

**Volatile Content of the Earth's Upper Mantle and
Roles of Hydrous Phases in Igneous Processes**

by

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3. **K. Shimizu**, A.E. Saal, C.E. Myers, A.N. Nagle, E.H. Hauri, D.W. Forsyth, V.S. Kamenetsky, and Y.L. Niu. Generation of mid-ocean-ridge basalts and the volatile content of the Earth's upper mantle. American Geophysical Union Fall Meeting 2014 (poster)
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Introduction

Various geological processes in the Earth can be studied using geochemistry. Melts derived from the mantle can be used to estimate the source composition to understand its physical properties such as its viscosity and seismic properties. Chemical tracers such as major, trace, volatile elements, and radiogenic isotopes can be used to understand the geological process that formed the mantle source of the melts as well as the shallow level processes that the melts have undergone. In addition, thermobarometry can be used to constrain the physical condition that a rock experienced. This dissertation research uses various methods to attempt to provide a better understanding of a wide range of geological processes in the Earth.

Chapter 1 (Shimizu et al., 2016) examines the generation process of mid-ocean ridge basalts (MORB) in the mantle and shallow level processes they undergo in the crust to make better estimates of the volatile contents in the Pacific upper mantle. Volatile contents in the Earth's upper mantle are key constraints on the origin of volatiles in the Earth and its evolution through time (Halliday, 2013; Hirschmann and Dasgupta, 2009; Javoy et al., 1986; Marty, 2012; Ozima, 1975; Tolstikhin and Marty, 1998). In addition, water content of the upper mantle is an important constraint for its solidus (Asimow and Langmuir, 2003; Dasgupta and Hirschmann, 2006; Dasgupta et al., 2013; Filiberto et al., 2014; Filiberto et al., 2012; Gaetani and Grove, 1998; Hirschmann et al., 2009; Tenner et al., 2012), viscosity (Hirth and Kohlstedt, 1996; Jung and Karato, 2001), and seismic properties (Jacobsen et al., 2008; Karato, 2012). The volatile contents in mid-ocean ridge basalts can be used to estimate those in the upper mantle. It is well known, however, that volatile contents in MORB may not necessarily reflect those in their source due to

processes such as degassing, shallow level contamination by seawater-derived material, sulfide saturation, and fractional crystallization (Kent et al., 1999; le Roux et al., 2006; Le Voyer et al., 2015; Michael and Cornell, 1998; Saal et al., 2002). In addition, melt homogenization in the mantle and crust may lead to underestimation of the range of volatile contents in the Earth's heterogeneous upper mantle. Hence, making accurate estimate of the Earth's upper mantle volatile contents requires careful assessment of the processes that MORB has gone through in the mantle and crust. In this chapter, we report volatile contents of MORB from Northern East Pacific Rise off-axis seamounts, Quebrada-Discovery-GoFar (QDG) transform fault system, and Macquarie Island in the East Pacific Rise (EPR) that are less homogenized compared to those from the ridge axis. After considering the effect of shallow level processes, the data suggests that Pacific MORB are mixtures of melts derived from a two-component upper mantle that are both peridotitic in lithology with the majority ultra-depleted in volatile and refractory incompatible elements (D-DMM) while the rest is enriched (E-DMM). The estimated composition of the E-DMM is shown to be consistent with its origin as a recycled oceanic lithosphere metasomatized by low degree melts.

Chapter 2 (Shimizu and Saal, in preparation) investigates the poorly understood effects of re-melting of a metasomatized oceanic lithosphere on the chemical composition of MORB using the data from chapter 1. Recent studies suggest that alkali rich lavas sampled at the Earth's surface previously interpreted to derive from the asthenospheric mantle (Hirose, 1997; Hirschmann et al., 2003; Takahashi and Kushiro, 1983) may actually derive from the lithosphere by melting of hydrous phases such as amphibole produced by metasomatism (Pilet et al., 2008). Despite the relatively small petrologic

evidence compared to continental environments, amphibole-bearing peridotites from the St. Paul's Rocks in the Mid-Atlantic Ridge shows that modal metasomatism of the oceanic lithosphere unrelated to ocean island volcanism does occur (Brunelli and Seyler, 2010; Kurz et al., 2009; Roden et al., 1984; Staudacher et al., 1989). Thus, MORB traditionally viewed as melts derived solely from the asthenosphere may not necessarily be the case, and contamination by re-melted lithosphere may affect its chemical composition. In this chapter, we show that EMORB from QDG transform fault characterized by its unique chemical composition might not originate from the asthenosphere, but instead originate from melting of a metasomatized oceanic lithosphere using geological evidences and geochemical modeling.

In chapter 3 (Shimizu et al., in review), we developed parameterized lattice strain models for REE partitioning between amphibole and silicate melt. Amphibole may be an important phase for the generation of alkali rich lavas (Pilet et al., 2008), and also for arc magma fractional crystallization based on the REE pattern of arc lavas (Davidson et al., 2007; Davidson et al., 2013). Previous models for REE partitioning between amphibole and melt have parameterized the partition coefficient solely based on the melt composition (Sisson, 1994; Tiepolo et al., 2007; Tiepolo et al., 2000), which is useful for predicting the REE partition coefficients when the equilibrium melt composition is available. These are difficult to constrain, however, for natural amphiboles found in cumulates and xenoliths. Further, previous models parameterized the partition coefficient for individual element independently, which makes it difficult to understand the general behavior of REE partitioning in amphibole and to develop accurate models for elements with sparse partitioning data (such as Gd and Tm). Our newly developed melt

composition model has a better reproducibility and a smaller number of coefficients to describe the REE partitioning between amphibole and silicate melt. Our mineral composition model provides an understanding of the REE substitution mechanism in amphibole, and it has an advantage of being applicable to natural samples without the knowledge of the melt composition.

In chapter 4 (Shimizu et al., in preparation), we developed a REE-in-amphibole-plagioclase thermometer. The distribution of rare earth elements (REE) between two coexisting minerals depends on temperature, pressure and mineral compositions (Lee et al., 2007; Liang et al., 2013; Seitz et al., 1999; Stosch, 1982; Sun and Liang, 2014; Witt-Eickschen and O'Neill, 2005), and can be used to develop REE-based thermobarometers (Liang et al., 2013; Sun and Liang, 2015). Crystallization temperature of amphiboles in crustal cumulates have been estimated using major element thermometers (e.g. Holland and Blundy, 1994; Putirka, 2016). Although these thermometers provide important information, there are situations where the major elements in minerals may be reset by subsolidus re-equilibration (Blundy and Holland, 1990; Dessimoz et al., 2012; Holland and Blundy, 1994). Application of our REE-in-amphibole-plagioclase thermometer to oceanic and continental gabbros shows that REE-based thermometer records a higher temperature compared to major element thermometers, and we examine the physical meaning of the recorded temperature.

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CHAPTER 1

Two-component mantle melting-mixing model for the generation of mid-ocean ridge basalts: implications for the volatile content of the Pacific upper mantle

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Abstract

We report major, trace, and volatile element (CO_2 , H_2O , F, Cl, S) contents and Sr, Nd, and Pb isotopes of mid-ocean ridge basalt (MORB) glasses from the Northern East Pacific Rise (NEPR) off-axis seamounts, the Quebrada-Discovery-GoFar (QDG) transform fault system, and the Macquarie Island. The incompatible trace element (ITE) contents of the samples range from highly depleted (DMORB, $\text{Th/La} \leq 0.035$) to enriched (EMORB, $\text{Th/La} \geq 0.07$), and the isotopic composition spans the entire range observed in EPR MORB. Our data suggest that at the time of melt generation, the source that generated the EMORB was essentially peridotitic, and that the composition of NMORB might not represent melting of a single upper mantle source (DMM), but rather mixing of melts from a two-component mantle (depleted and enriched DMM or D-DMM and E-DMM, respectively). After filtering the volatile element data for secondary processes (degassing, sulfide saturation, assimilation of seawater-derived component, and fractional crystallization), we use the volatiles to ITE ratios of our samples and a two-component mantle melting-mixing model to estimate the volatile content of the D-DMM ($\text{CO}_2 = 22$ ppm, $\text{H}_2\text{O} = 59$ ppm, F = 8 ppm, Cl = 0.4 ppm, and S = 100 ppm) and the E-DMM ($\text{CO}_2 = 990$ ppm, $\text{H}_2\text{O} = 660$ ppm, F = 31 ppm, Cl = 22 ppm, and S = 165 ppm). Our two-component mantle melting-mixing model reproduces the kernel density estimates (KDE) of Th/La and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for our samples and for EPR axial MORB compiled from the literature. This model suggests that: (1) 78% of the Pacific upper mantle is highly depleted (D-DMM) while 22% is enriched (E-DMM) in volatile and refractory ITE, (2) the melts produced during variable degrees of melting of the E-DMM controls most of the MORB geochemical variation, and (3) a fraction (~65 to

80%) of the low degree EMORB melts (produced by $\sim 1.3\%$ melting) may escape melt aggregation by freezing at the base of the oceanic lithosphere, significantly enriching it in volatile and trace element contents. Our results are consistent with previously proposed geodynamical processes acting at mid-ocean ridges and with the generation of the E-DMM. Our observations indicate that the D-DMM and E-DMM have (1) a relatively constant CO_2/Cl ratio of $\sim 57 \pm 8$, and (2) volatile and ITE element abundance patterns that can be related by a simple melting event, supporting the hypothesis that the E-DMM is a recycled oceanic lithosphere mantle metasomatized by low degree melts. Our calculation and model give rise to a Pacific upper mantle with volatile content of $\text{CO}_2 = 235$ ppm, $\text{H}_2\text{O} = 191$ ppm, $\text{F} = 13$ ppm, $\text{Cl} = 5$ ppm, and $\text{S} = 114$ ppm.

1. Introduction

The unique physical properties of the asthenosphere such as low seismic velocity (Nishimura and Forsyth, 1989), high electrical conductivity (Evans et al., 2005), and seismic anisotropy (Forsyth, 1975) have been attributed to either temperature (Priestley and McKenzie, 2006), grain size (Faul and Jackson, 2005), water content (Karato and Jung, 1998) or to the presence of a low melt fraction (Anderson and Spetzler, 1970). We rely on the composition of the asthenosphere to understand the parameters controlling the observed physical properties of this mechanically weak region of the upper mantle; and we resort to geochemical studies of Mid-Ocean Ridge Basalts (MORB) to unravel the composition of the asthenosphere.

In particular, the volatile element composition of the upper mantle provides an essential constraint for understanding mantle melting and melt compositions (Asimow

and Langmuir, 2003; Dasgupta and Hirschmann, 2006; Dasgupta et al., 2013; Filiberto et al., 2014; Filiberto et al., 2012; Gaetani and Grove, 1998; Hirschmann et al., 2009; Tenner et al., 2012), mantle viscosity (Hirth and Kohlstedt, 1996; Jung and Karato, 2001), mantle seismic velocity (Jacobsen et al., 2008; Karato, 2012), mantle heterogeneity (Cartigny et al., 2008; Hauri, 2002; Kingsley and Schilling, 1995; Saal et al., 2002; Simons et al., 2002), and crustal recycling (Dixon et al., 2002; Donnelly et al., 2004; Javoy et al., 1982).

The precise analysis of volatile elements (CO_2 , H_2O , F, Cl, S) in quenched MORB glasses can be used to estimate the volatile element composition of the upper mantle. However, due to the presence of long-lived magma chambers, axial MORB from fast spreading ridges like the East Pacific Rise (EPR), experience extensive fractional crystallization and homogenization of magmas through melt aggregation (Batiza and Niu, 1992; Langmuir et al., 1993; Niu et al., 1996; Sinton and Detrick, 1992). To make an accurate estimate of the volatile element composition of the upper mantle, it is important to determine to what extent the geochemical variations in axial MORB do represent a homogeneous mantle composition with variations in the physical conditions of magma generation and transport; or alternatively, whether they are inherited from mixing processes during the aggregation of melts originating from an heterogeneous upper mantle (Batiza et al., 1990; Hirschmann and Stolper, 1996; Niu et al., 1999; Niu et al., 2002; Shen and Forsyth, 1995). In contrast to axial MORB, lavas from intra-transform faults and seamounts share a common mantle source with axial MORB, but represent smaller melt volumes tapped locally from areas lacking steady-state magma chambers and along-axis transport (Batiza et al., 1990; Fornari et al., 1988; Langmuir and Bender,

1984; Niu et al., 2002; Perfit et al., 1996; Reynolds and Langmuir, 1997; Sims et al., 2002). Thus, these melts that experience relatively small amount of differentiation and homogenization provide better estimates of the volatile contents of the heterogeneous upper mantle.

Here we report major, trace, and volatile element and Sr, Nd, and Pb isotopic composition of primitive (high MgO) glassy basalt samples from the NEPR off-axis seamounts, the Quebrada-Discovery-GoFar (QDG) transform fault system, and the Macquarie Island. After filtering the volatile element data for secondary processes, we present a two-component (D-DMM and E-DMM) mantle melting-mixing model that successfully reproduces the trace and volatile element contents and isotopic composition of the EPR MORB and provides the volatile element budget of the Pacific upper mantle.

2. Samples and methods

The samples in this study are glassy basalts from the NEPR off-axis seamounts, the QDG transform fault system, and the Macquarie Island. Major elements, trace elements, and isotopic compositions of NEPR seamounts (Niu and Batiza, 1997; Niu et al., 2002) and Macquarie Island samples (Kamenetsky et al., 2000; Kamenetsky and Maas, 2002) have been previously analyzed and discussed, while those for the QDG transform fault samples are new data. Volatile elements for NEPR seamounts and QDG transform fault samples are new data, while those of Macquarie Island lavas (except for CO₂) have been previously analyzed and discussed (Kamenetsky et al., 2000). Except for the isotope data, all samples were reanalyzed for major, trace, and volatile elements on the same glass chips to avoid additional uncertainty of analyzing different elements in

different glass chips or bulk rock and inter-laboratory bias, therefore, previously published data have not been used in this study.

Forty-seven dredges of young, glassy basalt were collected by the R/V Knorr from the QDG study area. The QDG transform fault system on the EPR (3-5°S) is composed of three different transform faults that offset the fast-spreading EPR (134-140 mm/yr) by approximately 400 km, with at least 8 intra-transform spreading centers varying in length from <10 to 93 km (Fig. 1a).

Seventy-four glassy basalt samples from the NEPR seamounts in this study were collected by the R/V Thomas Washington between 5 and 15°N latitude from near-ridge seamounts on the 1988 Raitt 02 expedition (Batiza and Niu, 1992; Batiza et al., 1990) (Fig. 1b). Seamounts are located on both the Pacific and Cocos plates. All samples were collected within 180 km from the ridge axis and 78% of them were collected within 50 km.

The fifty-three glassy basalt samples from the Macquarie Island in this study were collected by B. J. Griffin, M. J. Rubenach, J. L. Everard and B. Goscombe (Fig. 1c). Macquarie Island (54°30'S, 158°56'E) is an exposure of the Macquarie Ridge located about 1200 km south of New Zealand. The island was formed in the last 10 Myrs by transpression due to difference in motion of the Australia and Pacific plates (Johnson and Molnar, 1972; Ruff et al., 1989). The island is considered an uplifted section of oceanic crust and mantle formed at an oceanic spreading center (e.g. Christodoulou et al., 1984; Goscombe and Everard, 1998; Varne et al., 2000; Varne et al., 1969).

We mounted three to six chips of fresh, clean, naturally quenched glass from each sample in indium metal and polished them using diamond paste down to 0.25 μm .

Multiple chips are used to determine the reproducibility of the measurements due to the analytical technique as well as the natural variation in the glasses. The major, trace, and volatile element measurements were made on the same glass chip. Although major and trace element data from previous studies (Kamenetsky and Maas, 2002; Niu et al., 2002) were not used to avoid potential sample heterogeneity and lab bias, the previous published and new data are very consistent with each other. The analytical error (2σ SE) of each samples were calculated from the measurements of three to six glass chips per sample.

Major elements were analyzed using the Cameca SX-100 electron microprobe at Brown University using a 2 μm spot size. Analyses were performed using a 15 keV accelerating voltage and 10nA beam current. Counting times for MgO , Al_2O_3 , MnO , P_2O_5 , and K_2O were 20s for peak and 10s for background. All other major elements, Na_2O , SiO_2 , FeO^* , TiO_2 , and CaO , used 10s peak and 5s background counting times. Standard used were Smithsonian basalts VG-A99B (USNM 113498) and VG-2B (USNM 111240) (Jarosewich et al., 1980). Average analytical error (2σ SE) of the major element analyses were <1% for SiO_2 , Al_2O_3 , and MgO , <2% for FeO and CaO , <3% for Na_2O and TiO_2 ; for K_2O and P_2O_5 the errors were significantly larger (1-20% and 2-30% respectively). Major element analyses of the NEPR seamount samples are on average within 6% of those from Niu and Batiza (1997) for all elements except MnO and K_2O (within 13% of published analyses). Analyses of the Macquarie Island seamount samples are on average within 8% of those from Kamenetsky et al. (2000) for all elements except MnO (within 18% of published analyses).

Trace elements were analyzed on the mounted glasses using the Quadrupole ICPMS X-Series II and 193 nm wavelength excimer Photon Machines Analyte G2 laser ablation system at Brown University. The standards used are BIR-1G, BHVO-2G, and BCR-2G, and the preferred values of elemental concentration from the GeoREM database (<http://georem.mpch-mainz.gwdg.de/>) were used. Analyses were conducted using a 160 μm spot size, the power output was 0.5mJ, and repetition rate of 20Hz. The background was measured for 30 s and then 20 s count time for pre-sputter and analysis. We used CaO as the internal standard. Average analytical error (2σ SE) of the samples was <6% for all elements. Trace element analyses of the NEPR seamount samples are on average within 20% of those from Niu and Batiza (1997). Analyses of the Macquarie Island seamount samples are on average within 10% of those from Kamenetsky et al. (2000) and Kamenetsky and Eggins (2012) for all elements, except for Li, V, Rb, Sr, Pb, and U (within 30% of published analyses). K concentrations of our samples measured using the electron microprobe and LA-ICP-MS are within 12% on average. For this study, the more precise K concentrations measured using LA-ICP-MS were used.

Volatile analyses for H_2O , CO_2 , F, Cl, and S were performed using the Cameca 6F ion probe at Carnegie Institution of Washington Department of Terrestrial Magnetism (for details on analytical techniques and standards see Hauri et al. (2002)). Each glass chip was analyzed using a 10-15nA Cs^+ primary beam with a 300 sec pre-sputter and 200 sec counting time. Detection limits for these analyses are < 0.5ppm for F, S, Cl and ~ 4-5ppm for H_2O , CO_2 . Average analytical precision (2σ SE) for volatile analyses was $\leq 5\%$ for all volatiles except Cl with 8%.

Sr and Nd isotopic measurements were made on a selected set of 27 QDG

transform fault samples. Pb isotopic measurements were made on a selected set of 4 QDG transform fault samples. Basaltic glasses were handpicked, leached with cold 6N HCl for 20 minutes, and then rinsed with Milli-Q water prior to dissolution. Nd, Sr, and Pb column chemistry were performed using Ln, Sr-spec, and AG1-X8 (100-200 mesh) resins respectively. Nd, Sr, and Pb isotopic compositions were measured on a Thermo Scientific NEPTUNE plus at Brown University. Sr and Nd were introduced to the mass spectrometer using a PFA 50µl nebulizer coupled with a glass spray chamber, while Pb was introduced with an APEX introduction system. The mass spectrometer was equipped with an H-skimmer cone and H-sampler cone. The baseline measurement was taken at -0.5 amu. $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ are corrected for instrumental mass fractionation using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ and $^{88}\text{Sr}/^{86}\text{Sr} = 0.1194$ respectively. Pb solution was spiked with NBS SRM-997 Tl solution with a Pb/Tl = 4 to correct for the mass fractionation using exponential law with a $^{203}\text{Tl}/^{205}\text{Tl} = 0.418922$. $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ of samples are reported relative to La Jolla Nd Standard $^{143}\text{Nd}/^{144}\text{Nd} = 0.511850$ and NBS SRM 987 $^{87}\text{Sr}/^{86}\text{Sr} = 0.71024$ respectively. $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ are reported relative to the NBS 981 Standard $^{206}\text{Pb}/^{204}\text{Pb} = 16.9356$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4891$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.7006$ (Todt et al., 1996). The internal precision of the Sr and Nd analyses is 5-10ppm and the external precision is 30ppm for Sr (2σ , $n = 75$) and 25ppm for Nd (2σ , $n = 104$). The internal precision of the Pb analysis is 20-45ppm and the external precision is 45-80ppm (2σ , $n = 75$). The Sr and Pb blanks were < 50 pg, and Nd blanks were < 30 pg. Sr, Nd, and Pb isotopic composition for a selection of NEPR seamounts and Macquarie Island basalts are from Niu et al. (2002) and Kamenetsky and Maas (2002) respectively.

3. Results

Major, trace, and volatile element concentrations of all samples are presented in Table S1, along with pressure of sample collection (P_{coll}), pressure of $\text{CO}_2\text{-H}_2\text{O}$ vapor saturation (P_{sat} calculated using the model of Dixon et al. (1995)) and Sr, Nd and Pb isotopic composition. The Macquarie Island samples were collected sub-aerially, however this does not correspond to their pressure of eruption since the eruption occurred under water prior to the tectonic uplift of the island (Duncan and Varne, 1988). Portner et al. (2010) estimated the paleo-ridge depth between 2000 to 3500 m.b.s.l. based on the benthic foraminifera from inter- and intra-pillow calcareous oozes (Quilty et al., 2008). Here we use an average of their estimated eruption pressure and assume a P_{coll} for Macquarie Island samples of 275 ± 75 bars.

The composition of the samples ranges from tholeiitic to alkalic basalts (Fig. 2a and Fig. S1). Most of the samples in this study have $\text{MgO} > 6.0$ wt% with a total range of 3.3 to 9.8wt%. The variation in major element composition of the samples with decreasing MgO generally follows a typical MORB differentiation trend (Fig. S2a~f, description of the model LLDs are given in section 4.4). Differences in major element content such as FeOt and Al_2O_3 for a given MgO are partly due to the large range in H_2O concentration (0.05-1.62 wt%) in our samples leading to variable delay of plagioclase saturation (e.g. Asimow and Langmuir, 2003; Sinton and Fryer, 1987). The samples with high H_2O content tend to have higher Al_2O_3 and lower FeOt than samples with low H_2O content for a given MgO due to greater delay of plagioclase crystallization. The differences in major element contents of our samples for a given MgO also reflect the

compositional variation of parental melt potentially due to variable pressure and temperatures of melt generation, mantle source composition, and mixing between melts.

We use the Th/La ratio of our samples as a proxy for the long-term geochemical enrichment/depletion of the mantle source instead of $(\text{La}/\text{Sm})_{\text{N}}$ and $\text{K}_2\text{O}/\text{TiO}_2$, which are more susceptible to fractionation at small degrees of melting. Based on the Th/La ratio, the samples are divided into three groups, EMORB ($\text{Th}/\text{La} \geq 0.07$), NMORB ($0.035 < \text{Th}/\text{La} < 0.07$), and DMORB ($\text{Th}/\text{La} \leq 0.035$) (Fig. 2a and 2b). Although not exact, the rough boundary between the three groups in terms of $(\text{La}/\text{Sm})_{\text{N}}$ and $\text{K}_2\text{O}/\text{TiO}_2$ ratios are as follows; EMORB ($(\text{La}/\text{Sm})_{\text{N}} \geq 1$ and $\text{K}_2\text{O}/\text{TiO}_2 \geq 0.15$), NMORB ($0.5 < (\text{La}/\text{Sm})_{\text{N}} < 1$ and $0.05 < \text{K}_2\text{O}/\text{TiO}_2 < 0.15$), and DMORB ($(\text{La}/\text{Sm})_{\text{N}} \leq 0.5$ and $\text{K}_2\text{O}/\text{TiO}_2 \leq 0.05$). For simplicity, from now on we will label the mantle source of NMORB, DMORB and EMORB as DMM, D-DMM, and E-DMM respectively.

The isotopic composition of the samples covers a large portion of the total range observed in EPR MORB (Fig. 3a and 3b). The EMORB samples tend to plot towards radiogenic Sr and Pb isotopic composition, and DMORB samples tend to plot towards unradiogenic Sr and Pb isotopic composition, suggesting that the Th/La of the samples can be used as a first order proxy for long-term ITE enrichment in the mantle source. However, Th/La is not always a good proxy for long-term mantle ITE enrichment since there are samples covering the whole range in Th/La with the isotopic composition of EMORB (Fig. 3c). This may suggest that these isotopically enriched DMORB and NMORB samples are derived from an E-DMM source that experienced recent depletion by fractional melting, where the incremental fractional melts did not completely aggregate before eruption.

4. The effect of secondary processes on volatiles

Previous studies have shown that volatile elements have bulk distribution coefficients similar to refractory ITEs during mantle melting: CO₂ has a bulk partition coefficient similar to Nb-Th-Ba, F to Nd-P, Cl to K-Nb, S to heavy REEs such as Dy, and H₂O to Ce-La (Danyushevsky et al., 2000; Dixon, 1997; Michael, 1988; Michael, 1995; Michael and Cornell, 1998; Rosenthal et al., 2015; Saal et al., 2002; Workman et al., 2006). A recent experimental study by Rosenthal et al. (2015) show that CO₂ behave more similar to Ba than Nb and F more similar to La than Nd. F/La is not used in this paper since the negative correlation between F/La and La/Sm might suggest a more incompatible behavior of La compared to F. The most commonly used ratios CO₂/Nb, H₂O/Ce, Cl/K, Cl/Nb, F/Nd, and S/Dy along with CO₂/Ba and Cl/Ba are used in this paper. These volatile to ITE ratios will change if the samples experience secondary processes that only affect the volatile elements, such as degassing, assimilation of hydrothermally altered materials, and sulfide saturation. Fractional crystallization may affect the volatile to ITE ratios in magmas depending on the extent of fractional crystallization and the difference in incompatibility of the elements in the crystallizing mineral. Once those processes are accounted for and the samples have been filtered for those processes, the volatile to trace element ratios can be used to determine the mantle source volatile abundances considering the small fractionation of these ratios during mantle melting.

4.1 Degassing: CO₂-H₂O saturation and P_{sat} vs. P_{coll}

At typical submarine pressures of eruption (> 50 bars), H_2O , Cl, F and S are relatively soluble in basaltic magma such that the effect of degassing is considered relatively small (Carroll and Webster, 1994; Danyushevsky et al., 2000; Edmonds et al., 2009; Lesne et al., 2011; Michael, 1995; Michael and Cornell, 1998; Schilling et al., 1980; Wallace and Carmichael, 1992). In contrast, the low solubility of CO_2 in basaltic magma results in significant CO_2 degassing during magma ascent and flow on the ocean floor (Dixon and Stolper, 1995; Soule et al., 2012). As a result, almost all MORB lavas are saturated or supersaturated with a CO_2 - H_2O rich vapor phase upon eruption.

The measured CO_2 and H_2O contents of the samples were used to calculate CO_2 - H_2O saturation pressures (P_{sat}) using the model of Dixon et al. (1995) (Fig. 4a). The comparison between P_{sat} and pressure of sample collection (P_{coll}) can be used to assess saturation/super-saturation/under-saturation of the samples in a CO_2 - H_2O vapor phase as well as the velocity of magma ascent relative to the magma-vapor equilibration rate. Samples with P_{sat} higher than P_{coll} are super-saturated in a CO_2 - H_2O vapor phase (Fig. 4b), which indicates that the magma ascent rate was too fast to allow magma-vapor equilibration (Dixon and Stolper, 1995; Dixon et al., 1995). Samples with P_{sat} equal to P_{coll} are saturated in a CO_2 - H_2O vapor phase, which indicates that the magma ascent rate was slow, allowing the magma-vapor equilibration. Samples with P_{sat} lower than P_{coll} indicates that the lavas are undersaturated in the CO_2 - H_2O vapor phase, assuming that the lavas did not erupt at a shallower depth reaching saturation and subsequently flowed down-slope. 95% of the samples are either saturated or super saturated with a CO_2 - H_2O vapor phase at the P_{coll} , therefore most likely they experienced CO_2 - H_2O degassing. Eight DMORB samples, most of which are from the QDG transform fault system, appear to be

undersaturated in CO₂-H₂O vapor phase (Fig. 4b). The vapor undersaturation of these DMORB samples is due to their low volatile contents and their deep eruption depth (avg. $P_{\text{coll}} = 385 \pm 77$). Five of the eight samples have depth of saturation shallower than 2400 m.b.s.l. (P_{sat} lower than 240 bars), which is the shallowest bathymetric depth for the areas of sample collection. Therefore, these five samples could not have erupted at a shallower depth (<2400 m.b.s.l.) and subsequently flowed down-slope. Thus, these five samples are undersaturated in a CO₂-H₂O vapor phase and their CO₂ content have not been affected by degassing. In contrast, three of the eight samples have depth of saturation 3500-3700 m.b.s.l. (P_{sat} of 350-370 bars), which is a common bathymetric depth that is found in the vicinity (< 10 km) of the area of samples collection. Although we cannot confidently rule out that these three samples could have erupted at shallower depth and flowed down-slope, we consider that the most likely explanation is that they are undersaturated in a CO₂-H₂O vapor phase given their high CO₂/Nb ratios (244 ± 26) similar to those measured in the other five CO₂-H₂O undersaturated samples and in the Siqueiros melt inclusions (Saal et al., 2002). In contrast, one NMORB from the NEPR seamount and one QDG EMORB samples with a P_{sat} below the P_{coll} (Fig. 4b) have very low CO₂/Nb (<20) suggesting significant CO₂ degassing. Therefore, we assumed they were erupted at shallow depth and transported down-slope.

Although solubility of H₂O is higher than CO₂ in basaltic magmas, degassing may affect the H₂O content of the samples with high mole fraction of H₂O in the vapor phase ($X_{\text{H}_2\text{O}}$) such as the Macquarie Island samples. We used the CO₂-H₂O degassing program (Solex) from Witham et al. (2012) to assess the effect of degassing on the H₂O content of the samples. To estimate the effect of degassing on the H₂O content of the lavas, we

assume the initial volatile content to be similar to those of the Macquarie Island samples 47963 with 1.41 wt% H₂O and an 7.32 wt% CO₂ (using a CO₂/Ba of 134 and the Ba content 546 ppm of the sample 47963, refer to section 5.3 for an explanation on the CO₂/Ba ratio) at a temperature of 1300 °C. According to the model, the melt after ~99.8% degassing of its CO₂ (128 ppm CO₂) still retains ~97.6% of its H₂O (1.38 wt%) assuming open system degassing. In contrast, close system degassing can lead to 72.9% loss of H₂O (final water content of 0.38 wt%), but the volume fraction of exsolved gas in such magma (79%) exceeds the critical fraction for magma fragmentation of 75% (Sparks, 1978; Wilson et al., 1980). We do not believe that the samples represent close system degassing because 1) although some of the Macquarie Island samples are hyaloclastites and others are glass pillow rims (Kamenetsky et al., 2000), we observe a strong correlation between H₂O and Ce (similar H₂O/Ce average and 2 sigma) in all the sample regardless of the eruption mechanism. 2) There is no correlation between the H₂O content and hydrogen isotopic composition of the samples (Bindeman et al., 2012). 3) Kamenetsky et al. (2002) analyzed the gas bubbles within the glasses using laser Raman spectroscopy and found that they had a CO₂ dominant composition. 4) Although some hyaloclastites in Macquarie Island formed by fragmentation due to explosive eruption, they formed mainly due to thermal shock granulation (Dickinson et al., 2009; Portner et al., 2010). Therefore, we conclude that degassing occurred under open system, and it had minimal effect on the H₂O content of our samples.

4.2 Chlorine and Water: Contamination process

Here we use Cl/K ratio to track shallow level processes such as assimilation of

hydrothermal circulation of seawater and seawater brines (Kent et al., 1999; Kent et al., 2002; Lassiter et al., 2002; le Roux et al., 2006; Michael and Cornell, 1998; Simons et al., 2002; Stroncik and Haase, 2004). Michael and Cornell (1998) define uncontaminated Cl/K ratios of 0.01-0.02 for NMORB and 0.08 for EMORB. When Cl/K ratios are compared to Th/La, the majority of the samples follow two distinct trends (Fig. 5a): One with a large range of Cl/K at roughly constant Th/La ratios in DMORB and NMORB samples indicative of assimilation of seawater or seawater brines (Kent et al., 1999; le Roux et al., 2006; Michael and Cornell, 1998). This trend is mostly defined by the DMORB and NMORB samples because they are the most susceptible samples to Cl contamination due to their low Cl concentration. The second trend is defined by the correlation between Cl/K and the extent of ITE enrichment. This trend includes as an extreme, the EMORB samples from Macquarie Island that consistently plots at a Cl/K of ~0.09 slightly above the mantle limit of 0.08 proposed by Michael and Cornell (1998) for the EMORB (Fig. 5b). This relatively constant Cl/K of ~0.09 is consistent with the measurement of the same sample set by Kendrick et al. (2012) and Kamenetsky and Eggins (2012). In contrast, EMORB samples with $Cl/K > 0.1$ are potentially contaminated since they have a considerably higher Cl/K compared to the rest of the EMORB samples. Therefore EMORB samples including the Macquarie Island samples with $Cl/K < 0.1$ are most likely not contaminated by assimilation of seawater or seawater brines, while the EMORB samples with $Cl/K > 0.1$ are potentially contaminated.

In addition to Cl, circulating hydrothermal fluids may also affect H₂O contents in the basalts, and figure 6 shows calculated effects of various contaminants on the Cl/K and H₂O/Ce ratios of a DMORB sample (D42A from QDG TF). The samples that have high

Cl/K (>0.1) can be explained by addition of up to 0.1~0.2% of a 15 to 50 wt% NaCl brine. Contamination by high salinity brine is a reasonable explanation for the high Cl/K, which increases this ratio much more than H_2O/Ce during contamination. It is possible to create very saline brines along the EPR where the hydrothermal circulation can occur at depths coincident with the top of the axial magma chamber along the ridge axis at ~ 4000 m.b.s.l (le Roux et al., 2006). This corresponds to a depth of 1200 meters into the oceanic crust, or a pressure of 620 bars (assuming 2800 m ocean depth, water density of 1000 kg/m^3 , and crust density of 2890 kg/m^3 (Carlson and Raskin, 1984)), which matches well with the highest P_{sat} recorded in our samples except for one NMORB sample that erupted at a deeper depth (Fig. 4b). At these pressures and temperatures, super-critical two-phase separation of seawater may occur, producing a vapor phase and dense, highly saline brine up to 50 wt% NaCl (Kelley and Delaney, 1987; Vanko, 1988). In terms of seawater assimilation, the DMORB and NMORB samples with high H_2O/Ce ratios often have high Cl/K (Fig. 6 inset), suggesting that high H_2O/Ce ratios of DMORB and NMORB samples may be due to assimilation of seawater. In contrast, the EMORB samples with the highest H_2O/Ce ratios have a relatively low Cl/K (Fig. 6 inset), which is inconsistent with the idea that assimilation of seawater is causing the high H_2O/Ce ratios in these samples.

The H_2O/Ce ratio of our unfiltered samples range from average Pacific MORB value of 150 (Dixon et al., 2002) up to ~ 400 (Fig. 7a). We filter DMORB and NMORB samples with Cl/K ratio higher than 0.04 and 0.06 respectively, since it is later shown in section 5.5.2 that samples with Cl/K as high as these values can be produced by magma mixing processes rather than assimilation of hydrothermal material. As discussed earlier in this section, EMORB samples with Cl/K ratio higher than 0.1 are also filtered for

contamination. After filtering the samples for contamination using the Cl/K ratios, it is apparent that a large fraction of the measured range in H_2O/Ce of DMORB and NMORB samples is due to contamination by hydrothermal circulation of seawater and seawater brine, but the range in H_2O/Ce of the EMORB samples persists (Fig. 7b).

4.3 Sulfur and Sulfide Saturation

The sulfur content at sulfide saturation (SCSS) of a melt depends on melt and sulfide compositions, fO_2 , fS_2 , temperature, and pressure (Carroll and Webster, 1994; Fortin et al., 2015; Liu et al., 2007; Mavrogenes and O'Neill, 1999; O'Neill and Mavrogenes, 2002; Wallace and Carmichael, 1992; Wykes et al., 2015). We calculated the SCSS of the samples using the sulfide saturation model of Fortin et al. (2015) and compared the results with the measured sulfur content (Fig. 8). We used the pressure of CO_2 - H_2O saturation (section 4.1), and the melt temperature was estimated based on the mole fractions of MgO and Al_2O_3 in the melt (Wallace and Carmichael, 1992) corrected for the effect of H_2O on the liquidus temperature (Medard and Grove, 2008). More than half of the samples (57%) are sulfide undersaturated according to the sulfide saturation model of Fortin et al. (2015). We have also calculated the SCSS using the model of Mavrogenes and O'Neill (1999) in conjunction with the model of O'Neill and Mavrogenes (2002), in which case all of our samples are sulfide undersaturated. These results do not change even if we calculate the SCSS of our samples using the pressure at the bottom of the oceanic crust of 1800 bars (assuming a 6.4 km thick oceanic crust and a crustal density of 2890 kg m^{-3} (Carlson and Raskin, 1984)). Although these results may seem at odds with the observation of sulfide blebs in MORB, these sulfides may not be in

equilibrium with the melt: they may be products of quench effects, magma mixing, crustal assimilation, etc. If this was the case, despite the observation of sulfide blebs in MORB, a majority of our samples may indeed be sulfide undersaturated.

