GEOCHEMICAL EVOLUTION OF EARTH'S CONTINENTAL CRUST

C. BRENNIN KELLER

A DISSERTATION
PRESENTED TO THE FACULTY
OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

RECOMMENDED FOR ACCEPTANCE
BY THE DEPARTMENT OF
GEOSCIENCES
ADVISER: BLAIR SCHOENE

NOVEMBER 2016

© Copyright by C. Brenhin Keller, 2016.

CC-BY-SA

This work is licensed under a Creative Commons Attribution-ShareAlike 4.0 License.

For more information about this license, visit:

<https://creativecommons.org/licenses/by-sa/4.0/>

Abstract

Earth’s unique continental crust represents the active interface between the deep earth and the surface earth system, and is crucial for the survival and diversification of life on Earth, both as a source for nutrients and a component in the silicate weathering feedback that stabilizes Earth’s equable climate on billion-year timescales. However, many open questions remain regarding the formation and secular temporal evolution of Earth’s crust – in part due to the extremely poorly-mixed nature of Earth’s continental crust such that compositional heterogeneity at any one point in geologic time typically dwarfs any systematic variation over time. New computational approaches enabled by the emergence of large, freely accessible geochemical datasets provide a way to see through this heterogeneity and extract quantitative information about underlying processes and variables that drive the evolution of Earth’s crust over geologic time.

Acknowledgements

The work presented in thesis was funded in large part by the DOE Computational Science Graduate Fellowship through Office of Science grant DE-FG02-97ER25308, with additional support from Princeton University and the Department of Geosciences.

I would particularly like to thank my adviser Blair Schoene, as well as professors Frederik Simons, Allan Rubin, and Adam Maloof. During my time in Guyot Hall, I have been fortunate to overlap with a great cohort of fellow students and postdocs to whom I am indebted in many ways, particularly including: Kyle Samperton for collaboration and camaraderie – we’ve been within a fifteen foot radius either in the office, the lab, or the field for much of the past six years, and it’s never gotten old; Blake Dyer, for constant discussion (scientific and otherwise) from the dining hall as first-year grad students to Geo-Bayesian Math Club and Jammin’ Crepes; Melanie Barboni, for Triumph, K-spar megacrysts, fondue, and showing how many zircons can be run on a TIMS if you know what you’re doing; my grad school role models Jon Husson, Catherine Rose, Garrett Tate, Suki Dorfman, Jessica Hawthorne, Nate Eichelberger, and Tobgay; and all of the members of the Earth History Journal Club.

Outside of the department, I would like to thank Barbara Ratschbacher, Callum McCulloch, and Patrick Boehnke, for working with me in the lab, in the field, and more; as well as the excellent community of CSGFers, especially Jeff Hammond for teaching me MPI.

I am also grateful to all of the people who have helped get me to the point where I could begin this dissertation, particularly including (but not limited to): Margaret Keller, for sharing her enthusiasm for geology, for rockhounding, and for science in general; Jim Mears for a remarkable introduction to micropaleontology; my friends Olof, Magnus, and Bjorn who taught me “Hello World” in C; Frank DiSalvo for opening his inorganic chemistry lab to me; my first geology professor Steve Spear from Palomar College; my undergraduate advisor Sue Kay; and Chris Andronicos and Linc Hollister for pointing me towards Blair.

Work from this thesis has been publicly presented at scholarly conferences as outlined in the following abstracts:

Keller, C.B., Schoene, B. and Boehnke, P. (2015). Temporal variation in average zircon saturation temperature over last 4 Gyr. *V.M. Goldschmidt Conference*, Goldschmidt Abstracts 2015, 1545.

Keller, C.B. and Schoene, B. (2014). Insights into the Formation of Archean Crust from Statistical Geochemistry of the Archean-Proterozoic Transition. *V.M. Goldschmidt Conference*, Goldschmidt Abstracts 2014, 1222.

Keller, C.B. et al. (2013). A statistical approach to the volcanic - plutonic connection. *V.M. Goldschmidt Conference*, Mineralogical Magazine 77, 1455.

Schoene, B. and Keller, C.B. (2012). Keynote: Multi-scale geochemical time series constraints on Archean lithosphere formation. *V.M. Goldschmidt Conference*, Mineralogical Magazine 76, 2342.

Keller, C.B. and Schoene, B. (2012). Secular geochemical evolution linked to atmospheric oxidation. *V.M. Goldschmidt Conference*, Mineralogical Magazine 76, 1927.

Contents

Abstract	iii
Acknowledgements	iv
List of Figures	ix
1 Introduction	1
2 Statistical Geochemistry and Atmospheric Oxidation	12
2.1 Abstract	12
2.2 Statistical geochemistry reveals disruption in secular lithospheric evolution about 2.5 Gyr ago	13
2.3 Methods	23
2.3.1 Database compilation	23
2.3.2 Monte Carlo analysis	24
2.3.3 Response of the Monte Carlo technique the distribution of the uncer- tainty of the data	28
2.3.4 Response of the Monte Carlo results to regions of missing data	30
2.3.5 Interpretation of major element trends	33
2.3.6 Redox partitioning calculations	41
3 Volcanic-Plutonic Parity and Crustal Differentiation	49
3.1 Abstract	49
3.2 Introduction	50

3.3	Quantifying Volcanic-Plutonic Parity	51
3.4	The Role of Water in Magma Eruptibility	53
3.5	Generation of the Felsic Continental Crust	59
3.6	Methods	66
3.6.1	MELTS simulations	71
3.6.2	Trace element calculations	77
3.6.3	Solidus temperature of hydrous and dry magmas	78
3.6.4	Causality of the plutonic water correlation	80
3.6.5	Eu anomalies	81
3.6.6	Melt extraction from crystal-rich magmas	82
3.7	Acknowledgements	83
3.8	Data Access	83
4	Continental Basalts and Plate Tectonics	93
4.1	Abstract	93
4.2	Introduction	94
4.3	Weighted Bootstrap Resampling Monte Carlo Analysis	98
4.4	Gradual secular variation in continental basaltic composition over Earth history	100
4.4.1	Sampling, preservation, and alteration	102
4.4.2	Variation in the extent of mantle melting	104
4.5	Rapid geochemical variation at the end of the Archean	111
4.5.1	Geochemical signatures of subduction	111
4.5.2	Trace element modelling	115
4.6	Discussion	119
4.6.1	Accuracy of temporal trends in average basaltic composition	119
4.6.2	Constraints on the prevalence of subduction through Earth history	120
4.6.3	Implications of ongoing subduction throughout the preserved rock record	124
4.7	Conclusions	125

4.8	Acknowledgements	127
4.9	Data Access	127
5	Zircon Saturation and the early Earth	138
5.1	Abstract	138
5.2	Temporal variation in relative zircon abundance throughout Earth history . .	139
5.3	Data Access	148
6	Conclusion	153
6.1	Secular geochemical evolution	153
6.2	Crustal differentiation	155
6.3	A stable Earth system	168

List of Figures

1.1	Proposed chronologies of Plate Tectonics and Crustal Growth	2
1.2	Time and Heterogeneity in the Earth Sciences	4
1.3	Geochemical correlation matrix	6
1.4	Change in geochemical correlation matrix from Archean to Phanerozoic . . .	8
2.1	Secular compositional evolution of mafic lithologies	16
2.2	Secular compositional evolution of felsic lithologies	18
2.3	Relationship of lithospheric evolution and atmospheric oxidation.	20
2.4	Constancy of mantle redox state	21
2.5	Schematic illustration of bootstrap resampling process	25
2.6	Prior and posterior sample distributions	27
2.7	Distribution of the mean	29
2.8	Response of Monte Carlo simulation to choice of uncertainty distribution . .	31
2.9	Sensitivity of geochemical trends produced by Monte Carlo analysis to choice of uncertainty distribution	32
2.10	Response of Monte Carlo simulation to incomplete data with stepwise starting distribution	34
2.11	Response of Monte Carlo simulation to incomplete data with stepwise starting distribution	35
2.12	Crustal contamination	37
2.13	Evolution of basalt fractionation trends through time	38

2.14	Pressure sensitivity of estimated percent mantle melt	40
3.1	Major element volcanic and plutonic Harker diagrams	54
3.2	Trace element volcanic and plutonic Harker diagrams	55
3.3	Fe-Mg differentiation systematics of arc and rift volcanic and plutonic rocks .	56
3.4	Water-saturated and-undersaturated solidi in granitic systems	60
3.5	Igneous rock abundance as a function of silica content	61
3.6	Comparison of observed and model differentiation trends	63
3.7	Cumulate compositions and curved differentiation trends	64
3.8	Volcanic and Plutonic Sample Locations	67
3.9	Volcanic and plutonic age distributions	69
3.10	Differentiation trends for volcanic and plutonic samples with known ages less than 100 Ma	70
3.11	Prior and Posterior Spatial Sample Distributions	72
3.12	Median differentiation trends	73
3.13	Volcanic and plutonic differentiation trends as a function of MgO	74
3.14	Inverted MELTS P-T paths	75
3.15	Calculated Sr, Ba, and Eu differentiation paths as a function of magma water content	79
4.1	Basaltic compatible and incompatible element trends	96
4.2	Schematic illustration of bootstrap resampling process	98
4.3	Trends in basaltic elemental abundances sorted by compatibility	101
4.4	Geochemical indicators of alteration and metasomatism in the igneous record	103
4.5	Deconvolving the effects of mantle melting and fractional crystallization . . .	106
4.6	Estimated average extent of mantle melting and mantle potential temperature through Earth history	109
4.7	Basaltic trace element discontinuities at the Archean-Proterozoic boundary .	112

4.8	Constant arc signatures in basalts throughout the preserved continental record	113
4.9	Mantle melting sytematics	116
4.10	Mantle trace element model	117
5.1	Factors influencing relative zircon abundance in igneous magmas over time .	142
5.2	Zircon saturation distributions as a function of melt fraction	144
5.3	Temporal variability in the distribution of zircon between mafic and felsic rocks	146
6.1	Temporal variation in the enrichment of plagioclase-associated major and trace elements during differentiation	156
6.2	Temporal variation in the enrichment of garnet-associated trace elements dur- ing differentiation	156
6.3	Mineral partition coefficients for a range of key trace elements	157
6.4	Temporal variation in the extent of Rb and K enrichment during differentiation	158
6.5	Temporal variation in the enrichment of saturation-limited trace elements during differentiation	158
6.6	Phanerozoic, Proterozoic, and Archean differentiation trends for incompatible elements	159
6.7	Plagioclase-associted Phanerozoic, Proterozoic, and Archean differentiation trends	161
6.8	Garnet-associated Phanerozoic, Proterozoic, and Archean differentiation trends	163
6.9	The crustal Daly Gap throughout the preserved rock record	164
6.10	The Daly gap in modern and accreted arcs	165
6.11	Phanerozoic, Proterozoic, and Archean compatible element differentiation trends	166

Chapter 1

Introduction

Time is the ultimate independent variable of the natural sciences: the only physical quantity whose value cannot be influenced, yet is not a fixed constant; the independent variable whose implacable progress directly underlies the fundamental concept of cause and effect. Few disciplines are more dependent on our ability to quantify the passage of time than the Earth sciences, where our primary record is a 4.5 billion year palimpsest shaped by processes that occur over characteristic timescales spanning at least 18 orders of magnitude – from gradual mantle cooling over $\sim 10^9$ years to volcanic and seismic events that initiate in a matter of $\sim 10^{-9}$ years. However, absolute time is far from ubiquitous as an independent variable in the geological literature, due in large part to the difficulty of quantifying the passage of time in the geologic record, compounded by the often diachronous nature of geological processes and materials. Where such obstacles can be overcome, observing the evolution of geological variables over time provides one of the most direct and intuitive approaches to understanding Earth system processes.

One central geological problem that has traditionally been lacking in well-quantified records of secular temporal variation involves the formation and differentiation of the continental crust – a question with fundamental (and perhaps under-appreciated) implications for the origin, evolution, and survival of life on Earth. Indeed, despite the apparently static

Figure 1.1: (A) Proposed onset times of plate tectonics, adapted from [Korenaga \[2013\]](#). (B) Compilation of proposed crustal growth curves, adapted from [Harrison \[2009\]](#)

nature of Earth's crust on human timescales, over million-year timescales and longer, the crust acts as an active boundary condition for the surface earth system, exerting (by virtue of its vastly greater mass) a strong control on the compositions of the atmosphere, biosphere, and hydrosphere.

In contrast to all other planets in the solar system, Earth possesses two compositionally, structurally, and morphologically distinct types of planetary crust, denoted as continental and oceanic crust [[Campbell and Taylor, 1983](#), [Lowman, 1989](#), [Taylor, 1989](#)]. Of these two, continental crust is markedly more felsic, with higher Si and lower Mg and Fe contents than the oceanic crust. As a result, continental crust is less dense and more buoyant than oceanic crust, producing via isostasy a bimodal topographic distribution (which, like continental crust itself, is largely unique to Earth) [[Rosenblatt et al., 1994](#), [Lorenz et al., 2011](#), [Rudnick and Gao, 2014](#)] featuring submarine exposure of oceanic crust and subaerial exposure of continental crust. In turn, this bimodal configuration facilitates the silicate weathering feedback that ultimately stabilizes liquid water on Earth over billion year (Gyr) timescales [[Walker et al., 1981](#), [Caldeira, 1995](#)].

The theory of plate tectonics provides the basic geological model for the operation of the solid Earth, including the continental and oceanic crust, at the present day. However, the operation of plate tectonics in the deep geologic past has remained a topic of debate, with proposed onset times ranging from ~ 0.85 Ga to >4.2 Ga (Figure 1.1a) [Korenaga, 2013]. Moreover, while the continental crust contains rocks ranging in age from just over four billion years [Bowring and Williams, 1999] to the present, there exists no consensus regarding how much continental crust may have existed in the past (Figure 1.1b) [Harrison, 2009]. While there is substantial overlap between proposed times of plate tectonic initiation and proposed times of most rapid crustal growth, the relationship between these two questions is not clear; plate tectonics requires plates, but these plates need not be continental.

In this context, the study of secular temporal variation has the potential to reveal substantial mechanistic insight. If we could accurately quantify change over time in average crustal composition, variation in this average should reflect changes underlying Earth system parameters such as mantle potential temperature and tectonic style. Moreover, a continuous temporal record would allow us to extrapolate back in time from the present in a qualified application of uniformitarianism, and examine questions of cause and effect. However, such an approach has traditionally been hindered by geological heterogeneity.

At the same time, substantial uncertainty has persisted regarding the process of crustal differentiation, regardless of tectonic style. In both continental and oceanic settings, mass is added to the crust through magmatism driven by partial melting of the underlying mantle. Such mantle melting produces basaltic magmas, but only oceanic crust reflects the basaltic composition of the input flux; reaching the average composition of continental crust requires an effective mechanism of crustal differentiation. While the potential range of underlying differentiation mechanisms such as partial melting and fractional crystallization was established nearly a century ago by early petrologists such as Bowen [1928], Daly [1914], and Read, no consensus exists regarding the relative contributions of different end-member processes, or the variation thereof over the 4.5 Gyr of Earth history.

Figure 1.2: (A) An example of a geochemical timeseries with clear temporal trends: Deuterium isotope record of the Vostok ice core, Antarctica, showing repeated cycles of glaciation (decreasing δD) and deglaciation (increasing δD) [Petit et al., 1999]. (B) An example of a geochemical timeseries where temporal trends over time are overwhelmed by the heterogeneity at any given time: Na_2O content over time from $\sim 67,000$ analyses of igneous whole-rock samples preserved in Earth's continental crust [this work].

As an analogy, we may consider for instance the Antarctic ice-core record of recent Pleistocene glaciations (Figure 1.2a) relative to the igneous whole-rock Na_2O record (Figure 1.2b). At the very shortest timescales (~ 1 kyr), variation in deuterium isotope composition is difficult to distinguish from noise, but over ~ 100 kyr timescales, clear cycles of glaciation and deglaciation become apparent. In contrast, in the igneous geochemical record of Earth's crust (Figure 1.2b), systematic temporal variation is difficult to distinguish from noise even over much longer (Gyr) timescales. In large part, this difference is attributable to the spatial heterogeneity of Earth's crust: while the atmosphere is well-mixed over less than kyr timescales, the crust is not effectively mixed over even Gyr timescales. As a result, spatial heterogeneity in crustal composition at any given time typically dwarfs any systematic variations over all of Earth history.

While confronted with a problem of geological heterogeneity, we have recently been presented with an overabundance of data. Open data repositories such as EarthChem [EarthChem, 2010] provide compilations spanning hundreds of thousands of independent geochemical analyses, representing many decades of cumulative published material. Taken in totality, this surfeit of data can be overwhelming, but it enables a variety of novel approaches.

Perhaps the best single graphical representation of this combined geochemical wealth may take the form of a full elemental covariance matrix such as that shown in Figure 1.3. A wide variety of petrological relationships can be observed from this microcosm of igneous geochemistry. Some are unsurprising – such as the positive covariances between elements with similar compatibility, or within the monolithic block of the rare-earth elements united by their common size and charge (save for Europium with its anomalous divalent redox state). Others are more subtle, such as the positive correlation of Eu and Sr with P_2O_5 (perhaps reflecting the substitution of Eu and Sr for Ca in Apatite), the negative correlation of Sr and Al with the heavy rare-earth elements, or the particular apparent antipathy of Ni and Ba. Ultimately however, this type of figure is static, illustrating relationships, but not cause and effect, and no passage of time.

Figure 1.3: Matrix of correlation coefficients for 48 major and trace elements, arranged roughly in order of compatibility (incompatible elements at top left, compatible elements at bottom right). Warm colors reflect a positive covariance for any given element pair, while cool colors reflect a negative covariance. Values along the diagonal are unity, as all elements are perfectly correlated with themselves.

As a first step towards temporal variation, we may simply consider the absolute difference in covariance relationships between two contrasting geologic time periods — in the case of Figure 1.4, the first and last geologic Eons with extant continental crust. Again, interesting relationships emerge: in the Archean, stronger correlations are observed of Na_2O , Al_2O_3 , Ba, and Sr with each other, with silica, and with the rare earth elements, as well as a greater slope for light/heavy rare earth element correlations with SiO_2 — all patterns somewhat suggestive of the Archean TTG signature [Martin et al. \[2005\]](#). Such relationships are intriguing (and provide a good basis for further investigation), but are highly abstract, and while some relationships are sufficiently systematic as a function of elemental chemistry that they appear likely to represent real changes in petrological process, it is difficult to evaluate the accuracy of, e.g., the anomalous correlations of Tantalum in the Archean relative to the Phanerozoic dataset (Figure 1.4).

In order to make sense of the abundance of continental whole-rock geochemical data at the global scale, we have developed a Monte Carlo approach of weighted bootstrap resampling, which both accounts for uncertainty in analytical data, and optimizes sampling distribution across the globe. This resampled data may then be binned as a function of any independent variable of choice (typically time), and the whole process repeated to obtain optimally representative estimates of mean and standard error of the mean. This method is introduced in Chapter 2, and is subsequently applied in some form throughout all other chapters of this thesis. In particular, Chapter 2 discusses the use of this method to quantify secular variation in crustal composition over time, along with an overview of some of the more intriguing results for both mafic and felsic lithologies, and the correlation thereof with other earth system events such as the Great Oxidation event. In Chapter 3, I apply similar techniques to better understand the process of crustal differentiation, and to answer the longstanding question of whether felsic plutonic rocks represent fully magmatic compositions, or are compromised by cumulate processes. Chapter 4 explores in more detail the temporal geochemical evolution of continental basalts introduced in Chapter 2, with significant ramifications for the question of

Figure 1.4: Absolute change in the matrix of correlation coefficients (as in Figure 1.3) between the Archean and the Phanerozoic. Positive values (warm colors) indicate a more positive correlation in the Archean than in the Phanerozoic, while negative values (cool colors) indicate a less positive (or more negative) correlation in the Archean than in the Phanerozoic.

Archean plate tectonics. Finally, chapter 5 discusses the particular consequences of temporal variation in average continental magmatic composition for the geochronologically important accessory mineral Zircon, with some implications for our understanding of Earth's oldest preserved minerals, the Jack Hills zircons.

References

- Norman L Bowen. *The Evolution of the Igneous Rocks* . Oxford University Press, 1928.
- Samuel A Bowring and Ian S Williams. Priscoan (4.00-4.03 Ga) orthogneisses from north-western Canada. *Contributions to Mineralogy and Petrology*, 134(1):3–16, January 1999.
- Ken Caldeira. Long-term control of atmospheric carbon dioxide; low-temperature seafloor alteration or terrestrial silicate-rock weathering? *American Journal of Science*, 295:1077–1114, 1995.
- I H Campbell and Stuart Ross Taylor. No water, no granites - No oceans, no continents. *Geophysical Research Letters*, 10(11):1061–1064, November 1983.
- Reginald Aldworth Daly. *Igneous rocks and their origin*. McGraw-Hill, 1914.
- EarthChem. EarthChem Portal, January 2010. URL <http://www.earthchem.org/>.
- T Mark Harrison. The Hadean Crust: Evidence from ≥ 4 Ga Zircons. *Annual Review of Earth and Planetary Sciences*, 37(1):479–505, May 2009.
- Jun Korenaga. Initiation and Evolution of Plate Tectonics on Earth: Theories and Observations. *Annual Review of Earth and Planetary Sciences*, 41(1):117–151, May 2013.
- Ralph D Lorenz, Elizabeth P Turtle, Bryan Stiles, Alice Le Gall, Alexander Hayes, Oded Aharonson, Charles A Wood, Ellen Stofan, and Randy Kirk. Hypsometry of Titan. *Icarus*, 211(1):699–706, January 2011.

- Paul D Lowman, Jr. Comparative planetology and the origin of continental crust. *Precambrian Research*, 44(3-4):171–195, October 1989.
- Hervé Martin, R Hugh Smithies, R Rapp, Jean-François Moyen, and D Champion. An overview of adakite, tonalite–trondhjemite–granodiorite (TTG), and sanukitoid: relationships and some implications for crustal evolution. *LITHOS*, 79(1-2):1–24, January 2005.
- J R Petit, J Jouzel, D Raynaud, N I Barkov, J M Barnola, I Basile, M Bender, J Chappellaz, M Davis, G Delaygue, M Delmotte, V M Kotlyakov, M Legrand, V Y Lipenkov, C Lorius, L PÉpin, C Ritz, E Saltzman, and M Stievenard. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature*, 399(6735):429–436, June 1999.
- P Rosenblatt, P C Pinet, and E Thouvenot. Comparative hypsometric analysis of Earth and Venus. *Geophysical Research Letters*, 21(6):465–468, March 1994.
- Roberta L Rudnick and S Gao. 4.1 Composition of the Continental Crust. In Roberta L Rudnick, editor, *Treatise on Geochemistry*, pages 1–51. Elsevier, 2014.
- Stuart Ross Taylor. Growth of planetary crusts. *Tectonophysics*, 161:147–156, 1989.
- James C G Walker, P B Hays, and J F Kasting. A negative feedback mechanism for the long-term stabilization of Earth’s surface temperature. *Journal of Geophysical Research*, 86(C10):9776–9782, 1981.

Chapter 2

Statistical Geochemistry and Atmospheric Oxidation

2.1 Abstract

Secular cooling of the Earth is required by surface heat loss and declining radiogenic heat production over the last 4.5 billion years. Igneous geochemistry has been used to understand how changing heat flux influenced Archean geodynamics [[Herzberg et al., 2007](#)], but records of systematic geochemical evolution are complicated by heterogeneity of the rock record and uncertainties regarding selection and preservation bias [[Hawkesworth and Kemp, 2006](#), [Condie and O'Neill, 2010](#), [Moyen, 2010](#)]. We apply statistical sampling techniques to a geochemical database of $\sim 70,000$ samples from the continental igneous rock record to produce the first comprehensive record of secular geochemical evolution throughout Earth history. Consistent with secular mantle cooling, compatible and incompatible elements in basalts record gradually decreasing mantle melt fraction through time. Superimposed on

This work has been published as: Keller, C. Brenhin, and Blair Schoene (2012), Statistical geochemistry reveals disruption in secular lithospheric evolution about 2.5 Gyr ago, *Nature*, *485*, 490–493.

this gradual evolution is a pervasive geochemical discontinuity ca. 2.5 Ga, including dramatic decreases in mantle melt fraction in basalts, and in deep crustal melting/fractionation indicators such as Na/K, Eu/Eu*, and La/Yb of felsic rocks. Along with increased preserved crustal thickness across the Archean-Proterozoic boundary [Artemieva, 2006, Durrheim and Mooney, 1991], these data are consistent with a model where high degree Archean mantle melting produced a thick, mafic lower crust and consequent deep crustal delamination and anatexis in turn resulting in abundant tonalite-trondhjemite-granodiorite (TTG) magmatism and a thin preserved Archean crust. Coincidence of the observed changes in geochemistry and crustal thickness with stepwise atmospheric oxidation [Kump, 2008] at the end of the Archean provides the most significant temporal link between deep earth geochemical processes and the rise of atmospheric oxygen on Earth.

2.2 Statistical geochemistry reveals disruption in secular lithospheric evolution about 2.5 Gyr ago

While it is generally expected that mantle potential temperatures were higher in the Archean, the ratio of terrestrial heat production to heat loss through time is very poorly constrained [KamLAND Collaboration, 2011]. The resulting lack of confidence in models of secular thermal evolution has contributed to uncertainty regarding the style of Archean geodynamics, given the temperature dependence of rock deformation mechanisms, mantle and crustal melting, and magma geochemistry [Herzberg et al., 2007]. The existence of high percent melt rocks such as komatiites, the predominance of the high-Na TTG series, and the purported structural evolution of granite-greenstone terranes have all been used to suggest that plate tectonics may have been different in style or even nonexistent during the Archean [Condie and Pease, 2008]. However, thermobarometric estimates of crustal geotherms similar to those of modern continents, geochronological evidence for tectonic-scale underthrusting, and the reported occurrence of subduction signatures such as high-field-strength element depletion

have led other authors to argue that plate tectonics has existed in its present state since at least 3.0 or as early as 3.8 Ga [Condie and Pease, 2008, de Wit, 1998].

Much like those generated in modern tectonic environments, rocks from preserved Archean crust are characterized by extreme geochemical heterogeneity. To obtain systematic trends from this record, studies of igneous geochemistry over Earth history have typically relied on small, carefully selected datasets from well characterized terranes [Condie, 2008, Condie and O'Neill, 2010, Li and Lee, 2004]. The present study takes a different approach on the basis that a sufficiently large, representative dataset can be used to define global geochemical averages very precisely; changes in this average over time should reflect the influence of long-term geodynamic drivers such as mantle temperature.

To this end, we have constructed a database of $\sim 70,000$ major and trace element whole-rock analyses from preexisting sources [Condie, 2008, Condie and O'Neill, 2010, Moyen, 2010, EarthChem, 2011] that report sample location as well as crystallization age and uncertainty. These data are superimposed on existing geophysical models Crust 2.0 [Bassin et al., 2000] and TC1 [Artemieva, 2006] that estimate present-day crustal and lithospheric parameters. Results for global mean geochemistry with time are generated by Monte Carlo analysis with weighted bootstrap resampling (Methods). Resampling weights are inversely related to spatiotemporal sample density in order to achieve a maximally uniform posterior sample density distribution and minimize selection bias. The result is a best estimate of the average igneous geochemistry of exposed continental crust through time, reported as means with associated 2- standard errors of the mean for 100 Ma intervals between 0 and 3.8 Ga. In order to distinguish between primary mantle melting and subsequent evolution and fractionation processes, we extract results from two silica ranges: 62-74% SiO_2 for intermediate to felsic samples and 43-51% SiO_2 for less fractionated mafic samples.

The results for the least fractionated (43-51% SiO_2) mafic samples preserved in the continental igneous rock record reveal a systematic decrease in compatible element concentration along with a corresponding increase in incompatible element concentration through time

Figure 2.1: Secular compositional evolution of mafic lithologies. Secular mantle cooling is illustrated by compatible (a-c) and incompatible (d-e) element trends over time in relatively unfractionated rocks (43-51% SiO₂), along with corresponding La/Yb (f) and percent melt (g). Error bars show 2- standard errors of the mean; shading illustrates density of the individual Monte Carlo simulations.

(Figure 2.1). These trends can be shown to reflect decreases in mantle partial melting through time, as a consequence of secular mantle cooling; alternative explanations such as a change in the degree of fractionation through time are found to be incompatible with the observed data (Methods; Figures 2.12-2.13). While such low silica samples do not generally represent primitive melts, compositional trends in these samples nonetheless reflect source processes given a representative dataset, allowing for the estimation of minimum percent mantle partial melting through time (Methods). In order to derive such minimum estimates, we applied least-squares optimization to match thermodynamic batch melting simulations of primitive mantle from MELTS [Ghiorso and Sack, 1995, Asimow and Ghiorso, 1998] with Monte Carlo simulations of basaltic major element concentrations through time (Methods). The results (Figure 2.1g) show a systematic decrease in mantle melt fraction from ~ 0.35 in the Archean to ~ 0.1 at the present. These results agree well with studies of mantle xenoliths which estimate that Archean subcontinental mantle lithosphere was produced through $\sim 40\%$ melt extraction [Walter, 1998].

In addition to the gradual trend expected from secular cooling, however, our results indicate a sudden, systematic ~ 10 percentage point decrease in average percent mantle melting at ~ 2.5 Ga (Figure 2.1g). Due to Earth's thermal inertia, it is unlikely that this event is the result of a rapid change in mantle potential temperature. While a rapid change in the style of tectonics and crust formation at ~ 2.5 Ga could provide one possible explanation for the rapid decrease in average mantle melting, an abrupt response in degree of melting to a gradual cooling path may provide a more parsimonious explanation; both experiments and thermodynamic models indicate substantially nonlinear mantle melting as a function of temperature, with notable inflections corresponding to clinopyroxene exhaustion [Hirschmann

et al., 1998]. Trace element geochemistry provides some additional insight: simple trace element modelling (Methods) suggests that the drastic increases in La/Yb (Figure 2.1f), La/Sm, and Sm/Yb cannot be explained by the trend in degree of mantle melting in Figure 2.1f alone, indicating a change in either trace element composition of the source or effective bulk partition coefficients.

