

**GEOCHEMISTRY OF THE GALÁPAGOS ARCHIPELAGO: UNRAVELING
DEEP MANTLE SIGNATURES FROM THE INFLUENCE OF SHALLOW
LEVEL PROCESSES**

BY

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-There are no mistakes, simply happy accidents

-Bob Ross

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INTRODUCTION

Plate tectonics have fueled almost continuous communication between the interior and the exterior geochemical reservoirs for most of the Earth's history. Oceanic melts erupt at the surface (recording the fractionating effects of melting and differentiation), are imprinted by the chemistry of the lithosphere, atmosphere and ocean (systems that have evolved through time), and are subducted back into the mantle. During subduction the material goes through an unconstrained amount of dehydration and metamorphism and is then mixed to some degree back into the chemistry of the mantle, beginning the cycle anew. Mantle heterogeneity, as a result, indisputably exists in the Earth, but the causes, effects and scale of this heterogeneity are poorly resolved. Therefore, one of the motivations of geochemical study is to determine how material collected at the surface reflects the composition of the mantle.

Ocean islands, or hotspots such as the Galapagos Archipelago, are ideal locations to study the mantle because these melting anomalies are thought to be the product of plumes of buoyantly upwelling material originating within the Earth from as deep as the core-mantle boundary (CMB) (Morgan, 1971). Ocean islands are generally associated with a large buoyancy flux, low velocity anomalies and thin transition zones (identified with seismic data) (e.g. Courtillot *et al.*, 2003, Hooft *et al.*, 2003, Villagomez *et al.*, 2007, Villagomez *et al.*, 2011, Rychert *et al.*, 2014, Villagomez *et al.*, 2014). These characteristics can be explained by the presence of greater than ambient mantle thermal anomalies (thus the term “hotspot”) originating at the CMB. Oceans islands are also unique in terms of their noble gas isotopic signatures with high $^3\text{He}/^4\text{He}$ ratios, solar-like Ne isotopes and unique heavier noble gas isotopes that are difficult to explain without the

presence of primitive mantle material (e.g. Kurz & Jenkins, 1981, Kurz *et al.*, 1982, Graham *et al.*, 1993, Kurz & Geist, 1999, Graham *et al.*, 2001, Georgen *et al.*, 2003, Kurz *et al.*, 2009, Colin *et al.*, 2011, Mukhopadhyay, 2012). In comparison to other geological settings, ocean island basalts in general exhibit extreme heterogeneity in their geochemical signatures. This is attributed to the presence of several isotopically unique reservoirs, hypothesized to be the result of both primitive mantle and recycled crustal material (Hofmann & White, 1982, Allègre *et al.*, 1983, Zindler & Hart, 1986, White *et al.*, 1993, Hofmann, 1997, White, 2010). Though it is hard to reconcile global mantle geochemical anomalies with a convecting mantle, material housed at the CMB is potentially isolated from the effects of convection, providing further support for ocean island basalts being the result of deep mantle plumes.

Unequivocally identifying specific mantle signatures in OIBs is difficult, however, due to an inadequate understanding of the extent to which upwelling melt is affected by interaction with the shallow crust and lithosphere. The resulting ambiguity in geochemical signatures calls the nature of ocean island basalts and their hypothesized origin at the CMB into question. This has led to a rift in the community between those that support and oppose using the plume theory to explain the characteristics of ocean islands (e.g. Anderson, 2000, Foulger, 2011).

In this dissertation, I have used a large geochemical data set of submarine glass, melt inclusions and whole rock, collected from across the Galapagos Archipelago, and a variety of techniques to explore the influence shallow level processes have on lavas erupted at the surface to then isolate the deep mantle signatures unique to the plume.

The Galapagos Archipelago, located < 200 km south of the Galapagos Spreading Center (GSC), contains 16 of 21 emergent volcanoes that have erupted since the Holocene, making it one of the most volcanically active areas in the world. Seismic studies have identified both a low-velocity anomaly and a thin transition zone in the mantle below the Galapagos Archipelago, characteristics attributed to a hot mantle plume column extending to at least as deep as the transition zone (Hoofstede *et al.*, 2003, Villagomez *et al.*, 2007, Villagomez *et al.*, 2011, Villagomez *et al.*, 2014). The plume column tilts towards the GSC, against the direction of plate motion (Villagomez *et al.*, 2014). This in conjunction with geochemical studies conducted along the ridge show the strong influence the Galapagos plume has on the GSC (Detrick *et al.*, 2002, Schilling *et al.*, 2003, Cushman *et al.*, 2004, Ingle *et al.*, 2010, Gibson *et al.*, 2015).

There are four main compositional components attributed to Galapagos plume that are concentrated in different geographical regions (White *et al.*, 1993, Hoernle *et al.*, 2000, Harpp & White, 2001, Werner *et al.*, 2003, Saal *et al.*, 2007). The western component is characterized by the lavas of Fernandina and is distinguishable by high $^3\text{He}/^4\text{He}$ isotopic ratios (Graham *et al.*, 1993, Kurz & Geist, 1999, Geist *et al.*, 2006, Kurz *et al.*, 2009). This component is generally compared to a relatively volatile-rich primitive mantle component (Kurz *et al.*, 1982, Farley *et al.*, 1992, Hart *et al.*, 1992, Hanan & Graham, 1996). There is a MORB-like component that, though it can be found across the archipelago, is focused in the central and eastern region and anchored by the composition of lavas from Genovesa (Harpp *et al.*, 2002, Harpp *et al.*, 2003, Geist *et al.*, 2005). The northern and southern components (illustrated by the lavas of Pinta and Floreana respectively) display enrichments in trace elements in addition to isotopic signatures

generally associated with ancient recycled material in the source. Floreana is most commonly compared to a HIMU component (high- μ = high $^{238}\text{U}/^{204}\text{Pb}$) due to enrichments in Pb isotopes (e.g. Harpp *et al.*, 2014). Pinta, in comparison, has low Nd and Hf isotopes with elevated $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ at a given $^{206}\text{Pb}/^{204}\text{Pb}$ ratio, akin to the DUPAL anomaly (Hart, 1984) and generally associated with an Enriched Mantle (EM) component (White *et al.*, 1993, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Schilling *et al.*, 2003). Lavas collected from the other islands and the submarine platform in the Galapagos have intermediate compositions, leading to the assumption that there is widespread mixing of these 4 end-members throughout the archipelago (e.g. Harpp & White, 2001, Gibson *et al.*, 2012).

Chapter one [Peterson, M., Saal, A., Nakamura, E., Kitagawa, H., Kurz, M. (2014). Origin of the ‘ghost plagioclase’ signature in Galapagos melt inclusions: new evidence from lead isotopes. *Journal of Petrology*. 55(11), 2193-2216. doi: 10.1093/petrology/egu054] focuses on identifying the origin of the “ghost plagioclase” signature using new Pb isotope analyses of olivine-hosted melt inclusions from Fernandina and Santiago that both show a trace element signature consistent with the presence of plagioclase cumulates. In the case of Santiago inclusions, there is evidence for simple plagioclase assimilation. Fernandina inclusions, in contrast, possess trace element contents indicative of the assimilation of plagioclase cumulates, without the expected major element signature (i.e. a “ghost plagioclase” trace element signature). Two competing hypotheses have emerged to explain the ghost plagioclase signature: 1. Incorporation of ancient, recycled plagioclase-rich cumulate (now eclogite) into the mantle and 2. Shallow-level interaction with plagioclase cumulates in the present-day

lower oceanic crust. We explore both hypotheses using Pb isotope measurements of the olivine-hosted inclusions from both islands. We find that melting and mixing models of ancient (~ 0.5 -1 Ga) recycled plagioclase-rich cumulates cannot reproduce the observed trace element and Pb isotope characteristics of the Fernandina inclusions with the ghost plagioclase signature. Shallow-level diffusive interactions between basalt and present-day plagioclase-rich cumulates, as a result, provide the simplest explanation for the observed trace element and isotopic compositions of melt inclusions from Fernandina and Santiago Islands.

Chapter 2 [Peterson, M., Saal, A., Kurz, M., Hauri, E., Blusztajn, J., Harpp, K., Werner, R., Geist, D., (submitted to Journal of Petrology). Determining the volatile budget of the Galapagos Plume: separating deep and shallow signatures] takes a broader approach by exploring the volatile contents of submarine glass collected from across the Galapagos Archipelago. Volatile elements assert a strong influence on processes such as mantle melting, magma crystallization, and style of eruption as well as the viscosity and rheology of the mantle (Hirth & Kohlstedt, 1996, Gaetani & Grove, 1998, Asimow & Langmuir, 2003, Asimow *et al.*, 2004). Surface processes such as degassing, sulfide saturation, and melt-crustal interaction, however, can significantly modify the primitive volatile/refractory element ratios of the melt (Michael, 1989, Dixon *et al.*, 1995, Dixon, 1997, Michael & Cornell, 1998, Dixon & Clague, 2001, Saal *et al.*, 2002, Stroncik & Haase, 2004, le Roux *et al.*, 2006, Workman *et al.*, 2006). Therefore we use new major, trace and isotopic measurements in conjunction with volatile element contents (H_2O , CO_2 , F, Cl, and S) of 118 glass chips to separate the signature of shallow level processes from the variation in volatile content of the Galapagos mantle plume.

Major, trace and isotopic measurements allow us to separate the samples into 2 broad arrays that range between the compositions of Fernandina and Sierra Negra/Cerro Azul (array 1) and between the composition of Genovesa and Pinta (array 2). Degassing has significantly decreased the CO₂ content of the magmas while having a minor affect on H₂O and S concentrations and no recognizable impact on Cl and F concentrations. Melts range from being just saturated with a sulfide liquid to being sulfide undersaturated at estimated pressures of crystal fractionation (~2 kbars). Assimilation of hydrothermally altered material, assessed with Cl/K ratios and the magnitude of the Sr anomaly ($Sr/Sr^* \geq 1$) in a primitive mantle normalized diagram, has significantly affected the samples of both arrays. The chemistry of array 2 further suggests that mixing of melts occurs after some degassing and contamination of the end-member compositions has taken place.

Once shallow level processes are accounted for we use ratios of volatile and refractory elements with similar incompatibilities to estimate the volatile budget of the Galapagos mantle plume. Distinctive H₂O/Ce and F/Nd ratios can differentiate the four main compositional components defined by the glasses of this study. Using the equations of Hirth and Kohlstedt (1996), the higher H₂O contents of the high ³He/⁴He Fernandina source will result in a mantle viscosity 5-7x lower than what we would predict for the depleted upper mantle component. The high ³He/⁴He end-member also shows C/³He ratios an order of magnitude higher than the depleted upper mantle and among the highest yet reported for OIB samples; a characteristic we attribute to a more carbonated source (Marty & Jambon, 1987, Trull *et al.*, 1993, Marty & Tolstikhin, 1998, Marty & Zimmermann, 1999, Shaw *et al.*, 2004, Barry *et al.*, 2014).

In Chapter 3 [Peterson, M., Kelley, K., Cottrell, L., Saal, A., Kurz, M. (in prep). The oxidation state of Fe in glasses from the Galapagos Archipelago: variation in oxygen fugacity as a function of mantle source] we build on the results of Chapter 2 by taking a subset of submarine glass chips measured for major, trace, and volatile contents and radiogenic isotopes from across the archipelago and using μ -XANES to measure new $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, proxy for $f\text{O}_2$ of the lavas. Oxygen fugacity ($f\text{O}_2$) is an intensive thermodynamic property that controls the speciation and partitioning of multi-valent elements and affects igneous processes such as magmatic phase relations during melting and crystallization, depth of melt initiation and the composition of volcanic gases (e.g. Ballhaus, 1993, Holloway & Blank, 1994, Canil, 1999). Our analysis reveals that $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios vary with the influence of shallow level processes, generally increasing with magmatic differentiation, decreasing with sulfur degassing and increasing with assimilation of hydrothermally altered material. After taking these processes into account, however, there is still variability in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of the isotopically different groups identified in Chapter 2. This translates into a magmatic $f\text{O}_2$ that ranges from $\Delta\text{QFM} = +0.16$ to $+0.74$, between the ranges identified for MORB ($-0.25 - +0.4$) and arc basalts ($+0.2 - +1.8$) (Kelley & Cottrell, 2009, Cottrell & Kelley, 2011, Kelley & Cottrell, 2012, Cottrell & Kelley, 2013, Brounce *et al.*, 2014). In general, the Sierra Negra/Cerro Azul component is more oxidized than the Pinta/Wolf, Darwin component. Both the Sierra Negra/Cerro Azul and Pinta mantle components are hypothesized to contain recycled material. The difference in oxidation state between these two sources and the correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and Pb isotopes suggest a difference in mantle lithology and therefore a difference in the type or influence of the recycled material on $f\text{O}_2$. The high

$^3\text{He}/^4\text{He}$ end-member is shown to have the most oxidized glasses ($\text{HHe} = 0.175 \pm 0.006$) of Chapter 3. The combination of the high $\text{C}/^3\text{He}$ ratios identified in Chapter 2 and the high $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios indicates that the high $^3\text{He}/^4\text{He}$ mantle source is both more carbonated and oxidized than previously thought for a primitive mantle component.

In Chapter 4 [Peterson, M., Wang, Z., Saal, A., Kurz, M., Eiler, J. (in prep). Oxygen isotopes in lavas from the Galapagos Archipelago: evaluating contributions from ancient and present-day crustal sources], we apply oxygen isotopes in olivine phenocrysts by laser fluorination in lavas collected from across the Galapagos Archipelago to isolate the deep mantle signatures from the effects of shallow level processes. Oxygen isotopes, in comparison to methods employed in Chapters 1-3, are uniquely suited to separate deep from shallow signatures due to the fact that measurable oxygen isotope fractionations only occur at low temperatures. As a result, deviations in $\delta^{18}\text{O}$ from the mantle source value (average upper mantle olivine = $5.0\text{-}5.4\text{‰}$, Matthey *et al.*, 1994, Eiler, 2001) are inferred to be the result of the presence of material that at one time resided on or near the surface. We find that Fernandina, Floreana, and Pinta, which represent three isotopic end-members of the Galapagos hotspot, have $\delta^{18}\text{O}$ values = $5.02 \pm 0.08\text{‰}$, within range of the oxygen isotope value of olivine in the upper mantle (Matthey *et al.*, 1994, Eiler, 2001). $\delta^{18}\text{O}$ values do not correlate with radiogenic isotopes, but there is an overall trend of increasing Sr/Sr^* and Ba/Nb ratios (indicators of the assimilation of plagioclase cumulates) with $\delta^{18}\text{O}$ values for the islands of San Cristobal, Sierra Negra, Darwin, and Santa Cruz. This suggests that the highest $\delta^{18}\text{O}$ values measured in olivines from San Cristobal ($5.34 \pm 0.05\text{‰}$) and the large ranges in $\delta^{18}\text{O}$ values identified for Sierra Negra, Darwin Volcano and Santa Cruz are the result of interaction with the shallow crust. Sierra

Negra, Alcedo, Darwin Volcano, Wolf Volcano and Ecuador, which have lower than upper mantle $\delta^{18}\text{O}$ values ($4.85 \pm 0.1\text{‰}$), do not show any correlations with radiogenic isotopes. For other ocean islands lower than upper mantle values for oxygen isotopes attributed to hydrothermally altered material in the source is accompanied by extreme isotopic heterogeneity (Eiler, 2001, Skovgaard *et al.*, 2001, Gurenko & Chaussidon, 2002, Cooper *et al.*, 2004, Thirlwall *et al.*, 2006, Day *et al.*, 2009, Day *et al.*, 2010, Gurenko *et al.*, 2011). Therefore, the low $\delta^{18}\text{O}$ values in the Galapagos are either being produced by a low $\delta^{18}\text{O}$ component with intermediate isotopes, in contrast to what is observed elsewhere, or are produced by interaction with a low $\delta^{18}\text{O}$ component in the shallow lithosphere. The olivines for these islands come from lavas with lower MgO that are more evolved. This suggests that the low $\delta^{18}\text{O}$ values of the olivines are due to the assimilation by the melt of a low $\delta^{18}\text{O}$ component in the volcanic edifice or shallow lithosphere. The lavas from these volcanoes, however, do not show unusual trace element or radiogenic isotope characteristics, making it difficult to unambiguously prove that assimilation is occurring in these samples. A small amount of assimilation of seawater ($\delta^{18}\text{O} = 0\text{‰}$) and/or hydrothermally altered gabbro without a cumulate component ($\delta^{18}\text{O} = +2.5/4.0\text{‰}$) can produce the low values for $\delta^{18}\text{O}$ without a large change to the trace element or radiogenic isotope composition of the melt, consistent with what is observed. These results show that while the Galapagos mantle has a generally homogenous $\delta^{18}\text{O}$ value indistinguishable from “normal” upper mantle, there is a more widespread affect of lithospheric contamination in melts than previously thought.

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CHAPTER 1

Origin of the “ghost plagioclase” signature in Galapagos melt inclusions: new evidence from lead isotopes

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ABSTRACT

Olivine-hosted melt inclusions from both Fernandina and Santiago islands in the Galapagos Archipelago have compositions indicating that plagioclase played an important role in the magmatic evolution of these volcanic islands. Major and trace element chemistry of Santiago melt inclusions indicates simple plagioclase assimilation. In contrast, Fernandina inclusions have compositions where the plagioclase appears to be only present as a ‘ghost’ trace element signature (i.e. “ghost plagioclase” signature). Two competing hypotheses have been proposed to explain this unique composition: **1)** incorporation of an ancient recycled plagioclase-rich cumulate (eclogite) into the mantle and **2)** shallow-level interaction between melts and plagioclase-rich cumulates in the present-day lower oceanic crust. Here we present new Pb isotope measurements of olivine-hosted melt inclusions from Fernandina and Santiago islands to distinguish between the two models. The new Pb isotope ratios are within the range previously reported for whole rock basalts from those islands. Melting and mixing models of ancient (~0.5-1 Ga) recycled plagioclase-rich cumulates cannot reproduce the observed trace element and Pb isotopic characteristics of Fernandina melt inclusions with a ghost plagioclase signature. Shallow-level diffusive interactions between basalt and present-day plagioclase-rich cumulates provide the simplest explanation for the observed trace element compositions and Pb isotope ratios of melt inclusions from Fernandina and Santiago islands.

Keywords: Galapagos; ghost plagioclase; mantle plume; melt inclusion; Pb isotopes

INTRODUCTION

The magmatism of the Galapagos Archipelago (Fig. 1) has conventionally been divided into four end-member components based on Sr, Nd, Pb, Hf and noble gas (He, Ne) isotopes (Vicenzi *et al.*, 1990, Bow & Geist, 1992, White *et al.*, 1993, Reynolds & Geist, 1995, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Geist *et al.*, 2002, Saal *et al.*, 2007, Kurz *et al.*, 2009, Gibson *et al.*, 2012). The end-member compositions are expressed at individual islands although several of these end-members are partially expressed at multiple volcanoes in the Archipelago. The two enriched mantle components are best represented by lavas from Pinta and Floreana islands, the high $^3\text{He}/^4\text{He}$ component is characteristic of Fernandina lavas and the depleted component, similar to MORB, is present in lavas from Genovesa Is. (Fig. 2). Previous geochemical studies of olivine-hosted melt inclusions and high-MgO basalts from the eastern central region of the Galapagos Archipelago show major, trace and isotope signatures consistent with interaction between basalt and plagioclase-rich cumulates during melt percolation through the oceanic lithosphere (Saal *et al.*, 2007, Koleszar *et al.*, 2009). In contrast, geochemical data of Fernandina and Isabela Island basalts in the western region of the archipelago do not show evidence of plagioclase assimilation. However, some Fernandina melt inclusions show strong trace element evidence of plagioclase assimilation, but the associated major-element signature of this process is absent.

Detailed trace element studies of basalts and melt inclusions from several oceanic islands (including the Galapagos Archipelago) and mid-ocean ridges have shown the presence of an unusual composition characterized by Sr, Ba, and Eu anomalies greater than one on primitive mantle normalized diagrams (Gurenko & Chaussidon, 1995,

Hofmann & Jochum, 1996, Kamenetsky *et al.*, 1998, Yang *et al.*, 1998, Chauvel & Hemond, 2000, Sobolev *et al.*, 2000, Huang *et al.*, 2005, Kent *et al.*, 2002, Danyushevsky *et al.*, 2003, Huang *et al.*, 2005; Ren *et al.*, 2005, MacLennan, 2008). Melting or crystallization will not significantly fractionate these elements from elements of comparable incompatibility unless plagioclase is present during these processes. Although the observed geochemical signature is typical of plagioclase-rich cumulates, many of these lavas and associated olivine-hosted melt inclusions show no indication of plagioclase accumulation or assimilation in their major element concentrations (e.g., uncommon enrichment of Al_2O_3 and depletion of FeO with decreasing MgO contents). Thus, this unusual composition was named the “ghost plagioclase” signature (Sobolev *et al.*, 2000).

Most lavas and melt inclusions with a ghost plagioclase signature are characterized by very primitive compositions (e.g., high-MgO contents). This suggests that a plagioclase-rich component is required either in the melt source region or in the crust through which the melt percolates. Two main hypotheses have been proposed to explain this signature. The first considers the presence of an ancient recycled oceanic crust with plagioclase-rich cumulate gabbro (now eclogite) as a component intrinsic to the convecting mantle (Hofmann & Jochum, 1996, Chauvel & Hemond, 2000, Sobolev *et al.*, 2000, Kent *et al.*, 2002, Ren *et al.*, 2005). The second argues for the interaction of melts with a plagioclase-rich cumulate during melt percolation through the present-day oceanic lithosphere (Danyushevsky *et al.*, 2003, Danyushevsky *et al.*, 2004, Saal *et al.*, 2007, MacLennan, 2008). Trace element contents of a 500-m gabbroic section of the oceanic crust drilled at site 735, Leg 118, have a clear plagioclase-rich cumulate

signature (“protolith” in Hart *et al.* (1999)). If this composition represents the lower oceanic crust, then both hypotheses give a reasonable explanation for the ghost plagioclase signature observed in oceanic basalts.

Pb isotopes provide an effective tool for determining which model best explains the ghost plagioclase signature. Basalts generated from a source containing an ancient (~0.5-1 Ga) recycled plagioclase-rich cumulate gabbro (now eclogite) will have a much higher $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ than present-day end-member MORB. This is due to the lower (U, Th)/Pb ratio of a plagioclase-rich cumulate (0.05 U/Pb and 0.114 Th/Pb based on average ‘protolith’ of Hart *et al.* (1999)) compared to that of the Earth’s depleted upper mantle (0.18 U/Pb and 0.439 Th/Pb based on DMM composition of Workman and Hart (2005)). In contrast, basaltic magmas percolating through the present-day oceanic lithosphere will obtain, at most, similar $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios to those of the plagioclase cumulate with which they interact.

In this report we present new Pb isotope data from geochemically well-characterized olivine-hosted melt inclusions from Santiago and Fernandina islands (representing the central/eastern and western regions of the Galapagos Archipelago, respectively) to test the origin of their ghost plagioclase trace element signature. Our Pb isotope data are consistent with the interaction between melts and a present day plagioclase-rich cumulate in the oceanic lithosphere.

Previous results

Samples

We used olivine-hosted melt inclusions picked from 2 samples collected from Fernandina and Santiago island basalts (Fig. 1). The Fernandina sample is AHA D25C, dredged from the western submarine flank of Fernandina ($00^{\circ}27.2'S$, $91^{\circ}44.6'W$, average 2750 meters depth) during the AHA-NEMO2 cruise in 2000. This dredge is part of the normal series lavas described in Geist *et al.* (2006) with a composition similar to the aphyric subaerial lavas erupted in Fernandina (Allan & Simkin, 2000). Both the subaerial and submarine lavas of Fernandina are noted for their compositional homogeneity, which is thought to be the result of mixing in a common magma chamber within the crust below Fernandina (Allan & Simkin, 2000, Geist *et al.*, 2006). The Santiago sample, STG06-29, was collected from a subaerial hornito ($0^{\circ}19'5.2''S$, $90^{\circ}35'1.7''W$) on the eastern side of Santiago, which is characterized by the MORB-like depleted component (Baitis & Swanson, 1976, White *et al.*, 1993, Koleszar *et al.*, 2009, Gibson *et al.*, 2012). Olivine-hosted melt inclusions were hand picked from crushed basalts under a binocular microscope, mounted in indium metal, exposed and then polished using diamond pastes down to $0.25\ \mu\text{m}$ (Fig. 3). The melt inclusions are naturally quenched to a homogeneous glass and have shapes that indicate a primary origin (Sobolev, 1996). They range in size from 50 to $250\ \mu\text{m}$ in diameter, with Santiago's inclusions being, on average, smaller ($\sim 60\ \mu\text{m}$) than those from Fernandina ($\sim 125\ \mu\text{m}$).

Major and Trace Element Compositions

The major and selected trace element contents of the melt inclusions, matrix glass and olivine host were reported in Koleszar *et al.* (2009). Complementary trace element data are reported here. The trace element data corrected for host olivine crystallization are

included in Supplementary Data Electronic Appendix S1 (supplementary data are available for downloading at <http://www.petrology.oxfordjournals.org>). Analytical errors (2σ) for triplicate analyses of representative melt inclusions are $<3\%$ for SiO_2 , CaO , Al_2O_3 , $<5\%$ for MgO , TiO_2 , and FeO and $<9\%$ for Na_2O . For the olivine hosts the error is $<2\%$ for SiO_2 , MgO , and FeO . Errors for the trace elements, determined from replicate analyses of matrix glasses and large melt inclusions, are typically $<5\%$ (2σ). Major and trace elements are corrected for olivine crystallization on the interior wall of the inclusion by numerically adding host olivine back into the melt inclusion composition in 0.1% increments until the inclusion and olivine host are in MgO-FeO equilibrium. Samples required only 2.6-16 %, averaging 7.0% olivine addition. For further information on the analytical techniques and corrections refer to Koleszar *et al.* (2009).

Olivine phenocrysts hosting the melt inclusions have Mg# (molar, $\text{MgO}/[\text{MgO}+\text{FeO}]*100$) averaging 85 ± 2 in the Fernandina sample and 86.6 ± 0.8 , with only two exceptions having Mg# of 82 and 85, in the Santiago lava (Koleszar *et al.*, 2009). In both samples, the Mg# of the olivine in equilibrium with the matrix glass is 78 and 82 for Fernandina and Santiago olivines respectively, indicating FeO–MgO disequilibrium between the phenocrysts and the host glasses.

The role of plagioclase: evidence from major and trace elements

Santiago Inclusions: After correction for olivine crystallization, both the major and trace element compositions of the Santiago inclusions evidence direct assimilation of plagioclase. Assimilation can be defined by a large decrease in FeO^* (FeO^* indicating total Fe) and a large increase in Al_2O_3 with decreasing MgO contents, trends that cannot

be reproduced by crystal fractionation processes (Fig. 4) (Koleszar *et al.*, 2009). Furthermore, almost all inclusions possess positive Sr, Ba, and Eu anomalies in a primitive mantle normalized diagram (Fig. 5) (Koleszar *et al.*, 2009). The magnitude of these anomalies correlates with Al_2O_3 contents, however they do not show any clear trend with very incompatible trace element ratios such as Nb/La suggesting a common source region (Fig. 6). If the variation in Al_2O_3 were the result of a different process from simple plagioclase assimilation, for example different degrees of melting, we would expect a large range in trace element ratios of highly to moderately incompatible elements (e.g., La/Yb) associated with the Al_2O_3 content. For most of the Santiago inclusions this correlation is not observed (Koleszar *et al.*, 2009). Inclusion STG06-29-19 represents an extreme case, with the lowest incompatible trace element contents and the strongest Sr and Eu anomalies. Only one Santiago inclusion (STG06-29-10, labeled Santiago enriched composition in the figures) has low Al_2O_3 and high FeO contents at low MgO coupled with a Sr anomaly lower than one, indicating possible plagioclase fractionation prior to entrapment.

Fernandina Inclusions: Although major element compositions of Fernandina melt inclusions indicate fractional crystallization, trace element compositions from a subgroup of inclusions have a ghost plagioclase signature. The major element contents of the inclusions, when combined with a compilation of Fernandina submarine glasses (Geist *et al.*, 2006), can be simply explained by olivine, olivine-plagioclase, and olivine-plagioclase-clinopyroxene crystallization (Fig. 4). However, trace element contents of the inclusions define two distinct groups: one with an enriched incompatible trace element composition typical of Fernandina lavas and a second group with an incompatible trace

element depleted composition. Eight of the eleven inclusions with depleted trace element compositions have positive Sr, Ba, and Eu anomalies in primitive mantle normalized diagram (Fig. 5 and 6), but their major element contents are inconsistent with the assimilation of plagioclase (i.e. ghost plagioclase signature). The magnitudes of Sr, Ba, and Eu anomalies do not correlate with Al_2O_3 contents (Fig. 6). However, a weak negative correlation exists between Sr/Sr^* ($\text{Sr}_{\text{PM}}/[(\text{Ce}_{\text{PM}}+\text{Nd}_{\text{PM}})/2]$) and Nb/La ratios, which indicates the presence of a trace element depleted melt in the creation of the ghost plagioclase signature.

LEAD ISOTOPE ANALYTICAL METHODS

Pb isotope analyses (Table 1) were performed using the Cameca 1270 SIMS at the Institute for the Study of the Earth's Interior, Okayama University, Misasa, Japan. In preparation for using the ion probe, mounts were submerged in 0.5M HNO_3 for 5 minutes to remove any sources of contamination from the surface. The samples were rinsed with MilliQ water three times, left under vacuum overnight to dry and coated with 300 Å of gold.

The samples were sputtered using a 30 nA focused beam of O^+ ions resulting in a 30 μm diameter pit. The primary beam (acceleration) energy was 23 keV, and the secondary accelerating voltage was 10 keV. Samples were analyzed at a mass resolution of 3000. Pb isotopes were collected using a multi-collection system equipped with five electron multipliers following the methods described in Kobayashi *et al.* (2004). Each analysis consisted of 3 minutes of pre-sputtering followed by 400 cycles of 10 seconds on Pb peaks. Mass positions were set by centering the ^{206}Pb peak at the beginning of each

analysis due to the high concentration of Pb in the standard. Background runs were measured using the settings of the run, but without the primary beam emission, and routinely checked throughout the session.

We used the synthetic basaltic glass standard FMSA (5 ppm Pb) to correct for the instrumental mass discrimination (Kobayashi *et al.*, 2004). The standard was measured repeatedly (≥ 9 times/day) over the course of the session. The daily external precision for the standard (2σ standard deviation of daily group of standard measurements) ranges from ± 0.27 (n = 16) to 0.35% (n = 9) for $^{207}\text{Pb}/^{206}\text{Pb}$ and 0.24 (n = 9) to 0.35% (n = 16) for $^{208}\text{Pb}/^{206}\text{Pb}$.

The Pb concentrations of the melt inclusions are all < 2 ppm, leading to low precision in the measured isotopic ratios. In the case of Santiago inclusions, with Pb concentrations of 0.6 to 0.9 ppm, the 2σ standard error in Pb isotope ranges from ± 0.6 to 1.5% for $^{207}\text{Pb}/^{206}\text{Pb}$ and ± 0.5 to 1.1% for $^{208}\text{Pb}/^{206}\text{Pb}$. For Fernandina inclusions, with Pb concentrations of 0.5 to 1.5 ppm, the errors are ± 0.4 to 2% and ± 0.3 to 1.6% $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ respectively. The low ^{204}Pb ion current yielded large uncertainties in the ^{204}Pb -normalized isotope ratios, rendering these ratios unusable.

RESULTS

The Pb isotopic compositions of the melt inclusions are consistent with those previously reported on whole rock samples from Fernandina and Santiago islands (White *et al.*, 1993, Harpp & White, 2001, Saal *et al.*, 2007, Gibson *et al.*, 2012) (Fig. 7).

For Santiago inclusions, $^{207}\text{Pb}/^{206}\text{Pb}$ ranges from 0.8261 to 0.8473, and $^{208}\text{Pb}/^{206}\text{Pb}$ from 2.0335 to 2.0678, which is within error of the range seen for Santiago whole rock

samples ($^{207}\text{Pb}/^{206}\text{Pb} = 0.8133\text{-}0.8381$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.0237\text{-}2.0569$) (White *et al.*, 1993, Saal *et al.*, 2007, Gibson *et al.*, 2012). There is no significant correlation between the Pb isotopes and the major and trace element contents indicative of plagioclase assimilation typical of these inclusions (Fig. 8). Inclusion STG06-29-10 (Santiago enriched inclusion with major and trace element evidence for plagioclase fractionation) has Pb isotope ratios within the range of the typical Santiago inclusions. STG06-29-19 (highest Sr anomaly) was too small in size to obtain reliable Pb isotope data.

In the case of Fernandina inclusions, $^{207}\text{Pb}/^{206}\text{Pb}$ ranges from 0.8113 to 0.8240 and $^{208}\text{Pb}/^{206}\text{Pb}$ from 2.010 to 2.042, which is within error of the range for Fernandina whole rock isotopic data reported in the literature ($^{207}\text{Pb}/^{206}\text{Pb} = 0.8136\text{-}0.8168$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.0281\text{-}2.0316$) (White *et al.*, 1993, Kurz & Geist, 1999, Saal *et al.*, 2007). The average of the melt inclusion range ($^{207}\text{Pb}/^{206}\text{Pb} = 0.8174$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.0315$, weighted for Pb concentration) falls close to the value of the host lava AHA D25C (Fig. 7). This is consistent with the host lava being an aggregate of a heterogeneous mixture with a varied geochemical composition that melt inclusions are sampling more fully (Saal *et al.*, 2005, MacLennan, 2008). There is no discernable correlation between the Pb isotopes, major, or trace element compositions of the inclusions (Fig. 8). The inclusions with depleted incompatible trace element contents we were able to measure have, at similar $^{207}\text{Pb}/^{206}\text{Pb}$, unusually high $^{208}\text{Pb}/^{206}\text{Pb}$. However, the large errors in these two analyses, due to the low Pb concentrations of the inclusions, do not allow us to discuss the implications of these results any further. From the eight inclusions with ghost plagioclase signature only four were large enough to measure the Pb isotopes. These four inclusions have $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ within the range of the other Fernandina inclusions.

DISCUSSION

Evidence for contamination by plagioclase cumulates: relationship between major, trace elements and Pb isotopes

Santiago melt inclusions (normal and enriched) have Pb isotopes that are within the range of those previously measured on whole rock lavas from this island indicating the presence of both trace element and Pb isotope enriched and depleted melt components (White *et al.*, 1993, Gibson *et al.*, 2012). Although the melt inclusions have major and trace element evidence for the assimilation and crystal fractionation of plagioclase, their Pb isotope ratios do not significantly correlate with any chemical indicators of these processes. There is, if any, only a very weak positive trend between Pb isotopes and both Al_2O_3 content and Sr/Sr^* (quantified by $\text{Sr}_{\text{PM}}/[(\text{Ce}_{\text{PM}}+\text{Nd}_{\text{PM}})/2]$) (Fig. 8). This indicates that the inclusions with depleted trace element and high $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ have been more affected by assimilation of plagioclase cumulates than the enriched inclusions, consistent with the hypothesis proposed by Saal *et al.*, (2007) using the whole rock geochemical data of basalts from the Galapagos Archipelago.

The assimilation of plagioclase is responsible for the observed range in Sr/Sr^* and Nb/La seen in the normal Santiago inclusions (Fig. 6); this process changes the Sr/Sr^* without significant modification of the Nb/La ratio in the melt. The exception is the depleted Santiago inclusion that has a Nb/La ratio much lower than the normal Santiago inclusions (0.4 compared to 0.8, respectively). This ratio cannot be explained by a normal Santiago melt undergoing simple plagioclase assimilation and therefore requires the presence of a more depleted melt (that will possess a low Nb/La) within the magmatic

plumbing system beneath Santiago. It is unfortunate that the depleted Santiago inclusion (STG06-29-19) was too small in size to obtain reliable Pb isotope data.

The Pb isotopic compositions of Fernandina inclusions fall within error of the range defined by the lavas from this island. This is expected for inclusions having major and trace element compositions analogous to Fernandina whole rock lavas. However, inclusions with a ghost plagioclase signature have Pb isotopes indistinguishable from those of normal Fernandina inclusions (Fig. 7 and 8). This suggests the process producing ghost plagioclase signatures in Fernandina inclusions also does not significantly affect Pb isotope ratios of the melt.

Evaluating the two theories for the origin of the Fernandina “ghost plagioclase signature”

With the new Pb isotopic constraint it is possible to evaluate the 2 proposed models for the origin for the ghost plagioclase signature: ancient recycled versus interaction with present-day plagioclase-rich cumulate. While both models are indistinguishable with respect to their trace/major element concentrations, their Pb-isotopes will be significantly different. Here, we evaluate both models for their ability to reproduce both the expected trace element and Pb isotopic signatures of the Fernandina inclusions.

Estimating the Pb isotope composition of ancient plagioclase cumulates

To estimate the Pb isotope ratios of an ancient (~ 0.5 -1 Ga) recycled plagioclase cumulate, we assume the cumulate is formed in the oceanic lithosphere during the crystallization of a range of MORB compositions. Using present-day Pb isotopes of

Pacific MORB and the U, Th, Pb contents estimated for the MORB mantle (E-DMM, N-DMM and D-DMM Donnelly *et al.*, 2004, Stracke *et al.*, 2005, Workman & Hart, 2005), we calculate Pb isotopes of the plagioclase-rich cumulate at the time of formation (~ 0.5 -1 Ga). We then use these calculated Pb isotopes with the measured U, Th and Pb concentrations of plagioclase-rich cumulates in the oceanic crust (Hart *et al.* 1999, Zimmer *et al.*, 1995) to calculate its present-day Pb isotopic compositions. Present day Pb isotope ratios of the ancient plagioclase cumulate calculated by this model are inconsistent with the values measured in Fernandina inclusions with ghost plagioclase signatures (Fig. 9).

The main variable parameters that control the isotopic evolution of the recycled gabbro in the calculation described above are the present-day isotopic and trace element composition of the MORB source, the trace element composition of the gabbro, and the time. The boundaries of the isotopic composition of the MORB source are defined by a compilation of Pacific MORB isotope data ($^{207}\text{Pb}/^{206}\text{Pb} = 0.82$ - 0.88 , $^{208}\text{Pb}/^{206}\text{Pb} = 2.026$ - 2.120) (Stracke *et al.*, 2005). These boundaries contain enriched (E), normal (N), and depleted (D) MORB isotopic values. As such, we change the U, Th, and Pb contents with the isotopic values to reflect the difference in trace element enrichment of EMORB versus N and D-MORB sources (Donnelly *et al.*, 2004, Workman and Hart, 2005). For the trace element composition of the gabbro we use reported U, Th, and Pb contents measured for what are considered pristine, unaltered protolith (i.e., Hp) and variably hydrothermally altered strip samples (i.e., Ps, Qs, Os) of lower crustal gabbros that show trace element evidence for plagioclase-rich cumulates reported in Hart *et al.*, (1999) and an average Gabbal Gerf plagioclase-rich gabbro composition (GG) as an additional

composition to test (Zimmer *et al.*, 1995). Therefore both a range in U/Pb (0.018-0.176) and Th/Pb ratios (0.032-0.484) were input into the calculation. We test ages of 500 Ma and 1Ga for the recycled gabbro. The 500 Ma minimum time of evolution is a conservative average minimum recycling time found through simultaneous analysis of multiple isotopic systems of other hotspots (e.g. McKenzie *et al.*, 2004), while material older than 1Ga did not show significant result improvement. All parameters are listed in Table 2 and results are shown in Fig. 9.

Though subduction may affect U, Th, and Pb contents of plagioclase-rich cumulate gabbros, what precisely this affect is remains largely unconstrained. The study of Becker *et al.* (2000) approached this problem by studying high-pressure eclogite bearing terranes. Those samples with a gabbroic protolith were comparable to samples gathered from the lower oceanic crust, which suggests subduction does not have a significant affect on U, Th, and Pb contents of subducted plagioclase cumulates. Other studies have tried to quantify trace element flux in a subduction zone using mass balance calculations (e.g. Kelley *et al.*, 2005, Chauvel *et al.*, 2009, Porter & White, 2009). Porter and White, (2009), using data from 8 different subduction zones for their trace element flux calculation found that, on average, 73-79% of U, Th, and Pb survived in to the deep mantle making changes to U/Pb, Th/Pb and Th/U small and not systematic. Therefore, for our model, we consider the U/Pb and Th/Pb ratios of the recycled plagioclase cumulate to be not significantly affected by subduction processes, which is consistent with the model of Sobolev *et al.*, (2000).

Using the parameters described above, the results of the model considering an ancient recycled plagioclase-rich cumulate do not produce isotopic values within what

has been found for Fernandina melt inclusions (Fig. 9). In order for a recycled gabbro to evolve to a Fernandina isotopic composition, the present-day MORB isotopic value has to be equal to the most enriched EMORB in the Pacific Ocean (which has a similar isotopic composition to Fernandina lavas; Fig. 9) and experience an incredibly short recycling time (≤ 152 Ma). This would avoid large changes in the initial isotopic value, but requires an improbably young recycled material. Alternatively, to stay within the more reasonable minimum age of recycling (500 Ma) we would have to expand the range in present-day MORB isotopic values to include the most enriched samples measured for Atlantic EMORB, samples which have been affected by the Sierra Leone plume (Schilling *et al.*, 1994). The very young age and/or the extreme isotopic composition necessary to reproduce the Fernandina Pb isotope values makes it unlikely that melt inclusions with the ghost plagioclase signature are sampling an ancient recycled plagioclase-rich cumulate in the source of the Galapagos plume. An additional melting/mixing step is needed, which will require us to expand our model to include trace elements in addition to Pb isotopes.

Melting of an ancient plagioclase cumulate: adding Pb isotopes to a critical melting model

To test whether melting of a plume mantle containing an ancient recycled plagioclase-rich cumulate could reproduce the trace element and Pb isotopic composition found in Fernandina melt inclusions with the ghost plagioclase signature, we use the model presented by Sobolev *et al.* (2000). The melting reactions, phase proportions and partition coefficients are presented in Table 3. This model considers that a quartz-eclogite

(recycled plagioclase-rich cumulate) entrained in a mantle plume starts to melt before the surrounding mantle during adiabatic upwelling. The resulting Si-rich melt infiltrates and reacts with the surrounding peridotite to form pyroxene (Yaxley & Green, 1998) transferring the trace element signature of the recycled plagioclase-rich cumulate to the peridotite. The subsequent melting of this hybrid mantle in the garnet stability field could then produce melts characterized by a ghost plagioclase trace element signature (Sobolev *et al.*, 2000).

Although Fernandina mantle has noble gasses consistent with a less degassed mantle composition (FOZO), we consider for the modeling two different mantle compositions, a trace element depleted DMM (Workman & Hart, 2005) and a primitive mantle (PM, McDonough & Sun, 1995) to better simulate a large range of possibilities. For the isotopes of the DMM mantle, we use the Pb isotopes of DMM from Stracke *et al.* (2005). For the PM mantle we use the average Pb isotopic composition for lavas from Fernandina (Saal *et al.*, 2007). For the remaining parameters (composition of ancient plagioclase, degree of melting for the eclogite, fraction of eclogite melt to peridotites used for mantle hybridization, and the degree of melting of the hybrid mantle) we test a range of values and present the results of the best-fit models in Fig. 10 and Table 4. The ancient recycled plagioclase-rich cumulate isotopic composition is calculated using the method and compositional ranges described in the previous section. The parameters for the cumulate calculation that yield the isotopic composition closest to the Fernandina melt inclusions isotopic composition are the extreme $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ of the EMORB Pacific ridge samples and the composition of either the gabbro strip Os (Hart *et al.*, 1999) or the average Gabal Gerf gabbro composition GG (Zimmer *et al.*, 1995) at an

age of 500 Ma and 1Ga. Following Sobolev *et al.* (2000) we consider that the eclogite melting has a residual porosity of 8%, which is reasonable for a high-Si melt (Yaxley and Green, 1998). Any fraction of melt above 8% will be removed to hybridize the surrounding mantle (either DMM or PM) at a ratio 0.1 melt to 0.9 peridotite. Though we tested our model using 9-50% instantaneous and aggregate eclogite melt, the results presented in Fig. 10 use the first weight percent past the porosity ($F = 9\%$) of instantaneous melt for hybridization because this produces the largest Sr anomaly. We also varied the proportion of eclogite melt to peridotites from 0.1:0.9 to 0.03:0.97, though this does not produce a significant change from what we show in Fig. 10. Following hybridization, we consider 5-15% accumulated critical melting of the hybrid mantle with 2% porosity. The resulting melt extracted from the mantle is mixed with typical Fernandina melt, in 10% increments. For the composition of the modeled melt originated from the hybrid mantle, the differences between 5 and 15% melting will not significantly affect the Sr/Sr* ratios, therefore we present an average value of 10% melting in Fig. 10. Results of each step of this model for the ideal parameters indicated above can be found in Table 4. None of the models were able to reproduce both the trace element and Pb isotope compositions of the ghost plagioclase inclusions. Over the range of tested parameters, the percentage of the eclogite needed to create the ghost plagioclase trace element signature force the Pb isotopes outside what we measured in the Fernandina inclusions with ghost plagioclase signature.

Present-day formation of a ghost plagioclase signature

In order to explain the similar Pb isotopic composition of the Fernandina melt inclusions with and without the ghost plagioclase, the process forming the ghost plagioclase signature must create both the observed trace element anomalies and isotopic ratios. For example, a plagioclase cumulate formed in the oceanic crust beneath Fernandina within the last few million years would have the present-day Pb isotope composition of Fernandina lavas. Therefore, a shallow-level diffusive interaction of a Fernandina melt with this plagioclase-rich cumulate would create the needed trace element anomalies while not affecting the Pb isotopes and the major element composition of the melt. To illustrate this, we've included a simple diffusion model that considers the approximate solution to the diffusion equations in a finite crystal-melt geometry (Hart, 1993) presented in Saal *et al.*, (2007) (Fig. 11). This model considers an end-member case of melt percolating through a troctolite mush with equal proportions of plagioclase and olivine. For simplicity, we neglect the effects of crystal dissolution and precipitation that may occur during diffusive re-equilibration of a partially molten system (Hart, 1993, Liang, 2003), namely we assume the melt is in major element equilibrium with the plagioclase cumulate (Saal et al., 2007). As a result, because of the low trace element budget of olivine, variations in the trace element content of the melt are due solely to diffusive exchange between plagioclase and melt.

There are 2 values for melt concentration that we must consider: the melt from which the plagioclase cumulate crystallizes and the composition of the melt interacting with the cumulate. The geochemistry of the Fernandina melt inclusions with ghost plagioclase signature (large positive Sr/Sr*, large range in Nb/La ratios, and Pb isotopes equal to those of Fernandina whole rock) limit what these melt compositions can be. A

large positive Sr anomaly, as is observed in the Fernandina melt inclusions with the ghost plagioclase signature, can be created by diffusion if the melt from which the plagioclase crystallized is much more enriched in trace element concentrations than the percolating melt. Therefore, for the cumulate composition, we considered the crystallization of plagioclase from an evolved Fernandina melt (AHA31A, Geist *et al.*, 2006) and we assume a Pb isotopic composition equivalent to that of Fernandina whole rock (Saal *et al.*, 2007). For the percolating melt we considered trace elements depleted melt because the Nb/La ratio in the depleted Fernandina melt inclusions with and without plagioclase ghost signature is much lower than those of the “normal” inclusions (Fig. 6 and 11). Although part of the Nb/La variation can be reproduced by the diffusive interaction of a percolating melt with the plagioclase cumulate due to the different diffusivity of Nb and La in plagioclase (Cherniak, 2003, Saal and Van Orman, 2004), the total variation in Nb/La ratios cannot be reproduced using reasonable parameters, suggesting that the percolating melt is depleted (i.e., low Nb/La). Therefore, for the percolating melt composition, we assumed a 12% aggregated fractional melt of the DMM composition (Workman and Hart, 2005) with a Nb/La ratio of 0.773 and with the average isotopic composition of Pacific MORB (Stracke *et al.*, 2005) (Fig. 9). Although we do not see erupted lavas with trace element depleted composition in Fernandina, the trace element depleted melt inclusions suggest the presence of low volume, trace element depleted melt composition in the plumbing system of this volcano.

In a crystal mush zone, either in a shallow crustal magma chamber or shallow regions of the mantle, the melt is expected to percolate by both reactive porous flow (low melt/rock ratio more susceptible to diffusive interaction with the crystal cumulate) and

channelized melt flow (high melt/rock ratio where the composition of the melt is similar to the erupted lavas) (e.g. Jaupart and Tait, 1995; Kelemen *et al.*, 1995). Therefore in a mush zone beneath Fernandina we would expect the presence of these two melts (channelized and reactive porous flow), which will progressively aggregate as presented in Fig. 11 reproducing the correlation between Nb/La and Sr/Sr* that is observed in the ghost plagioclase inclusions.

Other parameters include temperature, crystal size and melt to rock ratio. Based on the results of previous studies of the crust-mantle transition zone we set a temperature of 1200°C, grain size of 1 mm and use a melt to rock ratio of 1% (Boudier *et al.*, 1996, Dunn *et al.*, 2001). We further assume the temperature is constant, which is consistent with inefficient heat removal from the crust mantle transition zone (Dunn *et al.*, 2001). For the model we assume the solid is homogenous at the onset of diffusion. We also assume that the concentration in the middle of the grains is controlled by diffusion and that the mineral grains do not deform. Diffusion in the melt is considered instantaneous and the boundary between solid and melt is assumed to be in chemical equilibrium at all times (see Saal *et al.*, 2007 for further considerations). The values of all parameters used can be found in Table 5.

The results of this model (Fig. 11) demonstrate how the ghost plagioclase signature can be produced by diffusive interaction between a depleted melt and plagioclase cumulates and then the subsequent mixing of reacted melt with a normal composition Fernandina melt. The diffusivities of Sr and Pb, along with those of Ba, K and Eu⁺², are several orders of magnitude faster than the other trace elements (e.g., Th, Nb and REE), allowing a melt to develop a plagioclase-rich signature within a short

amount of time (Behrens *et al.*, 1990, Cherniak and Watson, 1994, Giletti and Casserly, 1994, Cherniak, 1995, Giletti and Shanahan, 1997, Cherniak, 2002, Cherniak, 2003, Saal and Van Orman, 2004). The fast diffusion of Pb also causes the rapid change in the Pb isotopes of the melt from the initial DMM value to a value within range of Fernandina. The rapid re-equilibration of Pb isotopes of the melt, however, necessitates that plagioclase cumulates have the Pb isotope composition of Fernandina. If we consider the opposite situation, where the plagioclase cumulate originated from a trace and isotopic composition similar to typical NMORB (e.g., crust created at the GSC), and the percolating melt has the isotopic and trace element composition of normal Fernandina lavas, the result will be a melt with the isotopic composition of NMORB and a negative Sr anomaly, thus not reproducing either the Pb isotopes or the trace element characteristics of the inclusions with ghost plagioclase signature. Alternatively, although quite unlikely, the plagioclase-rich cumulates formed at the ridge now under Fernandina might have had the extreme EMORB composition found in the Pacific Ocean, as this is similar to Fernandina whole rock. However, there is no evidence to support the existence of an extreme EMORB composition in the lithosphere beneath Fernandina.

It is clear that our simple model cannot reproduce the signature of the melt inclusion with the highest Sr/Sr* (D25C-2-29), but our model is limited by only considering diffusion. Burgess *et al.* (in preparation), explore an expansion of this model that includes dissolution/precipitation of plagioclase in addition to kinetic equilibration. The additional processes expand the number of starting compositions that allow a present-day interaction between melt and plagioclase cumulates to result in a ghost plagioclase signature and further highlights how interaction provides the simplest

explanation for the creation of a ghost plagioclase signature in the Galapagos Archipelago.

Presence of the ghost plagioclase signature in settings outside the Galapagos

The ghost plagioclase signature is a well-documented phenomenon that, despite only occurring in a small percentage of samples, can be found in suites of samples from multiple OIBs (Gurenko & Chaussidon, 1995, Hofmann & Jochum, 1996, Yang *et al.*, 1998, Chauvel & Hemond, 2000, Sobolev *et al.*, 2000, Kent *et al.*, 2002, Huang *et al.*, 2005, Ren *et al.*, 2005, MacLennan, 2008) and MORB (Kamenetsky *et al.*, 1998, Danyushevsky *et al.*, 2003, Danyushevsky *et al.*, 2004). However, very few studies report Pb isotopes in addition to trace and major elements. The study of MacLennan, (2008) reports Pb isotopes for a suite of Icelandic melt inclusions with several inclusions identified as possessing the ghost plagioclase signature. The Pb isotopes of the anomalous inclusions are within the range of isotope ratios measured for the normal composition inclusions. This led the authors to conclude that the ghost plagioclase inclusions were sampling a present-day process as opposed to an ancient recycled gabbro in the mantle source, consistent with the findings of our study. The study of Sobolev *et al.*, (2011) reports both Sr and Pb isotopes for a suite of melt inclusions from Hawaii that include several inclusions with large positive Sr anomalies on a primitive mantle normalized trace element diagram. The inclusions with the Sr anomalies did not fall outside of the Sr and Pb isotopic range defined by the inclusions with normal compositions, but the Sr anomaly correlates positively with Al_2O_3 content suggesting shallow-level interaction between melts and plagioclase-rich cumulates in the present-day

oceanic lithosphere beneath Hawaii. These few examples indicate that without the Pb or any other isotope data for the melt inclusions, it is difficult to unequivocally prove a recycled origin for the ghost plagioclase signature.

CONCLUSIONS

The major and trace element concentrations unique to the ghost plagioclase signature have been recreated equally well by models that invoke plagioclase-rich cumulate either as an ancient recycled component in the mantle or as present-day component in the oceanic lithosphere (Sobolev *et al.*, 2000, Danyushevsky *et al.*, 2003, Danyushevsky *et al.*, 2004). Because these two processes require vastly different ages, the Pb isotopes provide an excellent tool for evaluating these distinct models. Pb isotopes from the Galapagos basalts and melt inclusions suggest that the origin of a ghost plagioclase signature in basalts from the Galapagos Archipelago is not produced by the sampling of an ancient (~0.5-1 Ga) recycled plagioclase-rich cumulate within the mantle. Instead the trace elements and Pb isotopes are most consistent with a modern interaction between mantle melts and plagioclase-rich cumulates in the oceanic lithosphere. These results demonstrate that careful evaluation of the isotopic compositions of basalts and melt inclusions is required before unusual trace element anomalies such as Sr, Ba and Eu can be used to argue for the presence of ancient recycled crust in oceanic basalts.

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FIGURE CAPTIONS

Figure 1.

Map with the locations of the submarine dredge from Fernandina Island and the subaerial hornito from Santiago Island from which we picked the olivines containing the melt inclusions analyzed in this study.

Figure 2.

$^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ ratios obtained by TIMS and MC-ICPMS for whole rock and glass samples collected from the Galapagos archipelago. The data used are from: (Vicenzi *et al.*, 1990, Bow & Geist, 1992, White *et al.*, 1993, Reynolds & Geist, 1995, Harpp & White, 2001, Geist *et al.*, 2002, Saal *et al.*, 2007). Large open circles are the four end-members from the mantle tetrahedron projected onto the $^{208}\text{Pb}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ plane (Hart, 1988, Hart *et al.*, 1992, Workman *et al.*, 2004, Stracke *et al.*, 2005). FOZO is the approximate position for where the highest $^3\text{He}/^4\text{He}$ samples from the Galapagos plot in Pb-Pb space. Light grey fields represent most Galapagos volcanoes, while dark grey fields represent the data for Santiago and Fernandina islands.

Figure 3.

Photomicrographs of representative olivine-hosted melt inclusions from Fernandina and Santiago basalts taken in reflected light. In olivine grains with multiple exposed inclusions, a black arrow indicates the inclusion that was analyzed. Notice that there is no significant difference between the Fernandina melt inclusions with the ghost plagioclase signature, the depleted, and the normal inclusions (similar to matrix glass). Also notice

the same is true for the Santiago normal, enriched, and depleted inclusions. The small size of STG06-29-19 (extreme depletion) prevented us from analyzing this inclusion for Pb isotopes.

Figure 4.

Al_2O_3 and FeO^* (reported as total iron) versus MgO wt% for (a) Fernandina inclusions (Koleszar *et al.*, 2009) and compiled glass data (black plus sign, Geist *et al.*, 2006). Dark blue circles, melt inclusions with trace element compositions similar to Fernandina host glass (Fernandina normal composition); light grey circles, depleted trace element compositions; cyan circles, ghost plagioclase signature; violet star, Fernandina host glass composition. (b) Santiago inclusions (Koleszar *et al.*, 2009) and a compilation of Santiago subaerial lavas (black cross, data from <http://georoc.mpch-mainz.gwdg.de/georoc>). Dark green diamonds, melt inclusions with trace element composition similar to Santiago host glass (Santiago normal composition); yellow diamond, enriched trace element composition (STG06-29-10); brown diamond, extreme trace element depletion and plagioclase signature (STG06-29-19), pink star, Santiago host glass composition. Average 2σ error shown by grey plus symbol. Crystal fractionation trends have been calculated using PETROLOG (Danyushevsky, 2001, Danyushevsky and Plechov, 2011) for both Santiago and Fernandina inclusions at a pressure of 1.5 kbars for two different concentrations of water: dashed line uses 0.1 wt% and solid line 0.4 wt% water. Starting compositions for calculations were chosen to be high MgO content inclusions D25C-3-20 and STG06-29-06 for Fernandina and Santiago inclusions respectively. Note that, in general, Fernandina inclusions define a trend that

can be produced by magmatic differentiation of olivine, followed by olivine+plagioclase, followed by olivine+plagioclase+clinopyroxene. The inclusions with the ghost plagioclase signature also fall along this trend at major element concentrations indistinguishable from the normal Fernandina inclusions. In contrast, Santiago inclusions cannot be reproduced by simple magmatic differentiation; their increase in Al_2O_3 and decrease in FeO^* with decreasing MgO wt% cannot be reproduced by normal crystal fractionation and represents the assimilation of plagioclase of approximately An50.

Figure 5.

Primitive mantle-normalized trace element diagram for representative samples. (a) Fernandina: normal composition melt inclusion D25C-3-12 (MgO wt% = 8.51), depleted trace element composition D25C-2-24 (MgO wt% = 8.34), and ghost plagioclase composition D25C-3-34 (MgO wt% = 8.58). (b) Santiago: normal composition melt inclusion STG-06-29-17 (MgO wt% = 9.79), enriched composition STG06-29-10 (MgO wt% = 9.47), and most depleted trace element composition STG06-29-19 (MgO wt% = 9.10). Normalizing values are from McDonough and Sun (1995). Included in (a) and (b) is the lower crustal gabbro protolith (Hp) reported by Hart *et al.* (1999), which has one of the highest U/Pb ratios (magenta diamond).