Alternatively the model of Fortin et al. (2015) might be overestimating the SCSS of our samples. The strong partitioning of Cu and Ni found in sulfides in MORB (Patten et al., 2013) may reduce the $a\text{FeS}_{(\text{sulfide})}$ and stabilize sulfides in melts at lower SCSS compared to pure $\text{FeS}_{(\text{sulfide})}$ (Ariskin et al., 2013; Wykes et al., 2015). Therefore, SCSS models based on parameterization that do not consider Cu and Ni contents in sulfide may overestimate the SCSS of MORB samples. The $a\text{FeS}_{(\text{sulfide})}$ in sulfides found in MORB samples (Patten et al., 2013) calculated assuming the activity coefficient of $\text{FeS}_{(\text{sulfide})}$ is approximately 1.0 following Kiseeva and Wood (2015), ranges from 0.7 to 0.8. Although an $a\text{FeS}_{(\text{sulfide})}$ of 0.7 to 0.8 decreases the SCSS for our samples calculated using the model of Mavrogenes and O'Neill (1999) in conjunction with O'Neill and Mavrogenes (2002), they are still high compared to the measured sulfur content, suggesting that all our samples are sulfide undersaturated.

Despite this possibility that all our samples are sulfide undersaturated, we used the model of Fortin et al. (2015) to make conservative estimates of the SCSS of our samples given the observation of sulfide blebs in most MORB. After filtering our samples for sulfide saturation, the average S/Dy of the sulfide undersaturated DMORB, NMORB, and EMORB samples are 259 ± 64 (2σ), 247 ± 47 , and 189 ± 58 respectively (Fig. 9). Although there is significant overlap between groups, the more ITE enriched samples tend to have lower S/Dy ratio. In particular the average S/Dy of the most ITE enriched samples (Macquarie Island samples) is 179 ± 37 (2σ). This trend of decreasing

S/Dy with ITE enrichment is opposite of that expected from the higher modal abundance of garnet in the mantle during deeper melting of the E-DMM.

4.4 Fractional crystallization

Fractional crystallization is one of the processes that could potentially fractionate the volatile to trace elements ratios in a melt. To estimate the magnitude of this fractionation, the MELTS program (Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995) was used to model an isobaric fractional crystallization of model primitive DMORB and EMORB. For detailed explanation of the model LLDs, refer figure S2 caption. The major element composition of the model DMORB and EMORB LLDs generally follow the trends defined by our DMORB and EMORB samples showing the validity of this model in predicting the effect of fractional crystallization on the volatile to trace element ratios of our samples (Fig. S2a~f). However, the H₂O-rich Macquarie Island EMORB samples have higher Al₂O₃ and lower FeO_t for a given MgO compared to the model EMORB LLD suggesting a smaller amount of plagioclase crystallization in these samples due to their high H₂O contents of 1~1.5 wt%. We show that an alternative EMORB LLD using the same initial major element composition, but with high H₂O content (1.5wt%), reproduces the Macquarie samples (Fig. S2a~f).

The mineral-melt (except plagioclase-melt) partition coefficients for the volatile elements are from Hauri et al. (2006) (H₂O, F, and S) and Rosenthal et al. (2015) (CO₂) and those for the trace elements are from Kelemen et al. (2003). The incompatibility of Cl has been estimated to be similar to Ba and Rb (Schilling et al., 1980), thus the Ba partition coefficient from Kelemen et al. (2003) was used to simulate the behavior of Cl

during fractional crystallization. Furthermore CO₂ and Cl abundances correlate positively in the vapor undersaturated Siqueiros melt inclusion, which suggests a similarly incompatible behavior of CO₂ and Cl (Saal et al., 2002). Recent experimental results of Rosenthal et al. (2015) has shown that the bulk partition coefficient of CO₂ is slightly higher than Ba and more incompatible than Nb. For the CO₂ partition coefficient, experimental results of Rosenthal et al. (2015) are used. The plagioclase-melt partition coefficients for H₂O is from Johnson (2006) and those for the trace elements are from Blundy and Wood (1994). The experimental results of Bindeman et al. (1998) suggests the relatively compatible behavior of F and Cl in plagioclase, but even using their minimum partition coefficient would cause decreasing F/Nd and Cl/K ratios with decreasing MgO during plagioclase fractionation, which is not observed in our samples. Therefore, F and Cl, and S are assumed to be perfectly incompatible in plagioclase due to lack of reliable experimental data on their partitioning between plagioclase and basaltic melt.

The change in volatile to trace element ratios relative to the initial ratios (average ratios of all the DMORB samples and all the EMORB samples) after fractional crystallization to a MgO content in the melt of 5 wt% are ~11% for H₂O/Ce, ~18% for DMORB and 11% for EMORB for CO₂/Ba and Cl/Ba, 10% for F/Nd and 15% for S/Dy (Fig. S2g~m). The variation in CO₂/Ba and Cl/Ba ratios during fractional crystallization is noticeable due to the effect plagioclase and its dependence on the water content of the melt, but note that equivalent ratios such as CO₂/Nb, Cl/K, and Cl/Nb remain essentially constant. Thus, the use of CO₂/Ba and Cl/Ba may require a careful evaluation of fractional crystallization. Although non-trivial, the fractionation of H₂O/Ce, CO₂/Ba,

Cl/Ba, F/Nd, and S/Dy due to fractional crystallization is within the range of the analytical error for the measured ratios and the amount of fractionation listed above should be considered as the maximum fractionation of the ratios, since 93% of our samples have MgO content between 6 to 10 wt%. Therefore, the magnitudes of the fractionation of volatile to ITE ratios are not large enough to alter our interpretation of the data.

5. Discussion

5.1 The enriched component in the Pacific upper mantle (peridotite versus pyroxenite)

It is important to present some evidence that might help establish the lithology of the E-DMM. The origin of the enriched components in the source of MORB has been a topic of debate (e.g. Hirschmann and Stolper, 1996; Niu et al., 2002; Sobolev et al., 2007). Three samples from QDG TF have a very similar enriched isotopic composition indicative of derivation from an E-DMM, while their trace element pattern ranges from EMORB to DMORB (Fig. 10a and 10b). The range in trace element enrichment of these samples at an essentially constant isotopic composition suggests that the E-DMM melted incrementally without the aggregation of the different melt fractions, as expected at an intra-transform spreading settings (Morgan and Forsyth, 1988; Reynolds and Langmuir, 1997), producing melts with relatively constant isotopic composition but progressively depleted in ITE. This observation is reinforced by the composition of lavas used in this study, showing a range in Th/La ratios at relatively constant Nd, Sr, Pb isotopic composition, where the variation in Th/La increases from essentially a single value at the depleted isotopic ratio to the largest Th/La variation at the enriched isotopic ratio,

indicative of variable depletion in ITE during melting of the E-DMM (Fig. 3c). All the observations together support the statement that the E-DMM is melting incrementally without the aggregation of the different melt fractions. Furthermore, when we compare the DMORB samples produced from melting a source with isotopic composition indicative of E-DMM and of a D-DMM, we notice that both DMORB have essentially identical ITE concentration and very similar major element composition (Fig. 10c and 10d). These observations would be difficult to explain if the E-DMM and D-DMM sources were different lithologies (pyroxenite and peridotite respectively). Furthermore the δD of the Macquarie Island EMORB is similar to those of the D- and N-MORB (Bindeman et al., 2012), which is difficult to reconcile with the expected lower δD of a recycled oceanic crust dehydrated at a subduction environment (Shaw et al., 2008). Finally, the primitive major element composition of EMORB estimated by correction for fractional crystallization considering the water content of the melt is consistent with melting of a garnet peridotite (Appendix B and Fig. S3). The simple explanation for these observations is that the E-DMM is a peridotitic source.

Our statement does not rule out that recycled pyroxenites could have contributed to the generation of an E-DMM, but at the time of melt generation the source that melted to generate the EMORB was essentially peridotitic. Therefore, in this paper the lithology of E-DMM is considered a fertile peridotite rather than a pyroxenite. It is later shown in section 5.3 and 5.6 that this is supported by the relatively constant CO_2/Cl ratio of $\sim 57 \pm 8$ in E-DMM and D-DMM and by the fact that their volatile and ITE element abundance patterns can be related by a simple melting event; observations that are difficult to

reconcile with a pyroxenite generated during recycling of the oceanic crust affected by subduction processes as the origin for the EMORB source.

5.2 The origin of NMORB: The presence of an NMORB mantle (DMM) or melting and mixing of two mantle components (D-DMM and E-DMM)

The NMORB samples in this study have intermediate volatile and trace element contents and isotopic compositions between the DMORB and EMORB samples. A fundamental question is whether NMORB and its volatile and trace element contents represent either the melting of a single mantle source (DMM) or the mixture of DMORB and EMORB. The answer to such question has significant implications for the evolution and composition of the Pacific upper mantle. Pickle et al. (2009) in their study of the QDG TF system show that there is a significant correlation between the bathymetry, the calculated crustal thickness using residual mantle Bouguer anomaly (RMBA) and the composition of the erupted basalts in each ridge segment of the TF system. The shallow ridges have relatively thicker crust (i.e., higher magma flux) and lavas with intermediate compositions (NMORB) that underwent larger extent of magma differentiation (long lived magma chamber) compared to deeper ridges.

In fact, we do not have any real evidence for an NMORB mantle. The estimated probability density function defined by the Nd isotopes of clinopyroxene from abyssal peridotites (Warren et al., 2009 and references therein) are similar to that defined by lavas from the QDG transform fault, NEPR seamounts, and other MORB from seamounts and intra-transform faults (Brandl et al., 2012; Hall et al., 2006; Wendt et al., 1999) (Fig. 11). The more homogeneous isotopic composition of the lavas may be due to melt

aggregation either in the mantle or in magma chambers. Furthermore, the small length-scale of the isotopic variation (< 2 cm) in abyssal peridotites suggests a shallow level melt infiltration origin for the isotopic composition observed in clinopyroxenes from the lithospheric mantle rather than representing the compositional variation of the actual convecting mantle (Warren and Shimizu, 2010; Warren et al., 2009). All these observations strongly suggest that the NMORB might represent mixing of melts from a two-component D-DMM and E-DMM mantle (Niu and Batiza, 1997; Niu et al., 1996) rather than an actual DMM mantle source. To test this hypothesis we present a two-component mantle melting-mixing model in section 5.4.

5.3 The volatile contents of the two Pacific upper mantle components (D-DMM and E-DMM)

In order to evaluate the two-component mantle melting-mixing model, it is important to first establish the range of the volatile budget for the two components given the significant effect that volatiles have on the melting process (Asimow and Langmuir, 2003; Dasgupta and Hirschmann, 2006; Dasgupta et al., 2013; Filiberto et al., 2014; Filiberto et al., 2012; Gaetani and Grove, 1998; Hirschmann et al., 2009; Tenner et al., 2012). Here we establish the range of volatile element contents of the D-DMM and E-DMM using the volatile to trace element ratios of our samples.

The average CO_2/Nb for the eight DMORB samples undersaturated in $\text{CO}_2\text{-H}_2\text{O}$ vapor phase (258 ± 40 , 2σ) (Fig. 12a and 12b) is consistent with the average CO_2/Nb ratio of 239 ± 46 reported for primitive un-degassed melt inclusions from the Siqueiros transform fault (Saal et al., 2002). This ratio can be used to determine the CO_2 content of

the D-DMM. Assuming Nb concentration of 0.0864 ppm (D-DMM from Workman and Hart (2005)), the CO₂ content of D-DMM is 22.3 ± 3.5 (2 σ) ppm (Table 1). We obtain a similar D-DMM CO₂ content of 23.8 ± 14 (2 σ) ppm (Table 1) using the CO₂/Ba of the samples (105 ± 61) (Fig. 12c and 12d) and assuming Ba concentration of 0.227 ppm (D-DMM from Workman and Hart (2005)).

In contrast to the DMORB samples, the measured CO₂/Nb and CO₂/Ba of the EMORB samples cannot be directly used to determine their mantle CO₂ contents since their CO₂ has been significantly affected by degassing. Cartigny et al. (2008) estimated a higher CO₂/Nb of 537 ± 112 for EMORB by correcting the CO₂ content for degassing using their carbon isotopic composition (Fig. 12a). The measured CO₂/Nb and CO₂/Ba for our EMORB samples clearly deviate from this ratio due to degassing of the CO₂-rich vapor phase. In order to estimate the primitive CO₂ content in our EMORB, we use a different approach from that of Cartigny et al. (2008); namely, we use the correlation between CO₂ and Cl [$\text{CO}_2 = 22(\pm 14) + \text{Cl} \times 57(\pm 8)$] (uncertainties are 1 σ) observed in the primitive un-degassed melt inclusions from the Siqueiros transform zone (Saal et al., 2002). We use the Cl content of the uncontaminated Macquarie Island samples to calculate the CO₂ content of the EMORB prior to degassing since they are the most ITE enriched EMORB samples, and therefore, the most likely melts representative of the E-DMM. Once corrected for degassing the estimated CO₂/Nb and CO₂/Ba of EMORB are 744 ± 165 (2 σ) and 134 ± 23 (2 σ) respectively. Our estimated EMORB CO₂/Nb (744 ± 165) is within error of the EMORB CO₂/Nb (537 ± 112) estimated by Cartigny et al. (2008) using a completely different approach (Fig. 12a). Furthermore, when we calculate the CO₂/Ba of the samples in Cartigny et al. (2008), we obtain a value of 97.8 ± 28 that

compares well with our proposed value of 134 ± 23 (Fig. 12c). Using our EMORB CO_2/Nb and CO_2/Ba , the estimated CO_2 contents of the E-DMM are 990 ± 220 (2σ) ppm and 1010 ± 173 (2σ) ppm respectively (Table 1), assuming Nb and Ba content of 1.33 ppm and 7.54 ppm in the E-DMM (Donnelly et al., 2004). The consistent estimate of CO_2/Nb and CO_2/Ba for the E-DMM using two different methods suggests that the CO_2 -Cl relationship can be used to estimate the pre-degassing CO_2 content of Cl uncontaminated MORB samples. In addition, the fact that we can use the same CO_2 -Cl relationship for the DMORB and EMORB samples suggests that the CO_2/Cl ratio of Pacific upper mantle is relatively constant at $\sim 57 \pm 8$. Furthermore, the similar CO_2/Ba ratio of E-DMM (134 ± 23) and D-DMM (105 ± 61) suggests that the CO_2/Ba ratio is also relatively constant in the Pacific upper mantle, as first observed by Michael and Graham (2013).

The higher C content of the EMORB relative to the NMORB has been ascribed to recycling of C (e.g. Marty and Zimmermann, 1999). The relatively constant CO_2/Cl and CO_2/Ba ratio in the D-DMM and E-DMM suggests the lack of significant fractionation between CO_2 , Ba, and Cl during the formation of E-DMM. The C enrichment of E-DMM is difficult to explain by subduction processes since this process recycles C back into the mantle much more efficiently than the fluid mobiles Cl (Wallace, 2005) and Ba. The recycling of the oceanic mantle lithosphere previously metasomatized by low degree melt as the source of the E-DMM (Niu et al., 2002) is more consistent with our observation since CO_2 , Ba, and Cl are highly incompatible elements and do not significantly fractionate from each other during melting.

We obtain consistent D-DMM and E-DMM Cl contents using the Cl/K of the Cl-

uncontaminated samples. The Cl/K ranges from 0.01 to 0.1 (Fig. 5b). The range in Cl/K of the Cl-uncontaminated DMORB samples is 0.01 to 0.04, and the average Cl/K is 0.023 ± 0.015 (2σ). Based on this average Cl/K and assuming K content in the mantle source of 43.2 ppm (Based on K/Nb ratio of 500 in our DMORB samples and a Nb concentration of 0.0864 from D-DMM composition of Workman and Hart (2005)) the estimated Cl concentration of the D-DMM is 1.0 ± 0.64 (2σ) ppm (Table 1). The range in Cl/K of the Cl uncontaminated EMORB samples is 0.02 to 0.096 (Fig. 5b), and the average Cl/K is 0.078 ± 0.037 (2σ). The Cl content of the E-DMM is 19.6 ± 9.01 (2σ) ppm assuming K content in the mantle source of 253 ppm (Table 1) (Based on K/Nb ratio of 190 in our EMORB samples and a Nb concentration of 1.33 for the E-DMM of Donnelly et al. (2004)). We obtain similar D-DMM and E-DMM Cl contents using the Cl/Nb and Cl/Ba ratios of our samples (Table 1).

The total range of H_2O/Ce of the Cl uncontaminated samples ranges from 140 to 384 (Fig. 7b). The range in H_2O/Ce of the Cl uncontaminated DMORB samples is 140 to 220, and the average H_2O/Ce is 190 ± 41 (2σ). Based on this average H_2O/Ce and assuming Ce content in the D-DMM of 0.421 ppm (Workman and Hart, 2005) the estimated H_2O concentration of the D-DMM is 80 ± 17 (2σ) ppm (Table 1). The range in H_2O/Ce of the Cl uncontaminated EMORB samples is 165 to 384. Despite this large range in H_2O/Ce ratios of our EMORB samples, those having on average high H_2O/Ce ratios (QDG EMORB) are considered more representative of the E-DMM source. This assumption is based on the hypothesis that the range in H_2O/Ce ratio of EMORB has been produced by the diffusive loss of H_2O (H^+) during E-DMM storage or EMORB percolation through the ambient D-DMM as explained in detail in section 5.5.5 below.

The average $\text{H}_2\text{O}/\text{Ce}$ of the Cl uncontaminated QDG EMORB (high $\text{H}_2\text{O}/\text{Ce}$ EMORB) is 313 ± 112 (2σ). Using this $\text{H}_2\text{O}/\text{Ce}$ ratio, the average H_2O content of the E-DMM is 517 ± 184 (2σ) ppm (Table 1) assuming Ce content in the mantle source of 1.65 ppm (Donnelly et al., 2004).

Previously, the F/Nd ratios of oceanic basalts have been found to be fairly constant (20.1 ± 5.8) with no correlation between this ratio and isotopic data (Workman et al., 2006). The F/Nd ratio of our samples, however, ranges from 14.3 to 45.4, significantly outside the previous global range (Fig. 13). The samples are not filtered for Cl contamination since seawater and high salinity brine contains insignificant amount of F (Holland, 1984), and most likely did not affect the F/Nd beyond analytical error. The range in F/Nd of the DMORB samples is 14.3 to 21.0, and the average F/Nd is 17.2 ± 2.9 (2σ). Based on this average F/Nd and assuming Nd content in the D-DMM of 0.483 ppm (Workman and Hart, 2005) the estimated F concentration of the D-DMM is 8.3 ± 1.4 (2σ) ppm (Table 1). The range in F/Nd of the EMORB samples is 19.5 to 45.0, and the average F/Nd is 30.7 ± 12.7 (2σ). The average F content of the E-DMM is 37.8 ± 15.7 (2σ) ppm (Table 1) assuming Nd content of 1.23 ppm (Donnelly et al., 2004).

The total range in S/Dy of the sulfide undersaturated samples is 136 to 311 (Fig. 9). The range in S/Dy of the sulfide undersaturated DMORB samples is 204 to 311, and the average S/Dy is 259 ± 64 (2σ). Based on this average S/Dy and assuming Dy content in the D-DMM of 0.471 ppm (Workman and Hart, 2005) the estimated S concentration of the D-DMM is 122 ± 30 (2σ) ppm (Table 1). The range in S/Dy of the sulfide undersaturated EMORB samples is 136 to 283, and their average S/Dy is 189 ± 58 (2σ). The average S content of the E-DMM is 126 ± 39 (2σ) ppm (Table 1) assuming Dy

content in the mantle source of 0.666 ppm (Donnelly et al., 2004). These mantle S content estimates are consistent with previous estimates (Bézos et al., 2005; Chaussidon et al., 1989; Lorand, 1990; Morgan, 1986; Saal et al., 2002).

5.4 Two-component mantle melting-mixing model: Modeling method

We conducted near-fractional melting models for D-DMM and E-DMM using the pHMELTS program (Asimow et al., 2004; Ghiorso et al., 2002; Smith and Asimow, 2005) and subsequently mixed the calculated DMORB and EMORB following the method of Rudge et al. (2013). We used the major element composition of DMM from Workman and Hart (2005) for both the D- and E-DMM, based on the hypothesis that D- and E-DMM are both peridotitic (section 5.1) and the assumption that the differences in their major element composition has a small effect on their melting behavior compared to the significant difference in their H₂O content (section 5.3, Table 1). The trace element composition of D-DMM and E-DMM were taken from Workman and Hart (2005) and from Donnelly et al. (2004), respectively. The volatile element compositions of the D-DMM (CO₂ = 22 ppm, H₂O = 59 ppm, F = 8 ppm, Cl = 0.4 ppm, and S = 100 ppm) and of the E-DMM (CO₂ = 990 ppm, H₂O = 660 ppm, F = 31 ppm, Cl = 22 ppm, and S = 165 ppm) were obtained by running the model iteratively until it matches the observed geochemical data for D-, N- and EMORB. As can be seen in Table 1 the volatile contents used in the model are mostly within the range estimated from the measured volatile-refractory ITE ratios (Table 1). All volatile elements except for H₂O were considered as passive tracer elements. However, the H₂O concentration in the melt is also calculated as a tracer independent from that thermodynamic calculation by pHMELTS using the

partition coefficient from Hauri et al. (2006), and this tracer H₂O concentration is used in the following sections. The partition coefficients for H₂O and F are from Hauri et al. (2006) and the trace element partition coefficients are from Kelemen et al. (2003). For reasons given in section 4.4, the Ba partition coefficient from Kelemen et al. (2003) was used to simulate the behavior of Cl. For the CO₂ partition coefficient, experimental results of Rosenthal et al. (2015) are used. The SCSS model of Fortin et al. (2015) was used in conjunction with pHMELTS to calculate the S concentration of each one of the incremental D-DMM and E-DMM melts obtained from the model. The sulfur content at sulfide saturation (SCSS) was calculated for each incremental melt using their major element composition, H₂O content, P, and T obtained using pHMELTS. The S content of the incremental melts is set to zero when the sulfide in the mantle is consumed. The Sr, Nd, and Pb isotopic composition of the D-DMM are assumed to be those of sample GN10-3 from Garret transform fault (Wendt et al., 1999), which is a sample with one of the most depleted Sr, Nd, and Pb isotopic compositions in the EPR. The Sr, Nd and Pb isotopes used for the E-DMM are the highest Sr, and Pb isotopes and the lowest Nd isotopes measured for EPR EMORB. We used the Sr and Nd isotopic composition of the sample 3010-1502 from NERP seamount 6 (Brandl et al., 2012) and Pb isotopic composition of the Macquarie Island sample GG256 (Kamenetsky and Maas, 2002). Although this E-DMM is a hypothetical source since its isotopic composition is not defined by single sample, this is done only to reproduce some of the extreme isotopically enriched samples, and the results of our model does not significantly change by using a similar isotopic composition of a single sample (e.g., R78-6) from the NEPR seamount (Niu et al., 2002). We used a mantle potential temperature of 1350 °C. Melt extraction

starts when the degree of melting reaches 0.5 wt%, and 0.5 wt% melt (relative to the instantaneous solid mass) is retained in the mantle at each melting step (near fractional melting). The final pressure of melting, at the top of melting triangle, was set to the bottom of a 6.4 km oceanic crust, 1800 bars, assuming crustal density of 2890 kg m^{-3} (Carlson and Raskin, 1984). This is a simplification for the model, and in reality final depth of melting varies among distinct ridge settings (Morgan and Forsyth, 1988; Shen and Forsyth, 1992). For the description of the mixing model, refer to appendix C and for more details refer to Rudge et al. (2013).

We consider four main parameters in the two-component mantle melting-mixing model (Table 2): (1) The fraction of the D-DMM in the Pacific upper mantle (p_{DDMM}); for simplicity and following the traditional view of a well-mixed upper mantle (van Keken et al., 2002) we assumed a uniform distribution of D-DMM and E-DMM everywhere in our model (beneath the fracture zone, the seamounts and the ridge axis); hence p_{DDMM} is kept constant for these three different ridge settings. (2) The mixing parameter (N), indicating the extent of aggregation of the melts produced from both mantle sources. (3) The degree of melting below which we allow for a fraction of the EMORB to escape the aggregation within the melting triangle (F_{ext}); this melt is assumed to avert the aggregation at the wings of the melting triangle by forming part of the freezing front at the base of the oceanic lithosphere (Gregg et al., 2009; Hebert and Montesi, 2010; Hebert and Montesi, 2011; Katz, 2008; Katz and Weatherley, 2012; Montesi and Behn, 2007; Sparks and Parmentier, 1991). (4) The fraction of EMORB with $F < F_{\text{ext}}$ that is allowed to escape aggregation (f_{escape}).

The Kernel smoothed probability density estimates (KDE) of Th/La ratio and

$^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratio of the model and natural samples are used to assess the match between the model and (1) our QDG TF samples (Fig 14a and 14d), (2) our NEPR seamounts samples (Fig 14b and 14e), and (3) the compilation of EPR axial MORB (Gale et al., 2013; Mallick et al., in revision) (Fig. 14c and 14f). We tested two different variations of the two-component melting-mixing model to obtain the model KDEs that best matches those of natural samples. The first model is where no melt escape from the melting triangle and all the incremental melts are aggregated. Although the model can reproduce the KDEs for the $^{143}\text{Nd}/^{144}\text{Nd}$ of our samples, the Th/La KDEs are far too enriched compared to those of our samples (Fig. S4). The second model is where a fraction of the EMORB (f_{escape}), representing a low degree melting ($F < F_{\text{ext}}$), escapes the melt aggregation by forming part of the freezing front at the base of the oceanic lithosphere. The resulting model $^{143}\text{Nd}/^{144}\text{Nd}$ and Th/La KDEs can reproduce those of our QDG TF samples, our NEPR seamounts samples, and the compilation of EPR axial MORB (Fig. 14). The parameters required to obtain the best-matching model KDEs for the three ridge settings (transform fault, seamount and ridge axis) are as follow: QDG transform fault ($p_{\text{DDMM}} = 0.78$, $N = 16$, $F_{\text{ext}} = 1.3\%$, $f_{\text{escape}} = 0.65$), NEPR seamounts ($p_{\text{DDMM}} = 0.78$, $N = 40$, $F_{\text{ext}} = 1.3\%$, $f_{\text{escape}} = 0.75$), and compilation of EPR axial MORB ($p_{\text{DDMM}} = 0.78$, $N = 99$, $F_{\text{ext}} = 1.3\%$, $f_{\text{escape}} = 0.80$). The main parameter controlling the compositional difference of lavas from these three ridge settings is the mixing parameter N . We have explored a range of values of p_{DDMM} , F_{ext} , and f_{escape} , keeping the mixing parameter N constant for each ridge settings. The result of running 100 models for each ridge settings shows that in successful runs reproducing the natural KDEs, the parameters p_{DDMM} and F_{ext} negatively correlates with each other, while f_{escape} does not correlate well

with either p_{DDMM} or F_{ext} . The range of parameters that produces model KDEs that matches those of natural samples are as follows: $p_{DDMM} = 0.74\text{--}0.82$, $F_{\text{ext}} = 0.7\text{--}2.9\%$, $f_{\text{escape}} = 0.64\text{--}0.93$. Within these ranges, the values of the parameters given above for the three ridge settings best matches the KDEs of the natural samples assuming uniform distribution of D-DMM and E-DMM in a well-mixed upper mantle (van Keken et al., 2002). We did not attempt to reproduce the KDE of Macquarie Island samples because they mostly represent melts from a single E-DMM component (see appendix D).

Under the assumption that the compositions and uniform distribution of D-DMM and E-DMM used in this model are similar to those in the Pacific upper mantle, the results have potentially important implications on the melt transport processes beneath MOR, the control that the E-DMM melts have on the composition of axial MORB, the trace and volatile element budgets of the metasomatized oceanic lithosphere (Niu et al., 2002), the degree of melting and mixing at different ridge settings (transform fault, seamounts, ridge axis), and the composition of the Pacific upper mantle.

For all three ridge settings a fraction of a low degree melting of the E-DMM must escape melt aggregation, which has potential implications for melt transport process as well as the volatile and trace element budget of the oceanic lithosphere. A possible mechanism by which this melt could escape aggregation may be by low degree melts of a E-DMM produced at the wings of the melting triangle vertically migrating and freezing at the thermal boundary layer consistent with geodynamic models of the mid-ocean ridge (Gregg et al., 2009; Havlin et al., 2013; Hebert and Montesi, 2010; Hebert and Montesi, 2011; Montesi and Behn, 2007; Sparks and Parmentier, 1991). Therefore, it is quite plausible that a fraction of the EMORB (and perhaps DMORB, although we cannot

observe this geochemically) escapes the melt aggregation by freezing at the base of the oceanic lithosphere instead of erupting off-axis. The consequence of such a process is that the base of the oceanic lithosphere becomes enriched in volatile and trace elements, which will eventually be recycled back into the mantle at subduction zones and might be responsible for the generation of the E-DMM (Donnelly et al., 2004; Niu et al., 2002). Following this hypothesis, and to be consistent within our model, the fraction of EMORB that escaped the melt aggregation (65% to 80% of the $F < F_{\text{ext}} = 1.3\%$) is mixed with the bottom 22% of the oceanic lithospheric mantle (residual bottom $\sim 13\text{km}$ of a 60km thick oceanic lithosphere calculated using pHMELTS). The 22% fraction of the oceanic lithospheric mantle that is metasomatized is required to reproduce the proportion of E-DMM in the Pacific upper mantle estimated from our two-component mantle melting-mixing model. The major element composition of this metasomatized lithosphere is similar to that of E-DMM used as starting composition in our model (Table S2); as we mentioned earlier in this section; this is due to the small amount of melt added to the residual peridotite to form the E-DMM. Furthermore, the primitive mantle normalized trace element pattern of such a modeled metasomatized lithosphere (Fig. 15) closely resembles those of the E-DMM composition from Donnelly et al. (2004). Although we acknowledge the circularity in this model, the idea of a small amount of low degree melts escaping the aggregation by metasomatizing the lower oceanic lithosphere seems to be consistent with our two-component mantle melting-mixing model, the proposed processes acting at mid-ocean ridges and with the models for the generation of the E-DMM (Gregg et al., 2009; Hebert and Montesi, 2010; Hebert and Montesi, 2011; Katz, 2008; Katz and Weatherley, 2012; Montesi and Behn, 2007; Niu et al., 2002; Sparks and

Parmentier, 1991).

Another potential implication from the model result is that melting of a DMM mantle may not be necessary to explain the composition of NMORB, since the mixture of DMORB and EMORB can reproduce the composition of an NMORB. In other words, our model can reproduce the KDEs of a compilation of axial NMORB erupting at the EPR reasonably well. This may suggest that the extensive melt aggregation of DMORB and EMORB underneath the ridge produces a large amount of NMORB, whereas the lack of efficient melt aggregation at intra-transform spreading settings (Morgan and Forsyth, 1988; Reynolds and Langmuir, 1997) and seamounts (Fornari et al., 1988; Niu et al., 2002; Perfit et al., 1996) results in less NMORB and more DMORB and EMORB. Our model not only reproduces the KDEs of the samples, but also the trace element contents and isotopic composition of EPR MORB (Fig. 16a, b, c, and d). Note the “fan-shape” distribution of the samples in plots of very incompatible trace element ratios versus isotopes are pinned at the isotopic composition of the D-DMM and spreads as it gets closer to those of E-DMM (Fig. 16 b, c and d). This suggests that the melts produced during variable degrees of melting of the E-DMM controls most of the MORB geochemical variation. Although we cannot rule out the presence of an NMORB mantle source, we do not find any compelling argument to support its existence and by simply applying the Occam’s Razor principle, this hypothesis loses credence.

Although our model reproduces the KDEs and compositional range of our samples fairly well (Fig. 14 and 16) by considering several key assumptions (a uniform distribution of D-DMM and E-DMM, the escape of a fraction of the low degree melting from the E-DMM and different extent of melt aggregation at different ridge settings),

there are several other parameters that could influence the results, but for simplicity have not been considered yet. Exploration of parameters such as difference in the final depth of melting among distinct ridge settings (Morgan and Forsyth, 1988; Shen and Forsyth, 1992) and ridge migration over the mantle (Carbotte et al., 2004) are outside the scope of this paper and will be part of future work.

In the following section we explore the implications of the two-component mantle melting-mixing model on the evaluation of volatile-refractory trace element ratios of basalts and the volatile budget of the Pacific upper mantle.

5.5 Modelling of the volatile to trace element ratios

5.5.1 Carbon: Melting-mixing model

The two-component mantle melting-mixing model and the CO₂ concentration of D-DMM (22 ppm) and E-DMM (990 ppm) (Table 1 and section 5.3) reproduces the CO₂, Nb, and Ba of our most depleted DMORB samples, those estimated for Macquarie Island samples, and the samples corrected for degassing by Cartigny et al. (2008) (Fig. 17a, 17b, 17c, and 17d).

Deep low degree melts are more ITE enriched and have higher CO₂/Nb ratios than shallow high degree melts due to the more incompatible behavior of CO₂ than Nb (Rosenthal et al., 2015). Hence, CO₂/Nb ratio in the samples may differ from those in the source if the incremental melts of the source did not completely aggregate. However, this requires preferential loss or gain of extremely low degree melts, and also considering the uncertainty of ~20% in our estimated CO₂/Nb of D-DMM and E-DMM, the effect of this process may not be significant. Instead of using the CO₂/Nb ratio, the relatively constant

CO₂/Ba ratio of 105~134 in MORB can be used to estimate the primitive CO₂ concentration of MORB samples. However, fractional crystallization of plagioclase affects the CO₂/Ba ratio of magmas (section 4.4). Furthermore interaction of magmas with gabbro, especially gabbro with ITE enriched plagioclase derived from EMORB can affect the Ba concentration of the melt (Saal et al., 2007) . These processes may explain the larger variability in CO₂/Ba ratios of CO₂-H₂O vapor undersaturated DMORB in this study ($\pm 60\%$, 105 ± 61 (2σ)) compared to their less variable CO₂/Nb ratios ($\pm 16\%$, 258 ± 40 (2σ)). Larger variability in CO₂/Ba relative to CO₂/Nb is also observed in the Siqueiros melt inclusions (Saal et al., 2002). The opposite observation (CO₂/Ba variability < CO₂/Nb variability) is expected from a melting process since the CO₂-Ba pair behaves more similarly compared to CO₂-Nb pair (Rosenthal et al., 2015). CO₂/Nb ratio of MORB is less affected by either interaction with gabbro or by fractional crystallization, thus it is an alternative tool to estimate the primitive CO₂ concentration of degassed MORB samples.

The CO₂ content of the average oceanic crust was estimated using the two component melting-mixing model. Using the model parameters that reproduce the KDEs of EPR axial MORB compilation ($p_{DDMM} = 0.78$, $F_{\text{ext}} = 1.3\%$, $f_{\text{escape}} = 0.80$) and setting the mixing parameter N to ∞ (complete mixing), we obtain an average oceanic crust CO₂ content of 955 ppm. The average CO₂ flux from the ridge is 1.32×10^{12} mol yr⁻¹ or 58 Mt yr⁻¹ using a MOR mass flux of $21 \text{ km}^3 \text{ yr}^{-1}$ (Crisp, 1984) and oceanic crust density of 2890 kg/m³ (Carlson and Raskin, 1984). This compares well with the CO₂ flux of $2.2 \pm 0.9 \times 10^{12}$ mol yr⁻¹ calculated by Marty and Tolstikhin (1998) using the C³He ratio in MORB and the mid-ocean ridge He flux.

5.5.2 Chlorine: Melting-mixing model

The two-component mantle melting-mixing model and the Cl concentration of D-DMM (0.4 ppm) and E-DMM (22 ppm) (Table 1 and section 5.3) reproduces the Cl/K of QDG transform fault, NEPR seamount, and Macquarie Island samples (Fig. 18a and S5a). In figure 18a, note that some model mixtures do not plot within the area defined by the E- and D-DMM melting curves due to the curvature of the mixing between the model E- and DMORB.

The range of Cl/K produced by the model melts can be used to constrain the maximum Cl/K of the uncontaminated DMORB and NMORB samples at 0.04 and 0.06 respectively (Fig. 18a), which were used in section 5.3 to filter our samples for contamination. The highest Cl/K ratio for uncontaminated DMORB therefore could be much higher than previously defined (~ 0.01 of (Michael and Cornell, 1998; Saal et al., 2002)) due simply to the mixing process. Therefore, DMORB and NMORB samples with Cl/K below 0.04 and 0.06 may be potentially uncontaminated by high salinity brine or seawater. The model reproduces some but not all of the range in Cl/K for a given Th/La of the enriched samples (Fig. 18a). This is most likely due to the difference in partition coefficient between Cl (K_d similar to Ba) and K that becomes more evident in melts produced by low degree of melting of a E-DMM, such as the Macquarie Island lavas.

5.5.3 Fluorine: Melting-mixing model

The two-component mantle melting-mixing model using F concentration in the D-DMM and E-DMM of 8 ppm and 31 ppm respectively (Table 1 and section 4.3)

reproduce the F/Nd ratios of the QDG transform fault, NEPR seamount, and Macquarie Island samples (Fig. 18b and S5b). The high F/Nd ratio (~ 50) of the modeled low degree melting of the E-DMM source is due to the different partition coefficient between F and Nd (max. fractionation of $\sim$ factor of 2 from the E-DMM source F/Nd of 25) during melting in the presence of garnet, where Nd is more compatible than F. The most enriched model mixtures ($\text{Th/La} > \sim 0.10$) reproduces the high F/Nd ratio of Macquarie Island samples, consistent with the major, trace and isotopic composition of these samples strongly suggesting that they were low degree melts from an E-DMM that hardly mixed with DMORB melts (Fig. 16, 18, S1, S5b, Appendix D). Once garnet is no longer present in the source, F and Nd starts to behave more similarly producing a kink in the E-DMM melting curve at Th/La of ~ 0.095 . At higher degrees of melting after consumption of clinopyroxene, for both E-DMM and D-DMM, the bulk partition coefficient of fluorine becomes higher than Nd, resulting in a continuous increase in F/Nd with increasing degrees of melting. Thus, initially F/Nd decreases during melting in the garnet field and after clinopyroxene consumption F/Nd increases with the increasing degree of melting. Note that in a plot F/Nd versus Nd isotopes (Fig. S5b), the two-component melting-mixing produce non-linear mixing trends indicating that the observed compositional variation does not require more than two mantle source components (Brandl et al., 2012; Stracke and Bourdon, 2009). The model mixture, as expected, also reproduces the curved field defined by our samples in an Yb/Nd-La/Nd diagram (not shown), which was observed by Brandl et al. (2012).