Geochemical trends in high silica (62-74% SiO₂) rocks parallel many of those observed in basalts. Sodium, however, represents a notable exception. The high Na/K (Figure 2.2b) and Na/(Ca+Na+K), of the TTG series have pervaded the discussion of Archean crust formation [Condie, 2008, Condie and O'Neill, 2010, Drummond and Defant, 1990, Moyen, 2010, Moyen and Stevens, 2006, Petford and Atherton, 1996]. These geochemical signatures, along with high LREE/HREE ratios (e.g. La/Yb; Figure 2.2a), have been used to argue for the formation of TTG by high pressure (>40 km) partial melting of metabasalt at pressures above the Na-plagioclase stability field in the presence of restitic amphibole and/or garnet [Condie, 2008, Condie and O'Neill, 2010, Drummond and Defant, 1990, Moyen, 2010, Moyen and Stevens, 2006, Petford and Atherton, 1996]. Experimental data for partial melting of mafic rocks at mid to lower crustal pressures and temperatures have demonstrated a positive correlation between pressure and sodium concentration in the melt [Moyen and Stevens, 2006]. Trace element results from our dataset show correlations predicted by such a model: the secular evolution of Eu/Eu* and Sr (Figure 2.2c,d) parallels that of Na/K in felsic rocks, arguing that deep crustal melting (and/or high pressure fractional crystallization [Müntener et al., 2001]) played a larger role in forming preserved Archean crust than post-Archean crust.

The two most frequently proposed settings for such deep crustal anatexis and TTG generation are 1) melting of subducted oceanic crust, and 2) melting of overthickened mafic lower crust, which derives its basalt from mantle melting and crustal underplating [Drummond and Defant, 1990, Petford and Atherton, 1996]. Of these, the latter provides a potential genetic link between TTG generation and observed high percent mantle melting in the Archean: ex-

Figure 2.2: Secular compositional evolution of felsic lithologies. A shift in lithospheric evolution is suggested by trace element patterns in felsic rocks (62-73% SiO_2) (a-c) along with the relative abundance of Sr in rocks with 62-73% SiO_2 normalized to Sr in 43-51% SiO_2 samples (d). As Na, Eu, and Sr are all partitioned into plagioclase, higher abundance of these elements corresponds to decreased plagioclase fractionation. Error bars show 2- standard errors of the mean; shading illustrates density of the individual Monte Carlo simulations.

tensive basalt production could lead to a thicker and/or more mafic lower continental crust that would more often result in TTG generation. However, any process requiring a thick Archean crust creates an apparent dilemma: preserved Archean lithosphere is characterized by unusually thin crust [Durrheim and Mooney, 1991] (Figure 2.3a). Crustal delamination provides one potential solution, in which crustal thickening leads to a lower crust of dense garnet pyroxenite that can break off and founder into the mantle triggering an influx of hot asthenosphere that leads to lower crustal anatexis, crustal uplift, and magmatism [Kay and Kay, 1993]. Overthickening of mafic lower crust therefore leads to delamination, crustal thinning, and further deep crustal magmatism. Indeed, previous workers have suggested that lower crustal delamination was more prevalent in the Archean, a process that would have been facilitated by high Archean mantle potential temperatures [Petford and Atherton, 1996, Bédard, 2006]. Further, since delamination involves a pressure and temperature dependent critical crustal thickness [Bédard, 2006], delamination may relate gradual secular cooling to rapid change in the geochemical record. Archean delamination thus provides a link between high degree mantle melting, TTG abundance, dramatic geochemical shifts near the Archean/Proterozoic boundary, and thin preserved Archean crust.

While uncertainty in the timing of the observed geochemical transition is estimated to be on the order of 100 Ma, our results nonetheless reveal a striking temporal coincidence between a major discontinuity in the character of preserved continental lithosphere and the atmospheric great oxidation event (GOE) near the Archean/Proterozoic boundary (Figures 2.1-2.3). It is generally agreed that the atmosphere was mostly anoxic prior to ~ 2.4 Ga based on measurements of mass-independent sulfur isotope fractionation in pyritic shales [Farquhar et al., 2000], occurrence of banded iron formations [Fischer and Knoll, 2009], and the presence of reduced detrital grains (sulfides) in Archean sediment [Rasmussen and Buick, 1999] (Figure 2.3e). However, the cause of subsequent atmospheric oxidation remains a matter of debate; some indications suggest the GOE did not occur for at least several hundred million years after the evolution of photosynthesis, leading some to argue that

Figure 2.3: Relationship of lithospheric evolution and atmospheric oxidation. A notable temporal coincidence is observed between shifts in preserved crustal and lithospheric thickness (this study, based on the models of [Bassin et al. \[2000\]](#) and [Artemieva \[2006\]](#)), average percent mantle melting (this study), and atmospheric oxidation as shown by generalized atmospheric oxygen curve (adapted from [Kump \[2008\]](#)), $\delta^{33}\text{S}$ fractionation [[Farquhar et al., 2000](#)], and the presence of sedimentary of redox indicators [[Fischer and Knoll, 2009](#), [Rye and Holland, 1998](#), [Rasmussen and Buick, 1999](#)].

Figure 2.4: Mean V/Sc ratio through time for mafic (43-51% SiO₂) samples, illustrating the lack of a visible trend that would indicate changes in mantle oxygen fugacity.

an additional geological stimulus was required to trigger widespread atmospheric oxidation [Kasting et al., 1993, Kump and Barley, 2007].

Proposed mechanisms that could link the deep Earth to atmospheric oxidation at the end of the Archean include a change in mantle oxygen fugacity [Kasting et al., 1993], or a change in magma degassing style (subaerial vs. subaqueous) [Kump and Barley, 2007], where both influence the atmosphere via the flux of reduced volcanic volatiles. However, studies of mantle redox proxies such as V/Sc, including our own analysis (Figure 2.4), indicate that upper mantle oxygen fugacity has remained roughly constant over the last 3.8 Ga [Li and Lee, 2004]. The latter process remains plausible, but it is not immediately clear how this mechanism would link to our observed geochemical trends.

However, despite providing useful constraints on mantle oxygen fugacity, redox tracers such as V/Sc best record changes in oxygen fugacity of the mantleprimitive melt system, not subsequent magma fractionation and evolution; consequently, constraints on the redox state of magmas during evolution and fractionation in the crust are largely absent [Lee

et al., 2010]. Magmatic redox fractionation is controlled by mineral/melt $D\text{Fe}^{3+}/D\text{Fe}^{2+}$ distribution coefficients, which are very poorly characterized. However, as shown by experimental iron speciation studies, eclogitic minerals such as garnet and sodic clinopyroxene are capable of accommodating substantial Fe^{3+} , and have moderately elevated $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios compared other common restitic minerals such as olivine [Canil et al., 1994, Van Aken and Liebscher, 2002]. Consequently, melt extraction from an eclogitic or garnet pyroxenitic restite, as is expected during TTG genesis, could lead to lower melt $\text{Fe}^{3+}/\text{Fe}^{2+}$ relative to melt extracted from a low pressure restite rich in olivine (which contains substantial Fe but very low $\text{Fe}^{3+}/\text{Fe}^{2+}$) [Canil et al., 1994, Van Aken and Liebscher, 2002] and plagioclase (which contains high $\text{Fe}^{3+}/\text{Fe}^{2+}$ but very little total Fe) [Van Aken and Liebscher, 2002]. TTG magmatism may therefore leave more oxidizing power in eclogitic residue in the form of Fe^{3+} , while more reducing power is transported to the surface in the form of Fe^{2+} and equilibrated volatile species such as H_2S , CH_4 , and CO .

In this context, Archean deep crustal magmatism provides a potentially significant influence on surficial oxygen fugacity: simple stoichiometric calculations show that a 15% change in restitic $\text{Fe}^{3+}/\Sigma\text{Fe}$ for a modest $5 \text{ km}^3/\text{yr}$ magmatic flux would result in an increase in magma reducing capacity by approximately $4.0 \times 10^{12} \text{ mol } e^-/\text{yr}$, similar in magnitude to the entire present day volcanic volatile reducing flux (Methods). Although it is not simple to determine if the termination of this additional reducing flux at the end of the Archean would be sufficient to trigger atmospheric oxidation, the magnitude of the flux may be constrained by further study of restitic iron partitioning.

Though speculative, restitic redox partitioning provides a testable mechanism to explain the correlation of atmospheric oxidation with the $\sim 2.5 \text{ Ga}$ geochemical transition revealed by our analysis. It is not yet clear whether these changes represent a fundamental shift in the style of crust formation and tectonics or simply an abrupt response of melt production to gradual secular cooling. However, delamination and subsequent lower crustal anatexis provide potential explanations for the observed geochemical trends in felsic rocks that are

largely independent of the style of Archean tectonics. Our analysis illustrates the opportunity presented by recent efforts to make large amounts of published geochemical data readily available and amenable to statistical analysis. These initial results substantiate the existence of a period of profound change in the Earth system near the Archean/Proterozoic boundary with implications for crustal differentiation, atmospheric oxidation, and the habitability of Earth for complex aerobic biota.

2.3 Methods

2.3.1 Database compilation

A database of major and trace element analyses of $\sim 70,000$ igneous whole-rock samples was assembled from a number of preexisting sources, including ~ 2500 from [Condie \[2008\]](#), [Condie and O'Neill \[2010\]](#), ~ 1500 from [Moyen \[2010\]](#), [Moyen and Stevens \[2006\]](#), and the remaining majority from the EarthChem repository (encompassing samples from Navdat, Georoc, and the USGS) [[EarthChem, 2011](#)]. Each sample was paired with a geospatial location, with preexisting location data supplemented by new estimates when necessary. Geochemical data for individual samples was then coupled with crustal and lithospheric thickness, crustal V_p , V_s , and density by superimposing sample locations onto high spatial-resolution global crustal and lithospheric models CRUST 2.0 [[Bassin et al., 2000](#)] and TC1 [[Artemieva, 2006](#)], respectively. To minimize the chance of introducing any unintentional selection bias, outliers were not removed from the database except in cases where the recorded data was demonstrably unphysical. The result was a dataset including up to 98 defined variables (e.g. sample age, SiO_2 , La, crustal thickness, etc.) for each of the $\sim 70,000$ samples, for a total of more than 3.9 million defined datapoints.

2.3.2 Monte Carlo analysis

Estimates of all variables of interest were generated by Monte Carlo analysis with weighted bootstrap resampling, as illustrated for one scenario in Figure 2.5. Sample weights were assigned to be inversely dependent on spatiotemporal sample density according to the relationship

$$W_i \propto 1 / \sum_{j=1}^n \left(\frac{1}{((z_i - z_j)/a)^2 + 1} + \frac{1}{((t_i - t_j)/b)^2 + 1} \right) \quad (2.1)$$

where n is the number of samples in the database, z is spatial location, t is age of the rock, and a and b are normalization coefficients of 1.8 arc degrees (200 km) and 38 Ma, respectively. After calculation of weight W_i for each sample i in the database, bootstrap resampling was carried out in the following steps: (1) A subset of data were randomly selected such that the probability of inclusion in the resampled subset is directly proportional to sample weight. (2) A synthetic dataset for each sampled datapoint was drawn from a Gaussian distribution with a mean equal to the original value of the datapoint and standard deviation equal to the estimated 1-sigma uncertainty of the datapoint. (3) The resulting data was sorted into 100 Ma bins, with a mean and variance calculated for each variable. (4) Steps 1-3 were repeated 10,000 times. (5) A total mean and standard error of the mean were calculated for each variable in each bin. In order to distinguish between processes of mantle melting and subsequent evolution and fractionation, the entire procedure was conducted separately for samples from each of four silica ranges (43-51%, 51-62%, 62-74% and 74-80%).

Due to the large quantity of random numbers required for Monte Carlo simulation, randomness in steps 1 and 2 was simulated with the Mersenne Twister pseudorandom number generator [Matsumoto and Nishimura, 1998] as implemented by MATLAB. In order to assess the efficacy of the resampling procedure, prior and posterior density distributions were compared to the ideal case for latitude, longitude, and time, (Figure 2.6). The results suggest substantial improvement in sampling quality, although tradeoffs exist between uniform

Figure 2.5: Schematic illustration of Monte Carlo analysis for the example case of K_2O . (a) raw data; (b) results of 71 out of 10,000 weighted bootstrap-resampling Monte Carlo simulations, illustrating peak smearing due to uncertainties in reported sample ages; (c) sample means with 2-sigma standard errors of the mean. Note that figures are cropped at 3 wt. % K_2O but the averages shown in (c) are calculated from the full dataset.

sampling through time and uniform sampling in space. To evaluate the applicability of mean and standard error as appropriate statistics to characterize the results of Monte Carlo simulation, the distribution of sample means was examined and found to be approximately Gaussian as illustrated for one variable in Figure 2.7. This is expected as a consequence of the Central Limit Theorem; regardless of the distribution of a dataset, the distribution of the mean of the dataset will naturally tend towards a Gaussian distribution. Finally, to mitigate the undesirable statistical properties of ratios with small denominators and minimize the effect of outliers, geochemical ratios such as La/Yb were calculated first as fractions (e.g. $\text{La}/(\text{La}+\text{Yb})$) during Monte Carlo analysis and averaging, and subsequently converted to ratios for presentation; the resulting fractional averages are more robust than but not directly comparable to the average of a simple ratio.

In contrast to the widely-discussed episodic nature of crust formation (e.g. [Condie et al., 2011]), our analysis attempts to produce a uniform record by reducing the weight of abundantly sampled time periods or terranes. For instance, in accordance with Equation 2.1, rock samples from a time period poorly represented in the database will be bootstrap-resampled more heavily than those from periods where much crust is preserved. However, as Equation 2.1 attempts to balance optimal sampling through in space and optimal sampling through time, periods where very few data are preserved (e.g. 2.6-2.2 Ga) will remain more poorly sampled, resulting in larger standard errors of the mean at these times. Additionally, spatiotemporal sample weighting in conjunction with Monte Carlo sampling of rocks with large reported age uncertainties result in a continuous geochemical record that smooths out stochastic and stepwise transitions; the slopes of any abrupt trends presented herein are therefore minimum estimates. The nature of the Monte Carlo sampling process has the additional consequence that there is no uniform or single-valued age uncertainty for the resulting trends. However, temporal uncertainty in the results is generally on the order of 100 Ma.

Figure 2.6: Prior (original data; left) and posterior (after Monte-Carlo analysis; right) sampling distributions (histograms) compared to ideal distributions (solid lines), where the ideal spatial distributions are based on the current exposed area of the continents. Scale of the ideal curve is normalized to the height of the highest peak in the distribution for both the prior (raw data) and posterior (resampled data) cases. Since the true value of age distribution is unknown, no curve is shown for comparison. Instead, one sees that undersampled age ranges increase in importance during Monte Carlo simulation.

2.3.3 Response of the Monte Carlo technique the distribution of the uncertainty of the data

While our Monte Carlo analysis does not assume any specific statistical distribution for the geochemical, geochronological, or geophysical data, it is necessary to specify the distribution of the uncertainties associated with each individual data point in our database. Since this uncertainty will be a product of the convolution of multiple independent error sources, it is reasonable to conclude that the distribution of the uncertainty will approach a Gaussian distribution in accordance with the Central Limit Theorem (similar rationale explain why the distribution of the mean of the data approaches a Gaussian distribution (Figure 2.7) even though the distribution of the data is not Gaussian). In the sources from which we compiled the database, geochronological data is implied to be Gaussian in accordance with standard practice; no uncertainty is reported for individual geochemical data, but uncertainties for the analytical methods used are typically on the order of a few percent. Consequently we have conducted Monte Carlo analysis using the reported geochronological uncertainty for each data point, and assuming a 2sigma uncertainty of 4% with a Gaussian distribution for the geochemical data, as described in section 1.2 above. In order to ensure that the this choice of distribution does not bias the distribution of the results, two numerical experiments were carried out.

First, in order to demonstrate that the choice of error distribution used in Monte Carlo analysis does not bias the distribution of the data or its mean in the one-dimensional case, three Monte Carlo experiments were conducted using 1) a Gaussian distribution; 2) a lognormal distribution; and 3) a chi-squared distribution with 1 degree of freedom. Using two test datasets (MgO content of mafic igneous samples between 400 and 410 Ma, and a synthetic lognormal distribution), a 10,000-run Monte Carlo simulation was then conducted using each distribution for each data set to simulate the effect of 4% (two sigma) analytical error the same analytical error as is assumed for geochemical data in the Monte Carlo analysis of our 70000-sample geochemical dataset. As seen in Figure 2.8, for both the MgO data (a-d)

Figure 2.7: Histograms of the estimated mean MgO content of 43–51% SiO₂ samples in each of 10,000 Monte Carlo simulations for each 100 Ma bin between 0 and 4 Ga, illustrating the approximately Gaussian distribution of the means.

and the simulated distribution (e-h), while the choice of error distribution may influence the small-scale smoothness of the resulting data distribution, there is no bias to the overall distribution (as particularly evident in e-h), and no bias to the mean of the distribution (red vertical lines).

To further demonstrate that the choice of statistical distribution to represent analytical error does not bias our Monte Carlo results, we conducted our full Monte Carlo analysis (as in section 1.2) for three different combinations of error distributions. Figure 2.9 shows the results as a typical example for MgO in mafic samples (43-51% SiO₂) using (a) a Gaussian distribution for both geochemical error and geochronological error (as in Figures 2.1-2.3); (b) a Gaussian distribution for geochronological error and a log-normal distribution for geochemical error; and (c) a log-normal distribution for both geochemical error and geochronological error. As seen in Figure 2.9, the resulting trend in MgO through time is nearly identical in each case. We conclude that the choice of error distribution in our Monte Carlo analysis has little to no effect on the resulting trends.

2.3.4 Response of the Monte Carlo results to regions of missing data

Due to the well known paucity of early Proterozoic igneous rocks [Condie and Aster, 2010], it may be argued that the position and/or shape of the ~ 2.5 Ga geochemical transition that we observe may be influenced by a lack of data in this period. In our dataset, this lack of data is particularly pronounced between 2200 and 2600 Ma, a period during which the temporal density of geochemical data is only ~ 5 percent of that at the pronounced data peaks at 2100 and 2700 Ma. Consequently, we have conducted additional tests to examine the sensitivity of the Monte Carlo technique to periods of sparse data. First, a 10,000-point synthetic dataset was generated using a log-normal distribution, with an abrupt shift in the mean and variance of the data at 2500 Ma. Then, varying amounts of data were deleted in the period from 2200 to 2600 Ma, ranging from 100% of data present to 0% of data present (all deleted).

Figure 2.8: The results of Monte Carlo simulation of (1) MgO content of mafic igneous samples between 400 and 410 Ma (left, a-d), and (2) synthetic lognormal distribution with location parameter 0 and variance parameter 0.5 (right, e-h), where 4% (two sigma) analytical uncertainty is simulated using three different distributions for the analytical error. (a,e): distribution of the raw data; (b,f): distribution of Monte Carlo results when a Gaussian error distribution is used; (c,g): distribution of results when a log-normal distribution is used; (d,h): distribution of results when a chi-squared distribution is used. Red vertical lines show the position of the mean for each set of results; inset illustrates the distribution of individual means about that line (not to scale).

Figure 2.9: Monte Carlo simulation of MgO content through time in mafic (43-51% SiO₂) samples using (a) a Gaussian distribution for both geochemical error and geochronological error (as in Figures 1-3); (b) a Gaussian distribution for geochronological error and a log-normal distribution for geochemical error; and (c) a log-normal distribution for both geochemical error and geochronological error.

The dataset was then subjected to Monte Carlo analysis as in section 1.2 above, using an average age uncertainty of 22 Ma and 4% analytical error. As seen in Figure 2.10, an abrupt transition as seen in Figure 2.1g and Figure 2 b-d may may be preserved to some degree down to the point of 5% data remaining, with 1% and 0% of the data preserved, only a smooth transition is observed. Similarly, deleting data from a continuous starting distribution will not result in any discontinuity in the resulting Monte Carlo output, only a large increase in uncertainty in the data-poor region (Figure 2.11). Consequently, it appears unlikely that the observed abrupt transitions in secular geochemical evolution could be a product of the scarcity of early-Proterozoic data. More gradual transitions such as in Figure 1f may be influenced by a lack of data; although such trends still provide a convincing evidence for a major geochemical transition, the timing and rapidity of that transition is less certain. Although the dearth of data between ~ 2200 and ~ 2600 Ma may contribute in cases such as Figure 1f to the uncertainty in the timing of the observed geochemical transition, it remains the case that between the uncertainty in the timing of this transition and the uncertainty in the timing of the Great Oxidation Event, these two events easily overlap within uncertainty.

2.3.5 Interpretation of major element trends

Assuming our dataset provides a representative sample of the crust, four candidate mechanisms could explain the observed trends (Figure 1) in compatible and incompatible element composition of mafic rocks: (1) similar degree melting from a mantle that is more enriched now than in the past; (2) higher degrees of crustal contamination of otherwise identical basalts in the present; (3) higher degrees of fractionation in the present; or (4) higher mantle melt fraction in the past, due to either higher temperature or higher water content. A modern-day mantle that is more enriched now than in the Archean is inconsistent with well-established evidence from Nd, Sr, and Hf isotopic studies of mid-ocean ridge basalts [White and Hofmann, 1982, Vervoort and Blichert-Toft, 1999], eliminating mechanism (1). Increasing crustal contamination (2) should be reflected in ratios such as Nb/U and Pb/Ce

Figure 2.10: Monte Carlo analysis of simulated dataset with an abrupt change in mean and variance at 2500 Ma under the influence of varying degrees of data loss between 2200 and 2600 Ma (dashed blue lines) ranging from 100% of data preserved (a) to all data deleted (f). Background of plot (a) shows the initial synthetic dataset (note that data is cropped by the range of the plot). Note that in the case of a complete lack of input data between 2200 and 2600 Ma (0%), output data is only defined due to the age uncertainty of the adjacent input data.

Figure 2.11: Monte Carlo analysis of simulated dataset under the influence of varying degrees of data loss between 2200 and 2600 Ma (dashed blue lines) ranging from 100% of data preserved (a) to all data deleted (f) as in Figure 2.10, but with linear instead of stepwise trend in the initial simulated dataset. Note that in the case of a complete lack of input data between 2200 and 2600 Ma (0%), output data is only defined due to the age uncertainty of the adjacent input data.

[Hofmann et al., 1986] that are instead relatively constant through time (Figure 2.12). If increasing magma fractionation (3) was used to account for the entire observed trend, this would imply that modern basalts are on average created through fractionation of very high MgO magmas such as komatiites, which is clearly not the case. Indeed, if anything, a thick Archean crust as suggested by crustal depth-of-melting/fractionation indicators (Figure 2) as well as rapidly-cooling high-Mg mafic magmas suggest increased fractional crystallization in the Archean, in opposition to the observed trend. To address the issue more quantitatively, we mimic the approach of Klein and Langmuir [Klein and Langmuir, 1987], by applying our bootstrap resampling approach to reconstruct global mean MgO-Na₂O and MgO-CaO/Al₂O₃ trends for time periods between the Archean and the present day (Figure 2.13). Both trends are consistent with globally averaged fractionation paths, illustrating that substantial fractionation occurs at any given time, but parallel trends are shifted as a function of age. Following Klein and Langmuir [Klein and Langmuir, 1987], these parallel trends illustrate changes in mantle melt fraction. Given that decreasing average mantle melt fraction through time (4) is then the most compatible interpretation of the data, we are faced with two options: secular cooling or mantle dehydration. Evidence for a more hydrous Archean mantle is equivocal [Berry et al., 2008], and it has even been argued that the potentially undercompensated flux of water into the mantle at subduction zones suggests that the hydration state of the mantle is increasing through time, not decreasing [Peacock, 1990, Maruyama and Okamoto, 2007]. Secular cooling, on the other hand, presents no such caveats and is widely expected on the basis of physical constraints.

Mantle percent melt was estimated for each sample from 43-51% SiO₂ in all 10,000 simulations by numerical least squares optimization of the simulated major element data to that of slightly hydrous (0.1%) primitive mantle partial melts as calculated by MELTS [Ghiorso and Sack, 1995, Asimow and Ghiorso, 1998] for isobaric melting at a range of pressure conditions. Resulting percent melt estimates were found to agree within error despite order of magnitude differences in melting pressure (Figure 2.14), suggesting that the results are

Figure 2.12: Mean Pb/Ce and Nb/U through time for mafic lithologies, illustrating the lack of a clear trend that would be required to explain observed trends in compatible and incompatible element concentration through changes in degree of crustal contamination through time. Error bars represent 2-sigma standard errors of the mean from Monte-Carlo bootstrap resampling.

insensitive to changes in model pressure. Although MELTS does not extend to high enough pressures to directly simulate high-degree isentropic decompression melting, as long as the system is not far from equilibrium, percent melt and melt composition will be roughly state functions of pressure and temperature - that is, path independent. Consequently, at a given pressure (say, corresponding to the base of the crust) percent melt and melt composition will both be state functions of temperature. In this case, then, there will be a simple relationship between percent melt and melt composition, allowing for accurate estimation of percent melt from melt composition regardless of the exact melting path. This approach will break down in the case of fractional melt extraction, in which the melt cannot be in equilibrium with the solid; the absolute value of the results may therefore be inaccurate in the case of predominantly fractional melting, though relative trends would be expected to remain robust.

Since our analysis focuses on the trends in melt percentage over Earth history rather than the absolute values of these estimates, a number of sources of systematic error can be disregarded. We have intentionally not corrected basalt major element compositions for fractional crystallization to calculate primary melt compositions, as such an analysis has already been conducted on smaller datasets, and is only amenable to a small proportion of the available data [Herzberg et al., 2010]. By neglecting the effect of fractional crystallization, our estimates of percent melting through time are systematic underestimates. Nonetheless, absent major changes in the degree of fractional crystallization through time as is argued above, the results should accurately represent changes in percent melt over time. Herzberg et al. [Herzberg et al., 2010] analyzed a database of (n1500) basalts through early Earth history, identified those that could be corrected to primary mantle melts (n=33) to extract mantle potential temperature. The topology of a temperature curve corresponding to our degree-melting curve (Figure 2.1f) agrees well with Herzberg et al.s mantle potential temperature, though as expected they obtain higher mantle temperatures [Herzberg et al., 2010]. Further, our percent melting results generally agree with independent estimates of modern

Figure 2.14: Estimated percent mantle melt from 43-51% SiO_2 samples at (a) 0.2 GPa and (b) 2 GPa. Error bars are 2-sigma standard errors of the mean.

and Archean percent melting, suggesting that the degree of underestimation is not large [Walter, 2003, 1998].

In order to determine if observed trends in trace element ratios such as La/Yb in low silica samples could be generated solely by a single set of bulk partition coefficients given the estimated percent melting curve, linearized least squares regression was used to optimize bulk partition coefficients to fit percent melting and trace element curves with analytical non-modal batch melting equations. No single set of partition coefficients can reproduce the observed trace element ratios in basalts by varying melt fraction alone, showing that other variables such as temperature and mineralogy may have influenced partition coefficients, or that significant changes in source trace element composition (e.g. for the example of an arc setting, change in the trace element composition of the mantle wedge due to subduction erosion or sediment subduction) had an effect.

2.3.6 Redox partitioning calculations

To assess the potential for magmatic redox partitioning to affect surficial redox state, a simple stoichiometric redox balance of mantle restite was calculated for a modest 5 km³/yr magmatic flux (equivalent to estimates of modern arc magmatism; e.g. Crisp, 1984), assuming a magma density of 2500 kg/m³, 6 weight percent restitic Fe, and a ratio of 2 kg of restite to 1 kg of magma, as follows:

$$\begin{aligned} \frac{5 \text{ km}^3 \text{ magma}}{\text{yr}} * \frac{1000^3 \text{ m}^3}{\text{km}^3} * \frac{2500 \text{ kg}}{\text{m}^3} * \frac{2 \text{ kg restite}}{\text{kg magma}} * \dots \\ \dots \frac{0.06 \text{ kg Fe}}{\text{kg restite}} * \frac{1000 \text{ g}}{\text{kg}} * \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = \frac{2.68 * 10^{13} \text{ mol Fe}}{\text{yr}} \end{aligned} \quad (2.2)$$

Consequently, a fifteen percent increase in Fe³⁺/ΣFe of this restitic flux would liberate 4.02 * 10¹² mol e⁻ per year, or, stoichiometrically, consume 1.0 * 10¹² mol O₂/yr - similar in

magnitude to estimates of the entire present-day volcanic volatile flux of $\sim 5.6 * 10^{12}$ mol e^- /yr [Kump et al., 2001].

Notably, the Fe^{3+}/Fe^{2+} ratio of many magmas is low even at the present day, apparently not leaving much room for variation through time. However, theory and experiment suggest that oxygen fugacity is roughly proportional to the fourth power of ferric/ferrous ratio Nikolaev:1996wk. Consequently, a change in ferric/ferrous ratio from 0.1 to 0.01 would result in a roughly ten order of magnitude decrease in magmatic oxygen fugacity, with potentially major consequences for the production of volcanic volatiles.

References

- Irina M Artemieva. Global 1x1 thermal model TC1 for the continental lithosphere: implications for lithosphere secular evolution. *Tectonophysics*, 416:245–277, 2006.
- Paul D Asimow and Mark S Ghiorso. Algorithmic modifications extending MELTS to calculate subsolidus phase relations. *American Mineralogist*, 83:1127–1132, 1998.
- C Bassin, G Laske, and G Masters. The Current Limits of resolution for surface wave tomography in North America. *EOS Trans. AGU.*, 81:F897, 2000.
- Jean H Bédard. A catalytic delamination-driven model for coupled genesis of Archaean crust and sub-continental lithospheric mantle. *Geochimica et Cosmochimica Acta*, 70:1188–1214, 2006.
- Andrew J Berry, Leonid V Danyushevsky, Hugh St C O’Neill, Matt Newville, and Stephen R Sutton. Oxidation state of iron in komatiitic melt inclusions indicates hot Archaean mantle. *Nature*, 455:960–963, 2008.
- Dante Canil, Hugh St C O’Neill, D Graham Pearson, Roberta L Rudnick, William F McDonough, and D A Carswell. Ferric iron in peridotites and mantle oxidation states. *Earth and Planetary Science Letters*, 123:205–220, 1994.
- K C Condie and V Pease. When Did Plate Tectonics Begin on Planet Earth? - Google Books, 2008.