Figure 6.

(a) Sr/Sr^* ($\text{Sr}_{\text{PM}}/[(\text{Ce}_{\text{PM}}+\text{Nd}_{\text{PM}})/2]$) versus Al_2O_3 wt% for individual melt inclusions from both Fernandina and Santiago islands. Included inset shows a zoomed in view to better illustrate the correlation between Sr/Sr^* and Al_2O_3 in the Santiago inclusions. (b) Sr/Sr^*

vs Nb/La for Fernandina and Santiago inclusions. Included plagioclase-rich gabbro symbol (magenta diamond) is the value of protolith gabbro sample Hp (Hart *et al.*, 1999)

Figure 7.

$^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ ratios for individual melt inclusions from both Santiago and Fernandina islands. Results overlay the fields for Fernandina and Santiago islands for whole rock lavas (references as in Fig. 2). Also included is the Fernandina host glass AHA D25C (violet star), an average weighted for Pb concentration of both the Fernandina inclusions and Santiago inclusions (white star and labeled). Inset shows a zoomed out view of the results. Note that the inclusions with the ghost plagioclase signature plot in the same isotopic space as the inclusions from Fernandina with normal trace element compositions.

Figure 8.

(a) Sr/Sr^* ($\text{Sr}_{\text{PM}}/[(\text{Ce}_{\text{PM}}+\text{Nd}_{\text{PM}})/2]$) versus $^{207}\text{Pb}/^{206}\text{Pb}$ ratios for Fernandina and Santiago inclusions. A zoomed in view of Sr/Sr^* versus $^{207}\text{Pb}/^{206}\text{Pb}$ is also included. Note that Sr/Sr^* , an indicator of plagioclase signature, does not correlate with $^{207}\text{Pb}/^{206}\text{Pb}$ ratios for either inclusions from Fernandina or Santiago Islands. (b) Al_2O_3 wt% versus $^{207}\text{Pb}/^{206}\text{Pb}$ for Fernandina and Santiago inclusions. Note that only a very weak correlation might exist for only the Santiago inclusions. (c) Ba/Th ratios versus $^{208}\text{Pb}/^{206}\text{Pb}$ ratios for Fernandina and Santiago inclusions. Notice again the lack of trend between the Ba/Th ratios and isotopic ratios. Included is the plagioclase-rich gabbro composition of protolith

gabbro Hp from Hart *et al.*, (1999) with the isotopic composition of average DMM (Stracke *et al.*, 2005).

Figure 9.

$^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ ratios for individual melt inclusions from Fernandina Island with calculated possible trends for the isotopic evolution of ancient plagioclase cumulates. The field for MORB isotopes represents a compilation for the Pacific MORB (Stracke *et al.*, 2005 and references therein). Dashed lines in the field separates the Pacific compilation into fields of EMORB, NMORB, and DMORB compositions. Dotted lines show the back-calculation of the present-day $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ for the selected values of present-day Pacific MORB field (black square), to an initial isotopic value at 0.5 Ga (a, c, e) and 1.0 Ga (b, d, f) (white square), assumed to be the possible age of formation of the recycled gabbro. Starting Pacific MORB compositions (black square) for this calculation are separated between the panels into EMORB (a, b), NMORB (c, d) and DMORB (e, f). Solid lines show the evolution of the gabbro to its present-day isotopic composition for several different gabbro compositions. The gabbros chosen represent the extreme compositions for (U, Th)/Pb ratios from the compositions reported in Hart *et al.*, (1999). Also included is the average gabbro composition of the Gabal Gerf ophiolite (Zimmer *et al.*, 1995). Individual gabbro compositions are indicated by diamonds of different colors. In our isotopic calculation, for the back calculation to the isotopic composition of the gabbro at the time of formation, we tested all of the present-day isotopic values of Pacific MORB marked by the field, but have only included the results of calculation using the extreme minimum value of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios for

the field (EMORB), the extreme maximum $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ of the field (DMORB) and an average NMORB isotopic ratio, as these represent the boundaries of the calculation. Notice the results of all 6 models are well outside the field established by the Fernandina inclusions. Values of inputs can be found in Table 2.

Figure 10.

Comparison of Fernandina melt inclusion compositions with trends produced by mixing of a typical Fernandina basalt with lavas generated by partial melting of a mantle plume containing an ancient (~ 0.5 -1 Ga) recycled plagioclase-rich cumulate. (a-b) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. Large open circles are the end-members from the mantle tetrahedron projected onto the $^{208}\text{Pb}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ plane (Hart, 1988, Hart *et al.*, 1992, Hauri *et al.*, 1994, Workman *et al.*, 2004, Stracke *et al.*, 2005). (c-d) Sr/Sr* versus $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. Results of critical melting model using DMM (black open symbols) and PM compositions (black filled symbols) hybridized with ancient plagioclase cumulates (now eclogite) formed at 0.5 Ga (triangles) and 1 Ga (circles) (results presented in Table 4). Ancient cumulate is generated using the calculations described in the text. The parameters of the calculation are, for the starting composition, the extreme $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ of the EMORB Pacific samples and the two gabbro compositions that resulted in the isotope ratios closest to Fernandina: (a, c) ancient cumulate composition calculated using the Gabal Gerf average gabbro composition GG (Zimmer *et al.*, 1995), (b, d) ancient cumulate using the Os strip gabbro composition (Hart *et al.*, 1999). The model trends represent mixing of 10% aggregated critical melt of the hybrid mantle (Ag_EM_DM or Ag_EM_PM) with normal Fernandina melts in 10% increments (see

text for explanation of the model). End members of the hybrid mantle melt used for mixing (results of the critical melting model) are indicated by a larger symbol while smaller symbols denote 10% mixing steps. Note that the Pb isotope ratios and the Sr/Sr* cannot be simultaneously reproduced by this model.

Figure 11.

Comparison of Fernandina melt inclusion compositions with trends produced by diffusively reacting a 12% aggregated, fractional melt generated from a DMM source (Workman and Hart, 2005) with a plagioclase cumulate created from an evolved Fernandina melt (AHA31A Geist *et al.*, 2006) at 1200°C (see text for the description of the model and Table 5 for the model parameters). (a) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. (b) Sr/Sr* versus $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. (c) Sr/Sr* versus Nb/La ratios. Large purple circle indicates the composition of the percolating melt. Small purple circles represent the composition of the melt as diffusive equilibration with the plagioclase-rich cumulate progresses within a range of 1 to 400 years indicated by the numbers next to the small circles. Grey dashed lines represent mixing between the normal Fernandina melt (D25C-2-19B) and the percolating melt that reacted over 20 and 400 years; the grey diamonds denote 10% mixing steps.

FIGURES

Figure 1-1

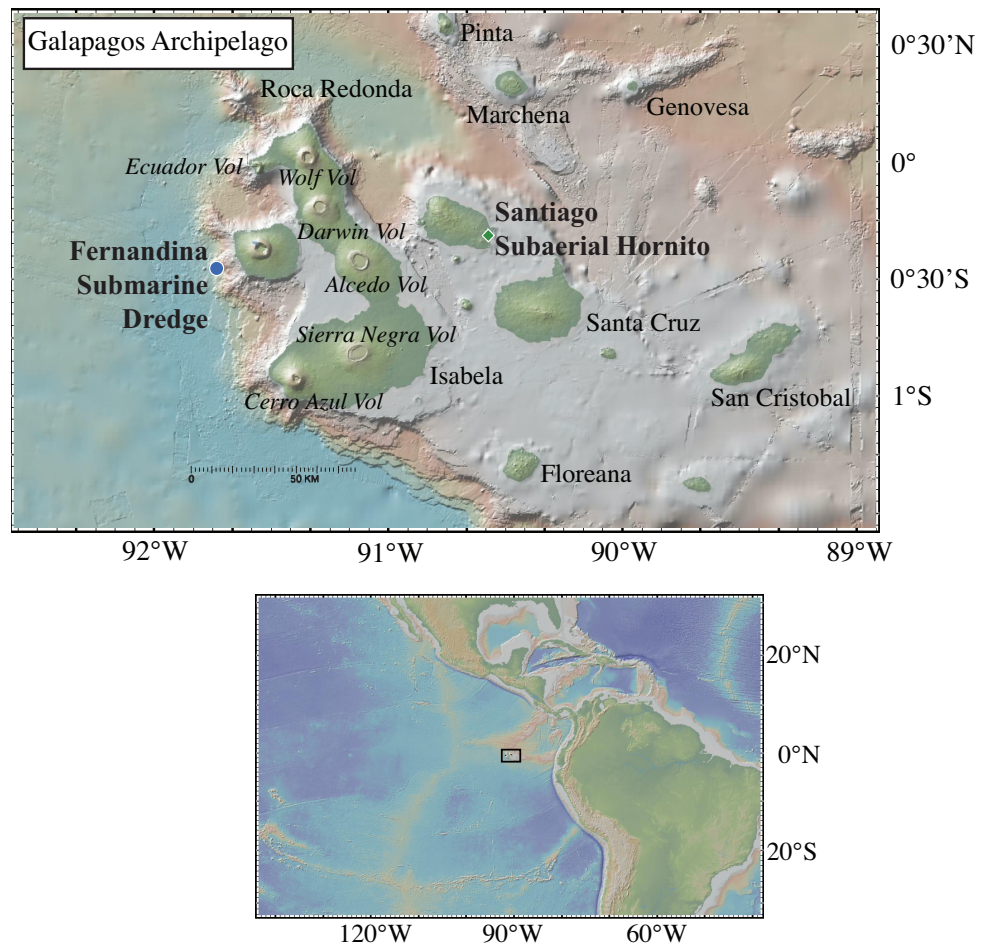


Figure 1-2

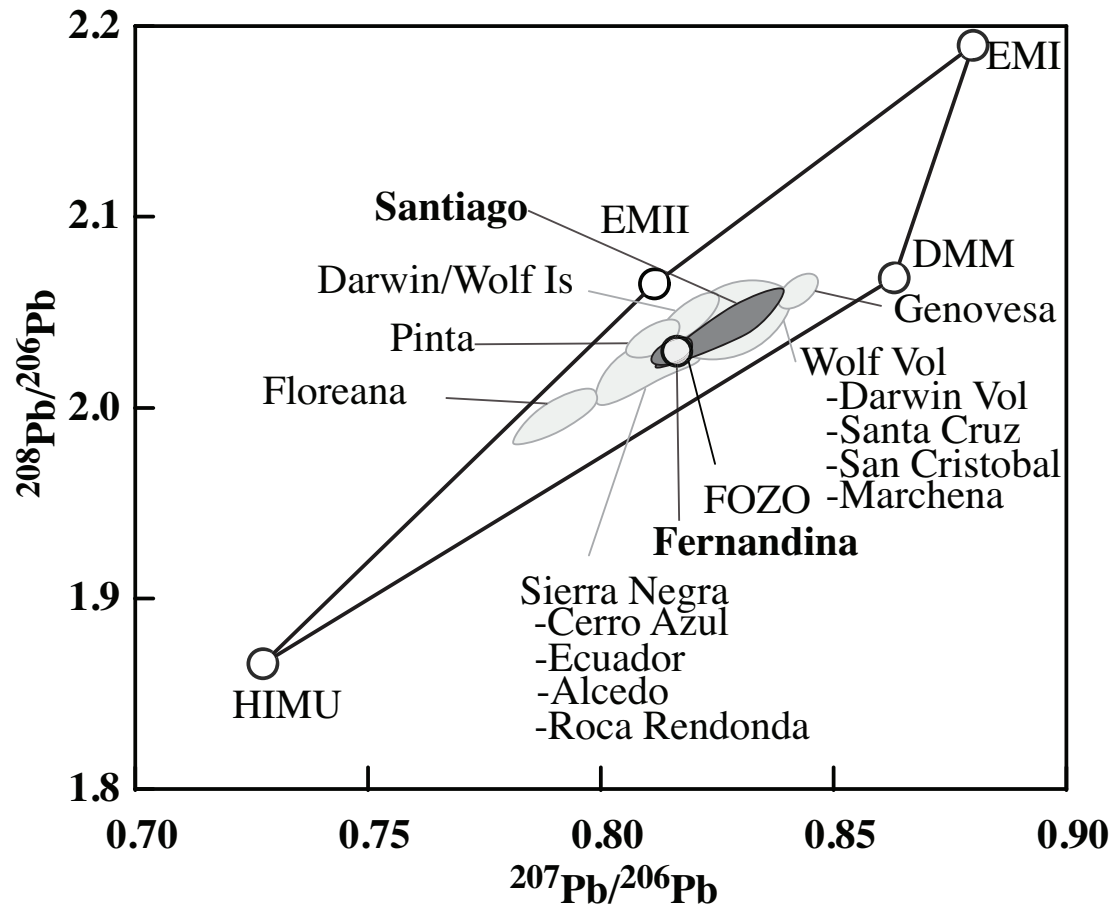
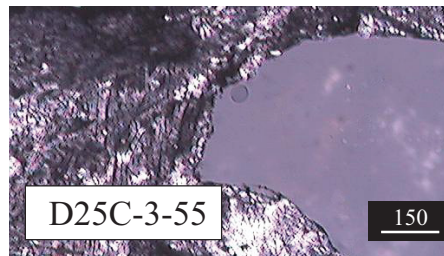
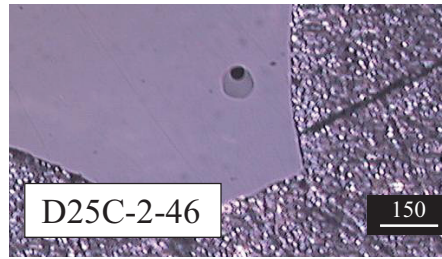
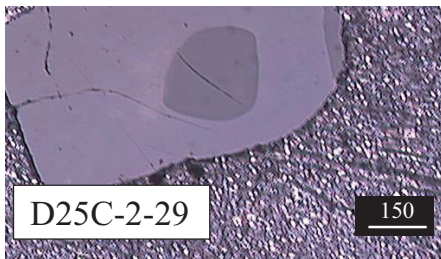
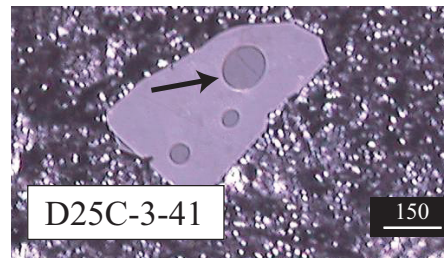
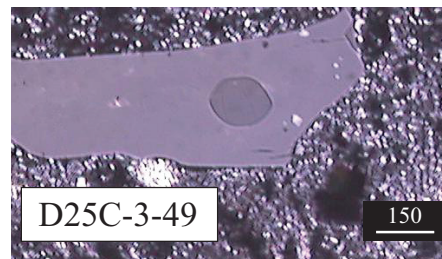
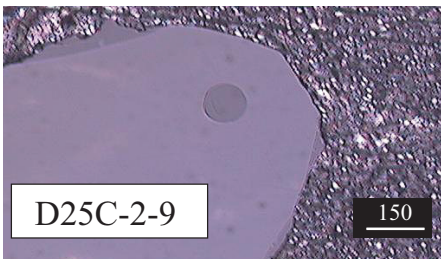


Figure 1-3

Ghost Plagioclase



Normal Fernandina



Depleted Fernandina

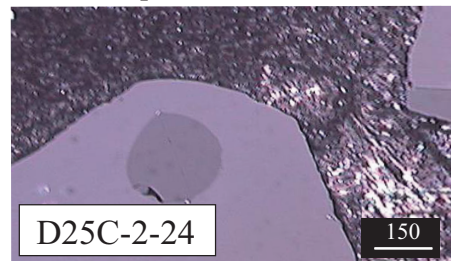
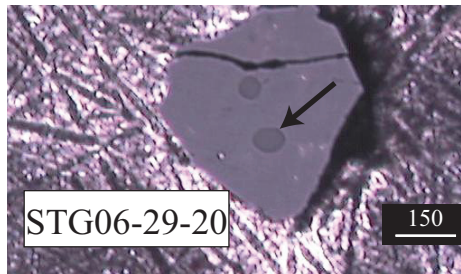
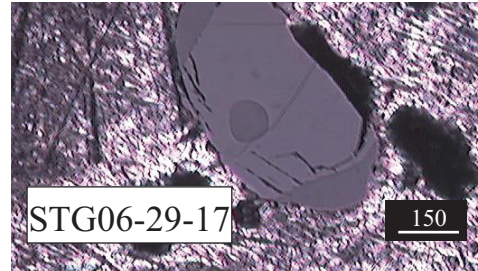
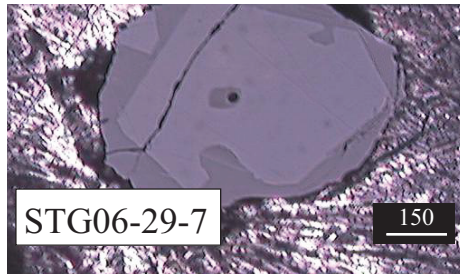
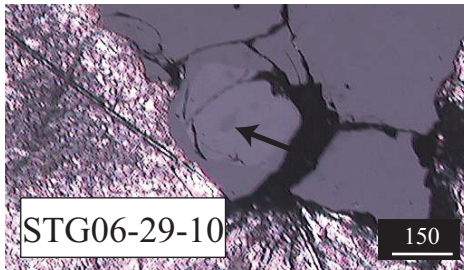


Figure 1-3 continued

Normal Santiago



Enriched Santiago



Ultra-depleted Santiago

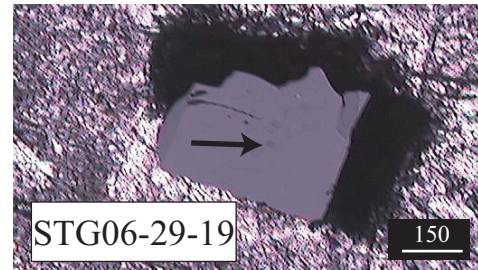


Figure 1-4

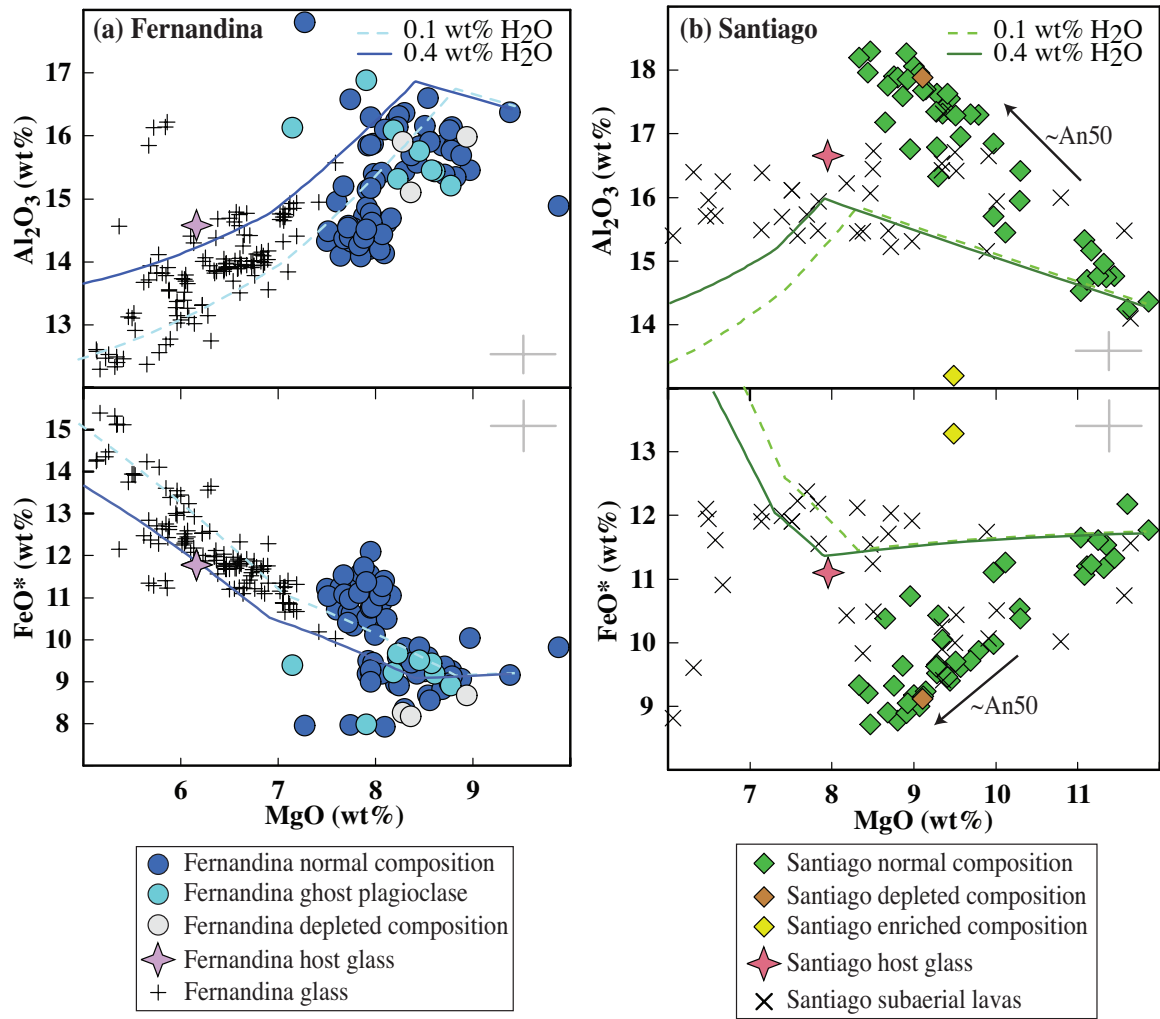


Figure 1-5

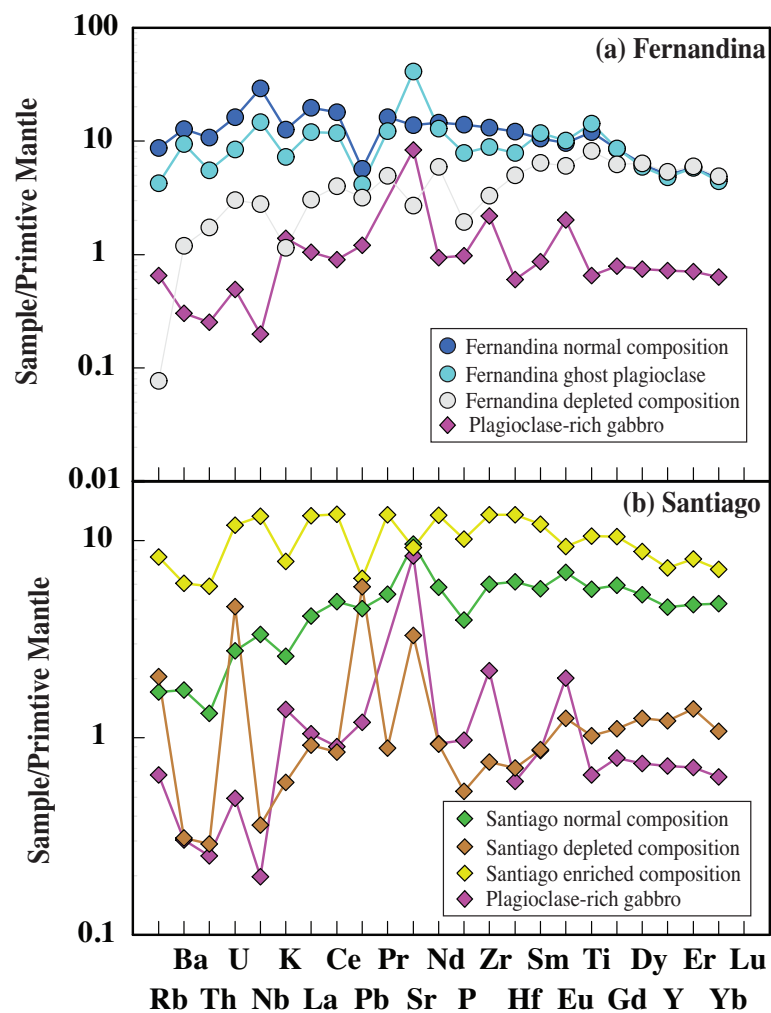


Figure 1-6

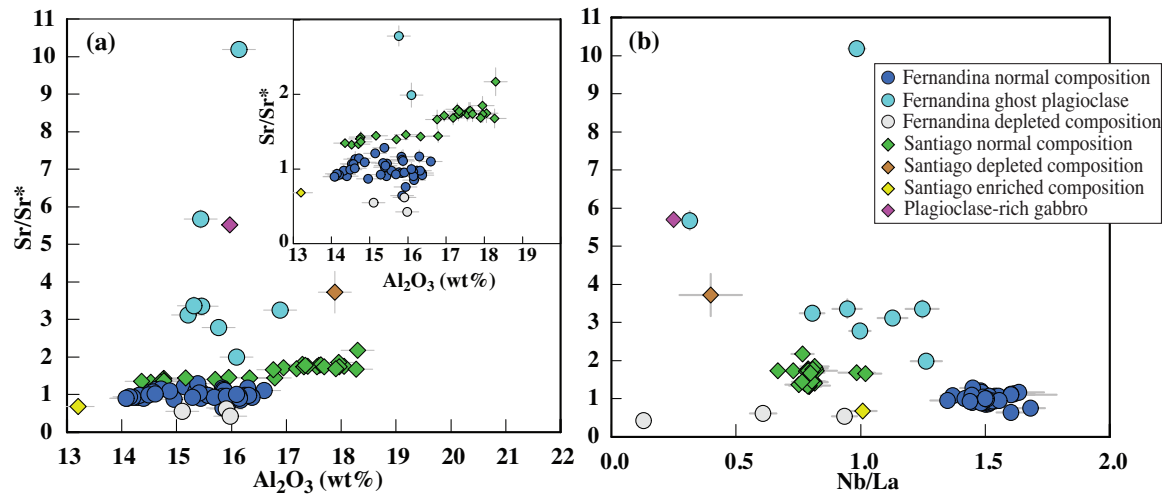


Figure 1-7

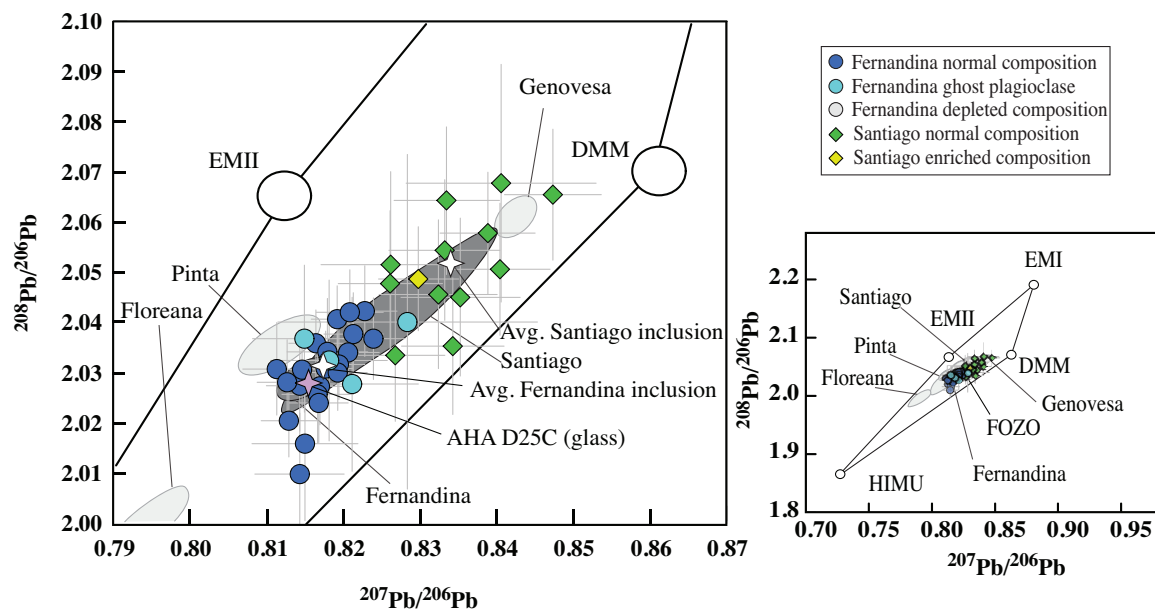


Figure 1-8

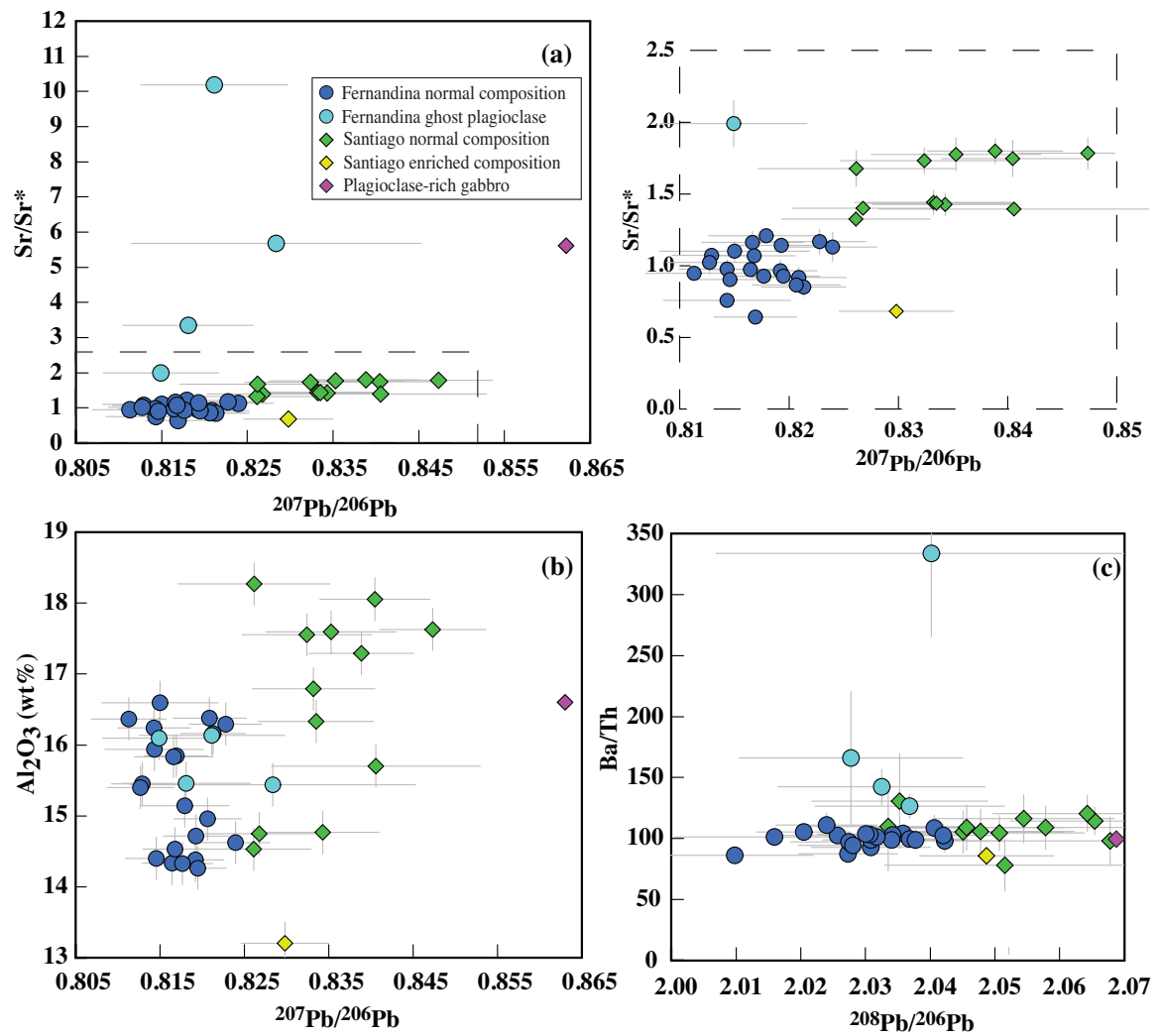


Figure 1-9

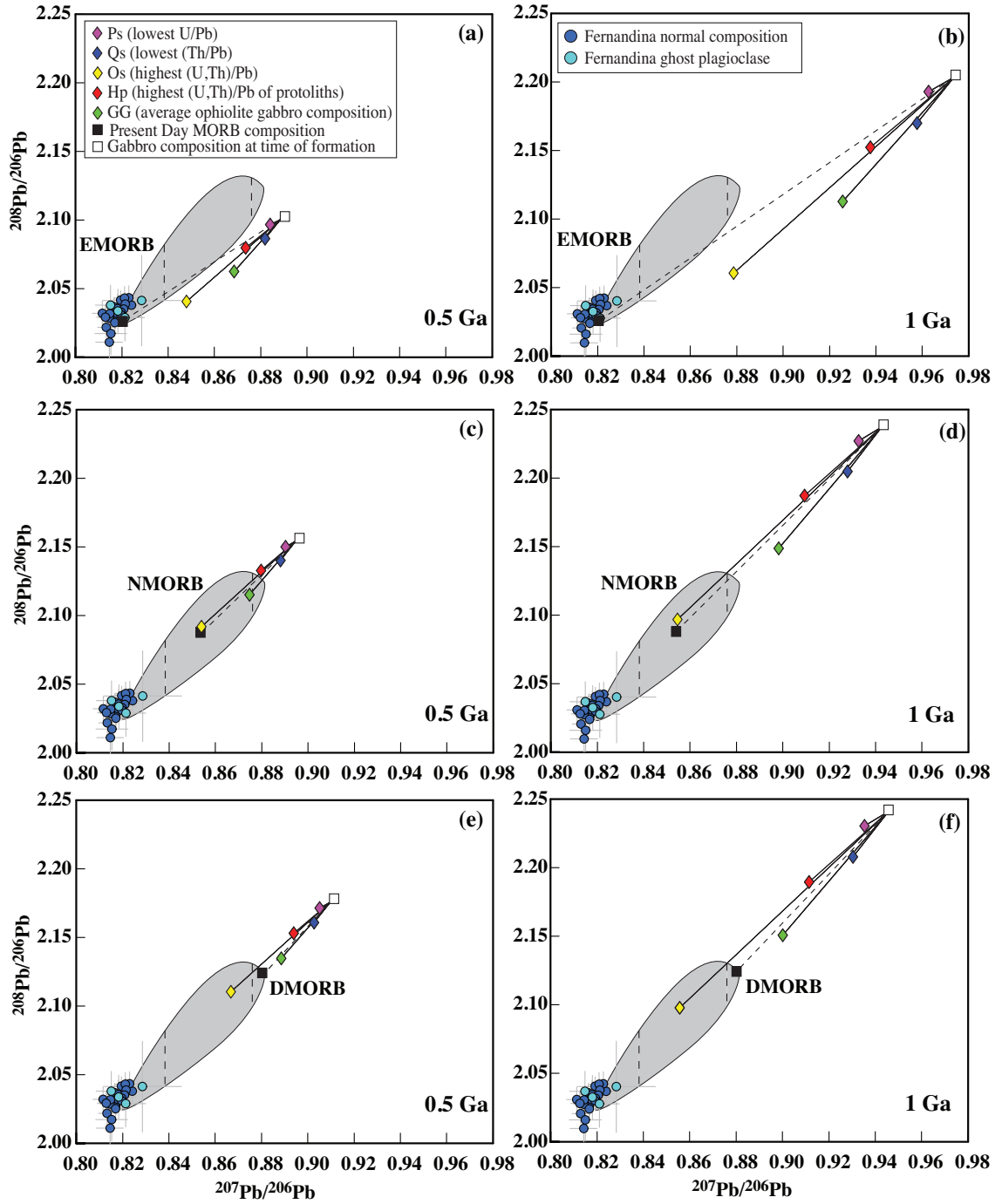


Figure 1-10

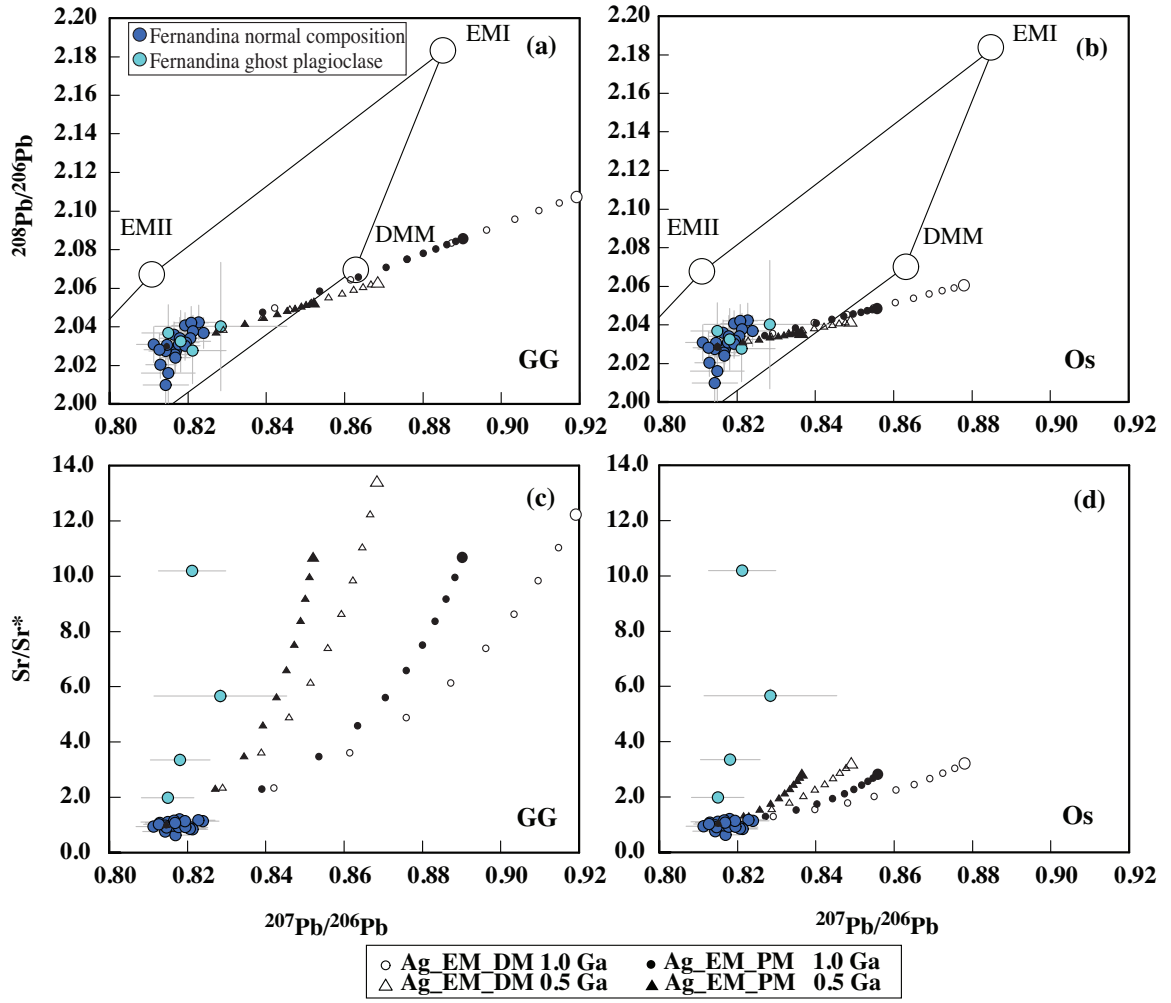
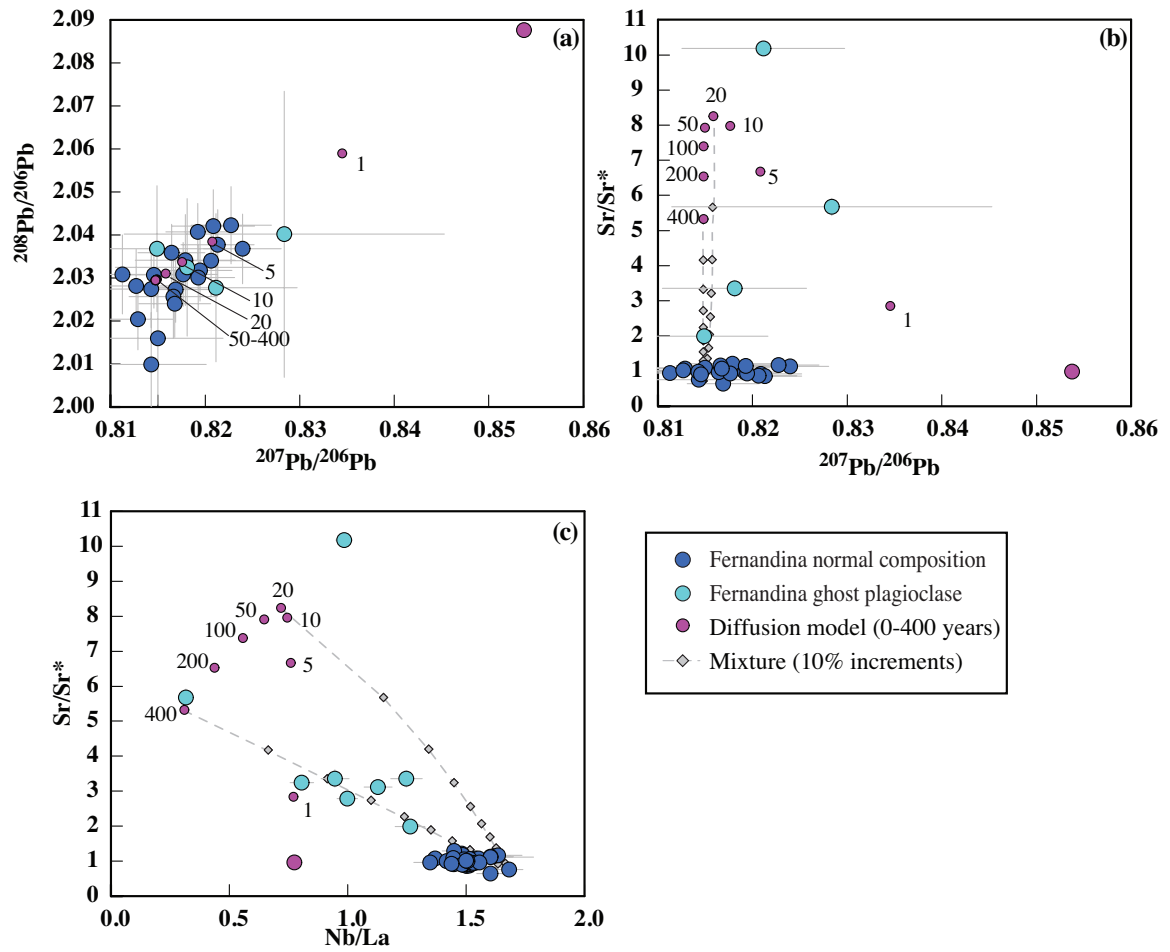


Figure 1-11



TABLES

Table 1. Pb isotope data of Santiago and Fernandina melt inclusion and Fernandina host glass

Sample	$^{207}\text{Pb}/^{206}\text{Pb}$	2σ	$^{208}\text{Pb}/^{206}\text{Pb}$	2σ
<i>Santiago</i>				
STG06-29-02A	0.8262	0.0090	2.052	0.019
STG06-29-02B	0.8343	0.0067	2.035	0.014
STG06-29-03	0.8405	0.0065	2.051	0.013
STG06-29-7	0.8473	0.0063	2.065	0.013
STG06-29-13	0.8268	0.0065	2.034	0.013
STG06-29-16B	0.8406	0.0124	2.068	0.024
STG06-29-16C	0.8335	0.0068	2.064	0.015
STG06-29-17	0.8389	0.0062	2.058	0.012
STG06-29-20	0.8353	0.0078	2.045	0.016
STG06-29-24	0.8324	0.0077	2.046	0.015
STG06-29-25	0.8261	0.0068	2.048	0.015
STG06-29-47	0.8332	0.0072	2.054	0.014
<i>Santiago Enriched</i>				
STG06-29-10	0.8298	0.0052	2.049	0.010
<i>Fernandina Normal</i>				
D25C-2-9	0.8194	0.0034	2.032	0.007
D25C-2-19A	0.8169	0.0038	2.027	0.008
D25C-2-19B	0.8143	0.0058	2.010	0.012
D25C-2-25A	0.8150	0.0069	2.016	0.015
D25C-2-27	0.8177	0.0036	2.031	0.007
D25C-2-30	0.8164	0.0035	2.036	0.007
D25C-2-52A	0.8113	0.0044	2.031	0.009
D25C-2-54	0.8129	0.0036	2.020	0.007
D25C-2-55	0.8179	0.0053	2.034	0.011
D25C-2-59	0.8206	0.0040	2.034	0.008
D25C-2-62	0.8146	0.0037	2.031	0.008
D25C-3-07	0.8228	0.0043	2.042	0.009
D25C-3-10	0.8240	0.0041	2.037	0.008
D25C-3-12	0.8213	0.0039	2.038	0.008
D25C-3-14	0.8192	0.0034	2.041	0.007
D25C-3-31	0.8193	0.0038	2.030	0.008
D25C-3-41A	0.8168	0.0038	2.024	0.008
D25C-3-42	0.8127	0.0039	2.028	0.009
D25C-3-43	0.8209	0.0043	2.042	0.008
D25C-3-49	0.8166	0.0047	2.026	0.010
D25C-3-52	0.8143	0.0043	2.027	0.009

Table 1 (*continued*)

Sample	$^{207}\text{Pb}/^{206}\text{Pb}$	2σ	$^{208}\text{Pb}/^{206}\text{Pb}$	2σ
<i>Fernandina Ghost Plagioclase</i>				
D25C-2-29	0.8211	0.0086	2.028	0.017
D25C-2-46	0.8284	0.0169	2.040	0.033
D25C-3-34	0.8181	0.0076	2.032	0.016
D25C-3-55	0.8149	0.0067	2.037	0.015
<i>Fernandina Depleted</i>				
D25C-2-24	0.8192	0.0135	2.050	0.028
D25C-2-57	0.8120	0.0153	2.052	0.034
<i>Host glass</i>				
AHA D25C glass	0.8155		2.031	

Pb isotopic ratios and error are 2σ standard error for Santiago melt inclusions and Fernandina melt inclusions. Fernandina inclusions separated into normal, ghost plagioclase, and depleted based on the differing trace element signatures of the inclusions. The Santiago inclusion with the trace element enriched composition is also separated from the normal composition Santiago inclusions.

Table 2. Inputs for Recycled Gabbro Isotopic Evolution

Trace Elements‡	E-DMM*	N-DMM**	D-DMM**		
U	0.023	0.0032	0.0018		
Th	0.086	0.0079	0.004		
Pb	0.075	0.018	0.014		
U/Pb	0.3067	0.1778	0.1286		
Th/Pb	1.1467	0.4389	0.2857		
Isotopes	EMORB°	NMORB°	DMORB°		
²⁰⁶ Pb/ ²⁰⁴ Pb	18.911	18.287	17.462		
²⁰⁷ Pb/ ²⁰⁴ Pb	15.514	15.613	15.341		
²⁰⁸ Pb/ ²⁰⁴ Pb	38.319	38.174	37.025		
²⁰⁷ Pb/ ²⁰⁶ Pb	0.8204	0.8538	0.8785		
²⁰⁸ Pb/ ²⁰⁶ Pb	2.0263	2.0875	2.1203		
Gabbro Trace Elements†	Ps°°	Qs°°	Os°°	Hp°°	GG^
U	0.003	0.008	0.043	0.010	0.026
Th	0.013	0.009	0.118	0.030	0.043
Pb	0.163	0.294	0.244	0.160	0.308
U/Pb	0.0184	0.0279	0.1762	0.0625	0.0831
Th/Pb	0.0798	0.0316	0.4836	0.1875	0.1404
Time (Ga)	0.5	1			

‡ In our isotopic calculation, for the back calculation to the isotopic composition of the gabbro at the time of formation, we tested all of the present-day isotopic values of Pacific MORB marked by the field in Fig. 9. Values below 0.8386 we considered EMORB and used trace element values listed for E-DMM for the calculation (bound is equal to the average Pacific EMORB value presented in Donnelly et. al., 2004). Values above 0.8766 we considered DMORB and used trace element values listed for D-DMM for the calculation (Workman and Hart, 2005). Fig. 9 shows the results of calculation using the extreme minimum ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios for the field (EMORB), the extreme maximum ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb of the field (DMORB) and an average NMORB isotopic ratio.

* Donnelly et al., 2004

** Workman and Hart, 2005

° Stracke et al., 2005

°° Hart 1999- Hp highest U/Pb ratio protolith, Ps, lowest U/Pb ratio strip sample, Qs, lowest Th/Pb ratio strip sample, Os, highest U/Pb and Th/Pb ratio strip sample

^ Zimmer, 1995

† at time of formation

Table 3. Partition coefficients, mineral modes and parameters used in critical melting model

Element	Kd solid-melt*				
	Ol	Opx	Cpx	Gt	Co
Ba	0.000005	0.000006	0.0003	0.00007	0
Th	0.000007	0.00002	0.0021	0.0021	0
Nb	0.00005	0.003	0.0089	0.011	0
K	0.00002	0.0001	0.001	0.01	0
La	0.0002	0.0031	0.054	0.0007	0
Sr	0.00004	0.0007	0.091	0.0007	0
Ce	0.00007	0.0021	0.086	0.0026	0
Nd	0.0003	0.0023	0.19	0.027	0
Zr	0.001	0.012	0.26	0.2	0
Sm	0.0009	0.0037	0.27	0.22	0
Eu	0.0005	0.009	0.43	0.61	0
Ti	0.015	0.086	0.4	0.6	0
Dy	0.0027	0.011	0.44	2	0
Y	0.0082	0.015	0.47	2	0
Er	0.0109	0.021	0.39	3.3	0
Yb	0.024	0.038	0.43	6.4	0
Pb	0.0003	0.0014	0.0075	0.0003	0
<i>Eclogite Melting</i>					
Start Mode ^a	0	0	0.4	0.5	0.1
Melting Mode ^b	0	0	0.6	0.1	0.3
α^{**}	0.08				
F(instant) [‡]	0.09				
<i>Lherzolite Melting^c</i>					
Reaction	-1.1	0.5	0.8	-0.2	0
Start Mode	0.53	0.14	0.265	0.065	0
Melting Mode	0.1	-0.3	1	0.2	0
α^{**}	0.02				
F(aggre) [¥]	0.1				

* Halliday et al. (1995) except for quartz (coesite) where partition coefficients were assumed to be zero.

^aEstimated using the thermodynamic model of Sobolev and Babeyko (1994).

^bTaken from the experiments of Yaxley and Green (1998).

** Porosity of the melting model. Represents the amount of melt retained by the solid matrix to prevent compaction

‡ Amount of instantaneous, eclogite melt extracted that hybridizes the overlying mantle

°The reaction coefficients represent the factors for each mineral that are multiplied by the fraction of eclogite melt to determine the amount those minerals are added or subtracted from the original mantle peridotite to obtain the mineral proportions of the hybridized mantle (Yaxley & Green, 1998, Sobolev et al., 2000, Sobolev and Babeyko, 1994). The model results presented in Fig. 10 use 0.1 as the fraction of eclogite melt to represent a 0.1:0.9 proportion of eclogite melt to peridotite. Quantitative modeling of the phase change that occurs during this reaction can be found in Sobolev et al. (2000). The starting mode for the lherzolite melting is taken from Hofmann (1988). This starting mode will change depending on the amount of melt created during eclogite melting. The melting mode was taken from Sobolev et al. (2000).

¥ Amount of aggregate melt extracted from the hybrid mantle, hypothesized by Sobolev et al. (2000) to ultimately form the ghost plagioclase signature.

Table 4a. Starting compositions and results of critical melting model, Gabbro Os.

Starting Compositions					Modeling Results					
Element	Gabbro: Os	9% EM	DM	PM	10/90 EM_DM	10/90 EM_PM	Ag_EM_DM	10% DM	Ag_EM_PM	10% PM
Ba	2.46	26.70	0.56	6.60	3.18	8.61		38.23		103.63
Th	0.12	1.26	0.01	0.08	0.13	0.20		1.60		2.38
Nb	0.76	7.58	0.15	0.66	0.89	1.35		10.60		16.05
K	500.04	5148.60	49.81	240.00	559.70	730.90		6725.00		8781.80
La	1.19	10.76	0.19	0.65	1.25	1.66		13.78		18.31
Sr	155.64	1264.10	7.66	19.90	133.30	144.30		1365.10		1477.90
Ce	4.50	36.78	0.55	1.68	4.17	5.19		43.09		53.54
Nd	3.51	20.67	0.58	1.25	2.59	3.19		21.13		26.04
Zr	19.00	68.20	5.08	10.50	11.39	16.27		76.79		109.65
Sm	1.23	4.21	0.24	0.41	0.64	0.79		4.24		5.25
Eu	0.53	0.98	0.10	0.15	0.18	0.24		0.89		1.14
Ti	1865.53	3565.70	716.30	1205.00	1001.20	1441.10		4547.80		6545.60
Dy	0.00	0.82	0.51	0.67	0.54	0.69		2.10		2.69
Y	12.70	10.29	3.33	4.30	4.02	4.90		15.07		18.34
Er	0.00	0.33	0.35	0.44	0.35	0.43		1.20		1.48
Yb	1.28	0.38	0.37	0.44	0.37	0.43		0.90		1.06
Pb	0.24	2.58	0.02	0.15	0.27	0.39		3.27		4.69
					0.5 Ga	0.5 Ga				
²⁰⁷ Pb/ ²⁰⁶ Pb	0.8479		0.8626	0.8147	0.8488	0.8362				
²⁰⁸ Pb/ ²⁰⁶ Pb	2.0405		2.0687	2.0291	2.0422	2.0365				
					1 Ga	1 Ga				
²⁰⁷ Pb/ ²⁰⁶ Pb	0.8788				0.8778	0.8556				
²⁰⁸ Pb/ ²⁰⁶ Pb	2.0606				2.0611	2.0491				

Table 4b. Starting compositions and results of critical melting model, Gabbro GG.

Element	Starting Compositions				Modeling Results				
	Gabbro: GG	9% EM	DM	PM	10/90 EM_DM	10/90 EM_PM	Ag_EM_DM	10% Ag_EM_DM	10% Ag_EM_PM
Ba	47.44	514.86	0.56	6.60	51.99	57.43	625.81	691.21	
Th	0.04	0.46	0.01	0.08	0.05	0.12	0.64	1.42	
Nb	0.73	7.26	0.15	0.66	0.86	1.32	10.22	15.67	
K	1577.19	16239.30	49.81	240.00	1668.80	1839.90	20051.40	22108.10	
La	1.33	12.06	0.19	0.65	1.38	1.79	15.21	19.74	
Sr	561.77	4562.80	7.66	19.90	463.20	474.20	4742.90	4855.70	
Ce	3.81	31.11	0.55	1.68	3.61	4.62	37.23	47.68	
Nd	2.56	15.07	0.58	1.25	2.03	2.63	16.56	21.48	
Zr	15.30	54.92	5.08	10.50	10.07	14.94	67.84	100.70	
Sm	0.72	2.46	0.24	0.41	0.46	0.61	3.08	4.08	
Eu	0.52	0.96	0.10	0.15	0.18	0.23	0.88	1.13	
Ti	5214.78	9967.30	716.30	1205.00	1641.40	2081.20	7455.50	9453.30	
Dy	0.95	0.78	0.51	0.67	0.53	0.68	2.08	2.68	
Y	6.48	5.25	3.33	4.30	3.52	4.40	13.18	16.46	
Er	0.53	0.29	0.35	0.44	0.34	0.42	1.18	1.47	
Yb	0.45	0.13	0.37	0.44	0.34	0.41	0.84	1.00	
Pb	0.31	3.25	0.02	0.15	0.34	0.46	4.08	5.49	
²⁰⁷ Pb/ ²⁰⁶ Pb	0.5 Ga				0.5 Ga	0.5 Ga			
²⁰⁸ Pb/ ²⁰⁶ Pb	0.8685		0.8626	0.8147	0.8682	0.852			
	2.0624		2.0687	2.0291	2.0627	2.0521			
²⁰⁷ Pb/ ²⁰⁶ Pb	1 Ga				1 Ga	1 Ga			
²⁰⁸ Pb/ ²⁰⁶ Pb	0.9258				0.9225	0.8899			
	2.1124				2.1101	2.0855			

Gabbro- starting plagioclase cumulate composition used for eclogite melting (Os-Hart et al., 1999, GG- Zimmer et al, 1995),
9%EM- is the result of 9% instantaneous melting of eclogite,
DM- depleted mantle composition (Workman & Hart, 2005),
PM- primitive mantle composition (Mcdonough & Sun, 1995),

10/90 EM_DM- composition of 10% eclogite melt, 90% DM forming a hybrid mantle
10/90 EM_PM- composition of 10% eclogite melt, 90% PM forming a hybrid mantle
10% Ag_EM_DM- results of 10% aggregate melting of hybrid eclogite melt/DM mantle
10% Ag_EM_PM- results of 10% aggregate melting of hybrid eclogite melt/PM mantle
Also shown are the resulting Pb isotope ratios of the hybrid mantle for plagioclase cumulates formed at 0.5 and 1 Ga. The Pb isotopes of DM are from Stracke et al., (2005), while the Pb isotopes of the PM mantle are taken to be equivalent to typical Fernandina basalt (Saal et al., 2007). Results of the melting of the hybrid mantle (both DM and PM) shown in figure 10.

