocks from the Tonga fore arc and trench. *Geochemistry, Geophys. Geosystems* 13, 1–17. Available at: https://doi.org/10.1029/2012GC004335.
- Minami M., Masuda A., Shimizu H. and Adachi M. (1995) Two Archean Sm-Nd ages of 3.2 and 2.5 Ga for the Marble Bar Chert, Warrawoona Group, Pilbara Block, Western Australia. *Geochem. J.* 29, 347–362. Available at: https://doi.org/10.2343/geochemj.29.347.
- Mole D. R., Barnes S. J., Yao Z., White A. J. R., Maas R. and Kirkland C. L. (2018) The Archean Fortescue Large Igneous Province: A result of komatiite contamination by a distinct Eo-Paleoarchean crust. *Precambrian Res.* 310, 365– 390. Available at: https://doi.org/10.1016/j.precamres.2018.02.017.

- Moorbath S. (1977) Ages, isotopes and evolution of Precambrian continental crust. *Chem. Geol.* **20**, 151–187. Available at: https://doi.org/10.1016/0009-2541(77)90042-0.
- Moorbath S., Taylor P. N. and Goodwin R. (1981) Origin of granitic magma by crustal remobilisation: Rb-Sr and Pb/Pb geochronology and isotope geochemistry of the late Archaean Qôrqut Granite Complex of southern West Greenland. *Geochim. Cosmochim. Acta* 45, 1051–1060. Available at: https://doi.org/10.1016/0016-7037(81)90131-9.
- Moorbath S., Whitehouse M. J. and Kamber B. S. (1997) Extreme Nd-isotope heterogeneity in the early Archaean—fact or fiction? Case histories from northern Canada and West Greenland—Reply. *Chem. Geol.* 135, 213–231. Available at: https://doi.org/10.1016/S0009-2541(96)00117-9.
- Moyen J. F. (2011) The composite Archaean grey gneisses: Petrological significance, and evidence for a non-unique tectonic setting for Archaean crustal growth. *Lithos* **123**, 21–36. Available at: https://doi.org/10.1016/j.lithos.2010.09.015.
- Moyen J. F., Laurent O., Chelle-Michou C., Couzinié S., Vanderhaeghe O., Zeh A., Villaros A. and Gardien V. (2017) Collision vs. subduction-related magmatism: Two contrasting ways of granite formation and implications for crustal growth. *Lithos* 277, 154–177. Available at: https://doi.org/10.1016/j.lithos.2016.09.018.
- Moyen J. F. and Martin H. (2012) Forty years of TTG research. *Lithos* **148**, 312–336. Available at: https://doi.org/10.1016/j.lithos.2012.06.010.
- Moyen J. F. and Stevens G. (2013) Experimental constraints on TTG petrogenesis: Implications for Archean geodynamics. *Archean Geodyn. Environ.*, 149–175. Available at: https://doi.org/10.1029/164GM11.
- Münker C., Weyer S., Scherer E. E. and Mezger K. (2001) Separation of high field strength elements (Nb, Ta, Zr, Hf) and Lu from rock samples for MC-ICPMS measurements. *Geochemistry Geophys. Geosystems* **1**. Available at: https://doi.org/10.1029/2001GC000183.
- Münker C., Wörner G., Yogodzinski G. and Churikova T. (2004) Behaviour of high field strength elements in subduction zones: Constraints from Kamchatka-Aleutian arc lavas. *Earth Planet. Sci. Lett.* **224**, 275–293. Available at: https://doi.org/10.1016/j.epsl.2004.05.030.
- Murphy D., Rizo H., O'Neil J., Hepple R., Wiemer D., Kemp A. and Vervoort J. D. (2021) Combined Sm-Nd, Lu-Hf, and ¹⁴²Nd study of Paleoarchean basalts from the East Pilbara Terrane, Western Australia. *Chem. Geol.* **578**, 120301. Available at: https://doi.org/10.1016/j.chemgeo.2021.120301.
- Murphy D. T., Kamber B. S. and Collerson K. D. (2003) A refined solution to the First Terrestrial Pb-isotope paradox. *J. Petrol.* **44**, 39–53. Available at: https://doi.org/10.1093/petrology/44.1.39.
- Næraa T., Scherstén A., Rosing M. T., Kemp A. I. S., Hoffmann J. E., Kokfelt T. F. and Whitehouse M. J. (2012) Hafnium isotope evidence for a transition in the dynamics of continental growth 3.2 Gyr ago. *Nature* **485**, 627–630. Available at:

https://doi.org/10.1038/nature11140.

- Nagel T. J., Hoffmann J. E. and Münker C. (2012) Generation of Eoarchean tonalitetrondhjemite-granodiorite series from thickened mafic arc crust. *Geology* **40**, 375– 378. Available at: https://doi.org/10.1130/G32729.1.
- Nakajima K. and Arima M. (1998) Melting experiments on hydrous low-K tholeiite: Implications for the genesis of tonalitic crust in the Izu-Bonin-Mariana arc. *Isl. Arc* 7, 359–373. Available at: https://doi.org/10.1111/j.1440-1738.1998.00195.x.
- Nakamura K. and Kato Y. (2002) Carbonate minerals in the Warrawoona group, Pilbara Craton: Implications for continental crust, life, and global carbon cycle in the early Archean. *Resour. Geol.* **52**, 91–100. Available at: https://doi.org/10.1111/j.1751-3928.2002.tb00122.x.
- Nakamura K. and Kato Y. (2004) Carbonatization of oceanic crust by the seafloor hydrothermal activity and its significance as a CO₂ sink in the Early Archean. *Geochim. Cosmochim. Acta* **68**, 4595–4618. Available at: https://doi.org/10.1016/j.gca.2004.05.023.
- Nash W. P. and Crecraft H. R. (1985) Partition coefficients for trace elements in silicic magmas. *Geochim. Cosmochim. Acta* **49**, 2309–2322. Available at: https://doi.org/10.1016/0016-7037(85)90231-5.
- Nebel O., Campbell I. H., Sossi P. A. and Van Kranendonk M. J. (2014) Hafnium and iron isotopes in early Archean komatiites record a plume-driven convection cycle in the Hadean Earth. *Earth Planet. Sci. Lett.* **397**, 111–120. Available at: https://doi.org/10.1016/j.epsl.2014.04.028.
- Nebel O., Mezger K., Scherer E. E. and Münker C. (2005) High precision determinations of ⁸⁷Rb/⁸⁵Rb in geologic materials by MC-ICP-MS. *Int. J. Mass Spectrom.* **246**, 10–18. Available at: https://doi.org/10.1016/j.ijms.2005.08.003.
- Nemchin A. A., Pidgeon R. T. and Whitehouse M. J. (2006) Re-evaluation of the origin and evolution of >4.2 Ga zircons from the Jack Hills metasedimentary rocks. *Earth Planet. Sci. Lett.* 244, 218–233. Available at: https://doi.org/10.1016/j.epsl.2006.01.054.
- Nisbet E. G. (1987) *The Young Earth*. eds. A. & Unwin and Boston., Available at: https://doi.org/10.1007/978-94-011-6489-4.
- Nutman A. P., Bennett V. C., Friend C. R. L., Van Kranendonk M. J. and Chivas A. R. (2016) Rapid emergence of life shown by discovery of 3,700-million-year-old microbial structures. *Nature* 537, 535–538. Available at: https://doi.org/10.1038/nature19355.
- Nutman A. P., Friend C. R. L., Bennett V. C., Wright D. and Norman M. D. (2010) ≥3700Ma pre-metamorphic dolomite formed by microbial mediation in the Isua supracrustal belt (W. Greenland): Simple evidence for early life? *Precambrian Res.* 183, 725–737. Available at: https://doi.org/10.1016/j.precamres.2010.08.006.
- Nutman A. P., McGregor V. R., Friend C. R. L., Bennett V. C. and Kinny P. D. (1996) The Itsaq Gneiss Complex of southern West Greenland; the world's most extensive

record of early crustal evolution (3900-3600 Ma). *Precambrian Res.* **78**, 1–39. Available at: https://doi.org/10.1016/0301-9268(95)00066-6.

O'Neil J., Carlson R. W., Francis D. and Stevenson R. K. (2008) Neodymium-142 evidence for hadean mafic crust. *Science* **321**, 1828–1831. Available at: https://doi.org/10.1126/science.1161925.

Oversby V. M. and Ringwood A. E. (1971) Time of formation of the Earth's core. *Nature* **234**, 463–465. Available at: https://doi.org/10.1038/234463a0.

- Palme H. and O'Neill H. St. C. (2014) 3.1 Cosmochemical estimates of mantle composition. In *Treatise on Geochemistry: Second Edition*, Elsevier Ltd., pp. 1– 39. Available at: https://doi.org/10.1016/B978-0-08-095975-7.00201-1.
- Palmer M. R. and Edmond J. M. (1989) The strontium isotope budget of the modern ocean. *Earth Planet. Sci. Lett.* **92**, 11–26. Available at: https://doi.org/10.1016/0012-821X(89)90017-4.
- Patchett P. J., Kouvo O., Hedge C. E. and Tatsumoto M. (1982) Evolution of continental crust and mantle heterogeneity: Evidence from Hf isotopes. *Contrib. to Mineral. Petrol.* 78, 279–297. Available at: https://doi.org/10.1007/BF00398923.
- Patchett P. J. and Tatsumoto M. (1980) Lu-Hf total-rock isochron for the eucrite meteorites. *Nature* **288**, 571–574. Available at: https://doi.org/10.1038/288571a0.
- Pearce J. A. (2008) Geochemical fingerprinting of oceanic basalts with applications to ophiolite classification and the search for Archean oceanic crust. *Lithos* **100**, 14–48. Available at: https://doi.org/10.1016/j.lithos.2007.06.016.
- Pearce J. A. (2014) Immobile element fingerprinting of ophiolites. *Elements* **10**, 101–108. Available at: https://doi.org/10.2113/gselements.10.2.101.
- Pearce J. A. and Norry M. J. (1979) Petrogenetic implications of Ti, Zr, Y, and Nb variations in volcanic rocks. *Contrib. to Mineral. Petrol.* **69**, 33–47. Available at: https://doi.org/10.1007/BF00375192.
- Pearce J. A. and Peate D. W. (1985) Tectonic implications of the composition of volcanic arc magmas. *Tectonics* 23, 251–284. Available at: https://doi.org/10.1146/annurev.ea.23.050195.001343.
- Peccerillo A. and Taylor S. R. (1976) Geochemistry of Eocene calc-alkaline volcanic rocks from the Kastamonu Area, Northern Turkey. *Contrib. to Mineral. Petrol.* 58, 63–81. Available at: https://doi.org/10.1007/BF00384745.
- Pelletier B. and Auzende J. M. (1996) Geometry and structure of the Vitiaz Trench Lineament (SW Pacific). *Mar. Geophys. Res.* 18, 305–335. Available at: https://doi.org/10.1007/BF00286083.
- Peter J. M. and Scott S. D. (1988) Mineralogy, composition, and fluid-inclusion microthermometry of seafloor hydrothermal deposits in the Southern Trough of Guaymas Basin, Gulf of California. *Can. Mineral.* 26 pt 3, 567–587.
- Petersson A., Kemp A. I. S., Gray C. M. and Whitehouse M. J. (2020) Formation of early Archean Granite-Greenstone Terranes from a globally chondritic mantle:

Insights from igneous rocks of the Pilbara Craton, Western Australia. *Chem. Geol.* **551**. Available at: https://doi.org/10.1016/j.chemgeo.2020.119757.

- Petersson A., Kemp A. I. S., Hickman A. H., Whitehouse M. J., Martin L. and Gray C. M. (2019) A new 3.59 Ga magmatic suite and a chondritic source to the east Pilbara Craton. *Chem. Geol.* 511, 51–70. Available at: https://doi.org/10.1016/j.chemgeo.2019.01.021.
- Peucker-Ehrenbrink B., Hofmann A. W. and Hart S. R. (1994) Hydrothermal lead transfer from mantle to continental crust: the role of metalliferous sediments. *Earth Planet. Sci. Lett.* **125**, 129–142. Available at: https://doi.org/10.1016/0012-821X(94)90211-9.
- Pin C. and Santos Zalduegui J. F. (1997) Sequential separation of light rare-earth elements, thorium and uranium by miniaturized extraction chromatography: Application to isotopic analyses of silicate rocks. *Anal. Chim. Acta* **339**, 79–89. Available at: https://doi.org/10.1016/S0003-2670(96)00499-0.
- Pirajno F. (1992) Hydrothermal Mineral Deposits. Springer-Verlag, Berlin. 702pp.
- Polat A. (2012) Growth of Archean continental crust in oceanic island arcs. *Geology* **40**, 383–384. Available at: https://doi.org/10.1130/focus042012.1.
- Polat A., Frei R., Appel P. W. U., Dilek Y., Fryer B., Ordóñez-Calderón J. C. and Yang Z. (2008) The origin and compositions of Mesoarchean oceanic crust: Evidence from the 3075 Ma Ivisaartoq greenstone belt, SW Greenland. *Lithos* 100, 293–321. Available at: https://doi.org/10.1016/j.lithos.2007.06.021.
- Polat A. and Hofmann A. W. (2003) Alteration and geochemical patterns in the 3.7-3.8 Ga Isua greenstone belt, West Greenland. *Precambrian Res.* **126**, 197–218. Available at: https://doi.org/10.1016/S0301-9268(03)00095-0.
- Polat A., Hofmann A. W. and Rosing M. T. (2002) Boninite-like volcanic rocks in the 3.7-3.8 Ga isua greenstone belt, West Greenland: Geochemical evidence for intraoceanic subduction zone processes in the early earth. *Chem. Geol.* **184**, 231–254. Available at: https://doi.org/10.1016/S0009-2541(01)00363-1.
- Polat A., Wang L. and Appel P. W. U. (2015) A review of structural patterns and melting processes in the Archean craton of West Greenland: Evidence for crustal growth at convergent plate margins as opposed to non-uniformitarian models. *Tectonophysics* 662, 67–94. Available at: https://doi.org/10.1016/j.tecto.2015.04.006.
- Puchtel I. S., Blichert-Toft J., Touboul M., Walker R. J., Byerly G. R., Nisbet E. G. and Anhaeusser C. R. (2013) Insights into early Earth from Barberton komatiites: Evidence from lithophile isotope and trace element systematics. *Geochim. Cosmochim. Acta* 108, 63–90. Available at: https://doi.org/10.1016/j.gca.2013.01.016.
- Puchtel I. S., Touboul M., Blichert-Toft J., Walker R. J., Brandon A. D., Nicklas R. W., Kulikov V. S. and Samsonov A. V. (2016) Lithophile and siderophile element systematics of Earth's mantle at the Archean-Proterozoic boundary: Evidence from 2.4 Ga komatiites. *Geochim. Cosmochim. Acta* 180, 227–255. Available at:

https://doi.org/10.1016/j.gca.2016.02.027.

- Qian Q. and Hermann J. (2013) Partial melting of lower crust at 10-15 kbar: Constraints on adakite and TTG formation. *Contrib. to Mineral. Petrol.* **165**, 1195–1224. Available at: https://doi.org/10.1007/s00410-013-0854-9.
- Quandt D., Micheuz P., Kurz W., Kluge T., Boch R., Hippler D., Krenn K. and Hauzenberger C. A. (2019) Geochemistry of vein calcites hosted in the Troodos Pillow Lavas and their implications for the timing and physicochemical environment of fracturing, fluid circulation, and vein mineral growth. *Geochemical Perspect. Lett.* 20, 5913–5938. Available at: https://doi.org/10.1029/2019GC008369.
- Ravindran A., Mezger K., Balakrishnan S., Kooijman E., Schmitt M. and Berndt J. (2020) Initial ⁸⁷Sr/⁸⁶Sr as a sensitive tracer of Archaean crust-mantle evolution: Constraints from igneous and sedimentary rocks in the western Dharwar Craton, India. *Precambrian Res.* **337**, 105523. Available at: https://doi.org/10.1016/j.precamres.2019.105523.
- Rehkämper M. and Mezger K. (2000) Investigation of matrix effects for Pb isotope ratio measurements by multiple collector ICP-MS: Verification and application of optimized analytical protocols. *J. Anal. At. Spectrom.* **15**, 1451–1460. Available at: https://doi.org/10.1039/b005262k.
- Richards J. R. (1983) Lead isotopes as indicators of old stable craton in Western Australia. *Geochem. J.* **17**, 247–255. Available at: https://doi.org/10.2343/geochemj.17.247.
- Richards J. R., Fletcher I. R. and Blockley J. G. (1981) Pilbara galenas: Precise isotopic assay of the oldest Australian leads; model ages and growth-curve implications. *Miner. Depos.* 16, 7–30. Available at: https://doi.org/10.1007/BF00206451.
- Rickard M. J. and Williams I. S. (2013) No zircon U-Pb evidence for a Precambrian component in the Late Eocene Yavuna trondhjemite, Fiji. *Aust. J. Earth Sci.* **60**, 521–525. Available at: https://doi.org/10.1080/08120099.2013.792295.
- Rizo H., Andrault D., Bennett N. R., Humayun M., Brandon A., Vlastelic I., Moine B., Poirier A., Bouhifd M. A. and Murphy D. T. (2019) ¹⁸²W evidence for core-mantle interaction in the source of mantle plumes. *Geochemical Perspect. Lett.* **11**, 6–11. Available at: https://doi.org/10.7185/geochemlet.1917.
- Rizo H., Boyet M., Blichert-Toft J. and Rosing M. T. (2011) Combined Nd and Hf isotope evidence for deep-seated source of Isua lavas. *Earth Planet. Sci. Lett.* **312**, 267–279. Available at: https://doi.org/10.1016/j.epsl.2011.10.014.
- Rizo H., Walker R. J., Carlson R. W., Touboul M., Horan M. F., Puchtel I. S., Boyet M. and Rosing M. T. (2016) Early Earth differentiation investigated through ¹⁴²Nd, ¹⁸²W, and highly siderophile element abundances in samples from Isua, Greenland. *Geochim. Cosmochim. Acta* 175, 319–336. Available at: https://doi.org/10.1016/j.gca.2015.12.007.
- Rodda P. (1994) Geology of Fiji. SOPAC Tech. Bull. Geol. Submar. Resour. Tonga-Lau-Fiji Reg. 8, 131–151.

- Rodda P. (1976) Geology of northern and central Viti Levu, Fiji. *Bull. Miner. Resour. Div.* **3**.
- Rodda P. (1967) Outline of the geology of Viti Levu. *New Zeal. J. Geol. Geophys.* **10**, 1260–1273. Available at: https://doi.org/10.1080/00288306.1967.10420217.
- Rodda P. and Lum J. (1990) Geological Evolution and Mineral Deposits of Fiji. In *Geologisches Jahrbuch*, pp. 37–66.
- Roerdink D. L., Ronen Y., Strauss H. and Mason P. R. D. (2022) Emergence of felsic crust and subaerial weathering recorded in Palaeoarchaean barite. *Nat. Geosci.* 15, 227–232. Available at: https://doi.org/10.1038/s41561-022-00902-9.
- Rollinson H. (2009) New models for the genesis of plagiogranites in the Oman ophiolite. *Lithos* **112**, 603–614. Available at: https://doi.org/10.1016/j.lithos.2009.06.006.
- Rollinson H. (2008) Ophiolitic trondhjemites: A possible analogue for Hadean felsic "crust." *Terra Nov.* **20**, 364–369. Available at: https://doi.org/10.1111/j.1365-3121.2008.00829.x.
- Rosing M. T. (1999) ¹³C-depleted carbon microparticles in ≥3700-Ma sea-floor sedimentary rocks from west Greenland. *Science* **283**, 674–676. Available at: https://doi.org/10.1126/science.283.5402.674.
- le Roux L. J. and Glendenin L. (1963) Half-Life of ²³²Th. In *Proc. Nat. Meet. on Nuclear Energy*, Pretoria, South Africa, April 1963. 83–94.
- Rudnick R. L. (1995) Making continental crust. *Nature* **378**, 571–578. Available at: https://doi.org/10.1038/378571a0.
- Rudnick R. L. and Gao S. (2014) 4.1 Composition of the continental crust. In *Treatise on Geochemistry: Second Edition*, Elsevier Ltd., pp. 1–51. Available at: https://doi.org/10.1016/B978-0-08-095975-7.00301-6.
- Ryder C. H., Gill J. B., Tepley F., Ramos F. and Reagan M. (2006) Closed- to open-system differentiation at Arenal volcano (1968-2003). *J. Volcanol. Geotherm. Res.* 157, 75–93. Available at: https://doi.org/10.1016/j.jvolgeores.2006.03.046.
- Satkoski A. M., Beukes N. J., Li W., Beard B. L. and Johnson C. M. (2015) A redoxstratified ocean 3.2 billion years ago. *Earth Planet. Sci. Lett.* **430**, 43–53. Available at: https://doi.org/10.1016/j.epsl.2015.08.007.
- Satkoski A. M., Fralick P., Beard B. L. and Johnson C. M. (2017) Initiation of modernstyle plate tectonics recorded in Mesoarchean marine chemical sediments. *Geochim. Cosmochim. Acta* 209, 216–232. Available at: https://doi.org/10.1016/j.gca.2017.04.024.
- Satkoski A. M., Lowe D. R., Beard B. L., Coleman M. L. and Johnson C. M. (2016) A high continental weathering flux into Paleoarchean seawater revealed by strontium isotope analysis of 3.26 Ga barite. *Earth Planet. Sci. Lett.* **454**, 28–35. Available at: https://doi.org/10.1016/j.epsl.2016.08.032.

Schellart W. P., Lister G. S. and Toy V. G. (2006) A Late Cretaceous and Cenozoic

reconstruction of the Southwest Pacific region: Tectonics controlled by subduction and slab rollback processes. *Earth-Science Rev.* **76**, 191–233. Available at: https://doi.org/10.1016/j.earscirev.2006.01.002.

- Scherstén A. and Garde A. A. (2013) Complete hydrothermal re-equilibration of zircon in the Maniitsoq structure, West Greenland: A 3001 Ma minimum age of impact? *Meteorit. Planet. Sci.* 48, 1472–1498. Available at: https://doi.org/10.1111/maps.12169.
- Schidlowski M., Hayes J. M. and Kaplan I. R. (1983) Isotopic interferences of ancient biochemistries: carbon, sulfur, hydrogen and nitrogen. In *Earth's Earliest Biosphere: Its Origin and Evolution* (ed. J. W. Schopf). Princeton University Press, Princeton, NJ., pp. 149–186.
- Schier K., Bau M., Münker C., Beukes N. and Viehmann S. (2018) Trace element and Nd isotope composition of shallow seawater prior to the Great Oxidation Event: Evidence from stromatolitic bioherms in the Paleoproterozoic Rooinekke and Nelani Formations, South Africa. *Precambrian Res.* 315, 92–102. Available at: https://doi.org/10.1016/j.precamres.2018.07.014.
- Schneider K. P., Hoffmann J. E., Boyet M., Münker C. and Kröner A. (2018) Coexistence of enriched and modern-like ¹⁴²Nd signatures in Archean igneous rocks of the eastern Kaapvaal Craton, southern Africa. *Earth Planet. Sci. Lett.* **487**, 54–66. Available at: https://doi.org/10.1016/j.epsl.2018.01.022.
- Schuth S., König S., and Münker C. (2011) Subduction zone dynamics in the SW Pacific plate boundary region constrained from hig-precision Pb isotope data. *Earth Planet. Sci. Lett.* **311**, 328-338. Available at: https://doi.org/10.1016/j.epsl.2011.09.006.
- Sdrolias M., Mueller R. D. and Gaina C. (2003) Tectonic evolution of the southwest Pacific using constraints from backarc basins. In *Evolution and Dynamics of the Australian Plate*, pp. 343–359. Available at: https://doi.org/10.1130/0-8137-2372-8.343.
- Segev A., Rybakov M. and Mortimer N. (2012) A crustal model for Zealandia and Fiji. *Geophys. J. Int.* **189**, 1277–1292. Available at: https://doi.org/10.1111/j.1365-246X.2012.05436.x.
- Shaw D. M. (1970) Trace element fractionation during anatexis. *Geochim. Cosmochim. Acta* **34**, 237–243. Available at: https://doi.org/10.1016/0016-7037(70)90009-8.
- Shibuya T., Tahata M., Kitajima K., Ueno Y., Komiya T., Yamamoto S., Igisu M., Terabayashi M., Sawaki Y., Takai K., Yoshida N. and Maruyama S. (2012) Depth variation of carbon and oxygen isotopes of calcites in Archean altered upperoceanic crust: Implications for the CO₂ flux from ocean to oceanic crust in the Archean. *Earth Planet. Sci. Lett.* **321–322**, 64–73. Available at: https://doi.org/10.1016/j.epsl.2011.12.034.
- Shields G. A. (2007) A normalised seawater strontium isotope curve and the Neoproterozoic-Cambrian chemical weathering event. *eEarth Discuss.* **2**, 69–84. Available at: https://doi.org/10.5194/eed-2-69-2007.

- Shields G. and Veizer J. (2002) Precambrian marine carbonate isotope database: Version 1.1. *Geochemistry, Geophys. Geosystems* **3**. Available at: https://doi.org/10.1029/2001GC000266.
- Shirey S. B. and Richardson S. H. (2011) Start of the wilson cycle at 3 Ga shown by diamonds from subcontinental mantle. *Science* **333**, 434–436. Available at: https://doi.org/10.1126/science.1206275.
- Siahi M., Hofmann A., Master S., Wilson A. and Mayr C. (2018) Trace element and stable (C, O) and radiogenic (Sr) isotope geochemistry of stromatolitic carbonate rocks of the Mesoarchaean Pongola Supergroup: Implications for seawater composition. *Chem. Geol.* **476**, 389–406. Available at: https://doi.org/10.1016/j.chemgeo.2017.11.036.
- Smith P. E., Farquhar R. M. and Halls H. C. (1992) U-Th-Pb isotope study of mafic dykes in the superior Province, Ontario, Canada: uniformity of initial Pb isotope ratios of the Hearst dykes. *Chem. Geol.* 94, 261–280. Available at: https://doi.org/10.1016/S0009-2541(10)80029-4.
- Smithies R. H. (2000) The Archaean tonalite-trondhjemite-granodiorite (TTG) series is not an analogue of Cenozoic adakite. *Earth Planet. Sci. Lett.* **182**, 115–125. Available at: https://doi.org/10.1016/S0012-821X(00)00236-3.
- Smithies R. H., Champion D. C. and Van Kranendonk M. J. (2009) Formation of Paleoarchean continental crust through infracrustal melting of enriched basalt. *Earth Planet. Sci. Lett.* 281, 298–306. Available at: https://doi.org/10.1016/j.epsl.2009.03.003.
- Smithies R. H., Champion D. C. and Van Kranendonk M. J. (2007a) The oldest wellpreserved felsic volcanic rocks on Earth: Geochemical clues to the early evolution of the Pilbara Supergroup and implications for the growth of a Paleoarchean protocontinent. *Dev. Precambrian Geol.* **15**, 339–367. Available at: https://doi.org/10.1016/S0166-2635(07)15042-8.
- Smithies R. H., Champion D. C., Van Kranendonk M. J., Howard H. M. and Hickman A. H. (2005a) Modern-style subduction processes in the Mesoarchaean: Geochemical evidence from the 3.12 Ga Whundo intra-oceanic arc. *Earth Planet. Sci. Lett.* 231, 221–237. Available at: https://doi.org/10.1016/j.epsl.2004.12.026.
- Smithies R. H., Van Kranendonk M. J. and Champion D. C. (2005b) It started with a plume - Early Archaean basaltic proto-continental crust. *Earth Planet. Sci. Lett.* 238, 284–297. Available at: https://doi.org/10.1016/j.epsl.2005.07.023.
- Smithies R. H., Van Kranendonk M. J. and Champion D. C. (2007b) The Mesoarchean emergence of modern-style subduction. *Gondwana Res.* **11**, 50–68. Available at: https://doi.org/10.1016/j.gr.2006.02.001.
- Smithies R. H., Lu Y., Johnson T. E., Kirkland C. L., Cassidy K. F., Champion D. C., Mole D. R., Zibra I., Gessner K., Sapkota J., De Paoli M. C. and Poujol M. (2019) No evidence for high-pressure melting of Earth's crust in the Archean. *Nat. Commun.* 10, 1–12. Available at: https://doi.org/10.1038/s41467-019-13547-x.