5.5.4 Water: Melting-mixing model

The two-component mantle melting-mixing model and the H₂O concentration of D-DMM (59 ppm) and E-DMM (660 ppm) (Table 1 and section 5.3) reproduces the H₂O/Ce of DMORB and NMORB samples, and the EMORB samples with higher H₂O/Ce (Fig. 18d and S5d). Similar to F/Nd, the consumption of clinopyroxene in the source at higher degrees of melting makes the bulk partition coefficient of water higher than Ce, which results in a continuous increase in H₂O/Ce with increasing degrees of fractional melting. The two-component mantle melting-mixing model cannot explain the entire range of H₂O/Ce in the EMORB samples. The lower H₂O/Ce EMORB samples may either be melts from a low H₂O/Ce E-DMM or they may be melts from a high H₂O/Ce E-DMM that experienced subsequent kinetic process that decreased its H₂O.

5.5.5 Water in E-DMM and EMORB: Fractionation of H₂O/Ce due to H⁺ diffusion

One likely explanation for the range in H₂O/Ce of the E-DMM might be different degrees of diffusive loss of H₂O (H⁺) during its storage in the ambient D-DMM (Workman et al., 2006). A 1D diffusion model was used to calculate the H₂O/Ce of an E-DMM within a semi-infinite ambient D-DMM as a function of its residence time and length-scale (Fig. 19). The initial H₂O content for E-DMM (660 ppm) and D-DMM (59 ppm) are used in the two-component mantle melting mixing model (section 5.4). We assume that the average temperature of the E-DMM is 1453 °C during its residence time (temperature at the mid-depth of the upper mantle assuming 0.5 °C/km mantle adiabat (McKenzie and Bickle, 1988) and potential temperature of 1350 °C (Ita and Stixrude, 1992)). Diffusivity of H⁺ in the D-DMM and E-DMM is assumed to be the same. We assume olivine controls the H⁺ diffusivity, and consider two H⁺ diffusion mechanisms

charge compensated by 1) flux of polarons-electrons in olivine (average diffusivity of $5.73 \times 10^{-9} \text{ m}^2/\text{s}$), and 2) diffusion of intrinsic point defects such as metal vacancy in olivine (average H diffusivity of $1.20 \times 10^{-9} \text{ m}^2/\text{s}$) (Kohlstedt and Mackwell, 1998). Diffusivity of Ce in clinopyroxene is slow (Van Orman et al., 2001) compared to H^+ , so the Ce concentration in the E-DMM is assumed to be constant. The model produces a range of $\text{H}_2\text{O}/\text{Ce}$ from ~ 350 to as low as 150 depending on the length-scale and residence time of the E-DMM (Fig. 19). Based on the mantle pseudo-isochron of Donnelly et al. (2004) the estimated residence time of the Pacific mantle E-DMM is $\sim 300\text{Ma}$, and thus, the mantle length-scale would range from ~ 2 to 25 km to reproduce the observed range in $\text{H}_2\text{O}/\text{Ce}$ observed in EMORB. Although our simple diffusion model does not consider other mantle phases such as clinopyroxene, which could decrease the hydrogen bulk diffusivity (Zhang and Liu, 2012), our model does not consider faster grain boundary diffusion of H^+ either, thus providing a simple but robust model. The observation of both low $\text{H}_2\text{O}/\text{Ce}$ EMORB samples and high $\text{H}_2\text{O}/\text{Ce}$ EMORB samples in all three sample locations (QDG TF, NEPR seamounts, and Macquarie Island) supports the hypothesis that the variation in the $\text{H}_2\text{O}/\text{Ce}$ of these samples is due to a diffusion process rather than a mantle source variation.

Another possible cause of the range in $\text{H}_2\text{O}/\text{Ce}$ is diffusive H^+ loss from the EMORB melts as it percolates through the D-DMM beneath the ridge. The E-DMM, enriched in volatile and trace elements, starts to melt deeper relative to the D-DMM (e.g. Asimow et al., 2004; Asimow and Langmuir, 2003; Green, 1976). Since the H_2O concentration gradient between the EMORB melts and the surrounding D-DMM is large, the diffusive loss of H^+ from the EMORB melt may be significant. Kogiso et al. (2004)

modeled this melt-solid diffusion process for Fe, Mg and Os to constrain the length scale of heterogeneity in the MORB mantle. This 1D model is applied here to H^+ diffusion to estimate the minimum length scale of a partially molten E-DMM that can preserve its primary melt H_2O content. The model calculates two important time-scales. The first time-scale is the 1D diffusion time-scale, which is the time required for the diffusing species, in this case H^+ in the EMORB, to reach $e/(e+1) \sim 73\%$ of its equilibrium concentration with the surrounding D-DMM (i.e., that is attained at $T = \infty$). The second time-scale is the 1D melt segregation time-scale, which is calculated using the compaction time (t_c) from the model of (McKenzie, 1984; McKenzie, 1985). This is the time required to reduce the mass of the melt by a factor of e (~ 2.718) in the partially molten region. If the melt segregation time-scale of the EMORB melt is shorter than its diffusion time-scale, the EMORB melt may be extracted from the partially molten E-DMM without significant diffusive loss of H_2O (H^+). The values of the parameters used are shown in Table 3. The model result suggests that $14.4 \text{ m} \times 14.4 \text{ m}$ (assuming an aspect ratio of melt height: width = 1:1 and H^+ diffusion mechanism charge compensated by flux of polarons-electrons in olivine) is the estimated minimum length scale of the partially molten E-DMM required for the segregation and extraction of the melt to occur without significant diffusive loss of H^+ (Fig. 20). The model results of using the H^+ diffusivity charge compensated by diffusion of intrinsic point defects such as metal vacancy in olivine (Mackwell and Kohlstedt, 1990) requires a smaller length scale of $8.8 \text{ m} \times 8.8 \text{ m}$ due to slower diffusivity of H^+ . These results may suggest that the large range in H_2O/Ce observed in our EMORB samples may be due to variable diffusive loss of H^+ (H_2O) from the EMORB melt to the surrounding D-DMM as a result of variable partially

molten E-DMM length scale. Alternatively diffusive loss of H^+ (H_2O) from the EMORB melt to the surrounding mantle may occur shallower at mantle lithospheric depths, which may be responsible for the high H_2O contents observed in abyssal peridotites (Warren and Hauri, 2014).

Diffusive loss of H^+ from the E-DMM and/or EMORB melt is also supported by the lack of other significant geochemical difference between the EMORB samples with different H_2O/Ce ratios. The process that produced the range in H_2O/Ce of the samples did not affect the other volatile and trace element contents and ratios in the mantle nor the melt produced from it, consistent with diffusive fractionation of H_2O/Ce due to the much faster diffusivity of H^+ compared to those of other elements.

5.5.6 Sulfur: Melting-mixing model

The two-component mantle melting-mixing model, and the S concentration of D-DMM (100 ppm) and E-DMM (165 ppm) (Table 1 and section 5.3) reproduces the range of S/Dy ratios in our DMORB and NMORB samples (Fig. 18c and S5c), but not the consistently low S/Dy ratios in the EMORB samples, in particular those from Macquarie Island. Instead, the model EMORB tend to have higher S/Dy due to both the effect of garnet and also the high SCSS calculated for H_2O rich model EMORB. Given the possibility of a lower H_2O E-DMM due to diffusive loss of H^+ in solid state discussed in the previous section (section 5.5.5), we ran our two component mantle melting-mixing model with an EDMM mantle that has a lower H_2O content of 264 ppm (calculated using H_2O/Ce ratio of 150 and Ce concentration of 1.65 ppm (Donnelly et al., 2004)). In this low H_2O model, the calculated EMORB with similar Th/La to those of the Macquarie

Island samples ($\text{Th/La} = 0.12\text{-}0.15$) have relatively high S/Dy ratios (237 ± 99 (2σ)) that does not match those in the Macquarie Island samples (163 ± 49 (2σ)).

Alternatively, the Macquarie Island samples might have had higher initial S/Dy ratios, which subsequently decreased due to sulfide saturation induced by diffusive loss of H^+ from the EMORB melts to the surrounding mantle as was discussed in the previous section. To test this hypothesis, we compared the measured sulfur content of the Macquarie Island samples to their calculated SCSS using the model of Fortin et al. (2015) and the measured H_2O content in the lavas at the P-T conditions along the melting path of EDMM from the AlphaMelts program (Antoshechkina et al., 2010; Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995; Smith and Asimow, 2005). The result is that our samples never reached sulfide saturation in the mantle with our measured S and H_2O contents. Furthermore, our samples show a negative correlation between their measured S and H_2O concentrations (Fig. S6), which is opposite to those expected from sulfide saturation due to the diffusive loss of H, since experimental results show higher SCSS in melts with higher H_2O content (Fortin et al., 2015). There is a possibility that the existing models overestimate the SCSS of our samples since the model parameterization does not consider Cu and Ni content in the sulfides as discussed in section 4.3.

Alternatively, degassing of S from the EMORB samples may explain their low S content and S/Dy ratios. Experimental data on the distribution of S between silicate melts and $\text{CO}_2\text{-H}_2\text{O}$ fluids at relatively reducing conditions similar to MORB (Fiege et al., 2015; Keppler, 2010; Lesne et al., 2011; Zajacz et al., 2012) suggests that S will degas under those conditions. This hypothesis is supported by our samples showing a negative correlation between their measured S and H_2O concentrations (Fig. S6). Furthermore, Fe-

Cu sulfides are found in CO₂-bearing bubbles decorating the bubble-glass interface in Macquarie Island samples suggesting that S and Cu are soluble in CO₂ rich fluid (Kamenetsky and Eggins, 2012).

The S content of the E-DMM estimated in our model (165 ppm) is the least well-constrained mantle volatile content in this study. In addition to the potential overestimation of SCSS by the models and the effect of S degassing discussed above, S/Dy of our two component melting-mixing model is not very sensitive to the initial S content of the EDMM. This is shown by the similarity between the S/Dy of our original model mixture (Fig. 18c) and those calculated using 3 times higher E-DMM S content of 510 ppm (Fig. S7) (calculated assuming Pacific upper mantle S content of 190 ppm, D-DMM S content of 100 ppm, and 78% D-DMM (22% E-DMM) in the Pacific upper mantle). Therefore, the estimated S content of the E-DMM (165 ppm) is a minimum estimate in our two-component melting mixing model.

5.6 Volatile content of the MORB mantle and implications

We use the results of our two-component mantle melting-mixing model to estimate the volatile contents of the Pacific upper mantle. Using the proportions of D-DMM (78%) and E-DMM (22%) and their estimated volatile element contents, we calculate the volatile element content of Pacific upper mantle as follows: CO₂ = 235 ppm, H₂O = 191 ppm, F = 13 ppm, Cl = 5 ppm, and S = 114 ppm (Table 1). This weighted average volatile content using the proportions of the two mantle components is within the range of the previous estimates made for the upper mantle volatile content (Fig. 21a and Table 4) (Beyer et al., 2012; Bézous et al., 2005; Dixon et al., 2002; Halliday, 2013;

Hirschmann and Dasgupta, 2009; Javoy and Pineau, 1991; le Roux et al., 2006; Le Voyer et al., 2015; Marty, 2012; Marty and Tolstikhin, 1998; Michael, 1988; Saal et al., 2002; Salters and Stracke, 2004; Schilling et al., 1980; Sobolev and Chaussidon, 1996; Workman and Hart, 2005).

The estimated volatile and refractory ITE content for the E-DMM relative to the D-DMM decreases as a function of increasing elemental peridotite-basaltic melt bulk partition coefficient (Fig. 21b), suggesting that the two sources can be related by a single melting event. One hypothesis for the origin of the E-DMM is the presence of recycled oceanic crust in the MORB source (e.g. Hirschmann and Stolper, 1996; Sobolev et al., 2007), and the higher C content of the EMORB relative to the NMORB has been ascribed to recycling of C (e.g. Marty and Zimmermann, 1999). However, dehydration of subducting oceanic crust alters its volatile and fluid mobile element abundances. For example, dehydration releases Cl from the subducting oceanic crust more efficiently than C (Wallace, 2005). Thus, a recycled oceanic crust should have characteristically higher CO_2/Cl ratio relative to D-DMM. Contrary to this prediction, the E-DMM and D-DMM have a relatively constant CO_2/Cl ratio of ~ 57 (section 5.3). An alternative proposed hypothesis for the origin of the E-DMM is metasomatism of the oceanic mantle lithosphere by a low degree mantle melt (Niu et al., 2002). In this scenario, the metasomatized oceanic lithosphere will have volatile and ITE element abundance pattern related to the D-DMM and E-DMM by simple melting, and this pattern will not largely change as they are protected from the dehydration process during recycling back to the mantle at subduction zones. Therefore, the origin of the E-DMM as a recycled oceanic lithosphere metasomatized by low degree melts (Niu et al., 2002) is a process that is

consistent with the observation that (1) the E-DMM and D-DMM have a relatively constant CO_2/Cl ratio of ~ 57 (section 4.3), and that (2) the volatile and refractory ITE for the E-DMM relative to the D-DMM simply decreases as a function of increasing elemental peridotite-basaltic melt bulk partition coefficient (Fig. 21b).

6. Conclusion

We have reported major, trace, and volatile element (CO_2 , H_2O , F, Cl, S) data as well as Sr, Nd, and Pb isotope composition of MORB glass samples from the Northern East Pacific Rise off-axis seamounts, Quebrada-Discovery-GoFar transform fault system, and Macquarie Island. The incompatible trace element (ITE) pattern of the samples range from highly depleted (DMORB, $\text{Th}/\text{La} \leq 0.035$) to enriched (EMORB, $\text{Th}/\text{La} \geq 0.07$), and the isotopic composition spans the entire range observed in EPR MORB.

At the time of melt generation, the source that generated the EMORB was essentially peridotitic. The variable incompatible trace element ratios (e.g., Th/La) of basalts with Sr, Nd and Pb isotope ratios similar to E-DMM suggests that the E-DMM melted incrementally without the aggregation of the different melt fractions. The identical major and trace elements composition of DMORB generated from both E-DMM and D-DMM, suggest that the E-DMM is a peridotitic source.

NMORB might represent mixing of melts from a two-component mantle (D-DMM and E-DMM), rather than an actual DMM mantle source. This is consistent with the similar frequency distribution of Nd isotopes generated from clinopyroxene from abyssal peridotites (at the centimeter spatial scale) and lavas from the QDG transform fault and NEPR seamounts. These observations when considered together with the

observed correlations between crustal thickness and extent of magma aggregation and differentiation (Pickle et al., 2009) strongly suggest that the NMORB might represent mixing of melts from a two-component D-DMM and E-DMM rather than melting an actual DMM mantle source.

After filtering the volatile data for secondary processes (volatile degassing, sulfide saturation, assimilation of seawater-derived component, and fractional crystallization), we use the volatile to trace element ratios of our samples and a two-component mantle melting-mixing model to estimate the volatile content of D-DMM ($\text{CO}_2 = 22$ ppm, $\text{H}_2\text{O} = 59$ ppm, $\text{F} = 8$ ppm, $\text{Cl} = 0.4$ ppm, and $\text{S} = 100$ ppm) and of the E-DMM ($\text{CO}_2 = 990$ ppm, $\text{H}_2\text{O} = 660$ ppm, $\text{F} = 31$ ppm, $\text{Cl} = 22$ ppm, and $\text{S} = 165$ ppm). A particularly important observation is the fairly constant CO_2/Cl ratio of $\sim 57 \pm 8$ in the D-DMM and E-DMM, which is difficult to reconcile with a recycled oceanic crust origin of E-DMM. Recycled oceanic mantle lithosphere metasomatized by a low degree mantle melt is a more consistent hypothesis with the observation.

Our two-component mantle melting-mixing model reproduces the trace, volatile element contents, and isotopic composition of our samples, in particular the kernel density estimates (KDE) of Th/La and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic composition of our samples and axial MORB data compiled from the literature. Moreover, our model suggests that the melts produced during variable degrees of melting of the E-DMM controls most of the MORB geochemical variation.

The parameters of the model required to match the observation suggests that (1) 78% of the upper mantle is highly depleted in volatile and refractory ITE (D-DMM) and 22% is enriched in volatile and refractory ITE (E-DMM), and (2) a fraction (~ 65 to 80%)

of the low degree EMORB melts ($\sim 1.3\%$) may escape melt aggregation by freezing at the base of the oceanic lithosphere significantly enriching it in volatile and trace elements, consistent with proposed geodynamical processes acting at mid-ocean ridges and with the generation and composition of the E-DMM.

Our two-component mantle melting-mixing model allows us to make the following statements. (1) The estimated primitive CO_2 content (955 ppm) of the average oceanic crust suggests a CO_2 flux from the ridge of $1.32 \times 10^{12} \text{ mol yr}^{-1}$ or 58 Mt yr^{-1} . (2) The Cl/K ratio for uncontaminated DMORB and NMORB may be higher than previously defined due to mixing of fractional melts of E-DMM and D-DMM. (3) The large range in F/Nd (14.3 to 45.4) of our samples is due to variation in the mantle source F/Nd ratio and also the significant fractionation of F/Nd during melting of garnet peridotite. (4) The negative correlation between S and H_2O content of our samples along with the failure of our model to reproduce the negative correlation between S/Dy and Th/La ratios of our samples suggests either the model of Fortin et al. (2015) might be overestimating the SCSS of our samples or our samples might have lost S due to some process other than sulfide saturation, such as S partitioning into the $\text{CO}_2\text{-H}_2\text{O}$ phase during degassing. (5) Our model does not reproduce the large range in $\text{H}_2\text{O/Ce}$ (150~400) of EMORB samples, indicating variable amounts of diffusive loss of H^+ from the E-DMM to the ambient D-DMM, or from the EMORB during percolation through the surrounding D-DMM. (6) The volatile and refractory ITE abundances in E-DMM normalized to D-DMM decreases as a function of increasing peridotite-basaltic melt bulk partition coefficient suggesting the two sources can be related by a single melting event. This observation and the relatively constant CO_2/Cl ratio of $\sim 57 \pm 8$ for the E-DMM and D-DMM is consistent with

the origin of the E-DMM as a recycled oceanic lithosphere metasomatized by low degree melts.

Using the proportion of D-DMM of 78% and E-DMM of 22% and the estimated D-DMM and E-DMM volatile element contents, we calculate the volatile element content of Pacific upper mantle ($\text{CO}_2 = 235$ ppm, $\text{H}_2\text{O} = 191$ ppm, $\text{F} = 13$ ppm, $\text{Cl} = 5$ ppm, and $\text{S} = 114$ ppm). The volatile element budget of the Pacific upper mantle presented in this paper provides a fundamental constraint to establish the origin and evolution of the volatile element budget in the Earth.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data (Tables S1 and S2) associated with this article can be found, in the online version, at

APPENDIX B. MAJOR ELEMENT CORRECTION FOR FRACTIONAL CRYSTALLIZATION

The major element composition of primitive melts provide useful information for estimating the mantle source lithology of the heterogeneous Earth's upper mantle. However, most MORB are not primitive melts since they experience variable degrees of fractional crystallization affecting the major element composition of the melts. Therefore, the major element composition of MORB must be corrected for fractional crystallization before interpreting them to infer mantle source lithology.

Previous method to correct the major element composition of MORB for fractional crystallization by Niu et al. (1999) assumes a single liquid line of decent (LLD) for melts that ranges from DMORB to EMORB. This assumption may lead to erroneous fractional crystallization correction since EMORB and DMORB have different LLDs due to the higher H₂O content in EMORB compared to DMORB (Danyushevsky, 2001; Michael and Chase, 1987). Thus, the correlation between the estimated primitive melt major element composition and their isotopic composition observed by Niu et al. (1999) (Fig. S3) may be an artifact of the fractional crystallization correction.

To take into account the different H₂O content of the samples, we fit a polynomial function to the LLDs calculated for DMORB (H₂O poor) and EMORB (H₂O rich) in section 4.4, and use these functions to correct the major element composition of samples for fractional crystallization to an Mg# of 72. We only correct the major element composition of DMORB and EMORB samples with Mg# higher than 60 using their respective LLDs to avoid the complicating effect of melt mixing in the more evolved samples and in the NMORB. Furthermore, we only use samples from NEPR seamounts

in order to make direct comparison between the results of our method and those of Niu et al. (1999). The estimated primitive major element composition of the DMORB and EMORB samples from NEPR seamounts are plotted against their isotopic composition (Fig S3), and are compared to those estimated by the method of Niu et al. (1999). The estimated primitive EMORB melt using our method is higher in FeOt, Na₂O, TiO₂, and K₂O, while lower in Al₂O₃ and CaO compared to estimated primitive DMORB; more importantly our trends for FeOt and Al₂O₃ are opposite to those using the method of Niu et al. (1999). Niu et al. (1999) interpreted the low FeOt and high Al₂O₃ of their estimated primitive EMORB to be consistent with low F melt of peridotite at relatively low pressure (10 kbar) (Baker et al., 1995), but their trends are most likely an artifact of not taking into account the effect of H₂O content on the delay of plagioclase saturation in EMORB. Instead, the lower Al₂O₃ and CaO and higher FeOt content in the primitive EMORB estimated using our method is consistent with melting of the E-DMM in the garnet stability at higher pressure than the D-DMM, consistent with experimental melt composition of garnet peridotite (Walter, 1998) having lower Al₂O₃ and CaO and higher FeOt content compared to spinel peridotite (Wasylenki et al., 2003). Therefore the estimated primitive EMORB major element composition is consistent with melting of E-DMM in the garnet stability field at high pressure.

APPENDIX C. TWO-COMPONENT MANTLE MELTING-MIXING MODEL

The incremental near fractional melts from the D-DMM and E-DMM were calculated using pHMELTS (Asimow et al., 2004; Ghiorso et al., 2002; Smith and Asimow, 2005) and are mixed following the method of Rudge et al. (2013). Here we

briefly describe the mixing method. We calculate 2000 weighted averages of the compositions of the individual fractional melts,

$$\hat{C} = \sum_{j=1}^m \sum_{i=1}^{n_j} \hat{r}_j^i \hat{c}_j^i, \quad (1)$$

where c_j^i are concentrations of the i th fractional melt of the j th mantle source, and $\hat{r}_j^i$ are random weights assigned for the i th fractional melt of the j th mantle source that has an expected value that takes into account the triangular geometry of the melting region and the masses of the individual incremental melts. Specifically for our case, the equation can be written as,

$$\hat{C} = \sum_{i=1}^{n_{DMORB}} \hat{r}_{DMORB}^i c_{DMORB}^i + \sum_{i=1}^{n_{EMORB}} \hat{r}_{EMORB}^i c_{EMORB}^i, \quad (2)$$

where c_{DMORB}^i and c_{EMORB}^i are i th fractional melts of the D-DMM and E-DMM, and

$\hat{r}_{DMORB}^i$ and $\hat{r}_{EMORB}^i$ are the randomly chosen weights that satisfy the conditions,

$$\hat{r}_{DMORB}^i \geq 0, \hat{r}_{EMORB}^i \geq 0, \quad (3)$$

$$\sum_{i=1}^{n_{DMORB}} \hat{r}_{DMORB}^i + \sum_{i=1}^{n_{EMORB}} \hat{r}_{EMORB}^i = 1, \quad (4)$$

$$E(\hat{r}_{DMORB}^i) = f_{DMORB} \tilde{\omega}_{DMORB}^i, \quad (5)$$

$$E(\hat{r}_{EMORB}^i) = f_{EMORB} \tilde{\omega}_{EMORB}^i, \quad (6)$$

where f_{DMORB} and (where $f_{EMORB} = 1 - f_{DMORB}$) are the average fraction of D-DMM and E-DMM melts that makes up the model melts, $\tilde{\omega}_{DMORB}^i$ and $\tilde{\omega}_{EMORB}^i$ are normalized weights, and $E(\hat{r}_{DMORB}^i)$ and $E(\hat{r}_{EMORB}^i)$ are the expected values of $\hat{r}_{DMORB}^i$ and $\hat{r}_{EMORB}^i$. The normalized weights $\tilde{\omega}_{DMORB}^i$ and $\tilde{\omega}_{EMORB}^i$ are normalized melt generation depth from the top of the melting region calculated for a triangle with a 45° angle from horizontal to the melting regime boundary. The fractions f_{DMORB} and f_{EMORB} are given by,

$$f_{DMORB} = \frac{p_{DDMM} \sum_{i=1}^{n_{DMORB}} \omega_{DMORB}^i}{p_{DDMM} \sum_{i=1}^{n_{DMORB}} \omega_{DMORB}^i + p_{EDMM} \sum_{i=1}^{n_{EMORB}} \omega_{EMORB}^i}, \quad (7)$$

$$f_{EMORB} = \frac{p_{EDMM} \sum_{i=1}^{n_{EMORB}} \omega_{EMORB}^i}{p_{DDMM} \sum_{i=1}^{n_{DMORB}} \omega_{DMORB}^i + p_{EDMM} \sum_{i=1}^{n_{EMORB}} \omega_{EMORB}^i}, \quad (8)$$

where p_{DDMM} and p_{EDMM} (where $p_{EDMM} = 1 - p_{DDMM}$) are the solid fractions of D-DMM and E-DMM in the Pacific upper mantle, ω_{DMORB}^i and ω_{EMORB}^i are melt generation depth from the top of the melting region. The random weights $\hat{r}_{DMORB}^i$ and $\hat{r}_{EMORB}^i$ are distributed as a Dirichlet distribution with parameters $\alpha_{DMORB}^{n_{DMORB}}$ and $\alpha_{EMORB}^{n_{EMORB}}$ given by,

$$\left\{ \hat{r}_{DMORB}^1, \dots, \hat{r}_{DMORB}^{n_{DMORB}}, \hat{r}_{EMORB}^1, \dots, \hat{r}_{EMORB}^{n_{EMORB}} \right\} \\ \sim \text{Dir} \left(\alpha_{DMORB}^1, \dots, \alpha_{DMORB}^{n_{DMORB}}, \alpha_{EMORB}^1, \dots, \alpha_{EMORB}^{n_{EMORB}} \right) \quad (9)$$

$$\alpha_{DMORB}^{n_{DMORB}} = (N - 1) f_{DMORB} \tilde{\omega}_{DMORB}^i, \quad (10)$$

$$\alpha_{EMORB}^{n_{EMORB}} = (N - 1) f_{EMORB} \tilde{\omega}_{EMORB}^i, \quad (11)$$

where N is the mixing parameter that controls the amount of mixing between the melts. $N = 1$ means no mixing while $N = \infty$ means complete mixing.

APPENDIX D. REASON FOR WHY WE DID NOT ATTEMPT TO REPRODUCE THE MACQUARIE ISLAND SAMPLES USING OUR MODEL

The samples from Macquarie Island are distinctly enriched compared to the other ridge settings (Fig. 2a and 3c). This enriched composition can be reproduced mostly by low degree EMORB melts ($F = 0.5\text{-}0.7\%$) that hardly mix with DMORB (0% to 30%); consistent with the tectonic origin of the Macquarie Island (Kamenetsky et al., 2000). Macquarie Island represents a transition from an extensional environment forming a mid-ocean ridge to transpressional conditions that tectonically uplifted it 5~10 Ma ago (e.g. Christodoulou et al., 1984; Goscombe and Everard, 1998; Johnson and Molnar, 1972; Ruff et al., 1989; Varne et al., 2000; Varne et al., 1969). During the last stages of spreading (5~10 Ma) the transpression produced a gradual shut off of the magmatism. During the shutting off of the magmatism the low degree melts from the E-DMM are most likely the last melts extracted at the sea floor. The eruption age of Macquarie Island lavas coincides with that of the tectonic uplift of the island (Duncan and Varne, 1988), supporting such an interpretation. Hence, the Macquarie Island samples are most likely the last melts from a E-DMM that were extracted at the surface after the shut off of the ridge magmatism; and therefore, it made no sense to reproduce the KDE of these samples

using our mixing model.

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Figure captions

Figure 1-1. (a) Bathymetric map of the QDG fracture zone system on the EPR (3-5°S) and **(b)** Northern EPR seamounts (5-15°N). **(c)** Macquarie Island located about 1200 km south of New Zealand. The symbols indicate sample locations and the colors indicate the degree of ITE enrichment; blue (DMORB, $\text{Th/La} \leq 0.035$), gray (NMORB, $0.035 < \text{Th/La} < 0.07$), and orange (EMORB, $\text{Th/La} \geq 0.07$).

Figure 1-2. (a) Th/La versus MgO for the samples. Most of the samples have $\text{MgO} > 6.0$ wt%. Samples are separated into three groups DMORB (blue, $\text{Th/La} \leq 0.035$), NMORB (gray, $0.035 < \text{Th/La} < 0.07$), and EMORB (orange, $\text{Th/La} \geq 0.07$). Error bars are 2σ SE. **(b)** Primitive mantle normalized trace element diagram of representative samples from each location and enrichment group. All plotted samples have between 7.5 and 8.5 wt% MgO. The grey field is the entire range of trace element abundance observed in a compilation of EPR axial MORB (Gale et al., 2013; Mallick et al., in revision) that have greater than 6 wt% MgO. Primitive mantle composition is from McDonough and Sun (1995).

Figure 1-3. (a) $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$, **(b)** $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ and **(c)** $^{143}\text{Nd}/^{144}\text{Nd}$ versus Th/La ratios for the samples in this study. In (a), (b), and (c), the small circles are EPR axial MORB (Gale et al., 2013; Mallick et al., in revision), small diamonds are Rano Rahi seamounts (Hall et al., 2006), small triangles are Seamount 6 (Brandl et al., 2012), and the circle with cross are Garrett transform fault (Wendt et al.,

1999). The isotopic composition for NEPR seamounts and Macquarie Island samples are from Niu et al. (2002) and (Kamenetsky and Maas, 2002) respectively. In (a) and (b) we also added the Pacific MORB data from a compilation by Stracke (2012). Error bars are 2σ for isotopic composition and 2σ SE for the Th/La ratios.

Figure 1-4. (a) CO_2 versus H_2O for the samples and their pressure of H_2O - CO_2 saturation. Isobars (solid lines) and isopleth of mole fraction of H_2O in the vapor phase ($X_{\text{H}_2\text{O}}$) (dashed lines) determined from the solubility model of Dixon et al. (1995). Error bars are 2σ SE. **(b)** Pressure of H_2O - CO_2 saturation (P_{sat}) versus pressure of collection (P_{coll}) for the samples. P_{sat} is calculated from the solubility model of Dixon et al. (1995). The black line is a 1:1 line. P_{coll} for Macquarie Island samples (not shown in fig. 4b) is 275 ± 75 bars, which is the estimated average paleo-ridge based on the benthic foraminifera from inter- and intra-pillow calcareous oozes (Quilty et al., 2008; Portner et al., 2010). Note that the lowest P_{sat} recorded in the Macquarie Island samples (273.5 bars) matches well with the estimated P_{coll} . Eight depleted samples plot below the 1:1 line outside of the error bars, indicating they are H_2O - CO_2 undersaturated. Sample D42A2 was not considered undersaturated since it is very close to the 1:1 line (8 bars). Samples that plot on the line are saturated, while those plotting above the line are supersaturated in CO_2 . Error bars for P_{sat} are based on the 2σ SE of the measured CO_2 and H_2O concentrations in the glasses. Error bars for P_{coll} are ± 15 bars.

Figure 1-5. (a) Cl/K versus Th/La ratios for the samples in this study. **(b)** Cl/K versus Th/La ratios for samples with Cl/K < 0.14. Two primary trends can be distinguished: One

with a large range of Cl/K at roughly constant Th/La representing Cl addition (the assimilation of seawater and seawater brines) and a second defined by a correlation between Cl/K and indicators of magmatic ITE enrichment. Error bars are 2σ SE.

Figure 1-6. Cl/K versus H₂O/Ce ratios for the samples in this study. The dashed lines represent the effects of seawater and NaCl brines of different concentrations contaminating a DMORB sample (D42A from QDG TF). Tick marks on the dashed lines shows the effect of 0.1 wt% assimilation of the contaminant. The compositions of the contaminants were taken from Kent et al. (1999) and le Roux et al. (2006). The inset shows samples with Cl/K < 0.2. Error bars are 2σ SE.

Figure 1-7. (a). H₂O/Ce versus Th/La ratios for all the samples. **(b).** H₂O/Ce versus Th/La ratios for samples uncontaminated by hydrothermal altered materials. DMORB samples with Cl/K > 0.04, NMORB samples with Cl/K > 0.06, and EMORB samples with Cl/K > 0.1 were filtered from the data set. We used Cl/K limits slightly higher than those proposed by Michael and Cornell (1998) for the D- and N-MORB samples, since we show in section 5.5.2 that values as high Cl/K ~ 0.04, for DMORB an ~ 0.06 for NMORB can be produced by the two component mantle melting mixing model and they may not necessarily indicate assimilation of hydrothermally altered material.

Figure 1-8. Sulfur content at sulfide saturation (SCSS) versus measured sulfur for the samples. The SCSS was calculated using the sulfide saturation model of Fortin et al. (2015). The solid line is the 1:1 line. The majority of the samples plot to the left of the

1:1 line indicating that they are sulfide undersaturated. Error bars of the sulfur content are 2σ SE. Error bars of the SCSS ($\pm 14\%$) for the calculated SCSS using the model of Fortin et al. (2015) are based on the average deviation of the calculated SCSS from the measured S content in the experiments with basaltic compositions and S contents similar to our samples (1000 to 1700 ppm).

Figure 1-9. S/Dy versus Th/La for the sulfide undersaturated samples based on the SCSS model of Fortin et al. (2015). The average S/Dy of the sulfide undersaturated DMORB, NMORB, and EMORB samples are 259 ± 64 , 247 ± 47 , and 189 ± 58 respectively, similar to the range of 225 ± 49 observed in depleted Siqueiros melt inclusions (Saal et al., 2002).

Figure 1-10. (a) Primitive mantle normalized trace element diagram and (b) Sr and Nd isotopic composition of five samples (DMORB samples D45A and D45B, NMORB samples D37A and D47A, and EMORB sample D8B). All five samples have MgO between 8.0-9.0wt%. (c) Primitive mantle normalized trace element diagram and (d) Sr and Nd isotopic composition of the isotopically depleted DMORB samples (blue, D44B and D10B) compared to isotopically enriched DMORB samples (dark blue, D45A and D45B). All four samples have MgO between 8.0-9.5wt%. Primitive mantle composition is from McDonough and Sun (1995). Symbols are as in figure 3.

Figure 1-11. Estimated probability density function of Nd isotopic composition in lavas from QDG transform fault, NEPR seamounts and other MORB from seamounts and

intra-transform faults (Brandl et al., 2012; Hall et al., 2006; Wendt et al., 1999) compared to clinopyroxene from abyssal peridotites (Warren et al., 2009 and references therein). The seamount and transform fault lavas and the clinopyroxene from abyssal peridotites display a similar frequency distribution.

Fig 1-12. (a) and (b) Measured and estimated CO₂ versus Nb of the samples. **(a)** is in logarithmic scale and **(b)** is in linear scale and zoomed in. CO₂ in Macquarie Island samples (filled square with cross) estimated from the CO₂-Cl correlation (see section 5.3). Also plotted are estimated CO₂ versus measured Nb in Mid-Atlantic Ridge MORB samples (open square with cross) from Cartigny et al. (2008). CO₂-undersaturated samples (light blue diamonds) define a constant CO₂/Nb ratio of 258 ± 40 (2σ) (dotted blue line), which is within error of the average CO₂/Nb (239 ± 46) of Siqueiros melt inclusions (gray field) from Saal et al. (2002). The CO₂ content estimated using the CO₂-Cl correlation (see section 5.3), versus measured Nb of Macquarie Island samples defines a CO₂/Nb of 744 ± 154 (2σ) (dotted orange line) consistent within error of the CO₂/Nb of 537 ± 112 defined independently by the Mid-Atlantic Ridge MORB samples from Cartigny et al. (2008). **(c) and (d)** Measured and estimated CO₂ versus Ba of the samples. Symbols as in **(a)** and **(b)**. **(c)** is in logarithmic scale and **(d)** is in linear scale and zoomed in. CO₂-undersaturated samples (light blue diamonds) define a CO₂/Ba ratio of 105 ± 60 (2σ), consistent with the Siqueiros melt inclusions (gray field) (Saal et al., 2002) with higher CO₂/Ba ratios compared to those with lower CO₂/Ba ratios that might have interacted with plagioclase (Saal et al., 2007). The CO₂ content estimated using the CO₂-Cl correlation (see section 5.3), versus measured Ba of Macquarie Island samples defines

a CO_2/Ba of 134 ± 23 (2σ) consistent within error of the CO_2/Ba of 97.8 ± 28 defined independently by the Mid-Atlantic Ridge MORB samples from Cartigny et al. (2008). The similar CO_2/Ba ratio of E-DMM (134 ± 23) and D-DMM (105 ± 61) suggests that the CO_2/Ba ratio is also relatively constant in the Pacific upper mantle (green field), as first observed by Michael and Graham (2013). Error bars are 2σ SE.