- Kent C Condie. Did the character of subduction change at the end of the Archean? Constraints from convergent-margin granitoids. *Geology*, 36(8):611–614, 2008.
- Kent C Condie and Richard C Aster. Episodic zircon age spectra of orogenic granitoids: The supercontinent connection and continental growth. *Precambrian Research*, 180:227–236, 2010.
- Kent C Condie and Craig O’Neill. The Archean-Proterozoic boundary: 500 my of tectonic transition in Earth history. *American Journal of Science*, 310:775–790, 2010.
- Kent C Condie, M E Bickford, Richard C Aster, Elena Belousova, and David W Scholl. Episodic zircon ages, Hf isotopic composition, and the preservation rate of continental crust. *GSA Bulletin*, 123:951–957, 2011.
- Maarten J de Wit. On Archean granites, greenstones, cratons and tectonics: does the evidence demand a verdict? *Precambrian Research*, 91:181–226, 1998.
- Mark S Drummond and Marc J Defant. A model for trondhjemite-tonalite-dacite genesis and crustal growth via slab melting: Archean to modern comparisons. *Journal of Geophysical Research*, 95(B13):21503–21521, December 1990.
- Raymond J Durrheim and Walter D Mooney. Archean and Proterozoic crustal evolution: evidence from crustal seismology. *Geology*, 19:606–609, 1991.
- EarthChem. EarthChem Portal, January 2011. URL <http://www.earthchem.org/>.
- James Farquhar, Huiming Bao, and Mark Thiemens. atmospheric influence of earth’s earliest sulfur cycle. *Science*, 289:756–758, 2000.
- Woodward W Fischer and Andrew H Knoll. An iron shuttle for deepwater silica in Late Archean and early Paleoproterozoic iron formation. *GSA Bulletin*, 121(1-2):222–235, 2009.

- Mark S Ghiorso and Richard O Sack. Chemical mass transfer in magmatic processes IV. A revised and internally consistent thermodynamic model for the interpolation and extrapolation of liquid-solid equilibria in magmatic systems at elevated temperatures and pressures. *Contributions to Mineralogy and Petrology*, 119(2-3):197–212, March 1995.
- Christopher J Hawkesworth and A I S Kemp. Evolution of the continental crust. *Nature*, 433:811–817, 2006.
- Claude Herzberg, Paul D Asimow, Nicholas T Arndt, Yaoling Niu, C M Leshner, J G Fitton, M J Cheadle, and A D Saunders. Temperatures in ambient mantle and plumes: Constraints from basalts, picrites, and komatiites. *Geochemistry Geophysics Geosystems*, 8(2), 2007.
- Claude Herzberg, Kent C Condie, and Jun Korenaga. Thermal history of the Earth and its petrological expression. *Earth and Planetary Science Letters*, 292:79–88, 2010.
- Marc M Hirschmann, Mark S Ghiorso, L E Wasylenki, Paul D Asimow, and Edward M Stolper. Calculation of Peridotite Partial Melting from Thermodynamic Models of Minerals and Melts. I. Review of Methods and Comparison with Experiments. *Journal of Petrology*, 39(6):1091–1115, 1998.
- Albrecht W Hofmann, K P Jochum, M Seufert, and William M White. Nb and Pb in oceanic basalts: new constraints on mantle evolution. *Earth and Planetary Science Letters*, 79(1-2):33–45, August 1986.
- KamLAND Collaboration. Partial radiogenic heat model for Earth revealed by geoneutrino measurements. *Nature Geoscience*, 4(9):647–651, July 2011.
- J F Kasting, D Eggler, and S Raeburn. Mantle redox evolution and the oxidation state of the Archean atmosphere. *The Journal of Geology*, 101:254–257, 1993.
- Robert Woodbury Kay and Suzanne Mahlburg Kay. Delamination and delamination magmatism. *Tectonophysics*, 219:177–189, 1993.

- E M Klein and Charles H Langmuir. Global correlations of ocean ridge basalt chemistry with axial depth and crustal thickness. *Journal of Geophysical Research*, 92(B8):8096–8115, 1987.
- Lee R Kump. The rise of atmospheric oxygen. *Nature*, 451:277–278, 2008.
- Lee R Kump and Mark E Barley. Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. *Nature*, 448:1033–1036, 2007.
- Lee R Kump, J F Kasting, and Mark E Barley. Rise of atmospheric oxygen and the “upside-down” Archean mantle. *Geochemistry Geophysics Geosystems*, 2, 2001.
- Cin-Ty Aeolus Lee, Peter Luffi, Véronique Le Roux, Rajdeep Dasgupta, F Albarède, and William P Leeman. The redox state of arc mantle using Zn/Fe systematics. *Nature*, 468:681–685, 2010.
- Zheng-Xue Anse Li and Cin-Ty Aeolus Lee. The constancy of upper mantle fO₂ through time inferred from V/Sc ratios in basalts. *Earth and Planetary Science Letters*, 228:483–493, 2004.
- Shigenori Maruyama and Kazuaki Okamoto. Water transportation from the subducting slab into the mantle transition zone. *Gondwana Research*, 11(1-2):148–165, January 2007.
- Makoto Matsumoto and Takuji Nishimura. Mersenne twister: a 623-dimensionally equidistributed uniform pseudo-random number generator. *ACM Transactions on Modelling and Computer Simulation*, 8(1):3–30, January 1998.
- Jean-François Moyen. The composite Archaean grey gneisses: Petrological significance, and evidence for a non-unique tectonic setting for Archaean crustal growth. *LITHOS*, 123(1-4):21–36, 2010.

- Jean-François Moyen and Gary Stevens. Experimental Constraints on TTG Petrogenesis: Implications for Archean Geodynamics. *Archean Geodynamics and Environment Geophysical Monograph Series*, 164:147–175, 2006.
- Othmar Müntener, Peter B Kelemen, and Timothy L Grove. The role of H₂O during crystallization of primitive arc magmas under uppermost mantle conditions and genesis of igneous pyroxenites: an experimental study. *Contributions to Mineralogy and Petrology*, 141(6):643–658, September 2001.
- Simon M Peacock. Fluid Processes in Subduction Zones. *Science*, 248:329–337, April 1990.
- Nick Petford and M Atherton. Na-rich partial melts from newly underplated basaltic crust: the Cordillera Blanca Batholith, Peru. *Journal of Petrology*, 37(6):1491–1521, 1996.
- Birger Rasmussen and Roger Buick. Redox state of the Archean atmosphere: Evidence from detrital heavy minerals in ca. 3250-2750 Ma sandstones from the Pilbara Craton, Australia. *Geology*, 27(2):115–118, 1999.
- Rob Rye and Heinrich D Holland. Paleosols and the evolution of atmospheric oxygen: a critical review. *American Journal of Science*, 298:621–672, 1998.
- P Van Aken and B Liebscher. Quantification of ferrous/ferric ratios in minerals: new evaluation schemes of Fe L 23 electron energy-loss near-edge spectra. *Physics and Chemistry of Minerals*, 29:188–200, 2002.
- Jeff D Vervoort and Janne Blichert-Toft. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. *Geochimica et Cosmochimica Acta*, 63(3-4): 533–556, February 1999.
- Michael J Walter. Melting of garnet peridotite and the origin of komatiite and depleted lithosphere. *Journal of Petrology*, 39(1):29–60, 1998.

-
- Michael J Walter. Melt Extraction and Compositional Variability in Mantle Lithosphere. In *Treatise on Geochemistry*, pages 363–394. Elsevier, 2003.
- William M White and Albrecht W Hofmann. Sr and Nd isotope geochemistry of oceanic basalts and mantle evolution. *Nature*, 296:821–825, April 1982.

Chapter 3

Volcanic-Plutonic Parity and Crustal Differentiation

3.1 Abstract

The continental crust is central to the biological and geological history of Earth. However, crustal heterogeneity has prevented a thorough geochemical comparison of its primary igneous building blocks—volcanic and plutonic rocks—and the processes by which they differentiate to felsic compositions. Our analysis of a comprehensive global dataset of volcanic and plutonic whole-rock geochemistry shows that differentiation trends from primitive basaltic to felsic compositions for volcanic versus plutonic samples are generally indistinguishable in subduction zone settings, but divergent in continental rifts. Offsets in major and trace element differentiation patterns in rift settings suggest higher water content in plutonic magmas and reduced eruptibility of hydrous silicate magmas. In both tectonic settings, our results indicate that fractional crystallization, rather than crustal melting, is predominantly respon-

This work has been published as: Keller, C. Brenhin, Blair Schoene, Melanie Barboni, Kyle M. Samperton, and Jon M. Husson (2015), Volcanic–plutonic parity and the differentiation of the continental crust, *Nature*, 523, 301–307.

sible for the production of intermediate and felsic magmas, emphasizing the role of mafic cumulates as a residue of crustal differentiation.

3.2 Introduction

Earth is the only planet in our solar system with a high-silica continental crust, which is complemented by a low-silica oceanic crust similar to that of the Moon, Mars and Venus [Taylor, 1989, Rudnick and Fountain, 1995]. The resulting bimodal topography [Rosenblatt et al., 1994] of oceans and continents is essential for regulating Earth's climate [Walker et al., 1981, Caldeira, 1995] and providing elemental nutrients to the biosphere [Froelich et al., 1982]. Igneous geochemistry drives our understanding of the formation and evolution of the continental crust, along with its depleted complement, the mantle [Rudnick and Fountain, 1995, Hofmann, 1997]. Detailed investigations of specific igneous systems have revealed that mantle-derived basaltic melts differentiate to higher silica contents through processes such as fractional crystallization, metamorphism, and remelting of crustal material. Though these processes are generally agreed to result in a geochemically-stratified lithosphere which increases in silica abundance from the crust-mantle boundary to the surface [Rudnick and Fountain, 1995, Christensen and Mooney, 1995], the compositional and geologic heterogeneity of the continents—scaling from kilometers to micrometers—has made it difficult to assess the relative importance of specific endmember processes. Solving this problem requires an understanding of why magmas a) ascend through the crust and erupt to form volcanic rocks, or b) stall and freeze at depth as plutons. Some models suggest that magma composition and volatile content dictate eruptibility [Carmichael, 2002, Miller et al., 2003], while others emphasize physical processes such as crystal/melt segregation in magma chambers [Bachmann et al., 2007] resulting in complementary volcanic and plutonic compositions. Alternatively, eruptibility may be controlled by thermal constraints whereby higher magma fluxes result in more magma reaching the surface [Annen, 2009], in which case systematic geochemical

differences between volcanic and plutonic rocks are not required. Here we test such models by taking advantage of increased availability of whole-rock compositional data to perform a comprehensive statistical analysis of the geochemical relationship between volcanic and plutonic rocks. We posit that this comparison provides insight not only into the predominant mechanisms of igneous differentiation and the origins of crustal stratification, but also since magmas that reach the Earth's surface are more efficiently recycled back into the mantle via erosion and subduction into crust-mantle geochemical evolution over billion-year timescales.

3.3 Quantifying Volcanic-Plutonic Parity

To determine if continental plutonic and volcanic rocks are compositionally equivalent, we have applied computational statistical techniques to a dataset of major and trace element geochemical analyses, with 122,751 plutonic and 171,690 volcanic whole-rock samples of the continental crust, extracted from the EarthChem database [EarthChem, 2010]. After filtering spurious data (Methods), each dataset was subjected to weighted bootstrap Monte Carlo analysis [Keller and Schoene, 2012] (Chapter 2), with sample weights inversely proportional to spatial sample density in order to obtain a uniform, maximally representative posterior sample distribution on the globe (Methods). This method maximises the accuracy of statistical parameters such as the mean and median, and minimises the effect of oversampling in regions that have been subjected to more intensive field study. Sampling bias is further minimised in our interpretations by focusing on intensive compositional variables, binned by differentiation proxies such as SiO_2 and MgO (Methods, Figures 3.1-3.2). Results are reported as the mean and 2 standard error of the mean for 2 weight percent (wt.%) SiO_2 bins.

The geochemistry of igneous rocks is known to correlate with tectonic setting [Pearce et al., 1984, Bebout, 2014], arising in part from different styles of mantle melting: water-driven flux melting in subduction zones (volcanic arcs) versus decompression melting in rifts

[Fyfe and McBirney, 1975, Bailey, 1983, Grove et al., 2012]. These contrasting processes form the basis of the classically-defined calc-alkaline versus tholeiitic differentiation series, as observed in both major and trace element systematics [Sisson and Grove, 1993, Bebout, 2014, Zimmer et al., 2010, Grove et al., 2012]. Since the proportion of volcanic versus plutonic magmatism may vary with tectonic setting, we have examined differentiation trends separately for arc and rift samples (based on geographic location for predominantly sub-200 Myr old samples; Methods) to prevent such an effect from biasing our geochemical analysis. The results (Figures 3.1-3.2) are shown along with mid-ocean ridge (MOR) differentiation trends as an endmember tholeiitic case for comparison.

Major and trace elements from both tectonic settings follow curvilinear differentiation trends (Figures 3.1-3.2), with rift volcanics falling closer to the tholeiitic MOR dataset. Elemental abundances consistently diverge for compositions more mafic than average primitive basalt (i.e., $< 50\%$ SiO_2), with plutonic rocks enriched in MgO and depleted in nominally incompatible major elements (Figure 3.1), consistent with the exposure of mafic plutonic cumulates. Enrichments in volcanic TiO_2 and K_2O at low silica may also suggest the influence of highly eruptible peralkaline volcanics with few intrusive equivalents. Above 55% SiO_2 , element compositions for arc plutonic and volcanic rocks follow overlapping trends at the 2-standard-error level, while rift volcanics reveal subtle enrichments in FeO and depletions in CaO and Al_2O_3 relative to rift plutonic samples. More dramatic differences between rift volcanic and plutonic rocks are observed in the trace element data, with offsets by up to a factor of two across a wide range of SiO_2 . Ba and Sr are significantly enriched in plutonic relative to volcanic rift rocks above 50% SiO_2 (Figure 3.2), while conversely, felsic rift plutonic rocks show depletions in Zr, Hf, and the heavy rare earth elements (HREE). Divergences in rift samples remain when sampling only rocks <100 Ma, such that plutonic compositions are not biased towards older, basement continental crust. In addition, while rift samples are generally associated with high heat fluxes [Morgan, 1982] that may permit anatexis of preexisting crust to produce incompatible element-enriched melts, average rift

differentiation trends in Figure 3.1 do not show a strong tendency towards S-type [White et al., 1986] signatures, e.g., with lower Al at high silica than in arcs.

As Zr and Hf are nominally incompatible in all major rock-forming minerals, the inflection toward decreasing Zr and Hf with increasing silica reflects saturation of zircon (ZrSiO_4) [Boehnke et al., 2013]. Yttrium and the HREE are similarly influenced by zircon fractionation, as well as by fractionation of amphibole and garnet [Schnetzer and Philpotts, 1970, GERM, 2013]. The large divalent cations Ba and Sr, meanwhile, are primarily compatible in feldspar, particularly high-Na plagioclase [GERM, 2013]. Consequently, decreased feldspar fractionation and increased zircon fractionation in rift plutonic relative to rift volcanic magmas could produce the observed offsets in Zr, Hf, HREE, and Sr at a given SiO_2 , consistent with a less dramatic but systematic depletion of CaO and Al_2O_3 in rift volcanics compared to plutonics (Figure 3.1).

3.4 The Role of Water in Magma Eruptibility

In one scenario for mineral fractionation between volcanic and plutonic rocks, eruptible felsic melt is extracted from a crystal-rich magma shortly prior to eruption, leaving behind a lower SiO_2 , cumulate-like plutonic residue [Bachmann et al., 2007]. This mechanism may be expected to enrich the plutonic residue, as is observed, in Ba and Sr due to feldspar accumulation. However, it is not obvious why such a process would be active in rift environments but completely absent in arcs.

Differences between rift and arc magmas indicate a higher proportion of anhydrous decompression melting in rifts compared to dominantly fluid driven flux melting beneath arcs [Fyfe and McBirney, 1975, Bailey, 1983, Grove et al., 2012]. As seen in Figure 3.1, rift volcanics consistently plot closer to the dry, tholeiitic MOR differentiation trend than other continental igneous rocks, with increased FeO^* and TiO_2 and decreased CaO and Al_2O_3 at a given silica content [Zimmer et al., 2010, Grove et al., 2012]. The tholeiitic character

Figure 3.1: Major element Harker diagrams showing mean and 2-standard-error uncertainties of the mean in 2% SiO_2 bins for plutonic (blue) and volcanic (red) samples from arc (left column) and rift (right column) tectonic settings. Mean and 2-standard-error confidence intervals for average MORB and felsic MOR differentiates are shown in grey for comparison.

Figure 3.2: Trace element Harker diagrams showing mean and 2-standard-error uncertainties of the mean in 2% SiO₂ bins for plutonic (blue) and volcanic (red) samples from arc (left column) and rift (right column) tectonic settings. Mean and 2-standard-error confidence intervals for average MORB and felsic MOR differentiates are shown in grey. Europium anomaly Eu/Eu* represents depletion (Eu/Eu* < 1) or enrichment (Eu/Eu* > 1) of Eu²⁺ relative to adjacent 3+ rare earth elements.

Figure 3.3: Fe-Mg systematics of arc and rift volcanic and plutonic rocks. Increasing FeO^* (total iron normalized as Fe^{2+}) during differentiation from 8% MgO to 4% MgO indicates a tholeiitic differentiation trend, while decreasing FeO^* indicates a calc-alkaline trend.

of rift volcanics relative to all other continental samples is illustrated most prominently in Figure 3.3, in which rift volcanic rocks show initial FeO enrichment with decreasing MgO that typifies the tholeiitic differentiation trend [Zimmer et al., 2010, Grove et al., 2012]. In contrast, rift plutonic and arc rocks show lower FeO^* at a given MgO and no FeO enrichment with decreasing MgO . Given the strong correlation between water content and the degree of tholeiitic versus calc-alkaline differentiation [Green and Ringwood, 1968, Sisson and Grove, 1993, Zimmer et al., 2010] this observation is consistent with a systematically more hydrous composition for plutonic rift relative to volcanic rift samples.

Dissolved water in silicate melts has the effect of lowering the liquidus and solidus temperatures such that most silicates saturate at lower temperatures [Yoder, 1965, Green and Ringwood, 1968, Burnham and Davis, 1974, Sisson and Grove, 1993, Thomson, 1996], with a particularly strong effect for sodic plagioclase [Yoder, 1965, Sisson and Grove, 1993]. In contrast, experiments reveal little to no effect of water content on the saturation tempera-

ture of minerals such as magnetite [Botcharnikov et al., 2008] and zircon [Boehnke et al., 2013]. Thus, at high water activity, crystallization of common silicates will be suppressed relative to these phases at a given temperature: zircon and magnetite are therefore expected to saturate at lower magma SiO_2 contents during hydrous fractionation. Increased fractional crystallization of magnetite relative to plagioclase and other silicates in hydrous magmas is responsible for FeO depletion in the calc-alkaline trend [Green and Ringwood, 1968, Sisson and Grove, 1993, Zimmer et al., 2010, Botcharnikov et al., 2008]. We argue that given the dominant control of zircon on magma Zr and Hf, combined with decreased partitioning of Ba and Sr in anorthite compared to albite [GERM, 2013], calc-alkaline differentiation also explains enrichment of Ba and Sr and depletion of Zr, Hf, and HREEs in the melt phase relative to differentiation at lower water contents.

If Ba and Sr contents are elevated in hydrous magmas due to suppressed plagioclase stability, the Eu anomaly (Eu/Eu^* ; Figure 3.2), typically viewed as an indicator of plagioclase fractionation during differentiation, may be expected to follow a less negative trend for hydrous differentiation. In apparent contradiction to the plagioclase fractionation hypothesis, the datasets show that Eu/Eu^* is identical in all plutonic and volcanic rocks above 52% SiO_2 regardless of tectonic setting. Surprisingly, however, arc Eu/Eu^* is observed to follow equally or even more negative differentiation trends than MOR samples (Figure 3.2). The relative lack of negative Eu/Eu^* in dry MORB tholeiites has been observed in other data compilations [Sun and McDonough, 1989], and may suggest that water availability in a differentiating magma has little effect on resulting Eu/Eu^* . Indeed, while plagioclase is often credited as the primary driver of magma Eu/Eu^* , a compilation of published partition coefficients [GERM, 2013] illustrates that, for instance, orthoclase may often have a higher $\text{Kd } \text{Eu}^{2+}/\text{Eu}^{3+}$ than plagioclase (Table 3.1). Consequently Eu/Eu^* is not directly diagnostic of plagioclase fractionation, and the lack of a more pronounced Eu anomaly in MOR and rift volcanic samples does not rule out increased plagioclase crystallization in these dry

lithologies relative to arc and plutonic samples if coupled with complementary H₂O-induced changes in the fractionation of other Eu/Eu*-active minerals.

Given the high fluid solubility of Ba and Sr [Tatsumi et al., 1986, Bebout, 2014], source enrichment by aqueous fluids provides an alternative origin of enhanced Ba and Sr concentrations in rift plutonics. Such metasomatic fluids may be released along with fluid-mobile elements such as Ba, Sr, Pb, and Rb [Tatsumi et al., 1986, Bebout, 2014] by rift-associated heating of mantle lithosphere or hydrous continental crust. However, enrichment in fluid-soluble elements cannot solely explain Ba and Sr offsets in rift plutonics given the lack of equivalent offsets in other fluid-soluble elements like Rb and Pb (Figure 3.2), which are observed to be strongly elevated in known cases of fluid-mobile element enrichment in metasomatic veins and aureoles [Bebout, 2014], and in experimental measurements of aqueous fluids produced by dehydration of oceanic crust [Tatsumi et al., 1986]. Enrichment by metasomatic fluids is consistent with the lack of Eu/Eu* offset associated with Ba and Sr enrichment, and may provide an initial water source for hydrous plutonic magmas in rifts. Melts enriched by these fluids would be driven towards calc-alkaline differentiation trends by the increased water content, with suppressed plagioclase fractionation and increased zircon fractionation generating a majority of observed volcanic-plutonic offsets.

Examination of the hydrous and anhydrous solidi for granitic compositions predicts a plutonic fate for hydrated granitoid magmas. Given the negative slope of the water-saturated solidus, hydrous magmas approach the solidus and may freeze upon decompression due to devolatilization, while decompression of dry magmas moves them away from the solidus towards greater degrees of partial melt (Figure 3.4; Supplementary Discussion) [Burnham and Davis, 1974, Thomson, 1996, Carmichael, 2002, Miller et al., 2003]. Consequently, water content may correlate with emplacement depth in settings where magmas with highly variable water contents are observed. In arcs, where magmas are almost ubiquitously hydrated [Plank et al., 2013] and often water-saturated by upper crustal depths for felsic compositions, the probability of eruption may instead be dictated by variables such as magma flux,

crustal stress and thermal state, as has been suggested based on geochronological, thermal, and structural considerations [Glazner et al., 2004, Annen, 2009, Petford et al., 1993] and as required by the identical arc volcanic and plutonic differentiation trends. Therefore, while dry tholeiitic magmas have been documented in arc settings [Grove et al., 2012], our analysis indicates that such melts do not affect average arc differentiation trends.

3.5 Generation of the Felsic Continental Crust

Despite the critical role of the continental crust on Earth, the relative contribution of two end-member processes responsible for crustal differentiation—fractional crystallization of mantle-derived basaltic magma and partial melting of older crust—remains uncertain [Chayes, 1963, Clague, 1978, Dufek and Bachmann, 2010, Lee and Bachmann, 2014]. The distribution of silica in crustal rocks, both globally (Figure 3.5) and regionally, reveals a pronounced gap in the abundance of intermediate compositions, generally referred to as the Daly Gap [Daly, 1925, Chayes, 1963, Clague, 1978, Reubi and Blundy, 2009, Dufek and Bachmann, 2010]. This bimodality initially suggests partial melting as the dominant mechanism of differentiation [Chayes, 1963]: low-degree melting of mantle-derived basalt with $\sim 50\%$ SiO_2 can produce granodioritic and trondhjemitic melts with $\sim 70\%$ SiO_2 or more—corresponding to the two observed peaks in the silica distribution [Green and Ringwood, 1968, Drummond and Defant, 1990]. In this model intermediate magmas are produced primarily by magma mixing between basaltic and granitic endmembers [Kent et al., 2010], as suggested by the observation of crystal-rich andesites [Reubi and Blundy, 2009]. Comparatively, fractional crystallization is less clearly predisposed to produce a bimodal silica distribution. Mechanisms have nonetheless been suggested by which compositional gaps may result from the systematics of crystal fractionation [Clague, 1978] or the dynamics of liquid-crystal separation [Dufek and Bachmann, 2010].

Figure 3.4: Water-saturated and-undersaturated solidi in granitic systems. Adapted from [Miller et al. \[2003\]](#) and [Thomson \[1996\]](#). Wet magmas, which are typically colder than dry magmas due to generation near the solidus of their protolith (supplementary discussion), move towards the solidus and may freeze upon decompression, while drier magmas with higher solidus temperatures move away from the solidus and may not crystallize until after eruption.

Figure 3.5: Histograms of rock abundance as a function of silica content for all igneous (a), volcanic (b) and plutonic (c) samples. While first observed in oceanic alkaline magma series [Daly, 1925, Chayes, 1963, Clague, 1978], compositional gaps clearly emerge in a spatiotemporally weighted whole-rock global dataset (a) with peak compositions equally spaced but systematically 5 wt. % SiO₂ lower than those observed in the melt inclusion histograms of [Reubi and Blundy, 2009] (blue line). The low-silica peak is dominant in volcanic samples (b), while the high-silica peak predominates in plutonic samples (c).

Fractional crystallization and partial melting models may be distinguished, however, in that the two mechanisms result in contrasting major and trace element differentiation trends at intermediate compositions. Given that intermediate magmas are produced by mixing between granitic and basaltic endmembers in the partial melting model, differentiation trends in this model must follow straight mixing lines, as physical mixing between two compositional endmembers invariably produces straight lines in element-element space [Langmuir et al., 1978]. Fractional crystallization, in contrast, produces curved trends through continuous differentiation [Bowen, 1928, Grove et al., 1997, Müntener et al., 2001, Alonso-Perez et al., 2009].

Consistent with a fractional crystallization model, the observed volcanic and plutonic differentiation trends follow distinctly curved paths, even at intermediate compositions (Figures 3.1-3.2). These curved paths resemble liquid lines of descent for fractional crystallization, overlapping with experimental batch fractional crystallization results (Figure 3.6a) [Grove et al., 1997, Müntener et al., 2001, Alonso-Perez et al., 2009]. Comparison of the observed trends to differentiation trends of primitive basalt subject to varying degrees of magma mixing suggest a maximum 40% contribution of magma mixing to the production of intermediate magmas relative to idealized continuous fractional crystallization (Figure 3.6a inset), decreasing to almost no allowed mixing relative to the experimental batch results. Abundant field and petrologic evidence for magma mixing [Eichelberger et al., 2000, Kent et al., 2010] suggests an underlying differentiation process intermediate in efficiency, on average, between batch and continuous fractional crystallization.

One first-order prediction of the fractional crystallization model is the production of abundant crystal cumulates as a by-product of magma differentiation, which will vary in mineralogy and composition as a function of the pressure, temperature, and extent of melt extraction [Bowen, 1928], but must be compositionally complementary to the extracted melt, resulting in divergent cumulate and melt compositions [Gelman et al., 2014]. As a result, the presence of cumulates in the plutonic record will produce observable compositional offsets

Figure 3.6: (a) Comparison of volcanic and plutonic MgO differentiation to experimental batch fractionation (yellow, from [Grove et al., 1997, Mintener et al., 2001, Alonso-Perez et al., 2009] as compiled by [Reubi and Blundy, 2009]) and calculated continuous fractionation trends (black, average of individual trends in (b)) from MELTS. (b-e) Results of 200 best-fitting MELTS simulations showing liquid fractionation trends (blue lines) and corresponding cumulate compositions (green points), with point size proportional to the volume of cumulates produced at each simulation step. Cumulate compositions are colored according to the silica content of the magma with which they are in equilibrium, but are plotted at their own (solid) SiO₂. Observed volcanic and plutonic differentiations trends (red and blue error-bars) in this figure include all samples regardless of tectonic environment. Fit is relative to volcanic path to avoid potential cumulate influence on melt composition.

Figure 3.7: Schematic illustration of instantaneous cumulate compositions required by fractionation trends, illustrating the offset between melt and cumulate trajectories for curved (a,c) and linear (b) fractionation trends. Instantaneous cumulate compositions will fall along blue line tangent to the melt curve, with the extent of offset along this line correlating with the efficiency of cumulate extraction. Relatively efficient fractionation, corresponding to a large compositional offset and a high-curvature differentiation trend, is suggested by the observed curvature of major and trace element differentiation trends (Figures 3.1-3.2); efficient differentiation is additionally consistent with thermal constraints [e.g., [Annen, 2009](#)] which indicate limited heat budgets for crustal differentiation.

between volcanic and plutonic averages for any nonlinear differentiation trends (e.g. Figure 3.7). Clear compositional divergence attributable to plutonic cumulates is observed below 50% SiO_2 in both arc and rift settings (e.g. MgO , Eu/Eu^*). However, compositional offsets between felsic (>62% SiO_2) volcanic and plutonic differentiation trends are absent in arcs (Figures 3.1-3.2) and are parsimoniously explained in rifts by the petrologic effects of water. This lack of a felsic cumulate signature suggests that any cumulates with more than 60% SiO_2 are either small in volume, minimal in degree of melt extraction, or extensively remobilized into the volcanic record - and thus of limited significance for crustal differentiation. Consequently, we propose that the production of even felsic magmas by fractional crystallization results in a predominantly mafic cumulate residue with <62% SiO_2 .

To test this prediction, we conducted geochemical modeling in which cumulate compositions, volatile contents, and P-T paths representative of average crustal differentiation are estimated by inversion of 1.36 million pMELTS [[Ghiorso et al., 2002](#), [Smith and Asimow, 2005](#)] simulations to fit the observed major element differentiation paths given in Figures 3.1-3.2 (Methods). As displayed in Figure 3.6b-e, felsic magmas with up to 80% SiO_2 are produced in equilibrium with a cumulate of no more than 60% SiO_2 . In addition to anticipated

outputs of MgO-enriched ultramafic olivine-clinopyroxene-garnet-spinel cumulates, MELTS modeling elucidates the origin of several previously unexplained features of our dataset (e.g., subtle plutonic K₂O enrichment between 52-62% SiO₂ due to orthoclase accumulation; Figure 3.6e) while reproducing observed differentiation trends.