Sommer H., Kröner A., Jacob D. E., Che X., Wong J. and Xie H. (2020) The formation

of TTGs by hydrous partial melting from a gabbroic mantle source in Viti Levu, Fiji islands. *Precambrian Res.* Available at: https://doi.org/10.1016/j.precamres.2020.105971.

- Sossi P. A., Eggins S. M., Nesbitt R. W., Nebel O., Hergt J. M., Campbell I. H., O'Neill H. S. C., Kranendonk M. Van and Rhodri Davies D. (2016) Petrogenesis and Geochemistry of Archean Komatiites. J. Petrol. 57, 147–184. Available at: https://doi.org/10.1093/petrology/egw004.
- Stacey J. S. and Kramers J. D. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planet. Sci. Lett.* 26, 207–221. Available at: https://doi.org/10.1016/0012-821X(75)90088-6.
- Staudigel H., Davies G. R., Hart S. R., Marchant K. M. and Smith B. M. (1995) Large scale isotopic Sr, Nd and O isotopic anatomy of altered oceanic crust: DSDP/ODP sites417/418. *Earth Planet. Sci. Lett.* **130**, 169–185. Available at: https://doi.org/10.1016/0012-821X(94)00263-X.
- Staudigel H., Muehlenbachs K., Richardson S. H. and Hart S. R. (1981) Agents of low temperature ocean crust alteration. *Contrib. to Mineral. Petrol.* **77**, 150–157. Available at: https://doi.org/10.1007/BF00636518.
- Steenfelt A., Hollis J., Kirkland C. L., Sandrin A., Gardiner N. J., Olierook H., Szilas K., Waterton P. and Yakymchuk C. (2021) The Mesoarchaean Akia terrane, West Greenland, revisited: New insights based on spatial integration of geophysics, field observation, geochemistry and geochronology. *Precambrian Res.* 352, 105958. Available at: https://doi.org/10.1016/j.precamres.2020.105958.
- Steiger R. H. and Jäger E. (1977) Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lett.* 36, 359–362. Available at: https://doi.org/10.1016/0012-821X(77)90060-7.
- Stern C. R. (2011) Subduction erosion: Rates, mechanisms, and its role in arc magmatism and the evolution of the continental crust and mantle. *Gondwana Res.* 20, 284–308. Available at: https://doi.org/10.1016/j.gr.2011.03.006.
- Stork A. (1984) Silicic magmatism in an island arc, Fiji, southwest Pacific: Implications for continental growth (rhyolite, trondhjemite). PhD thesis, University of California, Santa Cruz.
- Stracke A., Bizimis M. and Salters V. J. M. (2003) Recycling oceanic crust: Quantitative constraints. *Geochemistry, Geophys. Geosystems* 4. Available at: https://doi.org/10.1029/2001GC000223.
- Stracke A. and Bourdon B. (2009) The importance of melt extraction for tracing mantle heterogeneity. *Geochim. Cosmochim. Acta* 73, 218–238. Available at: https://doi.org/10.1016/j.gca.2008.10.015.
- Stracke A., Hofmann A. W. and Hart S. R. (2005) FOZO, HIMU, and the rest of the mantle zoo. *Geochemistry*, *Geophys. Geosystems* 6. Available at: https://doi.org/10.1029/2004GC000824.

Stratford J. M. C. and Rodda P. (2000) Late Miocene to Pliocene palaeogeography of

Viti Levu, Fiji Islands. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **162**, 137–153. Available at: https://doi.org/10.1016/S0031-0182(00)00109-7.

- Sun S.-s. and McDonough W. F. (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geol. Soc. London*, *Spec. Publ.* 42, 313–345. Available at: https://doi.org/10.1144/GSL.SP.1989.042.01.19.
- Sun S.-s. (1982) Chemical composition and origin of the earth's primitive mantle. *Geochim. Cosmochim. Acta* **46**, 179–192. Available at: https://doi.org/10.1016/0016-7037(82)90245-9.
- Suyehiro K., Takahashi N., Ariie Y., Yokoi Y., Hino R., Shinohara M., Kanazawa T., Hirata N., Tokuyama H. and Taira A. (1996) Continental crust, crustal underplating, and low-Q Upper Mantle beneath an oceanic island arc. *Science* 272, 390–392. Available at: https://doi.org/10.1126/science.272.5260.390.
- Szilas K., van Hinsberg V., McDonald I., Næraa T., Rollinson H., Adetunji J. and Bird D. (2017) Highly refractory Archaean peridotite cumulates: Petrology and geochemistry of the Seqi Ultramafic Complex, SW Greenland. *Geosci. Front.* 9, 689–714. Available at: https://doi.org/10.1016/j.gsf.2017.05.003.
- Szilas K., Kelemen P. B. and Bernstein S. (2015) Peridotite enclaves hosted by Mesoarchaean TTG-suite orthogneisses in the Fiskefjord region of southern West Greenland. *GeoResJ* 7, 22–34. Available at: https://doi.org/10.1016/j.grj.2015.03.003.
- Tachikawa K., Athias V. and Jeandel C. (2003) Neodymium budget in the modern ocean and paleo-oceanographic implications. *J. Geophys. Res. Ocean.* **108**, 1–13. Available at: https://doi.org/10.1029/1999jc000285.
- Tamura Y., Gill J. B., Tollstrup D., Kawabata H., Shukuno H., Chang Q., Miyazaki T., Takahashi T., Hirahara Y., Kodaira S., Ishizuka O., Suzuki T., Kido Y., Fiske R. S. and Tatsumi Y. (2009) Silicic magmas in the Izu-Bonin oceanic arc and implications for crustal evolution. *J. Petrol.* **50**, 685–723. Available at: https://doi.org/10.1093/petrology/egp017.
- Tamura Y. and Tatsumi Y. (2002) Remelting of an andesitic crust as a possible origin for rhyolitic magma in oceanic arcs: An example from the Izu-Bonin arc. *J. Petrol.* 43, 1029–1047. Available at: https://doi.org/10.1093/petrology/43.6.1029.
- Tani K., Dunkley D. J., Chang Q., Nichols A. R. L., Shukuno H., Hirahara Y., Ishizuka O., Arima M. and Tatsumi Y. (2015) Pliocene granodioritic knoll with continental crust affinities discovered in the intra-oceanic Izu-Bonin-Mariana Arc: Syntectonic granitic crust formation during back-arc rifting. *Earth Planet. Sci. Lett.* **424**, 84–94. Available at: https://doi.org/10.1016/j.epsl.2015.05.019.
- Tani K., Dunkley D. J., Kimura J.-I., Wysoczanski R. J., Yamada K. and Tatsumi Y. (2010) Syncollisional rapid granitic magma formation in an arc-arc collision zone: Evidence from the tanzawa plutonic complex, Japan. *Geology* 38, 215–218. Available at: https://doi.org/10.1130/G30526.1.

Tatsumoto M. (1978) Isotopic composition of lead in oceanic basalt and its implication
to mantle evolution. *Dev. Petrol.* **5**, 63–87. Available at: https://doi.org/10.1016/0012-821X(78)90126-7.

- Tatsumoto M., Knight R. J. and Allègre C. J. (1973) Time differences in the formation of meteorites as determined from the ratio of Lead-207 to Lead-206. *Science* **180**, 1279–1283. Available at: https://doi.org/10.1126/science.180.4092.1279.
- Taylor G. K., Gascoyne J. and Colley H. (2000) Rapid rotation of Fiji: Paleomagnetic evidence and tectonic implications. *J. Geophys. Res.* **105**, 5771–5781. Available at: https://doi.org/10.1029/1999JB900305.
- Taylor P. N., Moorbath S., Goodwin R. and Petrykowski A. C. (1980) Crustal contamination as an indicator of the extent of early Archaean continental crust: Pb isotopic evidence from the late Archaean gneisses of West Greenland. *Geochim. Cosmochim. Acta* 44, 1437–1453. Available at: https://doi.org/10.1016/0016-7037(80)90109-X.
- Taylor S. R. (1967) The origin and growth of continents. *Tectonophysics* **4**, 17–34. Available at: https://doi.org/10.1016/0040-1951(67)90056-X.
- Taylor S. R. and McLennan S. M. (1985) *The continental crust: its composition and evolution.*, Blackwell Scientific. Available at: https://doi.org/10.1017/S0016756800032167
- Taylor S. R. and McLennan S. M. (1995) The geochemical evolution of the continental crust. *Rev. Geophys.* **33**, 241–265. Available at: https://doi.org/10.1029/95RG00262.
- Tera F., Papanastassiou D. A. and Wasserburg G. J. (1974) Isotopic evidence for a terminal Lunar Cataclysm. *Earth Planet. Sci. Lett.* **22**, 1–21. Available at: https://doi.org/10.1016/0012-821X(74)90059-4.
- Terabayashi M., Masada Y. and Ozawa H. (2003) Archean ocean-floor metamorphism in the North Pole area, Pilbara Craton, Western Australia. *Precambrian Res.* **127**, 167–180. Available at: https://doi.org/10.1016/S0301-9268(03)00186-4.
- Thiemens M. M., Sprung P., Fonseca R. O. C., Leitzke F. P. and Münker C. (2019)
 Early Moon formation inferred from hafnium-tungsten systematics. *Nat. Geosci.* 12, 696–700. Available at: https://doi.org/10.1038/s41561-019-0398-3.
- Tiepolo M., Oberti R., Zanetti A., Vannucci R. and Foley S. F. (2007) Trace-element partitioning between amphibole and silicate melt. *Rev. Mineral. Geochemistry* **67**, 417–452. Available at: https://doi.org/10.2138/rmg.2007.67.11.
- Tilton G. R. and Kwon S. T. (1990) Isotopic evidence for crust-mantle evolution with emphasis on the Canadian Shield. *Chem. Geol.* **83**, 149–163. Available at: https://doi.org/10.1016/0009-2541(90)90277-E.
- Todd E., Gill J. B. and Pearce J. A. (2012) A variably enriched mantle wedge and contrasting melt types during arc stages following subduction initiation in Fiji and Tonga, southwest Pacific. *Earth Planet. Sci. Lett.* 335–336, 180–194. Available at: https://doi.org/10.1016/j.epsl.2012.05.006.
- Todd E., Stork A., Drewes-Todd E. K., Tani K., Allen C. M. and Gill J. B. (2021)

Geochemistry and geochronology of Cenozoic plutons of Viti Levu, Fiji, Version 1.0. *Interdiscip. Earth Data Alliance*. Available at: https://doi.org/10.26022/IEDA/111854.

- Toulkeridis T., Clauer N., Uysal I. T. and Kröner A. (2021) Sequential leaching of silicified Archaean carbonates: A Rb-Sr, Sm-Nd and Pb-Pb isotopic contribution to their tectonic-thermal history (Kaapvaal Craton, South Africa). *Precambrian Res.* 365. Available at: https://doi.org/10.1016/j.precamres.2021.106393.
- Trendall A. F. (2002) The Significance of Iron-Formation in the Precambrian Stratigraphic Record. *Precambrian Sediment. Environ.* **33**, 33–66. Available at: https://doi.org/10.1002/9781444304312.ch3.
- Trendall A. F. (1968) Three Great Basins of Precambrian banded iron formation deposition: A systematic comparison. *Bull. Geol. Soc. Am.* **79**, 1527–1544. Available at: https://doi.org/10.1130/0016-7606(1968)79[1527:TGBOPB]2.0.CO;2.
- Trendall A. F. and Blockley J. G. (1970) The iron formations of the Precambrian Hamersley Group, Western Australia. In *Geological Survey of Western Australia*, *Bulletin* **119**. 366p.
- Tusch J., Münker C., Hasenstab E., Jansen M., Marien C. S., Kurzweil F., van Kranendonk M. J., Smithies H., Maier W. and Garbe-Schönberg D. (2021) Convective isolation of Hadean mantle reservoirs through Archean time. *Proc. Natl. Acad. Sci. U. S. A.* **118**. Available at: https://doi.org/10.1073/pnas.2012626118.
- Tusch J., Sprung P., van de Löcht J., Hoffmann J. E., Boyd A. J., Rosing M. T. and Münker C. (2019) Uniform ¹⁸²W isotope compositions in Eoarchean rocks from the Isua region, SW Greenland: The role of early silicate differentiation and missing late veneer. *Geochim. Cosmochim. Acta* 257, 284–310. Available at: https://doi.org/10.1016/j.gca.2019.05.012.
- Van Kranendonk M. J. (2011) Onset of plate tectonics. *Science* **333**, 413–414. Available at: https://doi.org/10.1126/science.1208766.
- Van Kranendonk M. J. (2010) Three and a half billion years of life on Earth: A transect back into deep time. *Geological Survey of Western Australia, Record 2010/21*, 93 pp.
- Van Kranendonk M. J. (2006) Volcanic degassing, hydrothermal circulation and the flourishing of early life on Earth: A review of the evidence from c. 3490-3240 Ma rocks of the Pilbara Supergroup, Pilbara Craton, Western Australia. *Earth-Science Rev.* 74, 197–240. Available at: https://doi.org/10.1016/j.earscirev.2005.09.005.
- Van Kranendonk M. J., Collins W. J., Hickman A. and Pawley M. J. (2004) Critical tests of vertical vs. horizontal tectonic models for the Archaean East Pilbara Granite-Greenstone Terrane, Pilbara Craton, Western Australia. *Precambrian Res.* 131, 173–211. Available at: https://doi.org/10.1016/j.precamres.2003.12.015.
- Van Kranendonk M. J., Hickman A. H., Smithies R. H. and Nelson D. R. (2002) Geology and tectonic evolution of the Archean North Pilbara Terrain, Pilbara

Craton, Western Australia. *Econ. Geol.* **97**, 695–732. Available at: https://doi.org/10.2113/gsecongeo.97.4.695.

- Van Kranendonk M. J., Smithies R. H., Hickman A. H. and Champion D. C. (2007) Review: Secular tectonic evolution of Archean continental crust: interplay between horizontal and vertical processes in the formation of the Pilbara Craton, Australia. *Terra Nov.* 19, 1–38. Available at: https://doi.org/10.1111/j.1365-3121.2006.00723.x.
- Van Kranendonk M. J., Smithies R. H., Hickman A. H., Wingate M. T. D. and Bodorkos S. (2010) Evidence for Mesoarchean (~3.2 Ga) rifting of the Pilbara Craton: The missing link in an early Precambrian Wilson cycle. *Precambrian Res.* 177, 145–161. Available at: https://doi.org/10.1016/j.precamres.2009.11.007.
- Van Kranendonk M. J., Kirkland C. L. and Cliff J. (2015) Oxygen isotopes in Pilbara Craton zircons support a global increase in crustal recycling at 3.2Ga. *Lithos* 228– 229, 90–98. Available at: https://doi.org/10.1016/j.lithos.2015.04.011.
- Van Kranendonk M. J., Philippot P., Lepot K., Bodorkos S. and Pirajno F. (2008) Geological setting of Earth's oldest fossils in the ca. 3.5 Ga Dresser Formation, Pilbara Craton, Western Australia. *Precambrian Res.* 167, 93–124. Available at: https://doi.org/10.1016/j.precamres.2008.07.003.
- Van Kranendonk M. J., Smithies R. H. and Champion D. C. (2019) Paleoarchean development of a continental nucleus: The East Pilbara Terrane of the Pilbara Craton, Western Australia. *Earth's Oldest Rocks*, 437–462. Available at: https://doi.org/10.1016/B978-0-444-63901-1.00019-8.
- Van Kranendonk M. J., Webb G. E. and Kamber B. S. (2003) Geological and trace element evidence for a marine sedimentary environment of deposition and biogenicity of 3.45 Ga stromatolitic carbonates in the Pilbara Craton, and support for a reducing Archaean ocean. *Geobiology* 1, 91–108. Available at: https://doi.org/10.1046/j.1472-4669.2003.00014.x.
- Veizer J. (1989) Strontium isotopes in seawater through time. Annu. Rev. Earth Planet. Sci. 17, 141–167. Available at: https://doi.org/10.1146/annurev.ea.17.050189.001041.
- Veizer J. and Compston W. (1976) ⁸⁷Sr/⁸⁶Sr in Precambrian carbonates as an index of crustal evolution. *Geochim. Cosmochim. Acta* **40**, 905–914. Available at: https://doi.org/10.1016/0016-7037(76)90139-3.
- Veizer J., Hoefs J., Lowe D. R. and Thurston P. C. (1989b) Geochemistry of Precambrian carbonates: II. Archean greenstone belts and Archean sea water. *Geochim. Cosmochim. Acta* 53, 859–871. Available at: https://doi.org/10.1016/0016-7037(89)90031-8.
- Veizer J., Hoefs J., Ridler R. H., Jensen L. S. and Lowe D. R. (1989a) Geochemistry of Precambrian carbonates: I. Archean hydrothermal systems. *Geochim. Cosmochim. Acta* 53, 845–857. Available at: https://doi.org/10.1016/0016-7037(89)90030-6.
- Vervoort J. D. and Blichert-Toft J. (1999) Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. *Geochim. Cosmochim. Acta* **63**, 533–

556. Available at: https://doi.org/10.1016/S0016-7037(98)00274-9.

- Vervoort J. D. and Kemp A. I. S. (2016) Clarifying the zircon Hf isotope record of crust-mantle evolution. *Chem. Geol.* 425, 65–75. Available at: https://doi.org/10.1016/j.chemgeo.2016.01.023.
- Vervoort J. D., White W. M. and Thorpe R. I. (1994) Nd and Pb isotope ratios of the Abitibi greenstone belt: new evidence for very early differentiation of the Earth. *Earth Planet. Sci. Lett.* **128**, 215–229. Available at: https://doi.org/10.1016/0012-821X(94)90146-5.
- Viehmann S., Bau M., Bühn B., Dantas E. L., Andrade F. R. D. and Walde D. H. G. (2016) Geochemical characterisation of Neoproterozoic marine habitats: Evidence from trace elements and Nd isotopes in the Urucum iron and manganese formations, Brazil. *Precambrian Res.* 282, 74–96. Available at: https://doi.org/10.1016/j.precamres.2016.07.006.
- Viehmann S., Bau M., Hoffmann J. E. and Münker C. (2015) Geochemistry of the Krivoy Rog Banded Iron Formation, Ukraine, and the impact of peak episodes of increased global magmatic activity on the trace element composition of Precambrian seawater. *Precambrian Res.* 270, 165–180. Available at: https://doi.org/10.1016/j.precamres.2015.09.015.
- Viehmann S., Hoffmann J. E., Münker C. and Bau M. (2014) Decoupled Hf-Nd isotopes in Neoarchean seawater reveal weathering of emerged continents. *Geology* **42**, 115–118. Available at: https://doi.org/10.1130/G35014.1.
- Viehmann S., Reitner J., Tepe N., Hohl S. V., Van Kranendonk M., Hofmann T., Koeberl C. and Meister P. (2020) Carbonates and cherts as archives of seawater chemistry and habitability on a carbonate platform 3.35 Ga ago: Insights from Sm/Nd dating and trace element analysis from the Strelley Pool Formation, Western Australia. *Precambrian Res.* 344, 105742. Available at: https://doi.org/10.1016/j.precamres.2020.105742.
- Wacey D. (2010) Stromatolites in the ~3400 Ma Strelley Pool Formation, Western Australia: Examining biogenicity from the macro- to the nano-scale. *Astrobiology* 10, 381–395. Available at: https://doi.org/10.1089/ast.2009.0423.
- Walker J. C. G. (1985) Carbon dioxide on the early Earth. *Orig. Life Evol. Biosph.* **16**, 117–127. Available at: https://doi.org/10.1007/BF01809466.
- Wasserburg G. J. and DePaolo D. J. (1979) Models of earth structure inferred from neodymium and strontium isotopic abundances. *Proc. Natl. Acad. Sci.* **76**, 3594–3598. Available at: https://doi.org/10.1073/pnas.76.8.3594.
- Webb G. E. and Kamber B. S. (2010) On: Golding, S.D. (Ed.), Trace element geochemistry as a tool for interpreting microbialites. *Earliest Life Earth Habitats, Environ. Methods Detect.*, 127. Available at: https://doi.org/ 10.1007/978-90-481-8794-2_6.
- Webb G. E. and Kamber B. S. (2000) Rare earth elements in Holocene reefal microbialites: A new shallow seawater proxy. *Geochim. Cosmochim. Acta* 64, 1–9. Available at: https://doi.org/10.1016/S0016-7037(99)00400-7.

- Weyer S., Münker C., Rehkämper M. and Mezger K. (2002) Determination of ultra-low Nb, Ta, Zr and Hf concentrations and the chondritic Zr/Hf and Nb/Ta ratios by isotope dilution analyses with multiple collector ICP-MS. *Chem. Geol.* **187**, 295– 313. Available at: https://doi.org/10.1016/S0009-2541(02)00129-8.
- Wharton M. R., Hathway B. and Colley H. (1994) Volcanism associated with extension in an Oligocene-Miocene arc, southwestern Viti Levu, Fiji. *Geol. Soc. Spec. Publ.* 81, 95–114. Available at: https://doi.org/10.1144/GSL.SP.1994.081.01.06.
- Whelan P. M., Gill J. B., Kollman E., Duncan R. A. and Drake R. E. (1985)
 Radiometric dating of magmatic stages in Fiji. In Scholl, D.W., Vallier, T.L. (Eds.), Geology and offshore resources of Pacific island arcs; Tonga region, pp. 451–440.
- White W. M. (1993) 238U/204Pb in MORB and open system evolution of the depleted mantle. *Earth Planet. Sci. Lett.* **115**, 211–226. Available at: https://doi.org/10.1016/0012-821X(93)90223-V.
- Whitehouse M. J., Kamber B. S., Fedo C. M. and Lepland A. (2005) Integrated Pb- and S-isotope investigation of sulphide minerals from the early Archaean of southwest Greenland. *Chem. Geol.* 222, 112–131. Available at: https://doi.org/10.1016/j.chemgeo.2005.06.004.
- Whyatt L., Peters S., Pack A., Kirkland C. L., Balic-Zunic T. and Szilas K. (2020) Metasomatic reactions between archean dunite and trondhjemite at the seqi olivine mine in greenland. *Minerals* 10. Available at: https://doi.org/10.3390/min10010085.
- Wilde S. A., Valley J. W., Peck W. H. and Graham C. M. (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* **409**, 175–178. Available at: https://doi.org/10.1038/35051550.
- Willbold M., Hegner E., Stracke A. and Rocholl A. (2009) Continental geochemical signatures in dacites from Iceland and implications for models of early Archaean crust formation. *Earth Planet. Sci. Lett.* **279**, 44–52. Available at: https://doi.org/10.1016/j.epsl.2008.12.029.
- Wilson A. H., Shlrey S. B. and Carlson R. W. (2003) Archaean ultra-depleted komatiites formed by hydrous melting of cratonic mantle. *Nature* **423**, 858–861. Available at: https://doi.org/10.1038/nature01701.
- Windley B. F. (1986) The continental crust: its composition and evolution. *Phys. Earth Planet. Inter.* 42, 196–197. Available at: https://doi.org/10.1016/0031-9201(86)90093-2.
- Windley B. F., Kusky T. and Polat A. (2021) Onset of plate tectonics by the Eoarchean. *Precambrian Res.* 352, 105980. Available at: https://doi.org/10.1016/j.precamres.2020.105980.
- Wingate M. T. D. (1999) Ion microprobe baddeleyite and zircon ages for Late Archaean mafic dykes of the Pilbara Craton, Western Australia. *Aust. J. Earth Sci.* 46, 493– 500. Available at: https://doi.org/10.1046/j.1440-0952.1999.00726.x.