Figure 1-13. F/Nd versus Th/La ratios for the samples. F/Nd ratio of our samples ranges from 14.3 to 45.4, significantly outside the previously defined global constant F/Nd ratio of 20.1 ± 5.8 (Workman et al., 2006).

Figure 1-14. Kernel smoothed probability density estimates (KDE) for Th/La (**a, b, c**) and $^{143}\text{Nd}/^{144}\text{Nd}$ (**d, e, f**) using a model where a fraction of the EMORB melt ($f_{\text{escape}} = 65\%$ to 80%), representing a low degree melting ($F < F_{\text{ext}} = 1.3\%$), escape the melt aggregation by forming part of the freezing front at the base of the oceanic lithosphere (thick black line) reproducing KDEs of (**a, d**) our QDG TF samples (blue line), (**b, e**) our NEPR seamount samples (red line), and (**c, f**) compilation of EPR axial MORB (grey line) (Gale et al., 2013; Mallick et al., in revision), see section 5.4 in text for explanation of the models and parameters. The parameters required to obtain the best-matching model KDEs for the three ridge settings (transform fault, seamount and ridge axis) are as follow: QDG transform fault ($p_{\text{DDMM}} = 0.78$, $N = 16$, $F_{\text{ext}} = 1.3\%$, $f_{\text{escape}} = 0.65$), NEPR seamounts ($p_{\text{DDMM}} = 0.78$, $N = 40$, $F_{\text{ext}} = 1.3\%$, $f_{\text{escape}} = 0.75$), and compilation of EPR axial MORB ($p_{\text{DDMM}} = 0.78$, $N = 99$, $F_{\text{ext}} = 1.3\%$, $f_{\text{escape}} = 0.80$).

Figure 1-15. Primitive mantle normalized trace element diagram of a modeled E-DMM produced by addition of a fraction ($f_{\text{escape}} = 65\%$ to 80%) of low degree melt ($F < F_{\text{ext}} = 1.3\%$) to the bottom 22% of the model residual mantle (both calculated using pHMELTS). The E-DMM composition from Donnelly et al. (2004) is shown for comparison.

Figure 1-16. (a) Primitive mantle normalized trace element diagram of a randomly selected set of melt produced by the two-component mantle melting-mixing model (gray line with dot symbols), and representative composition of natural samples collected from each location. The grey field is the entire range of trace element abundance observed in a compilation of EPR axial MORB (Gale et al., 2013; Mallick et al., in revision) that have greater than 6 wt% MgO. The trace element concentrations of the model mixtures are increased by 81% (assuming perfect incompatibility of the trace elements in crystallizing phases) to take into account that our samples have experienced fractional crystallization. This is based on the fractional crystallization model using the MELTS program (Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995) (see section 4.4) that suggests a primitive melt with MgO of 12.5 wt% fractionally crystallizes 38 to 55% of its mass until reaching an MgO of 8.5 to 7.5wt%. **(b)** Nd, **(c)** Sr, and **(d)** Pb isotopic composition versus Th/La of our model results (grey points) and natural samples. The model melt mixture between incremental melts from the E-DMM (orange line) and the D-DMM (blue line) using pHMELTS reproduces the field defined by the EPR MORB (see section 5.4 for information about the model). The small circles are EPR axial MORB (Gale et al., 2013; Mallick et al., in revision), small diamonds are Rano Rahi seamounts (Hall et al., 2006),

small triangles are Seamount 6 (Brandl et al., 2012), and the circle with sticks are Garrett transform fault (Wendt et al., 1999). The model presented here is the one used for modeling the QDG TF samples with lowest degree of mixing ($N = 16$) that illustrate the largest compositional range. Error bars are 2σ SD for isotopic composition and 2σ SE for the Th/La ratios.

Figure 1-17. CO₂ versus Nb (**a, b**) and Ba (**c, d**) for the model mixture (grey points), incremental melting model of D-DMM (solid blue line), and E-DMM (solid orange line) using pHMELTS (see section 4.4 for model explanation) along with our samples and compilation of EPR MORB (small open diamonds) (Clog et al., 2013; Danyushevsky et al., 2000; Eiler et al., 2000; Michael, 1988; Saal et al., 2002; Soule et al., 2012; Wanless et al., 2011). CO₂ estimated for Macquarie Island samples (filled square with cross) using CO₂-Cl-Nb correlation (see section 5.3). Also plotted are the estimated CO₂ versus measured Nb and Ba for Mid-Atlantic Ridge MORB samples (open square with cross) from Cartigny et al. (2008). The model mixture reproduces our most depleted DMORB samples, the estimated Macquarie Island samples, and the Mid-Atlantic Ridge (MAR) MORB samples from Cartigny et al. (2008). (**b**) and (**d**) shows that the model mixture reproduces the CO₂/Nb and CO₂/Ba of our most depleted vapor undersaturated samples. In (**b**) and (**d**), the incremental melting models are discrete points rather than lines, but for clarity they are shown as lines.

Figure 1-18. (**a**) Cl/K, (**b**) F/Nd, (**c**) S/Dy, and (**d**) H₂O/Ce versus Th/La of the model mixture (grey points), incremental melting model of D-DMM (blue line), and E-DMM

(orange line) using pHMELTS (see section 5.4 for model explanation) along with our samples and EPR compilation (small open diamonds) (Clog et al., 2013; Danyushevsky et al., 2000; Eiler et al., 2000; Michael, 1988; Saal et al., 2002; Soule et al., 2012; Wanless et al., 2011). The kinks in the E-DMM melting model curves at Th/La of ~ 0.095 is due to the consumption of garnet in the source. The samples plotted in **(c)** and **(d)** are filtered for sulfide saturation (see section 4.3) and Cl contamination (see section 4.2) respectively. In **(a)**, the mixture limits the possible Cl/K of uncontaminated DMORB and NMORB samples at 0.04 and 0.06 respectively. In **(b)**, the model mixture reproduces the samples including the high F/Nd samples from Macquarie Island. Note that the F/Nd trend changes after clinopyroxene consumption. In **(c)** the model mixture reproduces the range of S/Dy ratios in our DMORB and NMORB, but not the consistently low S/Dy ratios in the EMORB samples in particular those from Macquarie Island (refer to section 5.5.6 for the explanation). In **(d)** the two-component mantle melting-mixing model reproduces the H_2O/Ce and Th/La of the DMORB, NMORB, and EMORB samples with high H_2O/Ce , but not the ones with low H_2O/Ce . This low H_2O/Ce may be due to variable diffusive loss of H_2O (H^+) from the E-DMM to the ambient D-DMM as a result of either variable residence time and length scale of the E-DMM or EMORB melt percolation and extraction (see section 5.5.5 and Fig. 19). Note H_2O/Ce change after clinopyroxene is consumed (18% melting for DDMM and 19.5% melting for EDMM).

Figure 1-19. Contour plot of H_2O/Ce of the E-DMM as a function of length-scale and residence time. The model is a 1D diffusion model of an E-DMM within a semi-infinite ambient D-DMM. The solid contour lines are the results (H_2O/Ce ratio of the E-DMM)

for which H diffusion is charge-compensated by the diffusion of intrinsic point defects such as metal vacancy, and the dashed contour lines are the results where it is charge compensated by flux of polarons-electrons (Kohlstedt and Mackwell, 1998).

Figure 1-20. Minimum length scale of the partially molten E-DMM required for the segregation and extraction of the melt to occur without significant diffusive H_2O (H^+) loss. Partially molten E-DMM of aspect ratio (height/width) and width to the right of the blue lines will extract the melt without significant diffusive H_2O (H^+) loss. The solid blue line is the result for which H^+ diffusion is charge-compensated by the diffusion of intrinsic point defects such as metal vacancy, and the dashed line is the result where it is charge compensated by flux of polarons-electrons (Kohlstedt and Mackwell, 1998). For example, assuming the H^+ diffusion is charge compensated by flux of polarons-electrons in olivine, the minimum length scale of a partially molten E-DMM with an aspect ratio of 1 is 14.8 meters $\times$ 14.8 meter. Parameters used for the model are given in Table 3.

Figure 1-21. (a) Carbonaceous chondrite normalized volatile element abundance in the D-DMM, E-DMM, and the Pacific upper mantle assuming 78% D-DMM and 22% E-DMM. The gray field is defined by the maximum and minimum estimates of the upper mantle volatile content from previous studies (Table 4) (Beyer et al., 2012; Bézous et al., 2005; Dixon et al., 2002; Halliday, 2013; Hirschmann and Dasgupta, 2009; Javoy and Pineau, 1991; le Roux et al., 2006; Le Voyer et al., 2015; Marty, 2012; Marty and Tolstikhin, 1998; Michael, 1988; Saal et al., 2002; Salters and Stracke, 2004; Schilling et al., 1980; Sobolev and Chaussidon, 1996; Workman and Hart, 2005). The carbonaceous

chondrite composition is from Anders and Grevesse (1989). **(b)** D-DMM normalized refractory and volatile element abundance of the E-DMM versus the element's bulk peridotite-basaltic melt partition coefficient. The abundances of elements in E-DMM relative to the D-DMM decreases as a function of increasing elemental peridotite-basaltic melt bulk partition coefficient, suggesting that the two sources can be related by a single melting event. The refractory trace element composition of D-DMM and E-DMM were taken from Workman and Hart (2005) from Donnelly et al. (2004), respectively and the volatile contents are from this study. Refractory trace and volatile element mineral-melt partition coefficient are from Kelemen et al. (2003), Hauri et al. (2006), and Rosenthal et al. (2015). Dy partition coefficient was used for the S partition coefficient since S behaves as a relatively compatible element during sulfide saturated E-DMM mantle melting (Fig. 18c). The mineral assemblage of the peridotite (55.2% olivine, 25.1% opx, 16.0% cpx, 3.6% spinel) is from pHMELTS model (Asimow et al., 2004; Ghiorso et al., 2002) for the D-DMM.

Figure 1-S1. Total alkali-silica (TAS) diagram (Le Bas et al., 1986). Alkali and tholeiitic basalt are separated by Macdonald and Katsura (1964) line (red dotted line). Most of the samples from QDG transform fault and NEPR seamounts are tholeiitic basalt, while most Macquarie Island samples are alkalic basalts.

Figure 1-S2. (a~f) Major element Harker diagrams of the samples. Liquid lines of descent (LLD) of the model DMORB (blue line) and EMORB (solid orange line for NEPR seamount and QDG TF EMORB, and dotted orange line for Macquarie Island EMORB).

The MELTS program (Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995) was used to model an isobaric fractional crystallization of model primitive DMORB and EMORB. The liquid lines of descent (LLDs) that best fit our DMORB and EMORB samples were calculated using the amoeba routine in the AlphaMelts program (Antoshechkina et al., 2010; Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995; Smith and Asimow, 2005). The primitive Siqueiros melt inclusion Siq1-6 (Saal et al., 2002) was used as the initial estimate of primary DMORB composition. The initial estimate of primary EMORB composition was calculated by adding olivine to the most primitive EMORB sample until its Mg# reached 76 using the PRIMELTS2 software (Herzberg and Asimow, 2008). To obtain the best-fit LLDs for the DMORB and EMORB samples, the initial estimated primary melt supplied to the amoeba routine is automatically adjusted until the misfit in the major elements and H₂O concentration between the model LLD and the group of samples with Mg# > 60 is minimized. A more detailed explanation of this routine is given by Cooper et al. (2004). The pressure at which fractional crystallization takes place was set to 600 bars, which is close to the highest P_{sat} recorded in our samples as well as the pressure at the top of the axial magma chamber (le Roux et al., 2006). The oxygen fugacity was set to QFM (Cottrell and Kelley, 2011). **(g~m)** Volatile to trace element ratios and MgO of our samples and model melts. The initial volatile to trace element ratios are average ratios of all the DMORB samples and all the EMORB samples. Refer to section 4.4 in text for the partition coefficients used for the calculation.

Figure 1-S3. Comparison of estimated primitive major element composition of DMORB and EMORB samples from NEPR seamounts considering the effect of water on the LLDs

in this study shown in Fig. S2 with those done by Niu et al. (1999) using only dry LLD. Solid (this study) and dashed lines (Niu et al., 1999) are linear fits to the correlation between the isotopic composition and estimated primitive major element composition estimated using the respective LLD.

Figure 1-S4. Kernel smoothed probability density estimates (KDE) for Th/La (left) and $^{143}\text{Nd}/^{144}\text{Nd}$ (right) using a model where all the melts are aggregated (thick black line). The KDEs of **(a, d)** QDG TF samples (blue line), **(b, e)** NEPR seamount samples (red line), and **(c, f)** EPR axial MORB compilation (grey line) (Gale et al., 2013; Mallick et al., in revision). Note that the model KDEs of $^{143}\text{Nd}/^{144}\text{Nd}$ matches the natural KDEs, but the model KDEs of Th/La are too enriched compared to the Th/La KDEs. The parameters required to obtain these model KDEs for the three ridge settings (transform fault, seamount and ridge axis) are as follow: QDG transform fault ($p_{DDMM} = 0.82$, $N = 16$), NEPR seamounts ($p_{DDMM} = 0.82$, $N = 40$), and compilation of EPR axial MORB ($p_{DDMM} = 0.82$, $N = 99$).

Figure 1-S5. **(a)** Cl/K, **(b)** F/Nd, **(c)** S/Dy, and **(d)** $\text{H}_2\text{O}/\text{Ce}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ for model mixture (grey points), incremental melting model of D-DMM (solid blue line), and E-DMM (solid orange line) using pHMELTS (see section 5.4 for model explanation) along with our samples and compilation of EPR MORB (small open diamonds) (Clog et al., 2013; Danyushevsky et al., 2000; Eiler et al., 2000; Michael, 1988; Saal et al., 2002; Soule et al., 2012; Wanless et al., 2011). The samples plotted in **(c)** and **(d)** are filtered for sulfide saturation and Cl contamination respectively. In **(a)** the mixture limits the

possible Cl/K of uncontaminated samples, and right panel shows same data zoomed out. In **(b)**, the model mixture reproduces the range of F/Nd in the samples for a given Nd isotopic composition. In **(c)** the model mixture reproduces the range of S/Dy ratios in our DMORB and NMORB, but not the relatively low S/Dy ratios in the EMORB samples in particular those from Macquarie Island (refer to section 5.5.6 for the explanation). In **(d)** the model reproduces the H₂O/Ce and Nd isotopic composition of the all samples except some EMORB with low H₂O/Ce. This low H₂O/Ce may be due to variable diffusive loss of H₂O (H⁺) from the E-DMM to the ambient D-DMM as a result of either variable residence time and length scale of the E-DMM or EMORB melt percolation and extraction (see section 5.5.5 and Fig. 19).

Figure 1-S6. S versus H₂O for sulfide undersaturated samples based on the SCSS model of Fortin et al. (2015). Also samples plotted have MgO > 7 wt% to avoid the effect of fractional crystallization. The negative correlation between S and H₂O content of our samples that were presumably sulfide saturated at the depth of generation, is opposite to the positive trend between SCSS and H₂O observed in the experimental data used in the study of (Fortin et al., 2015).

Figure 1-S7. S/Dy versus Th/La of the model mixture (grey points), incremental melting model of D-DMM (blue line), and E-DMM (orange line) using pHMELTS (see section 5.4 for model explanation) along with our samples and EPR compilation (small open diamonds) (small open diamonds) (Clog et al., 2013; Danyushevsky et al., 2000; Eiler et al., 2000; Michael, 1988; Saal et al., 2002; Soule et al., 2012; Wanless et al., 2011). The

E-DMM initial S content is 510 ppm (calculated assuming Pacific upper mantle S content of 190 ppm, D-DMM S content of 100 ppm, and 78% D-DMM (22% E-DMM) in the Pacific upper mantle) 3 times higher than the 165 ppm in our original model shown in figure 18c. Note that the S/Dy ratios of the model mixture do not significantly differ compared to those figure 18c suggesting that the model result is not very sensitive to the E-DMM S content.

Figures

Figure 1-1.

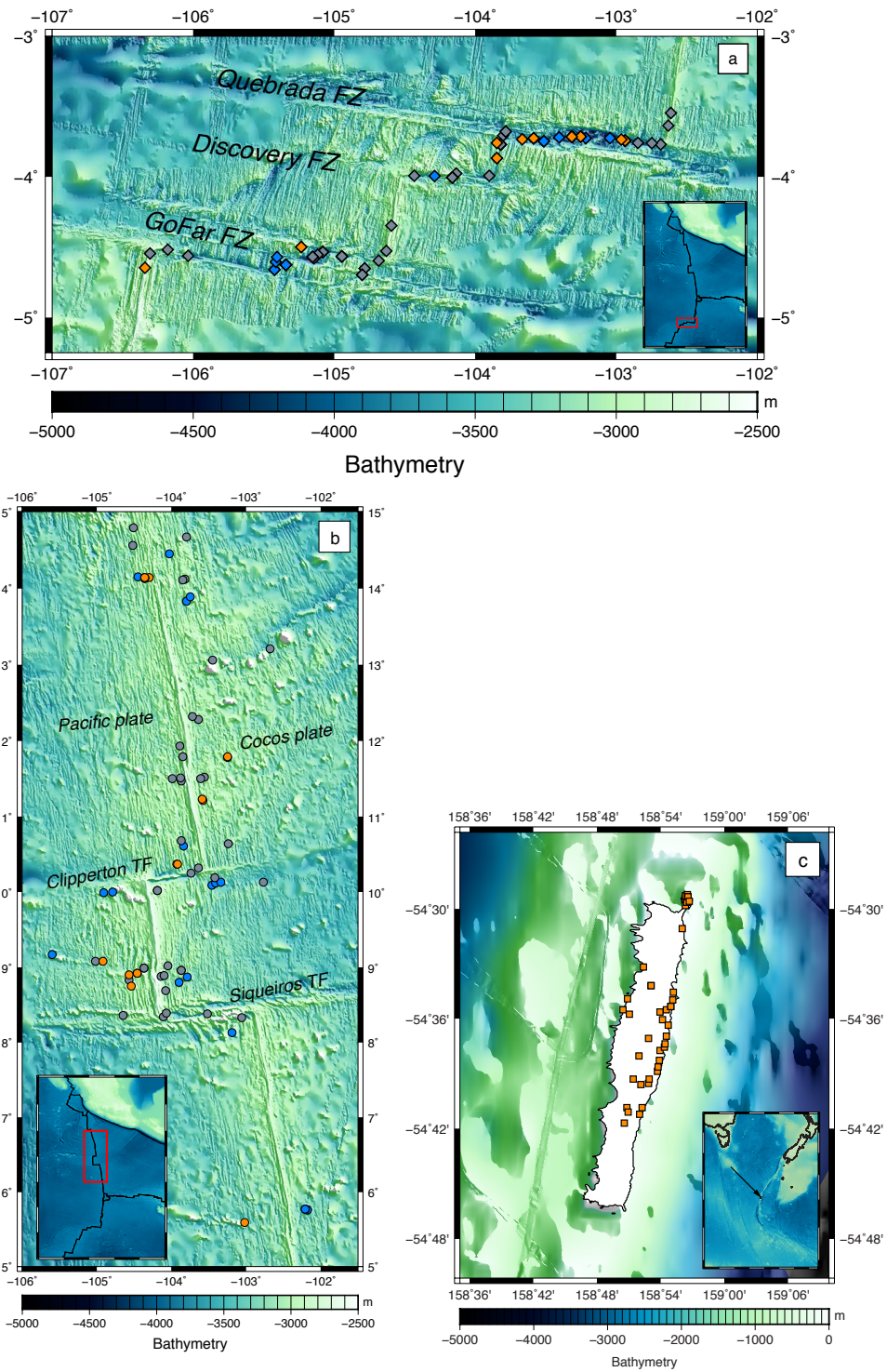


Figure. 1-2.

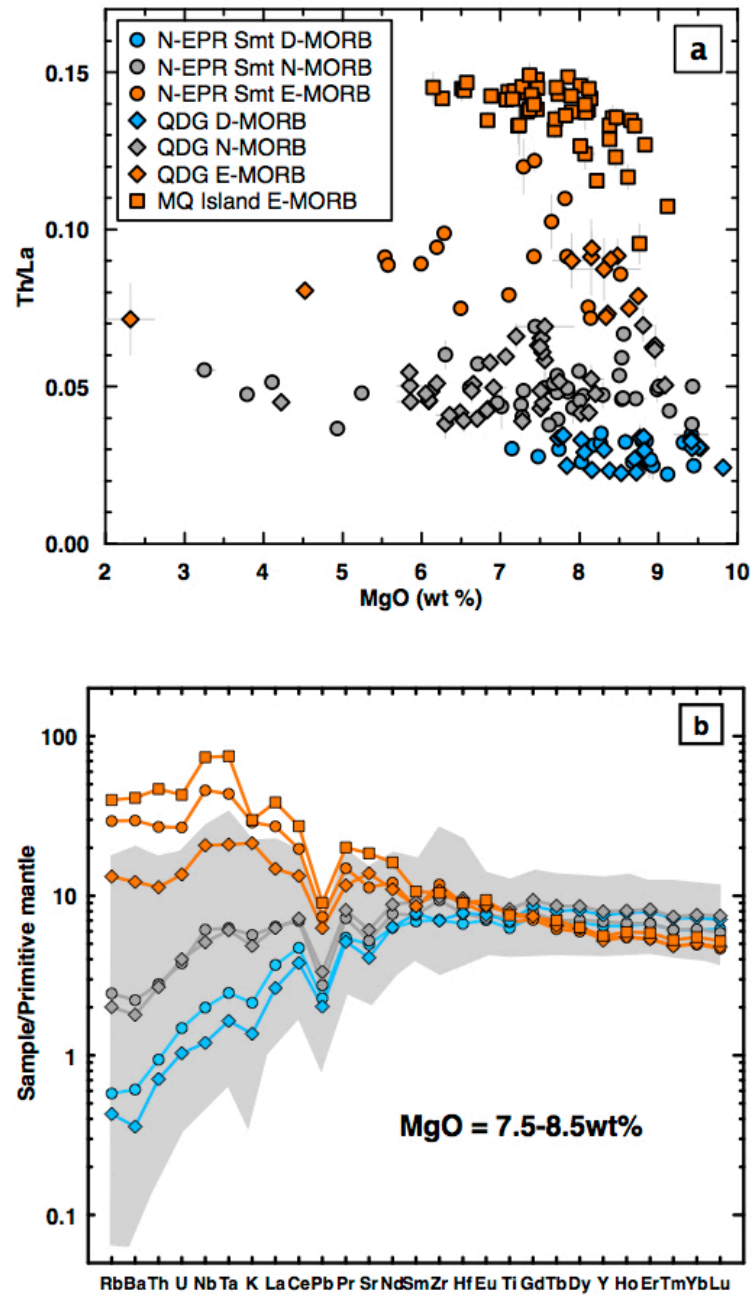


Figure 1-3.

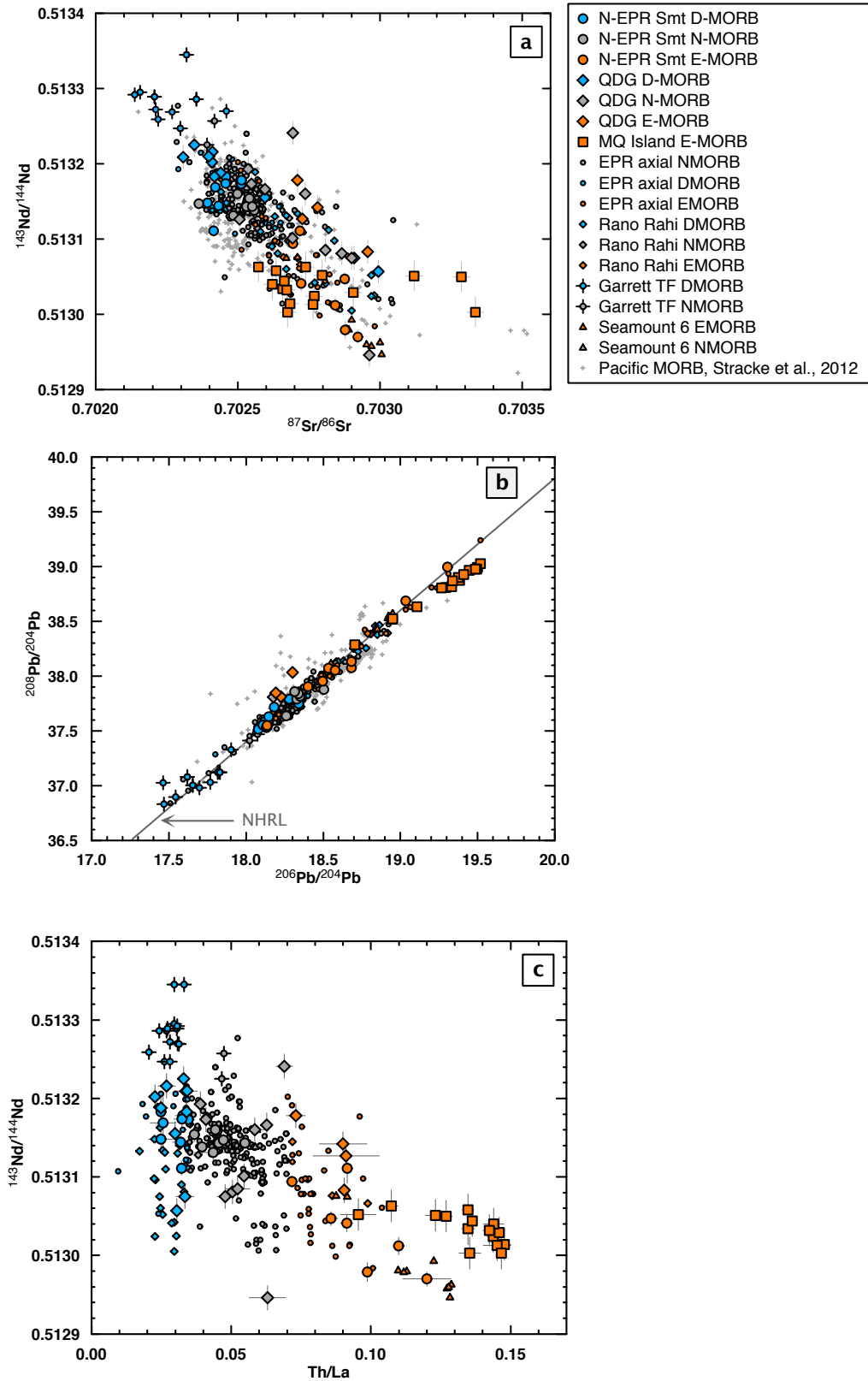


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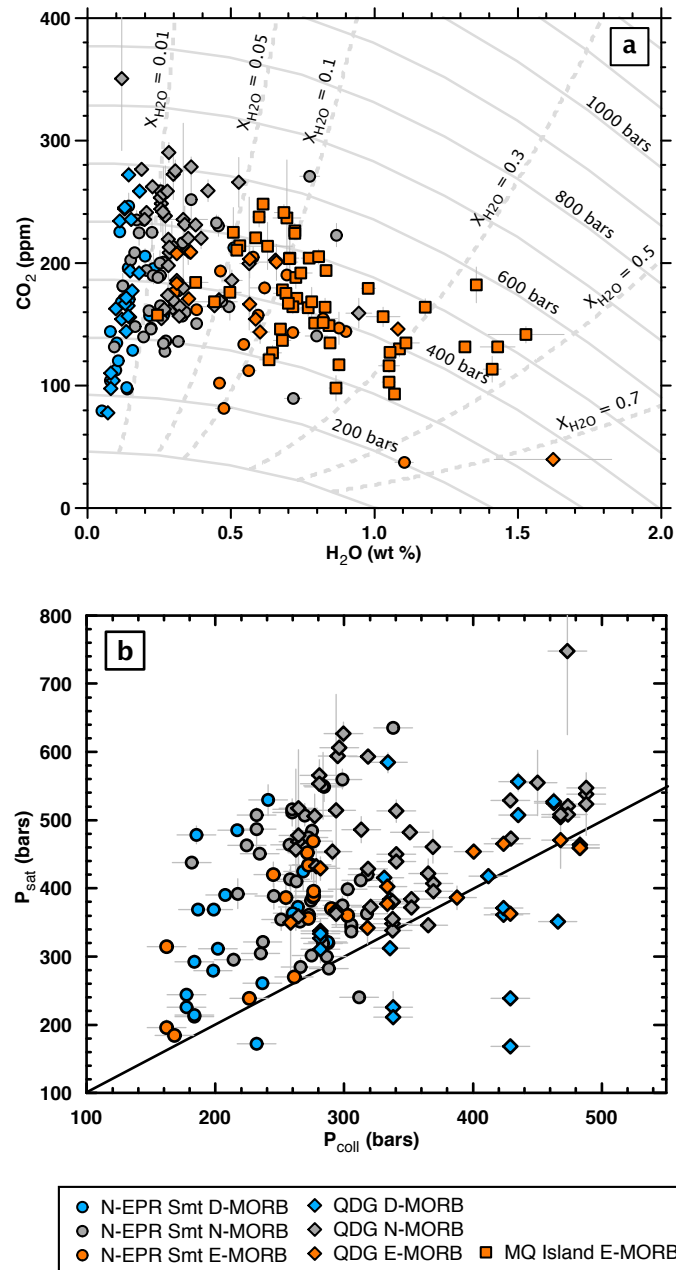


Figure 1-5.

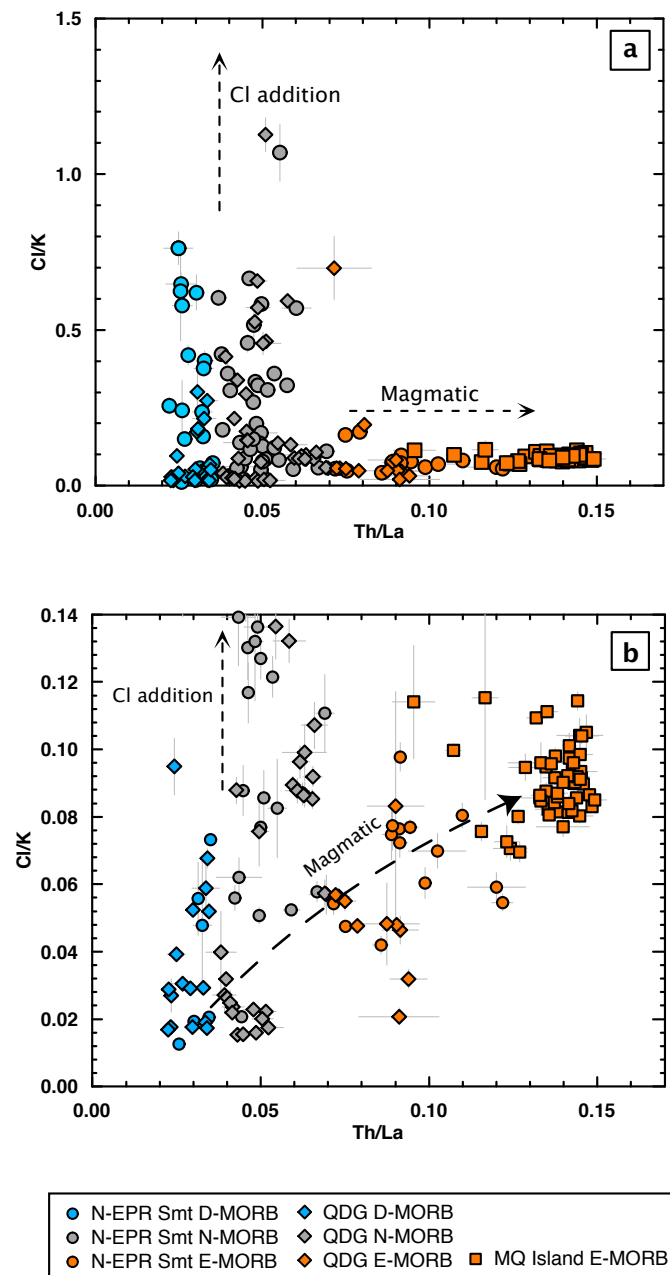


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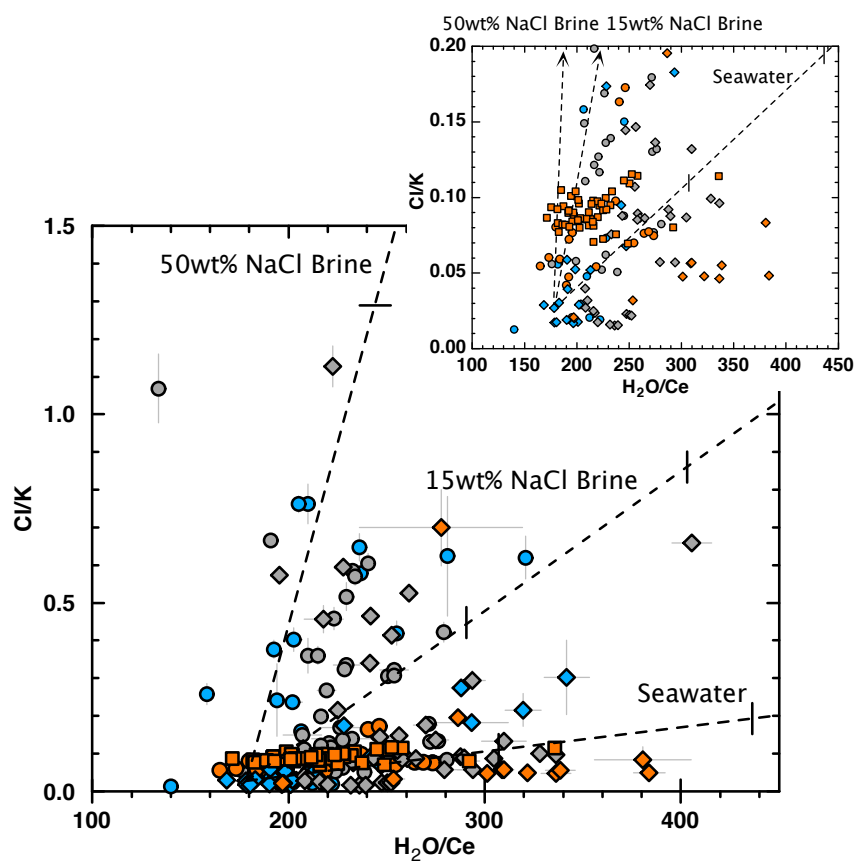


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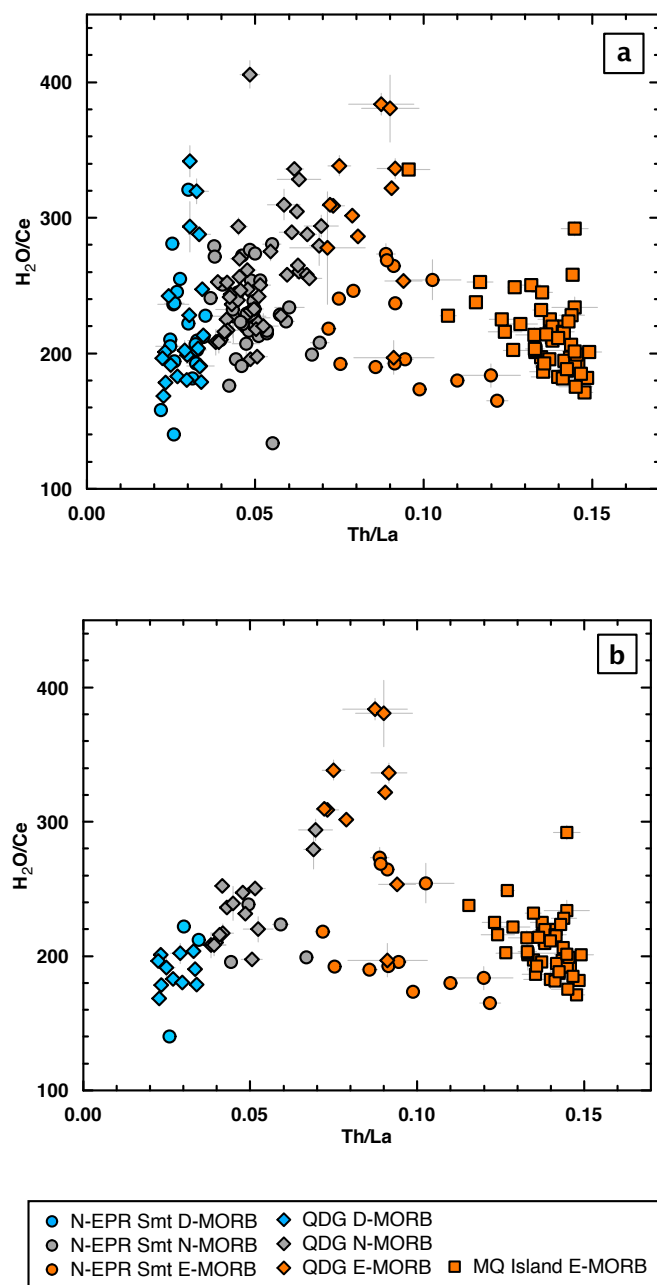


