

PETROLOGIC IMPLICATIONS FROM THE CHEMISTRY OF OLIVINE

PHENOCRYSTS

by

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Abstract of the Dissertation

Petrologic Implications from the Chemistry of Olivine Phenocrysts

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Source lithology of mantle plumes and other volcanic sources has been inferred from isotopic data for decades, however these studies cannot determine if the geochemical signature of pyroxenitic source is due to the presence of a pyroxenite, or if the geochemical signature had been imprinted upon peridotite by some metasomatic process (e.g. refertilization). Mn, Ca and Ni concentrations in olivines are used to infer the source lithology of primitive basalts. Secular cooling of the Galápagos hotspot has been established by petrologic modeling. An increase in the entrainment of relatively dense pyroxenite in the Galápagos plume over time may explain this trend in decreasing T_p with time, as pyroxenite entrainment would have a negative effect on the buoyancy of the plume. Analyses of olivines from Curacao indicates that pyroxenite was absent in the source of these Cretaceous age Galápagos plume lavas. Magmatism preserved at Quepos marks the transition of the Galápagos plume from the head (LIP) stage to the tail (hotspot track) stage. Major and trace element analyses of Quepos samples show a geochemical signal of a pyroxenite. The presence of pyroxenite as a distinct lithology in the source of these lavas is confirmed by olivine analyses. The extreme enrichment of radiogenic lead found in the lavas of Mangaia have long been interpreted as reflecting a component of ancient recycled crust and is representative of the isotopic endmember HIMU. Olivine

analyses of samples from Mangaia indicate that the source of these lavas is predominantly peridotite. If the source of Mangaia had a substantial pyroxenitic component, as inferred from isotopic data, then it is likely that it had its lithological identity destroyed. This may have been the result of the refertilization of mantle peridotite by the injection of silicic, pyroxenite source melt. Ni excess observed in the chemistry of olivines from various LIPs and hotspots contrast their Mn and Ca concentrations which are indicative of a peridotite source. High $^3\text{He}/^4\text{He}$ found in samples for which He analysis has been done, suggest a deep lower mantle source. The Ni excess may be due to the interaction between the lower mantle and the core.

Preface

The use of olivine trace element chemistry to infer source lithology first applied by Sobolev et al., 2005, constitutes the bulk of my PhD thesis work. This work as well as my masters thesis show that forward and inverse modeling of olivine chemistry is not only crucial for inferences of source lithology to be made, but also allows for the determination of magma chamber processes other than olivine crystallization (e.g. co-crystallization of other mineral phases, magma recharge and mixing). Below are summaries of my contributions to the 4 chapters of this dissertation as well as the contributions of other researchers.

Chapter 1:

This chapter is based on my modeling and interpretations of high precision EPMA olivine analyses I performed on samples from Curacao using the JXA-8200 superprobe at Rutgers University. These data were obtained from Curacao samples provided by A. Kerr from Cardiff University. Initial modeling of the pyroxenite primary magma was done by C. Herzberg and I performed all of the remaining petrologic modeling. I am responsible for the interpretations and the writing of this text. Although it may not be published in a journal in this form, this work is expected to constitute part of an article in collaboration with E. Gazel and J. Trela at Virginia Tech, to be submitted for publication in late 2014 or early 2015.

Chapter 2:

The study of the accreted terranes at Quepos was made possible by the acquisition of samples by E. Gazel. I performed analyses of olivines from these samples on the JXA-8200 superprobe at Rutgers University. Thin sections of eight Quepos picrites were provided by E. Gazel, while I made the remaining 2 thin sections from chips supplied by E. Gazel. The initial modeling of the pyroxenite source primary magmas was done by C. Herzberg and I did all of the remaining petrologic modeling presented in the appendix. Interpretations and the writing of the appendix is my work. The bulk of the chapter was written by J. Trela at Virginia Tech. I also contributed to the writing of the body of the manuscript. Ar ages discussed in the chapter were obtained by B. Jicha at the University of Wisconsin-Madison. Pb, Nd and Sr isotopic measurements were performed by M. Bezimis at the University of South Carolina. All of the co-authors had intellectual input to the manuscript. Chapter 2 will be submitted to Earth and Planetary Science Letters for publication in 2014 with J. Trela as the first author.

Chapter 3:

Samples from Mangaia were provided by M. Jackson and R. Cabral. Olivine analyses were performed by R. Cabral and me on the JXA-8200 superprobe at Rutgers University. I was the author of the paragraphs on the analytical method in section 2 of this chapter. C. Herzberg was the first author of this manuscript. All of the co-authors had intellectual input to this manuscript. This chapter was originally published in Earth and Planetary Science letters.

Herzberg, C., R.A. Cabral, M.G. Jackson, C. Vidito, J.M.D. Day and E.H. Hauri, (2014), Phantom Archean crust in Mangaia hotspot lavas and the meaning of

heterogeneous mantle: Earth and Planetary Science Letters, v. 396, no. 0, p. 97-106.

Chapter 4:

My contribution to this chapter consists of olivine analyses of Fernandina sample D-38 which were performed on the JXA-8200 at Rutgers University. This sample was obtained from D. Geist at the University of Idaho. I authored the section of the analytical method for measurements of sample D-38 in the Supplemental Material. C. Herzberg was the first author of this manuscript. All of the co-authors had intellectual input to this manuscript. This chapter was originally published in Nature.

Herzberg, C., P.D. Asimow, D.A. Ionov, C. Vidito, M.G. Jackson and D. Geist, (2013), Nickel and helium evidence for melt above the core-mantle boundary: Nature, v. 493, no. 7432, p. 393-398.

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First and foremost I would like to acknowledge my primary advisor Claude Herzberg. When Claude first approached me with the opportunity to work with him on the Galápagos project, I was in a position in which I did not know what I was going to do after my undergraduate degree. The opportunity to do extensive EPMA work in addition to doing a project in petrology immediately piqued my interest. However, given that I literally had no research experience the learning curve was very steep. Claude remained encouraging despite the numerous ups and downs I experienced over the last 5 years. I do not know if I would have made it this far had it not been for his optimism, extensive knowledge and confidence in me.

Esteban Gazel has been a collaborator of mine since the beginning and has always been willing to help me despite the fact that he is at a different college. The introduction he gave me to LA-ICP-MS not only expanded my analytical repertoire, but also gave me ideas to improve my EPMA analytical protocols.

The department turned to me when the need for a EPMA manager was needed. The opportunity given to me allowed me to expand my abilities, as the position required me to work with both internal and external users who worked on geologic problems very different than mine. The experience of managing this lab as well as the petrologic lab gave me experience beyond my own work which is invaluable to my CV. I am especially appreciative that the department allowed me to basically take over a room with petrographic equipment and set up a sample prep lab.

My research and working experience would have been far more difficult had it not been for the assistance of Jovani Reaves, Tonya Rufus and Danielle Parenti. It seemed like nearly every week I would contact them with a new problem I was having with the management of the lab and every time they provided me with what I needed. From the beginning of my time at Rutgers I have relied on my office mate Fara Lindsay and Jeremy Delaney for technical assistance. I will always be grateful for their willingness to discuss any given problem I was having.

Table of Contents	Page
Abstract of the Dissertation	ii
Preface	iv
Acknowledgments	vii
Table of Contents	ix
List of Figures	xiii
List of Tables	xvii

Chapter 1: Source Lithology of Cretaceous Picrites from the Caribbean

Large Igneous Province

Abstract	1
1. Introduction	1
2. Geologic Background	3
2.1. General CLIP	3
2.2. Curacao	6
3. Methods	8
3.1. Analytical Methods	8
3.2. Computational Methods	8
4. Results	9
5. Discussion	14
6. Conclusion	17
7. References	18
8. Figure Captions	26
9. Figures	30

10. Tables	38
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Chapter 2: A pyroxenite source in the Galapagos Plume at 70 Ma:

Implications for plume evolution

Abstract	49
1. Introduction	50
2. Geologic Background	52
3. Methods	56
4. Results	58
5. Discussion	60
6. Conclusions	64
7. References	65
8. Figure Captions	70
9. Figures	72
S.1. Supplementary Materials	78
S.1.1. Modeling	78
S.2.2. Results	80
S.2. References	82
S.3. Figure Captions	84
S.4. Figures	86

Chapter 3: Phantom Archean crust in Mangaia hotspot lavas and the meaning of heterogeneous mantle

Abstract	89
1. Introduction	90

2.	Samples, Analytical Methods and Results	92
3.	Petrologic Modeling	95
3.1.	Mangaia Primary Magma Composition	96
3.2.	Liquid Line of Descent (LLD)	97
3.3.	Olivines on the Liquid Line of Descent (OLLD)	98
3.4.	Comparison of model and observed olivine compositions	98
4.	Model Results and Evidence for Peridotite in the Mantle Source for Mangaia	98
5.	Evidence for Refertilized Peridotite in the Mantle Source for Mangaia	100
6.	Evidence for Pyroxenite in the Mantle Source for Mangaia	106
7.	Phantom, Fugitive and Possibly Stealth Recycled Crust as Recorded in Olivine Chemistry	107
8.	Conclusions	110
9.	Acknowledgements	111
10.	References	111
11.	Figure Captions	116
12.	Figures	120
13.	Tables	126
S.1.	Supplimentary Information	127
Chapter 4: Nickel and helium evidence for melt above the core–mantle boundary		
1.	Introduction	140
2.	Results	141

3.	Methods Summary	150
4.	References	151
	Figure Captions	154
6.	Figures	157
	Supplimentary Information	
S.1.	The Ni Content of Mantle Peridotite and Its Primary Magmas	160
S.2.	High Precision Olivine Analyses in Peridotite	161
S.3.	The Effects of Temperature, Pressure and Composition on the Partitioning of Ni between Olivine and Liquid	162
S.4.	Forward Models of Liquid Lines of Descent Involving Olivine and Clinopyroxene	166
S.5.	Phenocrysts from Isla Gorgona, Ontong Java Plateau and Fernandina	174
S.6.	Examples of Peridotite and Pyroxenite Source Lithologies Inferred from Olivine Phenocryst Composition	175
S.7.	References	176
S.8.	Figure Captions	180
S.9.	Figures	183
S.10.	Tables	195

List of Figures:

Chapter 1:

Figure 1: Map of the subareal exposures of Galapagos Hotspot tracks and the Caribbean Large Igneous Province	30
Figure 2: ITE ratios and T_p from the CLIP and present day Galapagos hotspot	31
Figure 3: Peridotite source modeling and the Curacao olivine data	32
Figure 4: Curacao Ca and Ni olivine data compared to modeled derivative magmas of various hybrid sources	33
Figure 5: AFC model compared to the olivine chemistry of Curacao	34
Figure 6: Magma mixing models compared to the olivine chemistry of Curacao	34
Figure 7: LLDs modeled from magma mixtures compared to hybrid models	35
Figure 8: Six cycles of magma fractionation followed by recharge in a system approaching a steady state	36
Figure 9: Progressive magma mixing models in which the degree of fractional crystallization is varied	37

Chapter 2:

Figure 1: Tectonic location of the study area	72
Figure 2: A) Chemical classification of samples using the total alkali versus silica diagram (TAS). B) CaO-MgO discrimination diagram between peridotite and pyroxenite derived magmas from Herzberg and Asimow (2008).	73
Figure 3: Multi-element spider diagram normalized to pyrolite mantle.	74

Figure 4: High-precision olivine composition from picrites of the Quepos terrane plotted in the Herzberg (2010) discrimination diagram	75
Figure 5: Age corrected Pb and Nd isotopes of picrite and basalt samples from the Quepos terrane	76
Figure 6: Galapagos plume secular cooling curve modified from Herzberg and Gazel, (2009)	77
Figure S1: Modeled olivine and derivative liquid compositions for Quepos	86
Figure S2: Olivine compositions of ten lavas from Quepos compared to modeled peridotite and pyroxenite source magmas	87
Figure S3: Modeling of mixtures of the peridotite and pyroxenite endmembers to estimate the proportion of pyroxenite in the source of Quepos	88

Chapter 3:

Figure 1: Mg-numbers versus Ni and Ca contents and Fe/Mn for calculated (Herzberg, 2011) and observed olivine	120
Figure 2: A model for fractional crystallization of a Mangaia primary magma, recharge and mixing in a magma chamber at 0.2 GPa	121
Figure 3: A model of olivine compositions that crystallize from primary magmas of peridotite that has been fertilized by variable addition of a dacite melt, and olivines that crystallize along a liquid line of descent (OLLD) at 0.2 GPa	122
Figure 4: A model of olivine compositions that crystallize from primary magmas of peridotite that has been fertilized by variable addition of a dacite melt, from Fig. 3, compared with selected observed olivines from the Canary Islands (Gurenko et al., 2009)	123

Figure 5: Olivines from Mangaia sample MG-1006 compared with model olivines 124
of a peridotite source, from Fig. 1

Figure 6: Summary of Ca contents and Mg-numbers for all measured Mangaia 125
olivine phenocrysts compared with olivines expected to crystallize from primary
magmas of a peridotite source that had variable amounts of dacite added, from
Fig. 3

Chapter 4:

Figure 1: Mg-numbers and Ni content for calculated (Herzberg, 2011) and 157
observed olivine

Figure 2: Mg-numbers and Ca, Mn and Fe/Mn contents for calculated (Herzberg, 158
2011) and observed olivine phenocrysts from MORBs (right panels) compared
with Baffin Island and West Greenland (Sobolev et al., 2007) (left panels)

Figure 3: Mg-numbers and Ni contents for calculated olivine (Herzberg, 2011) 159
and observed olivine phenocrysts

Figure S1: MgO and Ni contents of mantle peridotite and partial melts of mantle 183
peridotite (Herzberg, 2011)

Figure S2: A comparison of model and experimentally observed partition 184
coefficients for nickel

Figure S3: Measured versus calculated $D_{\text{NiO}}^{\text{Ol/L}}$ for equation (3) of Beattie et al. 185
(1991) and equations 7a,b,c of Putirka et al. (2011)

Figure S4: Measured versus calculated $D_{\text{NiO}}^{\text{Ol/L}}$ for equation (8) of Niu et al. 186
(2011).

Figure S5: Partition coefficients determined for clinopyroxene/liquid (blue 187
squares) and garnet/liquid (red circles) from experimental data listed in the text

Figure S6: Mg-numbers and Ni, Ca, Mn, and Fe/Mn for calculated olivine 188
(Herzberg, 2011) and observed olivine phenocrysts from Gorgona komatiites and
basalts from the Ontong Java Plateau (Sobolev et al., 2007)

Figure S7: Mg-numbers and Ni, Ca, Mn, and Fe/Mn for calculated olivine 189
(Herzberg, 2011) and observed olivine phenocrysts from a submarine sample
D38A from Fernandina in the Galapagos Islands (Table S1)

Figure S8: A comparison of olivine phenocryst compositions for Hawaii, West 190
Greenland, Baffin Island and Disko Island

Figure S9: A comparison of olivine phenocryst compositions for Hawaii and 191
Alexo komatiites of Archean age

Figure S10: Olivine phenocryst compositions from the Mexican Volcanic Belt 192
(Straub et al., 2008)

Figure S11: Olivine phenocryst compositions from the Komati Formation of the 193
Barberton greenstone belt compared with olivines expected to crystallize from
primary magmas of dry fertile peridotite (black form; 3.45% CaO)

Figure S12: Ca contents of olivine in experimental melts with various H₂O 194
contents

List of Tables:

Chapter 1:

Table 1: Secondary Standards, Primary Standards and Statistics	38
Table 2: Curacao Olivine Data	39
Table 3: Curacao Whole Rock and Calculated Primary Magma Compositions	44
Table 4: PRIMELT2 Primary Magmas and Trace Element Ratios for Figure 3	45

Chapter 3:

Table 1: Olivine/Liquid Ni Partition (D) Models & Their Uncertainties	126
Table S1: Major and trace elements for Mangaia lavas hosting olivine phenocrysts	127
Table S2: High precision Mangaia olivine phenocryst analyses	128

Chapter 4:

Table S1: High Precision Olivine Analyses for Peridotites	195
Table S2: Olivine Analyses from Fernandina Sample D38A	203

Chapter 1

Source Lithology of Curacao

Abstract:

The late Cretaceous to early Paleocene (Loewen et al., 2013; Sinton et al., 1998) lavas of Curacao are thought to be some of the earliest magmatism associated with the Galápagos plume (Geldmacher et al., 2003; Hauff et al., 2000; Kerr et al., 1996b). Presented here are olivine data obtained from two Curacao picrites. Petrologic modeling of olivine compositions indicates that the observed trends in Ca, Mn, Fe/Mn and Ni can not be explained by a pyroxenitic component. This differs from the modern Galápagos, which has pyroxenite in its source (Vidito et al., 2013). Results are consistent with the hypothesis that there have been secular changes in the amount of pyroxenite in the Galápagos plume. Additional modeling of magma chamber processes indicates that the geochemical trends observed in the olivine data could not have been caused by assimilation-fractional crystallization or Cpx crystallization alone. A process in which a peridotite source primary magma is allowed to crystallize olivine + Cpx + plagioclase followed by a recharge event best explains these trends. Modeled olivine compositions that crystallize over a range of mixtures of primary magma and evolved derivative magmas are consistent with the data.

1. Introduction

Large igneous provinces (LIPs) are formed by large outpourings of magma that may occur over short periods of time (Coffin and Eldholm, 1994). The potential for volcanic activity to affect the atmosphere and hydrosphere indicates that these large

magmatic events may be the cause of the extinctions which coincide temporally with them (e.g. Coffin and Eldholm, 1994; Richards et al., 1989; Sinton and Duncan, 1997; Wignall, 2005). Given the profound effect that magmatism can have on the planet it is essential to understand how these magmatic provinces are formed and how they evolve. Many LIPs may form due to the initial melting of a mantle plume head (Coffin and Eldholm, 1994; Hill et al., 1992; Richards et al., 1991; Sleep, 1996). Many hotspot tracks can be traced back to LIPs indicating that there is a genetic link between these different volcanic features (Richards et al., 1989).

Modeled mantle potential temperatures (T_p) of the present day Galápagos archipelago and the Caribbean Large Igneous Province (CLIP) show that over time the Galápagos plume has cooled (Herzberg and Gazel, 2009). The entrainment of dense recycled crust into a mantle plume may have a negative effect on the buoyancy of a mantle plume, thus allowing more heat to dissipate into the ambient mantle (Kumagai et al., 2008). Such a process would result in a decrease in T_p (Herzberg, 2011) and the degree of melting in a mantle plume. Inferences made from trace element olivine compositions of the present day Galápagos archipelago indicates that pyroxenite is present in the sources of most of the volcanoes produced from the tail stage of the plume (Vidito et al., 2013). Chapter 2 of this thesis shows that after the transition from plume head to plume tail at ~ 70 Ma, a clear signal of recycled crust or pyroxenite is seen. It is apparent that the melting of pyroxenite as well as the dynamic effects of pyroxenite entrainment is seen in the earliest preserved hotspot track as well as the present day Galápagos plume. In this study I present olivine analyses from older CLIP picrites from Curacao in order to determine if a recycled crust was present in the source of these CLIP

lavas. However, inferences about source lithology can be compromised by magma chamber processes, as discussed in this chapter.

2. Geologic Background

2.1. General CLIP

The CLIP consists of large masses of basaltic lavas that overlie and underplate the oceanic crust of the Caribbean plate (Mauffret and Leroy, 1997). A map of the sub-aerial exposures of the CLIP, accreted terranes (both CLIP and hotspot tracks) and the present day hotspot, are presented in Figure 1. Covering $\sim 0.8 \cdot 10^6 \text{ km}^2$ (Mauffret and Leroy, 1997), the CLIP reaches a maximum thickness of $\sim 20 \text{ km}$ at the Beata Ridge and the Nicaragua Rise (Edgar et al., 1971).

The generally accepted model for the timing of magmatism for the CLIP calls for a main pulse at $\sim 90 \text{ Ma}$ and that a second, smaller pulse occurred at $\sim 75 \text{ Ma}$ (Sinton et al., 1997). The hypothesis of two pulses of magmatism associated with this LIP may not be secure due to new $^{40}\text{Ar}/^{39}\text{Ar}$ ages from Haiti and Curacao, which indicate prolonged periods of magmatism without significant hiatuses (Loewen et al., 2014).

Establishing a clear link between the CLIP and the Galapagos hotspot is difficult due to the fact that older tracks of the Galápagos hotspot have been subducted in the Central American trench; thus they cannot be directly traced to the plateau. There are two schools of thought regarding tectonic reconstructions of the Galápagos hotspot. Some workers call for a model in which the CLIP was formed in-situ between the South American and North American continents (e.g. Meschede and Frisch, 1998) and thus is not related to the present day plume. Other reconstructions suggest that the plateau

formed on the Farallon plate in the Pacific. In the model of Duncan and Hargraves, 1984 the plateau formed in the present location of the Galápagos hotspot and then migrated eastward with the plate into its present position between the North and South American continents. “Pacific” models such as that of Duncan and Hargraves, 1984, support a genetic relationship between the present day Galápagos plume and the CLIP. Perhaps the strongest evidence against the fixist model comes from radiolaria fauna found in chert of the Bermeja complex on Puerto Rico that was of a Pacific origin and pre-date the opening of the Caribbean (Montgomery et al., 1994).

Apart from tectonic reconstructions, links between the present day Galápagos plume and the CLIP comes from isotopic data. Studies (Geldmacher et al., 2003; Hauff et al., 1997; Hauff et al., 2000; Hoernle et al., 2002; 2004; Lapierre et al., 2000; Sinton et al., 1998b; Thompson et al., 2004) show that exposures of the CLIP have Pb, Nd and Hf isotopic compositions that overlap those of the Galápagos Archipelago. Isotopic variations within the present day archipelago have been organized into isotopic domains (Hoernle et al., 2000) and characterized by a mixture of isotopic endmembers specific to the archipelago (Harpp and White, 2001). Geldmacher et al., 2003 showed that the central and eastern isotopic domains (Hoernle et al., 2000) existed in the main pulse of the CLIP, while the northern domain (Hoernle et al., 2000) persisted as far back as 65 Ma. In the CLIP the southern domain (Hoernle et al., 2000) isotopic signature is absent with the possible exception of Curacao (Geldmacher et al., 2003). The northern component (Hoernle et al., 2000) is not observed in the Galápagos magmas until the appearance of Quepos at ~65 Ma (Geldmacher et al., 2003). A component of recycled crust in CLIP lavas has been inferred by isotopic data (Geldmacher et al., 2003; Hauff et

al., 2000), however these studies are not able to determine if the recycled crust was present as separate lithological units (Herzberg, 2011).

Arguments for the presence of a LIP on the Caribbean plate are based primarily on the anomalously thick oceanic crust found in much of the region (see above) and trace element analysis. Basalts of the Caribbean Plateau typically have flat rare earth element (REE) patterns (Hauff et al., 1997; Hauff et al., 2000; Kerr et al., 1997), similar to other oceanic plateaus (e.g. Mahoney et al., 1993; Storey et al., 1992). Modeled mantle potential temperatures from the present day Galápagos archipelago and the CLIP, indicate that the mantle plume has cooled over the last 90 Ma (Herzberg and Gazel, 2009). Figure 2 shows that CLIP mantle potential temperatures modeled in PRIMELT2 (Herzberg and Asimow, 2008) are generally higher than those of the Galápagos archipelago. Moreover, the magmas of the present day Galápagos generally have higher La/Nd_N and Sm/Yb_N (Figure 2). Assuming a similar source for the CLIP and Galápagos hotspot, the depletion of more incompatible REEs (i.e. La/Nd_N and $\text{Sm/Yb}_N \sim 1$) in the CLIP relative to the present day Galapagos Archipelago, may be interpreted as evidence for higher degrees of melting in the Galápagos plume during the Cretaceous. Some workers propose that this high degree of melt was due in part to the plume head being in close proximity to a spreading center (Kerr et al., 1998; Lapierre et al., 2000).

The lower portions of the CLIP are thought to consist primarily of picrites and rare komatiites. More evolved basalts tend to be emplaced at the top of the sequence (Kerr et al., 1997; Kerr et al., 1998; Kerr et al., 1996a; Mauffret and Leroy, 1997). Primitive mafic and ultramafic rocks may be representative of early stage melts that had

erupted prior to the establishment of crustal magma chambers when the crust was still relatively thin. The higher density of these primitive magmas may prevent them from erupting after the crust has thickened and magma chambers have become well established, hence their absence at the top of the observed sequences (Kerr et al., 1997; Kerr et al., 1998).

2.2 Curacao

CLIP units found on Curacao consist primarily of a 5km sequence of pillow basalts of picritic to tholeiitic compositions (Beets et al., 1982; Klaver, 1987). The most primitive picrites are found near the base of the formation and lava compositions become increasingly evolved with stratigraphic height (Kerr et al., 1996a). Initial $^{40}\text{Ar}/^{39}\text{Ar}$ ages from the top and bottom of the formations at Curacao indicated that the lavas were emplaced in a relatively short interval consistent with the main pulse of the CLIP (Sinton et al., 1998a). The position of the emplacement of the units over a short period of time is strengthened by the presence of only a single intercalation of limestone (Kerr et al., 1997). Despite this evidence a more recent study conducted by Loewen et al., 2014 suggests that magmatism occurred over a longer period. The 16 new $^{40}\text{Ar}/^{39}\text{Ar}$ ages presented in this study shows that magmatism at Curacao occurred from ~63Ma to 92 Ma with few hiatuses (Loewen et al., 2013).

Picrites found at Curacao have major element trends that indicate that olivine was the only crystallizing phase (an olivine control line). Samples with the highest MgO contents are not representative of primary magmas, rather they thought to be cumulates (Kerr et al., 1996a). Rounded and resorbed olivines from the high MgO picrites is

indicative of olivine accumulation (Beets et al., 1982), while other picrites with dendritic olivines appear to have been formed through the rapid cooling of primitive magmas (Kerr et al., 1996a). An early interpretation of the occurrence of basaltic and ultramafic lavas at Curacao suggested that it was formed in the initial stages of a volcanic arc (Beets et al., 1982). However there is a lack of an ARC geochemical signal (e.g. K and Pb enrichment and Nb and Ta depletion). The Curacao lavas generally have flat REEs, similar to most CLIP samples (Beets et al., 1982; Kerr et al., 1996a) however Klaver, 1987 noted that REE abundances increased from the most primitive picrites to the tholeiitic basalts. Trace and major element trends were used in Klaver's thesis to show that the picrites may be representative of parental magmas to the more evolved tholeiites (Klaver, 1987). Since REEs are highly incompatible and major element trends indicate that plagioclase and clinopyroxene do not enter the LLD until the MgO contents reach 8-9% MgO, the sub-parallel trends in REEs can be explained by the formation of evolved magmas by fractional crystallization of a picritic parental magma (Kerr et al., 1996a). Furthermore, Klaver, 1987 interpreted the chemistry and petrography of the sequence at Curacao to be representative of open and continually replenished magma chambers.

ϵ_{Nd} and ϵ_{Hf} systematics indicate that most samples from Curacao are similar to the central domain (Hoernle et al., 2000), while a few samples have signatures that indicate a component of the southern domain (Geldmacher et al., 2003). This interpretation is complicated by the fact that none of the Curacao samples have the characteristic signal of radiogenic Pb enrichment associated with the southern domain (Geldmacher et al., 2003). Curacao picrites have a narrower range of ϵ_{Nd} , $^{87}\text{Sr}/^{86}\text{Sr}$ (Kerr et al., 1996a) and Pb isotopic ratios than the basalts (Hergt et al., 1994).

Variations in $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentrations led Kerr et al. to conclude that the basalts of Curacao had assimilated altered oceanic crust during the process of fractional crystallization. The possibility of contamination by a continental component was dismissed on the basis that Curacao is underlain by a basaltic basement (MORB) and that the Sr isotopic anomalies were not followed by a decrease in $^{143}\text{Nd}/^{144}\text{Nd}$. Repeated leachings of Curacao samples failed to yield analyses with significantly lower $^{87}\text{Sr}/^{86}\text{Sr}$, thus eliminating the possibility that the anomalous Sr signal was due to the alteration of the Curacao samples (Kerr et al., 1996a).

3. Methods

3.1 Analytical Methods

Major and minor element compositions were obtained from olivines using a modified version of the high precision EPMA protocol of Sobolev et al., 2007. These samples were analyzed with a focused beam (~1 μm) at 20 kV and 300 nA. On peak count times for all analyses are as follows: Si: 50s; Mg: 80s; Fe: 100s; Ni: 150s; Ca: 150s and Mn: 150s. In order to correct for instrumental drift the San Carlos olivine standard was analyzed at regular intervals during each run. A summary of the secondary standards, primary standards and statistics for the olivine analyses are given in Table 1.

3.2 Computational Methods

Liquid lines of descent (LLD), in which olivine is the sole crystallizing phase, were calculated using the algorithms of Herzberg, 2011. High pressure Cpx crystallization, occurring concurrently with olivine crystallization was calculated using algorithms of Herzberg et al., 2013. AFC modeling for the Curacao samples was done by

integrating the DePaolo, 1981 model into the algorithms of Herzberg, 2011 and Herzberg et al., 2013. Potential assimilants, which consisted of various lithologies from the oceanic lithosphere, were obtained from <http://georoc.mpch-mainz.gwdg.de>. R values (mass assimilant/mass crystallizing phases) < 1 were used for most models as it is assumed that latent heat of fusion from crystallization provides the heat required for assimilation (DePaolo, 1981). However, it has been shown that in the early stages of fractionation that R values can exceed 1 (Reiners et al., 1995). Magma mixing modeling was accomplished in 3 separate stages and is similar to the method given in Herzberg et al., 2014. The first stage consisted of LLD modeling in PETROLOG (Danyushevsky and Plechov, 2011). PETROLOG LLD modeling included olivine, clinopyroxene, and plagioclase crystallization at 1 atm. Olivine was modeled with the olivine liquidus temperature calculation from Beattie, 1993 together with the Fe/Mg exchange coefficient of Toplis, 2005. Plagioclase and clinopyroxene compositions were calculated with the models of Danyushevsky, 2001. In the subsequent step Ni, Ca and Mn was re-calculated for olivine using the partition coefficient calculations of Beattie, 1993 for Ni and Herzberg and O'Hara, 2002 for Ca and Mn. Ni was calculated for Cpx using the partition coefficient calculation of Herzberg et al., 2013. Ni, Ca and Mn concentrations in the liquids were also re-calculated at this step. Ranges of mixed magma compositions were then calculated, as were olivines in equilibrium with these mixed magmas.

4. Results

The two Curacao olivine populations (Figure 3) trend towards calculated olivine compositions from peridotite source primary magmas (Herzberg, 2011), this suggest that

the source of these Curacao magmas is peridotite. After performing inverse modeling of all of the possible primary magma compositions calculated from whole rock analyses (Kerr et al., 1996b; Klaver, 1987) in PRIMELT2 (Herzberg and Asimow, 2008), the solution for sample 79be028 (Klaver, 1987) was determined to be the most consistent with the olivine data. Nevertheless adjustments had to be made to the composition in order for it to be consistent with the olivine data. The affect of olivine sorting can have a dramatic effect on the Ni contents of whole rock, thus the Ni content of the peridotite source magma was calculated using the equation of Herzberg, 2011 (See Table 3). Additionally, Computed Mn and Ca show inconsistencies with the observed olivines which were corrected (Table 3). Modeled olivine trends which most closely match the measured olivines indicate that 70% to 90% Cpx crystallization with 30% to 10% olivine crystallization is required. This solution is unacceptable as dominant phenocryst phase in these samples is olivine (~50%) and it contradicts geochemical observations (Kerr et al., 1996b; Klaver, 1987). It is also possible that crystallization of olivine and Cpx occurred below the Moho (Herzberg et al., 2013; Geist et al., 1998; Vidito et al., 2014) and that when eruption occurred olivine crystallized, but Cpx did not. In such a case the geochemical signature of extensive Cpx crystallization would be preserved, but the amount of Cpx (if present at all) in the rock would not be proportional to this geochemical signature (e.g. Elthon et al., 1995; Thompson et al., 1980; O'Donnell and Presnall, 1980). Nevertheless, given the requirement of such a large proportion of cpx crystallization relative to olivine, other models are explored below.

The proportion of Cpx crystallization required by the LLD modeling may be reduced by the addition of pyroxenite source primary magma to the initial parental

magma. Of the samples which returned pyroxenite source errors in PRIMELT2 (Herzberg and Asimow, 2008), sample CUR36 (Kerr et al., 1996b) was chosen as a potential pyroxenite source magma. Computed Ni and Ca in olivine in equilibrium with this magma have consistent offsets with olivines of the peridotite primary magma. Mn contents however were much too high and were adjusted (Table 3) to be consistent with the offsets in Ca and Ni. Offsets in Mn, Ca and Ni relative to olivines in equilibrium with peridotite magmas and their derivative magmas has been interpreted as an indicator of a pyroxenite bearing source (Gurenko et al., 2010; Herzberg, 2011; Sobolev et al., 2005; Sobolev et al., 2007). Olivine compositions crystallized from the assumed pure pyroxenite primary magma are too far offset from the two Curacao samples, thus hybrid compositions were tested in subsequent models. Proportions of pyroxenite in the hybrid primary magma compositions were varied in 10% increments. Hybrid LLD models with 10% - 30% pyroxenite melt are shown for Ca and Ni (Figure 4). In all models the proportions of Cpx and olivine were adjusted to provide the optimum fit to the Ca contents of the measured olivines. The proportion of Cpx for the 10% pyroxenite hybrid (60-80%) is still too high for these picrites. The lack of internal consistency between Ca and Ni in these models becomes worse as the proportion of pyroxenite melt is increased. With as little as 30% pyroxenite melt in the hybrid, trends are not only inconsistent in their overlaps, but also in the slope of the modeled Ni trends compared to the slope of the observed Ni trends. It is obvious from these models that these Curacao samples could not have had a significant component of pyroxenite in its source.

Increasing Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ anomalies with progressive fractionation of the Curacao magmas has been interpreted as the assimilation of altered oceanic crust during

fractional crystallization (Kerr et al., 1996b). The effects of assimilation-fractional crystallization (AFC) on trace and isotopic compositions of magmas have been recognized for decades (e.g. Bohrsen and Spera, 2001, DePaolo, 1981 and Reiners et al., 1995). Although the effect of this process on major and minor elements is generally ignored, and the Sr signal of assimilation is absent in the picrites of Curacao (Kerr et al., 1996b), the possibility of AFC causing the unusual trends in olivine was tested. A number of different assimilant compositions consisting of samples crustal MORB and lithospheric mantle below MORB were tried. The only assimilants tested in this study that produced progressive offsets with increasing fractionation that were consistent with the observed data were harzburgites that had partially altered to talc. While these samples came from ODP-209 on the Mid-Atlantic Ridge (Paulick et al., 2006), the modeling is perfectly general for talc as an assimilant. AFC in which olivine was the sole crystallizing phase, could not reproduce the trends in the observed data even when $R > 1$. Only the solutions with AFC and high pressure, sub-Moho Cpx crystallization produced modeled olivine compositions consistent with the observed data (Figure 5).

The AFC model with Cpx crystallization provides an acceptable fit to the Curacao data with a peridotite primary magma and lower proportions of Cpx crystallization (30%-50%). Since the mode of these samples is dominated by olivine, this proportion of Cpx is more consistent with the petrography. However, given that Talc is a significant phase in this assimilant this solution is also unacceptable. Geochemical observations of Kerr et al., 1996b requires the hydrothermal alteration of the wall rock prior to assimilation. Although the harzburgite was indeed altered and high $^{87}\text{Sr}/^{86}\text{Sr}$ is found in the rocks recovered from ODP-209 (Paulick et al., 2006), the fact that Cpx must crystallize

concurrently with olivine and AFC precludes this model as a solution. In order for Cpx to be stable within the first 5% of fractional crystallization, the initial pressure would have to be ≥ 15 Kbars when the Cpx models of Danyushevsky, 2001 or Langmuir, 1992 are applied. Oxygen isotope measurements from the Oman Ophiolites indicate that hydrothermal alteration of oceanic crust is generally no greater than 6 km. Locally this alteration may penetrate deeper into ultramafic lithologies (Gregory and Taylor, 1981). Although ODP-209 is at a fracture zone in the Mid-Atlantic Ridge (Bach et al., 2004), it is still extremely unlikely that this alteration could penetrate to the required depth of ~55 km. Moreover, the mineralogical composition of the proposed assimilant could not exist at the required P/T conditions of the country rock. All the geotherm models of MacGregor and Basu, 1984 for oceanic lithosphere estimate a minimum temperature of 800°C at a pressure of 15 Kbars in the oceanic crust. At such conditions serpentine and talc breaks down and reverts to olivine, orthopyroxene and water vapor (Kitahara et al., 1966).

Herzberg et al., 2014 explained the deviation of olivines compositions from a typical calculated LLD by modeling the geochemical effects of magma recharge and mixing. Modeled olivine compositions with magma recharge and mixing in Figure 6, show excellent consistency with the observed Curacao olivine compositions without any co-crystallization of Cpx required. Mixtures of 60% to 40% primary magma and 60% - 40% evolved magmas with between 6.0% - 7.5% MgO are the best solutions.

The above recharge model suggests that after recharge, mixing within the magma chamber was imperfect and that further fractional crystallization prior to eruption was not

extensive. Variable mixing within the magma chamber is supported by the presence of olivines that individually have narrow forsterite ranges (avg. 1.5% variation core to rim) and normal, reverse and oscillatory zoning is present. Furthermore, if mixing were complete, yielding a homogeneous magma prior to subsequent fractional crystallization, the compositions of the olivines would not be in equilibrium with a range of mixtures as seen in Figure 6.

5. Discussion

If the magmas had homogenized and fractional crystallization had proceeded, the chemistry of the olivines would have been much different. Substantial fractional crystallization after recharge and perfect mixing would yield olivine compositions that form trends that would be sub-parallel to the original LLD in Figure 7. The scenario of perfect mixing followed by additional fractional crystallization is shown in Figure 7. Two mixtures (A and B) of the primary magma and a derivative liquid fractionated to 6.0% MgO were allowed to crystallize olivine, Cpx and plagioclase. Olivine compositions crystallized from hybrid sources, as well as the original peridotite source LLD, are included for comparison. The resulting trends of the modeled olivines are nearly parallel to olivines in equilibrium with the original LLD. Although there is a lack of internal consistency, such data could be mistaken for olivines derived from hybrid, pyroxenite bearing sources. Offsets in Ni and Ca for mixture A roughly coincide with hybrids with between 80% - 100% pyroxenite. Fe/Mn for this mixture however nearly overlaps the olivine compositions modeled from a hybrid with only 20% pyroxenite source melt.

The validity of the original LLD (dashed line in Fig 7) may be questionable. Mixing of a primary magma with the original LLD produced from a previous pulse of primary magma (as shown in Figure 6) may only hold true for the second pulse of magma into the magma chamber. If the system has undergone repeated cycles of magma recharge followed by fractional crystallization, then each subsequent recharge event would be followed by mixing of the new primary magma with a fractionated magma formed on an LLD from a mixed magma, not a primary magma. Modeling given in Figure 8 shows the effect of repeated cycles of fractional crystallization followed with magma mixing with 50% derivative liquid and 50% primary magma. With each cycle the the amount of fractional crystallization (olivine only) is kept constant. After the first cycle there is little change in the chemistry of the olivines and liquids. This is an unlikely scenario since in such a system there would be little variation observed in the chemistry of the erupted magmas or the mineral phases. Unlike the model of O'Hara 1977 in which regular batches of primary magma followed by fractional crystallization results in a steady state, the fact that the two samples in this study have different trends in olivine chemistry suggests that the degree of fractional crystallization between recharge events is not consistent.

A second scenario (Figure 9 A-C) in which with each successive cycle of fractionation and recharge, the amount of fractional crystallization increases. A progressive offset in Ca, Mn and Ni is observed in the modeled olivines with each cycle. Only olivine was allowed to crystallize in these models. This scenario is not possible for Curacao since with each cycle the trend in Ca is steeper. The Ca trend observed in the Curacao olivines is nearly horizontal which necessitates the presence of Cpx as a

crystallizing phase. Panels D-F in Figure 9 shows repeated cycles of fractionation and recharge in which olivine, Cpx and plagioclase are crystallizing phases. This model is consistent with the observed Ca, Fe/Mn and Ni trends in the Curacao samples. Models presented in Figure 6 and 9 while consistent with data are not the only possible recharge and mixing scenarios that could be consistent with the data. It is possible that the primary magma fractionated slightly prior to entering the magma chamber. This may be a viable model for sample 94-54 since Ni in these olivines appears to be trending to derivative liquids of a peridotite source. Also not considered are the effects of polybaric fractional crystallization, AFC and variable proportions of primary and derivative liquids in these multi-stage mixing models. Variable proportions of mixing may be supported by field observations near the base of the formation. The stratigraphic section presented in Kerr et al., 1996b shows that picritic lavas are interlain with more evolved tholeiites. If the models presented here apply to this stage in the magmatic history of Curacao, then it is likely that the mixtures of the more evolved liquids contained less primary magma. Nevertheless, different mixing scenarios does not compromise the interpretation of a peridotite source, since olivines crystallized along a mixing line with a primary magma (or derivative magma from a peridotite source) will invariably trend towards olivine compositions that are in equilibrium with the primary magma or their derivative magmas.

Kerr et al, 1996 notes that the eruption of picrites is inhibited by the high density of the magmas, but that a thin spot in the lithosphere (e.g. spreading center) or deep faulting may facilitate their eruption. Magma recharge and mixing may also provide a mechanism if not an additional factor by which the primitive picritic magmas had erupted to the surface. The injection of hot primitive magma into a magma chamber filled with

more evolved magma induces convection (Sparks et al., 1977) and increases the pressure within the magma chamber (Sparks et al., 1977; Blake, 1981). The increase in pressure may produce cracks in the overlying strata which provide pathways for the magma to escape and heat within the magma chamber decreases the viscosity and density of the magma making it easier to extrude to the surface (Sparks et al., 1977). Although the most evolved magmas modeled here are not particularly evolved (basaltic andesite) nor is a high volatile content expected, vesiculation triggered by magma mixing (Sparks et al., 1977) may not be necessary to trigger the eruptions as magma recharge alone may be adequate to produce the pressure increase required (Blake, 1981).

Although no satisfactory model in which AFC occurs was found to explain the olivine chemistry, this does not necessarily preclude the possibility of AFC. Potential assimilants tested included mid-ocean ridge basalt (MORB) samples with a range of compositions. In general it was found that the assimilation of basaltic country rock by a basaltic magma resulted only in subtle changes in the olivine chemistry. Thus assimilation may have occurred concurrently with crystallization, recharge and magma mixing, but the major and minor element chemistry of the assimilant must not have differed significantly from that of the plume derived magma.

6. Conclusions

The presence of a peridotite source for the magmas of Curacao supports the hypothesis of peridotite source for the head stage of the Galápagos plume, however much more work on CLIP is needed. The chemistry of the Curacao olivines reflects the mixing history and degree of fractionation of the previous batch of magma, as well as the

lithology of the primary magma. Of all the models tested, recharge and magma mixing in Curacao reproduced the observed olivine trends best. Crystallization of olivine from a range of magma mixtures is required. The variation in the observed trends suggests that this was a system in which the degree of fractionation between recharge events was variable. The lack of a satisfactory AFC model does not preclude the possibility of AFC, as it is likely that a crustal assimilant would have little impact on major and minor chemistry of olivines.

7. References

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8. Figure Captions

Figure 1: Map of the subareal exposures of Galápagos Hotspot tracks and the Caribbean Large Igneous Province. Locations covered in this study are in bold black letters. This map was produced in GeoMapApp (www.geomappapp.org) using the basemap of Ryan et al., 2009.

Figure 2: ITE ratios and T_p from the CLIP (Arndt et al., 1997; Brugmann et al., 1987; Donnelly et al., 1973; Escuder-Viruete et al., 2007; Hauff et al., 2000a; Hauff et al., 2000b; Jochum et al., 1991; Jolly et al., 2007; Kamenetsky et al., 2010; Kerr et al., 1997; Kerr et al., 2002; LaPierre et al., 1999; LaPierre et al., 2000; Mamberti et al., 2003; Millward et al., 1984; Millward et al., 1997; Revillon et al., 2000; Revillion et al., 2002; Sinton et al., 1997; Villagomez et al., 2002; White et al., 1999) and present day Galapagos hotspot (Baitis and Swanson, 1976; Bow, 1979; Bow and Geist, 1992; Geist et al., 1986; Geist et al., 2006; Gibson and Geist, 2010; Harpp et al., 2003; Kurz and Geist, 1999; Naumann et al., 2002; Saal et al., 2007; Teasdale et al., 2005; White et al., 1993). All trace elements have been normalized to primitive mantle (McDonough and Sun, 1995). Mantle potential temperatures (T_p) were modeled in PRIMELT2 (Herzberg and

Asimow, 2008). Tp is generally lower and ITE ratios higher than samples of the CLIP and Gorgona.

Figure 3: Peridotite source modeling and the Curacao olivine data. Analyses of Curacao olivine data plotted against olivines in equilibrium with modeled derivative magmas of a peridotite source primary magma. A reasonable match is obtained, however the requirement of a high proportion of Cpx early in the LLD is not supported by the mode of these samples.

Figure 4: Curacao Ca and Ni olivine data compared to modeled derivative magmas of various hybrid sources. Pyroxenite primary magma, calculated from sample CUR36 (Kerr et al., 1996b), was added to the original peridotite primary magma from Figure 1 in 10% increments to produce hybrid magmas. In each set of plots the proportion of Cpx/Ol is set such that the optimal fit with the Curacao Ca data is achieved. This illustrates the decrease in internal consistency between the modeled and observed Ca and Ni contents as the proportion of pyroxenite in the source is increased. This eliminates the possibility of a significant pyroxenite component in source of these two Curacao lavas.

Figure 5: AFC model compared to the olivine chemistry of Curacao. In addition to olivine and Cpx crystallization, LLDs represented by the blue lines have had an assimilant (1268A-15) added using the AFC model of DePaolo, 1981. These AFC models require less Cpx than the models shown in figure 1. Unfortunately since the assimilant lithology cannot exist in the T/P conditions required, this is not a valid solution for Curacao.

Figure 6: Magma mixing models compared to the olivine chemistry of Curacao. Curacao olivine data compared to modeled derivative magmas initially calculated using PETROLOG (Danyushevsky and Plechov, 2011) and then re-calculated following the algorithm of Herzberg et al., 2014. Calculated olivines in equilibrium with variably mixed primary and evolved derivative magmas provide the best fit to the data. The implication of this model is that fractionation during a magma recharge event is most likely to be responsible for the compositional trends.

Figure 7: LLDs modeled from magma mixtures compared to hybrid models. Olivine compositions modeled from mixtures of magmas from Figure 4, which were allowed to fractionate normally. Also plotted are modeled olivines that crystallized from various hybrid sources. This shows that olivines crystallized from mixed magmas can appear to have trends that are consistent with hybrid sources.

Figure 8: Six cycles of magma fractionation followed by recharge in a system approaching a steady state. The degree of fractional crystallization (olivine only) and proportions of derivative and primary magmas in magma mixing are kept relatively constant for all 6 cycles. This example shows that little change is observed in the olivine chemistry (and liquids) after the first cycle (labeled) provided that conditions remain constant.

Figure 9: Progressive magma mixing models in which the degree of fractional crystallization is varied. Panels A-C show six cycles of magma fractionation followed by recharge, in which olivine is the only crystallizing mineral phase. Olivine data from Curacao is not plotted in these three diagrams since with each successive cycle the trend

in Ca becomes increasingly steep, which is the opposite of what is observed in the olivine data. As seen in figure 8, there is an increase in the offset of Ni when recharge occurs with progressively fractionated liquids. Panels D-F show six cycles of magma fractionation followed by recharge in which Ol + Cpx + Plagioclase are allowed to crystallize on the LLD. As with all of the mixing models presented, Mn remains relatively insensitive to the effects of magma recharge and mixing. Ni and Ca show progressive offsets with increasing fractionation and with each successive cycle. Consistency between the Curacao data and the modeled mixing lines indicates that this process of continuous fractionation and recharge is also a viable model for these samples.