- Wingate M. T. D., Bodorkos S. and Van Kranendonk M. J. (2009) 178185: Gabbro sill, Sulphur Springs 804. *Geol. Surv. West. Aust.*, 4 p.
- de Wit M. J. (1998) On Archean granites, greenstones, cratons and tectonics: does the evidence demand a verdict? *Precambrian Res.* **91**, 181–226. Available at: https://doi.org/10.1016/S0301-9268(98)00043-6.
- Wood B. J. and Halliday A. N. (2005) Cooling of the Earth and core formation after the giant impact. *Nature* **437**, 1345–1348. Available at: https://doi.org/10.1038/nature04129.
- Wooden J. L. and Mueller P. A. (1988) Pb, Sr, and Nd isotopic compositions of a suite of Late Archean, igneous rocks, eastern Beartooth Mountains: implications for crust-mantle evolution. *Earth Planet. Sci. Lett.* 87, 59–72. Available at: https://doi.org/10.1016/0012-821X(88)90064-7.
- Woolnough W. G. (1903) The continental origin of Fiji. In *Proceedings of the Linnean Society of New South Wales*, pp. 457–540.
- Workman R. K. and Hart S. R. (2005) Major and trace element composition of the depleted MORB mantle (DMM). *Earth Planet. Sci. Lett.* **231**, 53–72. Available at: https://doi.org/10.1016/j.epsl.2004.12.005.
- Yakymchuk C., Kirkland C. L., Hollis J. A., Kendrick J., Gardiner N. J. and Szilas K. (2020) Mesoarchean partial melting of mafic crust and tonalite production during high-T–low-P stagnant tectonism, Akia Terrane, West Greenland. *Precambrian Res.* 339, 105615. Available at: https://doi.org/10.1016/j.precamres.2020.105615.
- Yamamoto K., Itoh N., Matsumoto T., Tanaka T. and Adachi M. (2004) Geochemistry of Precambrian carbonate intercalated in pillows and its host basalt: Implications for the REE composition of circa 3.4 Ga seawater. *Precambrian Res.* 135, 331– 344. Available at: https://doi.org/10.1016/j.precamres.2004.09.006.
- Zartman R. E. and Richardson S. H. (2005) Evidence from kimberlitic zircon for a decreasing mantle Th/U since the Archean. *Chem. Geol.* **220**, 263–283. Available at: https://doi.org/10.1016/j.chemgeo.2005.04.003.
- Zhang C., Holtz F., Koepke J., Wolff P. E., Ma C. and Bédard J. H. (2013) Constraints from experimental melting of amphibolite on the depth of formation of garnet-rich restites, and implications for models of Early Archean crustal growth. *Precambrian Res.* 231, 206–217. Available at: https://doi.org/10.1016/j.precamres.2013.03.004.
- Zhang J. B., Liu Y. S., Ducea M. N. and Xu R. (2020) Archean, highly unradiogenic lead in shallow cratonic mantle. *Geology* **48**, 584–588. Available at: https://doi.org/10.1130/G47064.1.
- Zhang J. and Nozaki Y. (1996) Rare earth elements and yttrium in seawater: ICP-MS determinations in the East Caroline, Coral Sea, and South Fiji basins of the western South Pacific Ocean. *Geochim. Cosmochim. Acta* **60**, 4631–4644. Available at: https://doi.org/10.1016/S0016-7037(96)00276-1.
- Zhao J. H. and Zhou M. F. (2008) Neoproterozoic adakitic plutons in the northern

margin of the Yangtze Block, China: Partial melting of a thickened lower crust and implications for secular crustal evolution. *Lithos* **104**, 231–248. Available at: https://doi.org/10.1016/j.lithos.2007.12.009.

Zindler A. and Hart S. (1986) Chemical geodynamics. *Ann. Re. Earth Planet. Sci.* **14**, 493–571. Available at: https://doi.org/10.1146/annurev.ea.14.050186.002425.

VI. APPENDIX

Appendix A

Table A1: Calculations for the ¹⁴³Nd/¹⁴⁴Nd isotope evolution for the primitive mantle⁴, depleted mantle⁵ and the respective PRIMA-normalized ϵ^{143} Nd⁶ with two different starting points, and the emergence of continental crust⁵ (see Fig. 1.11a). Initial ¹⁴⁷Sm/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd isotope composition for the primitive mantle is from Bouvier et al., (2008) and the decay constant of λ^{147} Sm = 6.54 × 10⁻¹² a⁻¹ (Lugmair and Marti, 1978) was used. The ¹⁴⁷Sm/¹⁴⁴Nd value for the depleted mantle is 0.220 (Workman and Hart, 2005) and for the Archean continental crust a ¹⁴⁷Sm/¹⁴⁴Nd = 0.1105 was used (Homeward Bound granite; Hasenstab et al., 2021).

	147Sm/144Nd	t (Ma)	4,560	4,200	3,700	3,400	3,000	2,500	0
primitive	0.196	143Nd/144Ndt	0.506697	0.507172	0.507829	0.508223	0.508747	0.509399	0.512630
mantle		$\epsilon^{\scriptscriptstyle 143}Nd_t$	0	0	0	0	0	0	0
depleted	0.220	$^{143}\mathrm{Nd}/^{144}\mathrm{Nd}_{\mathrm{t}}$		0.507172	0.507910	0.508352	0.508939	0.509672	0.513298
(4.2 Ga)		$\epsilon^{\scriptscriptstyle 143}Nd_t$		+0.00	+1.59	+2.53	+3.79	+5.35	+13.04
TTG	0.1105	$^{143}Nd/^{144}Nd_t$				0.508352	0.508647	0.509015	0.510836
extraction (3.4 Ga)		$\epsilon^{\scriptscriptstyle 143}Nd_t$				2.53	-1.96	-7.54	-34.99
depleted	0.220	$^{143}Nd/^{144}Nd_t$			0.507829	0.508271	0.508859	0.509591	0.513218
mantle (3.7 Ga)		$\epsilon^{\rm 143} Nd_t$			0	+0.95	+2.21	+3.77	+11.47
TTG	0.1105	$^{143}Nd/^{144}Nd_t$				0.508271	0.508566	0.508934	0.510756
extraction (3.4 Ga)		$\epsilon^{\rm 143}Nd_t$				0.95	-3.54	-9.13	-36.56

⁴ The ${}^{143}Nd/{}^{144}Nd_t$ isotope composition at time *t* for the *primitive mantle* was calculated using the following equation:

$$\left(\frac{^{143}Nd}{^{144}Nd}\right)_{(PRIMA; t=i)} = \left(\frac{^{143}Nd}{^{144}Nd}\right)_{(PRIMA; t=0)} - \left(\left(\frac{^{147}Sm}{^{144}Nd}\right)_{(PRIMA; t=0)} \times \left(e^{(\lambda^{147}Sm \times (t=i))} - 1\right)\right)$$

⁵ The ¹⁴³Nd/¹⁴⁴Nd_t isotope compositions at time *t* for the respective reservoir x (= *depleted mantle; continental crust*) were calculated using the following equation:

$$\begin{pmatrix} \frac{143}{Nd} \\ \frac{144}{Nd} \end{pmatrix}_{(x;\,t=i)} = \begin{pmatrix} \frac{143}{Nd} \\ \frac{144}{Nd} \end{pmatrix}_{(source;\,t=extraction)} + \left(\begin{pmatrix} \frac{147}{M} \\ \frac{144}{Nd} \end{pmatrix}_{x} \times \left(e^{(\lambda^{147}Sm \times (t=extraction))} - 1 \right) \right)$$
$$- \left(\begin{pmatrix} \frac{147}{M} \\ \frac{144}{M} \\ \frac{144}{$$

⁶ The $\varepsilon^{143}Nd_t$ value for the respective reservoir x (= *primitive mantle; depleted mantle; continental crust*) relative to the primitive mantle at time t was calculated using the following equation:

$$\varepsilon^{143} N d_{(x;t=i)} = \left(\left(\left(\begin{pmatrix} \binom{143}{Nd} \\ \frac{144}{Nd} \end{pmatrix}_{(x;t=i)} \\ \binom{143}{Nd} \\ \binom{143}{N$$

Table A2: Uranium-Th-Pb and Sm-Nd isotope evolution calculations for the primitive mantle⁷ (blue line) and depleted mantle⁷ from the Pilbara Craton (red line in Fig. 1.12; green line in Fig. 1.13). The μ_1 -, ω_1 -, and κ_1 -values for the primitive mantle are from the Apex clinopyroxene separate, whereas ¹⁴⁷Sm/¹⁴⁴Nd = 0.196 and ¹⁴³Nd/¹⁴⁴Nd_(today) = 0.51630 are from Bouvier et al. (2008). Initial Pb isotope compositions were calculated with a ²³⁸U/²³⁵U = 137.88 and the respective decay constants of λ^{235} U = 9.849 × 10⁻¹⁰ a⁻¹, λ^{238} U = 1.551 × 10⁻¹⁰ a⁻¹ (Jaffey et al., 1971), and λ^{232} Th = 4.948 × 10⁻¹¹ a⁻¹ (le Roux and Glendenin, 1963).

			primitive mantle		
	μ_1	ω ₁	κ_1	143Sm/144Nd	
	8.46	43.15	5.10	0.196	-
t (Ma)	²⁰⁶ Pb/ ²⁰⁴ Pbt	²⁰⁷ Pb/ ²⁰⁴ Pbt	²⁰⁸ Pb/ ²⁰⁴ Pbt	143Nd/144Ndt	ϵ^{143} Nd _t
4560	9.307	10.293	29.475	0.506697	0
4500	9.466	10.607	29.635	0.506776	0
4400	9.727	11.091	29.901	0.506908	0
4300	9.985	11.529	30.166	0.507040	0
4200	10.239	11.927	30.430	0.507172	0
4100	10.489	12.287	30.692	0.507303	0
4000	10.735	12.613	30.953	0.507435	0
3900	10.977	12.909	31.212	0.507567	0
3800	11.215	13.177	31.470	0.507698	Õ
3700	11.450	13 420	31,727	0.507829	Õ
3600	11.681	13.640	31,983	0.507961	Ő
3500	11 909	13 839	32 238	0 508092	Ő
3400	12 133	14 020	32.290	0.508223	Ő
3300	12 354	14 184	32 743	0 508354	Ő
3200	12.551	14 332	32.993	0 508485	Ő
3100	12.371	14 467	33 243	0.508616	0
3000	12.705	14.589	33 491	0.508747	0
2900	13 203	14.509	33 738	0.508877	0
2900	13.203	14.000	33.084	0.500077	0
2800	13.407	14.799	34 229	0.509008	0
2700	13.008	14.070	34.229	0.509158	0
2500	14.001	14.972	34.472	0.509209	0
2300	14.001	15.047	34.055	0.509599	0
2400	14.195	15.114	35 105	0.509529	0
2300	14.568	15 231	35 /3/	0.509059	0
2200	14.508	15.231	35.434	0.509790	0
2000	14.731	15.201	25.071	0.509920	0
2000	14.932	15.320	26 142	0.510049	0
1900	15.109	15.306	30.143	0.510179	0
1700	15.204	15.405	30.370	0.510309	0
1600	15.450	15.439	26.009	0.510459	0
1500	15.020	15.470	27.071	0.510508	0
1300	15.795	15.497	27.201	0.510098	0
1400	15.957	15.525	27,500	0.510627	0
1300	16.119	15.540	31.329	0.510957	0
1200	10.278	15.300	37.730	0.511080	0
1000	10.455	15.585	37.982	0.511215	0
1000	10.369	15.002	30.207	0.511544	0
900	10./41	15.01/	38.431	0.511475	0
800	10.891	15.031	38.033	0.511002	0
/00	17.039	15.044	38.8/3 20.005	0.511/51	0
500	17.184	15.055	39.095	0.511839	0
500	17.327	15.000	39.315	0.511988	0
400	1/.46/	15.6/5	39.533	0.512117	0
300	17.606	15.684	39.750	0.512245	0
200	17.742	15.692	39.966	0.512373	0
100	1/.8//	15.699	40.181	0.512502	0
0	18.009	15.705	40.395	0.512630	0

⁷ The *Pb* isotope composition (x = 6; 7; 8) at time *t* for the *primitive mantle* was calculated using the following equation with:

$$\begin{pmatrix} 2^{0x}Pb\\ \hline 2^{04}Pb \end{pmatrix}_{(1;t)} = \begin{pmatrix} 2^{0x}Pb\\ \hline 2^{04}Pb \end{pmatrix}_{(t=0)} - \left((\mu_1; \omega_1; \kappa_1)_{(t=0)} \times \left(e^{\left((\lambda^{238}U; \lambda^{235}U; \lambda^{232}Th) \times t \right)} - 1 \right) \right)$$

		depleted mantle					
	μ_2	ω_2	κ_2	143Sm/144Nd	-		
	6.46	39.08	6.05	0.220			
t (Ma)	206Pb/204Pbt	207Pb/204Pbt	208Pb/204Pbt	143Nd/144Ndt	$\epsilon^{143}Nd_t$		
3800	11.215	13.177	31.470	0.507698	0.00		
3700	11.395	13.362	31.703	0.508142	+0.32		
3600	11.571	13.530	31.935	0.507993	+0.63		
3500	11.745	13.683	32.165	0.508140	+0.95		
3400	11.916	13.821	32.394	0.508287	+1.26		
3300	12.085	13.946	32.623	0.508434	+1.58		
3200	12.250	14.059	32.850	0.508581	+1.89		
3100	12.414	14.162	33.076	0.508728	+2.21		
3000	12.575	14.255	33.301	0.508875	+2.52		
2900	12.733	14.339	33.524	0.509022	+2.84		
2800	12.889	14.416	33.747	0.509168	+3.15		
2700	13.042	14.485	33.969	0.509315	+3.46		
2600	13.194	14.548	34.189	0.509461	+3.78		
2500	13.342	14.605	34.408	0.509607	+4.09		
2400	13.489	14.656	34.627	0.509754	+4.40		
2300	13.633	14.703	34.844	0.509900	+4.71		
2200	13.775	14.745	35.060	0.510046	+5.02		
2100	13.915	14.784	35.275	0.510192	+5.33		
2000	14.053	14.818	35.489	0.510337	+5.65		
1900	14.189	14.850	35.702	0.510483	+5.96		
1800	14.322	14.878	35,914	0.510629	+6.27		
1700	14.454	14.904	36.125	0.510774	+6.57		
1600	14.583	14.928	36.335	0.510920	+6.88		
1500	14.710	14.949	36.543	0.511065	+7.19		
1400	14.836	14.968	36.751	0.511210	+7.50		
1300	14.959	14.986	36.958	0.511356	+7.81		
1200	15.081	15.001	37.163	0.511501	+8.12		
1100	15.201	15.016	37.368	0.511646	+8.42		
1000	15.319	15.029	37.572	0.511790	+8.73		
900	15 435	15.040	37.774	0.511935	+9.04		
800	15.549	15.051	37.976	0.512080	+9.34		
700	15.662	15.061	38,177	0.512224	+9.65		
600	15.773	15.070	38.377	0.512369	+9.96		
500	15.882	15.077	38,575	0.512513	+10.26		
400	15,989	15.085	38,773	0.512658	+10.57		
300	16.095	15.000	38,970	0.512802	+10.87		
200	16,199	15.097	39,165	0.512946	+11.17		
100	16 302	15.102	39 360	0.513090	+11.48		
0	16 403	15 107	39 554	0.513234	+11 78		

Table A2: (continued). Calculated upper mantle depletion⁸ starts at 3.8 Ga using μ_2 -, ω_2 -, and κ_2 -values from the Dalton Suite clinopyroxene separate. Depleted mantle ¹⁴⁷Sm/¹⁴⁴Nd of 0.220 is from Workman and Hart (2005).

⁸ The *Pb* isotope composition (x = 6; 7; 8) at time *t* for the *depleted mantle* was calculated using the following equation with:

$$\begin{pmatrix} \frac{2^{0x}Pb}{2^{04}Pb} \end{pmatrix}_{(2;(t=i))} = \begin{pmatrix} \frac{2^{0x}Pb}{2^{04}Pb} \end{pmatrix}_{(1;t=3.8\,Ga)} \\ + \left((\mu_2;\omega_2;\kappa_2) \times \left(e^{\left((\lambda^{238}U;\lambda^{235}U;\lambda^{232}Th) \times (t=3.8Ga) \right)} - 1 \right) \right) \\ - \left((\mu_2;\omega_2;\kappa_2) \times \left(e^{\left((\lambda^{238}U;\lambda^{235}U;\lambda^{232}Th) \times (t=i) \right)} - 1 \right) \right)$$

	ĺ		Depleted r	mantle		
					ω ₂	ω ₂
					20	60
	Ļ	12	μ	12	κ ₂	κ ₂
	3.	00	9.	.00	3.10	9.29
t (Ma)	206Pb/204Pbt	207Pb/204Pbt	206Pb/204Pbt	207Pb/204Pbt	208Pb/204Pbt	208Pb/204Pbt
3800	11.215	13.177	11.215	13.177	31.470	31.470
3700	11.298	13.263	11.465	13.435	31.589	31.828
3600	11.380	13.341	11.711	13.669	31.708	32.183
3500	11.461	13.412	11.953	13.882	31.826	32.537
3400	11.541	13.476	12.192	14.074	31.943	32.889
3300	11.619	13.534	12.426	14.248	32.060	33.239
3200	11.696	13.587	12.657	14.406	32.176	33.588
3100	11.772	13.634	12.885	14.549	32.292	33.935
3000	11.847	13.678	13.109	14.679	32.407	34.280
2900	11.920	13.717	13.330	14.796	32.521	34.624
2800	11.992	13.752	13.547	14.903	32.635	34.965
2700	12.064	13.784	13.761	14.999	32.749	35.306
2600	12.134	13.814	13.971	15.087	32.861	35.644
2500	12.203	13.840	14.179	15.166	32.974	35.981
2400	12.271	13.864	14.383	15.238	33.085	36.316
2300	12.338	13.886	14.584	15.303	33.197	36.649
2200	12.404	13.905	14.782	15.362	33.307	36.981
2100	12.469	13.923	14.977	15.415	33.417	37.311
2000	12.533	13.939	15.169	15.464	33.527	37.640
1900	12.596	13.954	15.358	15.508	33.636	37.967
1800	12.658	13.967	15.544	15.547	33.744	38.292
1700	12.719	13.979	15.727	15.583	33.852	38.616
1600	12.779	13.990	15.907	15.616	33.959	38.938
1500	12.838	14.000	16.085	15.646	34.066	39.258
1400	12.897	14.009	16.260	15.672	34.173	39.577
1300	12.954	14.017	16.432	15.697	34.278	39.895
1200	13.011	14.024	16.601	15.719	34.384	40.210
1100	13.066	14.031	16.768	15.739	34.488	40.525
1000	13.121	14.037	16.932	15.757	34.593	40.837
900	13.175	14.042	17.094	15.773	34.696	41.149
800	13.228	14.047	17.253	15.788	34.799	41.458
700	13.280	14.052	17.410	15.801	34.902	41.766
600	13.332	14.056	17.565	15.814	35.004	42.073
500	13.382	14.060	17.717	15.825	35.106	42.378
400	13.432	14.063	17.866	15.835	35.207	42.681
300	13.481	14.066	18.014	15.844	35.308	42.983
200	13.530	14.069	18.159	15.852	35.408	43.284
100	13.577	14.071	18.302	15.860	35.508	43.583
0	13.624	14.073	18.443	15.866	35.607	43.881

Table A2: (continued). Calculated upper mantle depletion starts at 3.8 Ga using a lower limit for $\mu_2 = 3.0$ and an upper limit of $\mu_2 = 9.0$, suggesting extreme and no U/Pb fractionation by partial melting of the upper mantle, respectively (Fig. 1.13c). Variation in ω_2 - and κ_2 -values are relative to a fixed $\mu_2 = 6.46$ (Fig. 1.13d).

Table A3: Alternative U-Th-Pb evolution calculation for the primitive mantle using the conditions, reported
by Maltese and Mezger (2020), suggesting the start of the Pb evolution after the Moon forming impact (at
4,491 Ma). Used μ_1 -, ω_1 -, and κ_1 -values are also from Maltese and Mezger (2020).

	I	primitive mantle	
	μ1		κ_1
	8.63	34.95	4.05
t (Ma)	²⁰⁶ Pb/ ²⁰⁴ Pbt	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
4491	9.345	10.370	29.510
4400	9.588	10.817	29.706
4300	9.851	11.264	29.921
4200	10.110	11.670	30.134
4100	10.364	12.037	30.346
4000	10.615	12.370	30.558
3900	10.862	12.672	30.768
3800	11.106	12.945	30.977
3700	11.345	13.193	31.185
3600	11.581	13.417	31.392
3500	11.813	13.621	31.598
3480	11.859	13.659	31.640
3300	12.267	13.972	32.008
3200	12.489	14.124	32.211
3100	12.707	14.261	32.413
3000	12.922	14.385	32.614
2900	13.133	14.498	32.814
2800	13.341	14.600	33.013
2700	13.547	14.692	33.211
2600	13.749	14.776	33.408
2500	13.947	14.852	33.605
2400	14.143	14.921	33.800
2300	14.336	14.984	33.994
2200	14.526	15.040	34.187
2100	14.713	15.091	34.380
2000	14.897	15.138	34.571
1900	15.078	15.180	34.761
1800	15.256	15.218	34.951
1700	15.432	15.253	35.139
1600	15.605	15.284	35.327
1500	15.775	15.312	35.514
1400	15.943	15.338	35.700
1300	16.108	15.361	35.884
1200	16.270	15.382	36.068
1100	16.430	15.402	36.251
1000	16.588	15.419	36.434
900	16.743	15.435	36.615
800	16.896	15.449	36.795
700	17.046	15.462	36.975
600	17.194	15.473	37.153
500	17.340	15.484	37.331
400	17.483	15.494	37.508
300	17.625	15.502	37.684
200	17.764	15.510	37.859
100	17.901	15.517	38.033
0	18.036	15.524	38.206

Table A4: Uranium-Th-Pb isotope evolution calculations for the primitive mantle (blue line) and depleted mantle for the SUC (red line in Fig. 1.15a; red area in Fig. 1.15b) using μ_{1-} , ω_{1-} , and κ_1 -values for the primitive mantle from Maltese and Mezger (2020) and μ_2 -value for the depleted mantle inferred from the Pilbara Craton (Apex Basalt clinopyroxene) with an upper κ_2 -value of 5 and a lower limit $\kappa_2 = 3$.

	primitive mantle		depleted mantle with higher κ_2			Depleted mantle with lower κ_2			
	μ1	ω ₁	κ ₁	μ ₂	ω ₂	κ ₂	μ ₂	ω ₂	κ ₂
	8.63	34.95	4.05	6.60	33.00	5.00	6.60	19.80	3.00
t (Ma)	²⁰⁶ Pb/ ²⁰⁴ Pb _t	$^{207}Pb/^{204}Pb_{t}$	²⁰⁸ Pb/ ²⁰⁴ Pb _t	²⁰⁶ Pb/ ²⁰⁴ Pb _t	$^{207}\text{Pb}/^{204}\text{Pb}_{t}$	²⁰⁸ Pb/ ²⁰⁴ Pb _t	$^{206}Pb/^{204}Pb_{t}$	207 Pb/ 204 Pb _t	208 Pb/ 204 Pb _t
4560	9.307	10.293	29.475						
4450	9.603	10.866	29.713						
4400	9.736	11.107	29.820						
4300	9.999	11.554	30.035						
4200	10.257	11.960	30.248	10.257	11.960	30.248	10.257	11.960	30.248
4100	10.512	12.327	30.460	10.452	12.241	30.449	10.452	12.241	30.368
4000	10.763	12.660	30.672	10.644	12.495	30.648	10.644	12.495	30.488
3900	11.010	12.962	30.882	10.833	12.726	30.847	10.833	12.726	30.607
3800	11.254	13.235	31.091	11.019	12.935	31.044	11.019	12.935	30.726
3700	11.493	13.483	31.299	11.202	13.124	31.241	11.202	13.124	30.844
3600	11.729	13.707	31.507	11.383	13.296	31.436	11.383	13.296	30.961
3500	11.961	13.911	31.713	11.560	13.452	31.631	11.560	13.452	31.078
3400	12.190	14.095	31.918	11.735	13.593	31.825	11.735	13.593	31.194
3300	12.415	14.262	32.122	11.907	13.720	32.017	11.907	13.720	31.310
3200	12.637	14.413	32.325	12.077	13.836	32.209	12.077	13.836	31.425
3100	12.855	14.551	32.527	12.244	13.941	32.400	12.244	13.941	31.539
2977	13.076	14.678	32.734	12.446	14.057	32.633	12.446	14.057	31.679

Table A5: U-Th-Pb isotope evolution calculations of the modern Earth's mantle (Fig. 1.16). Primitive mantle (blue line) is calculated in Table A2. Calculated depletion of the upper mantle starts at 3.8 and Pb isotope variations are calculated with μ_2 -, ω_2 -, and κ_2 -values from different clinopyroxene separates from the Pilbara Craton (red area). With the oxygenation of the oceans and atmosphere after the GOE (2.4 Ga; Lyons et al., 2014), highly oxidized U⁶⁺ is preferentially reintroduced into the mantle by subduction, changing the μ_3 - and κ_3 -values of the depleted mantle (green areas) to present values (White, 1993).

	> 2.4 Ga	depleted mantle	(reduced)	< 2.4 Ga depleted mantle (oxidized)			
	μ_2	ω ₂	κ ₂	μ ₃	ω3	κ ₃	
	5.64	15.85	2.81	11.2	29.90	2.67	
t (Ma)	²⁰⁶ Pb/ ²⁰⁴ Pb _t	²⁰⁷ Pb/ ²⁰⁴ Pb _t	²⁰⁸ Pb/ ²⁰⁴ Pb _t	²⁰⁶ Pb/ ²⁰⁴ Pb _t	²⁰⁷ Pb/ ²⁰⁴ Pb _t	²⁰⁸ Pb/ ²⁰⁴ Pb _t	
4560		-	-	-			
4500							
4400							
4300							
4200							
4100							
4000							
3900							
3800	11.215	13.177	31.470				
3700	11.372	13.339	31.565				
3600	11.526	13.486	31.658				
3500	11.678	13.619	31.752				
3400	11.827	13.739	31.845				
3300	11.974	13.848	31.938				
3200	12.119	13.947	32.030				
3100	12.262	14.037	32.121				
3000	12.402	14.118	32.212				
2900	12.540	14.192	32.303				
2800	12.676	14.258	32.393				
2700	12.811	14.319	32.483				
2600	12.942	14.374	32.573				
2500	13.072	14.423	32.662				
2400	13.200	14.468	32.750	13.200	14.468	32.750	
2300	13.326	14.509	32.838	13.326	14.509	32.838	
2200	13.450	14.546	32.926	13.450	14.546	32.926	
2100	13.573	14.580	33.013	13.573	14.580	33.013	
2000	13.693	14.610	33.100	13.693	14.610	33.100	
1900	13.811	14.637	33.186	13.811	14.637	33.186	
1800	13.928	14.662	33.272	13.928	14.662	33.272	
1700	14.043	14.685	33.358	14.043	14.685	33.358	
1600	14.156	14.705	33.443	14.156	14.705	33.443	
1500	14.267	14.724	33.527	14.267	14.724	33.527	
1400	14.376	14.741	33.612	14.376	14.741	33.612	
1300	14.484	14.756	33.695	14.484	14.756	33.695	
1200	14.590	14.770	33.779	14.590	14.770	33.779	
1100	14.695	14.782	33.862	14.695	14.782	33.862	
1000	14.798	14.794	33.944	14.798	14.794	33.944	
900	14.899	14.804	34.027	14.899	14.804	34.027	
800	14.999	14.815	34.108	14.999	14.815	34.108	
700	15.097	14.822	34.190	15.097	14.822	54.190 24.271	
500	15.194	14.829	34.271	15.194	14.829	34.271	
400	15.290	14.000	24.331	15.290	14.030	24.331	
400	15.383	14.843	34.431	15.383	14.843	34.431 34.511	
200	15.470	14.040	24.511	15.470	14.040	24.511	
200	15.507	14.000	34.391	15.507	14.033	34.391	
100	15.050	14.000	24.070	15.030	14.030	24.070	
U	13./44	14.802	34./48	13./44	14.802	34.748	

Table A5: (continued).