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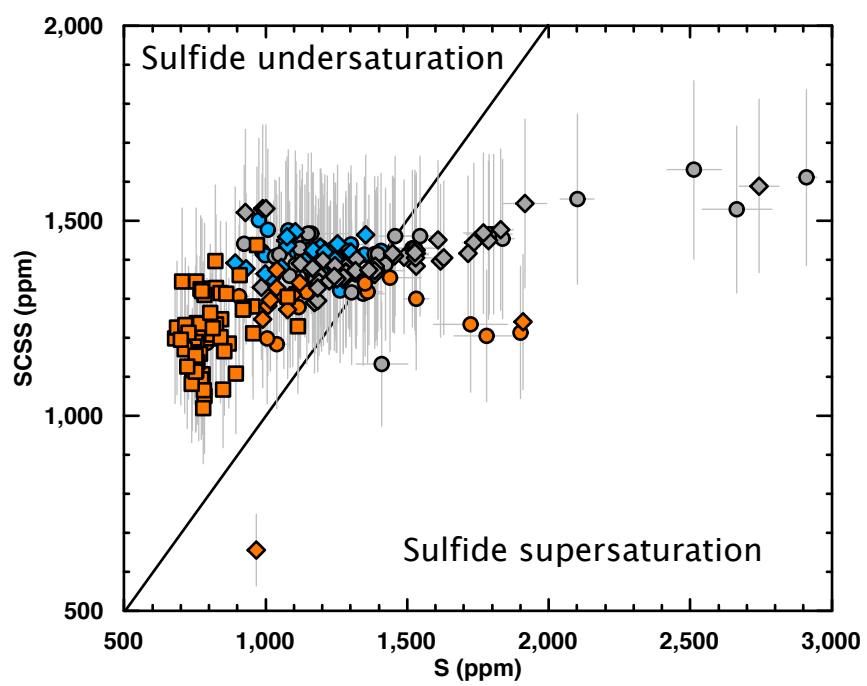


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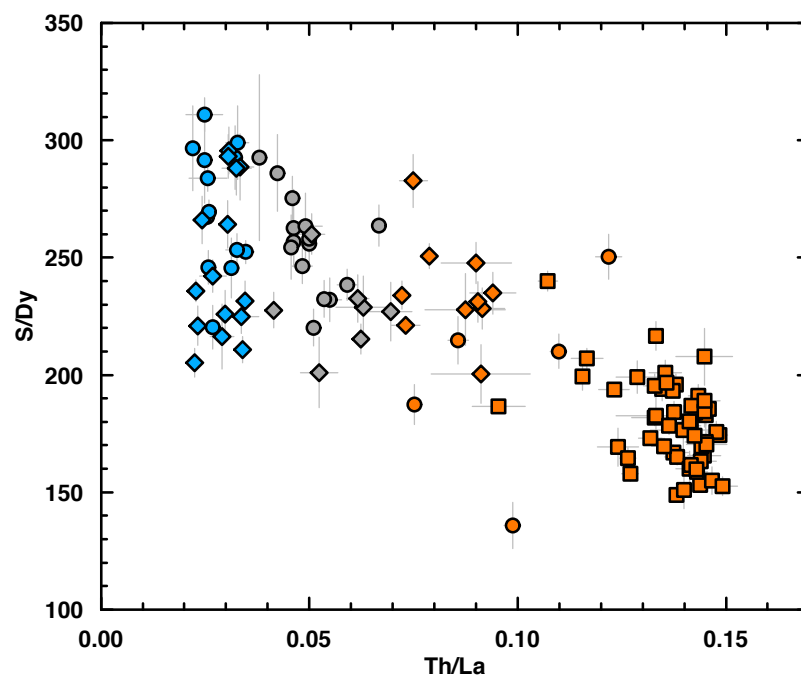


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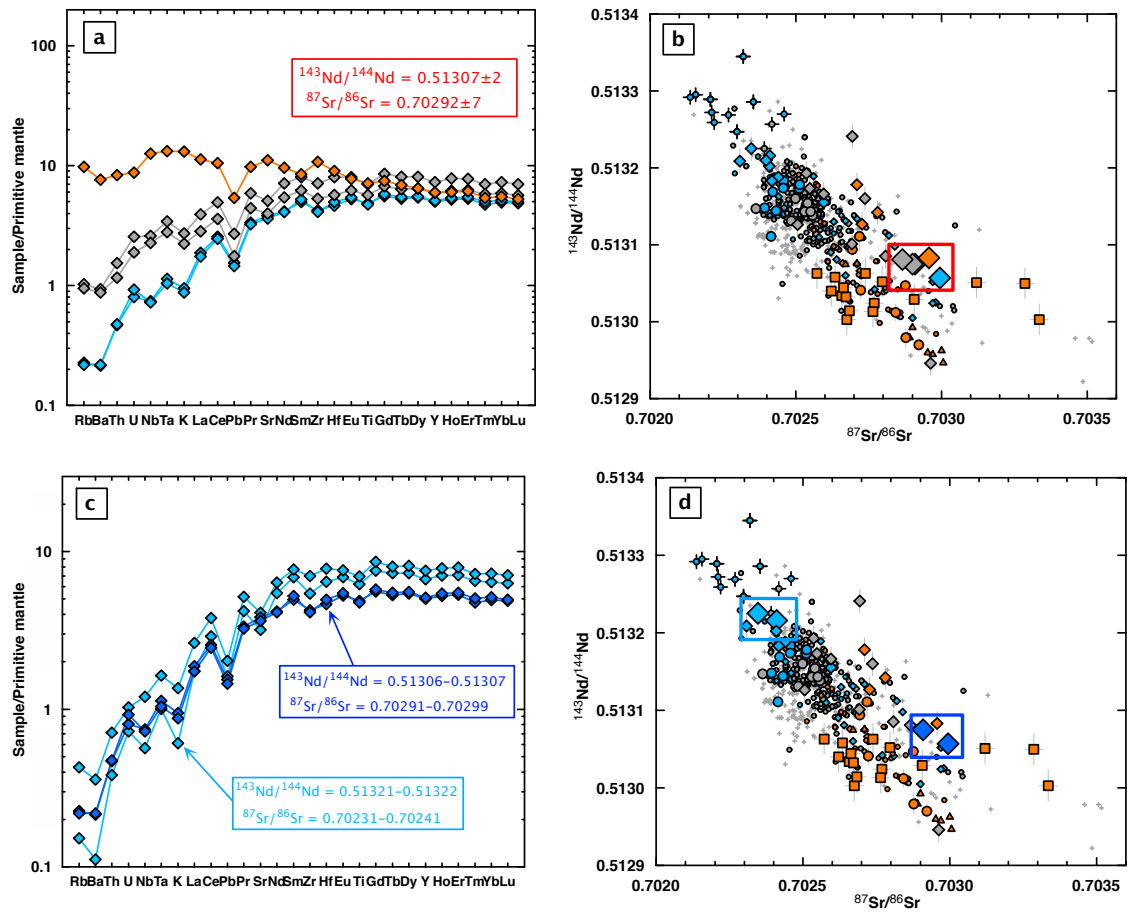


Figure 1-11.

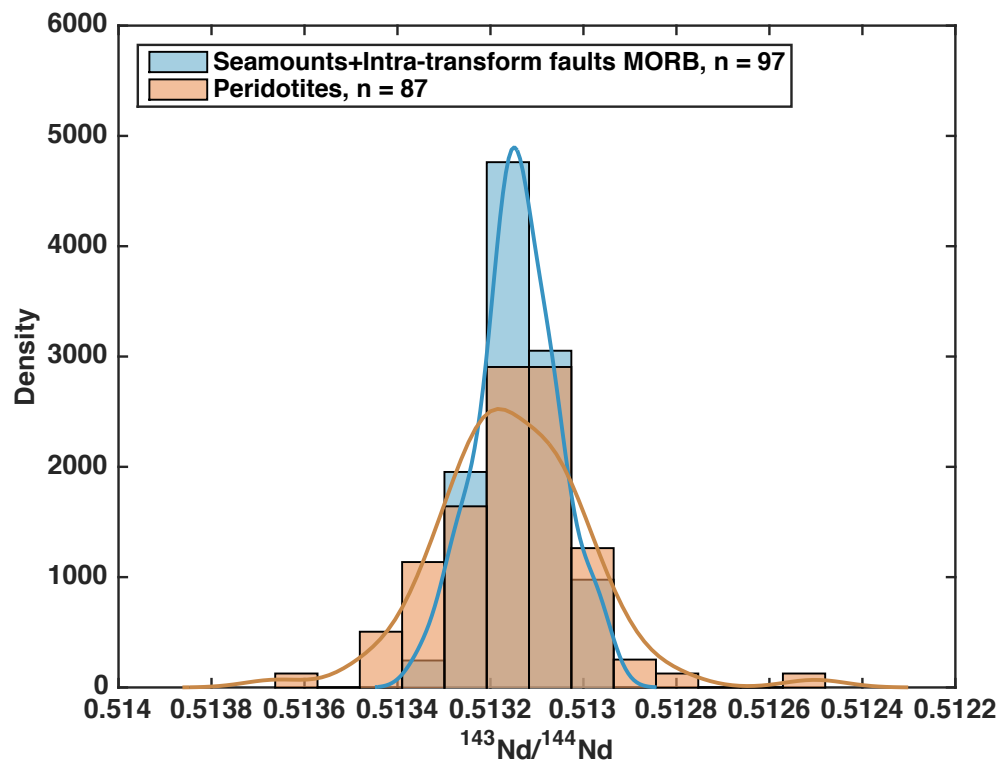


Figure 1-12.

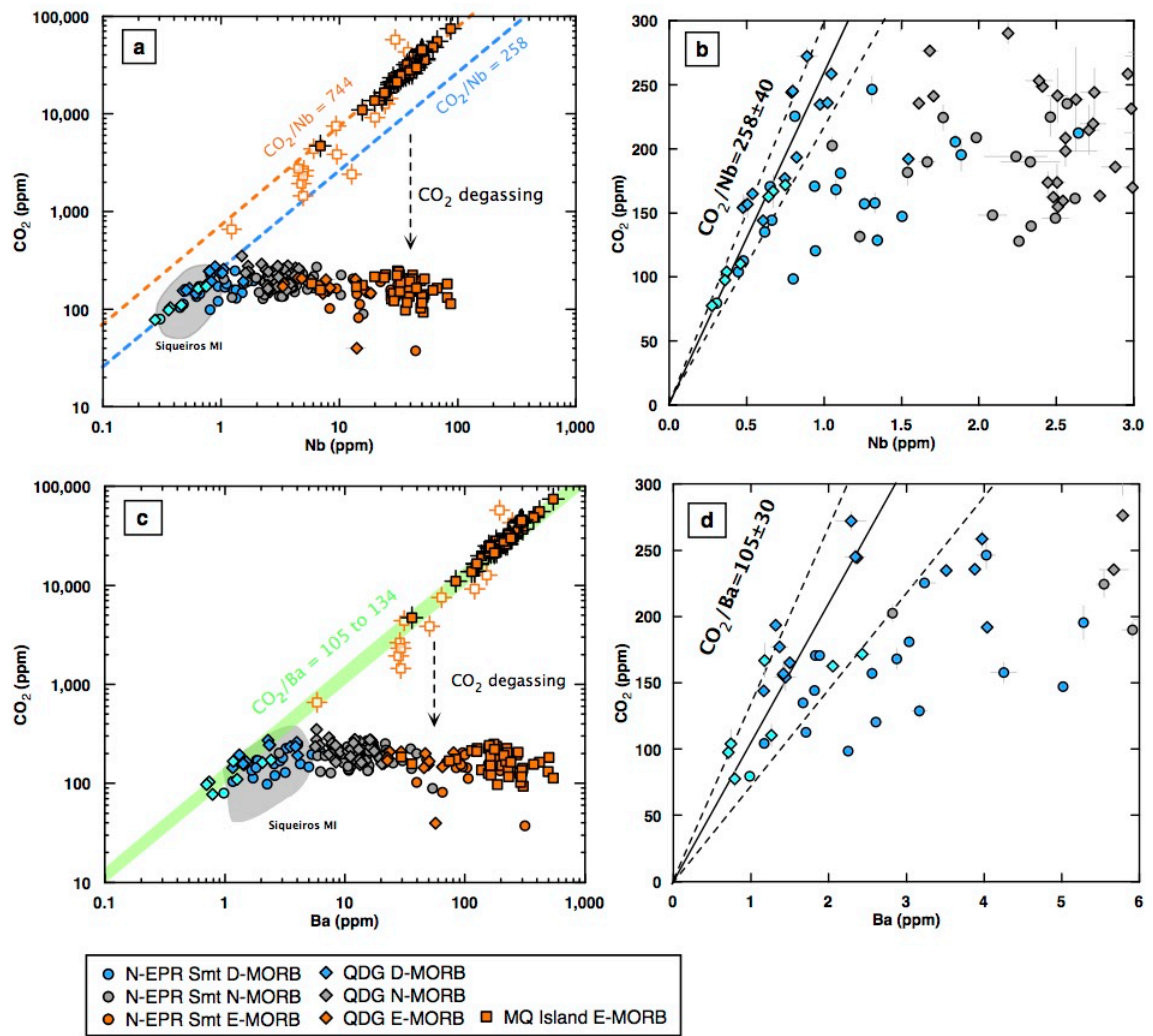


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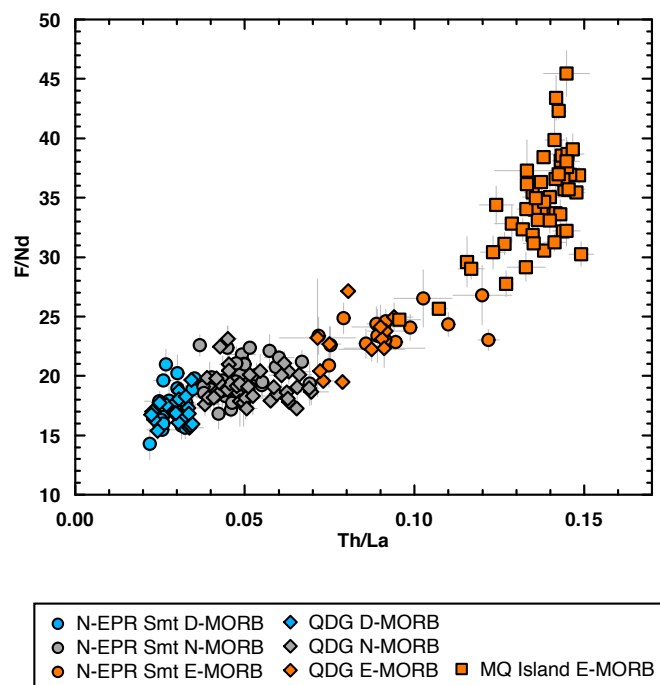


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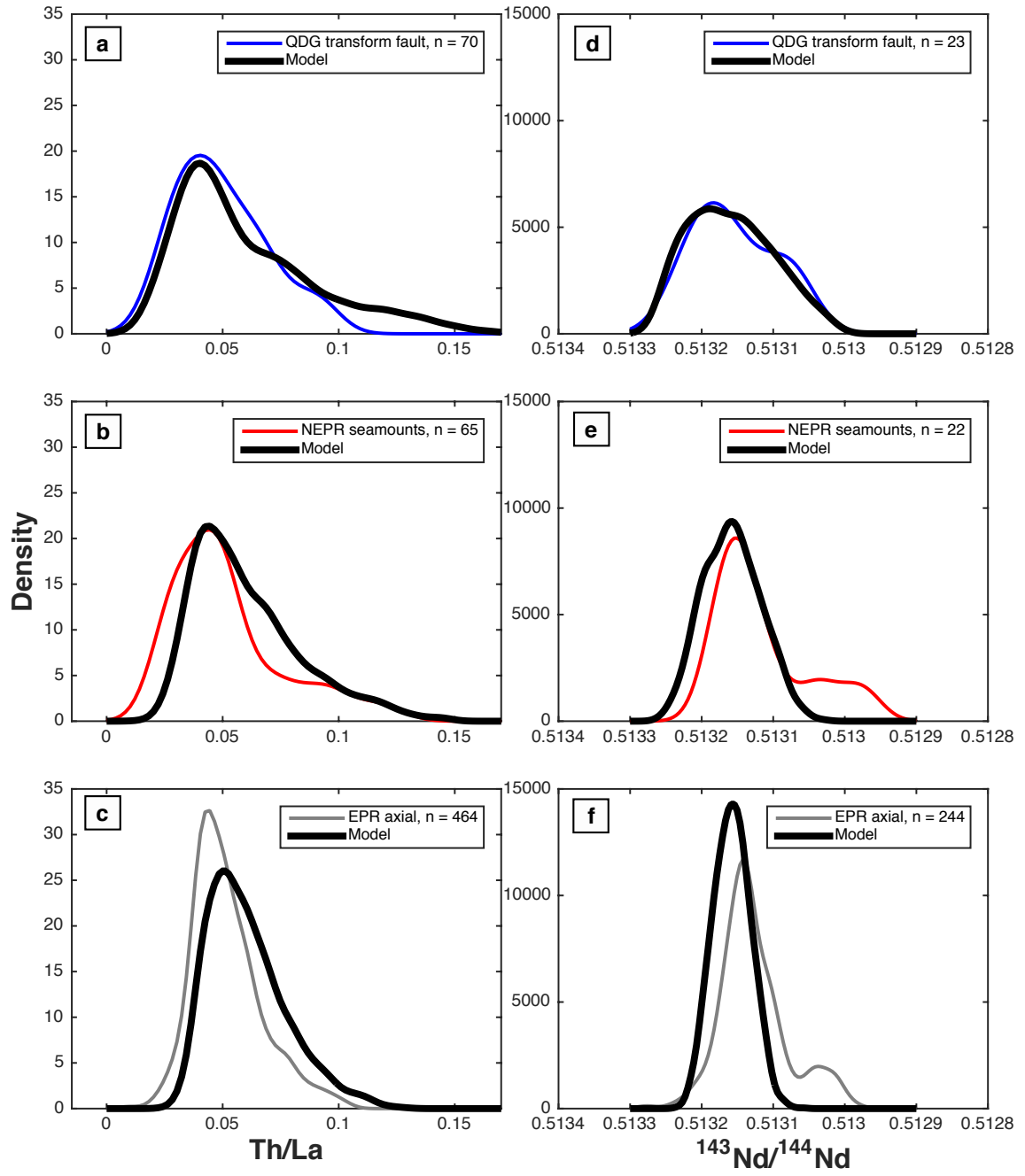


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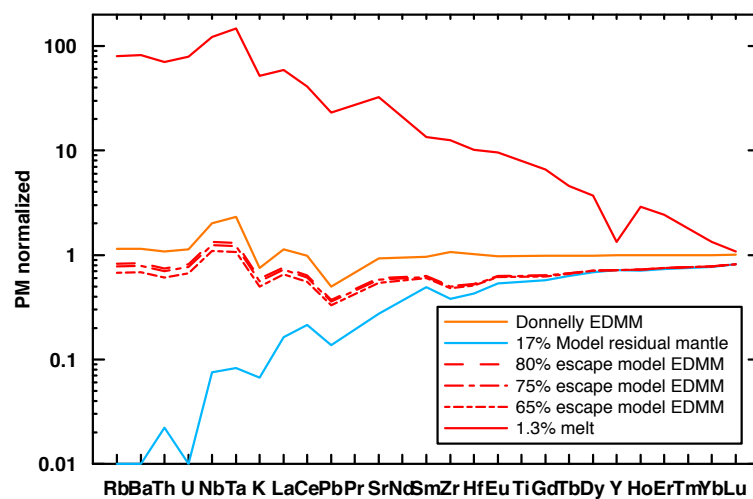


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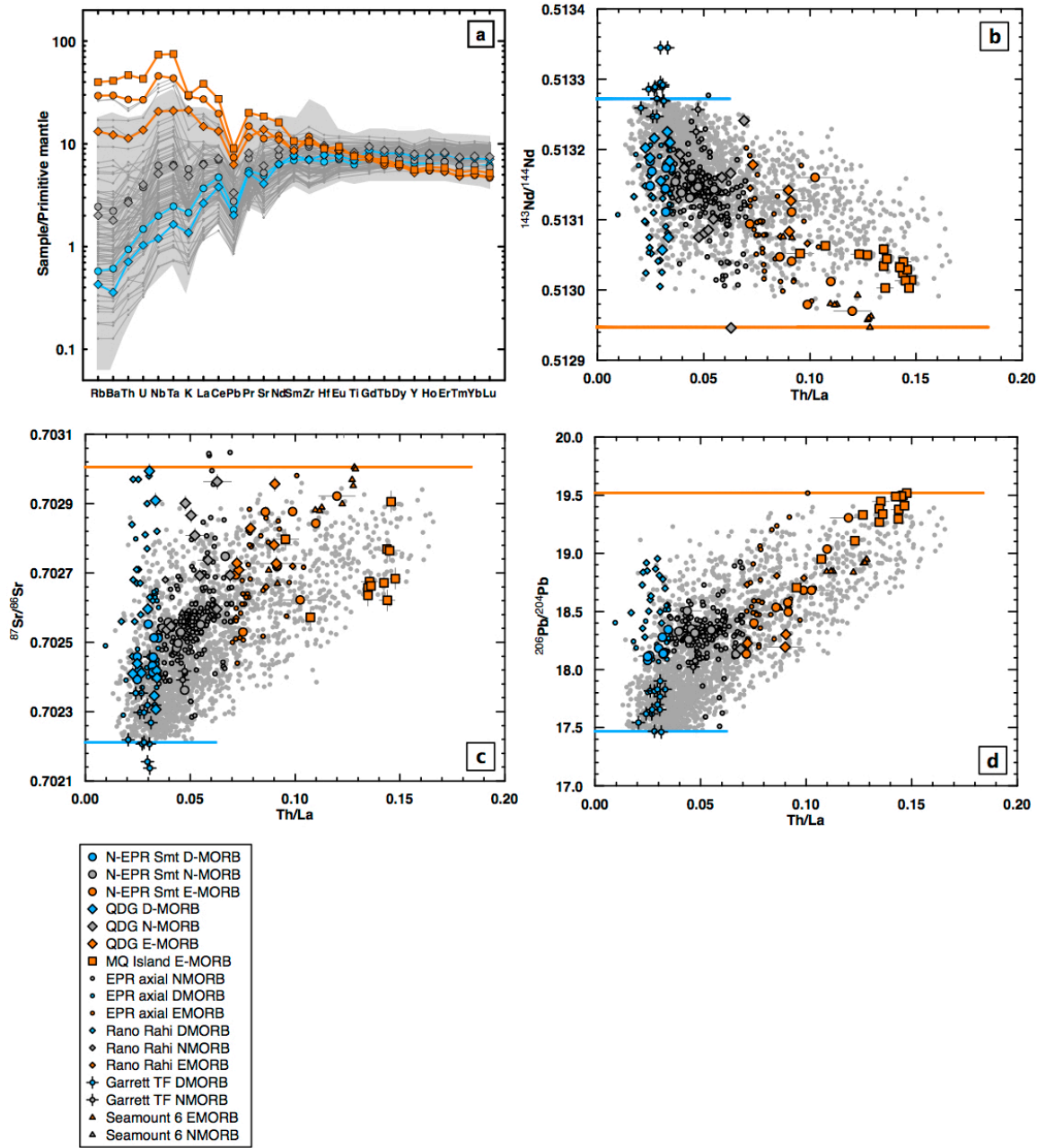


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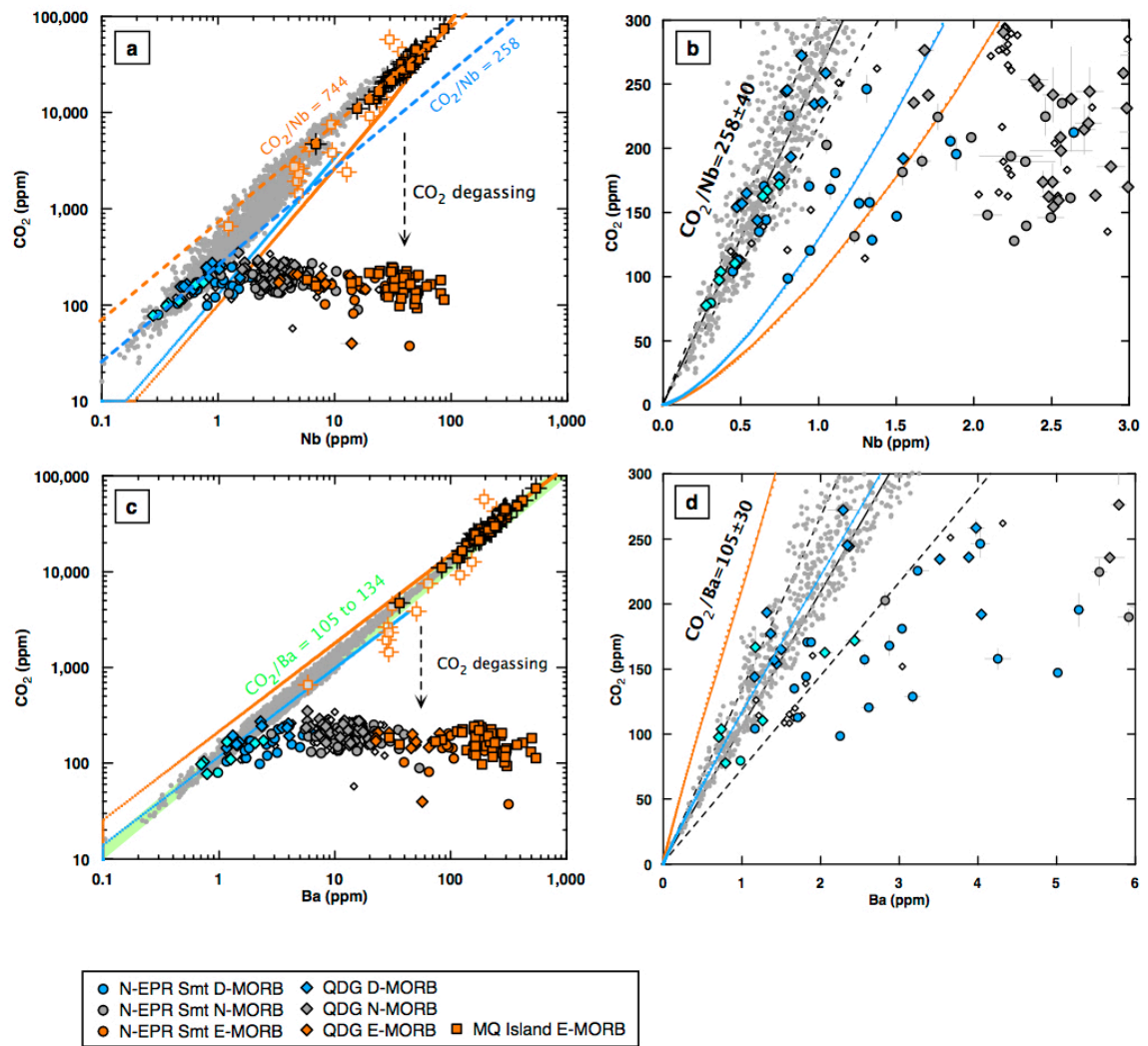


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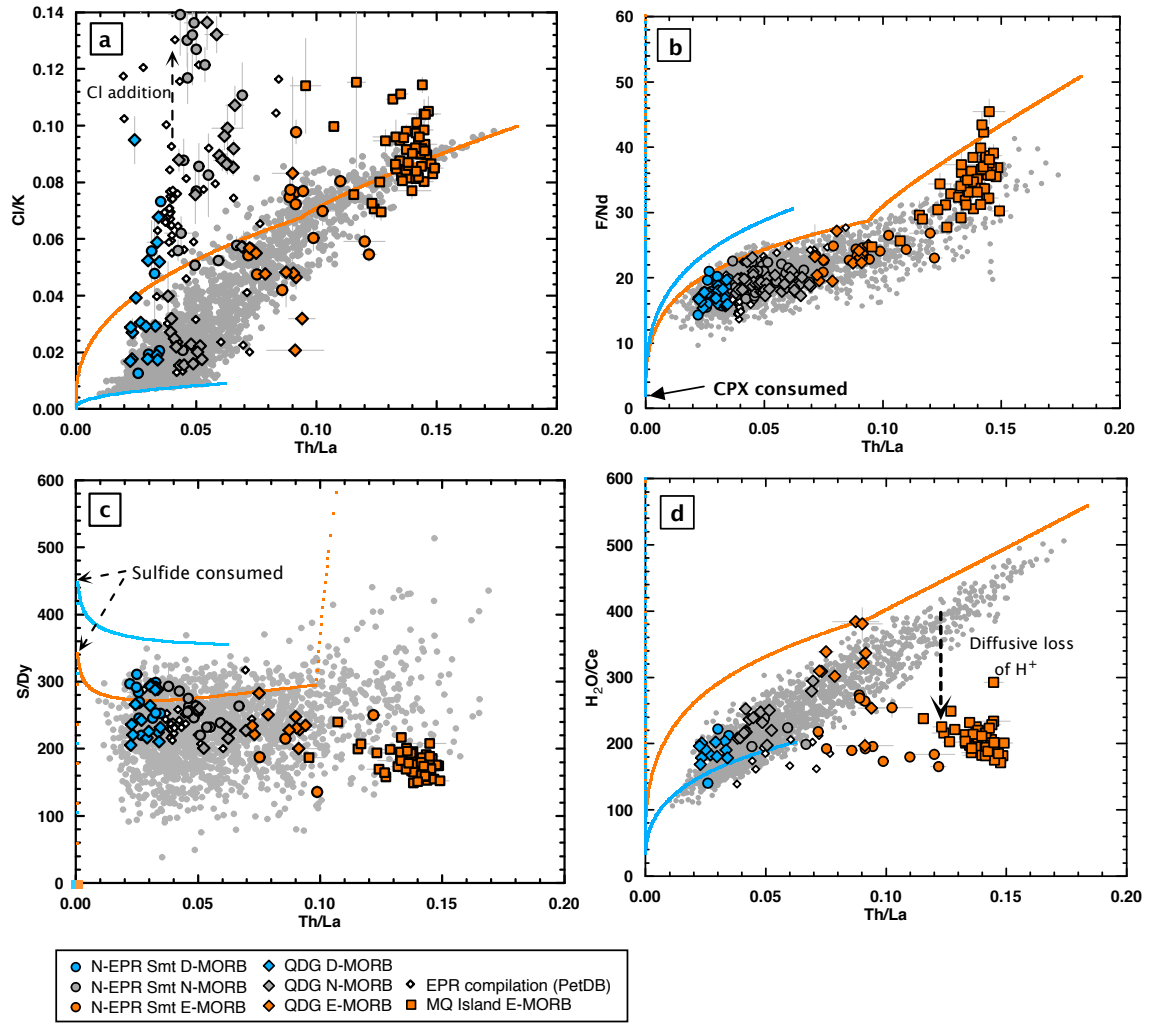


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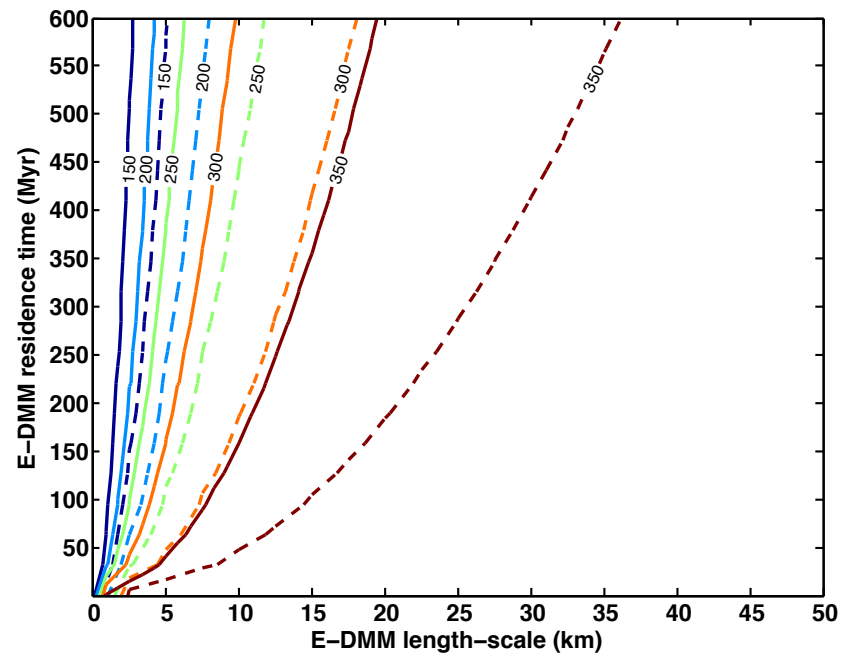


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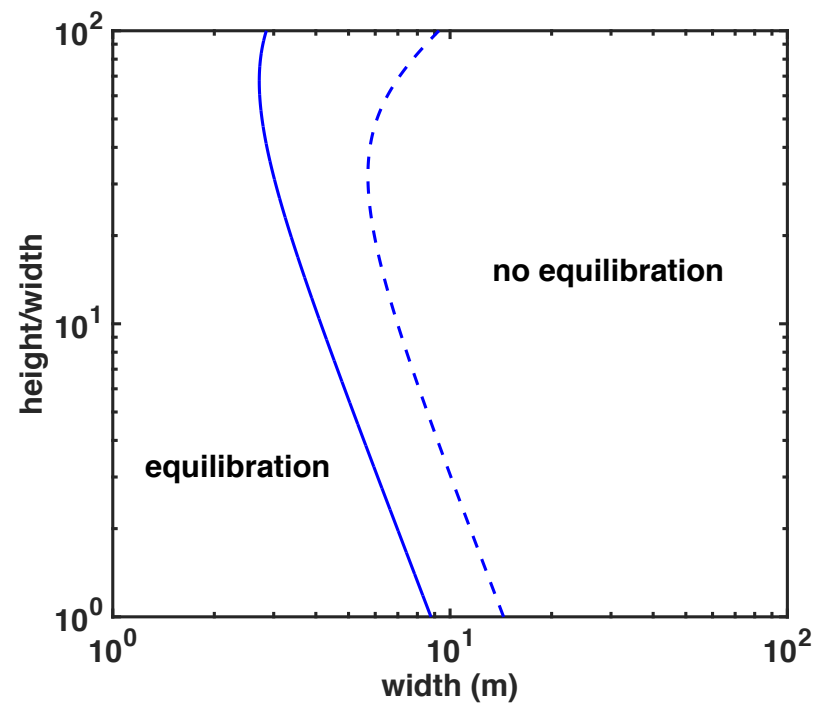


Figure 1-21.

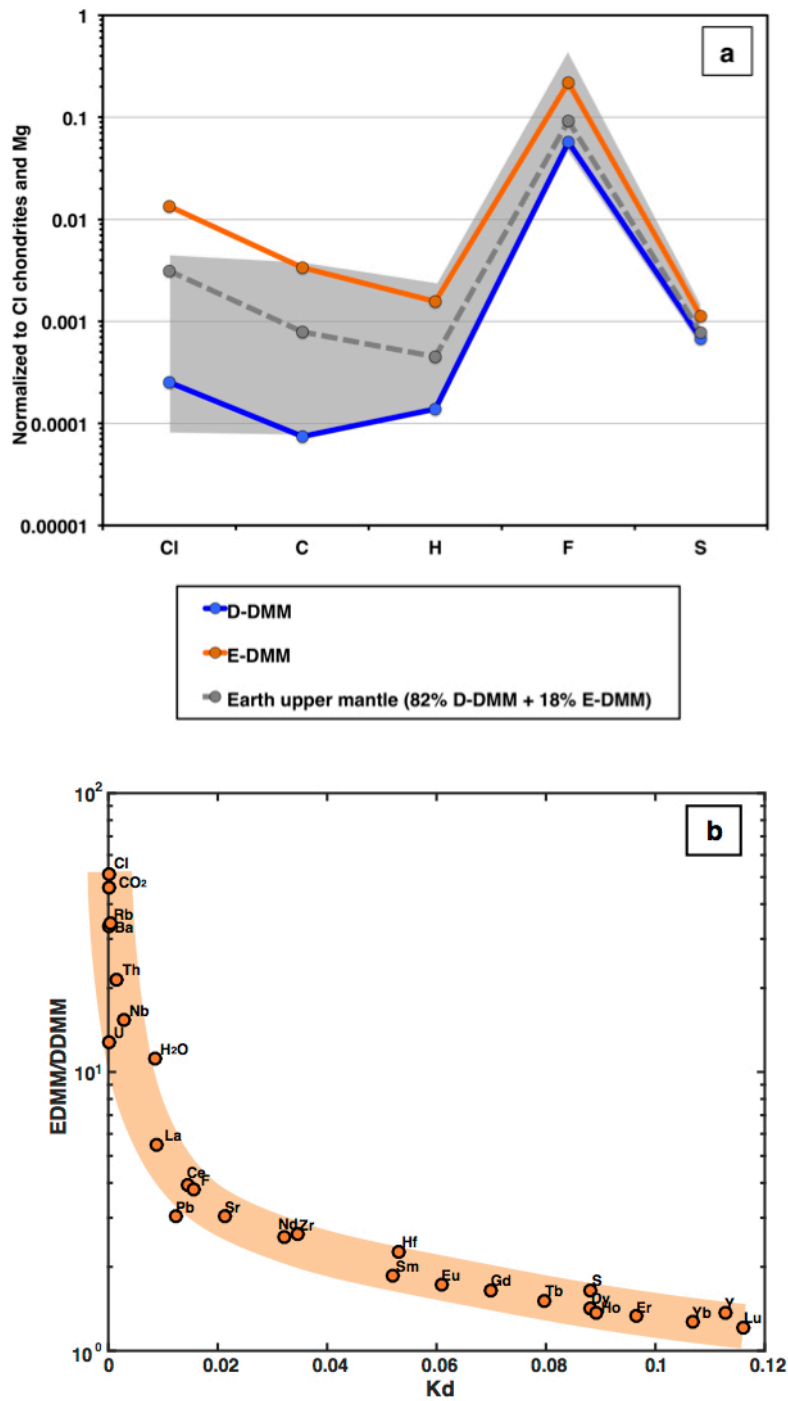


Figure 1-S1.