9. Figures

Figure 1:

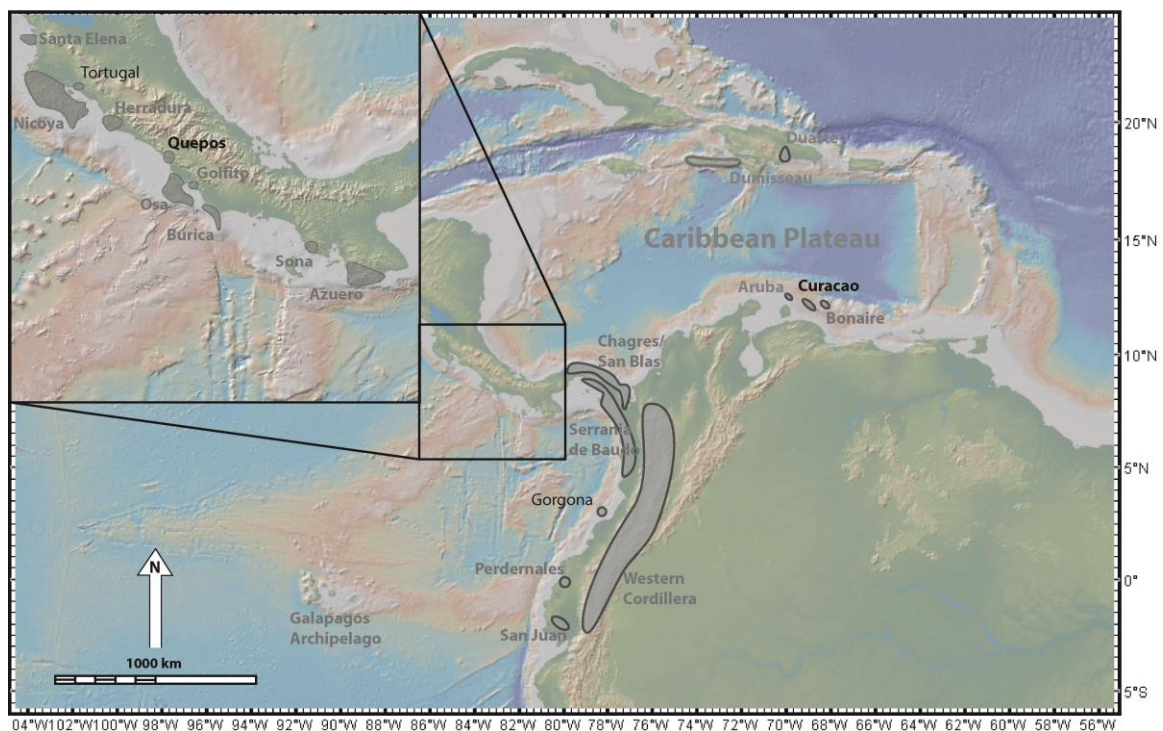


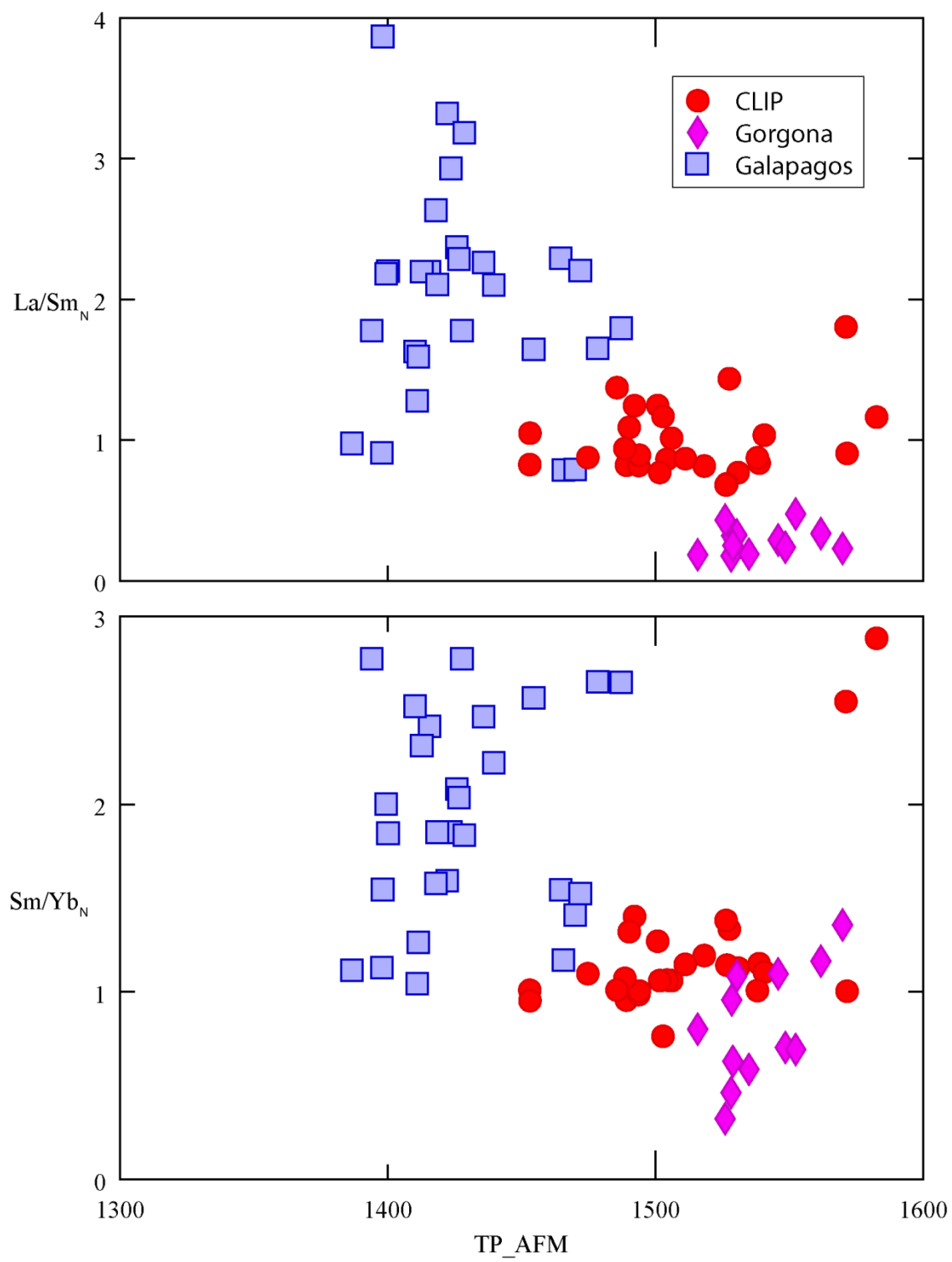
Figure 2:

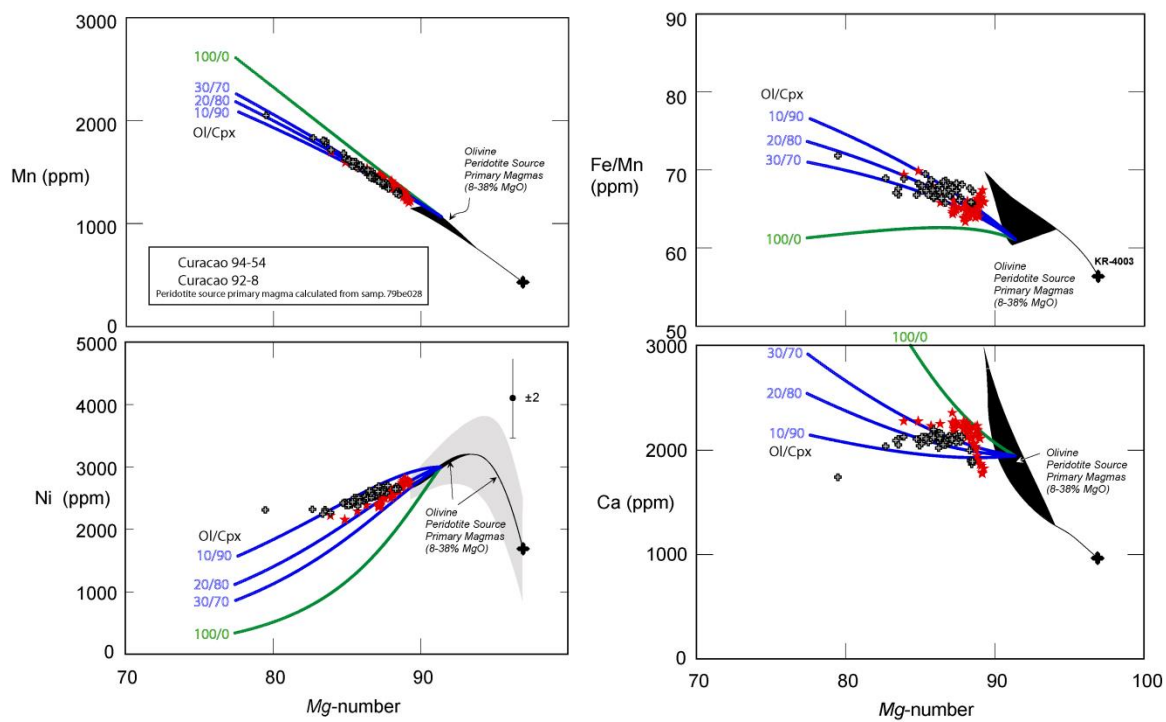
Figure 3:

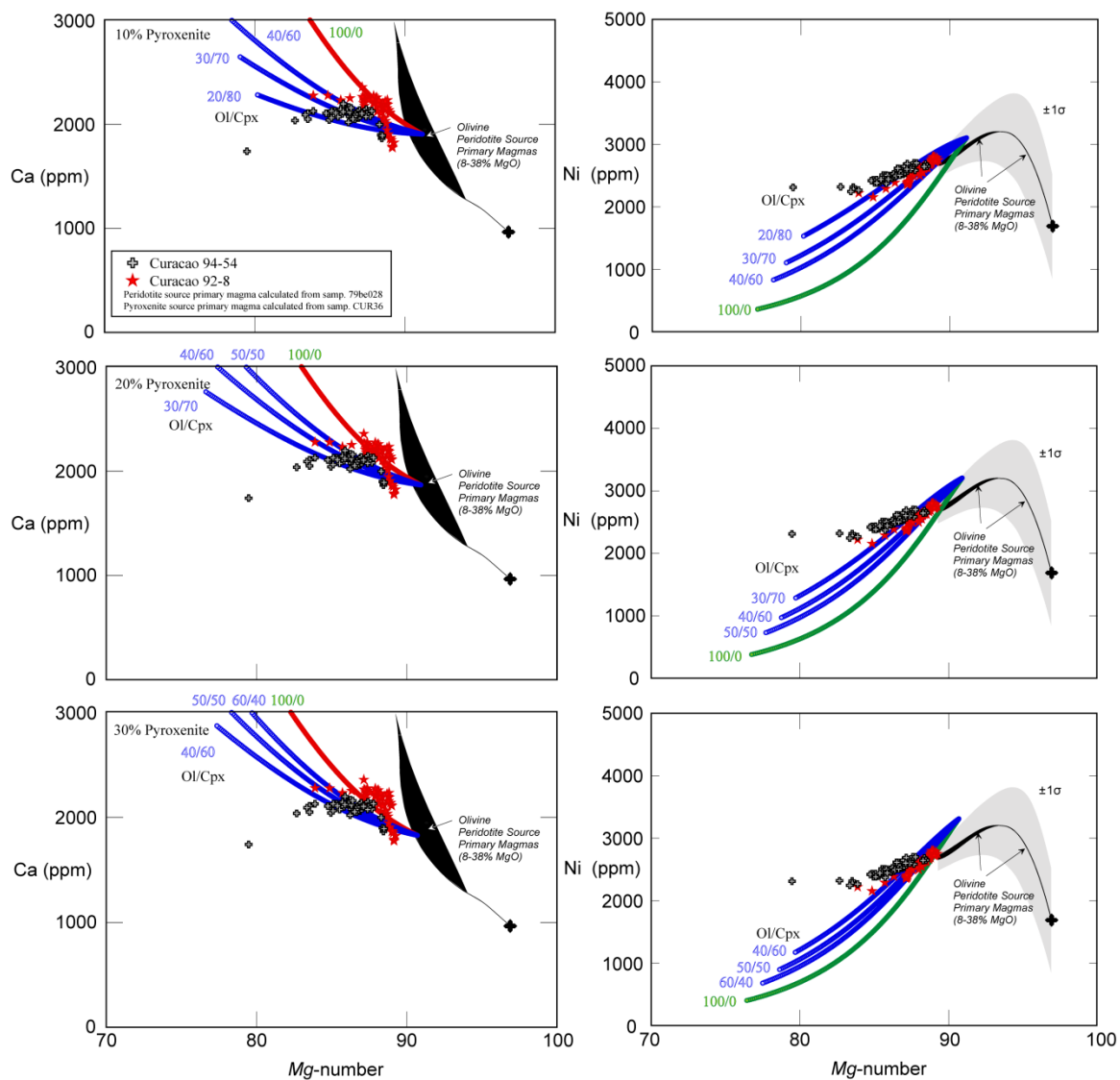
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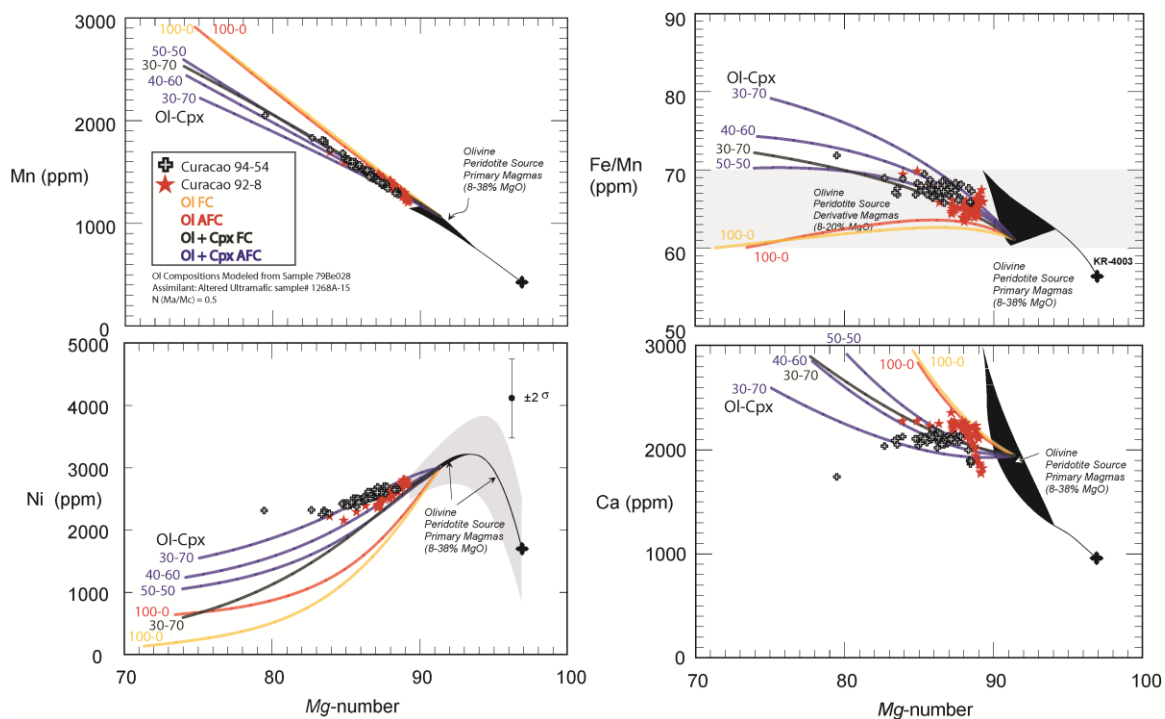
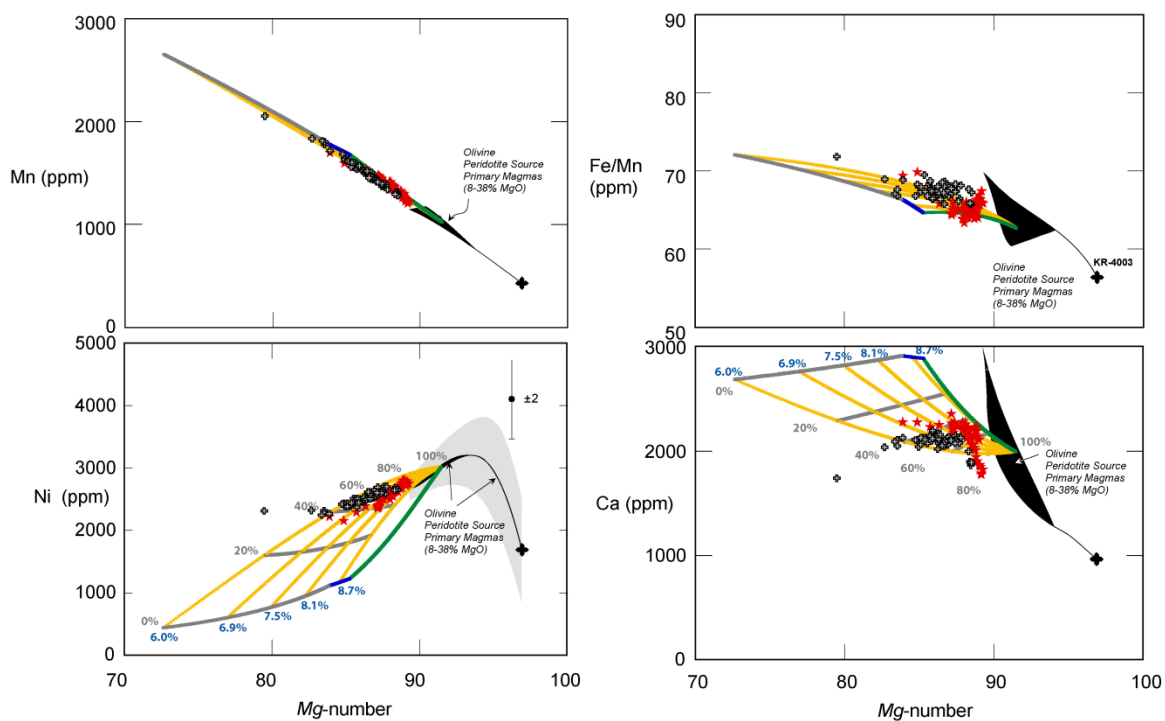
Figure 5:**Figure 6:**

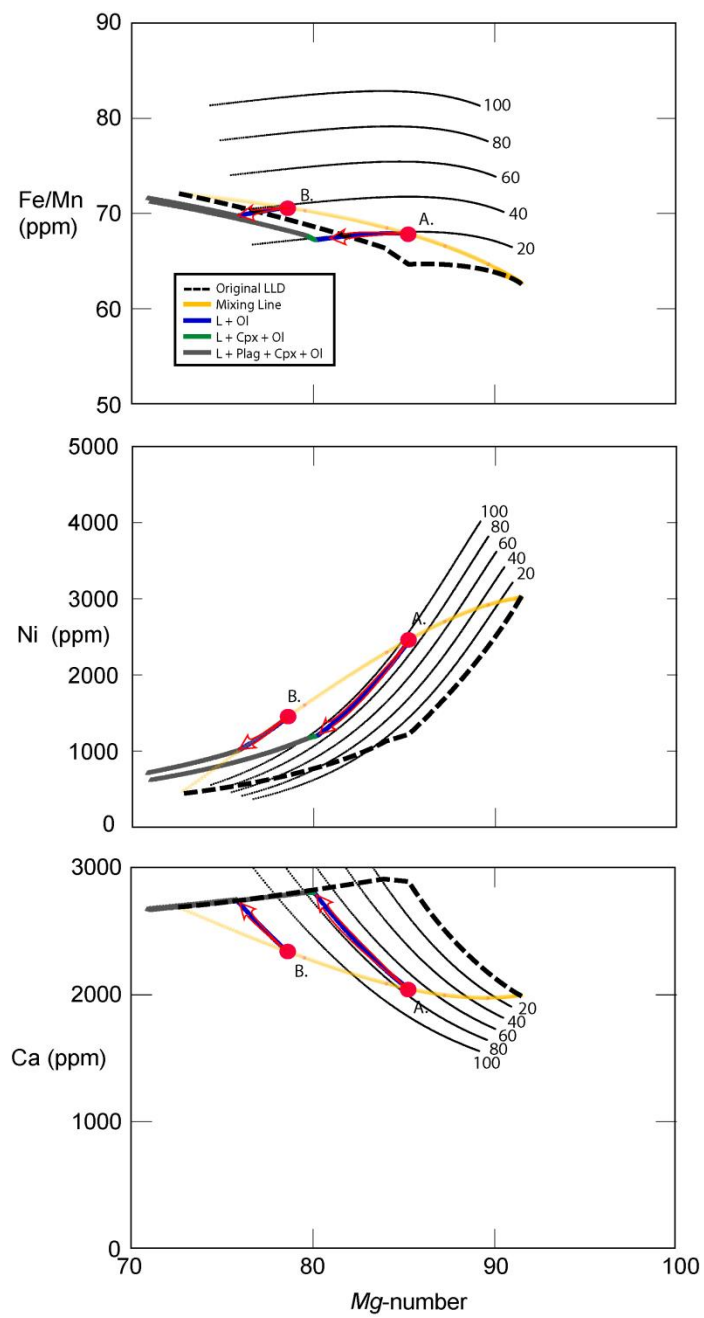
Figure 7:

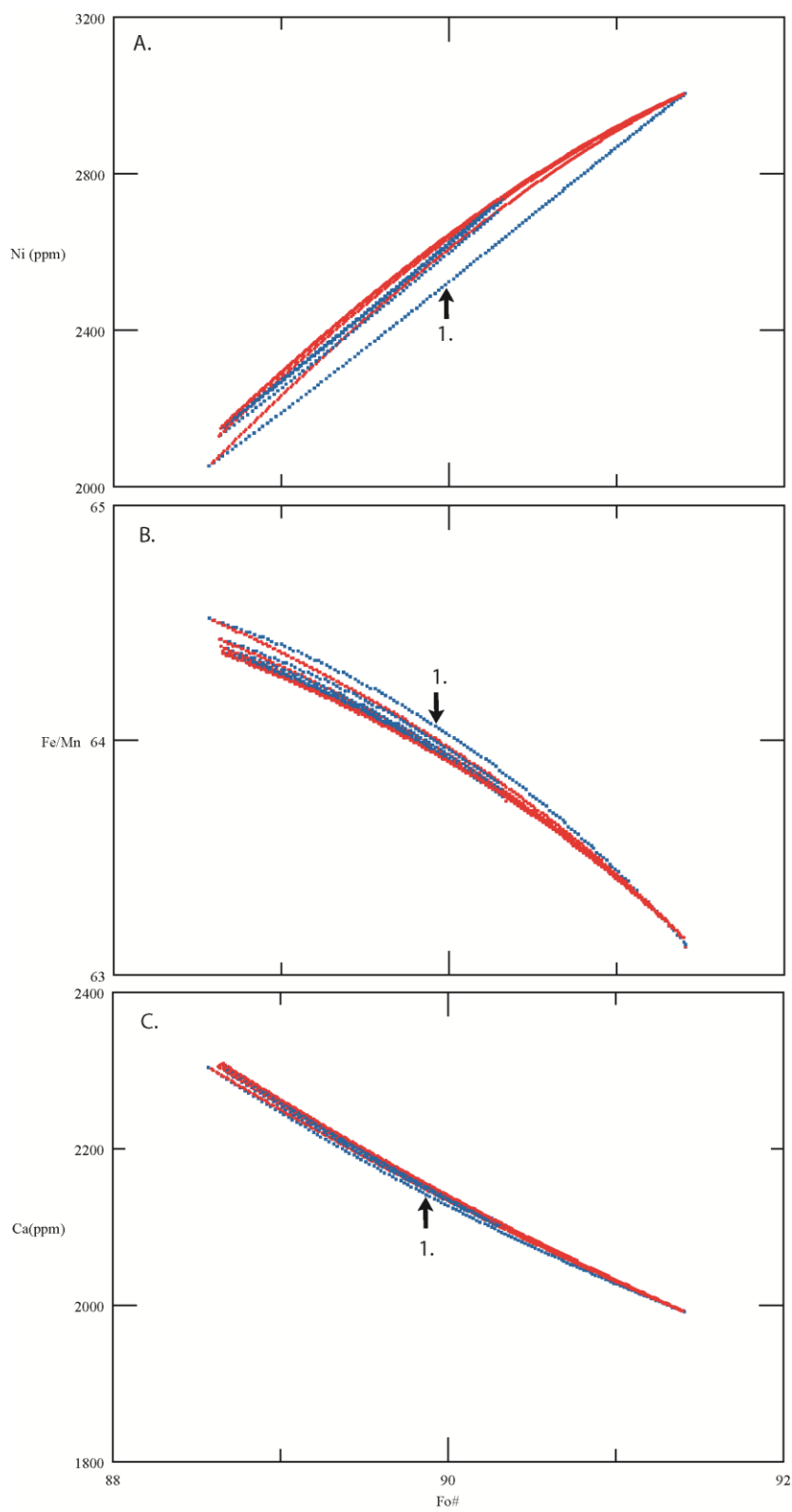
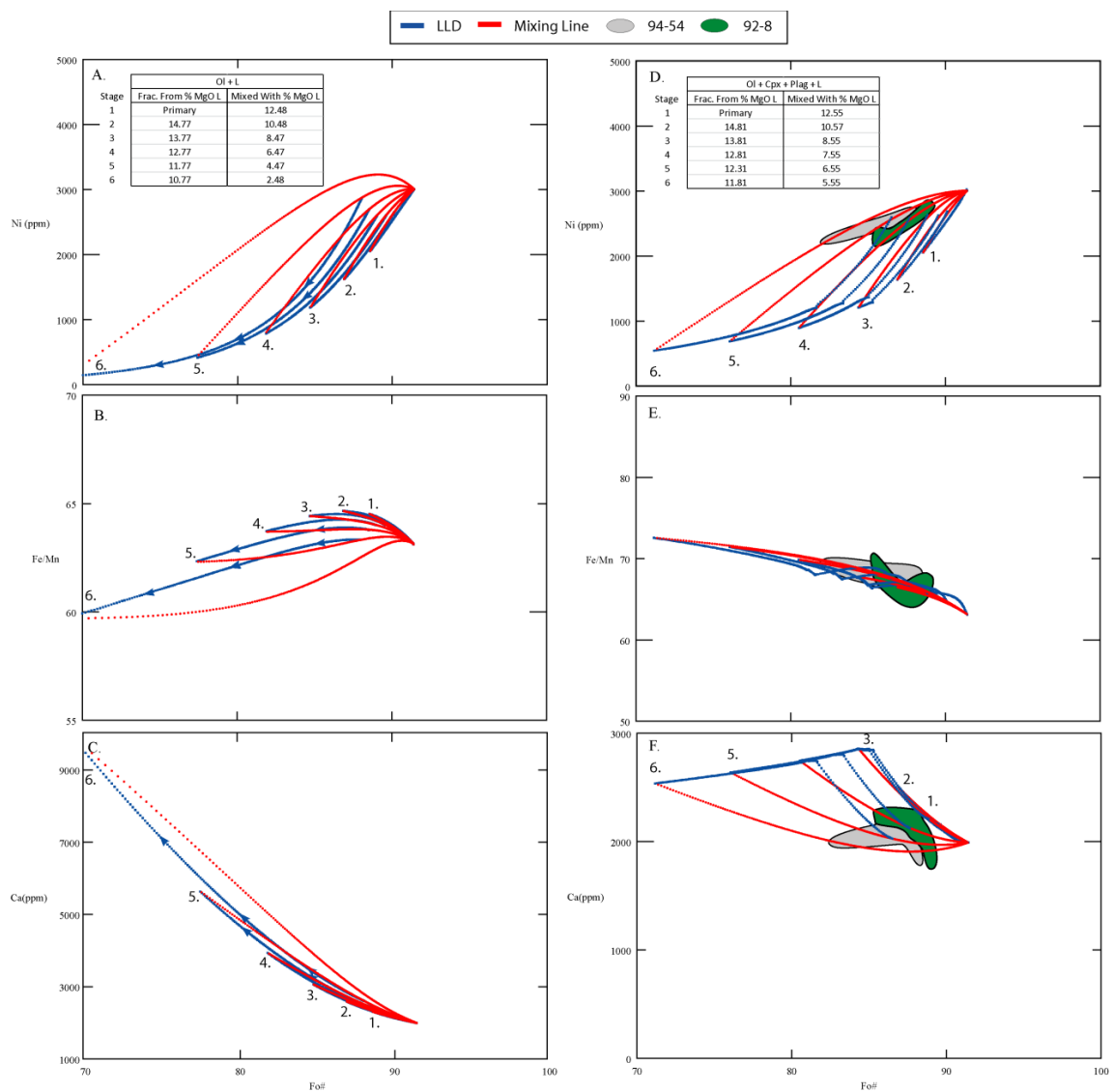
Figure 8:

Figure 9:



10. Tables

Table 1: Secondary Standards, Primary Standards and Statistics

	San Carlos Olivine, USNM 111312/44			
	Average (N=21)	1 Sigma	Average** (N=1788)	Published*
SiO₂ %	40.69	0.076	40.83	40.81
MgO %	49.05	0.096	48.90	49.42
FeO %	9.72	0.021	9.75	9.55
NiO %	0.356	0.0022	0.358	0.37
MnO %	0.132	0.0017	0.132	0.14
CaO %	0.063	0.0012	0.063	0.05
Fo #	90.0	0.0	89.9	90.2
Fe (ppm)	75532	160	75783	74233
Mn (ppm)	1019	13	1019	1084
Ni (ppm)	2798	17	2816	2907
Ca (ppm)	452	8	450	357
Fe/Mn	74.1	1	74.4	68.5

*Jarosewich et al., 1980

** All analyses of the RU SCOL standard at high currents and long count times over 4 years

***Jarosewich et al., 1987

	Primary Standards:	Avg. D.L. (3 σ)****	Avg. Percent Err. (1 σ)****
Si	Synthetic Fayalite (Takei)	0.0029	0.047
Mg	Synthetic Forsterite (Takei)	0.0041	0.076
Fe	Synthetic Fayalite (Takei)	0.0027	0.099
Ni	Synthetic Ni ₂ SiO ₄ (Boyd)	0.0017	0.739
Mn	Synthetic Tephroite (Takei)	0.0022	1.073
Ca	Chromian Augite, NMNH 164905	0.0023	0.621

****Statistics calculated in the Probe for EPMA software (Donovan, 2012)

Chromian Augite, NMNH 164905 (N=3)		
Average	1 σ	Published***
50.51	0.01	50.48
17.29	0.02	17.32
4.71	0.00	4.69
0.046	0.004	n.a.
0.127	0.003	0.12
<i>17.30</i>	<i>0.01</i>	<i>17.30</i>

Ca Standard

Kakanui Pyrope, USNM 143968 (N=3)			
	Average	1 σ	Published*
SiO2	41.62	0.47	41.46
MgO	19.02	0.15	18.51
FeO	10.34	0.04	10.68
NiO2	0.006	0.002	n.a.
MnO	0.322	0.006	0.28
CaO	5.09	0.02	5.17

	Augite 209 (N=3)		
	Average	1 σ	Published
SiO2	47.67	0.18	47.90
MgO	12.80	0.04	12.67
FeO	8.17	0.03	8.18
NiO2	0.006	0.005	n.a.
MnO	0.181	0.007	0.18
CaO	18.15	0.04	18.36

Table 2: Curacao Olivine Data

Sample	SiO ₂ %	MgO %	FeO %	NiO %	MnO %	CaO %	Fo#	Fe (ppm)	Mn (ppm)	Ni (ppm)	Ca (ppm)	Fe/Mn
92_8_Olivine1	40.38	47.34	11.46	0.332	0.177	0.308	88.0	89060	1372	2611	2204	64.9
92_8_Olivine1	40.32	47.27	11.59	0.331	0.179	0.308	87.9	90125	1383	2600	2201	65.2
92_8_Olivine1	40.00	46.17	13.02	0.304	0.198	0.315	86.3	101179	1537	2386	2248	65.8
92_8_Olivine2	40.44	47.99	10.74	0.353	0.166	0.306	88.8	83494	1282	2773	2186	65.1
92_8_Olivine2	40.37	48.04	10.77	0.347	0.163	0.312	88.8	83737	1262	2726	2229	66.4
92_8_Olivine2	40.35	48.00	10.82	0.349	0.166	0.307	88.8	84112	1287	2746	2194	65.3
92_8_Olivine2	40.34	47.93	10.90	0.344	0.171	0.310	88.7	84726	1326	2701	2217	63.9
92_8_Olivine3	40.36	48.22	10.61	0.355	0.159	0.295	89.0	82475	1233	2792	2106	66.9
92_8_Olivine3	40.44	48.12	10.63	0.356	0.162	0.295	89.0	82623	1256	2794	2111	65.8
92_8_Olivine3	40.38	48.12	10.69	0.350	0.164	0.299	88.9	83069	1267	2749	2134	65.6
92_8_Olivine3	40.36	48.13	10.69	0.351	0.168	0.298	88.9	83126	1299	2761	2131	64.0
92_8_Olivine3	40.37	48.01	10.80	0.350	0.167	0.301	88.8	83917	1296	2747	2152	64.7
92_8_Olivine3	40.40	47.95	10.83	0.345	0.169	0.300	88.8	84199	1308	2712	2146	64.4
92_8_Olivine4	40.29	47.42	11.46	0.333	0.179	0.315	88.1	89099	1389	2615	2248	64.2
92_8_Olivine4	40.27	46.87	12.04	0.319	0.186	0.315	87.4	93622	1438	2507	2250	65.1
92_8_Olivine4	40.30	47.30	11.58	0.327	0.182	0.307	87.9	90025	1411	2573	2195	63.8
92_8_Olivine4	40.20	46.81	12.18	0.304	0.189	0.313	87.3	94642	1463	2388	2238	64.7
92_8_Olivine5	40.20	47.47	11.53	0.318	0.183	0.309	88.0	89585	1414	2497	2210	63.4
92_8_Olivine5	40.37	47.45	11.37	0.327	0.173	0.310	88.1	88411	1339	2568	2216	66.0
92_8_Olivine6	40.34	47.43	11.42	0.325	0.174	0.311	88.1	88776	1350	2557	2220	65.8
92_8_Olivine6	40.25	47.51	11.42	0.331	0.179	0.315	88.1	88779	1385	2597	2255	64.1
92_8_Olivine6	40.25	47.33	11.60	0.326	0.182	0.317	87.9	90158	1410	2563	2269	63.9
92_8_Olivine7	40.54	48.26	10.45	0.349	0.156	0.248	89.2	81250	1205	2744	1771	67.4
92_8_Olivine7	40.49	48.27	10.48	0.354	0.159	0.250	89.1	81425	1234	2783	1784	66.0
92_8_Olivine7	40.55	48.10	10.58	0.352	0.160	0.260	89.0	82267	1236	2764	1859	66.6
92_8_Olivine7	40.48	48.04	10.70	0.356	0.165	0.266	88.9	83172	1277	2800	1901	65.1
92_8_Olivine7	40.41	47.97	10.83	0.345	0.169	0.280	88.8	84179	1311	2710	2004	64.2

Sample	SiO ₂ %	MgO %	FeO %	NiO %	MnO %	CaO %	Fo#	Fe (ppm)	Mn (ppm)	Ni (ppm)	Ca (ppm)	Fe/Mn
92_8_Olivine8	40.63	48.27	10.34	0.350	0.158	0.255	89.3	80402	1220	2751	1821	65.9
92_8_Olivine8	40.57	48.16	10.50	0.348	0.159	0.258	89.1	81647	1230	2731	1847	66.4
92_8_Olivine8	40.67	48.04	10.52	0.346	0.161	0.261	89.1	81759	1245	2718	1867	65.7
92_8_Olivine8	40.54	47.92	10.76	0.342	0.163	0.271	88.8	83626	1261	2685	1940	66.3
92_8_Olivine8	40.53	47.67	11.00	0.334	0.170	0.287	88.5	85532	1313	2622	2053	65.1
92_8_Olivine8	40.05	45.61	13.54	0.291	0.200	0.312	85.7	105231	1549	2290	2228	67.9
92_8_Olivine9	40.59	47.46	11.14	0.334	0.172	0.306	88.4	86593	1331	2625	2188	65.1
92_8_Olivine9	40.42	47.46	11.30	0.335	0.177	0.305	88.2	87842	1367	2635	2178	64.2
92_8_Olivine9	39.76	44.28	15.15	0.282	0.219	0.318	83.9	117742	1696	2219	2274	69.4
92_8_Olivine10	40.39	47.39	11.41	0.331	0.175	0.304	88.1	88716	1358	2604	2172	65.3
92_8_Olivine10	40.48	47.48	11.23	0.333	0.172	0.305	88.3	87280	1334	2615	2178	65.5
92_8_Olivine10	40.48	47.35	11.36	0.333	0.175	0.306	88.1	88272	1355	2618	2186	65.1
92_8_Olivine11	40.49	47.59	11.11	0.335	0.173	0.298	88.4	86377	1339	2630	2127	64.5
92_8_Olivine11	40.51	47.57	11.12	0.337	0.172	0.294	88.4	86436	1331	2650	2101	64.9
92_8_Olivine11	40.41	47.53	11.24	0.338	0.176	0.309	88.3	87334	1363	2658	2211	64.1
92_8_Olivine11	40.38	47.44	11.37	0.333	0.175	0.296	88.1	88395	1358	2620	2118	65.1
92_8_Olivine11	40.29	46.73	12.18	0.316	0.187	0.308	87.2	94643	1449	2483	2200	65.3
92_8_Olivine12	40.44	46.90	11.85	0.317	0.183	0.312	87.6	92106	1414	2493	2230	65.1
92_8_Olivine12	40.60	47.32	11.28	0.324	0.173	0.306	88.2	87647	1342	2550	2189	65.3
92_8_Olivine12	40.38	46.65	12.17	0.301	0.185	0.315	87.2	94569	1431	2367	2252	66.1
92_8_Olivine13	40.46	47.40	11.32	0.334	0.177	0.311	88.2	87969	1374	2628	2223	64.0
92_8_Olivine13	40.51	47.45	11.23	0.331	0.172	0.311	88.3	87297	1330	2604	2225	65.6
92_8_Olivine13	40.27	46.84	12.06	0.322	0.187	0.318	87.4	93771	1445	2529	2272	64.9
92_8_Olivine14	40.39	47.16	11.64	0.322	0.179	0.313	87.8	90473	1389	2532	2238	65.1
92_8_Olivine14	40.32	46.64	12.24	0.299	0.191	0.316	87.2	95141	1478	2353	2262	64.4
92_8_Olivine14	40.34	46.59	12.25	0.303	0.190	0.329	87.1	95199	1473	2384	2353	64.6
92_8_Olivine15	40.46	47.89	10.86	0.339	0.166	0.284	88.7	84421	1283	2665	2030	65.8
92_8_Olivine15	40.42	47.83	10.95	0.341	0.167	0.288	88.6	85138	1292	2676	2055	65.9

Sample	SiO ₂ %	MgO %	FeO %	NiO %	MnO %	CaO %	Fo#	Fe (ppm)	Mn (ppm)	Ni (ppm)	Ca (ppm)	Fe/Mn
92_8_Olivine15	40.41	47.63	11.15	0.337	0.172	0.294	88.4	86678	1329	2651	2101	65.2
92_8_Olivine15	40.20	46.87	12.14	0.307	0.187	0.304	87.3	94349	1452	2412	2175	65.0
92_8_Olivine15	40.15	46.81	12.25	0.306	0.189	0.300	87.2	95226	1465	2404	2141	65.0
92_8_Olivine15	39.83	45.05	14.32	0.274	0.206	0.318	84.9	111325	1594	2153	2273	69.9
95_54_Olivine1	39.85	45.79	13.56	0.302	0.201	0.297	85.8	105395	1558	2372	2125	67.7
95_54_Olivine1	39.03	41.21	18.96	0.294	0.265	0.243	79.5	147397	2052	2310	1737	71.8
95_54_Olivine2	39.94	45.83	13.41	0.315	0.203	0.307	85.9	104240	1570	2474	2193	66.4
95_54_Olivine2	39.38	43.54	16.26	0.295	0.237	0.285	82.7	126376	1833	2318	2033	68.9
95_54_Olivine3	40.39	47.74	11.11	0.338	0.170	0.260	88.5	86321	1313	2656	1861	65.7
95_54_Olivine3	40.57	47.53	11.12	0.341	0.169	0.265	88.4	86473	1312	2681	1895	65.9
95_54_Olivine3	40.31	47.84	11.08	0.337	0.165	0.264	88.5	86109	1280	2646	1888	67.3
95_54_Olivine3	40.26	47.70	11.26	0.336	0.167	0.279	88.3	87493	1293	2642	1994	67.7
95_54_Olivine3	40.30	47.11	11.79	0.329	0.178	0.290	87.7	91642	1378	2584	2075	66.5
95_54_Olivine4	39.80	45.73	13.66	0.310	0.201	0.294	85.6	106209	1555	2438	2101	68.3
95_54_Olivine4	39.86	45.61	13.71	0.312	0.206	0.297	85.6	106582	1595	2456	2121	66.8
95_54_Olivine4	39.95	45.04	14.21	0.303	0.210	0.285	85.0	110477	1625	2382	2037	68.0
95_54_Olivine5	39.96	46.13	13.10	0.314	0.193	0.303	86.3	101815	1498	2471	2162	68.0
95_54_Olivine5	39.91	46.01	13.27	0.318	0.198	0.299	86.1	103171	1531	2499	2138	67.4
95_54_Olivine5	39.74	45.68	13.76	0.319	0.207	0.290	85.5	106975	1602	2507	2069	66.8
95_54_Olivine6	40.02	45.98	13.19	0.313	0.196	0.298	86.1	102491	1520	2456	2127	67.4
95_54_Olivine6	39.68	44.03	15.47	0.294	0.230	0.295	83.5	120244	1778	2313	2105	67.6
95_54_Olivine7	39.72	45.13	14.33	0.309	0.211	0.294	84.9	111427	1632	2431	2101	68.3
95_54_Olivine7	39.64	45.08	14.46	0.308	0.217	0.294	84.7	112413	1683	2418	2102	66.8
95_54_Olivine7	39.58	44.12	15.49	0.290	0.233	0.286	83.5	120422	1802	2281	2046	66.8
95_54_Olivine8	40.23	46.93	12.03	0.330	0.177	0.300	87.4	93543	1369	2596	2141	68.3
95_54_Olivine8	40.17	46.53	12.49	0.330	0.186	0.297	86.9	97074	1439	2590	2123	67.4
95_54_Olivine8	40.08	46.09	13.03	0.320	0.196	0.290	86.3	101287	1517	2511	2072	66.8
95_54_Olivine9	40.22	47.10	11.86	0.344	0.180	0.298	87.6	92180	1394	2701	2126	66.1

Sample	SiO ₂ %	MgO %	FeO %	NiO %	MnO %	CaO %	Fo#	Fe (ppm)	Mn (ppm)	Ni (ppm)	Ca (ppm)	Fe/Mn
95_54_Olivine9	40.20	46.56	12.43	0.337	0.187	0.298	87.0	96584	1448	2647	2132	66.7
95_54_Olivine9	39.87	45.74	13.58	0.319	0.198	0.299	85.7	105555	1536	2507	2138	68.7
95_54_Olivine10	40.01	46.30	12.87	0.333	0.193	0.290	86.5	100043	1495	2614	2072	66.9
95_54_Olivine10	40.24	46.24	12.71	0.332	0.190	0.292	86.6	98757	1470	2611	2090	67.2
95_54_Olivine10	40.13	46.78	12.28	0.342	0.184	0.293	87.2	95418	1421	2690	2092	67.1
95_54_Olivine11	40.16	47.29	11.73	0.344	0.173	0.297	87.8	91173	1338	2700	2125	68.1
95_54_Olivine11	40.16	47.02	12.02	0.334	0.179	0.293	87.5	93413	1385	2623	2094	67.4
95_54_Olivine12	39.97	46.12	13.11	0.321	0.193	0.282	86.2	101937	1498	2525	2016	68.0
95_54_Olivine12	39.92	45.18	14.09	0.310	0.210	0.288	85.1	109528	1627	2432	2058	67.3
95_54_Olivine13	39.57	44.42	15.20	0.288	0.222	0.297	83.9	118128	1716	2265	2124	68.9
95_54_Olivine13	39.59	43.97	15.63	0.285	0.234	0.292	83.4	121513	1811	2243	2087	67.1
95_54_Olivine15	39.77	45.50	13.93	0.304	0.201	0.297	85.3	108288	1558	2391	2124	69.5
95_54_Olivine15	39.78	45.30	14.12	0.303	0.208	0.297	85.1	109728	1614	2381	2124	68.0
95_54_Olivine16	39.80	45.51	13.88	0.310	0.207	0.295	85.4	107907	1602	2438	2105	67.3
95_54_Olivine16	39.81	45.87	13.50	0.318	0.201	0.293	85.8	104968	1557	2502	2095	67.4
95_54_Olivine17	40.05	46.75	12.40	0.323	0.183	0.294	87.0	96424	1416	2535	2099	68.1
95_54_Olivine17	40.14	46.98	12.08	0.330	0.180	0.290	87.4	93881	1394	2597	2070	67.3
95_54_Olivine18	40.09	46.57	12.55	0.321	0.185	0.288	86.9	97541	1432	2520	2059	68.1
95_54_Olivine18	40.01	46.66	12.54	0.321	0.187	0.288	86.9	97473	1445	2522	2056	67.5
95_54_Olivine18	39.93	46.52	12.74	0.323	0.194	0.290	86.7	99054	1506	2538	2075	65.8
95_54_Olivine18	39.90	46.25	13.05	0.314	0.195	0.296	86.3	101433	1510	2470	2112	67.2
95_54_Olivine18	39.92	45.85	13.42	0.311	0.203	0.296	85.9	104353	1570	2441	2117	66.5
95_54_Olivine19	40.08	46.80	12.31	0.331	0.182	0.294	87.1	95700	1412	2601	2100	67.8
95_54_Olivine19	40.18	46.32	12.69	0.321	0.190	0.293	86.7	98627	1473	2519	2097	67.0
95_54_Olivine19	39.94	46.27	12.97	0.317	0.196	0.301	86.4	100844	1519	2494	2154	66.4
95_54_Olivine20	40.02	46.47	12.71	0.322	0.186	0.293	86.7	98776	1439	2533	2093	68.7
95_54_Olivine20	40.09	46.40	12.72	0.319	0.188	0.286	86.7	98867	1453	2503	2045	68.0
95_54_Olivine20	40.30	46.19	12.70	0.327	0.190	0.290	86.6	98731	1469	2571	2071	67.2

Sample	SiO ₂ %	MgO %	FeO %	NiO %	MnO %	CaO %	Fo#	Fe (ppm)	Mn (ppm)	Ni (ppm)	Ca (ppm)	Fe/Mn
95_54_Olivine20	40.25	46.15	12.80	0.332	0.187	0.287	86.5	99469	1451	2613	2048	68.5

Table 3: Curacao Whole Rock and Calculated Primary Magma Compositions

Sample	Data	Source	SiO2	TiO2	Al2O3	Cr2O3	Fe2O3	FeO	
79be028 (Klaver 1987)	Whole Rock		48.99	0.95	14.09	0		9.44	
Cur36 (Kerr et al., 1996b)	Whole Rock		50.69	1.2	14.28	0.02	1.36	11.04	
126A-8* (Paullick et al., 2006)	Whole Rock		59.27	0	0.9	0.36	0.61	4.57	
79be028	Primary Magma	peridotite	48.58	0.79	11.6	0	0.86	9.18	
CUR36	Primary Magma	pyroxenite	47.94	0.91	10.74	0.02	1.02	11.78	
Hybrid(90/10)***	Primary Magma	hybrid	48.55	0.8	11.53	0	0.88	9.45	
Hybrid(80/20)***	Primary Magma	hybrid	48.48	0.81	11.44	0	0.89	9.71	
Hybrid(70/30)***	Primary Magma	hybrid	48.42	0.82	11.35	0.01	0.91	9.97	
Hybrid(60/40)***	Primary Magma	hybrid	48.26	0.83	11.24	0.01	0.93	10.2	
Hybrid(40/20)***	Primary Magma	hybrid	48.15	0.86	11.08	0.01	0.96	10.73	
Hybrid(20/80)***	Primary Magma	hybrid	48.05	0.88	10.91	0.01	0.99	11.25	
Sample	Data	Source	MnO	MgO	CaO	Na2O	K2O	NiO	P2O5
79be028 (Klaver 1987)	Whole Rock		0.18	8.82	12.68	1.36	0	0.03	0.1
Cur36 (Kerr et al., 1996)	Whole Rock		0.19	7.49	11.2	2.5	0.06	0.01	0.01
126A-8* (Paullick et al., 2006)	Whole Rock		0.08	28.06	0.1	0.24	0.02	0.22	0.01
79be028	Primary Magma	peridotite	0.178/0.184**	17.07	10.8/10.48**	1.12	0	0.0673****	0
CUR36	Primary Magma	pyroxenite	0.175/0.191**	16.85	8.47	1.87	0.04	0.093	0.08
Hybrid(90/10)***	Primary Magma	hybrid	0.178	17.06	10.29	1.19	0	0.0699	0.01
Hybrid(80/20)***	Primary Magma	hybrid	0.178	17.03	10.09	1.27	0.01	0.0725	0.02
Hybrid(70/30)***	Primary Magma	hybrid	0.177	17.01	9.88	1.34	0.01	0.075	0.02
Hybrid(60/40)***	Primary Magma	hybrid	0.177	16.96	9.85	1.42	0.02	0.0775	0.03
Hybrid(40/20)***	Primary Magma	hybrid	0.176	16.92	9.39	1.57	0.03	0.0826	0.05
Hybrid(20/80)***	Primary Magma	hybrid	0.176	16.88	8.93	1.72	0.03	0.0878	0.06

*Assimilant for Curacao AFC Modeling

**Original Value/Adjusted Value

*** Peridotite/Pyroxenite

**** Calculated Ni Content using the Equation: $\text{Ni (ppm)} = 21.6\text{MgO} - 0.32\text{MgO}^2 + 0.051\text{MgO}^3$ (Herzberg, 2011)

Table 4: PRIMELT2 Primary Magmas and Trace Element Ratios for Figure 3

LOCATION	Reference	SAMPLE	SiO2	TiO2	Al2O3	Cr2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O
Burica (Galapagos)	Hauff et al., 2000a	BUR4	48.32	0.74	11.77	0.00	0.86	9.16	0.16	16.86	9.87	2.12	0.09
Cerro Azul (Galapagos)	Teasdale et al., 2005	54	47.06	1.56	13.89	0.13	1.01	8.42	0.16	13.83	11.51	1.87	0.34
Cerro Azul (Galapagos)	Naumann et al., 2002	CA-46	47.38	1.69	11.68	0.16	1.16	9.17	0.17	16.13	10.10	1.84	0.29
Cerro Azul (Galapagos)	Teasdale et al., 2005	16	46.87	1.53	14.12	0.11	0.98	8.43	0.15	13.76	11.56	1.93	0.34
Cerro Azul (Galapagos)	Teasdale et al., 2005	INTRACALDERA SCORIA	47.06	1.61	14.07	0.15	1.04	8.26	0.16	13.30	11.73	2.04	0.36
Cerro Azul (Galapagos)	Teasdale et al., 2005	50	47.10	1.54	14.28	0.11	0.96	8.27	0.15	13.40	11.69	1.92	0.35
Cerro Azul (Galapagos)	Teasdale et al., 2005	14	46.94	1.66	13.63	0.09	0.93	8.61	0.16	14.12	11.18	2.05	0.39
Cerro Azul (Galapagos)	Saal et al., 2007/Kurz and Geist, 1999	SG93-5	46.92	1.75	12.67	0.07	0.95	9.14	0.17	15.59	10.10	2.10	0.29
Cerro Azul (Galapagos)	Teasdale et al., 2005	42	47.34	1.60	14.46	0.13	0.94	7.97	0.15	12.68	12.03	2.11	0.37
Espanola (Galapagos)	White et al., 1993	G86-3	46.63	1.20	14.34	0.05	1.00	8.13	0.18	12.88	10.59	2.58	1.10
Fernandina (Galapagos)	Geist et al., 2006	AHA25 A	47.12	1.79	15.11	0.10	0.93	8.14	0.15	13.22	10.89	2.00	0.31
Fernandina (Galapagos)	Geist et al., 2006	AHA19 A	47.63	1.78	13.07	0.08	1.05	8.69	0.16	14.82	9.97	2.18	0.33
Fernandina (Galapagos)	Geist et al., 2006	AHA30 A	47.11	1.85	12.77	0.07	0.93	9.10	0.09	15.77	9.83	1.85	0.35
Floreana (Galapagos)	White et al., 1993	FL-29	45.22	1.77	15.30	0.13	1.05	8.69	0.18	13.63	10.05	2.81	0.91
Floreana (Galapagos)	Bow, 1979	FL-78	46.50	1.52	14.16	0.00	1.06	8.68	0.19	14.26	10.62	2.24	0.53
Floreana (Galapagos)	Bow, 1979	FL-30	46.23	1.60	14.13	0.00	1.04	8.71	0.17	13.68	10.94	2.47	0.74
Floreana (Galapagos)	Saal et al., 2007/Kurz and Geist, 1999	SG93-22	46.18	1.64	14.12	0.10	1.07	8.79	0.17	13.86	10.40	2.61	0.81
Floreana (Galapagos)	White et al., 1993	FL-26	45.97	1.27	13.67	0.05	0.98	9.38	0.18	15.50	10.67	2.00	0.16
Floreana (Galapagos)	White et al., 1993	FL-25	46.01	1.33	13.56	0.05	0.97	9.32	0.19	15.22	10.77	2.14	0.23
Floreana (Galapagos)	Saal et al., 2007/Kurz and Geist, 1999	SG93-19	46.55	1.73	14.05	0.12	1.05	8.52	0.18	13.79	11.16	2.15	0.48
Floreana (Galapagos)	Saal et al., 2007	NSK97-260	46.71	1.76	14.39	0.12	1.02	8.15	0.17	12.86	11.75	2.30	0.54
Floreana (Galapagos)	White et al., 1993	FL-3	46.96	1.21	14.49	0.04	1.00	8.09	0.18	12.82	10.70	2.60	1.10
Floreana (Galapagos)	Saal et al., 2007/Kurz and Geist, 1999	SG93-23	47.11	1.29	14.27	0.15	1.03	8.20	0.16	12.81	10.97	2.84	0.90
Floreana (Galapagos)	Bow, 1979	FL-33	47.45	1.15	14.65	0.00	1.00	8.26	0.17	13.49	10.32	2.61	0.64
San Cristobal (Galapagos)	Geist et al., 1986	SC-23	46.85	1.39	14.99	0.06	0.97	8.32	0.19	13.50	10.29	2.52	0.50
San Cristobal (Galapagos)	Saal et al., 2007	NSK97-126	46.64	1.07	16.12	0.06	0.95	8.21	0.16	13.26	10.68	2.34	0.32
San Cristobal (Galapagos)	Saal et al., 2007	NSK97-252	46.92	0.96	16.00	0.07	0.94	8.01	0.16	12.81	11.81	2.06	0.11
San Cristobal (Galapagos)	White et al., 1993	SC-75	47.20	1.05	16.46	0.08	0.93	7.79	0.17	12.44	11.56	2.01	0.18
San Cristobal (Galapagos)	Saal et al., 2007	NSK97-254	47.08	0.94	15.72	0.07	0.96	8.18	0.17	13.25	11.08	2.21	0.18
Santa Cruz (Galapagos)	White et al., 1993	SC-64	45.54	0.92	14.87	0.06	1.03	9.12	0.18	14.87	10.25	2.30	0.00
Santiago (Galapagos)	Baitis and Swanson, 1976	JH-86	46.07	1.12	14.19	0.00	0.99	9.22	0.18	15.42	10.64	2.02	0.05
Santiago (Galapagos)	Gibson and Geist, 2010	07DSG74	46.15	1.08	14.49	0.04	0.94	9.14	0.17	15.26	10.55	1.98	0.06
Gorgona (CLIP)	Revillion et al., 2000	GOR501	45.52	0.67	11.08	0.00	1.38	10.54	0.20	19.91	9.76	0.89	0.02
Gorgona (CLIP)	Brugmann et al., 1987/ Jochum et al., 1991	GOR-159	45.33	0.66	12.09	0.46	1.30	10.26	0.18	17.94	10.35	1.26	0.03
Gorgona (CLIP)	Kamenetsky et al., 2010	GOR-94-44	46.40	0.68	11.43	0.00	1.41	10.13	0.19	19.52	9.55	0.61	0.02
Gorgona (CLIP)	Brugmann et al., 1987/ Jochum et al., 1991	GOR-160	45.55	0.66	12.01	0.22	1.28	10.25	0.18	18.03	10.29	1.32	0.06