Table 5. Diffusion Model

	Kd (plag- melt) ^a	Dplag (1200°C,m ² /sec) ^b	Plagioclase melt ^c	Initial melt ^d	PM normalized output data*									
					1 yr	5 yr	10 yr	20 yr	50 yr	100 yr	200 yr	400 yr		
Ba	0.230	8.09E-19	271	4.69	0.75	0.88	1.06	1.40	2.41	4.03	7.04	9.79		
Th	0.050	3.10E-21	2.88	0.07	0.83	0.83	0.83	0.83	0.83	0.84	0.84	0.84		
U	0.024	3.10E-21	0.98	0.03	1.31	1.31	1.31	1.31	1.31	1.32	1.32	1.32		
Nb	0.030	3.10E-21	47.9	1.24	1.88	1.88	1.88	1.88	1.88	1.88	1.89	1.89		
Ta	0.030	3.10E-21	3.42	0.08	2.16	2.16	2.16	2.16	2.16	2.17	2.17	2.17		
K	0.171	4.38E-16	14693.6	408.33	18.79	47.21	53.76	54.84	54.86	54.86	54.86	54.86		
La	0.106	3.87E-19	35.14	1.60	2.48	2.52	2.57	2.67	2.96	3.44	4.39	5.32		
Ce	0.081	3.87E-19	79.68	4.57	2.73	2.76	2.79	2.86	3.05	3.38	4.01	4.64		
Pb	0.511	1.41E-17	2.48	0.15	1.84	4.76	7.57	11.25	15.11	15.89	15.94	15.94		
Pr	0.104		10.8	0.88	3.27	3.29	3.32	3.37	3.52	3.77	4.27	4.76		
Sr	1.813	3.37E-17	561	63.48	9.34	21.99	26.50	27.83	27.91	27.91	27.91	27.91		
Nd	0.084	2.92E-19	44.96	4.76	3.81	3.83	3.85	3.88	3.99	4.17	4.53	4.88		
Zr	0.004	3.10E-21	350	41.47	3.95	3.95	3.95	3.95	3.95	3.95	3.95	3.95		
Hf	0.015	3.10E-21	7.55	1.27	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50		
Sm	0.056	2.92E-19	10.27	1.88	4.62	4.63	4.63	4.65	4.70	4.77	4.93	5.08		
Eu	0.534	2.92E-19	3.19	0.74	5.43	7.51	9.29	11.21	12.64	13.01	13.53	14.00		
Ti	0.076	3.10E-21	24932.9	5310.42	4.41	4.41	4.41	4.41	4.41	4.41	4.41	4.41		
Gd	0.017		9.65	2.68	5.04	5.04	5.05	5.05	5.08	5.12	5.19	5.27		
Tb	0.038		1.43	0.49	5.25	5.25	5.25	5.25	5.27	5.29	5.32	5.36		
Dy	0.019	3.24E-19	7.78	3.37	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46		
Er	0.012		3.88	2.12	5.04	5.04	5.04	5.04	5.04	5.05	5.05	5.05		
Yb	0.015	5.06E-19	3.16	2.04	4.63	4.63	4.63	4.63	4.63	4.64	4.65	4.65		
²⁰⁷ Pb/ ²⁰⁶ Pb			0.8147	0.8538	0.8345	0.8208	0.8176	0.8159	0.8150	0.8148	0.8148	0.8148		
²⁰⁸ Pb/ ²⁰⁷ Pb			2.0291	2.0875	2.0587	2.0382	2.0334	2.0308	2.0294	2.0292	2.0292	2.0292		

Table 5 (continued)

a (m)	0.001
%melt to solid	1%
%Plag in solid	50%

^a Experimentally determined partition coefficients for plagioclase (An80) at 1200°C from Bedard (2006)

^b Diffusion coefficients from Cherniak and Watson (1994), Cherniak (1995), Cherniak (2002), Cherniak (2003), Giletti and Casserly (1994), and Giletti and Shanahan (1997) for plagioclase at 1200°C. For diffusion coefficients not determined experimentally we used estimates based on cation size and charge (Behrens *et al.*, 1990, Saal and Van Orman, 2004). We assumed diffusion coefficients for Nb, Ta, Zr, Hf, and Ti are similar to those of Th and U. We assumed Eu is 50% Eu+2 and that the diffusion coefficient for Eu+2 is similar to that of Sr

^c Geist *et al.*, (2006) composition AHA31A with isotopic composition of average Fernandina whole rock.

^d 12% aggregated fractional melt of DMM composition from Workman and Hart (2005) with the isotopic values of average Pacific DMM from Stracke *et al.* (2005)

* McDonough and Sun (1995)

CHAPTER 2

Determining the volatile budget of the Galapagos Plume: separating deep and shallow signatures.

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ABSTRACT

We report new major, trace and volatile element contents (H_2O , CO_2 , F, S, Cl), and new Sr, Nd, Pb and He isotopes on 118 submarine glass chips from the Galapagos Archipelago to evaluate the volatile budget of the Galapagos mantle plume. Major, trace and isotopic measurements identify two mixing arrays: Array 1 characterized by submarine glasses from near Fernandina (HHe: high $^3\text{He}/^4\text{He}$ component) and Sierra Negra/Cerro Azul volcanoes (ITE: incompatible trace element enriched component), and Array 2 defined by dredged samples from near Pinta/Wolf-Darwin lineament (WD: low $^3\text{He}/^4\text{He}$ ratios and high D7/4 D8/4 and Th/La ratios) and Genovesa Island (ITD: MORB-like component).

Degassing has significantly lowered the CO_2 content of the lavas and had some effect on the H_2O and S concentrations, but no recognizable impact on the F and Cl contents. The submarine glasses range from being saturated with a sulfide liquid to sulfide undersaturated at the estimated pressures for crystal fractionation (2 Kbars). Assimilation of hydrothermally altered material, assessed using Cl/K ratios and the magnitude of the Sr anomaly ($\text{Sr}/\text{Sr}^* > 1$), affected the volatile contents of a significant number of samples in both arrays. The chemistry of the samples in array 2 suggests shallow mixing occurred, after some degassing and contamination took place in the end-members.

Ratios between volatile and refractory elements with similar incompatibilities are used to estimate the mantle volatile budget of the Galapagos mantle plume. The Fernandina end-member shows a F/Nd ratio (20.1 ± 0.8) and $\text{H}_2\text{O}/\text{Ce}$ ratio (202 ± 26) similar to the value predicted for FOZO. The Sierra Negra/Cerro Azul end-member

shows a high F/Nd ratio (24.9 ± 0.7), and a slightly lower $\text{H}_2\text{O}/\text{Ce}$ ratio (174 ± 24), consistent with values previously considered for other mantle plumes with enriched mantle components. S/Dy and Cl/K ratios for these two end-members are very similar (HHe: S/Dy = 218 ± 21 , Cl/K = 0.057 ± 0.009 ITE: S/Dy = 237 ± 20 , Cl/K = 0.049 ± 0.010) consistent with ratios previously measured in lavas from other ocean islands. The Pinta-Wolf-Darwin end-member has a F/Nd (23.5 ± 0.4), Cl/K (0.066 ± 0.006) and S/Dy ratio (255 ± 40) similar to those of Sierra Negra/Cerro Azul but with a significantly higher $\text{H}_2\text{O}/\text{Ce}$ ratio (230 ± 35). The volatile content of the ITD glasses of the Genovesa end-member have been significantly affected by secondary processes with only few samples showing volatile/refractory element ratios close to those previously reported for MORB. $\text{C}/^3\text{He}$ ratios in Galapagos glasses from the HHe group are, on average, an order of magnitude higher than predicted values for DMM and ranges to the highest values measured for oceanic basalts, indicating that the Galapagos plume contains a mantle component that is more carbonated than the depleted upper mantle.

INTRODUCTION

Volatile elements (H₂O, CO₂, F, S, and Cl) assert a strong influence on mantle melting, magma crystallization, style of eruption, and on the viscosity and rheology of the mantle (Hirth & Kohlstedt, 1996, Gaetani & Grove, 1998, Asimow & Langmuir, 2003, Asimow *et al.*, 2004). A significant amount of research has been devoted to characterizing the volatile content of the mantle (e.g. Michael, 1989, Michael, 1995, Dixon *et al.*, 2002, Saal *et al.*, 2002, Stroncik & Haase, 2004). One approach is to assess variations in volatile to refractory element ratios that share similar incompatibility during mantle melting and fractional crystallization (Michael & Cornell, 1998, Saal *et al.*, 2002, Hauri *et al.*, 2006, e.g. Beyer *et al.*, 2012, Dalou *et al.*, 2012, Rosenthal *et al.*, 2015). However, surface processes, such as degassing, sulfide saturation and, melt-crustal interaction, can significantly modify magmatic volatile/refractory element ratios in the melt (Michael, 1989, Dixon *et al.*, 1995, Dixon, 1997, Michael & Cornell, 1998, Dixon & Clague, 2001, Saal *et al.*, 2002, Stroncik & Haase, 2004, le Roux *et al.*, 2006, Workman *et al.*, 2006). Therefore, it is important to evaluate these processes before extrapolating the observed variability of these ratios in the magmas to their mantle sources.

Oceanic hotspots, such as the Galapagos Archipelago, are ideal locations to study the volatile budget of the mantle because such melting anomalies contain several isotopically unique reservoirs, hypothesized to be the result of both recycled crustal and deep mantle material (e.g. Zindler & Hart, 1986, Hart *et al.*, 1992, Hofmann, 1997, White, 2010). However, only a limited number of studies have examined the volatile budget of mantle plumes in comparison to studies that have focused on mid-ocean ridge basalts (Schilling *et al.*, 1980, Jambon *et al.*, 1995, Dixon & Clague, 2001, Dixon *et al.*, 2002,

Lassiter *et al.*, 2002, Simons *et al.*, 2002, Stroncik & Haase, 2004, Workman *et al.*, 2006, Koleszar *et al.*, 2009, Cabral *et al.*, 2014, Kendrick *et al.*, 2014). These studies suggest that the mantle component characterized by high $^3\text{He}/^4\text{He}$ signature (sometimes called FOZO, PHEM or C and indicative of a "relatively undegassed" lower mantle; e.g. Kurz *et al.*, 1982b, Allègre *et al.*, 1983, Farley *et al.*, 1992, Hart *et al.*, 1992, Hanan & Graham, 1996), has a higher volatile content (H_2O , CO_2 , and Cl) relative to normal MORB (N-MORB) (Dixon *et al.*, 2002, Saal *et al.*, 2002, Simons *et al.*, 2002, Cartigny *et al.*, 2008, Koleszar *et al.*, 2009), while material with an isotopic signature associated with crustal recycling (high Sr and Pb and low Nd and Hf isotope ratios) is thought to be depleted in H_2O contents while possessing variable but higher Cl contents relative to N-MORB (Dixon & Clague, 2001, Dixon *et al.*, 2002, Saal *et al.*, 2002, Stroncik & Haase, 2004, Workman *et al.*, 2006, Cabral *et al.*, 2014, Kendrick *et al.*, 2014). The data is limited for S and F contents in plume basalts, with highly variable S/Dy ratios (ranging from less than to greater than expected N-MORB values) being explained by both degassing and sulfide fractionation. Equally variable F/Nd ratios are attributed to the presence of depleted mantle (F/Nd ~ 18), primitive mantle (F/Nd ~ 21), and variable amounts of recycled material in the source (for values higher than the primitive mantle) (Saal *et al.*, 2002, Workman *et al.*, 2006, Koleszar *et al.*, 2009, Cabral *et al.*, 2014, Kendrick *et al.*, 2014).

Isotopic studies of the Galapagos Archipelago and associated hotspot tracks have found the plume to be heterogeneous with four main isotopic components: a high $^3\text{He}/^4\text{He}$ component and 2 components (characterized by the melts of Pinta and Floreana Island in the Galapagos) with high Sr and Pb, and low Nd and Hf isotope ratios in addition to a

MORB-like end-member that is hypothesized to either be depleted upper mantle or a depleted component intrinsic to the Galapagos plume (e.g. Graham *et al.*, 1993, White *et al.*, 1993, Kurz & Geist, 1999, Hoernle *et al.*, 2000, Blichert-Toft & White, 2001, Harpp & White, 2001, Werner *et al.*, 2003, Saal *et al.*, 2007, Koleszar *et al.*, 2009, Kurz *et al.*, 2009, Vidito *et al.*, 2013). Koleszar *et al.* (2009) presented volatile data of melt inclusions on a sample set from Fernandina (high $^3\text{He}/^4\text{He}$ source) and Santiago islands (MORB-like end member) and found that the measured volatile/refractory element ratios were generally within the range observed in other high $^3\text{He}/^4\text{He}$ ocean island basalts (OIB) (Dixon & Clague, 2001, Simons *et al.*, 2002, Workman *et al.*, 2006), and MORB (Saal *et al.*, 2002), respectively. However, the data was limited to olivine-hosted melt inclusions picked from 1 sample collected at each location.

We present new geochemical information for 118 submarine glasses collected from across the Archipelago to obtain the volatile budget of the Galapagos plume. New major, trace and volatile element concentrations (H_2O , CO_2 , F, Cl, S) and new Sr, Nd, Pb and He isotope data provide new insights into the mantle beneath the archipelago. We first consider the effects of shallow level processes affecting the volatile contents of the basalts (crystal fractionation, degassing, sulfide saturation, and contamination with hydrothermally altered material) allowing us to identify the most pristine samples that let us evaluate the volatile variations in the different mantle sources that contribute to the Galapagos plume.

Geochemical Background

The Galapagos Archipelago is located in the equatorial Pacific <200 km south of the Galapagos Spreading Center (GSC). The archipelago contains 21 emergent volcanoes that sit on a shallow submarine platform. Of these volcanoes, 16 have erupted since the Holocene, making it one of the most active volcanic regions in the world.

The Galapagos Archipelago displays four main compositional components, two distinct end-members (having long-term enrichment of incompatible trace elements) occurring in the southern and northern regions, a high $^3\text{He}/^4\text{He}$ component occurring in the west, and a MORB-like end member prevalent in the center and northeast region of the archipelago (Swanson *et al.*, 1974, Vicenzi *et al.*, 1990, White *et al.*, 1993, Kurz & Geist, 1999, Hoernle *et al.*, 2000, Harpp & White, 2001, Harpp *et al.*, 2002, Harpp *et al.*, 2003, Saal *et al.*, 2007, Gibson *et al.*, 2012). The MORB-like end-member has been proposed to be either the depleted upper mantle or a depleted component intrinsic to the plume. The western component, found primarily near Fernandina Island, is characterized by intermediate $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios and high $^3\text{He}/^4\text{He}$ ratios reaching up to 29 Ra ($^3\text{He}/^4\text{He}$ ratio normalized to the atmospheric ratios, $1.4\text{e-}6$) (Graham *et al.*, 1993, White *et al.*, 1993, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Kurz *et al.*, 2009) corresponding to the FOZO component of Hart *et al.* (1992). The northern component, illustrated by the magmas collected from Pinta Island and the Wolf-Darwin lineaments' seamounts and islands, is intermediate to the other end-members in terms of $^{87}\text{Sr}/^{86}\text{Sr}$, but has elevated $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ at a given $^{206}\text{Pb}/^{204}\text{Pb}$ and represents the lowest $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratios yet measured in the Galapagos (Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Saal *et al.*, 2007). The low Nd and Hf

isotopes and the elevated Pb isotopes that deviate from the northern hemisphere reference line are within the range of the Dupal anomaly (Hart, 1984). The one $^3\text{He}/^4\text{He}$ measurement made for Pinta (6.9 Ra; (Kurz & Geist, 1999)) is at the lower values of the range defining MORB akin to the low variation seen in the southwest Indian Ridge (e.g. Kurz & Jenkins, 1981, Kurz *et al.*, 1982a, Graham *et al.*, 2001, Detrick *et al.*, 2002, Georgen *et al.*, 2003, Colin *et al.*, 2011, Graham *et al.*, 2013). Samples collected from Pinta have higher Pb and Sr isotope ratios than MORB, suggesting that the northern component of the Galapagos plume is not part of the MORB source but part of the plume. The southern component is defined mainly by the magmas of Floreana Island and is characterized by the highest $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ isotopic ratios found in the Galapagos with intermediate $^3\text{He}/^4\text{He}$ ratios (up to 14 Ra), $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios and unusually elevated $^{176}\text{Hf}/^{177}\text{Hf}$ ratios for the measured Nd isotopes (Bow & Geist, 1992, White *et al.*, 1993, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Kurz *et al.*, 2009, Harpp, 2014). This end-member is isotopically most similar to the HIMU mantle component, though its high $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios make it atypical in comparison to other HIMU magmas (Bow & Geist, 1992, Harpp & White, 2001, Harpp *et al.*, 2014). We note that, the radiogenic isotopes of this end-member are restricted to samples collected sub-aerially from the island itself, while the submarine platform near the island has an isotopic flavor similar to Sierra Negra and Cerro Azul Volcanoes (e.g. Harpp *et al.*, 2014). Sierra Negra and Cerro Azul Volcanoes, located on the southern half of the Isabela Island are characterized by intermediate compositions among those of Fernandina, Floreana and Pinta (White *et al.*, 1993, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Saal *et*

al., 2007, Harpp, 2014). The composition of Sierra Negra and Cerro Azul, is either the product of a mixture among several end-member compositions (e.g., Fernandina and Floreana), or a unique mantle source with an intermediate isotopic signature (e.g. White *et al.*, 1993, Harpp & White, 2001). The glasses of this study cover almost all the major geochemical domains in the Galapagos, with the exception of the Floreana component.

ANALYTICAL METHODS

Multiple glass chips were hand-picked from 118 dredged pillow basalts collected during dredging operations of the PLUME02 cruise in 1990 (Christie *et al.*, 1992), AHA-Nemo-2 cruise using the R/V Melville in 2000 (Geist *et al.*, 2006), the DRIFT04 cruise using the R/V Revelle in 2001 (Kurz *et al.*, 2001), and the R/V SONNE cruise SO 158 in 2001 (Werner, 2002). Locations of dredges are reported in Table 1 and shown in Figure 1.

Major, trace and volatile element concentrations were obtained by replicate analyses on 2-4 glass chips picked from the same sample. The glass chips were mounted in indium and analyzed for major, trace and volatile elements. Precision is reported as 2σ standard error. Major element concentrations were determined by the Cameca SX-100 electron microprobe at the Department of Geological Sciences, Brown University. Analyses were performed using 15 kV accelerating voltage, 15 nA beam intensity, and 5 μ m beam diameter for the glasses and PAP correction procedures (Pouchou & Pichoir, 1991, Devine, 1995). Primary standards used for calibration are USGS glasses BCR-2G, BIR-1G and AGV-2, Wilberforce apatite, Amelia albite (Purdue), fayalite (NMNH85276), rhodonite (NMNH104738), and synthetic samples of forsterite (FO97), rutile, and orthoclase (OR1). Smithsonian basaltic glasse VG-2B (USNM 111240) was

monitored as a secondary standard (included in Table 1). Precision for major elements is usually better than 2% for SiO₂, TiO₂, Al₂O₃, FeO, MgO, and CaO, better than 7% for K₂O and Na₂O, better than 10% for P₂O₅ and better than 20% for MnO. Trace elements analyses (Rb, Ba, Th, U, Nb, K, Pb, Sr, P, Zr, Hf, Ti, and REE) were conducted in 3 sessions. The first session was performed on the Cameca 6F Ion Probe at the Department of Terrestrial Magnetism, Carnegie Institution of Washington using techniques of Shimizu and Hart (1982). The second and third sessions were performed at the Graduate School of Oceanography, University of Rhode Island using a Thermo X-Series II quadrupole ICP-MS coupled with a New Wave UP 213 Nd-YAG laser ablation system, using a spot size of 80µm, 60% energy output and 10 Hz repeat rate. The second session was done on the glasses having depleted incompatible trace element contents previously analyzed by SIMS; we found the data to be consistent between both techniques while acquiring several new elements (Pr, Tb, Ho, Tm, Lu) using the LA-ICPMS. The third session was performed to expand the data set. Techniques and procedures used for reducing trace element data, gathered during the LA-ICPMS sessions are described in Kelley *et al.* (2003) using ⁴³Ca as an internal standard for the glasses. Calibration curves were generated using eight natural-composition glasses from the USGS (BIR-1G, BCR-2G, BHVO-2G) and the Max Planck Institute (KL2-G, ML3BG, StHs6/80-G, GOR132-G, T1-G; (Jochum *et al.*, 2006)). Precision for trace element analyses is better than 10%. Volatile element analyses (H₂O, CO₂, F, S, and Cl) were performed on the Cameca 6F Ion Probe at the Department of Terrestrial Magnetism, Carnegie Institution of Washington using a Cs⁺ primary beam. For volatile element analyses we used the technique and standards previously described in Hauri (2002). Precision is typically

better than 9% for H₂O, F, S, and Cl and better than 15% for CO₂.

Many isotope ratios and noble gas measurements are from the literature (Graham *et al.*, 1993, Harpp & White, 2001, Geist *et al.*, 2008, Kurz *et al.*, 2009). New isotope data are presented in Table 1 (new data in table are indicated by bold font). New Sr, Nd, Pb and He isotope analyses for samples collected during the DRIFT04 and AHA-Nemo-2 cruises were conducted at the Woods Hole Oceanographic Institution. Prior to dissolution for Sr-Nd-Pb isotopic analysis, chips were leached for 1 hour in 6N HCL. Conventional ion-exchange procedures were used and the isotope ratios were measured with a Thermo-Finnigan NEPTUNE MC-ICPMS. Typical procedural blanks are <100 pg for Sr analyses, < 30 pg for Nd analyses, and 30-50 pg for Pb analyses. Internal two sigma (2 σ) precision for Sr and Nd isotopic ratios is approximately 5-10 ppm and between 15 and 60 ppm for Pb. The external reproducibility, after normalization for NBS987 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710240$) and La Jolla standards ($^{143}\text{Nd}/^{144}\text{Nd} = 0.511847$), is ~25 ppm and ~15 ppm (2 σ) respectively. External reproducibility for Pb isotopes ranges from 150-200 ppm (2 σ). Two USGS standards (AGV-1: 18.9414, 15.6548, 38.5615 for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ respectively and BCR-1: 18.8215, 15.6356, 38.7309 for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ respectively) were used to verify the Pb procedure and yielded good agreement with literature values. Further information on isotope analytical procedures are given by Hart and Blusztajn (2006). Instrumental mass fractionation for isotopic analyses is corrected for by normalizing to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$, $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Pb isotope analyses were normalized to $^{206}\text{Pb}/^{204}\text{Pb} = 16.9356$, $^{206}\text{Pb}/^{204}\text{Pb} = 15.4891$, $^{206}\text{Pb}/^{204}\text{Pb} = 36.7006$. For He isotopic analyses, glasses are cleaned sonically once in distilled water, weak nitric acid and hydrogen peroxide, followed by a second cleaning in distilled water

and acetone. Chips were selected from cleaned glasses to be crushed in vacuum for measurement of helium abundance and isotopic composition using simultaneous collection of ^3He and ^4He in a fully automated mass spectrometer dedicated to helium measurements at the Woods Hole Oceanographic Institution. A subset of the powders that remained after crushing was melted in vacuum, which yielded the total helium concentration in the glasses and also allows a comparison with ion probe measurements in the glass. A description methods can be found in Kurz *et al.* (2004). Helium blanks measured during the course of the samples run were typically less than $5 \times 10^{-11} \text{ cm}^3 \text{ STP}$.

RESULTS

The major elements, trace element and isotopic compositions of the glasses in this study cover almost the entire compositional range reported for the Galapagos with the exception of the Floreana component (Bow & Geist, 1992, Graham *et al.*, 1993, White *et al.*, 1993, Geist *et al.*, 1998, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Saal *et al.*, 2007, Kurz *et al.*, 2009, Gibson *et al.*, 2012). The majority of the samples, collected from submarine dredges, fall on 2 distinct arrays that are distinguishable from each other both in terms of geographic location and in terms of major element, trace element and isotopic variations (see below). The first array (Array 1) consists of samples with compositions ranging between those from Fernandina Island and Sierra Negra/Cerro Azul volcanoes. The array is further divided into the high $^3\text{He}/^4\text{He}$ ratio (HHe) group and the incompatible trace element enriched (ITE) group using $^3\text{He}/^4\text{He}$ ratios above and below 22 Ra respectively. Samples of array 1 were collected exclusively from the western and southwestern edges of the Galapagos platform,

with the HHe group samples being concentrated around Fernandina Island (Fig. 1). The second array (Array 2) is comprised of samples that compositionally vary from incompatible trace element depleted samples (ITD group) similar to Genovesa Is (i.e., MORB), to incompatible trace element enriched glasses similar to samples from Pinta-Wolf-Darwin Is. (WD group) characterized by low $^3\text{He}/^4\text{He}$ ratios, high Th/La ratios and high D7/4, D8/4. ITD group samples from array 2 were mostly collected within the northeastern seamounts, with the samples of the WD group being exclusively collected in the area of the Wolf-Darwin lineaments. There are four samples collected just to the north of Wolf Volcano on Isabela Island that have unique compositions not matching those of either array; instead, these samples have geochemical characteristics similar to the lavas from Wolf Volcano.

The major element compositions of the glasses in this study indicate that the bulk of the samples are tholeiitic basalt with only a small subset of samples with an alkalic composition (Macdonald & Katsura, 1964). Glasses have MgO contents ranging between 5 and 9.85 wt%. Lavas from array 1 that fall between the compositions of Fernandina and Sierra Negra/Cerro Azul Volcanoes are generally more evolved (average MgO content of 6.16 wt%) than samples from array 2 that fall between the compositions of Genovesa and Pinta-Wolf-Darwin Is. (average MgO content of 8.00 wt%) (Fig. 2). This is consistent with an inferred higher magma flux near the plume center leading to the formation of well-developed magma chambers that produce more differentiated and homogenous lavas in the western sector of the archipelago (Geist *et al.*, 2014). In contrast, lavas from the north and northeastern sectors are generated under a lower magma flux that precludes the

formation of large magma chambers and promotes the eruption of less differentiated lavas.

In order to evaluate the effects of magma differentiation in array 1 and array 2, we calculated the liquid lines of descent (LLD) using PetroLog3 for progressive crystallization of olivine, plagioclase, and clinopyroxene (Danyushevsky & Plechov, 2011). We considered the compositions and water content of a trace element enriched (Fernandina inclusion) and a depleted melt inclusion (Santiago inclusion), compositions both reported in Table 2 (Koleszar *et al.*, 2009), because the isotope signatures of the two arrays are very different (which is discussed below). This indicates that several mantle sources are needed to produce the geochemical variability found in the glasses. Modeling was done for isobaric fractional crystallization at 2 Kbars. Pressure was chosen to be an average of the entrapment pressure of the Fernandina and Santiago melt inclusions that were found to be the least degassed. This is consistent with the average pressure of crystallization of Fernandina lavas from Geist *et al.* (2006) and provides a good fit to the data, though varying this pressure from 500-4000 bars does not significantly change the interpretation of the LLDs. The results of the modeling (Fig. 2) show that the major elements for arrays 1 and 2 cannot be produced by a single LLD. The same conclusion is reached if parameters such as the water content of the starting compositions are varied. Therefore modeled LLDs in addition to highly variable trace elements and isotopic signatures suggests that the glasses of the array 1 and of the array 2 are produced by melting different mantle sources followed by mixing of the melts.

A notable feature of the ITD glasses in array 2 is that, at high MgO contents, these glasses have much higher Al_2O_3 , lower TiO_2 and FeO contents than is predicted by the

LLD. These samples also overlap the range of the Santiago melt inclusions affected by plagioclase cumulate assimilation (Koleszar *et al.*, 2009, Peterson *et al.*, 2014) suggesting that the same process affected these glasses. This is consistent with the strong correlation between Sr/Sr^* ($\text{Sr}_{\text{PM}}/[(\text{Pr}_{\text{PM}}+\text{Nd}_{\text{PM}})/2]$) and Al_2O_3 contents shown by the samples (Fig. 3). Sr/Sr^* is the magnitude of the Sr anomaly on a primitive mantle (PM) normalized diagram and is a metric of plagioclase assimilation ($\text{Sr}/\text{Sr}^* > 1$) and fractionation ($\text{Sr}/\text{Sr}^* < 1$) (Fig. 4). The Santiago melt inclusions show progressive assimilation of plagioclase cumulates indicated by a negative correlation between Sr/Sr^* and MgO contents. The ITD samples have the opposite relationship between MgO and Sr/Sr^* . The highest MgO glasses in this study start out with very high Sr/Sr^* ratios that then decrease with decreasing MgO contents. This indicates that the glasses are most likely not primitive, uncontaminated submarine glasses and the least evolved samples underwent significant plagioclase assimilation (causing the high Sr/Sr^* of the highest MgO samples) followed by crystallization of plagioclase during subsequent differentiation (causing the positive correlation between MgO and Sr/Sr^*).

Array 1 between Fernandina and Sierra Negra/Cerro Azul: HHe Group and ITE Group

The samples that fall on array 1 between the compositions of Fernandina and Sierra Negra/Cerro Azul are enriched in incompatible trace elements (Fig. 4) and have high Nb/Zr (0.11-0.16) and Th/La ratios (0.07-0.10) (Supplementary Fig. S1). Nb can potentially be fractionated from Zr by low degrees of melting. The presence of several alkalic composition glasses implies that there is a range in the degree of melting for the

glasses of this study. However, the alkalic samples also possess distinct isotopic signatures, which suggest they are produced from a unique mantle source. Additionally, Nb/Zr and Th/La ratios are also correlated with isotopic ratios (Supplementary Fig. S2). Therefore variations in the degree of melting cannot entirely explain the range in compositions. As a result, both Nb/Zr and Th/La ratios, in conjunction with their isotopic compositions, reveal the incompatible trace element signatures of the mantle to be long-term characteristics. The high Sm/Yb ratios (1.85-2.75) in these lavas indicate deep melt generation within the garnet-lherzolite stability field. High-Ti anomalies on a primitive mantle normalized trace element diagram are cited as a characteristic of the FOZO mantle source (e.g. Saal *et al.*, 2007, Jackson *et al.*, 2008) therefore the large range in Ti/Gd ratios (2480-3216) could be reflecting the presence of FOZO end-member in the Fernandina mantle source. A recent study of Peters and Day (2014), questioned the significance of the Ti anomalies as a global indicator of a high $^3\text{He}/^4\text{He}$ mantle source, citing instead a combination of unique pressure-temperature melting conditions of OIB's and AFC processes. In the case of the Galapagos lavas, it is very difficult to explain the observed correlation (Supplemental Fig. S3) between $^3\text{He}/^4\text{He}$ and the Ti anomaly by magmatic processes. Therefore the Ti anomalies in the Fernandina samples most likely reflect a characteristic of the Fernandina mantle source.

The end-member compositions of the array 1 are distinctive isotopically, with samples that possess $^3\text{He}/^4\text{He}$ ratios between 22 Ra and 28.82 Ra (HHe group) showing, on average, lower Pb and Sr at similar Nd isotope ratios than samples with $^3\text{He}/^4\text{He}$ ratios less than 22 Ra (ITE group), consistent with previously measured isotopes for Fernandina

and Sierra Negra/Cerro Azul whole rock samples (Fig. 5) (White *et al.*, 1993, Kurz & Geist, 1999, Saal *et al.*, 2007, Kurz *et al.*, 2009).

Array 2 between Genovesa (MORB-like) and Pinta/Wolf, Darwin Islands: ITD Group and WD Group

The samples that fall on array 2 range between the compositions similar to Genovesa and Pinta-Wolf-Darwin Is., with incompatible trace element contents that span from depleted (ITD group), equivalent to those observed in MORB, to enriched compositions (WD group being slightly different from those measured in the ITE group) (Fig. 4, 5, S1 and S2). The maximum Nb/Zr (0.01-0.15) and Ti/Gd (1553-2648) ratios of array 2 overlap values seen in the HHe and ITE groups (Fig. S1). Sm/Yb ratios (0.73-1.77), however, are almost universally lower, which is most likely indicative of melting in the shallower spinel-lherzolite stability zone. The range in Th/La ratios (0.02-0.127) is the most distinctive characteristic of samples from array 2, reaching significantly higher (WD group) and lower (ITD group) than those of the HHe and ITE groups. The high Th/La ratio end-member is a characteristic of lavas from Pinta (Saal *et al.*, 2007), while the low Th/La ratio component is typical of MORB.

Samples from array 2 have $^3\text{He}/^4\text{He}$ ratios (6.87-8.81 Ra) within the range for MORB, with the lowest value found in samples from the WD group (Kurz & Jenkins, 1981, Kurz *et al.*, 1982b, Graham *et al.*, 1993, Kurz & Geist, 1999, Graham *et al.*, 2001, Detrick *et al.*, 2002, Georgen *et al.*, 2003, Kurz *et al.*, 2009, Colin *et al.*, 2011, Graham *et al.*, 2013). Glasses from the ITD group have Sr, Nd and Pb similar to those measured in MORB and Genovesa lavas (Fig. 5) (White *et al.*, 1993). Glasses from the WD group

have Sr, Nd and Pb isotope ratios that overlap with those measured in whole rock samples from Pinta Island and the Wolf-Darwin lineaments. The Pb isotopes are the most distinctive characteristic in samples from WD group with higher $^{207}\text{Pb}/^{204}\text{Pb} = 15.561\text{--}15.620$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.532\text{--}39.282$ for a given $^{206}\text{Pb}/^{204}\text{Pb}$ range = $18.852\text{--}19.366$ (high D7/4 and D8/4 as defined by Hart (1984)) (Cullen *et al.*, 1989a, White *et al.*, 1993, Harpp & White, 2001, Saal *et al.*, 2007). High Th/La ratios and D7/4 and D8/4 values are characteristics commonly been attributed to the presence of an older recycled crustal component in the source of OIB (e.g. Hofmann, 1997). A greater crustal component in the WD group over the lavas from the other groups is consistent with its low $^3\text{He}/^4\text{He}$, though, more data is required to confirm that the WD group has higher $\Delta 7/4$, D8/4 and lower $^3\text{He}/^4\text{He}$ than MORB. These characteristics are also consistent with plumes that contain an Enriched Mantle (EM) component such as the Samoa, Pitcairn and Society plumes (e.g. Stracke *et al.*, 2003, Workman *et al.*, 2006, Kendrick *et al.*, 2014). The range in trace element and isotopic compositions of array 2 completely overlaps with the composition demarcated by samples from the GSC (Figures 5, S1 and S2).

The compositions of submarine samples collected just north of Isabela island do not match the compositional range defined by either array, but they are consistent with those measured in whole rock lavas from Wolf Volcano. The glasses collected from north of Isabela have Th/La ratios and Sr, Nd and Pb isotopic compositions similar to MORB, but with higher Nb/Zr, Sm/Yb and Ti/Gd ratios consistent with a low degree of melting in the garnet-lherzolite stability field of a depleted mantle as previously proposed for Wolf Volcano lavas (Geist *et al.*, 2005, Saal *et al.*, 2007).

The 2 distinct arrays based on major and trace element contents and Sr, Nd, Pb and He isotope data implies that the glasses of this study define four end-members. The end-members of array 1 correspond to the trace element and isotopic compositions of Fernandina Island (HHe group) and Sierra Negra/Cerro Azul volcanoes (ITE group), while the end-members of array 2 correspond to Pinta-Wolf-Darwin Is. (WD group) and Genovesa Is. (ITD group). Thus the data will define volatile budget variations of these mantle source compositions contributing to the Galapagos plume.

Volatiles

There is a large range in volatile concentrations exhibited by the Galapagos submarine glasses, with H₂O concentrations varying from 0.10 to 1.23 wt%, CO₂ from 10.7 to 193.7 ppm, F from 61.4 to 840.7 ppm, S from 715 to 2185 ppm and Cl from 3.80 to 875 ppm. These concentrations are within the range found at other OIBs (Dixon & Clague, 2001, Dixon *et al.*, 2002, Hauri, 2002, Simons *et al.*, 2002, Workman *et al.*, 2006, Cabral *et al.*, 2014, Kendrick *et al.*, 2014). Concentrations of H₂O, F, Cl, and S generally increase with decreasing MgO wt% as is predicted by calculated LLDs from primitive melt inclusions representing the HHe and the ITD end member component (Koleszar *et al.*, 2009) (Fig. 6; parameters such as partition coefficients for volatile elements for LLD models included in Table 2), though the data do to deviate from the LLD models. This deviation is most likely due to a combination of shallow level processes and source heterogeneity. To overcome the effect of crystal fractionation we consider ratios of volatile to refractory elements with similar incompatibility during melting and crystallization (Nb, Ce, Nd, K, and Dy with CO₂, H₂O, F, Cl, and S, respectively, Fig. 6) (Schilling *et al.*, 1980, Michael,

1995, Michael & Cornell, 1998, Danyushevsky *et al.*, 2000, Saal *et al.*, 2002, Hauri *et al.*, 2006, Workman *et al.*, 2006). Once we account for the effect of shallow level processes such as degassing, sulfide saturation and assimilation of hydrothermally altered material, the volatile to refractory element ratios provide a straightforward approach to determine the volatile budgets of the different mantle components forming the Galapagos plume.

DISCUSSION

Shallow level process

Degassing

The partitioning of H₂O, CO₂, S, F, Cl from melt to a gas phase is controlled by the melt and gas composition, fO_2 , solubility and speciation of the volatiles, temperature and pressure (e.g. Unni & Schilling, 1978, Rowe & Schilling, 1979, Stolper & Holloway, 1988, Carroll & Webster, 1994, Dixon *et al.*, 1995, Dixon, 1997, Rosenthal *et al.*, 2015). Primitive CO₂/Nb ratios are predicted to range from ~300 - 600 (Saal *et al.*, 2002, Cartigny *et al.*, 2008). Only a few samples from the ITD group, those having the lowest Nb contents, are in this CO₂/Nb range, consistent with undegassed melt, with all other samples having much lower ratios (Fig. 6B). To assess the pressure of CO₂-H₂O saturation and the effects of degassing on the CO₂ and H₂O contents of the samples, we used the model of Dixon *et al.* (1995) to determine the pressure of CO₂-H₂O saturation and VolatileCalc (Newman & Lowenstern, 2002) to generate degassing paths that pass through the compositions of the samples. For the primitive compositions of the model, we used samples from the ITD and ITE groups with the highest concentrations of CO₂ (ITD group: PL02-9-29, ITE group: D49A). Calculated degassing paths for both open

and closed system degassing predict extensive degassing of CO₂ with only minor degassing of H₂O occurring during closed system degassing (Fig. 7A). To get changes in H₂O contents on the order of 26% (relative to the pressure), as is shown by the model, requires a melt to have a large H₂O content initially and be erupted at a lower pressure than is typical of the high H₂O content samples. Therefore, the samples are extensively degassed for CO₂ and minimally degassed for H₂O. The few samples in the ITD group with CO₂/Nb ratios ≥ 300 can potentially be used to assess the CO₂ content of the depleted component of the Galapagos mantle. The pressure of CO₂-H₂O vapor saturation ranges from 22 to 472 bars.

F, Cl and S are usually considered not to be affected by degassing processes in hotspot and ridge settings for samples erupted at pressures higher than ~ 50 bars (Unni & Schilling, 1978, Rowe & Schilling, 1979, Carroll & Webster, 1994). None of the Galapagos samples have unusually low F/Nd or Cl/K ratios, suggesting that they have not degassed significant amounts of these volatile elements. However, there are a number of samples that were collected over a range of pressures that have unusually low S/Dy ratios. By comparing the calculated CO₂-H₂O saturation pressure to S/Dy ratios of both the melt inclusion data from Koleszar *et al.* (2009) and the glass data of this study it becomes apparent that for pressure of saturation below ~ 400 bars S/Dy ratios switch from being relatively constant to decreasing with decreasing saturation pressure (Fig. 7B; samples of this study filtered for samples with Sr/Sr* > 1 , see section on Assimilation). The trend in the glasses and melt inclusions is not due to mixing of melts with variable S/Dy ratios because both melt inclusions from Santiago (MORB component) and Fernandina (high ³He/⁴He component) show relatively constant S/Dy ratios at high saturation pressures.

This suggests that S begins degassing at higher pressures than originally thought and that the low S/Dy ratios (<175) in the glasses of this study are the result of S degassing.

An interesting observation can be made when comparing the calculated CO₂-H₂O saturation pressure with the collection pressure for glasses from the Galapagos and other OIBs with MORB samples (Fig. 7C). Most samples erupted at mid-ocean ridges (EPR, GSC etc.) on average fall above a 1:1 line indicating that they are supersaturated with CO₂-H₂O vapor at the depth of eruption, representing melt that migrated from the magma chambers to the surface quickly enough to prevent melt-vapor diffusive equilibration (le Roux *et al.*, 2006 and references therein). This is also shown by the samples from the ITD group with all but one of the samples having CO₂/Nb ratios ≥ 300 being supersaturated at the pressure of eruption. In contrast, samples analyzed from different OIBs, including the Galapagos glasses in this study, fall along the 1:1 line, indicative of melts that were able to equilibrate at every pressure until eruption and quenching. This suggests a fundamental difference between OIB and MORB in the ratio of the melt transport rate to the CO₂-H₂O diffusive gas-melt equilibration rate, the implication being that melts are upwelling in OIBs at a rate that allows for continuous gas-melt re-equilibration or that the composition of OIB melt allows for faster CO₂ – H₂O diffusion.

Samples that fall below a 1:1 line between pressure of saturation and pressure of collection are thought to have either erupted at a shallower level and rolled down slope or are undersaturated in CO₂-H₂O. Of the samples from this study that fall below the 1:1 line, none of them are likely undersaturated in volatiles. All were either collected from local topographic lows or were collected from sections of steep topography, making it likely that these rolled downhill.

Sulfide Saturation

Sulfide saturation in basaltic melt is dependent on temperature, pressure, oxygen fugacity, sulfur fugacity and bulk composition (Wallace & Carmichael, 1992, Carroll & Webster, 1994, Mavrogenes & O'Neill, 1999, Holzheid & Grove, 2002, Liu *et al.*, 2007, Moune *et al.*, 2009).

To evaluate if the glasses reached sulfide saturation, we calculated the concentration of sulfur needed to saturate with a sulfide liquid using the model of Liu *et al.* (2007). The input parameters of this model include temperature, pressure, H₂O content in the melt and a compositional parameter referred to as MFM that describes the melt bulk composition using cation mole fractions to represent the ratio of network modifiers to network formers. To calculate the pre-eruptive temperature of the melt, we use an equation from Wallace and Carmichael (1992), which utilizes the predictable variation of Al₂O₃ and MgO content of a melt undergoing crystal fractionation, with an incorporated correction for the effect of H₂O content on the liquidus (Medard & Grove, 2008). Calculated temperatures vary from 1092-1255 °C with an estimated error in the calculation of 9 °C. We are interested in the pressure at which fractional crystallization is occurring and where sulfides could be separated from the melt. Therefore, we use 2 Kbars of pressure, which is the pressure used to calculate the LLDs in the results section above. Varying pressure between 2 Kbars and the pressure of vapor saturation (Dixon *et al.* (1995)) for individual samples does not significantly changes the results of the model and does not change our interpretation of those results. Model input H₂O contents are taken directly from measurements. We use an average value of Fe⁺³/ΣFe measured by μ-

XANES ($\text{Fe}^{+3}/\Sigma\text{Fe} = 0.17$) for the glasses (Peterson et al., in prep) to determine the amount of ferric and ferrous iron to input for the calculations. The total variation in MFM is 7.07-8.62. The sulfide saturation model of Liu *et al.* (2007) was independently verified by the experiments of Moune *et al.* (2009). We consider this the best approximation because it is the only available model that incorporates the effect of water on sulfide saturation. The samples range from just sulfide saturated to under-saturated in a sulfide liquid at 2 Kbars of pressure (Fig. 8). None of the samples identified as having partitioned S into a gas phase are sulfide saturated. It seems that samples from array 1 are closer to sulfide liquid saturation than those from Array 2.

Assimilation

The variation in volatile elements with refractory elements in Fig. 6 indicates that while H_2O , Cl, and S are correlated with Ce, K, and Dy, respectively, there is a large dispersion in the volatile data at a given refractory element value. Only F shows very little dispersion at a given value of Nd. Because degassing of H_2O , Cl, and S (for the majority of the glasses) has been shown to be negligible, the dispersion is likely indicative of a secondary process affecting the volatile element contents and/or variation in the volatile/refractory element ratios of primary melts.

High Cl/K and Cl/Nb ratios are used as indicators of assimilation of hydrothermally altered material due to the high concentration of Cl in seawater and brines percolating through the oceanic crust (Quinby-Hunt, 1983) compared to magmas. Uncontaminated mantle sources have Cl/K ratios that range from approximately 0.01 (MORB source) to 0.08 (enriched mantle source) (Michael, 1989, Michael & Cornell,

1998, Stroncik & Haase, 2004, Workman *et al.*, 2006). Oceanic lithosphere that has interacted with seawater tends to have large amounts of Cl, and thus, a much higher Cl/K ratio than uncontaminated melts (Michael, 1989, Jambon *et al.*, 1995, Michael & Cornell, 1998, Kent *et al.*, 1999a, Kent *et al.*, 1999b, Coogan *et al.*, 2003, Gillis *et al.*, 2003, Straub & Layne, 2003, Stroncik & Haase, 2004, le Roux *et al.*, 2006, Bonifacie *et al.*, 2008, John *et al.*, 2011). Therefore the assimilation of seawater-altered material is strongly reflected in the Cl/K ratios of the lavas.

All of the samples in this study show Cl enrichment to some degree beyond what would be expected for an uncontaminated melt. The ITD group (Cl/K = 0.024-0.772) and the WD group (Cl/K = 0.032-0.211) show large ranges in Cl/K. The ITE and HHe groups have overlapping ranges in Cl/K ratios (Cl/K = 0.033-0.149). While a Cl/K ratio up to 0.09 has been attributed to the mantle source of other ocean islands (Workman *et al.*, 2006), the total variations in Cl/K ratios of glasses analyzed for each compositional group do not correlate with any indicators of source or extent of melting (such as incompatible trace element and radiogenic isotope ratios). When considering only the samples with the lowest Cl/K ratios for each compositional group, then a very weak correlation is apparent between Cl/K ratios and Sr and Nd isotopes (Fig. 9). This suggests that the extreme variation in Cl/K within the different groups is not due to variation in the Cl concentration of the melt source, but rather is due to variable contamination by hydrothermally altered material, such as assimilation of 1.6% of a 50% NaCl brine, which could explain the highest Cl/K sample of the ITD group (Fig. 10).

There is a statistically significant correlation between Cl/K and H₂O/Ce for the samples from array 1 (ITE and HHe groups) (Fig. 10), suggesting that hydrothermally

altered material might have affected not only the Cl/K but also the H₂O/Ce ratios of the melts. The range in H₂O/Ce, like Cl/K for these groups overlaps (H₂O/Ce = 109-328) with the maximum measured ratios for the ITE and HHe group glasses being higher than previously observed in other trace element enriched OIB (Dixon *et al.*, 2002, Saal *et al.*, 2002, Simons *et al.*, 2002, Workman *et al.*, 2006). H₂O/Ce also does not correlate with isotopic ratios within a given group, as would be expected if the range in H₂O/Ce ratios within each group is due only to mixing between a volatile rich and volatile poor melt. Thus, the correlation of H₂O/Ce with Cl/K is most likely caused by the assimilation of hydrothermally altered rock in addition to any mixing that may be occurring. The samples in the ITE and HHe groups with Cl/K ratios lower than 0.08 (highest Cl/K ratio attributed to a plume source (Stroncik & Haase, 2004)), as a result, represent the least contaminated samples for Cl and H₂O. Cl/K ratios do not correlate with F/Nd or S/Dy ratios for these groups.

In the ITD group, CO₂/Nb, H₂O/Ce, F/Nd and S/Dy ratios weakly correlate with values of Sr/Sr* ≥ 1 , while Cl/K ratios are hugely variable reaching values up to 0.772, ten times higher than expected for uncontaminated samples (Fig. 11). The high Sr/Sr* values in the ITD group indicate that these samples have experienced interaction with a plagioclase-rich cumulate before subsequent crystallization of plagioclase (as is discussed in Results and shown in Fig. 3) (Saal *et al.*, 2007). Products of hydrothermal alteration, such as amphibole and serpentine, serve to concentrate volatile elements in the oceanic crust (e.g. Gillis & Meyer, 2001, Adam & Green, 2011, John *et al.*, 2011, Alt *et al.*, 2012). Although the mode produced by hydrothermal alteration is highly variable, plagioclase is ubiquitous in the oceanic crust, and occurs as both a primary (magmatic)

and secondary (hydrothermal) phase (Alt *et al.*, 1996a, Alt *et al.*, 1996b, Bach *et al.*, 2003, Coogan *et al.*, 2003, Barker *et al.*, 2008, Heft *et al.*, 2008, Kirchner & Gillis, 2012). The assimilation of plagioclase and associated hydrothermally altered cumulates, therefore, can produce Sr/Sr* values > 1 accompanied by high volatile/refractory element ratios. The high volatile refractory element ratios with the highest Sr/Sr* values in the ITD group lavas having high MgO content are, therefore, most likely caused by the early assimilation of hydrothermally altered crust followed by crystal fractionation. These results are supported by the extremely high Cl/K ratios an order of magnitude above the 0.02 expected for a MORB source (Michael, 1989, Michael & Cornell, 1998, Stroncik & Haase, 2004). The broadly positive correlation between Sr/Sr* and CO₂/Nb, H₂O/Ce, F/Nd and S/Dy, however, cannot be explained by crystal fractionation (which will only decrease Sr/Sr*), rather this correlation suggests the higher MgO melts that interacted with plagioclase cumulates are mixing with more evolved ITD melts less affected by contamination.

The dispersion in the volatile to refractory trace element ratios defined by the glasses from the WD group most likely are the result of mixing with an ITD melt after the ITD samples are contaminated and/or before they are degassed. The WD group end-member has Cl/K, H₂O/Ce, F/Nd and S/Dy ratios essentially consistent with those previously reported for other OIB (Cl/K ≤ 0.08, H₂O/Ce ~200, F/Nd ≥ 21, S/Dy ~260) (Dixon *et al.*, 2002, Simons *et al.*, 2002, Stroncik & Haase, 2004, Workman *et al.*, 2006, Koleszar *et al.*, 2009, Cabral *et al.*, 2014, Kendrick *et al.*, 2014). Mixing of this enriched end-member with melts from the ITD group would cause the increasing CO₂/Nb ratios and decreasing F/Nd ratios as WD samples approach the isotopic signature of the ITD

end-member (Fig. 13 and 15). Because the highest CO_2/Nb ratio of the ITD group represents the least degassed of the ITD glasses and may be the product of contamination (due to the high Sr/Sr^*) this is evidence that the mixing between the WD and ITD groups must have occurred after the ITD group was contaminated and/or before it degassed. The range in the WD group also overlaps the volatile variation of lavas from the GSC (Fig. 5, 9, S1 and S2).

Mantle Composition

A number of volatile studies in OIB indicate that isotopic heterogeneities in the mantle have well-defined, associated volatile/refractory element ratios (Dixon & Clague, 2001, Dixon *et al.*, 2002, Simons *et al.*, 2002, Workman *et al.*, 2006, Koleszar *et al.*, 2009, Cabral *et al.*, 2014, Kendrick *et al.*, 2014). In this study, after accounting for variability caused by shallow level processes, unique volatile/refractory element ratios are apparent in the end-member compositions of array 1 and 2 (Table 3). For array 1, the largest contrast is in F/Nd ratios (Fig. 12) and $\text{H}_2\text{O}/\text{Ce}$ ratios (Fig. 13). The HHe group end-member (Fernandina mantle component) possesses an $\text{H}_2\text{O}/\text{Ce}$ ratio (202 ± 26) and a F/Nd ratio (20.1 ± 0.8) that is close to that generally predicted for the FOZO mantle component based on a limited number of studies ($\text{F}/\text{Nd} \sim 21$, $\text{H}_2\text{O}/\text{Ce} \sim 200$, McDonough and Sun, 1995, Dixon *et al.*, 2002, Simons *et al.*, 2002, Koleszar *et al.*, 2009). The ITE group end-member (Sierra Negra/Cerro Azul mantle component), in contrast, shows a low $\text{H}_2\text{O}/\text{Ce}$ ratio ($\text{H}_2\text{O}/\text{Ce} = 174 \pm 24$) and the highest F/Nd ratio (24.9 ± 0.7) of all the samples analyzed. S/Dy ratios and Cl/K ratios are similar between the HHe group (S/Dy

$= 218 \pm 21$, $\text{Cl/K} = 0.057 \pm 0.009$) and the ITE group ($\text{S/Dy} = 237 \pm 20$, $\text{Cl/K} = 0.049 \pm 0.010$) end-members.

For the ITE group samples, there is a correlation between $^3\text{He}/^4\text{He}$ ratios and $\Delta 7/4$ (Fig. 12), which suggests that melts from the WD and HHe groups are influencing the composition of the ITE group samples. This is consistent with the lower $\text{H}_2\text{O/Ce}$ ratio of the ITE group, which is at the upper limit of what has been measured in OIB with EM mantle components, such as Samoa (58-157) (Workman *et al.*, 2006), Pitcairn (80) and Society (60) (Kendrick *et al.*, 2014), and EM-influenced MORB such as the Shona, Discovery and Great Meteor anomalies (<100) (Dixon *et al.*, 2002). The F/Nd ratio of the ITE end-member, however, is distinct from that of either the WD or HHe groups. The sample with the highest F/Nd ratio in the ITE group ($\text{F/Nd} = 26.5$), has a $^3\text{He}/^4\text{He}$ ratio = 13.1 Ra , whereas samples from this group having lower and higher $^3\text{He}/^4\text{He}$ ratios have lower F/Nd ratios (Fig. 12). It has also been suggested that the ITE mantle component could be the result of a mixture between the HHe group (Fernandina) and the HIMU mantle component of Floreana (e.g. Harpp and White, 2001). The F/Nd ratio of the ITE end-member, though higher than the HHe end-member, is lower than the value found for the HIMU end-member represented by Mangaia melt inclusions (Austral Islands) ($\text{F/Nd} = 30$) (Cabral *et al.*, 2014). The volatile/refractory element ratios of the ITE end-member can therefore be due to either a mixture of melts from several sources or a unique, intermediate composition.

The high $^3\text{He}/^4\text{He}$ ratio of the Fernandina group is thought to be due to the presence of a volatile-rich primitive mantle component. Using the volatile/refractory element ratios of the HHe end-member and the K, Ce, Nd, and Dy content of the

primitive mantle (240 ppm, 1.675 ppm, 1.25 ppm and 0.674 ppm respectively of (McDonough & Sun, 1995)) constrains the Cl, H₂O, F and S content of the HHe mantle source to 13.7 ± 2 ppm, 338 ± 44 ppm, 25.3 ± 1 ppm and 147 ± 14 ppm respectively. These values are generally lower than the estimated volatile content of the primitive mantle (17, 750, 25, 250 ppm) (McDonough & Sun, 1995). Understanding how the volatile/refractory element ratios of the ITE group are related to the volatile content of the ITE mantle component, in contrast, is more complex than the HHe group. The differences in F/Nd and H₂O/Ce between the ITE and HHe groups are probably not the result of a source with homogenous volatile contents and heterogeneous trace element contents because the isotopic signature of the ITE group would suggest that the ITE mantle source is enriched in trace elements over the source of the HHe group. This would produce both lower F/Nd and H₂O/Ce ratios, which is not observed. However, quantifying the difference in the volatile content of the ITE group mantle source from the HHe group mantle source is difficult because this end-member is either the product of a mixture (e.g., Fernandina and Floreana), or a unique intermediate mantle source, which makes the trace element composition of the source unconstrained. Therefore we limit the estimation of the volatile content of the ITE source to the volatile/refractory element ratios reported above.

For the samples that fall on array 2, the volatile contents of the end-member mantle compositions are difficult to estimate due to the strong evidence of contamination in the ITD group samples and mixing with the WD melts. For the ITD group, only the minimum Cl/K ratios (0.026 ± 0.002) and the corresponding F/Nd (17.3 ± 1.5) and S/Dy ratios (228 ± 16) of the glasses are within range of the Santiago melt inclusions analyzed

by Koleszar *et al.* (2009) (Fig. 13) and yield F (12.5 ± 1 ppm), Cl (1.3 ± 0.1 ppm) and S contents (115 ± 8) of the mantle source (using mantle contents of Nd = 0.703, K = 50 and Dy = 0.505, for the DMM of Workman and Hart (2005)) similar to those estimated for the depleted upper mantle (F = 16 ± 3 , Cl = 0.09 ± 0.63 , S = 146 ± 35 ; Saal *et al.* (2002)). The highest CO₂/Nb ratios of the ITD group are in the range found in MORB (Saal *et al.*, 2002, Cartigny *et al.*, 2008), but these glasses are not undersaturated in volatiles, so degassing will have decreased CO₂/Nb ratios and these glasses are associated with the highest values of Sr/Sr*, so contamination may have increased CO₂/Nb ratios (Fig. 11). In addition, all of H₂O/Ce ratios of the ITD group exceed what is expected of the depleted upper mantle (150-200; e.g. Dixon *et al.*, 2002, Saal *et al.*, 2002, Koleszar *et al.*, 2009). As a result, it is difficult to know how representative the CO₂/Nb and H₂O/Ce ratios of the ITD glasses are of the depleted mantle source in the Galapagos, therefore we restrict the values to what has previously been reported for the CO₂/Nb and H₂O/Ce ratios for this mantle component from melt inclusion studies (Koleszar *et al.*, 2009).

Samples from the WD group end-member that have the isotopic signature most similar to Pinta-Wolf-Darwin Is. are the least affected by mixing with contaminated melts from the ITD group. This yields S/Dy (255 ± 40) and Cl/K values (0.066 ± 0.006) similar to what has been reported for other ocean islands with evidence for recycled crustal material. The H₂O/Ce ratio (230 ± 35), while similar to ratios found in Mangaia melt inclusions and samples collected from Easter Island and the Salas y Gomez seamount chain (Simons *et al.*, 2002, Cabral *et al.*, 2014), is higher than what was found for other EM type sources such as Samoa, Pitcairn and Society (Workman *et al.*, 2006, Kendrick *et al.*, 2014). The F/Nd ratio (23.5 ± 0.5) is close to the ITE end-member, and higher than

what is estimated for the primitive mantle. Though the isotope signature of the Pinta-Wolf-Darwin end-member is indicative of a recycled crustal source, the exact trace element composition of this source is difficult to constrain, thereby limiting the estimation of the volatile content of this mantle component to the reported volatile/refractory element ratios for the WD end-member.

The effect of H₂O content on mantle rheology

The H₂O content of the mantle source will have a strong effect on the viscosity of the mantle. Despite the HHe group having a lower H₂O content than what is predicted for the primitive mantle, it is still 5x the concentration predicted for the MORB-source in the Galapagos (338 ppm versus 64 ppm based on a H₂O/Ce ratio for the depleted source of 117 (Koleszar *et al.*, 2009) and a DMM Ce content of 0.55 from Workman and Hart (2005)). These values can be used in conjunction with the power law form of the dependence of strain rate ($\dot{\epsilon}$) on differential stress (σ) of an olivine aggregate (Hirth & Kohlstedt, 1996, Hirth & Kohlstedt, 2003)

$$\dot{\epsilon} = A\sigma^n d^{-p} f_{H_2O}^r \exp\left(\frac{E^* + PV^*}{RT}\right) \quad (1)$$

where A is a material parameter, n is the stress exponent, d is grain size, p is the grain size exponent, f_{H_2O} is water fugacity, r is the water fugacity exponent, E* is the activation energy, V* is the activation volume, R is the gas constant and T is the absolute temperature, to estimate the difference in viscosity we would expect between the HHe component of the plume and the ITD component. For both the diffusion creep regime and

dislocation creep regime we can neglect the effect of the presence of melt on the strain rate at pressures greater than the estimated onset of carbonated melting (~200 km; Villagomez *et al.*, 2014). For a constant differential stress ($\sigma = 0.3$ MPa) and values for the wet diffusion creep regime listed in table 4, the viscosity of the HHe mantle component would be ~5x less than predicted for the ITD component. For the wet dislocation creep regime this number increases to ~7x less viscous. This has important implications for modeling plume ridge interaction, as a lower viscosity will increase the rate of solid flow, which will affect how plume material might flow towards the ridge, how melt is retained in the mantle, and melt production processes.