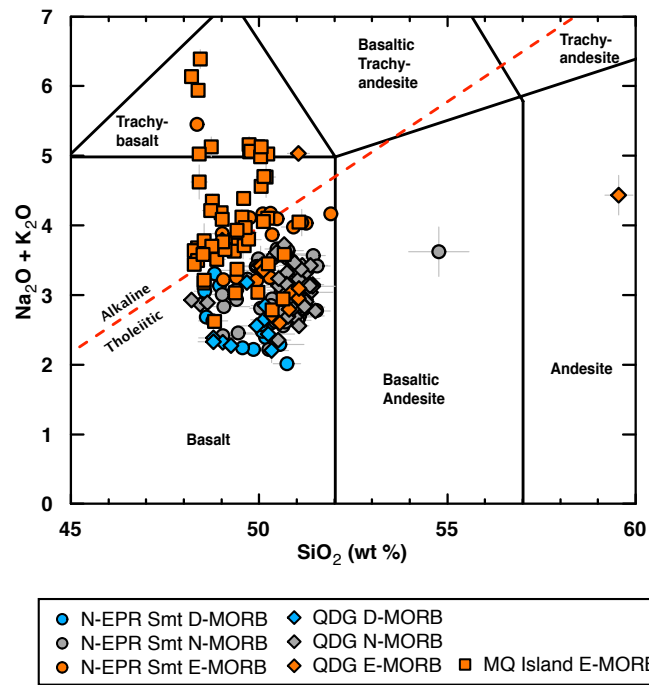


Figure 1-S2.

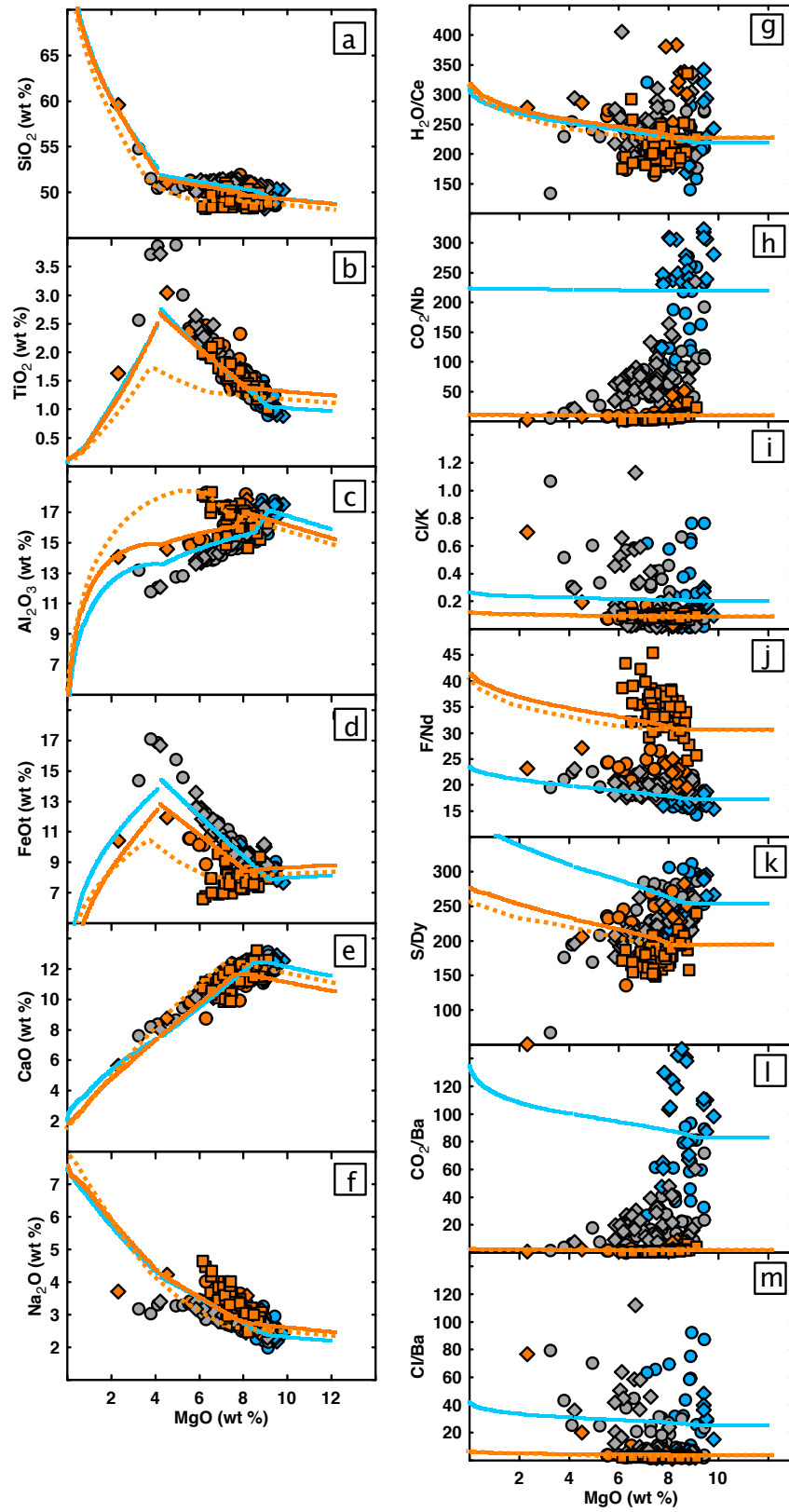


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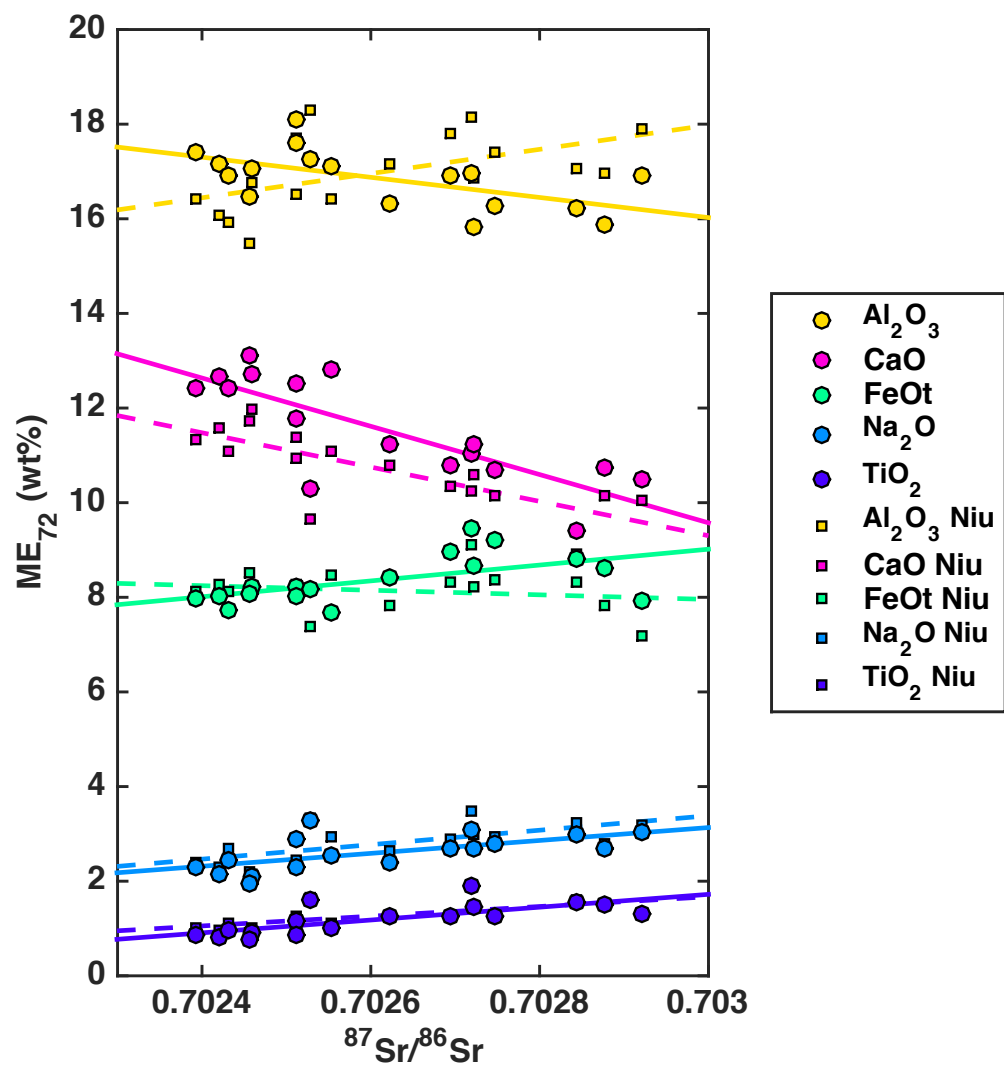


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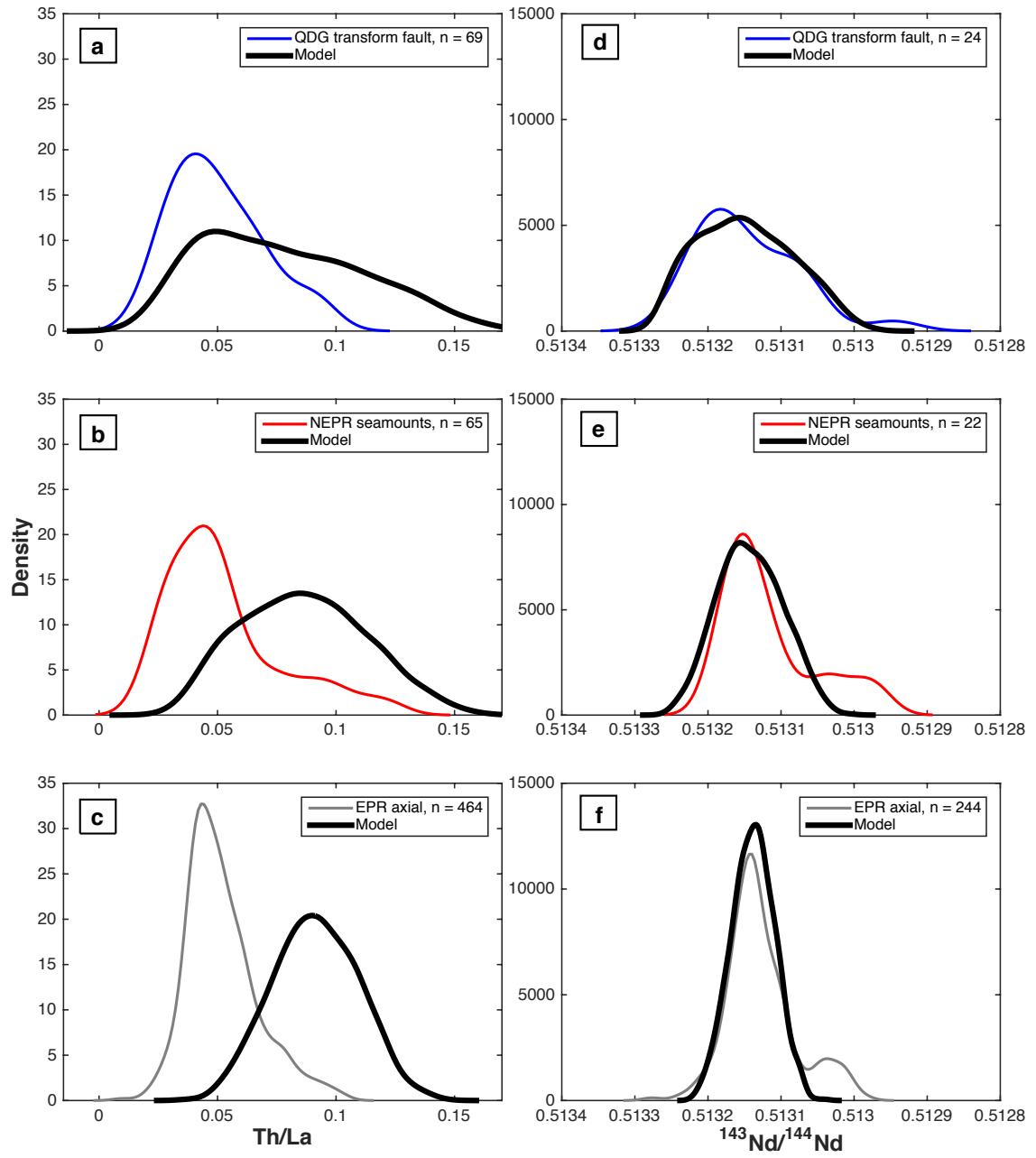


Figure 1-S5.

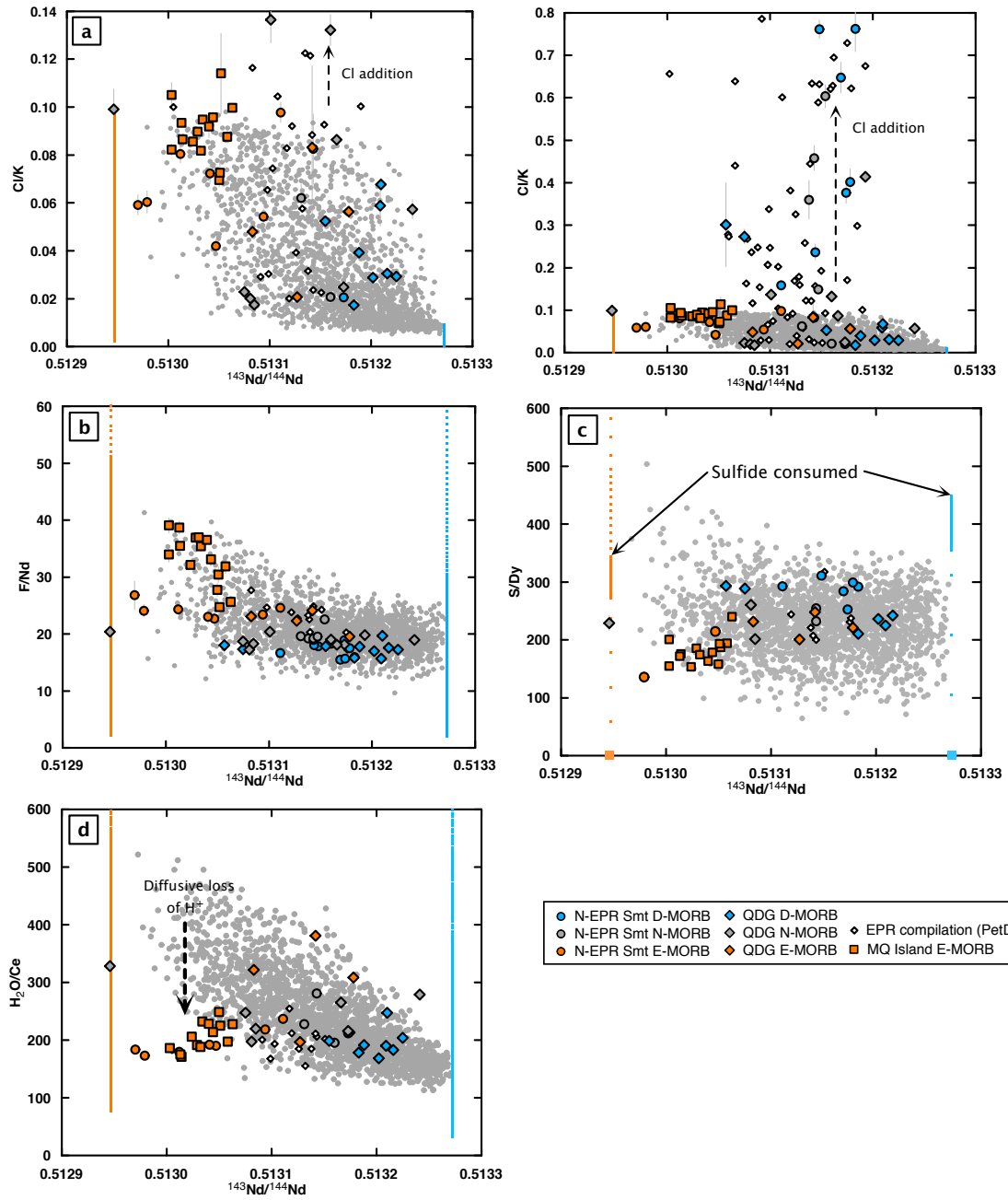


Figure 1-S6.

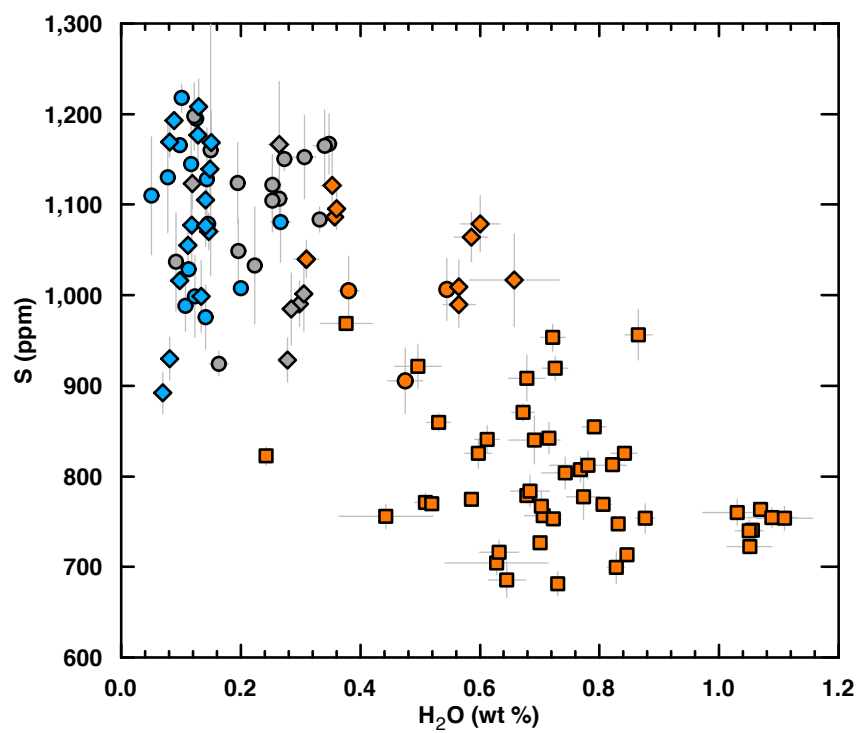


Figure 1-S7.

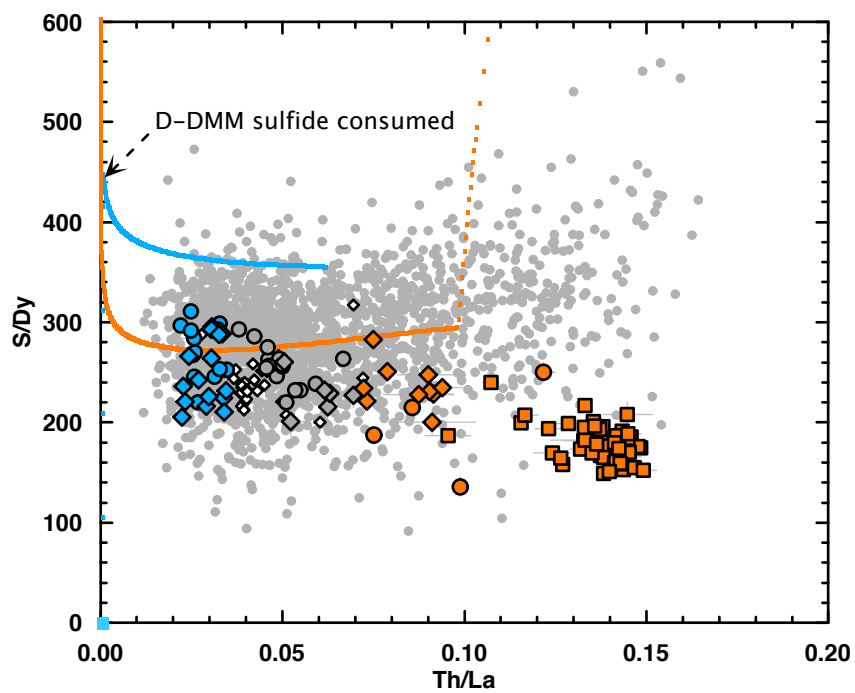


Table 1-1. Estimated volatile element concentration of D-DMM, E-DMM, and the Pacific upper mantle.

Element	D-DMM ^a			E-DMM ^b			Pacific upper mantle (78% D-DMM +22% E-DMM)
	Average (ppm)	Range (ppm)	2 σ (ppm)	Average (ppm)	Range (ppm)	2 σ (ppm)	
CO ₂ ^c	22.3	19.8–24.3	3.5	990	800–1219	220	
CO ₂ ^d	23.8	16.0–32.3	14	1010	866–1184	173	
CO₂	22			990			235
Cl ^e	1.0	0.54–1.70	0.64	19.6	5.24–25.2	9.01	
Cl ^f	0.76	0.33–1.26	0.54	19.5	9.48–32.7	9.59	
Cl ^g	0.87	0.31–1.81	0.91	19	8.75–32.9	8.43	
Cl	0.4			22			5
H ₂ O ^h	80	58.9–93.5	17	517	325–633	184	
H₂O	59			660			191
F ⁱ	8.3	6.9–10.1	1.4	37.8	24.0–55.9	15.7	
F	8			31			13
S ^j	122	97–147	30	126	91–188	39	
S	100			165			114

^aTrace element coccentration from Workman and Hart (2005)

^bTrace element concentration from Donnelly et al., (2004)

^cFrom CO₂/Nb ratio. For CO₂ content of the EMORB we used the CO₂-Cl correlation (refer to section 5.3 for explanation).

^dFrom CO₂/Ba ratio. For CO₂ content of the EMORB we used the CO₂-Cl correlation (refer to section 5.3 for explanation).

^eFrom Cl/K ratio

^fFrom Cl/Nb ratio

^gFrom Cl/Ba ratio

^hFrom H₂O/Ce ratio. For E-DMM H₂O content, we only used the QDG EMORB samples (refer to section 5.3 for explanation).

ⁱFrom F/Nd ratio

^jFrom S/Dy ratio

Bold numbers represent model values.

Table 1-2. Parameters used in the two-component mantle melting-mixing model^a

Parameter	Value	Description
p_{DDMM}	0.78	Solid fraction of D-DMM in the upper mantle
N	16 to 99	Extent of melt aggregation (N = 0 means no aggregation, N= ∞ means complete aggregation)
F_{ext}	1.3%	Degree of melting below which a fraction of EMORB may escape the melt aggregation
f_{escape}	0.65 to 0.8	Fraction of EMORB with $F < F_{\text{ext}}$ that escapes aggregation

^aBased on the model of Rudge et al. 2013

Table 1-3. Parameters used in the H⁺ diffusion model

Parameter	Value	Description
ϕ	0.01	Porosity
D_{ol}^a	2.97×10^{-9}	Diffusivity of H ⁺ in olivine (m ² /s)
D_m^b	8.13×10^{-5}	Diffusivity of H ⁺ in melt (m ² /s)
D_{eff}^c	4.80×10^{-5}	Effective diffusivity of H ⁺ in a partially molten E-DMM (m ² /s)
K_{bulk}^d	0.007	Bulk partition coefficient of H ₂ O between solid and melt
$d\phi/dz^e$	0.0333	Melt production rate of peridotite assuming 1kbar = 3km (%/km)
dz/dt	0.1	EPR mantle upwelling rate (m/yr)
$\zeta + 4/3\eta$	$10^{18f,g}$	Viscosity of EDMM solid matrix (Pa s)
η	$1^{g,h}$	Viscosity of EDMM partial melt (Pa s)
ρ_m	3300	Density of EDMM solid (kg/m ³)
ρ_s	2800	Density of EDMM melt (kg/m ³)
k_ϕ	$a^2\phi^2/3000^i$	Permeability
a	0.001	Grain size (m)
g	10	Acceleration due to gravity (m/s ²)

^aKohlstedt and Mackwell 1998, T = 1673K. Average diffusivity of H⁺ charge compensated by a flux of polarons-electrons in olivine.

^bZhang et al. 2007, T = 1673K, 1 wt% H₂O

^cEq. A12 from Lee 1995

^dHauri et al. 2006

^eAsimow et al. 2004 (0.1%/kbar)

^fJin et al. (2001).

^gMcKenzie (1985).

^hMurase and McBirney (1973).

ⁱMcKenzie (2000).

Reference	Mantle source	CO ₂ (ppm)	Cl (ppm)	H ₂ O (ppm)	F (ppm)	S (ppm)
This study	D-DMM	22	0.4	59	8	100
This study	E-DMM	990	22	660	31	165
This study	Pacific upper mantle (78% D-DMM +22% E-DMM)	235	5	191	13	114
Schilling et al., 1980	Large ion lithophile element depleted asthenosphere	-	7.3	-	65	-
Javoy and Pineau, 1991	Upper mantle	1100	-	-	-	-
Michael 1988	Incompatible-element-depleted upper mantle	-	-	140±40	-	-
Michael 1988	Incompatible-element enriched upper mantle	-	-	350±100	-	-
Sobolev and Chaussidon, 1996	depleted MORB mantle source	-	-	80 - 330	-	-
Sobolev and Chaussidon, 1996	T-MORB mantle source	-	-	190 - 290	-	-
Sobolev and Chaussidon, 1996	E-MORB mantle source	-	-	200 - 950	-	-
Marty and Tolstikhin 1998	Upper mantle	136±83	-	-	-	-
Marty and Tolstikhin 1998	EMORB type upper mantle	198±140	-	-	-	-
Dixon et al., 2002	DMM	-	-	100	-	-
Saal et al., 2002	MORB mantle source	72±19	1±0.5	142±85	16±3	146±35
Salters and Stracke, 2004	Depleted mantle	50.3±12	0.51±0.09	116±58	11±4.5	119±30
Workman and Hart, 2005	DMM	36±12	0.38±0.25	70 - 160	-	-
Bezos et al., 2005	Depleted mantle source	-	-	-	-	190±40
Le Roux et al., 2006	MORB mantle	-	5±1	128±5	17±1	129±6
Hirschmann and Dasgupta, 2009	DMM	60±35	-	110±55	-	-
Beyer et al., 2012	depleted MORB mantle	-	-	-	12	-
Marty et al., 2012	Depleted mantle	73±29	-	150±50	-	-
Halliday, 2013	Earth mantle (Model 3 - basaltic glass)	163±76	-	300±100	-	-
Le Voyer et al., 2015	DMM	-	1	110	12	-

[illegible]

^dFor the Macquarie Island samples, we use the estimated paleo-ridge depth between 2000 to 3500 m b.s.l. from Portner et al. (2010).

[illegible]

[illegible]

Location Sample Latitude Longitude Depth	0262-1F D13A -3.72 -103.41 4072-4148	0262-1F D45-A -4.63 -105.34 2564-3000	0262-1F D9A -3.72 -103.05 4608-4709	0262-1F D10A -3.72 -103.22 4545-4711	0262-1F D49-B -4.63 -105.34 2641-3000	0262-1F D45-C -4.63 -105.34 2614-3010	0262-1F D25-A -3.99 -104.20 3288-3378	0262-1F D12-B -3.72 -103.32 4670-4693	0262-1F D15A-B-C -3.73 -103.59 4169-4250	0262-1F D14A -3.75 -103.51 4267-4358	0262-1F D23A -3.98 -104.14 2749-2818	0262-1F D18-B -3.75 -103.51 4267-4358	0262-1F D2A -3.64 -102.63 2880-2963	0262-1F D24-C -4.01 -104.16 2594-2700
Major element (wt%)	SiO ₂ 49.88 Al ₂ O ₃ 15.46 FeO ^a 9.28 MgO 0.18 8.52 CaO 11.63 Na ₂ O 2.67 K ₂ O ^a 0.04 P ₂ O ₅ 0.01 Total 100.21	49.03 0.98 17.45 8.51 0.17 9.42 12.46 0.03 0.03 0.01 100.44	49.40 1.13 16.53 8.28 0.15 8.76 12.33 0.03 0.03 0.02 100.34	51.08 1.42 15.61 9.30 0.21 8.06 11.99 0.04 0.04 0.12 100.62	49.25 0.96 17.30 8.46 0.15 9.42 12.64 0.08 0.08 0.10 100.52	48.79 0.99 17.48 8.59 0.16 9.42 12.46 0.03 0.03 0.12 100.30	50.85 1.42 15.32 9.79 0.20 7.73 11.99 0.07 0.07 0.14 100.53	49.52 1.23 16.25 8.71 0.17 8.82 11.95 0.05 0.05 0.12 100.52	49.58 1.22 17.56 8.69 0.15 8.82 11.73 0.05 0.05 0.12 100.52	51.08 1.42 15.17 9.57 0.16 7.78 12.38 0.05 0.05 0.12 100.45	51.14 1.36 14.42 15.17 0.21 6.31 10.94 0.05 0.05 0.12 100.24	50.87 1.36 15.03 9.46 0.19 7.79 12.20 0.05 0.05 0.12 99.86	50.80 1.33 15.40 9.25 0.19 8.02 12.12 0.08 0.08 0.12 100.21	51.14 1.90 14.40 11.28 0.23 6.70 11.19 0.12 0.12 0.12 100.28
Trace element (ppm)	K ^a 342.66 Li 5.61 Sc 37.66 V 259.73 Cr 328.78 Mn 47.74 Ni 151.19 Cu 62.14 Zn 68.42 Rb 0.13 Sr 76.32 Y 21.59 Zr 82.73 Nb 0.82 Ba 1.32 La 2.07 Ce 4.53 Pr 1.45 Nd 84.7 Sm 3.31 Eu 1.20 Tb 0.81 Tm 0.52 Yb 0.48 Ho 3.65 Er 1.16 Tm 3.46 Yb 3.22 Hf 2.33 Ta 0.06 Pb 0.30 Th 0.05 U 0.02	227.23 4.31 34.14 199.02 328.78 46.19 92.90 58.91 14.14 76.32 21.59 44.69 0.49 0.80 0.42 2.22 4.53 5.20 2.52 2.01 0.81 0.52 0.48 0.78 2.33 0.50 2.18 1.31 0.04 0.23 0.04 0.02	241.63 5.05 38.21 228.53 328.78 42.12 140.95 63.34 0.21 76.32 26.52 56.90 0.64 0.64 2.05 1.42 1.72 1.03 6.38 2.52 1.01 0.67 0.54 0.96 2.83 0.41 2.70 1.76 0.05 0.24 0.05 0.02	323.61 5.79 27.80 277.80 328.78 40.60 110.49 71.34 0.26 76.32 32.53 73.55 0.84 2.34 1.72 1.30 7.96 3.10 1.20 0.80 0.80 3.46 3.18 2.10 1.34 0.06 0.29 0.05 0.02	210.78 4.37 34.24 264.51 328.78 47.00 92.96 59.58 0.13 76.32 21.94 43.14 0.48 1.44 1.13 0.83 5.14 2.12 0.84 0.54 0.54 2.40 3.8 2.27 1.40 0.04 0.22 0.04 0.02	239.22 4.27 33.63 197.61 328.78 43.45 156.39 92.76 0.14 76.32 21.34 45.31 0.51 1.41 1.24 0.87 5.21 2.08 0.82 0.54 0.54 2.31 2.22 1.34 0.04 0.24 0.04 0.02	573.33 6.50 30.58 260.58 328.78 42.45 90.02 72.18 0.39 76.32 36.17 97.55 1.55 4.04 2.86 1.74 9.95 3.71 1.28 0.87 0.87 3.79 3.51 2.22 1.56 0.11 0.41 0.10 0.03	374.55 53.2 38.86 263.45 328.78 41.85 154.50 72.11 0.38 76.32 21.67 66.92 1.55 3.51 1.84 1.64 1.30 7.66 2.88 0.74 0.74 3.15 2.88 2.07 2.00 0.28 0.06 0.02	294.59 4.96 32.66 219.02 328.78 41.74 158.07 75.41 0.27 76.32 25.62 75.79 0.75 2.43 2.62 1.39 8.29 1.08 0.66 0.66 3.15 2.80 2.38 2.07 0.36 0.36 0.02	388.71 5.61 39.17 285.17 328.78 42.42 58.75 81.93 72.05 0.44 76.32 29.76 70.82 1.05 3.98 2.06 1.35 7.81 2.96 1.12 0.74 0.74 3.19 3.00 2.01 0.33 0.07 0.03	1019.66 7.84 42.19 364.66 328.78 45.64 38.89 67.75 95.27 0.72 76.32 42.59 128.06 2.56 7.37 2.64 1.35 7.84 2.91 1.65 1.08 0.74 0.74 3.25 3.01 2.07 0.31 0.16 0.06	424.51 5.72 40.99 288.78 328.78 42.42 58.08 77.68 67.32 0.44 76.32 29.68 71.32 1.02 3.88 2.64 1.31 7.84 2.91 1.14 0.74 0.74 3.17 3.01 2.07 0.31 0.16 0.06	641.13 5.51 43.61 285.02 328.78 45.64 100.77 79.47 87.18 0.57 76.32 30.66 121.64 1.68 5.79 2.63 1.48 8.35 3.08 1.14 0.75 0.75 3.25 3.00 2.07 0.31 0.16 0.06	969.79 6.99 43.20 338.03 328.78 43.51 46.95 65.98 87.18 0.78 76.32 40.02 121.64 1.73 7.83 2.63 1.48 8.35 4.21 1.53 1.08 0.75 0.75 3.30 3.00 2.07 0.31 0.16 0.06
Isotopic composition ^b	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513094	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513057	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513209	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513075	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513075	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513077	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513077	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513183	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513077	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513211	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513183	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513211	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513211	¹⁴³ Nd/ ¹⁴⁴ Nd 0.513211
Volatiles (ppm)	H ₂ O (wt%) 191.35 F 141.55 S 1139.64 Cl 5.77 P ₂ O ₅ 41.8 P ₂ O ₅ 417.5	155.81 0.15 93.77 1070.45 14.22 281.5 351.5	162.67 0.10 99.83 1076.01 14.22 465.9 351.5	245.12 0.13 134.68 1176.89 14.22 462.8 527	154.15 0.12 89.02 1077.51 57.63 281.5 333.5	156.87 0.14 95.18 1076.49 51.41 281.5 311	191.96 0.18 162.27 124.25 10.90 331.3 415.5	234.49 0.11 116.29 1064.76 6.47 468.2 504.5	171.71 0.13 140.00 998.53 5.18 423.7 371.5	258.52 0.19 153.42 1319.34 26.33 435 586.5	198.13 0.26 235.07 1165.82 40.57 22.07 435	235.80 0.15 125.04 1185.82 137.80 264.2 507.5	276.42 0.19 155.59 1449.86 157.80 264.2 517.5	238.53 0.27 222.77 1449.86 30.91 264.2 517.5