	> 2.4	4 Ga depleted ma	antle	< 2.	4 Ga depleted ma	ntle
	μ_2	ω ₂	κ ₂	μ_3	ω ₃	κ ₃
	6.60	39.60	6.00	11.2	29.90	2.67
t (Ma)	²⁰⁶ Pb/ ²⁰⁴ Pb _t	²⁰⁷ Pb/ ²⁰⁴ Pb _t	²⁰⁸ Pb/ ²⁰⁴ Pb _t	²⁰⁶ Pb/ ²⁰⁴ Pb _t	²⁰⁷ Pb/ ²⁰⁴ Pb _t	²⁰⁸ Pb/ ²⁰⁴ Pb _t
4560						
4500						
4400						
4300						
4200						
4100						
4000						
3900						
3800	11.215	13.177	31.470			
3700	11.398	13.366	31.706			
3600	11.579	13.538	31.941			
3500	11.756	13.694	32.174			
3400	11.931	13.835	32.407			
3300	12.103	13.962	32.638			
3200	12.273	14.078	32.868			
3100	12.440	14.183	33.097			
3000	12.604	14.278	33.325			
2900	12.766	14.364	33.551			
2800	12.925	14.443	33.777			
2700	13.082	14.513	34.002			
2600	13.236	14.577	34.225			
2500	13.389	14.636	34.447			
2400	13.538	14.688	34.668	13.538	14.688	34.668
2300	13.686	14.736	34.888	13.788	14.769	34.835
2200	13.831	14.779	35.107	14.035	14.843	35.000
2100	13.974	14.818	35.325	14.277	14.909	35.164
2000	14.114	14.854	35.542	14.516	14.969	35.328
1900	14.253	14.886	35.758	14.751	15.024	35.491
1800	14.389	14.915	35.973	14.983	15.073	35.653
1700	14.524	14.942	36.186	15.211	15.118	35.814
1600	14.656	14.966	36.399	15.435	15.159	35.975
1500	14.786	14.987	36.610	15.656	15.196	36.135
1400	14.914	15.007	36.821	15.874	15.229	36.294
1300	15.041	15.025	37.030	16.088	15.259	36.452
1200	15.165	15.041	37.239	16.299	15.287	36.609
1100	15.287	15.056	37.446	16.506	15.312	36.766
1000	15.408	15.069	37.653	16.711	15.334	36.922
900	15.526	15.081	37.858	16.912	15.355	37.077
800	15.643	15.092	38.062	17.110	15.373	37.231
700	15.758	15.102	38.266	17.306	15.390	37.384
600	15.872	15.111	38.468	17.498	15.405	37.537
500	15.983	15.119	38.669	17.687	15.419	37.689
400	16.093	15.126	38.870	17.873	15.431	37.840
300	16.201	15.133	39.069	18.057	15.442	37.991
200	16.307	15.139	39.267	18.237	15.453	38.141
100	16.412	15.144	39.465	18.415	15.462	38.290
0	16.515	15.149	39.661	18.590	15.470	38.438

Appendix B



Figure B1: Shale-normalized (Ce/Ce*)_{SN} vs. $(Pr/Pr*)_{SN}$ ratios of the two carbonate groups and associated mafic rocks, Strelley Pool stromatolites and Archean shales from the Pilbara Craton (Nakamura and Kato, 2002; Van Kranendonk et al., 2003; Yamamoto et al., 2004; Allwood et al., 2006; Viehmann et al., 2020; Hasenstab et al., 2021; Tusch et al., 2021). Low-Mn Type II carbonates generally overlap with the Strelley Pool stromatolites, suggesting a strong seawater influence, whereas Type I carbonates show an intermediate composition between stromatolites and host rocks.



Figure B2: Initial ⁸⁷Sr/⁸⁶Sr vs. stable $\delta^{18}O_{VSMOW2}$ showing only small variations of the Euro Type II carbonates, whereas small variations are visible in $\delta^{18}O$. Meteoric water alteration would change the Sr isotope composition of the coexisting carbonate to radiogenic values and simultaneously to lighter $\delta^{18}O$. This is not applicable for any carbonate of this study. Radiogenic decay of ⁸⁷Rb to ⁸⁷Sr in a closed system, however, increases the Sr isotope composition of the carbonates without changing the $\delta^{18}O$. A positive covariation to lower Sr and O isotopes would suggest increasing influx of mantle derived fluids or fluid-rock interaction. This is not visible for the well-preserved Type II carbonates, but cannot be excluded for the Type I carbonates. Here however, radiogenic decay of ⁸⁷Rb obscured the initial Sr isotope composition.

Туре	High-Mn Type I					
Sample ID	Pil16-004	13613	Pil16-006	Pil16-006	Pil17-008d	Pil-17-008d
Formation	Euro	Euro	Euro	Euro	Euro	Euro
Age (Ma)	3340	3340	3340	3340	3340	3340
Latitude	21°21.407' S		21°21.407' S	21°21.407' S	21°21.407' S	21°21.407' S
Longitude	119°30.734' E		119°30.734' E	119°30.734' E	119°30.734' E	119°30.734' E
Rock type	calcite	ankerite	calcite	residue	calcite	quartz
SiO ₂ (wt.%)	0.00	8.40	1.15	-	0.92	99.18
Al ₂ O ₃ (wt.%)	0.02	0.01	0.02	-	0.02	0.00
FeO* (wt.%)	1.16	4.49	0.98	-	1.24	0.06
MnO (wt.%)	1.81	0.57	0.98	-	1.91	0.01
MgO (wt.%)	0.54	15.72	1.74	-	0.63	0.00
CaO (wt.%)	62.47	30.19	52.54	-	60.17	0.24
Na ₂ O (wt.%)	0.04	0.03	0.05	-	0.03	0.00
K ₂ O (wt.%)	0.00	0.00	0.00	-	0.00	0.00
Ca (ppm)	446492	215784	375485	-	430020	1715
Mn (ppm)	14018	4383	7620	-	14790	46.4
Al (ppm)	105	55.2	127	-	130	0.00
Fe (ppm)	8983	34877	7631	-	9632	435
Mg (ppm)	3286	94803	10509	-	3801	24.3
Na (ppm)	279	215	341	-	187	0.00
K (ppm)	313	240	382	-	209	0.00
Calcite (%)	94.44	61.68	93.58	-	93.84	-
Magnesite (%)	0.70	27.10	2.62	-	0.83	-
Siderite (%)	4.87	11.22	3.80	-	5.33	-
Li (ppm)	0.155	0.0335	0.186	-	0.144	1.78
Sc (ppm)	0.737	0.953	1.007	-	1.61	0.0127
Cr (ppm)	0.304	0.0783	0.190	-	0.935	0.0400
Mn (ppm)	11989	3127	10322	-	9146	12.8
Co (ppm)	0.611	0.523	0.770	-	0.612	0.0124
Ni (ppm)	3.72	21.6	7.26	-	6.39	0.276
Zn (ppm)	1.09	8.36	15.1	-	2.12	0.300
Rb (ppm)	0.0133	0.00135	0.0277	-	0.0196	3.11
Sr (ppm)	53.4	41.6	64.7	-	21.7	7.34
Y (ppm)	41.3	7.52	32.3	-	15.8	0.101
Zr (ppm)	0.00783	0.0114	0.0133	-	0.0128	0.0297
Mo (ppm)	0.179	0.0466	0.163	-	0.0102	0.00233
Cs (ppm)	0.00222	0.00287	0.00737	-	0.00441	0.0952
Ba (ppm)	19.4	1.10	43.2	-	2.31	6.40
La (ppm)	9.72	0.782	7.57	-	4.84	0.0659
Ce (ppm)	16.6	1.26	12.3	-	9.50	0.119
Pr (ppm)	1.72	0.152	1.40	-	1.11	0.0136
Nd (ppm)	6.43	0.763	5.68	-	4.46	0.0570
Sm (ppm)	1.58	0.234	1.52	-	1.06	0.0115
Eu (ppm)	0.614	0.0518	0.591	-	0.435	0.00596
Gd (ppm)	2.79	0.510	2.55	-	1.54	0.0130
Tb (ppm)	0.547	0.102	0.475	-	0.283	0.00207
Dy (ppm)	4.20	0.785	3.50	-	1.95	0.0131
Ho (ppm)	1.08	0.209	0.887	-	0.457	0.00282
Er (ppm)	3.66	0.659	2.84	-	1.46	0.00925
Tm (ppm)	0.583	0.101	0.447	-	0.233	0.00141
Yb (ppm)	3.91	0.675	2.81	-	1.59	0.0105
Lu (ppm)	0.631	0.117	0.460	-	0.263	0.00209
Pb (ppm)	0.218	0.337	0.218	-	0.111	0.0583
Th (ppm)	0.00217	0.000535	0.00140	-	0.00286	0.000988
U (ppm)	0.000634	0.00828	0.00323	-	0.00465	0.00167
ΣREE (ppm)	54.1	6.40	43.1	-	29.2	0.327
Y/Ho	38.4	36.0	36.5	-	34.5	35.7
Sm/Yb	0.405	0.346	0.539	-	0.668	1.098
Eu/Sm	0.388	0.222	0.390	-	0.409	0.519
La/La* _{CI}	1.45	1.97	1.52	-	1.20	1.40
Ce/Ce* _{SN}	0.927	0.839	0.870	-	0.944	0.915
Eu/Eu [*] SN	1.34	0.671	1.42	-	1.62	2.43
Pr/Pr* _{SN}	0.979	0.900	0.980	-	1.00	0.972

Table B1: Major (Micro-Probe), minor and trace element (ICP-MS) data for the interstitial carbonates, quartz, and certified reference material (JDo1). Normalization values by Taylor and McLennan (1985).

Table B1: (continued).

Type	High-Mn Type I					
Sample ID	Pil16-022b	Pil16-022b	13643	13643	13643	Pil17-002
Formation	Apex	Apex	Apex	Apex	Apex	Apex
Age (Ma)	3465	3465	3465	3465	3465	3465
Latitude	21°10.624' S	21°10.624' S				21°10.624' S
Longitude	119°41.762' E	119°41.762' E				119°41.762' E
Rock type	calcite	residue	calcite	ankerite	residue	calcite
SiO ₂ (wt.%)	1.76	-	5.89	0.00	-	0.00
Al ₂ O ₃ (wt.%)	0.03	-	0.02	0.03	-	0.05
FeO* (wt.%)	0.09	-	1.28	3.39	-	0.28
MnO (wt.%)	0.09	-	0.70	1.35	-	0.42
MgO (wt.%)	0.04	-	4.42	17.47	-	0.30
CaO (wt.%)	55.26	-	44.01	33.81	-	50.20
Na_2O (wt.%)	0.03	-	0.04	0.02	-	0.06
K_2O (wt.%)	0.00	-	0.00	0.00	-	0.00
Ca (ppm)	394931	-	314529	241605	-	358/64
Mn (ppm)	/18	-	5424	10461	-	3254
AI (ppm)	183	-	131	145	-	264
Fe (ppm)	08/	-	9984	20387	-	2152
Mg (ppiii)	230	-	20039	103570	-	1655
K (ppm)	215	-	209	132	-	410
Calaita (%)	00.58	-	88.21	62.05	-	430
Magnesite (%)	99.38	-	7 47	02.93	-	98.02
Siderite (%)	0.07	-	1.47	9.60	-	1.48
Li (ppm)	1.24		0.452	7.00		0.393
Sc (ppm)	0.480		1.24			0.668
Cr (ppm)	11.4	-	2.24	-	_	0.000
Mn (nnm)	4097	-	7292	-	_	4699
Co (ppm)	4 95	-	2.05	-	_	0.854
Ni (ppm)	26.7	-	15.3	-	-	7.29
Zn (ppm)	6.90	-	32.4	-	-	6.16
Rb (ppm)	0.0907	-	0.0359	-	-	0.0156
Sr (ppm)	263	-	42.6	-	-	35.1
Y (ppm)	11.6	-	26.7	-	-	14.9
Zr (ppm)	0.0468	-	0.0254	-	-	0.00758
Mo (ppm)	0.0634	-	0.101	-	-	0.0725
Cs (ppm)	0.0159	-	0.0139	-	-	0.0341
Ba (ppm)	15.0	-	357	-	-	66.6
La (ppm)	1.65	-	4.80	-	-	0.689
Ce (ppm)	3.10	-	7.49	-	-	1.56
Pr (ppm)	0.444	-	0.818	-	-	0.262
Nd (ppm)	2.34	-	3.35	-	-	1.54
Sm (ppm)	0.688	-	0.972	-	-	0.617
Eu (ppm)	0.552	-	0.432	-	-	0.230
Ga (ppm) Th (nnm)	1.25	-	1./1	-	-	1.22
To (ppiii) Dy (ppm)	0.190	-	0.556	-	-	0.219
Ho (ppm)	0.301	-	2.00	-	-	0.382
Fr (ppm)	0.844	-	2 237	-	-	1.18
Tm (ppm)	0.109	-	0.359	-	_	0.169
Yh (ppm)	0.647	-	2.416	-	-	1.05
Lu (ppm)	0.101	-	0.398	-	-	0.188
Pb (ppm)	0.247	-	0.269	-	-	0.288
Th (ppm)	0.00525	-	0.00416	-	-	0.000624
U (ppm)	0.00330	-	0.00462	-	-	0.0000100
ΣREE (ppm)	13.5	-	28.6	-	-	10.9
Y/Ho Y/Ho	38.5	-	39.0	-	-	39.1
Sm/Yb	1.064	-	0.402	-	-	0.590
Eu/Sm	0.803	-	0.445	-	-	0.373
La/La* _{CI}	1.60	-	1.66	-	-	1.53
Ce/Ce* _{SN}	0.832	-	0.862	-	-	0.821
Eu/Eu* _{SN}	3.12	-	1.53	-	-	1.27
Pr/Pr* _{SN}	0.931	-	0.961	-	-	0.912

Table B1: (continued).

Туре	High-Mn Type I			Low-Mn Type II		
Sample ID	Pil17-002	14613	Pil16-051b	Pil16-005	Pil16-005	Pil17-008a
Formation	Apex	Mt. Ada	Honeyeater	Euro	Euro	Euro
Age (Ma)	3465	3475	3180	3340	3340	3340
Latitude	21°10.624' S	21°07.696' S	21°07.696' S	21°21.407' S	21°21.407' S	21°21.407' S
Longitude	119°41.762' E	119°12.319' E	119°12.319' E	119°30.734' E	119°30.734' E	119°30.734' E
Rock type	residue	calcite	calcite	calcite	calcite	calcite
SiO ₂ (wt.%)	-	0.06	0.04	1.12	-	0.00
Al_2O_3 (wt.%)	-	0.03	0.07	0.00	-	0.00
FeO* (wt.%)	-	1.43	0.17	2.48	-	0.02
MnO (wt.%)	-	1.08	0.46	2.17	-	0.00
MgO (wt.%)	-	0.28	0.04	1.06	-	0.03
CaO (wt.%)	-	59.51	51.13	57.69	-	61.13
Na_2O (wt.%)	-	0.05	0.06	0.03	-	0.01
K_2O (wt.%)	-	0.00	0.01	0.01	-	0.01
Ca (ppm)	-	425295	365429	412311	-	436865
Mn (ppm)	-	8397	3584	16842	-	23.0
Al (ppm)	-	152	353	18.2	-	23.2
Fe (ppm)	-	11150	1314	19278	-	168
Mg (ppm)	-	1699	234	6387	-	163
Na (ppm)	-	341	427	244	-	66.8
K (ppm)	-	382	4/8	2/3	-	/4./
Calcite (%)	-	95.24	98.62	90.65	-	99.92
Magnesite (%)	-	0.38	0.06	1.40	-	0.04
Siderite (%)	-	4.38	1.32	7.94	-	0.04
Li (ppm)	-	0.422	0.150	0.283	-	-
Sc (ppm)	-	1.54	1.33	0.405	-	-
Cr (ppm)	-	0.381	1.18	0.531	-	-
Mn (ppm)	-	8273	3927	4826	-	-
Co (ppm)	-	0.626	0.961	0.753	-	-
\mathbf{N} (ppin) \mathbf{Z} n (ppin)	-	5.65 2.52	2.00	2.057	-	-
Zli (ppili) Ph (ppm)	-	2.32	2.08	2.037	-	-
Sr (ppm)	-	110	21.5	156	-	-
V (ppm)	-	12.0	6.11	3.87	-	-
T (ppiii) Zr (ppm)	-	0.0559	0.0364	0.0111	-	-
Mo (ppm)		0.120	0.0504	0.0878	-	-
Cs (ppm)	-	0.0238	0.00516	0.0070	-	_
Ba (nnm)	_	9.66	1 43	20.1	_	_
La (ppm)	_	1 43	0.291	0.778	_	_
Ce (ppm)	-	2.66	0.670	1.38	-	-
Pr (ppm)	-	0.372	0.101	0.183	-	-
Nd (ppm)	-	1.86	0.522	0.892	-	-
Sm (ppm)	-	0.628	0.196	0.260	-	-
Eu (ppm)	-	0.244	0.0916	0.0734	-	-
Gd (ppm)	-	1.01	0.375	0.404	-	-
Tb (ppm)	-	0.179	0.0782	0.0643	-	-
Dy (ppm)	-	1.31	0.632	0.421	-	-
Ho (ppm)	-	0.338	0.161	0.0960	-	-
Er (ppm)	-	1.03	0.536	0.275	-	-
Tm (ppm)	-	0.166	0.0877	0.0344	-	-
Yb (ppm)	-	1.07	0.558	0.211	-	-
Lu (ppm)	-	0.170	0.0962	0.0343	-	-
Pb (ppm)	-	0.441	0.0400	0.186	-	-
Th (ppm)	-	0.000756	0.00141	0.000748	-	-
U (ppm)	-	0.0100	0.00193	0.00501	-	-
ΣREE (ppm)	-	12.5	4.40	5.10	-	-
Y/Ho	-	38.3	37.8	40.2	-	-
Sm/Yb	-	0.585	0.351	1.231	-	-
Eu/Sm	-	0.389	0.467	0.282	-	-
La/La* _{CI}	-	1.47	1.18	1.55	-	-
Ce/Ce* _{SN}	-	0.842	0.884	0.842	-	-
Eu/Eu* _{sn}	-	1.49	1.49	1.16	-	-
Pr/Pr* _{SN}	-	0.953	0.961	0.951	-	-

Table B1: (continued).

Type	Low-Mn Type II				Certified Refere	nce Material
Sample ID	Pil17-008b	Pil17-008c	Pil17-008e	Pil16-073b	JDo1	JDo1
Formation	Euro	Euro	Euro	Bradley		
Age (Ma)	3340	3340	3340	3120		
Latitude	21°21.407' S	21°21.407' S	21°21.407' S	20°57.717' S		
Longitude	119°30.734' E	119°30.734' E	119°30.734' E	117°02.232' E		
Rock type	calcite	calcite	calcite	calcite		
SiO ₂ (wt.%)	0.00	0.00	0.00	0.00	-	-
Al ₂ O ₃ (wt.%)	0.03	0.03	0.03	0.02	-	-
FeO* (wt.%)	0.01	0.01	0.01	0.02	-	-
MnO (wt.%)	0.01	0.01	0.01	0.06	-	-
MgO (wt.%)	0.01	0.01	0.01	0.02	-	-
CaO (wt.%)	58.06	60.22	58.06	57.13	-	-
Na_2O (wt.%)	0.05	0.04	0.05	0.03	-	-
K_2O (wt.%)	0.01	0.01	0.01	0.00	-	-
Ca (ppm)	414974	430357	414975	408334	-	-
Mn (ppm)	49.2	53.0	49.1	495	-	-
Al (ppm)	145	147	145	85.3	-	-
Fe (ppm)	71.8	100	72.1	177	-	-
Mg (ppm)	81.0	42.2	81.1	113	-	-
Na (ppm)	388	313	388	252	-	-
K (ppm)	434	351	434	282	-	
Calcite (%)	99.95	99.95	99.95	99.81	-	-
Magnesite (%)	0.02	0.01	0.02	0.03	-	-
Siderite (%)	0.03	0.04	0.03	0.16	-	-
Li (ppm)	0.244	0.645	0.0213	0.0357	0.595	0.4-0.75
Sc (ppm)	0.375	0.211	0.127	0.190	0.393	0.13-0.5
Cr (ppm)	0.780	0.664	0.321	0.261	9.43	6.83-8.05
Mn (ppm)	85.0	49.0	13.7	420	58.426	44.000
Co (ppm)	1.30	0.829	0.635	0.557	0.592	0.14-03
Ni (ppm)	7.52	13.7	0.00	4.56	6.49	2.790
Zn (ppm)	2.69	3.09	1.08	1.28	37.565	31-38
KD (ppm)	0.0251	0.944	0.000	0.049	0.0714	0.081-0.14
Sr (ppm)	1063	903	1830	2485	129.885	108-118
Y (ppm)	5.59	4.70	10.90	0.303	12.108	8.9-10.4
Zr (ppiii) Mo (ppm)	0.00090	0.0071	0.00875	0.0110	0.333	0.4-3.5
$C_{\rm S}$ (ppm)	0.0118	-	-	0.00184	0.203	0.27-0.4
Cs (ppiii) Ba (ppm)	1.53	10.5	0.834	758 1	5.05	6.40-24
La (ppm)	0.302	0.340	0.816	0.0276	5.95 8.51	7.00-8.05
Ce (ppm)	0.302	0.549	1 10	0.0270	2 33	1 85-2 3
Pr (ppm)	0.410	0.005	0.170	0.00354	1.10	1.05-2.5
Nd (ppm)	0.190	0.418	0.874	0.0234	4.43	
Sm (ppm)	0.0562	0.145	0.302	0.00927	0.739	_
Eu (ppm)	0.0302	0.0256	0.0945	BaO	0.174	_
Gd (ppm)	0.187	0.308	0.727	0.0109	0.973	-
Th (ppm)	0.043	0.0600	0.141	0.00179	0.132	-
Dv (ppm)	0.424	0.465	1.09	0.0189	0.809	-
Ho (ppm)	0.137	0.118	0.279	0.00544	0.183	-
Er (ppm)	0.506	0.371	0.800	0.0201	0.497	-
Tm (ppm)	0.076	0.0522	0.0953	0.00520	0.0596	-
Yb (ppm)	0.449	0.305	0.478	0.0441	0.315	-
Lu (ppm)	0.0582	0.0367	0.0522	0.00932	0.0461	-
Pb (ppm)	0.0677	0.274	0.0279	0.0549	0.371	-
Th (ppm)	0.00177	0.0348	0.00134	0.00149	0.0493	-
U (ppm)	0.00870	0.0369	0.00109	0.000133	0.797	_
ΣREE (ppm)	2.90	3.41	7.11	0.211	20.3	-
Y/Ho	40.8	40.4	39.1	55.8	66.3	-
Sm/Yb	0.125	0.474	0.632	0.210	2.35	-
Eu/Sm	0.215	0.177	0.312	-	0.236	-
La/La* _{CI}	1.89	1.27	1.94	7.92	2.14	-
Ce/Ce* _{SN}	0.797	0.859	0.738	0.706	0.168	-
Eu/Eu* _{SN}	0.445	0.551	0.904	0.000	1.11	-
Pr/Pr* _{SN}	0.958	0.997	0.945	0.738	1.56	-

Туре	High-Mn Type I							
Sample ID	Pil16-004	13613	Pil16-006	Pil16-006	Pil17-008d	Pil-17-008d	Pil16-022b	Pil16-022b
Formation	Euro	Euro	Euro	Euro	Euro	Euro	Apex	Apex
Age (Ma)	3340	3340	3340	3340	3340	3340	3465	3465
Mineral	calcite	ankerite	calcite	residue	calcite	quartz	calcite	residue
Rb (ppm)	2.01	0.00276	0.00490	2.49	0.0477	3.70	0.09013	0.336
Sr (ppm)	53.4	64.4	69.8	2.58	25.5	4.88	253	1.03
Sm (ppm)	1.86	0.384	1.86	-	-	-	0.773	-
Nd (ppm)	7.46	1.18	6.87	-	-	-	2.56	-
⁸⁷ Rb/ ⁸⁶ Sr	0.1091	0.0001	0.0002	3.1716	0.0054	2.2101	0.0010	0.9523
⁸⁷ Sr/ ⁸⁶ Sr	0.706823 ± 13	0.718782 ± 15	0.707509 ± 85	0.720822 ± 65	0.706701 ± 10	0.758776 ± 8	0.710852 ± 12	0.763211 ± 49
${}^{87}{ m Sr}/{}^{86}{ m Sr}_{ m (i)}$	0.701523	0.718776	0.707499	0.566773	0.706438	0.651429	0.710800	0.715180
147Sm/144Nd	0.1502	0.1964	0.1620	-	-	-	0.1826	-
143Nd/144Nd	0.511657 ± 10	0.512530 ± 9	0.511924 ± 11	-	-	-	0.512363 ± 10	-
$\epsilon^{143} Nd$	-19.0 ± 0.4	-2.0 ± 0.4	-13.8 ± 0.4	-	-	-	-5.2 ± 0.4	-
${}^{143}Nd/{}^{144}Nd_{(i)}$	0.508340	0.508193	0.508346	-	-	-	0.508178	-
$\epsilon^{143}Nd_{(i)}$	$+0.8\pm0.4$	-2.1 ± 0.4	$+0.9\pm0.4$	-	-	-	$+0.8\pm0.4$	-
$\delta^{18}O$	$+11.21 \pm 0.012$	-	-	-	-	-	-	-
$\delta^{13}C$	-0.854 ± 0.007	-	-	-	-	-	-	-

Table B2: High-precision trace element, radiogenic Sr-Nd and stable ¹⁸O-¹³C isotope composition data of interstitial and vesicle filling carbonates, associated quartz, and host rock clinopyroxenes, respectively. Initial ϵ^{143} Nd values were calculated using the CHUR values ¹⁴⁷Sm/¹⁴⁴Nd = 0.1960 and ¹⁴³Nd/¹⁴⁴Nd = 0.51263, respectively (Bouvier et al., 2008) and a decay constant of λ^{147} Sm = 6.54 ×10⁻¹² a⁻¹ (Lugmair and Marti, 1978). For initial Sr isotope calculation a decay constant of λ^{87} Rb =1.42 × 10⁻¹¹ a⁻¹ (Steiger and Jäger, 1977) was used.