LOCATION	Reference	SAMPLE	NiO	P2O5	H2O	%ol add	T	TP AFM	KD	Xfo	F AFM	La/Sm _N	Sm/Yb _N
Burica (Galapagos)	Hauff et al., 2000a	BUR4	0.00	0.06	0.00	22.85	1386.1	1504.4	0.306	0.91	0.27	0.86	1.06
Cerro Azul (Galapagos)	Teasdale et al., 2005	54	0.05	0.16	0.00	2.75	1320.4	1427.7	0.299	0.91	0.08	1.78	2.78
Cerro Azul (Galapagos)	Naumann et al., 2002	CA-46	0.06	0.16	0.00	-2.93	1370.9	1487.2	0.303	0.91	0.18	1.80	2.65
Cerro Azul (Galapagos)	Teasdale et al., 2005	16	0.06	0.17	0.00	4.96	1318.9	1425.8	0.297	0.91	0.07	2.37	2.08
Cerro Azul (Galapagos)	Teasdale et al., 2005	INTRACALDERA SCORIA	0.04	0.17	0.00	-1.67	1308.4	1412.7	0.297	0.91	0.05	2.20	2.31
Cerro Azul (Galapagos)	Teasdale et al., 2005	50	0.06	0.17	0.00	5.01	1310.7	1415.6	0.298	0.91	0.06	2.20	2.41
Cerro Azul (Galapagos)	Teasdale et al., 2005	14	0.07	0.19	0.00	11.22	1327.0	1435.7	0.297	0.91	0.07	2.26	2.47
Cerro Azul (Galapagos)	Saal et al., 2007/Kurz and Geist, 1999	SG93-5	0.07	0.18	0.00	15.44	1359.3	1474.0	0.299	0.91	0.12	1.76	2.50
Cerro Azul (Galapagos)	Teasdale et al., 2005	42	0.05	0.17	0.00	3.95	1293.8	1394.0	0.297	0.91	0.04	1.78	2.78
Espanola (Galapagos)	White et al., 1993	G86-3	0.03	0.80	0.50	0.41	1298.5	1400.1	0.288	0.91	0.03	2.20	1.85
Fernandina (Galapagos)	Geist et al., 2006	AHA25 A	0.06	0.18	0.00	5.96	1306.4	1410.2	0.298	0.91	0.08	1.63	2.52
Fernandina (Galapagos)	Geist et al., 2006	AHA19 A	0.06	0.18	0.00	2.53	1342.7	1454.5	0.301	0.91	0.14	1.65	2.57
Fernandina (Galapagos)	Geist et al., 2006	AHA30 A	0.10	0.19	0.00	16.31	1363.2	1478.5	0.301	0.91	0.15	1.65	2.65
Floreana (Galapagos)	White et al., 1993	FL-29	0.05	0.22	0.00	1.66	1316.0	1422.2	0.285	0.91	0.00	3.32	1.59
Floreana (Galapagos)	Bow, 1979	FL-78	0.06	0.18	0.00	1.09	1330.2	1439.6	0.295	0.91	0.07	2.10	2.22
Floreana (Galapagos)	Bow, 1979	FL-30	0.06	0.24	0.00	2.99	1317.1	1423.6	0.291	0.91	0.01	2.93	1.85
Floreana (Galapagos)	Saal et al., 2007/Kurz and Geist, 1999	SG93-22	0.05	0.21	0.00	1.68	1321.1	1428.5	0.290	0.91	0.01	3.18	1.84
Floreana (Galapagos)	White et al., 1993	FL-26	0.07	0.11	0.00	15.07	1357.6	1471.9	0.295	0.91	0.06	2.20	1.52
Floreana (Galapagos)	White et al., 1993	FL-25	0.08	0.13	0.00	14.70	1351.3	1464.7	0.295	0.91	0.04	2.29	1.54
Floreana (Galapagos)	Saal et al., 2007/Kurz and Geist, 1999	SG93-19	0.04	0.19	0.00	0.53	1319.6	1426.6	0.295	0.91	0.05	2.29	2.03
Floreana (Galapagos)	Saal et al., 2007	NSK97-260	0.04	0.19	0.00	-0.87	1298.0	1399.4	0.293	0.91	0.02	2.18	2.00
Floreana (Galapagos)	White et al., 1993	FL-3	0.00	0.81	0.00	0.00	1297.1	1398.1	0.291	0.91	0.03	3.87	1.54
Floreana (Galapagos)	Saal et al., 2007/Kurz and Geist, 1999	SG93-23	0.04	0.23	0.00	-1.90	1296.8	1397.9	0.290	0.91	0.01	3.87	1.81
Floreana (Galapagos)	Bow, 1979	FL-33	0.05	0.22	0.00	2.02	1312.6	1418.0	0.295	0.91	0.08	2.63	1.58
San Cristobal (Galapagos)	Geist et al., 1986	SC-23	0.05	0.22	0.14	5.34	1313.0	1418.5	0.294	0.91	0.07	2.11	1.85
San Cristobal (Galapagos)	Saal et al., 2007	NSK97-126	0.05	0.14	0.00	5.85	1307.4	1411.4	0.295	0.91	0.06	1.59	1.26
San Cristobal (Galapagos)	Saal et al., 2007	NSK97-252	0.04	0.10	0.00	4.55	1296.8	1397.8	0.297	0.91	0.05	0.91	1.13
San Cristobal (Galapagos)	White et al., 1993	SC-75	0.04	0.10	0.00	2.30	1288.2	1386.6	0.298	0.91	0.06	0.98	1.11
San Cristobal (Galapagos)	Saal et al., 2007	NSK97-254	0.04	0.11	0.00	4.08	1307.1	1411.1	0.298	0.91	0.07	1.28	1.04
Santa Cruz (Galapagos)	White et al., 1993	SC-64	0.21	0.29	0.36	8.82	1343.8	1455.9	0.291	0.91	0.04	0.83	1.32
Santiago (Galapagos)	Baitis and Swanson, 1976	JH-86	0.00	0.09	0.00	12.94	1355.8	1469.9	0.296	0.91	0.08	0.79	1.41
Santiago (Galapagos)	Gibson and Geist, 2010	07DSG74	0.07	0.08	0.00	15.95	1352.2	1465.7	0.297	0.91	0.08	0.79	1.17
Gorgona (CLIP)	Revillion et al., 2000	GOR501	0.00	0.03	0.00	-8.10	1445.3	1569.9	0.296	0.92	0.25	0.23	1.36
Gorgona (CLIP)	Brugmann et al., 1987/ Jochum et al., 1991	GOR-159	0.10	0.04	0.00	-3.59	1407.7	1528.5	0.296	0.91	0.12	0.32	0.96
Gorgona (CLIP)	Kamenetsky et al., 2010	GOR-94-44	0.00	0.05	0.00	-17.85	1438.0	1561.8	0.302	0.92	0.30	0.33	1.16
Gorgona (CLIP)	Brugmann et al., 1987/ Jochum et al., 1991	GOR-160	0.10	0.05	0.00	-1.17	1409.5	1530.4	0.296	0.91	0.13	0.33	1.09

LOCATION	Reference	SAMPLE	SiO2	TiO2	Al2O3	Cr2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O
Gorgona (CLIP)	Revillion et al., 2000	GOR514	47.34	0.40	12.23	0.00	1.33	9.52	0.19	17.93	10.08	0.75	0.20
Gorgona (CLIP)	Revillion et al., 2000	GOR502	45.93	0.66	11.71	0.00	1.13	10.22	0.20	18.74	10.20	1.13	0.04
Gorgona (CLIP)	Arndt et al., 1997	GOR-94-26	46.61	0.67	11.68	0.00	1.24	9.98	0.18	19.06	9.58	0.82	0.12
Gorgona (CLIP)	Arndt et al., 1997	GOR-94-35	47.73	0.42	12.06	0.00	1.31	9.59	0.18	18.23	9.60	0.63	0.22
Gorgona (CLIP)	Arndt et al., 1997	GOR-94-32	47.72	0.41	12.30	0.00	1.31	9.45	0.18	17.82	10.03	0.65	0.08
Gorgona (CLIP)	Revillion et al., 2000	GOR519	46.99	0.45	11.92	0.00	1.11	9.56	0.19	17.96	10.06	1.18	0.56
Gorgona (CLIP)	Revillion et al., 2000	GOR520	46.79	0.43	11.44	0.00	0.91	9.93	0.19	18.88	10.08	1.30	0.03
Gorgona (CLIP)	Arndt et al., 1997/Revillion et al., 2002	GOR-94-7	48.19	0.45	12.21	0.00	1.08	9.29	0.17	17.36	10.16	1.00	0.05
Amaine (CLIP)	Villagomez et al., 2011	DV112	48.79	0.81	11.93	0.06	0.86	8.83	0.16	16.07	10.13	2.03	0.16
Amaine (CLIP)	Villagomez et al., 2011	DV111	48.56	0.69	11.79	0.06	0.86	9.08	0.18	16.79	10.49	1.27	0.07
Aruba (CLIP)	White et al., 1999	ARU96-21	48.32	0.80	12.11	0.00	0.93	9.15	0.18	16.93	9.93	1.50	0.09
Central Cordillera (CLIP)	Kerr et al., 2002	COL536	48.73	0.81	10.97	0.00	1.15	9.44	0.17	17.90	9.85	0.85	0.05
Central Cordillera (CLIP)	Millward et al., 1997	GTJ422	49.02	0.89	11.76	0.00	0.83	8.87	0.17	16.26	10.64	1.34	0.15
Central Cordillera (CLIP)	Kerr et al., 2002	COL311	50.11	0.65	12.82	0.00	0.84	8.25	0.16	14.77	10.65	1.61	0.08
Colombia (CLIP)	Villagomez et al., 2011	DV104	46.47	0.82	11.84	0.05	0.90	9.90	0.18	17.84	10.14	1.49	0.17
Colombia (CLIP)	Kerr et al., 1997	COL1	48.09	0.92	12.28	0.00	0.88	9.10	0.16	16.74	10.13	1.38	0.26
Colombia (CLIP)	Kerr et al., 1997	BAR7	49.68	0.75	11.76	0.00	0.84	8.86	0.16	16.34	10.19	1.30	0.06
Colombia (CLIP)	Kerr et al., 1997	BAR5	49.57	0.69	11.47	0.00	0.83	9.00	0.20	16.71	10.04	1.38	0.06
Colombia, Quillan	Mamberti et al., 2003	97G12	47.35	0.57	10.27	0.00	0.87	10.24	0.16	20.00	9.38	1.10	0.00
Duarte (CLIP)	Escuder-Virquete et al., 2007	JE9029	44.68	1.38	7.43	0.26	1.25	11.77	0.16	24.72	7.66	0.54	0.07
Duarte (CLIP)	LaPierre et al., 2000	96VD126*	46.40	1.21	8.66	0.00	1.05	10.83	0.18	19.98	9.83	1.67	0.08
Duarte (CLIP)	Escuder-Virquete et al., 2007	5JE37B	48.33	1.97	7.15	0.19	1.20	10.29	0.16	20.55	9.35	0.59	0.05
Duarte (CLIP)	LaPierre et al., 1999	97VD09	48.93	0.71	12.34	0.00	0.87	8.84	0.17	16.21	10.06	1.46	0.33
Herradura (CLIP)	Mamberti et al., 2003	AH1B	47.69	0.85	11.07	0.00	0.87	9.75	0.17	18.50	9.53	1.45	0.05
Herradura (CLIP)	Hauff et al., 2000a	BH11	48.51	0.76	12.38	0.00	0.88	8.89	0.18	16.19	10.12	1.96	0.07
Herradura (CLIP)	Mamberti et al., 2003	AH8	48.96	0.71	12.16	0.00	0.86	8.93	0.16	16.40	9.75	1.78	0.24
Nicoya (CLIP)	Mamberti et al., 2003	AN53	47.46	0.78	11.07	0.00	0.88	9.73	0.23	18.38	9.86	1.52	0.04
Nicoya (CLIP)	Mamberti et al., 2003	AN76	48.66	0.64	12.12	0.00	0.85	8.94	0.16	16.41	10.31	1.57	0.29
Nicoya (CLIP)	Hauff et al., 2000a	BN19	49.55	0.77	12.75	0.00	0.82	8.29	0.17	14.77	11.08	1.61	0.14
Nicoya (CLIP)	Sinton et al., 1997	NC93-20	48.82	0.78	11.42	0.00	0.85	9.21	0.19	17.16	10.03	1.45	0.05
Osa (CLIP)	Hauff et al., 2000a	OS9	49.63	0.81	12.29	0.00	0.91	8.60	0.16	15.62	10.03	1.79	0.09
Pedernales (CLIP)	Mamberti et al., 2003	99PE24	47.15	0.67	11.11	0.03	0.88	9.75	0.16	18.41	10.08	1.48	0.10
Site 146 (CLIP)	Jolly et al., 2007	CCBP146/43E	47.26	0.89	12.16	0.00	0.93	9.43	0.16	17.47	9.81	1.73	0.07
Venezuelan Basin (CLIP)	Hauff et al., 2000b	15-146-1	47.34	0.84	11.35	0.00	0.86	9.63	0.17	18.05	10.21	1.46	0.02
Venezuelan Basin (CLIP)	Donnelly et al., 1973	15-146-43R-1(131-143)	47.62	0.85	12.15	0.00	0.85	9.52	0.16	17.85	9.68	1.20	0.06

LOCATION	Reference	SAMPLE	NiO	P2O5	H2O	%ol add	T	TP AFM	KD	Xfo	F AFM	La/Sm	Sm/Yb
Gorgona (CLIP)	Revillion et al., 2000	GOR514	0.00	0.04	0.00	-16.39	1407.6	1528.3	0.308	0.92	0.29	0.18	0.46
Gorgona (CLIP)	Revillion et al., 2000	GOR502	0.00	0.04	0.00	12.48	1423.4	1545.8	0.298	0.92	0.21	0.29	1.10
Gorgona (CLIP)	Arndt et al., 1997	GOR-94-26	0.00	0.05	0.00	-1.18	1429.5	1552.4	0.303	0.92	0.30	0.47	0.69
Gorgona (CLIP)	Arndt et al., 1997	GOR-94-35	0.00	0.03	0.00	-12.61	1413.6	1535.0	0.311	0.92	0.31	0.19	0.59
Gorgona (CLIP)	Arndt et al., 1997	GOR-94-32	0.00	0.03	0.00	-14.98	1405.5	1526.0	0.311	0.92	0.30	0.43	0.32
Gorgona (CLIP)	Revillion et al., 2000	GOR519	0.00	0.03	0.00	6.74	1408.1	1528.9	0.303	0.92	0.29	0.25	0.63
Gorgona (CLIP)	Revillion et al., 2000	GOR520	0.00	0.03	0.00	27.53	1425.9	1548.6	0.302	0.92	0.29	0.24	0.70
Gorgona (CLIP)	Arndt et al., 1997/Revillion et al., 2002	GOR-94-7	0.00	0.04	0.00	6.22	1396.3	1515.8	0.311	0.91	0.30	0.18	0.80
Amaime (CLIP)	Villagomez et al., 2011	DV112	0.09	0.08	0.00	19.62	1369.6	1485.7	0.308	0.91	0.27	1.37	1.01
Amaime (CLIP)	Villagomez et al., 2011	DV111	0.09	0.06	0.00	21.94	1384.7	1502.8	0.311	0.91	0.29	1.17	0.76
Aruba (CLIP)	White et al., 1999	ARU96-21	0.00	0.06	0.00	17.46	1387.6	1506.1	0.309	0.91	0.28	1.01	1.06
Central Cordillera (CLIP)	Kerr et al., 2002	COL536	0.00	0.08	0.00	1.41	1407.0	1527.6	0.315	0.91	0.31	1.44	1.33
Central Cordillera (CLIP)	Millward et al., 1997	GTJ422	0.00	0.07	0.00	21.73	1373.6	1490.2	0.313	0.91	0.28	1.09	1.32
Central Cordillera (CLIP)	Kerr et al., 2002	COL311	0.00	0.05	0.00	14.92	1341.5	1453.1	0.316	0.91	0.28	1.05	0.95
Colombia (CLIP)	Villagomez et al., 2011	DV104	0.13	0.07	0.00	27.33	1405.9	1526.4	0.300	0.91	0.19	0.68	1.38
Colombia (CLIP)	Kerr et al., 1997	COL1	0.00	0.08	0.00	20.95	1383.6	1501.6	0.308	0.91	0.28	0.77	1.06
Colombia (CLIP)	Kerr et al., 1997	BAR7	0.00	0.06	0.00	21.03	1375.2	1492.2	0.317	0.91	0.29	1.24	1.40
Colombia (CLIP)	Kerr et al., 1997	BAR5	0.00	0.06	0.00	23.00	1382.9	1500.9	0.316	0.91	0.30	1.24	1.27
Colombia, Quillan	Mamberti et al., 2003	97G12	0.00	0.06	0.00	34.49	1446.9	1571.6	0.306	0.92	0.32	0.90	1.00
Duarte (CLIP)	Escuder-Viruete et al., 2007	JE9029	0.00	0.11	0.00	22.01	1524.5	1659.6	0.288	0.93	1.03	1.31	2.48
Duarte (CLIP)	LaPierre et al., 2000	96VD126*	0.00	0.12	0.00	25.81	1446.5	1571.2	0.299	0.92	0.20	1.80	2.55
Duarte (CLIP)	Escuder-Viruete et al., 2007	5JE37B	0.00	0.15	0.00	6.70	1456.9	1582.6	0.312	0.92	0.35	1.16	2.88
Duarte (CLIP)	LaPierre et al., 1999	97VD09	0.00	0.07	0.00	19.10	1372.6	1489.2	0.312	0.91	0.28	0.82	0.96
Herradura (CLIP)	Mamberti et al., 2003	AH1B	0.00	0.06	0.00	28.54	1418.8	1540.7	0.307	0.92	0.29	1.04	1.10
Herradura (CLIP)	Hauff et al., 2000a	BH11	0.00	0.06	0.00	18.43	1372.1	1488.6	0.307	0.91	0.27	0.94	1.07
Herradura (CLIP)	Mamberti et al., 2003	AH8	0.00	0.05	0.00	20.64	1376.7	1493.7	0.310	0.91	0.28	0.82	0.99
Nicoya (CLIP)	Mamberti et al., 2003	AN53	0.00	0.06	0.00	28.02	1416.5	1538.1	0.305	0.92	0.29	0.87	1.01
Nicoya (CLIP)	Mamberti et al., 2003	AN76	0.00	0.04	0.00	21.11	1376.8	1494.0	0.310	0.91	0.28	0.89	1.00
Nicoya (CLIP)	Hauff et al., 2000a	BN19	0.00	0.06	0.00	16.59	1341.5	1453.1	0.313	0.91	0.26	0.83	1.01
Nicoya (CLIP)	Sinton et al., 1997	NC93-20	0.00	0.06	0.00	24.07	1392.1	1511.2	0.312	0.91	0.29	0.87	1.15
Osa (CLIP)	Hauff et al., 2000a	OS9	0.00	0.06	0.00	13.10	1360.0	1474.7	0.313	0.91	0.28	0.88	1.10
Pedernales (CLIP)	Mamberti et al., 2003	99PE24	0.12	0.05	0.00	28.31	1417.1	1538.8	0.303	0.92	0.29	0.84	1.15
Site 146 (CLIP)	Jolly et al., 2007	CCBP146/43E	0.00	0.08	0.00	20.46	1398.5	1518.3	0.303	0.92	0.27	0.81	1.19
Venezuelan Basin (CLIP)	Hauff et al., 2000b	15-146-1	0.00	0.06	0.00	28.14	1410.0	1530.9	0.304	0.92	0.28	0.77	1.13
Venezuelan Basin (CLIP)	Donnelly et al., 1973	15-146-43R-1(131-143)	0.00	0.06	0.00	27.62	1406.1	1526.7	0.308	0.92	0.29	0.69	1.14

Chapter 2

A pyroxenite source in the Galapagos Plume at 70 Ma: Implications for plume evolution

Abstract

Plume-related magmas produced in OIB and LIPS and their connecting plume tracks provide evidence on the evolution on mantle temperature, size and composition of heterogeneities, and deep geochemical cycles. Here we provide new $^{40}\text{Ar}/^{39}\text{Ar}$ ages, radiogenic isotopes, major and trace element data, and high-precision olivine analyses for samples from the Quepos terrane (Costa Rica) to closely examine the critical LIP-OIB transitional phase of the Galapagos Plume. The new ages indicate that Quepos volcanism began at 70 Ma, persisting for 10 Ma. Our results suggest that a dominant pyroxenite (recycled oceanic crust) source lithology appeared in the Galapagos Plume during this transition. The maximum mantle potential temperature of the plume changed from ~1650 to ~1550 °C at 60-70 Ma. This change corresponds to the appearance of this dominant pyroxenite component that also correlates with increments in the high-field strength elements. Radiogenic isotope ratios (Nd-Pb) suggest that the Quepos terrane samples having both enriched (Northern Domain) and intermediate radiogenic signatures (Central Domain). The presence of a dense pyroxenite component may explain the observed decrease in T_p due to its effect on the plume's buoyancy, as well as the isotopic heterogeneity observed in Quepos lavas.

1. Introduction

The initial melting of mantle plumes produces unparalleled volumes ($5\text{--}40 \times 10^6 \text{ km}^3$) of lava that form continental and oceanic plateaus, which represent the most significant igneous structures on Earth (e.g., Coffin and Eldholm, 1994; Mahoney and Coffin, 1997; Saunders, 2005; Coffin et al., 2006). This type of intra-plate magmatism originates at a deep boundary layer below the upper mantle, (probably the core-mantle boundary) (e.g., Morgan, 1972; Tolstikhin and Hofmann, 2005; Torvik et al., 2010; Burke et al., 2011). During ascent, a plume may develop a volumetrically large “head”, followed by a narrower conduit or “tail”. Geodynamic models suggest that melting of a 500-2000 km wide plume head (Arndt, 2000) forms large igneous provinces (LIPs), characterized by high degrees of partial melting, high mantle potential temperatures (T_p), and widespread lava flows ($> 10^5 \text{ km}^2$) (Richards et al., 1989; Coffin and Eldholm, 1994, Herzberg and Gazel, 2009). These events are sometimes so large that they effect environmental change leading to catastrophic mass extinctions (e.g., Kerr, 2005). Subsequent melting of a plume conduit will form ocean island basalts (OIBs), which may manifest themselves as linear ocean island hotspot tracks. OIBs are magmatically less productive, formed by lower degrees of partial melting relative to plume heads (Herzberg and Gazel, 2009) of a narrow 100 km wide plume conduit or “tail” (Arndt, 2000).

The Galapagos hotspot provides unparalleled opportunities to reconstruct plume evolution due to the on-land accessibility of LIP terranes in the Caribbean and Costa Rica (Alvarado et al., 1997; Denyer and Gazel, 2009; Loewen et al., 2013) and accreted OIB terranes along the western coasts of Panama and Costa Rica (Hoernle et al., 2002).

Recent petrological studies showed that lavas part of the Caribbean LIP (CLIP) melted more extensively and at higher temperatures than lavas from the modern Galapagos Islands (Herzberg and Gazel, 2009). The T_p of the plume ranged from 1560-1620 °C during the Cretaceous and cooled to 1500 °C at present time (Herzberg and Gazel, 2009) at a rate of ~100 °C/Ma. The wide range in T_p for CLIP lavas depends on whether or not Gorgona komatiites were produced by the Galapagos plume (Herzberg and Gazel, 2009). This secular cooling may reflect either 1) more efficient conductive cooling of plume tails relative to heads (e.g., Nolet et al., 2006) or 2) a change in source lithology leading to a decrease in mantle potential temperatures due to plume buoyancy effects (e.g., Farnetani and Samuel, 2005). A change in source lithology may reflect contributions of a pyroxenite component. Entrained pyroxenite in the plume acts as an “anchor” reducing the vertical transit velocity of a plume, thus diffusing more heat relative to a purely peridotite plume due to longer travel times (Kumagai et al., 2008).

The amount, age, and contribution of this subducted slab reservoir fingerprinted in mantle plume geochemistry stands as a topic of great interest to geoscientists. Although a recycled crust signature has been identified in plumes through the use of radiogenic isotopes and trace-element signatures (Zindler and Hart, 1986; Hofmann, 1997; Chauvel et al., 2008) the exact nature of geochemical exchanges and mixing of pyroxenite with mantle endmembers requires further investigation. Global scale recycling of crustal material undoubtedly plays a key role in the development and evolution of deep geochemical reservoirs as well as affecting the thermodynamic cooling of Earth. Furthermore, when compared with a primitive mantle reference, typical OIB trace

element signatures show positive high field strength element (e.g., Nb and Ta anomalies), suggesting a subducted slab reservoir in the mantle (McDonough, 1991; Rudnick et al., 2000; Kamber and Collerson, 2000). This reservoir could represent the mantle domain component common in all plumes (e.g., C, FOZO) (Zindler and Hart, 1986; Hart et al., 1992; Strake et al., 2005).

Our objective in this study is to clarify the extent of pyroxenite derived melts present in the Quepos terrane, Costa Rica and its affect on T_p during the important CLIP-OIB transition of the plume. Using integrated petrological, isotopic, and olivine geochemical analyses, we show for the first time that a significant decrease in T_p (~100 °C) is evident in Quepos picobasalts and corresponds to the appearance of a pyroxenite component. Furthermore, previous studies suggested that the age of the Quepos terrane to be 65 Ma (Hauff et al., 2000). However, our new Ar-Ar data indicates that the age of the Quepos terrane is approximately 5 Ma older than previously suggested, at 70 Ma.

2. Geologic Background

The formation of the Caribbean Large Igneous Province (CLIP) began circa 95 Ma with the incipient melting of the Galapagos plume head (Duncan and Hargraves, 1984; Richards et al., 1989; Pindel and Barrett, 1990; Kerr, et al., 1996; Hauff et al., 1997; Sinton et al., 1997; Kerr et al., 1997; Hauff et al., 2000a;). The Caribbean plate represents an overthickened section of oceanic crust (~20 km) and is most likely the product of Cretaceous intraplate Galapagos hotspot magmatism (Duncan and Hargraves, 1984; Hauff et al., 1997, 2000a, b; Sinton et al., 1998; Kerr et al., 1996; Hoernle et al., 2002, 2004). The CLIP then migrated northeast with the Farallon Plate where it collided

with the Greater Antilles Arc (e.g., Duncan and Hargraves, 1984; Hauff et al., 2000; Geldmacher et al., 2003). This collision triggered a reversal in subduction polarity, which initiated subduction along the western edge of the CLIP margin (Geldmacher et al., 2003). The reversal in polarity facilitated the migration of the CLIP farther northeast between the converging North and South Americas between Late Cretaceous to Tertiary time (e.g., Duncan and Hargraves, 1984; Hauff et al., 2000a; Hoernle et al., 2002a; Geldmacher et al., 2003).

The exact age of incipient melting of the Galapagos plume still remains contested. Hoernle et al., 2002, 2004 proposed that the CLIP did not form from a single, voluminous pulse of magmatism, but rather through the gradual accretion of igneous structures such as hotspot tracks and plateaus. Their $^{40}\text{Ar}/^{39}\text{Ar}$ age results from the Nicoya Peninsula, Costa Rica extended the CLIP age range of volcanic activity to 70 Ma (139-69 Ma). It is now generally accepted that the main pulse of magmatism occurred at 89 Ma with a second, less voluminous pulse at 75 Ma (Hauff et al., 2000a; Hoernle et al., 2002; Kerr et al., 1996; Revillon et al., 2000; Sinton et al., 1997, 1998).

Petrological and geochemical investigations of the Burica, Osa, and Quepos terranes in western Costa Rica (Figure 1) together with Azuero and Sona terranes in Panama, provide strong evidence that these areas represent accreted Galapagos OIB terranes and aseismic ridges, which resulted from melting of the plume tail post CLIP formation. These terranes are markedly younger than CLIP related lavas (95 Ma) with $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 65-40 Ma (Sinton et al., 1997; Hauff et al., 2000a; Hoernle et al., 2002a) and represent the oldest Galapagos plume tail segments accreted to Central

America. Around 23 Ma the Farallon Plate broke up to form the Nazca and Cocos plates (e.g., Lonsdale, 2005). During the next 20 Ma the Galapagos hotspot and the Cocos-Nazca ridge experienced a series of complex interactions (Werner et al., 2003). The ridge-hotspot interactions subsequently formed the Cocos and Carnegie aseismic ridges located on the eastward moving Cocos and Nazca Plates respectively.

The present day archipelago is currently divided into four domains, characterized by unique isotopic variations in Nd-Sr-Pb and $^3\text{He}/^4\text{He}$ (Harpp and White, 2001; Hoernle et al., 2000). The Eastern Domain represents the most depleted isotopic end-member (Hoernle et al., 2000; Harpp and White, 2001) with compositions resembling those of mid ocean ridge basalt (MORB). The isotope depletion is thought to result from either a) continuous melt depletion as the plume migrates towards the Galapagos Spreading Center (Hoernle et al., 2002) or b) entrainment of asthenospheric material (White and Hofmann, 1978; Geist et al., 1998; White et al., 1993; Harpp and White, 2001). On the opposite end of the spectrum, lavas from the island Floreana define the most isotopically enriched endmember (Southern Domain) with high radiogenic $^{87}\text{Sr}/^{88}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (Harpp and White, 2001). This characteristic may reflect a HIMU component (Harpp and White, 2001) or hydrously altered oceanic crust (Harpp et al., 2013) present in the plume. Lavas in the Wolf-Darwin Lineament (Northern Domain) are probably the most enigmatic and the source of this endmember's characteristics remains unknown. These islands typically display small ^{207}Pb and ^{208}Pb enrichments (Harpp and White, 2001; Vidito et al., 2013) though are depleted in $^{87}\text{Sr}/^{88}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ relative to Floreana lavas (Harpp and White, 2001). Several possibilities exist including contributions of

recycled sediment (Dupré and Allegre, 1983) or subcontinental lithospheric mantle and recycled oceanic crust (Hart, 1984). Lavas from the Quepos terrane (focus of this study) closely resemble the Northern domain in terms of Nd, Hf and $^{206}\text{Pb}/^{204}\text{Pb}$, yet resemble Central Domain volcanics with respect to $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ (Hoernle et al., 2000; Geldmacher et al., 2003). Islands in the Central domain, e.g., Fernandina most likely resemble the true “plume” composition and show intermediate enrichments in Sr, Nd, Pb with high $^3\text{He}/^4\text{He}$ (Harpp and White, 2001). The northern domain $^3\text{He}/^4\text{He}$ ratios typically vary between 8.8-6.9 $\text{R}/\text{R}_\text{A}$, while the central domain $^3\text{He}/^4\text{He}$ ratios are as low as 13.7 (Geldmacher et al., 2003) and as high as 30.3 $\text{R}/\text{R}_\text{A}$ (Kurz et al., 2014). Furthermore, Hauff et al. (2000) measured $^3\text{He}/^4\text{He}$ ratios on two samples of Quepos olivine separates. Their results show that both samples have high initial $^3\text{He}/^4\text{He}$ ratios (11.4 and $11.7 \pm 0.3 \text{ R}/\text{R}_\text{A}$). These observed ratios are significantly greater than those measured from MORB ($\text{R}/\text{R}_\text{A} = 7\text{-}9$). It stands important to note that the Sr-Nd-Pb characteristics of the central domain isotopically resemble the C-PHEM-FOZO component common to mantle plumes e.g., Hart et al., 1992; Farley and Craig, 1992; Hanan and Graham, 1996. Olivine phenocrysts from Fernandina (central domain) also record the highest (30.3 $\text{R}/\text{R}_\text{A}$) helium ratios found in the archipelago. These observations suggest that central domain lavas originate from the hot, central part of the plume and indicate the primary magma composition of the source (Graham et al., 1993; Kurz and Geist, 1999; Harpp and White, 2001; Blichert-Toft and White, 2001; Kurz et al., 2014).

The Quepos terrane is one of six fault-bounded oceanic igneous terranes located on the Pacific Costa Rican coast (Figure 1). An intra-plate Galapagos origin is now

generally accepted to explain the formation of Quepos based on petrological (Hauff et al., 1997), field-based observations, and trace element data (Frisch et al., 1992) and represents the oldest accreted segments of the Galapagos OIB stage (Hauff et al., 1997). The lava stratigraphy of Quepos is dominated by a transitional tholeiitic series with incompatible trace element patterns indicative of an OIB source (Hauff et al., 2000).

3. Methods

Picrite, diabase, and basalt samples were collected at the Quepos terrane, from in-situ outcrops of fresh-meter size boulders next to outcrops the shoreline to take advantage of fresh surf erosion exposures. Outcrop location can be found in Table S1 in the Supplementary materials.

To obtain the $^{40}\text{Ar}/^{39}\text{Ar}$ data, groundmass and mineral separates were irradiated for 60 hours at the Oregon State University TRIGA-type reactor in the Cadmium-Lined In-Core Irradiation Tube. At the University of Wisconsin-Madison Rare Gas Geochronology Laboratory, incremental heating experiments were conducted using a 25 Watt CO_2 laser. Each step of the experiment included heating at a given laser power, followed by an additional 10 min for gas cleanup. The gas was cleaned with two SAES C50 getters, one of which was operated at $\sim 450^\circ\text{C}$ and the other at room temperature. Blanks were analyzed after every second laser heating step, and were less than 5×10^{-20} mol/V for ^{36}Ar and 2×10^{-17} mol/V for ^{40}Ar , respectively. Argon isotope analyses were performed using a MAP 215–50, and the isotope data was reduced using ArArCalc software version 2.5 (<http://earthref.org/ArArCALC/>). Ages were calculated from the blank-discrimination and decay-corrected Ar isotope data after correction for interfering

isotopes produced from potassium and calcium in the nuclear reactor (Supplementary Materials, Table S2). Ages are reported with 2σ uncertainties (includes the J uncertainty) and are calculated relative to a Fish Canyon standard age of 28.201 ± 0.046 Ma (Kuiper et al., 2008) and a value for $\lambda^{40}\text{K}$ of $5.463 \pm 0.107 \times 10^{-10} \text{ yr}^{-1}$ (Min et al., 2000) (Supplementary Table 1).

Alteration-free rock chips were selected under microscope and powdered in an alumina mill at the Department of Geosciences at Virginia Tech. From these powders, whole rock major (Figure 2A) and trace element composition (Figure 3) were collected at Washington State University by XRF and ICP-MS (protocols in Johnson et al., 1999) and are reported in Table S1.

Radiogenic isotope ratios for Pb, Nd, and Sr were collected on a Neptune multi collector ICPMS at Center for Elemental Mass Spectrometry (CEMS), University of South Carolina (USC). Pb isotope ratios were determined by the TI-addition technique (White et al., 2000). The NBS-981 was determined at $^{206}\text{Pb}/^{204}\text{Pb} = 16.936 \pm 0.001$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.490 \pm 0.001$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.694 \pm 0.003$ (2 standard deviations, $n = 13$). Isotopic ratios for Nd were normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ and the Nd standard JNd_i was measured at $^{143}\text{Nd}/^{144}\text{Nd} = 0.5121$ and 0.512112 ± 0.000007 ($n=6$) at USC. Isotopic ratios for Sr were normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and replicate analyses 0.710320 ± 0.000012 . All Sr measurements are reported relative to NBS-987 $^{87}\text{Sr}/^{86}\text{Sr} = 0.710250$.

Analyses of olivines from Quepos samples were conducted in Rutgers University's JEOL JXA-8200 Superprobe. A modified version of the protocol of (Sobolev et al., 2007) was utilized to obtain high precision trace-element data. Samples

were analyzed with a focused beam (~1 μm) at 20 kV and 300 nA. On peak count times were as follows: Si : 50s; Mg : 80s; Fe : 100s; Ni : 150s; Ca : 150s and Mn : 150s. The San Carlos olivine standard was analyzed at regular intervals during each run in order to correct for instrumental drift. A summary of the primary standards, statistics for the secondary standards and statistics for the olivine analyses are given in Tables 1A-C in Supplementary Materials. We modeled primary magmas to infer pyroxenite source contributions using PRIMELT-II software following method of Herzberg and Asimow, 2008. A detailed description of source magma determination is located in the Supplementary Materials section.

4. Results

The matrix of four samples from Quepos (three basalts and one picrite) were dated by $^{40}\text{Ar}/^{39}\text{Ar}$, and yielding plateau ages of 61.3 ± 0.75 , 61.5 ± 1.01 , 68.64 ± 0.28 , 70.1 ± 2.94 , and 70.50 ± 1.36 . Supporting data summarizing the $^{40}\text{Ar}/^{39}\text{Ar}$ age dating results is located in the Supplementary Materials section. Previously published $^{39}\text{Ar}/^{40}\text{Ar}$ ages of Quepos basalts yielded ages at 60.1 ± 0.7 Ma (Sinton et al., 2007) and 65.0 ± 0.4 (Hoernle et al., 2002). Plagioclase separates from a gabbro yield an age of 59.4 ± 1.8 Ma (Hauff et al., 2000). Our new measurements agree with the ~60 Ma pulse and extend the maximum age of Quepos volcanism to 70 Ma, indicating that the formation of this complex may have occurred over a 10 Ma interval.

New major and trace element results are summarized in Figures 2 and 3. Quepos lavas are both alkaline and sub-alkaline, with SiO_2 contents ranging from 44-54 wt% and with $\text{Na}_2\text{O}+\text{K}_2\text{O}$ ranging from 2-6 wt% (Figure 2). These lavas are classified as basalts,

basaltic-andesites, trachy-basalts, and one tephrite/basaltite (Figure 2). Quepos picrites are markedly lower in SiO_2 (43-48 wt%) and $\text{Na}_2\text{O}+\text{K}_2\text{O}$ (0.5-2 wt%), but fall well within the micro-basalt/basalt compositional fields (Figure 2). The vast majority of our Quepos samples plot below the peridotite-pyroxenite discrimination line (Figure 2B) defined by Herzberg and Asimow (2008). Primitive mantle normalized spider-diagrams from these samples display broad enrichment in incompatible elements (Figure 3). Quepos lavas show marked positive Ta, Nb, and Ti anomalies as well as depletions in fluid mobile elements (K, Rb, Th, U) relative to elements with similar compatibilities. Additionally, the trace element abundances of our samples closely resemble the incompatible element patterns of both the Cocos and Coiba Ridges (Galapagos tracks) (Figure 3).

High precision analyses of olivines from ten Quepos samples are presented in figure 4 plotted together with analyses from Mauna Kea (Sobolev et al., 2007). Offsets seen in both of these populations from calculated olivine compositions in equilibrium with primary and derivative magmas of a peridotite source (Herzberg, 2011) analyses strongly suggest that both were derived from a mantle source which contained pyroxenite as a separate lithology. Deviation from parallelism in both populations indicates that Cpx fractionation may be contributing to the offset (Herzberg, 2011), however these trends would not extrapolate to peridotite source primary magmas, thus it is impossible for the sources of these magmas to have been a pure peridotite source. Also, given that the offset in the Mauna Kea population is slightly greater, it may be assumed that these magmas were derived from melting of mantle which had more pyroxenite.

Eight new sets of Sr-Nd-Pb isotope ratios are provided in this study (Table X and

Figure 5). The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of our samples vary from 0.512934 to 0.512994. The $^{206}\text{Pb}/^{204}\text{Pb}$ ratios generally range from 18.934 to 19.513. The $^{208}\text{Pb}/^{204}\text{Pb}$ ratios generally range from 38.690 to 38.928. These ratios were age corrected using an average age of 65 Ma, and plotted in Figure 5 compared with modern Galapagos Plume isotopic domains (Hoernle et al. 2000; Harpp and White, 2001).

5. Discussion

The new $^{40}\text{Ar}/^{39}\text{Ar}$ ages presented in this study, suggested that Quepos volcanism lasted for approximately 10 Ma beginning at ~70 Ma and terminating at 60 Ma. Our new data suggest that the initial melting event, which formed this terrane, is ~5 Ma older than previously thought (Hoernle et al., 2002). The trace-element patterns reveal similarity to the current Galapagos hotspot tracks, Cocos, and Coiba Ridges (Figure 3). Therefore, the Quepos terrane is possibly the oldest accreted Galapagos OIB terrane found in Central America and records the transitional phase between CLIP and OIB type volcanism.

CaO-MgO bulk rock compositions can be used as a first order discrimination between peridotite and pyroxenite source derived melts (Herzberg and Asimow, 2008). Samples from the CLIP plot in the area consistent with a dominant peridotite source composition (Fig. 2B) (Sobolev et al. 2007; Herzberg et al., 2013). Our new samples from Quepos plot below that line in range with Mauna Kea (Hawaii) samples interpreted as derived from a pyroxenitic source (Sobolev et al., 2007; Herzberg, 2010). Meanwhile, modern Galapagos archipelago lavas plot in both areas consistent with presence of both peridotite and pyroxenite sources in the plume, as also confirmed by high-precision olivine data from Vidito et al. (2013).

New high-precision data from olivine phenocrysts from this terrane indicate elevated Ni and Fe/Mn and respectively lower Ca contents indicative of the presence of a pyroxenite component (Figure 4). Detailed petrological modeling of these data can be found in the Supplementary Materials. The olivine compositions are also in good agreement with samples from Mauna Kea, interpreted as deriving from a secondary stage pyroxenite, that resulted from the reaction of recycled eclogite-derived melts and peridotite (Sobolev et al., 2007).

Isotope variations in $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ reveal that the Quepos terrane is most similar to the classically defined Northern and Central Domains (Figure 5). In the modern archipelago the Central Domain is by far the most widespread and defines lavas from Fernandina and Isabella (Harpp and White, 2001). This component dominates the center of the archipelago, whereas the other components prevail in the peripheral areas (Harpp and White, 2001). The trace element chemistry, radiogenic isotope ratios, and $^3\text{He}/^4\text{He}$ ratios (Graham et al., 1993; Kurz and Geist, 1999) of Fernandina all suggest that lavas erupted in the western reaches of the archipelago represent the most undegassed, primitive part of Galapagos plume (Harpp and White, 2001).

The origin of the Northern Domain is possibly the most enigmatic of the four isotopic end-members. This domain only accounts for 3.3% of the total isotopic variation and is primarily found in the Wolf-Darwin Lineament and in Pinta Island of the present-day archipelago. Hoernle et al., (2000) first documented the existence of the Northern Domain at Quepos in 60-65 Ma. This Domain was later identified as a major part of the

submerged seamounts in the northern section of the Cocos Ridge offshore of Costa Rica (Werner et al., 2003). The Northern Domain stands unique relative to other Galapagos isotopic domains because it is intermediate in $^{87}\text{Sr}/^{86}\text{Sr}$, ϵNd , and $^{206}\text{Pb}/^{204}\text{Pb}$, but elevated in $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ for a given $^{206}\text{Pb}/^{204}\text{Pb}$ (Harpp and White, 2001). These high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are also observed in lavas from Kerguelen, Gough, Bouvet, and St. Paul, with compositions running sub-parallel to the MORB array (Dupré and Allégre, 1983; Hart, 1984). However, the high Rb/ Sr, U/Pb, and Th/U indicate that the origin of the anomalous Northern Domain transpired early in Earth's history (Harpp and White, 2001). Some possible mechanisms leading to the formation of this isotopically distinct domain include 1) recycling of entrainment of ancient oceanic crust into the plume (Hart, 1984) 2) recycling of subducted sediment (Dupré and Allégre, 1983) 3) delamination of subcontinental lithosphere (Hart, 1984) and 4) deep mantle heterogeneities related to the formation of continents (Hart, 1984). Based on the new data presented here, we favor the interpretation that recycled oceanic crust is responsible for the unique isotopic variability of the Northern Domain.

Our new $^{40}\text{Ar}/^{39}\text{Ar}$ ages and geochemical data provide valuable insight into a crucial phase during the life cycle of the Galapagos plume during CLIP-OIB stage transition, thereby elucidating “head-tail plume evolution”. A main question that remains is what affect does this pyroxenite contribution have on the evolutionary history of the Galapagos plume? Herzberg and Gazel (2009) proposed that lavas part of the CLIP melted hotter and more extensively than lavas from the 0-15 Ma archipelago and Carnegie and Cocos tracks (Figure 6A). A significant decrease in T_p (100 °C) is also

observed between ~70 Ma Quepos lavas and ~90 Ma CLIP lavas (Herzberg and Gazel, 2009). Interestingly, there is also an increasing trend in high-field strength elements concentration (Nb, Ta, Zr, Hf, etc) from 90 to 15 Ma (Figure 6B). Jackson et al., (2008) reported evidence for a global enriched HFSE reservoir commonly sampled by OIBs with correspondingly high $^3\text{He}/^4\text{He}$, and radiogenic $^{187}\text{Os}/^{188}\text{Os}$ that collectively suggest the existence of a mantle source with a refractory eclogite (pyroxenite) component (Jackson et al., 2008). This result advocates important implications for the development of global mantle geochemical heterogeneity. The high $^3\text{He}/^4\text{He}$ ratios of erupted lavas at some hotspots (Galapagos, Hawaii, Samoa, Iceland) are interpreted to originate from a relatively primitive, undegassed mantle reservoir (Kurz et al., 1982; Farley et al., 1992), named PHEM (Farley et al., 1992), FOZO (Hart et al., 1992), or C (Hanan and Graham, 1996). Understanding the nature of FOZO and the development of a nonprimitive (nonchondritic) mantle component is therefore crucial for understanding, the formation of the high HFSE signatures, $^3\text{He}/^4\text{He}$ domain frequently sampled by some plumes (Galapagos, Iceland, Hawaii, Samoa), balancing Earth's HFSE budget from subduction to deep recycling., and evaluating large-scale planetary differentiation processes (Jackson et al., 2008).

The results of this study suggest that the appearance of a pyroxenitic component at 70 Ma correlates with a substantial decrease in the Galapagos plume's T_p . Geodynamic models suggest that plumes which carry pyroxenite components will upwell at slower vertical velocities relative to purely peridotite plumes (Kumagai et al., 2008) and will diffuse more heat due to longer travel times. Since plumes cool via conductive heat loss

to their surroundings as they move vertically (Farnetani and Samuel, 2005; Nolet et al., 2006; Kumagai et al., 2008), those entraining a dense pyroxenite will cool more efficiently. A main question that remains is whether or not CLIP magmas also carried substantial pyroxenite contributions? It is theoretically possible that the “head” of the Galapagos plume did in fact entrain large amounts of recycled crust, although evidence of this may have been obliterated by high partial melt fractions during CLIP volcanism (Herzberg and Gazel, 2009).

6. Conclusions

The new ages constraints presented here indicate LIP-OIB transition occurred about 60-70 Ma in the history of the Galapagos Plume. Our results show that a dominant pyroxenite (recycled oceanic crust) source lithology is observed for the first time ~70 Ma in the record of the Quepos terrane.

The maximum mantle potential temperature of the plume changed from ~1650 to ~1550 °C at ~70 Ma. This change corresponds to the first appearance of the pyroxenite component in the Galapagos plume. Furthermore, there is also an increase in HFSE compositions throughout the evolution of the plume. The presence of a dense pyroxenite component may explain the observed 100 °C decrease in T_p at 70 Ma due to its effect on the plume’s buoyancy, as well as the isotopic heterogeneity observed in Quepos lavas.

Radiogenic isotope ratios (Nd-Pb) suggest that the Quepos terrane is sampled both enriched (Northern Domain) and intermediate radiogenic signatures (Central Domain). The enriched compositions are also consistent with a recycled component.

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8. Figure Captions

Figure 1: A) Tectonic location of the study area (modified from Denyer and Gazel, 2009). B) Map of the accreted oceanic complexes along the coast of Costa Rica and Panama (modified from Denyer and Gazel, 2009). C) Geological map of the Quepos terrane showing sample locations, structures, and areas underlain by basalts and picrites from Duran (2013).

Figure 2: A) Chemical classification of samples using the total alkali versus silica diagram (TAS). B) CaO-MgO discrimination diagram between peridotite and pyroxenite derived magmas from Herzberg and Asimow (2008). The shaded region represents primary magmas of fertile peridotite produced by accumulated fractional melting. Additional data from Stolper et al. (2004) and the Georoc database (<http://georoc.mpch-mainz.gwdg.de/georoc/>)

Figure 3: Multi-element spider diagram normalized to pyrolite mantle (McDonough and Sun, 1995). Note how the new data from Quepos overlap with the current Galapagos tracks, Cocos, Carnegie and Coiba Ridges. Additional data from Hoernle et al. (2000), Werner et al. (2003) and the Georoc database (<http://georoc.mpch-mainz.gwdg.de/georoc/>)

Figure 4: High-precision olivine composition from picrites of the Quepos terrane plotted in the Herzberg (2010) discrimination diagram. Quepos olivine compositions are not consistent with derivation of a peridotite source. Notice how the new Quepos data is within range of Mauna Kea data from Sobolev et al. (2007) interpreted as olivines that

crystallized from a pyroxenite derived primary magma. The green line shows a possible liquid line of descent from a pyroxenite source primary magma. More detailed modeling in the Supplementary Materials.

Figure 5: Age corrected Pb and Nd isotopes of picrite and basalt samples from the Quepos terrane. Most samples fall within the Northern and Central Galapagos Domains.

Figure 6: A) Galapagos plume secular cooling curve modified from Herzberg and Gazel, (2009). Note the drastic decrease in T_p at approximately 70-60 Ma. B) Evolution of the Nb contents (in ppm) vs. time (Ma). Notice as the plume cools down the Nb concentrations increased to a max. ~15 Ma.