C/³He ratios of the high ³He/⁴He mantle source

It is difficult to estimate the primitive CO₂ contents of the Galapagos glasses due to extensive degassing. Information about the mantle source, however, can be inferred by combining glass He concentrations of melt fractions, previously measured by Kurz *et al.* (2009) with glass CO₂ contents measured by SIMS. This is due to the similar solubilities of CO₂ and He in basaltic melt (Lux, 1987, Pan *et al.*, 1991, Dixon *et al.*, 1995, Jendrzejewski *et al.*, 1997), which results in C/³He ratios of the glass that reflect the C/³He ratio of the mantle. Because CO₂ measurements are obtained by SIMS, we are only able to calculate C/³He ratios for samples that have been measured for He isotopes utilizing a melting step, as this measures He retained in the glass matrix (as opposed to vesicles). This limits us mainly to glasses in the HHe group, with only a few samples from the ITE group and the one sample from the ITD group collected near Fernandina. C/³He ratios can be found in Table 1.

Calculated $C^3\text{He}$ ratios of Galapagos glass average $4.37 \pm 9 \times 10^{10}$, though this number is skewed by one low He concentration glass (AHA19A). When this glass is excluded the average shifts to $3.10 \pm 6 \times 10^{10}$. This number is an order of magnitude higher than the canonical upper mantle value ($\text{DMM } C^3\text{He} = \sim 2 \pm 1 \times 10^9$; (Marty & Jambon, 1987, Marty & Tolstikhin, 1998, Shaw *et al.*, 2004, Barry *et al.*, 2014)), and values measured for mantle plumes ($2\text{--}20 \times 10^9$ (Trull *et al.*, 1993, Marty & Tolstikhin, 1998, Marty & Zimmermann, 1999, Barry *et al.*, 2014)).

Possible causes for variations in $C^3\text{He}$ ratios include degassing, assimilation of shallow lithospheric material, or variation in the mantle source. Degassing could fractionate the $C^3\text{He}$ of the residual melt due to the slightly higher solubility of He in comparison to CO_2 ($S_{\text{He}} = 6.4 \times 10^{-4} \text{ cm}^3 \text{ STP/g}$ while $S_{\text{CO}_2} = 2.7 \times 10^{-4} \text{ cm}^3 \text{ STP/g}$ experimentally derived solubility constants at 1 atm (Lux, 1987, Pan *et al.*, 1991, Dixon *et al.*, 1995, Jendzejewski *et al.*, 1997)). This would cause a decrease in the $C^3\text{He}$ ratio of the melt as degassing progresses, which does not explain the higher $C^3\text{He}$ ratios of Galapagos glasses. Assimilation of either a carbonate rich source in the crust or sediments could cause the higher $C^3\text{He}$ ratios (Shaw *et al.*, 2004). However, assimilation of crust or sediment should manifest in other trace element proxies, such as elevated Sr/Ce ratios that would potentially correlate with $C^3\text{He}$ ratios in Galapagos glasses, neither of which is observed. The most likely explanation for the higher $C^3\text{He}$ ratios in the Galapagos glasses is that a high $^3\text{He}/^4\text{He}$ mantle source component in the Galapagos plume is more carbonated than other oceanic basalts. This explanation is consistent with geochemical modeling that invokes a carbonatite mechanism for helium displacement in plume settings (Hofmann *et al.*, 2011) and recent melt modeling of the Galapagos hotspot

by Villagomez *et al.* (2014), who invoke the production of carbonatite to explain the low velocity anomalies at greater than 150 km depth identified by seismic imaging.

CONCLUSIONS

The geochemical data presented in this paper define two mixing arrays: array 1 ranging between the composition of Fernandina Island and Sierra Negra/Cerro Azul volcanoes (HHe group and ITE group respectively) and array 2 between the composition of Pinta-Wolf-Darwin Islands and Genovesa Island (WD and ITD groups respectively). 4 samples from Wolf Volcano did not fall on either array, but this volcano has been shown to be anomalous geochemically in many respects, because it is isotopically depleted but has enriched incompatible trace element concentrations (Geist *et al.*, 2005). The principle findings of this study can be summarized as follows:

- 1.) All of the glasses, except for the subset of samples from the ITD group that are supersaturated with $\text{CO}_2\text{-H}_2\text{O}$ fluid, have extensively degassed CO_2 . There is minimal degassing of the other volatile species, except for a subset of samples that have degassed S in addition to CO_2 .
- 2.) The pressure of $\text{CO}_2\text{-H}_2\text{O}$ vapor saturation versus the pressure of sample collection for the samples, in combination with data previously published for other oceanic basalts, reveal a fundamental difference between MORB and OIB; where either lower melt upwelling rate or faster C and H diffusion in the melt allowed for the continuous equilibration of vapor and melt in OIB compared to MORB.

- 3.) The Galapagos submarine glasses range from sulfide saturated to undersaturated.
- 4.) Assimilation of hydrothermally altered material has affected the Cl contents of a subset of glasses from all of the groups. Cl/K ratios are correlated with H₂O/Ce ratios for the HHe and ITE groups showing that H₂O also might be affected by assimilation of hydrothermally altered material. Furthermore samples from the ITD group with the highest Sr/Sr* ratios have the correspondingly highest H₂O/Ce, CO₂/Nb, F/Nd, and S/Dy ratios. This suggests that the assimilation of plagioclase-rich cumulates is accompanied by the assimilation of volatile rich phases in the shallow lithosphere.
- 5.) The correlations between CO₂/Nb and F/Nd and isotopes in the glasses of the WD group suggests that melts from the WD group are mixing with variably contaminated and/or less degassed samples from the ITD group at depth.
- 6.) The new data yields a first-order estimate of source volatile contents of the end-members defining the two geochemical arrays
 - a. For the samples of array 1, the HHe group end-member (Fernandina) shows a H₂O/Ce ratio (202 ± 26) and F/Nd ratio (20.1 ± 0.8). The ITE end-member (Sierra Negra/Cerro Azul), in contrast, shows a higher F/Nd ratio (24.9 ± 0.7) and a H₂O/Ce ratio (174 ± 24) that is lower but within error of the HHe end-member, similar to that previously reported for an enriched mantle source, which may be indicative of recycled crust. S/Dy and Cl/K ratios for the two end-members of the array 1 are very similar ($S/Dy = 218 \pm 21$, $Cl/K = 0.057 \pm 0.009$ and $S/Dy = 226 \pm 20$, $Cl/K = 0.048 \pm 0.011$ for the HHe and ITE groups respectively).

- b. The estimated $\text{H}_2\text{O}/\text{Ce}$ ratio for the primitive Galapagos mantle beneath Fernandina, if it has a refractory trace element composition similar to the PM, indicates that the H_2O , F, Cl, and S contents for the source of the HHe samples are generally lower than what is predicted for the primitive mantle.
 - c. Only the minimum Cl/K (0.026 ± 0.002), F/Nd ratios (17.3 ± 1.5), and S/Dy ratios (228 ± 16) of the Genovesa end-member (ITD group) from array 2 fall within range of MORB.
 - d. The Pinta-Wolf-Darwin end-member (WD group) has high $\Delta 7/4$, $\Delta 8/4$ and Th/La ratios and low $^3\text{He}/^4\text{He}$ ratios suggesting the presence of a recycled crustal component. The volatile data for this end-member yield a similar S/Dy ratio (255 ± 40) to those of the end-members in array 1, have slightly higher Cl/K ratio (0.066 ± 0.006), an $\text{H}_2\text{O}/\text{Ce}$ ratio (230 ± 35), and a F/Nd ratio (23.5 ± 0.04) that is higher than the estimate ratio for the Fernandina mantle component, but lower than what was found for the ITE end-member.
- 7.) The higher H_2O contents of the Fernandina HHe source will result in a mantle viscosity 5-7x lower than what we would predict for the ITD mantle component.
- 8.) $\text{C}/^3\text{He}$ ratios in the glasses of the Fernandina HHe end-member are, on average, an order of magnitude higher than what has been found previously for MORB and other OIB suggesting that the Galapagos plume contains a mantle component that is carbonated.

Distinctive $\text{H}_2\text{O}/\text{Ce}$ and F/Nd ratios, as a result, can differentiate the four main compositional components defined by the glasses of this study. The generally higher $\text{H}_2\text{O}/\text{Ce}$ ratios of the HHe, ITE, and WD groups suggests that the H_2O contents of these sources is higher than the depleted upper mantle which will affect the physical properties of the mantle such as the variability of mantle viscosity. These effects in addition to the high $\text{C}/^3\text{He}$ ratios of the HHe group will be important to consider in future modeling plume-ridge interactions and mantle flow.

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FIGURE CAPTIONS

Figure 1. Map of the Galapagos archipelago with locations of sample dredges. Bathymetry is indicated by the color scale on the left side on the map and prominent features are labeled. Array 1 consists of samples that range between the compositions of Fernandina Island and Sierra Negra/Cerro Azul volcanoes that are further divided into HHe and ITE groups based on samples with $^3\text{He}/^4\text{He}$ ratios above and below $^3\text{He}/^4\text{He} = 22 \text{ Ra}$, respectively. Array 2 consists of samples that range between the compositions of Genovesa Island and Pinta, Wolf and Darwin Islands that have been divided into the ITD group (samples with more MORB-like compositions) and the WD group (samples characterized by high Th/La ratios and high $\Delta 7/4$, $\Delta 8/4$). Samples that have a composition similar to Wolf Volcano on Isabela are also shown separately. Map created using GeoMapApp <http://www.geomapapp.org> (Ryan *et al.*, 2009).

Figure 2. (A-F) Major element concentrations plotted against MgO wt% of individual glasses. FeO* indicates total Fe content. Superimposed on the glass data are the predicted liquid lines of descent (LLD) calculated using PetroLog3 (Danyushevsky & Plechov, 2011). The calculations are performed isobarically at 2 Kbars of pressure for 2 different starting compositions, which can be found in table 2. Notice the entire range in major elements cannot be reproduced by a single LLD. Blue LLD calculated from primitive melt inclusion AHA-D25C-3-43 (indicated by a grey triangle outlined in blue), collected from a submarine dredge with an enriched composition similar to those of Fernandina lavas. Green LLD calculated from a primitive melt inclusion STG06-29-06 (indicated by

a grey triangle outlined in green), collected from Santiago, with a depleted composition similar to MORB. Compositions were chosen so that LLDs would bracket the range in data. Melt inclusion compositions reported in Koleszar *et al.* (2009) are shown by labeled grey fields. Errors are 2σ standard error.

Figure 3. Sr/Sr* versus A.) Al₂O₃ wt% and B.) MgO wt% of individual glasses. Sr/Sr* is quantified by $Sr_{PM}/(((Pr_{PM}+Nd_{PM})/2))$. Included in both figures are grey fields that represent melt inclusion data from Santiago and Fernandina reported in Koleszar *et al.* (2009) and Peterson *et al.* (2014) and LLDs as calculated in Figure 2. Notice that the data from the ITD group fall outside the area defined by the LLD. In Fig. 2A ITD Group data follow the same trend between Sr/Sr* and Al₂O₃ defined by the Santiago melt inclusions, which were found to undergo simple plagioclase assimilation. However in Fig. 2B the ITD Group samples define the opposite trend to the Santiago melt inclusions, with only the highest MgO content and Sr/Sr* glasses overlapping with the middle of the field defined by the melt inclusions. This indicates that the glasses with the highest MgO wt% have initially assimilated plagioclase cumulates and later began to crystallize plagioclase out, causing the opposite trend to the Santiago melt inclusions in Sr/Sr* versus MgO wt%. Errors are 2σ standard error.

Figure 4. Primitive mantle normalized trace element diagram. Samples representing the different groups (HHE Group: D24A, D28C, ITE Group: D6G, D8A, WD Group: PL02-29-3, PL02-28-11, ITD Group: DR70-1, PL02-10-8) have similar MgO contents (6.08-7.84 wt %) and trace element contents representative of the overall characteristics of each

group. For example, notice the positive Ti anomaly in the HHe Group samples. The grey field shows the range in previously collected trace element data in whole rocks from across the Galapagos Archipelago limited to samples with MgO contents between 6.0 and 8.0 wt % (McBirney *et al.*, 1969, Baitis & Lindstrom, 1980, Cullen *et al.*, 1989b, Vicenzi *et al.*, 1990, Bow & Geist, 1992, White *et al.*, 1993, Geist *et al.*, 1995, Reynolds & Geist, 1995, Standish *et al.*, 1998, Geist *et al.*, 2002, Schilling *et al.*, 2003, Saal *et al.*, 2007, Gibson *et al.*, 2012). Inset shows the high MgO content ITD and WD Group glasses that have the largest Sr anomalies and have been affected by plagioclase assimilation. Normalization values from McDonough and Sun (1995).

Figure 5. (A-C) $^{143}\text{Nd}/^{144}\text{Nd}$ and (D-F) $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^3\text{He}/^4\text{He}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{208}\text{Pb}/^{204}\text{Pb}$. Notice glass samples with $^3\text{He}/^4\text{He} > 22\text{Ra}$ correspond to the Pb isotope composition indicative of Fernandina whole rocks. Notice also that the WD and ITD Groups define a compositional range from near Genovesa to near Pinta-Wolf-Darwin Islands. Some of the isotopic data is reported in Geist *et al.*, (2008) and Harpp and White, (2001); the rest is new data. Both previously reported and new data are presented in Table 1. The grey fields are defined by previously published isotope data on whole rocks basalts from different islands and the GSC (Cullen *et al.*, 1989b, White *et al.*, 1993, Reynolds & Geist, 1995, Blichert-Toft & White, 2001, Schilling *et al.*, 2003, Saal *et al.*, 2007, Ingle *et al.*, 2010) while the yellow and green fields show the position of unpublished isotopic data for the ITD and WD groups respectively from the SONNE SO158 cruise (Hoernle, personal communication).

Figure 6. Volatile contents versus MgO wt% and refractory trace elements with similar incompatibility. LLDs, represented by blue and green lines shown in the volatile versus MgO wt% plots, are calculated as in Figure 2. Partition coefficients for volatile elements presented in Table 2. (A-B) CO₂ ppm versus MgO wt% and Nb ppm. Notice that Santiago inclusion chosen for LLD modeling is degassed for CO₂. An inclusion with a higher CO₂ content was not chosen for modeling because they were both more evolved and showed a larger signature of assimilation (higher Sr/Sr*). (C-D) H₂O wt% versus MgO wt% and Ce ppm. (E-F) F ppm versus MgO wt% and Nd ppm. (G-H) Cl ppm versus MgO wt% and K ppm. (I-J) S ppm versus MgO wt% and Dy ppm. Black lines delineate the volatile/refractory element ratios that bracket the data (in the case of H₂O versus Ce, F versus Nd, Cl versus K, and S versus Dy) or are commonly cited mantle values for ratios of volatiles and refractory elements (in the case of CO₂ versus Nb). Notice that while H₂O, F, Cl, and S contents increase with decreasing MgO wt%, indicating that crystal fractionation has some control over the volatile content, the CO₂ content is relatively constant, indicating CO₂ is controlled by degassing.

Figure 7. A.) CO₂ ppm versus H₂O wt% concentrations of the glasses. In addition to the data are the CO₂-H₂O equilibrium saturation pressures (horizontally curved black lines) and equilibrium vapor phase compositions (vertically curved black lines) from the model of Dixon *et al.* (1995), and three degassing paths calculated using the model of Newman and Lowenstern (2002). Dashed red lines show open system degassing, calculated from the composition of two samples with the highest CO₂ content from the ITD and ITE Groups (PL02-9-29, D49A respectively). Dashed and dotted red line shows the closed

system degassing path calculated from D49A (assuming 1.8 wt% vapor exsolved). Errors are 2σ standard errors. B.) S/Dy ratios versus pressure of CO₂-H₂O vapor saturation, calculated from the model shown in panel A (Dixon *et al.*, 1995) for individual glasses. Melt inclusions from Koleszar *et al.* (2009) are also included. Notice that for P saturation values < 400 bars S/Dy ratios switch from being relatively constant to gradually decreasing, which suggests S degassing. C.) Pressure of CO₂-H₂O vapor saturation, calculated from the model shown in panel A (Dixon *et al.*, 1995), versus individual pressures of collection. The error in the pressure of saturation is based on the error in the analysis of CO₂. The error on the pressure of collection represents the depth change over the course of each dredge. Fields for the Galapagos spreading center (GSC), the East Pacific Rise (EPR), the Loihi seamount, Pitcairn Island and from different islands in Samoa and Society archipelagos are plotted for comparison (Dixon & Clague, 2001, Schilling *et al.*, 2003, Cushman *et al.*, 2004, le Roux *et al.*, 2006, Workman *et al.*, 2006, Ingle *et al.*, 2010, Kendrick *et al.*, 2014, Shimizu *et al.*, In preparation). Solid black line is a 1:1 line.

Figure 8. Log values of measured sulfur concentrations versus log of calculated S concentration at sulfide saturation (SCSS) using the model of Liu *et al.* (2007). The calculation is based on the major element composition, pressure, temperature, and the concentration of water of a sample (see text for in depth discussion of model). Black solid line is the 1:1 line at and above which samples are considered sulfide saturated. Black dashed lines represent the 200 ppm error of the model based on the experiments of

Moune *et al.* (2009). Based on this model, the glasses range from sulfide saturated to undersaturated. Included error represents the average 2σ standard error of S measurement.

Figure 9. Volatile/refractory element ratios versus (A-F) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and (G-L) $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for individual glasses. Also included are grey fields representing previously reported data from the GSC (Ingle *et al.*, 2010) and yellow and green fields showing the position of unpublished isotopic data for the ITD and WD groups respectively from the SONNE SO158 cruise (Hoernle, personal communication). Errors are 2σ standard errors.

Figure 10. Cl/K ratios versus $\text{H}_2\text{O}/\text{Ce}$ ratios of the ITE and HHe Group lavas. Black solid line shows calculated York regression. The relatively good linear correlation shows that assimilation of hydrothermally altered material might be simultaneously affecting Cl and H_2O contents of the glasses. Dashed box shows the expected mantle limits of a trace element enriched source (Dixon *et al.*, 2002, Simons *et al.*, 2002, Stroncik & Haase, 2004, Workman *et al.*, 2006). Inset shows Cl/K ratios versus $\text{H}_2\text{O}/\text{Ce}$ ratios for all the glasses of this study. Lines show compositional effect of adding seawater (SW) (Cl = 1.935 wt%, H_2O = 97.5 wt%, K = 340.2 ppm, and Ce = 0.001 ppb), a 15% NaCl brine (Cl = 9.9 wt%, H_2O = 85 wt%, K = 2075 ppm, and Ce = 0.006 ppb), and a 50% NaCl brine (Cl = 30.3 wt%, H_2O = 50 wt%, K = 6474 ppm, and Ce = 0.02 ppb) (Kent *et al.*, 1999a, Kent *et al.*, 1999b) to the composition of sample D20a. Ticks are labeled for the percent material mixed. Errors are 2σ standard errors.

Fig. 11. Volatile/refractory element ratios versus Sr/Sr* for individual glasses. Errors are 2 σ standard errors.

Figure 12. $^3\text{He}/^4\text{He}$ ratios versus A.) $\Delta 7/4$ and B.) F/Nd ratios. $\Delta 7/4$ calculations are based on equations found in Hart (1984) and represent positive and negative deviations from the northern hemisphere reference line. Errors are 2 σ standard errors.

Figure 13. Volatile/refractory element ratios versus (A-E) $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ and (F-J) Th/La ratios for individual glasses and array end-member compositions. $^{208}\text{Pb}^*/^{206}\text{Pb}^* = (^{208}\text{Pb}/^{204}\text{Pb} - 29.4761)/(^{206}\text{Pb}/^{204}\text{Pb} - 9.3066)$. End-member compositions for the ITE, HHe, and WD groups are determined from samples filtered to Cl/K ratios ≤ 0.08 and S/Dy ratios ≥ 175 that are not sulfide saturated. Additionally, for ITE group, end-member components are the mean and median of the samples with the highest F/Nd ratios. These represent an end-member of the correlation between F/Nd and $^3\text{He}/^4\text{He}$ ratios defined by array 1 (Fig. 13). For the HHe group, because the in-group F/Nd ratio variation is lower, the end-member components are the average and median values of the filtered samples. The WD end-member is defined by the mean and median values of the samples with the isotopic composition closest to the Pinta component. F/Nd, Cl/K and S/Dy ratios of the ITD end-member composition are set by the samples with the lowest Cl/K ratios. CO_2/Nb ratios are set by the expected CO_2/Nb ratio of a MORB source (Saal *et al.*, 2002) and $\text{H}_2\text{O}/\text{Ce}$ end-member set by the average value of Santiago normal inclusions reported in Koleszar *et al.* (2009). End-member compositions presented in Table 3 Dashed lines show the values generally cited for the FOZO and MORB sources (e.g. Dixon *et al.*, 2002,

Saal *et al.*, 2002, Simons *et al.*, 2002). Yellow and green fields showing the position of unpublished isotopic data for the ITD and WD groups respectively from the SONNE SO158 cruise (Hoernle, personal communication). Errors bars showing the 1 standard deviation of samples used to set end-member compositions.

Supplementary Figure 1. Th/La ratios versus A.) Sm/Yb ratios, B.) Ti/Gd ratios and C.) Nb/Zr ratios of individual glasses plotted with fields defining the ranges of previously measured whole rock and glass samples from the Galapagos Archipelago and the Galapagos Spreading Center (GSC) (references as in Fig. 4). Notice that glasses of this study cover almost the entire geochemical range shown by the literature data from trace element depleted to enriched signatures. Errors are 2σ standard error.

Supplementary Figure 2. (A-D) $^{87}\text{Sr}/^{86}\text{Sr}$, (E-H) $^{143}\text{Nd}/^{144}\text{Nd}$, and (I-L) $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ versus Sm/Yb, Ti/Gd, Th/La, and Nb/Zr ratios of individual glasses with a field showing the range of data collected from the GSC and for selected islands from the Galapagos Archipelago. $^{208}\text{Pb}^*/^{206}\text{Pb}^* = (^{208}\text{Pb}/^{204}\text{Pb} - 29.4761) / (^{206}\text{Pb}/^{204}\text{Pb} - 9.3066)$ is the ratio of the radiogenic additions to the initial terrestrial Pb. Trace element ratios are correlated with isotopic ratios indicating that the trace element variations are long-lived characteristics of the mantle sources. Notice 2 distinct arrays of data; the first array being composed of the HHe and ITE Groups and the second one being composed of the WD and ITD groups. Yellow and green fields showing the position of unpublished isotopic data for the ITD and WD groups respectively from the SONNE SO158 cruise (Hoernle, personal

communication). References for fields and isotopic data as in Figure 4. Errors are 2σ standard error.

Supplementary Figure 3. $^3\text{He}/^4\text{He}$ versus Ti/Gd of individual glasses. Notice the weak trend between $^3\text{He}/^4\text{He}$ and Ti/Gd. This is often cited as a characteristic of the FOZO mantle source. References are reported in Figure 6. Errors are 2σ standard error.

FIGURES

Figure 2-1

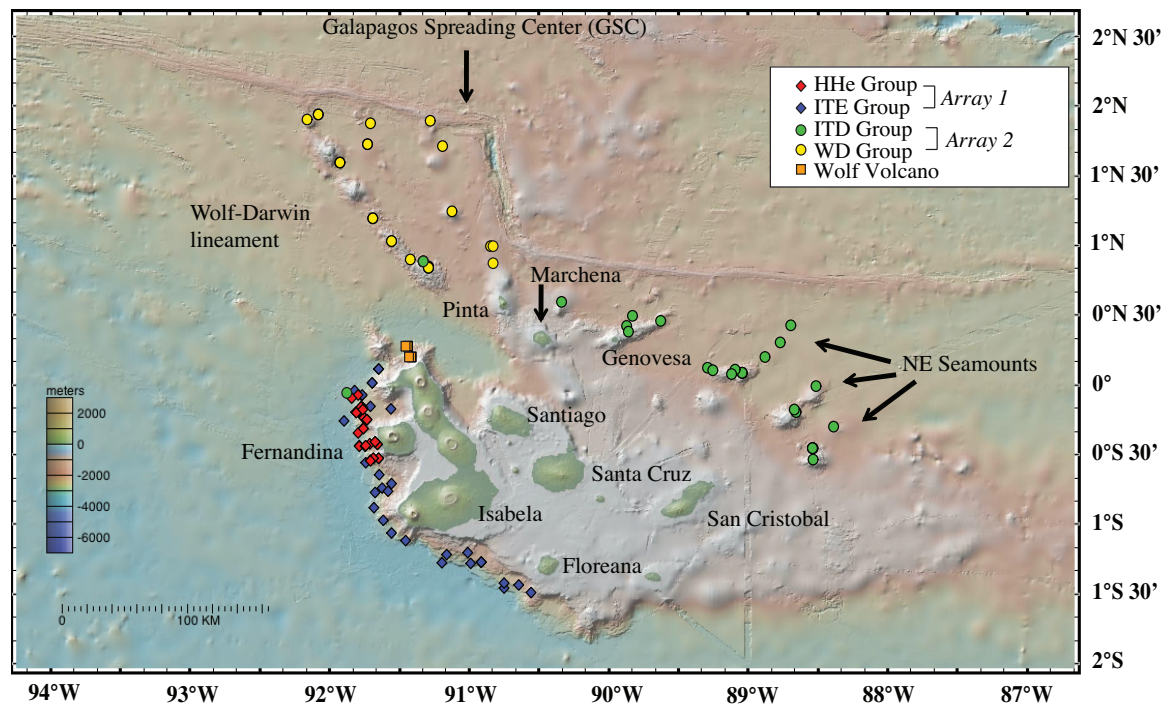


Figure 2-2

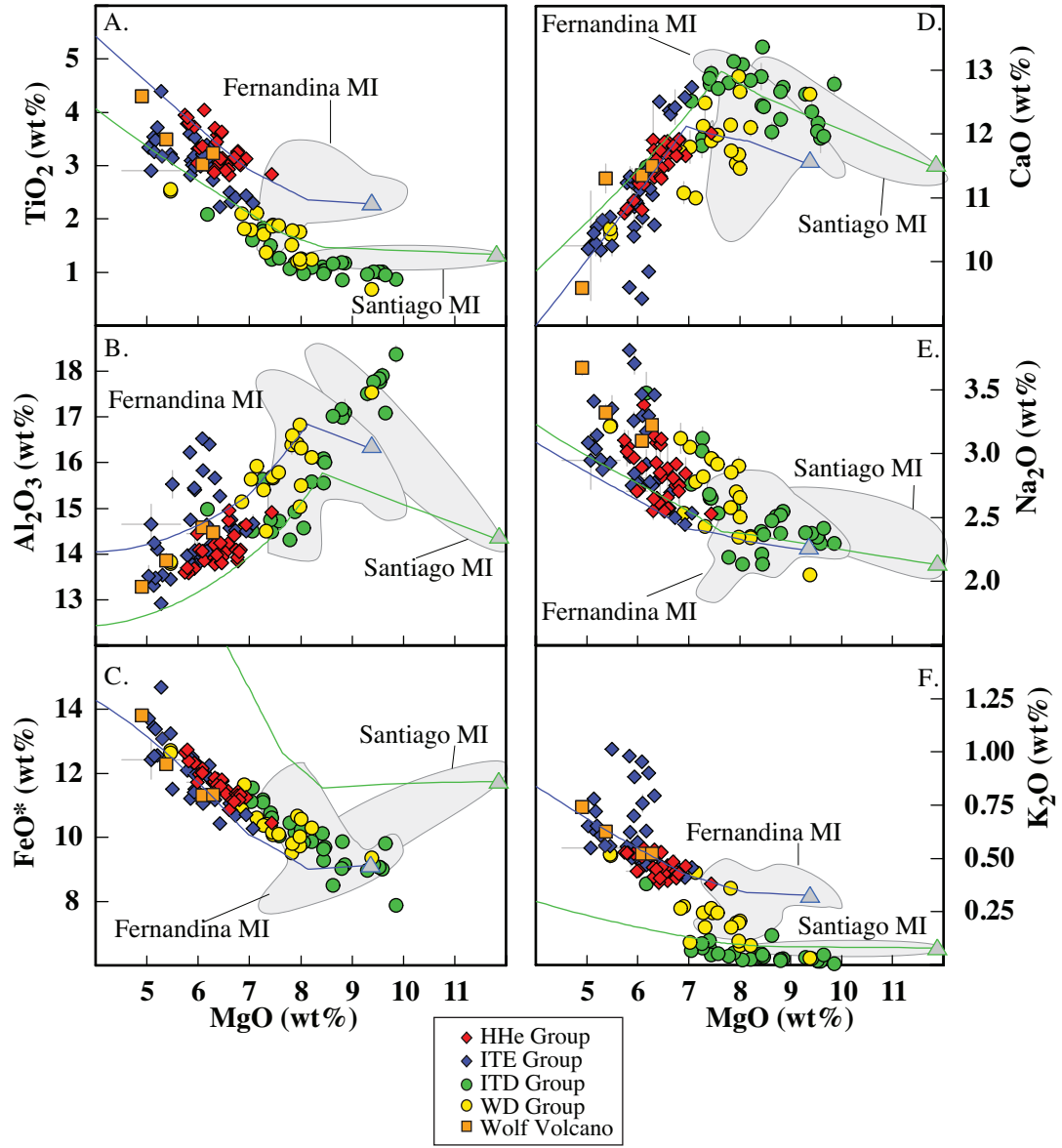


Figure 2-3

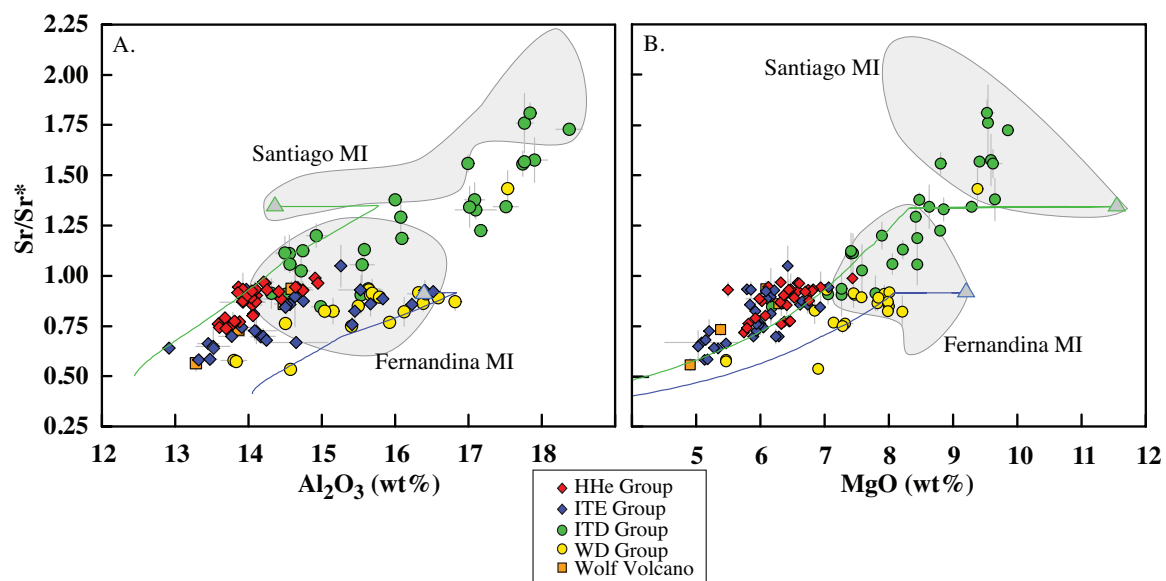


Figure 2-4

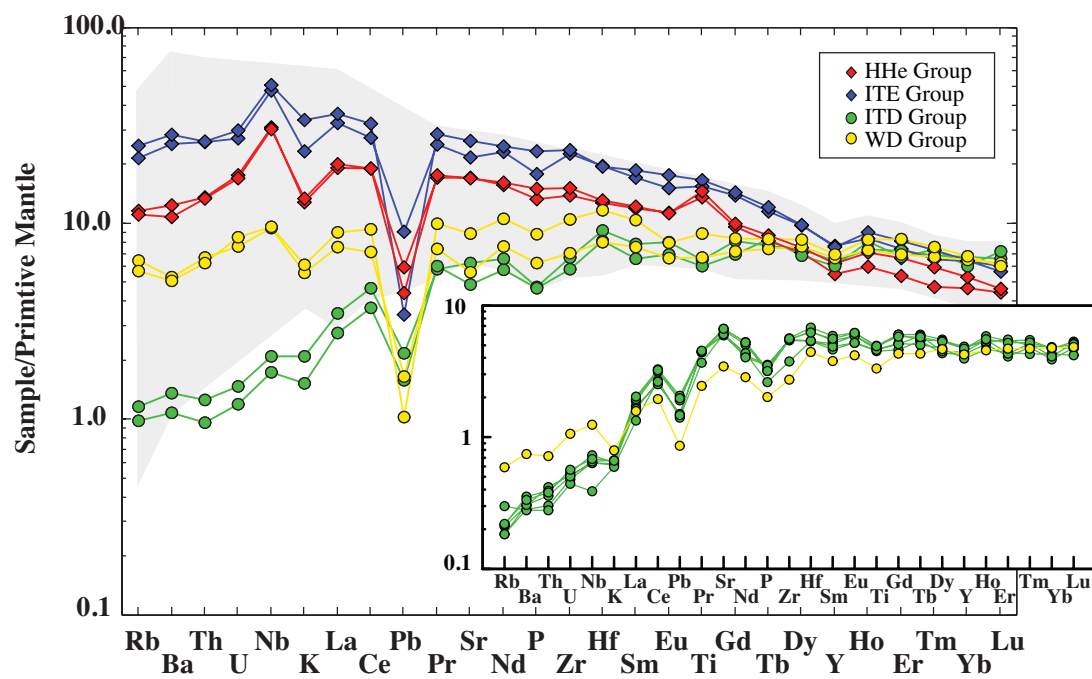


Figure 2-5

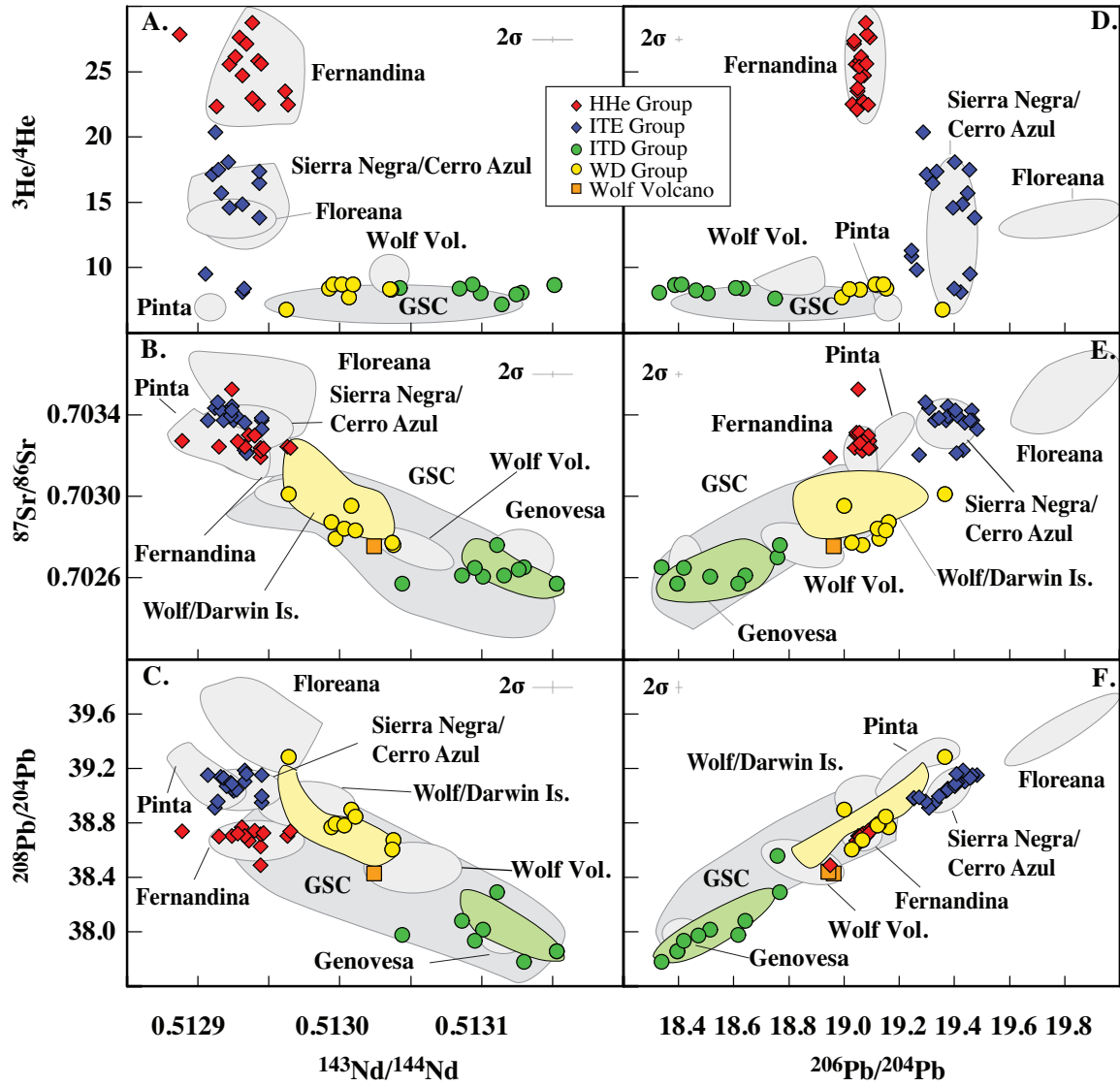


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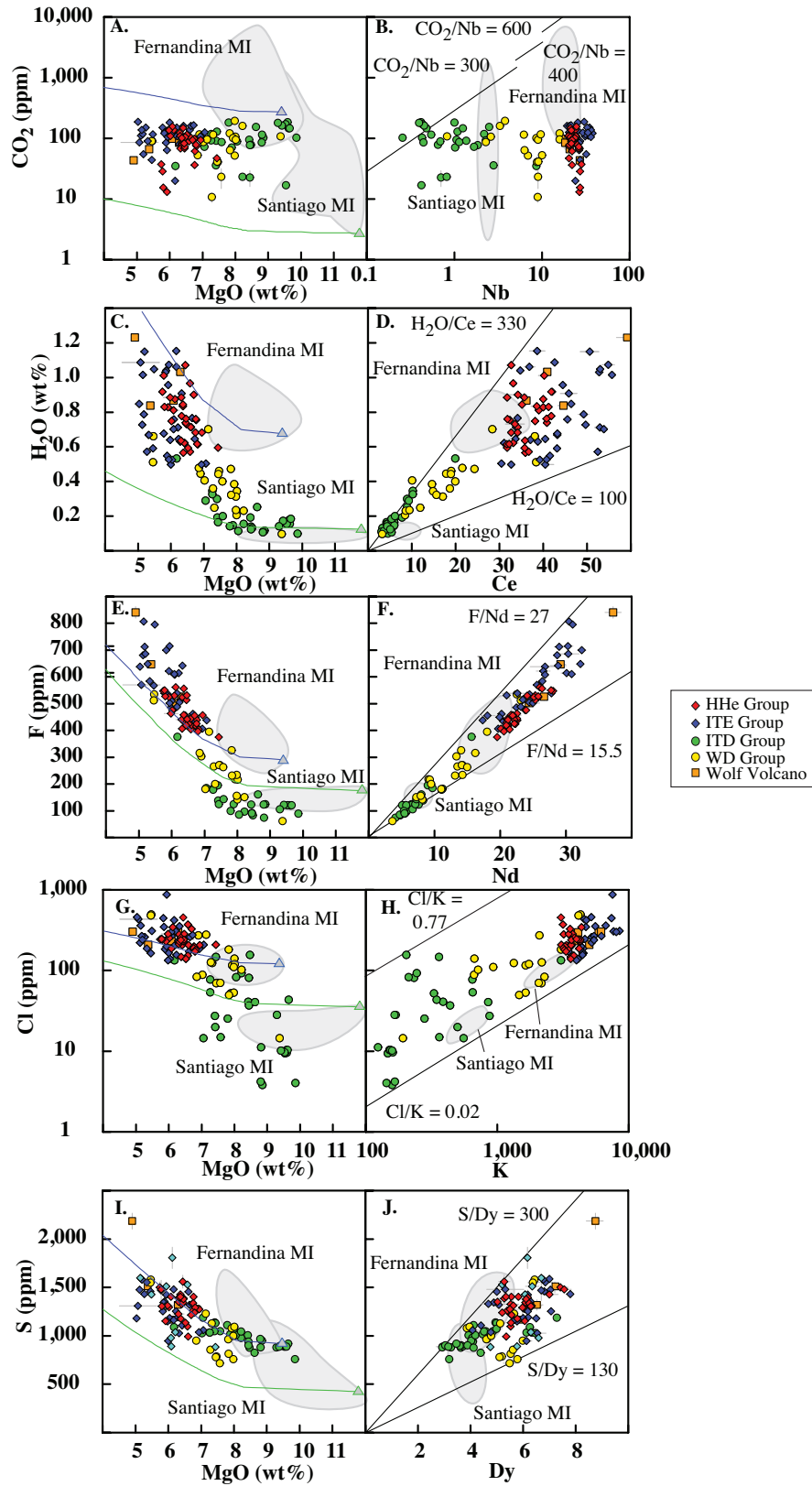


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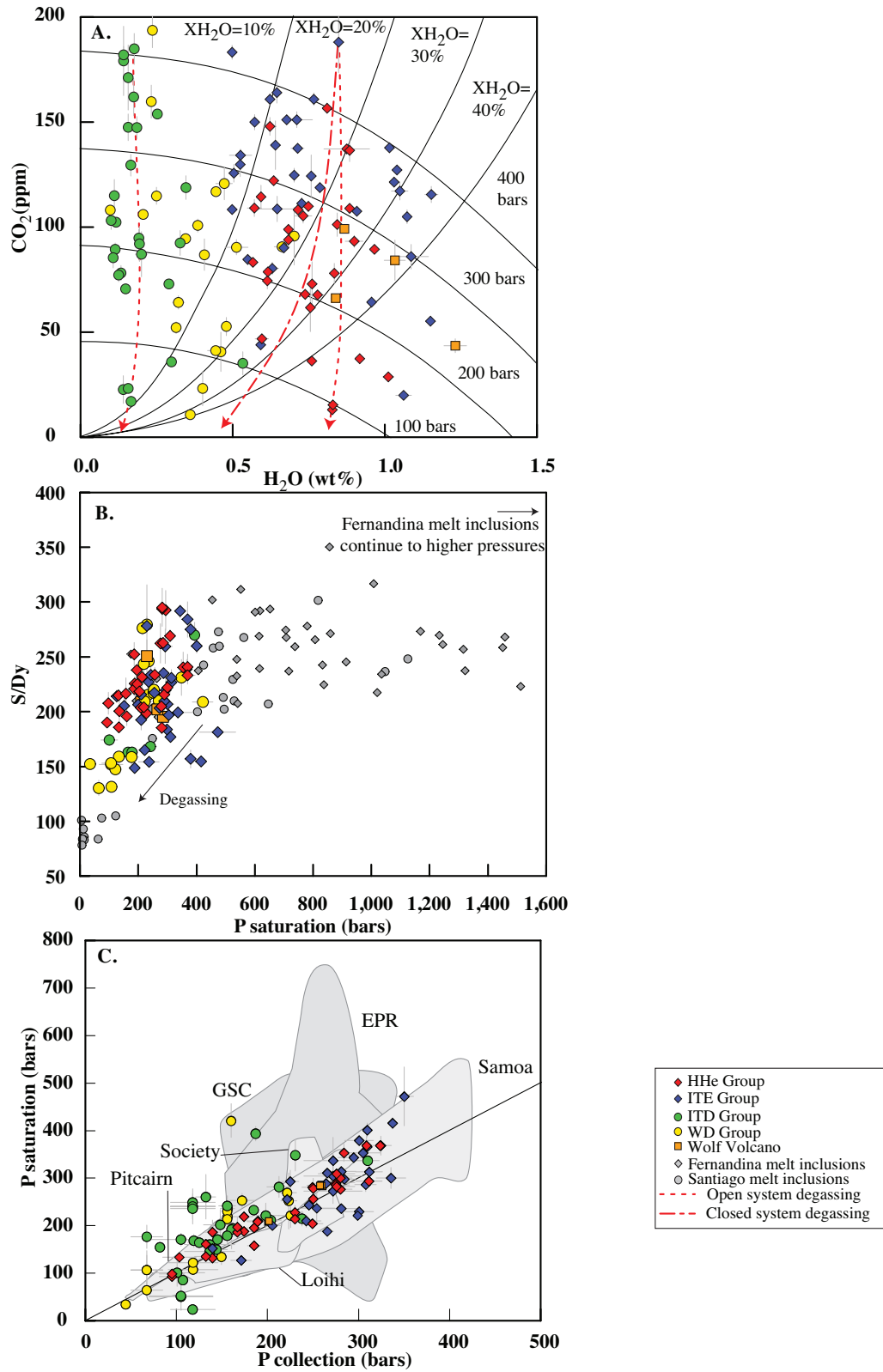


Figure 2-8

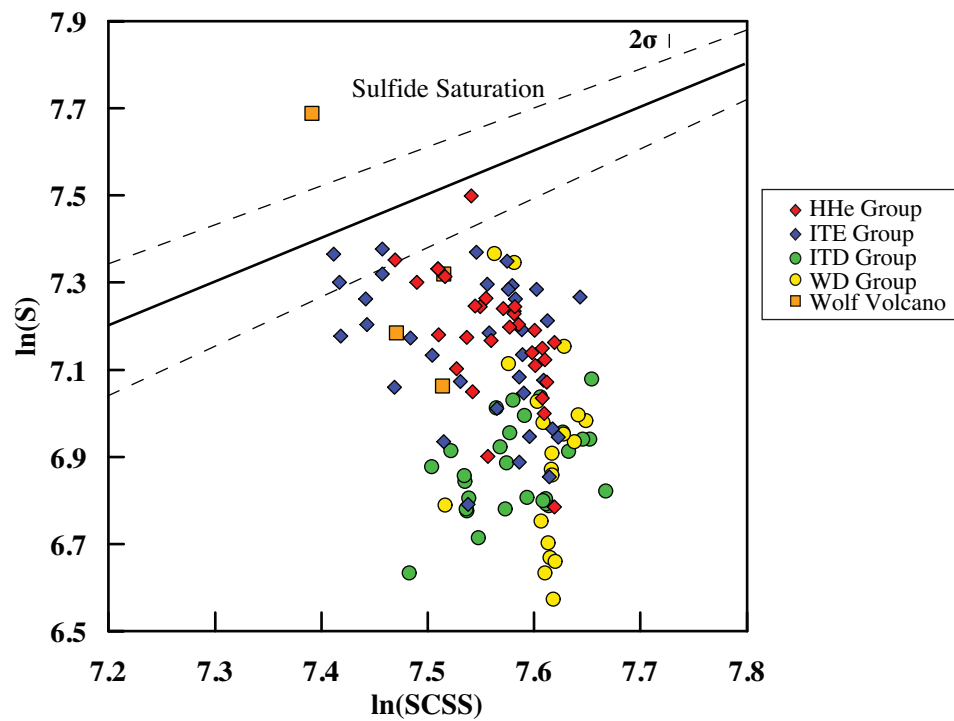


Figure 2-9

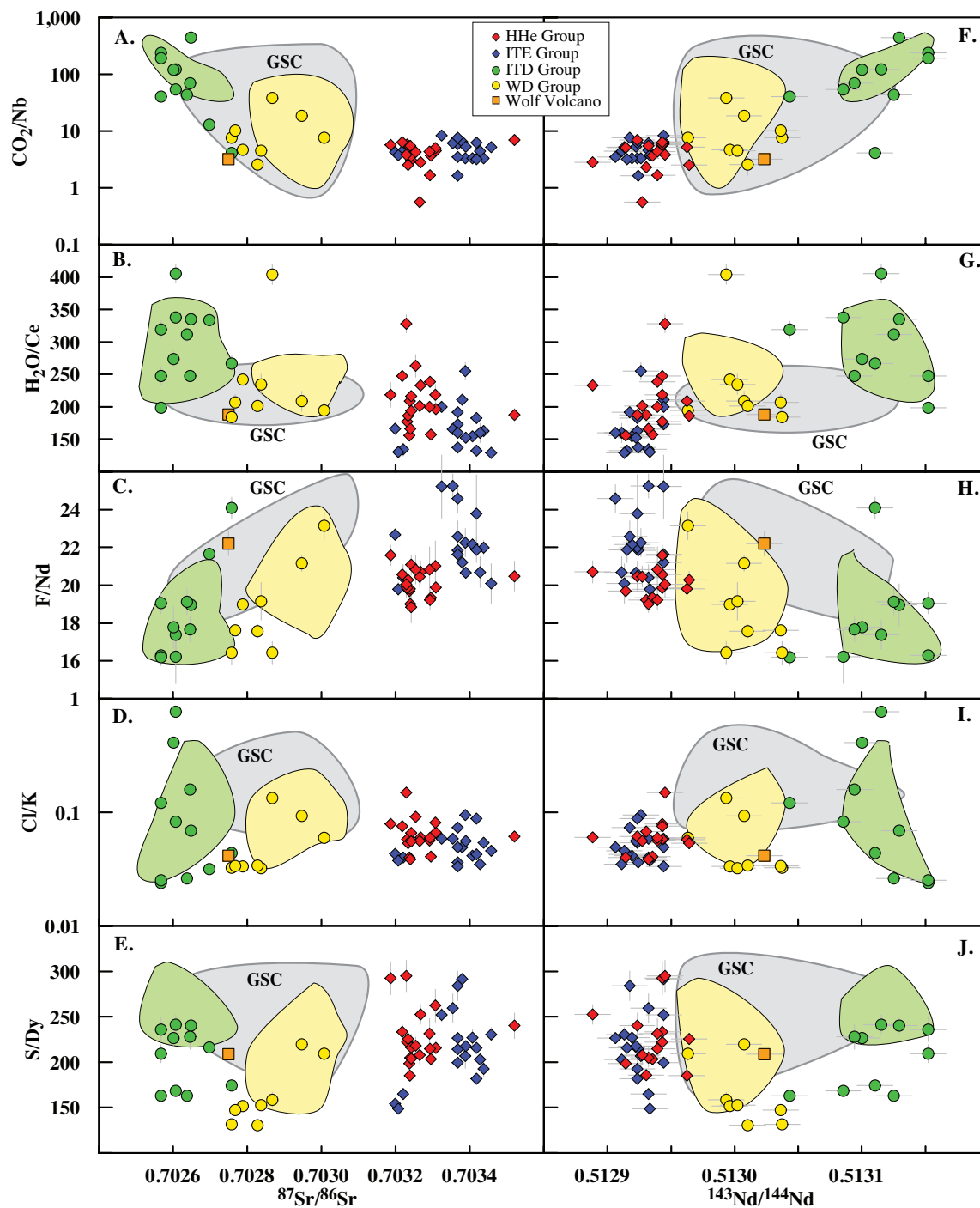


Figure 2-10

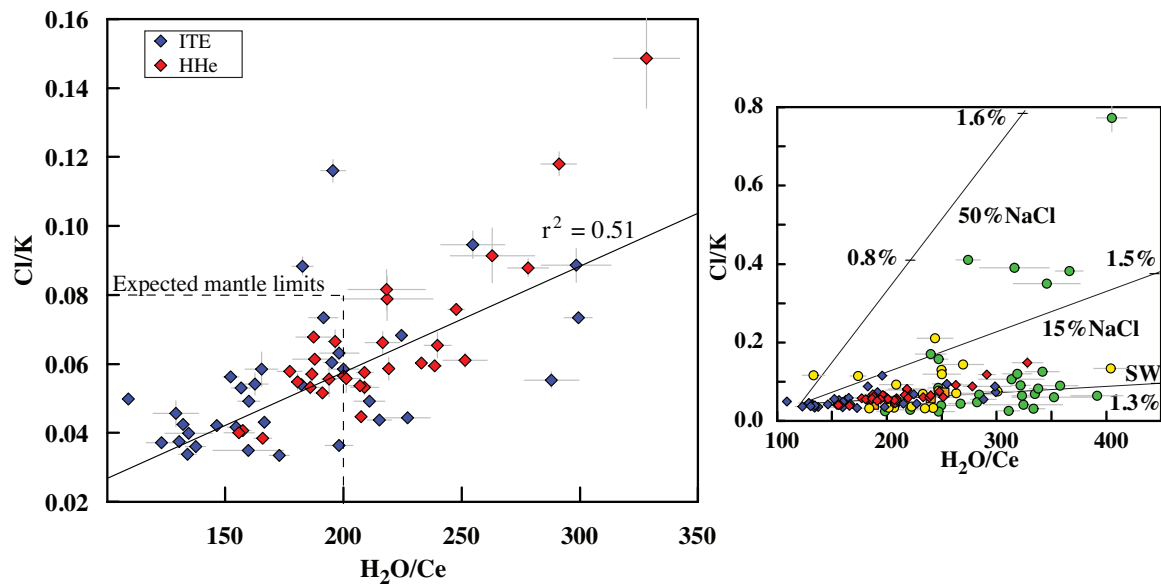


Figure 2-11

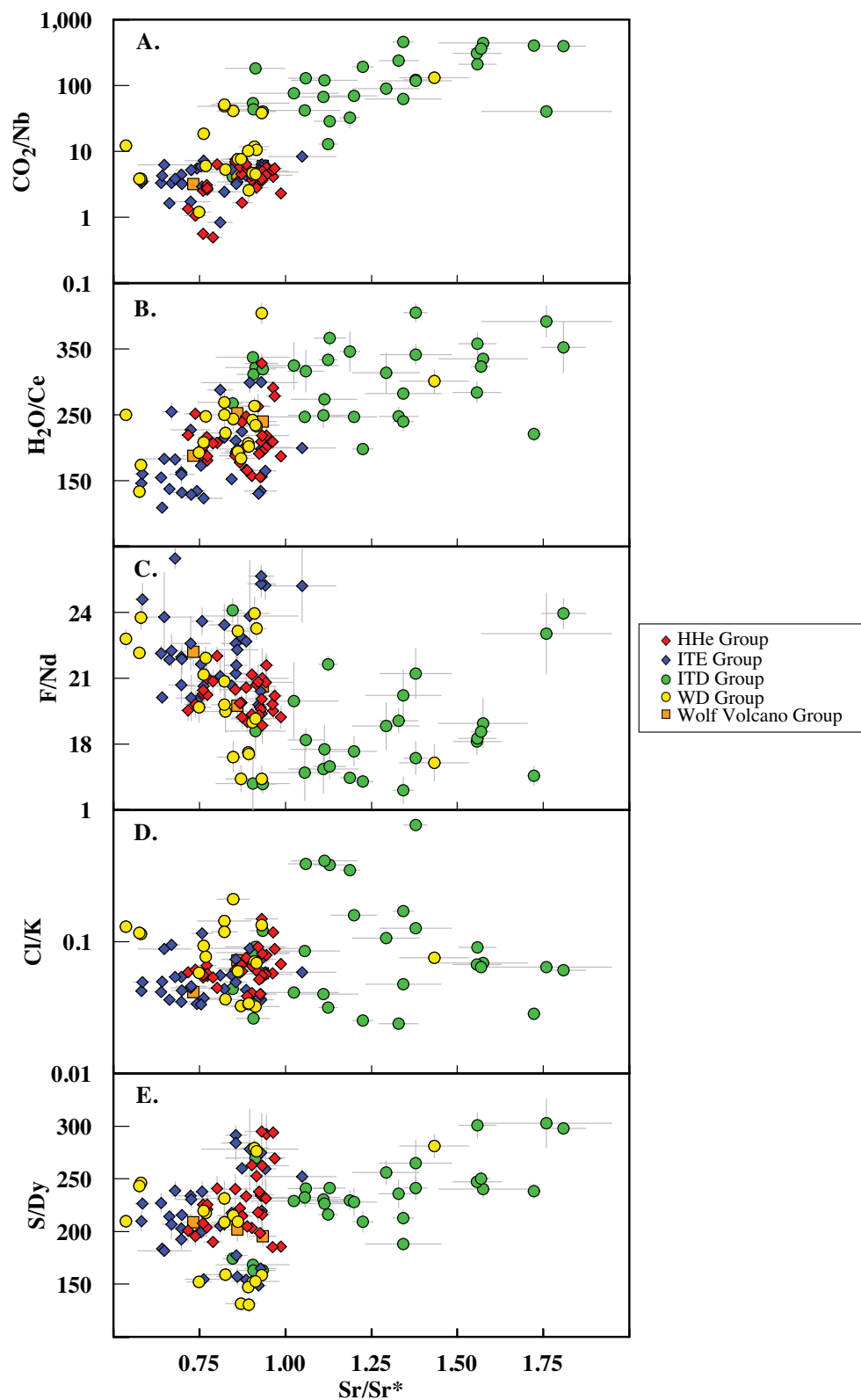


Figure 2-12

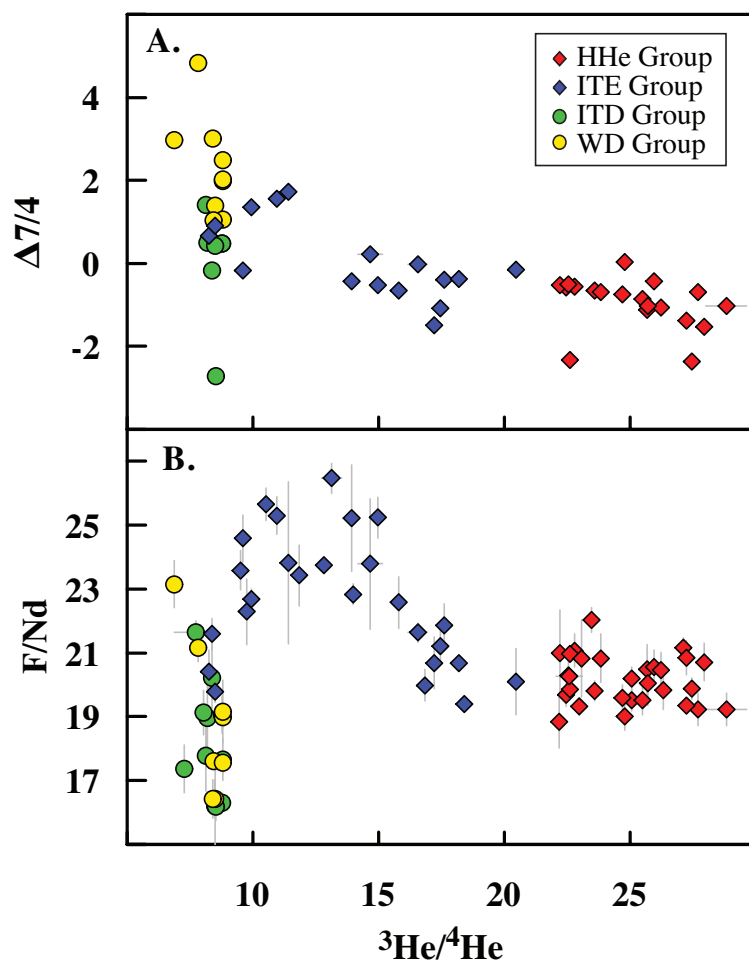
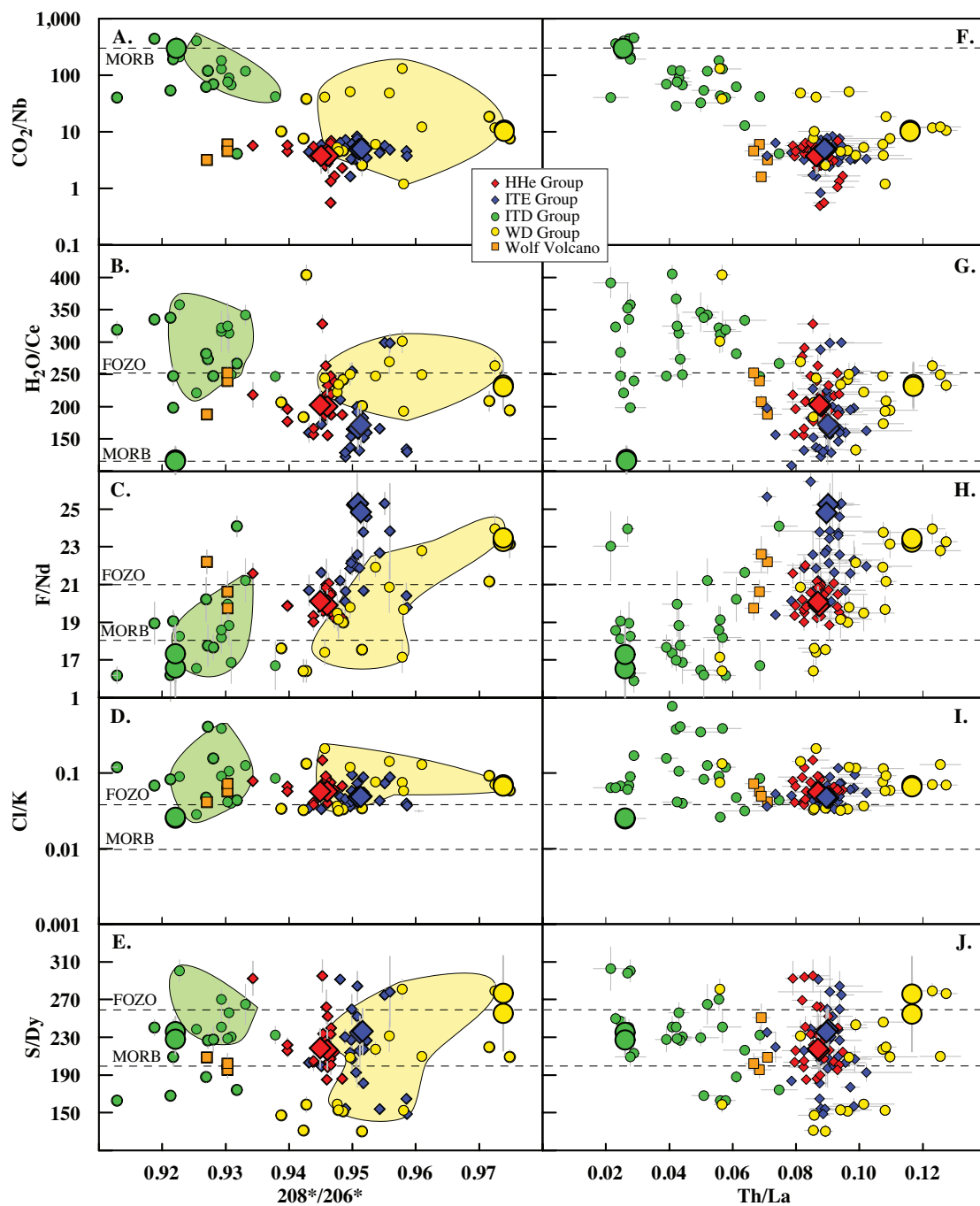
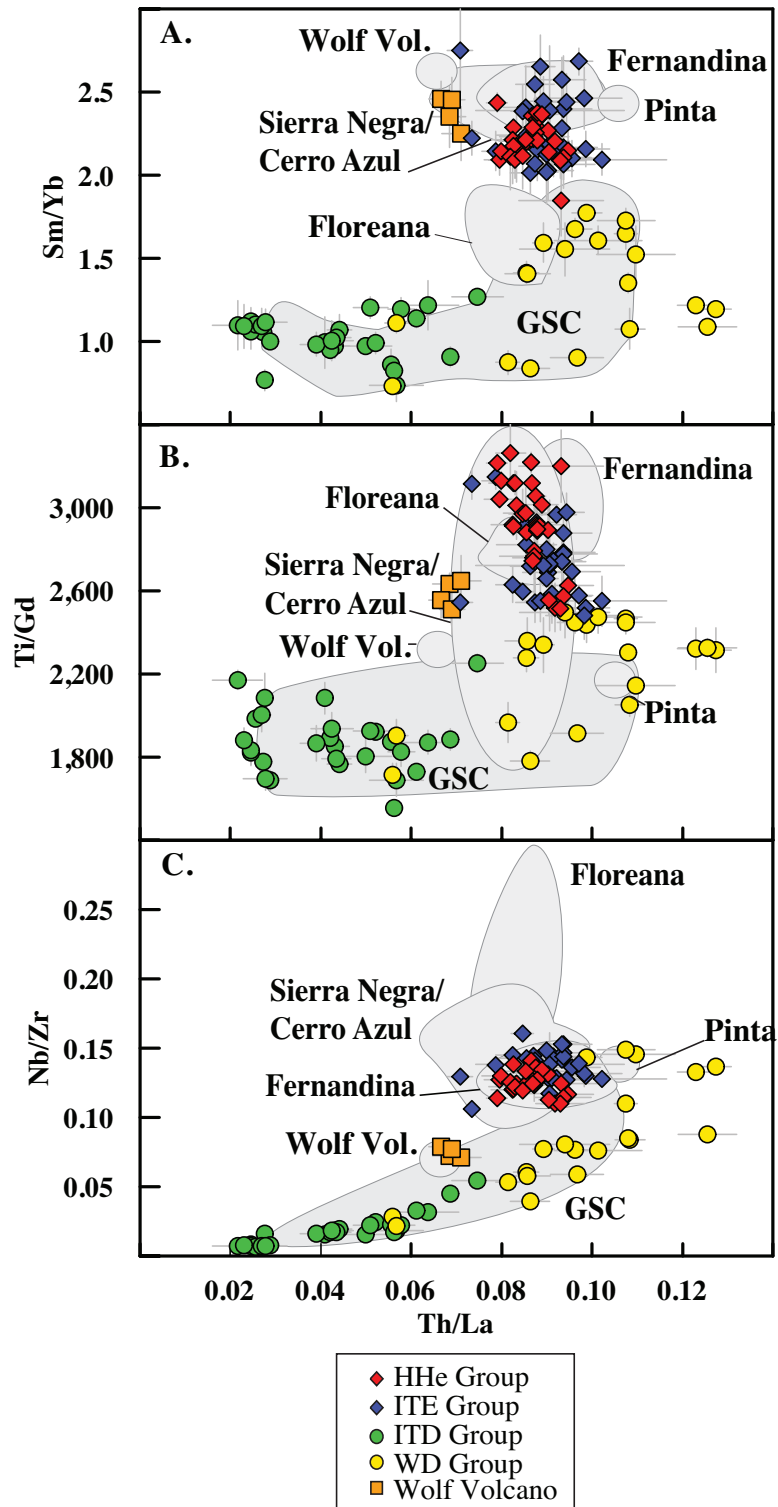