The production of intermediate and felsic crust by fractional crystallization is therefore consistent with both the curvature of observed differentiation trends and the existence of mafic cumulates in the plutonic record. However, questions remain regarding crustal silica distributions in a fractional crystallization scenario. As shown in Figure 3.5, the compositional gap in crustal igneous rocks is largely driven by the contrasting silica distributions of volcanic and plutonic rocks, with a high-silica peak in plutonic samples and a low-silica peak in volcanic samples. This relationship is the opposite of that predicted by proposed mechanisms of compositional gap formation by mineral-melt separation [Clague, 1978, Dufek and Bachmann, 2010], and may indicate that the global whole-rock compositional gap is distinct from that observed in some individual volcanic suites [Daly, 1925, Dufek and Bachmann, 2010]. The global Daly Gap as reflected in exposed igneous rocks appears to originate instead from superimposing a mantle-derived primitive basaltic distribution with a peak at ~52% SiO₂ onto a differentiated plutonic silica distribution skewed towards high silica.

While mafic cumulates clearly exist in the plutonic record, the higher average silica of plutonic samples is significant in the context of differentiation by fractional crystallization, and suggests that the majority of the mafic residue from crustal differentiation is lost from or otherwise not represented in the plutonic record. This is one expression of a widely-acknowledged problem in crustal mass balance: namely, the production of continental crust with ~61% SiO₂ from basaltic mantle inputs with ~50% SiO₂ [Kay and Kay, 1991, Rudnick and Fountain, 1995]. This issue is not unique to a fractional crystallization origin of the felsic crust, but can be averted in some crustal melting models by mechanisms where the mafic residue never leaves the mantle, e.g. slab melting [Drummond and Defant, 1990]. In a fractional crystallization model (and most crustal melting models), however, a mechanism

by which cumulates are physically removed from the continental crust is required, e.g., lower crustal delamination [Kay and Kay, 1991].

Further implications for the evolution of the crust-mantle system arise from the observed differences in volcanic and plutonic differentiation in rift settings. Because volcanic rocks are more easily eroded and removed from the crust, the tendency towards higher water in rift plutonic rocks should bias the mean crustal composition towards calc-alkaline, thus downplaying the importance of intracontinental magmatism to crustal growth. Meanwhile, the weatherable volcanics are more readily recycled and incorporated into surface biogeochemical cycles - for instance, elevated phosphorous in mafic volcanics (Figure 3.1) will necessarily contribute to increased phosphate availability over geologic timescales. Conversely, the preferential sequestration of elements enriched in plutonic rocks in the continental crust, such as K, Ba, and Sr (Figures 3.1-3.2), when compounded over billions of years, influences the crust-mantle elemental budget and radiogenic isotope mass balance, and provides additional constraint for quantitative models of crustal growth from the Archean to the present.

Although our results emphasize the distinction between arc and rift magmatism, the curvature of differentiation trends underscores the importance of fractional crystallization in both environments. Given the exclusively Phanerozoic age of surveyed arc and rift samples, our results suggest that it is possible to produce a bulk andesitic crust by processes of fractional crystallization and subsequent loss of mafic cumulates in modern tectonic settings, consistent with a fundamentally uniformitarian origin of the crust by processes now in operation.

3.6 Methods

In order to elucidate the geochemical relationship between volcanic and plutonic rocks, we have prepared and analyzed a dataset of major and trace element compositional data for 171,690 volcanic and 122,751 plutonic whole-rock samples together with location and litho-

logical information (Supplementary Table 1). Data was obtained from the freely-accessible EarthChem Portal, including samples from NavDat, Georoc, PetDB, and the US Geological Survey [EarthChem, 2010]. Oceanic samples were extracted to calculate tholeiitic MOR differentiation trends, while continental samples were separated into volcanic and plutonic datasets based on reported lithology. Volcanic and Plutonic samples were further classified by cross-correlating sample location with present-day tectonic environment, using a geospatially referenced tectonic setting map modified from the USGS Global Crustal Database [USGS, 1997] (Figure 3.8).

As illustrated in Figure 3.8, only samples from active oceanic and continental arcs are included in the arc category, while samples from active rifts along with some well-established failed rifts (aulacogens) and plume-associated continental large igneous provinces were included in the rift category. Consequently, rift samples represent those whose parental basaltic magma was produced primarily by decompression melting of the mantle, while arc samples are characterized by the contributions of flux melting in the arc mantle wedge. Continental samples whose original tectonic environment could not be discerned (grey area in Figure 3.8) were excluded from plots of arc versus rift geochemistry, but included in the trends of Figure 3.6.

In contrast to the dataset of Keller and Schoene [2012] (Chapter 2), a substantial proportion (~40%) of the whole-rock samples in our larger volcanic-plutonic dataset are not associated with age constraints. Tectonic setting assignments based on present-day location are, naturally, only valid for samples produced in their current setting, limiting the accuracy of assignments for samples older than a few hundred million years. If numerous, mis-assigned samples would likely blur the distinction between arc and rift subsets. However, based on the distribution of known sample dates (Figure 3.9), the proportion of older inherited samples in modern arc and rift settings is negligible in our dataset. This dominantly Phanerozoic age distribution has the additional benefit of increasing the probability that the process of tectonics and crust formation has not changed within the period of our analysis. Accord-

Figure 3.8: Sample locations and tectonic setting assignments. a: All volcanic and plutonic sample locations ($n=294,347$). b: Tectonic setting map modified from the USGS Global Crustal Database [USGS, 1997] c: Assigned arc and rift volcanic and plutonic sample locations ($n=141,561$). d: Oceanic (MOR) sample locations ($n=48,605$). Plutonic samples are plotted above and may obscure full range of volcanic samples. Samples not originating in explicit arc or rift provinces (grey area in b) were excluded from setting-specific differentiation trends, but included in the general volcanic and plutonic differentiation trends of Figure 3.6.

ingly, differentiation diagrams including only samples with known ages in the last 100 Ma (Figure 3.10) display the same trends and offsets as those including all available data, only with somewhat larger standard errors of the mean due to smaller sample size.

Due to the large size of the dataset, spurious data was filtered both manually and algorithmically (Supplementary Code 1). Although outlier removal may introduce bias by rejecting valid but exceptional data, the presence of extreme outliers (e.g., several orders of magnitude farther from the median than the 25% C.I. and likely not representing real bulk rock compositions) necessitated a method of outlier rejection to produce optimally accurate distributions of crustal composition. Consequently, conservative outlier rejection bounds were set manually in severe cases. Data representing physically impossible conditions (e.g. compositional normalization $>>100\%$.) was not considered meaningful, and thus deleted categorically.

Data were then subjected to a modified version of the statistical approach of Keller and Schoene [2012] (Chapter 2). Since geochronological constraints are not available for many samples in the volcanic-plutonic dataset, resampling weights were based only on sample location, rather than location and age as in Keller and Schoene [2012] (Chapter 2), to obtain an optimally uniform posterior spatial distribution (Figure 3.11). Although elemental distributions in the dataset are often not Gaussian (Figures 3.12-3.13), the arithmetic mean of a set of sample compositions nonetheless has unique physical significance, representing the bulk composition that would be produced by physically homogenizing that sample set. Further, in contrast to the distribution of the elemental data, the distribution of the mean for each element is nearly Gaussian, due to the effects of the central limit theorem. Consequently, Figures 3.1-3.2 show the arithmetic mean of binned volcanic and plutonic samples, along with the two-sigma standard error of the mean; equivalent plots based instead on the median are shown in Figure 3.12, with congruent results.

As the single dominant oxide component of most igneous rocks, wt.% SiO_2 is simpler to interpret and easier to correlate with observed rock compositions than most alternative

Figure 3.9: Age distributions for plutonic (a) and volcanic (b) samples with known ages. Both are dominated by Phanerozoic (<540 Ma) samples, with a slightly greater proportion of pre-200 Ma samples in the plutonic distribution.

Figure 3.10: Mean major (a-g) and trace element (h-n) differentiation trends a function of SiO_2 (binned in 2 wt.% intervals) along with 2-standard-error uncertainties (error bars) for volcanic (red) and plutonic (blue) samples with known ages less than 100 Ma, along with tholeiitic mid ocean ridge differentiates (grey outline).

Figure 3.11: Prior (original data, a-d) and posterior (after Monte-Carlo analysis, e-h) sample distributions in log scale for both volcanic and plutonic samples. Ideal distributions given uniform sampling of the continents (black line) shown for comparison. Since bootstrap resampling probabilities are weighted to reject no more than 90% of samples, improvement in posterior distribution is limited to roughly one log unit.

Figure 3.12: Median major (a-g) and trace element (h-n) differentiation trends as a function of SiO_2 , (error bars) with elemental distributions (lines) for volcanic (red) and plutonic (blue) samples, along with tholeiitic mid ocean ridge differentiates (grey outline). Error bars and MOR outline show median and two-standard-error uncertainties in 2 wt.% SiO_2 bins, while distributions are shown for 5 wt. % SiO_2 bins.

Figure 3.13: Mean major (a-g) and trace element (h-n) differentiation as a function of MgO, (error bars) with elemental distributions (lines) for volcanic (red) and plutonic (blue) samples, along with tholeiitic mid ocean ridge differentiates (grey outline). Error bars and MOR outline show median and two-standard-error uncertainties in 1 wt.% MgO bins, while distributions are shown for 1.25 wt. % MgO bins.

differentiation indicators. Nonetheless, similar volcanic-plutonic trends to those in the Harker diagrams (Figures 3.1-3.2) may be observed as well with wt% MgO as the independent variable (Figure 3.14), with decreasing MgO corresponding to increasing differentiation.

3.6.1 MELTS simulations

To test our predictions regarding the influence of fractional crystallization on average differentiation trends, the characteristics of cumulates in the plutonic record, and the effect of water on differentiation, we have conducted trace and major element geochemical modelling using high-performance computational resources at the DOE's National Energy Research Supercomputing Center and the Princeton Institute for Computational Science and Engineering. The massive parameter space and the nonlinear, discontinuous equations of igneous differentiation processes such as fractional crystallization lead to highly nonunique solutions which cannot be obtained analytically except in the simplest cases. Consequently, we have approached the problem through a brute-force Monte Carlo approach, minimizing 1.36 million MELTS fractionation paths with differing starting compositions and P-T paths to fit the observed crustal differentiation trends. These simulations were conducted using the alphaMELTS [Smith and Asimow, 2005] v1.4.1 command-line version of the MELTS and pMELTS thermodynamic modelling software [Ghiorso et al., 2002] along with parallel scripting codes (Supplementary Code 1, Supplementary Table 2). As each forward MELTS simulation is independent, the computation is inherently highly parallel, with minimal communication requirements between processes. However, due to the design of MELTS and alphamelts, numerous small configuration, input, and output files must be written for each simulation, such that networked filesystem performance may be a limiting factor for scalability. The average primitive oceanic basalt of Kelemen et al. [2014] was used as a starting composition, with varying initial H₂O, CO₂ contents and P-T conditions. Initial H₂O and CO₂ contents were drawn from uniform distributions between 0-4% by weight for H₂O and

Figure 3.14: Comparison of inverted MELTS parameters and compositional paths from $\sim 1.3 \times 10^6$ MELTS simulations with initial oxygen fugacity set by the Fayalite-Magnetite-Quartz buffer (FMQ, left) versus another $\sim 1.3 \times 10^6$ simulations with initial oxygen fugacity one log unit above the FMQ buffer (FMQ+1, right). a-b: Initial and average volatile distributions of 350 best-fitting simulations. c-d: P-T and P-SiO₂ paths of 350 best-fitting MELTS simulations. e-f: Major element melt and cumulate compositions for 200 best-fitting MELTS simulations.

between 0-1% for CO₂. Initial oxygen fugacity was equilibrated at the Fayalite-Magnetite-Quartz buffer (FMQ) but subsequently allowed to evolve in response to mineral fractionation.

Pressure ranges of differentiation were set following the assumption that basaltic magmas must be generated in the mantle (conservatively, at depths greater than ~33 km) and solidify in the crust. Maximum pressure is limited in a typical arc setting by the depth of the subducted slab (~100 km) but was constrained slightly shallower in practice so as not to greatly exceed the calibration range of pMELTS. Consequently, initial and final pressures were drawn from uniform random distributions between 1-2.5 and 0-1 GPa, respectively, with initial temperature set by the primitive basalt liquidus and a final temperature of 700 °C. Pseudorandom P-T paths were then generated by selecting five points from a uniform distribution for both pressure and temperature between the previously generated minima and maxima for each simulation, subject to the constraint that subsequent points must be non-increasing in both pressure and temperature. Each P-T path was then constructed by linearly interpolating between these seven points. The production simulations were then run using alphaMELTS v1.2 with a fractionation threshold of 0.005 and a 10 °C cooling step size. To explore the effect of oxygen fugacity, an equivalent set of simulations was conducted with an initial oxygen fugacity one log unit above the Fayalite-Magnetite-Quartz buffer (FMQ+1). The initial volatile compositions, average volatile compositions, and P-T paths of the best-fitting 350 simulations out of 1.36×10^6 simulations for initial oxygen fugacities of FMQ and FMQ+1 are shown in Figure 3.14, along with a comparison of best-fitting major element paths for these two different initial redox states. Results elsewhere throughout the text show the FMQ version.

Given the large compositional and physical parameter space sampled, some simulations will inevitably fall in regions where MELTS is poorly calibrated. In addition, saturation of hydrous mafic phases (largely amphibole) is likely underestimated in general, while at high silica MELTS may underestimate the saturation of quartz and overestimate that of potassium feldspar; rhyolite-MELTS, which addresses the latter two problems [Gualda et al., 2012] (not

available in an alphasELTS scripted version at time of our simulations) may result in different inversion results. Consequently, our simulations should be reproduced with multiple versions of MELTS before assigning particular significance to second-order results such as the inverted optimal P-T paths or water contents shown in Figure 3.14. Nonetheless, the MELTS results do unequivocally demonstrate that fractionation of the the calculated cumulate compositions can accurately reproduce the observed average major element differentiation trends.

3.6.2 Trace element calculations

In order to additionally simulate trace element fractionation, we calculated representative average mineral/melt partitioning using partition coefficients from the the GERM partition coefficient database [GERM, 2013] (Supplementary Table 3). Due to the strong compositional dependence of most trace element partition coefficients (mineral/melt partition coefficients tend to increase with increasing magma silicate network strength), partition coefficients were binned and interpolated as a function of magma SiO₂ content, propagating errors through unweighted Monte Carlo bootstrap resampling (supplementary code).

Trace element differentiation paths were calculated for ideal fractional crystallization using mineral phase proportions from the best-fit MELTS simulations. As seen in Figure 3.15, calculated fractionation paths conform to the expectation of increasing Sr, and to a lesser degree Ba with increasing magma water content. As seen in Table 3.1, the compiled partition coefficient data reveals high Kd Eu/Eu* in orthoclase as well as plagioclase feldspar, resulting in no clear correlation of magma water content with Eu anomaly during differentiation (Figure 3.15).

3.6.3 Solidus temperature of hydrous and dry magmas

While the opposing slopes of the hydrous vs. dry solidi are unambiguously determined (as seen in Figure 3.4) from experimental data [Green, 1973, Thomson, 1996], connecting these solidi to the preferential stalling of hydrous magmas upon decompression also requires

Figure 3.15: Simulated Sr (a) Ba (b) and Eu (c) differentiation paths (blue lines) and corresponding cumulate compositions (green points) calculated by applying GERM partition coefficients [GERM, 2013] to the mineral percentages derived from 200 MELTS simulations with best-fitting major element trends out of 1.36 million MELTS simulations with varying initial H₂O, CO₂, and P-T paths (methods) and initial oxygen fugacity set by the Fayalite-Magnetite-Quartz (FMQ) buffer. The diameter of each cumulate point is proportional to the volume of cumulates produced at each simulation step.

lower average temperatures for hydrous magmas. The assumption of colder temperatures in hydrous magmas is somewhat justified since these magmas inevitably derive from systems with suppressed solidi and liquidi. As an example, let us consider an arbitrary silicate protolith to which a finite quantity of heat is added, sufficient to produce an extractable proportion of silicate magma over a geologically relevant temporal and spatial scale. Two factors suggest that, in this scenario, final magma temperature will be linked to the solidus and liquidus temperatures of the protolith. Holland:2011vm Firstly, for processes within the solid earth, rates of heat transport are competitive with those of heat addition. Once the solidus is reached in one region of the protolith, heat can diffuse and advect to adjacent regions of unmelted protolith, until the available heat is consumed as latent heat of fusion. This is demonstrated by the extreme rarity of terrestrial supersolidus magmas, which are thought to be produced only in cases of extremely rapid heat addition such as large bolide impacts [Zieg and Marsh, 2005]. Secondly, the molar heat capacity C_p [J/mol K] of most silicates is much lower (by two to three orders of magnitude) than their molar latent heat of fusion H_f [kJ/mol] [Holland and Powell, 2011]. In this sense, a difference in solidus temperature is equivalent in terms of heat consumed to a comparatively small change in the extent of protolith melting. As long as the liquidus is not exceeded, then, the final magma temperature will be a consistent offset above the solidus over a range of solidus temperatures. In other words, once the solidus is reached, the remaining available heat is primarily used to produce more magma, not raise magma temperature. We may then infer that the addition of heat to a hydrous (low-T solidus) vs. dry (high-T solidus) protolith will result in a relatively similar extent of melting - and thus a similar position relative to the appropriate solidus - but with higher temperature for the dry magma due to its higher solidus temperature. The same reasoning holds for the addition of water to an existing magma: the addition of water will promote further melting (of entrained crystals, if any, or of the surrounding wall rock), decreasing magma temperature as the melting reaction consumes the available excess enthalpy.

3.6.4 Causality of the plutonic water correlation

If our observed correlation between plutonic emplacement and geochemical signatures of higher water content is not fortuitous, there are at least two plausible causal mechanisms we must consider, with opposite directions of causality: that plutonic magmas are hydrous because they are not degassed near the surface, or that their higher water content forces them to stall at depth. Given that the solubility of water in silicate magma increases with increasing pressure [Hamilton et al., 1964], there is an inherent bias towards higher water content in magmas differentiated and emplaced at higher pressure. However, our geochemical evidence for higher water in plutonic magmas requires increased water content during the period of differentiation, rather than that of final emplacement. The apparent dearth of cumulates in the upper crust (Figures 3.1-3.2) may indicate that proportionately little differentiation occurs in shallow subvolcanic magma chambers, partially decoupling depth of emplacement from depth of differentiation. If, despite these considerations, greater emplacement depth does contribute significantly to higher water content in plutonic magmas during differentiation, this effect and the associated geochemical signatures of higher water content in plutonic magmas during differentiation should be observed equally in both arc and rift environments, which is not what our data show. In contrast, higher water content leading to an increased likelihood of plutonic emplacement invokes no such contradiction if arc magmas are (as expected) uniformly hydrous at crustal depths. Such considerations, combined with a thermodynamic expectation for the stalling of hydrous magmas as discussed in the section on solidus temperature lead us to favor the latter direction (plutonic because hydrous) of causality.

3.6.5 Eu anomalies

Although negative Eu anomalies in magmas are typically attributed to plagioclase fractionation [Philpotts and Schnetzler, 1968, Weill and Drake, 1973], plagioclase is not the only mineral with substantial potential effect on Eu/Eu*. Instead, as observed in Table 3.1,

	Kd Eu / Kd Eu*	Kd Eu
Orthoclase	69.19	3.22
Anorthite	11.79	1.32
Orthopyroxene	1.043	0.478
Biotite	0.947	0.316
Amphibole	0.8682	1.36
Clinopyroxene	0.8005	3.22
Olivine	0.5560	0.259
Sphene	0.4997	73.7
Allanite	0.4432	124.6
Apatite	0.3927	9.81
Garnet	0.2183	1.28

Table 3.1: Mineral/melt partition coefficients at 70% SiO₂, interpolated from data of the Geochemical Earth Reference Model Kd Database[GERM, 2013].

minerals such as orthoclase, sphene, apatite, allanite, clinopyroxene, and garnet may also substantially both the Eu budget and Eu/Eu* ratio [GERM, 2013] (Supplementary Table 3). One potential explanation for the apparent lack of a systematic difference in Eu anomaly between dry and hydrous magmas hinges on the relative abundance of orthoclase and plagioclase feldspar. While water suppresses plagioclase stability (other factors held constant), it also increases the relative proportion - and possibly the absolute proportion - of orthoclase feldspar. Given the substantially greater Kd Eu/Eu* and Kd Eu of orthoclase relative to anorthite (Table 3.1), the increased partitioning of Eu into orthoclase may offset the decrease in Eu fractionation by plagioclase, resulting in an equally negative Eu anomaly of the magma even in the case of decreased plagioclase fractionation. Such an explanation is not without caveats: for instance, considering only the feldspars, this mechanism would predict that any water-related Ba offset produced by plagioclase suppression would be similarly negated by orthoclase, which is not observed. However, the lack of any difference in Eu anomaly between arc and rift (including MOR) samples for a given silica range demonstrates that, whatever its cumulative effects on mineral stability, water activity evidently does not substantially alter magma Eu anomalies (Figure 3.2).

3.6.6 Melt extraction from crystal-rich magmas

One potentially significant mechanism for the production of compositional offsets between volcanic and plutonic compositions is the extraction of mobile (and potentially eruptible) melt from a magma, leaving a cumulate plutonic residue [Bachmann et al., 2007, Gelman et al., 2014]. At low silica, plutonic cumulates would be expected to be enriched in minerals such as olivine and pyroxene relative to non-cumulate volcanic magmas, resulting in enrichments of compatible elements such as Mg and Ni. Meanwhile, accumulation of plagioclase and pyroxene, as in (similarly mafic) anorthosites and cumulate gabbros would be expected to result in positive plutonic Eu anomalies. Evidence of such mafic cumulate processes is evident in the geologic record [Hunter and Sparks, 1987, Ashwal, 1993, Jagoutz and Schmidt, 2012] as well as from our analysis of geochemistry in both arc and rift environments (Figures 3.1-3.2).

At higher silica, a similar process of melt extraction would be expected to leave plutonic cumulates enriched in feldspar along with potentially lesser proportions of amphibole, biotite, and quartz. This feldspar accumulation would enrich the felsic plutonic residue in Ba and Sr [Gelman et al., 2014], as is observed in rift settings. However, felsic plutonic cumulates resulting from shallow melt extraction would not readily account for the occurrence of plutonic Ba and Sr enrichments only in rift (and not arc) settings, nor the additional volcanic enrichments of Zr and Hf in rift settings. While plagioclase saturation may be suppressed in arcs relative to rifts due to higher overall water content, plagioclase remains a dominant rock-forming mineral in arcs. Accordingly, suppression of plagioclase in arc settings is evidently not so dramatic as to prevent or even markedly reduce the formation of anorthosite or leucogabbro-like mafic cumulates with positive Eu anomalies in arcs (Figure 3.2), and would not be expected to prevent or reduce the formation of feldspathic-cumulates at higher silica when magma temperatures have fallen farther into the feldspar stability range. As such, melt extraction in should be expected to result in Ba and Sr enrichment of the residue in arc settings as much as in rifts. Consequently, although shallow volcanic melt extraction leaving

a plutonic residue has been argued to occur in some scenarios [Bachmann, 2004] (and our results should not be taken to indicate otherwise), it does not appear to be a volumetrically significant mechanism for the production and differentiation of felsic crust.

3.7 Acknowledgements

C.B.K. was supported by a Computational Science Graduate Fellowship through U.S. Department of Energy Office of Science grant DE-FG02-97ER25308. Computational resources were provided by the National Energy Research Scientific Computing Center under DOE Office of Science Contract No. DE-AC02-05CH11231, and by the Princeton Institute for Computational Science and Engineering. Thanks to Patrick Boehnke for valuable discussion and feedback throughout the project.

3.8 Data Access

The full datasets for volcanic and plutonic whole rock composition, partition coefficients, and MELTS simulation output are provided as supplementary data, and are freely available along with all associated source code under a GNU GPL v2.0 open-source license on GitHub at <https://github.com/PrincetonUniversity/VolcanicPlutonic>

References

- R Alonso-Perez, Othmar Müntener, and Peter Ulmer. Igneous garnet and amphibole fractionation in the roots of island arcs: experimental constraints on andesitic liquids. *Contributions to Mineralogy and Petrology*, 157:541–558, 2009.
- Catherine Annen. From plutons to magma chambers: Thermal constraints on the accumulation of eruptible silicic magma in the upper crust. *Earth and Planetary Science Letters*, 284:409–416, 2009.
- Lewis D Ashwal. *Anorthosites*. Minerals and Rocks. Springer-Verlag, 1993.
- Olivier Bachmann. On the Origin of Crystal-poor Rhyolites: Extracted from Batholithic Crystal Mushes. *Journal of Petrology*, 45(8):1565–1582, July 2004.
- Olivier Bachmann, Calvin F Miller, and S L de Silva. The volcanic–plutonic connection as a stage for understanding crustal magmatism. *Journal of Volcanology and Geothermal Research*, 167:1–23, 2007.
- D K Bailey. The chemical and thermal evolution of rifts. *Tectonophysics*, 94(1-4):585–597, May 1983.
- Gray E Bebout. 4.20 Chemical and Isotopic Cycling in Subduction Zones. In Roberta L Rudnick, editor, *Treatise on Geochemistry*, pages 703–747. Elsevier, 2014.
- Patrick Boehnke, E Bruce Watson, Dustin Trail, T Mark Harrison, and Axel K Schmitt. Zircon saturation re-revisited. *Chemical Geology*, 351:324–334, August 2013.

- R E Botcharnikov, R R Almeev, J Koepke, and F Holtz. Phase relations and liquid lines of descent in hydrous ferrobalt—implications for the Skaergaard intrusion and Columbia River flood basalts. *Journal of Petrology*, 49(9):1687–1727, 2008.
- Norman L Bowen. *The Evolution of the Igneous Rocks*. Oxford University Press, 1928.
- C Wayne Burnham and N F Davis. The role of H₂O in silicate melts; II, Thermodynamic and phase relations in the system NaAlSi₃O₈ - H₂O to 10 kilobars, 700 degrees to 1100 degrees C. *American Journal of Science*, 274(8):902–940, October 1974.
- Ken Caldeira. Long-term control of atmospheric carbon dioxide; low-temperature seafloor alteration or terrestrial silicate-rock weathering? *American Journal of Science*, 295:1077–1114, 1995.
- Ian S E Carmichael. The andesite aqueduct: perspectives on the evolution of intermediate magmatism in west-central (105–99°W) Mexico. *Contributions to Mineralogy and Petrology*, 143(6):641–663, September 2002.
- F Chayes. Relative abundance of intermediate members of the oceanic basalt-trachyte association. *Journal of Geophysical Research*, 68(5):1519–1534, March 1963.
- Nikolas I Christensen and Walter D Mooney. Seismic velocity structure and composition of the continental crust: A global view. *Journal of Geophysical Research*, 100(B6):9761–9788, June 1995.
- D A Clague. The Oceanic Basalt-Trachyte Association: An Explanation of the Daly Gap. *The Journal of Geology*, 86(6):739–743, November 1978.
- Reginald Aldworth Daly. The Geology of Ascension Island. *Proceedings of the American Academy of Arts and Sciences*, 60(1):3–80, June 1925.

- Mark S Drummond and Marc J Defant. A model for trondhjemite-tonalite-dacite genesis and crustal growth via slab melting: Archean to modern comparisons. *Journal of Geophysical Research*, 95(B13):21503–21521, December 1990.
- Josef Dufek and Olivier Bachmann. Quantum magmatism: Magmatic compositional gaps generated by melt-crystal dynamics. *Geology*, 38(8):687–690, July 2010.
- EarthChem. EarthChem Portal, January 2010. URL <http://www.earthchem.org/>.
- John C Eichelberger, Darren G Chertkoff, Scott T Dreher, and Christopher J Nye. Magmas in collision: Rethinking chemical zonation in silicic magmas. *Geology*, 28(7):603–606, 2000.
- P N Froelich, M L Bender, N A Luedtke, and G R Heath. The marine phosphorus cycle. *American Journal of Science*, 282:474–511, 1982.
- W S Fyfe and A R McBirney. Subduction and the structure of andesitic volcanic belts. *American Journal of Science*, 275A:285–297, 1975.
- Sarah E Gelman, Chad D Deering, Olivier Bachmann, Christian Huber, and Francisco J Gutierrez. Identifying the crystal graveyards remaining after large silicic eruptions. *Earth and Planetary Science Letters*, 403:299–306, October 2014.
- GERM. Geochemical Earth Reference Model Partition Coefficient Database, January 2013. URL <http://www.earthref.org/KDD/>.
- Mark S Ghiorso, Marc M Hirschmann, Peter W Reiners, and Victor C Kress, III. The pMELTS: A revision of MELTS for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa. *Geochemistry Geophysics Geosystems*, 3(5):1–36, May 2002.
- Allen F Glazner, John M Bartley, Drew S Coleman, Walt Gray, and Ryan Z Taylor. Are plutons assembled over millions of years by amalgamation from small magma chambers? *GSA Today*, 14(4/5):4–11, 2004.

- D H Green. Experimental melting studies on a model upper mantle composition at high pressure under water-saturated and water-undersaturated conditions. *Earth and Planetary Science Letters*, 19(1):37–53, May 1973.
- Trevor H Green and A E Ringwood. Genesis of the calc-alkaline igneous rock suite. *Contributions to Mineralogy and Petrology*, 18(2):105–162, 1968.
- Timothy L Grove, Julie M Donnelly-Nolan, and T Housh. Magmatic processes that generated the rhyolite of Glass Mountain, Medicine Lake volcano, N. California. *Contributions to Mineralogy and Petrology*, 127:205–223, 1997.
- Timothy L Grove, Christy B Till, and M J Krawczynski. The role of H₂O in subduction zone magmatism. *Annual Review of Earth and Planetary Sciences*, 40:413–439, March 2012.
- Guilherme A R Gualda, Mark S Ghiorso, R V Lemons, and T L Carley. Rhyolite-MELTS: a Modified Calibration of MELTS Optimized for Silica-rich, Fluid-bearing Magmatic Systems. *Journal of Petrology*, 53(5):875–890, April 2012.
- D L Hamilton, C Wayne Burnham, and E F Osborn. The Solubility of Water and Effects of Oxygen Fugacity and Water Content on Crystallization in Mafic Magmas. *Journal of Petrology*, 5(1):21–39, 1964.
- Albrecht W Hofmann. Mantle geochemistry: the message from oceanic volcanism. *Nature*, 385:219–229, January 1997.
- TJB Holland and R Powell. An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids. *Journal of Metamorphic Geology*, 29:333–383, 2011.
- R H Hunter and R S J Sparks. The differentiation of the Skaergaard Intrusion. *Contributions to Mineralogy and Petrology*, 95(4):451–461, April 1987.