9. Figures

Figure 1:

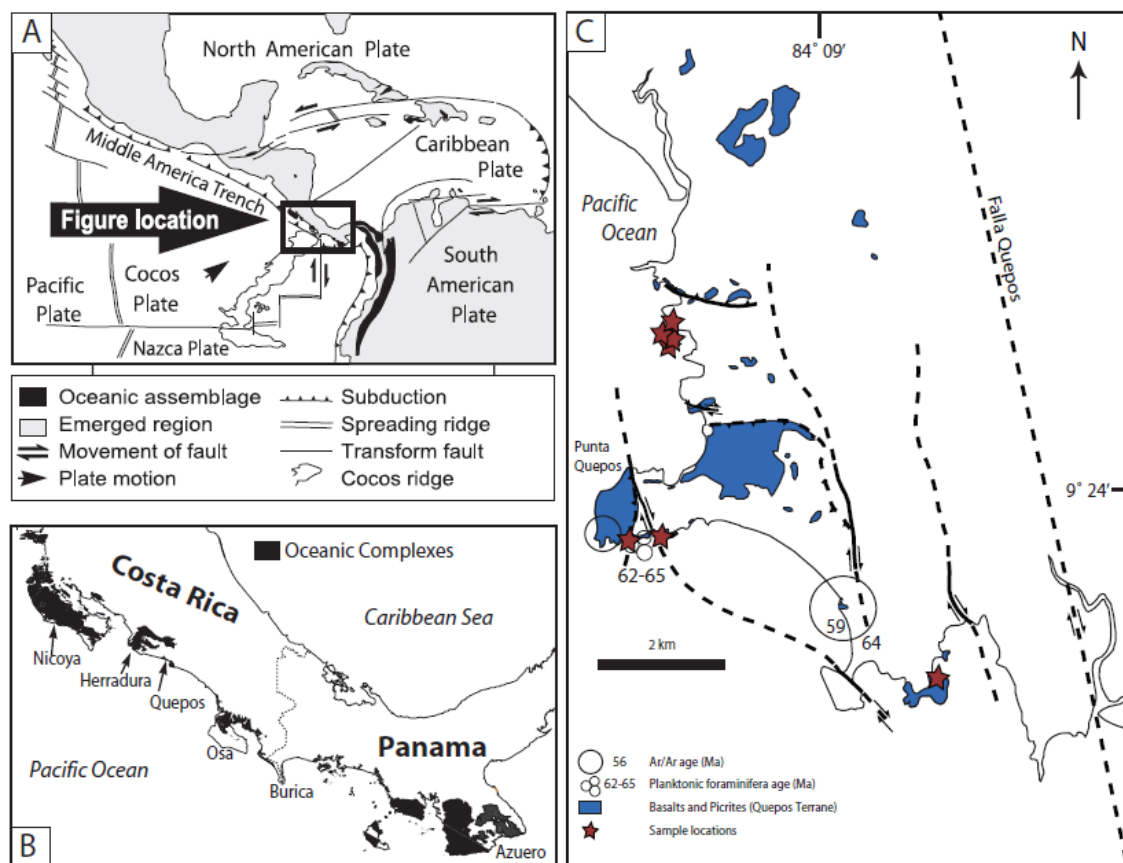


Figure 2:

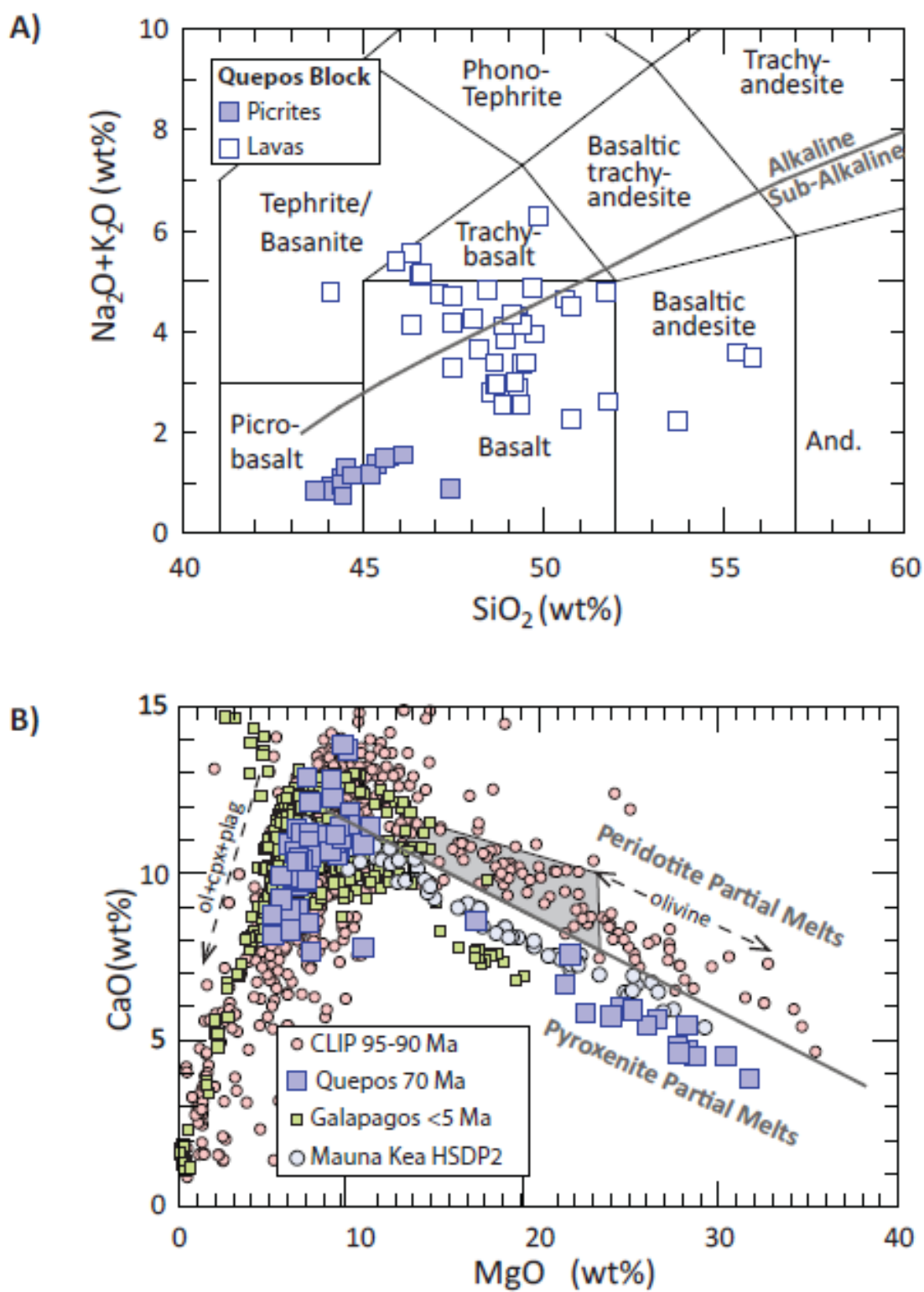


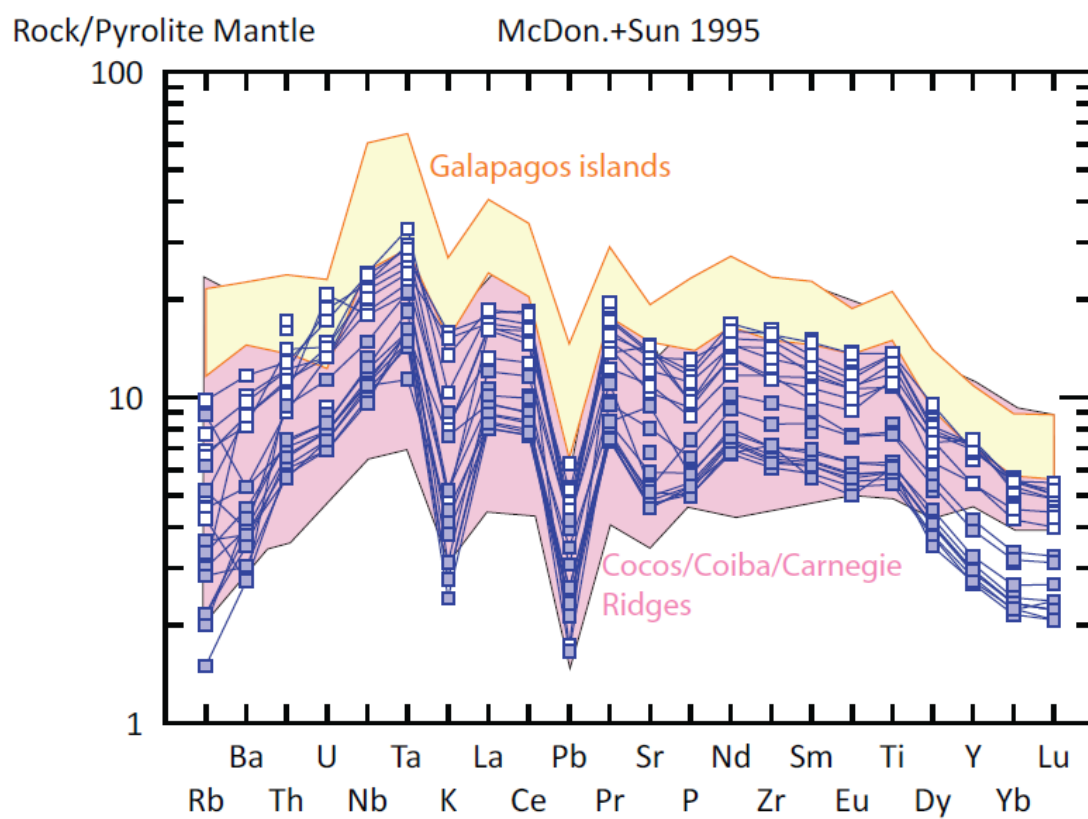
Figure 3:

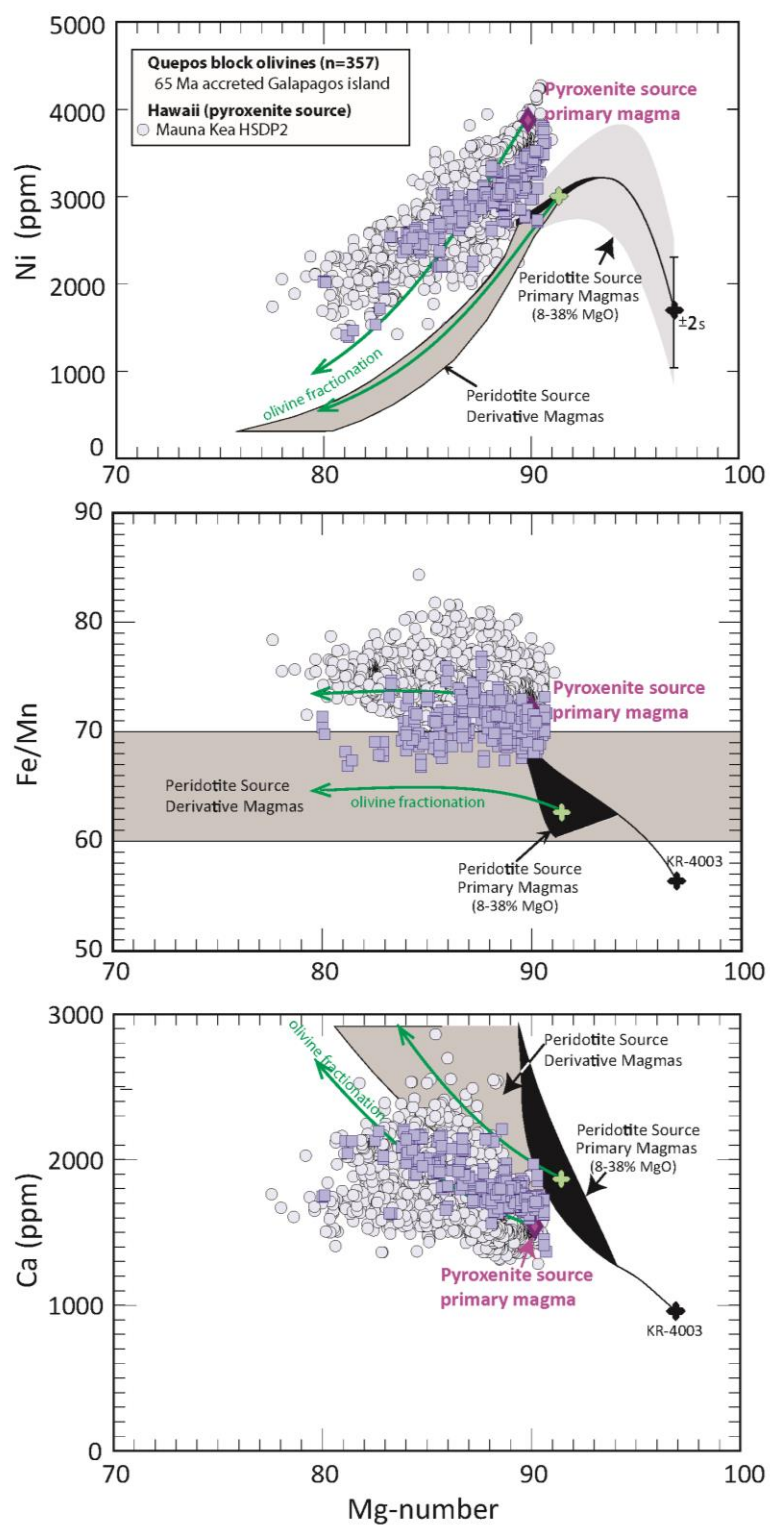
Figure 4:

Figure 5:

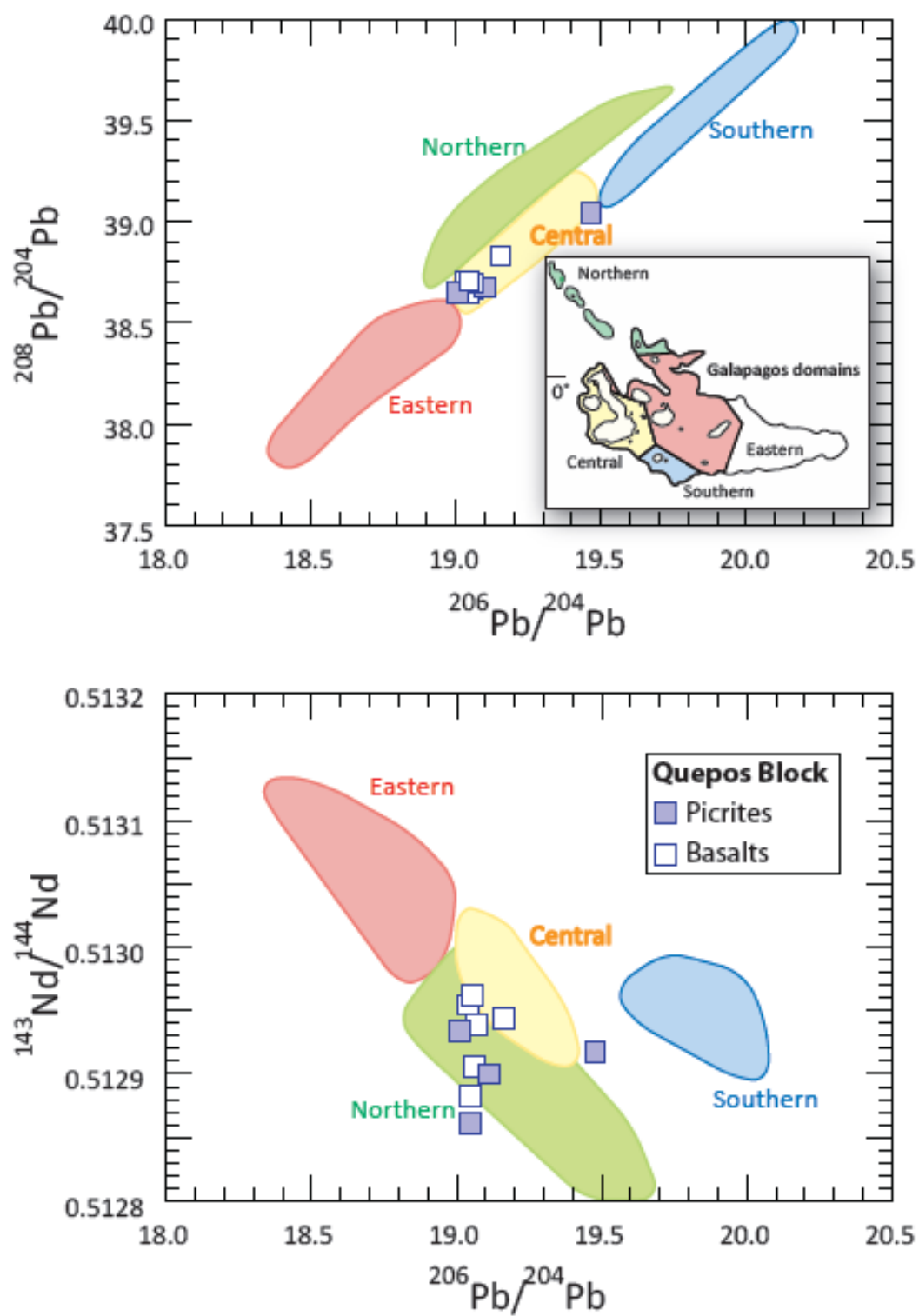
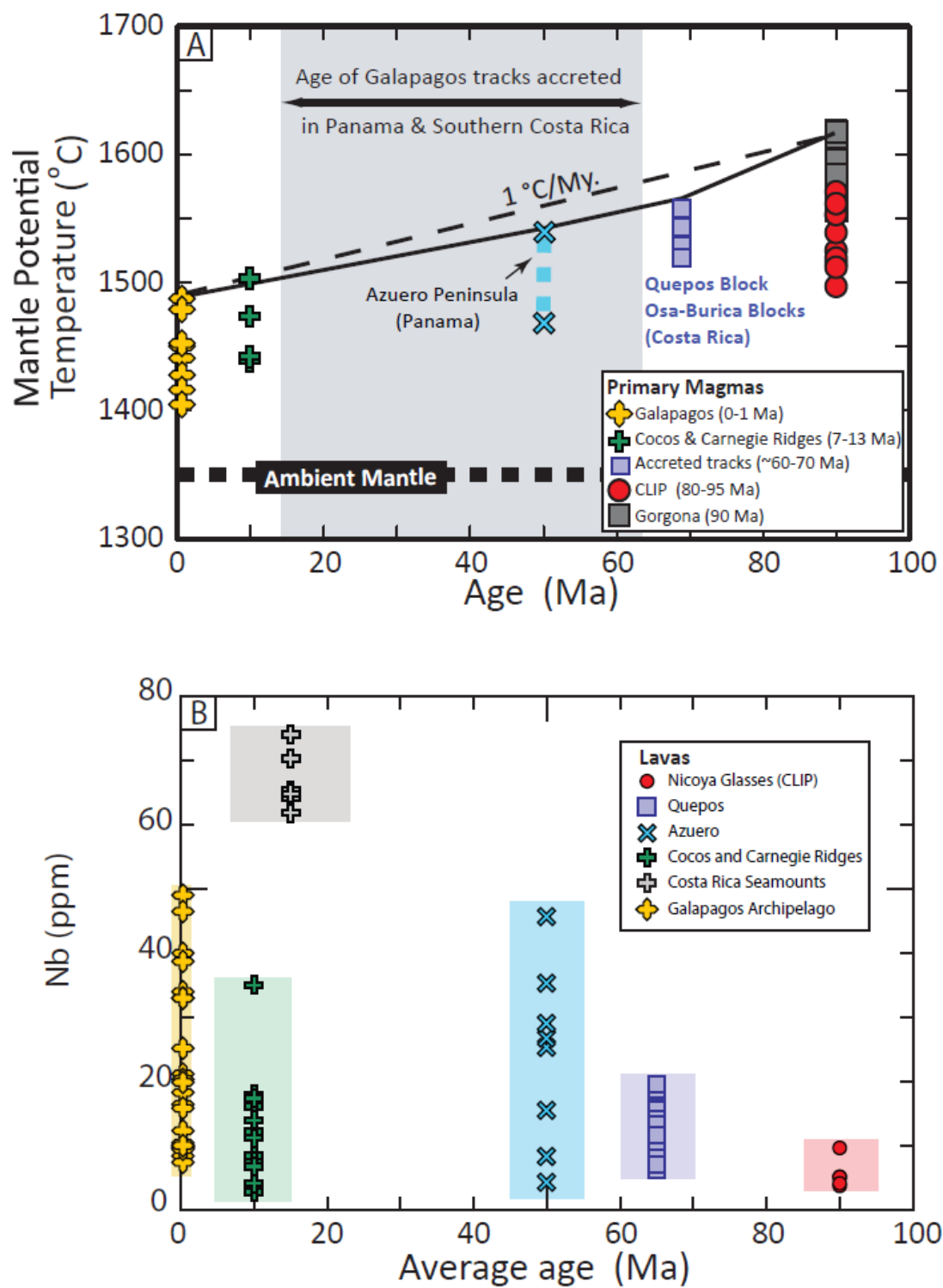


Figure 6:



S.1. Supplemental Materials

S.1.1. Modeling

Fields representing olivine compositions of peridotite source magmas (Pacific Ocean and Indian Ocean MORB (Sobolev et al., 2007)) and pyroxenite source magmas (Mauna Kea (Sobolev et al., 2007)) are presented in Figure 1B along with measures olivine compositions from Quepos sample QP-121311-13. The measured olivine compositions from this study overlaps both fields, thus initially the source of Quepos is ambiguous without modeling. The presence of pyroxenite in the source of Quepos is suggested in the whole rock data of Quepos (Appel, 1990; Kussmaul et al., 1982; Tournon and Azema, 1984; Wildberg, 1984; Meschede and Frisch, 1994; Sinton et al., 1997; Hauff et al., 2000 and this study) plotted in Figure 1A along with the discrimination line of Herzberg and Asimow, 2008.

We infer the source lithology of Quepos through the comparison of Mn, Fe/Mn Ni and Ca measured in olivine phenocrysts against modeled olivine compositions. Figure 1 below provides a visual example of the modeling procedure. Such modeling, first presented in Herzberg, 2011, starts with the calculation of primary magmas. A peridotite source primary magma was calculated from CR372T92 (Tournon and Azema, 1984) in PRIMELT2 (Herzberg and Asimow, 2008). In this first step, olivine is added (blue symbols) and subtracted (red symbols) from the starting composition (yellow cross) incrementally. The peridotite source primary magma (Herzberg and Gazel, 2009), represented by the red star, is obtained when ~26.5% olivine is added to the whole rock analysis. The criteria used for the determination of the primary magma were given in

(Herzberg and Asimow, 2008) and will not be repeated here. Since the Ni content of a magma is easily modified by olivine sorting (Herzberg, 2011), the Ni content of the peridotite primary magma solution is calculated with the following equation from Herzberg 2011:

$$\text{Ni (ppm)} = 21.6\text{MgO} - 0.32\text{MgO}^2 + 0.051\text{MgO}^3$$

Computed Mn of the olivine in equilibrium with this peridotite source primary magma was too high, thus the Mn concentration of the primary magma was adjusted. The array of olivine compositions computed in PRIMELT2 (Herzberg and Asimow, 2008) forms a trend that is sub-parallel to the measured olivine crystals therefore it is improbable that the crystals of QP-121311-13 crystallized from a pure, peridotite source magma.

When observed olivine phenocryst compositions are higher in Ni and Fe/Mn and lower in Ca and Mn than phenocrysts crystallized from a peridotite source primary magma a pyroxenite-bearing source is inferred (Herzberg, 2011; Sobolev et al., 2007). A whole rock analysis of QP-121311-13 was the starting composition for the modeling of a pyroxenite source primary magma. As with PRIMELT2 (Herzberg and Asimow, 2008) olivine is added and subtracted incrementally, however in this calculation the composition of the primary magma is determined when the composition of the liquid reaches the pyroxenite cotectic (Herzberg, 2011). The first LLD calculated from the primary magma of QP-121311-13 (green star) only consists of Ol + L (black line). While

the Ca concentrations of the resulting modeled trend is much more consistent with the observed olivine compositions, the slope of the trend does not match the trend in the observed olivine well. The crystallization of Cpx in addition to olivine causes the Ca content of a magmatic liquid to be lower than if olivine crystallized alone. This results in olivines that are progressively lower in Ca. Cpx compositions were computed using equations for partition coefficients presented in (Herzberg et al., 2013). LLDs in which fixed amounts of Cpx relative to Ol crystallize (green lines), produces trends consistent with the observed olivine crystals of QP-121311-13. A successful solution is when there is a reasonable degree of agreement between the modeled Mn, Fe/Mn, Ni and Ca olivine contents and the measured olivine crystals.

S.1.2. Results

LLDs calculated from the hybrid primary magma of QP-121311-13 plots on top of olivine compositions measured from all 10 Quepos samples (Figure 2). This suggests that this primary magma composition may be representative of the primary magma of these samples and perhaps Quepos in general. Trends in Ni and Ca require high pressure, sub-moho Cpx crystallization that occurred concurrently with olivine crystallization (Herzberg et al., 2013). Modeled Ni and Ca however do not produce trends consistent with the observed olivines that have the same proportions of Olivine/Cpx. The best fit between the observed trend in Ca and the calculated LLDs suggests a ratio of Ol/Cpx of 50/50 in the crystallizing assemblage. Ni on the other hand produces a trend that indicates a higher proportion of Cpx relative to Ol is required in the LLD (Figure 2).

Determining the proportion of pyroxenite in Quepos is not a simple matter. Unfortunately, no isotopic data exists for MS90 (Meschede and Frisch, 1994) so any modeling of source endmembers for Quepos is based entirely on major and minor elements. Petrologic modeling of the endmember proportions is made more complicated by the fact that the amount of Ni and Ca in MS90 appears to be much too high (Figure S3). Also, the proportions of peridotite and pyroxenite in the hybrid primary magmas required to reproduce the Mn trend in the olivines, differ from the proportions required to reproduce the Ca trend in the olivines. The calculated proportion of pyroxenitic melt in the source of Quepos, based on Mn alone, is 24%. If Ca is used 64%, pyroxenitic melt is required.

In order to address the inconsistencies between Ca, Mn and Ni, mixtures of variably fractionated peridotite and pyroxenite source primary magmas was tested. The degree of olivine crystallization for either component is limited by the requirement that the resulting mixture has to be in equilibrium with olivine that has a forsterite content no lower than 90%. LLDs produced from the modeled mixtures, which included only olivine addition and subtraction, were plotted against the olivine composition that is in equilibrium with the hybrid primary magma (QP-121311-13). If olivine is allowed to crystallize from the peridotite source primary magma prior to mixing, the resulting hybrid magmas have higher Ni contents. This is the opposite of what is required. When both endmember primary magmas are allowed to crystallize equal proportions olivine prior to mixing, the difference between the resulting LLDs from the mixture of evolved liquids and the LLD of original mixture of the primary magma endmembers is negligible if the

proportions of the components are equal. The best solution is obtained when the peridotite endmember magma is left as primary and the pyroxenite endmember is allowed to crystallize olivine until the magma has reached ~11.5% MgO. Under these conditions, a mixture of 30% derivative pyroxenitic magma and 70% peridotite primary magma closely approximates the hybrid calculated from QP-121311-13.

The main difficulty with the modeling in figure 3 is how to explain the fractionation of only one magmatic endmember component, given that it is assumed that both endmember primary magmas were produced in the same source region. It may be that extreme composition of MS90 does not accurately represent the true pyroxenite endmember. Instead, this sample may be representative of a different pyroxenite body within the Galapagos plume at ~65 Ma. The disproportionately high Ca content and low Mn in the primary magma of MS90 may point to a pyroxenite source that had a lower modal concentration of Cpx and a higher modal concentration of garnet, than the actual pyroxenitic component in the hybrid magmas. Another possibility is that the relatively low Ni content of the hybrid pyroxenite primary magma is a result of a pyroxenitic component that is not completely free of olivine.

S.2. References

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S.3. Figure Captions

Figure S1: Modeled olivine and derivative liquid compositions for Quepos. Pacific Ocean and Indian Ocean MORB (Sobolev et al., 2007) are included as examples of peridotite source magmas, while Mauna Kea (Sobolev et al., 2007) is included as an example of a pyroxenite source primary magma. The modeling of the peridotite source primary magma (red star) is done by olivine addition (blue circles) and subtraction (red circles) from the whole rock composition (yellow cross) in PRIMELT2 (Herzberg and Asimow, 2008). Since the trend in the measured olivines (orange circles) are sub-parallel to the olivines modeled in PRIMELT2 (Herzberg and Asimow, 2008) a different primary magma (blue star) is computed by subtracting olivine from the whole rock analysis of QP-121311-13. An LLD of Ol + L is calculated from this primary magma as well as Ol + Cpx + L. The consistency with this second model suggests that these olivines crystallized from a pyroxenite-bearing source.

Figure S2: Olivine compositions of ten lavas from Quepos compared to modeled peridotite and pyroxenite source magmas. Modeled olivine compositions from derivative magmas of a peridotite source are sub-parallel to measured olivine compositions in all 4 plots. Good internal consistency between modeled olivine compositions of QP-121311-13 and measured olivines, suggest that this primary magma is representative of the source of these magmas. The largest observed offset of any primary magma from the expected peridotite source compositions indicates that this magma may have been derived from a relatively pure pyroxenite source.

Figure S3: Modeling of mixtures of the peridotite and pyroxenite endmembers to estimate the proportion of pyroxenite in the source of Quepos. These plots show the LLD of a hybrid magma composition consisting of a mixture of 70% peridotite primary magma and 30% of a derivative magma obtained from a pyroxenite primary magma which has crystallized olivine until the MgO content reached ~11.4%. A solution for a mixture of the pure pyroxenite endmember was not possible do to the extremely high Ni content of this primary magma.

S.4. Figures

Figure 1:

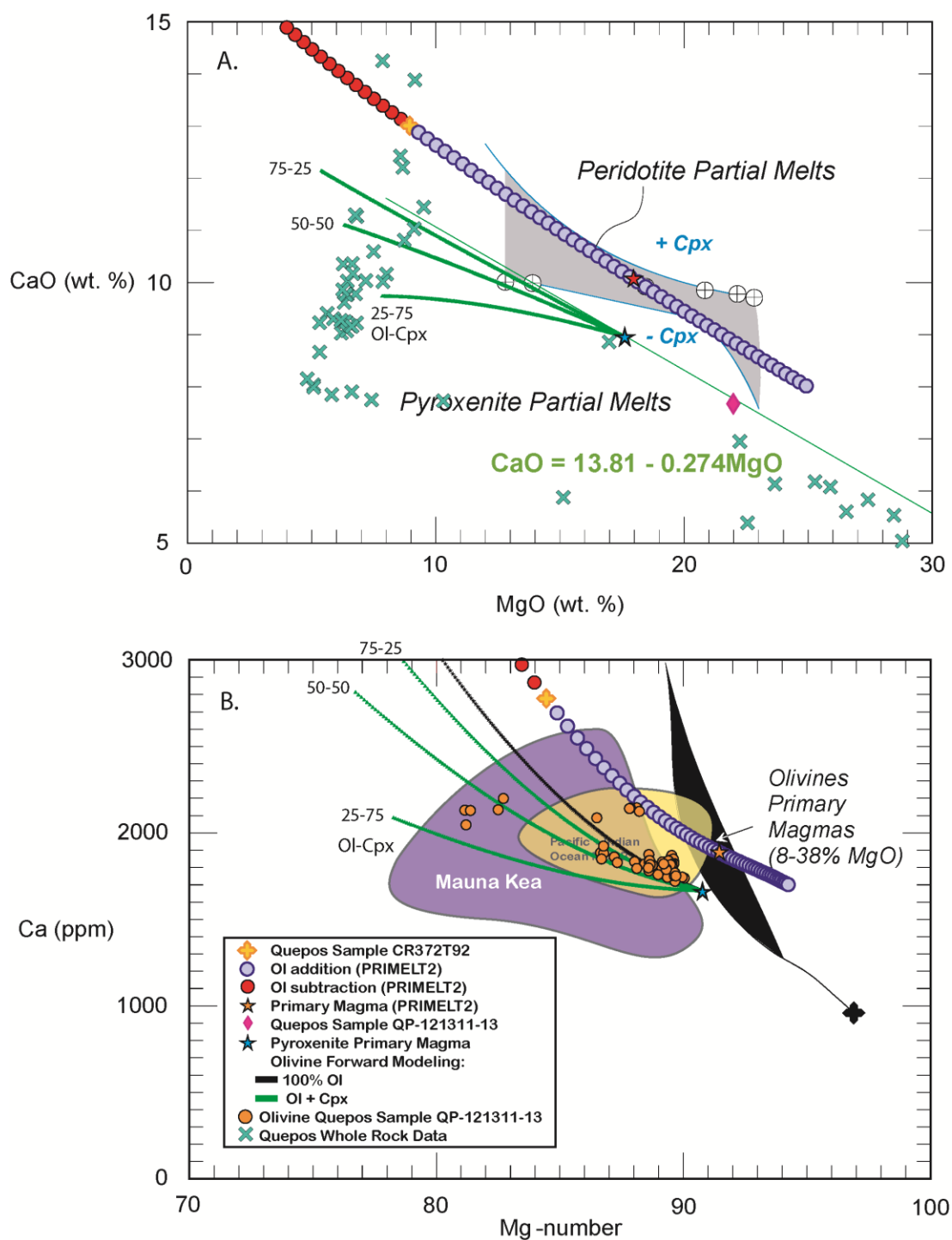


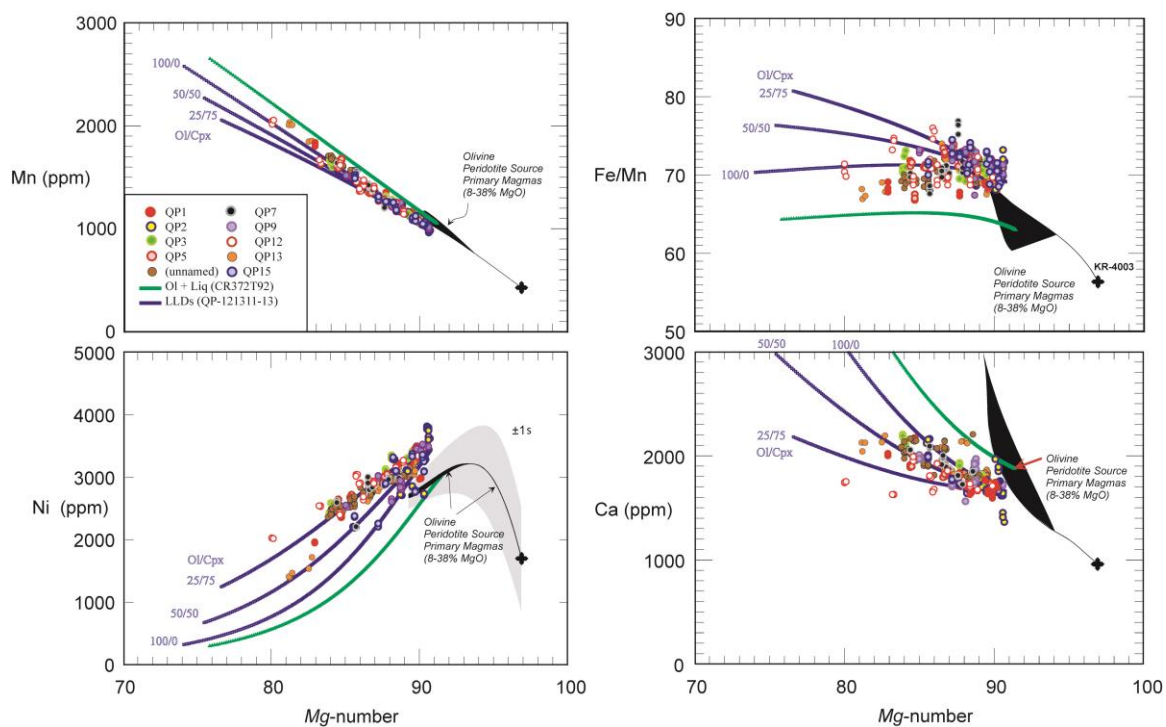
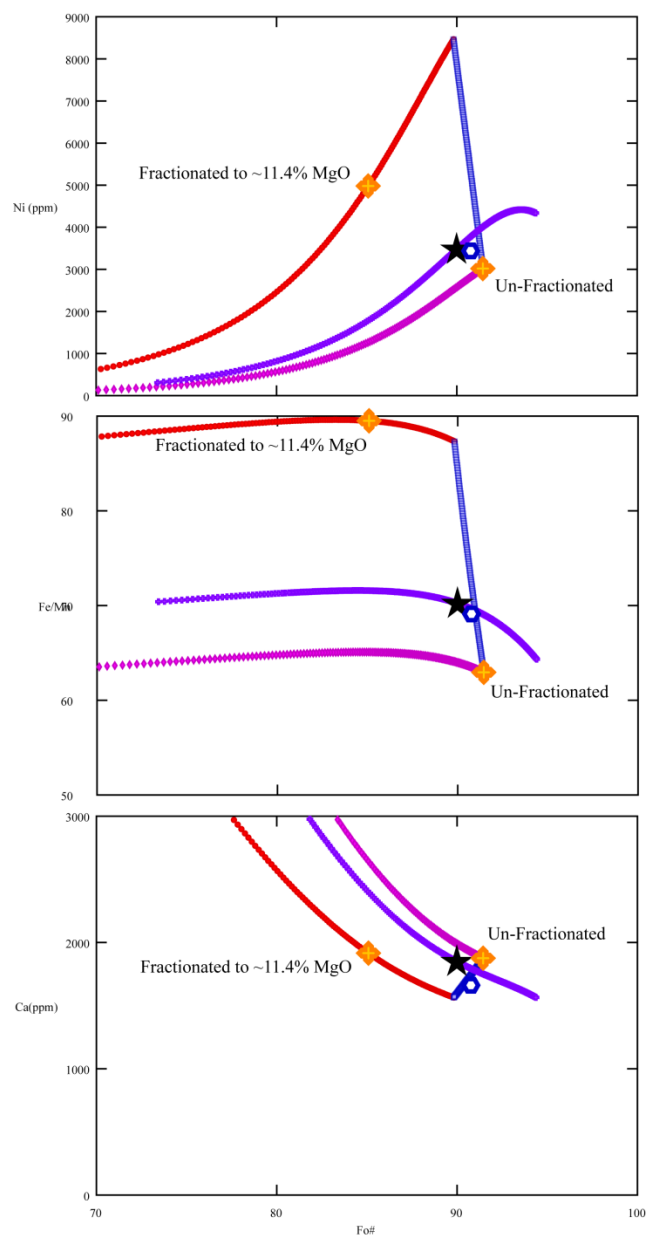
Figure 2:

Figure 3:

Chapter 3

Phantom Archean crust in Mangaia hotspot lavas and the meaning of heterogeneous mantle

Abstract

Lavas from Mangaia in the Cook-Austral island chain, Polynesia, define a HIMU (or high μ , where $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$) global isotopic end-member among ocean island basalts (OIB) with the highest ${}^{206,207,208}\text{Pb}/{}^{204}\text{Pb}$. This geochemical signature is interpreted to reflect a recycled oceanic crust component in the mantle source. Mass independently fractionated (MIF) sulfur isotopes indicate that Mangaia lavas sampled recycled Archean material that was once at the Earth's surface, likely hydrothermally-modified oceanic crust. Recent models have proposed that crust that is subducted and then returned in a mantle plume is expected to transform to pyroxenite/eclogite during transit through the mantle. Here we examine this hypothesis for Mangaia using high-precision electron microprobe analysis on olivine phenocrysts. Contrary to expectations of a crustal component and, hence pyroxenite, results show a mixed peridotite and pyroxenite source, with peridotite dominating. If the isotopic compositions were inherited from subduction of recycled oceanic crust, our work shows that this source has phantom-like properties in that it can have its lithological identity destroyed while its isotope ratios are preserved. This may occur by partial melting of the pyroxenite and injection of its silicic melts into the surrounding mantle peridotite, yielding a refertilized peridotite. Evidence from one sample reveals that not all pyroxenite in the melting region was destroyed. Identification of source lithology using olivine phenocryst chemistry can be further compromised by

magma chamber fractional crystallization, recharge, and mixing. We conclude that the commonly used terms mantle “heterogeneities” and “streaks” are ambiguous, and distinction should be made of its lithological and isotopic properties.

1. Introduction

Oceanic plates, including crust and mantle lithosphere, enter the mantle at subduction zones. Integrated over geologic time, subduction of oceanic crust has generated a large reservoir of crustal material that must now reside in the Earth’s mantle. Regions of buoyantly upwelling mantle, called mantle plumes, are thought to return some of the crustal material to the shallow mantle, where it melts and is erupted at hotspots (Morgan, 1971; Hofmann and White, 1982; White and Hofmann, 1982). In order to evaluate this hypothesis for deep recycling, it is important to detect petrological and geochemical signatures of ancient subducted materials in hotspot lavas.

Lavas from the island of Mangaia, located in the Cook Islands, have the most radiogenic Pb isotope compositions amongst both the HIMU end-member and OIB globally (Woodhead, 1982; Chauvel et al., 1997). This isotopic signature, together with trace element compositions, has been interpreted to reflect a recycled oceanic crust component in the mantle source of Mangaia lavas (Zindler and Hart, 1986; Chauvel et al., 1992; 1995; Hauri and Hart, 1993; Hofmann, 1997; Weaver, 1991; Willbold and Stracke, 2006). Supporting this hypothesis, MIF sulfur isotope signatures, which were uniquely generated in the Earth’s atmosphere in the Archean, were recently discovered in olivine-hosted sulfide inclusions from Mangaia lavas (Cabral et al., 2013). This signature provides the strongest evidence yet for deep recycling of surface materials into the mantle

source of hotspot lavas. Armed with this evidence for deep recycling—from subduction zones to mantle plumes—it is important to characterize the present-day mantle that sourced Mangaia lavas.

The Pb isotope ratios that characterize the HIMU component in OIB must involve a process that strongly fractionates U/Pb and Th/Pb. Loss of Pb during subduction-driven dewatering of the oceanic crust is one such process (Chauvel et al., 1992; 1995; Hofmann, 1997). OIB that sample a region of the mantle with subducted crust, preserved as pyroxenite/eclogite, are expected to crystallize olivine with high Ni, low Ca, low Mn and high Fe/Mn compared to melts of peridotite (Sobolev et al., 2005; 2007; Gurenko et al., 2009; 2010; Herzberg, 2011), and may also be expressed in terms of distinctive trace-element and isotope systematics (Gurenko et al., 2009; Day et al., 2009; 2010; Day and Hilton, 2011). An important question, therefore, is whether HIMU lavas, which sample recycled oceanic crust, crystallize olivine that implicates a pyroxenite protolith.

While recycled crust may contribute to the HIMU component in OIB, it may not be expressed as a distinct pyroxenite lithology. Recycled crust that is mixed into its host peridotite during convective stirring might produce a fertilized peridotite (Jackson et al., 2008; Gurenko et al., 2009; Parai et al., 2009). Understanding the source lithology of HIMU magmas can therefore place constraints on the long-term involvement of recycled crust, whether it is direct in the form of pyroxenite melting beneath a hotspot or indirect in the form of peridotite melting. Inferences about source lithology are now a tractable problem using the composition of olivine phenocrysts as a tracer. Using olivine phenocryst compositions, we draw first-order conclusions about the source lithology of

the HIMU isotopic reservoir using samples from Mangaia, the HIMU type locality, and we discuss implications for the preservation of recycled crust as a pyroxenite lithology in the mantle.

2. Samples, Analytical Methods and Results

Five lavas from the island of Mangaia were examined in this study, and they are all porphyritic olivine- and clinopyroxene-bearing alkali basalts. Two of the lavas, MGA-B-25 and MGA-B-47, were collected in the 1990 field season and were previously characterized geochemically by Hauri and Hart (1993; 1997), and both host MIF sulfur anomalies (Cabral et al., 2013). Point counting of phenocrysts in petrographic thin sections reveals 20% olivine and 20% clinopyroxene in MGA-B-25, and 60% olivine and 10% clinopyroxene in MGA-B-47. New samples were collected during a field campaign in 2010, and they have the following phenocryst modes: MG-1001 (40% olivine and 10% clinopyroxene), MG-1002 (20% olivine and 30% clinopyroxene), and MG-1006 (20% olivine and 10% clinopyroxene). Additionally, all samples contain opaque phases, most likely as chrome-rich spinels as revealed in positive correlations of whole rock MgO-Cr₂O₃.

Major and select trace element (Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb, U, and Th) compositions for samples MG-1001, MG-1002, and MG01006 were measured by XRF at Franklin and Marshall College using a *PW 2404 PANalytical XRF* vacuum spectrometer following the procedures outlined in Boyd and Mertzmann (1987). Briefly, major element analyses by XRF involved standard lithium tetraborate fusion techniques using 3.6:0.4 g LiBO₄:sample powder. Ferrous iron

concentrations were determined by titration with potassium dichromate. Trace element analyses involved standard copolywax preparation (7 g powder: 1.4 g copolywax). Additional details of analytical methods are given at <http://www.fandm.edu/earth-and-environment/major-element-technique>. Whole rock data for MG-B-47 and MG-B-25 were given in Hauri and Hart (1997; 1993).

We analyzed olivine phenocrysts in 7 samples from Mangaia. A total of 316 high precision analyses were obtained from olivine phenocrysts of varying sizes and forsterite contents. Single core analyses were taken from olivine phenocrysts identified as homogeneous from backscatter images. Traverses were taken from olivines that exhibited zoning.

Olivine, major element, and trace element data were obtained using a slightly modified method of Sobolev et al. (2007). Analyses were conducted on the Jeol JXA-8200 electron microprobe at Rutgers University. A current of 300 nA and an accelerating voltage of 20 kV were used for all analyses. Count times on the elements are as follows: 50 s for Si, 80 s for Mg, 100 s for Fe, and 150 s for Mn, Ni, and Ca. We calibrated on synthetic fayalite or tephroite for Si; synthetic forsterite for Mg; synthetic fayalite for Fe; synthetic tephroite for Mn; synthetic Ni_2SiO_2 or SRM 126c (36% Ni) for Ni and Kakanui Augite (USNM 122142) for Ca. We used a San Carlos olivine standard only for drift correction, and it was analyzed at regular intervals throughout every run. Detection limits at a 3σ (99%) confidence level and errors (2σ) were obtained from the Probe for EPMA program (Donovan, 2012). Average detection limits for Si, Mg, and Fe are 30, 22 and 32 ppm, respectively. Average detection limits for trace elements Ni, Mn,

and Ca are 23, 22, and 19 ppm, respectively. Analyses of major elements Si, Mg, and Fe have an average relative 2σ error of $\sim 0.09\%$, $\sim 0.09\%$, and $\sim 0.18\%$ respectively. Average 2σ errors for trace elements Ni, Mn, and Ca are 25 ppm, 31 ppm, and 33 ppm respectively. 2 standard deviations of Ni, Mn, Ca and Fo# for the San Carlos olivine analyses (n=97) in our study are 57 ppm, 31 ppm, 19 ppm and 0.1% respectively. Analyses with oxide totals greater than $\pm 2\%$ deviation from 100% were excluded. Chemical formulas were calculated for all analyses. Analyses with deviations in stoichiometry greater than $\pm 1\%$ were excluded.

Olivine compositions are shown in Fig. 1 for MG-1001, MG-1002, MGA-B-25 and MGA-B-47; they are homogeneous or they display modest normal zoning, with Mg-numbers decreasing from the cores to rims. Results for MG-1006 differ and they will be discussed separately.

3. Petrological Modeling

Our goal is to use high precision olivine data shown in Fig. 1 to infer the lithology of the source that melted to produce the Mangaia lavas. When olivine Mg-numbers are greater than 90, pyroxenite sources are often revealed in olivine phenocrysts with high Ni, low Ca, low Mn and high Fe/Mn compared to olivines that crystallize from melts of peridotite (Sobolev et al., 2005; 2007; Gurenko et al., 2009; 2010; Herzberg, 2011). For example, olivine in mantle peridotite from a wide range of tectonic environments typically contain ~ 3000 ppm Ni (Herzberg et al., 2013); these are similar to olivine in primitive MORB from the East Pacific Rise and olivines that have been inferred to have crystallized from primary magmas of Archean komatiites (Herzberg, 2011; Herzberg et

al., 2013). The inference of source lithology becomes more challenging when interpreting olivine phenocrysts with Mg numbers < 90 , like those from Mangaia (i.e., 79-86; Fig. 1). For example, extraction of heat from a peridotite-source primary magma can be accomplished by fractional crystallization of both olivine and clinopyroxene. When clinopyroxene participates, the derivative magma will be relatively enriched in Ni and depleted in Ca and Mn (Herzberg et al., 2013; Vidito et al., 2013). Olivines that crystallize from such derivative magmas will also be relatively enriched in Ni and depleted in Ca and Mn, a signal that might be confused with a pyroxene-rich source. For Mangaia, the case for clinopyroxene crystallization is obvious in their observed phenocrysts. We assume that clinopyroxene crystallized in a shallow magma chamber below Mangaia, but acknowledge that in other cases it can occur in the mantle (O'Hara, 1968; Albarède et al., 1997; Geist et al., 1998; Herzberg and Asimow, 2008; Herzberg et al., 2013; Vidito et al., 2013). The effects of fractional crystallization must be evaluated in order to draw conclusions about the mantle source (O'Hara, 1968), and this involves petrological modeling.

A detailed description of the method we adopt for petrological modeling (Herzberg, 2011; Herzberg et al., 2013), and is given again in a somewhat abbreviated form. The petrological model has the following components: 1) identification of a primary magma composition, 2) calculation of a liquid line of descent after variable proportions of olivine and clinopyroxene have been subtracted, 3) calculation of the compositions of olivine that crystallize from these derivative magmas, 4) comparison of model and observed olivine compositions.

3.1. Mangaia Primary Magma Composition

Primary magma compositions for peridotite-sources have been computed from primitive lava compositions using PRIMELT2 (Herzberg and Asimow, 2008) and results for lavas from the Cook-Austral Islands were reported earlier (Herzberg and Asimow, 2008; Herzberg and Gazel, 2009). However, successful solutions for Mangaia could not be obtained because the published lava database is limited. Furthermore, implementation of PRIMELT2 inverts the effects of fractional crystallization of olivine in order to restore primary magma composition (Herzberg and O'Hara, 2002), and the method is restricted to primitive lavas and glasses that gained or lost only olivine. This excludes Mangaia lavas because of their substantial content of clinopyroxene phenocrysts, and we know of no method that reliably inverts clinopyroxene crystallization because crystal sorting can yield considerable variation in phenocryst mode. Furthermore, we will show that the olivine phenocryst compositions are consistent with magma chamber dynamics that include fractional crystallization, recharge and mixing, processes that rule out the possibility of properly restoring primary magma composition.

Given that an inverse model is not tractable for Mangaia, a forward model strategy is adopted that assumes a peridotite-source primary magma composition. We begin by identifying a glass produced in experiment 40.06 by Walter (1998) on fertile peridotite KR-4003 as our assumed Mangaia peridotite-source primary magma composition. The experiment was run at 4 GPa and 1590°C, the residuum mineralogy is olivine + clinopyroxene + garnet, the glass contains 18.58 % MgO and it was produced by 9.2% equilibrium melting of peridotite (Walter, 1998). It is understood that the exact

matching of Mangaia's primary magma with any experimental melt is unlikely for many reasons. We will show that Walter's melt composition is slightly low in CaO; TiO_2 is also too low most, likely because it does not capture contributions from recycled crust (Prytulak and Elliott, 2007). Walter did not report Ni in his experiments, so we assumed the Ni content using $\text{Ni (ppm)} = 21.6\text{MgO} - 0.32\text{MgO}^2 + 0.051\text{MgO}^3$ for a peridotite source (Herzberg, 2011). However, Walter's melt 40.06 is very similar in composition to a successful PRIMELT2 solution listed in Herzberg and Gazel (2009) for basalt sample RRT-B-21 from Rurutu in the Cook-Austral chain (Hauri and Hart, 1997), which is similarly high in MgO (18.8%) and exhibits a strong HIMU flavor. A successful PRIMELT2 solution was also obtained for one sample from Tubuaii which is located closer to Mangaia and for which 16.4% MgO was obtained for the primary magma; however, this solution yielded model olivine compositions that were much lower in Ni and higher in Fe/Mn than observed Mangaia olivines.

3.2. Liquid Line of Descent (LLD)

We assumed that fractional crystallization of our primary magma occurred strictly in a shallow magma chamber at 0.2 GPa, and computed the liquid line of descent using PETROLOG (Danyushevsky and Plechov, 2011). To keep the LLD geochemically faithful to Walter's experimental melt composition, we assumed that crystallization was anhydrous and with all iron as FeO. Olivine is the liquidus phase, and it is followed by clinopyroxene and plagioclase, a result that is also obtained using pMELTS (Ghiorso et al., 2002). Clinopyroxene dominates over olivine when it begins to crystallize, and this is revealed by a break in the LLD for CaO and Ni (Fig. 2). PETROLOG permits the user to

input the olivine/melt distribution coefficients for Ni (D_{Ni}), and we have chosen the Beattie-Jones model (Jones, 1984; Beattie et al., 1991) because it provides consistency with previous work (Herzberg, 2011; 2013). There are other olivine/liquid distribution models, and all are parameterizations of experimental data. But the Beattie-Jones model has the minimum root mean square error (Table 1), and it is the most accurate. For clinopyroxene and liquid, we assumed D_{Ni} varies with the composition of the liquid (Herzberg et al., 2013; Supplementary Information), yielding D values that are in good agreement with experimental measurements of LeRoux et al. (2011).

3.3. Olivines on the Liquid Line of Descent (OLLD)

The compositions of olivine that crystallizes along the liquid line of descent (OLLD) were calculated for Ni using the Beattie-Jones model and for Ca and Mn using distribution coefficients reported in Herzberg and O'Hara (2002).

3.4. Comparison of model and observed olivine compositions

Model olivine compositions on the liquid line of descent are now compared with observed olivine compositions for MG-1001, MG-1002, MGA-B-25 and MGA-B-47. As mention above, results for MG-1006 differ and they will be discussed separately.

4. Model Results and Evidence for Peridotite in the Mantle Source for Mangaia

Fig. 1 illustrates that, within the precision of measurement, Fe/Mn in observed olivines are well-matched with model olivines as well as those from East Pacific Rise MORB for which a peridotite source has been inferred (Sobolev et al., 2007; Herzberg, 2011). However, observed olivines differ from model olivines on the liquid line of

descent in having higher Ni and lower Ca at any given Mg-number. And like Mangaia, work on mid ocean ridge basalts reveals that their geochemistry also cannot be explained solely by fractional crystallization, but must include recharge of the magma chamber with primary magma and subsequent mixing with liquid on the LLD (O'Hara, 1977; O'Neill and Jenner, 2013). We now include magma chamber recharge of our primary magma and mixing with liquids on the LLD (Fig. 2), and calculate the olivine compositions that would crystallize from these new liquid compositions (Fig. 1). Results show that this process yields a field of mixed magmas that would crystallize olivines that are a good match to observed olivines when we used a derivative liquid having 6% MgO. While the calculation was made to produce an optimum match, it may be no coincidence that lavas from the Cook-Austral chain also have maximum FeO contents at around 6% MgO, dropping at lower MgO contents owing to magnetite fractionation. Application of PETROLOG to our primary magma, modified for an oxygen fugacity at the QFM buffer, and calculation of magma density (Lang and Carmichael, 1987) along the LLD reveals the production of FeO-rich liquids with maximum densities at around 6% MgO. Such derivative liquids may have settled to the magma chamber floor where they were exposed to and mix with subsequent batches of primary melt.

The Ca contents of observed olivines are generally higher than model olivines that crystallize from either the LLD or mixed magmas (Fig. 1). This misfit likely arises because the CaO content of our assumed Mangaia primary magma is too low. A better result is obtained by increasing CaO in Walter's experimental composition a small amount, from 10.31 to 11.31% (Figs. 1, 2). It is possible that a carbonated peridotite

might be a better source because its partial melts are higher in CaO than volatile-free peridotite (Dasgupta et al., 2007). Primitive high-Mg lavas from the Cook-Austral chain consist of a continuum of compositions from basalts having ~ 48% SiO₂ to nephelinites with 38% SiO₂. The lavas display negative SiO₂-CaO correlations, indicating they are related by partial melting of a carbonated peridotite source (Dasgupta et al., 2007). However, the lavas have higher alkalis than the experimental melts of Dasgupta et al. (2007) and negative SiO₂-La/Yb correlations, a difference that might be attributed to refertilization or metasomatism of a peridotite source from recycled crust (Jackson and Dasgupta, 2008).

The most important conclusion drawn from petrological modeling is that the Mangaia lavas are reasonably well-described by a model that involves a peridotite source, and one that was likely carbonated. Fractional crystallization of the Mangaia primary magma occurred in a shallow magma chamber which was replenished by subsequent batches of primary magma. A model of magma mixing and crystallization yields olivines that are a good match with observed olivine compositions. We now evaluate whether this peridotite source model is unique.

5. Evidence for Refertilized Peridotite in the Mantle Source for Mangaia

The evidence from olivine of a peridotite source for Mangaia appears to be at odds with isotopic evidence for a role played by recycled crust. We now seek a resolution to this paradox by examining prior hypotheses for the origin of a peridotite source for HIMU lavas from the Canary Islands (Gurenko et al., 2009; 2010; Day et al., 2009; 2010). While there is no compelling reason to assume the sources of Mangaia and

the Canary Islands were identical, it is worth noting that the models for the later differ in details that may be relevant to the present discussion.

Gurenko et al. (2009; 2010) form HIMU peridotite by mixing of recycled crust into peridotite, similar to that proposed by Parai et al. (2009) for the Cook-Austral Islands. Based on Pb-Os isotope systematics Hauri and Hart (1993) estimated a HIMU Mangaia source as a basalt-peridotite mixture, the proportions of which depend on the age of the crust (~20% for ancient basaltic crust). Day et al. (2009; 2010) and Hanyu et al. (2011) propose a mixed peridotite-pyroxenite source, partial melting of the recycled crust, and metasomatic injection and reaction of the melts into the host peridotite in order to comply with the severe constraints on total crustal source material imposed by Os isotopes. This model was originally proposed by Yaxley and Green (1998) who showed that recycled basaltic crust can partially melt at 3 GPa to yield dacite, an experimental observation that has been reproduced (Pertermann and Hirschmann, 2003; Spandler et al., 2008). At 3 GPa, SiO₂-rich melts of quartz eclogite have been observed to react with the peridotite host to produce orthopyroxene-rich layers (Yaxley and Green, 1998); if such melts percolate into the peridotite, they may react out of existence, forming a solid refertilized peridotite enriched in orthopyroxene, clinopyroxene and garnet (Yaxley and Green, 1989). This process was examined experimentally by Mallik and Dasgupta (2012; 2013) who showed that the infiltrated melts can evolve to silica-deficient compositions. In nature, whether dacitic melts produce layers of pyroxenite or refertilized peridotite will likely depend on the mode of melt transport; porous flow is expected to yield refertilized peridotite whereas pyroxenite is likely to be produced by channel flow. Evidence for

production of pyroxenite veins by peridotite-dacite melt has been documented in mantle xenoliths (Liu et al., 2005). Prytulak and Elliott (2009) suggested that peridotite refertilized by dacitic melts might be an ideal way to reconcile the low melt productivity of Pico Island in the Azores as inferred from ^{238}U - ^{230}Th and ^{235}U - ^{231}Pa disequilibria with the geochemical evidence for involvement of recycled crust. And evidence for peridotite refertilization by melts of pyroxenite have been documented in orogenic peridotite (Marchesi et al., 2013). The essential question is whether olivine phenocryst compositions can be used to distinguish partial melts of fertilized peridotite or pyroxenite. Sobolev et al. (2005; 2007) and later Herzberg (2011) proposed that partial melts olivine-free pyroxenites will crystallize olivines in Hawaii and other occurrences with elevated Ni and low Ca and Mn. But how do such olivines compare with those that crystallize from partial melts of refertilized peridotite? We now examine this model computationally because there presently exist no high precision olivine data on experimental melts of fertilized peridotite appropriate to Mangaia.

The model setup is similar to that which was described previously (Herzberg and O'Hara, 2002; Herzberg, 2013), and consists of the following components: 1) a dacite melt composition A200K from Pertermann and Hirschmann (2003) is mixed with peridotite KR-4003 in 10 weight % increments to yield a variety of source compositions that range from refertilized peridotite to pyroxenite; Ni contents were not measured, so we calculated it assuming the dacite is in equilibrium with mantle olivine having 0.36%, similar to that described by Wang and Gaetani (2008); 2) the compositions of liquids extracted from residues of olivine and olivine + orthopyroxene were computed by mass

balance solutions to the equation for accumulated fractional melting using bulk distribution coefficients derived from distribution coefficients of olivine and orthopyroxene weighted in variable proportions in the peridotite-dacite mixes; 3) olivine phenocryst compositions are computed as described above for olivines that crystallize along a liquid line of descent at 0.2 GPa. We emphasize that the model has its limitations because residual clinopyroxene and garnet have not been included owing to the added computational complexity; nevertheless, it provides a bound on the possible olivine compositions and the effects of residual clinopyroxene and garnet can be estimated qualitatively. Results are shown in Fig. 3.

When increasing amounts of dacite are added to peridotite, the partial melts crystallize olivines with increasing Ni, decreasing Ca, and increasing Fe/Mn (Fig. 3). For Ni, the effect is similar to that explored by Kelemen et al. (1998) wherein Ni-rich melts in equilibrium with orthopyroxene are produced by the reaction of a silica – rich melt with olivine in peridotite. Fe/Mn in olivine is high because Mn is low owing to preferential partitioning into orthopyroxene. Ca decreases because the dacite composition and the variable mixtures are low in Ca. When the amount of dacite added to peridotite reaches about 40%, the mixture becomes nearly olivine-free pyroxenite and the olivines that crystallize from their partial melts become similar in composition to many olivine phenocrysts from Koolau volcano in Hawaii and El Hierro in the Canary Islands (Fig. 3; Sobolev et al., 2007; Gurenko et al., 2009; Herzberg, 2011). The effect of including clinopyroxene and garnet would be to further increase Ni and Fe/Mn and decrease Ca, based on partition coefficients given in Herzberg et al. (2013).