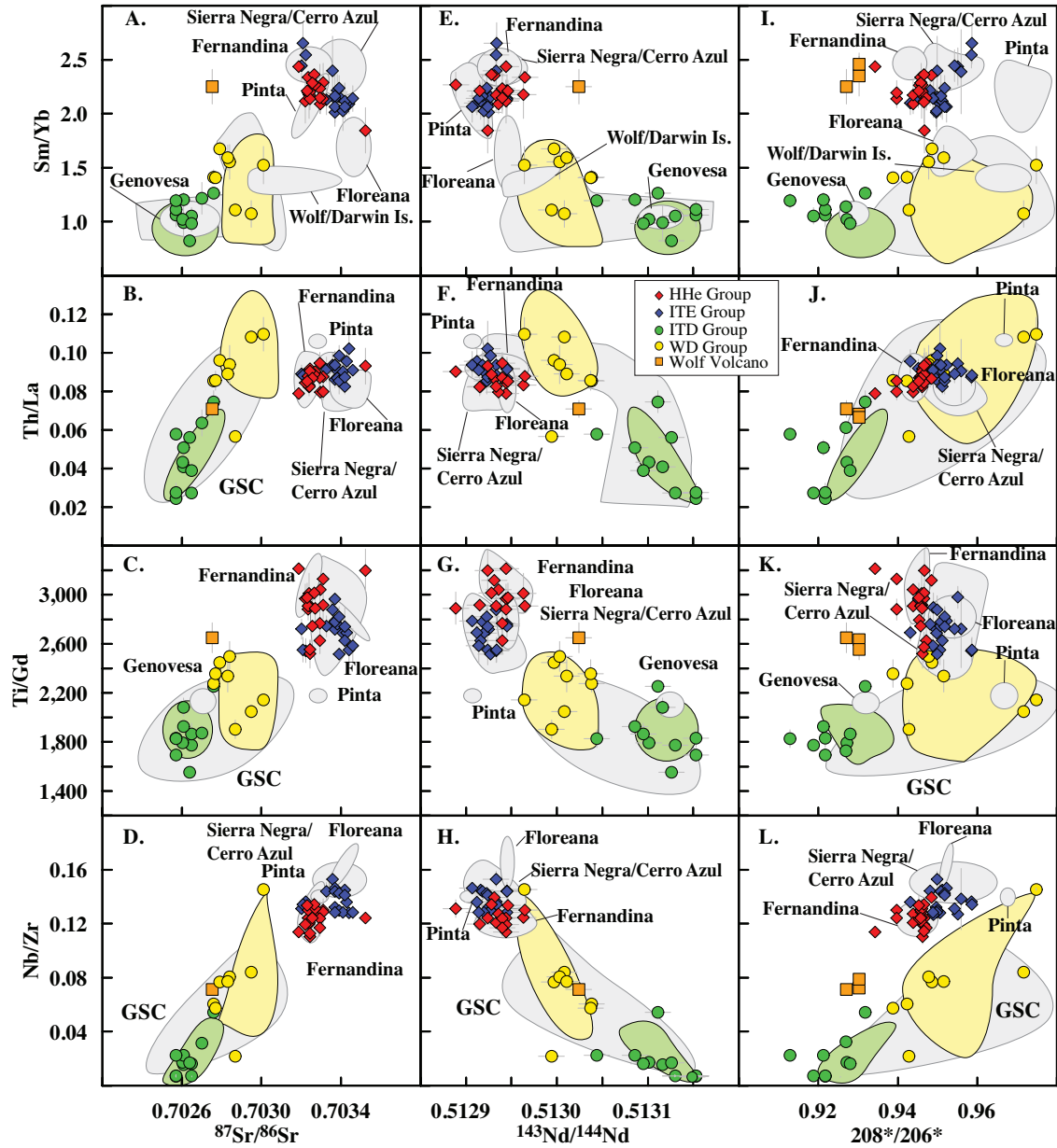
Figure 2-13



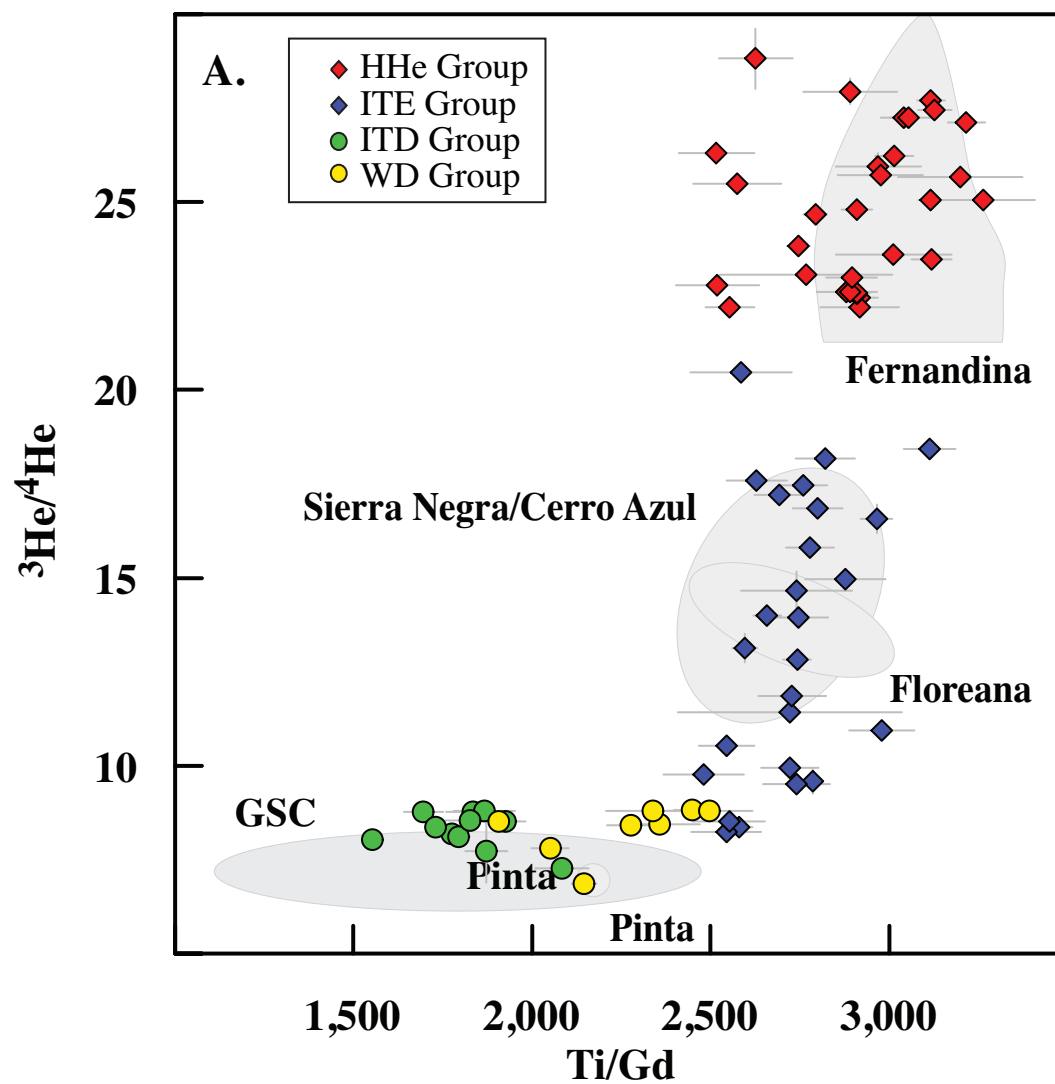
Supplementary Figure 2-1



Supplementary Figure 2-2



Supplementary Figure 2-3



TABLES

Table 1. Sample Information and chemical data for Galapagos glasses

Group	HHe Group	HHe	HHe	HHe	HHe	HHe	HHe	HHe	HHe
Sample	AHA18a	AHA18b	AHA19a	AHA19b	AHA20a	AHA20b	AHA21a	AHA21b	AHA22a
Cruise	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2
Latitude	-0.17	-0.17	-0.21	-0.21	-0.24	-0.24	-0.24	-0.25	-0.19
Longitude	-91.77	-91.77	-91.81	-91.80	-91.75	-91.75	-91.75	-91.75	-91.76
Average									
Depth (m)	2500	2500	2800	2800	1740	1740	1670	1670	2300
<i>Major Elements (wt%)</i>									
SiO ₂	49.11	49.22	49.01	49.42	48.76	48.74	48.80	48.76	48.56
TiO ₂	2.90	3.10	2.92	3.14	3.57	3.70	3.61	3.64	3.13
Al ₂ O ₃	14.04	14.09	13.92	13.92	13.88	13.78	13.82	13.81	14.64
FeO*	11.38	11.37	11.74	11.77	11.83	11.86	11.76	11.80	11.24
MnO	0.21	0.20	0.21	0.20	0.23	0.18	0.21	0.20	0.17
MgO	6.53	6.75	6.31	6.47	6.37	6.33	6.45	6.46	6.94
CaO	11.88	11.78	11.90	11.46	11.40	11.32	11.33	11.30	11.66
Na ₂ O	2.55	2.75	2.55	2.82	3.09	3.14	3.07	3.11	2.84
K ₂ O	0.43	0.44	0.46	0.46	0.52	0.54	0.53	0.53	0.46
P ₂ O ₅	0.30	0.31	0.33	0.33	0.36	0.42	0.40	0.39	0.33
Total	99.31	98.15	99.35	98.62	97.85	98.22	98.12	98.26	98.00
<i>Volatile Content</i>									
H ₂ O (wt%)	0.593	0.683	0.635	0.732	0.834	0.779	0.738	0.761	0.683
CO ₂ (ppm)	114.42	98.90	122.10	105.31	77.97	67.73	68.04	72.88	94.02
F (ppm)	424.55	415.20	440.48	441.45	555.83	523.26	513.49	531.55	456.63
S (ppm)	1135.16	1260.73	1224.45	1386.20	1428.27	1395.42	1344.32	1378.54	1273.68
Cl (ppm)	139.21	183.57	213.02	284.83	255.32	227.89	230.26	240.64	206.22
P saturation (bars)	279	256	300	277	219	188	186	197	214

Trace Elements (ppm)

Rb	6.88	8.16	6.99	8.22	9.19	10.24	10.05	10.01	8.37
Ba	83.20	89.04	84.26	90.40	103.33	111.12	109.14	109.39	93.69
Th	1.21	1.19	1.27	1.20	1.60	1.49	1.46	1.46	1.25
U	0.378	0.388	0.409	0.413	0.456	0.499	0.493	0.497	0.411
Nb	20.84	20.79	21.20	21.04	25.29	27.03	26.24	26.24	21.68
K	3615.31	3452.39	3684.44	3493.89	3857.63	4278.76	4197.14	4216.56	3642.82
La	14.62	13.67	14.87	13.74	17.44	16.95	16.56	16.58	14.34
Ce	35.73	32.69	35.84	33.54	38.51	41.88	40.87	40.79	34.13
Pb	0.57	1.04	0.56	1.08	1.28	1.29	1.26	1.26	1.14
Sr	347.00	337.22	337.82	341.80	338.38	345.22	343.52	343.32	355.79
Nd	22.33	21.20	22.18	21.02	26.37	25.79	25.35	25.35	21.93
P	1373.22	1224.27	1383.01	1192.77	1482.54	1515.61	1497.55	1491.89	1356.24
Zr	172.50	168.23	170.66	163.40	229.47	207.91	202.67	202.13	174.86
Hf	4.09	4.01	4.09	3.83	5.44	4.80	4.77	4.70	4.15
Sm	5.83	5.41	5.67	5.30	6.75	6.43	6.31	6.31	5.46
Eu	1.92	1.84	1.93	1.84	2.19	2.21	2.15	2.16	1.89
Ti	17836.84	16653.09	17706.29	16537.20	19420.25	20085.96	19689.78	19696.36	16940.13
Gd	6.13	5.96	6.14	5.67	7.71	6.90	6.77	6.82	6.12
Dy	5.54	5.39	5.51	5.29	7.00	6.18	6.09	6.12	5.50
Y	28.88	28.32	28.62	27.28	36.58	32.46	31.92	31.75	28.60
Er	3.13	2.78	3.08	2.69	3.64	3.15	3.11	3.13	2.84
Yb	2.68	2.39	2.58	2.31	3.07	2.75	2.69	2.65	2.44
Pr		4.63		4.66	5.62	5.76	5.62	5.62	4.79
Tb		0.93		0.89	1.19	1.08	1.05	1.06	0.95
Ho		1.07		1.03	1.38	1.21	1.20	1.19	1.07
Tm		0.38		0.37	0.50	0.44	0.43	0.43	0.40
Lu		0.37		0.34	0.48	0.42	0.41	0.40	0.37

Isotopes

$^3\text{He}/^4\text{He}^b$	24.79	24.68	22.62	22.20	22.79	22.55	22.59	22.61	23.07
1σ	0.14	0.12	0.13	0.08	0.14	0.12	0.26	0.10	0.10
C^3/He	4.27E+09	4.26E+09	4.61E+11	4.06E+10	7.92E+09	3.39E+09	5.48E+09	6.09E+09	5.97E+09
$^{87}\text{Sr}/^{86}\text{Sr}^c$	0.70324		0.70323	0.70331	0.70324	0.70324			0.70329

$^{143}\text{Nd}/^{144}\text{Nd}^c$	0.512933		0.512944		0.512965		0.512994	
ϵNd	5.76		5.97		6.38		5.89	
$^{206}\text{Pb}/^{204}\text{Pb}^c$	19.082		19.039		19.097		19.079	
$^{207}\text{Pb}/^{204}\text{Pb}^c$	15.560		15.532		15.556		15.554	
$^{208}\text{Pb}/^{204}\text{Pb}^c$	38.702		38.622		38.734		38.723	
Group	HHe	HHe	HHe	HHe	HHe	HHe	HHe	HHe
Sample	AHA22b	AHA23a	AHA23b	AHA25a	AHA25c	AHA26a	AHA27a	AHA27c
Cruise	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2
Latitude	-0.18	-0.26	-0.26	-0.45	-0.45	-0.43	-0.42	-0.42
Longitude	-91.76	-91.73	-91.73	-91.78	-91.74	-91.71	-91.67	-91.67
Average								
Depth (m)	2300	1395	1395	2750	2750	1890	950	950
<i>Major Elements (wt%)</i>								
SiO ₂	48.57	49.28	49.27	48.21	49.07	49.04	49.31	49.40
TiO ₂	2.93	3.27	3.24	4.05	3.33	3.16	3.72	3.80
Al ₂ O ₃	14.74	13.85	13.92	13.86	14.10	14.11	13.68	13.59
FeO*	11.27	11.43	11.32	12.08	11.98	11.65	12.32	12.39
MnO	0.18	0.19	0.21	0.16	0.19	0.19	0.22	0.21
MgO	6.59	6.77	6.76	6.12	6.03	6.38	5.92	5.81
CaO	11.67	11.66	11.65	11.21	11.23	11.70	10.95	10.83
Na ₂ O	2.66	2.78	2.92	3.38	2.72	2.65	2.97	3.06
K ₂ O	0.47	0.42	0.41	0.55	0.44	0.45	0.52	0.53
P ₂ O ₅	0.32	0.33	0.31	0.38	0.33	0.34	0.37	0.38
Total	99.41	98.25	98.50	97.93	99.40	99.66	98.34	98.40
<i>Volatile Content</i>								
H ₂ O (wt%)	0.571	0.755	0.760	0.875	0.749	0.566	0.827	0.830
CO ₂ (ppm)	109.09	61.73	36.23	137.23	109.91	83.29	13.04	15.38
F (ppm)	444.55	439.06	425.69	561.14	475.93	437.88	524.43	527.79
S (ppm)	1096.73	1401.60	1337.36	1805.47	1296.13	1177.93	1152.91	1306.23
Cl (ppm)	153.10	197.77	189.76	345.18	251.60	147.90	229.66	239.87
P saturation (bars)	228	187	132	294	289	209	93	98

Trace Elements (ppm)

Rb	7.16	7.77	7.59	9.31	8.79	7.99	7.52	10.28	10.33
Ba	86.92	84.18	82.67	99.81	91.78	86.15	82.39	107.05	107.77
Th	1.25	1.24	1.37	1.25	1.20	1.25	1.19	1.43	1.49
U	0.406	0.398	0.384	0.451	0.432	0.425	0.370	0.487	0.512
Nb	21.28	22.07	22.00	23.97	23.52	24.24	22.59	26.69	27.24
K	3814.26	3278.95	3187.74	4375.60	3661.56	3781.60	3625.93	4282.16	4294.73
La	15.16	13.69	14.43	15.84	13.90	15.60	14.98	16.33	16.72
Ce	36.66	32.41	31.85	40.03	35.16	38.12	35.94	39.97	41.24
Pb	0.51	1.00	1.01	1.44	1.18	0.50	0.58	1.31	1.35
Sr	368.06	331.05	319.62	420.13	344.38	363.97	355.44	345.56	342.83
Nd	22.58	21.20	22.15	26.00	21.67	23.94	22.64	25.15	25.80
P	1446.11	1188.44	1303.16	1600.48	1481.84	1559.53	1469.68	1629.50	1627.12
Zr	177.64	168.43	188.25	210.80	166.34	186.18	177.33	195.96	202.76
Hf	4.14	4.07	4.64	4.82	3.93	4.39	4.13	4.58	4.70
Sm	5.79	5.41	5.83	6.58	5.39	6.08	5.77	6.12	6.44
Eu	1.89	1.85	1.89	2.28	1.89	2.04	2.01	2.14	2.22
Ti	18009.30	17577.94	17782.20	22223.24	18935.84	20355.43	19296.46	20288.15	20827.68
Gd	6.17	6.08	6.77	6.92	5.89	6.51	6.35	6.64	6.91
Dy	5.52	5.55	6.23	6.17	5.34	6.01	5.79	6.07	6.29
Y	28.82	28.97	32.64	32.04	27.90	30.98	29.60	31.47	32.58
Er	3.07	2.80	3.27	3.14	2.75	3.33	3.22	3.09	3.19
Yb	2.62	2.39	2.71	2.70	2.43	2.84	2.76	2.72	2.73
Pr		4.58	4.68	5.71	4.81			5.57	5.72
Tb		0.95	1.06	1.08	0.92			1.05	1.08
Ho		1.08	1.24	1.20	1.05			1.18	1.23
Tm		0.39	0.44	0.43	0.38			0.42	0.44
Lu		0.37	0.42	0.41	0.37			0.41	0.41

Isotopes

$^3\text{He}/^4\text{He}^b$	22.45	27.94	28.82		27.11	27.44	27.24	27.25	26.23
1σ	0.10	0.17	0.40		0.11	0.12	0.11	0.09	0.11
$\text{C}/^3\text{He}$	6.57E+09	2.36E+10	1.53E+10		6.62E+10	6.21E+10	5.79E+09	2.08E+10	3.25E+10
$^{87}\text{Sr}/^{86}\text{Sr}^c$	0.70324	0.70327	0.70330	0.70319		0.70331	0.70330		0.70327

$^{143}\text{Nd}/^{144}\text{Nd}^c$	0.512915	0.512889	0.51294	0.512944	0.512936	0.512922	5.66
ϵ_{Nd}	5.40	4.90	5.89	5.97	5.81		
$^{206}\text{Pb}/^{204}\text{Pb}^c$	19.055	19.092	19.088	18.949	19.046		19.070
$^{207}\text{Pb}/^{204}\text{Pb}^c$	15.551	15.545	15.550	15.533	15.532		15.548
$^{208}\text{Pb}/^{204}\text{Pb}^c$	38.699	38.734	38.741	38.485	38.628		38.718
Group	HHe	HHe	HHe	HHe	HHe	HHe	HHe
Sample	AHA29a	AHA29b	AHA30a	AHA30b	AHA32a	D11a	D24a-2
Cruise	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	AHA-Nemo- 2	DRIFT04	DRIFT04
Latitudea	-0.54	-0.54	-0.54	-0.54	-0.56	-0.08	-0.33
Longitudea	-91.65	-91.65	-91.68	-91.68	-91.71	-91.79	-91.75
Average							
Depth (m)	1325	1325	1852.5	1852.5	2495	2842	2758
<i>Major Elements (wt%)</i>							
SiO ₂	49.05	48.88	49.14	49.35	49.30	49.16	49.02
TiO ₂	3.95	3.90	3.01	3.04	2.82	3.06	3.05
Al ₂ O ₃	13.60	13.70	14.10	14.05	14.95	14.05	14.23
FeO*	12.66	12.75	11.34	11.18	10.87	11.59	11.45
MnO	0.19	0.22	0.19	0.20	0.19	0.19	0.19
MgO	5.74	5.79	6.82	6.80	6.60	6.41	6.58
CaO	10.77	10.83	11.91	11.91	11.52	11.72	11.89
Na ₂ O	3.10	3.01	2.75	2.71	2.57	2.62	2.88
K ₂ O	0.53	0.53	0.43	0.43	0.44	0.39	0.40
P ₂ O ₅	0.38	0.41	0.30	0.32	0.29	0.31	0.30
Total	98.48	98.04	97.73	98.25	99.55	99.50	97.71
<i>Volatile Content</i>							
H ₂ O (wt%)	0.918	1.011	0.614	0.616	0.714	0.622	0.966
CO ₂ (ppm)	37.37	28.73	74.42	78.70	108.30	147.93	89.42
F (ppm)	547.42	549.83	404.57	396.94	420.39	429.53	404.18
S (ppm)	1501.25	1479.85	1291.11	1240.35	993.33	1326.72	1528.25
Cl (ppm)	243.37	244.60	179.63	172.18	207.21	206.20	372.35
P saturation (bars)	135	161	158	195	281	205	283

Trace Elements (ppm)

Rb	10.22	9.79	7.43	7.66	6.39	8.36	6.90	6.60	7.02
Ba	110.16	106.22	83.62	84.83	81.38	92.61	74.86	71.05	83.49
Th	1.72	1.70	1.27	1.17	1.18	1.25	1.27	1.06	1.08
U	0.499	0.485	0.381	0.389	0.367	0.403	0.379	0.344	0.369
Nb	28.11	27.17	20.36	20.42	20.74	21.96	21.26	19.90	21.64
K	4150.04	4005.53	3229.27	3336.98	3600.35	3572.23	3358.00	3194.48	3154.62
La	18.39	18.26	14.03	13.28	14.15	14.33	13.67	12.93	13.12
Ce	41.85	40.22	31.66	32.25	34.17	34.21	33.14	31.78	33.17
Pb	1.27	1.26	1.00	1.02	0.52	1.15	1.11	0.66	0.97
Sr	338.39	339.49	334.45	328.11	357.89	347.79	310.76	337.77	348.76
Nd	28.03	27.74	21.46	20.55	21.22	21.89	20.98	20.11	20.70
P	1562.19	1493.66	1153.63	1179.49	1387.56	1247.62	1474.85	1343.55	1252.86
Zr	245.44	247.45	180.61	160.17	166.73	176.83	171.18	158.20	156.50
Hf	5.70	5.82	4.42	3.83	3.91	4.11	3.98	3.69	3.79
Sm	7.13	7.19	5.58	5.17	5.39	5.54	5.21	4.91	5.21
Eu	2.34	2.29	1.87	1.81	1.94	1.91	1.79	1.73	1.83
Ti	21325.69	20703.51	16463.21	16528.05	17638.06	16882.28	18513.67	17545.56	17630.86
Gd	8.29	8.23	6.45	5.71	5.86	6.15	5.79	5.38	5.66
Dy	7.48	7.57	5.97	5.21	5.36	5.57	5.52	5.02	5.20
Y	40.31	40.76	31.28	27.35	27.47	29.18	29.13	26.70	26.37
Er	3.95	3.99	3.08	2.67	3.02	2.82	3.04	2.90	2.62
Yb	3.38	3.44	2.61	2.34	2.47	2.43	2.82	2.32	2.28
Pr	6.01	5.86	4.60	4.49		4.81			4.57
Tb	1.29	1.29	1.00	0.91		0.97			0.89
Ho	1.50	1.50	1.16	1.02		1.09			0.99
Tm	0.54	0.56	0.42	0.37		0.39			0.36
Lu	0.53	0.53	0.41	0.35		0.38			0.33

Isotopes

$^3\text{He}/^4\text{He}^b$	25.48	26.31	22.19	22.99	23.60	23.83	25.67	25.05	25.05
1σ	0.10	0.14	0.08	0.12	0.11	0.10	0.14	0.13	0.13
$C^3\text{He}$	1.11E+10	5.00E+09	1.23E+10	1.08E+10	5.97E+09	4.04E+09	2.95E+10	6.66E+10	

P saturation (bars)	283	133	369	369	152	294	244
<i>Trace Elements (ppm)</i>							
Rb	6.74	6.94	7.28	8.09	8.74	8.98	10.69
Ba	82.11	81.48	84.81	93.16	92.96	93.38	129.05
Th	1.14	1.07	1.26	1.34	1.32	1.26	1.82
U	0.353	0.357	0.379	0.431	0.447	0.423	0.576
Nb	21.63	20.22	21.53	24.73	23.95	23.78	31.80
K	3049.36	3067.02	3754.05	4193.80	3672.79	4636.01	5408.79
La	13.33	12.37	14.90	16.19	15.03	17.18	21.39
Ce	32.66	31.80	35.68	39.04	36.87	43.21	50.60
Pb	0.94	0.89	0.90	0.94	1.17	0.51	1.34
Sr	335.59	340.16	346.73	339.73	326.84	445.13	392.77
Nd	20.92	19.54	22.54	24.09	23.12	27.80	30.36
P	1181.65	1191.46	1489.46	1741.10	1404.72	1679.66	2152.53
Zr	161.91	145.20	180.28	202.15	180.89	223.71	255.16
Hf	3.94	3.60	4.16	4.40	4.25	5.17	5.52
Sm	5.26	4.83	5.55	5.91	5.82	6.87	7.74
Eu	1.85	1.74	1.92	1.98	1.99	2.34	2.52
Ti	17502.83	16260.21	18475.01	20273.80	18277.50	23511.46	23356.17
Gd	5.88	5.22	6.22	6.50	6.24	7.55	8.01
Dy	5.29	4.76	5.63	5.82	5.67	6.70	6.77
Y	27.21	23.57	29.40	31.15	29.21	33.55	36.87
Er	2.70	2.35	3.02	3.27	2.91	3.62	3.91
Yb	2.38	2.05	2.62	2.82	2.55	3.09	3.21
Pr	4.58	4.33			5.12		
Tb	0.91	0.80			0.97		
Ho	1.02	0.89			1.11		
Tm	0.37	0.32			0.40		
Lu	0.35	0.30			0.38		
<i>Isotopes</i>							
$^3\text{He}/^4\text{He}^b$	25.71	27.71	25.94	23.47		18.42	11.84
1σ	0.11	0.09	0.18	0.12		0.08	0.04
$C/^3\text{He}$			9.05E+09			3.42E+11	

$^{87}\text{Sr}/^{86}\text{Sr}^c$ **0.70323**
 $^{143}\text{Nd}/^{144}\text{Nd}^c$ **0.512946**
 ϵNd **6.01**
 $^{206}\text{Pb}/^{204}\text{Pb}^c$ **19.089**
 $^{207}\text{Pb}/^{204}\text{Pb}^c$ **15.550**
 $^{208}\text{Pb}/^{204}\text{Pb}^c$ **38.723**

0.70322
0.512944
5.97
19.066
15.554
38.714

0.512931
5.72
19.103
15.555
38.767

Group	ITE	ITE	ITE	ITE	ITE	ITE	ITE	ITE	ITE	ITE
Sample	D20a	D27a	D31a	D34a	D36	D38a	D39a	D40a	D42a	
Cruise	DRIFT04	DRIFT04	DRIFT04	DRIFT04	DRIFT04	DRIFT04	DRIFT04	DRIFT04	DRIFT04	
Latitude	-0.27	-0.57	-0.79	-0.76	-0.72	-0.72	-0.78	-0.89	-0.99	
Longitude	-91.89	-91.74	-91.67	-91.62	-91.55	-91.55	-91.58	-91.68	-91.61	
Average										
Depth (m)	3375	3078	3049	2645	2250	2218	3097		2947	

Major Elements (wt%)

SiO ₂	49.29	47.99	48.54	48.80	49.48	48.94	49.10	48.74	49.08
TiO ₂	3.32	3.14	4.39	2.23	3.54	2.30	2.44	3.25	2.50
Al ₂ O ₃	13.79	15.53	12.92	15.26	13.32	14.67	14.50	14.25	14.57
FeO*	12.26	11.50	14.69	10.44	13.44	10.28	10.72	12.55	11.07
MnO	0.21	0.19	0.23	0.18	0.23	0.17	0.18	0.22	0.18
MgO	6.00	5.49	5.28	6.42	5.13	7.06	6.93	5.14	6.62
CaO	10.91	10.25	10.19	12.51	10.27	12.73	12.57	10.45	12.36
Na ₂ O	2.79	3.35	2.95	2.81	3.06	2.54	2.45	3.41	2.57
K ₂ O	0.58	1.01	0.61	0.47	0.64	0.46	0.41	0.78	0.43
P ₂ O ₅	0.38	0.86	0.46	0.50	0.43	0.28	0.28	0.43	0.32
Total	99.53	99.32	100.24	99.61	99.53	99.42	99.58	99.22	99.69

Volatile Content

H ₂ O (wt%)	0.498	1.049	0.572	0.622	0.727	0.504	0.498	1.015	0.713
CO ₂ (ppm)	183.25	117.22	149.96	160.89	111.27	125.64	108.41	137.82	137.50
F (ppm)	509.74	795.56	648.49	455.49	681.26	437.67	406.96	806.52	434.30
S (ppm)	947.55	1426.94	1432.22	1108.79	1475.36	1058.34	1038.08	1599.16	1456.49
Cl (ppm)	165.85	309.19	260.44	240.03	219.99	208.37	185.67	361.91	171.67

P saturation (bars)	416	286	298	353	289	293	256	367	343
<i>Trace Elements (ppm)</i>									
Rb	9.33	13.21	12.29	7.66	12.27	6.12	6.51	13.90	6.87
Ba	101.14	160.23	117.19	100.33	117.55	80.81	76.83	164.43	80.13
Th	1.49	1.60	1.73	1.27	2.00	1.26	1.20	2.12	1.27
U	0.457	0.584	0.559	0.351	0.534	0.417	0.359	0.616	0.398
Nb	25.54	31.32	35.00	19.32	33.70	20.39	20.47	36.08	21.35
K	4456.29	8502.93	5219.53	4098.08	5223.79	3562.81	3302.41	6693.08	3491.39
La	16.97	22.63	22.06	13.84	21.49	13.48	14.03	25.08	14.61
Ce	40.45	52.97	52.49	31.09	49.70	30.49	32.71	55.69	33.81
Pb	1.79	0.86	1.04	0.59	1.12	2.30	0.62	0.95	0.63
Sr	332.95	522.03	364.32	344.54	304.27	300.47	296.04	389.83	311.56
Nd	24.70	31.01	32.21	18.07	28.69	17.34	19.69	30.47	20.48
P	1676.40	2340.49	2129.75	1121.90	1890.65	1143.74	1115.05	1873.33	1196.60
Zr	201.97	241.82	254.47	134.31	237.51	133.23	143.48	224.55	147.81
Hf	4.54	5.12	5.97	3.26	5.45	3.20	3.44	5.15	3.56
Sm	6.44	7.22	7.88	4.54	7.25	4.34	5.02	7.37	5.04
Eu	2.10	2.59	2.63	1.62	2.44	1.42	1.67	2.59	1.79
Ti	19890.15	18989.62	27116.31	13506.32	21618.82	13183.85	14478.65	19832.54	14956.26
Gd	6.86	7.46	8.62	4.92	7.88	4.58	5.13	7.64	5.42
Dy	6.13	6.07	7.79	4.40	7.04	4.08	4.78	6.69	4.99
Y	32.15	30.83	40.26	23.37	37.20	21.72	24.53	34.13	25.09
Er	3.44	3.22	4.35	2.42	4.00	2.20	2.63	3.59	2.67
Yb	3.00	2.63	3.68	2.13	3.18	1.81	2.24	3.09	2.27
Pr									
Tb									
Ho									
Tm									
Lu									
<i>Isotopes</i>									
$^3\text{He}/^4\text{He}^b$		10.52		13.94	12.83	14.97	18.19	13.13	17.46
1σ		0.05		0.06	0.11	0.11	0.12	0.20	0.12
$C/^3\text{He}$									

$^{87}\text{Sr}/^{86}\text{Sr}^c$	0.70333	0.70336	0.70339	0.70338
$^{143}\text{Nd}/^{144}\text{Nd}^c$	0.512945	0.512933	0.512923	0.512945
ϵNd	5.99	5.76	5.56	5.99
$^{206}\text{Pb}/^{204}\text{Pb}^c$	19.151	19.438	19.409	19.345
$^{207}\text{Pb}/^{204}\text{Pb}^c$	15.566	15.593	15.591	15.577
$^{208}\text{Pb}/^{204}\text{Pb}^c$	38.817	39.100	39.092	38.993
Group	ITE	ITE	ITE	ITE
Sample	D47a	D48a	D49a	D50a
Cruise	DRIFT04	DRIFT04	DRIFT04	DRIFT04
Latitude	-1.08	-1.13	-1.22	-1.29
Longitude	-91.55	-91.45	-91.01	-90.99
Average				
Depth (m)	3098	3244	3504	3358
<i>Major Elements (wt%)</i>				
SiO ₂	48.95	48.85	48.92	50.23
TiO ₂	2.32	2.41	3.33	2.97
Al ₂ O ₃	14.75	14.52	13.52	14.08
FeO*	10.84	10.70	13.72	11.96
MnO	0.18	0.18	0.22	0.19
MgO	6.65	6.73	5.03	5.94
CaO	12.31	12.42	10.20	11.35
Na ₂ O	2.70	2.50	3.09	2.84
K ₂ O	0.46	0.47	0.65	0.63
P ₂ O ₅	0.28	0.54	0.70	0.35
Total	99.44	99.31	99.39	99.98
<i>Volatile Content</i>				
H ₂ O (wt%)	0.767	0.645	0.848	1.086
CO ₂ (ppm)	160.91	164.06	188.12	134.18
F (ppm)	461.41	448.90	638.23	501.92
S (ppm)	1318.62	1328.72	1179.33	1425.46
Cl (ppm)	261.29	276.12	459.70	198.45

P saturation
(bars)

	401	369	472	314	210	379	230	314	301
<i>Trace Elements (ppm)</i>									
Rb	7.92	7.81	11.96	11.87	10.66	7.48	10.88	9.45	9.87
Ba	97.75	89.06	121.45	128.71	104.98	115.03	135.09	93.08	99.65
Th	1.35	1.37	1.75	1.99	1.46	1.44	1.43	1.58	1.79
U	0.399	0.387	0.570	0.592	0.457	0.430	0.452	0.499	0.503
Nb	20.58	21.38	30.33	33.71	26.61	22.46	23.88	25.60	26.15
K	3826.29	3759.21	5201.98	5437.47	4307.37	4716.95	4757.21	4346.69	4583.43
La	14.98	14.63	19.98	21.21	17.75	15.27	15.75	17.38	18.12
Ce	34.15	33.72	46.42	49.21	41.56	34.74	38.64	40.79	42.62
Pb	0.64	0.57	0.83	0.88	1.65	1.93	1.18	2.24	1.73
Sr	317.90	306.68	317.28	305.80	308.46	347.22	367.02	320.25	305.66
Nd	20.20	19.88	26.83	28.98	24.44	20.97	22.60	24.98	25.61
P	1158.40	1194.54	1811.95	1976.02	1453.36	1568.53	1416.03	1472.68	1510.29
Zr	138.87	148.71	214.73	230.07	183.42	176.83	172.70	199.17	201.27
Hf	3.25	3.32	4.99	5.36	4.40	4.06	4.11	4.60	4.85
Sm	4.82	4.89	6.46	6.87	6.17	5.40	5.53	6.26	6.51
Eu	1.77	1.62	2.36	2.37	2.09	1.92	1.94	2.11	2.10
Ti	14045.58	14363.08	20477.95	21148.47	18392.65	16389.17	16192.90	17922.82	17477.76
Gd	5.28	5.17	7.47	7.59	7.00	5.50	5.95	6.93	6.94
Dy	5.07	4.68	6.50	7.00	6.28	4.89	5.32	6.18	6.33
Y	25.75	24.77	35.27	36.99	31.94	26.72	26.95	31.79	33.49
Er	2.82	2.57	3.72	3.78	3.54	2.80	2.59	3.34	3.48
Yb	2.39	2.26	3.13	3.32	2.91	2.21	2.31	2.92	3.02
Pr							5.14		
Tb							0.93		
Ho							0.99		
Tm							0.35		
Lu							0.34		

Isotopes

³He/⁴He^b

1σ

C/³He

	11.42	20.46
	0.04	0.09
		5.29E+09

P saturation (bars)	127	210	237	380	236	222	188	311	304
<i>Trace Elements (ppm)</i>									
Rb	10.70	9.41	10.53	12.93	11.06	14.78	14.86	18.44	9.67
Ba	103.55	93.60	148.94	166.79	98.27	184.74	187.14	208.56	104.75
Th	1.59	1.70	1.77	2.06	1.65	2.02	2.07	2.36	1.50
U	0.471	0.461	0.520	0.548	0.490	0.570	0.604	0.637	0.441
Nb	27.11	24.17	29.17	31.17	27.13	32.81	33.29	37.91	23.45
K	4545.03	4274.15	6213.40	5582.29	4515.26	7684.09	8056.29	7412.03	4116.54
La	18.45	16.63	19.89	20.97	18.24	23.17	23.38	24.31	16.69
Ce	43.12	38.78	45.54	45.81	43.26	52.95	53.81	52.80	39.20
Pb	2.08	1.75	1.69	1.36	2.03	0.41	0.51	1.63	0.28
Sr	306.77	290.69	428.98	431.82	298.42	514.04	521.44	489.77	313.88
Nd	25.97	23.42	26.81	28.83	26.39	30.09	30.87	32.39	23.82
P	1552.60	1384.11	1934.43	1604.41	1561.72	2005.62	2087.33	1929.09	1370.40
Zr	205.00	188.84	222.48	237.14	211.32	240.44	247.77	273.45	175.90
Hf	4.94	4.31	5.00	5.52	5.02	5.23	5.48	6.26	4.55
Sm	6.49	6.04	6.50	6.92	6.72	7.14	7.54	7.77	6.09
Eu	2.26	2.01	2.36	2.33	2.23	2.75	2.70	2.61	1.84
Ti	19726.31	16499.00	18880.15	18587.69	19599.45	19407.38	19873.34	20897.84	18515.70
Gd	7.26	6.47	6.94	7.49	7.29	7.63	7.79	8.10	6.61
Dy	6.81	6.19	5.78	6.54	6.85	6.29	6.59	7.07	6.01
Y	35.44	31.32	30.30	32.85	35.42	31.67	32.30	35.08	29.49
Er	3.86	3.40	3.22	3.23	3.87	3.36	3.54	3.40	3.51
Yb	3.22	2.89	2.66	2.81	3.32	2.81	2.84	2.89	2.86
Pr				6.39				7.26	
Tb				1.13				1.24	
Ho				1.24				1.29	
Tm				0.44				0.46	
Lu				0.41				0.42	
<i>Isotopes</i>									
$^3\text{He}/^4\text{He}^b$			9.95	9.76		8.24	8.51	8.37	16.84
1σ			0.04	0.08		0.05	0.06	0.07	0.11
$C/^3\text{He}$			3.99E+10			1.12E+10	1.06E+10		

$^{87}\text{Sr}/^{86}\text{Sr}^c$	0.70337	0.70344	0.70320	0.70341	0.70322	0.70321		
$^{143}\text{Nd}/^{144}\text{Nd}^c$	0.512925	0.512924		0.51292	0.512933	0.512934		
ϵNd	5.60	5.58		5.50	5.76	5.77		
$^{206}\text{Pb}/^{204}\text{Pb}^c$	19.371	19.377	19.271	19.402	19.432	19.407		
$^{207}\text{Pb}/^{204}\text{Pb}^c$	15.592	15.593	15.594	15.595	15.604	15.604		
$^{208}\text{Pb}/^{204}\text{Pb}^c$	39.033	39.048	38.985	39.065	39.181	39.159		
Group	ITE	ITE	ITD Group	ITD	ITD	ITD	ITD	ITD
Sample	PL02-24-32	PL02-24-37	D10a	D22a	PL02-10-8	PL02-11-5	PL02-12-1	PL02-13-24
Cruise	PLUME02	PLUME02	DRIFT04	DRIFT04	PLUME02	PLUME02	PLUME02	PLUME02
Latitude	-1.29	-1.29	-0.08	0.37	-0.55	-0.19	-0.21	0.07
Longitude	-90.91	-90.91	-91.95	-89.85	-88.53	-88.67	-88.65	-89.04
Average								
Depth (m)	2719	2719	3100	819	1074	1006	1251	1050
<i>Major Elements (wt%)</i>								
SiO ₂	49.46	49.26	50.22	50.39	49.98	49.26	49.49	49.25
TiO ₂	3.05	3.00	1.16	1.17	1.50	2.08	1.60	1.03
Al ₂ O ₃	13.76	14.20	17.02	14.92	14.74	14.99	14.50	16.09
FeO*	12.29	11.83	8.50	10.16	10.38	11.32	11.54	9.28
MnO	0.20	0.20	0.20	0.17	0.23	0.20	0.24	0.17
MgO	5.98	6.24	8.63	7.89	7.41	6.17	7.05	8.44
CaO	10.95	11.15	12.03	13.13	12.87	11.48	12.51	12.44
Na ₂ O	2.77	2.78	2.48	2.58	2.68	3.47	2.76	2.21
K ₂ O	0.51	0.51	0.14	0.06	0.11	0.38	0.07	0.04
P ₂ O ₅	0.46	0.31	0.13	0.09	0.14	0.29	0.18	0.04
Total	99.43	99.47	100.51	100.55	100.05	99.64	99.95	98.99
<i>Volatile Content</i>								
H ₂ O (wt%)	0.640	0.646	0.252	0.148	0.299	0.533	0.290	0.140
CO ₂ (ppm)	139.07	108.65	153.80	70.64	35.79	35.15	72.91	22.61
F (ppm)	486.13	505.26	161.64	125.05	194.57	376.27	185.01	91.28
S (ppm)	1149.12	1253.89	823.55	1015.30	1049.24	1090.64	1187.18	938.56
Cl (ppm)	134.07	155.46	40.66	52.10	27.50	133.74	14.47	81.30

P saturation
(bars)

	337	273	337	155	282	85	101	165	51
<i>Trace Elements (ppm)</i>									
Rb	8.70	9.66	1.53	9.17	2.44	1.34	5.95	0.79	0.38
Ba	83.91	119.29	11.63	5.32	5.36	14.94	60.42	8.39	4.46
Th	1.45	1.61	0.18	0.06	0.07	0.19	0.56	0.15	0.05
U	0.421	0.470	0.051	0.024	0.029	0.057	0.199	0.038	0.018
Nb	23.35	24.75	2.49	1.02	1.08	2.80	8.59	1.68	0.70
K	4008.54	4448.10	852.20	329.57	360.31	873.08	3049.16	552.99	232.27
La	15.74	16.85	2.98	1.64	1.71	2.98	7.50	2.69	1.06
Ce	37.04	40.43	8.95	5.99	6.03	8.95	19.94	9.33	4.05
Pb	0.33	0.26	0.39	0.31	0.30	0.34	0.53	0.34	0.19
Sr	301.22	303.38	156.86	110.27	101.93	140.15	205.56	120.01	80.97
Nd	22.47	24.42	8.00	7.08	7.01	8.99	15.62	9.67	5.55
P	1413.42	1420.12	542.80	379.69	362.30	594.15	1135.83	549.51	261.48
Zr	182.12	182.00	76.20	62.89	63.18	88.98	158.25	98.48	44.63
Hf	4.28	4.65	1.91	2.00	2.11	2.48	3.68	2.74	1.92
Sm	5.68	6.12	2.91	2.54	2.92	3.30	4.62	3.75	2.34
Eu	2.05	1.95	1.09	1.06	1.14	1.24	1.59	1.39	0.94
Ti	18380.36	18267.52	6772.97	6906.85	7314.44	8555.03	12190.16	9297.61	6087.44
Gd	6.20	6.79	3.92	3.70	4.08	4.57	5.41	5.98	3.37
Dy	5.77	6.17	4.38	4.46	4.99	4.85	6.26	7.28	4.09
Y	30.26	30.52	21.92	26.19	28.14	27.86	37.41	36.45	22.86
Er	3.05	3.56	2.63	2.75	3.04	2.89	3.91	4.71	2.58
Yb	2.65	2.91	2.56	2.59	2.86	2.71	3.64	4.54	2.41
Pr			1.62	1.21	1.19	1.90		1.90	0.83
Tb			0.68	0.69	0.70	0.87		1.11	0.61
Ho			0.95	0.99	1.01	1.18		1.67	0.90
Tm			0.41	0.43	0.44	0.50		0.72	0.39
Lu			0.39	0.41	0.41	0.47		0.74	0.37

Isotopes

³He/⁴He^b

1σ

C/³He

7.72
0.42

8.12
0.04

8.79
0.06

8.36
0.06
5.88E+10

17.21
0.13

16.56
0.19

$^{87}\text{Sr}/^{86}\text{Sr}^c$	0.70337	0.70343	0.70265	0.70260	0.70270	0.70276	0.70264
$^{143}\text{Nd}/^{144}\text{Nd}^c$	0.512945	0.512912	0.513095	0.513101		0.513111	0.513126
ϵNd	5.99	5.35	8.92	9.03		9.23	9.52
$^{206}\text{Pb}/^{204}\text{Pb}^c$	19.329	19.307	18.471	18.514	18.758	18.766	18.790
$^{207}\text{Pb}/^{204}\text{Pb}^c$	15.586	15.569	15.492	15.512	15.584	15.541	15.629
$^{208}\text{Pb}/^{204}\text{Pb}^c$	38.948	38.908	37.971	38.013	38.554	38.290	38.692
Group	ITD	ITD	ITD	ITD	ITD	ITD	ITD
Sample	PL02-13-25	PL02-13-27	PL02-14-3	PL02-27-1	PL02-27-17	PL02-9-20	PL02-9-33
Cruise	PLUME02	PLUME02	PLUME02	PLUME02	PLUME02	PLUME02	PLUME02
Latitude	0.07	0.07	0.10	0.88	0.88	-0.47	-0.47
Longitude	-89.04	-89.04	-89.09	-91.32	-91.32	-88.53	-88.53
Average							
Depth (m)	1050	1050	1365	1557	1557	1180	1180
<i>Major Elements (wt%)</i>							
SiO ₂	50.02	49.57	48.11	48.76	48.61	47.34	47.41
TiO ₂	1.03	1.10	1.17	1.83	1.77	0.99	1.01
Al ₂ O ₃	16.00	15.58	17.10	15.53	15.64	17.77	17.90
FeO*	9.68	9.87	9.15	11.17	11.11	9.07	9.00
MnO	0.17	0.19	0.17	0.22	0.22	0.16	0.17
MgO	8.47	8.21	8.86	7.27	7.26	9.54	9.59
CaO	12.42	12.83	12.73	11.93	11.82	12.17	12.49
Na ₂ O	2.36	2.35	2.55	3.12	3.02	2.34	2.30
K ₂ O	0.04	0.03	0.03	0.08	0.10	0.02	0.01
P ₂ O ₅	0.19	0.07	0.19	0.14	0.33	0.11	0.14
Total	100.39	99.80	100.05	100.05	99.87	99.51	99.45
<i>Volatile Content</i>							
H ₂ O (wt%)	0.133	0.156	0.117	0.346	0.327	0.166	0.156
CO ₂ (ppm)	78.18	23.18	102.27	118.84	92.44	16.99	184.84
F (ppm)	82.78	97.19	124.20	182.10	178.89	120.53	120.27
S (ppm)	876.18	978.52	950.44	1032.48	1033.03	886.88	891.12
Cl (ppm)	156.92	93.00	3.80	53.61	77.62	9.38	10.37

P saturation (bars)	171	52	160	146	242	179	24	240	249
<i>Trace Elements (ppm)</i>									
Rb	0.36	0.43	0.19	0.22	1.10	1.08	0.11	0.13	0.13
Ba	3.52	4.55	2.37	2.71	12.49	10.40	1.87	1.99	2.34
Th	0.04	0.05	0.03	0.03	0.16	0.17	0.02	0.03	0.03
U	0.016	0.020	0.010	0.010	0.050	0.054	0.010	0.011	0.011
Nb	0.65	0.81	0.43	0.44	2.18	2.27	0.42	0.42	0.48
K	203.19	243.64	158.79	166.10	648.53	644.26	146.63	150.97	153.71
La	0.92	1.13	1.07	1.21	3.10	3.01	1.11	1.22	1.27
Ce	3.29	4.25	4.71	5.39	10.24	10.24	4.25	5.25	5.49
Pb	0.15	0.21	0.22	0.26	0.40	0.36	0.22	0.29	0.31
Sr	79.22	79.91	106.17	113.25	136.02	139.01	117.70	128.60	132.86
Nd	4.77	5.72	6.52	7.59	11.23	11.05	5.24	6.34	6.62
P	255.30	272.38	310.57	310.37	652.76	625.00	319.82	286.97	296.77
Zr	41.31	47.49	60.28	61.83	97.12	101.49	57.26	57.32	59.28
Hf	1.44	1.93	1.91	2.43	3.18	2.99	1.51	1.81	1.92
Sm	2.04	2.29	2.54	2.94	4.09	4.16	1.89	2.19	2.39
Eu	0.85	0.94	1.08	1.16	1.55	1.56	0.80	0.91	0.95
Ti	5896.57	6383.48	6681.36	7009.40	10787.35	10587.87	5435.53	5796.76	5950.51
Gd	2.83	3.37	3.64	4.13	5.60	5.79	2.50	3.26	3.26
Dy	3.63	4.06	4.03	4.63	6.13	6.34	2.93	3.71	3.65
Y	21.84	23.82	25.14	25.85	34.39	35.65	18.29	20.02	20.95
Er	2.28	2.58	2.59	2.89	3.85	3.85	1.80	2.37	2.41
Yb	2.05	2.42	2.39	2.64	3.40	3.48	1.72	2.07	2.13
Pr	0.77	0.90	1.19	1.20	2.01	1.95	1.14	1.13	1.12
Tb	0.55	0.60	0.67	0.74	1.01	1.03	0.54	0.59	0.54
Ho	0.77	0.86	0.95	1.06	1.39	1.40	0.76	0.87	0.79
Tm	0.32	0.37	0.40	0.46	0.58	0.57	0.33	0.37	0.34
Lu	0.31	0.34	0.39	0.43	0.53	0.55	0.32	0.36	0.32
<i>Isotopes</i>									
$^3\text{He}/^4\text{He}^b$	7.27		8.78	8.78	8.51	8.53		8.19	
1σ	0.04		0.05	0.05	0.05	0.05		0.05	
$C/^3\text{He}$									