- Oliver Jagoutz and Max W Schmidt. The formation and bulk composition of modern juvenile continental crust: The Kohistan arc. *Chemical Geology*, 298-299:79–96, 2012.
- Robert Woodbury Kay and Suzanne Mahlburg Kay. Creation and destruction of lower continental crust. *Geologische Rundschau*, 80(2):259–278, 1991.
- Peter B Kelemen, K Hanghøj, and A R Greene. 4.21 One View of the Geochemistry of Subduction-Related Magmatic Arcs, with an Emphasis on Primitive Andesite and Lower Crust. In Roberta L Rudnick, editor, *Treatise on Geochemistry*, pages 749–806. Elsevier, 2014.
- C Brenhin Keller and Blair Schoene. Statistical geochemistry reveals disruption in secular lithospheric evolution about 2.5Gyr ago. *Nature*, 485(7399):490–493, May 2012.
- Adam J R Kent, Cristina Darr, Alison M Koleszar, Morgan J Salisbury, and Kari M Cooper. Preferential eruption of andesitic magmas through recharge filtering. *Nature Geoscience*, 3(9):631–636, August 2010.
- Charles H Langmuir, Robert D Vocke, Jr., Gilbert N Hanson, and Stanley R Hart. A general mixing equation with applications to Icelandic basalts. *Earth and Planetary Science Letters*, 37(3):380–392, January 1978.
- Cin-Ty Aeolus Lee and Olivier Bachmann. How important is the role of crystal fractionation in making intermediate magmas? Insights from Zr and P systematics. *Earth and Planetary Science Letters*, 393:266–274, May 2014.
- Calvin F Miller, Susanne Meschter McDowell, and Russell W Mapes. Hot and cold granites? Implications of zircon saturation temperatures and preservation of inheritance. *Geology*, 31(6):529–532, 2003.
- P Morgan. Heat flow in rift zones. In G Pálmason, editor, *Continental and Oceanic Rifts, Geodynamics Series*, pages 107–122. American Geophysical Union, 1982.

- Othmar Müntener, Peter B Kelemen, and Timothy L Grove. The role of H₂O during crystallization of primitive arc magmas under uppermost mantle conditions and genesis of igneous pyroxenites: an experimental study. *Contributions to Mineralogy and Petrology*, 141(6):643–658, September 2001.
- Julian A Pearce, Nigel B W Harris, and Andrew G Tindle. Trace Element Discrimination Diagrams for the Tectonic Interpretation of Granitic Rocks. *Journal of Petrology*, 25(4):956–983, November 1984.
- Nick Petford, Ross C Kerr, and John R Lister. Dike transport of granitoid magmas. *Geology*, 21(9):845–848, 1993.
- John A Philpotts and C C Schnetzler. Europium anomalies and the genesis of basalt. *Chemical Geology*, 3:5–13, 1968.
- Terry Plank, Katherine A Kelley, Mindy M Zimmer, Erik H Hauri, and Paul J Wallace. Why do mafic arc magmas contain 4 wt. percent water on average? *Earth and Planetary Science Letters*, 364:168–179, February 2013.
- Olivier Reubi and Jonathan D Blundy. A dearth of intermediate melts at subduction zone volcanoes and the petrogenesis of arc andesites. *Nature*, 461(7268):1269–1273, October 2009.
- P Rosenblatt, P C Pinet, and E Thouvenot. Comparative hypsometric analysis of Earth and Venus. *Geophysical Research Letters*, 21(6):465–468, March 1994.
- Roberta L Rudnick and David M Fountain. Nature and composition of the continental crust: A lower crustal perspective. *Reviews of Geophysics*, 33(3):267–309, August 1995.
- C C Schnetzler and John A Philpotts. Partition coefficients of rare-earth elements between igneous matrix material and rock-forming mineral phenocrysts—II. *Geochimica et Cosmochimica Acta*, 34(3):331–340, March 1970.

- T W Sisson and Timothy L Grove. Experimental investigations of the role of H₂O in calc-alkaline differentiation and subduction zone magmatism. *Contributions to Mineralogy and Petrology*, 113:143–166, 1993.
- Paula M Smith and Paul D Asimow. Adiabatic 1ph: A new public front-end to the MELTS, pMELTS, and pHMELTS models. *Geochemistry Geophysics Geosystems*, 6(1):1–8, 2005.
- S Sun and William F McDonough. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In A D Saunders and M J Norry, editors, *Magmatism in the Ocean Basins, Geological Society Special Publication*, pages 313–345. Geological Society, 1989.
- Y Tatsumi, D L Hamilton, and R W Nesbitt. Chemical characteristics of fluid phase released from a subducted lithosphere and origin of arc magmas: evidence from high-pressure experiments and natural rocks. *Journal of Volcanology and Geothermal Research*, 29:293–309, 1986.
- Stuart Ross Taylor. Growth of planetary crusts. *Tectonophysics*, 161:147–156, 1989.
- Alan Bruce Thomson. Fertility of crustal rocks during anatexis. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, 87:1–10, 1996.
- USGS. US Geological Survey Global Crustal Database Geologic Province and Thermo-Tectonic Age Maps, January 1997. URL <http://earthquake.usgs.gov/research/structure/crust/maps.php>.
- James C G Walker, P B Hays, and J F Kasting. A negative feedback mechanism for the long-term stabilization of Earth’s surface temperature. *Journal of Geophysical Research*, 86(C10):9776–9782, 1981.
- D F Weill and M J Drake. Europium Anomaly in Plagioclase Feldspar: Experimental Results and Semiquantitative Model. *Science*, 180(4090):1059–1060, June 1973.

- A J R White, J D Clemens, J R Holloway, L T Silver, Bruce W Chappell, and V J Wall. S-type granites and their probable absence in southwestern North America. *Geology*, 14(2):115, 1986.
- H S Yoder, Jr. Diopside-Anorthite-Water at Five and Ten Kilobars and Its Bearing on Explosive Volcanism. *Year Book of the Carnegie Institution of Washington*, 64:82–89, 1965.
- Michael J Zieg and Bruce D Marsh. The Sudbury Igneous Complex: Viscous emulsion differentiation of a superheated impact melt sheet. *Geological Society of America Bulletin*, 117(11):1427–1450, 2005.
- Mindy M Zimmer, Terry Plank, Erik H Hauri, Gene M Yogodzinski, Peter Stelling, Jessica Larsen, Brad S Singer, Brian Jicha, Charles Mandeville, and Christopher J Nye. The Role of Water in Generating the Calc-alkaline Trend: New Volatile Data for Aleutian Magmas and a New Tholeiitic Index. *Journal of Petrology*, 51(12):2411–2444, 2010.

Chapter 4

Continental Basalts and Plate Tectonics

4.1 Abstract

Basaltic magmas constitute the primary mass flux from Earth's mantle to its crust, carrying information about the conditions of mantle melting through which they were generated. As such, changes in the average geochemistry of basalts through time reflect changes in underlying parameters such as mantle potential temperature and the geodynamic setting of mantle melting. However, sampling bias, preservation bias, and geological heterogeneity complicate the calculation of statistically representative average compositions. Here we use weighted bootstrap resampling Monte Carlo analysis to minimize sampling bias over the heterogeneous rock record and obtain maximally representative average basaltic compositions through time. Over the approximately 4 Ga preserved in the continental rock record, the average composition of preserved continental basalts has evolved along a generally smooth curve, with decreasing compatible element concentrations and increasing incompatible element concentrations, punctuated by a rapid step in some variables such as La/Yb ratios and Zr, Hf, and Ti abundances approximately 2.5 Ga ago. Despite the abrupt nature of many geochemical

changes at the end of the Archean, geochemical modelling of mantle melting systematics and trace element partitioning suggests that these observations can be explained most parsimoniously by discontinuous changes in the mineralogy of mantle partial melting driven by a gradual decrease in mantle potential temperature without appealing to any change in tectonic process. This interpretation is supported by the geochemical record of slab fluid input to continental basalts, which indicates no long-term change in the global proportion of arc versus non-arc basaltic magmatism at any time in the preserved rock record.

4.2 Introduction

Systematic changes in crustal composition and juvenile magma chemistry between the Archean and the present have long been advanced on the basis of geochemical, structural, and field observations. Observed differences between Archean and post-Archean crust – including the preponderance of granite-greenstone terranes, high-Na Trondhjemite-Tonalite-Granodiorite plutons, and ultramafic komatiite lavas in the Archean – have led to much discussion about the style and rate of Archean tectonics [Green, 1975, Hargraves, 1976, Wilson et al., 1978, Sleep, 1992, de Wit, 1998, Hamilton, 1998, Bédard, 2006, Pease et al., 2008, Condie and Kröner, 2008, Stern, 2008]. One interpretational paradigm invokes the abundance of TTGs, komatiites, and apparent lack of preserved blueschists and ophiolites in the Archean along with vertical tectonic interpretations of dome-and-keel granite-greenstone terranes as evidence for a fundamentally different tectonic regime in the Archean [Hamilton, 1998, Bédard, 2006, Stern, 2008]. In contrast, a more uniformitarian paradigm holds that qualitative differences between Archean and Proterozoic lithologies can be satisfactorily explained by secular changes in variables such as mantle temperature or water content in an essentially modern plate tectonic setting, backed by evidence for modern subduction-like geotherms in the Archean and horizontal tectonic interpretations of Archean terranes,

especially the Kaapvaal Craton and the Superior Province [Sleep, 1992, de Wit, 1998, Pease et al., 2008, Condie and Kröner, 2008].

Given conflicting structural models for Archean tectonics, some studies have turned to major and trace element geochemistry of Archean rocks as a way to infer tectonic setting based on modern associations [e.g. Atherton and Petford, 1993, Condie, 2005, Martin et al., 2005, Moyen and Stevens, 2006]. Such approaches have been stymied by two fundamental problems: 1) geochemical signatures are potentially nonunique and may not have the same genetic implications 4 Ga ago that they have today, and 2) systematic temporal variations in geochemistry can be dwarfed by the variance of the rock record at any one time. The resulting uncertainties have in turn limited our ability to apply modern chemotectonic signatures [e.g. Pearce and Cann, 1973, Pearce et al., 1984] to the Archean.

In order to obtain meaningful temporal trends from the heterogeneous rock record, one traditionally productive approach has been to prioritize quality over quantity, for instance obtaining a well-constrained primitive magma composition by tracing a liquid line of descent from samples that have only fractionated olivine [Herzberg et al., 2010], or by focusing on the composition of carefully screened and geologically well-understood suites of samples [Condie and O'Neill, 2010].

For instance, using 33 primary melt solutions culled from a dataset of 1500 “non-arc” basalt analyses, Herzberg et al. [2010] found primary magma temperatures consistent with a smooth trend in mantle potential temperature from ~ 1530 C in the Eoarchean to ~ 1350 C today, with a potential period of increasing mantle temperature in the early Archean in accordance with the models based on scaling laws of Korenaga [2008].

If, however, one can obtain a sufficiently large, representative sample dataset, then an alternative inclusive approach becomes possible. Given a perfectly representative sample set of the continental crust, the arithmetic mean of a compositional variable from this set has unique physical significance corresponding to the bulk composition of the crust — that is, the composition that would result from physically homogenizing the entire crust. Consequently,

Figure 4.1: Secular evolution of compatible (a) and incompatible (b) element abundances in basalt over the past 4 Ga, following the methods of Keller and Schoene [2012] (Chapter 2)

changes in the average composition of new igneous crust over time contain valuable information about the processes of crust formation: at long time scales, changes in the mean reflect secular variation in fundamental terrestrial parameters such as mantle potential temperature, crustal thickness, and tectonic mechanism of crust formation. A continuous temporal record of average crustal geochemistry would thus allow for the critical examination of temporal variations in such Earth system parameters and, consequently, the extrapolation of modern geologic processes back through Earth history in a conditional application of uniformitarianism. However, the quantification of systematic changes in mean crustal composition has been impeded by the difficulty of obtaining a representative sample population in the face of the vast heterogeneity of magmatic processes preserved in the igneous rock record, and persistent questions about sampling and preservation bias.

Recently, increasing availability of large geochemical datasets, such as EarthChem, Georoc, and Navdat, has provided a new opportunity to better quantify crustal composition by employing a greatly enlarged sample set. Our previous work [Keller and Schoene, 2012] (Chapter 2) took advantage of these freely-available datasets to construct and analyze a $\sim 70,000$ -sample whole-rock geochemical record of secular crustal evolution over the past

4 Ga, using weighted bootstrap resampling Monte Carlo analysis to obtain maximally representative temporal trends. First-order results revealed smooth decreases in compatible element abundance and increases in incompatible element abundance in basaltic samples (Figure 4.1), along with some indication of more discontinuous processes at the end of the Archean. While many indications of rapid geochemical variation across the Archean-Proterozoic boundary were specific to the felsic record, changes in the estimated degree of average mantle melting and in basaltic La/Yb ratio circa 2.5 Ga suggested a potentially discontinuous event in the mafic record as well [Keller and Schoene, 2012] (Chapter 2).

Given the petrological complexities involved, our previous work did not present any definitive conclusion on the origin and significance of this potential discontinuity in the mafic record. However, many additional geochemical constraints are available due to the breadth of the underlying dataset. Consequently, in order to better understand the implications of the new record of crustal evolution provided by statistical geochemistry, we focus here in more depth on the $\sim 30,000$ -sample mafic subset of our previous database with between 43% and 51% SiO_2 , here termed basaltic (*sensu lato*). As the product of 4 Ga of partial mantle melting, this mafic record preserves the most direct account of mantle conditions through time, and provides the necessary foundation for any interpretation of subsequent processes of crustal differentiation. Our analysis of this record combines weighted bootstrap resampling Monte Carlo analysis with major- and trace-element geochemical modeling. This statistical analysis allows us to study global-scale variations in the process and setting of basaltic magma production over geologic time, in turn providing insight into the style and existence of plate tectonics throughout Earth history.

Figure 4.2: Illustration of the weighted bootstrap resampling Monte Carlo method

4.3 Weighted Bootstrap Resampling Monte Carlo Analysis

In order to minimize sampling bias and accurately represent uncertainties in the dataset to obtain an optimal estimate of the compositional distribution of Earth’s exposed crust, we followed the weighted bootstrap resampling Monte Carlo analysis method of [Keller and Schoene \[2012\]](#) (Chapter 2), demonstrated in Figure 4.2. As in our previous work, this technique was applied to a 70,000-sample record of crustal whole-rock major and trace element geochemistry, including $\sim 67,000$ samples from the EarthChem repository, $\sim 2,500$ samples from [Condie and O’Neill \[2010\]](#), and ~ 1500 from [Moyen \[2010\]](#) including age estimates and geospatial sample locations for each sample. Although outliers were not rejected categorically, the dataset was manually screened to identify suspicious data patterns and exclude any physically implausible data (e.g. concentrations <0 or $>100\%$). We consider only samples collected from the present-day continental crust, focusing (except where otherwise noted) on samples with between 43-51 wt. % SiO_2 . This silica range is chosen to include a majority of mantle-derived basalts, but exclude many ultramafic cumulates; however the exact mafic silica range chosen has relatively little influence on the results (Supplementary Figure S1). To minimize any filtering-induced interpretational complications, no geochemical filtering was conducted beyond the limited outlier screening and silica binning described here.

To obtain an optimally even spatiotemporal sample weighting, each sample was assigned a weight inversely proportional to its (l^2 -norm) proximity to other samples in space and time. Subsequently, the data were resampled (with replacement) in accordance with this weight such that data points from sparsely represented regions of the crust are resampled more frequently, while those from densely sampled regions are resampled less frequently. Meanwhile, analytical uncertainty is accurately represented at each resampling step by the addition of Gaussian noise with appropriate variance for each variable in the dataset. The result is a continuous temporal record of the composition of preserved, exposed crust, represented as mean and two-standard-error uncertainty of the mean for 100 Ma time intervals over the last 4 Ga.

While such weighted resampling reduces sampling bias, it cannot eliminate it completely (e.g., rocks that were never collected by a geologist cannot be included in the dataset). Similarly, rocks that have been lost from the crustal record or are otherwise not presently exposed on Earth's surface are also necessarily absent from our record. The resulting preservation and exposure bias cannot be corrected without quantitative knowledge of the relationship between preservation / exposure potential and composition. The displayed two-standard-error uncertainties throughout this paper show only how well we know the average composition for basaltic rocks of a given age assuming a random, unbiased sampling of the crust, and thus must be treated as minimum uncertainties. Consequently, sampling, preservation, and exposure bias should be kept in mind throughout the following discussion.

These limitations notwithstanding, the quantification of average compositions for preserved, surficially exposed continental crust through time provides an invaluable window into the deeper workings of the Earth system due to the ability of averages to isolate meaningful signals of secular variation from the heterogeneous rock record. Reducing a geochemical variable to a single global average scalar necessarily discards information. However, this reduction in complexity mitigates the effect of many confounding processes (e.g. local variability in structural/tectonic setting, mantle heterogeneity, partitioning within the sample

set, etc.) such that the resulting average value is a more representative estimator of underlying secular variation. This follows directly from the significance of the arithmetic mean as an analogue for physical homogenization, and can be considered to reflect the inverse relationship between sample size and signal/noise ratio.

This above effect is crucial for our purposes, since temporal variations in crustal composition are typically dwarfed by the instantaneous geochemical variability of the igneous rock record at any given time. Even though our resampled averages are not perfectly representative, they are the most representative data available at present, and are observed to display properties consistent with first-principles expectations, e.g, for secular temporal variation in mantle potential temperature. Consequently, we present the best quantitative record of basaltic crustal evolution available to date, and explore the results with geochemical modelling, including alphaMELTS major element and mantle mineralogy calculations [Ghiorso et al., 2002, Smith and Asimow, 2005] combined with GERM trace element partitioning [GERM, 2013], in an effort to develop and test a parsimonious and internally consistent narrative of the processes and conditions of continental basalt generation over the past 4 Ga.

4.4 Gradual secular variation in continental basaltic composition over Earth history

The results of this statistical analysis (Figures 4.1 - 4.8) reveal a diverse array of statistically significant trends in average basaltic composition, ranging from smooth and continuous to abrupt and discontinuous at the 4-Ga scale. Considering first the continuous trends, we observe what may be summarized as a consistent increase in incompatible element abundance accompanied by a decrease in compatible element abundance for average basalts and gabbros of a constant silica range (43-51% SiO₂) over the last 4 Ga. In addition to the observations of Keller and Schoene (Figure 4.1), such trends persist for a wide range of

Figure 4.3: Extended systematic comparison of basaltic compatible and incompatible element abundance trends, sorted by relative compatibility

compatible and incompatible elements (Figure 4.3), hinting at an igneous origin for these first-order variations.

When interpreting the following results, it is worth bearing in mind that neither mid-ocean ridge basalts nor mantle plume basalts are common in the continental record. Since we include only samples geographically originating from present-day continental crust, non-continental basalts such as mid-ocean ridge basalts and ocean island basalts are excluded from our record except where they have been incorporated into the continental crust by natural geologic processes such as obduction. This exclusion is fully intentional, given that we are attempting to understand in particular the formation of the continental crust. Consequently, no subsequent geochemical interpretations should be considered representative of non-continental basalts such as MORB or OIB, nor the source mantle thereof.

4.4.1 Sampling, preservation, and alteration

In principle, systematic changes in average basaltic composition may represent igneous variations in average crustal basaltic composition, secondary variations in the composition of preserved basalts due to increasing alteration or metamorphism of older samples, or illusory variations driven only by sampling or preservation bias. Evidence that variations in basaltic compatible and incompatible element abundances since 4 Ga represent magmatic signatures, and are not overly influenced by alteration or weathering, is provided by the matching variations in element pairs with matching silicate mineral/melt partition coefficients but with very different chemical properties. Figure 4.4 illustrates a number of such element pair ratios: U and La, both highly incompatible but with dramatically different redox chemistry; K and Sm, both incompatible but very distinct in abundance, charge, and ionic radius; and Sc and Co, both compatible but with distinct size, charge, and redox chemistry. Differences in ionic radius, charge, and redox chemistry will greatly influence elemental mobility and solubility during alteration and metasomatism, yet all ratios remain nearly invariant over the last 4 Ga.

Figure 4.4: Ratios of major and trace elements with equivalent silicate mineral/melt partition coefficients but dramatically different chemical properties during weathering and alteration, showing broad invariance over time. **(a)** Uranium / Lanthanum, both highly incompatible. **(b)** Potassium / Samarium, both incompatible. **(c)** Scandium / Cobalt, both compatible. Here and throughout, ratios are calculated using the method of [Keller and Schoene \[2012\]](#) (Chapter 2), starting with fractions $a/(a+b)$ (to avoid numerical instability) for each whole-rock analysis with both elements defined, then resampled and averaged before converting back ratio space a/b .

Further, while sampling and preservation bias are difficult to rule out even with our weighted bootstrap resampling methods, there is no known *a priori* reason that either sampling or preservation bias should favor more mafic compositions in the past and more felsic compositions towards the present. While difficult to quantify given its dependence on the collective sampling behavior of the geological community, the expected distribution of sampling bias in silica space is relatively flat, and is likely to disproportionately favor less common rock types – acting counter to any underlying changes in lithology. Meanwhile, preservation bias should favor (if anything) more felsic samples over time, given the increased chemical weathering rate and greater density of mafic rocks, which make mafic crust more vulnerable both to erosional loss at the surface and convective loss at the base of the crust.

4.4.2 Variation in the extent of mantle melting

Given an igneous interpretation, the most straightforward hypothesis to explain the systematic temporal trends in basaltic compatible and incompatible element abundance observed by Keller and Schoene [2012] (Chapter 2) is that secular mantle cooling has decreased the average extent of mantle partial melting through time, resulting in increasing incompatible element concentrations and decreasing compatible element concentrations as seen in Figure 4.1. However, a range of confounding factors could bias these trends, including changes in mantle depletion, basaltic magma differentiation, and magma water content.

Since Earth’s mantle forms the depleted complement to the silicic continental crust, the mantle has become depleted in incompatible elements as a result of crust formation [Rudnick and Fountain, 1995, Hofmann, 1997]. While terrestrial crustal growth rates remain actively debated, nearly all models agree that the crust has either grown or remained constant in volume since the end of the Hadean [Hawkesworth et al., 2010, Belousova et al., 2010], consistent with isotopic evidence for relatively constant mantle composition [White and Hofmann, 1982, Vervoort and Blichert-Toft, 1999]. Constant or increasing crustal volume would result in either constant or increasingly depleted mantle composition. Any increase in

Figure 4.5: Deconvolving the effects of mantle melting and fractional crystallization. Observed trends throughout this figure were produced by binning the full dataset of Keller and Schoene [2012] (Chapter 2) – by SiO_2 in **a-b** and by MgO in **c-f**. The binning schemes are chosen only to display a region of interest, and as such the absolute values of highest and lowest displayed bins should not be assigned any particular significance. Further methodology is described in the text. **(a)** MgO decreases as a function of silica content during fractional crystallization, converging at high SiO_2 . Reductions in mantle melting over the the last 4 Ga decrease MgO at nearly constant silica, producing offsets between different age differentiation trends at high angle to the differentiation trend. **(b)** FeO^*/MgO ratio increases with silica during fractional crystallization, but decreases at nearly constant silica during partial melting, producing systematic offsets between fractionation trends of different ages that cannot be explained by changes in basalt differentiation. **(c)** Relative effects of partial melting and fractional crystallization on FeO^* as a function of MgO . **(d)** Changes in mantle partial melting and basalt fractional crystallization have distinct slopes in $\text{CaO}/\text{Al}_2\text{O}_3 - \text{MgO}$ space, producing resolvable offsets in differentiation trends over time. **(e)** The systematic offset between Archean and modern $\text{MgO}-\text{TiO}_2$ differentiation trends is not well explained by changes in either extent of mantle melting or fractional crystallization, but instead suggests increasing average mantle melting pressure through time. **(f)** Similar offsets between Archean and later $\text{MgO}-\text{Na}_2\text{O}$ differentiation trends again suggest increasing mantle melting pressure over the past 4 Ga. Notably, Archean basalts have lower Na_2O for a given MgO , despite the well-known high Na signatures of Archean granitoids.

mantle depletion would not, however, explain the observed trends: an increasingly depleted mantle would result in decreasing incompatible element concentrations in basalts over time, opposite the trends observed from our dataset.

A more subtle point concerns the possibility for changes in the extent or process of basaltic magma differentiation. For many elements, *increasing* magma differentiation by fractional crystallization and *decreasing* degree of primary mantle melting produce similar changes in elemental abundance. As a result, differentiating the contributions of these two processes may be problematic. In order to resolve such processes, we may turn to a variety of differentiation diagrams featuring elements or ratios that behave differently to some extent during mantle partial melting as opposed to basalt fractional crystallization (Figure 4.5).

It is important to note that the differentiation trends shown in Figure 4.5 are not liquid lines of descent, but rather the average of very many different lines of descent from different magmas under different conditions. As such, the interpretation is somewhat different from

a traditional liquid line of descent, but changes in the average extent of mantle melting or average trend of differentiation will still be clearly visible. Due to the heterogeneity of mantle-derived basalt compositions, a single “primitive” starting point is not shown, but in general mantle-derived basalts will originate on the left and differentiate to the right in Figure 4.5a-b, and originate on the right and differentiate to the left in 4.5c-f, as illustrated by the schematic “fractional crystallization” arrows. The directions of the accompanying mantle “melting extent” and mantle “melting pressure” were established by pMELTS-mode alphaMELTS simulations of isobaric batch mantle melting from solidus to liquidus at a range of pressures between 1 and 3 GPa using the primitive mantle composition of [McDonough and Sun \[1995\]](#) with varying bulk mantle water contents between 0.1% and 1% H₂O (e.g., Figure S2). Variation in water content over this range resulted in substantial differences in primitive magma composition for some elements, but neither varying water content nor varying oxygen fugacity substantially changes the overall vector of mantle melting extent and melting pressure at the scale of the schematic effect vectors.

As seen in Figure 4.5, differentiation trends from successive 1-Ga periods of Earth history are offset perpendicular to the observed direction of differentiation, indicating changes in mantle partial melt composition at an angle (in elemental cross-plot space) to the prevailing differentiation trend [c.f. [Klein and Langmuir, 1987](#)]. In particular, changing degree of mantle melt appears to have little effect on primary magma silica content relative to other major elements such as MgO (e.g., Figure S2), such that binning basaltic magmas by silica serves as a relatively robust way to extract the effects of mantle partial melting for magmas which have undergone a similar degree of differentiation (Figure 4.5).

Ruling out changes in mantle depletion or basaltic differentiation, a final caveat stems from the ability of water to decrease mantle solidus temperature [e.g. [Mysen and Boettcher, 1975](#), [Grove et al., 2006](#)]. Decreasing mantle water content could in principle lead to decreasing mantle melting extent for a constant potential temperature, with solidus temperature increasing in response to ongoing mantle degassing. However, changing mantle water con-

tent also has major predictions for subsequent magma differentiation. Notably, increased magmatic water activity promotes magnetite saturation relative to the major rock-forming silicate minerals, changing magma Fe/Mg ratios during differentiation [Sisson and Grove, 1993, Botcharnikov et al., 2008]. As demonstrated in Figure 4.5b-c, neither the $\text{FeO}^*/\text{MgO}^*$ slope during differentiation nor the relative occurrence of magnetite saturation in FeO^* – MgO space is significantly altered over the past 4 Ga. Consequently, declining extent of mantle melting in response to secular mantle cooling remains the simplest explanation for the observed first-order variations in average basaltic geochemistry through time.

If it is possible to calculate the approximate extent of mantle melting for each basaltic sample in the database, we can use this information to produce a temporal record of global average mantle melting extent, which in turn provides insight into the global heat budget and associated geodynamic processes. Along these lines, one simple methodology is to compare (in a least-squares sense) the major element composition of each whole-rock sample to pMELTS simulations of primitive mantle melting and find the best-fit extent of mantle melting for each basaltic sample. Graphically, this procedure is equivalent to finding the closest point on the calculated MELTS mantle melting line in n -dimensional major element space for each whole rock composition, where each of the n major elements is standardized to unit variance. A representative average record through time is then produced by the usual weighted bootstrap resampling technique [Keller and Schoene, 2012] (Chapter 2). As an added benefit, this approach naturally produces a corresponding estimate of mantle melting temperature for each sample, allowing for the calculation of apparent mantle potential temperature through time. This inclusive approach makes no attempt to either exclude basaltic samples that have undergone small degrees of fractional crystallization or crystal accumulation, or to numerically correct back to a primitive magma composition. Since most basaltic magmas have undergone some degree of fractional crystallization, this approach likely results in an underestimation of mantle melting extent. However, in the absence of changes

Figure 4.6: Estimated average extent of mantle melting ((a)) and mantle potential temperature ((b)) through time, determined by least-squares comparison of observed major element concentrations for each basaltic sample in the database (43-54% SiO_2) to those of calculated basalt compositions corresponding to 0 to 100% partial melting of primitive mantle. Mantle melting was simulated by pMELTS-mode alphaMELTS isobaric equilibrium batch melting calculations using the primitive mantle composition of [McDonough and Sun \[1995\]](#) with 0.15 wt.% initial H_2O at 2.2, 2.7 and 3.2 GPa.

in degree of fractional crystallization through time, this underestimation results in only a systematic offset with little influence on relative temporal trends.