A role for pyroxenite melting has been recognized for Koolau and El Hierro using a wide variety of geochemical, isotopic, and petrological approaches (Sobolev et al., 2007; Gurenko et al., 2009; Herzberg, 2011; Day et al., 2009; 2010; Hauri, 1996; Lassiter and Hauri, 1998; Blichert-Toft et al., 1999; Huang and Frey, 2005; Jackson et al., 2012). Melts of pyroxenite can be SiO₂-rich like Koolau and SiO₂-poor like El Hierro and Mangaia (Herzberg, 2011), and it is important to understand how they can be related. At high pressures the pyroxene-garnet plane is a thermal divide that separates SiO₂-rich and -poor pyroxenite, and it is not possible to derive a partial melt of one from the other. A typical basalt, for example, is SiO₂-rich and will consist of quartz or coesite eclogite which, when melted can produce dacitic SiO₂-rich melts. The following are different petrological pathways that can yield El Hierro or Koolau type basalts: 1) dacitic melts can react with peridotite to make a second stage pyroxenite consisting of Cpx+Gt+Opx+Qz(Cs); partial melts are MgO- and SiO₂-rich basalts similar to Koolau primary magmas; they plot to the SiO₂-rich side of the pyroxene-garnet plane, or within the plane (Herzberg, 2011); olivine phenocrysts from such melts will have maximum Ni contents (Fig. 3). 2) the infiltration of low degree SiO₂-rich melts or advanced melts into surrounding peridotite will react with it, producing a refertilized peridotite which, when melted, can yield an SiO₂-poor alkali melt (Yaxley and Green, 1978;); addition of CO₂ is expected to further lower SiO₂ (Dasgupta et al., 2007) and will likely contribute to the wide range of silica deficient rock types in the Canary and Cook-Austral Islands. 3) bimineralec eclogite residues of advanced melts of the basalt protolith will be in spatial contact with peridotite, producing a local region of olivine-poor pyroxenite which will

can also yield SiO₂-poor melts (Mallik and Dasgupta, 2012; 2013). Olivine phenocrysts of refertilized peridotite can have high Ni, depending on the mass fraction of infiltrated SiO₂-rich melt (Fig. 3).

Mangaia lavas share the alkalic properties of El Hierro, and both have olivines with overlapping Ni at Mg-numbers in the 79-83 range. As discussed below, this might be evidence for a pyroxenite source origin for Mangaia. However, the evidence is contradictory in that Mangaia olivines exhibit a Ni trend towards those expected of a peridotite source. Mangaia Ca contents are similar to some olivines from El Hierro and fertilized peridotite, but others have much higher Ca contents and Mg-numbers (Fig. 3). Mangaia olivines have lower Fe/Mn than those expected of fertilized peridotite (Fig. 3), but this may be an artifact of spinel crystallization. The drop in Fe/Mn in El Hierro and Koolau is likely the result of spinel fractionation because spinel contains no Mn; its fractionation will drop Fe/Mn in the derivative magmas and the olivines from which they crystallize. For Mangaia, while the variation in Fe/Mn is within the precision of measurement, there is a hint of a refertilized peridotite source as seen by the distinct positive trend towards ~ 10% dacite addition (Fig. 3); the positive trend in Fe/Mn may be accounted for by some combination of olivine and spinel fractionation.

Olivine compositions for the Canary Islands (Gurenko et al., 2009) shown in Fig. 4 are good examples of olivine crystallization from a refertilized peridotite source provenance. They are particularly helpful because the olivines extend to higher Mg-numbers than those from Mangaia, and provide a more secure inference about source lithology. For purposes of preserving clarity, we restrict this analysis to olivine

populations with well-separated compositions; we have also excluded Mangaia samples MG-1001, MG-1002, MGA-B-25 and MGA-B-47, but the reader can readily draw comparisons with Fig. 1. Many olivines from La Gomera have high Ca contents and Mg-numbers that are similar to Mangaia, and trend in a direction that is consistent with a peridotite that has been refertilized by about 10-20% dacite. Peridotite melting is most pronounced and yet, relative to other volcanoes in the Canary Islands, the lavas from La Gomera have the most radiogenic Nd, Sr, and Pb isotopic compositions (Gurenko et al., 2009).

6. Evidence for Pyroxenite in the Mantle Source for Mangaia

Mangaia sample MG-1006 stands out as different from all others (Fig. 5). It is complex in that its olivines are both normally and inversely zoned in terms of Mg-number, it contains skeletal olivines, and large clinopyroxene phenocrysts that are spongy and embayed. Zoning is most pronounced near phenocryst edges and zoning profiles were obtained on 4 to 5 individual core-rim analyses. Reversely zoned olivines are generally larger than normally zoned olivines, and many are clearly separated from the normally zoned olivines in having anomalously low Ca and Mg-number. However, some of the reversely zoned grains trend towards the normally zoned population from core to rim, and develop high Ca contents characteristic of normally zoned olivines. A similar core-rim pattern is revealed in Fe/Mn (Fig. 5). Normally zoned olivines show a trend where Fe/Mn is positively correlated with Mg-number, reversely zoned olivines show a negative trend, and the two olivine populations converge at an Mg-number of about 80. We interpret these trends as olivines that crystallized from separate batches of magma

that mixed; the reversely zoned olivines have compositions that are similar to many olivines from El Hierro. The normally zoned olivines have attributes of both peridotite and pyroxenite sources; the highest Ca contents and lowest Fe/Mn are similar to those of a peridotite source; however, in detail they define trends in the direction of olivines from Koolau volcano, and there is some overlap with olivines from El Hierro (Fig. 5). It is possible that the entire olivine population in MG-1006 originated from the mixing of separate batches of pyroxenite-source magmas. To relate them, it is likely that the early batch crystallized olivines with the lowest Mg-numbers settled as antacrysts in the next batch of magma, and partial reequilibration was expressed as reversed zoning along the rims.

The signal of recycled crust in sample MG-1006 as a pyroxenite lithology is consistent with isotopic and trace element evidence presented by many workers and reviewed above. It also point to deficiencies in our use of Walter's (1998) model peridotite source primary magma for Mangaia samples MG-1001, MG-1002, MGA-B-25 and MGA-B-47. Our primary magma would predict basaltic compositions that are significantly lower in TiO_2 than observed, a misfit that also points to a role played by recycled crust (Prytulak and Elliott, 2007). A carbonated peridotite source is more likely, with CO_2 originating from recycled carbonate associated with recycled crust (Jackson and Dasgupta, 2008; Dasgupta et al., 2007; Dasgupta and Hirschmann, 2010).

7. Phantom, Fugitive and Possibly Stealth Recycled Crust as Recorded in Olivine Chemistry

Fig. 6 captures the similarities and differences in olivine Ca contents for all Mangaia samples that were studied. Olivines from Mangaia samples MG-1001, MG-1002, MGA-B-25 and MGA-B-47 have Ca contents that are high and trend to high Mg-numbers characteristic of crystallization from derivative melts of peridotite or refertilized peridotite. If the isotopic compositions were inherited from subduction of recycled oceanic crust, then this crust can be considered phantom because its lithological identity has been destroyed. A mechanism for partial crust destruction that is compatible with the olivine chemistry has partial melting of recycled crust and metasomatic injection of silicic melts into the surrounding peridotite (Yaxley and Green, 1998; Spandler et al., 2008; Prytulak and Elliott, 2009; Day et al., 2009; 2010; Hanyu et al., 2011; Mallik and Dasgupta, 2012; 2013). For Mangaia, direct evidence for a role played by recycled crust is in olivine chemistry of sample MG-1006. Olivines in this sample can have lower Ca contents, and trend in directions that are consistent with a pyroxenite source. Given that the crustal lithological identity had successfully escaped destruction by partial melting, we refer to this as “fugitive” recycled crust.

For the entire olivine database with normal zoning, there is converge to a common Ca content and Mg-number of ~ 80 (Fig. 6); they are also similar in Fe/Mn and Ni (Figs. 1, 4). Clearly, no inferences about source lithology would be secure from this population of data having a restricted composition. It is consistent with magma chamber fractional crystallization, recharge, and mixing of magmas of a variably fertilized peridotite source (Fig. 1, 3). But it may also be consistent with pyroxenite melts that undergo similar magma chamber processes; unfortunately, we cannot identify an appropriate lava

composition for which a liquid line of descent can be computed. It is further conjectured that the convergent olivines may have crystallized from the mixing of peridotite- and pyroxenite-sources that fractionated to a common LLD. Whatever the correct explanation may be, it is clear that information concerning the source lithologies of primary magmas can be destroyed by both magma chamber and deep partial melting processes. If the details in our analysis of the problem seem unsatisfactory, they are given in the spirit of trying to give substance and definition to a phantom.

This analysis has been restricted to the formation of stage 2 pyroxenite and refertilized peridotite by dacitic melt production from recycled basalt. It is a successful way of explaining many petrological and geochemical features, but it may not be unique. Advanced or total melts of a pyroxenite protolith with a basaltic composition must necessarily yield basaltic compositions, not dacite (Pertermann and Hirschmann, 2003; Spandler et al., 2008). Stage 2 pyroxenite that forms by reaction of basalt with peridotite will have lower Ni and higher Ca contents and higher Fe/Mn, as will their partial melts and crystallizing olivines (Herzberg, 2011). We term this class of pyroxenite as “stealth pyroxenite” in that it may melt and crystallize olivine phenocrysts with compositions similar to those of melts from mantle peridotite. And, it is expected to be similar to phantom pyroxenite in that it has the isotopic and geochemical characteristics of recycled crust, but olivine compositions that are confused with a peridotite provenance. The possible formation of stealth pyroxenite requires further study from both a computational and experimental point of view. If verified, it will place important restrictions on the use of olivine chemistry to infer source lithology.

8. Conclusions

Inferences have been drawn about possible mantle source lithologies that melted to yield lavas from Mangaia in the Cook-Austral island chain, Polynesia. The method involves a comparison of olivine phenocryst chemistry with forward calculations of olivine compositions that are expected to crystallize from primary magmas of peridotite that has been variably fertilized by a dacite melt produced by partial melting of pyroxenite. Olivine phenocrysts have Mg-numbers that are too low to have been direct precipitates from primary magmas, and inferences about source lithology require an evaluation of the effects of magma chamber fractional crystallization, recharge, and mixing. Results show that most olivine phenocrysts from Mangaia have Ni and Ca contents and Fe/Mn ratios that are consistent with crystallization of magmas that originated from a peridotite or fertilized peridotite source.

If the isotopic compositions were inherited from subduction of recycled oceanic crust, then its lithological identity has been destroyed. A mechanism for partial crust destruction that is compatible with the olivine chemistry has partial melting of recycled crust and metasomatic injection of silicic melts into the surrounding peridotite (Yaxley and Green, 1998; Spandler et al., 2008; Prytulak and Elliott, 2009; Day et al., 2009; 2010; Hanyu et al., 2011). Direct evidence in support of this model has been found in olivines from one Mangaia sample that have preserved the chemical signature of pyroxenite. We conclude that the commonly used terms mantle “heterogeneities” and “streaks” are ambiguous, and distinction should be made of its lithological and isotopic properties.

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11. Figure Captions:

Figure 1: Mg-numbers versus Ni and Ca contents and Fe/Mn for calculated (Herzberg, 2011) and observed olivine. An Mg-number is defined as $100\text{MgO}/(\text{MgO} + \text{FeO})$ in mole per cent. Black forms = calculated Ni and Ca in olivines that crystallize from all primary melts derived from a fertile peridotite source having 1960 ppm Ni, 3.45% CaO and 0.13% MnO (Herzberg, 2011); the $\pm 1\sigma$ uncertainty for Ni is discussed in Herzberg et al.

(2013). The gray lines are olivine compositions that crystallize from an assumed Mangaia primary magma that subsequently fractionated olivine, clinopyroxene and plagioclase at 0.2 GPa, an olivine liquid line of descent (OLLD). The fields bounded by the broken lines and OLLD simulate the range of olivine compositions that would crystallize by magma chamber fractional crystallization, recharge, and mixing. Mangaia olivines are from samples MGA-B-25, MGA-B-47, MG-1001, MG-1002, normalized to 100%. Precision in Ca and Ni is about the size of the symbols. Small variations in Mn propagate to significant variations in Fe/Mn as represented by the bracket. Olivines from the East Pacific Rise MORB are from Sobolev et al., (2007).

Figure 2: A model for fractional crystallization of a Mangaia primary magma, recharge and mixing in a magma chamber at 0.2 GPa. Black lines are computed liquid lines of descent (LLD) using PETROLOG (Danyushevsky and Plechov, 2011) on a Mangaia primary magma that is assumed to have the compositions of Walter's (1998) 40.06 experimental composition, modified also by 1% CaO addition. Walter's melt composition was performed on fertile peridotite KR-4003. Broken lines are mixed end-members that, together with the LLD, provide bounds on the fields of mixed magmas. Whole rock analyses for lavas from Managaia: open circles are compiled whole rock compositions (Wood, 1997; Woodhead, 1996; Dupuy et al., 1989; Kogiso et al., 1997; Hauri and Hart (1993; 1997)). Black squares are new whole rock data for MG-1001, -1002, and -1006 reported in this paper (Table A1) and MGA-B-47 reported by Hauri and Hart (1997); analysis MGA-B-25 (Hauri and Hart (1993) plots off scale and is unreliable owing to extensive alteration.

Figure 3: A model of olivine compositions that crystallize from primary magmas of peridotite that has been fertilized by variable addition of a dacite melt, and olivines that crystallize along a liquid line of descent (OLLD) at 0.2 GPa. Model olivines are compared with observed Mangaia olivines from samples MGA-B-25, MGA-B-47, MG-1001, MG-1002 and those from Koolau and El Hierro (Sobolev et al., 2007; Gurenko et al., 2009).

Figure 4: A model of olivine compositions that crystallize from primary magmas of peridotite that has been fertilized by variable addition of a dacite melt, from Fig. 3, compared with selected observed olivines from the Canary Islands (Gurenko et al., 2009). Note the general compatibility between observed olivines from La Gomera and La Palma with model olivines of a peridotite source that has been fertilized with ~ 10-20% dacite melt. This is supporting evidence that Mangaia olivines having the highest Ca contents and Mg-numbers (Fig. 3) crystallized from a fertilized peridotite source, not pyroxenite.

Figure 5: Olivines from Mangaia sample MG-1006 compared with model olivines of a peridotite source, from Fig. 1. Core compositions of reversely zoned olivines, indicated by the white crosses, are similar to those from Koolau and El Hierro, for which a pyroxenite source was inferred (Sobolev et al., 2007; Gurenko et al., 2009). Rim compositions of reversely zoned olivines are similar to those of normally zoned olivines. Ca contents and Mg-numbers of normally zoned olivines, indicated by the black squares, trend in a direction towards olivines of a pyroxenite source provenance.

Figure 6: Summary of Ca contents and Mg-numbers for all measured Mangaia olivine phenocrysts compared with olivines expected to crystallize from primary magmas of a

peridotite source that had variable amounts of dacite added, from Fig. 3. Ca contents of observed olivine phenocrysts trend in directions that point towards fertilized peridotite and pyroxenite sources.

12. Figures:

Figure 1:

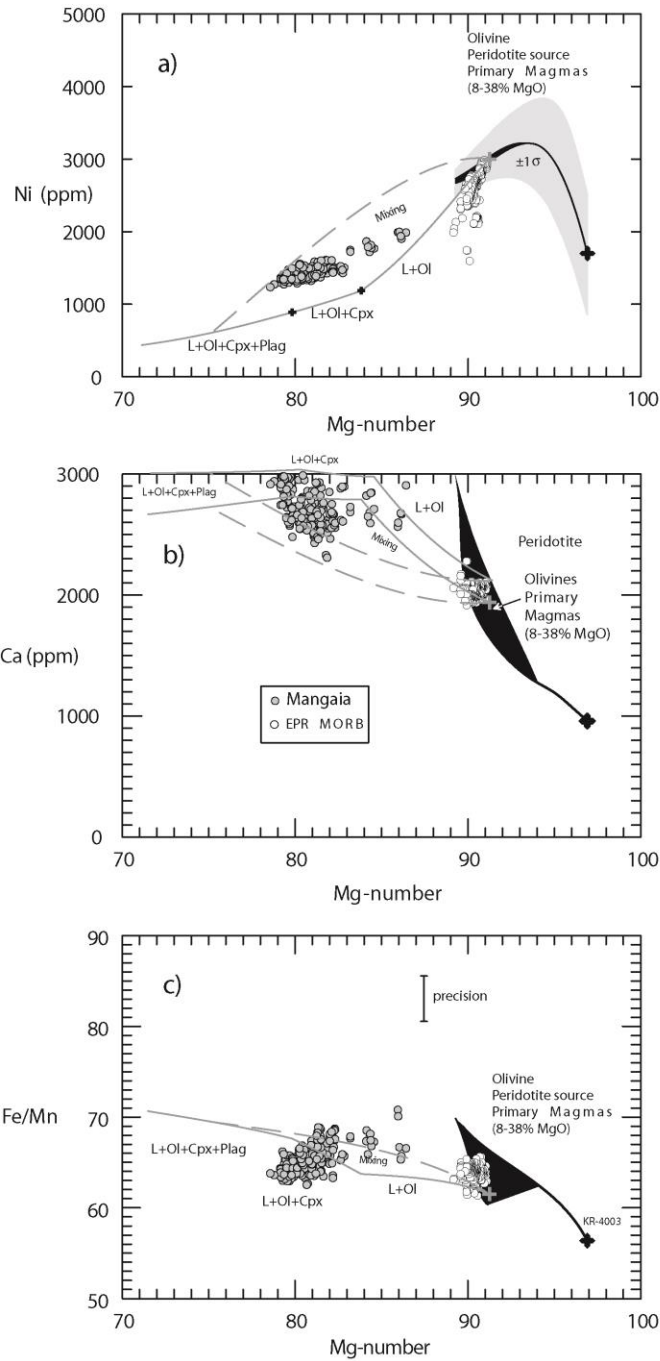


Figure 1

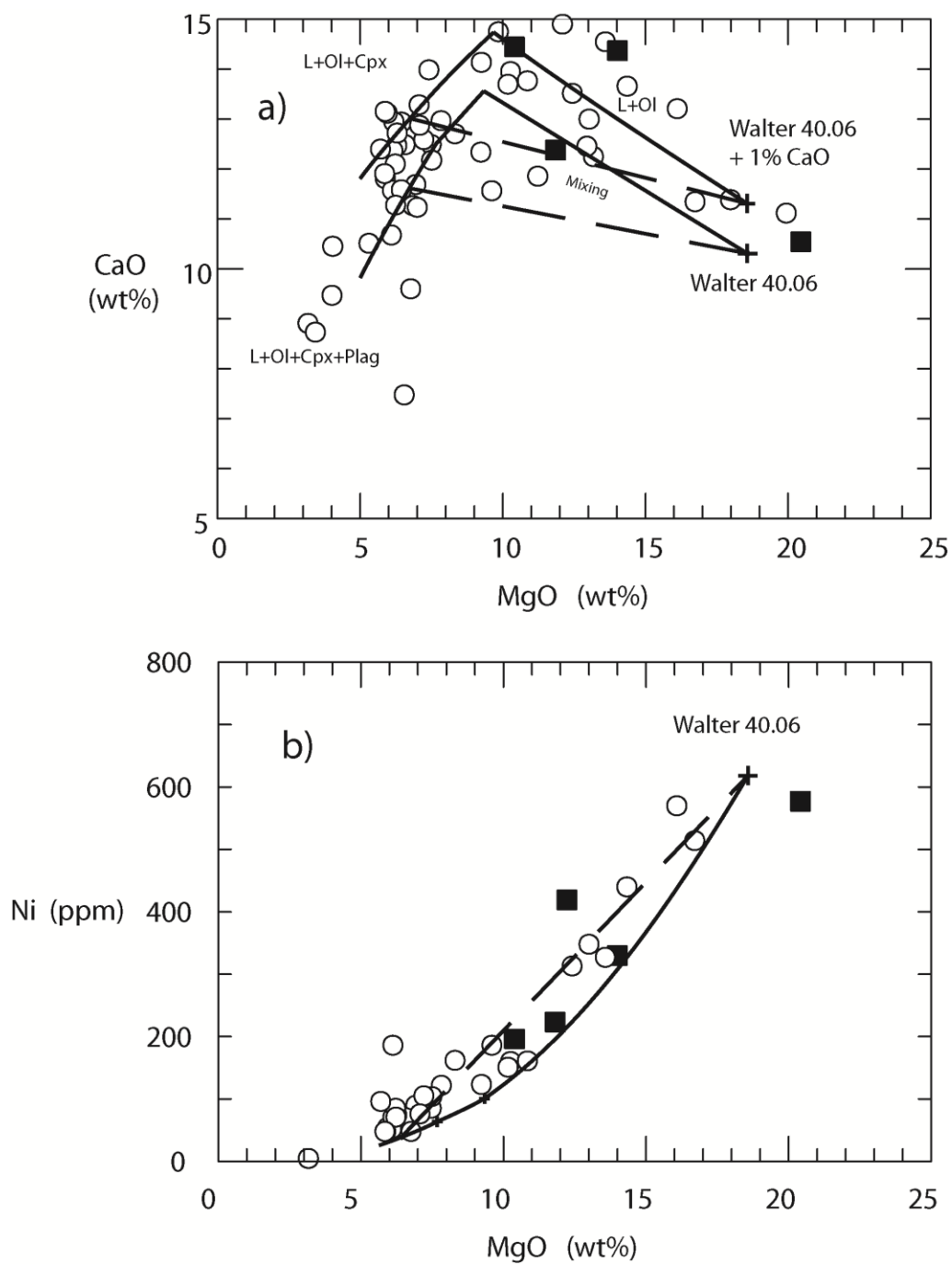
Figure 2:**Figure 2**

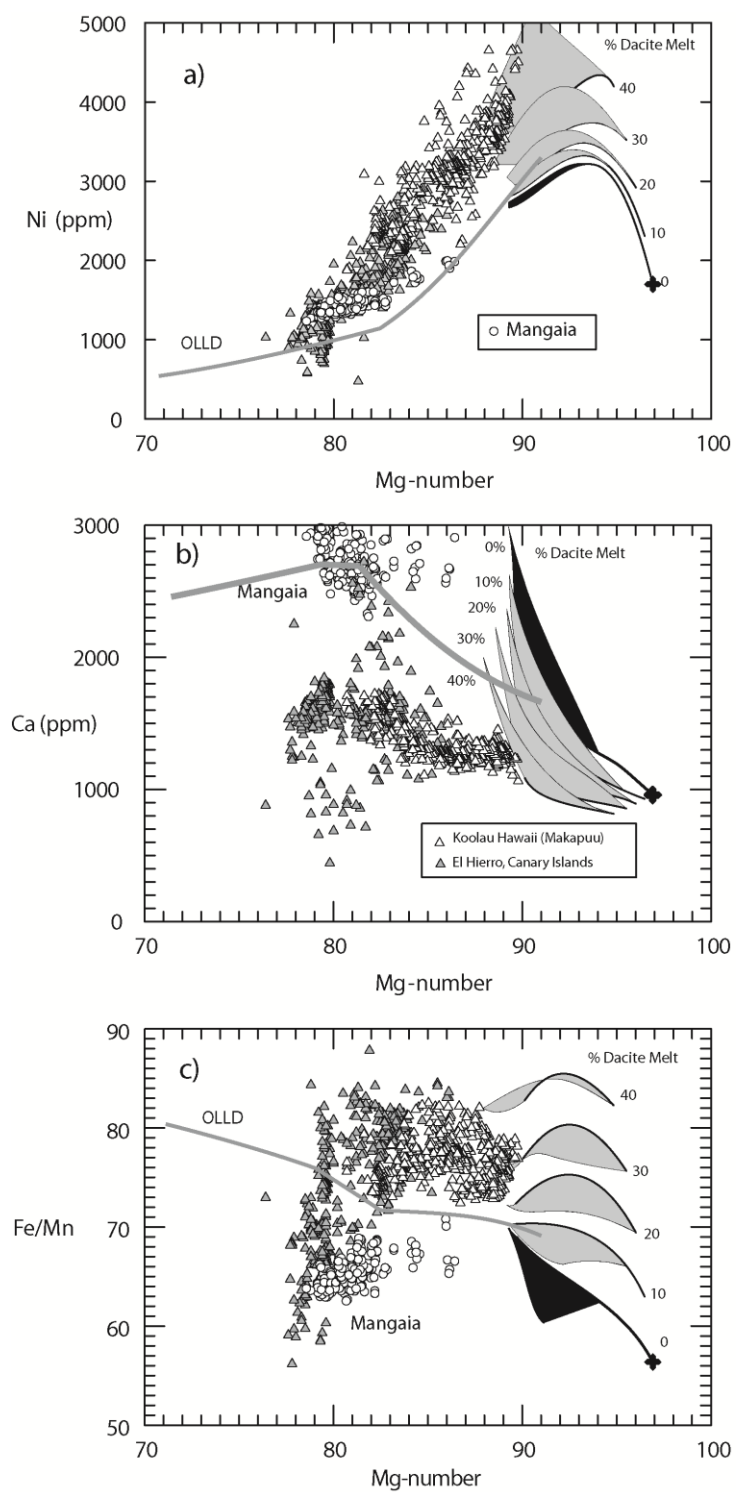
Figure 3:**Figure 3**

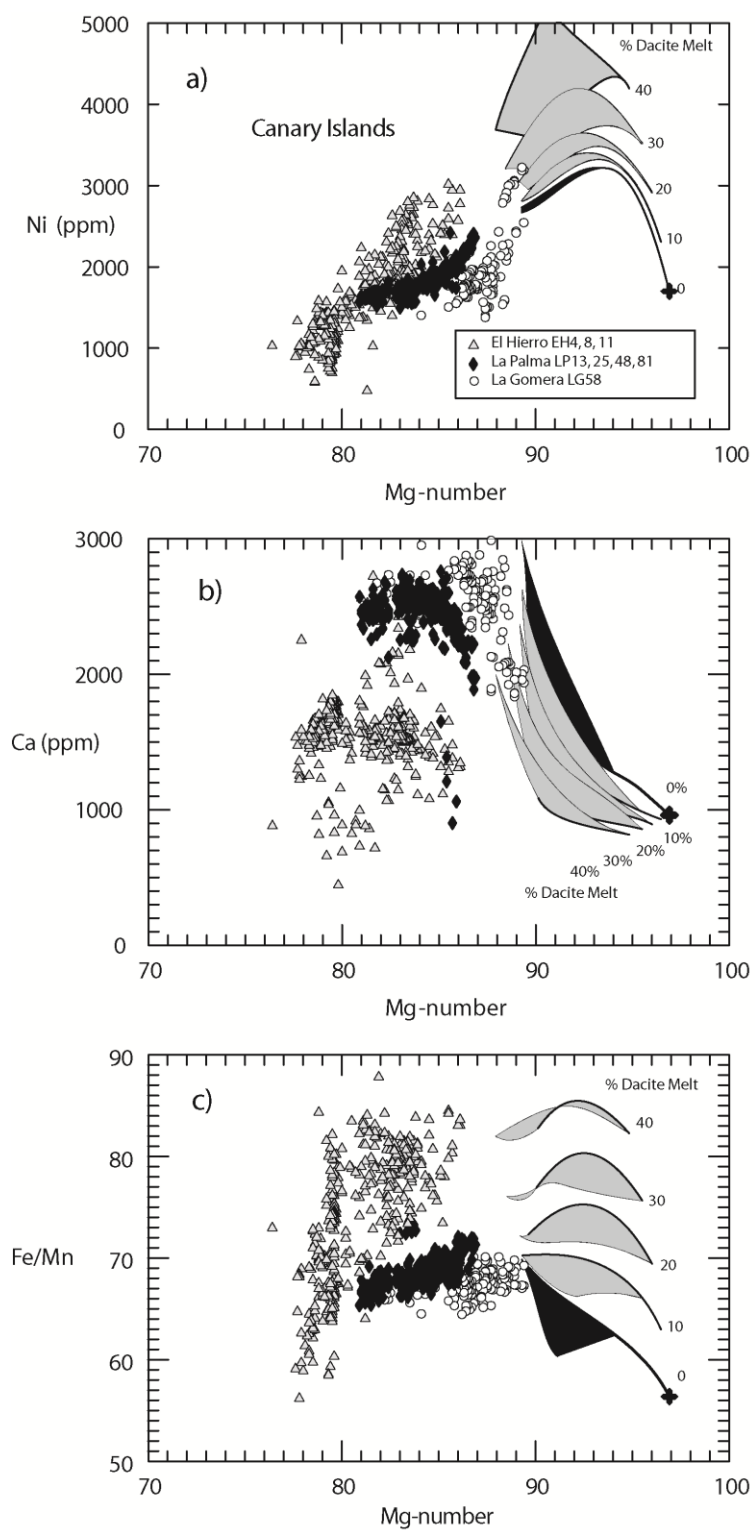
Figure 4:**Figure 4**

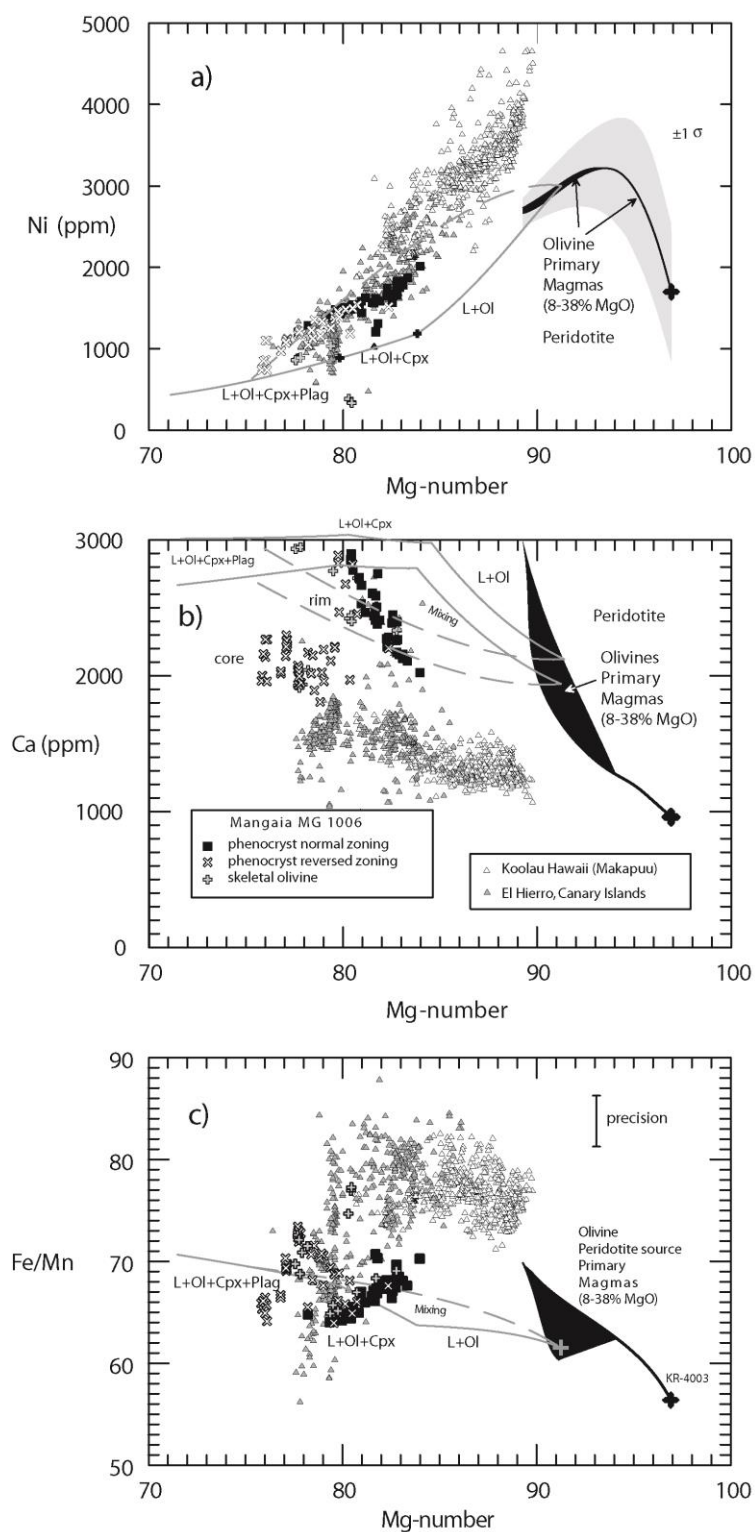
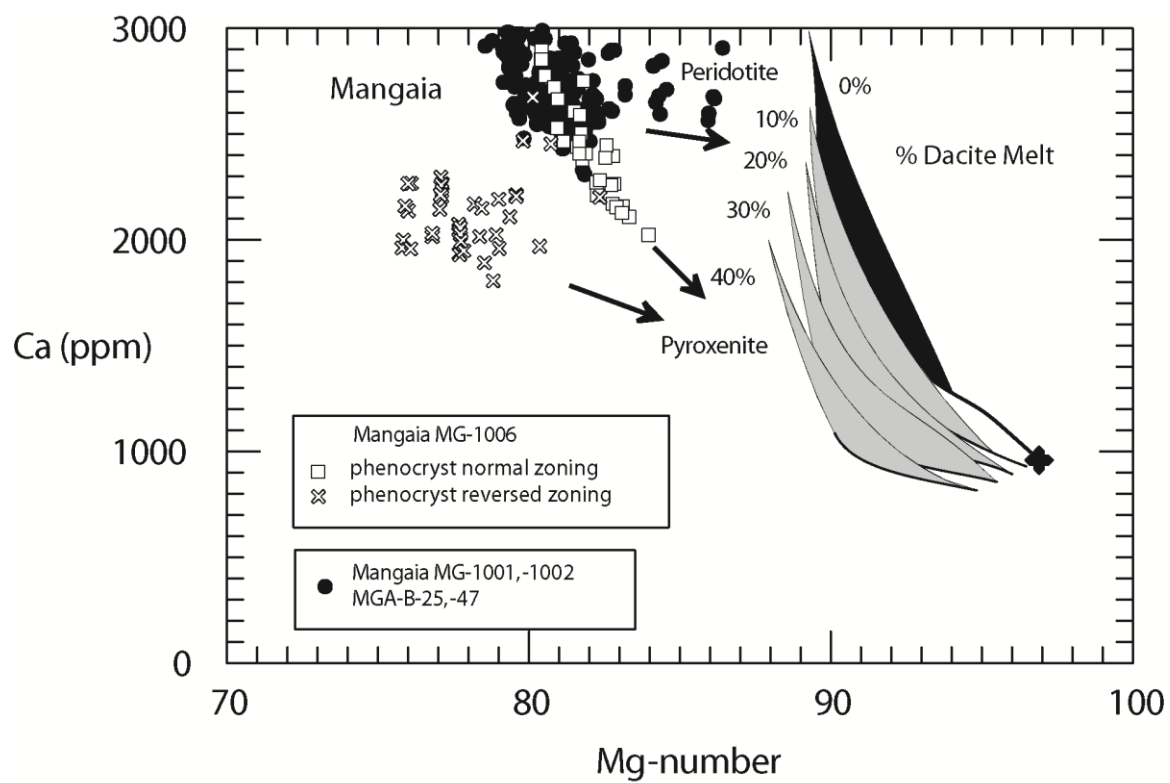
Figure 5:**Figure 5**

Figure 6:**Figure 6**

13. Tables:

Table 1: Olivine/Liquid Ni Partition (D) Models & Their Uncertainties

Model	RMSE
Beattie et al. (1993)	1.1
Li and Ripley (2010)	1.4
Putirka et al. (2011; equation 2a)	2.7
Putirka et al. (2011; equation 2b)	2.0
Putirka et al. (2011; equation 2c)	2.9
Matzen et al. (2013)	2.5
Hart and Davis (1978)	4.2
Niu et al. (2011)*	2.1

RMSE = Root Mean Square Error

$$1 \text{ RMSE} = (\Sigma(\text{model D Ni} - \text{experimental D Ni})^2 / N)^{0.5}$$

N = 271 experiments listed in Herzberg et al. (2013)

together with 13 experiments in Matzen et al. (2013)

* does not include data at 1 atmosphere

S.1.Supplimentary Information:

Table A1: Major and trace elements for Mangaia lavas hosting olivine phenocrysts

Specimen	MG1001	MG1002	MG1006	MGA-B-47	MGA-B-25
SiO₂	43.57	43.35	43.23	44.5	44.23
TiO₂	2.22	2.61	2.92	1.74	2.13
Al₂O₃	9.50	11.57	11.76	7.99	8.54
Fe₂O₃T	13.73	14.40	14.8	14.29	14.2
MnO	0.19	0.22	0.2	0.19	0.21
MgO	13.81	10.26	11.7	20.67	12.26
CaO	14.15	14.24	12.22	10.65	17.92
Na₂O	1.86	2.29	2.23	1.68	1.32
K₂O	0.52	0.68	0.71	0.48	0.35
P₂O₅	0.28	0.37	0.41	0.23	
Total	99.83	99.99	100.18	102.42	
LOI	8.80	6.78	2.29		
FeO	7.96	8.89	8.94		
Fe₂O₃	4.88	4.52	4.86		
Rb	6	10	12	11	
Sr	377.0	659.0	483	270	
Y	23	27	28.8	16	
Zr	133	177	204	112	
V	266	285	308	211	
Ni	320	190	217	574	
Cr	1125.0	512.0	559	1499	
Nb	27.8	43.7	50.6	30	
Ga	12	14	15.2	11	
Cu	103	107	148	106	
Zn	127	179	101	89	
Co	71	60	67		
Ba	163	247	235	108	
La	12	16	17	18.8	
Ce	43.0	42.0	40	37.1	
U	<0.5	<0.5	1.6	0.52	
Th	2	<0.5	7	1.96	
Sc	40	36	36	38	
Pb	5	<1	5	1.82	

MGA-B-47 is from Hauri and Hart (1997)

Sample MGA-B-25 is from Hauri and Hart (1993). Analysis is unreliable as it is heavily altered

Table S2: High precision Mangaia olivine phenocryst analyses.

Sample	SiO ₂	MgO	FeO	CaO	MnO	NiO	Cr ₂ O ₃	Al ₂ O ₃	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG-1001	39.1	40.93	18.92	0.4	0.291	0.172	0.017	0.027	99.86	79.41	1351	2254	2859	147123
MG-1001	39.11	40.63	18.85	0.406	0.292	0.176	0.013	0.024	99.5	79.35	1383	2262	2902	146579
MG-1001	39.12	40.91	18.96	0.397	0.297	0.174	0.012	0.028	99.9	79.36	1367	2301	2838	147434
MG-1001	39.11	41.17	18.64	0.416	0.292	0.171	0.012	0.024	99.84	79.74	1343	2262	2974	144946
MG-1001	39.21	41.2	18.75	0.414	0.299	0.172	0.014	0.025	100.08	79.66	1351	2316	2959	145801
MG-1001	39.09	41.06	18.84	0.411	0.3	0.169	0.021	0.027	99.92	79.53	1328	2324	2938	146501
MG-1001	39.08	40.88	18.77	0.407	0.295	0.171	0.015	0.029	99.64	79.52	1343	2285	2909	145956
MG-1001	39.21	40.94	18.74	0.416	0.297	0.176	0.011	0.027	99.82	79.57	1383	2301	2974	145723
MG-1001	39.29	41.26	18.93	0.381	0.296	0.173	0.011	0.018	100.36	79.53	1359	2293	2723	147201
MG-1001	39.23	41.41	18.66	0.427	0.288	0.172	0.016	0.026	100.23	79.82	1351	2231	3052	145101
MG-1001	39.11	41.08	19.14	0.417	0.305	0.166	0.01	0.027	100.26	79.28	1304	2363	2981	148834
MG-1001	39.2	41.22	19.1	0.397	0.298	0.172	0.014	0.029	100.43	79.37	1351	2308	2838	148523
MG-1001	39.05	40.8	19.09	0.403	0.298	0.168	0.017	0.033	99.86	79.21	1320	2308	2881	148445
MG-1001	38.97	40.64	19.1	0.407	0.298	0.165	0.015	0.032	99.63	79.13	1296	2308	2909	148523
MG-1001	39.22	40.89	18.96	0.457	0.299	0.162	0.009	0.024	100.03	79.35	1273	2316	3267	147434
MG-1001	39.46	42.21	17.3	0.383	0.266	0.188	0.023	0.031	99.86	81.3	1477	2060	2738	134526
MG-1001	39.36	42.39	17.21	0.382	0.261	0.189	0.018	0.033	99.85	81.45	1485	2022	2731	133826
MG-1001	39.35	42.41	17.02	0.38	0.262	0.189	0.021	0.031	99.66	81.62	1485	2029	2716	132348
MG-1001	39.21	41.5	18.26	0.413	0.281	0.177	0.021	0.028	99.89	80.2	1390	2177	2952	141991
MG-1001	38.95	41.06	18.54	0.403	0.284	0.172	0.016	0.027	99.45	79.79	1351	2200	2881	144168
MG-1001	39.03	41.3	18.71	0.397	0.288	0.176	0.016	0.026	99.95	79.73	1383	2231	2838	145490
MG-1001	38.92	40.93	18.86	0.394	0.29	0.174	0.016	0.039	99.63	79.46	1367	2246	2816	146656
MG-1001	38.93	40.83	18.85	0.403	0.294	0.17	0.012	0.025	99.51	79.43	1335	2277	2881	146579
MG-1001	39.26	41.07	19.17	0.402	0.304	0.173	0.009	0.025	100.41	79.25	1359	2355	2873	149067
MG-1001	39.11	40.98	19.01	0.398	0.298	0.171	0.017	0.04	100.02	79.35	1343	2308	2845	147823
MG-1001	39.22	41.29	19.12	0.402	0.3	0.172	0.015	0.021	100.54	79.38	1351	2324	2873	148678
MG-1001	39.16	41.29	18.84	0.425	0.295	0.165	0.012	0.027	100.22	79.62	1296	2285	3038	146501

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG-1001	39.05	40.82	18.74	0.37	0.286	0.178	0.014	0.03	99.49	79.52	1398	2215	2645	145723
MG-1001	39.17	41.2	18.73	0.36	0.286	0.18	0.02	0.029	99.99	79.68	1414	2215	2573	145645
MG-1001	39.05	41.1	18.7	0.362	0.291	0.179	0.016	0.03	99.73	79.66	1406	2254	2588	145412
MG-1001	39.12	41.27	18.69	0.368	0.295	0.177	0.013	0.027	99.96	79.74	1390	2285	2630	145334
MG-1001	39.14	41.46	18.63	0.402	0.288	0.173	0.017	0.029	100.13	79.86	1359	2231	2873	144868
MG-1001	39.41	41.55	18.26	0.363	0.276	0.196	0.017	0.034	100.1	80.22	1540	2138	2595	141991
MG-1001	39.22	41.71	18.12	0.357	0.272	0.192	0.019	0.037	99.94	80.4	1508	2107	2552	140902
MG-1001	39.38	41.65	18.45	0.375	0.282	0.185	0.016	0.026	100.36	80.09	1453	2184	2680	143468
MG-1001	39.33	42.1	18.1	0.369	0.287	0.178	0.017	0.034	100.41	80.57	1398	2223	2638	140747
MG-1001	39.28	41.66	18.03	0.374	0.277	0.182	0.016	0.033	99.84	80.46	1430	2146	2673	140202
MG-1001	39.27	41.71	17.95	0.369	0.28	0.183	0.018	0.031	99.81	80.55	1438	2169	2638	139580
MG-1001	39.23	41.8	18.23	0.386	0.279	0.178	0.017	0.031	100.15	80.34	1398	2161	2759	141757
MG-1001	39.37	41.36	18.57	0.376	0.287	0.172	0.011	0.029	100.18	79.88	1351	2223	2688	144401
MG-1001	39.35	41.92	18.69	0.374	0.295	0.179	0.019	0.028	100.86	79.99	1406	2285	2673	145334
MG-1001	39.37	41.84	18.76	0.382	0.297	0.173	0.014	0.031	100.86	79.9	1359	2301	2731	145879
MG-1001	39.28	41.59	18.81	0.396	0.296	0.174	0.013	0.032	100.59	79.76	1367	2293	2831	146267
MG-1001	39.27	41.52	18.77	0.381	0.298	0.174	0.018	0.029	100.47	79.77	1367	2308	2723	145956
MG-1001	39.27	41.29	18.58	0.347	0.286	0.172	0.019	0.03	99.99	79.84	1351	2215	2480	144479
MG-1001	39.51	42.73	16.58	0.385	0.247	0.188	0.022	0.029	99.69	82.12	1477	1913	2752	128927
MG-1001	39.44	42.77	16.7	0.345	0.255	0.194	0.023	0.035	99.76	82.03	1524	1975	2466	129860
MG-1001	39.13	42.5	16.77	0.352	0.256	0.191	0.029	0.048	99.27	81.87	1500	1983	2516	130404
MG-1001	39.52	42.9	16.9	0.357	0.261	0.196	0.023	0.033	100.19	81.9	1540	2022	2552	131415
MG-1001	39.39	42.4	17.36	0.353	0.268	0.197	0.02	0.032	100.01	81.32	1548	2076	2523	134992
MG-1001	39.01	40.95	18.75	0.388	0.299	0.176	0.015	0.029	99.62	79.56	1383	2316	2773	145801
MG-1001	39.32	42.56	17.43	0.377	0.263	0.19	0.024	0.029	100.2	81.32	1493	2037	2695	135537
MG-1001	39.44	42.8	17.62	0.375	0.272	0.194	0.021	0.031	100.76	81.24	1524	2107	2680	137014
MG-1001	39.57	42.65	17.71	0.392	0.266	0.192	0.026	0.027	100.84	81.1	1508	2060	2802	137714
MG-1001	39.48	42.88	17.4	0.395	0.257	0.197	0.034	0.041	100.69	81.45	1548	1991	2823	135303

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG-1001	39.5	42.44	17.44	0.385	0.259	0.198	0.031	0.032	100.28	81.26	1555	2006	2752	135614
MG-1001	39.16	41.74	18.21	0.38	0.281	0.185	0.027	0.05	100.03	80.34	1453	2177	2716	141602
MG-1001	39.51	42.37	17.94	0.377	0.273	0.186	0.02	0.035	100.71	80.8	1461	2115	2695	139502
MG-1001	39.52	42.6	17.67	0.34	0.268	0.202	0.034	0.038	100.67	81.12	1587	2076	2430	137403
MG-1001	39.36	42.35	17.59	0.347	0.269	0.194	0.03	0.038	100.18	81.1	1524	2084	2480	136781
MG-1001	39.39	42.48	17.38	0.379	0.271	0.189	0.028	0.034	100.15	81.33	1485	2099	2709	135148
MG-1001	39.23	41.4	19.14	0.414	0.304	0.167	0.014	0.032	100.7	79.4	1312	2355	2959	148834
MG-1001	39.33	41.61	19.05	0.433	0.298	0.173	0.015	0.03	100.94	79.56	1359	2308	3095	148134
MG-1001	39.37	41.59	19.01	0.394	0.297	0.174	0.018	0.03	100.88	79.59	1367	2301	2816	147823
MG-1001	39.25	41.51	18.9	0.406	0.299	0.173	0.016	0.03	100.59	79.65	1359	2316	2902	146967
MG-1001	39.15	41.49	18.96	0.364	0.298	0.188	0.02	0.032	100.49	79.59	1477	2308	2602	147434
MG-1001	39.24	41.6	19	0.364	0.297	0.182	0.022	0.045	100.74	79.6	1430	2301	2602	147745
MG-1001	39.2	41.04	19.08	0.385	0.299	0.179	0.021	0.028	100.23	79.31	1406	2316	2752	148367
MG-1001	39.08	40.93	19.2	0.404	0.3	0.174	0.019	0.028	100.14	79.16	1367	2324	2888	149300
MG-1001	39.27	40.95	19.2	0.408	0.304	0.171	0.011	0.028	100.34	79.17	1343	2355	2916	149300
MG-1001	39.02	42.03	17.03	0.379	0.259	0.191	0.023	0.03	98.97	81.48	1500	2006	2709	132426
MG-1001	39.74	43.13	16.99	0.367	0.258	0.194	0.028	0.033	100.74	81.9	1524	1998	2623	132115
MG-1001	39.42	42.74	17.02	0.363	0.259	0.195	0.025	0.035	100.06	81.74	1532	2006	2595	132348
MG-1001	39.93	42.99	16.55	0.373	0.249	0.191	0.027	0.036	100.35	82.24	1500	1929	2666	128694
MG-1001	39.46	42.88	16.8	0.399	0.26	0.197	0.032	0.028	100.05	81.98	1548	2014	2852	130638
MG-1001	38.97	41.09	18.91	0.369	0.295	0.174	0.015	0.031	99.86	79.48	1367	2285	2638	147045
MG-1001	38.89	40.63	18.66	0.397	0.289	0.181	0.014	0.026	99.1	79.51	1422	2239	2838	145101
MG-1001	39.2	41.81	18.19	0.376	0.282	0.184	0.015	0.028	100.09	80.38	1445	2184	2688	141446
MG-1001	39.12	41.22	18.23	0.38	0.28	0.184	0.017	0.023	99.46	80.12	1445	2169	2716	141757
MG-1001	39.08	40.69	19.1	0.384	0.3	0.172	0.01	0.029	99.77	79.15	1351	2324	2745	148523
MG-1001	39.93	44.33	14.72	0.375	0.218	0.219	0.04	0.032	99.86	84.3	1720	1689	2680	114463
MG-1001	39.46	42.04	17.92	0.4	0.275	0.19	0.014	0.029	100.34	80.7	1493	2130	2859	139347
MG-1001	39.05	41.18	19.1	0.417	0.301	0.171	0.012	0.027	100.26	79.35	1343	2332	2981	148523

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG-1001	39.02	41.18	18.93	0.402	0.295	0.17	0.015	0.028	100.03	79.5	1335	2285	2873	147201
MG-1001	39.35	42.6	17.16	0.383	0.265	0.196	0.021	0.031	100.01	81.57	1540	2053	2738	133437
MG-1001	39.38	41.98	17.58	0.383	0.267	0.194	0.021	0.03	99.83	80.97	1524	2068	2738	136703
MG-1001	40.77	40.63	17.04	0.363	0.254	0.187	0.017	0.057	99.32	80.95	1469	1967	2595	132504
MG-1001	39.37	41.81	18.26	0.374	0.276	0.195	0.017	0.028	100.33	80.32	1532	2138	2673	141991
MG-1001	39.29	41.15	18.54	0.38	0.284	0.19	0.015	0.024	99.87	79.82	1493	2200	2716	144168
MG-1001	39.31	41.88	18.14	0.376	0.277	0.182	0.016	0.028	100.21	80.45	1430	2146	2688	141058
MG-1001	39.21	42.23	17.37	0.367	0.264	0.184			99.62	81.25	1445	2045	2623	135070
MG-1001	39.19	42.22	17.45	0.372	0.265	0.183			99.68	81.18	1438	2053	2659	135692
MG-1001	39.06	42.29	17.15	0.357	0.263	0.18			99.3	81.46	1414	2037	2552	133359
MG-1001	39.01	42.71	17.13	0.359	0.256	0.181			99.64	81.63	1422	1983	2566	133204
MG-1001	39.2	42.33	17.41	0.364	0.267	0.182			99.75	81.25	1430	2068	2602	135381
MG-1001	39.16	42.35	17.53	0.371	0.268	0.178			99.85	81.15	1398	2076	2652	136314
MG-1001	39.29	42.69	16.95	0.326	0.256	0.205			99.71	81.78	1610	1983	2330	131804
MG-1001	39.41	42.8	16.92	0.323	0.258	0.204			99.92	81.85	1603	1998	2309	131571
MG-1001	39.13	41.97	18.02	0.359	0.278	0.172			99.93	80.59	1351	2153	2566	140124
MG-1001	39.12	42.11	18.07	0.36	0.276	0.175			100.11	80.6	1375	2138	2573	140513
MG-1001	39.41	42.54	17.66	0.349	0.279	0.173			100.41	81.11	1359	2161	2495	137325
MG-1001	39.3	42.65	17.36	0.364	0.272	0.178			100.13	81.41	1398	2107	2602	134992
MG-1001	39.25	41.98	18.24	0.362	0.288	0.169			100.28	80.4	1328	2231	2588	141835
MG-1001	39.06	41.72	18.24	0.362	0.287	0.17			99.83	80.3	1335	2223	2588	141835
MG-1001	39.18	42.49	17.28	0.35	0.267	0.183			99.76	81.42	1438	2068	2502	134370
MG-1001	39.24	42.42	17.27	0.349	0.266	0.184			99.73	81.41	1445	2060	2495	134292
MG-1001	39.17	42.13	17.82	0.381	0.281	0.171			99.96	80.82	1343	2177	2723	138569
MG-1001	39.49	42.33	17.8	0.379	0.281	0.168			100.45	80.91	1320	2177	2709	138414
MG-1001	39.35	42.45	17.41	0.37	0.264	0.176			100.03	81.29	1379	2043	2646	135381
MG-1001	39.46	42.55	17.51	0.373	0.266	0.18			100.33	81.24	1412	2061	2668	136159
MG-1001	39.41	42.28	17.33	0.361	0.264	0.177			99.82	81.3	1387	2043	2579	134759