P saturation (bars)	241	236	168	202	171	221	150	195	394
<i>Trace Elements (ppm)</i>									
Rb	0.11	0.13	0.88	0.69	0.47	0.1136	0.18	0.36	0.53
Ba	2.02	2.21	10.63	8.88	5.82	2.8114	1.83	4.70	6.70
Th	0.03	0.03	0.12	0.10	0.08	0.0233	0.02	0.06	0.07
U	0.010	0.012	0.037	0.030	0.024	0.0092	0.009	0.016	0.019
Nb	0.43	0.45	1.83	1.37	1.06	0.5427	0.26	0.69	1.00
K	160.03	158.94	436.56	499.36	386.62	124.007	143.28	212.27	278.98
La	1.06	1.32	1.76	2.24	1.80	0.8426	0.87	0.97	1.27
Ce	4.44	5.40	5.05	7.76	6.13	3.1035	4.51	3.62	4.39
Pb	0.22	0.30	0.18	0.32	0.25	0.1194	0.21	0.14	0.24
Sr	120.42	132.11	77.51	123.93	114.31	78.8355	120.67	62.35	62.66
Nd	5.05	6.56	5.45	8.23	6.54	4.0398	5.44	4.70	5.35
P	315.18	287.70	282.71	425.04	340.43	188.3518	235.07	264.90	289.20
Zr	57.90	58.70	40.67	69.96	56.90	33.2839	39.39	37.48	44.01
Hf	1.53	1.77	1.82	2.58	2.01	1.2754	1.51	1.64	1.98
Sm	1.98	2.27	2.06	3.16	2.32	1.4307	2.08	1.82	2.14
Eu	0.80	0.95	0.85	1.23	0.94	0.693	0.91	0.83	0.83
Ti	5556.45	5931.13	5640.78	7789.73	6348.72	4652.3108	5593.19	5609.10	6214.21
Gd	2.77	3.16	2.99	4.41	3.43	2.2304	2.82	3.32	3.32
Dy	3.03	3.59	3.88	4.94	3.93	2.9287	3.19	4.18	4.11
Y	19.00	20.23	22.19	27.36	22.37	18.5673	16.98	21.93	24.29
Er	1.88	2.28	2.37	3.15	2.54	1.9272	1.94	2.54	2.76
Yb	1.81	2.08	2.27	2.95	2.38	1.8625	1.89	2.47	2.49
Pr	1.13	1.15	0.93	1.47	1.29	0.80	0.94	0.86	0.97
Tb	0.58	0.57	0.56	0.76	0.69	0.49	0.50	0.67	0.70
Ho	0.82	0.83	0.83	1.09	0.98	0.75	0.69	1.02	1.08
Tm	0.35	0.36	0.36	0.46	0.43	0.34	0.29	0.43	0.46
Lu	0.35	0.34	0.35	0.44	0.42	0.33	0.28	0.42	0.46

Isotopes
 $^3\text{He}/^4\text{He}^b$
 1σ
 $C/^3\text{He}$

$^{87}\text{Sr}/^{86}\text{Sr}^c$
 $^{143}\text{Nd}/^{144}\text{Nd}^c$
 ϵNd
 $^{206}\text{Pb}/^{204}\text{Pb}^c$
 $^{207}\text{Pb}/^{204}\text{Pb}^c$
 $^{208}\text{Pb}/^{204}\text{Pb}^c$

Group	ITD	ITD	ITD	ITD	WD Group	WD	WD	WD	WD	WD
Sample	DR79-1	DR80-2	DR83-6	DR83-6	PL02-26-16	PL02-26-21	PL02-26-25	PL02-26-7	PL02-28-1	PL02-28-11
Cruise	SO 158	SO 158	SO 158	SO 158	PLUME02	PLUME02	PLUME02	PLUME02	PLUME02	PLUME02
Latitude	0.42	-0.02	-0.31	-0.31	0.83	0.83	0.83	0.84	1.02	1.02
Longitude	-88.69	-88.51	-88.39	-88.39	-91.29	-91.29	-91.29	-91.29	-91.55	-91.55
Average										
Depth (m)	2377	1606	1321	1321	676	676	676	676	1183	1183
<i>Major Elements (wt%)</i>										
SiO ₂	47.87	50.56	47.89	47.89	49.13	49.47	48.64	49.32	48.69	48.49
TiO ₂	0.95	1.27	0.96	0.96	1.87	1.87	1.79	1.89	1.76	1.78
Al ₂ O ₃	17.08	14.72	17.51	17.51	15.69	15.78	15.64	15.67	16.82	16.59
FeO*	9.82	10.04	8.97	8.97	10.17	10.10	11.11	10.08	9.74	9.80
MnO	0.16	0.20	0.16	0.16	0.17	0.20	0.18	0.21	0.16	0.16
MgO	9.65	7.58	9.29	9.29	7.45	7.57	7.03	7.46	7.98	7.84
CaO	11.96	12.71	12.62	12.62	11.89	11.98	11.80	11.97	11.68	11.74
Na ₂ O	2.42	2.53	2.38	2.38	2.96	2.92	3.05	2.95	2.90	2.85
K ₂ O	0.05	0.05	0.03	0.03	0.26	0.25	0.11	0.25	0.20	0.18
P ₂ O ₅	0.06	0.10	0.07	0.07	0.20	0.20	0.36	0.18	0.19	0.18
Total	100.02	99.77	99.89	99.89	99.80	100.34	99.72	99.99	100.13	99.62
<i>Volatile Content</i>										
H ₂ O (wt%)	0.185	0.200	0.141	0.141	0.444	0.401	0.407	0.461	0.314	0.322
CO ₂ (ppm)	147.36	87.12	179.13	179.13	41.14	23.17	86.83	40.7	52.14	64.1
F (ppm)	120.81	144.06	105.93	105.93	270.79	262.58	181.46	270.36	234.07	231.4
S (ppm)	917.63	1048.25	880.49	880.49	780.52	715.78	1026.42	787.06	759.39	814.09
Cl (ppm)	43.45	14.95	28.29	28.29	69.78	70.61	88.85	70.05	53.29	49.63

P saturation (bars)	215	192	261	106	64	177	107	108	122
<i>Trace Elements (ppm)</i>									
Rb	0.52	0.58	0.2185	4.3099	4.3832	1.07	4.3881	3.6079	3.4015
Ba	8.40	7.06	2.4501	49.7096	49.9265	10.89	48.222	38.4638	33.3533
Th	0.09	0.08	0.0404	0.7122	0.7072	0.18	0.7242	0.5462	0.4975
U	0.026	0.024	0.0156	0.2155	0.2358	0.052	0.203	0.1777	0.1714
Nb	1.25	1.13	0.3938	9.0863	8.9781	2.28	8.7721	6.9053	6.2984
K	344.67	362.23	165.5492	2167.4007	2070.7699	663.66	2095.6714	1640.82	1467.5311
La	1.72	1.78	1.4002	7.5789	7.9264	3.10	7.5265	6.3928	5.8035
Ce	5.41	6.15	5.8641	18.9457	19.9004	10.07	19.0325	17.0915	15.5883
Pb	0.21	0.23	0.2387	0.1542	0.1931	0.34	0.1614	0.1599	0.1529
Sr	106.76	96.32	117.9786	205.5402	212.0721	137.55	204.6942	187.1786	175.7391
Nd	5.69	7.21	6.6622	14.1379	14.9552	11.05	14.2343	14.2505	13.1395
P	285.72	418.73	292.4683	827.2338	862.4216	636.26	841.2189	825.4759	788.8159
Zr	50.60	61.15	52.3018	112.5106	116.5399	104.00	114.2235	114.0026	109.4997
Hf	1.63	2.28	1.7579	3.2915	3.4859	3.06	3.1139	3.6078	3.2884
Sm	1.98	2.67	2.4588	4.0461	4.4965	3.97	4.413	4.4087	4.2039
Eu	0.80	1.06	1.0246	1.2688	1.3099	1.49	1.2404	1.26	1.219
Ti	5542.24	7271.43	5905.574	11254.6069	11334.5612	10831.36	11215.4798	10887.4561	10661.6578
Gd	2.88	3.75	3.4962	4.5072	4.845	5.68	4.5813	4.7833	4.5212
Dy	3.46	4.58	4.1353	5.1057	5.4858	6.47	5.1861	5.7824	5.5199
Y	19.67	25.90	18.9853	27.5403	28.7964	35.91	27.4486	30.2221	29.6103
Er	2.23	2.94	2.6251	3.2456	3.5035	3.90	3.16	3.5737	3.6198
Yb	2.00	2.66	2.4582	2.6021	2.8197	3.57	2.6355	3.1181	2.9872
Pr	1.25	1.53	1.19			1.98			
Tb	0.62	0.82	0.63			1.07			
Ho	0.93	1.19	0.93			1.45			
Tm	0.39	0.50	0.40			0.60			
Lu	0.38	0.48	0.39			0.57			
<i>Isotopes</i>									
$^3\text{He}/^4\text{He}^b$				8.79	8.80	8.51	8.81	8.42	8.45
1σ				0.05	0.05	0.05	0.05	0.05	0.05
$C/^3\text{He}$									

$^{87}\text{Sr}/^{86}\text{Sr}^c$	0.70284	0.70283	0.70287	0.70279	0.70276	0.70277
$^{143}\text{Nd}/^{144}\text{Nd}^c$	0.513003	0.513011	0.512994	0.512997	0.513038	0.513037
ϵNd	7.12	7.28	6.94	7.00	7.80	7.78
$^{206}\text{Pb}/^{204}\text{Pb}^c$	19.121	19.152	19.161	19.127	19.067	19.028
$^{207}\text{Pb}/^{204}\text{Pb}^c$	15.584	15.592	15.582	15.575	15.588	15.564
$^{208}\text{Pb}/^{204}\text{Pb}^c$	38.778	38.844	38.766	38.791	38.673	38.602

Group	WD	WD	WD	WD	WD	WD
Sample	PL02-29-3	PL02-30-1	DR40-1	DR40-3	DR41-A-1	DR46-A-1
Cruise	PLUME02	PLUME02	SO 158	SO 158	SO 158	SO 158
Latitude	1.90	1.59	0.98	0.98	1.24	1.71
Longitude	-92.16	-91.92	-90.84	-90.84	-91.12	-91.19
Average						
Depth (m)	1723	2256	1560	1560	445	2235

Major Elements (wt%)

SiO_2	50.25	48.34	49.15	49.44	50.17	49.01	50.22	50.21	48.93
TiO_2	1.38	1.52	1.21	1.18	1.72	2.11	1.25	1.82	1.24
Al_2O_3	14.51	16.38	16.42	16.32	15.41	15.92	15.04	14.57	16.12
FeO^*	10.41	9.52	10.67	10.58	10.38	10.60	10.03	11.64	10.30
MnO	0.19	0.19	0.17	0.19	0.18	0.19	0.20	0.22	0.21
MgO	7.32	7.82	7.93	8.01	7.28	7.14	7.98	6.90	8.21
CaO	12.48	12.14	11.54	11.46	12.12	11.00	12.90	11.08	12.10
Na_2O	2.43	2.58	2.70	2.66	2.82	2.78	2.35	2.53	2.34
K_2O	0.18	0.36	0.20	0.21	0.24	0.43	0.11	0.27	0.09
P_2O_5	0.37	0.32	0.12	0.15	0.16	0.33	0.13	0.26	0.15
Total	99.52	99.18	100.12	100.19	100.48	99.51	100.21	99.51	99.69

Volatile Content

H_2O (wt%)	0.249	0.472	0.385	0.345	0.360	0.702	0.236	0.445	0.232
CO_2 (ppm)	114.9	120.75	100.78	94.44	10.73	95.68	193.72	116.94	159.74
F (ppm)	200.19	325.69	217.55	216.52	265.00	395.15	155.88	303.49	151.04
S (ppm)	1127.04	964.90	1078.48	1093.09	855.38	1228.66	999.99	1279.18	1045.01
Cl (ppm)	123.93	181.75	115.98	120.36	126.42	278.27	110.98	272.66	102.55

P saturation (bars)	253	222	230	214	34	252	421	270	349
<i>Trace Elements (ppm)</i>									
Rb	3.8423	6.8494	4.9368	5.12	4.67	6.77	1.78	6.19	1.54
Ba	34.9704	87.8552	59.4427	62.54	56.53	97.67	24.09	58.63	19.06
Th	0.5294	1.204	0.8013	0.86	0.83	1.30	0.33	0.90	0.26
U	0.1539	0.3114	0.1922	0.211	0.249	0.350	0.094	0.235	0.075
Nb	6.1775	15.868	8.5886	9.00	8.95	15.87	3.79	9.61	3.30
K	1338.0145	3057.23	1641.6904	1740.38	2174.95	3623.12	931.32	2094.54	713.95
La	4.8853	10.98	6.5166	6.75	7.67	12.10	3.42	7.19	3.14
Ce	11.9439	24.28	14.6067	14.82	18.70	28.41	9.44	17.83	8.62
Pb	0.245	0.23	0.1716	0.19	0.19	0.21	0.31	0.17	0.30
Sr	111.6015	220.97	144.668	148.58	163.53	239.72	97.78	113.61	89.48
Nd	9.463	14.07	9.0857	9.30	13.46	18.03	7.88	13.32	7.24
P	560.2203	897.10	519.7734	516.92	806.37	1237.91	472.95	906.50	440.69
Zr	73.464	109.11	64.6133	65.85	105.54	144.27	64.28	109.26	61.79
Hf	2.2616	2.60	2.1215	2.32	3.35	3.79	2.28	3.50	2.21
Sm	3.0594	3.81	2.5899	2.62	4.26	5.01	2.62	4.02	2.50
Eu	1.0151	1.35	0.9007	0.98	1.30	1.55	0.99	1.20	0.97
Ti	8005.1267	8890.25	7157.9846	7254.28	10531.18	12825.14	7496.73	10984.16	7232.57
Gd	3.9043	4.14	3.0823	3.13	4.57	5.20	3.92	4.72	3.68
Dy	5.1269	4.61	3.8605	3.96	5.62	5.65	4.79	6.10	4.52
Y	28.4253	25.44	21.3247	21.51	30.11	30.36	25.19	35.76	26.58
Er	3.0279	2.69	2.6033	2.64	3.76	3.67	2.98	4.18	2.93
Yb	2.846	2.50	2.1235	2.19	3.15	3.05	2.91	3.69	2.87
Pr							1.57		1.51
Tb							0.76		0.70
Ho							1.11		1.05
Tm							0.47		0.46
Lu							0.46		0.46

Isotopes
³He/⁴He^b
1σ
C/³He

6.87
0.08

7.81
0.05

$^{87}\text{Sr}/^{86}\text{Sr}^c$ 0.70295 0.70301
 $^{143}\text{Nd}/^{144}\text{Nd}^c$ 0.513008 0.512964
 ϵNd 7.22 6.36
 $^{206}\text{Pb}/^{204}\text{Pb}^c$ 19.001 19.366
 $^{207}\text{Pb}/^{204}\text{Pb}^c$ 15.599 15.620
 $^{208}\text{Pb}/^{204}\text{Pb}^c$ 38.895 39.282

Group	WD	WD	WD	WD	WD	Wolf Volcano	Wolf Volcano	Wolf Volcano	Wolf Volcano
Sample	DR60-1	DR62-2	DR65-1	DR68-3	DR68-4	D3a	D3a-2	D4a	D4a
Cruise	SO 158	SO 158	SO 158	SO 158	SO 158	DRIFT04	DRIFT04	DRIFT04	DRIFT04
Latitude	1.72		0.89		0.86				0.19
Longitude	-91.72	-91.69	-91.42	-90.84	-90.84				-91.41
Average									
Depth (m)	1848	2038	1493	1561	1561	2595	2595	2595	2015

Major Elements (wt%)

SiO ₂	49.81	48.75	49.05	50.19	50.35	48.91	49.07	48.85	48.95
TiO ₂	1.25	0.68	2.10	2.53	2.55	3.02	3.50	3.23	4.30
Al ₂ O ₃	15.50	17.53	15.15	13.80	13.83	14.59	13.86	14.48	13.28
FeO*	10.24	9.36	10.85	12.72	12.64	11.32	12.29	11.34	13.81
MnO	0.22	0.17	0.18	0.20	0.21	0.18	0.19	0.19	0.23
MgO	8.00	9.38	6.85	5.47	5.46	6.08	5.38	6.28	4.90
CaO	12.66	12.63	11.71	10.43	10.51	11.35	11.31	11.50	9.59
Na ₂ O	2.50	2.05	3.12	3.22	3.21	3.10	3.32	3.22	3.67
K ₂ O	0.09	0.03	0.27	0.52	0.52	0.52	0.63	0.52	0.74
P ₂ O ₅	0.15	0.09	0.24	0.32	0.30	0.36	0.46	0.38	0.53
Total	100.42	100.68	99.52	99.38	99.59	99.45	100.00	97.53	98.04

Volatile Content

H ₂ O (wt%)	0.206	0.098	0.479	0.662	0.512	0.867	0.839	1.033	1.2317
CO ₂ (ppm)	106.02	108.15	52.68	90.59	90.44	99.15	66.18	84.25	43.5488

F (ppm)	141.67	61.40	315.35	535.08	512.15	502.78	647.46	526.06	840.6638
S (ppm)	1072.59	887.88	951.72	1582.37	1549.65	1168.1	1510.5	1318.57	2185.0281
Cl (ppm)	140.95	14.48	83.35	493.31	482.14	230.65	207.91	297.46	303.9469
P saturation (bars)	233	212	134	236	219	285	210	266	230
<i>Trace Elements (ppm)</i>									
Rb	1.43	0.35	4.80	9.55	9.72	5.6781	7.0773	6.76	10.1489
Ba	17.20	4.90	55.00	121.04	119.66	55.0504	65.3289	66.48	85.8537
Th	0.25	0.06	0.86	1.78	1.65	0.9846	1.2619	1.01	1.5163
U	0.066	0.022	0.244	0.472	0.454	0.3581	0.4539	0.382	0.6116
Nb	2.60	0.82	9.97	23.86	23.47	16.5052	20.6707	18.34	26.9698
K	667.41	191.39	2281.94	4293.91	4150.27	3996.7644	5014.1729	4120.73	6155.6629
La	2.86	1.02	8.53	16.52	16.73	14.3924	17.7609	15.18	21.9666
Ce	8.45	3.26	21.53	38.08	38.38	36.1482	44.6224	40.94	59.3694
Pb	0.27	0.13	0.20	0.28	0.30	1.785	1.8253	1.37	1.9228
Sr	97.57	68.53	211.90	235.27	236.68	381.852	364.4298	391.62	361.9929
Nd	8.14	3.58	16.19	22.51	23.10	24.3693	29.1668	26.65	37.1913
P	453.54	181.92	953.19	1339.56	1359.47	1670.7093	2070.1348	1583.62	2287.9665
Zr	66.07	28.80	131.14	160.24	163.79	228.4943	290.2098	232.21	348.0472
Hf	2.27	1.26	3.80	4.46	4.44	5.0699	6.2698	5.36	7.5852
Sm	2.74	1.54	4.82	5.77	5.77	6.4207	7.283	6.80	9.2496
Eu	1.05	0.65	1.41	1.82	1.87	1.9359	2.46	2.39	3.1334
Ti	7467.33	4009.74	12581.17	15536.64	15511.46	17993.7745	20957.4181	18612.71	24759.5253
Gd	4.19	2.34	5.09	6.35	6.37	6.829	7.9125	7.28	9.8653
Dy	4.99	3.16	5.99	6.43	6.37	5.9788	7.2362	6.53	8.7207
Y	27.67	18.34	31.13	34.20	34.90	31.9168	37.6285	32.59	44.3709
Er	3.23	2.06	3.69	4.03	4.08	3.2925	3.8514	3.16	4.273
Yb	3.26	2.10	3.00	3.35	3.25	2.7326	3.2357	2.77	3.7715
Pr	1.49	0.62						5.78	8.22
Tb	0.83	0.43						1.13	1.53
Ho	1.25	0.68						1.22	1.63
Tm	0.55	0.32						0.43	0.58
Lu	0.55	0.33						0.39	0.54

Table 2. Fractional Crystallization model

	Starting Composition		
	Enriched Composition ^a	Depleted Composition ^b	
Major Elements (wt%)			
SiO ₂	47.48	46.46	
TiO ₂	2.29	1.34	
Al ₂ O ₃	16.38	14.36	
FeO*	9.16	11.77	
MnO	0.12	0.20	
MgO	9.38	11.86	
CaO	11.58	11.50	
Na ₂ O	2.25	2.14	
K ₂ O	0.33	0.08	
P ₂ O ₅	0.26	0.07	
H ₂ O (wt%)	0.68	0.12	
Volatile Elements (ppm)			
CO ₂	279.76	2.74	
F	293.36	176.48	
S	923.26	420.41	
Cl	118.42	34.54	
Starting Parameters ^c			
Volatile Kds ^d			
	Ol	CPX	PLAG
CO ₂	5.00E-06	3.00E-04	0
F	0.00259	0.0464	0.084
S	0.0027	0.44	0.019
Cl	5.00E-06	3.00E-04	0
Pressure	2kbars		
Temperature	1200		
Oxygen Fugacity	QFM		

^a Composition of melt inclusion AHA D25C-3-43 reported in Koleszar et al., (2009)

^b Composition of melt inclusion STG06-29-06 reported in Koleszar et al., (2009)

^c Models used in PETROLOG: Ol, CPX, PLAG- Danyushevsky, 2001, Melt density- Lange and Carmichael, 1987, Melt viscosity- Bottinga & Weill 1972. Oxygen fugacity set at QFM and then run closed for oxygen

^d CO₂, S, and Cl partition coefficients (Kd) for olivine (Ol) and clinopyroxene (CPX) based on the partition coefficients of Ba and Dy from Halliday et al. [1995]. Kd's for Ol and CPX for fluorine based on values of Hauri et al., [2006]. Plagioclase Kd's for F and S based on Nd and Dy values from Bedard (2006)

Table 3. End-member compositions

Group ^a		CO ₂ /Nb †	1σ	H ₂ O/Ce	1σ	F/Nd	1σ	Cl/K	1σ	S/Dy	1σ
HHe group	mean	4	2	202	26	20.1	0.8	0.057	0.009	218	21
	median	4	2	200	26	19.9	0.8	0.057	0.009	216	21
ITE group ^b	mean	5	2	174	24	24.9	0.7	0.049	0.010	237	20
	median	4	2	165	24	25.2	0.7	0.049	0.010	235	20
WD group ^c	mean	10	2	230	35	23.5	0.4	0.066	0.006	255	40
	median	10	2	233	35	23.3	0.4	0.069	0.006	276	40
ITD group ^d	mean	300*		117°		17.3	1.5	0.026	0.002	228	16
	median	300*		117°		16.6	1.5	0.025	0.002	236	16

† values are mean and median of extensively degassed samples and therefore do not represent mantle compositions

* set by expected value for MORB mantle (Saal *et al.*, 2002)

° set by average value of Santiago melt inclusions (Koleszar *et al.*, 2009)

^a End-member compositions for HHe, ITE, and WD group determined from samples that have been filtered to Cl/K < 0.08, S/Dy > 175, Sr/Sr* ≤ 1, and are not within error of being sulfide saturated. Further conditions exist where indicated. Further conditions exist where indicated. 1σ standard deviation between samples used to define end-member are indicated.

^b Determined from a subset of samples that represent the end-member composition determined from F/Nd ratios: D36, D51a, D34a, D38a, D27a

^c Determined from a subset of samples with an isotopic composition closest to the Pinta component

^d Determined from a subset of samples with the lowest Cl/K ratios: PL02-14-3, PL02-14-8, DR72-A-1

Table 4. Calculation of mantle viscosity: Wet diffusion/dislocation creep with constant [OH]

Rheological Parameters ^a				
	Diffusion		Calculation	
	creep regime	Dislocation creep regime	Strain Rate ($\dot{\epsilon}$)	Viscosity (Pa*s)
A	1.00E+06	90		
n	1	3.5		
P	3	0		
r	1	1.2		
E* (kJ/mol)	335	480		
V* (m ³ /mol)	4.00E-06	0.000011		
P (Pa)	7.00E+09	7.00E+09		
R	8.314	8.314		
T (°C)	1400	1400		
d (μm)	10000	10000		
σ (MPa)	0.3	0.3		
Diffusion creep regime	PM	H2O (ppm) 338.35	C(OH) = H/10 ⁶ Si ^b 5532.0225	7.69E-15
	DDMM	64.35	1052.1225	1.46E-15
Dislocation creep regime	PM	338.35	5532.0225	1.68E-13
	DDMM	64.35	1052.1225	2.29E-14
				1.79E+18
				1.31E+19

^a Parameters found in Table 1 of Hirth and Kohlstedt (2003)

^b Calculated for OI (Fo90)L 1ppm H2O = 16.35H/10⁶ Si (Paterson, 1982)

CHAPTER 3

The oxidation state of Fe in glasses from the Galapagos Archipelago: variation in oxygen fugacity as a function of mantle source.

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ABSTRACT

The oxidation state of the Earth's mantle plays an intrinsic role in the magmatic evolution of the Earth. Heterogeneity in magmatic oxidation has been recognized in lavas from mid-ocean ridges with variable isotopic enrichment. This suggests that isotopically diverse ocean island basalts may also preserve a large variability in their magmatic oxidation state. Here we present new μ -XANES measurements of $\text{Fe}^{3+}/\Sigma\text{Fe}$ (a proxy for system $f\text{O}_2$), using a geochemically diverse suite of submarine glasses from the Galapagos Archipelago. Utilizing previously presented major elements, trace elements, dissolved volatiles and isotopic data we show that $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios vary with the influence of shallow level processes. $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios generally increase with magmatic differentiation, but still show a large variation at a given MgO, which suggests other shallow level processes are affecting $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the melt. Progressive degassing of sulfur is shown to accompany decreasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, while assimilation of hydrothermally altered crust is shown to increase $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. Even after taking these processes into account there is still variability in the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of the isotopically distinct sample suites studied, yielding a magmatic $f\text{O}_2$ that ranges from $\Delta\text{QFM} = +0.16$ to $+0.74$ and showing that oxidation state varies as a function of mantle source composition in the Galapagos hotspot system. After correcting back to a common MgO content = 8.0 wt%, the trace element depleted group similar to MORB (ITD), and the trace element enriched group similar to Pinta (WD = high Th/La, $\Delta 7/4$, $\Delta 8/4$ ratios) show $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios within range of MORB (ITD = 0.162 ± 0.003 and WD = 0.164 ± 0.006). The other trace element enriched group similar to Sierra Negra and Cerro Azul (ITE) shows evidence of mixing between an oxidized and reduced source with the reduced end-

member showing a radiogenic isotope signature similar to Pinta (maximum ITE = 0.177 ± 0.008). This suggests that mantle sources in the Galapagos that are thought to contain recycled components (WD and ITE) are different in terms of their oxidation state. The high $^3\text{He}/^4\text{He}$ Fernandina samples are shown to have the most oxidized glasses (HHe = 0.175 ± 0.006) with high C/ ^3He ratios indicating the primitive mantle may be a more carbonated and oxidized source than previously thought.

INTRODUCTION

Oxygen fugacity (fO_2) is an intensive thermodynamic property that provides a measure of a system's redox potential at equilibrium. fO_2 controls the speciation and partitioning of multi-valent elements and affects igneous processes such as magmatic phase relations during melting and crystallization, depth of melt initiation and the composition of volcanic gases (e.g. Ballhaus, 1993, Holloway & Blank, 1994, Canil, 1999). Therefore, understanding fO_2 variability in space and time can potentially constrain the evolution of the mantle, as well as present-day mantle melting conditions .

The preservation of magmatic and mantle source fO_2 remains a topic of considerable debate (Ballhaus, 1993, Canil, 2002, Lee *et al.*, 2005, Cottrell *et al.*, 2009, Kelley & Cottrell, 2009, Lee *et al.*, 2010, Cottrell & Kelley, 2011, Kelley & Cottrell, 2012, Cottrell & Kelley, 2013). Using $Fe^{3+}/\Sigma Fe$ ratios as a proxy for fO_2 , a large variation is found in measured $Fe^{3+}/\Sigma Fe$ ratios in mid-ocean ridge basalts (MORB) and arc basalts (Bezous & Humler, 2005, Kelley & Cottrell, 2009, Cottrell & Kelley, 2011, Kelley & Cottrell, 2012, Cottrell & Kelley, 2013, Brounce *et al.*, 2014, Le Voyer *et al.*, 2015). Shallow level processes can account for some of this variation and can be tracked by variations in major, trace and volatile elements (H_2O , CO_2 , F, S, and Cl). Magmatic differentiation can change $Fe^{3+}/\Sigma Fe$ ratios due to early crystallizing phases, such as olivine, partitioning Fe^{2+} over Fe^{3+} and thereby concentrating Fe^{3+} in the melt, which causes an increase in $Fe^{3+}/\Sigma Fe$ ratios as magma evolves. Degassing has the potential to affect $Fe^{3+}/\Sigma Fe$ ratios when there is an oxidation state difference between volatile species dissolved in the melt and the major degassing species of volatile (Anderson & Wright, 1972, Kelley & Cottrell, 2012, Brounce *et al.*, 2014). Assimilation of wall rock by the

melt can also affect $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios as melt interacts with oxidized crust. Shallow level processes, however, are shown to inadequately recreate the total variation between measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of MORB and arc basalts, which suggests the mantle source $f\text{O}_2$ of these settings is fundamentally different (Kelley & Cottrell, 2012, Brounce *et al.*, 2014).

Recently, $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios were shown to vary systematically as a function of source composition in MORB with more enriched MORB (EMORB) mantle domains with higher Pb isotope ratios being more reduced than depleted MORB domains (samples filtered to only non-plume influenced MORB by Cottrell and Kelley (2013)). Ocean island basalts (OIB) are derived from several global geochemically distinct mantle reservoirs and display extensive regional geochemical heterogeneity (e.g. Hofmann, 1997, Stracke *et al.*, 2005, White, 2010). If the mantle can indeed preserve long-lived heterogeneities in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, OIBs have the potential to record large variations in and the possible evolution of mantle source oxidation state. However, whether OIB melt from a source that contains more primitive mantle that houses high $^3\text{He}/^4\text{He}$ and solar-like neon isotopes and/or recycled crustal components preserve measurably different oxidation state from either depleted upper mantle or arc mantle has yet to be extensively tested.

The goal of this study is to evaluate the oxidation state of the Galapagos mantle using μ -XANES to measure $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of submarine basaltic glass collected from across the archipelago. By using major, trace and volatile elements in addition to radiogenic isotope ratios, we show that some of the variation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios that we measure is due to shallow level processes such as magmatic differentiation, degassing,

and assimilation of hydrothermally altered material. However, shallow level processes cannot explain all of the variation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. There is evidence for variable oxidation states between the isotopically unique end-members in the Galapagos mantle source. The trace element depleted end-member in the Galapagos lavas has $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios comparable to MORB values at similar MgO contents (Cottrell & Kelley, 2011, Le Voyer *et al.*, 2015). The high $^3\text{He}/^4\text{He}$ end-member and the trace element and isotope enriched end-member similar to Sierra Negra and Cerro Azul have the highest $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of this study, while the trace element enriched end-member similar to Pinta (high Th/La and $\Delta 7/4$, $\Delta 8/4$) has intermediate $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios to these and the depleted end-member at similar MgO contents. These results place new constraints on the $f\text{O}_2$ relevant for OIB magmas. We will explore the implications of these findings in terms of mechanisms controlling $f\text{O}_2$ of the OIB mantle during plume melting.

GEOLOGIC BACKGROUND AND PREVIOUS WORK

In the Galapagos Archipelago, located on the equatorial Pacific, 16 of the 21 emergent volcanoes have erupted since the Holocene, making the Galapagos one of the most active volcanic regions in the world. The islands and seamounts sit on a shallow submarine platform 100-200 km to the south of the Galapagos Spreading Center (GSC), on the Nazca plate which is moving eastward with respect to a hotspot reference frame (Gripp & Gordon, 2002). Seismic studies have identified both a low-velocity anomaly and a thin transition zone in the mantle below the Galapagos Archipelago, characteristics attributed to a hot mantle plume column extending to at least as deep as the transition zone (Hooft *et al.*, 2003, Villagomez *et al.*, 2007, Villagomez *et al.*, 2011, Villagomez *et al.*, 2014).

The plume column tilts towards the GSC, against the direction of plate motion (Villagomez *et al.*, 2014). This in conjunction with geochemical studies conducted along the ridge show the strong influence the Galapagos plume has on the GSC (Detrick *et al.*, 2002, Schilling *et al.*, 2003, Cushman *et al.*, 2004, Ingle *et al.*, 2010, Gibson *et al.*, 2015).

There are four main compositional components that are generally distinguishable geographically from each other in the Galapagos Archipelago. The western component, found primarily near Fernandina Island, is characterized by high $^3\text{He}/^4\text{He}$ ratios reaching up to 29 Ra ($^3\text{He}/^4\text{He}$ ratio normalized to the atmospheric ratios, $1.4\text{e-}6$) in addition to intermediate $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios (Graham *et al.*, 1993, White *et al.*, 1993, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Kurz *et al.*, 2009) analogous to a minimally degassed, primitive mantle component (e.g. Kurz *et al.*, 1982, Farley *et al.*, 1992, Hart *et al.*, 1992, Hanan & Graham, 1996). The northern component, characterized by the lavas of Pinta Island and the Wolf/Darwin lineaments, is discernible by elevated $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ at a given $^{206}\text{Pb}/^{204}\text{Pb}$, resulting in high $\Delta 7/4$ and $\Delta 8/4$ as defined by Hart (1984), and the lowest $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratios yet measured in the Galapagos (Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Saal *et al.*, 2007). The southern component, characterized by lavas from Floreana Island with the highest $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ isotopic ratios found in the Galapagos with intermediate $^3\text{He}/^4\text{He}$ ratios (up to 14 Ra), $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios and unusually elevated $^{176}\text{Hf}/^{177}\text{Hf}$ ratios for the measured Nd isotopes (Bow & Geist, 1992, White *et al.*, 1993, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Kurz *et al.*, 2009, Harpp, 2014). While the Pb isotopes of this component

are typical of a HIMU mantle component, the high $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are unusual in comparison to other HIMU localities (Bow & Geist, 1992, Harpp & White, 2001, Harpp *et al.*, 2014). There is also a strong presence of a depleted component similar to MORB throughout the Galapagos, which is concentrated in the central and northeastern region of the archipelago. In general, lavas from Genovesa Island characterize this component, which is hypothesized to be either the product of depleted upper mantle, or a depleted component intrinsic to the plume.

The submarine basaltic glass measured for $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios for this study have been previously characterized for major, trace, and volatile elements, as well as isotopic ratios (Harpp & White, 2001, Geist *et al.*, 2006, Kurz *et al.*, 2009, Peterson *et al.*, submitted to Journal of Petrology). Glass chips were taken from dredges collected during the PLUME02 cruise in 1990 (Christie *et al.*, 1992), AHA-Nemo-2 cruise using the R/V Melville in 2000 (Geist *et al.*, 2006), the DRIFT04 cruise using the R/V Revelle in 2001 (Kurz *et al.*, 2001), and the R/V SONNE cruise, SO 158 in 2001 (Werner, 2002) from depths ranging from 445-3504 m below sea level. The samples are collected from across the archipelago (Fig. 1) and generally fall on 2 compositional trends. These trends cover almost the entire range reported in the Galapagos, with the exception of the Floreana component, which was not sampled.

The first array (Array 1) ranges between the compositions of Fernandina Islands and Sierra Negra/Cerro Azul Volcanoes. Lavas from Sierra Negra/Cerro Azul, located on the southern half of Isabela Island, are geochemically intermediate between the compositions of Fernandina, Floreana and Pinta (White *et al.*, 1993, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Saal *et al.*, 2007, Harpp, 2014). The

compositions of Sierra Negra and Cerro Azul are thus either the result of a mixture of melts from several end-members or the product of a unique mantle source with an intermediate composition. Though it is possible that a unique composition exists (Vidito *et al.*, 2013), samples from Sierra Negra and Cerro Azul fall over a large compositional space making it more likely they are the result of mixing of melts from several sources. Array 1 is sub-divided into the high $^3\text{He}/^4\text{He}$ ratio (HHe) group and the incompatible trace element enriched (ITE) group using $^3\text{He}/^4\text{He}$ ratios above and below 22 Ra respectively. Array 1 is characterized by samples that are enriched in incompatible trace elements (high Th/La ratios) and show characteristics consistent with generation in the garnet stability field (high Sm/Yb ratios) (Fig. 2). The HHe group also possesses a higher average Ti/Gd ratio than the ITE group, consistent with proposed high Ti characteristic of the a deep primitive mantle source (e.g. Kurz & Geist, 1999, Saal *et al.*, 2007, Jackson *et al.*, 2008). The samples of array 1, in terms of volatile/refractory element variations, are mainly distinguishable in terms of F/Nd and $\text{H}_2\text{O}/\text{Ce}$ ratios with the HHe group falling at higher $\text{H}_2\text{O}/\text{Ce}$ (202 ± 26) and lower F/Nd (20.1 ± 0.8) than the ITE group ($\text{H}_2\text{O}/\text{Ce} = 174 \pm 24$, F/Nd = 24.9 ± 0.7), while showing similar S/Dy and Cl/K ratios (HHe: S/Dy = 218 ± 21 , Cl/K = 0.057 ± 0.009 , ITE: S/Dy = 226 ± 20 , Cl/K = 0.048 ± 0.011) (Peterson *et al.*, submitted to Journal of Petrology). Volatile elements are often reported as ratios between a given volatile element and a refractory element of similar incompatibility (Nb, Ce, Nd, K, and Dy with CO_2 , H_2O , F, Cl, and S, respectively) to overcome the variation in concentrations during crystal fractionation and melting (Schilling *et al.*, 1980, Michael, 1995, Michael & Cornell, 1998, Danyushevsky *et al.*, 2000, Saal *et al.*, 2002, Hauri *et al.*, 2006, Workman *et al.*, 2006). The samples of array 1 have extensively degassed CO_2 , but

$C/{}^3\text{He}$ ratios calculated for samples from the HHe group are, on average, an order of magnitude higher than MORB and among the highest yet reported for OIB samples (Marty & Jambon, 1987, Trull *et al.*, 1993, Marty & Tolstikhin, 1998, Marty & Zimmermann, 1999, Shaw *et al.*, 2004, Barry *et al.*, 2014, Peterson *et al.*, submitted to Journal of Petrology). C and ${}^3\text{He}$ have similar solubilities in basaltic melt (Lux, 1987, Pan *et al.*, 1991, Dixon *et al.*, 1995, Jendrzewski *et al.*, 1997) and, therefore, will not be greatly fractionated during degassing. The high $C/{}^3\text{He}$ ratios, as a result, imply that the HHe end-member of array 1 comes from a carbonated mantle source. The samples of array 1 with ${}^3\text{He}/{}^4\text{He}$ ratios above 22Ra have lower Pb and Sr at similar Nd isotope ratios than samples with ${}^3\text{He}/{}^4\text{He}$ ratios less than 22 Ra (ITE group), consistent with previously measured isotopes for Fernandina and Sierra Negra/Cerro Azul whole rock samples (Fig. 3) (White *et al.*, 1993, Kurz & Geist, 1999, Saal *et al.*, 2007).

The second array (Array 2) ranges between the compositions of Genovesa and Pinta Is./Wolf, Darwin lineaments. The array is subdivided into the incompatible trace element depleted (ITD) group similar to MORB and an enriched composition (different from the ITE group) that displays the characteristics of the Pinta-Wolf-Darwin mantle end-member (WD group). The samples of array 2 range from trace element depleted to trace element enriched with the WD group having higher Th/La ratios than either the ITE or HHe groups (Fig. 2; high Th/La ratios are a characteristic of Pinta; Saal *et al.*, 2007). The WD group has a F/Nd (23.5 ± 0.4), Cl/K (0.066 ± 0.006) and S/Dy ratio (255 ± 40) similar to those of Sierra Negra/Cerro Azul but with a significantly higher $\text{H}_2\text{O}/\text{Ce}$ ratio (230 ± 35). In comparison, secondary processes have significantly affected the volatile content of the ITD glasses with only few samples showing volatile/refractory element

ratios close to those previously reported for MORB (Peterson *et al.*, submitted to Journal of Petrology). The samples of the ITD group have isotope ratios similar to MORB while the WD group display elevated $\Delta 7/4$ and $\Delta 8/4$ and low $^3\text{He}/^4\text{He}$ ratios (Fig. 3), consistent with the Pinta-Wolf-Darwin mantle end-member in the Galapagos and other plumes that contain an EM component (e.g. Stracke *et al.*, 2003, Workman *et al.*, 2006, Kendrick *et al.*, 2012).

SAMPLE PREPARATION AND METHODS

For microbeam analysis, individual samples were handpicked under a microscope to select glass that is free of alteration, mounted in epoxy and doubly polished to a thickness that created a large pool of glass (thickness variation = 30-100 μm) to ensure the presence of a crystal free path for the beam. Photographs were taken of wafered glass in reflected, plane-polarized and cross-polarized light.

Fe K-edge XANES spectra were collected at station X26A (bending magnet) at the National Synchrotron Light Source (NSLS), Brookhaven National Lab (BNL) in two sessions. NSLS operates at 2.8 GeV and 300 mA and we achieved energy selection using a Si (311) channel-cut monochromator. XANES spectra were collected in fluorescence mode using a 9x5 μm spot size. A minimum of 3 spectra were taken on independent spots per Galapagos glass sample to allow for a quantitative assessment of reproducibility and precision. Each spectra was inspected for evidence of crystal interference, which, if identified, resulted in rejection of that spectra from further analysis. Centroid precisions are determined by simultaneously fitting the baseline with a linear function, constrained to have a positive slope, and a damped harmonic oscillator (DHO) function and fitting the

pre-edge peaks with two Gaussian functions over a 7110-7118 eV sub-sample of the pre-edge region. To correct for monochromator energy drift over the course of each session, multiple spectra were taken of reference glass LW_0. We define centroid energy for LW_0 as 7112.3 and model energy drift as a linear function between each analysis. Use of the drift monitor allows for the direct comparison of centroid and $\text{Fe}^{3+}/\Sigma\text{Fe}$ determinations between beam sessions. Further details of spectral collection and fitting are given in Cottrell *et al.* (2009).

We are able to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of Galapagos glasses by referencing the drift-corrected centroid (area-weighted energy of the pre-edge $1s \rightarrow 3d$ multiplet) of individual analyses to a calibration curve constructed from experimental glasses. Experimental basaltic glasses were equilibrated at 1 atm at multiple oxygen fugacities from 2 log units below to 4.5 log units above the Quartz-Fayalite-Magnetite (QFM) buffer (Kress & Carmichael, 1991). 1σ uncertainty of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of Galapagos glasses averaged ± 0.0037 .

RESULTS

The 27 glass chips from the Galapagos prepared for analysis range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from 0.153-0.194 (Fig. 4 and presented in table 1). The six ITD glasses with MORB-like compositions have an average $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.162 ± 0.003 , which is comparable to ratios previously reported for MORB glass (average $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.16$) (Bezous & Humler, 2005, Kelley & Cottrell, 2009, Cottrell & Kelley, 2011, Le Voyer *et al.*, 2015). Of the remaining 21 samples, the 6 samples from the WD group (characterized by high Th/La ratios, $\Delta 7/4$ and $\Delta 8/4$ and low $^3\text{He}/^4\text{He}$ ratios) have an average $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.161 \pm 0.008$,

similar to MORB, while the one sample from Wolf volcano has the highest measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio = 0.194. In comparison, the 9 samples from the ITE group (characterized by an enriched trace element and isotopic composition similar to Sierra Negra/Cerro Azul) and the 5 samples from the HHe group (characterized by $^3\text{He}/^4\text{He}$ ratios above 22Ra) are both slightly more oxidized than MORB at comparable MgO contents ($\text{Fe}^{3+}/\Sigma\text{Fe} = 0.178 \pm 0.007$, and $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.182 \pm 0.005$ respectively). These values are most similar to the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of back-arc basin basalts and Mariana trough basalts (0.171 ± 0.011) while being less oxidized than values reported for volcanic front basalts (0.236 ± 0.021) (Kelley & Cottrell, 2009, Kelley & Cottrell, 2012, Brounce *et al.*, 2014).

Using the empirical expression of Sack *et al.* (1980) and the regression coefficients of Kress and Carmichael (1991), $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of a basalt can be related to $f\text{O}_2$ for a specified temperature and composition. We calculated magmatic $f\text{O}_2$ values for the glasses of this study at a pressure of 2 kbars (determined from the average pressure of entrapment of high MgO melt inclusions from the Galapagos measured by Koleszar *et al.* (2009)) and temperature of the melt calculated using an equation provided in Wallace and Carmichael (1992), that uses the predictable variation in Al_2O_3 and MgO content of a melt undergoing crystal fractionation, with an included correction for the effect of H_2O content of the liquidus temperature (Medard & Grove, 2008). Resulting $f\text{O}_2$ values varied from $\Delta\text{QFM} = +0.02$ to $+0.74$ (ΔQFM referring to the log unit difference in $f\text{O}_2$ of a sample from the quartz-fayalite-magnetite buffer). Similar to $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, this is slightly more oxidized than the range found for MORB (-0.25 - $+0.4$; Christie *et al.*, 1986, Bezos & Humler, 2005, Cottrell & Kelley, 2011, Cottrell & Kelley, 2013, Le Voyer *et al.*,

2015), but less oxidized than the range stated for arc mantle (+1 - +1.8; Kelley & Cottrell, 2009, Kelley & Cottrell, 2012, Brounce *et al.*, 2014).

There is a large variation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios within each compositional group. Due to the correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and MgO, some of this variation can be attributed to crystal fractionation. Some of this variation, however, occurs at the same or over a small range of MgO contents. This implies that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of the glasses of this study are varying in terms of degree of melting, sampling other shallow level processes, such as degassing or assimilation of shallow lithospheric material, or there is an inherent heterogeneity in mantle source redox.

DISCUSSION

Magmatic Oxidation during differentiation and partial melting

Magmatic differentiation can cause changes in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios because of the differences in partitioning behavior of Fe^{2+} and Fe^{3+} for different crystallizing phases (e.g. Sugawara, 2001, Lundgaard & Tegner, 2004, Mallmann & O'Neill, 2009). There is a clear increase in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios with decreasing MgO contents for the glasses of this study (Fig. 4). This is consistent with partitioning Fe^{2+} over Fe^{3+} in early crystallizing phases such as olivine and clinopyroxene and therefore concentrating Fe^{3+} in the melt. At a given MgO content, however, there is a large range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios between and within the different groups of glasses. We have calculated possible liquid lines of descent (LLD) using PetroLog3 (Danyushevsky & Plechov, 2011) in order to assess the extent to which fractional crystallization can change $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios.

For this modeling we assume isobaric fractional crystallization occurring at 2 kbars of pressure (Koleszar *et al.*, 2009) (varying the pressure between 0.5-4 Kbars does not change our interpretation of the results). We also use the compositions of both an olivine-hosted melt inclusion taken from Fernandina and one from Santiago (composition presented in Table 2 and reported in Koleszar *et al.* (2009)) in order to generate the LLD of an enriched melt and a depleted melt respectively. The water content and minor/trace element enrichment of the Fernandina mantle component is higher than the depleted mantle component in the Galapagos (e.g. White *et al.*, 1993, Koleszar *et al.*, 2009, Peterson *et al.*, submitted to Journal of Petrology). This will change the overall trajectory of the LLD, especially because water can have a large effect on plagioclase and clinopyroxene crystallization. We used 2 different compositions to better bracket the data. We ran the model as a system closed to oxygen. Implicit in the assertion that fractional crystallization can change $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios is the assumption that the system has remained closed to oxygen exchange with the environment. This assumption is supported by a global study of MORB glass with well-defined LLDs within single suites of data, that are well reproduced by fractional crystallization of olivine $\pm$ plagioclase $\pm$ clinopyroxene in a system closed to oxygen (Cottrell & Kelley, 2011, Cottrell, personal communication). Finally, we assume $D(\text{olivine})^{\text{Fe}^{3+}} = 0$, $D(\text{plagioclase})^{\text{Fe}^{3+}} = 0.3$, $D(\text{clinopyroxene})^{\text{Fe}^{3+}} = 0.45$, based on current experimentally determined partition coefficients for Fe^{3+} (Sugawara, 2001, Lundgaard & Tegner, 2004, Mallmann & O'Neill, 2009). The results of the modeling show that despite the differences in the LLD of an enriched versus a depleted melt, fractional crystallization over a decrease in MgO content of ~ 9.3 -5.0 wt% is only predicted to increase $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios by 0.03. For the ITE and WD groups (the

groups with the largest variation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios), the samples of each group have MgO contents within 2 wt. % and yet cover the same range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of ~ 0.03 and ~ 0.02 respectively. This variation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios therefore, cannot be explained by crystal fractionation of olivine $\pm$ plagioclase $\pm$ clinopyroxene alone.

Crystallization of Fe-oxides such as magnetite (Fe_3O_4) can have a large effect on $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. Although magnetite has a mixed valence composition, it is dominantly ferric ($2\text{Fe}^{3+}: 1\text{Fe}^{2+}$); therefore, crystallization of magnetite in a system closed to oxygen would lead to a decrease in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of the melt. For the glasses of this study, however, magnetite is not predicted to saturate before MgO ~ 6 wt%, which is only applicable to the ITE and HHe groups. These groups do not show the other predicted effects of magnetite fractionation, such as a strong decrease in TiO_2 or FeO^* (e.g. Berndt *et al.*, 2005, Jenner *et al.*, 2010, Zimmer *et al.*, 2010). Therefore we conclude that magnetite fractionation cannot explain the range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios that we see for samples at similar MgO contents.

The samples of this study have experienced different levels of crystal fractionation, so to account for these effects we recalculate $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios to an arbitrary MgO content = 8 wt%, with $\text{Fe}^{3+}/\Sigma\text{Fe}_{(8)}$ being analogous to $\text{Na}_2\text{O}_{(8)}$ in the style of Klein and Langmuir (1987). Because the samples of this study do not define a well-constrained LLD for $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, we use a linear regression of the data presented here in addition to $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of MORB samples measured with the XANES techniques described in Cottrell *et al.* (2009) to define the slope of the correction for all of the samples (Cottrell *et al.*, 2009, Cottrell & Kelley, 2011, Le Voyer *et al.*, 2015; Cottrell and Kelley, unpublished data). The slope is approximately equivalent to that defined by olivine only

fractionation. MORB data can be used to define the regression because they are well modeled by the sequence olivine $\pm$ plagioclase $\pm$ clinopyroxene, similar to MORB and EMORB samples, although the isotopic and trace element enriched groups in the Galapagos do show a slightly different trajectory for the LLD from MORB samples (as explored in Peterson *et al.* (submitted to Journal of Petrology)). Therefore a regression solely defined by Galapagos plume samples should have a similar slope to that defined by the MORB data from the literature. We also use a single slope for all the groups of this study because even though the predicted LLD of an enriched versus a depleted melt defines two slightly differently sloped trends, the partition coefficients for Fe^{3+} are defined by a limited number of studies and there is a large uncertainty in the predicted LLDs. Also, the difference in $\text{Fe}^{3+}/\Sigma\text{Fe}_{(8)}$ ratios calculated using the 1 slope defined by the data of this study in combination with MORB data reported in the literature and the 2 slopes defined by predicted LLDs is generally less than 2.5%. This ultimately results in a primary $f\text{O}_2$ difference of 0.18 log units, which is within the 0.5 log unit uncertainty expected using the method of Kress and Carmichael (1991) to predict oxygen fugacity.

$\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios have not been found to vary with degree of melting in other settings despite the fact that Fe^{3+} is more incompatible than Fe^{2+} during melting (e.g. Bezos & Humler, 2005, Cottrell & Kelley, 2011, Dauphas *et al.*, 2014). $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios within the groups of this study do not vary with La/Yb ratios, implying that $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are not varying with degree of melting (not shown). La/Yb ratios are sensitive to the degree of melting due to the large differences in the incompatibility of La relative to Yb. The one sample collected just north of Isabela with the composition of Wolf Volcano shows the highest $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio (0.194) at a given MgO content. This sample is

characterized by low Th/La ratios and more depleted Sr, Nd and Pb isotopic compositions than the compositions of the other volcanoes of Isabela, but with higher Nb/Zr, Sm/Yb and Ti/Gd ratios than MORB. The trace elements and isotopic ratios are consistent with a low degree of melting in the garnet stability field of a depleted mantle (Geist *et al.*, 2005, Saal *et al.*, 2007, Peterson *et al.*, submitted to Journal of Petrology). The high $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the one sample with the composition of Wolf Volcano may be evidence that low degrees of melting can have a measurable effect on the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios that has not been previously recognized. Alternatively, the high $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of Wolf Volcano may be evidence for the presence of an unusual depleted source in the plume that is more oxidized than depleted upper mantle or this sample may have been altered after emplacement. However, it is difficult to constrain the origin of the high $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio because only one sample with this composition has been measured, and more measurements will thus be required to explain the $f\text{O}_2$ of the mantle source contributing to Wolf Volcano.

The role of volatiles in magmatic oxidation

Volatiles, such as sulfur, have the potential to play a role in determining magmatic oxidation. For example, the large electronic difference between oxidized sulfate (S^{+6}) and reduced sulfide (S^{2-}) means that, despite its low abundance, sulfur has the potential to drive changes in redox through the Fe-S redox couple:

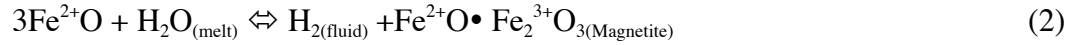


The speciation of S in the melt will determine whether sulfide fractionation or degassing can change the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. For the estimated range of oxygen fugacity in ocean island basalts ($\Delta\text{QFM} = 0 - +2$; Ballhaus (1993)), S is dissolved in basaltic melt as a mixture of S^{2-} and SO_4^{2-} (e.g. Metrich *et al.*, 2009, Jugo *et al.*, 2010). Magnetite fractionation has been shown to shift equation 1 to the right and cause the initiation of sulfide fractionation, which subsequently produces Fe^{3+} (Jenner *et al.*, 2010). In their analysis of the volatile contents of the glasses of this study, Peterson *et al.* (submitted to Journal of Petrology), determined that the melt was just saturated with a sulfide liquid to sulfide undersaturated (using the model of Liu *et al.* (2007) and an $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio = 0.17 to determine sulfur content at sulfide saturation (SCSS)). Recalculation of the SCSS using the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios measured in this study maintains this result. Only glasses that are sulfide undersaturated were chosen for XANES analysis.

Sulfur degassing also has the potential to affect the oxidation state of the melt. The 2 main species of S that degas are SO_2 (S^{4+}) and H_2S (S^{2-}), though for the glasses of this study at the pressure at which the melt is in equilibrium with a CO_2 - H_2O vapor phase (23-472 bars calculated using the model of Dixon *et al.* (1995) and discussed in Peterson *et al.* (submitted to Journal of Petrology)) we would expect the gas phase to be mainly composed of SO_2 (Carroll & Webster, 1994, Symonds *et al.*, 1994, Moretti *et al.*, 2003, Oppenheimer, 2003, Wallace, 2005). Degassing, as a result, will cause a redistribution of electrons in the melt and change the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. Peterson *et al.* (submitted to Journal of Petrology), when comparing S/Dy ratios to the H_2O - CO_2 pressure of saturation, found that S begins to degas at approximately 400 bars of pressure. When S/Dy ratios are

compared to $\text{Fe}^{3+}/\Sigma\text{Fe}_{(8)}$ ratios there is a distinct reduction trend with decreasing S contents (Fig. 5). If S is mainly degassing as SO_2 , this implies that S is mainly dissolved in the melt as S^{2-} consistent with the parameterization of Jugo *et al.* (2010) for the magmatic $f\text{O}_2$'s calculated for the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of this study.

Degassing of other volatiles (H-C-O-Cl species) could also potentially affect $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. Degassing of H_2 could drive the oxidation of a basaltic melt through the redox couple:



This reaction will cause the melt to oxidize as H_2 escapes the system. For the vapor phase to have a significant proportion of H_2 , the melt must be much more reduced ($< \Delta\text{QFM} -1$) than the magmatic $f\text{O}_2$ calculated for the glasses of this study and, in general, predicted for OIB and MORB (Carmichael, 1991, Cottrell *et al.*, 2009, Zhang & Duan, 2009). The process is also self-limiting as increasing the oxidation of the melt will drive the proportion of H_2 in the fluid down. Finally, this reaction requires the precipitation of magnetite, for which there is no evidence in the glasses of this study. As a result, it is unlikely that H_2 degassing is affecting the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. It is also unlikely that CO_2 degassing is affecting the melt $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. At $\text{QFM} > -1$, graphite is not stable in the melt, therefore C will be speciated as carbonate (CO_3^{2-}) (e.g. Stagno *et al.*, 2013). As a result, CO_2 degassing will be redox neutral. This is consistent with the fact that CO_2 degassing is not correlated with changes in oxidation in the glasses of this study (such as

variation in CO₂/Nb with Fe³⁺/ΣFe ratios, not shown). Cl degassing also has the potential to oxidize the melt through the redox couple (Bell & Simon, 2011):



However, there is no evidence of Cl degassing from the melts of this study such as a correlation between Cl/K ratios and CO₂-H₂O saturation pressure (not shown). Therefore, it is unlikely that Cl degassing is affecting Fe³⁺/ΣFe ratios.

Magmatic Oxidation during assimilation of hydrothermally altered material

Reactions with seawater have been shown to oxidize the crust (e.g. Alt, 1995), therefore assimilation of hydrothermally altered crust and/or seawater has the potential to oxidize melt. There is a clear correlation between increasing values of Sr/Sr* >1 (Sr anomaly on a primitive mantle normalized diagram = Sr_{pm}/[(Nd_{pm} + Ce_{pm})/2] (McDonough & Sun, 1995)) and increasing Fe³⁺/ΣFe₍₈₎ ratios (Fig. 6). Sr/Sr* can be used as a measure for plagioclase fractionation (<1) and assimilation of plagioclase cumulates (>1). Sr/Sr* is shown to correlate with increasing volatile/refractory element ratios and thus is a good indicator of the assimilation of hydrothermally altered crust in the Galapagos (Peterson *et al.*, submitted to Journal of Petrology). The correlation between Fe³⁺/ΣFe₍₈₎ ratios and Sr/Sr* is therefore consistent with assimilation of hydrothermally altered crust.