Location	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	QMG-ITF	
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Location Sample Latitude Longitude Depth	Q05-TF 481-8002	Q06-TF 461-8600	Q08-TF 2700-2774	Q09-TF 3008-1185	Q09-TF 3600-7949	Q09-TF 3471-3551	Q09-TF 2770-2823	Q09-TF 3583-3724	Q09-TF 3044-3126	Q09-TF 2858-3005	Q09-TF 4600-4861	Q09-TF 4400-4601	Q09-TF 2592-2649	Q09-TF 3341-3403
Major element (wt%)														
SiO ₂	51.14	50.77	51.26	51.36	51.37	50.51	51.12	50.46	50.66	51.23	50.51	50.90	50.06	51.27
TiO ₂	1.71	1.44	2.08	2.19	1.98	2.48	2.26	2.49	3.72	2.09	1.15	1.66	2.63	1.51
Al ₂ O ₃	15.24	15.76	14.46	13.86	14.44	14.27	14.01	13.62	12.10	14.10	13.90	13.54	13.62	14.89
FeO	10.30	10.49	10.30	10.30	10.30	10.30	10.30	10.30	10.30	10.30	10.30	10.30	10.30	10.30
MgO	0.19	0.20	0.21	0.25	0.23	0.22	0.21	0.22	0.29	0.23	0.15	0.18	0.24	0.18
MnO	7.50	8.12	6.66	6.05	6.92	6.63	6.19	5.85	4.22	6.87	9.08	5.84	6.87	7.51
CaO	11.54	11.96	10.99	9.95	11.63	10.08	10.44	10.31	8.02	11.07	12.34	11.67	10.12	12.26
Na ₂ O	2.79	2.62	3.19	3.29	2.92	3.18	3.18	3.40	3.41	2.79	2.28	2.66	3.18	2.74
K ₂ O	0.11	0.08	0.14	0.13	0.12	0.16	0.19	0.21	0.31	0.14	0.06	0.14	0.23	0.10
P ₂ O ₅	0.16	0.12	0.21	0.23	0.20	0.24	0.21	0.31	0.46	0.30	0.10	0.19	0.30	0.11
Total	100.55	100.61	100.20	99.85	100.81	99.46	99.95	99.63	99.86	100.57	100.42	100.53	99.79	100.32
Trace element (ppm)														
Li	921.04	647.62	1172.88	1084.39	1017.59	1329.98	1637.43	1761.13	2601.86	1186.63	534.16	1167.20	1927.75	806.92
Sc	6.52	5.62	6.23	8.51	7.68	8.70	7.75	8.86	14.00	7.85	4.96	5.83	9.23	5.56
Se	41.80	37.02	40.81	45.51	46.18	42.12	41.12	41.43	38.79	37.52	38.16	38.78	40.45	41.02
V	276.58	357.73	401.50	454.57	388.75	414.57	397.96	383.71	472.62	360.52	254.13	301.90	440.50	301.08
Cr	247.85	308.90	144.20	18.66	183.78	213.57	58.13	62.92	0.37	182.19	396.62	304.38	32.23	304.38
Mn	38.57	118.11	40.47	59.58	63.14	97.34	46.63	32.71	9.09	62.81	159.45	132.27	33.69	69.61
Zn	67.94	70.11	34.47	59.42	63.14	50.34	60.25	61.59	35.88	75.92	60.31	64.75	58.84	76.76
Cu	80.12	72.23	101.16	101.16	88.15	102.87	91.79	110.84	153.89	90.15	66.56	72.70	114.08	70.61
Rb	0.86	0.57	1.31	1.24	1.35	1.63	1.84	1.99	2.70	1.32	0.57	2.31	2.31	1.51
Sr	113.75	92.93	121.59	119.11	107.40	108.35	120.01	143.23	120.26	92.73	79.57	121.43	132.03	108.27
Y	36.32	32.81	46.56	52.87	46.28	58.16	60.31	57.71	58.25	48.72	29.48	54.07	54.18	34.07
Zr	18.33	18.33	18.33	18.33	18.33	18.33	18.33	18.33	18.33	18.33	18.33	18.33	18.33	18.33
Nb	2.51	1.61	3.39	3.30	2.88	4.17	4.53	5.47	7.42	3.65	1.49	3.37	5.77	2.51
Ba	8.37	5.67	11.81	11.26	11.09	13.03	16.96	19.24	21.21	12.10	5.79	11.83	21.96	13.58
La	3.57	2.42	5.12	4.90	4.20	5.80	5.95	7.53	10.46	5.21	1.84	7.00	13.58	3.43
Ce	1.15	7.89	15.19	15.16	13.34	17.92	17.36	23.09	32.20	15.84	6.01	12.01	20.47	9.81
Pr	2.01	1.42	2.63	2.72	2.30	3.11	2.92	3.67	5.29	2.72	1.12	2.07	3.42	1.71
Nd	1.86	1.38	2.53	2.54	2.14	2.92	2.56	3.25	4.68	2.56	0.93	1.71	2.80	1.30
Sm	3.94	3.00	4.86	5.43	4.65	5.93	5.40	6.38	9.23	5.54	2.53	3.44	5.89	3.44
Eu	1.39	1.13	1.58	1.83	1.61	1.89	1.75	2.16	2.89	1.70	0.96	1.31	2.00	1.25
Tb	0.92	0.72	1.15	1.32	1.16	1.42	1.23	1.48	2.04	1.22	0.63	0.85	1.35	0.84
Gd	5.53	4.27	6.63	7.29	6.63	8.34	7.29	8.84	12.34	7.53	3.66	5.11	8.08	4.93
Dy	6.29	4.92	7.82	8.97	7.87	9.65	8.47	10.00	14.02	8.81	4.32	5.80	9.22	5.87
Ho	3.43	2.63	4.18	4.78	3.86	5.18	4.58	5.48	7.48	4.58	1.78	2.53	4.18	2.53
Er	3.96	3.06	4.96	5.62	5.06	6.01	5.33	6.65	9.23	5.48	2.75	3.60	5.63	3.67
Tm	0.56	0.43	0.70	0.87	0.73	0.87	0.75	0.88	1.26	0.77	0.40	0.50	0.80	0.52
Yb	3.68	2.88	4.73	5.33	4.66	5.68	5.00	5.77	8.17	5.04	2.59	3.34	5.38	3.30
Lu	0.54	0.43	0.70	0.82	0.69	0.83	0.75	0.85	1.24	0.76	0.38	0.50	0.78	0.51
Hf	2.85	2.00	3.76	4.05	3.47	4.56	4.08	5.08	7.31	4.05	1.61	2.72	4.41	2.44
Th	0.17	0.13	0.26	0.23	0.21	0.28	0.28	0.38	0.58	0.27	0.10	0.21	0.38	0.17
U	0.07	0.04	0.09	0.07	0.07	0.09	0.10	0.15	0.17	0.10	0.04	0.13	0.13	0.06
Major element (ppm)														
CO ₂	241.63	235.49	231.51	220.33	185.81	220.18	259.04	183.94	159.28	278.57	350.63	266.47	199.65	173.60
H ₂ O (wt%)	0.26	0.30	0.34	0.40	0.31	0.35	0.42	0.36	0.95	0.36	0.12	0.26	0.36	0.28
F	201.17	159.88	278.56	289.97	235.19	333.04	304.86	374.73	653.52	278.26	117.43	281.30	371.32	185.48
Cl	14.68	14.19	1321.78	570.25	76.92	76.11	76.05	804.48	76.05	76.05	76.05	76.05	76.05	76.05
P ₂ O ₅	488.1	473.6	277	313.2	369.4	351.1	280.9	364.4	318.5	296.1	748	450.4	262.4	337.6
Isotopic composition ^a														
⁸⁷ Si/ ²⁸ Si	523.5	508.5	506	486	407.5	482.5	553.5	422	428.5	606.5	748	555	457	380
¹³ C/ ¹² C														
¹⁵ N/ ¹⁴ N														
¹⁸ O/ ¹⁶ O														
²⁰⁷ Pb/ ²⁰⁶ Pb														
²⁰⁸ Pb/ ²⁰⁶ Pb														

[illegible]

Location Sample Latitude ^a Longitude ^a Depth Major element (wt%)	Maesquet Island G138 2000-5000	Maesquet Island 38511 -54.583 158.919 2000-5001	Maesquet Island G923b 2000-5500	Maesquet Island 66596 -54.629 158.899 2000-5500	Maesquet Island G893 -54.606 158.912 2000-5500	Maesquet Island 47974 -54.491 158.939 2000-5500	Maesquet Island 47990 -54.601 158.903 2000-5500	Maesquet Island AC23b -54.488 158.939 2000-5500	Maesquet Island G492a -54.494 158.941 2000-5500	Maesquet Island G565a -54.626 158.875 2000-5500	Maesquet Island 47979 -54.497 158.939 2000-5500	Maesquet Island G866a1 -54.57 158.885 2000-5500	Maesquet Island G4253 -54.626 158.906 2000-5500	Maesquet Island 66011 -54.487 158.942 2000-5500
SiO ₂	48.38	49.16	49.03	50.24	50.66	49.59	48.41	49.78	50.05	49.41	48.82	49.72	49.62	50.13
TiO ₂	1.38	1.18	1.38	1.58	1.54	1.71	1.67	1.80	1.71	1.40	1.01	1.64	1.40	1.82
Al ₂ O ₃	16.89	15.62	16.67	15.32	15.39	16.96	17.38	17.10	16.99	15.95	16.38	15.91	16.62	17.36
FeO	7.92	7.60	7.45	8.28	8.17	7.97	6.98	7.56	7.91	8.23	7.92	7.98	7.31	7.61
MnO	0.17	0.14	0.14	0.16	0.17	0.16	0.14	0.15	0.14	0.16	0.16	0.15	0.14	0.15
MgO	8.14	8.61	8.07	7.24	7.27	7.46	7.07	7.37	7.41	8.46	9.11	7.15	7.89	7.15
CaO	12.14	13.19	11.86	11.89	11.54	10.45	11.61	9.92	10.42	11.49	12.59	11.29	12.30	10.03
Na ₂ O	2.25	2.25	3.12	2.85	2.25	3.86	3.96	3.86	3.72	3.24	2.48	3.72	3.27	3.60
K ₂ O	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32
P ₂ O ₅	0.27	0.17	0.30	0.32	0.34	0.42	0.49	0.53	0.60	0.23	0.10	0.23	0.31	0.52
Total	98.62	98.90	98.78	98.47	98.47	99.11	98.77	99.27	99.60	98.71	98.62	98.51	99.56	99.48
Trace element (ppm)														
K ⁺	3938.73	2234.32	5908.54	4201.24	4841.13	6841.60	9177.90	8752.07	6992.81	3313.55	8231.77	4393.26	5564.25	8985.39
Li	4.19	3.74	4.38	4.30	4.72	4.81	4.40	4.77	4.70	3.60	3.80	4.54	4.40	4.65
Sc	54.24	39.88	34.74	34.30	36.67	30.39	31.00	27.81	29.82	35.38	35.92	34.56	35.13	27.78
Y	32.00	18.50	25.00	25.00	26.67	18.50	18.50	18.50	18.50	18.50	18.50	18.50	18.50	18.50
Co	211.30	362.54	236.10	256.19	241.11	210.57	169.58	191.51	190.07	222.72	327.80	222.06	248.18	181.14
Cu	36.41	37.43	32.84	33.62	33.41	32.79	30.42	32.08	32.27	38.23	42.17	34.51	33.17	31.99
Ni	118.14	109.56	92.51	73.89	84.91	110.12	86.62	115.56	102.59	131.40	152.80	97.43	99.84	111.65
Zn	68.22	99.59	77.35	77.35	71.77	55.96	67.44	53.17	56.22	68.85	54.14	69.03	73.71	47.42
Sb	56.27	51.60	52.48	59.47	61.02	59.41	47.72	56.18	59.61	58.70	54.14	55.11	49.92	56.79
Se	18.52	18.52	18.52	18.52	18.52	18.52	18.52	18.52	18.52	18.52	18.52	18.52	18.52	18.52
Y	25.30	21.34	25.07	25.07	25.39	27.35	25.35	25.76	26.12	25.82	20.03	28.12	23.92	25.67
Zr	185.10	185.10	234.47	185.03	163.42	247.89	407.98	45.80	144.65	172.56	18.86	193.04	275.87	412.05
Nb	95.24	74.91	107.72	108.26	125.39	141.70	132.35	152.25	134.67	97.00	58.47	118.16	100.41	152.22
Ba	31.70	13.93	41.06	33.00	40.26	39.04	61.54	49.23	37.41	113.80	6.92	33.37	39.05	48.54
La	16.71	8.40	21.04	17.32	21.01	21.83	31.55	26.02	21.55	11.41	3.62	163.28	217.57	29.02
Ce	17.73	11.40	17.73	17.73	17.73	17.73	17.73	17.73	17.73	17.73	17.73	17.73	17.73	17.73
Pr	3.73	2.21	4.46	4.79	4.76	4.79	6.29	5.43	4.79	3.01	1.56	4.09	4.31	5.54
Nd	15.57	10.34	17.91	17.69	20.14	19.70	24.32	21.52	19.79	13.51	7.57	17.60	17.30	22.09
Sm	3.66	2.78	3.91	4.43	4.47	4.43	4.75	4.61	4.51	3.51	2.38	4.11	3.92	4.65
Eu	1.27	1.01	1.34	1.38	1.45	1.53	1.60	1.72	1.53	1.25	0.89	1.45	1.33	1.57
Tb	0.67	0.57	0.66	0.71	0.78	0.78	0.70	0.72	0.75	0.66	0.52	0.74	0.64	0.72
Dy	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43
Ho	0.92	0.74	0.89	0.95	1.03	0.96	0.84	0.88	0.94	0.93	0.72	0.89	0.85	0.89
Er	2.55	2.20	2.55	2.73	3.06	2.84	2.37	2.37	2.51	2.64	2.19	2.56	2.49	2.56
Tm	0.37	0.31	0.36	0.33	0.42	0.39	0.33	0.35	0.38	0.36	0.29	0.41	0.35	0.36
Yb	2.36	2.05	2.31	2.52	2.86	2.58	2.09	2.24	2.49	2.44	2.01	2.75	2.30	2.54
Lu	0.43	0.39	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43
Hf	2.38	2.46	2.46	2.46	2.46	2.46	2.46	2.46	2.46	2.46	2.46	2.46	2.46	2.46
Ta	1.75	1.80	1.79	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
Pb	0.93	0.54	1.16	1.01	1.42	1.32	1.65	1.32	1.35	1.06	0.42	0.95	1.09	2.65
Th	2.37	2.94	2.94	2.36	3.05	3.02	4.46	3.60	3.02	1.40	0.49	3.74	2.87	3.74
U	0.50	0.34	0.88	0.50	0.62	0.71	0.97	0.86	0.76	0.33	0.12	0.54	0.64	0.92
Volatiles element (ppm)														
H ₂ O (wt %)	241.26	168.52	200.72	175.38	151.14	134.90	156.19	127.08	117.09	214.70	157.19	151.56	167.22	102.85
F	0.68	0.44	0.70	0.69	0.79	0.85	1.03	1.06	0.88	0.53	0.24	1.05	0.70	1.05
S	569.56	299.67	628.00	699.77	719.48	602.08	969.51	745.85	618.15	410.52	194.31	548.74	639.95	743.94
Cl	755.71	767.27	783.75	840.11	854.67	713.60	760.30	740.77	753.49	859.78	726.47	812.56	739.80	754.33
P ₂ O ₅	257.75	257.75	455.41	404.46	503.22	587.78	846.52	761.21	540.54	240.54	82.13	488.78	455.50	754.33
P ₂ O ₅	275 ± 75	275 ± 75	482.5	421	384	358	372	382	325.5	484.5	318.5	389.5	404.5	329
Isotopic composition ^b														
¹⁴³ Nd/ ¹⁴⁴ Nd										0.70312	0.70372	0.70372	0.70372	
²⁰⁶ Pb/ ²⁰⁴ Pb										0.51305	0.51305	0.51305	0.51305	
²⁰⁷ Pb/ ²⁰⁴ Pb										19.108	18.951	19.108	15.572	
²⁰⁸ Pb/ ²⁰⁴ Pb										38.634	38.523	38.634	38.676	

Location	Maquisette Island	Maquisette Island	Maquisette Island	Maquisette Island	Maquisette Island	Maquisette Island
Sample	G955b	G929a	Z5638	61410	G705c	G937
Latitude	-54.681	-54.638	-54.689	-54.689	-54.689	-54.648
Longitude	134.931	134.931	134.931	134.931	134.931	134.931
Depth	2000-3500	2000-3500	2000-3500	2000-3500	2000-3500	2000-3500
Major element (wt%)						
SiO ₂	49.41	48.74	48.55	50.04	50.05	49.03
TiO ₂	1.68	1.41	1.24	1.80	1.80	1.34
Al ₂ O ₃	15.92	16.89	16.76	16.90	17.11	16.87
FeO ^a	8.24	7.68	7.40	7.64	7.67	7.56
MgO	0.18	0.16	0.16	0.15	0.16	0.14
MnO	0.18	0.17	0.17	0.17	0.17	0.17
Na ₂ O	11.18	11.54	12.56	9.88	9.49	11.92
K ₂ O ^a	0.58	0.65	0.43	1.09	1.11	0.78
P ₂ O ₅	0.35	0.30	0.23	0.53	0.53	0.31
Total	98.70	98.92	98.80	99.29	99.76	98.91
Trace element (ppm)						
K ^a	4503.58	4987.76	3356.01	8367.26	8761.67	6159.14
Li	4.68	4.42	3.89	4.82	4.90	3.92
Sc	32.43	32.43	32.43	32.43	32.43	32.43
V	198.88	172.84	176.04	146.30	151.42	170.84
Cr	257.33	231.85	287.29	185.25	184.40	198.08
Co	33.86	15.30	36.57	31.76	31.28	31.92
Ni	113.91	116.91	112.25	112.64	108.03	76.26
Cu	68.08	73.86	79.16	51.24	50.74	70.26
Zn	146.05	146.05	146.05	146.05	146.05	146.05
Br	15.22	15.22	15.22	15.22	15.22	15.22
Rb	190.71	226.25	1172.59	426.34	427.49	290.55
Sr	29.82	25.20	22.67	26.25	26.66	23.20
Y	126.83	97.77	86.95	154.66	158.85	114.69
Zr	32.86	39.34	23.96	49.97	49.67	44.66
Nb	162.98	211.56	123.51	299.03	296.88	240.12
Ba	127.42	127.42	127.42	127.42	127.42	127.42
La	33.94	36.89	25.54	49.65	49.72	41.19
Ce	4.12	4.22	3.11	5.64	5.74	4.80
Pr	17.76	17.05	13.09	23.04	22.54	19.33
Nd	3.83	3.16	4.74	4.91	4.26	3.48
Sm	1.45	1.32	1.14	1.66	1.60	1.45
Eu	0.79	0.68	0.57	0.95	0.91	0.79
Gd	4.90	4.26	3.66	4.97	4.91	4.64
Dy	5.16	4.56	3.94	4.72	4.79	4.58
Ho	1.07	0.89	0.80	0.94	0.93	0.94
Er	3.08	2.54	2.32	2.65	2.70	2.81
Tm	0.43	0.36	0.34	0.37	0.38	0.39
Yb	2.78	2.29	2.21	2.47	2.45	2.60
Lu	0.43	0.37	0.34	0.37	0.37	0.37
Hf	2.85	2.23	2.04	3.32	3.35	2.64
Ta	1.81	2.11	1.37	2.78	2.74	2.50
Pb	0.98	1.02	0.78	1.55	1.58	1.18
Th	2.56	2.90	1.77	3.88	3.85	3.43
U	0.54	0.63	0.40	0.94	0.92	0.73
Volatiles (ppm)						
CO ₂	188.11	191.87	210.34	134.85	116.13	163.96
H ₂ O (wt %)	0.71	0.74	0.52	1.11	1.05	0.83
F	587.98	669.21	445.64	774.31	745.92	524.27
S	919.31	803.95	769.69	753.47	722.40	584.95
Cl	491.11	289.99	803.24	790.69	790.69	523.84
P ₂ O ₅	275 ± 75	275 ± 75	400.5	275 ± 75	357.5	275 ± 75
Isotopic composition ^b						
¹³⁴ Sm/ ¹⁴⁷ Sm	0.703653					
¹⁴³ Nd/ ¹⁴⁴ Nd	0.513044					
²⁰⁶ Pb/ ²⁰⁴ Pb	19.317					
²⁰⁷ Pb/ ²⁰⁴ Pb	15.567					
²⁰⁸ Pb/ ²⁰⁴ Pb	38.87					

Table 1-S2. Calculation of the model E-DMM major, trace, and volatile element composition and the mass balance of the low degree melt metasomatism.

	DDMM ^a	Initial EDMM ^b	1.3% aggregated melt of EDMM	Bottom 22% of the mantle lithosphere ^d	Calculated EDMM by metasomatism of mantle lithosphere (mantle lithosphere plus 1.04% ^c of low F melt of EDMM)
SiO ₂	44.71	44.71	41.20	44.72	44.68
TiO ₂	0.13	0.13	1.12	0.12	0.13
Al ₂ O ₃	3.98	3.98	9.32	3.91	3.97
FeO ^t	8.18	8.18	13.27	8.17	8.23
MnO	0.13	0.13	0.12	0.13	0.13
MgO	38.73	38.73	19.41	38.90	38.70
CaO	3.17	3.17	8.04	3.12	3.17
Na ₂ O	0.13	0.13	0.40	0.10	0.11
Cr ₂ O ₃	0.57	0.57	3.84	0.57	0.61
NiO	0.24	0.24	0.07	0.24	0.24
K ₂ O ^c	0.005	0.030	2.101	0.001	0.02
Rb	0.020	0.684	48.1	0.003	0.50
Ba	0.227	7.54	537.2	0.01	5.60
Th	0.004	0.086	5.6	0.00	0.06
U	0.0018	0.023	1.6	0.00	0.02
Nb	0.0864	1.33	81.1	0.05	0.89
Ta	0.0056	0.073	4.46	0.003	0.05
La	0.134	0.737	38.8	0.10	0.50
Ce	0.421	1.65	70.7	0.36	1.09
Pb	0.014	0.075	3.5	0.02	0.06
Pr	0.087	0.31	7.73	0.09	0.17
Nd	0.483	1.23	30.9	0.48	0.80
Sr	6.092	18.51	665.1	5.54	12.40
Zr	4.269	11.2	143.5	4.64	6.09
Hf	0.127	0.288	3.1	0.14	0.17
Sm	0.210	0.392	5.8	0.21	0.27
Eu	0.086	0.149	1.6	0.09	0.10
Ti	650.0	779.2	6720	631.87	695.19
Gd	0.324	0.536	4.0	0.34	0.37
Tb	0.064	0.097	0.5	0.07	0.07
Dy	0.471	0.666	2.8	0.48	0.51
Ho	0.108	0.148	0.5	0.11	0.11
Y	3.129	4.28	6.7	3.24	3.28
Er	0.329	0.437	1.2	0.33	0.34
Yb	0.348	0.441	0.7	0.35	0.36
Lu	0.056	0.068	0.1	0.06	0.06
H ₂ O	59	660	33389.8	56	402.61
CO ₂	22	990	69183.4	4.3	723.79
F	8	31	1231.9	7.3	20.03
Cl	0.4	22	1567.4	0.02	16.32
S	100	165	4497.8	89.1	134.98

^aMajor elements (DMM) (except for K₂O) and trace elements (DDMM) from Workman and Hart (2005) and volatile elements from this study^bMajor elements (DMM) (except for K₂O) from Workman and Hart (2005), trace elements from Donnelly et al., (2004), and volatile elements from this study^cK₂O content for DDMM and EDMM calculated using the K/Nb ratios of our D- and E-MORB samples and Nb concentration of DDMM (Workman and Hart, 2005) and EDMM (Donnelly et al., 2004) (refer to section 5.3).^dWeighted average of the DDMM residue (78%) and EDMM residue (22%) at depth of 47 to 60km (bottom 22% of oceanic lithosphere) calculated using pHMELTS (Asimow et al., 2004, Ghiorso et al., 2002, Smith & Asimow 2005) and SCSS model of Fortin et al., (2015)^eBased on the mass balance calculation below (80% escape model).

low F melt of EDMM (aggregated 1.3% melt of EDMM)	Bottom 22% of residual mantle	Mass ratio low F melt/residual mantle (%)
100×0.22×0.013×0.8 =0.2288 (22% EDMM, F = 1.3%, and 80% melt escape)	22	1.04
100×0.22×0.013×0.75 =0.2145 (22% EDMM, F = 1.3%, and 75% melt escape)	22	0.98
100×0.22×0.013×0.65 =0.1859 (22% EDMM, F = 1.3%, and 65% melt escape)	22	0.85

CHAPTER 2

The role of the metasomatized oceanic lithosphere on the composition of mid-ocean ridge basalts from the East Pacific Rise

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Abstract

In the present study, we sought to better understand the effect of melting of a metasomatized oceanic lithosphere on the chemical composition of MORB using the East Pacific Rise (EPR) mid-ocean ridge basalts (MORB) from the Quebrada-Discovery-GoFar (QDG) transform fault, Northern EPR (NEPR) seamounts, and Macquarie (MQ) Island. The QDG EMORB, characterized by high H_2O/Ce , K/Nb , Rb/Th ratios and lower Nb/Th , Ce/Pb , Ba/Th , define a different magma component from other MORB. The unique chemical composition of EMORB from QDG transform fault might suggest melting of a metasomatized oceanic lithosphere most likely triggered by formation of intra-transform spreading ridges due to clockwise rotation in Pacific-Nazca plate relative motion. We quantitatively test this hypothesis using a model assuming a two component asthenospheric mantle (DDMM and EDMM) and formation of hydrous cumulates in the oceanic lithosphere by crystallization of low degree melts of the EDMM. The model suggests that re-melting of the hydrous cumulates can reproduce the composition of EMORB from the QDG transform fault. Geological evidence for metasomatism of the oceanic lithosphere by the EDMM is found in St. Paul's Rocks where magmatic amphiboles in peridotites have enriched trace element pattern and radiogenic isotopic composition suggesting derivation from the EDMM. In addition, compositions of lavas recently erupted (<9.2 Ma) on the Pacific Plate near the Japan Trench are shown to have geochemical signature that suggest mixing between an EM-1 type mantle derived melt and re-melted metasomatized oceanic lithosphere. The previously unrecognized process of re-melting of metasomatized oceanic lithosphere may significantly affect the chemical composition of MORB, and suggests that the common assumption for the purely

asthenospheric origin of MORB could lead to erroneous estimates of the asthenospheric mantle composition. We also show that amphiboles in oceanic peridotites and off-craton continental xenoliths have average isotopic composition that limits the average age of the metasomatism to within ~200 Myrs assuming the amphiboles were produced from metasomatism by EDMM derived melts. The relatively young age of globally observable metasomatism could suggest a hydration induced weakening of the continental lithospheric mantle by metasomatism, and preferential delamination of the metasomatized continental lithospheric mantle within ~200 Myrs of the metasomatic event.

1. Introduction

Hydrous and carbonated melt metasomatism significantly affects the chemical composition (e.g. Halliday et al., 1995), seismic velocity (e.g. Thybo, 2006), and rheology (e.g. Li et al., 2008) of the lithospheric mantle. Hydrous and carbonated melts formed at a significantly deeper depth than the dry mantle solidus (e.g. Dasgupta et al., 2013; Gaetani and Grove, 1998), migrate upwards and metasomatize the overlying oceanic and continental lithospheric mantle, resulting in significant enrichment of its volatile and trace element contents (Donnelly et al., 2004; Green and Wallace, 1988; Halliday et al., 1995; Hirschmann, 2010; Menzies et al., 1987; Niu et al., 2002; Pilet et al., 2008). This metasomatic melt may crystallize volatile-rich minerals such as amphibole in the lithospheric mantle (Nielson and Noller, 1987; Pilet et al., 2011; Pilet et al., 2008; Wilshire, 1987). Amphibole has been suggested to potentially produce the sharp seismic velocity drops observed in oceanic environments (Green et al., 2011) and

in continental environments (Selway et al., 2015). In addition, experimental studies show that alkalic lavas (e.g. basanite, nephelinite, and alkali basalts) commonly viewed as products of low degree asthenospheric mantle melting, can also form by partial melting of an amphibole rich lithology in the lithospheric mantle (Pilet et al., 2011; Pilet et al., 2008). Thus, lavas observed at the surface may not necessarily originate in the asthenospheric mantle, but some may instead represent partial melts from a metasomatized lithospheric mantle. Therefore, understanding the process of lithospheric mantle metasomatism and partial melting is important for constraining the chemical composition of the lithospheric mantle, interpreting the geophysical observations, as well as making accurate estimates of the asthenospheric mantle composition using the composition of oceanic and continental basalts.

In this study we used our recently published geochemical data of submarine basaltic glasses (Shimizu et al., 2016) to evaluate the role of the metasomatized oceanic lithosphere on the composition of mid-ocean ridge basalts (MORB) from the East Pacific Rise (EPR). We identify a common magma component, present at transform fault systems, seamounts, and magma-starved ridges over a very large region of the Pacific basin. We propose that melting of a previously metasomatized oceanic lithosphere generates this common component, which significantly modifies the chemical composition of MORB.

2. Samples and methods

In this study we used our recently published geochemical data on submarine basaltic glasses from Quebrada/Discovery/GoFar (QDG) transform fault system located

on 3°-5°S EPR (Shimizu et al., 2016), the NEPR seamounts collected between 5-15°N (Batiza et al., 1990), and the Macquarie Island (54°30'S, 158°56'E) collected by B. J. Griffin, M. J. Rubenach, J. L. Everard, and B. Goscombe. The major, trace, and volatile elements and isotopic composition of the samples were reported in Shimizu et al. (2016).

Here, we briefly describe the analytical methods (for more details refer to Shimizu et al. (2016)). We mounted three to six chips of fresh, clean, naturally quenched glass from each sample in indium metal and polished them using diamond paste down to 0.25 μm . Major elements were analyzed using the Cameca XS-100 electron microprobe at Brown University. Average analytical error (2σ SE) of the major element analyses were <1% for SiO_2 , Al_2O_3 , and MgO , <2% for FeO and CaO , <3% for Na_2O and TiO_2 ; for K_2O and P_2O_5 the errors were significantly larger (1-20% and 2-30% respectively). Trace elements were analyzed in-situ using the Quadrupole ICPMS X-Series II and 193 nm wavelength excimer Photon Machines Analyte G2 laser ablation system at Brown University. Average analytical error (2σ SE) of the trace element analyses were <6% for all elements. The concentrations of K (0.5-9.2%, 2σ SE) and P (0.4-12.2%, 2σ SE) measured using the LA-ICP-MS are used in this study given the better precision compared measurements using the EMP. Volatiles (H_2O , CO_2 , F, Cl, and S) were analyzed using the Cameca 6F ion probe at Carnegie Institution of Washington Department of Terrestrial Magnetism. Average analytical precision (2σ SE) for volatile analyses was $\leq 5\%$ for all volatiles except Cl with 8%. Sr, Nd, and Pb isotopic composition were made on a selected set of QDG samples using the Thermo Scientific NEPTUNE plus at Brown University. The internal precision of the Sr and Nd analyses is 5-10ppm and the external precision is 30ppm for Sr (2σ , $n = 75$) and 25ppm for Nd (2σ , n

= 104). The internal precision of the Pb analysis is 20-45ppm and the external precision is 45-80ppm (2σ , $n = 75$). The Sr and Pb blanks were < 50 pg, and Nd blanks were < 30 pg.

3. Results

Most of the samples in this study have $\text{MgO} > 6.0 \text{ wt\%}$ (Fig. 1a), ranging from tholeiitic to alkalic basalts. Based on the Th/La ratio, the samples are divided into three groups, EMORB ($\text{Th/La} > 0.07$), NMORB ($0.035 \leq \text{Th/La} \leq 0.07$), and DMORB ($\text{Th/La} < 0.035$) (Fig. 1a and 1b). The isotopic composition of the samples covers a large portion of the total range observed in EPR MORB (Fig. 2a and 2b). The EMORB samples tend to plot towards radiogenic Sr and Pb isotopic composition, and DMORB samples tend to plot towards unradiogenic Sr and Pb isotopic composition, suggesting that the Th/La of the samples can be used as a first order proxy for long-term ITE enrichment in the mantle source. However, Th/La is not always a good proxy for long-term mantle ITE enrichment since incomplete aggregation of incremental fractional melts of a long-term mantle ITE enriched source can produce isotopically enriched samples with a range of Th/La ratios (Shimizu et al., 2016).

Previous studies have shown that volatile elements have bulk distribution coefficients similar to refractory ITEs during mantle melting: CO_2 has a bulk partition coefficient similar to Nb-Th-Ba, F to Nd-P, Cl to K-Nb, S to heavy REEs such as Dy, and H_2O to Ce-La (Danyushevsky et al., 2000; Dixon, 1997; Dixon et al., 2002; Hauri et al., 2006; Michael, 1988; Michael, 1995; Michael and Cornell, 1998; Rosenthal et al., 2015; Saal et al., 2002; Workman et al., 2006). These volatile to ITE ratios will change if the

samples experience secondary processes that only affect the volatile elements, such as degassing, assimilation of hydrothermally altered materials, and sulfide saturation. To evaluate the volatile contents of the lavas and their sources we applied in this paper the most commonly used ratios CO_2/Nb , $\text{H}_2\text{O}/\text{Ce}$, Cl/K , F/Nd , and S/Dy (Danyushevsky et al., 2000; Dixon, 1997; Michael, 1988; Michael, 1995; Michael and Cornell, 1998; Rosenthal et al., 2015; Saal et al., 2002; Workman et al., 2006).

The effect of the shallow level processes on the samples were evaluated by Shimizu et al. (2016). We filtered samples with $\text{Cl}/\text{K} > 0.04$ for DMORB, > 0.06 for NMORB, and > 0.11 for EMORB and for samples indicating sulfide saturation using the sulfur content at sulfide saturation model of Fortin et al. (2015) (Kent et al., 1999; Kent et al., 2002; Lassiter et al., 2002; le Roux et al., 2006; Michael and Cornell, 1998; Saal et al., 2002; Simons et al., 2002; Stroncik and Haase, 2004). Although our filtering may result in underestimating the roles that apatite and sulfides within the metasomatized lithospheric mantle (Pilet et al., 2011) could have on the composition of MORB, we chose to use filtered data to avoid the effect of assimilation of seawater and brine and sulfide saturation. Filtering the samples using these limits for the Cl/K ratios reduces the range in $\text{H}_2\text{O}/\text{Ce}$ ratio in the DMORB and NMORB samples while not the range in $\text{H}_2\text{O}/\text{Ce}$ of the EMORB samples, and the general trends in the data persists (Fig. S1). This is because DMORB and NMORB samples with very high Cl/K tend to have high $\text{H}_2\text{O}/\text{Ce}$ consistent with assimilation of seawater and brine, while EMORB samples with high $\text{H}_2\text{O}/\text{Ce}$ tend to have low Cl/K . Hence, contamination by hydrothermal material cannot explain the unusually the high $\text{H}_2\text{O}/\text{Ce}$ ratios in some EMORB samples.

In general, although there is some overlap, EMORB samples from QDG transform fault have higher $\text{H}_2\text{O}/\text{Ce}$ ratios (~ 350) than those from NEPR seamounts and MQ Island (from 150 to 250) (Fig. 3a). The $\text{H}_2\text{O}/\text{Ce}$ ratios of EMORB samples negatively correlate with their $\delta_{\text{alkalinity}}$ (Fig. S2), opposite to the positive correlation expected from the more compatible behavior of Ce relative to H_2O in garnet (Hauri et al., 2006). This is because low degree melts of garnet peridotite with high $\delta_{\text{alkalinity}}$ should have high $\text{H}_2\text{O}/\text{Ce}$ ratios, while the progressively higher degree melts with lower $\delta_{\text{alkalinity}}$ should have progressively lower $\text{H}_2\text{O}/\text{Ce}$. Shimizu et al. (2016) hypothesized that the distinct $\text{H}_2\text{O}/\text{Ce}$ ratios between these two EMORB groups results from various degrees of diffusive loss of H^+ from either the EMORB or its mantle source (EDMM) to the surrounding DMORB mantle source (DDMM). The QDG EMORB with high $\text{H}_2\text{O}/\text{Ce}$ ratios were interpreted as those that survived diffusive loss of H^+ due to either the larger size of EDMM or its shorter residence time in the DDMM, while NEPR seamount and MQ Island EMORB were interpreted as those that diffusively lost H^+ to the surrounding DDMM.

Although this is a plausible hypothesis to explain the distinct $\text{H}_2\text{O}/\text{Ce}$ ratios in the two EMORB groups, $\text{H}_2\text{O}/\text{Ce}$ is not the only geochemical characteristic that distinguishes EMORB from the QDG transform fault from those from the NEPR seamounts and MQ Island. QDG EMORB are more depleted in incompatible trace elements and have unusual positive K anomaly (i.e. high K/La) in primitive mantle normalized diagrams (Fig. 1b and 3b). Furthermore QDG EMORB generally have higher K/Nb, K/U, Rb/Th, Rb/Ba, and Rb/Nb ratios and lower Nb/Th, Ce/Pb, Ba/Th, Ba/La, and $\text{K}_2\text{O}/\text{H}_2\text{O}$ ratios compared to those from NEPR seamounts and MQ Island (Fig. 4). Sr-Nd-Pb isotopic

compositions of QDG EMORB are also distinct from those of the NEPR seamount and MQ Island MORB. QDG EMORB are more radiogenic in Nd isotopes for a given Sr isotopic composition (Fig. 2a), and their $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are generally less radiogenic with high $\Delta 8/4$ and similar $\Delta 7/4$ to the NEPR seamounts and MQ Island (Fig. 2b). In addition, QDG EMORB have lower Cl/K and F/Nd and higher S/Dy ratios compared to those of NEPR seamounts and MQ Island EMORB (Fig. S3). MQ Island EMORB are distinctly higher in F/Nd and lower in S/Dy compared to QDG transform fault and NEPR seamount EMORB, which may be due to low degree melting in the garnet stability field and S degassing respectively (Shimizu et al., 2016).

Although EMORB from QDG transform fault vs. NEPR seamounts and MQ Island are chemically distinct from each other as a group, some EMORB from NEPR seamounts and MQ Island have high $\text{H}_2\text{O}/\text{Ce}$ ratios similar to those from QDG transform fault suggesting a continuum between the two groups of EMORB (Fig. 3a). Furthermore, the EMORB from QDG transform fault shows a trend towards the DMORB (Fig. 5). The two trends are fairly well reproduced with mixing lines between three end-members, a MQ Island EMORB (sample 47963), a QDG EMORB (sample D19A) and a QDG DMORB (sample D44A) (Fig. 5), and further mixing between the two trends would reproduce the intermediate samples. The QDG DMORB sample was chosen as an end-member given its similar trace element characteristics to DMORB from Garrett transform fault, which are melts that likely best reflect the depleted component of EPR MORB mantle (depleted DMM or D-DMM) as shown by their depleted trace element and isotopic composition (Wendt et al., 1999). The influence of a high $\text{H}_2\text{O}/\text{Ce}$ QDG type

EMORB observed in NEPR seamounts and MQ Island may suggest that EMORB with high H₂O/Ce from QDG transform fault is a common component in the Pacific MORB.

4. Discussion

The differences between EMORB from QDG and those from the NEPR seamounts and MQ Island in trace element and isotopic composition in addition to volatile/refractory ITE ratios, suggests that diffusive loss of H⁺ alone does not fully explain their distinct geochemical characteristics. Instead, high H₂O/Ce and other unique geochemical characteristics (e.g. positive K anomaly, high Rb/Ba, and low Nb/Th) of the QDG EMORB suggest a different component that affected the composition of the Pacific MORB. We envision two possible origins for this component, (1) a different mantle source within the convecting mantle and (2) a metasomatized oceanic lithospheric mantle affected by hydrous and carbonated melt.

4.1 Potential asthenospheric mantle sources of QDG EMORB

The high H₂O/Ce ratio in QDG EMORB may suggest its derivation from a less degassed volatile rich mantle, although this might not be supported by the ³He/⁴He ratio of the QDG EMORB are ~8 Ra (M.D. Kurz 2015, personal communication) suggesting its derivation from an upper mantle source and not a less degassed deeper mantle. A mantle that has been fluxed by slab derived fluids at subduction zones may have a high H₂O/Ce ratio. However, the QDG EMORB have a positive Nb anomaly opposite of that expected for a mantle fluxed by slab derived fluids (Fig. 1b). QDG EMORB have the low Ba/Nb (5.68 ± 1.99 (2 σ)) and Rb/Nb (0.67 ± 0.25 (2 σ)) compared to those expected in a

mantle fluxed by slab derived fluids ($\text{Ba/Nb} = 86.8 \pm 35.7$ (2σ) and $\text{Rb/Nb} = 6.40 \pm 2.01$ (2σ)) in global subducting sediment composition (GLOSS) (Plank and Langmuir, 1998). Although we acknowledge that it might be possible to explain the geochemical characteristics of QDG EMORB with an asthenospheric mantle source produced by complicated processes in the subduction zone that is difficult to constrain, in this study, we explore shallow magmatic processes in the lithosphere to provide a simpler alternative hypothesis.