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG-1001	39.36	41.77	17.98	0.365	0.274	0.175			99.92	80.55	1378	2122	2608	139813
MG-1001	39.45	41.93	17.9	0.364	0.273	0.17			100.09	80.68	1333	2115	2603	139191
MG-1001	38.65	40.82	18.35	0.368	0.286	0.169			98.64	79.86	1328	2217	2631	142691
MG-1001	38.58	40.94	18.4	0.372	0.283	0.171			98.75	79.86	1340	2189	2656	143079
MG-1001	38.65	40.99	18.41	0.368	0.284	0.171			98.88	79.87	1343	2197	2628	143157
MG-1001	38.6	41.05	18.17	0.372	0.284	0.164			98.65	80.11	1287	2201	2662	141291
MG-1001	38.59	40.9	18.12	0.37	0.285	0.168			98.44	80.09	1317	2208	2641	140902
MG-1001	38.54	41.03	18.15	0.373	0.283	0.171			98.55	80.12	1344	2191	2663	141135
MG-1001	39.39	42.87	16.78	0.359	0.248	0.19			99.84	81.99	1495	1924	2568	130482
MG-1001	39.54	43.08	16.73	0.361	0.246	0.192			100.15	82.11	1511	1905	2577	130093
MG-1001	39.72	42.78	17.83	0.351	0.272	0.174			101.14	81.05	1368	2105	2511	138647
MG-1001	39.83	42.85	17.76	0.353	0.272	0.176			101.24	81.13	1379	2105	2523	138103
MG-1001	39.61	42.6	17.79	0.355	0.274	0.176			100.81	81.02	1383	2125	2539	138336
MG-1001	39.75	42.82	17.82	0.352	0.272	0.178			101.2	81.07	1397	2104	2513	138569
MG-1001	39.45	42.52	17.55	0.367	0.274	0.177			100.34	81.2	1390	2119	2626	136470
MG-1001	39.48	42.59	17.45	0.373	0.27	0.176			100.33	81.31	1381	2093	2665	135692
MG-1001	39.05	42.27	17.13	0.36	0.25	0.177			99.24	81.47	1391	1940	2570	133204
MG-1001	38.98	42.06	17.1	0.353	0.25	0.179			98.92	81.43	1404	1933	2522	132970
MG-1001	38.91	41.78	17.17	0.367	0.264	0.186			98.68	81.26	1460	2048	2620	133515
MG-1001	39.1	42.19	17.2	0.375	0.264	0.187			99.32	81.38	1465	2043	2680	133748
MG-1001	38.9	41.96	16.6	0.361	0.248	0.181			98.25	81.84	1423	1923	2583	129082
MG-1001	40.05	43.63	16.74	0.364	0.249	0.191			101.22	82.29	1497	1929	2598	130171
MG-1001	40.12	43.63	16.74	0.363	0.245	0.189			101.28	82.29	1483	1894	2591	130171
MG-1001	39.85	43.38	16.78	0.366	0.249	0.184			100.81	82.17	1444	1928	2613	130482
MG-1001	40.25	43.67	16.73	0.358	0.245	0.189			101.44	82.31	1485	1895	2557	130093
MG-1001	38.21	40.14	18.12	0.367	0.286	0.172			97.29	79.79	1348	2215	2620	140902
MG-1001	39.75	42.67	17.53	0.367	0.271	0.183			100.78	81.27	1434	2098	2622	136314
MG-1001	39.99	42.82	17.45	0.37	0.268	0.18			101.07	81.39	1412	2074	2645	135692

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG-1001	39.4	42.15	17.49	0.369	0.27	0.184			99.86	81.12	1445	2094	2637	136003
MG-1001	39.32	42.08	17.7	0.367	0.274	0.173			99.91	80.91	1360	2121	2620	137636
MG-1001	39.36	42.2	17.69	0.369	0.276	0.173			100.07	80.96	1356	2138	2634	137558
MG-1001	39.72	43.18	16.74	0.358	0.246	0.191			100.43	82.13	1501	1909	2558	130171
MG-1001	39.66	43.14	16.76	0.357	0.247	0.19			100.35	82.1	1491	1910	2555	130327
MG-1001	39.45	42.8	16.44	0.361	0.241	0.192			99.48	82.27	1505	1866	2579	127838
MG-1001	39.56	42.76	16.38	0.363	0.243	0.189			99.49	82.31	1487	1885	2597	127372
MG-1001	39.6	43.1	16.86	0.373	0.251	0.189			100.38	82	1483	1946	2666	131104
MG-1001	39.63	43.12	16.87	0.373	0.249	0.191			100.42	82	1500	1925	2667	131182
MG-1001	39.35	42.26	17.35	0.347	0.255	0.192			99.75	81.28	1511	1975	2481	134914
MG-1001	39.49	42.48	17.37	0.344	0.253	0.197			100.12	81.34	1548	1961	2462	135070
MG-1001	39.2	42.25	17	0.36	0.258	0.184			99.26	81.58	1444	1999	2576	132193
MG-1001	38.98	42.1	17.04	0.362	0.257	0.188			98.93	81.49	1474	1988	2584	132504
MG-1001	39.53	42.72	16.55	0.374	0.256	0.187			99.61	82.14	1465	1982	2672	128694
MG-1001	39.6	42.73	16.51	0.374	0.25	0.189			99.66	82.18	1483	1934	2673	128383
MG-1001	39.09	41.44	17.36	0.361	0.269	0.18			98.7	80.97	1415	2084	2582	134992
MG-1001	39.33	41.85	17.53	0.361	0.272	0.18			99.52	80.97	1411	2103	2577	136314
MG-1001	38.94	41.64	17.72	0.36	0.284	0.172			99.11	80.73	1350	2198	2570	137792
MG-1001	38.73	41.18	17.59	0.355	0.282	0.175			98.32	80.67	1371	2187	2536	136781
MG-1001	39.33	42.2	17.15	0.354	0.266	0.176			99.48	81.43	1379	2064	2529	133359
MG-1001	39.39	42.24	17.14	0.354	0.269	0.175			99.58	81.46	1372	2084	2528	133281
MG-1001	39.8	43.37	16.23	0.366	0.249	0.184			100.2	82.65	1448	1930	2619	126205
MG-1001	39.95	43.46	16.14	0.365	0.247	0.182			100.34	82.76	1430	1913	2608	125505
MG-1001	39.35	42.65	16.48	0.374	0.26	0.185			99.3	82.18	1451	2016	2674	128149
MG-1001	39.27	42.74	16.52	0.374	0.262	0.183			99.34	82.18	1435	2029	2675	128460
MG-1001	39.07	42.21	17.04	0.385	0.263	0.183			99.15	81.53	1438	2040	2754	132504
MG-1001	38.85	42.08	17	0.382	0.266	0.182			98.76	81.52	1429	2063	2731	132193
MG-1002	39.25	41.74	18.05	0.36	0.28	0.181			99.86	80.47	1422	2169	2573	140358

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG-1002	39.3	41.73	18.17	0.369	0.281	0.178			100.03	80.37	1398	2177	2638	141291
MG-1002	38.82	41.82	17.15	0.373	0.255	0.2			98.63	81.29	1569	1976	2665	133359
MG-1002	39.01	42.36	16.45	0.376	0.242	0.204			98.64	82.11	1602	1871	2685	127916
MG-1002	38.73	40.7	18.97	0.384	0.288	0.171			99.25	79.27	1346	2228	2744	147512
MG-1002	38.71	40.84	18.97	0.394	0.289	0.171			99.38	79.33	1342	2238	2814	147512
MG-1002	38.28	40.17	19.28	0.412	0.304	0.162			98.61	78.78	1274	2357	2941	149922
MG-1002	38.24	39.94	19.43	0.408	0.306	0.157			98.48	78.56	1233	2368	2916	151089
MAGB-25	39.17	41.6	17.41	0.4	0.265	0.178			99.02	80.98	1398	2053	2859	135381
MAGB-25	39.44	42.12	17.47	0.4	0.267	0.179			99.88	81.12	1408	2066	2856	135848
MAGB-25	39.77	42.07	18.25	0.393	0.281	0.175			100.93	80.42	1375	2173	2808	141913
MAGB-25	39.8	42.04	18.24	0.393	0.282	0.173			100.93	80.42	1360	2184	2809	141835
MAGB-25	39.66	41.95	18.27	0.392	0.279	0.176			100.73	80.36	1379	2160	2800	142068
MAGB-25	39.85	42.79	17.3	0.404	0.265	0.181			100.78	81.51	1419	2056	2885	134526
MAGB-25	39.52	42.55	17.33	0.41	0.265	0.184			100.26	81.4	1447	2052	2930	134759
MAGB-25	38.96	42.18	16.92	0.386	0.268	0.189			98.91	81.63	1485	2073	2762	131571
MAGB-25	38.63	41.93	17.01	0.369	0.267	0.191			98.39	81.46	1499	2067	2640	132271
MAGB-25	39.85	43.43	16.05	0.405	0.245	0.191			100.18	82.83	1504	1899	2897	124806
MAGB-25	39.74	43.29	16.22	0.403	0.25	0.194			100.1	82.63	1522	1933	2881	126128
MAGB-25	39.03	42.09	17.31	0.409	0.266	0.182			99.28	81.25	1429	2060	2921	134603
MAGB-25	39.21	42.12	17.38	0.41	0.274	0.176			99.57	81.2	1386	2119	2929	135148
MAGB-25	39.62	43.17	16.06	0.405	0.245	0.188			99.68	82.73	1474	1895	2896	124883
MAGB-47	38.81	41.09	18.05	0.384	0.274	0.191			98.8	80.23	1502	2124	2743	140358
MAGB-47	39.16	41.62	18.14	0.39	0.279	0.194			99.78	80.35	1522	2158	2791	141058
MAGB-47	39.15	41.74	17.11	0.378	0.252	0.201			98.83	81.3	1580	1949	2705	133048
MAGB-47	39.4	42.02	17	0.377	0.253	0.204			99.26	81.5	1601	1957	2695	132193
MAGB-47	39.87	42.56	17.52	0.377	0.259	0.192			100.78	81.24	1509	2005	2691	136236
MAGB-47	39.87	42.37	17.37	0.373	0.261	0.194			100.43	81.3	1523	2024	2663	135070
MAGB-47	39.44	43.72	14.7	0.395	0.215	0.238			98.72	84.13	1867	1668	2824	114308

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MAGB-47	39.48	43.48	14.63	0.395	0.218	0.237			98.44	84.12	1863	1689	2821	113764
MAGB-47	39.53	41.76	17.55	0.39	0.263	0.19			99.67	80.92	1492	2039	2784	136470
MAGB-47	39.19	41.67	17.65	0.395	0.272	0.19			99.37	80.8	1495	2106	2821	137247
MAGB-47	40.26	44.85	14.83	0.363	0.219	0.229			100.75	84.35	1800	1692	2594	115319
MAGB-47	40.63	45.21	14.71	0.379	0.22	0.225			101.38	84.56	1766	1700	2710	114386
MAGB-47	39.11	43.1	15.52	0.376	0.23	0.222			98.55	83.19	1746	1784	2686	120684
MAGB-47	38.97	42.9	15.45	0.382	0.229	0.22			98.16	83.19	1724	1770	2728	120140
MAGB-47	40.47	46.03	13.42	0.359	0.19	0.253			100.72	85.94	1990	1474	2565	104355
MAGB-47	40.56	46.12	13.43	0.364	0.192	0.253			100.92	85.96	1987	1490	2598	104432
MAGB-47	39.38	41.81	18	0.413	0.272	0.195			100.08	80.54	1532	2108	2950	139969
MAGB-47	39.44	41.85	18.14	0.418	0.277	0.192			100.31	80.44	1505	2143	2989	141058
MAGB-47	40.21	44.83	14.76	0.398	0.222	0.226			100.64	84.41	1775	1718	2847	114774
MAGB-47	40.17	44.82	14.8	0.398	0.22	0.231			100.64	84.37	1815	1706	2844	115086
MAGB-47	39.23	41.79	18.31	0.356	0.278	0.198			100.16	80.27	1557	2156	2547	142379
MAGB-47	39.31	41.81	18.34	0.357	0.277	0.196			100.29	80.25	1541	2143	2550	142613
MAGB-47	39.34	44.94	13.01	0.42	0.196	0.254			98.16	86.03	1997	1517	3001	101166
MAGB-47	40.08	45.97	12.88	0.407	0.194	0.253			99.77	86.42	1987	1505	2907	100156
MAGB-47	40.1	45.44	13.02	0.373	0.199	0.242			99.38	86.15	1901	1541	2668	101244
MAGB-47	39.96	45.34	13.03	0.375	0.2	0.247			99.15	86.11	1937	1551	2677	101322
MAGB-47	39.73	44.37	14.83	0.371	0.226	0.228			99.75	84.21	1790	1750	2650	115319
MG1006_Norm_Zone_Olivine1	39.65	43.01	16.55	0.318	0.247	0.209			99.99	82.24	1642	1913	2273	128694
MG1006_Norm_Zone_Olivine1	39.29	41.68	18.12	0.399	0.278	0.189			99.95	80.39	1485	2153	2852	140902
MG1006_Norm_Zone_Olivine1	39.46	42.33	17.53	0.345	0.267	0.207			100.14	81.15	1626	2068	2466	136314
MG1006_Norm_Zone_Olivine1	39.51	42.67	16.99	0.35	0.253	0.203			99.98	81.74	1595	1960	2502	132115
MG1006_Norm_Zone_Olivine1	39.3	41.68	18.34	0.45	0.286	0.191			100.25	80.2	1500	2215	3217	142613
MG1006_Norm_Zone_Olivine2	39.72	43.65	16.19	0.337	0.238	0.211			100.35	82.77	1658	1844	2409	125894
MG1006_Norm_Zone_Olivine2	39.6	43.4	16.31	0.343	0.244	0.209			100.1	82.59	1642	1890	2452	126827
MG1006_Norm_Zone_Olivine2	39.43	42.61	17.22	0.365	0.26	0.2			100.08	81.52	1571	2014	2609	133904

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG1006_Norm_Zone_Olivine2	38.86	40.12	19.94	0.529	0.309	0.164			99.91	78.19	1288	2393	3781	155054
MG1006_Norm_Zone_Olivine3	39.21	42.41	16.94	0.36	0.241	0.153			99.31	81.69	1202	1867	2573	131726
MG1006_Norm_Zone_Olivine3	39.34	42.6	16.91	0.383	0.241	0.166			99.65	81.79	1304	1867	2738	131493
MG1006_Norm_Zone_Olivine3	39.08	41.91	17.57	0.371	0.265	0.182			99.38	80.96	1430	2053	2652	136625
MG1006_Norm_Zone_Olivine3	38.73	40.78	18.64	0.465	0.292	0.187			99.09	79.59	1469	2262	3324	144946
MG1006_Norm_Zone_Olivine3	38.72	40.07	18.17	0.54	0.288	0.177			97.97	79.72	1390	2231	3860	141291
MG1006_Norm_Zone_Olivine4	39.86	44.32	15.08	0.283	0.215	0.256			100.01	83.97	2011	1665	2023	117263
MG1006_Norm_Zone_Olivine4	39.59	43.36	16.04	0.316	0.236	0.225			99.77	82.81	1767	1828	2259	124728
MG1006_Norm_Zone_Olivine4	39.18	41.27	18.44	0.453	0.288	0.187			99.82	79.96	1469	2231	3238	143390
MG1006_Norm_Zone_Olivine4	39.21	41.52	18.18	0.427	0.281	0.187			99.81	80.28	1469	2177	3052	141369
MG1006_Norm_Zone_Olivine5	39.09	41.97	17.61	0.352	0.264	0.201			99.49	80.94	1579	2045	2516	136936
MG1006_Norm_Zone_Olivine5	38.98	41.29	18.39	0.446	0.287	0.191			99.58	80.01	1500	2223	3188	143002
MG1006_Norm_Zone_Olivine6	39.56	43.52	15.78	0.301	0.233	0.232			99.63	83.1	1822	1805	2152	122706
MG1006_Norm_Zone_Olivine6	39.57	43.33	16.11	0.315	0.24	0.22			99.78	82.74	1728	1859	2252	125272
MG1006_Norm_Zone_Olivine6	39.36	42.45	17.07	0.34	0.255	0.198			99.68	81.59	1555	1975	2430	132737
MG1006_Norm_Zone_Olivine6	39.25	41.62	18.06	0.404	0.279	0.194			99.81	80.42	1524	2161	2888	140435
MG1006_Norm_Zone_Olivine7	39.61	43.43	16.12	0.304	0.232	0.233			99.93	82.76	1830	1797	2173	125350
MG1006_Norm_Zone_Olivine7	39.5	43.08	16.55	0.309	0.244	0.222			99.91	82.27	1744	1890	2209	128694
MG1006_Norm_Zone_Olivine7	39.18	41.7	17.97	0.387	0.275	0.196			99.7	80.53	1540	2130	2766	139736
MG1006_Norm_Zone_Olivine7	38.97	40.82	18.94	0.474	0.297	0.176			99.68	79.34	1383	2301	3388	147278
MG1006_Norm_Zone_Olivine8	39.6	43.5	15.99	0.301	0.234	0.223			99.84	82.9	1752	1813	2152	124339
MG1006_Norm_Zone_Olivine8	39.4	42.52	17.01	0.344	0.258	0.205			99.74	81.67	1610	1998	2459	132271
MG1006_Norm_Zone_Olivine8	39.27	41.71	18.1	0.399	0.282	0.192			99.97	80.42	1508	2184	2852	140747
MG1006_Norm_Zone_Olivine8	39.11	41.15	18.48	0.452	0.286	0.181			99.66	79.87	1422	2215	3231	143701
MG1006_Norm_Zone_Olivine9	39.77	43.85	15.64	0.295	0.232	0.238			100.03	83.33	1870	1797	2109	121617
MG1006_Norm_Zone_Olivine9	39.64	43.59	15.83	0.297	0.233	0.227			99.82	83.07	1783	1805	2123	123095
MG1006_Norm_Zone_Olivine9	39.61	43.18	16.49	0.319	0.245	0.213			100.06	82.35	1673	1898	2280	128227
MG1006_Norm_Zone_Olivine9	39.4	42.06	17.79	0.381	0.275	0.192			100.09	80.82	1508	2130	2723	138336

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG1006_Norm_Zone_Olivine10	39.4	42.69	16.96	0.333	0.254	0.202			99.84	81.77	1587	1967	2380	131882
MG1006_Norm_Zone_Olivine10	39.47	43.22	16.31	0.333	0.247	0.199			99.78	82.53	1563	1913	2380	126827
MG1006_Norm_Zone_Olivine10	39.36	42.75	16.86	0.336	0.249	0.201			99.76	81.88	1579	1929	2402	131104
MG1006_Norm_Zone_Olivine11	39.4	42.59	17.04	0.336	0.256	0.204			99.83	81.67	1603	1983	2402	132504
MG1006_Rev_Zone_Olivine0	38.01	38.12	21.31	0.3115	0.334	0.137			98.21	76.12	1079	2584	2227	165676
MG1006_Rev_Zone_Olivine0	37.79	38.12	21.40	0.3110	0.331	0.138			98.09	76.05	1080	2564	2223	166424
MG1006_Rev_Zone_Olivine0	38.70	38.62	21.79	0.2986	0.329	0.110			99.85	75.95	862	2549	2134	169469
MG1006_Rev_Zone_Olivine0	38.46	38.41	21.80	0.3005	0.331	0.108			99.42	75.85	847	2564	2148	169517
MG1006_Rev_Zone_Olivine0	38.72	39.21	21.11	0.2814	0.319	0.124			99.77	76.80	977	2472	2012	164163
MG1006_Rev_Zone_Olivine0	38.60	39.13	21.09	0.2829	0.317	0.123			99.55	76.78	965	2458	2022	163998
MG1006_Rev_Zone_Olivine1	38.85	39.84	20.39	0.27	0.283	0.154			99.79	77.69	1210	2192	1930	158554
MG1006_Rev_Zone_Olivine1	38.78	39.79	20.34	0.269	0.279	0.153			99.6	77.71	1202	2161	1923	158165
MG1006_Rev_Zone_Olivine1	38.86	39.98	20.29	0.272	0.28	0.15			99.83	77.84	1178	2169	1944	157776
MG1006_Rev_Zone_Olivine1	39.05	40.77	19.29	0.274	0.274	0.167			99.83	79.02	1312	2122	1959	150000
MG1006_Rev_Zone_Olivine1	39.26	41.51	18.35	0.374	0.28	0.189			99.96	80.13	1485	2169	2673	142691
MG1006_Rev_Zone_Olivine2	38.51	38.65	21.95	0.279	0.337	0.097			99.82	75.84	762	2610	1994	170684
MG1006_Rev_Zone_Olivine2	38.58	38.73	22.04	0.275	0.336	0.094			100.06	75.8	738	2603	1966	171384
MG1006_Rev_Zone_Olivine2	38.5	38.83	21.76	0.273	0.332	0.094			99.79	76.08	738	2572	1951	169207
MG1006_Rev_Zone_Olivine2	38.8	40.42	20.09	0.304	0.308	0.134			100.05	78.19	1053	2386	2173	156221
MG1006_Rev_Zone_Olivine2	39.02	41.08	18.84	0.425	0.296	0.178			99.84	79.53	1398	2293	3038	146501
MG1006_Rev_Zone_Olivine3	39.01	41.14	19.06	0.295	0.276	0.16			99.94	79.37	1257	2138	2109	148212
MG1006_Rev_Zone_Olivine3	39.04	41.28	18.88	0.31	0.275	0.174			99.96	79.58	1367	2130	2216	146812
MG1006_Rev_Zone_Olivine3	39.04	41.34	18.91	0.309	0.276	0.173			100.04	79.58	1359	2138	2209	147045
MG1006_Rev_Zone_Olivine3	39.27	42.18	17.95	0.344	0.273	0.196			100.21	80.73	1540	2115	2459	139580
MG1006_Rev_Zone_Olivine4	38.64	39.97	20.46	0.286	0.282	0.151			99.79	77.69	1186	2184	2044	159098
MG1006_Rev_Zone_Olivine4	38.74	39.99	20.47	0.286	0.28	0.15			99.92	77.69	1178	2169	2044	159176
MG1006_Rev_Zone_Olivine4	38.79	40.07	20.54	0.291	0.284	0.15			100.12	77.66	1178	2200	2080	159720
MG1006_Rev_Zone_Olivine4	38.67	39.96	20.41	0.287	0.285	0.152			99.76	77.73	1194	2208	2051	158709

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG1006_Rev_Zone_Olivine4	38.9	40.9	19.38	0.307	0.288	0.163			99.94	79	1280	2231	2194	150700
MG1006_Rev_Zone_Olivine4	38.96	41.24	18.67	0.403	0.286	0.185			99.75	79.74	1453	2215	2881	145179
MG1006_Rev_Zone_Olivine5	38.92	40.81	19.54	0.253	0.279	0.147			99.95	78.82	1155	2161	1808	151944
MG1006_Rev_Zone_Olivine5	39.21	41.86	18.23	0.276	0.269	0.151			100	80.36	1186	2084	1973	141757
MG1006_Rev_Zone_Olivine5	39.44	43.18	16.49	0.308	0.245	0.193			99.86	82.35	1516	1898	2202	128227
MG1006_Rev_Zone_Olivine5	39.08	41.72	18.02	0.393	0.279	0.19			99.69	80.49	1493	2161	2809	140124
MG1006_Rev_Zone_Olivine6	38.63	39.48	20.93	0.321	0.304	0.139			99.79	77.07	1092	2355	2294	162753
MG1006_Rev_Zone_Olivine6	38.71	39.61	20.93	0.317	0.301	0.143			100.02	77.13	1123	2332	2266	162753
MG1006_Rev_Zone_Olivine6	38.65	39.54	20.94	0.316	0.302	0.141			99.89	77.09	1108	2339	2259	162830
MG1006_Rev_Zone_Olivine6	38.7	39.6	20.94	0.312	0.304	0.142			100	77.12	1115	2355	2230	162830
MG1006_Rev_Zone_Olivine6	38.71	39.57	20.94	0.308	0.303	0.141			99.98	77.11	1108	2347	2202	162830
MG1006_Rev_Zone_Olivine6	38.76	39.61	21.01	0.31	0.304	0.139			100.13	77.06	1092	2355	2216	163375
MG1006_Rev_Zone_Olivine6	38.65	39.51	20.98	0.3	0.299	0.137			99.88	77.05	1076	2316	2144	163142
MG1006_Rev_Zone_Olivine6	38.91	40.51	19.84	0.301	0.292	0.143			100	78.44	1123	2262	2152	154277
MG1006_Rev_Zone_Olivine6	39.07	41.23	18.71	0.466	0.289	0.186			99.96	79.71	1461	2239	3331	145490
MG1006_Rev_Zone_Olivine7	38.76	39.95	20.39	0.283	0.283	0.152			99.82	77.74	1194	2192	2023	158554
MG1006_Rev_Zone_Olivine7	38.77	40.04	20.42	0.279	0.281	0.154			99.94	77.75	1210	2177	1994	158787
MG1006_Rev_Zone_Olivine7	38.79	40.41	19.88	0.281	0.282	0.156			99.79	78.37	1225	2184	2009	154588
MG1006_Rev_Zone_Olivine7	38.92	41.32	18.71	0.395	0.284	0.184			99.81	79.74	1445	2200	2823	145490
MG1006_Rev_Zone_Olivine8	38.9	40.6	19.79	0.265	0.278	0.173			100	78.52	1359	2153	1894	153888
MG1006_Rev_Zone_Olivine8	38.88	40.73	19.41	0.282	0.275	0.17			99.74	78.9	1335	2130	2016	150933
MG1006_Rev_Zone_Olivine8	39.06	41.29	18.62	0.344	0.272	0.176			99.77	79.81	1383	2107	2459	144790
MG1006_Skeletal_Olivine1	39.09	41.77	18.28	0.338	0.246	0.049			99.77	80.29	385	1905	2416	142146
MG1006_Skeletal_Olivine1	39.16	41.88	18.16	0.341	0.237	0.044			99.82	80.43	346	1836	2437	141213
MG1006_Skeletal_Olivine1	39.15	41.91	18.15	0.335	0.236	0.043			99.81	80.45	338	1828	2395	141135
MG1006_Skeletal_Olivine2	38.77	39.98	20.48	0.27	0.283	0.157			99.94	77.68	1233	2192	1930	159253
MG1006_Skeletal_Olivine2	38.77	40	20.41	0.267	0.284	0.156			99.89	77.74	1225	2200	1909	158709
MG1006_Skeletal_Olivine2	38.88	40.19	20.3	0.271	0.288	0.152			100.09	77.92	1194	2231	1937	157854

Sample	SiO2	MgO	FeO	CaO	MnO	NiO	Cr2O3	Al2O3	Total	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
MG1006_Skeletal_Olivine2	38.87	40.32	20.04	0.285	0.281	0.148			99.94	78.19	1163	2177	2037	155832
MG1006_Skeletal_Olivine2	39.12	41.17	18.93	0.388	0.289	0.175			100.06	79.49	1375	2239	2773	147201
MG1006_Skeletal_Olivine2	39.1	41.25	18.67	0.43	0.288	0.188			99.92	79.75	1477	2231	3074	145179
MG1006_Skeletal_Olivine3	39.48	43.32	16.07	0.325	0.234	0.217			99.65	82.77	1705	1813	2323	124961
MG1006_Skeletal_Olivine3	39.3	42.6	16.99	0.35	0.25	0.202			99.68	81.71	1587	1936	2502	132115
MG1006_Skeletal_Olivine3	39.1	41.89	17.82	0.379	0.267	0.189			99.64	80.73	1485	2068	2709	138569
MG1006_Skeletal_Olivine4	38.8	39.84	20.55	0.41	0.296	0.11			100.01	77.55	864	2293	2931	159798
MG1006_Skeletal_Olivine4	38.77	40.01	20.34	0.412	0.297	0.113			99.94	77.81	888	2301	2945	158165
MG1006_Skeletal_Olivine4	39.01	41.03	19.02	0.441	0.294	0.132			99.93	79.36	1037	2277	3152	147900

Chapter 4

Nickel and helium evidence for melt above the core–mantle boundary

1. Introduction

High $^3\text{He}/^4\text{He}$ ratios in some basalts have generally been interpreted as originating in an incompletely degassed lower-mantle source (Kurz et al., 1982; Class and Goldstein, 2005; Tolstikhin and Hofmann, 2005; Labrosse et al., 2007; Gonnermann and Mukhopadhyay, 2009; Kurz et al., 2009; Jackson et al., 2010; Coltice et al., 2011; Jackson and Carlson, 2011). This helium source may have been isolated at the core–mantle boundary region since Earth’s accretion (Tolstikhin and Hofmann, 2005; Labrosse et al., 2007; Coltice et al., 2011). Alternatively, it may have taken part in whole-mantle convection and crust production over the age of the Earth (Class and Goldstein, 2005; Gonnermann and Mukhopadhyay, 2009; Jackson and Carlson, 2011); if so, it is now either a primitive refugium at the core–mantle boundary or is distributed throughout the lower mantle (Class and Goldstein, 2005; Gonnermann and Mukhopadhyay, 2009). Here we constrain the problem using lavas from Baffin Island, West Greenland, the Ontong Java Plateau, Isla Gorgona and Fernandina (Galapagos). Olivine phenocryst compositions show that these lavas originated from a peridotite source that was about 20 per cent higher in nickel content than in the modern mid-ocean-ridge basalt source. Where data are available, these lavas also have high $^3\text{He}/^4\text{He}$. We propose that a less-degassed nickel-rich source formed by core–mantle interaction during the crystallization of a melt-rich layer or basal magma ocean (Labrosse et al., 2007; Coltice et al., 2011), and that this source continues to be sampled by mantle plumes. The spatial distribution of this source

may be constrained by nickel partitioning experiments at the pressures of the core–mantle boundary.

2. Results

Primitive mantle has been estimated to contain 1,960 p.p.m. nickel (Ni) (McDonough and Sun, 1995), and this is similar to estimates for depleted peridotite (Salters and Stracke, 2004), which makes up the average mid-ocean-ridge basalt (MORB) source. It is also similar to the Ni content of fertile peridotite (which has less basalt than primitive peridotite but more melt than depleted peridotite so more basalt can be extracted during partial melting) obtained from recent high-quality measurements (Ionov, 2007) (Supplementary Fig. 1 and Supplementary section 1), which can be described by:

$$\text{Ni (p.p.m.)} = 568.6\text{MgO (weight per cent)} - 630 \quad (1)$$

Equation (1) fits the Ni contents of 110 fertile and depleted peridotite compositions to 92 p.p.m. ($\pm 2\sigma$); we refer to this as normal Ni peridotite. High-precision olivine analyses from these fertile and depleted peridotites¹² yield 2,800–3,100 p.p.m. Ni and magnesium (Mg)-numbers of 89–92 (that is, $100\text{MgO}/(\text{MgO} + \text{FeO})$ in mole per cent; Fig. 1a, Supplementary Table 1 and Supplementary Information section 2). These olivines from mantle peridotite are very similar to primitive olivine phenocryst compositions from East Pacific Rise (EPR) basalts (Fig. 1a). They are also very similar to model Ni contents (Herzberg, 2011) shown by the black line in Fig. 1, which is appropriate for olivine

phenocrysts of primary magmas having 8%–38% MgO and for melting of both fertile and depleted upper-mantle peridotite. Model olivines are also similar to observed olivine phenocrysts in hot Archaean komatiites from Alexo (Sobolev et al., 2007; Arndt et al., 2008) (Fig. 1b) and other occurrences of high-temperature magmas (Methods), demonstrating restricted compositions over a broad temperature range (Sobolev et al., 2007).

Olivines from the Palaeocene-epoch picrites in Baffin Island and West Greenland, on the other hand, have higher Ni contents (up to 3,800 p.p.m.) than those from MORBs, Archaean komatiites, and mantle peridotite (Fig. 1c). Those with high Mg-numbers are also higher in Ni than olivines that are expected to crystallize from any partial melt of normal mantle peridotite, as indicated by Ca, Mn and Fe/Mn (Fig. 2). Primary magma major-element compositions were estimated from modelling of whole-rock lava compositions (Herzberg and Gazel, 2009), but sorting of olivine phenocrysts in lava flows compromises reliable Ni estimates with this method. However, the Ni contents and Mg-numbers of the olivine phenocrysts themselves are unaffected by crystal sorting. We estimated a typical Ni content of the primary magma that is required to crystallize olivines with the observed Ni and highest Mg-numbers. The high-Ni olivines require a fertile peridotite source having 2,360 p.p.m. Ni (Methods Summary). This is about 20% higher than normal Ni peridotite with 1,960 p.p.m. Ni and is well outside the 2σ uncertainty bounds of equation (1). The range of olivine compositions at low Mg-numbers and Ni contents is a consequence of variable olivine and clinopyroxene fractionation from primary magmas (Fig. 1c and Supplementary Information section 4).

The excess-Ni problem is not confined to Baffin Island and West Greenland. Although high-precision Ni data for olivine in intraplate occurrences are limited, we find high Ni in olivines from the Ontong Java plateau, Gorgona komatiites, and the Fernandina volcano in the Galapagos Islands (Fig. 3). In all cases a peridotite source provenance is indicated by Ca, Mn and Fe/Mn (Sobolev et al., 2007; Herzberg, 2011) in olivine (Fig. 2 and Supplementary Information). The high Ni in Gorgona olivines is clearly seen because the sample suite includes olivines with very high Mg-numbers, close to those expected for early crystals from the primary magmas. The high Ni in olivines from the other occurrences is less clear, owing to their lower Mg-numbers. For these we modelled the Ni contents of olivines that would crystallize from primary magmas and their liquid lines of descent. Using primary magma compositions from Herzberg and Gazel, 2009 with the Ni contents adjusted to those expected in melts from normal fertile peridotite containing 1,960 p.p.m. Ni (Fig. 1), the Ni contents of olivines that crystallize along liquid lines of descent are always lower than those observed in olivines from the Ontong Java plateau or the Fernandina volcano, regardless of the proportions of crystallizing olivine and clinopyroxene. Rather, all successful solutions require Ni-rich fertile peridotite sources having Ni contents up to 2,360 p.p.m.

Mantle that has been depleted by prior melting events can be high in both MgO and NiO compared with more fertile sources (see equation (1)). However, the Ni contents of partial melts of highly depleted peridotite and fertile peridotites are indistinguishable at liquid MgO < 25 weight per cent (Herzberg, 2011) (Supplementary Fig. 1) and the

olivines of primary melts shown in Fig. 1c should be generally applicable. Therefore, Ni-rich olivine phenocrysts cannot crystallize from melts of normal depleted peridotite.

Excess Ni in olivine has also been attributed to high temperatures and pressures of melting (Putirka et al., 2011). However, this is not consistent with olivines from Archaean komatiites from Alexo (Sobolev et al., 2007) (Fig. 1b) and Barberton (see Methods), which are thought to be among the hottest magmas ever erupted on Earth (Arndt et al., 2008), and yet have normal Ni concentrations. Appealing to the formation of Alexo komatiites in a cool and wet environment does not solve the problem because they are compositionally similar to komatiites from the Belingwe greenstone belt (Puchtel et al., 2009) for which melt inclusion studies point to a hot and dry origin (Berry et al., 2008). Furthermore, Barberton komatiites separated from a deep garnet-bearing residue that was hot and dry, and yet there is no excess Ni (Methods); low-temperature hydrous melting models are also not consistent with olivine phenocryst compositions (Methods). Consequently, the high Ni contents of the Baffin Island and West Greenland olivines are more plausibly related to composition rather than temperature-pressure effects.

Shield volcanoes from Hawaii also contain olivine phenocrysts with increased Ni (Arndt et al., 2008; Putirka et al., 2011), and there is general agreement that Hawaii is melting from a source that is hotter than the ambient mantle (Herzberg and Gazel, 2009; Putirka et al., 2011). High Ni contents in Hawaiian olivines have been used to infer both pyroxenite melting in the source (Sobolev et al., 2007; Herzberg, 2011) and high temperatures and pressures of peridotite melting (Putirka et al., 2011). Comparably high

mantle potential temperatures have been inferred for both Hawaii and West Greenland occurrences (1,500–1,600 °C; (Herzberg and Gazel, 2009)) and both erupted through thick lithosphere (Supplementary Information). If increased temperature and pressure is the main mechanism for producing olivine phenocrysts with high Ni contents (Putirka et al., 2011), there should be similar Ni, Mn, Fe/Mn and Ca contents in olivines from Hawaii and from Baffin Island and West Greenland. This is not observed (Supplementary Fig. 8). Hawaiian olivines are higher in Ni by ~1,000 p.p.m. and they have substantially lower calcium (Ca) and manganese (Mn) and higher Fe/Mn contents than those from West Greenland and Baffin Island. For the latter, a peridotite source provenance is clearly indicated (Fig. 2 and Supplementary Fig. 8). By contrast, low Ca and low Mn and high Fe/Mn contents for Hawaiian olivines are an expected consequence of pyroxenite source melting, owing to residuum retention of Ca in clinopyroxene and Mn in garnet (Supplementary Fig. 5). It is pyroxenite that contributes to high Ni in Hawaiian olivines (Sobolev et al., 2007; Herzberg, 2011), not temperature and pressure effects (Putirka et al., 2011). However, a possible role for mixed Ni-rich and Ni-poor peridotite with pyroxenite remains to be evaluated for Hawaii.

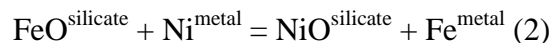
We conclude that high Ni coupled to peridotite-generated levels of Ca, Mn and Fe/Mn (Figs 1–3 and Supplementary Figs 6 and 7) point to Ni-rich peridotite sources for Baffin Island, West Greenland, Ontong Java plateau, Isla Gorgona and Fernandina in the Galapagos Islands. By ‘Ni-rich’, we refer to Ni contents that are significantly higher than those described by equation (1), in contrast with normal-Ni peridotite sources that melt to make modern oceanic crust at mid-ocean ridges (Fig. 1a).

Current estimates of the Ni content of fertile mantle peridotite (McDonough and Sun, 1995; Salters and Stracke, 2004) are based on averages which can vary by about 300 p.p.m. (Herzberg, 2011); the Ni content of olivine in such peridotites obtained from open-access web sources is also large (Putirka et al., 2011). Although our estimated Ni content for Ni rich peridotite is roughly within this range, we emphasize that this coincidence has no meaning because whole-rock and olivine Ni data are often compiled from sources of questionable accuracy (Herzberg, 2011), and there is much less uncertainty in our more recent work (Ionov, 2007) (Fig. 1 and Supplementary Fig. 1). Random 6300 p.p.m. variations in the Ni content of peridotite can result in olivines with Ni as low as 2,200 p.p.m. (Herzberg, 2011). Such low Ni contents have never been reported from high precision olivine analyses in unmetasomatized mantle peridotite (Fig. 1a) and, when found in olivine phenocrysts (Sobolev et al., 2007), other explanations are more plausible. For example, some MORB olivines can be low in Ni (Fig. 1a), but this is plausibly explained by sequestration of Ni into a residual sulphide phase (Herzberg, 2011), which can remain stable in the residue up to 15% melting (Bezous et al., 2005).

Lavas exhibiting Ni excess are also associated with elevated $^3\text{He}/^4\text{He}$. Picrites from Baffin Island and West Greenland have $^3\text{He}/^4\text{He}$ up to 50 times the atmospheric value (R_a) (Starkey et al., 2009), and they also have primitive Nd and Pb isotopic compositions (Jackson et al., 2010). For the others, the maximum $^3\text{He}/^4\text{He}$ (R_a) is 29 for Fernandina (Kurz et al., 2009) and 18 for Gorgona (Revillon et al., 2002). No helium data are currently available for lavas from the Ontong Java plateau, but they also have primitive Nd and Pb isotopic ratios (Jackson and Carlson, 2011).

We now explore a model that might produce a Ni-rich peridotite with increased $^3\text{He}/^4\text{He}$. We have tested the formation of Ni-rich peridotite in a magma ocean by perovskite subtraction and/or ferropericlasite addition. Although such models can yield high Ni contents, they produce a peridotite source that is too low in SiO_2 and Fe/Mn that is too high. More work on intra-mantle differentiation scenarios informed by accurate high-pressure phase equilibria and partitioning data are warranted (Coltice et al., 2011), but here we propose a core–mantle interaction model.

Evidence for melting at the present-day core–mantle boundary includes the coincidence of recent determinations of the peridotite solidus with the estimated temperature at the top of the outer core (Fiquet et al., 2010) and seismic observations of ultralow-velocity zones (Williams and Garnero, 1996). As even more melt is expected in an early hotter Earth, present-day ultralow-velocity zones may represent the terminal stages in the crystallization of a long-lived magma ocean, and they provide a possible mechanism for preserving primitive mantle (Labrosse et al., 2007; Coltice et al., 2011). This model predicts an equilibrium exchange of Ni between liquid metal in the core and liquid silicate in the mantle, which can be described by :



The present-day Ni content of fertile mantle peridotite (1,960 p.p.m.) may have been established by core formation at, 30–60 GPa (Siebert et al., 2012). Silicate melt in contact

with liquid metal would be enriched in Ni at 135 GPa as the exchange is driven from left to right with increasing pressure at constant oxidation state of iron (Walker, 2005; Rubie et al., 2011; Siebert et al., 2012). We propose that a Ni-rich and less-degassed domain was formed by core–mantle interaction during the late stages of the crystallization of a basal magma ocean (Labrosse et al., 2007) or melt layer, and that some part of this source continues to be sampled by mantle plumes. Another tracer for core–mantle interaction may be the addition of tungsten and osmium (Os) isotopes from the core to the mantle (Brandon et al., 2003; Walker, 2005). Gorgona is the only location examined here with available $^{186}\text{Os}/^{188}\text{Os}$ data, and there is an ^{186}Os anomaly that has been attributed to core influence (Brandon et al., 2003). There is no shortage of plausible mechanisms of core–mantle interaction, and the challenge is to understand how they are geochemically expressed (Walker, 2005).

Earth's mantle may have become oxidized by disproportionation of FeO in a deep magma ocean during crystallization of Fe^{3+} -rich Mg-perovskite and loss of metallic Fe to the core (Wade and Wood, 2005). The Ni-rich peridotite source for West Greenland is also oxidized, having produced melts more oxidizing than MORB and within one log unit of the nickel–nickel oxide oxygen fugacity buffer (Larsen and Pedersen, 2000). Although it is counterintuitive, we propose that these oxidized magmas had an origin that began above the core–mantle boundary, in a location where Ni-rich silicate melt and Fe^{3+} -rich Mg-perovskite were in equilibrium with the outer core. Mantle plumes that sample this region and ascend above the melting zone would solidify to Ni-rich ferropericlase, Ca perovskite and Fe^{3+} -rich Mg-perovskite, transforming further to Ni-rich and oxidized

peridotite in the upper mantle. Partial melting will yield magmas like those from West Greenland that are both Ni-rich and more oxidizing than MORB.

The spatial distribution of elevated $^3\text{He}/^4\text{He}$ in the mantle might be constrained by understanding the origin of a Baffin Island and West Greenland source with 2,360 p.p.m. Ni. Although core formation in a single stage is not likely (Rubie et al., 2011), its prediction of 3,580 p.p.m. Ni (Rubie et al., 2011) in the mantle at 135 GPa may be a guide to the Ni content of silicate melt at the present time. A source with 2,360 p.p.m. Ni would then require mixing of this high-Ni endmember with the canonical, 1,960 p.p.m. Ni from elsewhere in the mantle. In this scenario, the Ni-rich and high- $^3\text{He}/^4\text{He}$ source may be widely distributed (Class and Goldstein, 2005; Gonnermann and Mukhopadhyay, 2009) or it may take the form of a halo around the core. Alternatively, the isolation of the Baffin Island and West Greenland source as a refuge from convection near the core–mantle boundary (Tolstikhin and Hofmann, 2005; Jackson et al., 2010; Coltice et al., 2011; Jackson and Carlson, 2011) is plausible if it can be demonstrated that 2,360 p.p.m. Ni in a silicate melt is in equilibrium with the core. In any case, interaction of the core with a silicate melt is a plausible mechanism for production of oxidized Ni rich peridotite, and it provides evidence for a long-lived melt layer or basal magma ocean (Labrosse et al., 2007; Coltice et al., 2011).

3. Methods Summary

The method for calculating model olivine Ni compositions is given elsewhere (Herzberg, 2011) and in the Supplementary Information. Primary magma compositions are calculated first, followed by the olivines that they crystallize. The compositions of Ni

in liquids extracted from dunite [liquid+olivine] and harzburgite [liquid+olivine+orthopyroxene] residues were computed by mass balance solutions to the equation for accumulated fractional melting:

$$C_L = C_o[1 - (1-F)^{1/D}]/F$$

where C_L is weight per cent NiO in the liquid (primary magma), C_o is the initial NiO in the peridotite source composition (0.25%, (McDonough and Sun, 1995); 1,960 p.p.m.), F is the melt fraction, and D is the bulk distribution coefficient from the Beattie–Jones model (Supplementary Information). Ni contents for near-solidus melts were calculated from the MgO contents of near-solidus melts, together with a solidus olivine composition having 0.36% NiO (Herzberg, 2011) (Supplementary Information). Ni contents of near-solidus primary magmas are nearly indistinguishable from those of primary magmas for liquid+olivine and liquid+olivine+orthopyroxene assemblages, and the full range of possible Ni contents are shown in Supplementary Fig. 1.

The Ni content of olivine that crystallizes as a phenocryst at one atmosphere from a primary magma C_L was calculated using olivine/liquid Ni distribution coefficients from the Beattie–Jones model (Supplementary Information). Results are displayed in Figs 1 and 3 for a fertile peridotite having $C_o = 1,960$ p.p.m. Ni. Olivines have 2,800–3,100 p.p.m. Ni, and they provide an excellent description of olivine in normal mantle peridotite, primitive olivine phenocrysts in modern MORB, and olivine phenocrysts in

Archaean komatiites. However, they fail to describe the much higher Ni contents of olivines from Baffin Island, West Greenland, the Ontong Java Plateau, Isla Gorgona and Fernandina (Galapagos) (Figs 1c and 3). For these, excellent agreement between computed and observed olivine Ni contents could be obtained with $C_o = 0.30\%$ NiO (2,360 p.p.m. Ni), a Ni-rich peridotite source.

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5. Figure Captions:

Figure 1: Mg-numbers and Ni content for calculated (Herzberg, 2011) and observed olivine. An Mg-number is defined as $100\text{MgO}/(\text{MgO} + \text{FeO})$ in mole per cent. The black curve represents the calculated Ni content in olivines that crystallize from all primary melts derived from a fertile peridotite source having a whole-rock Ni content of 1,960 p.p.m. (Herzberg, 2011); the $\pm 1\sigma$ uncertainty (grey shading) is discussed in Supplementary Information section 3. The black hatched area represents the calculated Ni content in olivines from olivine fractionated derivative liquids from primary magmas having 8–13% MgO. **a**, The green circles are 203 high-precision analyses of olivine in mantle peridotite from various tectonic settings (Supplementary Information); the blue and red circles are high-precision olivine phenocrysts in MORBs from the Pacific (the

EPR) and Indian oceans (Sobolev et al., 2007; Putirka et al., 2011). **b**, The red circles are high-precision olivine phenocrysts from the Archaean Alexo komatiites (Sobolev et al., 2007). The green curves are calculated Ni contents in olivines from olivine-fractionated derivative liquids from primary magmas having 20–30% MgO (Herzberg, 2011), as indicated (green numbers); primary magmas for Alexo contained 26–30% MgO (Herzberg, 2011; Arndt et al., 2008). **c**, The white circles are high-precision olivine phenocrysts from West Greenland and Baffin Island (Sobolev et al., 2007); the uncertainty is only slightly greater than the size of the open circles. The red crosses are the Ni contents of olivine phenocrysts expected to crystallize from primary melts derived from Ni-rich fertile peridotite having 2,360 p.p.m. Ni. The green and blue lines are olivine compositions that will crystallize from these primary magmas by fractionation of olivine and clinopyroxene in the weight proportions indicated (Supplementary Information). A low-Ni population comes from one sample (ID 27142) from West Greenland (Sobolev et al., 2007), and it represents 28% of the database, having Mg number. 90. There is little overlap between this sample and the more Ni-rich types. The difference between the low- and high-Ni populations most probably reflects mantle source heterogeneity, but there are no independent geochemical data for these samples with which to test this possibility.

Figure 2: Mg-numbers and Ca, Mn and Fe/Mn contents for calculated (Herzberg, 2011) and observed olivine phenocrysts from MORBs (right panels) compared with Baffin Island and West Greenland (Sobolev et al., 2007) (left panels). The black regions are calculated olivines from primary melts (8–38% MgO) derived by peridotite

melting (Herzberg, 2011). The black hatched area in **f** and the grey shading in **c** and **d** represent the calculated olivines from olivine-fractionated derivative liquids from primary magmas having 8–20% MgO. The green and blue lines in **a**, **c** and **e** are olivine compositions that crystallize from primary magmas that fractionated olivine and clinopyroxene in the weight proportions indicated (Supplementary Information). The inset in **b** shows how Ca in olivine changes owing to olivine and clinopyroxene fractionation from the primary magmas. The MORBs in **b**, **d** and **f** are from the EPR (white circles) and Indian Ocean (yellow circles). Although a wide range of Ca contents are theoretically possible for olivines that crystallize from peridotite-source primary magmas, most have ~2,000 p.p.m. Ca—similar to those found in MORBs, Baffin Island and West Greenland. Primitive and depleted peridotites contain ~1,000 p.p.m. Mn (McDonough and Sun, 1995; Salters and Stracke, 2004) and, although olivines with $\text{Fe/Mn} = 55\text{--}70$ can crystallize from primary magmas, more usually the range is restricted to 60–65 (Herzberg, 2011).

Figure 3: Mg-numbers and Ni contents for calculated olivine (Herzberg, 2011) and observed olivine phenocrysts. **a**, Gorgona (Sobolev et al., 2007), **b**, the Ontong Java Plateau (Sobolev et al., 2007), and **c**, Fernandina (this work; Supplementary Information section 5 and Supplementary Table 2). The black curves represent the calculated Ni content in olivines of primary magmas of fertile peridotite having 1,960 p.p.m. Ni (Herzberg, 2011); the grey shaded regions ($\pm 1\sigma$) represent a possible range of Ni contents in olivine that may arise from uncertainties in the calculation (Supplementary Information). The red crosses are olivines that would crystallize from Ni-rich fertile

peridotite-source primary magmas; the green and blue lines are olivine compositions that crystallize from primary magmas that fractionated olivine and clinopyroxene in the weight proportions indicated (Supplementary Information section 4).