The sample with the highest Cl/K ratio (PL02-13-25; Cl/K = 0.77) is also indicated in Figure 6. This sample has most probably assimilated brine or seawater in addition to hydrothermally altered crust (Kent *et al.*, 1999, Stroncik & Haase, 2004,

Peterson *et al.*, submitted to Journal of Petrology). This sample is not significantly more oxidized than the other samples (whose Cl/K ratios range from 0.025 - 0.069). In addition, there is no evidence for a correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}_{(8)}$ ratios and Cl/K ratios in the glasses of this study. Therefore, it is more likely that assimilation of hydrous components in the crust are causing the increase in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios as opposed to assimilation of seawater or brine.

Mantle source variation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios

After accounting for the major processes that can affect $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in the melt, the different groups of glasses still show variation outside of analytical uncertainty (Fig. 7). The ITD and WD groups have similar $\text{Fe}^{3+}/\Sigma\text{Fe}_{(8)}$ ratios to each other (ITD = 0.162 ± 0.003 and WD = 0.164 ± 0.006) and MORB values (Bezos & Humler, 2005, Cottrell & Kelley, 2011, Le Voyer *et al.*, 2015), while the HHe group (Fernandina source) are more oxidized (HHe = 0.175 ± 0.006 , maximum value = 0.179) than MORB, but less oxidized than reported for arc basalts (Kelley & Cottrell, 2009, Kelley & Cottrell, 2012, Brounce *et al.*, 2014). The ITE group (Sierra Negra/Cerro Azul) have the largest range in $\text{Fe}^{3+}/\Sigma\text{Fe}_{(8)}$ ratios (average = 0.169 ± 0.008 , maximum = 0.177), which ranges to more oxidized than the ITD and WD groups but more reduced relative to the HHe group. This could suggest mixing with melts from the WD mantle source as $\text{Fe}^{3+}/\Sigma\text{Fe}_{(8)}$ ratios broadly correlate with $\Delta 7/4$ values.

Both the Pinta (WD group) and Sierra Negra/Cerro Azul mantle end-members (ITE group) are hypothesized to contain recycled components (e.g. White *et al.*, 1993, Harpp & White, 2001, Schilling *et al.*, 2003, Harpp *et al.*, 2014). The Pinta component

has an isotopic signature similar to an EM mantle end-member. The Sierra Negra/Cerro Azul end-member is either the product of a mixture, between the Floreana, Fernandina and Pinta end-members, or alternatively a unique component with an intermediate isotopic composition. The differences in $\text{Fe}^{3+}/\Sigma\text{Fe}_{(8)}$ ratios and the correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}_{(8)}$ ratios and Pb isotopes for the ITE group between an oxidized end-member and a reduced end-member similar to the WD group suggests that the source material of these two end-members is intrinsically different and that there are long-lived, heterogeneous redox domains in the mantle, consistent with the conclusions of Cottrell and Kelley (2013).

The HHe group is the most oxidized group within the glasses of this study. The characteristics of the source material for the HHe group (Fernandina mantle end-member) are consistent with a mantle component that is generally attributed to less-degassed, primitive lower mantle material (e.g. Allègre *et al.*, 1983, Farley *et al.*, 1992, Hart *et al.*, 1992, Hanan & Graham, 1996). Peterson *et al.* (submitted to Journal of Petrology) also showed that the high $^3\text{He}/^4\text{He}$ end-member in the Galapagos is more carbonated than MORB and other oceanic islands using the high $\text{C}/^3\text{He}$ ratios of this end-member. The more oxidized nature of the HHe group may be due to the higher carbon content of the mantle source. Stagno *et al.* (2013) demonstrates with experimental and natural data that carbon hosted as graphite or diamond in the upwelling mantle will oxidize to produce carbonate melt through the reduction of Fe^{3+} . As a result, the depth of carbonate melt formation is dependent on the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the bulk rock. In the Galapagos, lavas with the highest $^3\text{He}/^4\text{He}$ ratios are located above a seismic low velocity zone that is at a depth of 200-250km, which is estimated to be the result of the initiation of carbonate

melting (Villagomez *et al.*, 2014). At this depth, a mantle containing 30 ppm C (estimated C content of the MORB mantle source) would require a $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of at least 6-7% to stabilize a carbonated melt phase (Stagno *et al.*, 2013). Subsequent oxidation of the carbon would then cause a ~1% reduction in the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of the mantle source. Increasing the carbon content of a source without changing the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio would therefore result in a more reduced melt. If the $\text{Fe}^{3+}/\Sigma\text{Fe}_{(8)}$ ratios of the glasses of this study are representative of the mantle, then to end with an $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio more oxidized than MORB for a source that contains an order of magnitude more carbon (as observed in the HHe group) would require an even more oxidized $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio than the 6-7% hypothesized for MORB by Stagno *et al.* (2013) and much more than the 0.036 estimated for the primitive mantle from peridotite and pyroxenite xenoliths (Canil *et al.*, 1994).

CONCLUSIONS

Galapagos glass compositions show a range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from MORB-like to more oxidized than MORB, within the range of back-arc basin basalts and Mariana trough basalts, but less oxidized than volcanic front basalts. Some of this variability can be attributed to crystal fractionation, but not variable degrees of melting, consistent with previous studies. There is also evidence that S degassing causes magmatic reduction, while assimilation of hydrothermally altered crust is causing magmatic oxidation. After accounting for these shallow level processes, the different isotopic groups still vary from each other in their $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of this study result in a magmatic $f\text{O}_2$ for the Galapagos Archipelago that varies from $\Delta\text{QFM} = +0.16 - +0.74$, intermediate

to the MORB and arc systems. The ITD group has a $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio within range of what has been found for MORB. The WD group was also found to possess a $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio within the range of MORB while the ITE group is generally more oxidized. The WD and ITE groups have both been hypothesized to contain recycled components in their mantle sources, but the difference in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of these groups and the correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and Pb isotopes suggest that their mantle source compositions are intrinsically different. The HHe group is the most oxidized group of this study with the highest $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. This in combination with the more carbonated nature of the source could be evidence that less degassed, primitive lower mantle (the source of the high $^3\text{He}/^4\text{He}$ ratios of the HHe group) is inherently more oxidized than depleted upper mantle.

The new data suggest that the observed $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios reflect mantle source variations instead of simply lithospheric processes. This has important implications for the preservation of long-lived mantle heterogeneities in oxidation state and simultaneously implies that the mantle is neither a well-mixed homogenous source nor a well-buffered system.

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FIGURE CAPTIONS

Figure 1. Map of the Galapagos archipelago with locations of sample dredges and prominent features labeled. Scale bar and bathymetry color scale are included the left side on the map. Array 1 consists of samples that range between the compositions of Fernandina Island and Sierra Negra/Cerro Azul volcanoes that are further divided into HHe and ITE groups based on samples with $^3\text{He}/^4\text{He}$ ratios above and below $^3\text{He}/^4\text{He} = 22 \text{ Ra}$, respectively. Array 2 consists of samples that range between the compositions of Genovesa Island and Pinta, Wolf and Darwin Islands that have been divided into the ITD group (samples with more MORB-like compositions) and the WD group (samples characterized by high Th/La ratios and high $\Delta 7/4$, $\Delta 8/4$). Samples that have a composition similar to Wolf Volcano on Isabela are shown separately. Map created using GeoMapApp <http://www.geomapapp.org> (Ryan *et al.*, 2009).

Figure 2. Th/La ratios versus A.) Ti/Gd ratios and B.) Sm/Yb ratios of individual glasses plotted over fields that represent ranges of previously measured whole rock and glass samples from the Galapagos Archipelago (Cullen *et al.*, 1989, Vicenzi *et al.*, 1990, Bow & Geist, 1992, White *et al.*, 1993, Geist *et al.*, 2002, Saal *et al.*, 2007, Gibson *et al.*, 2012). Errors shown are 2σ standard error for individual glasses. Inset shows larger submarine glass data set analyzed in Peterson *et al.*, (submitted to Journal of Petrology).

Figure 3. (A-B) $^{143}\text{Nd}/^{144}\text{Nd}$ and (C-E) $\Delta 7/4$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ and $^3\text{He}/^4\text{He}$. Notice glass samples with $^3\text{He}/^4\text{He} > 22\text{Ra}$ correspond to the isotope composition indicative of

Fernandina whole rocks. Notice also that the WD and ITD Groups define a compositional range from near Genovesa to near Pinta-Wolf-Darwin Islands (isotopic data for individual glasses reported in Harpp & White, 2001, Schilling *et al.*, 2003, Geist *et al.*, 2008, Peterson *et al.*, submitted to Journal of Petrology). The grey fields are defined by previously published isotope data on whole rocks basalts from different islands (Cullen *et al.*, 1989, White *et al.*, 1993, Reynolds & Geist, 1995, Blichert-Toft & White, 2001, Schilling *et al.*, 2003, Saal *et al.*, 2007, Ingle *et al.*, 2010). Average 2σ standard error indicated by the grey plus sign in each panel. Inset shows larger submarine glass data set analyzed in Peterson *et al.*, (submitted to Journal of Petrology).

Figure 4. MgO wt% versus A.) TiO_2 wt %, B.) $\text{Fe}^{+3}/\Sigma\text{Fe}$ ratios, C.) Al_2O_3 wt% and D.) K_2O wt% for individual glasses from this study. Superimposed on the data are predicted liquid lines of descent (LLD) for olivine (olv) - olv + plagioclase (plag) – olv + plag + clinopyroxene (cpx) (solid red and green lines, where black dot on the lines indicates the appearance of a new crystal phase in the fractionating mineral assemblage). Calculations were performed in PetroLog3 (Danyushevsky & Plechov, 2011) isobarically at 2 Kbars of pressure using 2 different starting compositions, which can be found in Table 2. Red LLD is calculated from an enriched Fernandina composition, while green LLD is calculated from a depleted Santiago composition. LLDs for $\text{Fe}^{+3}/\Sigma\text{Fe}$ ratios calculated using mineral/melt partition coefficients $D_{\text{olv}} = 0$, $D_{\text{plag}} = 0.35$, $D_{\text{cpx}} = 0.45$ (Sugawara, 2001, Lundgaard & Tegner, 2004, Mallmann & O'Neill, 2009) in a system closed to oxygen. Notice in panel B that at a given MgO content there is a large range in $\text{Fe}^{+3}/\Sigma\text{Fe}$ ratios between and within different groups showing that the variation in $\text{Fe}^{+3}/\Sigma\text{Fe}$ ratios

cannot be explained by differentiation alone. Grey field covers the range in $\text{Fe}^{+3}/\Sigma\text{Fe}$ ratios reported for MORB (Cottrell & Kelley, 2011, Le Voyer *et al.*, 2015). Errors are 2σ standard error for TiO_2 , Al_2O_3 , and K_2O and 1σ for $\text{Fe}^{+3}/\Sigma\text{Fe}$ ratios.

Figure 5. S/Dy ratios versus A.) Pressure of CO_2 - H_2O vapor saturation and B.) $\text{Fe}^{+3}/\Sigma\text{Fe}_{(8)}$ ratios showing that S degassing correlates with magmatic reduction. Pressure of saturation calculated using the model of Dixon *et al.* (1995). Glass data shown in panel A include all the data reported in Peterson *et al.*, (submitted to Journal of Petrology) filtered for samples affected by assimilation of hydrothermally altered material, which will independently affect S/Dy ratios. Also shown are melt inclusion data from Koleszar *et al.* (2009). Error for S/Dy ratios are 2σ standard error, error for $\text{Fe}^{+3}/\Sigma\text{Fe}_{(8)}$ ratios are 1σ standard error. Error for $\text{H}_2\text{O} - \text{CO}_2$ P saturation calculated from the 2σ standard error of CO_2 measurements.

Figure 6. $\text{Fe}^{+3}/\Sigma\text{Fe}_{(8)}$ ratios versus Sr/Sr* for individual glasses. Notice the clear trend between increasing Sr/Sr* (proxy for plagioclase assimilation) and magmatic oxidation. Also labeled is the ITD sample with the highest Cl/K ratio (PL02-13-25 collected from the eastern seamounts). Cl/K is used as an indicator of assimilation of hydrothermally altered material. While this sample is oxidized, it is not unusually oxidized in comparison to the other affected samples in the ITD group. This is consistent with assimilation of shallow, hydrothermally altered, lithospheric material causing magmatic oxidation as opposed to simply assimilating seawater.

Figure 7. $\text{Fe}^{+3}/\Sigma\text{Fe}_{(8)}$ ratios versus A.) $^{87}\text{Sr}/^{86}\text{Sr}$, B.) $^{143}\text{Nd}/^{144}\text{Nd}$, C.) $^3\text{He}/^4\text{He}$, and D.) $\Delta 7/4$ for individual glasses. Small symbols indicate samples whose $\text{Fe}^{+3}/\Sigma\text{Fe}_{(8)}$ ratio has been identified as being affected by shallow processes. Notice the broad correlation between isotope signature and $\text{Fe}^{+3}/\Sigma\text{Fe}_{(8)}$ ratios.

FIGURES

Figure 3-1

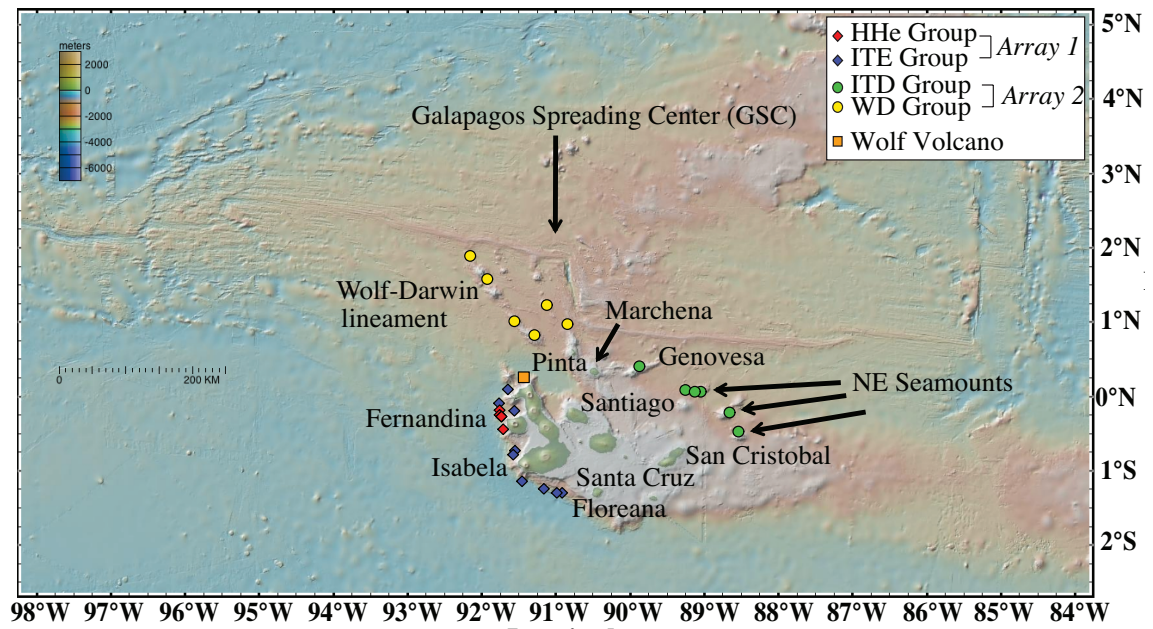


Figure 3-2

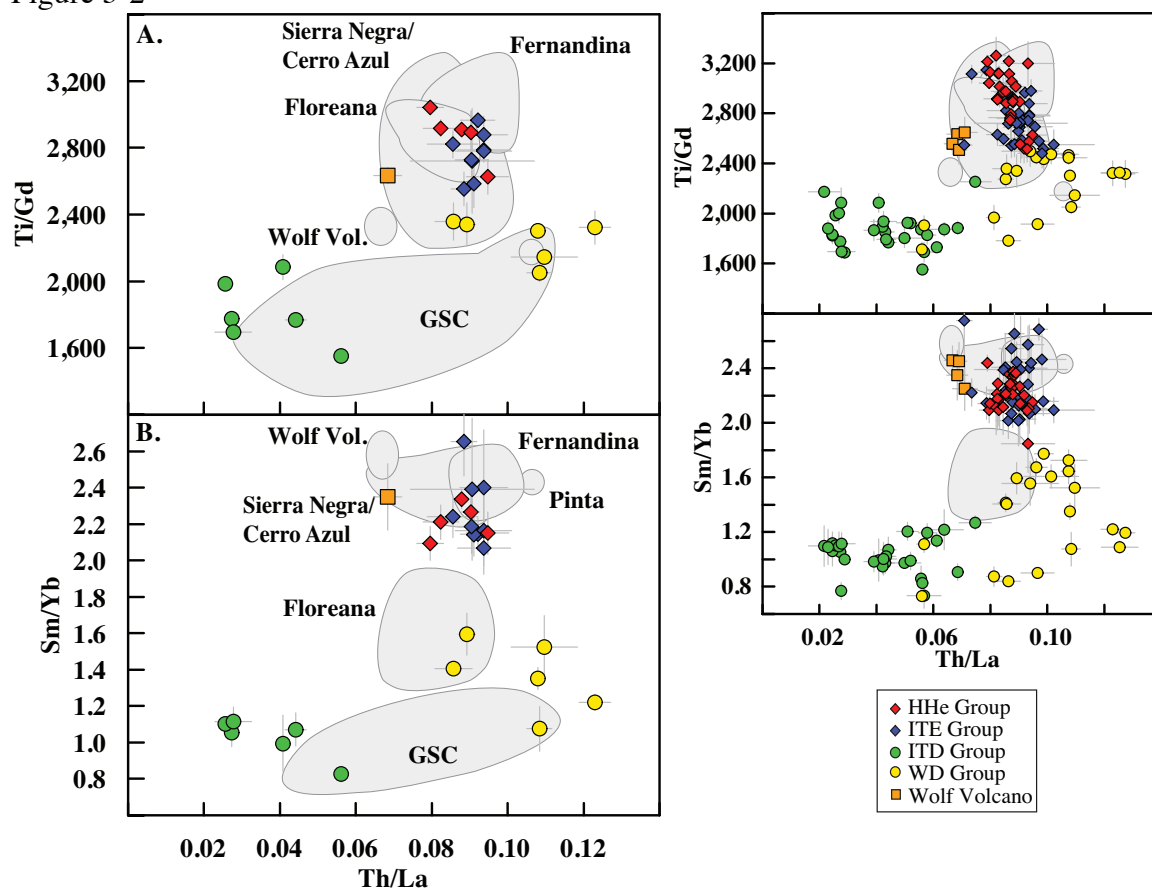


Figure 3-3

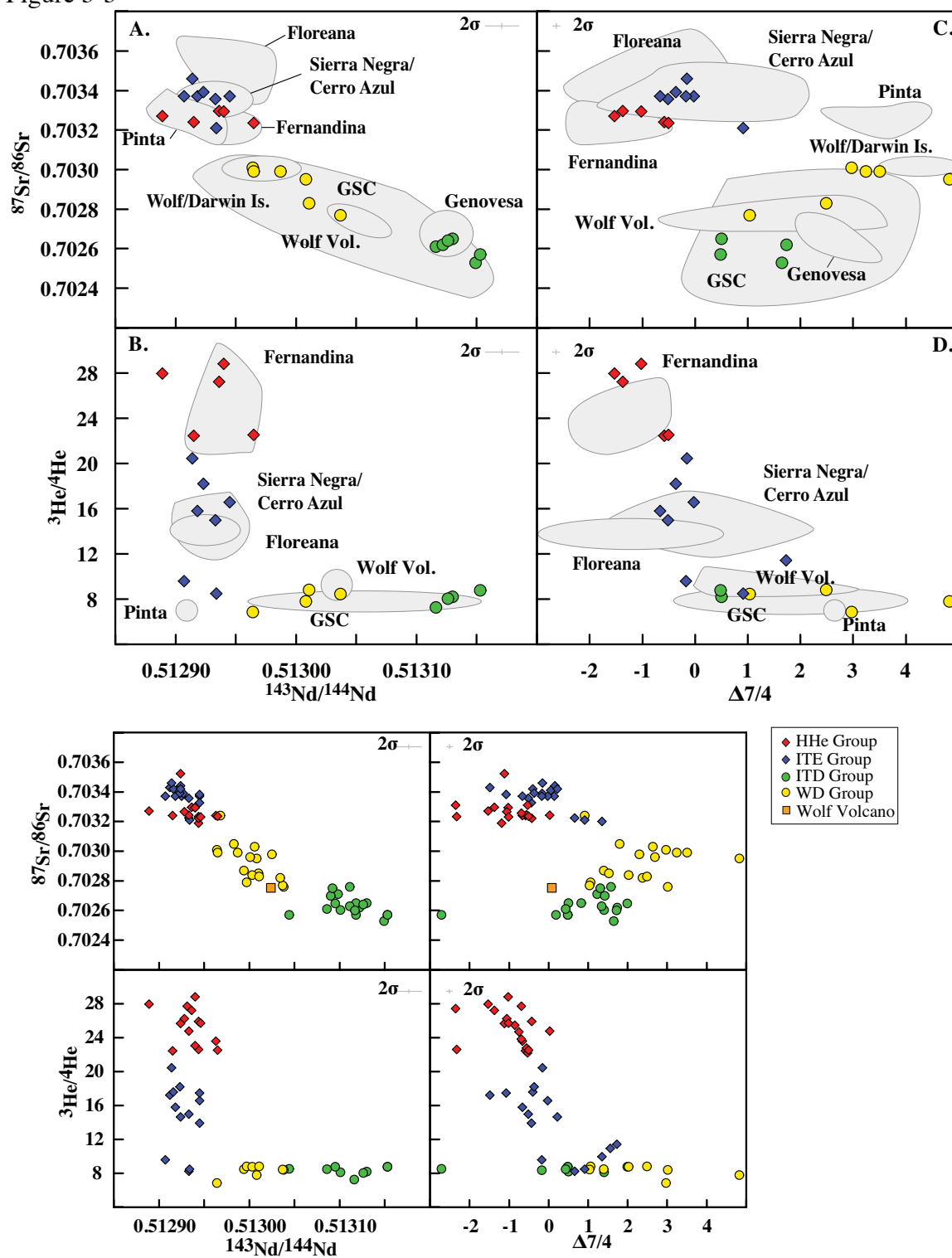


Figure 3-4

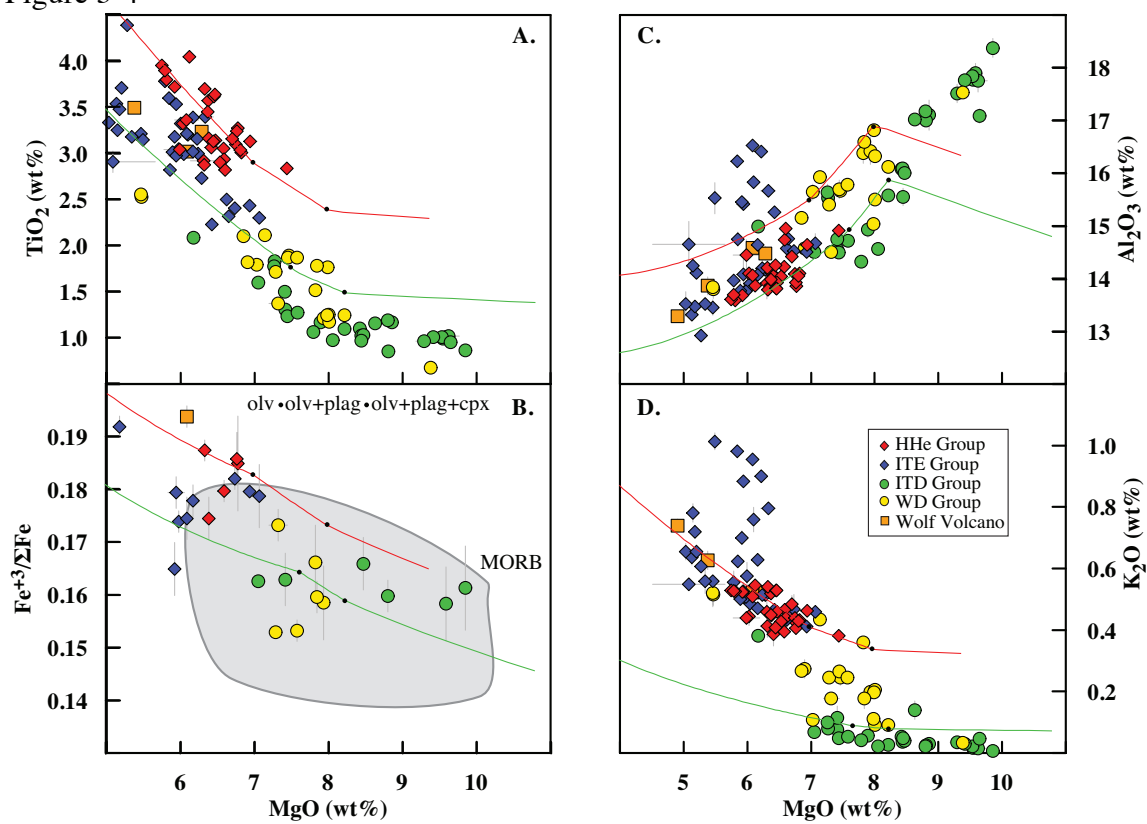


Figure 3-5

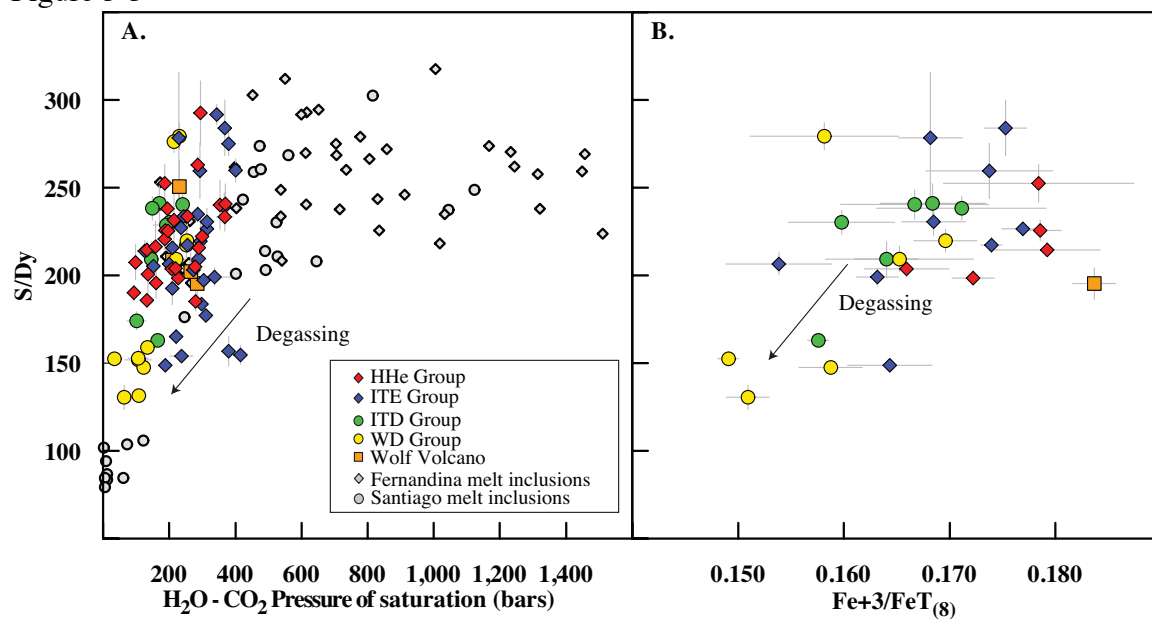


Figure 3-6

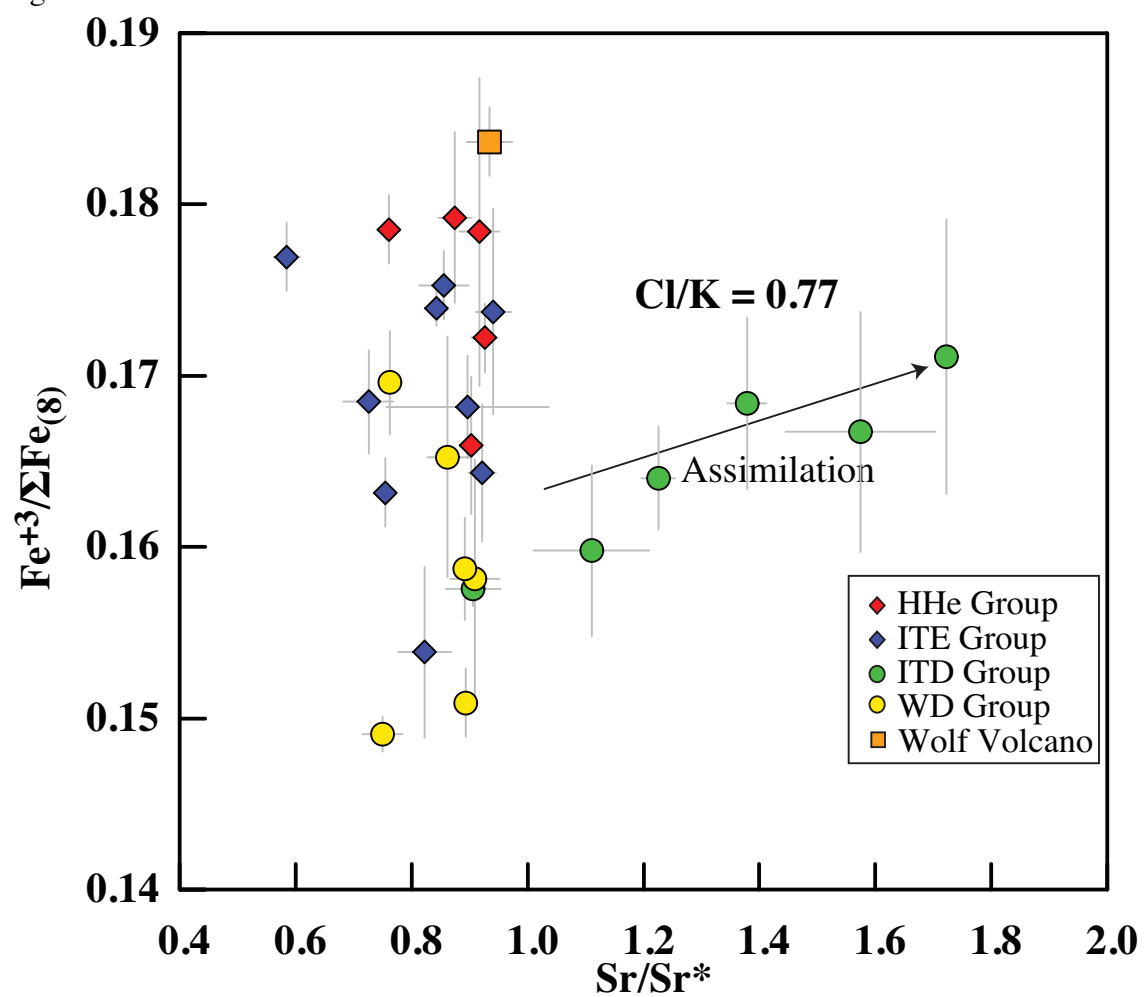
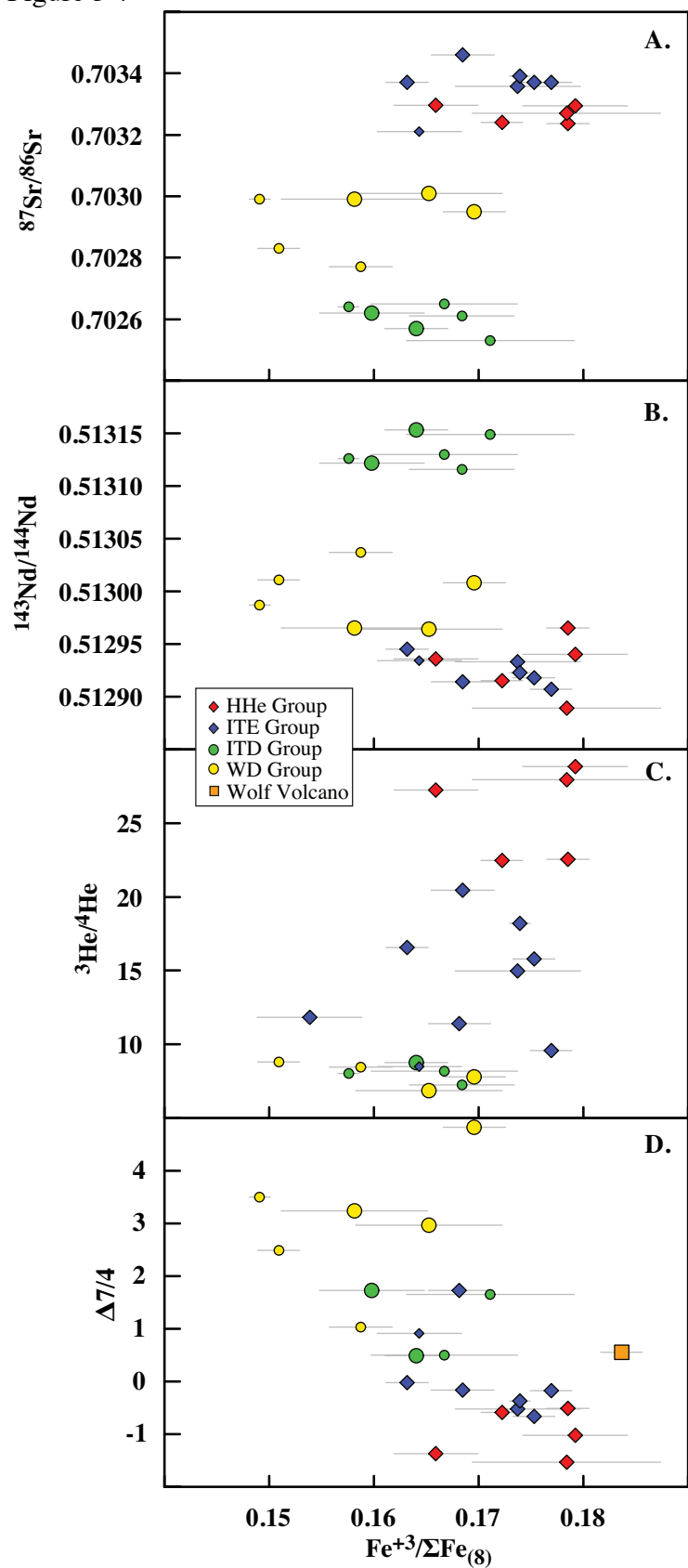


Figure 3-7



TABLES

Table 1. $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios as measured by XANES and calculated deviations in $f\text{O}_2$ from the Quartz-Fayalite-Magnetite Buffer (ΔQFM) for the samples of this study

Sample ID*	Latitude	Longitude	Group	$\text{Fe}^{3+}/\Sigma\text{Fe}$	1σ	ΣdX_i^a	Temperature ($^{\circ}\text{C}$) ^b	$\Delta\text{QFM}^c_{(\text{magmatic})}$
PL02-12-1	-0.21	-88.65	ITD	0.163	0.001	0.228	1164	0.19
PL02-13-25	0.07	-89.04	ITD	0.166	0.005	0.208	1208	0.29
PL02-14-8	0.07	-89.12	ITD	0.160	0.003	0.221	1226	0.17
PL02-9-29	-0.47	-88.53	ITD	0.158	0.007	0.172	1245	0.25
DR70-2	0.41	-89.87	ITD	0.163	0.005	0.243	1176	0.16
DR72-A-1	0.09	-89.25	ITD	0.161	0.008	0.212	1254	0.21
D3a	0.27	-91.43	Wolf	0.194	0.002	0.227	1123	0.66
PL02-26-21	0.83	-91.29	WD	0.153	0.002	0.230	1178	0.03
PL02-28-11	1.02	-91.55	WD	0.160	0.003	0.210	1195	0.18
PL02-29-3	1.90	-92.16	WD	0.173	0.003	0.230	1172	0.35
PL02-30-1	1.59	-91.92	WD	0.166	0.007	0.223	1187	0.26
DR40-1	0.98	-90.84	WD	0.159	0.007	0.182	1191	0.23
DR41-A-1	1.24	-91.12	WD	0.153	0.001	0.229	1171	0.02
D13b	-0.19	-91.55	ITE	0.165	0.005	0.197	1123	0.29
D38a	-0.72	-91.55	ITE	0.179	0.006	0.256	1158	0.38
D39a	-0.78	-91.58	ITE	0.180	0.001	0.238	1154	0.43
D48a	-1.13	-91.45	ITE	0.182	0.002	0.238	1145	0.46
D51a	-1.23	-91.16	ITE	0.192	0.002	0.178	1102	0.74
D5g	0.10	-91.64	ITE	0.178	0.003	0.233	1112	0.41
D60a	-1.29	-90.99	ITE	0.179	0.003	0.193	1130	0.52
D8a	-0.09	-91.76	ITE	0.175	0.004	0.162	1146	0.52
PL02-24-32	-1.29	-90.91	ITE	0.174	0.002	0.190	1125	0.44

	Latitude	Longitude	Group	Fe ³⁺ /ΣFe	1σ	Σd _i X _i ^a	Temperature (°C) ^b	ΔQFM ^c _(magmatic)
AHA20b	-0.24	-91.75	HHe	0.187	0.002	0.230	1125	0.56
AHA22b	-0.18	-91.76	HHe	0.180	0.002	0.210	1147	0.49
AHA23a	-0.26	-91.73	HHe	0.185	0.009	0.221	1134	0.54
AHA23b	-0.26	-91.73	HHe	0.186	0.005	0.229	1134	0.54
AHA26a	-0.43	-91.71	HHe	0.175	0.004	0.212	1138	0.41

* Sample ID's have been shortened to not include cruise information; IDs beginning with PL02 are from the PLUME02 cruise, DR are from the R/V SONNE cruise, D are from the DRIFT04 cruise, and AHA are from the AHA-Nemo-2 cruise.

^a Σd_iX_i parameterizes the basalt composition: sum of coefficients (d_i) multiplied by the oxide mole fractions (X_i), as defined in Kress and Carmichael (1991)

^b Temperature of melt calculated from calculation of Wallace and Carmichael (1992) with a correction for the effect of water content on the liquidus from Medard and Grove (2008)

^c ΔQFM calculated using the regression coefficients of Kress and Carmichael (1991) at a pressure of 2 Kbars and calculated temperature of the melt

Table 2. Fractional crystallization model

Major Elements (wt%)	Starting Composition	
	Enriched Composition ^a	Depleted Composition ^b
SiO ₂	47.48	46.46
TiO ₂	2.29	1.34
Al ₂ O ₃	16.38	14.36
FeO*	9.16	11.77
MnO	0.12	0.20
MgO	9.38	11.86
CaO	11.58	11.50
Na ₂ O	2.25	2.14
K ₂ O	0.33	0.08
P ₂ O ₅	0.26	0.07
H ₂ O (wt%)	0.68	0.12
Fe ³⁺ /ΣFe ^c	0.165	0.141
Pressure ^d	2kbars	
Temperature	1200	

^a Composition of melt inclusion AHA D25C-3-43 reported in Koleszar et al., (2009)

^b Composition of melt inclusion STG06-29-06 reported in Koleszar et al., (2009)

^c derived by taking an average (for the enriched composition) of the HHe, ITE, and WD group Fe³⁺/ΣFe ratios and (for the depleted composition) taking an average of the ITD group glasses and correcting this back to the MgO content of the inclusions using the slope of a linear regression through the data of this study in addition to Fe³⁺/ΣFe ratios reported for MORB in Cottrell and Kelley (2011)

^d Models used in PETROLOG: Ol, CPX, PLAG- Danyushevsky, 2001, Melt density- Lange and Carmichael, 1987, Melt viscosity- Bottinga & Weill 1972. Oxygen fugacity set at QFM and then run closed for oxygen

Chapter 4

Oxygen isotopes in lavas from the Galapagos Archipelago: evaluating contributions from ancient and present-day crustal sources

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ABSTRACT

New measurements of oxygen isotopes in olivine phenocrysts collected across the Galapagos Archipelago show a larger range in $\delta^{18}\text{O}$ values than previously reported. Fernandina, Floreana, and Pinta, which represent the main isotopic end-members of the Galapagos hotspot, and Cerro Azul and Santiago, which have more intermediate compositions, have $\delta^{18}\text{O}$ values = $5.02 \pm 0.08\text{‰}$, within the accepted range of the oxygen isotope value of upper mantle olivine. Therefore, $\delta^{18}\text{O}$ values do not correlate with radiogenic isotopes, but there is an overall trend of increasing Sr/Sr* and Ba/Nb ratios with $\delta^{18}\text{O}$ values for Sierra Negra, Darwin Volcano, Santa Cruz and San Cristobal. This suggests that the high $\delta^{18}\text{O}$ values of San Cristobal ($5.34 \pm 0.05\text{‰}$) and the large ranges in $\delta^{18}\text{O}$ values for Sierra Negra and Darwin volcanoes and Isla Santa Cruz are the result of the assimilation of plagioclase cumulates. Olivines from Sierra Negra, Alcedo, Darwin, Wolf and Ecuador volcanoes with $\delta^{18}\text{O}$ values lower than upper mantle values ($4.85 \pm 0.1\text{‰}$), in comparison, do not show unique trace element or isotopic signatures making it difficult to unambiguously identify the occurrence of assimilation for these melts. Assimilation of a small amount of seawater ($\delta^{18}\text{O} = 0\text{‰}$) and/or hydrothermally altered gabbro without a cumulate component ($\delta^{18}\text{O} = +2.5/4.0\text{‰}$), however, can produce the low values for $\delta^{18}\text{O}$ without a large change in the trace element or isotopic composition of the melt. These results show that while the three end member components of the Galapagos mantle have a generally homogenous $\delta^{18}\text{O}$ value indistinguishable from “normal” upper mantle, there is a more widespread affect of lithospheric contamination in melts than previously thought.

INTRODUCTION

One of the main concerns when inferring mantle compositions from lavas is distinguishing between signatures of melt/rock interaction in the shallow lithosphere from the signature of recycled material in the mantle source. Oxygen isotopes are uniquely suited to address this because many crustal materials have oxygen isotope ratios that are measurably different from those that are characteristic of the mantle due to low temperature weathering and water-rock interaction. As a result, deviations in $\delta^{18}\text{O}$ ($\delta^{18}\text{O} = 1000[^{18}\text{O}/^{16}\text{O}_{\text{sample}}/^{18}\text{O}/^{16}\text{O}_{\text{VSMOW}} - 1]$, where VSMOW is the Vienna standard mean ocean water at an $^{18}\text{O}/^{16}\text{O} = 0.0020052$) from the mantle source value (average upper mantle olivine = 5.0-5.4‰, Matthey *et al.*, 1994, Eiler, 2001) are inferred to indicate the presence of material that at one time resided at or near the surface.

Ocean island basalts (OIB) display a wider range in $\delta^{18}\text{O}$ values than mid-ocean ridge basalts (2.9-7.5‰ versus $5.7 \pm 0.2\%$; Harmon & Hoefs, 1995, Eiler, 2001). The large range in $\delta^{18}\text{O}$ values have been explained both by meteoric water/seawater interaction with magma and interaction with lower (^{18}O -depleted) and/or upper (^{18}O -enriched) hydrothermally altered oceanic crust as either a magmatic contaminant sampled during a melt's passage through the lithosphere or as a recycled component in the mantle source (e.g. Taylor & Forester, 1979, Eiler, 2001, Kent *et al.*, 2004, Bindeman *et al.*, 2006, Wang & Eiler, 2008, Workman *et al.*, 2008). Correlations between oxygen isotopes and radiogenic isotopes and trace element ratios are essential in distinguishing between variable $\delta^{18}\text{O}$ values of the mantle and shallow level contamination. Differentiating between mantle and lithospheric sources of oxygen can thus constrain the composition of

mantle plumes and also reveal details of the magmatic plumbing system transporting magma to the surface.

The Galapagos Archipelago is the eruption site of a mantle plume that has 4 isotopically distinct mantle end-members (e.g. White *et al.*, 1993, Blichert-Toft & White, 2001, Harpp & White, 2001, Saal *et al.*, 2007). These components are generally isolated to the northern, western, southern, and central/eastern regions of the archipelago. The western component is characterized by the lavas of Fernandina and is distinguishable by high $^3\text{He}/^4\text{He}$ isotopic ratios (Graham *et al.*, 1993, Kurz & Geist, 1999, Kurz *et al.*, 2009). This component is generally compared to a relatively volatile-rich primitive mantle component (Kurz *et al.*, 1982, Farley *et al.*, 1992, Hart *et al.*, 1992, Hanan & Graham, 1996). There is a MORB-like component that is concentrated in the central and eastern region and anchored by the lavas of Genovesa, though it can be found across the archipelago (Harpp *et al.*, 2002, Harpp *et al.*, 2003, Geist *et al.*, 2005). The northern and southern components (illustrated by the lavas of Pinta and Floreana respectively) display enrichments in trace elements in addition to isotopic signatures generally associated with ancient recycled material in the source. Floreana is most commonly compared to a HIMU component (high- μ = high $^{238}\text{U}/^{204}\text{Pb}$) due to enrichments in Pb isotopes, despite radiogenic Sr and Hf isotopes which are atypical of a HIMU source (e.g. Harpp *et al.*, 2014). Pinta, in comparison, has low Nd and Hf isotopes with elevated $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ at a given $^{206}\text{Pb}/^{204}\text{Pb}$ ratio, which are characteristics generally associated with an Enriched Mantle (EM) component. Lavas collected from the other islands and the submarine platform in the Galapagos have intermediate compositions suggesting widespread mixing of these 4 end-members throughout the archipelago (e.g. Harpp &

White, 2001, Gibson *et al.*, 2012). However, shallow lithosphere can also influence the geochemistry of erupted basalts (Peterson *et al.*, 2014, Peterson *et al.*, In prep, Peterson *et al.*, submitted to Journal of Petrology).

The limited previous work on Galapagos Archipelago oxygen isotopes has revealed very little regional variation in $\delta^{18}\text{O}$ values, despite variable radiogenic isotopic signatures. This has led to the conclusion that magmas in the Galapagos are derived from a source with homogenous $\delta^{18}\text{O}$ values, within error of MORB, and that significant assimilation of hydrothermally altered crustal material is not occurring (Geist *et al.*, 1995, Geist *et al.*, 1998). Only rhyolites from Alcedo with evidence for magnetite crystallization (which will increase $\delta^{18}\text{O}$ of the melt) and hydrothermally altered xenoliths from Cerro Azul and the plume influenced Galapagos Spreading Center (GSC) have $\delta^{18}\text{O}$ values above (in the case of the rhyolites and Cerro Azul) and below (in the case of the GSC) what has been measured for MORB (Geist *et al.*, 1995, Geist *et al.*, 1998).

We present new $\delta^{18}\text{O}$ values of olivine phenocrysts taken from subaerial eruptions sampled across the Galapagos Archipelago. Results are combined with the previously published geochemistry and petrogenesis of the Galapagos lavas from which the olivine grains derive (Kurz & Geist, 1999, Saal *et al.*, 2007). With this expanded dataset we show that there is a larger range in $\delta^{18}\text{O}$ values in the Galapagos and evidence for a more widespread affect of contamination of melt with lithospheric material than previously suspected.

METHODS AND PREVIOUS RESULTS

Samples from 12 volcanoes in the Galapagos Archipelago were selected for this analysis (Fig. 1, Islands listed in Table 1). Lavas from Fernandina, Floreana and Pinta represent the main isotopic end-members both within the 12 volcanoes sampled and in the Galapagos Archipelago (as described above, Fig. 2). Cerro Azul, Sierra Negra, Ecuador and Alcedo (volcanoes located on Isabela) are intermediate in their isotopic composition to Fernandina, Floreana, and Pinta, (White *et al.*, 1993, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Saal *et al.*, 2007, Kurz *et al.*, 2009). Lavas from Darwin Volcano and Wolf Volcano on Isabela, and Santiago, which is in the central part of the archipelago, have lower Sr isotope and higher Nd isotope ratios than the other volcanoes on Isabela, with Pb isotopes that range from MORB-like to similar to Wolf and Darwin Islands and $^3\text{He}/^4\text{He}$ ratios that are slightly elevated in comparison to MORB (White *et al.*, 1993, Kurz & Geist, 1999, Blichert-Toft & White, 2001, Harpp & White, 2001, Saal *et al.*, 2007, Gibson *et al.*, 2012). Santa Cruz, located in the central part of the archipelago east of Santiago, has similar isotopic characteristics to Santiago, but on average is more MORB-like (White *et al.*, 1993, Blichert-Toft & White, 2001, Harpp & White, 2001, Saal *et al.*, 2007). San Cristobal is an island in the southeastern end of the archipelago (Fig. 1). Lavas from San Cristobal fall over a range in geochemical compositions from similar to MORB to more intermediate, comparable to the range of Santa Cruz, but with higher Sr isotopes at a given value for $^{143}\text{Nd}/^{144}\text{Nd}$ (Fig. 2; White *et al.*, 1993, Saal *et al.*, 2007). Sample ID's refer to the lava from which olivines were picked. Geochemistry and petrogenesis of the lavas have been previously reported in the literature (Kurz & Geist, 1999, Saal *et al.*, 2007).

Coarse olivine grains (≥ 1 mm in size) free of inclusions and alteration were hand-picked under a binocular microscope. Oxygen isotope analyses were conducted at the California Institute of Technology using previously described CO₂-laser fluorination techniques (Sharp, 1990, Valley *et al.*, 1995, Eiler *et al.*, 2000a, Eiler *et al.*, 2000b). Measurements of working standards UWG garnet (2-4 times per day) and SCO olivine (2-6 times per day) were interspersed with measurements of unknown samples. Results for these standards yielded $\delta^{18}\text{O}$ values of $5.78 \pm 0.09\text{‰}$ (UWG, $n = 22$) and $5.29 \pm 0.07\text{‰}$ (SCO, $n=27$), which are within the accepted values of UWG (5.80‰) and SCO (5.25‰) (Valley *et al.*, 1995, Eiler *et al.*, 2000a, Eiler *et al.*, 2000b). All standard deviations are 1σ and refer to long-term reproducibility of raw measurements. All $\delta^{18}\text{O}$ values for unknown samples on a given day were corrected by the difference between the measured and accepted values for standards on that day. Duplicated measurements (2-3) were performed on each unknown sample with 1σ standard deviations typically less than 0.1‰ (standard deviations for each sample reported in Table 1).

RESULTS

Oxygen isotope data from olivine grains are presented in Table 1. The $\delta^{18}\text{O}$ values for the total data set (4.74-5.40‰) fall over a greater range than previously reported for phenocryst $\delta^{18}\text{O}$ values in the Galapagos (4.64-5.04‰; range reported in Geist *et al.* (1998) for plagioclase cumulates from several locations in the Galapagos converted to the range in equilibrium olivine values using a $\Delta_{\text{plagioclase-olivine}} = 0.7\text{‰}$ (Eiler, 2001 and references therein)). This range also exceeds the range of pristine, “normal” mantle olivine ($5.2 \pm 0.2\text{‰}$; Matthey *et al.*, 1994).

In general, olivine from Fernandina, Pinta and Floreana (which represent the non-MORB mantle end-members in the Galapagos) show a narrow range of $\delta^{18}\text{O}$ values (4.97-5.11‰; Fig. 2). Olivine from Cerro Azul and Santiago also fall within to lower than this range. The highest $\delta^{18}\text{O}$ values can be found in the 3 olivine samples from San Cristobal (maximum $\delta^{18}\text{O} = 5.40\text{‰}$). The lowest $\delta^{18}\text{O}$ values can be found in the one sample from Ecuador Volcano and one of the samples from Sierra Negra (4.74‰), (White *et al.*, 1993, Reynolds & Geist, 1995, Blichert-Toft & White, 2001, Harpp & White, 2001, Saal *et al.*, 2007). However, Sierra Negra also displays one of the largest ranges in $\delta^{18}\text{O}$ values for a given island in this study (4.74-4.95‰), along with Darwin Volcano (4.78-5.04‰), Cerro Azul Volcano (4.86-5.13) and Santa Cruz (4.75-5.22‰). In the following discussion we will examine $\delta^{18}\text{O}$ values within individual islands as well as across the archipelago as a region.

DISCUSSION

Fractional Crystallization and Partial Melting

Magmatic differentiation tends to cause only small changes in $\delta^{18}\text{O}$ values because common crystallizing phases have both positive, in the case of plagioclase, and negative, in the case of olivine and clinopyroxene, isotopic mineral-magma fractionation factors (e.g. Chiba *et al.*, 1989, Harris *et al.*, 2000, Eiler, 2001, Cooper *et al.*, 2004). To test the expected effects of fractional crystallization on $\delta^{18}\text{O}$ values, the liquid line of descent (LLD) is calculated for both a trace element depleted and enriched composition using PetroLog3 (Fig. 3; Danyushevsky & Plechov, 2011). The isobaric LLD is calculated at 2 kbar in a system closed to oxygen. For the modeling, we use the trace element depleted

composition of a high MgO olivine-hosted melt inclusion from Santiago Island and the trace element enriched composition of a high MgO inclusion from Fernandina (reported in table 2 and Koleszar *et al.* (2009)). While these compositions do not represent the entire range in major element data found in the Galapagos, these compositions include measurements for H₂O contents, which can have a great effect on crystallization trends, and generally bracket the major element data thus providing end-member cases for the expected $\delta^{18}\text{O}$ fractionation (Fig. 3). The pressure is based on an average pressure of entrapment of melt inclusions collected from Fernandina and Santiago, though changing the pressure between 0.5 and 4 kbars does not change the interpretation. The variation in $\delta^{18}\text{O}$ for Rayleigh distillation is calculated using the fractionation factors presented in table 2 for crystallizing minerals, recalculating the bulk fractionation factor (α) at each step based on the modal abundances of crystallizing phases. These values are assumed to be constant over the course of fractional crystallization to simplify the calculation. For tholeiitic basalts and a temperature change $< 200^\circ\text{C}$ at magmatic temperatures this has found to be a valid simplification (Chiba *et al.*, 1989, Harris *et al.*, 2000, Eiler, 2001, Wang & Eiler, 2008). The primary $\delta^{18}\text{O}$ values of the crystallizing melt are fixed so that resulting trends pass through the measured value for Santiago and Fernandina, though changing this value does not effect the total change in $\delta^{18}\text{O}$ over the course of the LLD. The results of the calculation show that the $\delta^{18}\text{O}$ of olivine in equilibrium with the crystallizing melt can only be expected to change by a maximum of 0.15‰, which inadequately addresses the range we measure in $\delta^{18}\text{O}$ values.

Variations in the degree of partial melting are also not predicted to appreciably increase the $\delta^{18}\text{O}$ values of a melt by more than $\sim 0.1\text{‰}$ (Eiler, 2001). Large increases in

$\delta^{18}\text{O}$ values due to partial melting are the result of an increasing albitic component in the melt and only become a concern at very small degrees of melt. For this study, the $\delta^{18}\text{O}$ values within a given island do not vary with La/Yb or Sm/Yb values (trace element ratios sensitive to degree and depth of melting, Fig. 4). This includes volcanoes that show large variations in $\delta^{18}\text{O}$, such as Santa Cruz, with very little variation in Sm/Yb or La/Yb, and volcanoes that show large variations in Sm/Yb and La/Yb, but change very little in $\delta^{18}\text{O}$, such as is the case for Floreana. Lavas from Wolf Volcano tend to have values in Sm/Yb and La/Yb equivalent to lavas from trace element enriched components such as Fernandina, but are isotopically more similar to Genovesa. These characteristics are attributed to low degree melts of a depleted mantle source (Geist *et al.*, 2005). The $\delta^{18}\text{O}$ values from the Wolf Volcano olivines are slightly lower than normal upper mantle values ($4.89 \pm 0.04\text{‰}$), opposite to what would be predicted if a low degree of melting were greatly affecting $\delta^{18}\text{O}$ values. Samples from Santa Cruz (which show the largest range in $\delta^{18}\text{O}$ values) also show this trend, with the two samples with the slightly higher La/Yb ratios (and presumably lower degree of melting) also having lower $\delta^{18}\text{O}$ values. Fractional crystallization and partial melting, as a result, are not the major factors controlling $\delta^{18}\text{O}$ variation in the Galapagos Archipelago.

$\delta^{18}\text{O}$ variation of the main isotopic end-members in the Galapagos

Samples from the main isotopic mantle end-members in the Galapagos (Fernandina, Floreana, and Pinta) cover a large range in radiogenic isotopes, but only show a narrow range in $\delta^{18}\text{O}$ values (4.97-5.11‰), within error of the range found for upper mantle olivine (Fig. 2; Matthey *et al.*, 1994, Eiler, 2001). This range is at the lower end of the

upper mantle range, similar to high $^3\text{He}/^4\text{He}$ olivine from Baffin Island (Kent *et al.*, 2004). This suggests that the Galapagos mantle has a homogenous value for $\delta^{18}\text{O}$. This value is at the lower end of the range predicted for normal upper mantle olivine, and is consistent with previous studies of oxygen isotopes in the Galapagos (Geist *et al.*, 1995, Geist *et al.*, 1998).

Assimilation

$\delta^{18}\text{O}$ values greater than normal upper mantle

Oxygen isotope fractionation between minerals and water is temperature dependent. As a result, low temperature ($< 200^\circ\text{C}$) hydrothermal alteration leads to ^{18}O enrichment while high temperature alteration ($> 250^\circ\text{C}$) leads to ^{18}O depletion of crust relative to unaltered basalts (e.g. Muehlenbachs & Clayton, 1976, Muehlenbachs, 1998, Alt & Bach, 2006). Recrystallization of cumulates can also lead to oxygen exchange with seawater and has been shown in the case of plagioclase cumulates to increase $\delta^{18}\text{O}$ values up to 7.4‰ (Alt & Bach, 2006, Gao *et al.*, 2006). Interaction with different parts of the crust, as a result, can potentially lead to different variations in $\delta^{18}\text{O}$ values (Garcia *et al.*, 1998, Wang *et al.*, 2003, Gaffney *et al.*, 2005, Wang & Eiler, 2008, Genske *et al.*, 2013).