	Туре	High-Mn Type I							Low-Mn Type II	
	Sample ID	13643	13643	13643	Pil17-002	Pil17-002	14613	Pil16-051b	Pil16-005	Pil16-005
	Formation	Apex	Apex	Apex	Apex	Apex	Mt. Ada	Honeyeater	Euro	Euro
	Age (Ma)	3465	3465	3465	3465	3465	3475	3180	3340	3340
	Mineral	calcite	ankerite	residue	calcite	residue	calcite	calcite	calcite	calcite
	Rb (ppm)	0.0357	-	3.58	0.0144	0.620	0.0114	0.00851	0.00114	0.0160
	Sr (ppm)	56.1	-	3.18	46.3	0.602	99.1	13.1	215	123
	Sm (ppm)	1.33	-	-	0.872	-	0.551	0.157	-	-
	Nd (ppm)	4.73	-	-	2.21	-	1.74	0.444	-	-
	87Rb/86Sr	0.0018	-	3.2832	0.0009	3.0159	0.0003	0.0019	0.000015	0.00037
	⁸⁷ Sr/ ⁸⁶ Sr	0.706976 ± 11	-	0.791860 ± 25	0.709343 ± 14	0.828457 ± 40	0.702455 ± 12	0.710959 ± 39	0.701050 ± 12	0.702093 ± 14
	$^{87}Sr/^{86}Sr_{(i)}$	0.706885	-	0.626274	0.709298	0.676354	0.702438	0.710870	0.701049	0.702075
	147Sm/144Nd	0.1698	-	-	0.2390	-	0.1912	0.2137	-	-
	143Nd/144Nd	0.512223 ± 13	-	-	0.513856 ± 11	-	0.512568 ± 10	0.513082 ± 19	-	-
	$\epsilon^{143}Nd$	-7.9 ± 0.4	-	-	$+23.9\pm0.4$	-	-1.2 ± 0.4	$+8.8\pm0.4$	-	-
ued).	${}^{143}Nd/{}^{144}Nd_{(i)}$	0.508331	-	-	0.508378	-	0.508173	0.508591	-	-
contin	$\epsilon^{143}Nd_{(i)}$	$+3.8\pm0.4$	-	-	$+4.7\pm0.4$	-	$+1.0\pm0.4$	$+1.6\pm0.4$	-	-
B2: (c	$\delta^{18}O$	-	-	-	$+16.66 \pm 0.010$	-	-	$+9.253 \pm 0.019$	$+13.178 \pm 0.025$	$+13.178 \pm 0.025$
Table	$\delta^{13}C$	-	-	-	$+0.068 \pm 0.060$	-	-	-1.831 ± 0.011	$+1.039 \pm 0.010$	$+1.039 \pm 0.010$

226

Туре	Low-Mn Type II					Host rock clinopy	roxene	
Sample ID	Pil17-008a	Pil17-008b	Pil17-008c	Pil17-008e	Pil16-073b	Pil17-010	Pil17-010	Pil16-022a
Formation	Euro	Euro	Euro	Euro	Bradley	Mt. Ada	Mt. Ada	Apex
Age (Ma)	3340	3340	3340	3340	3120	3475	3475	3465
Mineral	calcite	calcite	calcite	calcite	calcite	clinopyroxene	clinopyroxene	clinopyroxene
Rb (ppm)	0.00887	0.00840	0.136	0.00309	0.0217	0.633	1.35	0.303
Sr (ppm)	1278	1275	825	1746	2516	9.51	13.1	25.9
Sm (ppm)	-	-	0.172	0.231	0.00648	1.20	1.75	0.417
Nd (ppm)	-	-	0.538	0.693	0.0231	3.08	4.45	0.910
⁸⁷ Rb/ ⁸⁶ Sr	0.000038	0.000019	0.0000045	0.00000019	0.000025	0.1934	0.2981	0.0338
⁸⁷ Sr/ ⁸⁶ Sr	0.701063 ± 9	0.701098 ± 11	0.701063 ± 12	0.701071 ± 13	0.701373 ± 19	0.710124 ± 10	0.715787 ± 15	0.706957 ± 17
${}^{87}Sr/{}^{86}Sr_{(i)}$	0.701062	0.701097	0.701063	0.701071	0.701372	0.700341	0.700710	0.705253
147Sm/144Nd	-	-	0.2017	0.2020	0.1698	0.2351	0.2375	0.2774
143Nd/144Nd	-	-	0.512817 ± 11	0.512839 ± 12	0.512294 ± 245	0.513547 ± 9	0.513581 ± 8	0.514492 ± 16
$\epsilon^{143} Nd$	-	-	3.7 ± 0.4	4.1 ± 0.4	-6.5 ± 2.5	$+17.9\pm0.4$	$+18.5\pm0.4$	$+36.3\pm0.4$
$^{143}Nd/^{144}Nd_{(i)} \\$	-	-	0.508362	0.508378	0.508794	0.508143	0.508120	0.508134
$\epsilon^{143}Nd_{(i)}$	-	-	1.2 ± 0.4	1.5 ± 0.4	4.0 ± 2.5	$+0.4\pm0.4$	$\textbf{-0.1} \pm 0.4$	$\textbf{-0.1} \pm 0.4$
$\delta^{18}O$	$+10.540\pm\ 0.007$	$+10.548 \pm 0.005$	$+10.974 \pm 0.009$	11.205 ± 0.017	$+9.101 \pm 0.023$	-	-	-
$\delta^{13}C$	$+0.274 \pm 0.057$	$+0.521 \pm 0.059$	$+1.371 \pm 0.059$	0.490 ± 0.008	-0.371 ± 0.006	-	-	-

Туре	Host rock clinopy	roxene		
Sample ID	Pil16-052a	Pil16-52b	Pil16-69	Pil16-71
Formation	Honeyeater	Honeyeater	Bradley	Bradley
Age (Ma)	3180	3180	3123	3123
Mineral	clinopyroxene	clinopyroxene	clinopyroxene	clinopyroxene
Rb (ppm)	0.0315	0.129	0.446	1.36
Sr (ppm)	3.12	7.24	25.0	21.1
Sm (ppm)	0.304	0.457	2.13	1.61
Nd (ppm)	0.677	1.07	6.35	4.28
⁸⁷ Rb/ ⁸⁶ Sr	0.0292	0.0516	0.0516	0.1869
⁸⁷ Sr/ ⁸⁶ Sr	0.709270 ± 22	0.712534 ± 14	0.705780 ± 14	0.710523 ± 17
${}^{87}Sr/{}^{86}Sr_{(i)}$	0.707920	0.710151	0.703440	0.702049
147Sm/144Nd	0.2719	0.2588	0.2003	0.2254
143Nd/144Nd	0.514325 ± 10	0.514066 ± 10	0.512812 ± 13	0.513319 ± 17
$\epsilon^{143}Nd$	$+33.1 \pm 0.4$	$+28.0\pm0.4$	$+3.5\pm0.4$	$+13.4\pm0.4$
$^{143}Nd/^{144}Nd_{(i)} \\$	0.508612	0.508628	0.508678	0.508667
$\epsilon^{143}Nd_{(i)}$	$+2.0\pm0.4$	$+2.3\pm0.4$	$+1.8\pm0.4$	$+1.6\pm0.4$
$\delta^{18}O$				
$\delta^{13}C$				

VI. Appendix

Table B2: (continued).

	ACA-9	99.8%	99.0%	97.0%	95.0%	90.0%	85.0%	75.0%	50.0%	Pil16-53a
La (ppm)	0.259	0.271	0.321	0.445	0.570	0.880	1.19	1.81	3.37	6.47
Ce (ppm)	0.286	0.319	0.453	0.786	1.12	1.95	2.79	4.46	8.63	16.966
Pr (ppm)	0.0339	0.0388	0.0588	0.109	0.159	0.283	0.408	0.657	1.28	2.53
Nd (ppm)	0.165	0.189	0.287	0.530	0.774	1.38	1.99	3.21	6.26	12.3
Pm (ppm)	-	-	-	-	-	-	-	-	-	-
Sm (ppm)	0.0571	0.0642	0.0928	0.164	0.236	0.414	0.593	0.951	1.84	3.63
Eu (ppm)	0.0359	0.0384	0.0483	0.0730	0.0977	0.159	0.221	0.345	0.654	1.27
Gd (ppm)	0.158	0.167	0.201	0.287	0.373	0.588	0.803	1.23	2.31	4.46
Tb (ppm)	0.0239	0.0255	0.0318	0.0477	0.0635	0.103	0.143	0.222	0.419	0.815
Dy (ppm)	0.169	0.180	0.223	0.331	0.439	0.709	0.979	1.52	2.87	5.57
Y (ppm)	3.86	3.92	4.166	4.79	5.41	6.96	8.52	11.6	19.4	34.9
Ho (ppm)	0.0489	0.0513	0.0607	0.0843	0.108	0.167	0.226	0.343	0.638	1.23
Er (ppm)	0.182	0.189	0.216	0.284	0.352	0.522	0.693	1.03	1.88	3.59
Tm (ppm)	0.0305	0.0315	0.036	0.046	0.057	0.083	0.109	0.161	0.292	0.553
Yb (ppm)	0.220	0.227	0.255	0.325	0.396	0.571	0.746	1.10	1.98	3.73
Lu (ppm)	0.0434	0.0445	0.0488	0.0597	0.0706	0.098	0.125	0.179	0.315	0.587
Zr (ppm)	0.0817	0.288	1.111	3.169	5.23	10.4	15.5	25.8	51.5	103
Fe (ppm)	12500	12720	13599	15796	17994	23488	28982	39970	67440	122380
Mn (ppm)	6300	6291	6255	6166	6076	5852	5628	5180	4060	1820
Al (ppm)	1000	1144	1722	3165	4608	8216	11824	19040	37080	73160
Y/Ho	78.8	76.4	68.6	56.8	50.2	41.8	37.7	33.8	30.4	28.5
Eu/Sm	0.63	0.60	0.52	0.44	0.41	0.38	0.37	0.36	0.35	0.35
Sm/Yb	0.26	0.28	0.36	0.50	0.60	0.73	0.79	0.87	0.93	0.97
La/Sm	4.53	4.22	3.46	2.71	2.42	2.12	2.01	1.91	1.83	1.78
Eu/Eu* _{sn}	1.94	1.90	1.80	1.68	1.63	1.57	1.54	1.52	1.51	1.50
ΣREE	1.71	1.84	2.33	3.57	4.81	7.92	11.02	17.22	32.73	63.75

Table B3a: Seawater-rock mixing⁹, inferred by mixing of carbonate (ACA-9; Allwood et al., 2010) and pillow basalt (Pill6-53a; Tusch et al., 2021).

Table B3b: Seawater-hydrothermal fluid mixing, inferred by mixing of modern seawater (489 m; Zhang and Nozaki, 1996) and hydrothermal fluids (BS-13-4/2; Bau and Dulski, 1999).

	ACA-9	99.8%	99.0%	97.0%	95.0%	90.0%	85.0%	75.0%	50.0%	Pil16-53a	
La (ppm)	0.00000176	0.0000023	0.0000045	0.0000101	0.0000157	0.0000296	0.0000435	0.0000713	0.0001408	0.00027976	
Ce (ppm)	0.00000024	0.0000017	0.0000074	0.0000217	0.0000360	0.0000717	0.0001075	0.0001790	0.0003578	0.00071529	
Pr (ppm)	0.00000023	0.0000004	0.0000011	0.0000028	0.0000045	0.0000087	0.0000129	0.0000214	0.0000425	0.00008483	
Nd (ppm)	0.00000109	0.0000018	0.0000044	0.0000111	0.0000178	0.0000345	0.0000511	0.0000845	0.0001679	0.00033479	
Pm (ppm)	-	-	-	-	-	-	-	-	-	-	
Sm (ppm)	0.00000027	0.0000004	0.0000010	0.0000025	0.0000040	0.0000077	0.0000114	0.0000188	0.0000374	0.00007458	
Eu (ppm)	0.0000008	0.0000006	0.0000026	0.0000077	0.0000129	0.0000256	0.0000384	0.0000640	0.0001278	0.00025560	
Gd (ppm)	0.00000040	0.0000006	0.0000012	0.0000028	0.0000043	0.0000082	0.0000122	0.0000200	0.0000396	0.00007878	
Tb (ppm)	0.00000007	0.0000001	0.0000002	0.0000004	0.0000006	0.0000011	0.0000016	0.0000026	0.0000052	0.00001038	
Dy (ppm)	0.00000056	0.0000007	0.0000011	0.0000021	0.0000031	0.0000057	0.0000083	0.0000134	0.0000263	0.00005200	
Y (ppm)	0.00001062	0.0000110	0.0000127	0.0000170	0.0000212	0.0000317	0.0000423	0.0000634	0.0001161	0.00022164	
Ho (ppm)	0.00000017	0.0000002	0.0000002	0.0000004	0.0000006	0.0000009	0.0000013	0.0000021	0.0000040	0.00000785	
Er (ppm)	0.00000060	0.0000006	0.0000008	0.0000011	0.0000014	0.0000022	0.0000030	0.0000046	0.0000087	0.00001673	
Tm (ppm)	0.00000009	0.0000001	0.0000001	0.0000001	0.0000002	0.0000003	0.0000004	0.0000006	0.0000011	0.00000203	
Yb (ppm)	0.00000062	0.0000006	0.0000007	0.0000009	0.0000011	0.0000015	0.0000019	0.0000028	0.0000049	0.00000922	
Lu (ppm)	0.00000011	0.0000001	0.0000001	0.0000001	0.0000002	0.0000002	0.0000003	0.0000003	0.0000006	0.00000106	
Zr (ppm)	-	-	-	-	-	-	-	-	-	-	
Fe (ppm)	-	-	-	-	-	-	-	-	-	-	
Mn (ppm)	-	-	-	-	-	-	-	-	-	-	
Al (ppm)	-	-	-	-	-	-	-	-	-	-	
Y/Ho	62.5	59.6	51.6	42.4	38.2	33.8	32.0	30.3	29.0	28.2	Ī
Eu/Sm	0.3	1.4	2.6	3.1	3.2	3.3	3.4	3.4	3.4	3.4	
Sm/Yb	0.4	0.7	1.4	2.8	3.8	5.2	6.0	6.8	7.6	8.1	
La/Sm	6.4	5.5	4.5	4.0	3.9	3.8	3.8	3.8	3.8	3.8	
Eu/Eu* _{SN}	1.1	6.0	12.3	15.4	16.2	16.9	17.2	17.4	17.5	17.6	
ΣREE	-	-	-	-	-	-	-	-	-	-	

⁹ For Table B3a-d the following Mixing-equation

$$C_i^x = \left(C_i^A x\right) + \left(C_i^B (1-x)\right)$$

was used, where (C_i^X) is calculated concentration of trace element (*i*) at the mixing ratio of *x* parts of the trace element *i* of the source *A* and of *1-x* of rock source *B*.

	Pil17- 008d	99%	90%	80%	70%	60%	50%	40%	30%	20%	Pil16- 022a
Sc (ppm)	1.60	1.99	5.46	9.32	13.2	17.0	20.9	24.8	28.6	32.5	40.2
Mn (ppm)	14790	14653	13424	12058	10692	9326	7961	6595	5229	3863	1131
Zr (ppm)	0.0128	0.306	2.94	5.87	8.80	11.7	14.7	17.6	20.5	23.4	29.3
Sr (ppm)	21.7	22.5	29.3	36.8	44.4	52.0	59.6	67.1	74.7	82.3	97.4
Th (ppm)	0.00286	0.00417	0.0159	0.0290	0.0421	0.0552	0.0682	0.0813	0.0944	0.107	0.134
U (ppm)	0.00465	0.00496	0.00783	0.0110	0.0142	0.0174	0.0206	0.0238	0.0270	0.0302	0.0365
Nd (ppm)	4.46	4.45	4.32	4.17	4.03	3.88	3.74	3.60	3.45	3.31	3.02
Al (ppm)	130	717	6002	11875	17747	23620	29492	35364	41237	47109	58854
ΣREĒ	29.2	29.1	27.9	26.7	25.4	24.1	22.8	21.6	20.3	19.0	16.5

Table B3c: Calculation for mafic rock contamination (Pil16-022a; Tusch et al., 2021).

Table B3d: Calculation for shale contamination (Pil16-38; Tusch et al., 2021).

	Pil17- 008d	99%	90%	80%	70%	60%	50%	40%	30%	20%	Pil16- 38
Sc (ppm)	1.60	1.86	4.22	6.84	9.46	12.1	14.7	17.3	19.9	22.6	27.8
Mn (ppm)	14790	14644	13329	11868	10407	8946	7485	6024	4563	3102	180
Zr (ppm)	0.0128	1.27	12.6	25.2	37.8	50.4	63.0	75.6	88.2	101	126
Sr (ppm)	21.7	22.8	32.9	44.2	55.4	66.6	77.9	89.1	100	112	134
Th (ppm)	0.00286	0.132	1.29	2.58	3.87	5.16	6.45	7.74	9.03	10.3	12.9
U (ppm)	0.00465	0.0289	0.247	0.489	0.731	0.973	1.22	1.46	1.70	1.94	2.43
Nd (ppm)	4.46	4.71	7.01	9.55	12.1	14.6	17.2	19.7	22.3	24.8	29.9
Al (ppm)	130	1352	12347	24564	36781	48998	61215	73431	85648	97865	122299
ΣREE	29.2	30.6	43.1	57.0	70.9	84.7	98.6	113	126	140	168

Appendix C







Figure C2: Tera-Wasserburg Concordia plots of SHRIMP-analyzed zircons. Error ellipses represent 68.3 % confidence levels (approximately one standard deviation). Solid ellipse: analysis used in weighted mean age calculation; dotted ellipse: analysis excluded. Dashed lines represent linear projections from weighted mean ages to common lead compositions estimated using the two-stage common-Pb model of (Stacey and Kramers, 1975).



Figure C3: Chondrite-normalized REE compositions of selected zircons of Todd et al. (2021). All zircons show typical magmatic REE patterns.



Figure C4: Nb/Yb vs. U/Yb diagram of zircons (after Barth et al., 2017) showing the subduction zone related character of the Fijian felsic rocks in comparison to detrital zircons from Izu-Bonin (Barth et al., 2017) and the Andean Northern Volcanic Zone (NVZ; Dilles et al., 2015). Arc-derived zircons and their felsic host rocks extend to lower Nb/Yb than in basalts from mid-ocean ridge or oceanic intraplate settings that lie within the mantle array. Uranium/Yb ratios above the mantle array reflect the slab-derived U in arcs, but less than in continental margin zircons.



Figure C5: ⁸⁷Sr/⁸⁶Sr vs. SiO₂ diagram showing an increase of the Sr isotope composition for Korolevu (LDsuite) that might hint at small degrees of altered oceanic or early arc crustal assimilation, whereas all samples of the LE- and EE-suites nearly retain their original Sr isotope compositions. However, some samples with higher Sr isotope compositions correlate with L.O.I. (Fig. 3.9a) and show mineral replacements of mafic minerals to chlorite and epidote, and plagioclase to sericite and epidote, respectively, which rather suggest post-depositional alteration.

Suite	LE-suite					
Sample ID	DGG5	YV 06	T24	T24 (dupl.)	T25	T25 (dupl.)
Pluton	Yavuna	Yavuna	Wainivalau	-	Wainivalau	-
Age (Ma)	37.25 ± 0.63		10.74 ± 0.24		11.28 ± 0.20	
Latitude	17.833 °S	17.838 °S	17.889 °S		17.882 °S	
Longitude	177.542 °E	177.546 °E	178.205 °E		178.199 °E	
Rock type	Med-K trondhi	Med-K trondhi	Med-K tonal.		Med-K tonal.	
SiO ₂ (wt.%)	73.01	74.85	68.58		72.76	
TiO ₂ (wt.%)	0.25	0.26	0.51		0.39	
Al ₂ O ₃ (wt.%)	14.27	13.86	15.11		13.51	
FeO* (wt.%)	2.34	2.23	4.60		3.14	
MnO (wt.%)	0.07	0.07	0.10		0.08	
MgO(Wt.%)	0.75	0.62	1.75		1.25	
VaO(wt.%)	2.07	5.47	4.10		3.57	
$K_{2}O(wt.\%)$	1.62	1.10	1.60		1.50	
P_2O_5 (wt.%)	0.08	0.06	0.11		0.10	
L.O.I. (wt.%)	1.15	1.06	0.75		0.61	
Total (wt.%)	99.61	98.41	99.52		100.27	
Sc (ppm)	n/a	6.36	11.2	n/a	5.96	n/a
V (ppm)	n/a	n/a	93.3	n/a	54.3	n/a
Cr (ppm)	n/a	n/a	20.4	n/a	10.9	n/a
Co (ppm)	n/a	n/a n/a	9.57	n/a	5.38	n/a
Cu (ppm)	n/u n/a	n/a	5 58	n/a	4.07	n/a n/a
Zn (ppm)	n/a n/a	n/a	34.8	n/a	22.9	n/a
Rb (ppm)	18.6	13.0	15.4	24.6	13.9	24.3
Sr (ppm)	153	119	181	199	187	198
Y (ppm)	20.3	22.1	19.7	21.9	12.1	14.0
Zr (ppm)	120	120	110	131	70.9	111.0
Nb (ppm)	n/a	1.53	2.10	n/a	1.86	n/a
Mo (ppm)	n/a	n/a	1.47	n/a	0.404	n/a
Cs (ppm)	0.0862	0.0332	0.210	0.220	0.165	0.170
La (ppm)	8.93	9.82	11.0	83	7 01	6.80
Ce (ppm)	18.6	20.3	20.0	18.3	12.8	14.3
Pr (ppm)	2.32	2.56	2.76	2.44	1.81	1.81
Nd (ppm)	9.21	10.5	11.5	10.2	7.42	7.19
Sm (ppm)	2.21	2.65	2.75	2.53	1.73	1.62
Eu (ppm)	0.730	0.886	0.885	0.787	0.743	0.642
Gd (ppm)	2.68	2.94	3.02	3.29	1.86	2.08
To (ppm)	0.476	0.530	0.505	0.551	0.304	0.354
Ho (ppm)	0.662	0.783	0.710	0 741	0.429	0.463
Er (ppm)	2.02	2.37	2.09	2.06	1.29	1.34
Tm (ppm)	0.320	0.372	0.333	0.333	0.214	0.212
Yb (ppm)	2.13	2.56	2.32	2.17	1.54	1.45
Lu (ppm)	0.321	0.441	0.362	0.319	0.252	0.228
Hf (ppm)	n/a	3.44	2.82	n/a	1.84	n/a
Ta (ppm)	n/a	0.119	0.175	n/a	0.180	n/a
W (ppm)	1.55 n/a	0.981	0.126	1.02 n/a	0.980	1.200 n/a
Th (ppm)	1.92	1.56	1.76	1.68	1.98	1.66
U (ppm)	0.497	0.576	0.659	0.604	0.770	0.605
Eu/Eu*	0.908	0.963	0.930	0.826	1.25	1.06
Ba/Th	124	111	93.0	101	73.5	93.6
(La/Sm) _{PRIMA}	2.57	2.36	2.53	2.09	2.57	2.66
(La/Yb) _{PRIMA}	2.93	2.68	3.31	2.68	3.18	3.28
Dy/Yb	1.42	1.37	1.42	1.60	1.29	1.47
Dy/Dy* Zr/V	0.672	0.000 5.47	0.050	0.780	0.594	0.672
Nh/La	5.91 n/a	0.164	0.04	5.99 n/a	0.07	1.91 n/a
Nb/Ta	n/a	13.3	12.4	n/a	9.57	n/a
Zr/Hf	n/a	34.8	34.6	n/a	35.0	n/a
Nb/Yb	n/a	0.598	0.913	n/a	1.17	n/a
Th/Yb	0.904	0.608	0.761	0.776	1.29	1.15
Sr/Y	7.55	5.40	9.20	9.11	15.4	14.1
Zr/Sm	54.3	45.6	39.7	51.8	49.5	68.4

Table C1: Major (XRF; dry), minor and trace element (ICP-MS) data for the Fijian plutons and certified reference materials. Normalization values by Palme and O'Neill (2014).