The results (Figure 4.6) are recalculated using the method of [Keller and Schoene \[2012\]](#) (Chapter 2) for isobaric batch melting at pressures between 2.2 and 3.2 GPa using the primitive mantle composition of [McDonough and Sun \[1995\]](#) with 0.15 wt.% initial H_2O . Percent melt estimates display a clear decrease from nearly 40% mantle melting in the Archean to ~10% today, in agreement with independent estimates of modern and Archean mantle melting [[Kelley et al., 2010](#), [Portnyagin et al., 2007](#), [Walter, 1998](#), [Bernstein et al., 2007](#)] despite the lack of a fractionation correction, suggesting that the degree of underestimation is minor. Over the same time period, the corresponding mantle potential temperature record cooled from approximately 1500 °C in the Archean to 1330 °C at present, following a trend intermediate between the models of [Korenaga \[2008\]](#) and [Davies \[2009\]](#), which are based on scaling laws for the mantle heat budget through time. Although average basaltic water content appears not to have changed substantially over the past 4 Ga (no change in FeO/MgO

differentiation slope in Figure 4.5b-c, discussed further in section 4.1), the same cannot be said for mantle melting pressure; systematic offsets in MgO–TiO₂ and MgO–Na₂O differentiation trends (Figure 4.5e-f) suggest increasing average mantle melting pressure through time. If present, a systematic increase in mantle melting pressure would allow a smaller range of mantle cooling to explain the observed decrease in mantle melting extent. Nonetheless, the total magnitude of average mantle cooling (~ 170 °C) is generally consistent with that suggested by both Grove and Parman [2004] and Herzberg et al. [2010], despite major differences in methodology.

The general agreement of these results with previous estimates is arguably surprising, given that we include a wide range of basaltic compositions not restricted to primitive basalt. Moreover, rejecting samples with high least-squares residuals results in surprising congruent (though potentially less representative) inversion results (Figure S3). While the results appear to fall within an *a-priori* reasonable range, their accuracy is in part dependent on the degree of correlation among the error terms introduced for each separate major element record by each potential confounding igneous process (fractional crystallization, phenocryst accumulation, assimilation, slab fluid input, etc.). In the simplest case of fully uncorrelated errors for N elements, error in the end result (e.g., mantle melting extent) would decrease by a factor of $\sqrt{N}$. Fully correlated errors, which would arise if the effects of confounding processes such as fractional crystallization were fully parallel to the mantle melting path in N -dimensional major element space, would allow for no reduction in the confounding bias. In reality, each of the above confounding processes acts neither parallel nor perpendicular to the mantle melting path, resulting in real errors that will be both correlated and anticorrelated to largely unknown degrees. Consequently, the true accuracy of the resulting mantle melting curves is not well determined. The results in Figure 4.6 thus should not be taken as absolute, and potential igneous biases should be kept in mind throughout, including those schematically illustrated in the same figure.

4.5 Rapid geochemical variation at the end of the Archean

While the estimated decreases in melting temperature generally follow a smooth curve over the past 4 Ga, a marked discontinuity (at the two-standard-error level) is observed in average apparent mantle percent melt across the Archean/Proterozoic boundary at 2.5 Ga (Figure 4.6a). The large thermal inertia of the mantle to resist sudden changes in temperature, as well as the absence of any discontinuity in the corresponding temperature record, suggest that if representative of a real phenomenon, this discontinuity is not likely to be produced by a change in mantle temperature, but rather a threshold change in process, mineralogy, or rate.

In addition to the apparently discontinuous mantle melting extent in Figure 4.6a, a number of basaltic trace elements display changes in ratio or abundance at or near the Archean-Proterozoic boundary much more abrupt than the smooth compatible and incompatible element trends of Figure 4.1. This effect was first observed for La/Yb ratio, where trace element calculations indicate that the rapid increase in average basaltic La/Yb at the end of the Archean cannot be explained by changes in percent mantle melting alone without either a change in partition coefficients or source composition [Keller and Schoene, 2012] (Chapter 2). As seen in Figure 4.7a-c, rapid, almost step-like increases in rare earth fractionation (for both light/middle and middle/heavy rare earth elements) are demonstrated by average basaltic La/Yb, La/Sm, and Sm/Yb ratios. Similarly abrupt trends are observed in the abundance of a number of incompatible high-field-strength elements such as Zr (Figure 4.7d) and Ti.

4.5.1 Geochemical signatures of subduction

One potential model for the observed 2.5 Ga discontinuity involves the initiation of modern-style subduction at the end of the Archean, which could increase average basaltic La/Yb,

Figure 4.7: Basaltic trace elements and ratios showing rapid changes near the end of the Archean. **(a-c)**: increasing rare earth fractionation, including light/heavy (La/Yb; **(a)**), light/middle (La/Sm; **(b)**), and middle/heavy (Sm/Yb; **(c)**) rare earth element enrichment. **(d)**: Basaltic Zr abundance.

Figure 4.8: Constancy of arc vs. non-arc geochemical signatures in basalts over time. **(a)**: Basaltic Nb/Th ratio. **(b)**: Basaltic Rb/Nb ratio. **(c)**: Tholeiitic Index [Zimmer et al., 2010]– FeO* for samples 4 wt. % MgO divided by FeO* for samples 8 wt. % MgO. **(d)**: Proportion of basaltic samples with “arc-like” Nb/Th. Ratios are calculated as in Figure 4.4, while Tholeiitic index is calculated using bins of 4 ± 0.5 and 8 ± 0.5 wt. % MgO

La/Sm, and Sm/Yb by addition of high La/Yb slab fluids and subducted sediment. It has been suggested that such a scenario could also produce a decrease in apparent degree of mantle melting due to the introduction of cold subducted slabs into the mantle [Condie and O'Neill, 2010]. If this is the case, the same basaltic samples should also record a dramatic change in subduction signatures which record the effect of slab fluids due to the relative insolubility of high field strength elements such as Nb and Ta compared to large ion lithophiles like K and Rb.

In particular, Condie and O'Neill [2010] have suggested the use of the Nb/Th ratio, which unlike many other high field strength/large ion lithophile ratios is relatively insensitive to changing percent melt due to the similar incompatibility of Nb and Th in the mantle. In particular, Nb/Th ratios below 5 are generally associated with a subduction setting, where slab fluids are abundant, while Nb/Th ratios above 7 are associated with melts produced in the absence of slab fluids. However, as seen in Figure 4.8, both the average Nb/Th and the percentage of high- and low-Nb/Th basalts are essentially constant throughout recorded Earth history. Alternative subduction signatures such as K/Hf and Rb/Nb — also with matching peridotite/melt partition coefficients but with even higher solubility contrast [Tatsumi et al., 1986] — similarly show no major discontinuity across the Archean-Proterozoic boundary and no clear trend over geologic time (Figure 4.8b-c).

Further insight into the prevalence of subduction over geologic time is provided by the record of calc-alkaline vs. tholeiitic magma series. It is generally considered that more hydrous, more oxidized magmas saturate Fe-Mg oxides such as magnetite and ilmenite sooner relative to the major rock-forming silicate minerals, driving the remaining magma composition away from the Fe axis and resulting in a calc-alkaline differentiation trend [Sisson and Grove, 1993, Botcharnikov et al., 2008]. Consequently, calc-alkaline differentiation is observed to correlate strongly with magmatic water content [Zimmer et al., 2010]. While tholeiitic magmas may occur in multiple tectonic settings, the calc-alkaline series is restricted almost exclusively to subduction zones, where it is a dominant differentiation trend. Conse-

quently, the initiation of subduction in the rock record should coincide with an increase in the abundance of the calc-alkaline series.

Quantitatively, [Zimmer et al. \[2010\]](#) have proposed the “tholeiitic index” as a numerical measure for the degree of tholeiitic vs. calc-alkaline differentiation in a given magma series, defined as total Fe at 4% MgO over total Fe at 8% MgO for magmas of the same series (e.g. as in Figure 4.5c). Extending this metric to consider the average tholeiitic index of the continental crust — comparing the FeO content of magmas with 4 wt.% MgO to those with 8 wt. % MgO for each 100 Ma time bin — should allow us to discern any systematic changes in the abundance of calc-alkaline versus tholeiitic differentiation. Remarkably, as seen in Figure 4.8d, the average tholeiitic index of juvenile basalts have remained relatively constant over the last ~ 3.8 Ga, strongly suggesting that average basaltic water content has remained relatively constant for most of Earth history. These results, including an average THI of ~ 0.9 are entirely consistent with the predominantly calc-alkaline average differentiation trends observed in Figure 4.5b-c.

4.5.2 Trace element modelling

If tectonic setting and magma water activity are constant over the last ~ 4 Ga, one possible remaining source of discontinuous threshold processes in the basaltic record involves melting systematics — the modal mineralogy of the residual mantle as a function of melt extraction. Although our earlier results suggested that the observed La/Yb trends could not be fit with a constant set of partition coefficients [[Keller and Schoene, 2012](#)] (Chapter 2), bulk peridotite/melt partition coefficients are not constant during mantle melting, nor is melt productivity linear as a function of mantle temperature. Instead, as is well known from both experimental and theoretical studies, the relationship of mantle percent melt to melting temperature is markedly non-linear, with discontinuities in slope corresponding to the exhaustion of peridotite minerals upon progressive melting, most notably at the point

Figure 4.9: Mantle melting systematics as modeled by pMELTS as a function of melting extent at 2.7 GPa. **(a)**: Modal mineral abundances as a weight percentage of the remaining solid. **(b)**: Mantle melting temperature as a function of melting extent, displaying strong nonlinearity. **(c)**: Peridotite/melt partition coefficients based on mineral percentages from **(a)** and GERM mineral/melt partition coefficients

Figure 4.10: Comparison of observed and calculated basaltic trace element abundances for (a) La/Yb ratio, (b) Sr abundance, (c) Zr abundance, and (d) Nb abundance. Calculated values are obtained (as described in the text) using the mantle melting extents from Figure 4.6, mineral proportions as in Figure 4.9, GERM partition coefficients, and a constant mantle composition

of clinopyroxene exhaustion around 25-30% melt [Herzberg and Zhang, 1996, Hirschmann et al., 1998, 1999].

In order to investigate the effects of mantle melting systematics on melt productivity and partition coefficients, we paired the pMELTS mantle melting simulations from Section 3.2 with trace element partitioning calculations. To this end, we first extracted the relative mass of melt and residue present for each temperature step, as well as the proportion of each rock-forming mineral in the corresponding mantle residue. Trace element concentrations in the melt were then calculated using the equilibrium batch melting equation along with mineral/melt partition coefficients derived from the GERM partition coefficient database [GERM, 2013] interpolated as a function of SiO_2 as in Keller et al. [2015] (Chapter 3) by bootstrap resampling. While partition coefficients were not adjusted in any way, the initial primitive mantle trace element composition was scaled to best fit the basaltic record. Compared to standard primitive mantle trace element estimates [e.g. McDonough and Sun, 1995], this inversion resulted in moderately higher trace element abundances – likely due to the effect of processes such as enriched slab fluid input on the basaltic trace element record. This constant mantle trace element composition was used for all timesteps.

The results reveal that at pressures typical for mantle wedge flux melting, garnet and clinopyroxene are both exhausted in the residuum at $\sim 30\%$ melt (Figure 4.9a), resulting in a discontinuous break in slope for both melt productivity (Figure 4.9b) and peridotite/melt partition coefficients (Figure 4.9c). The nonlinearity and discontinuous slope of the percent melt–temperature relationship in Figure 4.9b are responsible for reconciling the discontinuous percent melt–time curve in Figure 4.6a with the smooth temperature–time curve in Figure 4.6b. Applying the partition coefficients from Figure 4.9c to the percent melt–time trend from Figure 4.7a accurately reproduces observed trace element trends, as seen in Figure 4.10, with no fitting or adjustment of partition coefficients.

4.6 Discussion

4.6.1 Accuracy of temporal trends in average basaltic composition

As demonstrated throughout the previous sections, weighted bootstrap resampling Monte Carlo analysis of a sufficiently large global dataset reveals a consistent set of clear temporal trends in average basaltic composition over Earth history. These trends are resolvable only thanks to the statistical properties of large sample sets, demonstrated in the general case by the law of large numbers. Although individual basalt compositions may vary widely from the true population mean due to geological (and to a lesser degree analytical) sources of variance, the effect of this variance on the mean of the observed sample set diminishes in proportion to the number of independent data in the set; equivalently, the standard error of the observed mean decreases as the *square root* of the number of independent data. Consequently, while it is impractical to exclude all low-quality data from a large dataset, even highly uncertain data provide new information about the population mean as long as individual sample compositions are independent and accurate to within their stated uncertainty. Since both geological and analytical uncertainty are the result of successive convolutions of many independent sources of error, the central limit theorem indicates that uncertainty on each data point is likely to approach a symmetric Gaussian distribution which would not systematically bias the observed mean. Moreover, even drawing from a highly non-Gaussian distribution of geochemical *data*, the probability distribution of the *mean* will also approach a Gaussian distribution in accordance with the central limit theorem, such that variance and standard deviation are appropriate parameters with which to characterize the variability of the mean [Keller and Schoene, 2012] (Chapter 2). The result is a statistically robust record of secular geochemical evolution on which to build interpretations of geologic process.

Given an accurate record of continental basalt composition through time, arguably the critical interpretational variable is magma water content, which influences a wide range of petrologic properties from magma viscosity, density and solidus temperature to mineral sat-

uration order. Since water acts to lower the solidus temperature of silicate magmas [Yoder, 1965, Mysen and Boettcher, 1975, Thomson, 1996], increasing average water content during mantle basalt generation would increase the average extent of mantle partial melting at a constant mantle potential temperature. If not taken into account when estimating mantle potential temperatures from basalt geochemistry, increasing basaltic water content over time would lead to a systematic underestimation of the extent of mantle cooling; conversely, decreasing water content would lead to an overestimation. Substantial uncertainty persists regarding the magnitude of both the volcanic flux of mantle water to the surface and the subduction-driven return flux via altered oceanic crust [Wallace, 2005, Maruyama and Okamoto, 2007, van Keken and Hacker, 2011, Parai and Mukhopadhyay, 2012], providing little constraint on mantle water content through time at the Ga scale. Nevertheless, our calculated mantle melting extent and mantle potential temperature trends (Figure 4.6) fall well within the range of previous independent estimates [Kelley et al., 2010, Portnyagin et al., 2007, Walter, 1998, Bernstein et al., 2007, Korenaga, 2008, Davies, 2009], suggesting little systematic bias from sources such as differentiation of non-primitive basalts or changes in average basaltic water content. Moreover, all indications from our geochemical record suggest that average continental basaltic water content has remained largely constant over much of Earth history: multiple measures of the relative extent of wet calc-alkaline versus dry tholeiitic magma differentiation as well as trace element signatures of slab fluid input (Figures 4.5b-c, 4.8) all indicate no measurable change over the past ~ 4 Ga.

4.6.2 Constraints on the prevalence of subduction through Earth history

The initiation of subduction and modern-style plate tectonics would directly precipitate a major increase in average basaltic water content due to the addition of wet basaltic magmas produced by flux melting with $\sim 4.0\%$ H_2O [e.g. Plank et al., 2013] to the preexisting population of dry rift and plume basalts produced by decompression melting with only $\sim 0.2\%$ H_2O

[e.g. [Sobolev and Chaussidon, 1996](#)], corresponding to a decrease in tholeiitic index from 1.8 at 0.2% H₂O towards 0.8 at 4.0% H₂O [[Zimmer et al., 2010](#)]. However, no such trend is observed in our results (Figure 4.8d). Instead, average tholeiitic index has held roughly constant at THI $\simeq$ 0.9 since the earliest Archean, indicating a consistent predominance of calc-alkaline differentiation (Figure 4.8d). This conclusion is strongly supported by a wide range of fluid-sensitive trace element signatures including Nb/Th, K/Hf, and Rb/Nb (Figure 4.8a-c,e), all of which show no systematic variation in the relative extent of slab fluid input since the earliest Archean. Indeed, since arc basalts today display higher degrees of melting than coeval rift and plume basalts [[Watson and McKenzie, 1991](#), [Kelley et al., 2010](#)] due to the increased water content of arc basalts, the sudden addition of hydrous arc basalts to the geologic record would arguably result in a rapid increase in average mantle melting extent, which is not observed at any time in the preserved rock record (Figure 4.6).

Objections to Archean plate tectonics have been raised on a wide variety of grounds, notably among them the absence from the preserved Archean record of certain rock types considered characteristic of plate tectonics [[Hamilton, 1998](#), [Stern, 2008](#)]. For example, blueschists and ultra-high pressure (UHP) metamorphic terranes, considered to form exclusively at subduction zones, first appear in the early Neoproterozoic, broadly concomitant with an increase in the occurrence of preserved ophiolites [[Stern, 2008](#), [Brown, 2007](#), [Harlow et al., 2015](#)]. However, a Neoproterozoic start to plate tectonics would conflict with an abundance of geologic evidence thought to reflect modern-style horizontal tectonics well before this time, including the formation of the well-established supercontinent Rodinia [e.g. [Hoffman, 1988](#), [Li et al., 2008](#)]. Such conflicts may be resolved by incomplete preservation in the geologic record: in light of preservation bias, the first appearances of plate tectonic hallmarks supply only one-sided constraints – providing evidence of plate tectonic processes at a given date, without necessarily ruling out earlier operation. This effect of preservation bias is broadly applicable to a wide range of records. For example, [Shirey and Richardson \[2011\]](#) provide a global record of lithospheric inclusions in diamond, identifying eclogitic inclusions

as old as 3.0 Ga, but only peridotitic inclusions prior to that time. Due to Os isotopic enrichment, the eclogitic inclusions provide evidence for subduction and underplating of basaltic crust [Richardson et al., 2001]. However, the absence of eclogitic inclusions older than 3 Ga need not argue against subduction before this date; unlike depleted lithospheric peridotite, eclogite is denser than the underlying asthenosphere and thus subject to delamination – a process which is only expedited by higher mantle temperatures [Jull and Kelemen, 2001] which likely prevailed in the Archean.

Moreover, the existing constraints are highly temporally heterogeneous. Consider, for example, the first known appearance of jadeitites by 520 Ma [Harlow et al., 2015]; UHP metamorphic terranes by ~ 620 Ma [Liou et al., 2014]; lawsonite-bearing blueschists by ~ 750 Ma [Tsuji-mori and Ernst, 2014]; complete ophiolites by 1998 Ma [Scott et al., 1992]; seismically-imaged crustal sutures by 2.69 Ga [Calvert et al., 1995]; paired metamorphic belts by ~ 2.7 Ga [Brown, 2006]; isotopically evolved, underplated eclogites by 2.89 Ga [Richardson et al., 2001]; continental rifting by 3.2 Ga [Van Kranendonk and Smithies, 2007]; boninites and fragmentary ophiolite-like accreted oceanic terranes by 3.7 Ga [Polat et al., 2002, Komiya et al., 1999, Furnes et al., 2007]; and crust/mantle isotopic recycling by at least 3.9 Ga [Shirey et al., 2008]. Compared to geochemical and isotopic signatures that are readily preserved even after extensive metamorphism, many of the earlier entries in this list display poor preservation potential.

Jadeitites, blueschists, and other very high pressure, low temperature metamorphic rocks are thermodynamically fragile – far out of thermodynamic equilibrium at any depth in a crustal geotherm – and are difficult to successfully exhume and preserve even under modern arc geotherms [Ernst, 2003]; such assemblages may have never formed in ancient subduction zones given higher mantle temperatures and more Mg-rich oceanic crust [Palin and White, 2015]. Ophiolites, meanwhile, remain recognizable after more extensive metamorphism and alteration, but are susceptible to erosion due to their high chemical weatherability and their emplacement by obduction on top of existing continental crust. At the other extreme,

geochemical subduction signatures and isotopic tracers of crustal recycling can be preserved in principle as far back in time as the earliest surviving rocks and minerals. If the pervasive diachroneity of these data is the result of preservation bias, we should then be led to conclude that the oldest preserved constraint is the most accurate. Although it may be possible to construct a model in which the progressive appearance of plate tectonic hallmarks develops due to a progressively changing style of tectonics, preservation bias appears to provide one parsimonious interpretation.

Meanwhile, the constraints from our geochemical record are difficult to escape (Figures 4.5, 4.8). The effect of water on the extent of calc-alkaline differentiation is well understood, and the major elements by which this effect is quantified are not readily biased [e.g. [Sisson and Grove, 1993](#), [Zimmer et al., 2010](#)]. The effect of slab fluids to produce relative enrichment of fluid-mobile elements and depletion of non-mobile elements is similarly well established [[Perfit et al., 1980](#), [Tatsumi et al., 1986](#), [McCulloch and Gamble, 1991](#), [Pearce and Peate, 1995](#), [Schmidt and Poli, 2014](#)], with no clear mechanism available to mask the absence of such arc signatures from the geologic record in the absence of subduction. If anything, the progressive leaching of fluid-soluble elements such as Rb from older rocks would only enhance such an effect. Together, we are left to conclude that the global long-term average proportion of flux and dehydration melting has not changed systematically at any time in the preserved rock record, and that subduction of oceanic crust has likely been in operation since at least the earliest Archean.

Nonetheless, it is worthwhile to note that nothing in our interpretation argues directly against the operation of novel, possibly nonuniformitarian processes in the Archean – e.g., widespread intracrustal diapirism [[Van Kranendonk and Smithies, 2007](#)] – as long as such processes are compatible with the constant observed proportion of flux and decompression melting preserved in the continental basaltic record. Some of the most intriguing features of Earth’s igneous rock record are endemic to the Archean, including granite-greenstone terranes, trondhjemites and komatiites. While our results suggest that basalts are generated by

largely the same processes today as they were in the Archean, rapid discontinuities in granitic trace element compositions 2.5 Ga ago [Keller and Schoene, 2012] (Chapter 2) appear to suggest a change in the process of crustal differentiation, coincident with widespread atmospheric oxidation at the end of the Archean.

4.6.3 Implications of ongoing subduction throughout the preserved rock record

In the context of ongoing plate tectonics since at least 3.8 Ga, several features of the geochemical record become more readily explicable. For instance, TiO_2 – MgO and Na_2O – MgO systematics (Figure 4.5e-f) indicate a continual, progressive increase in the average depth of mantle melting over Earth history, the opposite of what would result from secular mantle cooling in a mantle decompression melting scenario [Iwamori et al., 1995]. In a plate tectonic flux melting regime, by contrast, the depth of flux melting is generally thought to decrease with increasing mantle potential temperature due to dehydration of the slab at lower pressures if all else is held constant [Peacock, 1990, Schmidt and Poli, 1998]. One complication to the standard picture arises from the fact that the composition of subducting slabs has not been constant through Earth history. Recently, Palin and White [2015] have suggested that more Mg-rich Archean slabs contain more stable hydrous minerals that can carry more water to greater depths, acting counter to the effect of increased mantle potential temperature. Mantle lithosphere, which may control the depth of last magma equilibration with the convecting mantle, provides another potential complication. Given that preserved continental lithosphere is roughly coeval with its overlying crust [Pearson, 1999], and increases in thickness towards the Archean [Artemieva, 2006], one might expect deeper depths of last magma equilibration in the Archean – also contrary to the observed pressure trends. However, this complication applies in detail only to decompression melting below preexisting continental crust with an extant mantle lithosphere; the depth of last equilibration in modern arc settings appears to be set instead by crustal thickness [Plank and Langmuir, 1988], suggesting

that a highly rigid mantle lithosphere is not yet present in arc settings. While there is much room for further research, the trend in melting pressure suggested by Figure 4.5e-f may well be most consistent with a predominance of flux melting in the continental basaltic record, as is suggested by the consistently calc-alkaline ($\text{THI} < 1$) average observed tholeiitic index in Figure 4.8d.

Other features of the observed basaltic record, such as the rapid shift in trace element ratios (La/Yb, etc.), are similarly internally consistent with a plate tectonic setting, given that mineral stability thresholds in an arc mantle wedge setting readily explain the observed trends (Figure 4.10). While we have not attempted to quantify the extent of the apparent increase in average mantle melting pressure, one notable consequence would be to shift the site of flux melting from the garnet peridotite stability field towards the spinel peridotite stability field in early Earth history – though potentially to little effect given the apparent extent of mantle melting beyond the point of garnet and clinopyroxene exhaustion in the Archean (Figures 4.6, 4.9).

Even within a plate tectonic regime, the apparently constant average basaltic water content since ~ 4 Ga is remarkable, suggesting a roughly constant proportion of arc and non-arc magmatism in the preserved continental record. If accurate, these results demonstrate that a constant ratio of flux to decompression melting is a persistent feature of terrestrial plate tectonics on Ga timescales.

4.7 Conclusions

The integration of large, freely available geochemical datasets with computational statistical methods that minimize sampling bias and accurately reflect data uncertainties has allowed for the quantification of systematic changes in average basaltic composition over time (Figures 4.1-4.8), including gradual (Figure 4.1), abrupt (Figure 4.7), and invariant (Figure 4.8) trends at the 4-Ga scale. Although it is not possible to demonstrate complete independence

of these results from sampling and preservation bias, weighted bootstrap resampling Monte Carlo analysis provides a robust method to obtain maximally representative information from the heterogeneous rock record. Internal consistency of the resulting trends, along with observed trends contrary to expected weathering and preservation biases, provides some confirmation that the results likely reflect secular variation in underlying drivers of the Earth system. These trends represent a significant advance in our ability to quantify changes in the composition of Earth's crust over time; their continuous nature allows for a qualified application of uniformitarianism, working backwards through Earth history from the known state of the present.

Due to the lack of any systematic variation in abundance ratio for elemental pairs with matching igneous partitioning behavior but contrasting mobility during alteration and weathering (Figures 4.4, 4.7a-b), it is reasonable to consider that these trends likely reflect original igneous variability attributable to systematic changes in igneous processes over Earth history. An igneous origin for observed basaltic major and trace element geochemical trends is consistent with the interpretation of Keller and Schoene [2012] (Chapter 2) that the smoothly decreasing compatible and increasing incompatible element trends of average basalt over the past 4 Ga (Figure 4.1) reflect decreasing average extent of mantle melting driven by secular mantle cooling. This interpretation is supported by the distinct observed signature of decreased partial melting relative to increased magma differentiation (Figure 4.4) and the lack of apparent variation in average basaltic magma water content since 4 Ga (Figure 4.5b-c, 4.8). Moreover, when properly accounting for the effects of mineral stability bounds on trace element partitioning and melt productivity, (Figures 4.9), it is observed that even the most abrupt observed discontinuities in trace element geochemistry are consistent with smooth, continuous mantle cooling as observed in Figure 4.10.

Consequently, we propose that the geochemistry of the preserved basaltic crustal record can be most parsimoniously explained by essentially modern plate tectonic processes modified by secular mantle cooling. In this interpretation, rapid variations in the geochemical record

at the end of the Archean are effectively explained by the discontinuous effects of mineral stability thresholds on the petrologic processes of magma generation and differentiation, specifically garnet and clinopyroxene exhaustion during mantle partial melting. In addition to the consistent reproduction of observed trace element geochemistry (Figure 4.10), support for this model comes from its reconciliation of a discontinuous (at the 2-standard-error level) percent melt trend with a smooth and continuous mantle melting temperature trend as observed in Figure 4.6.

This model is strongly supported by the invariance of geochemical slab fluid input signatures through geologic time (Figure 4.8a-c,d) which indicate a roughly constant proportion of crust produced in subduction zones over the entirety of the preserved rock record. Together, this evidence favors a horizontal, uniformitarian model of Archean tectonics. Given the profound geologic consequences of a planetary transition from a stagnant lid or vertical tectonic regime to horizontal plate tectonics, the invariance of slab fluid signatures and the absence of any dramatic changes in the basaltic record that cannot be explained by secular mantle cooling indicates that subduction and associated horizontal tectonics had already begun on Earth by at least 3.8 Ga and have operated consistently since.

4.8 Acknowledgements

C.B.K. was supported by a Computational Science Graduate Fellowship through US Department of Energy Office of Science grant DE-FG02-97ER25308.

4.9 Data Access

The full dataset and all computational source code is available at <https://github.com/brenhinkeller/StatisticalGeochemistry> under an MIT open-source license.

References

- Irina M Artemieva. Global 1x1 thermal model TC1 for the continental lithosphere: implications for lithosphere secular evolution. *Tectonophysics*, 416:245–277, 2006.
- M Atherton and Nick Petford. Generation of sodium-rich magmas from newly underplated basaltic crust. *Nature*, 362:144–146, 1993.
- Jean H Bédard. A catalytic delamination-driven model for coupled genesis of Archaean crust and sub-continental lithospheric mantle. *Geochimica et Cosmochimica Acta*, 70:1188–1214, 2006.
- Elena Belousova, Y Kostitsyn, W L Griffin, G C Begg, Suzanne Y O’Reilly, and N J Pearson. The growth of the continental crust: Constraints from zircon Hf-isotope data. *LITHOS*, 2010.
- Stefan Bernstein, Peter B Kelemen, and K Hanghøj. Consistent olivine Mg# in cratonic mantle reflects Archean mantle melting to the exhaustion of orthopyroxene. *Geology*, 35(5):456–462, 2007.
- R E Botcharnikov, R R Almeev, J Koepke, and F Holtz. Phase relations and liquid lines of descent in hydrous ferrobalt—implications for the Skaergaard intrusion and Columbia River flood basalts. *Journal of Petrology*, 49(9):1687–1727, 2008.
- M Brown. Metamorphic Conditions in Orogenic Belts: A Record of Secular Change. *International Geology Review*, 49(3):193–234, March 2007.

- Michael Brown. Duality of thermal regimes is the distinctive characteristic of plate tectonics since the Neoproterozoic. *Geology*, 34(11):961, 2006.
- A J Calvert, E W Sawyer, W J Davis, and J N Ludden. Archean subduction inferred from seismic images of a mantle suture in the Superior Province. *Nature*, 375(6533):670–674, June 1995.
- Kent C Condie. TTGs and adakites: are they both slab melts? *LITHOS*, 80:33–44, 2005.
- Kent C Condie and Alfred Kröner. When did plate tectonics begin? Evidence from the geologic record. In Kent C Condie and Victoria Pease, editors, *When Did Plate Tectonics Begin on Planet Earth?: Geological Society of America Special Paper 440*, pages 281–294. Geological Society of America, 2008.
- Kent C Condie and Craig O'Neill. The Archean-Proterozoic boundary: 500 my of tectonic transition in Earth history. *American Journal of Science*, 310:775–790, 2010.
- Geoffrey F Davies. Effect of plate bending on the Urey ratio and the thermal evolution of the mantle. *Earth and Planetary Science Letters*, 287(3-4):513–518, October 2009.
- Maarten J de Wit. On Archean granites, greenstones, cratons and tectonics: does the evidence demand a verdict? *Precambrian Research*, 91:181–226, 1998.
- W G Ernst. High-pressure and ultrahigh-pressure metamorphic belts—Subduction, recrystallization, exhumation, and significance for ophiolite study. In Y Dilek, editor, *Ophiolite Concept and the Evolution of Geological Thought: GSA Special Paper 373*. Geological Society of America, 2003.
- H Furnes, Maarten J de Wit, H Staudigel, Minik T Rosing, and K Muehlenbachs. A Vestige of Earth's Oldest Ophiolite. *Science*, 315(5819):1704–1707, March 2007.
- GERM. Geochemical Earth Reference Model Partition Coefficient Database, January 2013. URL <http://www.earthref.org/KDD/>.