The island of San Cristobal, which has the highest $\delta^{18}\text{O}$ values measured here, is identified by Saal *et al.* (2007) as having interacted with plagioclase-rich cumulates during melt transport through the oceanic lithosphere. This is indicated by positive Sr, Ba and Eu anomalies on a primitive mantle normalized diagram (elements that are difficult to fractionate from other trace elements with similar incompatibility without the presence of plagioclase). Using $\text{Sr}/\text{Sr}^* \geq 1$ ($\text{Sr}_{\text{PM}}/[(\text{Ce}_{\text{PM}} + \text{Nd}_{\text{PM}})/2]$), and Ba/Nb ratios as indicators

of assimilation of plagioclase cumulates, the data of this study show a positive correlation between increasing $\delta^{18}\text{O}$ values and increasing amounts of assimilation (Fig. 5). This includes the islands with large $\delta^{18}\text{O}$ variability, such as Sierra Negra and Santa Cruz. There is also a weak correlation between increasing $\delta^{18}\text{O}$ values and $\Delta 7/4$ ratios (measure of the deviation of $^{207}\text{Pb}/^{204}\text{Pb}$ from the Northern Hemisphere Reference Line and defined in Hart (1984); Fig. 2c, 2f). The $\Delta 7/4$ ratios, however, are in range of the values of Genovesa, which is MORB-like, rather than Pinta, which is characterized by high $\Delta 7/4$. Sr isotopes show this as well, with San Cristobal falling at low values of $^{87}\text{Sr}/^{86}\text{Sr}$, closer to the Genovesa end of the array. If the high $\delta^{18}\text{O}$ values were due to ancient recycled material in the mantle source, a stronger correlation of $\delta^{18}\text{O}$ values with more radiogenic isotopes would be expected. Samples from Floreana, which also show high values of Sr/Sr^* and Ba/Nb , do not show correspondingly high $\delta^{18}\text{O}$ values. Therefore the higher $\delta^{18}\text{O}$ values of San Cristobal and the volcanoes that display large ranges in $\delta^{18}\text{O}$ values are more consistent with the assimilation of plagioclase cumulates with the isotopic composition of Genovesa in the present-day lithosphere.

$\delta^{18}\text{O}$ values lower than normal upper mantle

Samples with the lowest $\delta^{18}\text{O}$ values come from Sierra Negra, Ecuador, Alcedo, Darwin, Wolf and Santa Cruz volcanoes which produce lavas with intermediate isotopic compositions to Fernandina, Floreana, and Pinta (Fig. 2). $\delta^{18}\text{O}$ values that are outside the accepted upper mantle range that are explained by the presence of recycled hydrothermally altered material in the mantle source are often accompanied by very radiogenic isotopic signatures (e.g. Eiler, 2001, Skovgaard *et al.*, 2001, Cooper *et al.*,

2004, Workman *et al.*, 2008, Day *et al.*, 2009, Day *et al.*, 2010). Therefore the lowest $\delta^{18}\text{O}$ values in the Galapagos would be predicted to reside in the Floreana and/or Pinta mantle sources that are thought to contain recycled material and have some of the most extreme radiogenic isotopes in the Galapagos. However, what is observed is that the lowest $\delta^{18}\text{O}$ values are found in lavas with intermediate isotopic compositions. Therefore, the low $\delta^{18}\text{O}$ values are either being produced by a low $\delta^{18}\text{O}$ component with intermediate isotopes, in contrast to what is observed elsewhere, or are produced by interaction with a low $\delta^{18}\text{O}$ component in the shallow lithosphere.

The lighter $\delta^{18}\text{O}$ olivine from Sierra Negra, Ecuador, Alcedo, Darwin, Wolf and Santa Cruz volcanoes come from lavas that are more evolved and have experienced fractional crystallization (Fig. 3). These lavas range in terms of enrichment with Darwin and Wolf Volcanoes anchoring the more depleted, MORB-like end of the variability. Assimilation will often occur concurrently with fractional crystallization (e.g. Depaolo, 1981). The lavas from these volcanoes, however, do not show unusual trace element or radiogenic isotope characteristics, making it difficult to unambiguously prove that assimilation is occurring in these samples. Meteoric water, seawater and gabbro that has interacted with seawater at high temperatures will have $\delta^{18}\text{O}$ values lower than upper mantle olivine and can potentially be sources of low $\delta^{18}\text{O}$ in the Galapagos (Gao *et al.*, 2006, Thirlwall *et al.*, 2006), but this interaction must not create a significant change in the trace element or radiogenic isotope characteristics of the melt.

Meteoric water has been shown to impart a $\delta^{18}\text{O}$ value distinct from that of seawater in areas where precipitation leads to an active hydrothermal system. This is illustrated in Hawaii where there is a correlation between areas of greater precipitation

and lower $\delta^{18}\text{O}$ values in olivine (Wang & Eiler, 2008). In the Galapagos, however, there does not appear to be a correlation with precipitation patterns. In Santa Cruz, for example, two of the three samples were collected in the dry lowlands (area of low precipitation) while one sample was collected in the humid highlands (area of greatest precipitation) (Kurz & Geist, 1999, Saal *et al.*, 2007, Trueman & d'Ozouville, 2010). The sample collected in the humid highlands shows the highest value for $\delta^{18}\text{O}$ in contrast to what would be predicted if the source of low $\delta^{18}\text{O}$ in the Galapagos were the result of the meteoric hydrothermal system.

Seawater and gabbro that is hydrothermally altered at high temperatures can impart a low $\delta^{18}\text{O}$ value to melt (Kent *et al.*, 2004, Gao *et al.*, 2006, Thirlwall *et al.*, 2006, Bindeman *et al.*, 2008). To test the effects of each of these assimilants on Galapagos melt, we model a mixture of the composition of GI92-19 (Sierra Azul) with seawater and 1 hydrothermally altered gabbro composition with 2 different $\delta^{18}\text{O}$ values. GI92-19 is set to have an initial $\delta^{18}\text{O}$ value equal to the melt composition in equilibrium with the average olivine values measured for Fernandina, Floreana and Pinta (5.52‰). For seawater the $\delta^{18}\text{O} = 0\text{‰}$ while the gabbro composition (composition Bp; Hart *et al.*, 1999), uses both a minimum $\delta^{18}\text{O}$ value (+2.5‰) found for hydrothermally altered gabbro and the global average $\delta^{18}\text{O}$ value (+4.0‰) (compositions of assimilants presented in Table 3). We chose a gabbro composition without a strong plagioclase cumulate trace element signature so as to produce the smallest change in the composition of the melt. The gabbro composition has an assigned $^{87}\text{Sr}/^{86}\text{Sr}$ ratio equivalent to Genovesa to model a gabbro created at the GSC. To reproduce the $\delta^{18}\text{O}$ value of GI92-19 requires 18% mixing with the gabbro with the global average $\delta^{18}\text{O}$, 10% for the gabbro with the minimum value for

$\delta^{18}\text{O}$, and only 2.5% mixing with seawater (Fig. 6). This is close to the amount of seawater that would be needed to produce the full range in Cl/K ratios of the submarine glass with the composition of Sierra Negra/Cerro Azul reported in Peterson *et al.* (submitted to Journal of Petrology). Mixing with each of these three components does not greatly affect the radiogenic isotope or trace element composition of the melt, which is consistent with the samples not having unusual compositions outside of their oxygen isotope signatures. Therefore interaction with seawater and hydrothermally altered gabbro could potentially be the source of low $\delta^{18}\text{O}$ values in the Galapagos Archipelago.

Alternative explanation for light $\delta^{18}\text{O}$ in the Galapagos

The presence of pyroxenite in the mantle source of a given hotspot has been invoked to explain variations in $\delta^{18}\text{O}$ values both above and below the upper mantle range (e.g. Eiler, 2001, Skovgaard *et al.*, 2001, Cooper *et al.*, 2004, Thirlwall *et al.*, 2006, Day *et al.*, 2009, Day *et al.*, 2010). The low $\delta^{18}\text{O}$ values of these studies, however, are correlated with highly radiogenic isotopic signatures. In the Galapagos, the low $\delta^{18}\text{O}$ values are associated with lavas of intermediate isotopic compositions to Fernandina, Floreana and Pinta (that have $\delta^{18}\text{O}$ values within the accepted range of pristine upper mantle). This suggests, as we have argued, that these values are indicative of interaction with the present-day shallow level crust as opposed to being a characteristic of the mantle source. The study of Vidito *et al.* (2013), however, using the minor element composition of olivine collected across the archipelago argues that source lithology and the presence of pyroxenite in the Galapagos is not evidenced by the radiogenic isotope signatures of lavas. Pyroxenite in the source of OIBs is thought to be the product of eclogite melt

reacting with peridotite in the mantle to form a pyroxene-rich source. Olivine formed from partial melts of this reacted source record the hybridization by retaining high Ni and Si contents, but low Mn and Ca contents. Because clinopyroxene has a negative mineral-magma fractionation factor (Chiba *et al.*, 1989, Eiler, 2001) it is conceivable that a pyroxene-rich source would produce a light $\delta^{18}\text{O}$ melt. Vidito *et al.* (2013) used measurements of Ni, Si, Mn and Ca in olivine collected from across the Galapagos Archipelago to create a map of proposed areas with high concentrations of pyroxenite in the mantle. They identified Sierra Negra, Ecuador, Darwin, Alcedo, Santiago and Roca Redonda as having > 40% pyroxenite in the source. With the exception of Santiago, these cover almost all of the locations that exhibit low $\delta^{18}\text{O}$ values in this study. Though the study of Vidito *et al.* (2013) only reports on one sample from Santiago (which produces lavas with a large range in compositions), it has a similar composition to the sample from Santiago analyzed here. Santiago, however has $\delta^{18}\text{O}$ values within range of normal upper mantle, in contrast to the hypothesis that pyroxenite in the mantle source is the cause low $\delta^{18}\text{O}$. Wolf volcano, which also has olivine with low $\delta^{18}\text{O}$ values, is identified as a purely peridotite source and would therefore require a different source of low $\delta^{18}\text{O}$. If the low $\delta^{18}\text{O}$ values of the samples of this study are the result of the presence of pyroxenite in the source that has an intermediate isotopic composition, the olivines with low $\delta^{18}\text{O}$ should also show enrichments in Ni and Si but depletions in Mn and Ca. These measurements will therefore be the focus of future measurements.

CONCLUSIONS

New oxygen isotope data measured in olivine grains taken from 12 different volcanoes/islands in the Galapagos Archipelago show a larger range in $\delta^{18}\text{O}$ values than previously measured. The main non-MORB isotopic mantle end-members in the Galapagos (Fernandina, Floreana, and Pinta) show $\delta^{18}\text{O}$ values ($5.02 \pm 0.08\text{‰}$) within range of olivine from pristine upper mantle. Generally, $\delta^{18}\text{O}$ values do not correlate with radiogenic isotopes, which indicates that variation above and below normal mantle values is more likely due to interaction with shallow, hydrothermally altered material than the presence of low $\delta^{18}\text{O}$ components in the mantle source. This is corroborated for $\delta^{18}\text{O}$ values above the accepted mantle limit by the trend of increasing Sr/Sr* and Ba/Nb ratios, which are indicators of the assimilation of plagioclase cumulates, with increasing $\delta^{18}\text{O}$ values. Therefore the high $\delta^{18}\text{O}$ values of San Cristobal (maximum = 5.40‰) and the large range in $\delta^{18}\text{O}$ values of Sierra Negra Santa Cruz and Darwin Volcano are the result of the assimilation of plagioclase cumulates. The $\delta^{18}\text{O}$ values of Sierra Negra, Alcedo, Darwin, Wolf and Ecuador volcanoes that fall below the mantle limit ($4.85 \pm 0.1\text{‰}$), do not exhibit geochemical characteristics indicative of assimilation which makes it difficult to unambiguously identify this process as the cause of the low $\delta^{18}\text{O}$ values in the Galapagos. However, a small amount of assimilation of seawater ($\delta^{18}\text{O} = 0\text{‰}$) and/or hydrothermally altered gabbro without a cumulate component ($\delta^{18}\text{O} = +2.5/4.0\text{‰}$) can produce the low values for $\delta^{18}\text{O}$ without a large change to the trace element or radiogenic isotope composition of the melt and assimilation of hydrothermally altered material and/or seawater is consistent with volatile/refractory element variations previously measured in the Galapagos. These results show that interaction with the hydrothermally

altered crust is a widespread phenomenon in the Galapagos Archipelago and should be considered when inferring mantle geochemistry of lavas erupted at the surface.

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FIGURE CAPTIONS

Figure 1. Map of the Galapagos archipelago with prominent features labeled. Scale bar and bathymetry color scale are included the left side on the map. Volcanoes where olivine grains were collected are indicated by symbols used for geochemical plotting. Map created using GeoMapApp <http://www.geomapapp.org> (Ryan *et al.*, 2009).

Figure 2. $^{87}\text{Sr}/^{86}\text{Sr}$, $^3\text{He}/^4\text{He}$, and $\Delta 7/4$ versus (A-C) $^{143}\text{Nd}/^{144}\text{Nd}$ and (D-F) $\delta^{18}\text{O}$ values of olivine phenocrysts. Isotope ratios for lava associated with the $\delta^{18}\text{O}$ of olivine phenocrysts were reported Saal *et al.*, (2007) and Kurz and Geist (1999). Grey field in panels D-F show the range of typical upper mantle olivine $\delta^{18}\text{O}$ (Mattey *et al.*, 1994, Eiler, 2001). Notice that samples from Floreana, Fernandina, and Pinta (representing the extreme enriched isotopic end-members in the Galapagos) are within the upper mantle field. Errors shown for $\delta^{18}\text{O}$ values are 1σ .

Figure 3. MgO wt% versus A.) TiO_2 wt %, and B.) $\delta^{18}\text{O}$ values for individual samples. Major element data for lava associated with the $\delta^{18}\text{O}$ of olivine phenocrysts were reported in (Saal *et al.*, 2007)). Superimposed on the data are predicted liquid lines of descent (LLD) for olivine (olv) - olv + plagioclase (plag) – olv + plag + clinopyroxene (cpx) (solid black and purple lines, where black circle indicates the appearance of a new fractionating crystal phase). Calculations were performed in PetroLog3 (Danyushevsky & Plechov, 2011) isobarically at 2 Kbars of pressure using 2 different starting compositions, which can be found in Table 2. Black LLD is calculated from an enriched Fernandina

composition, while purple LLD is calculated from a depleted Santiago composition.

LLDs for $\delta^{18}\text{O}$ values was calculated using mineral/melt fractionation factors presented in Table 2 and described in the text. Notice in panel B that at a given MgO content there is a large within island variation in $\delta^{18}\text{O}$ values. Errors shown for $\delta^{18}\text{O}$ values are 1σ .

Figure 4. $\delta^{18}\text{O}$ values versus A.) Sm/Yb and B.) La/Yb for individual olivines. Trace element data for lava associated with the $\delta^{18}\text{O}$ of olivine phenocrysts were reported in Saal *et al.* (2007) Notice there is very little within island variation in trace element ratios with $\delta^{18}\text{O}$ values. Errors shown for $\delta^{18}\text{O}$ values are 1σ .

Figure 5. $\delta^{18}\text{O}$ values versus A.) Sr/Sr* ($\text{Sr}_{\text{PM}} / [(\text{Ce}_{\text{PM}} + \text{Nd}_{\text{PM}}) / 2]$) and B.) Ba/Nb ratios for individual samples. Also shown is the composition of plagioclase-rich gabbro Fp and Hp reported in Hart *et al.* (1999) with the maximum value for $\delta^{18}\text{O}$ measured for hydrothermally altered plagioclase cumulates (Alt & Bach, 2006, Gao *et al.*, 2006). Samples Fp and Hp are unaltered, lower crustal protolith gabbros from the 500 m gabbroic section drilled at site 735 during Leg 118 (Ocean Drilling Project) in the SE Indian Ridge. Inset at left shows a zoomed in version of panels A and B. Notice the trend of increasing Sr/Sr* and Ba/Nb ratios towards the values of the gabbro with increasing $\delta^{18}\text{O}$. This suggests $\delta^{18}\text{O}$ values are being increased by the assimilation of plagioclase cumulates. Errors shown for $\delta^{18}\text{O}$ values are 1σ .

Figure 6. $\delta^{18}\text{O}$ values versus A.) $^{87}\text{Sr}/^{86}\text{Sr}$ and B.) Ba/Nb ratios for individual samples. Also included are simple mixing lines between lava composition of GI92-8 ($\delta^{18}\text{O}$ value

set to melt in equilibrium with average olivine value from Fernandina, Floreana, and Pinta) and both seawater and an unaltered protolith lower crustal gabbro composition that does not show trace element signature of plagioclase cumulate (Bp; Hart *et al.*, 1999) with 2 different values for $\delta^{18}\text{O}$ (2.5 and 4.0 ‰ explained in text). Each point along mixing lines represent 1% mixing. Notice that the trends are hyperbolic, which allows the $\delta^{18}\text{O}$ value of the melt to change without greatly affecting the isotopic or trace element composition. Inset shows zoomed out view of panels A and B. Errors shown for $\delta^{18}\text{O}$ values are 1σ .

FIGURES

Figure 4-1

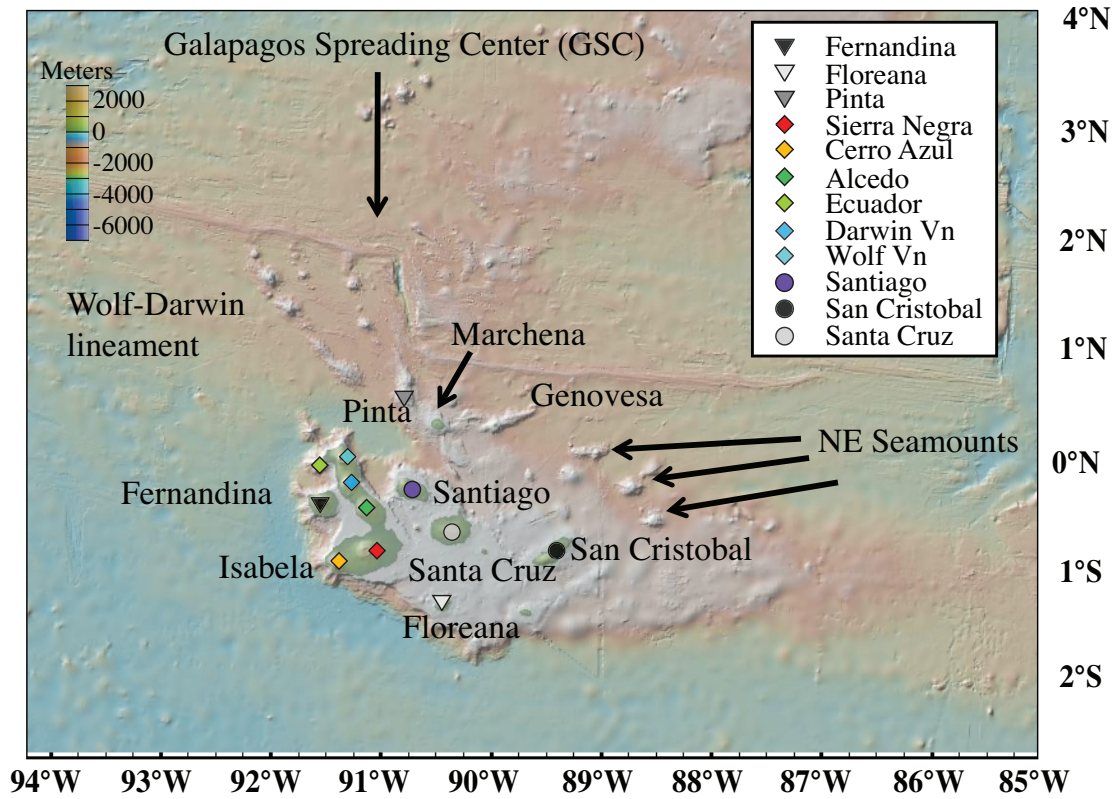


Figure 4-2

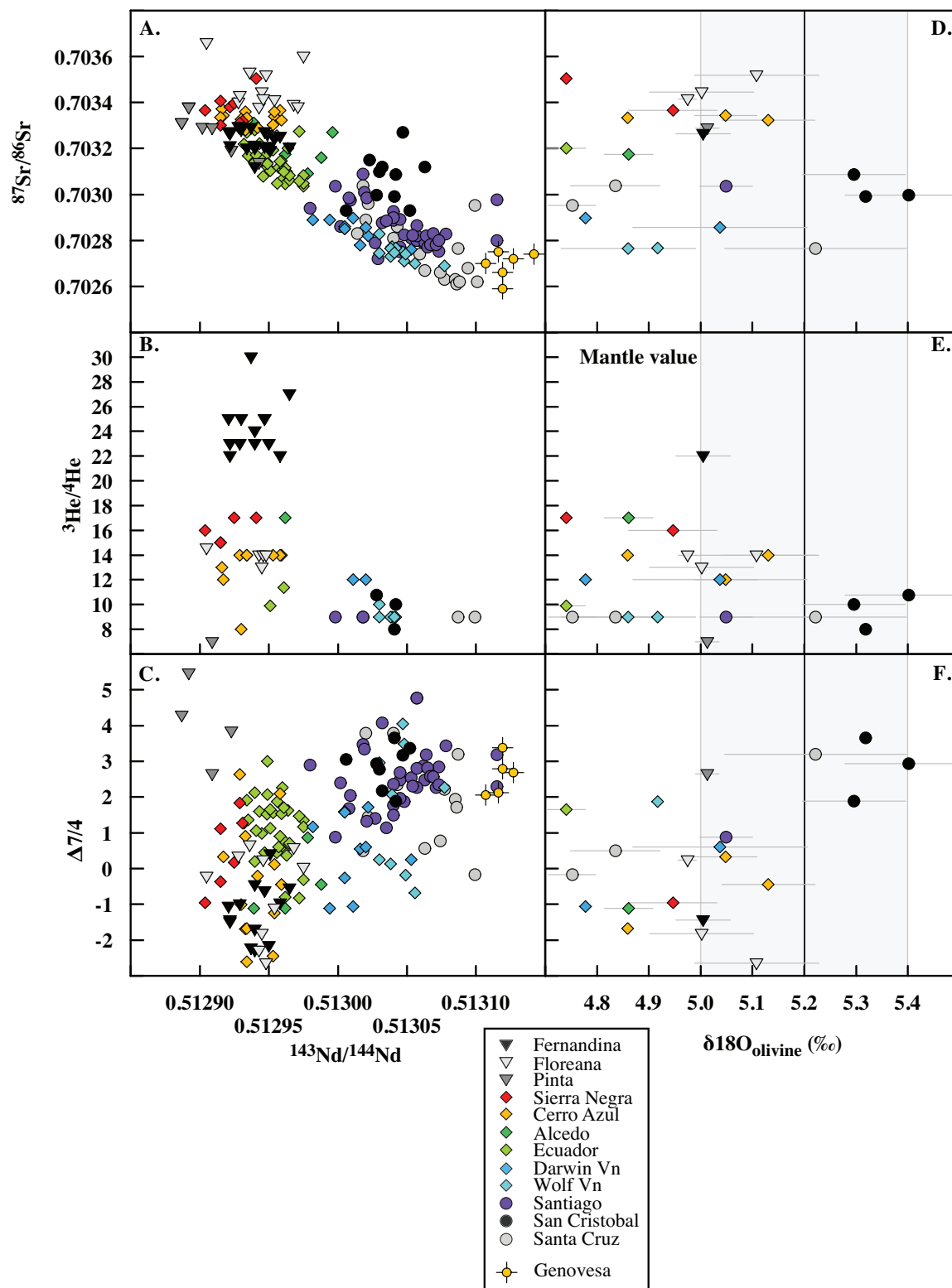


Figure 4-3

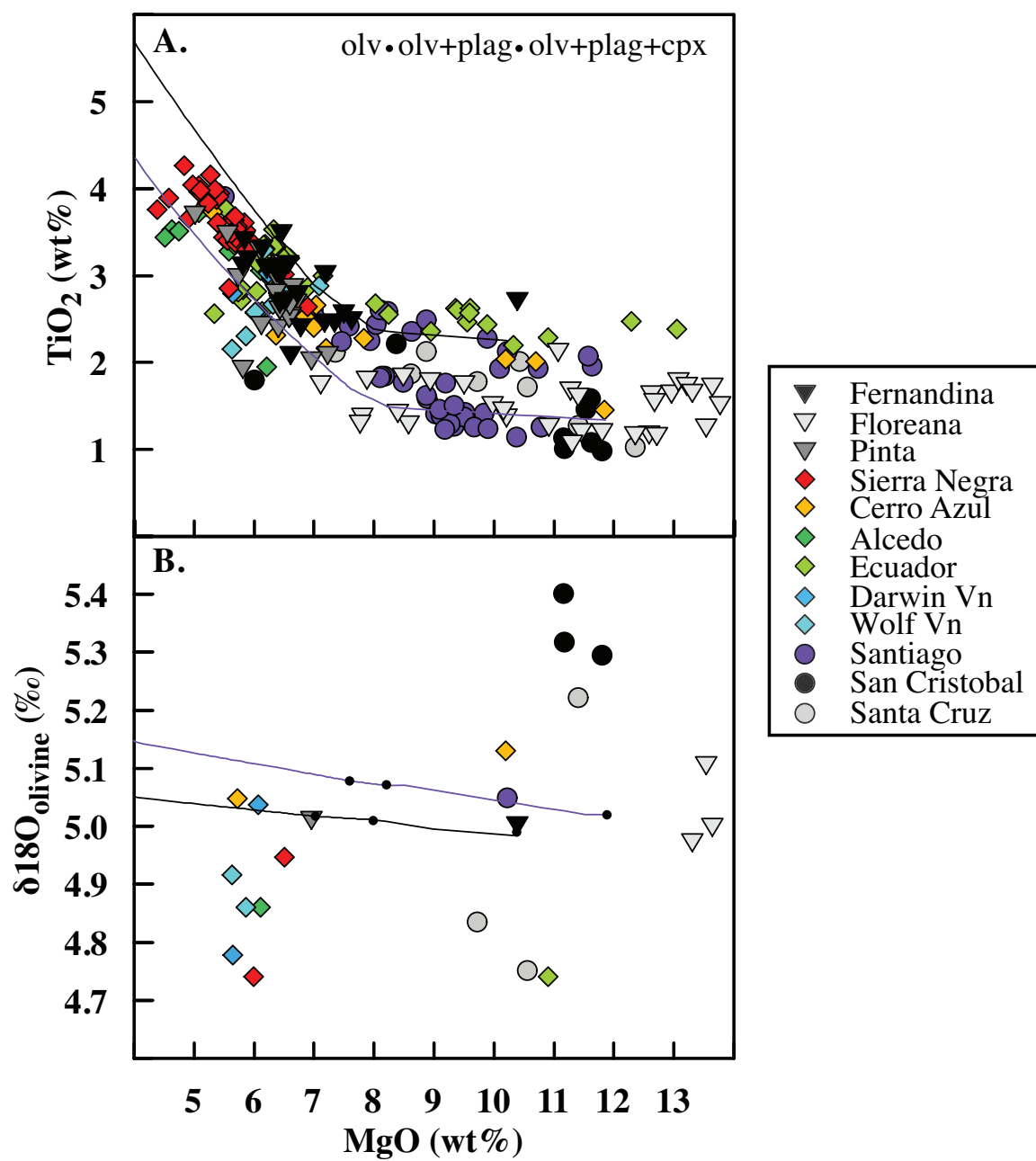


Figure 4-4

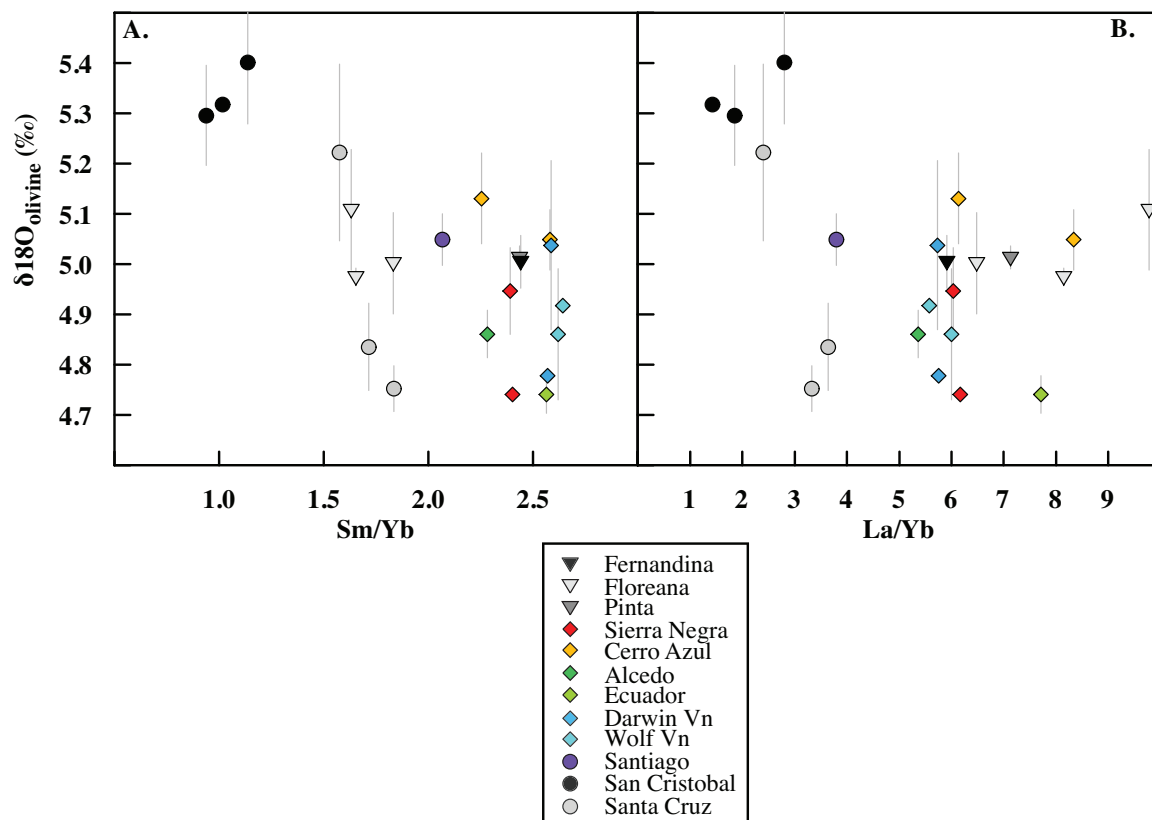


Figure 4-5

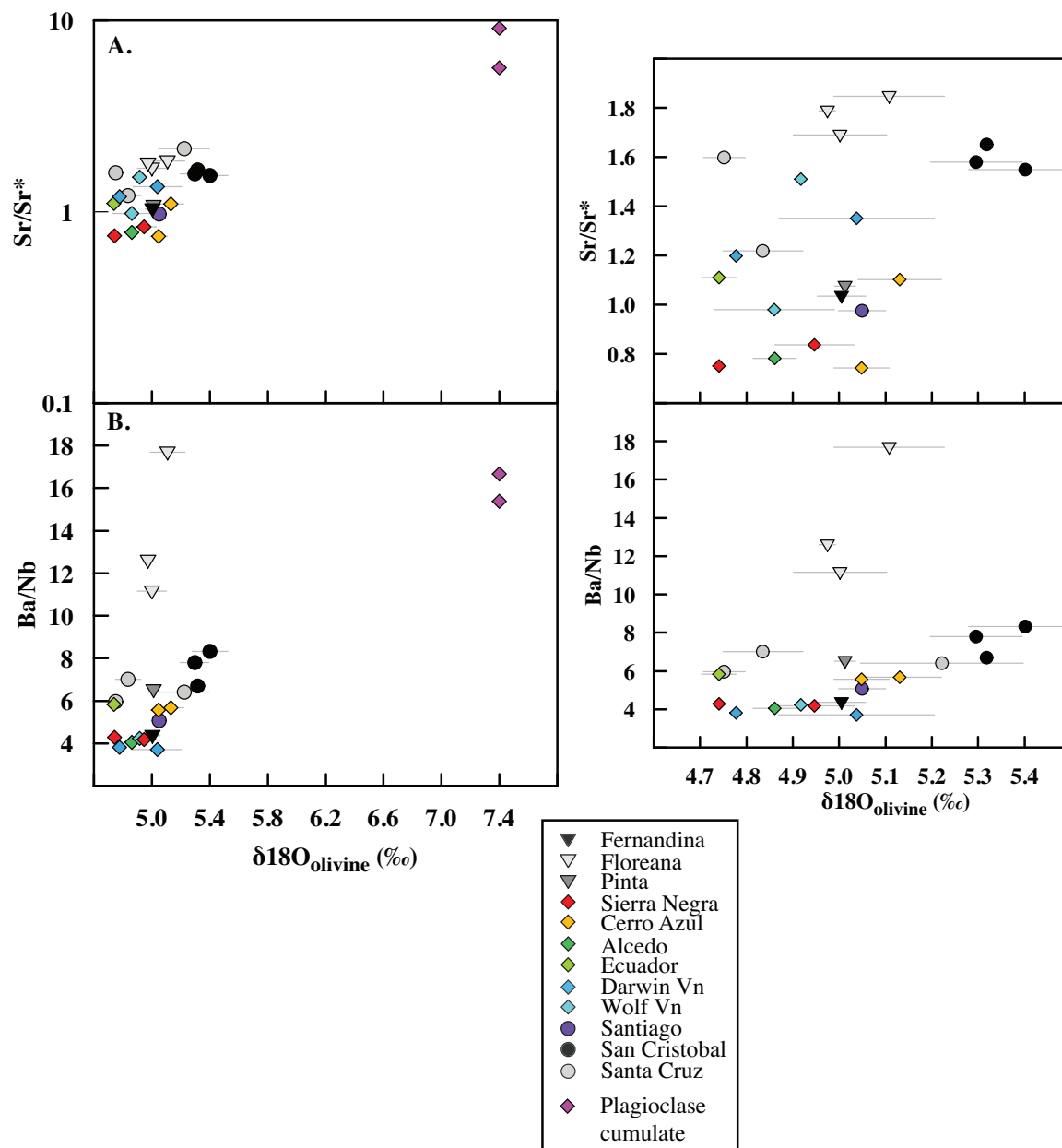
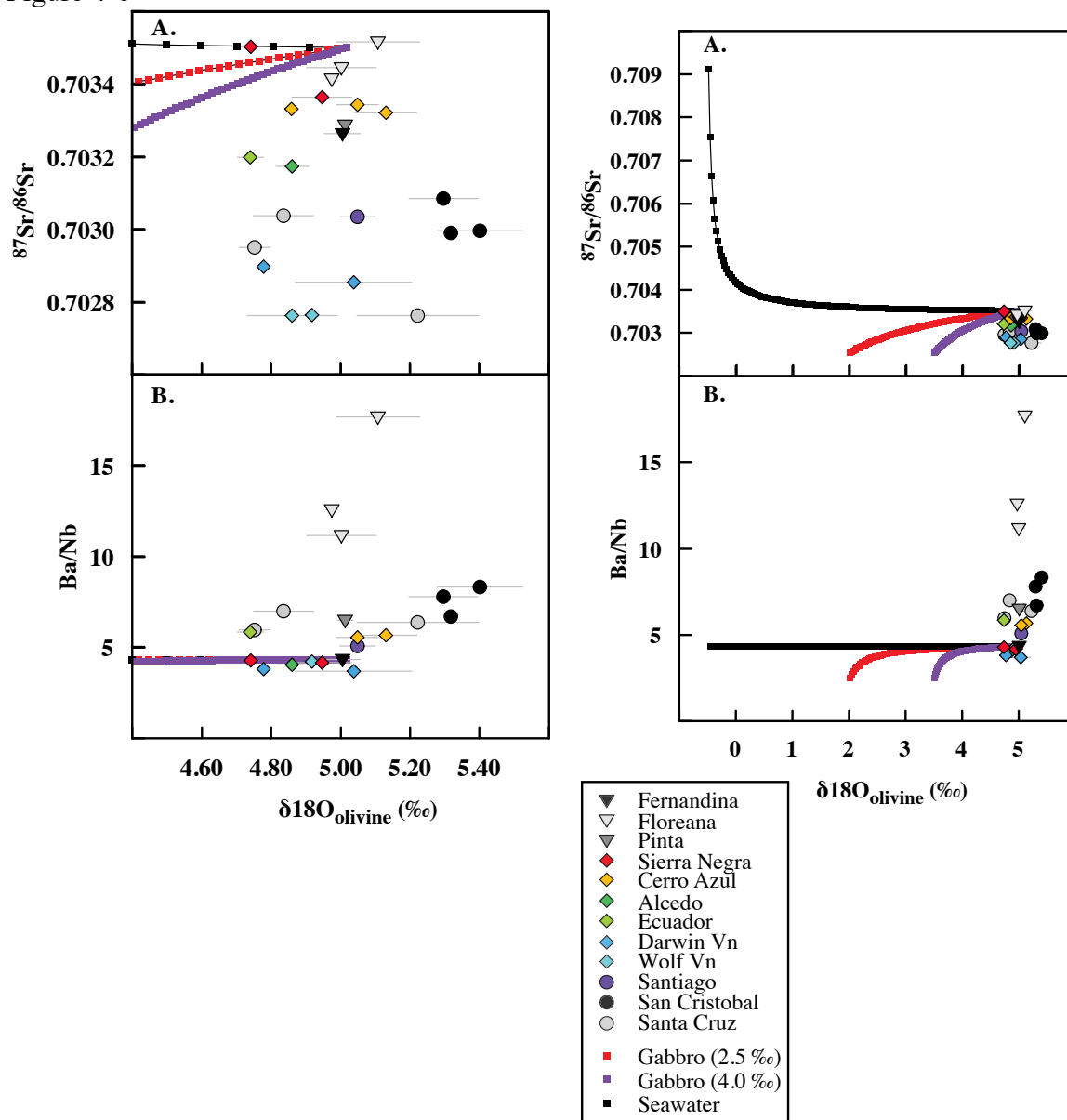


Figure 4-6



TABLES

Table 1. Results of in situ analysis for oxygen isotope compositions of individual olivine grains from subaerial lavas collected across the Galapagos Archipelago

Sample ID	Island	$\delta^{18}\text{O}$ (‰)	1σ (‰)
GI92-16	Alcedo	4.86	0.05
CA90-19-1	Cerro Azul	4.86	0.20
SG 93-12	Cerro Azul	5.05	0.06
SG 93-5	Cerro Azul	5.13	0.09
GI92-17	Darwin Vn	4.78	0.01
GI92-18	Darwin Vn	5.04	0.17
GI92-19	Ecuador	4.74	0.04
NSK97-215	Fernandina	5.00	0.05
SG93-19	Floreana	5.00	0.10
SG93-22	Floreana	4.97	0.02
SG93-23	Floreana	5.11	0.12
SKV98-108	Pinta	5.01	0.02
NSK97-126	San Cristobal	5.40	0.12
NSK97-252	San Cristobal	5.32	
NSK97-254	San Cristobal	5.30	0.10
GI92-04	Santa Cruz	5.22	0.18
GI92-1	Santa Cruz	4.75	0.05
GI92-2A	Santa Cruz	4.84	0.09
NSK97-238	Santiago	5.05	0.05
GI92-5	Sierra Negra	4.95	0.09
GI92-8	Sierra Negra	4.74	
W95-74	Wolf Vn	4.92	0.01
W95-75-R	Wolf Vn	4.86	0.13

Refer to Saal et al., (2007) for detailed description of geochemistry

Table 2. Fractional crystallization model

	Starting Composition	
	Enriched Composition ^a	Depleted Composition ^b
Major Elements (wt%)		
SiO ₂	47.11	46.46
TiO ₂	2.23	1.34
Al ₂ O ₃	15.97	14.36
FeO*	9.21	11.77
MnO	0.12	0.2
MgO	10.34	11.86
CaO	11.29	11.5
Na ₂ O	2.19	2.14
K ₂ O	0.32	0.08
P ₂ O ₅	0.25	0.07
H ₂ O (wt%)	0.68	0.12
Pressure ^c	2kbars	
$\delta^{18}\text{O}_{\text{o-melt}}^{\text{d}}$	5.5	5.62
Equilibrium fractionation factors ^e		
	Δ	α
plagioclase	0.2	1.0002000
clinopyroxene	-0.2	0.9998000
olivine	-0.5	0.9995001

^a Composition of melt inclusion AHA D25C-3-43 reported in Koleszar et al., (2009), but modified to an MgO = 10.3 wt% (value of Fernandina lava with olivine grain measured for oxygen isotopes). Modification was done by adding equilibrium olivine back into the composition in 0.5% increments. Correction required 2.5% olivine addition.

^b Composition of melt inclusion STG06-29-06 reported in Koleszar et al., (2009)

^c Models used in PETROLOG: Ol, CPX, PLAG- Danyushevsky, 2001, Melt density- Lange and Carmichael, 1987, Melt viscosity- Bottinga & Weill 1972. Oxygen fugacity set at QFM and then run closed for oxygen

^d Initial $\delta^{18}\text{O}$ values of the melt set to pass through the $\delta^{18}\text{O}$ values measured for Santiago and Fernandina compositions

^e Equilibrium fractionation factors based on the results of Eiler (2001) and Chiba *et al.*, (1989). $\Delta = 1000 \cdot \ln \alpha$

Table 3. Simple mixing model compositions

	GI92-8*	Gabbro Composition (Bp) ^a	Seawater ^b
Major Elements (wt%)			
SiO ₂	49.06	41.20	
TiO ₂	3.36	6.12	
Al ₂ O ₃	14.18	9.61	
FeO*	12.71	24.69	
MnO	0.21	0.33	
MgO	5.99	6.46	
CaO	10.62	8.85	
Na ₂ O	3.03	2.63	
K ₂ O	0.49	0.06	
P ₂ O ₅	0.344	0.05	
H ₂ O (wt%)			97.5
Ba (ppm)	115	5	0.00117
Nb (ppm)	26.82	2.05	0
Sr (ppm)	302	122	7.8
⁸⁷ Sr/ ⁸⁶ Sr	0.7035	0.70253	0.7091
δ18O _o	5.52	2.5/4	0

* δ¹⁸O_o of GI92-8 set to the melt value in equilibrium with the average δ¹⁸O value of olivine from Fernandina, Floreana and Pinta

^a Gabbro composition is a prisitine unaltered lower crustal gabbro composition without a strong cumulate trace element signature from Hart *et al.* (1999). Sr isotope is set to be equal to Genovesa which is the MORB-like component in the Galapagos to simulate a gabbro created at the GSC. Both a δ¹⁸O = +2.5 and +4.0‰ are tested to see relative amounts of assimilant needed.

^b Seawater trace element composition taken from Quinby-Hunt (1983). Isotopic composition taken from (Farrell *et al.*, 1995).

SYNTHESIS

The geochemistry of ocean islands basalts begins with a mantle source derived from complex materials with unknown quantities of recycled components from as deep as the core-mantle boundary (CMB). Separating the signatures of the deep mantle source from the effects of shallow level processes is difficult without high quality data gathered to specifically address the amount of communication occurring between mantle and surface reservoirs. In this dissertation, I have used a large geochemical data set of submarine glass, melt inclusions and whole rock, collected from across the Galapagos Archipelago, to explore the influence of shallow level processes on lavas erupted at the surface and to isolate deep mantle signatures unique to the Galapagos plume.

Chapter 1 uses Pb isotopes measured on melt inclusions from Fernandina and Santiago to explore the origin of the “ghost plagioclase” signature. While commonly explained by invoking an ancient recycled gabbro (now eclogite) in the mantle source, the Pb isotope variations of the Santiago and Fernandina inclusions are more easily explained by melt interaction with plagioclase cumulates in the plumbing system of the islands.

Chapter 2 sets out to characterize the volatile contents of the different isotopic end-members lavas using new major, trace, and volatile content (H_2O , CO_2 , F, Cl, S) radiogenic and He isotope measurements of 118 submarine glasses collected across the Galapagos Archipelago. The samples geographically and geochemically define 2 arrays that span the signatures of Fernandina and Sierra Negra/Cerro Azul (array 1) and Genovesa and Pinta, Wolf, and Darwin Islands (array 2). Due to the effects of degassing, the samples are found to have significantly lowered CO_2 concentrations, with minimal

lowering of H₂O and S, but no observable affect on F or Cl. The samples range from just saturated with a sulfide liquid to sulfide undersaturated. Assimilation of hydrothermally altered material, traced using Cl/K ratios and the magnitude of the Sr anomaly on a primitive mantle normalized diagram (Sr/Sr*), is found to have affected most of the glasses of the study, but only the isotopically depleted glasses have significantly contaminated signatures. Despite the affects of shallow level processes there is still a measurable variation in ratios of volatile and refractory elements with similar incompatibilities between the isotopically unique groups of glasses. The most distinctive differences are found in H₂O/Ce ratios and F/Nd ratios. The high ³He/⁴He Fernandina end-member in the Galapagos is found to have higher water contents than the MORB end-member of array 2. This results in a 5-7x lower viscosity of the Fernandina mantle in comparison to depleted upper mantle which has implications for mantle flow and plume-ridge interaction. The high ³He/⁴He Fernandina end-member also shows an order of magnitude larger C/³He ratio than what has been measured for the depleted upper mantle and among the highest yet reported for OIB samples. This suggests that the Galapagos mantle component hosting the high ³He/⁴He ratio is more carbonated than in other settings.

Chapter 3 reports on new Fe³⁺/ΣFe ratios (a proxy for *f*O₂) on a subset of glasses measured for major, trace, isotopic and volatile contents in Chapter 2. Utilizing the results from Chapter 2 and the new measurements of Chapter 3, we are able to identify the influence shallow level processes have on Fe³⁺/ΣFe ratios. Generally, Fe³⁺/ΣFe ratios increase with magmatic differentiation, decrease with sulfur degassing and increase with assimilation of hydrothermally altered material. After accounting for shallow level

processes, there is still a measurable variation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios between the different isotopic end member groups which translates into a magmatic $f\text{O}_2$ that ranges from $\Delta\text{QFM} = +0.16$ to $+0.74$, between the ranges identified for MORB and arc basalts. In general, the Sierra Negra/Cerro Azul component is more oxidized than the Pinta/Wolf, Darwin component. Both the Sierra Negra/Cerro Azul and Pinta mantle components are hypothesized to contain recycled material. The difference in oxidation state between these two sources and the correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and Pb isotopes suggest a difference in mantle lithology and therefore a difference in the type or influence of the recycled material on $f\text{O}_2$. The high $^3\text{He}/^4\text{He}$ end-member is found to be the most oxidized. The combination of the high $\text{C}/^3\text{He}$ ratios identified in Chapter 2 and the high $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios indicates that the high $^3\text{He}/^4\text{He}$ mantle source is both more carbonated and oxidized than previously thought for a primitive mantle component.

In Chapter 4 we present new oxygen isotope of olivine phenocrysts taken from lava collected across the Archipelago. The main isotopic end-members in the Galapagos, (Fernandina, Floreana, and Pinta) have $\delta^{18}\text{O}$ values within the narrow range found for the upper mantle and, in general, $\delta^{18}\text{O}$ values do not correlate with radiogenic isotopes. We take this as evidence that the Galapagos mantle has a homogenous $\delta^{18}\text{O}$ within range of the upper mantle, consistent with previous findings in the Galapagos (Geist *et al.*, 1995, Geist *et al.*, 1998). The positive correlation of Sr/Sr* and Ba/Nb ratios with $\delta^{18}\text{O}$ values suggest that the maximum oxygen isotope values are the result of plagioclase cumulates. The low $\delta^{18}\text{O}$ values of Sierra Negra, Alcedo, Darwin, Wolf and Ecuador volcanoes ($4.85 \pm 0.1\text{‰}$), do not exhibit geochemical characteristics indicative of assimilation making it difficult to unambiguously identify the occurrence of this process. However, a small

amount of assimilation of seawater ($\delta^{18}\text{O} = 0\text{‰}$) and/or hydrothermally altered gabbro without a cumulate component ($\delta^{18}\text{O} = +2.5/4.0\text{‰}$) can produce the low values for $\delta^{18}\text{O}$ without a large change to the trace element or radiogenic isotope composition of the melt.

These results show that interaction with the hydrothermally altered crust is a widespread phenomenon in the Galapagos Archipelago and should be considered when inferring mantle geochemistry of lavas erupted at the surface. However, the results of this thesis have also isolated mantle signatures that are distinct in the Galapagos from mid-ocean ridge basalts in terms of volatile elements and oxidation state. These results further the conclusion that ocean islands basalts come from a reservoir unique from the depleted upper mantle and have important implications for ability of the mantle to preserve long-lived heterogeneities. This is consistent with plume theory and implies that the mantle is neither a well-mixed homogenous source nor a well-buffered system.

FUTURE DIRECTIONS

The scientific findings of these chapters pose several immediate questions for future research in the Galapagos as well as having implications for broader areas of research. The following discussion is a summary of those ideas.

The results of chapter 1 highlight the importance of presenting isotopic measurements when trying to identify ancient recycled material in the mantle. The ghost plagioclase signature is a well-documented phenomenon that, despite only occurring in a small percentage of samples, can be found in suites of samples from multiple OIBs (Gurenko & Chaussidon, 1995, Hofmann & Jochum, 1996, Yang *et al.*, 1998, Chauvel & Hemond, 2000, Sobolev *et al.*, 2000, Kent *et al.*, 2002, Huang *et al.*, 2005, Ren *et al.*,

2005, MacLennan, 2008, Sobolev *et al.*, 2011) and MORB (Kamenetsky *et al.*, 1998, Danyushevsky *et al.*, 2003, Danyushevsky *et al.*, 2004). Only a few of these studies present isotopic measurements in addition to major and trace elements, yet many claim there is recycled gabbro in the mantle source of the area being studied. Without isotopic measurements these conclusions are ambiguous, as shown in Chapter 1. Therefore it will be worthwhile to return to these areas where the ghost plagioclase signature has been recognized and measure these inclusions for Pb isotopes.

The results of Chapters 2 and 3 present interesting characterizations of volatile contents and oxidation state of the high $^3\text{He}/^4\text{He}$ end-member, the trace element enriched end-member characterized by the lavas of Pinta (low $^3\text{He}/^4\text{He}$ ratios, high Th/La, $\Delta 7/4$ and $\Delta 8/4$), and the trace element depleted end-member anchored by the lavas of Genovesa, which represent 3 of the 4 major isotopic end-members in the Galapagos. The fourth end-member identified in the submarine glasses has the composition of Sierra Negra/Cerro Azul, which, while enriched in comparison to MORB, has a signature that is isotopically intermediate to Floreana, Pinta, and Fernandina (White *et al.*, 1993, Blichert-Toft & White, 2001, Harpp & White, 2001, Geist *et al.*, 2006, Saal *et al.*, 2007, Geist *et al.*, 2008, Kurz *et al.*, 2009, Harpp *et al.*, 2014). This signature is therefore either the product of mixing of melts from several end-members or a unique but isotopically intermediate mantle source. The Floreana end-member, as a result, remains uncharacterized for volatiles or oxidation state.

Floreana is dynamically and geochemically unique in the Galapagos. The eruption style is the most explosive, lavas are much more alkaline and it has the most radiogenic Sr and Pb isotopes measured in the archipelago (McBirney *et al.*, 1969, Bow & Geist,

1992, White *et al.*, 1993, Harpp & White, 2001, Lyons *et al.*, 2007, Harpp, 2014). The explosive eruption style, in particular, has led to the hypothesis that the Floreana mantle component is volatile-rich in comparison to the other components of the Galapagos plume. If the composition of Sierra Negra/Cerro Azul is the result of mixing between melts from the Floreana, Pinta and Fernandina end-members, then the higher F/Nd ratio and lower H₂O/Ce ratio than either the Pinta or Fernandina end-members may be the result of the influence of Floreana on the geochemical signature of the lavas. This is inconsistent, however, with the hypothesis that the Floreana mantle source is enriched in volatiles. A means to test this would be to measure a combination of submarine glass with the isotopic composition of Floreana and sub-aerially collected olivine-hosted melt inclusions from the Floreana Island for volatile contents. The former of these 2 measurements is planned for the summer of 2015.

In addition to volatile measurements, measuring Fe³⁺/ΣFe ratios for samples with the isotopic composition of Floreana would also provide an interesting future direction for research. In the study of Cottrell and Kelley (2013), submarine glass from mid-ocean ridges that show enrichments in Pb isotopes were found to be more reduced in terms of Fe³⁺/ΣFe ratios than normal MORB samples (Fe³⁺/ΣFe = 0.12 in comparison to the average value of 0.16 found for MORB (Cottrell & Kelley, 2011, Le Voyer *et al.*, 2015)). The hypothesis put forth by the authors was that carbon subducted into the mantle prior to 2.3 Ga would be reduced due to the presence of an anoxic atmosphere during this time period (Kasting *et al.*, 1993), resulting in reduced carbon domains in the mantle. The samples with low Fe³⁺/ΣFe ratios, as a result, are purported to be sampling this ancient reduced domain. An obvious test of this hypothesis would be to measure isotopically

HIMU samples, like the Floreana component, for $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. The HIMU mantle source is hypothesized to contain material that was at the surface at 1.8-2.3 Ga (e.g. Hanyu *et al.*, 2011, Cabral *et al.*, 2013, Hanyu *et al.*, 2013). Because the Floreana component is atypical in comparison to other HIMU plumes (Blichert-Toft & White, 2001, Harpp & White, 2001, Harpp *et al.*, 2014), it would be essential to combine these measurements with measurements from a separate hotspot such as the Austral Island chain, to better characterize the $f\text{O}_2$ of the HIMU mantle source.

The results of Chapters 2 and 3 also make the Galapagos a unique location to measure highly siderophile elements (HSE: Os, Ir, Ru, Pt, Pd, Rh, Re, and Au). Residual sulfide in the source, crystallization of sulfide from the melt and degassing of sulfur exerts a strong control on the variation of HSE in a melt (Barnes *et al.*, 1985, Bockrath *et al.*, 2004, Mungall & Su, 2005, Ballhaus *et al.*, 2006, Fonseca *et al.*, 2007, Brenan, 2008, Dale *et al.*, 2009, van Acken *et al.*, 2010). The presence of sulfide in the source and melt, as well as the partitioning of HSE into sulfide, is dependent on sulfur content and $f\text{O}_2$ of the source (Mavrogenes & O'Neill, 1999, Holzheid & Grove, 2002, Liu *et al.*, 2007, Righter *et al.*, 2008). The subset of samples from the Galapagos that have been measured for both volatile concentrations and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are thus uniquely constrained for S content and $f\text{O}_2$ which are the controlling parameters for HSE fractionation. Variations can be correlated with isotopic values making the Galapagos an ideal location to explore the HSE budget of the mantle.

Measuring Re-Os and Pt-Os isotopes on samples characterized for volatile elements and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios is also an interesting direction for research in the Galapagos. For the Re-Os isotope system ($^{187}\text{Re} - ^{187}\text{Os} + \beta^-$; $t_{1/2} = 4.16 \times 10^{10}$) and the Pt-Os isotope

system ($^{190}\text{Pt} - ^{186}\text{Os} + \alpha$; $t_{1/2} = 4.5 \times 10^{11}$), Re, Pt and Os are all HSE, but Re and Pt are both moderately compatible elements, while Os is a highly incompatible element (Hauri & Hart, 1997, Shirey & Walker, 1998, Fonseca *et al.*, 2007, Mallmann & O'Neill, 2007). To generate coupled, high time-integrated Re/Os and Pt/Os ratios and therefore high $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ ratios in basaltic glass and whole rock we measure at the surface requires specific conditions for fractionation. Combining variations in Os isotopes with trace elements, other radiogenic isotopes, volatile elements and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, as a result, allows us to examine the mantle for components such as recycled, crustal materials, contributions from the core, or a cumulate pile at the core-mantle boundary that has trapped liquid metal from the outer core (Ireland *et al.*, 2011). For example, Floreana, could be expected to show high $^{187}\text{Os}/^{188}\text{Os}$ ratios (up to 0.17) predicted for ancient recycled oceanic crust and lithosphere and in the range of other HIMU OIBs (Day, 2013). However, if the atypical Sr and Hf isotopes are due to the presence of recycled sediment (which would contain low $^{187}\text{Os}/^{188}\text{Os}$ isotopes in relation to the isotopes expected of recycled lithosphere due to the moderate compatibility of Re) lower $^{187}\text{Os}/^{188}\text{Os}$ ratios (between 0.14-0.17) could be expected. Fernandina, in comparison, may show more radiogenic $^{186}\text{Os}/^{188}\text{Os}$ ratios in comparison to chondritic values (0.1198373 ± 49) and the other regional mantle end-members if the component housing the high $^3\text{He}/^4\text{He}$ component has trapped liquid from the outer core which would have the high concentration of Pt needed to produce high $^{186}\text{Os}/^{188}\text{Os}$ ratios (Ireland *et al.*, 2011). Therefore the combination of $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ ratios with measurement of relative and absolute abundances of HSE can elucidate characteristic differences between primitive mantle sources in terms of HSE and therefore inform on the evolution

of HSE elements in the mantle. Os isotopes are also highly sensitive tracers of interaction with the crust, which would continue to build on the results of this thesis.

The results of chapter 4 provide an interesting snapshot of oxygen isotope variation in the Galapagos, with compelling results that require further investigation. The origin of low $\delta^{18}\text{O}$ values, in particular, could be better examined with a more focused study. In addition to measuring the olivine grains for their major and minor element compositions, focusing in on a pair of volcanoes, such as Sierra Negra and Cerro Azul that have similar trace element and radiogenic isotope signatures but variable $\delta^{18}\text{O}$, and collecting both subaerial and submarine samples would provide a means to test hypotheses for the origin of the low $\delta^{18}\text{O}$ component. If the light ^{18}O component is a pyroxenite in the mantle source, this should produce olivine with enrichments in Ni and Si and depletions in Mn and Ca due to the formation of pyroxenite from eclogite melts reacting with peridotite (Sobolev *et al.*, 2005, Sobolev *et al.*, 2007, Vidito *et al.*, 2013). Sierra Negra, which has shown lower $\delta^{18}\text{O}$ values than Cerro Azul, would therefore be predicted to show a measurably higher Ni and Si content and lower Mn and Ca content than olivine from Cerro Azul. If the light component, however, is apart of the volcanic edifice or lithosphere then the Fo contents of olivine from Sierra Negra should not show unusual composition and be correlated with $\delta^{18}\text{O}$ values (Wang & Eiler, 2008, Genske *et al.*, 2013).

If submarine samples from Sierra Negra with melt inclusions can be identified, it would also be interesting to combine oxygen isotope measurements with XANES measurements of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. The Sierra Negra/Cerro Azul component examined in Chapter 3, showed the largest variation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of any of the groups with few

compelling correlations between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and indicators of shallow level processes. However, the results of Chapter 4 suggest that melt from Sierra Negra has interacted with hydrothermally altered lithosphere. As a result, combining $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of melt inclusions with the $\delta^{18}\text{O}$ values of their host olivine, may provide evidence for shallow level contamination causing changes in the oxidation state of a melt. This type of study would add to the continuing discussion of the ability of lavas to preserve magmatic and source $f\text{O}_2$ (Ballhaus, 1993, Canil, 2002, Lee *et al.*, 2005, Cottrell *et al.*, 2009, Kelley & Cottrell, 2009, Lee *et al.*, 2010, Cottrell & Kelley, 2011, Kelley & Cottrell, 2012, Cottrell & Kelley, 2013).

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