Suite	LE-suite					
Sample ID	T44	T22	T10	T41	T8	T36
Pluton	Wainivalau	Wainivalau	Wainivalau	Wainivalau	Wainivalau	Wainivalau
Age (Ma)	11.73 ± 0.07			11.41 ± 0.20		11.73 ± 0.18
Latitude	17.942 °S	17.943 °S		17.949 °S		17.887 °S
Longitude	178.182 °E	178.225 °E		178.186 °E		178.159 °E
Rock type	Med-K	Low-K	Med-K	Med-K	Med-K	Med-K
	trondhjemite	trondhjemite	trondhjemite	trondhjemite	trondhjemite	trondhjemite
S_1O_2 (wt.%)	73.32	74.26	75.17	75.90	76.08	76.96
$110_2 (Wt.\%)$	0.32	0.30	0.30	0.28	0.25	0.25
AI_2O_3 (wt.%) $E_2O_3^*$ (wt.%)	15.76	2.54	2.40	2.18	12.98	15.11
MnO(wt.%)	2.17	2.34	2.40	2.18	1.80	0.05
M_{gO} (wt %)	0.88	0.03	0.54	0.69	0.03	0.05
CaO (wt.%)	2.59	2.21	1.91	1.77	1.90	0.84
Na ₂ O (wt.%)	4.74	5.57	3.85	3.84	3.61	3.79
K ₂ O (wt.%)	2.07	0.99	2.29	1.76	2.77	2.67
P_2O_5 (wt.%)	0.10	0.09	0.06	0.06	0.04	0.04
L.O.I. (wt.%)	n/a	n/a	1.12	1.44	0.46	0.35
Total (wt.%)	99.90	99.56	99.62	99.43	99.77	98.59
Sc (ppm)	n/a	4.01	4.06	3.74	3.79	n/a
V (ppm)	n/a	28.8	25.4	29.7	19.7	n/a
Cr (ppm)	n/a	39.0 2.71	10.8	10.1	1/.0	n/a
Ni (ppm)	n/a n/a	2.71	4.28	2.18	4.77	n/a n/a
$C_{\rm II}$ (ppm)	n/a	95 3	11.57	4 93	2.11	n/a
Zn (ppm)	n/a	55.3	21.8	14.5	19.9	n/a
Rb (ppm)	23.3	13.4	18.6	17.8	23.7	36.4
Sr (ppm)	155	116	112	114	108	121
Y (ppm)	19.6	19.5	20.4	16.8	17.8	16.2
Zr (ppm)	134	120	114	115	119	125
Nb (ppm)	n/a	2.67	2.73	2.33	2.93	n/a
Mo (ppm)	n/a	1.05	0.771	0.685	2.11	n/a
Cs (ppm)	0.112	0.0412	0.119	0.0585	0.166	0.281
Ба (ppm) La (ppm)	218	145	218	230	288	230
Ce (ppm)	22.6	15.9	26.1	16.9	18.5	25.0
Pr (ppm)	2.98	2.66	4.08	2.41	2.52	3.08
Nd (ppm)	11.8	11.2	16.4	9.96	10.2	11.5
Sm (ppm)	2.42	2.60	3.51	2.30	2.19	2.41
Eu (ppm)	0.755	0.747	0.727	0.727	0.761	0.562
Gd (ppm)	2.95	2.70	3.30	2.36	2.30	2.68
Tb (ppm)	0.494	0.453	0.526	0.397	0.392	0.431
Dy (ppm)	3.00	2.99	3.30	2.59	2.57	2.63
Fr (ppill)	0.048	0.005	0.707	0.370	0.385	0.327
Tm (ppm)	0.301	0.338	0.358	0.306	0.318	0.255
Yb (ppm)	2.00	2.44	2.59	2.27	2.41	1.68
Lu (ppm)	0.280	0.444	0.461	0.419	0.427	0.244
Hf (ppm)	n/a	3.27	3.18	3.10	3.41	n/a
Ta (ppm)	n/a	0.238	0.24	0.213	0.284	n/a
Pb (ppm)	1.40	2.99	1.59	1.33	1.25	2.12
W (ppm)	n/a	0.0898	0.188	0.0962	0.193	n/a
In (ppm)	1./6	1.58	1.94	1./3	2.07	2.87
U (ppiii) Eu/Eu*	0.722	0.855	0.648	0.800	1.03	0.700
Ba/Th	124	91 7	112	136	139	89.2
(La/Sm)ppima	2.62	2.18	2.61	2.37	2.77	3.13
(La/Yb) _{PRIMA}	3.48	2.55	3.88	2.64	2.77	4.93
Dy/Yb	1.50	1.22	1.27	1.14	1.07	1.56
Dy/Dy*	0.674	0.605	0.553	0.557	0.516	0.630
Zr/Y	6.33	7.14	5.13	5.36	5.15	5.62
Nb/La	n/a	0.283	0.187	0.265	0.295	0.228
Nb/Ta 7-/11	n/a	10.3	11.1	10.6	9.87	9.87
Lr/Hf Nb/Vb	n/a	55.4 1.61	51.0	55.1 1 25	<i>30.3</i>	30.5 1.17
Th/Yh	0.879	1.01	0.911	1.25	1.05	1.17
Sr/Y	7.94	5.95	5 49	6.78	6.07	7.50
Zr/Sm	46.2	48.0	36.7	37.4	29.9	42.2

Table C1: (continued). Ratios in *italics* are calculated with high-precision HFSE data of Table C2.
Suite	LE-suite			LD-suite		
Sample ID	T08-29	T08-29 (dupl.)	69-858	DGG3	ST99	ST107
Pluton	W. Stocks		Noikoro	Korolevu	Korolevu	Korolevu
Age (Ma)	7.94 ± 0.39			9.46 ± 0.21		
Latitude	17.98 °S		17.935 °S	18.168 °S	18.149 °S	18.149 °S
Doughtude	1/7.55 E		1//.040 E	1//./08 E	177.732 E	177.055 E
Rock type	Med-K tonalite		Med-K tonalite	gabbro	Qtz-gabbro	Low-K tonalite
S_1O_2 (wt.%)	68.50		/0.39	54.83	57.27	67.10
$110_2 (W1.\%)$	0.40		0.57	0.08	0.44	15.00
FeO* (wt %)	4 15		3 22	9.73	8 24	5 70
MnO (wt.%)	0.06		0.07	0.24	0.20	0.15
MgO (wt.%)	1.88		1.16	5.39	5.26	1.56
CaO (wt.%)	4.69		3.95	9.94	10.04	5.43
Na ₂ O (wt.%)	3.50		4.05	1.96	2.68	3.84
K ₂ O (wt.%)	1.43		1.77	0.20	0.25	0.18
P_2O_5 (wt.%)	0.08		0.08	0.14	0.02	0.12
L.O.I. (wt.%) Total (wt.%)	1.20 97.28		0.65 99.03	n/a 99.25	0.57 99.57	0.31 99.14
Sc (ppm)	9.71	11.1	7.88	n/a	39.5	20.0
V (ppm)	83.7	n/a	58.8	n/a	216	104
Cr (ppm)	16.2	n/a	7.28	n/a	n/a	n/a
Co (ppm)	7.11	n/a	4.73	n/a	28.1	10.2
Ni (ppm)	4.97	n/a	1.59	n/a	n/a	n/a
Cu (ppm)	30.5	n/a	6.31	n/a	69.0	27.8
Zn (ppm) Ph (ppm)	27.1	n/a 24.5	33.0	n/a 1.71	/9.9	/0./
$\mathbf{K} \mathbf{b}$ (ppiii) $\mathbf{S} \mathbf{r}$ (ppm)	206	24.5	11.7	1.71	1.92	0.505
\mathbf{Y} (ppm)	14 7	15 30	17.0	21.6	29.7	26.6
Zr (ppm)	107	114	80.1	41.0	27.1	21.4
Nb (ppm)	1.45	1.36	1.83	n/a	0.320	0.443
Mo (ppm)	0.585	n/a	0.603	n/a	0.710	0.710
Cs (ppm)	0.103	0.0979	0.118	0.0486	0.0264	0.0228
Ba (ppm)	383.6	408	274	50.7	62.7	57.4
La (ppm)	6.23	6.46	7.05	1.50	1.30	1.65
Ce (ppm)	12.7	14.3	15.2	4.45	4.25	4.55
Pr (ppm)	1.92	1.93	2.12	0.818	0.853	1.00
Nu (ppili) Sm (ppm)	8.20	0.17 1.00	9.15	4.54	2.51	0.10
Eu (ppm)	0.628	0.618	0.697	0.687	0.785	2.47
Gd (ppm)	2.17	2.24	2.41	2.81	3.59	3.56
Tb (ppm)	0.364	0.384	0.412	0.536	0.707	0.656
Dy (ppm)	2.36	2.54	2.68	3.56	5.06	4.54
Ho (ppm)	0.502	0.549	0.588	0.782	1.12	0.987
Er (ppm)	1.46	1.55	1.77	2.22	3.29	2.83
Tm (ppm)	0.236	0.243	0.295	0.341	0.513	0.431
Yb (ppm)	1.64	1.61	2.12	2.32	3.47	2.84
Lu (ppm)	0.203	3.06	0.348	0.324	1.09	0.429
Ta (ppm)	0.129	0.135	0.177	n/a n/a	0.0194	0.0285
Pb (ppm)	1.31	1.29	2.12	1.01	0.872	0.714
W (ppm)	0.157	n/a	0.0975	n/a	0.209	0.212
Th (ppm)	1.06	0.955	1.47	0.143	0.111	0.103
U (ppm)	0.356	0.349	0.652	0.102	0.083	0.096
Eu/Eu*	0.912	0.887	0.915	0.951	0.811	1.19
Ba/Th	361	427	186	354	564	556
(La/Sm) _{PRIMA}	1.98	2.07	2.03	0.559	0.345	0.426
$(La/1D)_{PRIMA}$	2.05	2.81	2.32	0.451	0.262	0.405
Dy/10 Dy/Dy*	0.702	1.30	0.643	1.35	1.40	1.39
Z_r/Y	6.64	7.46	4.35	1.90	0.836	0.732
Nb/La	0.228	0.223	0.266	n/a	0.238	0.261
Nb/Ta	10.8	10.8	10.7	n/a	15.1	15.8
Zr/Hf	35.1	35.1	29.3	n/a	24.8	23.4
Nb/Yb	0.846	0.846	0.880	n/a	0.0921	0.153
Th/Yb	0.647	0.593	0.693	0.0617	0.0320	0.0363
Sr/Y	14.0	15.5	11.1	5.84	3.69	4.51
Zr/Sm	48.7	49.7	33.4	24.0	10.4	7.9

Table C1: (continued).

Suite	LD-suite			EE-suite		
Sample ID	DGG4	ST87	LK01	FJ05-06	FJ05-06 (dupl.)	FJ06-07
Pluton	Korolevu	Korolevu	Korolevu	Momi		Momi
Age (Ma)	9.63 ± 0.18			20.79 ± 0.34		20.98 ± 0.31
Latitude	18.182 °S	18.163 °S	18.19°S	17.943 °S		17.942 °S
Longitude	1//.693 °E	1//.6/8 °E	1//.84 °E	1//.2/0 °E		1//.26/ °E
Rock type	LOW-K trondhiomito	LOW-K trondhiamita	med-K	Low-K tonalite		LOW-K trondhiomito
\mathbf{SiO} (wit 0 /)	72.52	74.10	78.06	71.12		
$\operatorname{TiO}_2(\operatorname{wt}, \%)$	0.45	0.47	0.27	0.48		0.19
Al_2O_2 (wt %)	13 53	13 56	11.40	13 71		12 11
FeO^{*} (wt.%)	3.70	2.97	1.65	3.85		1.24
MnO (wt.%)	0.12	0.08	0.03	0.12		0.04
MgO (wt.%)	0.77	0.63	0.27	0.41		0.09
CaO (wt.%)	2.91	2.65	4.06	8.43		1.00
Na ₂ O (wt.%)	4.28	4.25	2.03	1.68		5.52
K ₂ O (wt.%)	0.62	0.67	1.29	0.06		1.04
P_2O_5 (wt.%)	0.10	0.06	0.04	0.13		0.03
L.O.I. (wt.%)	-	0.55	4.86	1.33		0.86
Total (wt.%)	97.14	97.01	94.13	99.38	11.6	3.06
Sc (ppiii)	n/a	9.59	9.94 n/a	0.39 40.3	11.0 n/a	5.90
Cr (ppm)	n/a	$\frac{20.1}{n/a}$	n/a n/a	6 10	n/a	4 64
Co (ppm)	n/a	4 23	n/a	3.40	n/a	1.19
Ni (ppm)	n/a	n/a	n/a	12.1	n/a	0.667
Cu (ppm)	n/a	4.18	n/a	3.89	n/a	57.7
Zn (ppm)	n/a	34.2	n/a	41.0	n/a	10.1
Rb (ppm)	5.97	3.37	11.0	0.777	0.834	3.90
Sr (ppm)	109	81.6	73.0	411.5	436	43.4
Y (ppm)	41.5	46.6	30.7	54.6	56.6	53.1
Zr (ppm)	79	114	101	196	194	295
Nb (ppm)	n/a	0.861	0.643	2.785	2.67	3.64
Mo (ppm)	n/a	1.55	n/a	0.208	n/a	0.125
Cs (ppiii) Ba (ppm)	108	0.0918	102	0.0541	0.0232	213
La (ppm)	2 23	3 52	2 61	10.5	11.8	10.4
Ce (ppm)	7.51	8.99	7.76	26.3	27.6	23.0
Pr (ppm)	1.44	2.07	1.34	4.24	4.64	4.32
Nd (ppm)	8.57	11.7	7.07	21.0	22.6	20.3
Sm (ppm)	3.38	4.34	2.49	6.22	6.66	5.90
Eu (ppm)	1.08	0.981	0.657	1.91	2.08	0.967
Gd (ppm)	5.45	5.81	3.55	7.55	8.21	6.88
Tb (ppm)	1.02	1.10	0.723	1.33	1.51	1.29
Dy (ppm)	6.65	7.67	5.15	8.92	9.85	9.01
Ho (ppm)	1.48	1.68	1.1/	1.91	2.16	1.99
Er (ppm) Tm (ppm)	4.10	4.99	3.51	5.59	6.06 0.017	6.02
Thi (ppiii) Vh (ppm)	4.07	5.43	3.67	5.92	5.88	6.992
Lu (ppm)	0.589	0.873	0.600	0.991	0.927	1.15
Hf (ppm)	n/a	3.50	3.33	4.91	5.24	7.83
Ta (ppm)	n/a	0.0676	0.0531	0.193	0.200	0.276
Pb (ppm)	1.28	1.157	1.68	3.20	2.96	1.13
W (ppm)	n/a	0.259	n/a	13.0	n/a	8.08
Th (ppm)	0.107	0.380	0.341	1.03	1.10	1.40
U (ppm)	0.039	0.249	0.233	0.489	0.489	0.845
Eu/Eu*	0.760	0.592	0.669	0.846	0.852	0.460
Ba/In	1014	311	299	26.9	24.9	151
$(La/SIII)_{PRIMA}$	0.420	0.510	0.000	1.07	1.15	1.12
Dv/Yb	1.63	1 41	1.40	1.51	1.67	1.29
Dy/Dy*	1.45	1.19	1.15	0.931	0.994	0.840
Zr/Y	1.90	2.25	3.93	3.38	3.42	5.24
Nb/La	n/a	0.245	0.327	0.259	0.225	0.339
Nb/Ta	n/a	14.1	12.9	14.8	13.3	12.9
Zr/Hf	n/a	28.8	29.6	36.0	37.0	34.0
Nb/Yb	n/a	0.159	0.280	0.459	0.454	0.504
Th/Yb	0.0262	0.0700	0.0931	0.175	0.187	0.201
Sr/Y	2.63	1.75	2.378	7.54	7.70	0.819
Zr/Sm	20.6	24.1	51.8	29.6	29.1	4/.1

Suite	EE-suite					
Sample ID	FJ06-07 (dupl.)	FJ06-07 (dupl.)	KL02	T47	ST15	ST14
Pluton		· · ·	Near Momi	S-Wainivalau	S-Wainivalau	S-Wainivalau
Age (Ma)			21.75 ± 0.99			
Latitude			17.888 °S	17.950 °S	17.949 °S	17.948 °S
Longitude			177.305 °E	178.207 °E	178.149 °E	178.162 °E
D 1 -			Med-K			Low-K
Rock type			rhyolite	Med-K tonalite	Med-K tonalite	trondhjemite
SiO_2 (wt.%)			76.30	71.70	74.47	74.63
TiO ₂ (wt.%)			0.25	0.46	0.44	0.40
Al_2O_3 (wt.%)			13.96	14.17	13.49	13.13
FeO* (wt.%)			2.04	3.58	2.28	2.46
MnO (wt.%)			0.03	0.06	0.12	0.03
MgO (wt.%)			1.25	1.27	0.94	0.63
CaO (wt.%)			0.63	2.94	3.24	1.81
Na ₂ O (wt.%)			3.82	3.85	4.91	6.43
K ₂ O (wt.%)			1.69	1.85	0.02	0.42
P_2O_5 (wt.%)			0.03	0.11	0.08	0.06
L.O.I. (wt.%)			3.05	0.62	2.01	0.78
Total (wt.%)			95.26	98.57	99.17	99.30
Sc (ppm)	3.94	8.55	8.60	8.49	7.45	9.56
V (ppm)	6.02	n/a	9.33	64.1	36.0	n/a
Cr (ppm)	4.62	n/a	1.33	40.6	13.5	n/a
Co (ppm)	1.19	n/a	0.636	3.91	8.10	n/a
Ni (ppm)	0.681	n/a	0.160	3.77	6.69	n/a
Cu (ppm)	57.6	n/a	n/a	2.59	3.54	n/a
Zn (ppm)	9.90	n/a	65.0	20.2	45.3	n/a
Rb (ppm)	3.92	6.97	17.8	3.79	0.440	5.77
Sr (ppm)	41.6	62.8	138	149	182	135
Y (ppm)	51.2	77.8	46.0	27.4	37.2	37.8
Zr (ppm)	299	282	151	127	170	202
Nb (ppm)	2.94	3.50	2.92	3.01	3.72	3.74
Mo (ppm)	0.117	n/a	n/a	0.733	1.05	n/a
Cs (ppm)	0.0245	0.0173	0.209	0.190	0.0332	0.0528
Ba (ppm)	212	221	188	199	58.2	92.2
La (ppm)	9.62	17.3	10.3	6.99	8.13	11.2
Ce (ppm)	20.4	42.1	13.1	16.3	10.3	25.8
Pr (ppm)	4.00	0.90	3.23 12.5	2.00	2.85	3.00
Nu (ppiii) Sm (nnm)	19.3	51.7	15.5	12.0	15.1	13.0
Sili (ppili) Eu (ppm)	0.026	9.20	5.40 1.07	5.50	5.71	4.55
Ed (ppm)	6.68	1.47	1.07	2.940	1.01	5.10
Th (ppm)	1.26	2.06	4.55	0.672	4.05	0.971
Dy (ppm)	8.72	13.7	5 71	4.50	5.83	6.50
Ho (ppm)	1.90	3.04	1 35	0.971	1 27	1.40
Er (ppm)	5 77	8.83	4 10	2.88	3.81	3.96
Tm (ppm)	0.946	1 40	0.618	0.463	0.613	0.610
Yb (ppm)	6.64	9.15	4.05	3.24	4.27	4.05
Lu (ppm)	1.14	1.45	0.629	0.507	0.702	0.683
Hf (ppm)	7.81	8.18	3.85	3.33	4.59	5.81
Ta (ppm)	0.266	0.293	0.226	0.227	0.258	0.307
Pb (ppm)	1.13	1.23	1.04	1.234	1.992	0.98
W (ppm)	4.60	n/a	n/a	0.176	0.245	n/a
Th (ppm)	1.23	2.01	1.151	1.592	1.289	1.70
U (ppm)	0.814	0.935	0.334	0.818	0.782	0.770
Eu/Eu*	0.459	0.451	0.820	0.773	0.735	0.561
Ba/Th	172	110	163	125	45.2	54.2
(La/Sm) _{PRIMA}	1.07	1.19	1.90	1.27	1.39	1.63
(La/Yb) _{PRIMA}	1.01	1.32	1.78	1.51	1.33	1.93
Dy/Yb	1.31	1.50	1.41	1.39	1.37	1.61
Dy/Dy*	0.863	0.909	0.778	0.806	0.825	0.865
Zr/Y	5.46	3.63	3.28	4.25	4.27	5.33
Nb/La	0.339	0.202	0.283	0.283	0.423	0.453
Nb/Ia	13.2	11.9	12.7	13.5	14.9	12.7
Zr/Hf	54.1	34.5	39.2	34.0	<i>33.3</i>	54.4
IND/YD Th (Nth	0.529	0.383	0.721	0.911	0.803	0.880
1 II/ 1 D Sr/V	0.180	0.219	0.284	0.491	0.302	0.420
SI/ I Zu/Sux	0.813	0.808	5.01	5.45	4.88	5.57
Zr/Sm	48.9	30.5	43.5	55.5	42.9	40.3

Table C1: (continued).

Suite	EE-suite		Certified Reference	e Materials		
Sample ID	ST14 (dupl.)	ST12	JG-1		BIR-1	
Pluton		S-Wainivalau	Japan		USA	
Age (Ma)						
Latitude		17.947 °S				
Longitude		178.193 °E				
Rock type		LOW-K	granodiorite		basalt	
S:O (wt 0/)		trondnjemite	<u> </u>			
SIO_2 (wt.%)		/0.52				
$A_{1}O_{2}$ (wt.%)		12 59				
FeO* (wt %)		1 98				
MnO (wt.%)		0.03				
MgO (wt.%)		0.36				
CaO (wt.%)		2.20				
Na ₂ O (wt.%)		5.73				
K ₂ O (wt.%)		0.45				
P_2O_5 (wt.%)		0.04				
L.O.I. (wt.%)		1.36				
Total (wt.%)	10.05	100.31	1.67		12.1	
Sc (ppm)	10.07	7.28	4.67	6.54	43.4	44
v (ppm) Cr (ppm)	n/a	n/a n/a	23.4	25 64.6	319	313
Cr (ppiii)	n/a	n/a	3 36	4.0	51.2	51.4
Ni (ppm)	n/a	n/a	6.62	4	161	166
C_{11} (ppm)	n/a	n/a	2.07	15	114	126
Zn (ppm)	n/a	n/a	36.9	41.5	67.7	71
Rb (ppm)	5.75	6.65	145	181	0.224	0.212
Sr (ppm)	137	130	157	184	114	104
Y (ppm)	38.8	39.1	30.2	28.5	15.7	16
Zr (ppm)	203	163	131	114	15.6	14
Nb (ppm)	3.71	3.71	11.4	12.6	0.539	0.55
Mo (ppm)	n/a	n/a	1.07	1.46	0.061	0.50
Cs (ppm)	0.0455	0.0580	10.3	10.2	0.00855	0.005
Ba (ppm)	93.0	111	448	462	0.96	5.83
La (ppiii) Ce (ppm)	11.5	25.8	53.2 62.8	22.4 45.0	1.024	0.02
Pr (nnm)	3.63	3 45	8 35	5 21	0.388	0.38
Nd (ppm)	16.0	14.4	31.6	19.5	2.50	2.5
Sm (ppm)	4.43	3.68	6.77	4.67	1.17	1.1
Eu (ppm)	0.893	0.757	0.691	0.74	0.550	0.54
Gd (ppm)	5.29	4.36	6.01	4.2	1.88	1.85
Tb (ppm)	0.995	0.825	0.929	0.83	0.372	0.36
Dy (ppm)	6.62	5.73	5.39	3.93	2.65	2.5
Ho (ppm)	1.43	1.32	1.05	0.83	0.582	0.57
Er (ppm)	4.03	4.02	2.92	1.83	1.68	1.7
Im (ppm) Vh (nnm)	0.023	0.043	2.05	0.44	0.255	0.20
I U (ppm)	4.13	4.33	0.567	0.39	0.261	0.26
Hf (ppm)	5.84	4.50	3.96	3.79	0.567	0.581
Ta (ppm)	0.304	0.350	1.46	1.7	0.0390	0.035
Pb (ppm)	1.00	2.00	24.1	26.2	2.96	3.08
W (ppm)	n/a	n/a	1.08	1.7	0.0287	0.07
Th (ppm)	1.73	2.99	17.0	13.5	0.0344	0.03
U (ppm)	0.795	0.810	2.68	3.3	0.0141	0.01
Eu/Eu*	0.559	0.573	0.328	0.506	1.13	1.15
Ba/Th	54.2	37.1	26.4	34.2	203	194
$(La/Sm)_{PRIMA}$	1.63	2.01	3.31	3.05	0.341	0.359
(La/YD) _{PRIMA}	1.92	1.88	8.07	0.29	0.259	0.263
Dy/10 Dy/Dy*	1.01	1.32	1.//	1.38	1.38	1.32
Zr/Y	5 3 3	4 27	4 33	4 00	0.989	0.875
Nb/La	0.318	0.307	0.325	0.563	0.864	0.887
Nb/Ta	12.7	11.1	7.84	7.41	13.8	15.7
Zr/Hf	34.4	36.0	33.1	30.1	27.5	24.1
Nb/Ýb	0.880	0.824	3.75	5.06	0.320	0.333
Th/Yb	0.419	0.691	5.57	5.42	0.0204	0.0182
Sr/Y	3.53	3.33	5.18	6.46	7.245	6.50
Zr/Sm	46.3	45.4	19.4	24.4	13.4	12.7

Suite	Certified Refere	ence Materials			Procedural blanks	5
Sample ID	BCR-2		G-2		blank 1	blank 2
Pluton	USA					
Age (Ma)						
Latitude						
Longitude						
Rock type	basalt		granite			
SiO_2 (wt.%)						
TiO_2 (wt.%)						
Al ₂ O ₃ (wt.%)						
FeO* (wt.%)						
MnO (wt.%)						
MgO (wt.%)						
CaO(Wt.%)						
$K_{2}O(wt.\%)$						
$R_2O(wt.\%)$ $P_2O_5(wt.\%)$						
L.O.I. (wt.%)						
Total (wt.%)						
Sc (ppm)	33.3	33	n/a		0.055	0.056
V (ppm)	424	416	n/a		0.020	0.035
Cr (ppm)	23.1	18	n/a		2.180	2.096
Co (ppm)	37.4	37	n/a		0.017	0.016
Cu (ppm)	12.2	12 - 17.7	n/a		0.070	0.079
Zn (ppm)	13.5	127.00	n/a		0.094	0.298
Rb (ppm)	47.3	46.9 - 48	150	169	0.025	0.024
Sr (ppm)	349	340 - 346	464	475	0.273	0.276
Y (ppm)	34.7	37.00	9.23	9.88	0.004	0.004
Zr (ppm)	194	184 - 188	n/a		0.042	0.031
Nb (ppm)	12.0	12.60	n/a		0.006	0.005
Mo (ppm)	256.5	248 - 250	n/a	1.24	0.028	0.020
Cs (ppm)	1.18	1.10	1.53	1.34	0.005	0.005
La (ppm)	25.6	25.00	85.0	88.4	0.038	0.017
Ce (ppm)	53.7	53.00	155	160	0.005	0.005
Pr (ppm)	6.93	6.7 - 6.8	15.6	16.9	0.004	0.004
Nd (ppm)	29.8	28 - 28.7	49.1	53.8	0.021	0.022
Sm (ppm)	6.84	6.58 - 6.7	6.38	7.19	0.023	0.024
Eu (ppm)	2.08	1.96 - 2	1.33	1.40	0.008	0.008
Gd (ppm)	7.00	6.75 - 6.8	4.52	4.23	0.023	0.025
Tb (ppm)	1.09 6.54	1.07	0.459	0.495	0.004	0.004
Ho (ppm)	1 32	1.28 - 1.33	0.335	0.373	0.013	0.013
Er (ppm)	3.60	3.66	0.783	0.927	0.012	0.012
Tm (ppm)	0.533	0.54	0.109	0.123	0.004	0.004
Yb (ppm)	3.47	3.38 - 3.5	0.589	0.722	0.018	0.018
Lu (ppm)	0.534	0.503 - 0.51	0.0715	0.102	0.016	0.013
Hf (ppm)	4.72	4.8 - 4.9	n/a		0.018	0.017
Ta (ppm)	0.741	0.74	n/a	20 P	0.007	0.008
Pb (ppm)	0.554	11.00	30.3	30.0	0.015	0.010
Th (ppm)	6.03	6.00	24.2	24.5	0.023	0.007
U (ppm)	1.69	1.69	1.74	1.96	0.007	0.007
Eu/Eu*	0.912	0.909	0.752	0.769		
Ba/Th	116		78.1	76.7		
(La/Sm) _{PRIMA}	2.38	2.42	8.48	7.82		
(La/Yb) _{PRIMA}	5.17	5.17	101	85.6		
Dy/Yb	1.89	1.90	3.65	3.16		
Dy/Dy*	0.751	0.754	0.581	0.529		
Zr/Y	5.59	5.08				
Nb/La	0.469	0.504				
Nb/Ta	16.2	17.0				
Zr/Hf	41.1	39.2 2 7 2				
IND/ID Th/Yh	3.4/	3./3 1.79	41.1	24.0		
111/10 Sr/V	1.74	1./0	41.1	34.U 48 1		
Zr/Sm	28.3	28.6	50.5	40.1		
21/0111	20.5	20.0			1	

Table C1: (continued).