- Mark S Ghiorso, Marc M Hirschmann, Peter W Reiners, and Victor C Kress, III. The pMELTS: A revision of MELTS for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa. *Geochemistry Geophysics Geosystems*, 3(5):1–36, May 2002.
- D H Green. Genesis of Archean Peridotitic Magmas and Constraints on Archean Geothermal Gradients and Tectonics. *Geology*, 3(1):15, 1975.
- Timothy L Grove and Stephen Parman. Thermal evolution of the Earth as recorded by komatiites. *Earth and Planetary Science Letters*, 2004.
- Timothy L Grove, Nilanjan Chatterjee, Stephen W Parman, and Etienne Medard. The influence of H₂O on mantle wedge melting. *Earth and Planetary Science Letters*, 249(1-2):74–89, September 2006.
- W Hamilton. Archean magmatism and deformation were not products of plate tectonics. *Precambrian Research*, 1998.
- R B Hargraves. Precambrian Geologic History. *Science*, 193(4251):363–371, July 1976.
- George E Harlow, Tatsuki Tsujimori, and Sorena S Sorensen. Jadeitites and Plate Tectonics. *Annual Review of Earth and Planetary Sciences*, 43(1):105–138, May 2015.
- Christopher J Hawkesworth, B Dhuime, A B Pietranik, Peter A Cawood, A I S Kemp, and C D Storey. The generation and evolution of the continental crust. *Journal of the Geological Society*, 167(2):229–248, March 2010.
- Claude Herzberg and Jianzhong Zhang. Melting experiments on anhydrous peridotite KLB-1: Compositions of magmas in the upper mantle and transition zone. *Journal of Geophysical Research*, 101(B4):8271, 1996.
- Claude Herzberg, Kent C Condie, and Jun Korenaga. Thermal history of the Earth and its petrological expression. *Earth and Planetary Science Letters*, 292:79–88, 2010.

- Marc M Hirschmann, Mark S Ghiorso, L E Wasylenki, Paul D Asimow, and Edward M Stolper. Calculation of Peridotite Partial Melting from Thermodynamic Models of Minerals and Melts. I. Review of Methods and Comparison with Experiments. *Journal of Petrology*, 39(6):1091–1115, 1998.
- Marc M Hirschmann, Paul D Asimow, Mark S Ghiorso, and Edward M Stolper. Calculation of Peridotite Partial Melting from Thermodynamic Models of Minerals and Melts. III. Controls on Isobaric Melt Production and the Effect of Water on Melt Production. *Journal of Petrology*, 40(5):831–851, May 1999.
- Paul F Hoffman. United Plates of America, The Birth of a Craton: Early Proterozoic Assembly and Growth of Laurentia. *Annual Review of Earth and Planetary Sciences*, 16(1):543–603, May 1988.
- Albrecht W Hofmann. Mantle geochemistry: the message from oceanic volcanism. *Nature*, 385:219–229, January 1997.
- H Iwamori, Dan McKenzie, and E Takahashi. Melt generation by isentropic mantle upwelling. *Earth and Planetary Science Letters*, 1995.
- M Jull and Peter B Kelemen. On the conditions for lower crustal convective instability. *Journal of Geophysical Research*, 106(B4):6423–6446, 2001.
- C Brenhin Keller and Blair Schoene. Statistical geochemistry reveals disruption in secular lithospheric evolution about 2.5Gyr ago. *Nature*, 485(7399):490–493, May 2012.
- C Brenhin Keller, Blair Schoene, Melanie Barboni, Kyle M Samperton, and Jon M Husson. Volcanic–plutonic parity and the differentiation of the continental crust. *Nature*, 523(7560):301–307, July 2015.

- Katherine A Kelley, Terry Plank, S Newman, Edward M Stolper, Timothy L Grove, Stephen Parman, and Erik H Hauri. Mantle melting as a function of water content beneath the Mariana Arc. *Journal of Petrology*, 2010.
- E M Klein and Charles H Langmuir. Global correlations of ocean ridge basalt chemistry with axial depth and crustal thickness. *Journal of Geophysical Research*, 92(B8):8096–8115, 1987.
- Tsuyoshi Komiya, Shigenori Maruyama, Toshiaki Masuda, Susumu Nohda, Mamoru Hayashi, and Kazuaki Okamoto. Plate Tectonics at 3.8–3.7 Ga: Field Evidence from the Isua Accretionary Complex, Southern West Greenland. *The Journal of Geology*, 107(5):515–554, September 1999.
- Jun Korenaga. Plate tectonics, flood basalts and the evolution of Earth’s oceans. *Terra Nova*, 2008.
- Z X Li, S V Bogdanova, A S Collins, and A Davidson. Assembly, configuration, and break-up history of Rodinia: A synthesis. *Precambrian Research*, 2008.
- Juhn G Liou, Tatsuki Tsujimori, Jingsui Yang, R Y Zhang, and W G Ernst. Recycling of crustal materials through study of ultrahigh-pressure minerals in collisional orogens, ophiolites, and mantle xenoliths: A review. *Journal of Asian Earth Sciences*, 96:386–420, December 2014.
- Hervé Martin, R Hugh Smithies, R Rapp, and Jean-François Moyen. An overview of adakite, tonalite-trondhjemite-granodiorite (TTG), and sanukitoid: relationships and some implications for crustal evolution. *LITHOS*, 79:1–24, 2005.
- Shigenori Maruyama and Kazuaki Okamoto. Water transportation from the subducting slab into the mantle transition zone. *Gondwana Research*, 11(1-2):148–165, January 2007.

- M T McCulloch and J A Gamble. Geochemical and geodynamical constraints on subduction zone magmatism. *Earth and Planetary Science Letters*, 1991.
- William F McDonough and S Sun. The composition of the Earth. *Chemical Geology*, 1995.
- Jean-François Moyen. The composite Archaean grey gneisses: Petrological significance, and evidence for a non-unique tectonic setting for Archaean crustal growth. *LITHOS*, 123 (1-4):21–36, 2010.
- Jean-François Moyen and Gary Stevens. Experimental Constraints on TTG Petrogenesis: Implications for Archean Geodynamics. *Archean Geodynamics and Environment Geophysical Monograph Series*, 164:147–175, 2006.
- Bjorn O Mysen and A L Boettcher. Melting of a Hydrous Mantle: I. Phase Relations of Natural Peridotite at High Pressures and Temperatures with Controlled Activities of Water, Carbon Dioxide, and Hydrogen. *Journal of Petrology*, 16(1):520–548, January 1975.
- Richard M Palin and Richard W White. Emergence of blueschists on Earth linked to secular changes in oceanic crust composition. *Nature Geoscience*, December 2015.
- Rita Parai and S Mukhopadhyay. How large is the subducted water flux? New constraints on mantle regassing rates. *Earth and Planetary Science Letters*, 317-318:396–406, February 2012.
- Simon M Peacock. Fluid Processes in Subduction Zones. *Science*, 248:329–337, April 1990.
- Julian A Pearce and J R Cann. Tectonic setting of basic volcanic rocks determined using trace element analyses. *Earth and Planetary Science Letters*, 19(2):290–300, June 1973.
- Julian A Pearce and D W Peate. Tectonic Implications of the Composition of Volcanic Arc Magmas. *Annual Review of Earth and Planetary Sciences*, 23(1):251–285, May 1995.

- Julian A Pearce, Nigel B W Harris, and Andrew G Tindle. Trace Element Discrimination Diagrams for the Tectonic Interpretation of Granitic Rocks. *Journal of Petrology*, 25(4): 956–983, November 1984.
- D Graham Pearson. The age of continental roots. *LITHOS*, 48(1-4):171–194, September 1999.
- Victoria Pease, John Percival, R Hugh Smithies, Gary Stevens, and Martin J Van Kranendonk. When did plate tectonics begin? Evidence from the orogenic record. In Kent C Condie and Victoria Pease, editors, *When Did Plate Tectonics Begin on Planet Earth?: Geological Society of America Special Paper 440*, pages 199–228. Geological Society of America, 2008.
- M R Perfit, D A Gust, A E Bence, R J Arculus, and Stuart Ross Taylor. Chemical characteristics of island-arc basalts: Implications for mantle sources. *Chemical Geology*, 30(3): 227–256, September 1980.
- Terry Plank and Charles H Langmuir. An evaluation of the global variations in the major element chemistry of arc basalts. *Earth and Planetary Science Letters*, 90:349–370, 1988.
- Terry Plank, Katherine A Kelley, Mindy M Zimmer, Erik H Hauri, and Paul J Wallace. Why do mafic arc magmas contain 4 wt. percent water on average? *Earth and Planetary Science Letters*, 364:168–179, February 2013.
- A Polat, Albrecht W Hofmann, and M T Rosing. Boninite-like volcanic rocks in the 3.7–3.8 Ga Isua greenstone belt, West Greenland: geochemical evidence for intra-oceanic subduction zone processes in the early Earth. *Chemical Geology*, 184(3-4):231–254, April 2002.
- Maxim Portnyagin, Kaj Hoernle, Pavel Plechov, Nikita Mironov, and Sergey Khubunaya. Constraints on mantle melting and composition and nature of slab components in volcanic arcs from volatiles (H₂O, S, Cl, F) and trace elements in melt inclusions from the Kamchatka Arc. *Earth and Planetary Science Letters*, 255(1-2):53–69, March 2007.

- S H Richardson, Steven B Shirey, J Harris, and Rick W Carlson. Archean subduction recorded by Re–Os isotopes in eclogitic sulfide inclusions in Kimberley diamonds. *Earth and Planetary Science Letters*, 191(3–4):257–266, September 2001.
- Roberta L Rudnick and David M Fountain. Nature and composition of the continental crust: A lower crustal perspective. *Reviews of Geophysics*, 33(3):267–309, August 1995.
- Max W Schmidt and S Poli. Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. *Earth and Planetary Science Letters*, 163:361–379, 1998.
- Max W Schmidt and S Poli. 4.19 Devolatilization During Subduction. In Roberta L Rudnick, editor, *Treatise on Geochemistry*, pages 669–701. Elsevier, 2014.
- D J Scott, H Helmstaedt, and M J Bickle. Purtuniq ophiolite, Cape Smith belt, northern Quebec, Canada: A reconstructed section of Early Proterozoic oceanic crust. *Geology*, 20(2):173, 1992.
- Steven B Shirey and S H Richardson. Start of the Wilson Cycle at 3 Ga Shown by Diamonds from Subcontinental Mantle. *Science*, 333(6041):434–436, July 2011.
- Steven B Shirey, B S Kamber, and M J Whitehouse. A review of the isotopic and trace element evidence for mantle and crustal processes in the Hadean and Archean: Implications for the onset of plate tectonic subduction. *When did plate tectonics begin on planet Earth?: GSA Special Paper 440*, pages 1–29, 2008.
- T W Sisson and Timothy L Grove. Experimental investigations of the role of H₂O in calc-alkaline differentiation and subduction zone magmatism. *Contributions to Mineralogy and Petrology*, 113:143–166, 1993.
- Norman H Sleep. Archean plate tectonics: what can be learned from continental geology? *Canadian Journal of Earth Sciences*, 1992.

- Paula M Smith and Paul D Asimow. Adiabatic 1ph: A new public front-end to the MELTS, pMELTS, and pHMELTS models. *Geochemistry Geophysics Geosystems*, 6(1):1–8, 2005.
- Alexander V Sobolev and Marc Chaussidon. H₂O concentrations in primary melts from supra-subduction zones and mid-ocean ridges: Implications for H₂O storage and recycling in the mantle. *Earth and Planetary Science Letters*, 137(1-4):45–55, January 1996.
- Robert J Stern. Modern-style plate tectonics began in Neoproterozoic time: An alternative interpretation of Earth’s tectonic history. In Kent C Condie and Victoria Pease, editors, *When Did Plate Tectonics Begin on Planet Earth?: Geological Society of America Special Paper 440*, pages 265–280. Geological Society of America, 2008.
- Y Tatsumi, D L Hamilton, and R W Nesbitt. Chemical characteristics of fluid phase released from a subducted lithosphere and origin of arc magmas: evidence from high-pressure experiments and natural rocks. *Journal of Volcanology and Geothermal Research*, 29: 293–309, 1986.
- Alan Bruce Thomson. Fertility of crustal rocks during anatexis. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, 87:1–10, 1996.
- Tatsuki Tsujimori and W G Ernst. Lawsonite blueschists and lawsonite eclogites as proxies for palaeo-subduction zone processes: a review - Tsujimori - 2013 - Journal of Metamorphic Geology - Wiley Online Library. *Journal of Metamorphic Geology*, 32:437–454, 2014.
- Peter E van Keken and Bradley R Hacker. Subduction Factory: 4. Depth-dependent flux of H₂O from subducting slabs worldwide. *Journal of Geophysical Research: Solid Earth*, 116:1–15, 2011.
- Martin J Van Kranendonk and R Hugh Smithies. Review: secular tectonic evolution of Archean continental crust: interplay between horizontal and vertical processes in the formation of the Pilbara Craton, Australia. *Terra Nova*, 19:1–38, 2007.

- Jeff D Vervoort and Janne Blichert-Toft. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. *Geochimica et Cosmochimica Acta*, 63(3-4): 533–556, February 1999.
- Paul J Wallace. Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. *Journal of Volcanology and Geothermal Research*, 2005.
- Michael J Walter. Melting of garnet peridotite and the origin of komatiite and depleted lithosphere. *Journal of Petrology*, 39(1):29–60, 1998.
- Sarah Watson and Dan McKenzie. Melt Generation by Plumes: A Study of Hawaiian Volcanism. *Journal of Petrology*, 32(3):501–537, June 1991.
- William M White and Albrecht W Hofmann. Sr and Nd isotope geochemistry of oceanic basalts and mantle evolution. *Nature*, 296:821–825, April 1982.
- J F Wilson, J L Orpen, M J Bickle, Christopher J Hawkesworth, A Martin, and E G Nisbet. Granite-greenstone terrains of the Rhodesian Archaean craton. *Nature*, 271(5640):23–27, January 1978.
- H S Yoder, Jr. Diopside-Anorthite-Water at Five and Ten Kilobars and Its Bearing on Explosive Volcanism. *Year Book of the Carnegie Institution of Washington*, 64:82–89, 1965.
- Mindy M Zimmer, Terry Plank, Erik H Hauri, Gene M Yogodzinski, Peter Stelling, Jessica Larsen, Brad S Singer, Brian Jicha, Charles Mandeville, and Christopher J Nye. The Role of Water in Generating the Calc-alkaline Trend: New Volatile Data for Aleutian Magmas and a New Tholeiitic Index. *Journal of Petrology*, 51(12):2411–2444, 2010.

Chapter 5

Zircon Saturation and the early Earth

5.1 Abstract

Zircon is the dominant chronometer of absolute geologic time on Earth, and provides our only direct window into the Hadean Eon. However, the quantity of zircon crystallized per unit mass of magma is highly variable, complicating interpretation of the terrestrial zircon archive as a record of the antecedent crust or magma. Here we combine zircon saturation simulations with a dataset of $\sim 70,000$ igneous whole-rock geochemical analyses to quantify secular variation in relative zircon abundance throughout Earth history. We find increasing zircon abundance per mass of magma through geologic time, suggesting that the zircon record underestimates past crustal volume even if preservation bias is eliminated. In early Earth history, zircons were even less likely to crystallize from low-silica magmas than they are today, consistent with a felsic origin for Hadean zircons.

5.2 Temporal variation in relative zircon abundance throughout Earth history

The accessory mineral zircon is ubiquitous, refractory, and can be radiometrically dated to high precision and accuracy through the U and Th decay systems. This unique trinity of properties has made zircon into a standard mineral tracer of geologic time, capable of covering timescales from Gyr to kyr through the related U-Th/Pb and U-series geochronometers [Schoene, 2014, Schmitt, 2011]. Zircon grains constitute the oldest known terrestrial material, providing a glimpse of Earth in the Hadean Eon which has been argued to reveal a remarkably modern environment, complete with liquid water [Mojzsis et al., 2001], continents [Wilde et al., 2001], and felsic crust [Harrison, 2009]. In the subsequent geologic record, zircon provides crucial absolute time constraints for processes ranging from evolution and mass extinction [Gradstein et al., 2012, Shen et al., 2011] to magmatism and crustal differentiation [Hoskin, 2003, Kemp et al., 2007, Samperton et al., 2015].

Given its ubiquity in igneous rocks, zircon has been used as a proxy for magma crystallization, crust production, and even crustal composition [Condie et al., 2009, Cawood et al., 2013, Lee et al., 2016]. However, quantity of zircon is not a direct substitute for quantity of magma or crust. Instead, zircon abundance in the igneous record is a function of magma composition, which is both spatially and temporally heterogeneous. Moreover, due to the high closure temperatures of the U-Th/Pb and U-series systems, ages from these geochronometers exclusively date zircon crystallization [Schoene, 2014, Schmitt, 2011], which need not coincide with the crystallization of other silicate minerals. Consequently, zircon saturation systematics must be taken into account at both large and small spatiotemporal scales, from interpreting global zircon age spectra to establishing the age of a single igneous hand sample [Harrison et al., 2007].

The temperature T_{sat} at which zircon saturates in an igneous magma can be accurately predicted by an empirical equation of the form

$$\frac{a}{T_{sat}} = \ln \left(\frac{[Zr]_{zircon}}{[Zr]_{melt}} \right) + bM + c$$

where a , b , and c are constants, $[Zr]$ is zirconium concentration, and M is a compositional measure of magma polymerization defined on a molar basis as

$$M = \frac{[Na] + [K] + 2[Ca]}{[Al] * [Si]}$$

[[Watson and Harrison, 1983](#), [Boehnke et al., 2013](#)]. Purely stochastic heterogeneity in magma composition would produce no meaningful temporal variation in zircon saturation behavior. However, on sufficiently long geologic timescales, decreasing mantle potential temperature is reflected in systematic variations in average magma composition, including increasing abundance of incompatible elements such as Zr [[Keller and Schoene, 2012](#)] (Chapter 2).

Even within a closed system, magma composition (including M and $[Zr]_{melt}$) will vary systematically throughout crystallization as a function of pressure, temperature, and melt fraction, such that a single bulk zircon saturation temperature is insufficient to characterize the zircon saturation behavior of even the simplest igneous systems. Accordingly, in order to examine the effects of temporal variations in magma composition throughout Earth history on zircon saturation behavior, we combine zircon saturation calculations with alphaMELTS [[Ghiorso et al., 2002](#), [Smith and Asimow, 2005](#)] major element simulations on 52,300 whole-rock compositions spanning the preserved rock record from modern to Archean. While generally incompatible in silicate minerals, zirconium mineral/melt partition coefficients vary widely between common silicate minerals and may be as high as 0.3-0.5 for clinopyroxene, amphibole, and garnet. Consequently, to ensure accurate zircon saturation calculations, mineral-specific GERM partition coefficients [[GERM, 2013](#)] were used when calculating melt Zr concentrations at each temperature step of each alphaMELTS simula-

tion. Finally, to obtain temporal trends, the results of zircon saturation simulations were subjected to weighted bootstrap resampling following the approach of [Keller and Schoene, 2012] (Chapter 2) to calculate accurate estimates of the mean and standard error of the mean for each independent variable of interest.

The primary forcings on zircon abundance over Gyr timescales are illustrated in Figure 5.1a as averages for igneous whole-rock samples preserved in the present-day continental crust. Over the past 4 Gyr, average igneous zirconium content has increased, while average M-value has decreased. These changes are a consequence of secular mantle cooling, which has resulted in lower average mantle melting extent, leading to increased average concentrations of incompatible elements such as Zr [Keller and Schoene, 2012] (Chapter 2), and generally more highly polymerized magmas with lower M value. Combined, these forcings should result in substantially increased zircon concentration in the igneous record (mass of zircon crystallized per mass of magma) since the early Archean.

While zircon saturation is largely independent of magma pressure and water content [Boehnke et al., 2013], the crystallization of other silicate minerals is not, with higher pressure and lower water content generally increasing crystallization temperatures. Consequently, in drier or deeper magmas, most silicate minerals will crystallize earlier relative to zircon [Keller et al., 2015] (Chapter 3), and such magmas will be more likely to fully crystallize to the solidus without ever reaching zircon saturation. Correspondingly, our saturation calculations run at higher pressures or lower magma water contents display lower total zircon abundance at any given time, as shown in Figure 5.1b. However, common temporal trends are revealed across a wide range of P and H₂O values, with the mass of zircon saturated per mass of magma increasing substantially since the early Archean, by as much as a factor of 5 (Figure 5.1b).

The strong influence of crystallization pressure and magma water content on final whole-rock zircon abundance limits our ability to unambiguously reconstruct past magma volumes from the zircon record. Average continental magma crystallization pressure throughout Earth history is poorly known for plutonic igneous rocks, and is controlled by factors such

Figure 5.1: (a) Average zirconium and M value throughout the preserved rock record for continental igneous rocks with 40-80% SiO₂. (b) Calculated average zircon concentration (micrograms of zircon per gram of whole rock) as a function of time, under a range of crystallization conditions. (c) The effect of applying a relative zircon abundance correction to the detrital zircon age spectrum of Belousova et al. [2010] for varying crystallization conditions.

as crustal density structure, magma composition, regional geothermal gradient, local stress state, and ultimately limited by crustal thickness. However, deeper average crystallization depths in the past corresponding with thicker original crust [Keller and Schoene, 2012] (Chapter 2) would only accentuate the trends observed here. Given that the exposed Phanerozoic igneous rock record is dominated by upper crustal batholiths, it appears unlikely that average crystallization depths were dramatically shallower for preserved Archean plutons. Meanwhile, magma water content may vary greatly between different tectonic settings at any one time, though recent geochemical evidence suggests that the global average water content (and the global ratio of mantle flux melting to mantle decompression melting) for continental magmas has remained roughly constant throughout the preserved rock record (Chapter 4). As discussed in Chapter 4, this result is contrary to non-plate-tectonic models for the Archean, but even if such models were correct, the resulting lack of water in Archean magmas would enhance, not diminish, the trends in Figure 5.1b.

Consequently, it appears safe to conclude that compared to the present day, average continental magmas in the Archean crystallized much less zircon per unit mass of magma. If not taken into account, this systematic trend in relative zircon abundance would lead to substantial underestimation of the amount of crust required to produce Earth's early zircon record. The impact of this trend on preserved zircon age spectra is shown in Figure 5.1c, which illustrates what the largely detrital zircon age spectrum of Belousova et al. [2010] would look like if all magmas crystallized zircon at present-day average rates, under a range of model conditions. For magmas crystallizing at a given set of P, H₂O conditions, this result is equivalent to the true magma age spectrum required to produce the observed detrital zircon age spectrum in the absence of preservation bias – with true average crystallization conditions likely intermediate between the shallow/wet and deep/dry endmembers shown in Figure 5.1c. Regardless of exact P, H₂O conditions, the zircon abundance correction increases the magmatic significance of the Archean and Proterozoic zircon record – an effect that is only enhanced if preservation bias is considered as well. As peaks in global zircon age

Figure 5.2: Zircon saturation distributions during magma crystallization as a function of percent melt for varying silica ranges, calculated at 6 kilobar and 3 wt.% H_2O . Relative zircon abundance is reported as micrograms of zircon saturated per gram of magma per percentage-point decrease in residual melt fraction.

spectra are often interpreted as times of increased global magmatic activity, correlated with the plate-tectonic Wilson cycle [Condie and Aster, 2010, e.g.], the corrected age spectrum would appear to imply a more steady-state supercontinent cycle with equivalent peaks in magmatic activity back to ~ 3 Ga, or (depending on the strength of preservation bias) even before.

In addition to zircon age spectra, this correction applies to any model of crustal growth based on the abundance of zircon in the preserved rock record, but does not apply to the models of e.g. Belousova et al. [2010] or Dhuime et al. [2012], as these models do not, in fact, use the observed zircon abundance spectra as an estimate of magmatic activity through time, but rather assume by default a constant rate of igneous activity throughout Earth history when integrating their isotopically-derived "juvenile crust proportion" curves.

Changing average zirconium concentration and M value over the past ~ 4 Gyr has additional consequences for the position of zircon in the magma crystallization sequence. In general, mafic magmas require greater extents of in-situ differentiation to reach zircon saturation, and thus crystallize zircon at lower residual melt fractions (Figure 5.2). As observed

in Figure 5.2, zircon saturation in Archean magmas of any given silica range is further delayed and diminished due to lower average $[Zr]$ and higher M -values. Unsurprisingly, delayed zircon saturation is directly correlated with lower total zircon mass saturated (Figure 5.2), an effect that is accentuated if a magma is not allowed to cool fully to its solidus, either due to eruptive quenching or residual melt extraction.

Due to non-Newtonian magma rheology, magmas containing less than $\sim 37\%$ melt are disproportionately unlikely to erupt [Caricchi et al., 2007]; common volcanic rocks are typically well above this threshold. As residual melt is largely quenched to an amorphous glass upon eruption, any mineral phases crystallizing below the eruptive melt fraction will be absent from the volcanic record. Given that basalts display the greatest delay in zircon saturation and are substantially overrepresented in the volcanic record [Keller et al., 2015] (Chapter 3), the effect of eruptive quenching on zircon saturation will be most noticable in the mafic record. Phanerozoic basalts typically erupt with fewer than 30% phenocrysts by volume [e.g., Bryan, 1983], and at the time of eruption contain little or no zircon, consistent with the predictions of Figure 5.2. Delayed zircon saturation in Archean lithologies should result in an even more pronounced dearth of zircons in the Archean volcanic record for magmas of any given silica content.

Although zircons are characteristically much more abundant in felsic magmas, the traditional view of the Hadean has held little place for the tectonic environments that tend to produce evolved, felsic magmas [Sleep, 2000, O'Neill and Debaille, 2014] – leading to proposals that Earth's earliest zircons may have formed either directly from a mafic protolith [Compston and Pidgeon, 1986, Kemp et al., 2010] or indirectly via processes such as the differentiation of an impact melt sheet [Darling et al., 2009, Marchi et al., 2014].

However, if the thermal evolution of the early Earth followed a trend of secular cooling as observed in the post-Hadean continental rock record [Keller and Schoene, 2012] (Chapter 2), then Hadean mafic magmas would be predicted to saturate very little zircon due to even lower average whole-rock $[Zr]$ and higher M -values. As observed in Figure 5.3a, Archean

Figure 5.3: Temporal variability in the distribution of zircon between igneous rocks of different silica contents, calculated at 6 kilobar and 3 wt. % H_2O . (a) Temporal variation in relative zircon abundance as a function of silica. (b) The mass of zircon saturated per mass of mafic magma (40-50% SiO_2) relative to that saturated in an equivalent mass of coeval felsic magma (60-70% SiO_2). The likelihood of saturating zircon in mafic lithologies was dramatically lower (by nearly factor of 5) in the earliest Archean than it was today.

mafic magmas on average saturated very little zircon per mass of whole-rock both relative to either Archean felsic rocks or post-Archean mafic rocks when crystallized to their solidus at a given set of P, H₂O conditions. This dramatic deficit in zircon saturation in Archean relative to modern magmas is observed to be equivalent to a difference of roughly 10 wt.% silica in whole-rock composition, such that, e.g., a 3-4 Ga granodiorite with 65 wt. % SiO₂ saturates only as much zircon as a 0-1 Ga basaltic andesite with 55 wt. % SiO₂ (Figure 5.3a).

Moreover, while felsic magmas in Figure 5.3a consistently saturate more zircon on average than their mafic counterparts at all times in Earth history, this relative imbalance was stronger in the Archean. Figure 5.3b illustrates the calculated average mass of zircon saturated during complete crystallization of a given mass of mafic magma (40-50% SiO₂) relative to that saturated in an equal mass of coeval felsic magma (60-70% SiO₂). As observed in Figure 5.3b, the discrepancy between mafic and felsic zircon abundance is roughly three times greater in the Archean – with Archean mafic magmas crystallizing on average little more than a tenth of the zircon mass saturated in an equal mass of coeval felsic magma when both are fully crystallized. This inequality between Archean mafic and felsic zircon abundance is exacerbated when considering magmas that do not fully crystallize, due to the greatly delayed zircon saturation of Archean mafic magmas (Figure 5.2a) – an effect that would be further compounded by the apparent prevalence of volcanic lithologies in the Archean mafic record [e.g., [de Wit and Ashwal, 1997](#)].

If Hadean mantle potential temperatures were similar to or higher than those in the early Archean, we conclude that zircon saturation was inhibited in Hadean mafic magmas by a factor similar to or greater than that observed in the early Archean, decreasing the likelihood that any given Hadean zircon originated from a mafic lithology by more than a factor of three relative to an equivalent model where systematic temporal trends in whole-rock geochemistry are neglected. This result is consistent with evidence for felsic inclusion suites and low crystallization temperatures from the Hadean zircon record [[Harrison, 2009](#)].

Together, our results emphasize the significance of the extant zircon record of early Earth history, given the comparative difficulty of saturating zircon under early Earth conditions due to lower average magma zirconium content and lower silicate magma polymerization state. Under such conditions, zircon saturation is delayed and diminished, especially in mafic lithologies. Consequently more crust is required to explain preserved zircon age spectra, and felsic crust is favored as the likely origin of the Hadean zircons which represent the oldest known terrestrial material.

5.3 Data Access

All data computational source code is available at <https://github.com/brenhinkeller/meltstzirc>

References

- Elena Belousova, Y Kostitsyn, W L Griffin, G C Begg, Suzanne Y O'Reilly, and N J Pearson. The growth of the continental crust: Constraints from zircon Hf-isotope data. *LITHOS*, 2010.
- Patrick Boehnke, E Bruce Watson, Dustin Trail, T Mark Harrison, and Axel K Schmitt. Zircon saturation re-revisited. *Chemical Geology*, 351:324–334, August 2013.
- W B Bryan. Systematics of modal phenocryst assemblages in submarine basalts: Petrologic implications. *Contributions to Mineralogy and Petrology*, 83(1-2):62–74, August 1983.
- L Caricchi, L Burlini, Peter Ulmer, and T Gerya. Non-Newtonian rheology of crystal-bearing magmas and implications for magma ascent dynamics. *Earth and Planetary Science Letters*, 2007.
- Peter A Cawood, Christopher J Hawkesworth, and B Dhuime. The continental record and the generation of continental crust. *Geological Society of America Bulletin*, 125(1-2):14–32, January 2013.
- W Compston and R T Pidgeon. Jack Hills, evidence of more very old detrital zircons in Western Australia. *Nature*, 321(6072):766–769, June 1986.
- Kent C Condie and Richard C Aster. Episodic zircon age spectra of orogenic granitoids: The supercontinent connection and continental growth. *Precambrian Research*, 180:227–236, 2010.