6. Figures

Figure 1:

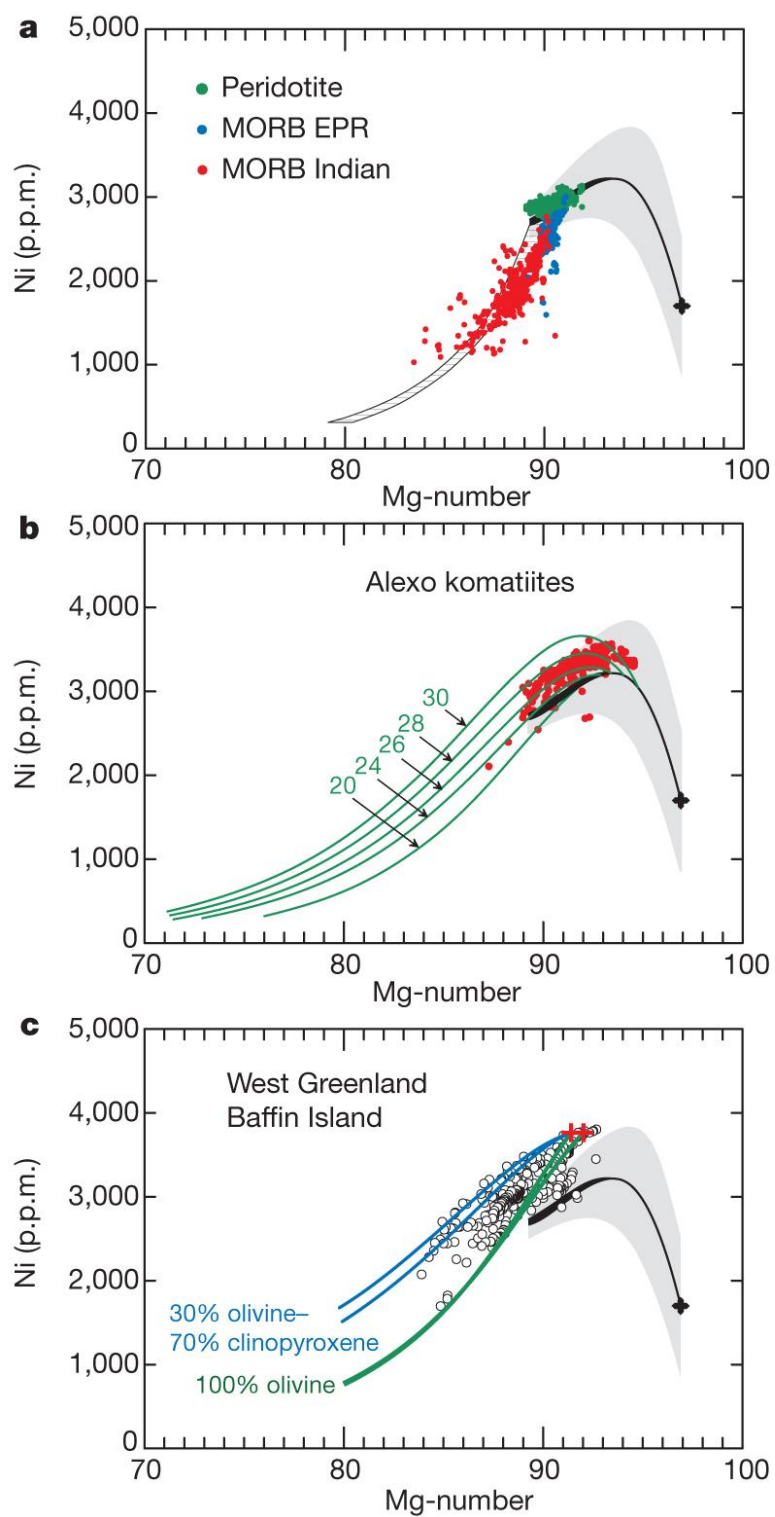


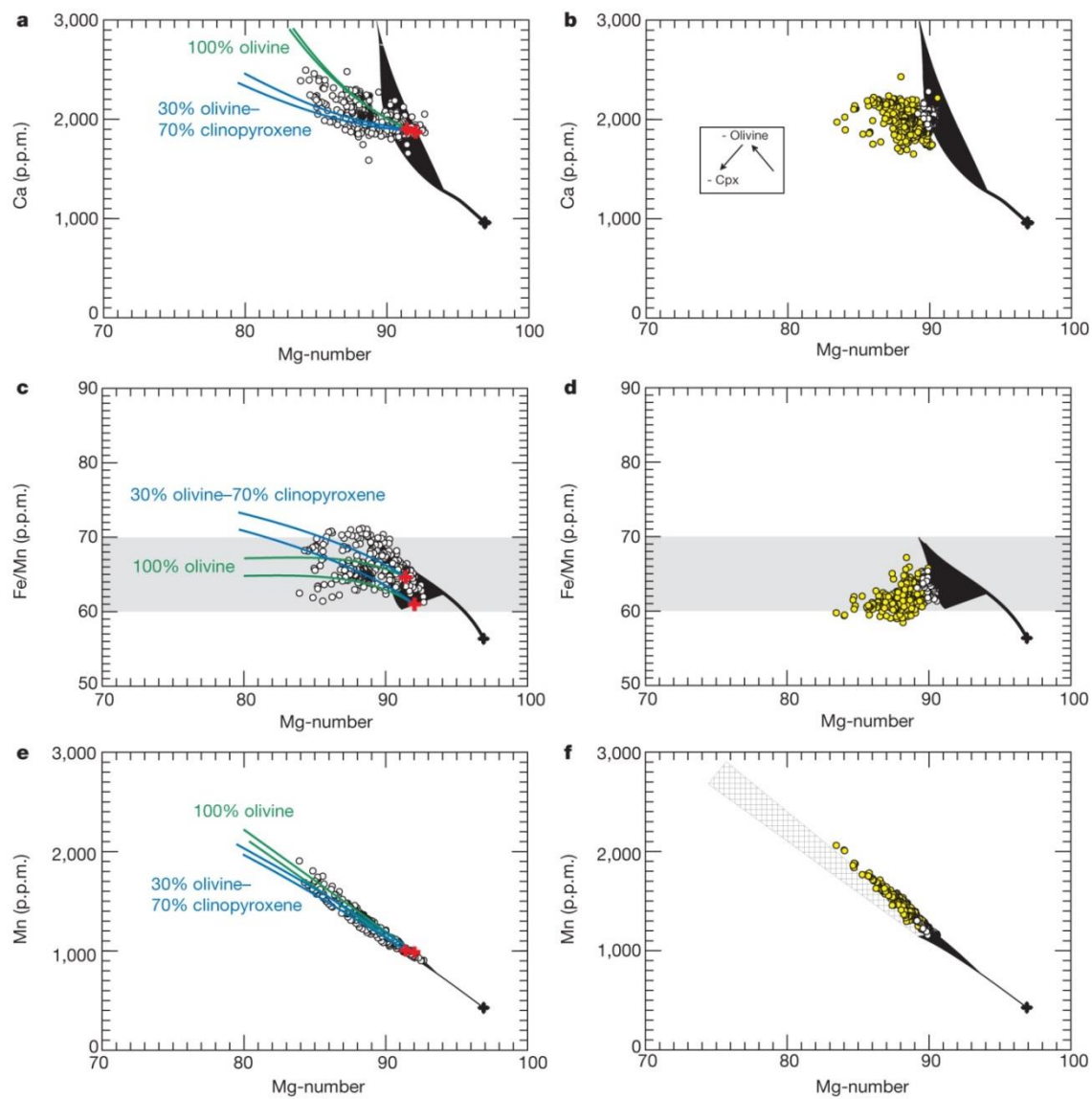
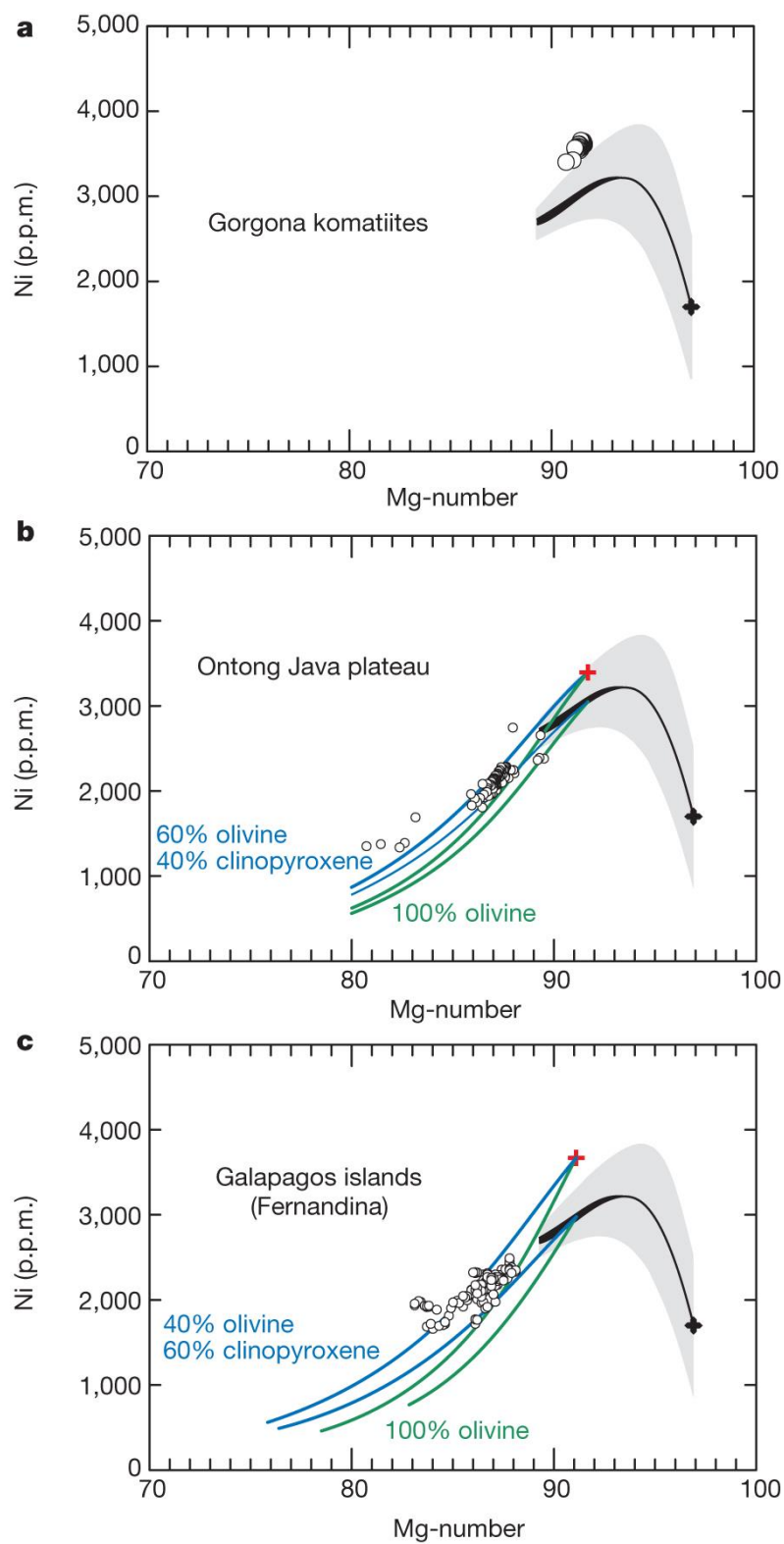
Figure 2:

Figure 3:

Supplemental Information:

S.1. The Ni Content of Mantle Peridotite and Its Primary Magmas

Of the 590 whole rock spinel and garnet peridotite analyses from off-craton xenolith and tectonic occurrences compiled by Herzberg (1993), 407 contain Ni data and these are shown in Fig. S1. Fertile peridotite has 0.03% K₂O (McDonough and Sun, 1995), and most of the peridotites have higher K₂O, indicating that they were modified by metasomatism. There are 264 analyses with K₂O < 0.03%, and these generally have more uniform NiO contents than the metasomatised types. Nevertheless, many of the measurements in this database were obtained in the 1960s by analytical methods that predated the XRFs, and the variation in Ni shown in Fig. S1 likely reflects uncertainties in analytical method. For example, peridotites with K₂O < 0.03% can be described by the equation: Ni (ppm) = 71.7MgO – 844, and the uncertainty is ± 254 ppm (1σ).

The old database of Herzberg (1993) can now be compared with the more recent determinations of off-craton peridotite xenoliths from Asia (Ionov, 2007; 2010; Ionov and Hofmann, 2007; Ionov et al., 2005). Most Ionov data were obtained using wavelength-dispersive X-ray fluorescence spectrometry at the University of Mainz. Data quality is greatly improved (Fig. S1), and can be described by the equation: Ni (ppm) = 68.6MgO – 630 where the uncertainty of 110 fertile and depleted peridotite compositions is ± 46 ppm (1σ). Using this equation and 37.7% MgO in pyrolite (McDonough and Sun, 1995), we obtain 1957 ppm Ni, virtually indistinguishable from the McDonough and Sun (1995) canonical value of 1960 ppm.

S.2. High Precision Olivine Analyses in Peridotite

Ionov (2007, 2010) and Ionov et al. (2005) published high-precision analyses of olivine in intraplate peridotite xenoliths from Tariat (Mongolia) and Tok (SE Siberia), and subduction xenoliths from Avacha (Kamchatka), using protocols similar to those reported by Sobolev et al. (2007). We have compiled these data and add high precision analyses of olivine from other off-craton spinel and garnet peridotites from Asia. Results from abyssal peridotites will be reported by Ionov and Sobolev separately, and are similar to intraplate and subduction occurrences, demonstrating homogeneity of Ni in all tectonic settings. Table S1 lists individual olivine analyses in some cases and also averages. Replicate analyses using the method of Sobolev et al. (2007) are in good agreement, and will be reported elsewhere by Ionov and Sobolev. Results of 203 analyses shown in Fig. 1 of the text reveal substantial homogeneity of Ni in peridotite olivine. They are in excellent agreement with model Ni contents of olivine (Fig. 1; Herzberg, 2011), although they are slightly higher in Ni in some cases, indicating the possible influence of Ni exchange with orthopyroxene on cooling (Herzberg, 1999). Overall olivine Ni homogeneity is in contrast with a wide range of Ni contents in olivines from peridotites compiled by Putirka et al. (2011) from GEOROC. While we concur that Ni-rich peridotite sources can be important in intraplate magmatism, we conclude the evidence for it can be weak in existing peridotite databases owing to questionable accuracy.

S.3. The Effects of Temperature, Pressure and Composition on the Partitioning of Ni between Olivine and Liquid

The partitioning of Ni between olivine and liquid depends on temperature, pressure, and composition of the melt (Hart and Davis, 1978; Beattie et al., 1991; Herzberg and Zhang, 1996; Wang and Gaetani, 2008; Filiberto et al., 2009; Putirka et al., 2011; Li and Ripley, 2010; Longhi et al., 2010; Niu et al., 2011). In particular, $D_{\text{Ni}}^{\text{Ol/L}}$ goes down with increasing MgO content of the melt. But as increasing temperatures and pressures of melting yield melts with higher MgO contents (O'Hara, 1968), it can be difficult to resolve the separate T-P-X effects. This problem has given rise to a plethora of parameterizations of experimental data that have calibrated $D_{\text{Ni}}^{\text{Ol/L}}$ as a function of T-P-X. It is important to resolve because elevated Ni contents of olivine phenocrysts have been used to infer pyroxenite melting in the source (Sobolev et al., 2005; 2007; Herzberg, 2011), elevated temperatures and pressures in mantle plumes (Li and Ripley, 2010; Putirka et al., 2011; Matzen et al., 2012) and elevated pressures (Niu et al., 2011).

We adopt a model of Ni partitioning that provides the minimum error when recovering experimental data. This is a temperature-independent model first formulated by Jones (1984), later calibrated by Beattie et al. (1991), and corroborated in subsequent studies (Wang and Gaetani, 2008; Filiberto et al., 2009; Longhi et al., 2010). We call this a Beattie-Jones model, which is described by:

$$D_{\text{NiO}}^{\text{Ol/L}} = \text{NiO}^{\text{Ol}}/\text{NiO}^{\text{L}} \quad (1)$$

$$D_{\text{MgO}}^{\text{OL}} = \text{MgO}^{\text{Ol}}/\text{MgO}^{\text{L}} \quad (2)$$

and

$$D_{\text{NiO}}^{\text{Ol/L}} = 3.346 D_{\text{MgO}}^{\text{Ol/L}} - 3.665 \quad (3)$$

where NiO^{OL} , Ni^{OL} , MgO^{Ol} , Mg^{OL} refer to mole fractions of NiO and MgO in the phases liquid (L) and olivine (Ol), based on one metal cation per oxide (i.e., SiO_2 , MgO , $\text{AlO}_{1.5}$, $\text{NaO}_{0.5}$ etc.; Beattie et al., 1991). The constants in equation (3) have been obtained from a parameterization of experimental data (Beattie et al., 1991), which we have tested using the experimental database on Fe-bearing compositions collated by Li and Ripley (2010). To this database was added:

- 11 experiments of Longhi et al. (2010; 1554 to 2015°C and 1.6 to 6.0 GPa).
- 11 experiments of Taura et al. (1998; 1600 to 2000°C and 3.0 to 14.4 GPa using both electron microprobe and SIMS analyses)
- 6 experiments of Le Roux et al. (2011; 1300 to 1500 °C and 1.5 to 2.0 GPa)
- 10 experiments of Matzen et al. (2011; 1301 to 1500 °C and 1 atmosphere)

There are a total of 271 experiments with temperatures in the 1122-2050°C range and pressures in the 1 atmosphere to 13 GPa range. To these experiments, the olivine/liquid

distribution coefficients $D_{\text{NiO}}^{\text{Ol/L}}$ were calculated according to the Beattie-Jones equation (3). For the entire database ($N = 271$) we calculate:

$$1 \text{ standard deviation } (1\sigma) = (\Sigma(D_{\text{NiO,calculated}} - D_{\text{NiO,observed}})^2 / (N-1))^{0.5} \quad (4)$$

and obtain $1\sigma = 1.1$. However, the difference between calculated and observed $D_{\text{NiO}}^{\text{Ol/L}}$ is clearly related to temperature as shown in Fig. S2. This likely reflects the effects of temperature on promoting equilibrium during the course of an experiment, and differences between calculated and observed partitioning are minimized and approximately constant at $T > 1500^\circ\text{C}$. We have developed an empirical expression for computing the effects of temperature on σ by binning the experimental database in 100°C increments. At $T > 1500^\circ\text{C}$:

$$1 \text{ standard deviation } (1\sigma) = 0.4 \quad (5)$$

and $T < 1500^\circ\text{C}$:

$$1 \text{ standard deviation } (1\sigma) = -9.308 + 0.0179T - 0.0000075T^2 \quad (6)$$

The results of this uncertainty analysis on the Ni content of olivine in equilibrium with partial melts of mantle peridotite was shown in Fig. 1 of the main body of this paper.

It was shown by Herzberg (2011) that the method of Beattie et al. (1991; equation 3) provides a better description of experimental data than the method of Li and Ripley (2010) which contains independently adjustable temperature and composition terms. Similarly, Putirka et al. (2011) have expressed the partitioning of NiO on a weight % basis, and parameterized it according to both temperature (°C) and composition (wt%). They parameterized 81 experiments with:

$$D_{\text{NiO}}^{\text{Ol/L}} = \exp[-3.257 + 6800/T] \quad (7a)$$

49 experiments with:

$$D_{\text{NiO}}^{\text{Ol/L}} = \exp[-4.75 + 0.033(\text{SiO}_2)^{\text{L}} + 6829/T] \quad (7b)$$

and 81 experiments with:

$$D_{\text{NiO}}^{\text{Ol/L}} = \exp[-1.78 + .04(\text{SiO}_2)^{\text{L}} - 0.04(\text{MgO})^{\text{L}} + 3236/T] \quad (7c)$$

These equations were labeled as 2a, 2b, and 2c in Putirka et al. (2011). Results shown in Fig. S3 demonstrate that the Beattie – Jones parameterization of equation (3) yields a more accurate description of the experimental database than Putirka et al. (2011). For mantle peridotite having 1960 ppm Ni that melts at high temperatures appropriate to a mantle plume, use of the Putirka et al. (2011) parameterization will yield primary magmas with Ni contents that are too high.

Niu et al. (2011) suggested that the Ni content of olivine is a function of the pressure at which melting stops at the base of the lithosphere, which covers the 0 to 3 GPa range. They provided the following parameterization of a limited and unspecified number of experiments:

$$D_{\text{NiO}}^{\text{Ol/L}} = 4.6914P^{-0.5357} \quad (8)$$

As their equation (8) intercepts the y-axis at infinity, we restrict this analysis to experiments in the 0.5 to 3.2 GPa. Results shown in Fig. S4 demonstrate that the Niu et al. (2011) parameterization is not as successful as the method of Beattie et al. (1991) in describing the experimental database.

The most successful method for describing the Ni content of olivine phenocrysts to crystallize from magmas is provided by Beattie et al. (1991), and it is the one we have adopted in this work. The method has the advantage of requiring only the composition of the melt from which olivine crystallizes. There are no independently adjustable temperature and pressure terms, which are themselves model-dependent. We conclude that the high Ni contents of olivines in Baffin Island, Disko Island, West Greenland, the Ontong Java Plateau, Isla Gorgona, and Fernandina originated from a Ni-rich peridotite source, and are not artifacts of elevated temperatures and pressures of melting.

S.4. Forward Models of Liquid Lines of Descent Involving Olivine and Clinopyroxene

The problem of inferring source lithology is tractable when Mg-numbers of olivine phenocrysts are high, generally > 89 (Herzberg, 2011). For example, olivine phenocrysts for shield building lavas on Hawaii are higher in Ni and Fe/Mn, and lower in Mn and Ca than those expected of a normal peridotite source (Sobolev et al., 2005; 2007; Herzberg, 2011). In contrast, maximum Mg-numbers for olivine phenocrysts from many intraplate volcanoes are typically in the 80-88 range, and can result from the crystallization of both olivine and clinopyroxene from primary magmas. The problem is to compare high precision olivine analyses with those that are expected to crystallize from such magmas. This is solved by a forward model of the liquid line of descent, and the calculation of olivine that crystallizes along it.

The importance of sub Moho clinopyroxene fractionation in ocean island and MORB petrogenesis has been recognized previously (Albarède et al., 1997; Geist et al., 1998; Herzberg, 2004a; Herzberg and Asimow, 2008). The effect of decompression is to expand the liquidus crystallization fields of olivine and clinopyroxene (O'Hara, 1968; Herzberg, 1992), and both can crystallize when primary magmas interact with wall rocks during transit. Relative to olivine only crystallization, deep fractionation of clinopyroxene can produce derivative magmas with lower CaO, SiO₂, higher FeO, lower MnO, and higher NiO. Olivine that crystallizes from such melts at the surface will exhibit depletions in Ca and Mn, elevated Fe/Mn, and elevated Ni. The erroneous interpretation can be made that this olivine points to a pyroxenite source lithology even if the primary magmas melted from a peridotite source. The problem is how to distinguish the effects of

clinopyroxene as a crystallizing phase from clinopyroxene a residual phase in pyroxenite source.

The method for calculating a liquid line of descent begins with identification of a primary magma composition. Primary magma compositions for peridotite-sources have been computed from primitive lava compositions that differed by olivine addition and subtraction using PRIMELT2 (Herzberg and Asimow, 2008). Results for many ocean islands and large igneous provinces were reported by Herzberg and Gazel (2009). In most cases it was sufficient to obtain primary magmas from the raw lava compositions. For Fernandina, most lava compositions were too differentiated to obtain primary magma compositions owing to plagioclase and augite fractionation. The few remaining primitive samples had unusually variable Mn, and primary magma Mn was adjusted slightly to optimize the match with observed olivine phenocryst compositions. Additionally, whole rock NiO contents often provide unreliable primary magma NiO contents due to olivine sorting; for primary magmas of peridotite-sources, we use $\text{Ni (ppm)} = 21.6\text{MgO} - 0.32\text{MgO}^2 + 0.051\text{MgO}^3$ (Herzberg, 2011).

From these identified primary magmas, both olivine and clinopyroxene were permitted to crystallize along a liquid line of descent. The Ol:Cpx proportions have been varied arbitrarily because the exact T-P paths at which melts interact with wall rocks are not known. We assume perfect fractional crystallization, and the extraction of olivine and clinopyroxene was accomplished computationally by removing them incrementally by 0.1%. Of course, the compositions of olivine and clinopyroxene need to be computed at

each step in order to compare with observed phenocryst compositions. This is accomplished with partition coefficients as discussed now.

The method for computing the compositions of Ni, Ca, Mn, and Fe in olivine in equilibrium with both the primary magmas and their derivative liquids was reported in Herzberg (2011), and is repeated here because it is an appropriate introduction to the calculation of clinopyroxene composition. As discussed above, we make use of the partition coefficient:

$$D_i^{Ol/L} = X_i^{Ol} / X_i^L \quad (9)$$

where X_i refers to the mole fraction of oxide component i in the phases liquid (L), olivine (Ol), based on one metal cation per oxide (i.e., SiO_2 , MgO , $AlO_{1.5}$, $NaO_{0.5}$ etc.). We used the temperature-independent Beattie-Jones parameterization model (Jones, 1984; Beattie et al., 1991):

$$D_i^{Ol/L} = A_i^{Ol/L} D_{MgO}^{Ol/L} + B_i^{Ol/L} \quad (10)$$

where $D_{MgO}^{Ol/L} = MgO^{Ol}/Mg^{Ol}$ and the A and B constants have been parameterized from experimental data. Parameterized results for Ni reported by Beattie *et al.* (1991) were

discussed above (equation 3). Results for Mn and Ca are from Herzberg and O'Hara (2002), and we use a 1 atmosphere Fe/Mg exchange coefficient from Toplis (2005).

The method for calculating Cpx fractionation is similar to that for Ol addition/subtraction calculations (Herzberg and Asimow, 2008; Herzberg, 2011) except that the partition coefficients are different. We have parameterized high quality high pressure experimental data for Cpx/L from the following sources: Walter (1998), Longhi (2002), Pertermann and Hirschmann (2003), Keshav et al. (2004), Gerbode and Dasgupta (2010) and Le Roux et al. (2011). For Fe and Mn, we follow the Jones-Beattie method of parameterizing partition coefficients as discussed above for olivine:

$$D_{\text{FeO Cpx/L}} = 0.215 D_{\text{MgOCpx/L}} + 0.181 \quad (R = 0.98) \quad (11)$$

$$D_{\text{MnO Cpx/L}} = 0.284 D_{\text{MgOCpx/L}} + 0.294 \quad (R = 0.91) \quad (12)$$

And

$$D_{\text{CaO Cpx/L}} = 0.395 D_{\text{MgOCpx/L}} + 0.503 \quad (R = 0.85) \quad (13)$$

where R refers to the correlation coefficient. Results show that D for FeO and MnO are well-correlated with D for MgO (Fig. S5), as indicated also by the high correlation coefficients. Equations (11) and (12) describe equally well the partitioning of Fe and Mn in melting experiments for which 3-4% H₂O was reported in the liquid (Balta et al., 2011). However, as discussed by Balta et al. (2011), clinopyroxene in these wet experiments contain unusually high CaO compared with anhydrous experiments; as it is

not likely that intraplate magmas are this wet (Herzberg and Asimow, 2008), the Balta results for CaO were not included in the parameterization. For all other experiments, the lower correlation coefficients for CaO may result in part from vacant sites (Hirschmann and Petermann, 2003). But there are also less satisfactory correlations of $D_{\text{MgO}}^{\text{Cpx/L}}$ with D_s for TiO_2 , $\text{AlO}_{1.5}$, and $\text{NaO}_{0.5}$, indicating limitations in application of the Jones-Beattie method to coupled ionic substitutions. Improved correlations were obtained empirically with the following equations:

$$D_{\text{TiO}_2}^{\text{Cpx/L}} = 0.215 D_{\text{CaO}}^{\text{Cpx/L}} - 0.047 \quad (R = 0.87) \quad (14)$$

$$D_{\text{AlO}_{1.5}}^{\text{Cpx/L}} = -1.114 D_{\text{SiO}_2}^{\text{Cpx/L}} + 1.859 \quad (R = 0.77) \quad (15)$$

and

$$D_{\text{NaO}_{0.5}}^{\text{Cpx/L}} = 1.304 D_{\text{AlO}_{1.5}}^{\text{Cpx/L}} - 0.412 \quad (R = 0.93) \quad (16)$$

D values for CaO, SiO_2 , $\text{AlO}_{1.5}$, and $\text{NaO}_{0.5}$ are computed from mole fractions of these components in Cpx and Liquid in the usual manner; however, sodium partitioning depends on aluminum partitioning and equation (15) must be solved before equation (16).

Clinopyroxene compositions that were computed with the above partition coefficients were assumed to be stoichiometric, with no site vacancies, and all plot exactly within the pyroxene-garnet plane.

It is useful to compare the partitioning behavior of garnet and clinopyroxene, and results are shown in Fig. S5 and listed below.

	$A^{Gt/L}$	$B^{Gt/L}$	R (correlation coefficient)
FeO	0.589	-0.135	0.99
MnO	1.169	-0.375	0.98
CaO	0.20	0.31	0.96
NiO (see below)			

Included in Fig. S5 are data for majorite garnet/liquid from experiments in the range 15.5-22.5 GPa and 2135-2375°C (Herzberg and Zhang, 1996). These extreme T-P data are fully consistent with others in the 2.5 to 7.0 GPa range, demonstrating the success of the Jones-Beattie model in capturing the partitioning of Fe, Mn, Mg, and Ca between garnet and liquid over all conditions of magma genesis.

Manganese is strongly partitioned into garnet, whereas it displays both compatible and incompatible behavior in clinopyroxene. Furthermore, MnO is more compatible in Cpx and Gt than is FeO (Fig. S5). The ability of garnet and clinopyroxene to preferentially accept Mn over Fe during melting and crystallization will yield liquids with elevated Fe/Mn. Olivines that crystallize from such liquids will also be elevated in Fe/Mn and can indicate a garnet pyroxenite source during partial melting (Sobolev et al., 2007; Herzberg, 2011). Alternatively, olivines with elevated Fe/Mn can indicate garnet pyroxenite crystallization from melts of a peridotite source.

There are very few experiments that constrain the partitioning of Ni for Cpx/L and Gt/L. However, Canil (1999) reported variable $D_{\text{NiO}}^{\text{Gt/Ol}}$ in subsolidus experiments, reaching a maximum of 0.11 at 1500°C and 5 GPa. Using Canil's data, Sobolev et al. (2005) estimated $D_{\text{NiO}}^{\text{Gt/Ol}}$ in the 0.10-0.14 range appropriate to Walter's (1998) experiments for which no NiO data were reported; similarly, they estimated $D_{\text{NiO}}^{\text{Gt/Cpx}}$ of about 0.5. For the case of L + Ol + Cpx \pm Gt, we can estimate $D_{\text{NiO}}^{\text{Cpx/L}}$ and $D_{\text{NiO}}^{\text{Gt/L}}$ from $D_{\text{NiO}}^{\text{Gt/Ol}}$ and $D_{\text{NiO}}^{\text{Cpx/Ol}}$ and $D_{\text{NiO}}^{\text{Ol/L}}$ (Beattie et al., 1991; equation 1). Results are:

$$D_{\text{NiO}}^{\text{Cpx/Ol}} = 0.250 D_{\text{NiO}}^{\text{Ol/L}} \quad (17)$$

and

$$D_{\text{NiO}}^{\text{Gt/L}} = 0.125 D_{\text{NiO}}^{\text{Ol/L}} \quad (18)$$

There is only one experiment for which high quality Ni data are reported for all phases for L + Ol + Cpx, that being G107 of Le Roux et al. (2011). Results show $D_{\text{NiO}}^{\text{Cpx/Ol}} = 0.28 D_{\text{NiO}}^{\text{Ol/L}}$ using Ni in olivine and liquid in experiment G107. The distribution of Ni between Ol and L in this experiment (8.32) is in good but not perfect agreement with the parameterization of Beattie et al. (1991; 9.32) at the $D_{\text{MgO}}^{\text{Ol/L}}$ in G107 (3.88). Using Beattie's parameterized $D_{\text{NiO}}^{\text{Ol/L}}$, we obtain for experiment G107 $D_{\text{NiO}}^{\text{Cpx/Ol}} = 0.250 D_{\text{NiO}}^{\text{Ol/L}}$, in excellent agreement with equation (17).

S.5. Olivine Phenocrysts from Isla Gorgona, Ontong Java Plateau and Fernandina

Olivine phenocryst compositions from Isla Gorgona komatiites were provided by Sobolev et al. (2007) and are shown in Fig. S6. These have very high *Mg*-numbers, similar to those expected for early crystals from the primary magmas, and peridotite source provenance is indicated by Ca, Mn, and Fe/Mn (Herzberg, 2011; Sobolev et al., 2007). However, they distinctly enriched in Ni, and require crystallization of magmas of a Ni-rich peridotite source.

Olivine phenocryst compositions from the Ontong Java Plateau were also provided by Sobolev et al. (2007) and are also shown in Fig. S6. They have lower *Mg*-numbers than olivines from Gorgona, and there is some indication that both olivine and clinopyroxene fractionation has affected their compositions. Relative to olivine-only fractionation, the effects of variable clinopyroxene fractionation is to lower Ca and Mn, and raise both Ni and Fe/Mn.

Olivine phenocryst compositions for Fernandina are new and reported in Table S2 and shown in Fig. S7. These were obtained from a submarine sample D38A from Fernandina in the Galapagos Islands (Geist et al., 2006). Major and trace element data were obtained using the method of Sobolev 2007 on Rutgers University's Joel JXA-8600 electron microprobe. Detection limits were obtained from the Probe for Windows for all elements. Average detection limits for Si, Mg and Fe are 53, 36 and 40 ppm respectively. Average detection limits for trace elements Ni, Mn and Ca are 26, 28 and 16 ppm respectively. 2σ error for all elements was calculated from repeated analyses of the San Carlos olivine standard. Analyses of Si, Mg and Fe have a relative 2σ error of $\sim 1.75\%$,

~0.51% and ~0.57% respectively. Analyses of trace elements Ni, Mn and Ca have a relative 2σ error of 2.02%, 2.68% and 3.06% respectively. The relative 2σ error for the Fo# is ~0.12%. Analyses with oxide totals $> \pm 2\%$ deviation from 100% were excluded. Chemical formulas were calculated for all analyses. Analyses with deviations in stoichiometry $> \pm 1\%$ were excluded. Relative to olivine-only fractionation, the effects of variable clinopyroxene fractionation (Geist et al., 1998) is to lower Ca and Mn, and raise both Ni and Fe/Mn.

S.6. Examples of Peridotite and Pyroxenite Source Lithologies Inferred from Olivine Phenocryst Composition

Comparably high mantle potential temperatures have been inferred for both Hawaii and West Greenland occurrences (TP = 1500-1600°C; Herzberg and Asimow, 2008; Herzberg and Gazel, 2009), and both erupted over thick lithosphere (Larsen and Pedersen, 2000; Li et al., 2000; 2004). If elevated temperature and pressure is the main mechanism for producing olivine phenocrysts with high Ni contents, then it is to be expected olivine phenocryst compositions from Hawaii and West Greenland occurrences will have similar Ni, Mn, Fe/Mn, and Ca. This is not observed (Fig. S8). Hawaiian olivines are higher in Ni by ~ 1000 ppm, they are substantially lower Ca and Mn and higher Fe/Mn compared with those from West Greenland, Baffin Island and Disko Island.

Olivine phenocrysts from Alexo komatiites of Archean age have Ni contents that are somewhat higher than those of expected from olivines of primary peridotite-source magmas with 26-30% MgO (Fig. S9). However, the effect of minor olivine fractionation is to initially raise Ni then lower it, producing an array that is concaved toward the Mg-

number axis (Herzberg, 2011). This sense of curvature computed from the Beattie-Jones Ni partitioning model is captured in olivines from Alexo (Fig. S9), a remarkable level of agreement. It is also clear from Fig. S9 that olivine phenocrysts from Hawaii and Alexo komatities have very different Ca, Mn, and Fe/Mn. For Alexo, a peridotite source provenance is clearly indicated (Fig. S9). In contrast, low Ca and Mn and high Fe/Mn for Hawaiian olivines are not consistent with peridotite-source melting.

Olivine phenocrysts in subduction zone andesites from the Mexican Volcanic Belt have the highest Ni contents ever reported (Straub et al., 2008), and greatly exceed the Ni contents of normal mantle peridotite (Fig. S10). Straub et al. (2008) interpreted these high Ni contents with a pyroxenite source lithology that formed by reaction of SiO₂-rich slab fluids with peridotite in the mantle wedge. Ni maxima are observed for 4 sub parallel arrays, and those with the lowest Mg-numbers exclude the possibility of formation from a peridotite source lithology. Most relevant to the present discussion is that it is not probable that these olivine Ni contents can be interpreted by any temperature- and pressure-melting and crystallization process that operated on a normal Ni peridotite source.

S.7. References:

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S.8. Figure Captions:

Figure S1:

MgO and Ni contents of mantle peridotite and partial melts of mantle peridotite (Herzberg, 2011).

Figure S2:

A comparison of model and experimentally observed partition coefficients for nickel.

Figure S3:

Measured versus calculated $D_{\text{NiO}}^{\text{Ol/L}}$ for equation (3) of Beattie et al. (1991) and equations 7a,b,c of Putirka et al. (2011).

Figure S4:

Measured versus calculated $D_{\text{NiO}}^{\text{Ol/L}}$ for equation (8) of Niu et al. (2011).

Figure S5:

Partition coefficients determined for clinopyroxene/liquid (blue squares) and garnet/liquid (red circles) from experimental data listed in the text. Note that FeO contents of garnets in experimental data from Keshav et al.(2004; orange circles) are highly discrepant, unlike MnO, and were not included in the regression.

Figure S6:

Mg-numbers and Ni, Ca, Mn, and Fe/Mn for calculated olivine (Herzberg, 2011) and observed olivine phenocrysts from Gorgona komatiites and basalts from the Ontong Java Plateau (Sobolev et al., 2007). Black regions are calculated olivines from primary magmas of peridotite (Herzberg, 2011). Green and blue lines are olivine compositions that crystallize from primary magmas that fractionated olivine and clinopyroxene in the weight proportions indicated. Hi Ni refers to olivine crystallization from a primary melt of a high Ni mantle peridotite.

Figure S7:

Mg-numbers and Ni, Ca, Mn, and Fe/Mn for calculated olivine (Herzberg, 2011) and observed olivine phenocrysts from a submarine sample D38A from Fernandina in the Galapagos Islands (Table S1). Black regions are calculated olivines from primary magmas of peridotite (Herzberg, 2011). Green and blue lines are olivine compositions that crystallize from primary magmas that fractionated olivine and clinopyroxene in the weight proportions indicated. Hi Ni refers to olivine crystallization from a primary melt of a high Ni mantle peridotite.

Figure S8:

A comparison of olivine phenocryst compositions for Hawaii, West Greenland, Baffin Island and Disko Island. All data are from Sobolev et al. (2007).

Figure S9:

A comparison of olivine phenocryst compositions for Hawaii and Alexo komatiites of Archean age. All data are from Sobolev et al. (2007).

Figure S10:

Olivine phenocryst compositions from the Mexican Volcanic Belt (Straub et al., 2008).

Figure S11:

Olivine phenocryst compositions from the Komati Formation of the Barberton greenstone belt compared with olivines expected to crystallize from primary magmas of dry fertile peridotite (black form; 3.45% CaO). Red arrow labeled F reflects lower Ca content of olivine with increasing melt fraction F. Low Ca olivine outliers may have grown in heterogeneous melts formed at high melt fractions or from melts of more depleted peridotite (grey form; 2.14% CaO; melt solutions in Herzberg (2004b) except calculated for accumulated fractional melting). It is notable that depleted isotopic compositions do not correlate with depleted major element compositions of peridotite sources (e.g., Salters and Stacker, 2004), and the olivine Ca contents should cover the full range of possibilities. Model depleted and fertile peridotite compositions have ~ 8% FeO (Herzberg and O'Hara, 2002). An ancient FeO-depleted source is expected to yield olivines with similar CaO but higher Mg-numbers.

Figure S12: Ca contents of olivine in experimental melts with various H₂O contents.

S.9. Figures:

Figure S1:

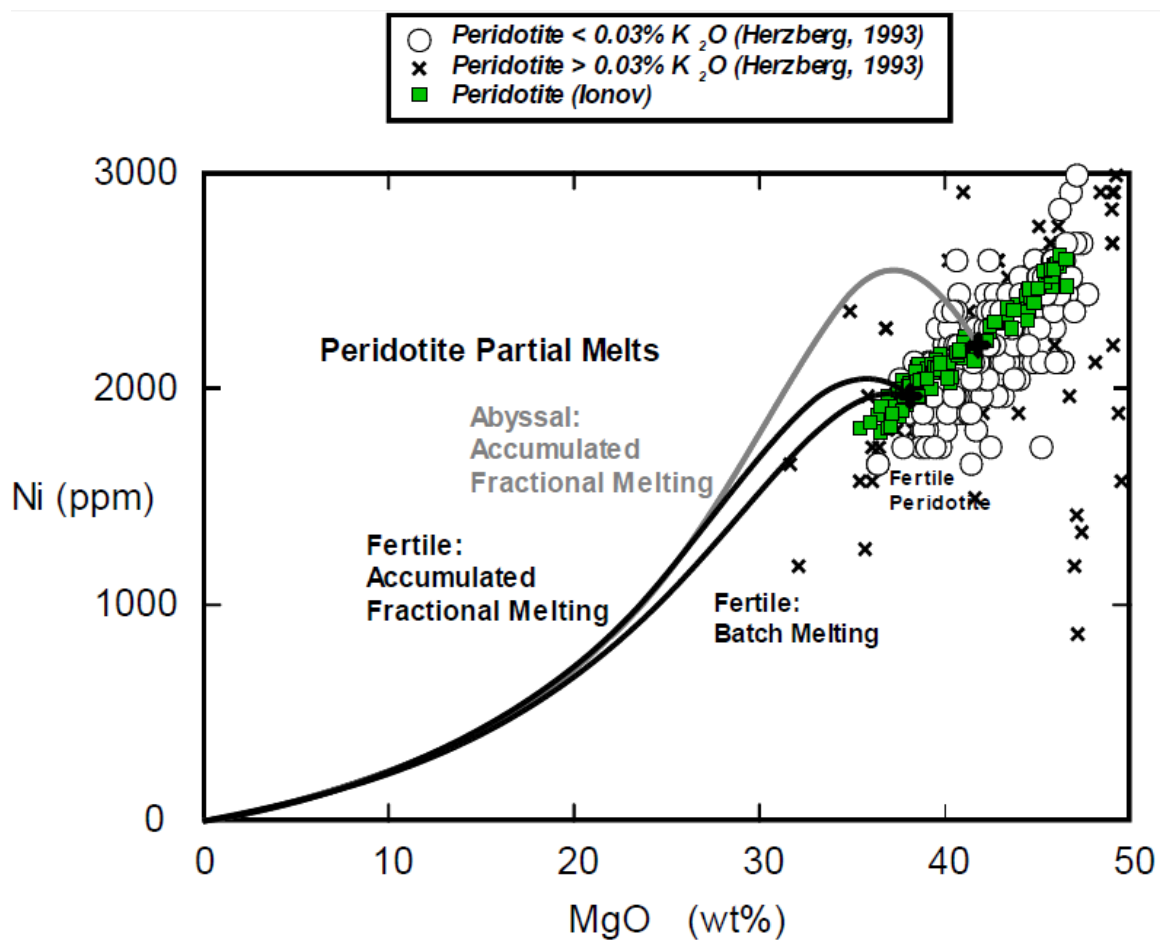


Figure S2:

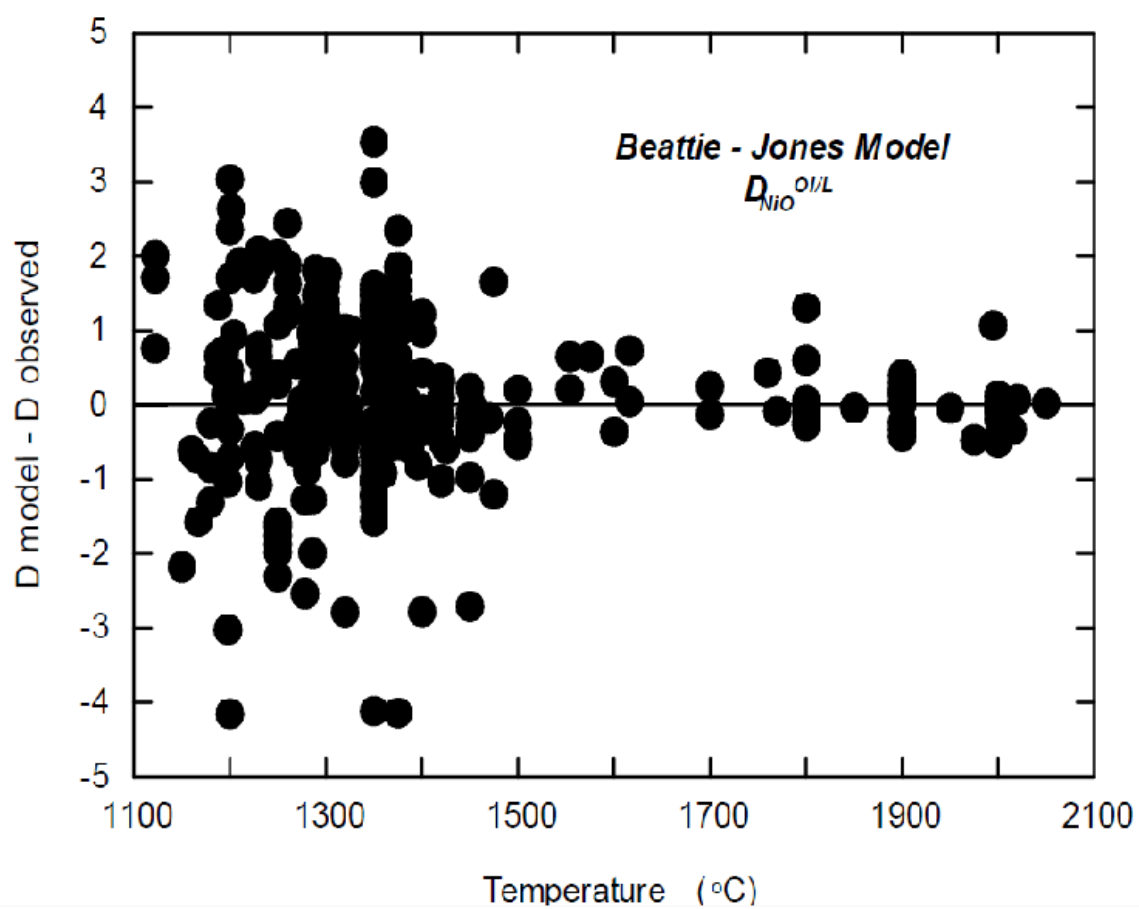


Figure S3:

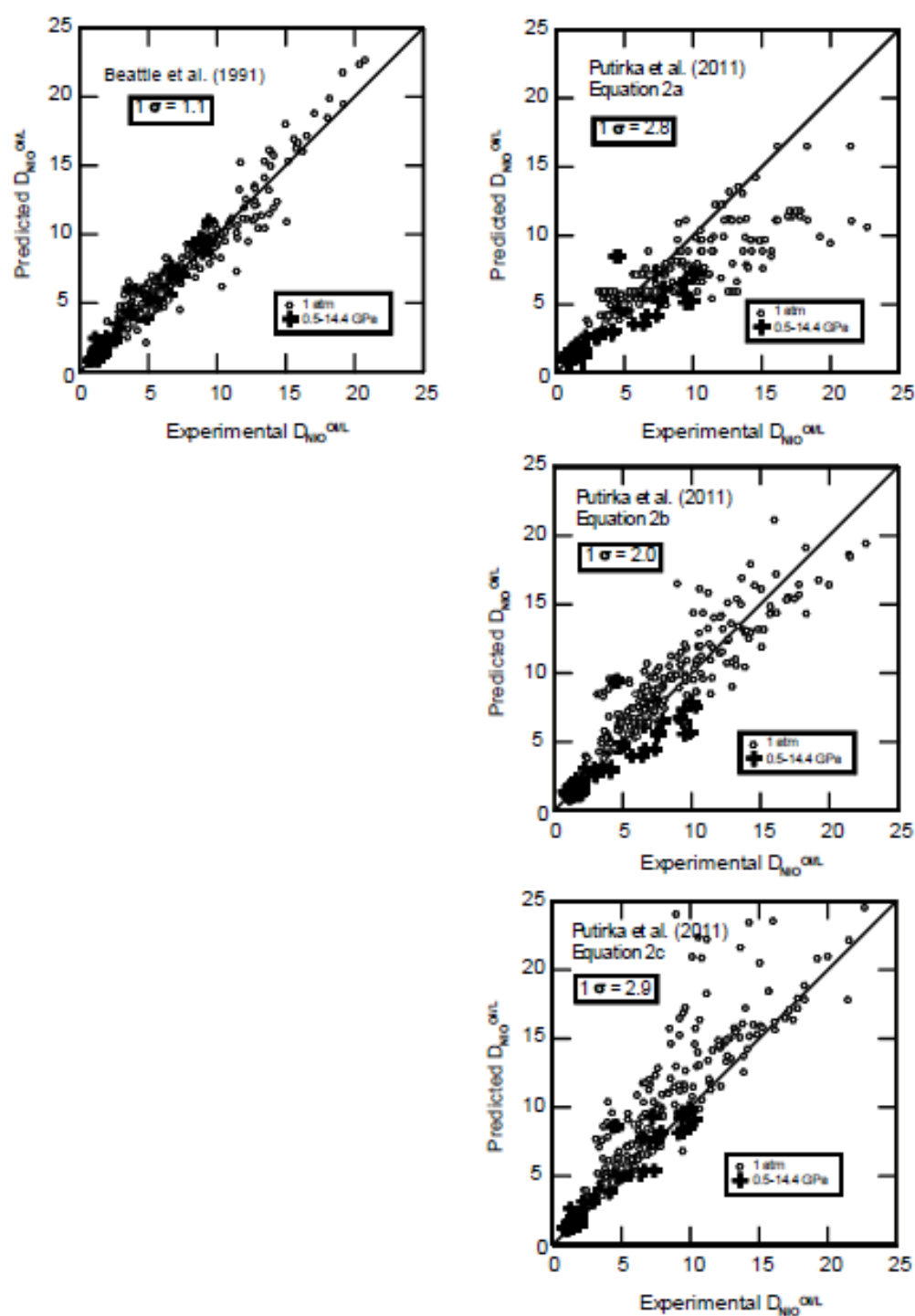


Figure S4:

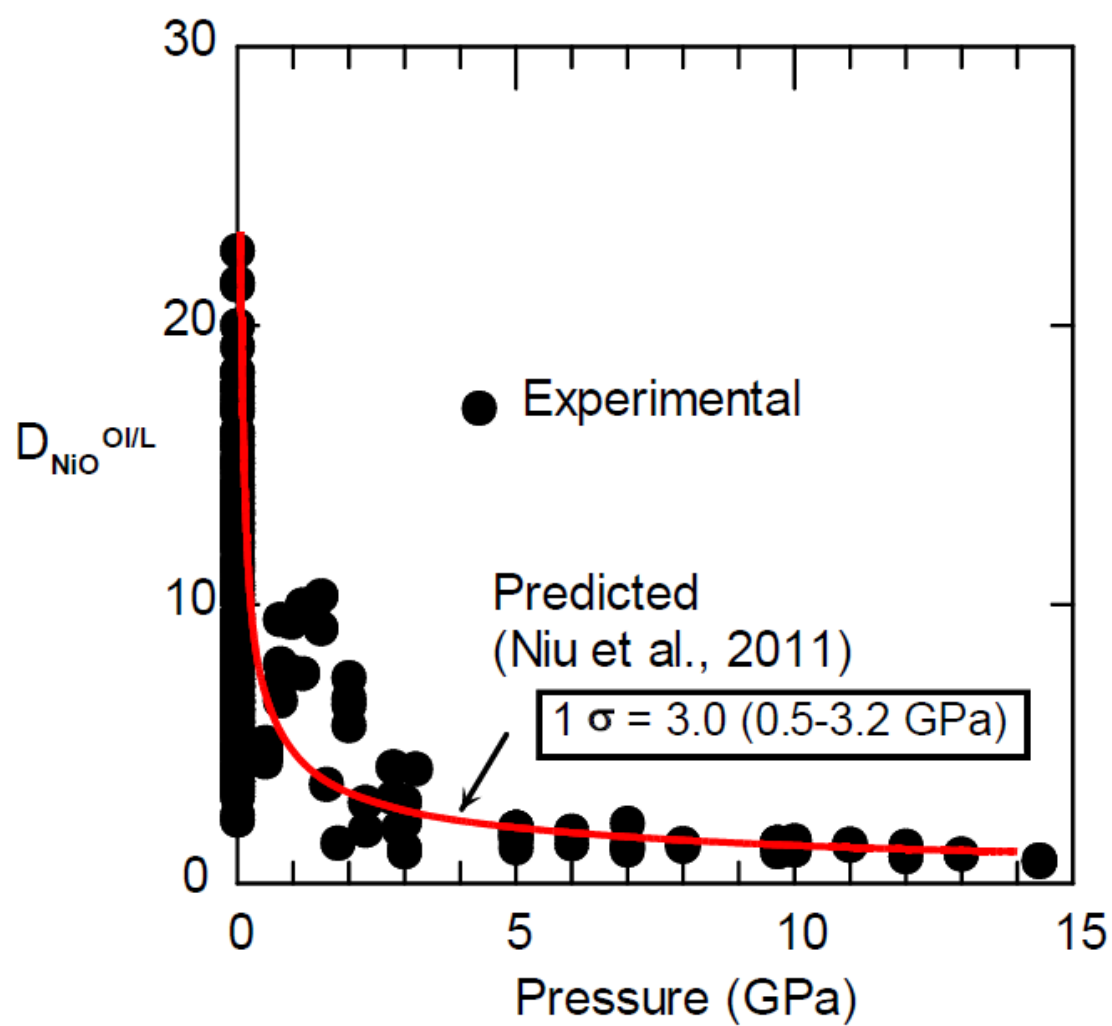


Figure S5:

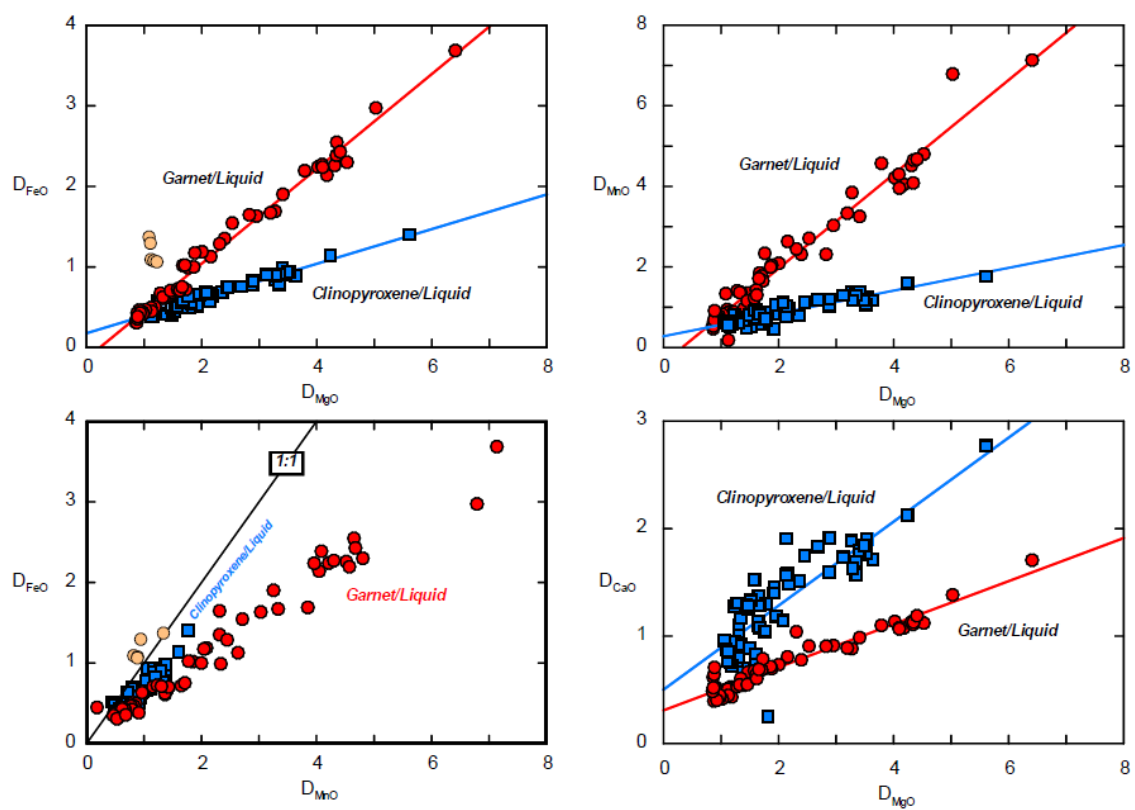


Figure S6:

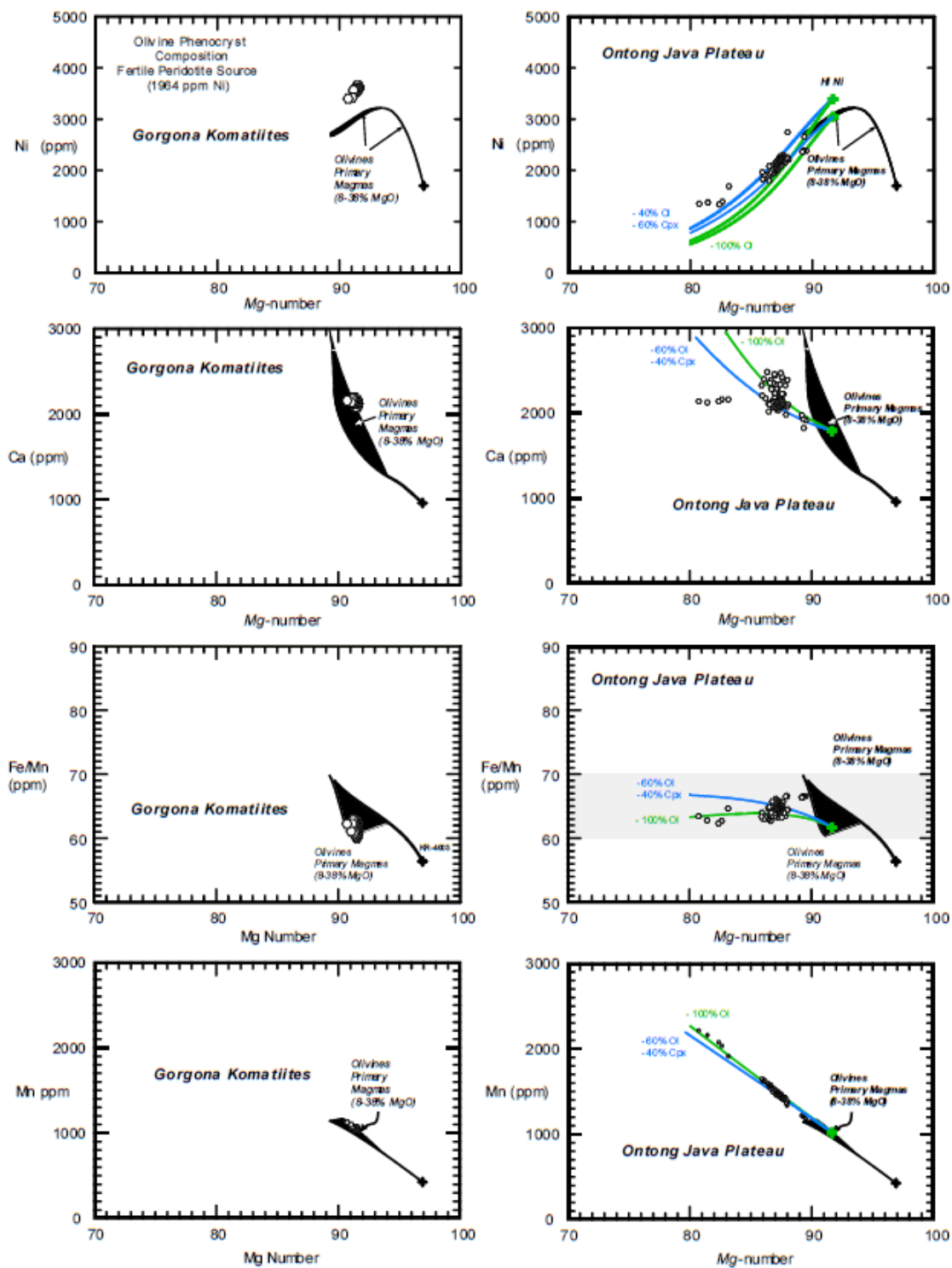


Figure S7:

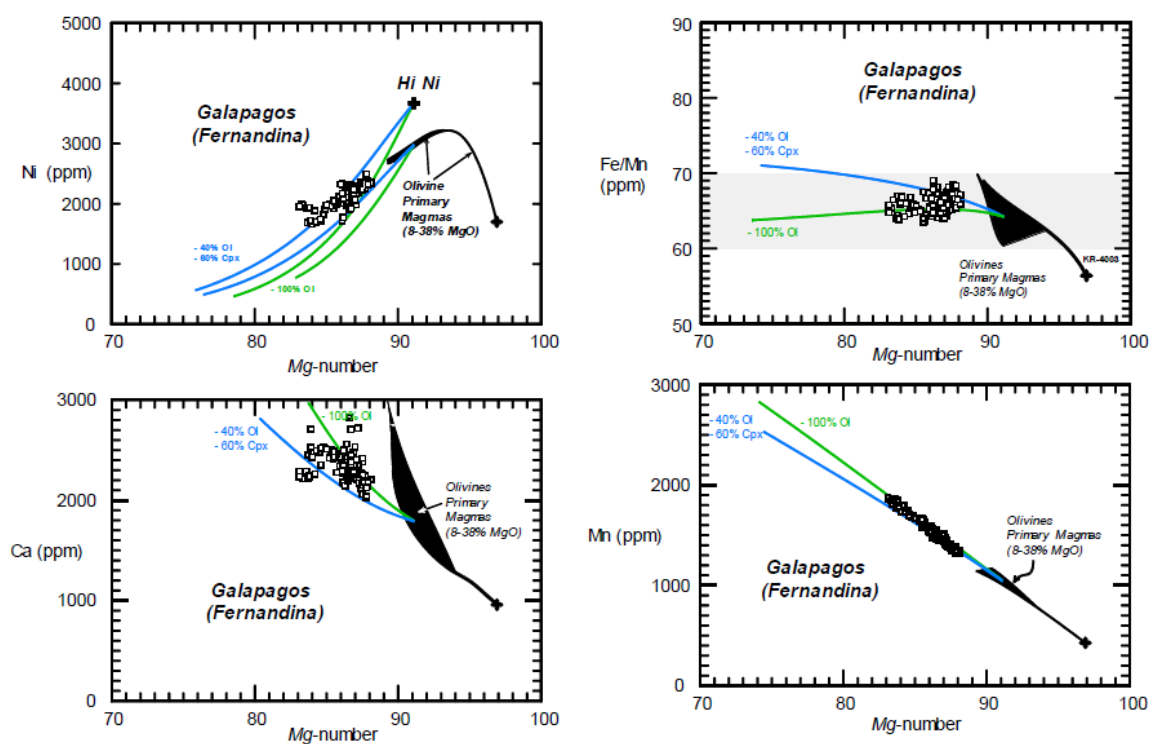


Figure S8:

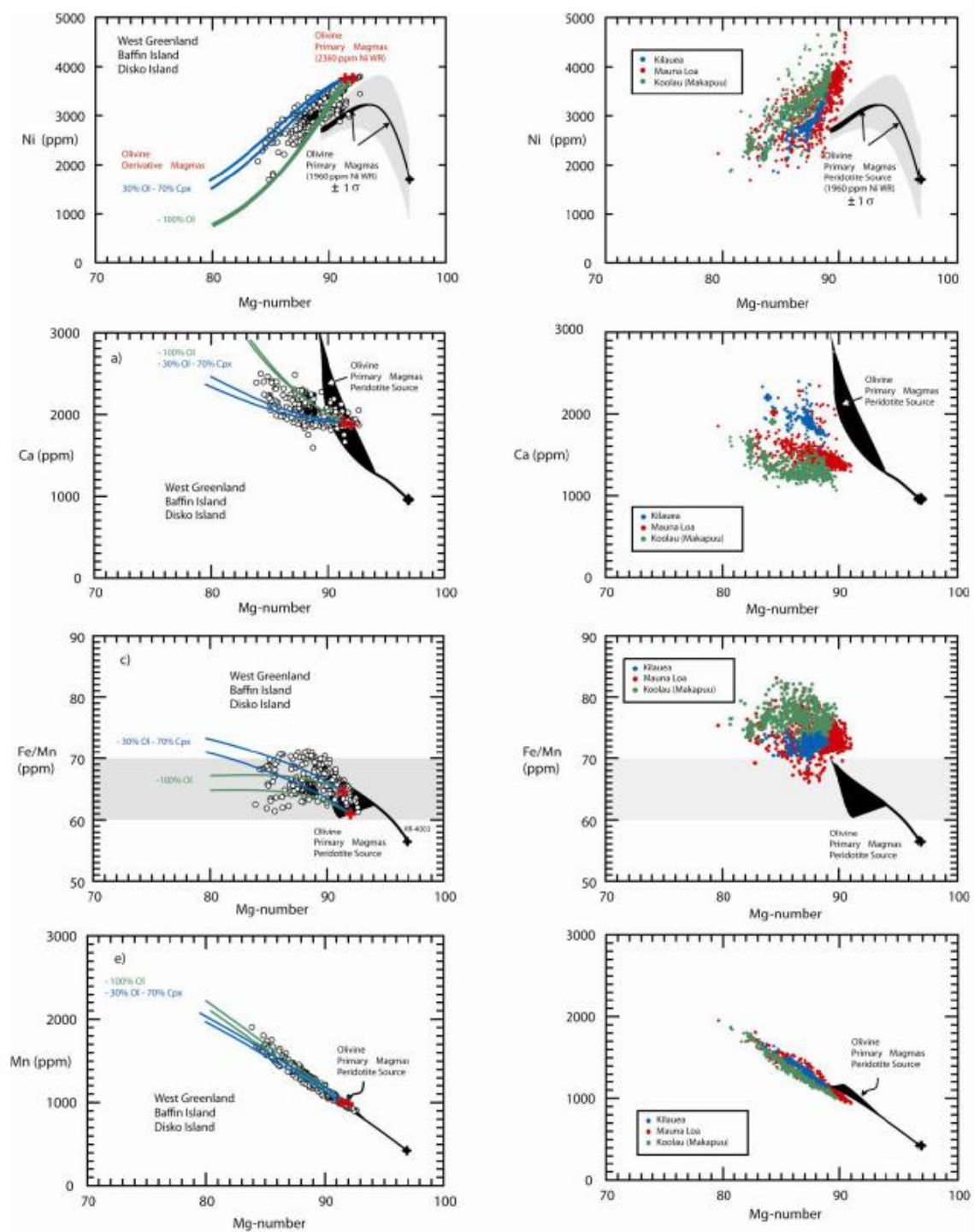


Figure S9:

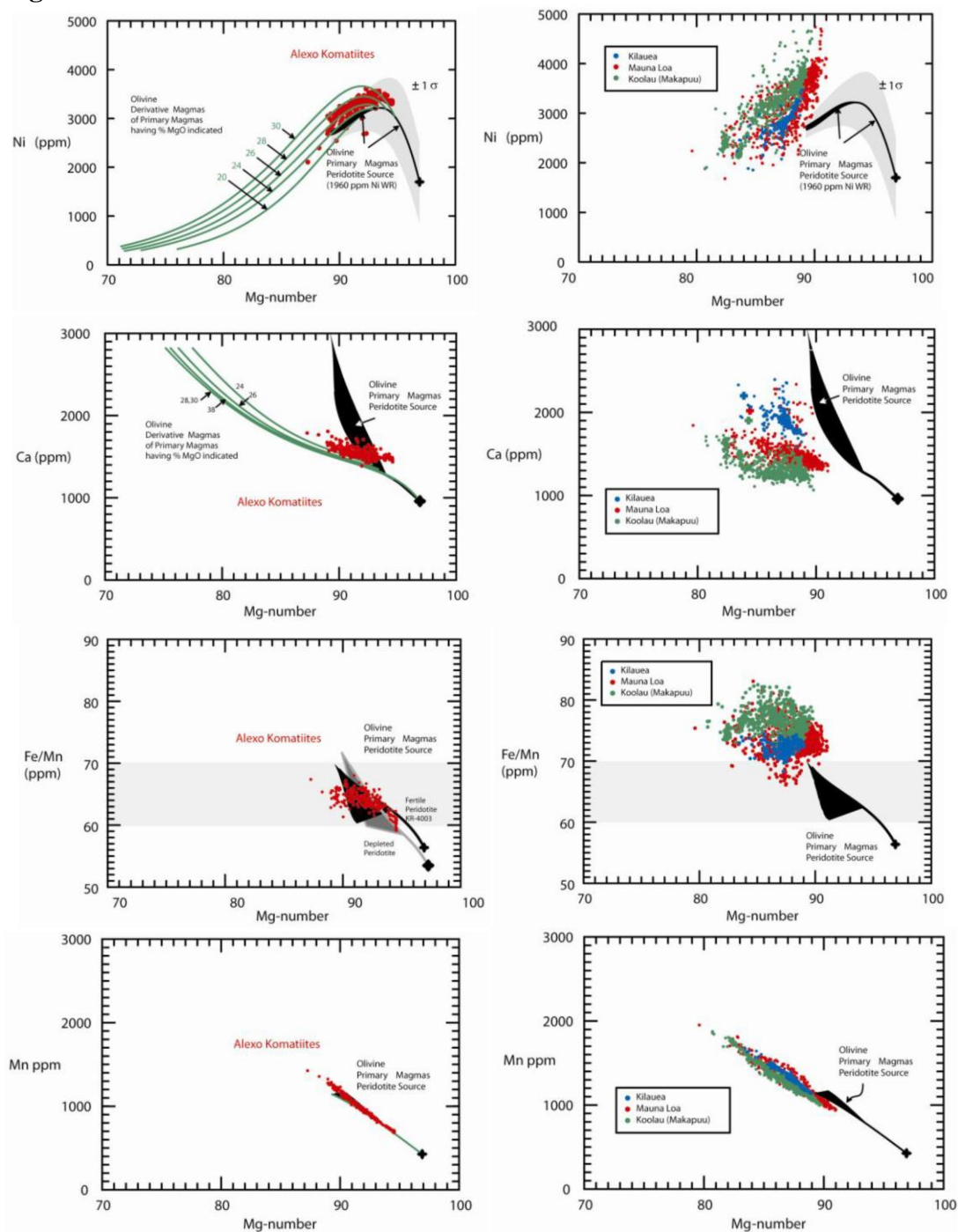


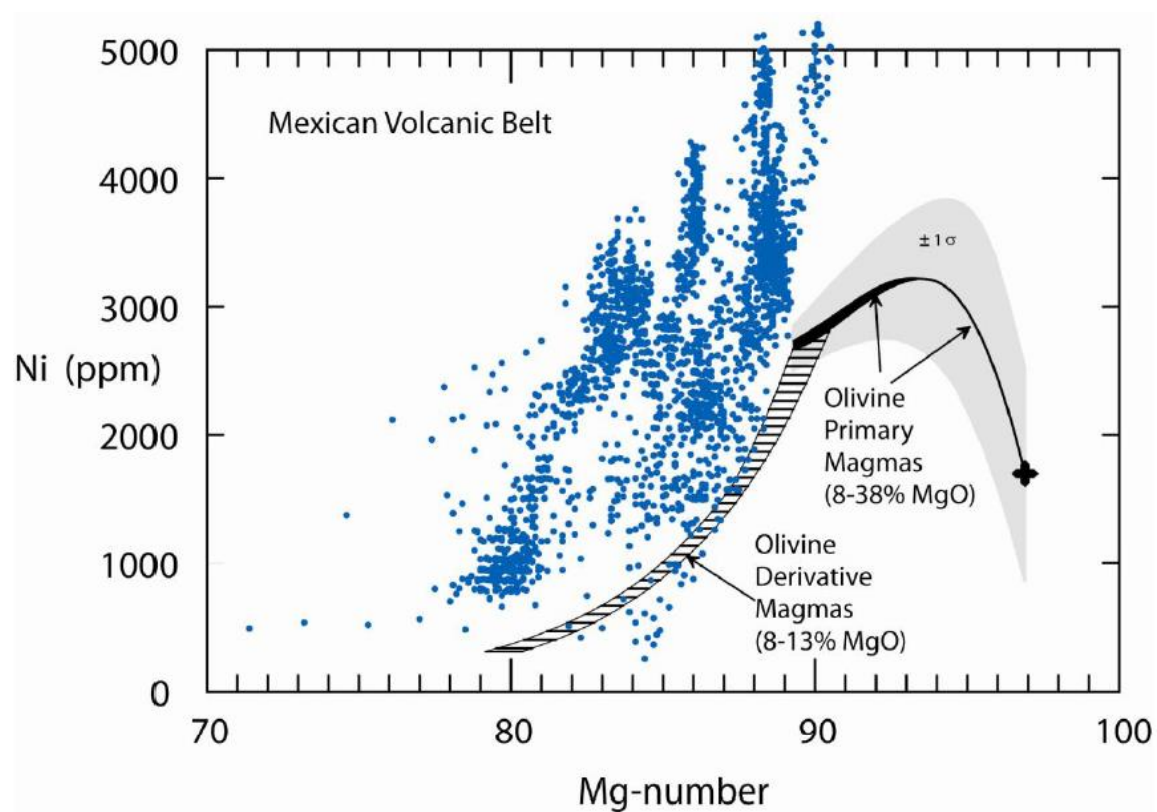
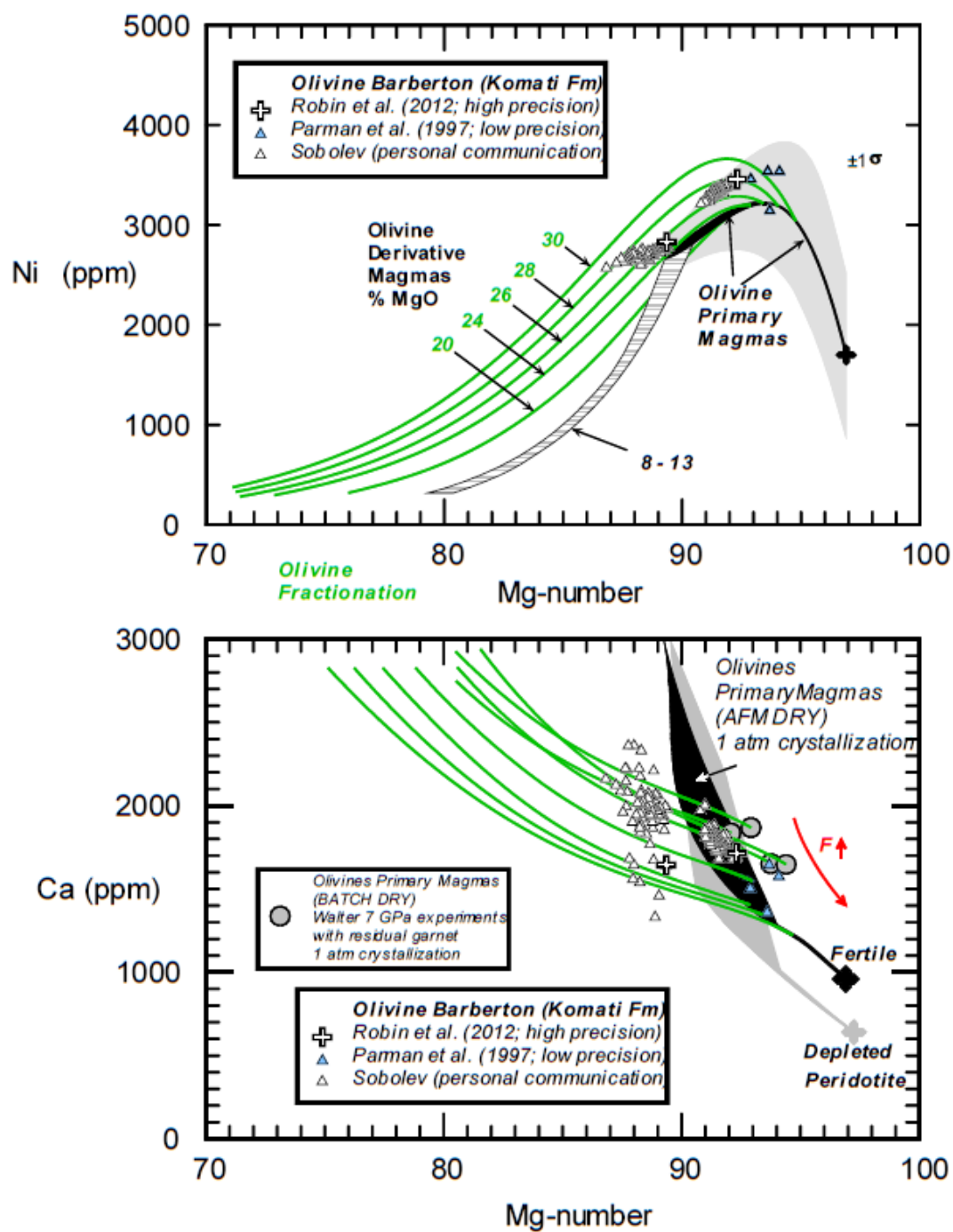
Figure S10:

Figure S11:



S.10. Tables:**Table S1: High Precision Olivine Analyses for Peridotites**

Off-Craton Spinel Peridotites

Sample Number	SiO ₂	NiO	MgO	Total	Mg-number	Ni (ppm)
Vitim, southern Siberia, (east of Lake Baikal):						
Spinel lherzolites in Miocene tuffs						
314-56ol7	40.28	0.373	49.03	100.4	89.3	2933
314-58ol7	40.39	0.371	49.42	100.3	89.9	2915
314-59ol8	40.52	0.368	49.77	100.3	90.4	2888
314-71ol7	40.37	0.374	50.11	100.0	91.0	2938
314-72ol7	40.48	0.375	49.83	100.3	90.4	2945
Spl lherzolites in young basaltic lavas						
86-1ol7	40.45	0.357	49.49	100.3	90.0	2807
302-10 ol7	40.49	0.371	49.16	100.4	89.6	2913
302-403 ol9	40.71	0.364	49.23	100.7	89.6	2861
559-43 ol8	40.79	0.373	49.49	100.5	90.1	2933
621-11 ol10	40.69	0.370	49.16	100.7	89.5	2905
621-24 ol9	40.68	0.364	49.37	100.4	90.0	2863
621-36 ol8	40.90	0.381	50.54	100.4	91.5	2990
623-10 ol7	40.75	0.372	49.47	100.5	90.0	2923
623-14 ol9	40.79	0.359	49.58	100.5	90.3	2823
625-1 ol av6	40.88	0.352	49.31	100.7	89.9	2764
Southern Baikal region, southern Siberia:						
8601-13 ol7	40.96	0.386	50.03	100.8	90.7	3033
8603-2ol7	40.64	0.362	49.00	100.7	89.3	2846
83-36ol7	40.72	0.366	49.34	100.7	89.7	2873
83-50ol7	40.86	0.362	49.55	100.8	90.0	2847
601-1 ol av8	40.98	0.386	50.24	100.6	91.1	3033
604-2 ol av8	40.94	0.374	49.75	100.4	90.7	2936

Mongolia:

Dariganga (SE Mongolia)

bn8ol7	41.12	0.389	50.90	100.6	91.8	3059
bn9ol8	40.98	0.377	50.31	100.6	91.1	2960
bn10ol8	40.99	0.375	49.87	100.7	90.6	2946
bn12ol6	40.97	0.363	50.36	100.6	91.1	2853
bn24ol7	40.67	0.370	49.41	100.5	89.9	2909
bn38ol6	40.56	0.369	49.87	100.4	90.4	2902
by24 ol6	40.92	0.382	50.04	100.5	90.8	2998
by26ol7	40.89	0.372	50.11	100.5	91.0	2921
by31ol7	40.51	0.379	49.80	100.1	90.6	2975
by35ol7	40.44	0.394	50.14	100.1	90.9	3095
by36ol7	40.68	0.378	49.76	100.5	90.3	2965
by40ol7	40.42	0.377	49.48	100.2	90.0	2960
db10ol8	40.81	0.375	50.27	100.6	91.0	2946
db11ol7	40.86	0.382	50.06	100.8	90.6	3002
db12ol7	40.89	0.392	50.22	100.7	90.8	3079
db15ol7	41.14	0.387	50.64	100.9	91.4	3040
db17ol7	40.97	0.369	50.28	100.7	91.0	2901
db18ol7	41.11	0.393	50.52	101.1	91.0	3088
db19ol7	41.01	0.375	50.27	101.0	90.7	2948
db22 ol6	40.80	0.364	49.94	100.7	90.5	2858
db23ol7	41.04	0.382	50.31	100.8	91.0	3001
db24ol7	40.99	0.372	50.16	100.9	90.7	2923
ats68 ol av7	40.26	0.365	49.44	99.9	90.1	2870
ats73 ol av6	40.42	0.384	49.53	99.8	90.5	3017
ats76 ol av6	40.47	0.378	49.35	99.9	90.2	2972
ats77 ol av4	40.53	0.365	49.06	99.9	90.0	2865
ats78 ol av4	40.14	0.367	49.28	99.2	90.4	2887
ats79 ol av3	40.64	0.373	49.69	100.0	90.7	2930

Dariganga (SE Mongolia)

Ats80 ol av3	40.56	0.375	49.21	100.3	89.7	2944
9429-7ol6	40.89	0.381	49.74	100.8	90.2	2990
9429-11 ol7	41.04	0.388	50.27	100.8	91.0	3047
9429-12ol7	40.98	0.384	50.03	100.6	90.8	3013
9429-13 ol5	40.81	0.377	49.99	100.5	90.6	2965
9429-36ol7	41.11	0.373	50.23	100.8	90.9	2929

Tariat, central Mongolia:

Shavaryn-Tsaram eruption center

Mo-79-4 ol7	41.20	0.370	49.78	100.9	90.5	2905
Mo-88 ol8	41.10	0.395	50.00	100.5	91.0	3102
Mo-89 ol9	41.03	0.372	49.98	100.6	90.8	2924
mo90ol6	40.70	0.377	49.93	100.1	90.9	2960
mo91ol5	40.40	0.367	49.60	99.8	90.5	2883
mo92ol5	40.40	0.378	50.13	99.6	91.3	2973
mo93ol5	40.30	0.377	50.02	99.4	91.3	2962
Mo-94a ol6	41.19	0.371	50.26	100.7	91.1	2915
mo94a ol6	40.53	0.357	49.64	99.9	90.6	2808
Mo-95 ol6	41.09	0.378	50.23	100.8	90.9	2969
Mo-96 ol11	41.03	0.366	49.95	100.7	90.7	2872
Mo-99 ol6	40.89	0.366	48.93	100.7	89.4	2875
Mo-101 ol7	41.09	0.366	48.77	100.9	89.3	2875
Mo-102 ol8	40.95	0.384	49.86	100.5	90.7	3015
Mo-103 ol8	40.91	0.374	49.51	100.5	90.3	2937
Mo-104 ol8	41.13	0.385	49.93	100.6	90.8	3027
MOG-1 ol7	40.85	0.379	49.56	100.5	90.3	2978
MOG-2 ol7	40.70	0.367	48.78	100.6	89.2	2880
MOG-3 ol7	40.92	0.369	49.48	100.4	90.3	2896
MOG-4 ol7	41.12	0.373	49.05	101.0	89.6	2928
MOG-5 ol7	40.95	0.365	48.79	100.6	89.5	2871

Shavaryn-Tsaram eruption center

MOZ-1 ol7	40.69	0.371	48.84	100.5	89.3	2911
4399-23 ol8	41.12	0.382	50.23	100.5	91.3	3003
4500-8 ol7	40.83	0.367	48.77	100.7	89.3	2886
4500-17 ol8	41.00	0.376	50.00	100.6	90.8	2956
4500-18 ol av9	41.33	0.392	50.94	100.8	91.9	3082
4500-21 ol7	40.87	0.371	48.98	100.6	89.6	2917
4594-4 ol8	41.14	0.395	50.63	100.3	91.9	3103
4594-6 ol7	40.84	0.370	49.13	100.7	89.6	2907

Other Tariat volcanoes, averages of 6-7 analyses (Ionov 2007)

Z-5	40.79	0.368	49.07	100.6	89.6	2891
Z-6	40.82	0.373	49.21	100.7	89.7	2930
Z-7	40.81	0.358	49.14	100.6	89.8	2812
Z-8	40.88	0.372	49.07	100.6	89.7	2922
Z-11	40.77	0.365	48.85	100.5	89.5	2867
Z-12	40.98	0.365	49.49	100.7	90.2	2867
Z-14	40.72	0.368	48.67	100.6	89.1	2891
Z-15	40.81	0.367	48.95	100.5	89.6	2883
Z-16	40.65	0.375	49.06	100.5	89.6	2946
Z-17	40.74	0.372	49.15	100.5	89.7	2922
Z-18	40.74	0.357	48.9	100.7	89.3	2804
Z-65	40.71	0.368	48.86	100.6	89.3	2891
Z-71	40.78	0.361	49.24	100.7	89.7	2836
Z-72	40.72	0.365	49.01	100.6	89.5	2867
Hr-4	41.16	0.372	49.29	100.9	89.9	2922
Hr-6	40.98	0.365	48.66	100.7	89.3	2867
Hr-12	41.07	0.363	48.6	100.9	89.1	2852
Hr-18	41.15	0.371	49.34	100.8	90.0	2914
Hr-20	40.9	0.360	48.8	100.7	89.4	2828
Hr-22	40.78	0.365	48.59	100.3	89.4	2867

Other Tariat volcanoes, averages of 6-7 analyses (Ionov 2007)

Hr-26	41.06	0.364	48.9	100.9	89.4	2859
St-0	40.77	0.367	48.89	100.7	89.3	2883
St-3	40.7	0.375	49.06	100.4	89.6	2946
St-23	40.71	0.369	48.9	100.6	89.4	2899
Ts-14	40.86	0.365	49.19	100.6	89.8	2867
Ts-21	40.84	0.366	48.85	100.8	89.2	2875

Russian Far East:

Tok, LH series, averages of 8 analyses each (Ionov et al. 2005)

Sa.N°	SiO ₂	NiO	MgO	Total	Mg#	Ni, ppm
9501-2	40.97	0.390	50.41	100.5	91.3	3067
9501-3	41.00	0.371	50.29	100.5	91.2	2917
9502-9	41.14	0.376	50.51	100.7	91.4	2956
9505-3	41.45	0.365	50.07	101.6	90.4	2870
9506-0	40.74	0.367	50.46	99.7	91.9	2879
9506-1	41.24	0.361	49.38	101.6	89.5	2836
9506-2	41.27	0.363	49.39	101.6	89.5	2849
9506-3	41.43	0.394	50.54	101.6	90.9	3097
9507-1	41.27	0.375	50.53	101.2	91.1	2947
9507-5	40.75	0.365	49.42	100.4	90.1	2866
9508-1	40.82	0.373	49.58	100.4	90.4	2928
9508-2	40.88	0.378	49.69	100.3	90.6	2967
9508-5	40.73	0.363	49.38	100.4	90.1	2853
9508-6	40.73	0.360	49.01	100.5	89.6	2825
9508-7	40.95	0.373	49.97	100.2	91.1	2933
9508-11	40.98	0.381	50.10	100.2	91.3	2994
9508-31	41.01	0.382	50.50	100.3	91.6	2997
9508-39	40.63	0.359	48.91	100.4	89.4	2820
9508-40	41.12	0.383	50.27	100.5	91.3	3008

9508-50	40.82	0.376	50.08	100.2	91.2	2952
Tok, LH series, averages of 8 analyses each (Ionov et al. 2005)						
9510-2	41.12	0.371	50.48	100.5	91.5	2911
9510-4	41.03	0.382	50.41	100.5	91.4	3001
9510-8	40.87	0.375	50.07	100.6	90.8	2948
9510-17	40.97	0.354	49.90	100.6	90.7	2781
9510-19	41.14	0.380	50.28	100.7	91.1	2988
River Ussuri:						
8802-1ol7	40.56	0.363	49.51	100.5	90.0	2850
8802-2ol7	40.64	0.354	49.31	100.7	89.7	2782
8803-1ol8	40.87	0.376	50.67	100.5	91.6	2955
8803-2ol9	40.79	0.375	50.34	100.4	91.2	2942
8803-3ol8	40.81	0.373	50.30	100.5	91.0	2929
8803-4ol9	40.78	0.377	50.21	100.5	90.9	2962
Zeya-Amur region (averages of 7 analyses each)						
f1	40.67	0.388	49.77	100.0	90.8	3048
f2	40.67	0.395	50.01	99.9	91.1	3103
f3	40.42	0.375	49.13	100.0	89.9	2946
f4	40.52	0.377	49.55	99.8	90.6	2962
f5	40.26	0.383	48.89	99.7	89.8	3009
f6	40.32	0.374	48.74	99.8	89.5	2938
f7	40.34	0.370	48.72	99.9	89.4	2907
f8	40.83	0.399	50.53	99.9	91.9	3134
f9	40.63	0.374	49.57	100.1	90.5	2938
fev-1 ol5	40.67	0.366	49.32	100.4	89.9	2938
en-1 ol4	40.80	0.369	49.44	100.6	90.0	2938
en-2 ol5	40.66	0.375	49.30	100.4	90.0	2938
sv-1 ol6	40.76	0.376	49.38	100.5	90.0	2938

Sources of published data: Ionov (2007; 2010); Ionov et al., (2005)

Off-Craton Garnet and Garnet-Spinel Peridotites

Sample Number	SiO ₂	NiO	MgO	Total	Mg-number	Ni (ppm)
Vitim, southern Siberia (east of lake Baikal)						
313-1ol6	40.88	0.371	49.67	100.8	90.1	2912
313-2ol10	40.74	0.376	49.61	100.3	90.4	2954
313-3 ol9	40.92	0.368	49.56	100.8	90.1	2892
313-5ol6	40.79	0.361	49.64	100.7	90.2	2836
313-6ol7	40.82	0.363	49.46	100.5	90.2	2848
313-7ol6	40.92	0.366	49.49	100.8	90.0	2876
313-8 ol11	40.81	0.369	49.50	100.5	90.3	2898
313-37ol7	40.68	0.374	49.56	100.6	90.1	2938
313-54ol7	40.83	0.368	49.40	100.6	90.0	2892
313-102ol9	40.67	0.362	49.29	100.5	89.9	2844
313-104ol8	40.59	0.361	49.28	100.4	89.9	2838
313-106ol7	40.38	0.363	49.50	100.1	90.1	2855
313-110ol6	40.81	0.364	49.92	100.7	90.4	2859
313-112ol7	40.82	0.374	49.53	100.6	90.1	2941
313-240ol7	40.37	0.352	49.43	100.0	90.2	2765
313-241ol7	40.69	0.356	49.43	100.4	90.1	2795
31474ol6	40.90	0.370	50.15	100.7	90.9	2909
314-230 av.3	40.98	0.375	49.45	100.7	90.2	2946
314-580 av.3	40.84	0.371	49.34	100.4	90.2	2914
621-10 ol9	40.89	0.362	49.35	100.7	89.9	2840
621-19 ol10	40.63	0.363	48.67	100.7	89.1	2855
Dariganga (SE Mongolia)						
8508-6ol7	40.92	0.364	49.67	100.7	90.3	2859
by18ol7	40.95	0.374	50.19	100.8	90.8	2940
by27ol7	40.52	0.366	49.14	100.3	89.7	2876
8504-24ol7	40.57	0.365	49.58	100.5	90.0	2866

Dariganga (SE Mongolia)

db8ol7	40.82	0.367	49.78	100.8	90.3	2882
db13ol7	40.90	0.369	50.11	100.8	90.7	2896
db20ol7	40.60	0.369	49.73	100.6	90.2	2898
db21ol7	40.88	0.375	49.95	100.9	90.4	2944

Shavaryn-Tsaram, Tariat (central Mongolia)

4334-11 ol9	40.82	0.358	48.81	100.6	89.4	2815
53389 ol8	40.84	0.361	48.93	100.5	89.6	2836
200-81 ol av8	40.87	0.379	49.36	100.7	90.0	2974

Spinel peridotite xenoliths from subduction zones

Sample Number	SiO ₂	NiO	MgO	Total	Mg-number	Ni (ppm)
Subduction zone peridotites: Avacha volcano, Kamchatka, Russia (Ionov et al. 2010)						
Av-1	40.70	0.38	50.08	100.10	91.0	2975
Av-2	40.72	0.39	50.19	100.26	91.1	3080
Av-3	40.58	0.38	50.05	100.07	90.9	3012
Av-4	40.77	0.40	49.89	100.31	90.7	3107
Av-5	40.65	0.40	50.20	100.35	90.9	3122
Av-6	40.53	0.39	50.16	100.07	91.0	3024
Av-7	40.67	0.38	50.16	100.21	91.0	2991
Av-8	40.80	0.39	50.27	100.12	91.3	3024
Av-9	40.77	0.38	50.20	100.27	91.1	2963
Av-10	40.74	0.39	50.09	100.10	91.1	3043
Av-11	40.74	0.38	50.18	100.11	91.2	3013
Av-12	40.67	0.38	50.20	100.16	91.1	3006
Av-13	40.77	0.39	50.21	100.21	91.2	3027
Av-14	40.67	0.38	50.25	100.21	91.1	2985
Av-15	40.67	0.38	50.10	100.11	91.0	2949
Av-16	40.87	0.40	50.62	100.16	91.8	3124
Av-17	40.76	0.39	50.37	100.10	91.4	3038

Table S2: Olivine Analyses from Fernandina Sample D38A

	SiO ₂ %	MgO %	FeO %	CaO %	MnO %	NiO %	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
D38A Phen 1	40.44	46.58	11.53	0.302	0.175	0.303	87.8	2380	1352	2156	89640
D38A Phen 1	40.52	46.80	11.57	0.298	0.174	0.308	87.8	2420	1349	2132	89936
D38A Phen 1	40.43	46.86	11.56	0.298	0.170	0.311	87.8	2446	1318	2127	89890
D38A Phen 1	40.19	45.61	12.65	0.324	0.190	0.291	86.5	2284	1468	2312	98383
D38A Phen 2	40.64	47.17	11.65	0.299	0.179	0.311	87.8	2442	1386	2138	90623
D38A Phen 3	39.73	44.99	13.03	0.336	0.202	0.258	86.0	2029	1561	2398	101287
D38A Phen 4	40.07	45.71	13.36	0.328	0.205	0.270	85.9	2121	1586	2344	103890
D38A Phen 5	40.35	46.77	11.87	0.287	0.177	0.288	87.5	2266	1369	2053	92339
D38A Phen 6	40.26	46.62	11.85	0.332	0.180	0.287	87.5	2255	1394	2371	92161
D38A Phen 6	40.35	46.62	11.92	0.337	0.179	0.291	87.5	2290	1384	2411	92707
D38A Phen 6	40.47	46.59	12.15	0.380	0.184	0.286	87.2	2243	1426	2719	94483
D38A Phen 7	40.55	46.93	11.51	0.298	0.172	0.303	87.9	2378	1330	2133	89481
D38A Phen 8	40.22	45.72	13.16	0.334	0.201	0.274	86.1	2149	1557	2386	102305
D38A Phen 8	40.13	45.55	13.12	0.334	0.199	0.268	86.1	2107	1541	2388	102052
D38A Phen 8	40.12	44.96	13.93	0.338	0.215	0.253	85.2	1986	1662	2418	108310
D38A Phen 9	40.39	46.33	12.15	0.329	0.186	0.276	87.2	2171	1440	2349	94502
D38A Phen 9	40.37	45.76	12.86	0.328	0.190	0.265	86.4	2083	1474	2342	99968
D38A Phen 9	40.36	45.60	13.75	0.339	0.204	0.246	85.5	1931	1584	2421	106903
D38A Phen 10	40.36	46.28	12.10	0.327	0.187	0.276	87.2	2169	1450	2337	94085
D38A Phen 12	40.04	44.06	15.28	0.343	0.229	0.215	83.7	1691	1775	2454	118854
D38A Phen 13	40.61	46.29	12.39	0.347	0.187	0.275	86.9	2162	1447	2483	96338
D38A Phen 14	40.29	46.45	11.93	0.294	0.177	0.298	87.4	2345	1374	2104	92763
D38A Phen 15	40.54	46.43	12.14	0.319	0.182	0.283	87.2	2226	1409	2279	94415
D38A Phen 16	40.38	45.74	12.74	0.331	0.188	0.269	86.5	2114	1453	2367	99059
D38A Phen 18	40.53	46.85	11.92	0.305	0.179	0.288	87.5	2262	1387	2179	92664
D38A Phen 19	40.34	46.33	12.29	0.333	0.189	0.274	87.0	2151	1466	2378	95598
D38A Phen 19	40.41	46.40	12.26	0.321	0.184	0.277	87.1	2177	1427	2296	95337
D38A Phen 19	40.53	45.71	13.09	0.318	0.190	0.256	86.2	2011	1476	2273	101797

	SiO ₂ %	MgO %	FeO %	CaO %	MnO %	NiO %	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
D38A Phen 21	40.65	46.69	12.01	0.318	0.181	0.289	87.4	2272	1400	2270	93419
D38A Phen 21	40.75	46.96	11.77	0.314	0.178	0.288	87.7	2259	1380	2246	91499
D38A Phen 21	40.56	45.84	12.93	0.319	0.198	0.279	86.3	2189	1534	2283	100537
D38A Phen 22	40.53	45.71	12.79	0.326	0.198	0.250	86.4	1964	1530	2327	99422
D38A Phen 22	40.74	46.15	12.86	0.333	0.200	0.253	86.5	1986	1552	2381	100034
D38A Phen 22	40.74	46.36	12.27	0.337	0.192	0.252	87.1	1981	1484	2407	95403
D38A Phen 23	40.62	44.14	15.64	0.314	0.236	0.255	83.4	2004	1829	2248	121603
D38A Phen 23	40.57	43.85	15.69	0.313	0.241	0.255	83.3	2005	1867	2236	122043
D38A Phen 23	40.75	43.90	15.91	0.317	0.243	0.250	83.1	1964	1882	2267	123717
D38A Phen 23	40.50	43.55	15.77	0.322	0.244	0.251	83.1	1970	1891	2305	122606
D38A Phen 23	41.04	44.76	15.29	0.360	0.233	0.223	83.9	1752	1804	2574	118884
D38A Phen 24	41.42	46.17	13.33	0.323	0.206	0.222	86.1	1748	1593	2309	103630
D38A Phen 24	41.23	46.03	13.27	0.331	0.202	0.229	86.1	1796	1568	2365	103218
D38A Phen 24	41.29	46.08	13.25	0.335	0.205	0.229	86.1	1796	1590	2393	103028
D38A Phen 24	41.21	46.04	13.17	0.340	0.200	0.228	86.2	1790	1549	2428	102385
D38A Phen 24	40.90	44.43	15.09	0.344	0.227	0.214	84.0	1681	1755	2457	117303
D38A Phen 25	41.32	46.44	12.05	0.315	0.182	0.291	87.3	2288	1411	2249	93733
D38A Phen 26	41.26	46.32	12.36	0.328	0.191	0.283	87.0	2225	1477	2342	96097
D38A Phen 27	40.93	45.65	13.06	0.333	0.199	0.269	86.2	2109	1541	2377	101548
D38A Phen 28	41.27	46.02	13.17	0.335	0.201	0.271	86.2	2133	1553	2395	102404
D38A Phen 28	41.19	45.86	13.07	0.334	0.202	0.271	86.2	2128	1561	2389	101600
D38A Phen 28	40.88	45.69	12.78	0.325	0.196	0.269	86.4	2117	1518	2326	99375
D38A Phen 28	40.92	45.88	12.50	0.323	0.188	0.270	86.7	2125	1453	2310	97227
D38A Phen 29	40.84	44.54	14.40	0.302	0.221	0.253	84.6	1986	1709	2159	111961
D38A Phen 30	41.07	45.66	13.26	0.346	0.199	0.268	86.0	2102	1544	2472	103107
D38A Phen 31	41.13	46.20	12.42	0.322	0.192	0.285	86.9	2240	1490	2305	96555
D38A Phen 32	41.18	46.86	12.09	0.308	0.180	0.290	87.4	2282	1398	2202	94044
D38A Phen 33	40.97	46.55	12.12	0.306	0.182	0.293	87.3	2303	1406	2190	94266
D38A Phen 34	40.97	46.57	12.06	0.308	0.181	0.290	87.3	2275	1405	2199	93752
D38A Phen 35	40.32	44.45	14.43	0.329	0.220	0.218	84.6	1716	1707	2349	112194

	SiO ₂ %	MgO %	FeO %	CaO %	MnO %	NiO %	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
D38A Phen 36	40.38	44.50	14.57	0.348	0.226	0.218	84.5	1710	1752	2485	113262
D38A Phen 37	40.76	45.44	13.56	0.320	0.204	0.256	85.7	2008	1581	2289	105475
D38A Phen 38	40.82	46.44	12.23	0.310	0.186	0.294	87.1	2308	1438	2213	95070
D38A Phen 38	41.03	46.68	12.28	0.311	0.187	0.291	87.1	2289	1445	2221	95461
D38A Phen 38	40.86	46.66	12.24	0.317	0.187	0.290	87.2	2282	1446	2267	95169
D38A Phen 38	40.55	46.24	11.75	0.313	0.181	0.283	87.5	2226	1403	2236	91336
D38A Phen 38	40.61	44.89	14.34	0.355	0.219	0.233	84.8	1827	1694	2540	111500
D38A Phen 39	40.59	46.27	12.27	0.315	0.182	0.276	87.1	2168	1413	2254	95395
D38A Phen 39	40.62	46.69	12.25	0.309	0.182	0.284	87.2	2232	1408	2210	95241
D38A Phen 39	40.50	46.74	12.07	0.304	0.178	0.286	87.3	2243	1379	2172	93888
D38A Phen 39	40.45	46.21	12.63	0.318	0.190	0.272	86.7	2136	1470	2272	98218
D38A Phen 40	40.70	46.99	11.97	0.302	0.179	0.285	87.5	2239	1387	2161	93088
D38A Phen 41	39.93	45.36	13.07	0.314	0.197	0.292	86.1	2295	1529	2246	101636
D38A Phen 41	40.16	45.74	13.16	0.304	0.198	0.295	86.1	2314	1534	2173	102308
D38A Phen 41	40.25	45.87	13.14	0.304	0.194	0.296	86.2	2325	1506	2173	102190
D38A Phen 41	39.78	44.03	15.07	0.378	0.229	0.219	83.9	1716	1774	2699	117165
D38A Phen 42	40.22	46.19	12.29	0.321	0.184	0.283	87.0	2221	1424	2296	95534
D38A Phen 43	40.23	45.82	13.18	0.325	0.205	0.297	86.1	2330	1586	2323	102505
D38A Phen 44	40.23	45.53	13.23	0.335	0.205	0.295	86.0	2320	1592	2393	102900
D38A Phen 45	40.06	45.54	13.11	0.332	0.202	0.269	86.1	2112	1566	2376	101953
D38A Phen 46	40.03	45.52	13.07	0.330	0.199	0.269	86.1	2113	1540	2362	101671
D38A Phen 47	40.33	46.46	12.41	0.318	0.187	0.287	87.0	2253	1446	2276	96530
D38A Phen 48	40.07	45.91	12.67	0.325	0.190	0.279	86.6	2189	1474	2324	98549
D38A Phen 49	40.25	46.55	11.67	0.304	0.176	0.297	87.7	2335	1362	2174	90768
D38A Phen 50	40.28	46.76	11.84	0.304	0.174	0.300	87.6	2353	1344	2174	92070
D38A Phen 51	40.42	47.02	11.66	0.296	0.177	0.317	87.8	2489	1375	2118	90646
D38A Phen 52	40.46	45.93	13.39	0.329	0.200	0.265	85.9	2085	1546	2349	104148
D38A Phen 53	40.54	46.07	12.87	0.327	0.192	0.276	86.4	2169	1487	2336	100112
D38A Phen 53	40.45	45.81	13.12	0.330	0.203	0.268	86.2	2104	1573	2360	102024
D38A Phen 53	40.61	46.09	12.95	0.340	0.195	0.269	86.4	2115	1509	2433	100674

	SiO ₂ %	MgO %	FeO %	CaO %	MnO %	NiO %	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
D38A Phen 54	40.75	45.90	13.14	0.325	0.200	0.270	86.2	2118	1552	2320	102188
D38A Phen 54	40.51	45.69	13.03	0.321	0.198	0.270	86.2	2120	1531	2293	101294
D38A Phen 54	40.61	45.91	13.20	0.332	0.200	0.272	86.1	2139	1552	2376	102650
D38A Phen 54	40.37	45.14	13.24	0.339	0.204	0.268	85.9	2106	1578	2421	102928
D38A Phen 55	41.02	46.01	13.27	0.327	0.201	0.273	86.1	2142	1557	2334	103180
D38A Phen 56	40.86	46.13	13.25	0.334	0.207	0.273	86.1	2143	1603	2385	103022
D38A Phen 57	40.60	45.74	12.90	0.300	0.192	0.275	86.3	2164	1490	2143	100331
D38A Phen 58	40.61	45.04	13.79	0.350	0.213	0.251	85.3	1970	1649	2503	107215
D38A Phen 58	40.73	45.31	13.62	0.345	0.215	0.262	85.6	2057	1665	2467	105908
D38A Phen 58	41.05	45.69	13.64	0.348	0.212	0.264	85.7	2070	1646	2490	106032
D38A Phen 58	40.93	44.98	14.22	0.356	0.220	0.245	84.9	1923	1707	2543	110606
D38A Phen 59	40.83	45.43	13.64	0.343	0.214	0.260	85.6	2043	1660	2451	106064
D38A Phen 59	40.84	45.46	13.76	0.342	0.218	0.263	85.5	2066	1686	2447	106990
D38A Phen 59	40.73	45.27	13.70	0.349	0.215	0.262	85.5	2057	1665	2498	106565
D38A Phen 59	40.69	44.32	14.77	0.350	0.225	0.217	84.3	1707	1740	2505	114820
D38A Phen 60	42.01	47.61	11.16	0.287	0.167	0.307	88.4	2409	1291	2048	86769
D38A Phen 61	41.53	46.33	12.92	0.318	0.201	0.270	86.5	2121	1554	2276	100484
D38A Phen 61	41.09	45.96	12.92	0.319	0.194	0.272	86.4	2133	1499	2280	100486
D38A Phen 61	40.75	46.15	12.85	0.318	0.198	0.271	86.5	2128	1536	2272	99925
D38A Phen 61	40.66	46.25	12.97	0.315	0.198	0.274	86.4	2151	1535	2251	100884
D38A Phen 61	40.68	46.25	12.88	0.318	0.202	0.271	86.5	2128	1561	2270	100165
D38A Phen 62	40.80	46.32	12.74	0.399	0.195	0.244	86.6	1915	1512	2848	99104
D38A Phen 62	40.56	46.13	12.60	0.379	0.193	0.244	86.7	1921	1492	2709	98012
D38A Phen 62	40.64	46.10	12.93	0.360	0.194	0.261	86.4	2048	1506	2572	100533
D38A Phen 63	40.81	46.15	12.87	0.309	0.199	0.284	86.5	2232	1540	2210	100092
D38A Phen 63	41.01	46.32	12.92	0.313	0.193	0.287	86.5	2258	1497	2236	100500
D38A Phen 63	40.85	46.09	12.68	0.314	0.195	0.283	86.6	2220	1509	2242	98626
D38A Phen 63	41.04	46.42	12.48	0.313	0.193	0.280	86.9	2203	1496	2240	97060
D38A Phen 63	40.90	46.12	12.60	0.316	0.194	0.288	86.7	2260	1504	2256	97976
D38A Phen 64	40.19	45.91	12.87	0.328	0.197	0.267	86.4	2101	1529	2342	100095

	SiO ₂ %	MgO %	FeO %	CaO %	MnO %	NiO %	OL Mg#	Ni ppm	Mn ppm	Ca ppm	Fe ppm
D38A Phen 64	40.01	46.06	12.87	0.325	0.194	0.273	86.4	2143	1504	2321	100106
D38A Phen 64	40.22	46.03	12.92	0.333	0.199	0.278	86.4	2181	1545	2379	100435
D38A Phen 64	40.24	45.75	13.06	0.349	0.203	0.273	86.2	2141	1569	2493	101571
D38A Phen 65	40.61	46.67	11.56	0.283	0.177	0.300	87.8	2357	1373	2020	89856
D38A Phen 66	40.58	46.81	11.64	0.284	0.171	0.299	87.8	2346	1324	2033	90520
D38A Phen 67	40.21	45.65	12.81	0.319	0.196	0.267	86.4	2095	1516	2278	99592
D38A Phen 67	40.44	45.80	13.10	0.329	0.194	0.273	86.2	2147	1500	2349	101847
D38A Phen 67	40.38	45.69	13.00	0.319	0.199	0.264	86.2	2075	1539	2281	101114
D38A Phen 67	40.76	46.62	12.55	0.331	0.192	0.278	86.9	2180	1490	2365	97626
D38A Phen 68	40.21	44.70	14.53	0.353	0.218	0.222	84.6	1746	1692	2523	113021
D38A Phen 69	40.41	46.07	12.61	0.326	0.195	0.294	86.7	2311	1512	2332	98041
D38A Phen 69	40.13	45.95	12.58	0.328	0.194	0.290	86.7	2278	1499	2343	97813
D38A Phen 69	40.27	46.28	12.68	0.333	0.193	0.293	86.7	2300	1492	2382	98592
D38A Phen 69	39.98	45.90	12.53	0.340	0.195	0.287	86.7	2254	1508	2432	97426
D38A Phen 69	39.67	44.24	13.87	0.346	0.212	0.248	85.0	1946	1641	2472	107833
D38A Phen 70	39.67	43.71	15.21	0.310	0.237	0.242	83.7	1904	1837	2219	118250
D38A Phen 71	39.66	43.52	15.20	0.317	0.239	0.244	83.6	1918	1849	2269	118224
D38A Phen 71	39.75	43.73	15.05	0.310	0.236	0.243	83.8	1907	1828	2214	117055
D38A Phen 71	39.92	43.92	15.21	0.311	0.239	0.245	83.7	1926	1848	2220	118259
D38A Phen 71	39.89	43.84	15.09	0.312	0.237	0.245	83.8	1928	1836	2233	117318
D38A Phen 71	39.81	43.96	14.74	0.314	0.230	0.238	84.2	1873	1783	2244	114584
D38A Phen 72	40.41	46.93	11.28	0.306	0.169	0.295	88.1	2318	1307	2189	87727
D38A Phen 72	40.47	46.61	11.27	0.306	0.172	0.297	88.1	2331	1331	2187	87660
D38A Phen 72	40.40	46.66	11.40	0.303	0.172	0.293	87.9	2298	1333	2163	88665
D38A Phen 72	39.86	45.24	12.98	0.317	0.195	0.274	86.1	2150	1514	2264	100965
D38A Phen 73	39.97	46.01	12.33	0.313	0.189	0.285	86.9	2241	1467	2240	95878
D38A Phen 74	39.76	46.03	12.33	0.316	0.194	0.281	86.9	2209	1499	2258	95911
D38A Phen 75	39.68	45.88	12.24	0.349	0.192	0.259	87.0	2035	1487	2497	95192