×
•=
Ч
Ē
T
Ō
b
0
1
7
Ι
\sim

Table C2: High-precision trace element concentration data and radiogenic Hf-Nd-Sr-Pb isotope composition data of Fijian plutons and two certified reference standards (JG-1; G-2). Calculated ε^{176} Hf and ε^{143} Nd values are relative to CHUR with 176 Hf/ 177 Hf = 0.282785 and 143 Nd/ 144 Nd = 0.512630, respectively (Bouvier et al., 2008). **Bold** values are used for the figures in **Chapter 3**.

Suite	LE-suite							
Sample	DGG5	YV 06	YV 06 (dupl.)	T24	T24 (dupl.)	T24 (dupl.)	T25	T25 (dupl.)
Pluton	Yavuna	Yavuna		Wainivalau			Wainivalau	
Rock Type	Med-K trondhiemite	Med-K trondhiemite		Med-K tonalite			Med-K tonalite	
Age (Ma)	37.25 ± 0.63			10.74 ± 0.24			11.28 ± 0.20	
Zr (ppm)	-	120.9	-	101.1	109.4	-	64.88	-
Nb (ppm)	-	1.464	-	2.114	2.097	-	1.920	-
Ta (ppm)	-	0.1104	-	0.1702	0.1637	-	0.2007	-
Lu (ppm)	-	0.4169	-	0.3619	0.3604	-	0.2516	-
Hf (ppm)	-	3.471	-	2.920	2.911	-	1.856	-
¹⁷⁶ Lu/ ¹⁷⁷ Hf	-	0.0170	-	0.0176	0.0176	-	0.0192	-
176Hf/177Hf	0.283119 ± 8	0.283135 ± 6	0.28312 ± 6	$\textbf{0.283188} \pm \textbf{8}$	0.283194 ± 7	0.283162 ± 12	0.283217 ± 12	0.283154 ± 10
$\epsilon^{176} Hf$	11.8 ± 0.4	12.4 ± 0.4	11.8 ± 0.4	14.3 ± 0.4	14.5 ± 0.4	13.3 ± 0.4	15.3 ± 0.4	13.0 ± 0.4
143Nd/144Nd	0.513067 ± 6	0.513024 ± 7	0.513031 ± 6	0.513081 ± 10	-	0.513087 ± 8	0.513094 ± 9	0.513082 ± 8
$\epsilon^{143} Nd$	$\textbf{8.4} \pm \textbf{0.4}$	7.5 ± 0.4	$\textbf{7.7} \pm \textbf{0.4}$	$\textbf{8.6} \pm \textbf{0.4}$	-	8.8 ± 0.4	8.9 ± 0.4	$\textbf{8.7} \pm \textbf{0.4}$
⁸⁷ Sr/ ⁸⁶ Sr	0.703599 ± 6	0.703744 ± 11	0.703824 ± 12	0.703212 ± 9	-	$\textbf{0.703012} \pm \textbf{8}$	0.703190 ± 7	0.703141 ± 7
²⁰⁶ Pb/ ²⁰⁴ Pb	19.010	-	19.029	-	-	18.864	-	18.898
²⁰⁷ Pb/ ²⁰⁴ Pb	15.579	-	15.568	-	-	15.578	-	15.584
²⁰⁸ Pb/ ²⁰⁴ Pb	38.610	-	38.648	-	-	38.373	-	38.407

Suite	LE-suite								
Sample	T44	T22	T22 (dupl.)	T10	T41	T41 (dupl.)	T8	T36	T36 (dupl.)
Pluton	Wainivalau	Wainivalau		Wainivalau	Wainivalau		Wainivalau	Wainivalau	
Rock Type	Med-K trondhiemite	Low-K trondhiemite		Med-K	Med-K		Med-K	Med-K	
Age (Ma)	11.73 ± 0.07				11.41 ± 0.20			11.73 ± 0.18	
Zr (ppm)	-	109.8	128.8	104.9	106.4	-	108.3	115.7	-
Nb (ppm)	-	2.614	2.517	2.693	2.271	-	2.809	2.710	-
Ta (ppm)	-	0.2383	0.2435	0.2417	0.2137	-	0.2847	0.2728	-
Lu (ppm)	-	0.4438	0.3851	0.4608	0.4186	0.3205	0.4265	0.3707	-
Hf (ppm)	-	3.421	3.857	3.321	3.213	2.933	3.548	3.496	-
¹⁷⁶ Lu/ ¹⁷⁷ Hf	-	0.0184	0.0142	0.0197	0.0185	0.0190	0.0170	0.0151	-
¹⁷⁶ Hf/ ¹⁷⁷ Hf	0.283154 ± 12	0.283159 ± 11	0.283173 ± 6	0.283180 ± 17	0.283182 ± 11	0.283191 ± 11	0.283179 ± 13	0.283209 ± 10	0.283164 ± 8
$\epsilon^{176} Hf$	13.0 ± 0.4	13.2 ± 0.4	13.7 ± 0.4	$+13.0\pm0.4$	$+14.1\pm0.4$	$+14.4\pm0.4$	$+14.0\pm0.4$	$+15.0\pm0.4$	$+13.4\pm0.4$
143Nd/144Nd	0.513095 ± 12	0.513057 ± 6	-	0.513067 ± 10	0.513072 ± 14	-	$\textbf{0.513083} \pm 7$	0.513054 ± 4	0.513073 ± 13
$\epsilon^{143}Nd$	$\textbf{8.9} \pm \textbf{0.4}$	$\textbf{8.2} \pm \textbf{0.4}$	-	$+8.4\pm0.4$	$+8.5\pm0.4$	-	$+8.7\pm0.4$	$+8.1\pm0.4$	$+8.5\pm0.4$
⁸⁷ Sr/ ⁸⁶ Sr	0.703175 ± 8	0.703278 ± 12	-	0.703275 ± 10	0.703157 ± 8	-	0.703291 ± 8	0.703199 ± 12	0.703235 ± 9
²⁰⁶ Pb/ ²⁰⁴ Pb	18.807	-	-	-	-	-	-	-	18.783
²⁰⁷ Pb/ ²⁰⁴ Pb	15.564	-	-	-	-	-	-	-	15.555
²⁰⁸ Pb/ ²⁰⁴ Pb	38.334	-	-	-	-	-	-	-	38.309

Suite	LE-suite	LD-suite							
Sample	69-858	DGG3	ST99	ST99 (dupl.)	ST107	ST107 (dupl.)	DGG4	ST87	LK 01
Pluton	Noikoro		Korolevu		Korolevu		Korolevu	Korolevu	Korolevu
Rock Type	Med-K tonalite	gabbro	Qtz-gabbro		Low-K tonalite		Low-K	Low-K	rhyolite
Age (Ma)		9.46 ± 0.21					9.63 ± 0.18	nonumennie	
Zr (ppm)	74.00	-	24.84	29.07	19.44	18.79	-	104.9	97.45
Nb (ppm)	1.873	-	0.3198	0.3096	0.4303	0.4083	-	0.8623	0.6181
Ta (ppm)	0.1748	-	0.01747	0.02041	0.02723	0.02413	-	0.06131	0.04804
Lu (ppm)	0.3475	-	0.5218	0.5241	0.4290	0.4460	-	0.8729	0.5659
Hf (ppm)	2.528	-	1.072	1.174	0.8322	0.8334	-	3.643	3.293
176Lu/177Hf	0.0195	-	0.0689	0.0634	0.0729	0.0740	-	0.0340	0.0244
¹⁷⁶ Hf/ ¹⁷⁷ Hf	0.283196 ± 19	0.283186 ± 10	0.283209 ± 12	0.283228 ± 6	$\textbf{0.283278} \pm \textbf{14}$	0.283289 ± 11	0.283173 ± 10	0.283210 ± 12	0.283221 ± 7
$\epsilon^{176} Hf$	14.5 ± 0.4	14.2 ± 0.4	15.0 ± 0.4	15.7 ± 0.4	17.4 ± 0.4	17.8 ± 0.4	13.7 ± 0.4	15.0 ± 0.4	15.4 ± 0.4
143Nd/144Nd	0.513110 ± 7	0.513112 ± 8	0.513099 ± 6	-	$\textbf{0.513087} \pm \textbf{5}$	-	0.513149 ± 10	$\textbf{0.513099} \pm \textbf{5}$	0.513108 ± 6
$\epsilon^{143} Nd$	$+9.2\pm0.4$	9.2 ± 0.4	9.0 ± 0.4	-	$\textbf{8.8} \pm \textbf{0.4}$	-	10.0 ± 0.4	9.0 ± 0.4	9.2 ± 0.4
⁸⁷ Sr/ ⁸⁶ Sr	0.703436 ± 8	0.703727 ± 9	$\textbf{0.703490} \pm 11$	-	0.703663 ± 18	-	$\textbf{0.703838} \pm \textbf{9}$	0.703965 ± 12	0.704403 ± 11
²⁰⁶ Pb/ ²⁰⁴ Pb	-	18.8210	-	-	-	-	18.8060	-	-
²⁰⁷ Pb/ ²⁰⁴ Pb	-	15.5770	-	-	-	-	15.5730	-	-
²⁰⁸ Pb/ ²⁰⁴ Pb	-	38.5070	-	-	-	-	38.4950	-	-

Table C2: (continued).

Suite	LD-suite	EE-suite							
Sample	LK 01 (dupl.)	FJ05-06	FJ05-06 (dupl.)	FJ06-07	FJ06-07 (dupl.)	FJ06-07 (dupl.)	KL02	T47	ST15
Pluton		Momi		Momi			Near Momi	S-Wainivalau	S-Wainivalau
Rock Type		Low-K tonalite		Low-K trondhjemite			rhyolite	Med-K tonalite	Low-K tonalite
Age (Ma)		20.79 ± 0.34		20.98 ± 0.31			21.75 ± 0.99		
Zr (ppm)	-	184.2	-	277.8	279.7	-	-	116.3	159.1
Nb (ppm)	-	2.719	-	3.524	3.510	-	-	2.956	3.684
Ta (ppm)	-	0.1842	-	0.2725	0.2663	-	-	0.2198	0.2474
Lu (ppm)	-	0.8946	-	1.392	1.410	-	-	0.5070	0.7020
Hf (ppm)	-	5.124	-	8.177	8.196	-	-	3.419	4.784
¹⁷⁶ Lu/ ¹⁷⁷ Hf	-	0.0248	-	0.0242	0.0244	-	-	0.0252	0.0208
¹⁷⁶ Hf/ ¹⁷⁷ Hf	0.283174 ± 4	0.283156 ± 10	$\textbf{0.283147} \pm \textbf{4}$	0.283141 ± 9	0.283161 ± 10	0.283144 ± 4	0.283142 ± 6	0.283185 ± 5	0.283173 ± 13
$\epsilon^{176} Hf$	13.8 ± 0.4	13.1 ± 0.4	$+12.8\pm0.4$	$+12.6\pm0.4$	$+13.3\pm0.4$	$+12.7\pm0.4$	$+12.6 \pm 0.4$	$+14.1 \pm 0.4$	$+13.7\pm0.4$
143Nd/144Nd	0.513085 ± 8	0.513013 ± 7	0.513062 ± 4	0.513028 ± 8	-	$\textbf{0.513057} \pm \textbf{6}$	0.513050 ± 10	$\textbf{0.513074} \pm 10$	0.513061 ± 4
$\epsilon^{143} Nd$	$\textbf{8.7} \pm \textbf{0.4}$	7.3 ± 0.4	$+8.3\pm0.4$	$+7.6\pm0.4$	-	$+8.2\pm0.4$	$+8.0\pm0.4$	$+8.5\pm0.4$	$+8.2\pm0.4$
⁸⁷ Sr/ ⁸⁶ Sr	0.704426 ± 22	0.703824 ± 8	$\textbf{0.703827} \pm 9$	$\textbf{0.703803} \pm \textbf{9}$	-	0.703935 ± 43	-	0.703219 ± 9	0.703737 ± 12
²⁰⁶ Pb/ ²⁰⁴ Pb	18.790	-	18.670	-	-	18.705	18.737	-	-
²⁰⁷ Pb/ ²⁰⁴ Pb	15.565	-	15.552	-	-	15.569	15.565	-	-
²⁰⁸ Pb/ ²⁰⁴ Pb	38.483	-	38.301	-	-	38.375	38.406	-	-

	Suite	EE-suite					Certified Reference Material Procedural blanks			ks
	Sample	ST15 (dupl.)	ST14	ST14 (dupl.)	ST12	ST12 (dupl.)	JG-1	G2	blank 1	blank 2
	Pluton		S-Wainivalau		S-Wainivalau		Japan	USA		
-	Rock Type		Low-K		Low-K		granodiorite	granite	in (ng/g)	in (ng/g)
	Age (Ma)		Ironamenine		fronamennie					
	Zr (ppm)	187.8	201.4	-	167.1	-	120.7	-	0.951	0.425
	Nb (ppm)	3.419	3.565	-	3.567	-	11.42	-	0.009	0.989
	Ta (ppm)	0.2577	0.2799	-	0.3226	-	1.433	-	0.012	0.092
	Lu (ppm)	0.6128	0.6578	-	0.6390	-	0.4940	-	0.096	0.076
	Hf (ppm)	5.390	5.846	-	4.637	-	4.088	-	0.034	0.029
	176Lu/177Hf	0.0161	0.0160	-	0.0196	-	0.0191	-	-	-
	¹⁷⁶ Hf/ ¹⁷⁷ Hf	0.283171 ± 5	0.283177 ± 4	0.283161 ± 4	0.283179 ± 6	0.283160 ± 6	0.282761 ± 9	0.282521 ± 4	-	-
	$\epsilon^{176} Hf$	13.6 ± 0.4	13.9 ± 0.4	13.3 ± 0.4	$+13.9\pm0.4$	$+13.3 \pm 0.4$	-0.8	-9.3	-	-
	143Nd/144Nd	-	0.513061 ± 4	0.513066 ± 6	0.513047 ± 4	0.513069 ± 6	0.512432 ± 8	0.512235 ±	-	-
	$\epsilon^{143} Nd$	-	$\textbf{8.3} \pm \textbf{0.4}$	8.3 ± 0.4	$+8.0\pm0.4$	$+8.4\pm0.4$	-4.0 ± 0.4	-7.9 ± 0.4	-	-
ued).	⁸⁷ Sr/ ⁸⁶ Sr	-	0.703785 ± 11	0.703807 ± 13	0.703254 ± 12	0.703240 ± 26	0.711033 ±	0.709725 ±	-	-
contin	²⁰⁶ Pb/ ²⁰⁴ Pb	-	-	18.755	-	18.750	-	18.633	-	-
C2: ((²⁰⁷ Pb/ ²⁰⁴ Pb	-	-	15.552	-	15.552	-	15.539	-	-
Table	²⁰⁸ Pb/ ²⁰⁴ Pb	-	-	38.311	-	38.311	-	38.245	-	-

Element	D_i^{Opx}	D_i^{Ol}	$\mathbf{D}_{i}^{\mathrm{Pl}}$	$\mathrm{D_{i}^{Amph}}$	${\rm D_i}^{\rm CPx}$	$\mathrm{D_i}^{\mathrm{Magn}}$	$\mathbf{D}_{\mathrm{i}}^{\mathrm{Ilm}}$	D_i^{Qtz}	$D_i{}^{Ap}$	D_i^{Grt}
Th	0.13	0.003	0.095	0.055	0.104	0.02	0.09	0.008	23	0.0075
Nb	0.001	0.00007	0.239	0.44	0.007	0.86	0.88	-	0.05	0.04
Та	0.008	0.0004	0.053	0.22	0.028	0.95	1.47	-	0.05	0.08
La	0.0003	0.0001	0.358	0.319	0.028	0.015	0.015	0.014	12	0.028
Ce	0.0007	0.001	0.339	0.56	0.059	0.016	0.012	0.006	15	0.08
Pr	0.0014	0.002	0.316	0.898	0.0116	0.018	0.011	0.006	17	0.15
Sr	0.047	0.001	2.9	0.389	0.032	0.022	0.0022	-	1.4	0.019
Nd	0.0028	0.003	0.289	1.32	0.115	0.026	0.01	0.009	19	0.222
Zr	0.074	0.002	0.078	0.781*	0.125	0.56	0.8	-	16	0.537
Hf	0.15	0.004	0.069	0.781	0.208	0.65	1.24	-	16	0.431
Sm	0.0085	0.002	0.237	2.09	0.259	0.024	0.009	0.008	20	1.43
Eu	0.68	-	2.17	1.79	0.341	0.025	0.01	0.031	13	1.54
Gd	0.02	0.003	0.192	2.53	0.422	0.018	0.011	0.007	20	4.84
Tb	0.03	0.004	0.17	2.6	0.502	0.019	0.018	0.007	19	7.8
Dy	0.043	0.006	0.15	2.55	0.57	0.018	0.02	0.01	18	11.5
Y	0.054	0.008	0.138	2.47	0.603	0.018	0.037	-	17.5	14.1
Ho	0.06	0.009	0.132	2.41	0.616	0.018	0.035	0.01	16.8	15.3
Er	0.079	0.012	0.117	2.22	0.64	0.018	0.067	0.01	15.5	18.8
Tm	0.101	0.018	0.104	2	0.644	0.018	0.102	0.01	14.2	21.5
Yb	0.125	0.05	0.094	1.79	0.635	0.018	0.13	0.012	13	23.2
Lu	0.149	0.041	0.085	1.59	0.617	0.018	0.19	0.02	10	24.1

Table C3a: Partition coefficients $D_i^{\phi \ 10}$ used to model fractional crystallization and anataxis of basalt (Nash and Crecraft, 1985; <u>Adam and Green, 2006</u>; Bédard, 2006; **Klemme et al., 2006**; *Foley, 2008*).

$$D_i = \frac{C_i^C}{C_i^L}$$

¹⁰ The ratio of the concentration of trace element *i* in a mineral (C_i^C) relative to the concentration of the same trace element *i* in the liquid/melt (C_i^L) is called partition coefficient (D_i) of a specific mineral (φ) where

If $D_i \ll 1$, the element behaves incompatible and is preferentially concentrated in the liquid in partial melting or fractional crystallization processes. Vice versa, if $D_i \gg 1$, the element beave compatible and remains preferentially in the solid phases in partial melting processes or preferentially crystallizes in fractional crystallization processes.

Table C3b: Calculated stable mineral assemblages (adapted to 10 % melt increments) during 400 MPa crystal fractionation (Blatter et al., 2013).

Melt	Xopx	\mathbf{X}_{Pl}	X_{Amph}	X _{CPx}	Xol	X _{Magn}	X _{Ilm}	X_{Ap}	Sum of cryst.
90 %	-	11	-	6	6	-	-	-	23.0
80 %	-	11	-	6	6	-	-	-	23.0
70 %	-	11	-	6	6	-	-	-	23.0
60 %	-	25	-	14	6	2	-	-	47.0
50 %	-	25	-	14	6	2	-	-	47.0
40 %	-	23	-	17	5	3	-	0.2	48.2
30 %	-	23	-	17	5	3	-	0.2	48.2
20 %	11	34	19	12	-	4	-	0.2	80.2
10 %	9	31	32	9	-	2	-	0.2	83.2

Relative mineral fractions $X\phi$ for each 10 % melt increment

Melt	X _{Opx}	X_{Pl}	X_{Amph}	X _{CPx}	Xol	X _{Magn}	X _{Ilm}	X_{Ap}
90 %	0.0000	0.4783	0.0000	0.2609	0.2609	0.0000	0.0000	0.0000
80 %	0.0000	0.4783	0.0000	0.2609	0.2609	0.0000	0.0000	0.0000
70 %	0.0000	0.4783	0.0000	0.2609	0.2609	0.0000	0.0000	0.0000
60 %	0.0000	0.5319	0.0000	0.2979	0.1277	0.0426	0.0000	0.0000
50 %	0.0000	0.5319	0.0000	0.2979	0.1277	0.0426	0.0000	0.0000
40 %	0.0000	0.4772	0.0000	0.3527	0.1037	0.0622	0.0000	0.0041
30 %	0.0000	0.4772	0.0000	0.3527	0.1037	0.0622	0.0000	0.0041
20 %	0.1372	0.4239	0.2369	0.1496	0.0000	0.0499	0.0000	0.0025
10 %	0.1082	0.3726	0.3846	0.1082	0.0000	0.0240	0.0000	0.0024

Mean partition coefficients \overline{D}_{l}^{11} *for each 10 % melt increment*

Element	D(90%)	D(80%)	$\frac{1}{\overline{D}}(70\%)$	D(60%)	D(50%)	D(40%)	D(30%)	D (20%)	<u>D</u> (10%)
Th	0.073	0.073	0.073	0.083	0.083	0.179	0.179	0.145	0.138
Nb	0.116	0.116	0.116	0.166	0.166	0.170	0.170	0.250	0.280
Та	0.033	0.033	0.033	0.077	0.077	0.095	0.095	0.127	0.131
La	0.179	0.179	0.179	0.199	0.199	0.231	0.231	0.262	0.288
Ce	0.178	0.178	0.178	0.199	0.199	0.246	0.246	0.324	0.385
Pr	0.155	0.155	0.155	0.173	0.173	0.227	0.227	0.392	0.506
Sr	1.396	1.396	1.396	1.553	1.553	1.402	1.402	1.337	1.243
Nd	0.169	0.169	0.169	0.189	0.189	0.259	0.259	0.502	0.674
Zr	0.070	0.070	0.070	0.103	0.103	0.183	0.183	0.315	0.403
Hf	0.088	0.088	0.088	0.127	0.127	0.214	0.214	0.338	0.419
Sm	0.181	0.181	0.181	0.204	0.204	0.289	0.289	0.687	0.970
Eu	1.127	1.127	1.127	1.257	1.257	1.211	1.211	1.522	1.639
Gd	0.203	0.203	0.203	0.229	0.229	0.325	0.325	0.797	1.141
Tb	0.213	0.213	0.213	0.241	0.241	0.339	0.339	0.816	1.167
Dy	0.222	0.222	0.222	0.251	0.251	0.349	0.349	0.805	1.147
Y	0.225	0.225	0.225	0.255	0.255	0.353	0.353	0.786	1.115
Ho	0.226	0.226	0.226	0.256	0.256	0.352	0.352	0.770	1.090
Er	0.226	0.226	0.226	0.255	0.255	0.348	0.348	0.722	1.013
Tm	0.222	0.222	0.222	0.250	0.250	0.339	0.339	0.664	0.923
Yb	0.224	0.224	0.224	0.246	0.246	0.329	0.329	0.609	0.837
Lu	0.212	0.212	0.212	0.235	0.235	0.305	0.305	0.551	0.751

¹¹ If more than one mineral is responsible for the distribution of a specific trace element (*i*), the behaviour of the trace element may be described by a mean partition coefficient (\overline{D}_i) where

$$\overline{D}_i = \sum_{\varphi} X_{\varphi} D_i^{\varphi}$$

 $(X\varphi)$ is the relative weight fraction of the mineral (φ) and (D_i^{φ}) is the partition coefficient for trace element (i) in mineral (φ) .

Melt	X _{Opx}	\mathbf{X}_{Pl}	X_{Amph}	X _{CPx}	Xol	X _{Magn}	X _{Ilm}	X _{Ap}	Sum of cryst.
90 %	-	3	-	15	3	1	-	-	22.0
80 %	-	3	-	15	3	1	-	-	22.0
70 %	-	20	-	20	7	2	-	-	49.0
60 %	-	20	-	20	7	2	-	-	49.0
50 %	-	20	-	20	7	2	-	-	49.0
40 %	9	22	14	16	0	3	-	0.2	64.2
30 %	9	22	14	16	0	3	-	0.2	64.2
20 %	12	28	27	11	0	2	-	0.2	80.2
10 %	7	27	39	9	0	1	-	0.2	83.2

Table C3c: Calculated stable mineral assemblages (adapted to 10 % melt increments) during 700 MPa crystal fractionation (Blatter et al., 2013).

Relative mineral fractions $X\phi$ for each 10 % melt increment

Melt	X _{Opx}	X_{Pl}	X_{Amph}	X _{CPx}	X _{Ol}	X_{Magn}	X_{Ilm}	X_{Ap}
90 %	0.0000	0.1364	0.0000	0.6818	0.1364	0.0455	0.0000	0.0000
80 %	0.0000	0.1364	0.0000	0.6818	0.1364	0.0455	0.0000	0.0000
70 %	0.0000	0.4082	0.0000	0.4082	0.1429	0.0408	0.0000	0.0000
60 %	0.0000	0.4082	0.0000	0.4082	0.1429	0.0408	0.0000	0.0000
50 %	0.0000	0.4082	0.0000	0.4082	0.1429	0.0408	0.0000	0.0000
40 %	0.1402	0.3427	0.2181	0.2492	0.0000	0.0467	0.0000	0.0031
30 %	0.1402	0.3427	0.2181	0.2492	0.0000	0.0467	0.0000	0.0031
20 %	0.1496	0.3491	0.3367	0.1372	0.0000	0.0249	0.0000	0.0025
10 %	0.0841	0.3245	0.4688	0.1082	0.0000	0.0120	0.0000	0.0024

Mean partition coefficients \overline{D} for each 10 % melt increment

meanpa	mean partment excipterents 2 for each 10 / o men merement									
Element	D(90%)	D (80%)	D(70%)	D(60%)	D(50%)	D (40%)	D (30%)	D (20%)	<u>D</u> (10%)	
Th	0.085	0.085	0.082	0.082	0.082	0.161	0.161	0.143	0.134	
Nb	0.076	0.076	0.136	0.136	0.136	0.220	0.220	0.254	0.295	
Та	0.070	0.070	0.072	0.072	0.072	0.119	0.119	0.121	0.136	
La	0.069	0.069	0.158	0.158	0.158	0.237	0.237	0.267	0.298	
Ce	0.087	0.087	0.163	0.163	0.163	0.301	0.301	0.353	0.415	
Pr	0.052	0.052	0.135	0.135	0.135	0.361	0.361	0.457	0.566	
Sr	0.418	0.418	1.198	1.198	1.198	1.099	1.099	1.159	1.134	
Nd	0.119	0.119	0.166	0.166	0.166	0.476	0.476	0.610	0.771	
Zr	0.122	0.122	0.106	0.106	0.106	0.315	0.315	0.372	0.456	
Hf	0.181	0.181	0.140	0.140	0.140	0.347	0.347	0.394	0.470	
Sm	0.210	0.210	0.204	0.204	0.204	0.666	0.666	0.874	1.134	
Eu	0.530	0.530	1.026	1.026	1.026	1.356	1.356	1.542	1.669	
Gd	0.315	0.315	0.252	0.252	0.252	0.789	0.789	1.030	1.344	
Tb	0.367	0.367	0.276	0.276	0.276	0.815	0.815	1.056	1.377	
Dy	0.411	0.411	0.295	0.295	0.295	0.812	0.812	1.041	1.353	
Y	0.432	0.432	0.304	0.304	0.304	0.799	0.799	1.015	1.315	
Ho	0.440	0.440	0.307	0.307	0.307	0.786	0.786	0.993	1.285	
Er	0.455	0.455	0.311	0.311	0.311	0.744	0.744	0.927	1.192	
Tm	0.457	0.457	0.309	0.309	0.309	0.692	0.692	0.849	1.084	
Yb	0.453	0.453	0.305	0.305	0.305	0.640	0.640	0.774	0.980	
Lu	0.439	0.439	0.293	0.293	0.293	0.583	0.583	0.697	0.876	

VI. Appendix

Table C3d: Calculated stable mineral assemblages during 800 MPa partial melting of N-MORB (Hoffmann	
et al., 2019).	