- Kent C Condie, Elena Belousova, W L Griffin, and Keith N Sircombe. Granitoid events in space and time: Constraints from igneous and detrital zircon age spectra. *Gondwana Research*, 15(3-4):228–242, June 2009.
- J Darling, C Storey, and C Hawkesworth. Impact melt sheet zircons and their implications for the Hadean crust. *Geology*, 37(10):927–930, October 2009.
- Maarten J de Wit and Lewis D Ashwal. Greenstone belts. Oxford University Press, 1997.
- B Dhuime, Christopher J Hawkesworth, Peter A Cawood, and C D Storey. A Change in the Geodynamics of Continental Growth 3 Billion Years Ago. *Science*, 335(6074):1334–1336, March 2012.
- GERM. Geochemical Earth Reference Model Partition Coefficient Database, January 2013. URL <http://www.earthref.org/KDD/>.
- Mark S Ghiorso, Marc M Hirschmann, Peter W Reiners, and Victor C Kress, III. The pMELTS: A revision of MELTS for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa. *Geochemistry Geophysics Geosystems*, 3(5):1–36, May 2002.
- Felix M Gradstein, James G Ogg, Mark D Schmitz, and Gabi M Ogg. *The Geologic Time Scale 2012*, volume 1-2. Elsevier B.V., 2012.
- T Mark Harrison. The Hadean Crust: Evidence from ≥ 4 Ga Zircons. *Annual Review of Earth and Planetary Sciences*, 37(1):479–505, May 2009.
- T Mark Harrison, E Bruce Watson, and Amos B Aikman. Temperature spectra of zircon crystallization in plutonic rocks. *Geology*, 35(7):635, 2007.
- P W O Hoskin. The Composition of Zircon and Igneous and Metamorphic Petrogenesis. *Reviews in Mineralogy and Geochemistry*, 53(1):27–62, January 2003.

- C Brenhin Keller and Blair Schoene. Statistical geochemistry reveals disruption in secular lithospheric evolution about 2.5Gyr ago. *Nature*, 485(7399):490–493, May 2012.
- C Brenhin Keller, Blair Schoene, Melanie Barboni, Kyle M Samperton, and Jon M Husson. Volcanic–plutonic parity and the differentiation of the continental crust. *Nature*, 523(7560):301–307, July 2015.
- A I S Kemp, Christopher J Hawkesworth, G L Foster, B A Paterson, J D Woodhead, J M Hergt, C M Gray, and M J Whitehouse. Magmatic and Crustal Differentiation History of Granitic Rocks from Hf-O Isotopes in Zircon. *Science*, 315(5814):980–983, February 2007.
- A I S Kemp, S A Wilde, Christopher J Hawkesworth, C D Coath, A Nemchin, R T Pidgeon, J D Vervoort, and S A DuFrane. Hadean crustal evolution revisited: New constraints from Pb–Hf isotope systematics of the Jack Hills zircons. *Earth and Planetary Science Letters*, 296(1-2):45–56, July 2010.
- Cin-Ty Aeolus Lee, Laurence Y Yeung, N Ryan McKenzie, Y Yokoyama, Kazumi Ozaki, and Adrian Lenardic. Two-step rise of atmospheric oxygen linked to the growth of continents. *Nature Geoscience*, 9(6):417–424, May 2016.
- S Marchi, W F Bottke, L T Elkins-Tanton, M Bierhaus, K Wuennemann, A Morbidelli, and D A Kring. Widespread mixing and burial of Earth’s Hadean crust by asteroid impacts. *Nature*, 511(7511):578–582, July 2014.
- Stephen J Mojzsis, T Mark Harrison, and Robert T Pidgeon. Oxygen-isotope evidence from ancient zircons for liquid water at the Earth’s surface 4,300 Myr ago. *Nature*, 409(6817):178–181, January 2001.
- Craig O’Neill and V Debaille. The evolution of Hadean–Eoarchaeon geodynamics. *Earth and Planetary Science Letters*, 406:49–58, November 2014.

- Kyle M Samperton, Blair Schoene, John M Cottle, C Brenhin Keller, James L Crowley, and Mark D Schmitz. Magma emplacement, differentiation and cooling in the middle crust: Integrated zircon geochronological–geochemical constraints from the Bergell Intrusion, Central Alps. *Chemical Geology*, 417:322–340, December 2015.
- Axel K Schmitt. Uranium Series Accessory Crystal Dating of Magmatic Processes. *Annual Review of Earth and Planetary Sciences*, 39(1):321–349, May 2011.
- Blair Schoene. 4.10 U–Th–Pb Geochronology. In Roberta L Rudnick, editor, *Treatise on Geochemistry*, pages 341–378. Elsevier, 2014.
- S z Shen, Jim L Crowley, Y Wang, Samuel A Bowring, D H Erwin, P M Sadler, C q Cao, D H Rothman, J Ramezani, H Zhang, Y Shen, X d Wang, W Wang, L Mu, W z Li, Y g Tang, X l Liu, L j Liu, Y Zeng, Y f Jiang, and Y g Jin. Calibrating the End-Permian Mass Extinction. *Science*, 334(6061):1367–1372, December 2011.
- Norman H Sleep. Evolution of the mode of convection within terrestrial planets. *Journal of Geophysical Research: Solid Earth*, 105(E7):17563–17578, 2000.
- Paula M Smith and Paul D Asimow. Adibat 1ph: A new public front-end to the MELTS, pMELTS, and pHMELTS models. *Geochemistry Geophysics Geosystems*, 6(1):1–8, 2005.
- E Bruce Watson and T Mark Harrison. Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types. *Earth and Planetary Science Letters*, 64(2):295–304, August 1983.
- Simon A Wilde, John W Valley, William H Peck, and Colin M Graham. Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature*, 409(6817):175–178, January 2001.

Chapter 6

Conclusion

6.1 Secular geochemical evolution

Throughout the preceding chapters, we have observed a range of the results that may be obtained from statistical analysis of large geochemical datasets, particularly via the technique (first introduced in Chapter 2) of weighted bootstrap resampling. Using this technique to obtain maximally representative compositional estimates, a first-order overview of average preserved continental igneous whole-rock geochemistry reveals two sets of clear trends in composition over the past 4 Gyr:

1) a gradual, continuous record of decreasing compatible element abundance and increasing incompatible element abundance, consistent with a greater extent of mantle melting in early Earth history, best observed in mafic lithologies; and

2) rapid, discontinuous geochemical variations across the Archean-Proterozoic boundary, best observed in felsic lithologies in the form of an Archean “TTG” signature of increased Na, Sr, Eu/Eu^* and La/Yb in Archean granitoids (Chapter 2).

While (1) is fully expected as a direct consequence of secular mantle cooling, the origin of (2) is substantially more obscure. Given the geochemical associations of the involved trace elements, we proposed in Chapter 2 that the observed trends in average felsic geochemistry

were driven by the fractionation of less plagioclase and more garnet during the process of crustal differentiation in the Archean due to differentiation at greater depth – a hypothesis which, if correct, could help explain the end-Archean atmospheric Great Oxidation Event.

These results of Chapter 2 further emphasized the importance throughout Earth history of crustal differentiation – a process which, as the source of the felsic continental crust is largely responsible for Earth’s bimodal topography and the silicate weathering feedback that maintains the stability of liquid water on billion-year timescales [Taylor, 1989, Walker et al., 1981, Caldeira, 1995]. Consequently, in order to better understand the crucial process of crustal differentiation, Chapter 3 explored in some detail the average differentiation systematics of relatively modern volcanic and plutonic magmas across a range of tectonic settings. The results emphasized the importance of fractional crystallization (as opposed to partial melting) as a mechanism of crustal differentiation, but found the abundance of plutonic cumulates preserved in the continental crust severely lacking. As a result, supported by a range of experimental, thermal, and mass-balance considerations (Section 3.5) along with suggestive MELTS pressure-temperature path inversions (Section 3.6.1), we proposed differentiation by fractional crystallization at the base of thick arc crust (followed by delamination of ultramafic cumulates) as the dominant mechanism and setting of crustal differentiation. Additional consequences of the apparent dearth of plutonic cumulates included the rehabilitation of felsic plutonic rocks as broadly representative of solidified magmas; indeed, in arc settings, no substantial deviation between average volcanic and plutonic whole-rock compositions is observed above 50% SiO₂. Deviations between felsic volcanic and plutonic whole-rock compositions where they are observed in rift settings are better attributed to differences in water content, with wet magmas more likely to stall upon decompression due to devolatilization.

Crustal differentiation driven by fractional crystallization is consistent in principle with the hypothesis of increased garnet fractionation and decreased plagioclase fractionation in the Archean. However, the picture of Phanerozoic crustal differentiation presented in Chapter 3

of deep crustal differentiation at the base of thick continental crust, with residues removed by delamination, is remarkably similar to that proposed for the Archean in Chapter 2. If correct, this consistency in the setting of crustal differentiation would substantially limit the degrees of freedom available to explain a wide variety of discontinuous geochemical trends observed at the end of the Archean (e.g., Figures 2.1f-g, 2.2).

One diverse category of explanations for abrupt geochemical changes across the Archean-Proterozoic boundary invokes a change in the occurrence or style of plate tectonics. This possibility is examined in more depth in Chapter 4, which focuses on the continental basaltic record as the direct product of tectonically-driven mantle melting. In this chapter, a wide range of rapid variations in mafic trace element geochemistry (Figure 4.7) are observed to coincide with the onset of the felsic Archean TTG signature from Chapter 2. However, no change is observed in either major or trace element records of slab fluid input (Figure 4.8), requiring roughly constant proportions of flux and decompression magmatism, and thus the continuous occurrence of largely modern-style subduction magmatism. Moreover, despite the necessarily gradual nature of secular mantle cooling, we observed in Section 4.5 that even abrupt trace element signatures in the mafic record may arise from a smooth decrease in mantle potential temperature when considering the effects of mantle mineral stability thresholds (e.g., Figures 4.9-4.10).

6.2 Crustal differentiation

Having established that subduction magmatism was likely operative in the Archean, and largely explicated the geochemical variations in primary (i.e., igneous, mantle-derived) continental basalts as a consequence of secular mantle cooling, we are left to satisfactorily explain the TTG signature of Archean granitoids as a function of differentiation. If Archean granitoids were largely derived by fractional crystallization (as modern granitoids appear to be, following Chapter 3), granitoids throughout earth history should be largely derived from

Figure 6.1: Temporal variation in the enrichment of plagioclase-associated major and trace elements during differentiation from average basaltic (43-51% SiO₂) to granitic (62-74% SiO₂) whole-rock compositions.

Figure 6.2: Temporal variation in the enrichment of garnet-associated trace elements during differentiation from average basaltic (43-51% SiO₂) to granitic (62-74% SiO₂) whole-rock compositions.

Figure 6.3: Mineral/melt partition coefficients for a range of key trace elements and rock-forming minerals from the GERM partition coefficient database [GERM, 2013], interpolated for 65% SiO_2 melt compositions.

essentially coeval basalts. On timescales coarser than the (rapid, $\lesssim 10$ Myr) timescales of fractional crystallization, we may then examine the extent to which different elements are enriched or depleted during differentiation by simply dividing average granitic and basaltic compositions. A systematic examination of temporal trends in elemental differentiation via this method reveals clear, temporally coincident discontinuities at the end of the Archean in the enrichment of a wide range of major and trace elements related to plagioclase (Figure 6.1) and garnet (Figure 6.2). As illustrated in Figure 6.1, elements such as Na_2O , Sr, Eu, and Al_2O_3 that are abundant in plagioclase feldspar are all more strongly enriched during differentiation in the Archean, suggesting a relative dearth of Archean plagioclase fractionation. Meanwhile, signatures of garnet fractionation (La/Yb, Sm/Yb enrichment, Lu depletion; Figure 6.1) are all enhanced in the Archean.

Moreover, a discontinuity in enrichment level is not a general feature of the Archean-Proterozoic boundary for all elements, but rather appears specific to major and trace elements associated with either garnet or plagioclase. For instance, as demonstrated in Figure 6.4, the enrichment level of the highly incompatible alkali metals Rb and K_2O is essen-

Figure 6.4: Temporal variation in the extent of incompatible element enrichment during differentiation from average basaltic (43-51% SiO_2) to granitic (62-74% SiO_2) whole-rock compositions.

Figure 6.5: Temporal variation in the enrichment of saturation-limited minor elements during differentiation from average basaltic (43-51% SiO_2) to granitic (62-74% SiO_2) whole-rock compositions.

tially constant throughout Earth history, suggesting no major change in the abundance of K-hosting minerals such as orthoclase and biotite during differentiation. In contrast to Rb and K_2O , the extent of Ba enrichment has decreased significantly through time. Considering the mineral/melt partition coefficients of relevant major phases (Figure 6.3), this may reflect either diminished fractionation of Albite plagioclase in the Archean, or (given the higher mineral/melt compatibility of Ba relative to Rb in silicate minerals other than olivine) the generally delayed saturation of complex silicates due to greater past mantle melting extents.

Figure 6.6: Average Phanerozoic, Proterozoic, and Archean differentiation trends as a function of SiO_2 for saturation-limited (a-c) and other incompatible (d-f) elements.

A range of other mineral-specific minor and trace elements show distinct temporal trends in enrichment level, but (like Rb and K_2O) absent any discontinuity at the Archean-Proterozoic boundary. Specifically, the elements Zr, TiO_2 , and P_2O_5 all show generally decreasing levels of differentiative enrichment since the early Archean. These elements share a set of notable petrologic properties, in that all are incompatible during mantle melting but sufficiently abundant that they are able to saturate their own accessory mineral phase in sufficiently differentiated magmas: zircon for Zr, rutile or sphene for TiO_2 , and apatite for P_2O_5 . As such, their abundance in felsic magmas is limited by saturation, while their abundance in mafic magmas is controlled by the extent of mantle melting; the greater extent of enrichment during Archean differentiation thus likely reflects their lower abundance prior to differentiation in high melt-fraction Archean mafic magmas.

Examination of average differentiation trends as a function of SiO_2 for the Phanerozoic, Proterozoic, and Archean (Figure 6.6a-c) broadly confirms this proposal. Abundances of each element increase markedly as a function of time widely at low SiO_2 , before plateauing or converging at high silica. Meanwhile, as suspected from Figure 6.4 above, differentiation trends as a function of SiO_2 for Rb and K_2O (Figure 6.6d-e) confirm that there has been no substantial change in the differentiation systematics of these elements from the Archean to the present, with roughly parallel differentiation trends offset (as expected for incompatible elements) to lower concentrations in the Archean by higher mantle melting extents.

Analogous differentiation trends for plagioclase-associated (Figure 6.7) and garnet-associated (Figure 6.8) elements *do* show major changes in differentiation trend between the Archean and the Proterozoic, providing some mechanistic insight into the temporal trends observed in Figures 6.1-6.2. In the Phanerozoic, the onset of plagioclase fractionation is likely responsible for the decrease in Sr and Al_2O_3 abundance circa $\sim 55\%$ SiO_2 , as well as the coincident plateau in Na_2O (Figure 6.7). In the Archean, this does not happen until above 65% SiO_2 , suggesting that plagioclase saturation during magmatic differentiation was greatly delayed in the Archean. Accordingly, average Archean and post-Archean Eu/Eu^*

Figure 6.7: Average Phanerozoic, Proterozoic, and Archean differentiation trends as a function of SiO_2 for plagioclase-associated major and trace elements. Eu / Eu^* reflects europium abundance relative to expected europium abundance if all Eu were trivalent, as interpolated from the chondrite-normalized abundance of adjacent rare-earth elements Sm and Gd.

differentiation trends diverge above 55% SiO₂ as seen in Figure 6.7d, with essentially constant Archean Eu/Eu* between 55-70% SiO₂ suggesting limited fractionation of feldspar within this silica range.

In theory, delayed plagioclase saturation during magmatic differentiation could be attributed to either increased magmatic water content or increased pressure [Yoder, 1965, Green and Hibberson, 1970, Goldsmith, 1980]. However, in practice the former may require the latter, as arc magmas appear to be frequently water-saturated during differentiation at present (Chapter 3). Since the average water content of continental basaltic magmas does not appear to have changed substantially throughout the preserved rock record (Chapter 4), a change in depth is likely the efficient cause of any changes in plagioclase stability during magmatic differentiation, both directly and via greater magmatic water solubility at depth. In this context, the abundance of plagioclase in Archean mafic rocks may be taken to suggest that the average depth of differentiation was much greater than the depth of emplacement for such lithologies.

Over the same silica range (55-65% SiO₂) where plagioclase fractionation appears to be suppressed, Archean differentiation trends display distinct evidence of garnet fractionation (Figure 6.8). Light/heavy rare earth ratios (La/Yb, La/Sm, Sm/Yb) increase far more rapidly during differentiation over this silica range in the Archean than in any later time period. This signature includes depletion of heavy rare earth elements both in absolute terms (Lu; Figure 6.8c) and relative to the middle rare earth elements (Sm/Yb; 6.8d), a signature unique to garnet among major rock-forming minerals (Figure 6.3). While it may appear fortuitous that plagioclase suppression and enhanced garnet fractionation during Archean differentiation should occur over the same silica range (55-65% SiO₂), this correlation is likely not coincidental: as the dominant Al-bearing major silicate phases at magmatic temperatures, garnet and plagioclase are stoichiometrically related in many metamorphic reactions; in this context, increased Al availability from plagioclase suppression directly promotes gar-

Figure 6.8: Average Phanerozoic, Proterozoic, and Archean differentiation trends as a function of SiO_2 for garnet-related trace elements.

net stability via Le Chatelier's principle, compounding the direct effect of pressure to promote garnet growth.

In light of the foregoing evidence, I find little recourse but to conclude that crustal differentiation occurred at greater pressure in the Archean. Given the abrupt onset of this apparent high-pressure differentiation signature at the Archean-Proterozoic boundary (Figures 6.1-6.2), one may be led to suspect an entirely different mechanism or setting of crustal differentiation in the Archean. Indeed, crustal differentiation by high-pressure partial melting of subducting slabs of oceanic crust [Drummond and Defant \[1990\]](#) or the base of a thick

Figure 6.9: Two-dimensional histogram of the number of whole-rock analyses in the Earth-Chem database as a function of age and silica content. To illustrate relative abundance as a function of silica content, the histogram for each time step is normalized.

Figure 6.10: Histograms of the number of whole-rock analyses in the EarthChem database from active (a) and accreted (b) arc terranes. Silica distribution of melt inclusions in active arcs from [Reubi and Blundy, 2009] is overlain in blue in (a)

mafic crust [Barker and Arth, 1976] has long been proposed to explain the unique characteristics of Archean granitoids, with the bimodal silica distribution of Archean granite-greenstone terrains held to be emblematic of differentiation by partial melting [e.g., Barker and Arth, 1976, Hawkesworth et al., 2016].

However, a systematic examination of crustal silica distribution through time (Figure 6.9) reveals that such a bimodal silica distribution (the crustal Daly Gap) is by no means unique to the Archean, but rather first appears in the Phanerozoic, for all crust older than ~ 250 Ma. While the crustal Daly Gap is absent in samples collected at the surface of active arcs, it becomes readily apparent both in melt inclusions entrapped at depth in active arcs [Reubi and Blundy, 2009] and in accreted arc terranes (Figure 6.10). Considering this, it

Figure 6.11: Average Phanerozoic, Proterozoic, and Archean differentiation trends as a function of SiO₂ for MgO (a) and Cr₂O₃ (b), showing pronounced curvature throughout differentiation for all time periods.

appears more likely that the lack of a substantial Daly gap in the youngest crustal record reflects exposure level bias, a hypothesis notably consistent with the P-SiO₂ inversion results of Figure 3.14.

Moreover, following the approach of Chapter 3.5, the curvature of observed average crustal differentiation trends (e.g., Figure 6.7a-b, 6.11) would seem to require that fractional crystallization was the predominant mechanism of differentiation in the Archean – apparently ruling out slab melting. Confounding the issue, mantle melting pressure for continental basalts appears to have decreased through time, (Chapter 4.4.2) further constraining the depth at which differentiation can occur. Together, suggestions for deeper crustal differentiation and shallower mantle melting lead towards a narrow critical process zone near the base of the crust.

Considering the range of above constraints, we appear to be led back towards a largely uniformitarian model where fractional crystallization at or near the base of thick arc crust is the predominant mechanism of crustal differentiation throughout the entire preserved rock record. If correct, this would leave only two potential explanations for the greater depth of differentiation in the Archean: (1) thicker arc crust or (2) melt ponding and fractional

crystallization in the shallow arc mantle. The first option (1) would run counter to traditional (but perhaps unfounded) notions that the Archean crust was too weak to support high topography, but would be consistent with the notion of crustal thickness correlating with mantle melting extent as discussed originally in Chapter 2. Absent an abrupt change in crustal thickness, this approach would require average arc crustal thickness to cross an abrupt threshold in plagioclase and garnet stability to explain the rapid changes in differentiation systematics observed at the Archean-Proterozoic boundary. A catalytic delamination mechanism as proposed in Chapter 2 might still be invoked, but may be severely limited by the observations of Chapter 4 that indicate a constant ratio of flux to decompression melting. The second option (2) would have to overcome the density contrast between differentiating magmas and mantle peridotite in order to stall the ascending magmas long enough to differentiate, a task that may be made easier by the presence of a lighter, stronger Archean mantle lithosphere. However, the role of mantle lithosphere in arc settings is notoriously nebulous even at present, hindering the evaluation of this hypothesis.

Attempts to place the mantle melting pressure trends of Figure 4.5 and the crustal differentiation pressure trends suggested by Figures 6.1-6.8 in a quantitative framework through comparison to simulations and experiments may allow us to distinguish between differentiation at the base of thick arc crust versus thin arc mantle lithosphere. Better estimation of Archean crustal rheology given reevaluated data for Archean crustal composition and crustal heat production may also help test the proposal of thick Archean arc crust. Examination of correlations between preserved crustal thickness and apparent differentiative enrichment may provide additional insight, though complicated by orogeny, rifting, erosion, and delamination. In this area, much work remains to be done.

6.3 A stable Earth system

While indirect, the observation from Chapter 4 that a mantle melting curve derived from major element systematics can accurately predict the evolution of highly incompatible trace elements in basalts with a constant mantle composition (e.g., Figure 4.10) provides some tentative support for a roughly constant crustal volume throughout the preserved continental record. Since the continental crust is estimated to contain roughly half the terrestrial budget of highly incompatible trace elements [Rudnick and Fountain, 1995] but less than 0.4% of Earth's major element budget, crustal growth over the past 4 Ga could cause dramatic mantle trace element depletion with almost no corresponding change in mantle major element composition. In the event of crustal growth since 4 Ga, major-element based mantle melting curves (e.g., Figure 4.6) when combined with a constant primitive mantle composition could therefore result in model basaltic trace element abundances that over-predict the true abundances of highly incompatible elements such as Zr and Sr in young basalts by up to a factor of two – which is not observed (Figure 4.10b-c).

Since the continental basaltic record appears to predominantly sample arc basalts, which derive their trace elements not only from the mantle but also from the subducted slab via slab fluids, the results in Figure 4.10 cannot provide absolute constraints on the extent of mantle depletion. However, the influence of slab fluids will be minimized for highly fluid-immobile incompatible elements such as Zr and Nb, where still no systematic deviation from the constant mantle composition model is observed over the past 4 Ga.

The results of Chapter 5 similarly suggest that the volume of felsic crust on the early Earth may have been systematically underestimated since the Hadean, with potentially steady-state supercontinent-cycle peaks in magmatism back to at least 3 Ga (Figure 5.1). Steady-state crustal volume would not be entirely surprising in the context of ongoing subduction since the earliest Archean, since modern-day plate tectonics appears to produce little or no net crustal growth [von Huene and Scholl, 1991], consistent with a recycling-dominated crustal growth curve such as that of Armstrong and Harmon [1981] or Warren [1989]. Rather, in

a plate tectonic system, constant crustal volume may be maintained by negative feedback: for a constant global ridge length, increasing crustal volume drives continental arcs closer to spreading ridges, leading to subduction of younger oceanic crust and concomitantly higher average subduction erosion at the global scale.

Additional insight into the long-term dynamics of the terrestrial tectonic system may be obtained from the observed mantle cooling trend. Mantle thermal models suggest that concave-down mantle temperature trends may occur as a result of strong negative feedbacks limiting mantle convection and oceanic spreading rates at high mantle potential temperature, driven by, e.g., the flexural resistance of dehydrated oceanic mantle lithosphere [Korenaga, 2008]. In the absence of such a feedback, the mantle cooling trend may revert to a concave-up asymptotic form, driven by primordial heat loss and the exponential decay of radiogenic heat production. Given the numerous uncertainties involved in the production of our apparent mantle temperature record, any observations derived from the form of this curve should be considered suggestive at best. However, it has not escaped notice that the apparent record from Figure 4.6 does appear to display concave-down curvature in the Archean.

The observed trend (Figure 4.6) is intermediate between the endmember models of Davies [2009] and Korenaga [2008] in both absolute value and curvature. Such a trend is consistent with the operation a stabilizing negative feedback on oceanic spreading rate, though perhaps not as strong as that of Korenaga [2008]. A transition from concave-down to concave-up mantle cooling is characteristic of such hybrid models, denoting the time at which standard thermal constraints overtake the tectonic negative feedback as the rate-limiting variable [Davies, 2009].

Since greater mantle heat flux is readily dissipated by either greater total mid-ocean ridge length or faster spreading rate, the existence of a negative feedback limiting the rate of subduction would seem to favor greater ridge length as the mechanism for accommodating greater mantle heat flux on the early Earth – consistent with the predictions of Hargraves [1986]. This greater ridge length (and thus greater arc length) could be accommodated

through more extensive oceanic arcs, or (as suggested by Hargraves) a large number of smaller continents, which have higher perimeter-to-surface-area ratios. However, if increased ridge length were accommodated by increasing oceanic arc length rather than by increasing continental perimeter, this would help to offset the presumable increase in subduction-erosion driven by greater plate bending resistance in the Archean, increasing the proportion of potentially crust-producing oceanic arcs relative to crust-consuming continental arcs.

If such observations are valid, we are tentatively led towards a model in which a system of negative feedbacks stabilizes the operation of plate tectonics over Ga timescales despite substantial mantle cooling, helping to reconcile indications of a remarkably modern-looking early Earth [Harrison, 2009] with high mantle potential temperatures shortly after Earth accretion. The existence of such feedback mechanisms would not be surprising *a priori*, since negative feedbacks are crucial to the persistence of a dynamic system on billion-year timescales. In this context, the stabilizing feedback mechanisms that maintain the operation of plate tectonics over Gyr timescales may join the silicate weathering feedback [Walker et al., 1981] among the processes that maintain the habitability of Earth over geologic time.

References

- Richard Lee Armstrong and R S Harmon. Radiogenic Isotopes: The Case for Crustal Recycling on a Near-Steady-State No-Continental-Growth Earth [and Discussion]. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 301(1461):443–472, May 1981.
- Fred Barker and Joseph G Arth. Generation of trondhjemitic-tonalitic liquids and Archean bimodal trondhjemite-basalt suites. *Geology*, 1976.
- Ken Caldeira. Long-term control of atmospheric carbon dioxide; low-temperature seafloor alteration or terrestrial silicate-rock weathering? *American Journal of Science*, 295:1077–1114, 1995.
- Geoffrey F Davies. Effect of plate bending on the Urey ratio and the thermal evolution of the mantle. *Earth and Planetary Science Letters*, 287(3-4):513–518, October 2009.
- Mark S Drummond and Marc J Defant. A model for trondhjemite-tonalite-dacite genesis and crustal growth via slab melting: Archean to modern comparisons. *Journal of Geophysical Research*, 95(B13):21503–21521, December 1990.
- GERM. Geochemical Earth Reference Model Partition Coefficient Database, January 2013. URL <http://www.earthref.org/KDD/>.
- J R Goldsmith. The melting and breakdown reactions of anorthite at high pressures and temperatures. *American Mineralogist*, 65(3-4):272–284, April 1980.

- D H Green and W Hibberson. The instability of plagioclase in peridotite at high pressure. *LITHOS*, 3(3):209–221, January 1970.
- R B Hargraves. Faster spreading or greater ridge length in the Archean? *Geology*, 14(9):750–752, 1986.
- T Mark Harrison. The Hadean Crust: Evidence from ~ 4 Ga Zircons. *Annual Review of Earth and Planetary Sciences*, 37(1):479–505, May 2009.
- Christopher J Hawkesworth, Peter A Cawood, and B Dhuime. Tectonics and crustal evolution. *GSA Today*, 2016.
- Jun Korenaga. Plate tectonics, flood basalts and the evolution of Earth’s oceans. *Terra Nova*, 2008.
- Olivier Reubi and Jonathan D Blundy. A dearth of intermediate melts at subduction zone volcanoes and the petrogenesis of arc andesites. *Nature*, 461(7268):1269–1273, October 2009.
- Roberta L Rudnick and David M Fountain. Nature and composition of the continental crust: A lower crustal perspective. *Reviews of Geophysics*, 33(3):267–309, August 1995.
- Stuart Ross Taylor. Growth of planetary crusts. *Tectonophysics*, 161:147–156, 1989.
- Roland von Huene and David W Scholl. Observations at convergent margins concerning sediment subduction, subduction erosion, and the growth of continental crust. *Reviews of Geophysics*, 1991.
- James C G Walker, P B Hays, and J F Kasting. A negative feedback mechanism for the long-term stabilization of Earth’s surface temperature. *Journal of Geophysical Research*, 86(C10):9776–9782, 1981.
- Paul H Warren. Growth of the continental crust: a planetary-mantle perspective. *Tectonophysics*, 161(3-4):165–199, April 1989.

- H S Yoder, Jr. Diopside-Anorthite-Water at Five and Ten Kilobars and Its Bearing on Explosive Volcanism. *Year Book of the Carnegie Institution of Washington*, 64:82-89, 1965.