Temp.	Xopx	X_{Pl}	XAmph	X _{CPx}	Xol	X _{Magn}	X _{Ilm}	X _{Qtz}	Sum of cryst.
655 °C	-	12.6	67	7.2	-	0.5	1	9.8	98.1
825 °C	-	20.3	55.9	12.1	-	0.5	1.1	5.7	95.6
870 °C	3.9	23	44.4	15.1	-	1	1.1	2.5	91.0
900 °C	9.2	24.9	31.9	17.5	-	1	1.3	0	85.8
945 °C	10.7	23.7	25.7	18.8	-	1	1.3	0	81.2

Relative mineral fractions for each Temperature increment

Temp.	X _{OPx}	X_{Pl}	X_{Amph}	X _{CPx}	X_{Ol}	X _{Magn}	X _{Ilm}	X _{Qtz}
655 °C	0.0000	0.1284	0.6830	0.0734	0.0000	0.0051	0.0102	0.0999
825 °C	0.0000	0.2123	0.5847	0.1266	0.0000	0.0052	0.0115	0.0596
870 °C	0.0429	0.2527	0.4879	0.1659	0.0000	0.0110	0.0121	0.0275
900 °C	0.1072	0.2902	0.3718	0.2040	0.0000	0.0117	0.0152	0.0000
945 °C	0.1318	0.2919	0.3165	0.2315	0.0000	0.0123	0.0160	0.0000

Mean partition coefficients \overline{D} for each Temperature increment

Element	D(650°C)	D(825°C)	D(870°C)	D(900°C)	D(945°C)
Th	0.059	0.067	0.075	0.085	0.088
Nb	0.345	0.324	0.296	0.258	0.235
Та	0.179	0.165	0.154	0.137	0.128
La	0.268	0.267	0.252	0.229	0.212
Ce	0.431	0.407	0.369	0.319	0.290
Pr	0.656	0.594	0.520	0.428	0.380
Sr	0.641	0.847	0.930	0.998	0.983
Nd	0.948	0.849	0.737	0.599	0.530
Zr	0.564	0.501	0.441	0.365	0.328
Hf	0.573	0.515	0.462	0.395	0.363
Sm	1.478	1.306	1.124	0.900	0.792
Eu	1.530	1.553	1.509	1.438	1.369
Gd	1.784	1.574	1.354	1.085	0.958
Tb	1.835	1.621	1.397	1.122	0.993
Dy	1.804	1.596	1.379	1.113	0.989
Y	1.749	1.550	1.343	1.088	0.970
Ho	1.710	1.516	1.315	1.067	0.953
Er	1.580	1.405	1.224	1.000	0.897
Tm	1.429	1.275	1.115	0.918	0.828
Yb	1.284	1.149	1.010	0.838	0.760
Lu	1.146	1.029	0.909	0.761	0.694

						F					
	Melt	90.0%	80.0%	70.0%	60.0%	50.0%	40.0%	30.0%	20.0%	10.0%	rel. F
Element	69-920	90.0%	88.9%	87.5%	85.7%	83.3%	80.0%	75.0%	66.7%	50.0%	
Th	0.32	0.35	0.39	0.45	0.51	0.61	0.73	0.92	1.30	2.37	
Nb	1.00	1.10	1.22	1.37	1.56	1.81	2.18	2.77	3.76	6.19	
Та	0.08	0.09	0.10	0.11	0.13	0.15	0.19	0.24	0.35	0.64	
La	3.90	4.25	4.68	5.23	5.91	6.84	8.12	10.13	13.67	22.38	
Ce	10.20	11.12	12.25	13.68	15.47	17.91	21.19	26.32	34.63	53.06	
Pr	1.66	1.81	2.00	2.24	2.55	2.96	3.52	4.40	5.63	7.93	
Sr	272.00	260.90	249.02	236.21	216.90	196.09	179.25	159.66	139.25	117.69	
Nd	8.33	9.09	10.03	11.20	12.69	14.72	17.36	21.49	26.30	32.96	
Zr	52.00	57.35	63.99	72.44	83.19	97.97	117.57	148.73	196.37	297.04	
Hf	1.53	1.68	1.88	2.12	2.42	2.84	3.39	4.25	5.55	8.31	
Sm	2.66	2.90	3.19	3.56	4.03	4.66	5.46	6.69	7.60	7.76	
Eu	0.92	0.91	0.89	0.88	0.85	0.81	0.77	0.72	0.59	0.38	
Gd	3.09	3.36	3.69	4.11	4.62	5.32	6.19	7.51	8.16	7.40	
Tb	0.56	0.61	0.67	0.74	0.83	0.96	1.11	1.34	1.45	1.29	
Dy	3.29	3.57	3.91	4.34	4.87	5.59	6.46	7.79	8.43	7.62	
Y	22.60	24.52	26.86	29.79	33.42	38.28	44.23	53.27	58.11	53.65	
Ho	0.71	0.77	0.84	0.94	1.05	1.20	1.39	1.67	1.84	1.73	
Er	2.21	2.40	2.63	2.91	3.27	3.74	4.33	5.22	5.84	5.79	
Tm	0.33	0.36	0.39	0.44	0.49	0.56	0.65	0.79	0.90	0.95	
Yb	2.12	2.30	2.52	2.80	3.14	3.60	4.19	5.08	5.95	6.66	
Lu	0.32	0.35	0.38	0.42	0.48	0.55	0.64	0.78	0.94	1.11	
La/Sm	1.47	1.47	1.47	1.47	1.47	1.47	1.49	1.51	1.80	2.88	
(La/Yb) _{PRIMA}	1.29	1.29	1.30	1.31	1.32	1.33	1.36	1.39	1.61	2.35	
Yb _{PRIMA}	4.44	4.82	5.28	5.86	6.58	7.55	8.77	10.63	12.46	13.95	
Dy/Yb	1.55	1.55	1.55	1.55	1.55	1.55	1.54	1.53	1.42	1.14	
Dy/Dy*	0.95	0.95	0.94	0.94	0.94	0.94	0.93	0.91	0.81	0.58	
Zr/Y	2.30	2.34	2.38	2.43	2.49	2.56	2.66	2.79	3.38	5.54	
Nb/La	0.26	0.26	0.26	0.26	0.26	0.27	0.27	0.27	0.27	0.28	
Nb/Ta	12.5	12.4	12.3	12.1	12.0	11.8	11.6	11.3	10.8	9.7	
Zr/Hf	34.0	34.1	34.1	34.2	34.3	34.5	34.7	35.0	35.4	35.8	
Nb/Yb	0.47	0.48	0.48	0.49	0.50	0.50	0.52	0.55	0.63	0.93	
Th/Yb	0.15	0.15	0.16	0.16	0.16	0.17	0.17	0.18	0.22	0.36	
Sr/Y	12.04	10.64	9.27	7.93	6.49	5.12	4.05	3.00	2.40	2.19	
Zr/Sm	19.5	19.8	20.0	20.3	20.7	21.0	21.6	22.2	25.8	38.3	

Table C4a: Calculation of 400 MPa fractional crystallization¹² (see Table C3b) using WA-B-source rock **69-920** (Todd et al., 2021) for the EE-suite (Momi pluton).

$$C_i^L = C_i^0 \times F^{(\overline{D}_i - 1)}$$

¹² During the process of fractional crystallization using the Raleigh equation

it is possible to change concentration of trace element (*i*) in the melt (C_i^L). F is the fraction of the original melt that remains, \overline{D}_i is the mean partition coefficient for component *i*, and C_i^{θ} is the concentration of the specific trace element *i* in the melt before any crystallization has occurred.

						F					
	Melt	90.0%	80.0%	70.0%	60.0%	50.0%	40.0%	30.0%	20.0%	10.0%	rel. F
Element	69-48	90.0%	88.9%	87.5%	85.7%	83.3%	80.0%	75.0%	66.7%	50.0%	•
Th	0.10	0.11	0.12	0.14	0.16	0.19	0.23	0.29	0.41	0.74	
Nb	0.36	0.40	0.44	0.49	0.56	0.65	0.79	1.00	1.35	2.23	
Та	0.02	0.02	0.02	0.03	0.03	0.04	0.05	0.06	0.09	0.16	
La	1.39	1.52	1.67	1.86	2.11	2.44	2.90	3.61	4.87	7.98	
Ce	4.30	4.69	5.17	5.77	6.52	7.55	8.93	11.10	14.60	22.37	
Pr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Sr	137.00	131.41	125.43	118.97	109.25	98.77	90.29	80.42	70.13	59.28	
Nd	4.64	5.06	5.59	6.24	7.07	8.20	9.67	11.97	14.65	18.36	
Zr	28.00	30.88	34.45	39.01	44.79	52.75	63.31	80.09	105.74	159.94	
Hf	1.26	1.39	1.54	1.74	2.00	2.34	2.79	3.50	4.57	6.84	
Sm	1.81	1.97	2.17	2.42	2.74	3.17	3.71	4.55	5.17	5.28	
Eu	0.62	0.61	0.60	0.59	0.57	0.54	0.52	0.49	0.39	0.25	
Gd	2.44	2.65	2.92	3.24	3.65	4.20	4.89	5.93	6.44	5.84	
Tb	0.47	0.51	0.56	0.62	0.70	0.80	0.93	1.13	1.21	1.08	
Dy	3.02	3.28	3.59	3.99	4.47	5.13	5.93	7.15	7.74	6.99	
Y	21.70	23.55	25.79	28.61	32.09	36.76	42.47	51.15	55.79	51.52	
Ho	0.69	0.75	0.82	0.91	1.02	1.17	1.35	1.63	1.79	1.68	
Er	2.05	2.22	2.44	2.70	3.03	3.47	4.01	4.84	5.42	5.37	
Tm	0.30	0.33	0.36	0.40	0.44	0.51	0.59	0.71	0.82	0.86	
Yb	2.06	2.24	2.45	2.72	3.05	3.50	4.07	4.93	5.78	6.47	
Lu	0.31	0.34	0.37	0.41	0.46	0.53	0.62	0.76	0.91	1.08	
La/Sm	0.77	0.77	0.77	0.77	0.77	0.77	0.78	0.79	0.94	1.51	
(La/Yb) _{PRIMA}	0.47	0.47	0.48	0.48	0.48	0.49	0.50	0.51	0.59	0.86	
Yb _{PRIMA}	4.32	4.68	5.13	5.69	6.39	7.33	8.52	10.33	12.11	13.55	
Dy/Yb	1.47	1.47	1.47	1.47	1.47	1.46	1.46	1.45	1.34	1.08	
Dy/Dy*	1.22	1.22	1.22	1.21	1.21	1.21	1.19	1.17	1.04	0.75	
Zr/Y	1.29	1.31	1.34	1.36	1.40	1.44	1.49	1.57	1.90	3.10	
Nb/La	0.26	0.26	0.26	0.26	0.27	0.27	0.27	0.28	0.28	0.28	
Nb/Ta	18.0	17.8	17.7	17.5	17.2	17.0	16.7	16.3	15.5	14.0	
Zr/Hf	22.2	22.3	22.3	22.4	22.4	22.5	22.7	22.9	23.1	23.4	
Nb/Yb	0.17	0.18	0.18	0.18	0.18	0.19	0.19	0.20	0.23	0.34	
Th/Yb	0.05	0.05	0.05	0.05	0.05	0.05	0.06	0.06	0.07	0.11	
Sr/Y	6.31	5.58	4.86	4.16	3.40	2.69	2.13	1.57	1.26	1.15	
Zr/Sm	15.5	15.7	15.9	16.1	16.3	16.7	17.1	17.6	20.4	30.3	

Table C4b: Calculation of 400 MPa fractional crystallization (see Table C3b) using WA-A-source rock **69-48** (Todd et al., 2021) for the LD-suite (Korolevu pluton).

		F									
	Melt	90.0%	80.0%	70.0%	60.0%	50.0%	40.0%	30.0%	20.0%	10.0%	rel. F
Element	69-920	90.0%	88.9%	87.5%	85.7%	83.3%	80.0%	75.0%	66.7%	50.0%	
Th	0.32	0.35	0.39	0.44	0.51	0.60	0.73	0.93	1.31	2.39	
Nb	1.00	1.10	1.23	1.38	1.58	1.84	2.20	2.75	3.72	6.06	
Та	0.08	0.09	0.10	0.11	0.13	0.15	0.19	0.24	0.34	0.62	
La	3.90	4.30	4.80	5.37	6.12	7.13	8.45	10.53	14.17	23.06	
Ce	10.20	11.23	12.50	13.98	15.91	18.53	21.66	26.49	34.43	51.64	
Pr	1.66	1.83	2.05	2.30	2.63	3.08	3.55	4.27	5.32	7.19	
Sr	272.00	289.19	309.69	301.62	292.56	282.20	276.06	268.35	251.60	229.21	
Nd	8.33	9.14	10.14	11.33	12.89	15.00	16.86	19.60	22.97	26.91	
Zr	52.00	57.04	63.26	71.28	81.81	96.30	112.21	136.67	176.28	256.96	
Hf	1.53	1.67	1.84	2.06	2.35	2.75	3.18	3.84	4.91	7.09	
Sm	2.66	2.89	3.17	3.53	3.99	4.61	4.97	5.47	5.76	5.25	
Eu	0.92	0.97	1.02	1.02	1.01	1.01	0.93	0.84	0.68	0.42	
Gd	3.09	3.32	3.60	3.98	4.46	5.12	5.36	5.70	5.63	4.44	
Tb	0.56	0.60	0.64	0.71	0.79	0.91	0.94	1.00	0.97	0.75	
Dy	3.29	3.50	3.75	4.12	4.60	5.23	5.45	5.75	5.66	4.43	
Y	22.60	23.99	25.65	28.15	31.34	35.58	37.21	39.42	39.19	31.51	
Но	0.71	0.75	0.80	0.88	0.98	1.11	1.17	1.24	1.25	1.02	
Er	2.21	2.34	2.50	2.74	3.04	3.45	3.65	3.93	4.05	3.55	
Tm	0.33	0.35	0.37	0.41	0.45	0.52	0.55	0.60	0.64	0.61	
Yb	2.12	2.25	2.40	2.63	2.92	3.32	3.60	3.99	4.37	4.43	
Lu	0.32	0.34	0.36	0.40	0.44	0.51	0.56	0.63	0.71	0.77	
La/Sm	1.47	1.49	1.51	1.52	1.53	1.55	1.70	1.92	2.46	4.39	
(La/Yb) _{PRIMA}	1.29	1.34	1.40	1.43	1.46	1.50	1.64	1.84	2.26	3.63	
Yb _{PRIMA}	4.44	4.70	5.02	5.50	6.13	6.95	7.54	8.36	9.16	9.29	
Dy/Yb	1.55	1.56	1.57	1.57	1.57	1.57	1.51	1.44	1.29	1.00	
Dy/Dy*	0.95	0.94	0.93	0.93	0.92	0.92	0.86	0.79	0.66	0.44	
Zr/Y	2.30	2.38	2.47	2.53	2.61	2.71	3.02	3.47	4.50	8.16	
Nb/La	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	0.26	
Nb/Ta	12.5	12.5	12.5	12.4	12.3	12.1	11.8	11.5	10.9	9.8	
Zr/Hf	34.0	34.2	34.4	34.6	34.8	35.0	35.3	35.6	35.9	36.2	
Nb/Yb	0.47	0.49	0.51	0.52	0.54	0.56	0.61	0.69	0.85	1.37	
Th/Yb	0.15	0.16	0.16	0.17	0.17	0.18	0.20	0.23	0.30	0.54	
Sr/Y	12.04	12.05	12.07	10.71	9.34	7.93	7.42	6.81	6.42	7.27	
Zr/Sm	19.5	19.7	19.9	20.2	20.5	20.9	22.6	25.0	30.6	49.0	

Table C4c: Calculation of 700 MPa fractional crystallization (see Table C3c) using WA-B-source rock **69-920** (Todd et al., 2021) for the EE-suite (S-Wainivalau pluton).

				F		
	Melt	1.9%	4.4%	9.0%	14.2%	18.8%
Element	T08-21					
Th	0.36	4.65	3.32	2.27	1.68	1.39
Nb	0.63	1.76	1.78	1.75	1.73	1.66
Та	0.04	0.21	0.20	0.17	0.15	0.14
La	3.26	11.64	10.92	10.23	9.64	9.04
Ce	8.31	18.77	19.15	19.50	19.99	19.61
Pr	1.29	1.95	2.11	2.29	2.53	2.60
Sr	155.32	231.39	174.15	158.64	148.75	150.77
Nd	6.34	6.69	7.42	8.34	9.67	10.26
Zr	42.45	74.11	81.06	86.44	93.24	93.37
Hf	1.20	2.06	2.24	2.35	2.49	2.49
Sm	2.00	1.36	1.55	1.80	2.19	2.41
Eu	0.70	0.53	0.58	0.63	0.71	0.75
Gd	2.42	1.37	1.56	1.83	2.26	2.51
Tb	0.42	0.23	0.26	0.31	0.38	0.42
Dy	2.67	1.49	1.70	1.99	2.43	2.69
Y	16.88	9.72	11.06	12.86	15.70	17.31
Но	0.59	0.35	0.40	0.46	0.56	0.61
Er	1.71	1.09	1.23	1.42	1.71	1.87
Tm	0.25	0.18	0.20	0.23	0.27	0.29
Yb	1.64	1.28	1.44	1.63	1.90	2.04
Lu	0.24	0.21	0.23	0.26	0.30	0.32
La/Sm	1.63	8.54	7.05	5.69	4.41	3.76
(La/Yb) _{PRIMA}	1.39	6.34	5.31	4.40	3.54	3.10
Yb _{PRIMA}	3.44	2.69	3.01	3.40	3.99	4.27
Dy/Yb	1.63	1.16	1.19	1.22	1.28	1.32
Dy/Dy*	0.97	0.43	0.47	0.51	0.57	0.62
Zr/Y	2.51	7.62	7.33	6.72	5.94	5.39
Nb/La	0.19	0.15	0.16	0.17	0.18	0.18
Nb/Ta	15.8	8.6	9.0	10.1	11.3	12.1
Zr/Hf	35.4	35.9	36.3	36.7	37.4	37.6
Nb/Yb	0.38	1.37	1.24	1.08	0.91	0.82
Th/Yb	0.22	3.62	2.31	1.40	0.88	0.68
Sr/Y	9.20	23.80	15.75	12.33	9.48	8.71
Zr/Sm	21.2	54.4	52.4	48.1	42.6	38.8

Table C4d: Calculation of 800 MPa dehydration melting¹³ (see Table C3d) using YV-IAT source rock **T08-21** (Todd et al., 2012) for the LE-suite (Yavuna pluton).

¹³ The concentration of a trace element (*i*) in a melt (C_i^L) during the partial melting using Shaw's (1970) equation:

$$C_i^L = C_i^0 \times \frac{1}{\overline{D}_i (1-F) + F}$$

Where F is the melt fraction, \overline{D}_i is the mean partition coefficient for trace element (*i*), and (C_i^{θ}) is the initial concentration of trace element (*i*) in the rock prior to any melting.

				F		
	Melt	1.9%	4.4%	9.0%	14.2%	18.8%
Element	69-920					
Th	0.32	4.15	2.96	2.02	1.49	1.23
Nb	1.00	2.80	2.83	2.78	2.75	2.64
Та	0.08	0.41	0.40	0.35	0.31	0.27
La	3.90	13.86	13.03	12.23	11.53	10.82
Ce	10.20	23.08	23.53	23.94	24.53	24.07
Pr	1.66	2.51	2.71	2.95	3.26	3.34
Sr	272.00	420.10	318.44	290.40	272.45	275.70
Nd	8.33	8.78	9.74	10.95	12.70	13.48
Zr	52.00	90.93	99.40	105.94	114.22	114.38
Hf	1.53	2.63	2.85	3.00	3.18	3.17
Sm	2.66	1.81	2.06	2.39	2.91	3.20
Eu	0.92	0.61	0.60	0.63	0.67	0.71
Gd	3.09	1.75	1.99	2.34	2.88	3.20
Tb	0.56	0.31	0.35	0.41	0.51	0.56
Dy	3.29	1.84	2.10	2.45	3.00	3.32
Y	22.60	13.02	14.81	17.22	21.01	23.17
Но	0.71	0.42	0.48	0.55	0.67	0.74
Er	2.21	1.41	1.59	1.84	2.21	2.41
Tm	0.33	0.23	0.26	0.30	0.36	0.38
Yb	2.12	1.66	1.86	2.10	2.46	2.63
Lu	0.32	0.28	0.31	0.35	0.40	0.43
La/Sm	1.47	7.65	6.33	5.11	3.96	3.38
(La/Yb) _{PRIMA}	1.29	5.84	4.91	4.07	3.27	2.87
Yb _{PRIMA}	4.44	3.47	3.89	4.40	5.16	5.52
Dy/Yb	1.55	1.11	1.13	1.16	1.22	1.26
Dy/Dy*	0.95	0.43	0.46	0.50	0.56	0.60
Zr/Y	2.30	6.98	6.71	6.15	5.44	4.94
Nb/La	0.26	0.20	0.22	0.23	0.24	0.24
Nb/Ta	12.5	6.8	7.1	8.0	8.9	9.6
Zr/Hf	34.0	34.6	34.9	35.3	35.9	36.1
Nb/Yb	0.47	1.69	1.53	1.32	1.12	1.00
Th/Yb	0.15	2.50	1.59	0.96	0.61	0.47
Sr/Y	12.04	32.25	21.50	16.86	12.96	11.90
Zr/Sm	19.5	50.2	48.3	44.3	39.3	35.7

Table C4e: Calculation of 800 MPa dehydration melting (see Table C3d) using WA-B source rock **69-920** (Todd et al., 2021) for the LE-suite (N-Wainivalau pluton).

VII. ACKNOWLEDGEMENTS

I am particularly grateful to my supervisor, Carsten Münker, who has provided the funding, the guidance, and offered me the chance to travel the world in the name of Science.

I want to thank Reiner Kleinschrodt and J. Elis Hoffmann for co-supervising this thesis, as well as my previous theses. A special thanks goes to Frank Wombacher for managing the clean lab, the maintenance of the MC-ICP-MS, and his support in times when Horst was once again a Horst.

Furthermore, I thank all people that scientifically contributed to this dissertation, above all Jim B. Gill (University of California Santa Cruz), Kristoffer Szilas (University of Copenhagen), and Martin J. Van Kranendonk (University of New South Wales). I am grateful for giving me the chance to work on these highly interesting rocks from the most exotic locations. A special thanks goes to Beth Drewes-Todd, Erin Todd, Allen Stork, Tani Kenichiro, Charlotte M. Allen, Sebastian (Fumi) Viehmann, Jakub Surma, and Oliver Jäger for their support and contributions to the shared publications.

I want to express my gratitude to my PhD siblings, Jonas Tusch, Sebastian Kommescher, Maxwell M. Thiemens, and Jens Barosch. In addition, a special thank is directed to Bo-Magnus Elfers and Markus Pfeifer. You all have been a great help and I cherish the shared time with Mauerbiere, cooking events, movie nights, and board game nights. "Qapla!"

I appreciate the work, discussions and shared time (in alphabetical order) with Alessandro, Alex, Almut, Carina, Christiane, Christina, Daniel, Daniela, Dominik, Eric, Florian, Ina, Julia, Laura with Paul, Maria, Marina, Mario, Mike, Ninja, Peter, Ramon, Stefan, and Vicky. Financial support for this thesis has been provided by the German Research Foundation (DFG) grant to C. Münker as part of the priority program 1833 *"Building a Habitable Earth"* (Mu 1406/181) and by the European Research Council (ERC) grant 669666 *"Infant Earth"*.

An meine Familie: vielen Dank für die Unterstützung und die zahlreichen schönen Momente, die ich durch euch erhalten habe!

VIII. ERKLÄRUNG

Ich versichere, dass ich die von mir vorgelegte Dissertation selbständig angefertigt, die benutzten Quellen und Hilfsmittel vollständig angegeben und die Stellen der Arbeit – einschließlich Tabellen, Karten und Abbildungen –, die anderen Werken im Wortlaut oder dem Sinn nach entnommen sind, in jedem Einzelfall als Entlehnung kenntlich gemacht habe; dass diese Dissertation noch keiner anderen Fakultät oder Universität zur Prüfung vorgelegen hat; dass sie – abgesehen von unten angegebenen Teilpublikationen – noch nicht veröffentlicht worden ist, sowie, dass ich eine solche Veröffentlichung vor Abschluss des Promotionsverfahrens nicht vornehmen werde.

Die Bestimmungen der Promotionsordnung sind mir bekannt. Die von mir vorgelegte Dissertation ist von Prof. Dr. Carsten Münker betreut worden.

Nachfolgend genannte Teilpublikationen liegen vor:

- Marien, C.S.; Drewes-Todd, E.K.; Stork, A.; Todd, E.; Gill, J.B.; Hoffmann J.E.; Tani, K.; Allen, C.M.; Münker, C. (2022), *Geochimica et Cosmochimica Acta* 320, 339-365 - Juvenile continental crust evolution in a modern oceanic arc setting: Petrogenesis of Cenozoic felsic plutons in Fiji, SW Pacific. <u>https://doi.org/10.1016/j.gca.2021.11.033</u> (Chapter 3, Appendix C)
- Marien, C.S., Jäger, O., Tusch, J., Viehmann, S., Surma, J.; Van Kranendonk, M.J.; Münker, C. (2023), *Precambrian Research*, **394**, 107109 - Interstitial carbonates in pillowed metabasaltic rocks from the Pilbara Craton, Western Australia: A vestige of Archean seawater chemistry and seawater-rock interactions. <u>https://doi.org/10.1016/j.precamres.2023.107109</u> (Chapter 2; Appendix B)

Köln, den 29.10.2023

Ort, Datum

Unterschrift