4.2 Lithospheric mantle origin of QDG EMORB: Hypothesis

The unique volatile and incompatible trace element signatures, and isotopic composition of the QDG EMORB in conjunction with their specific geological setting of a transform fault system may suggest a lithospheric mantle derivation for these lavas. As previously suggested (Donnelly et al., 2004; Halliday et al., 1995; Niu et al., 2002; Shimizu et al., 2016), the oceanic lithosphere could be metasomatized at the wings of the melting region where low degree melts may migrate vertically and freeze at the thermal boundary layer (Gregg et al., 2009; Havlin et al., 2013; Hebert and Montesi, 2010; Hebert and Montesi, 2011; Katz, 2008; Montesi and Behn, 2007; Sparks and Parmentier, 1991). The low degree melts rich in volatile and trace elements may fractionally crystallize in the cold shallow lithospheric mantle (Pilet et al., 2011). Fractional crystallization of nominally anhydrous minerals will further concentrate the residual melt in incompatible trace and volatile elements, eventually saturating it in hydrous phases such as amphibole and phlogopite. This lithology rich in hydrous mineral upon melting may produce melts with geochemical characteristics consistent with the observation in the QDG EMORB.

Intra-transform spreading centers at the QDG transform fault formed and grew to accommodate the clockwise rotation in Pacific-Nazca plate relative motion (e.g. Lonsdale, 1989), which lead to the “leakiness” (i.e. melt extraction) in small intra-transform spreading ridges. This melt extraction may have allowed the melting of pre-existing hydrous mineral rich lithology in the oceanic lithosphere. Therefore an amphibole rich lithology in the lithospheric mantle could be a plausible source of the QDG EMORB both based on the geological setting of the QDG transform fault and the unique geochemical signatures observed in the QDG EMORB. Furthermore, DMORB and EMORB asthenosphere derived melt, seems to mix a common component that is a QDG like EMORB with high H_2O/Ce derived from the hydrous mineral rich layer at the wings of the melting region (Fig. 5). The stronger signature of this common component at the QDG transform fault may be due to the smaller flux of asthenospheric melt owing to the slower mantle upwelling rate underneath a transform fault (Morgan and Forsyth, 1988) relative to the NEPR seamounts and MQ Island where QDG type EMORB signatures might be more diluted due to the larger melt flux.

One of the petrological evidences for metasomatism of the oceanic lithosphere is found at the St. Paul’s Rocks located 1°N and 29°20’W on the Mid-Atlantic Ridge (MAR) just north of the St. Paul fracture zone. The peridotites from St. Paul’s Rocks commonly contain magmatic amphibole (magmatic amphibole-bearing peridotites and hornblendites), and they are enriched in alkalis and incompatible elements (Melson et al., 1972). The Sr-Nd-Pb isotopic composition of the magmatic amphibole-bearing peridotites and hornblendites (Roden et al., 1984) are similar to those of EPR EMORB (Fig. 6a and 6b) (Shimizu et al., 2016). The He isotopic composition of these ultramafic

rocks are similar to the MORB samples found close the St. Paul archipelago (Graham et al., 1992; Staudacher et al., 1989), and their Ne isotopic composition plots along the MORB line (Kurz et al., 2009) both suggesting a MORB mantle origin of these rocks. Based on these observations and the trace element pattern of the samples, the amphibole-bearing peridotites and hornblendites have been interpreted as products of metasomatism of the oceanic lithosphere by alkali rich melts derived from an EMORB mantle (Brunelli and Seyler, 2010) similar to our metasomatism hypothesis. In addition to amphibole, the ultramafic rocks contain minerals such as apatite and phlogopite (Roden et al., 1984). Therefore the amphibole-bearing peridotites and hornblendites from St. Paul archipelago is an evidence of oceanic lithosphere metasomatism that supports our hypothesis for the generation of the QDG EMORB samples.

4.3 Lithospheric mantle origin of QDG EMORB: Model

We quantitatively test whether melting of an amphibole rich lithology in the lithospheric mantle can produce the QDG EMORB. We do this using a model that is based on a Monte Carlo model developed by Pilet et al. (2011). Our model still assumes a two-component upper mantle composed of DDMM and EDMM. However, the EMORB produced by low degree melting of the EDMM that escapes melt aggregation towards the ridge (e.g. Shimizu et al., 2016) is assumed metasomatize the lithosphere forming anhydrous and hydrous cumulates by fractional crystallization. We then assume that a subsequent heating event (e.g. due to infiltration of melt) melts the hydrous cumulate to form a lithosphere derived melt. We test whether or not this lithosphere derived melt that is compositionally distinct from the asthenosphere- (DDMM- and EDMM-) derived melts

can explain the unique composition of QDG EMORB. The trace element composition of the EDMM is from Donnelly et al. (2004) and the volatile element composition is from Shimizu et al. (2016) except for the H₂O concentration. The H₂O concentration in the EDMM estimated in Shimizu et al. (2016) was based on the highest H₂O/Ce ratio measured in the QDG EMORB, but given the potential lithospheric origin of QDG EMORB, we use a H₂O/Ce ratio of 160 in the NEPR seamount and MQ Island EMORB to estimate the water content of the EDMM. This results in an H₂O concentration in EDMM of 264 ppm (assuming Ce concentration of 1.65 ppm in E-DMM from Donnelly et al. (2004)). The Sr, Nd and Pb isotopes used for the EDMM are not from one sample, but represent the highest Sr, Pb and lowest Nd isotopes for the EMORB. We used the Sr and Nd isotopic composition of the sample 3010-1502 from NERP seamount 6 (Brandl et al., 2012) and Pb isotopic composition of the sample GG256 (Kamenetsky and Maas, 2002). Although this E-DMM is a hypothetical source since its isotopic composition is not defined by single sample, the results of our model does not significantly change by using a similar isotopic composition of a single sample (e.g., R78-6) from the NEPR seamount (Niu et al., 2002). The Sr, Nd, and Pb isotopic composition of the D-DMM are assumed to be those of sample GN10-3 from Garret transform fault (Wendt et al., 1999). The values selected for DDMM and EDMM are one of the most depleted and enriched isotopic compositions in the EPR, respectively.

The parameters in the model are listed in Table 1. In the model, the initial asthenospheric melt is derived from an EDMM mantle with degrees of melting ranging from 1 to 2%. This is based on the estimated degree of melting of EDMM below which some amount of melt escapes melt aggregation at the ridge towards the base of the

lithosphere (Shimizu et al., 2016). The initial melt derived from the EDMM mantle fractionally crystallizes in three steps (following Pilet et al. (2011)). The first step is the fractional crystallization of anhydrous phases (e.g. olivine, clinopyroxene, garnet, etc. listed in Table 1) that forms the anhydrous cumulate. This is followed by fractional crystallization of predominantly amphibole (>60%) along with anhydrous phases (e.g. clinopyroxene, plagioclase, etc.), and accessory phases (e.g. apatite, phlogopite, allanite, carbonate etc.) that forms the first hydrous cumulate. The next step is similar except zircon and orthopyroxene also crystallizes as an accessory phase forming the second hydrous cumulate (Table 1). The residual liquid after the formation of the second hydrous cumulate is assumed to cryptically metasomatize the surrounding peridotite. The hydrous cumulates and a portion of the residual melt is combined to simulate a metasomatized hydrous lithosphere (MHL). We envision that melting of this MHL to occur in two possible processes that are (1) percolation of DMORB through the lithosphere melting the MHL or (2) direct melting of the metasomatized lithosphere including the buffering effect of the depleted peridotitic matrix, both of which are process that cannot be precisely modeled given their complexity. In order to model these processes in a simple way, we melt the MHL and mix the MHL melt (5 to 20%) with DMORB (80 to 95%) (QDG DMORB D7A-A with MgO = 9.8 wt%) to produce the QDG EMORB. The parameters in the model (Table 1) were randomly varied using a Monte-Carlo method. For details of the model, refer to Appendix A and to Pilet et al. (2011).

The results of the model were compared to the most enriched QDG EMORB samples in characteristic volatile/refractory and trace element ratios (H_2O/Ce , K/Nb , K/U , Rb/Th , Rb/Ba , Rb/Nb , Nb/Th , Ce/Pb , Ba/Th , Ba/La , and K_2O/H_2O) that distinguish

the QDG EMORB from those in the NEPR seamounts and MQ Island. Using these ratios, the normalized chi-squared values were calculated for each model result to assess their goodness of fit. The range of parameter values that best reproduces the QDG EMORB (model results with lowest normalized chi-squared) are shown in Table 2. The model melts reproduces the H₂O/Ce, Th/La, and K/La ratios due to the melting of hydrous phases such as amphibole and phlogopite (Fig. 7a and 7b). Furthermore the model melts reproduces the characteristic volatile/refractory and trace element ratios of QDG EMORB (H₂O/Ce, K/Nb, K/U, Rb/Th, Rb/Ba, Rb/Nb, Nb/Th, Ce/Pb, Ba/Th, Ba/La, and K₂O/H₂O) (Fig. 8), and also the relatively depleted trace element pattern of QDG EMORB with the positive K anomaly (Fig. 9). The model melts have F/Nd, Cl/K, and S/Dy ratios similar to QDG EMORB consistent with the observation (Fig. S3). This mixing also produces melts with more radiogenic Nd isotopes for a given Sr isotopic composition due to the higher Sr/Nd ratio in the MHL melts relative to that in the DMORB (Fig. 10a, orange mixing curve). In contrast, mixing between DMORB and typical asthenospheric EMORB (Sr/Nd = 17, F = 5% melting of EDMM from Donnelly et al. (2004)) does not produce a significant curvature (Fig. 10a, green mixing curve). The mixing between the MHL melt and DMORB fails to reproduce the Pb isotopic composition of QDG EMORB that is more radiogenic in ²⁰⁸Pb/²⁰⁴Pb for a given ²⁰⁶Pb/²⁰⁴Pb (Fig. 10b). However, the composition of the DDMM is not well constrained, and the most depleted DMORB samples from Garrett transform fault may suggest the existence of a DDMM source with more radiogenic ²⁰⁸Pb/²⁰⁴Pb for a given ²⁰⁶Pb/²⁰⁴Pb. In addition, assimilation of sulfides with highly unradiogenic Pb (Burton et al., 2012) and interaction with the highly depleted peridotites (Malaviarachchi et al., 2008) may also result in a more radiogenic ²⁰⁸Pb/²⁰⁴Pb

for a given $^{206}\text{Pb}/^{204}\text{Pb}$ observed in the QDG EMORB (Fig. 10b). Furthermore, direct melting of the metasomatized lithosphere including the effect of depleted peridotite in the lithosphere (Malaviarachchi et al., 2008) is an alternative process by which the QDG EMORB may acquire the relatively depleted trace element pattern (Fig. 9) as well as the more radiogenic Nd isotopes for a given Sr isotopic composition (Fig. 10a).

The model results also reproduces the general characteristics of the major element composition of QDG EMORB samples (Fig. 11). Mixing between the DMORB (QDG DMORB D7A-A with $\text{MgO} = 9.8 \text{ wt\%}$) and the MHL melts with a relatively low MgO content (4-6 wt%) reproduces the slightly more differentiated composition of QDG EMORB compared to DMORB, and its general major element characteristics (e.g. low SiO_2 and FeO_t , high Al_2O_3). Alternatively mixing between lithospheric peridotite melt (isobaric melt of KLB-1 at 1GPa from Sorbadere et al. (2013)) and MHL melts would produce similar results (Fig. 11), suggesting that contribution of the depleted peridotite in the lithosphere may also play a role. The major element composition of experimental melts of amphibole-bearing peridotite (Pilet et al., 2008; Sorbadere et al., 2013) and amphibole-wherlite (Médard et al., 2006; Sorbadere et al., 2013) brackets the composition of QDG EMORB (except for TiO_2 content in Pilet et al. (2008)), which supports the potential contribution of peridotite in the melting of the MHL. Therefore, we cannot distinguish between the mixing of DMORB and MHL melts as opposed to the contribution of peridotite in the melting process of MHL.

In summary, our model simulated (1) the metasomatism of the oceanic lithosphere by low degree melts of the asthenospheric mantle by producing a hydrous cumulate in the oceanic lithosphere (MHL or metasomatized hydrous lithosphere), and (2) melting of the

MHL and mixing between this melt with a DMORB. For a certain range of model parameters, this mixture reproduces the unique volatile and trace element signatures ($\text{H}_2\text{O}/\text{Ce}$, K/Nb , K/U , Rb/Th , Rb/Ba , Rb/Nb , Nb/Th , Ce/Pb , Ba/Th , Ba/La , and $\text{K}_2\text{O}/\text{H}_2\text{O}$), certain volatile to trace element ratios ($\text{H}_2\text{O}/\text{Ce}$, S/Dy , Cl/K and F/Nd), and isotopic composition of the QDG EMORB (more radiogenic Nd isotopes for a given Sr isotopic composition). The model also reproduces the general major element characteristics (e.g. low SiO_2 and FeO , high Al_2O_3) of QDG EMORB. As shown in the results section, QDG type EMORB with high $\text{H}_2\text{O}/\text{Ce}$ also exist in the NEPR seamounts and MQ Island (Fig. 5), and they may derive from the hydrous mineral rich at the wings of the melting region. Therefore, oceanic lithosphere metasomatized by low degree melts derived from the EDMM may be a common component that affects the composition of Pacific MORB.

4.4 Lithospheric mantle origin of QDG EMORB: Geological evidences

The aforementioned evidence for metasomatism of the oceanic lithosphere in the amphibole bearing peridotites from the St. Paul's Rocks supports our model of metasomatism of the oceanic lithosphere by low degree melts derived from the EDMM. Furthermore, the chemical composition of lavas from the “petit spot” volcanoes located near the Japan Trench (Hirano et al., 2006) could provide additional evidence of metasomatism of the oceanic lithosphere. The Petit-spot volcanoes form as a result of melt extraction through lithospheric fractures produced by plate flexure at subduction zones (Hirano et al., 2006; Yamamoto et al., 2014). The melts are extracted from the bottom of the lithosphere (~100 km) where a Pacific mantle EDMM rich in H_2O and CO_2

would melt to ~1–2 wt% (Dasgupta et al., 2013). The geochemical characteristics of such melt would be similar the MQ Island EMORB samples, which is distinctly different from those of the Petit spot lavas (Fig. 12) requiring an alternative source other than an EDMM. The petit-spot lavas define a trend where Sr, Nd, and Pb isotopes correlate with the LILE/HFSE enrichment (e.g. Ba/Nb) ranging from a component isotopically similar to the EM-1 mantle component to another component more radiogenic in Pb and Nd isotopes while less radiogenic in Sr isotope. It has been argued that this correlation observed in petit spot lavas suggest melts derived from recycled materials accumulating and mixing at the top of the asthenosphere (Machida et al., 2009; Machida et al., 2015). Alternatively, it may suggest mixing between a percolating melt derived from a recycled material in the asthenosphere and re-melted metasomatized oceanic lithosphere (Buchs et al., 2013). In fact, a subset of the petit spot lavas (group 3) has certain trace element ratios that match the characteristics of the QDG EMORB (e.g. Nb/Th, Ce/Pb, K/Nb, K/U, Rb/Nb), different from the other group 1 and 2 (Fig. 11). In order to evaluate whether or not the group 3 samples can be explained by re-melting of the oceanic lithosphere that was metasomatized at the ridge, we calculate the Sr, Nd, and Pb isotopic composition of the metasomatized hydrous lithosphere (MHL) modeled in section 4.3 assuming it was produced from a melt derived from an EDMM 130 Myrs ago at the ridge (e.g. age of oceanic lithosphere at the petit spot volcano (Müller et al., 2008)). We back calculate the isotopic composition of the EDMM 130 Myrs ago using a current day EPR EMORB type isotopic composition (sample 3010-1502 from Brandl et al. (2012)) and parent-daughter ratios of the EDMM from Donnelly et al. (2004). Using this isotopic composition of EDMM 130 Myrs ago and the parent daughter ratios in the MHL formed in section 4.3,

we calculate the Sr, Nd, and Pb isotopic composition of the MHL today. A melt derived from such MHL have trace element and isotopic composition that lies along the extension of the correlation between Ba/Th, Ce/Pb, Nd and Pb isotopic composition defined by the petit spot lavas (Fig. 13). Although the Sr isotopic composition of the MHL is more radiogenic than the petit spot lavas, our model is not unique, e.g., a larger amount of phlogopite in the MHL would lead to a more radiogenic Sr isotopic composition today due to its high Rb/Sr ratio. The result suggests that EPR type EMORB may produce an MHL at the ridge that can later re-melt by interaction with asthenosphere derived melts to produce correlations between trace element ratios (e.g. Ba/Th, Ce/Pb) and isotopic compositions similar to the ones observed in the lavas sampled at the surface.

There is ample evidence of lithospheric mantle metasomatism in continental xenoliths containing amphibole as well as plagioclase, phlogopite, apatite, and carbonate (e.g. Coltorti et al., 2004; Coltorti et al., 2000; Ionov et al., 1993; Wulff-Pedersen et al., 1996; Wulff-Pedersen et al., 1999). These xenoliths are from intraplate regions far from current subduction zones, where there is relatively weak decompression of the mantle (e.g., Basin and Range and Middle Atlas). Similar to the wings of the melting triangle, this weak decompression of the mantle may produce small degree melts of the asthenospheric mantle that migrate upwards and crystallize amphibole in the shallow mantle lithosphere (Green et al., 2011; Pilet et al., 2008; Pilet et al., 2010).

A compilation of Sr-Nd-Pb isotopic composition of the amphiboles in the off-craton continental xenoliths suggest that at least some continental lithospheric metasomatism may be caused by low degree melts from an EDMM similar to what may occur in the oceanic lithosphere. The average Sr and Nd isotopic composition of the

amphiboles in xenoliths (Fig. 6a) is similar to those of the EDMM and amphibole-bearing ultramafic rocks from the St. Paul's Rocks (Roden et al., 1984), and at least some amphiboles in xenoliths have radiogenic Pb isotopic composition fairly similar to the oceanic amphiboles (Fig. 6b). On average amphiboles in xenolith have more unradiogenic Nd and Pb isotopic compositions and more radiogenic Sr isotopic composition compared to those in oceanic amphiboles. This can be explained by the older metasomatism age for continental amphiboles of 10–200 Myrs assuming the parent daughter ratios in EDMM of Donnelly et al. (2004) and in amphibole from our model (section 4.3). The similar isotopic composition between amphiboles in continental xenolith, the EDMM, and the St. Paul's Rocks might suggest the global distribution of lithosphere metasomatism by an EDMM like source.

5. Conclusions

The potential derivation of QDG EMORB from a metasomatized lithospheric mantle, the presence of QDG type EMORB at both NEPR seamounts and MQ Island, and the geologic evidence of wide spread metasomatism of the lithospheric mantle suggests that metasomatized lithospheric mantle might be a common component that affects the chemical composition of many MORB. Therefore the common assumption that composition of MORB solely reflects melting of an asthenospheric mantle source may not always be true, and this assumption could lead to an erroneous estimation of the asthenospheric mantle composition. For example, whether QDG EMORB and its volatile and trace element contents represent melting of a lithospheric mantle or an actual asthenospheric mantle (EDMM) has significant implications for the volatile content in

the EDMM and the Earth's upper mantle. Assuming the latter, Shimizu et al. (2016) estimated the H₂O contents the asthenospheric EDMM and bulk upper mantle to be 660 ppm and 191 ppm respectively (using the proportion of DDMM:EDMM of 78:22 and H₂O content in DDMM of 59 ppm from Shimizu et al. (2016)). However if the QDG EMORB are derived from a lithospheric mantle, these values must be revised using the samples that are more likely derived from the asthenospheric mantle such as NEPR seamount and MQ Island EMORB. In this case the H₂O content of the EDMM may be as low as 264 ppm using an H₂O/Ce ratio of 160 (H₂O/Ce of the most enriched NEPR seamount EMORB) and Ce content of 1.65 in the EDMM (Donnelly et al., 2004). Using the EDMM H₂O content of 264 ppm, the upper mantle H₂O content would be 104 ppm, lower by approximately a factor of two than the 191 ppm previously estimated by Shimizu et al. (2016). Therefore it is important to understand whether QDG EMORB represent melting of a lithospheric mantle or an actual asthenospheric mantle.

Also the evidence of lithospheric mantle metasomatism in the oceanic lithosphere by melts derived from the EDMM along with the potential evidence of its global distribution might have significant implications for the geodynamic evolution and interpretation of geophysical observations of the oceanic and continental lithospheric mantle. Amphibole has been invoked to potentially cause the sharp decrease in seismic velocity in oceanic (Green et al., 2011) and continental (Selway et al., 2015) environments. The similarity in average isotopic composition between the amphiboles observed in oceanic and continental regions limits the average age of the metasomatism to within ~200 Myrs assuming the amphiboles were produced from metasomatism by EDMM derived melts. This is because longer residence time of the amphiboles in

continental lithosphere leads to ingrowth of the isotopic composition, and thus different isotopic composition between amphiboles in oceanic and continental environments. The relatively young age of globally observable metasomatism could suggest a hydration induced weakening of the continental lithospheric mantle by metasomatism (e.g. Li et al., 2008), and preferential delamination of the metasomatized continental lithospheric mantle within ~200 Myrs of the metasomatic event. Delamination of the metasomatized continental lithospheric mantle would cause upwelling and decompression melting of the asthenospheric mantle, and the produced asthenospheric melts would metasomatize the overlying freshly exposed lithospheric mantle. This process would be able to keep the age of amphiboles in the lithosphere to within ~200 Myrs preventing its isotopic composition to differ significantly compared to the oceanic amphiboles and the EDMM.

Appendix A. Mantle metasomatism model (for details refer to Pilet et al. (2011))

As described in section 4.3, the initial asthenospheric mantle melt derived from the E-DMM mantle fractionally crystallizes in three steps in our model to form the MHL (metasomatized hydrous lithosphere), which is then melted to form the MHL melt.

For the phases crystallized, in addition to the those considered in Pilet et al. (2011), an additional phase carbonate and additional elements K and the volatiles (H_2O , CO_2 , F, Cl, S) were considered. The partition coefficient of the elements used and their references are listed in Table S2. K_2O - H_2O , S, and CO_2 are treated as major elements in phases such as amphibole and phlogopite, sulfide, and carbonate respectively, in the same manner that TiO_2 , Zr, and Hf are treated as a major element in Ti-rich phases (titanite, rutile, and ilmenite) and zircon respectively in the model of Pilet et al. (2011).

The composition of the MHL melt was modeled by combining (a) partial melt of the hydrous cumulate and (b) the residual melt (assuming that the composition of melt derived from a cryptically metasomatized peridotite is similar to those of the melt that metasomatized the peridotite). The composition of (a) the partial melt of the hydrous cumulate is calculated by combining (a1) the melt formed by incongruent melting of amphibole (forming a melt and producing clinopyroxene, olivine, and minor spinel) and (a2) the composition of minor and accessory phases (all phases other than amphibole) in the hydrous cumulate that are completely melted out during melting of the hydrous cumulate.

The major element composition of (a1) the melt formed by incongruent melting of amphibole was taken from the melt pocket from Aliani et al. (2009). They used mass-balance calculation to show that the melt pockets are the product of incongruent melting of amphibole, which produces melt, clinopyroxene, olivine, and minor spinel. The experimental results of incongruent melting of amphibole from Pilet et al. (2008) were not used since we envision the amphibole in the MHL veins (cm scale) to be equilibrated in major element with the surrounding peridotite similar to those in Aliani et al. (2009), whereas amphibole used in the experiments by Pilet et al. (2008) are hornblendites that are much larger scale and are in disequilibrium with the surrounding peridotite. The trace and volatile element composition of the (a1) amphibole melt was calculated using the composition of amphibole from the crystallization model and the incongruent melting reaction from Aliani et al. (2009). The major element compositions of (a2) minor and accessory phases are an average composition of these phases found in mantle xenolith database from PetDB. The trace and volatile element composition of (a2) minor and

accessory phases are simply those calculated in the crystallization model.

The major element composition of the (b) residual melt was calculated using the experimental liquids from (Pilet et al., 2010), which were parameterized as a function of the mass fraction of liquid relative to the initial liquid mass left after crystallization using a polynomial fit. The trace and volatile element composition of (b) residual liquid is simply those calculated in the crystallization model.

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Figure captions

Figure 2-1. (a) Th/La versus MgO for the samples. Most of the samples are relatively primitive with MgO > 6.0 wt%. Samples are separated into three groups DMORB (blue, Th/La ≤ 0.035), NMORB (gray, 0.035 < Th/La < 0.07), and EMORB (orange for QDG transform fault and green for NEPR seamount and MQ Island samples, Th/La ≥ 0.07). Error bars are 2σ SE. **(b)** Primitive mantle normalized trace element diagram of representative samples from each location and enrichment group. All plotted samples have between 7.5 and 8.5 wt% MgO. Primitive mantle composition is from McDonough and Sun (1995).

Figure 2-2. (a) $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for the samples. **(b)** $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for the samples. Northern hemisphere reference line as defined by Hart (1984). Small gray crosses are compilation of pacific MORB from Stracke (2012). Error bars are 2σ.

Figure 2-3. H₂O/Ce ratios versus **(a)** Th/La and **(b)** K/La ratios for samples uncontaminated by hydrothermal altered materials. DMORB samples with Cl/K > 0.04, NMORB samples with Cl/K > 0.06, and EMORB samples with Cl/K > 0.11 were removed from the data set (Shimizu et al., 2016). Error bars are 2σ SE.

Figure 2-4. H₂O/Ce and trace element ratios (K/Nb, K/U, Rb/Th, Ba/Nb, Rb/Nb, Nb/Th, Ce/Pb, Ba/Th, Ba/La, K₂O/H₂O) for the EMORB from QDG transform fault, NEPR seamounts, and MQ Island. DMORB and N-MORB samples are not shown for clarity.

Note that QDG EMORB generally have a higher K/Nb, K/U, Rb/Th, Rb/Ba, Rb/Nb and lower in Nb/Th, Ce/Pb, Ba/Th, Ba/La, K₂O/H₂O compared to NEPR seamount and MQ Island EMORB. Error bars are 2 σ SE.

Figure 2-5. H₂O/Ce and trace element ratios (F/Nd, Th/La, Th/U, La/Sm, Ce/Pb, Nb/U, Sm/Nd, Ba/La, Yb/Ce, La/Nd) for QDG transform fault, NEPR seamounts, and MQ Island samples. The blue line is a mixing trend between a QDG EMORB sample with high H₂O/Ce (D19A) and a QDG DMORB sample (D44A). The green line is a mixing trend between the same QDG EMORB sample (D19A) and a MQ Island EMORB sample (47963). Error bars are 2 σ SE.

Figure 2-6. (a) ¹⁴³Nd/¹⁴⁴Nd versus ⁸⁷Sr/⁸⁶Sr and **(b)** ²⁰⁸Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb for our samples and for a compilation of amphiboles in oceanic peridotites (gray circles) and continental xenoliths (gray crosses) from PetDB. Small gray crosses are compilation of pacific MORB from Stracke (2012). The black square is the average isotopic composition of amphibole in peridotites from the St. Paul's Rocks (Roden et al., 1984), which in (b), is equivalent to the average isotopic composition of amphiboles in oceanic peridotite.

Error bars are 2 σ .

Figure 2-7. H₂O/Ce ratios versus **(a)** Th/La and **(b)** K/La ratios for the results of the MHL model (orange dots) and samples.

Figure 2-8. H₂O/Ce and refractory/refractory element ratios (K/Nb, K/U, Rb/Th, Ba/Nb, Rb/Nb, Nb/Th, Ce/Pb, Ba/Th, Ba/La, K₂O/H₂O) for the results of the MHL model (orange dots), and EMORB samples from QDG transform fault, NEPR seamounts and MQ Island. DMORB and N-MORB samples are not shown for clarity.

Figure 2-9. Primitive mantle normalized trace element diagram of results of MHL model (gray lines) and QDG EMORB. D-MORB and N-MORB samples from the QDG transform fault and NEPR seamounts and NEPR seamounts E-MORB are not shown for clarity. All plotted samples have between 7.5 and 8.5 wt% MgO. Primitive mantle composition is from McDonough and Sun (1995).

Figure 2-10. (a) ¹⁴³Nd/¹⁴⁴Nd versus ⁸⁷Sr/⁸⁶Sr for the samples and for the results of the MHL model (orange dots). The orange line with the stronger curvature is the mixing line between DMORB and MHL melts, while the green line with less curvature is that between DMORB and a typical asthenospheric EMORB (5% melting of EDMM from Donnelly et al. (2004)). **(b)** ²⁰⁸Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb for the samples and the results of the MHL model (orange dots). Also shown are the Horoman peridotite (Malaviarachchi et al., 2008) and sulfides included in silicate minerals (Burton et al., 2012) with highly unradiogenic ²⁰⁶Pb/²⁰⁴Pb isotopic composition and plotting above the NHRL (Hart, 1984). Blue arrow shows the qualitative effect of assimilating these materials to our MHL model results.

Figure 2-11. Major element composition of our samples, MHL melts (red open diamonds), MHL model (orange open diamonds, mixture between MHL melts and QDG DMORB D7A-A with MgO = 9.8 wt%). Also shown are curve fits by eye to experimental melt composition of Médard et al. (2006) (olivine+clinopyroxene+amphibole (OCA2) at 0.5-1.0 GPa (green line)), Sorbadere et al. (2013) (pure OCA2 (red line) and pure peridotite KLB-1 (orange line), and mixtures of OCA2 and peridotite KLB-1 (blue line and yellow triangle) all at 1 GPa), and Pilet et al. (2008) (Sandwich experiment with hornblendite (AG4) and peridotite (DMM1) at 1.5 GPa (gray line)).

Figure 2-12. Th/La and trace element ratios (Nb/Th, Ce/Pb, P/Nd, K/Nb, K/U, Rb/Th) for the Petit-spot lavas (gray (groups 1&2) and black (group 3) diamonds) (Hirano et al., 2006; Machida et al., 2015), and samples from QDG transform fault, NEPR seamounts and MQ Island.

Figure 2-13. Ce/Pb and Ba/Th versus (a, b) $^{143}\text{Nd}/^{144}\text{Nd}$, (c, d) $^{206}\text{Pb}/^{204}\text{Pb}$, and (e, f) $^{87}\text{Sr}/^{86}\text{Sr}$ for the samples, petit spot seamounts (gray (groups 1&2) and black (group 3) diamonds) (Hirano et al., 2006; Machida et al., 2015), and melt derived from the MHL (red circle). The MHL composition is from the model in section 4.3, and the isotopic composition was calculated assuming formation of MHL 130 Myrs ago from a melt derived from an EDMM. The isotopic composition of EDMM 130 Myrs ago was calculated using a current day EPR EMORB type isotopic composition (sample 3010-

1502 from Brandl et al. (2012)) and the parent-daughter ratios of the EDMM from Donnelly et al. (2004).

Figure 2-S1. H₂O/Ce ratios versus Ba/La for **(a)** all the samples and **(b)** samples filtered for contamination by hydrothermal materials. Error bars are 2 σ SE.

Figure 2-S2. H₂O/Ce versus alkalinity index (deviation in wt% Na₂O and K₂O from the Macdonald and Katsura (1964) line) for our samples. Note that the negative trend between H₂O/Ce and $\delta_{\text{alkalinity}}$ is opposite to the positive trend expected from lower degree melting of garnet peridotite due to the lower melt productivity at lower degrees of melting of a wetter mantle (Asimow et al., 2004; Asimow et al., 1997) and higher partition coefficient of Ce relative to H₂O in garnet (Hauri et al., 2006) if we assume melting of a single mantle source.

Figure 2-S3. **(a)** H₂O/Ce, **(b)** Cl/K, **(c)** F/Nd, and **(d)** S/Dy ratios versus Th/La ratios for the results of the MHL model (orange dots) (refer to section 4.3) and Cl-uncontaminated samples. In (d), samples are filtered for sulfide saturation using the SCSS model of Fortin et al. (2015).

Table headings

Table 2-1. Parameters used in the mantle metasomatism model based on the model of Pilet et al. (2011).

Table 2-2. Range of parameters required to reproduce the QDG E-MORB

Table 2-3. Mineral-melt partition coefficients used in the model

Table footnotes

Table 2-3.

^aRefractory trace elements (RTE) from a compilation Kelemen et al. (2003). H₂O, Cl, F, and S from Hauri et al. 2006 and CO₂ from Rosenthal et al. (2015).

^bRTE except REE from Dalpé and Baker (2000) (experiment FM10). REE from Shimizu et al. (in review) (recommended partition coefficient at 1100°C). F and Cl from Dalou (2011). TiO₂, K₂O and H₂O treated as major elements.

^cRTE from Foley et al. (1996) (experiment Phl-4). F and Cl from Dalou (2011). TiO₂, K₂O and H₂O treated as major elements.

^dRTE from Bindeman and Davis (2000) (experiment 99-1). H₂O from Johnson (2005). F and Cl from Dalou et al. (2012). S assumed perfectly incompatible due to lack of experimental data.

^eRTE from Pilet et al. (2011).

^fTiO₂ treated as major element following Pilet et al. (2011).

^gVolatile elements assumed to be perfectly incompatible.

^hH₂O, F, and Cl from Mathez and Webster (2005). S assumed perfectly incompatible.

ⁱZr and Hf treated as major element following Pilet et al. (2011).

^jRTE from Pilet et al. (2011), except for Pb *D* of 50 (within range of experimental and natural observation such as Wood et al. (2008), Lagos et al. (2008), Li and Audétat (2012), Patten et al. (2013), Hart and Gaetani (2016)).

^kS treated as a major element.

^lRTE calculated using apparent cmt/melt *D* from Ionov (1998) (sample 4-36-9). Ba and U partition coefficients were decreased and increased by factor of 10 respectively to better reproduce natural carbonate RTE content.

^mCO₂ treated as a major element.

ⁿ*D* values assumed same as Nb partition coefficient for certain phases due to lack of measurements.

Figures

Figure 2-1.

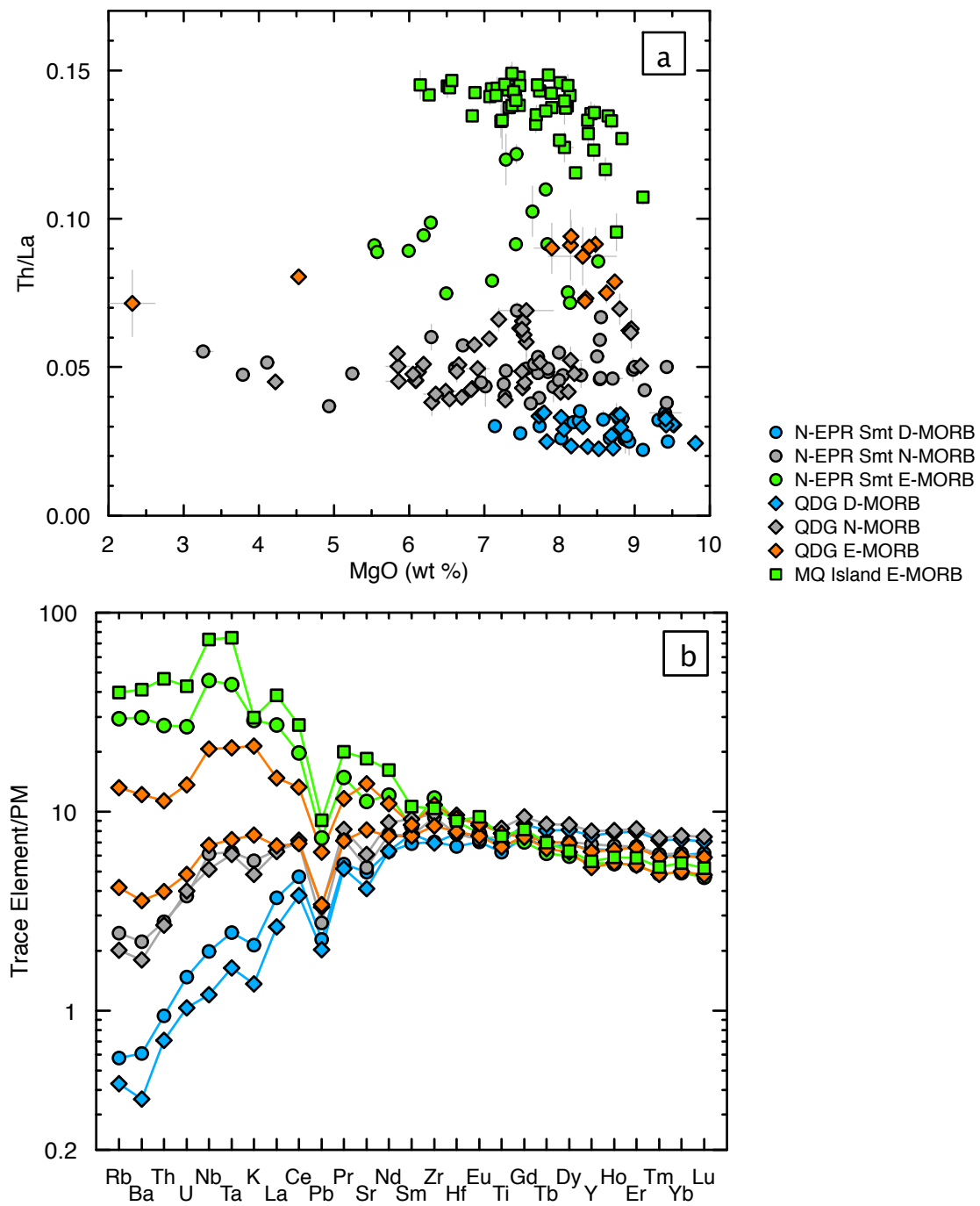


Figure 2-2.

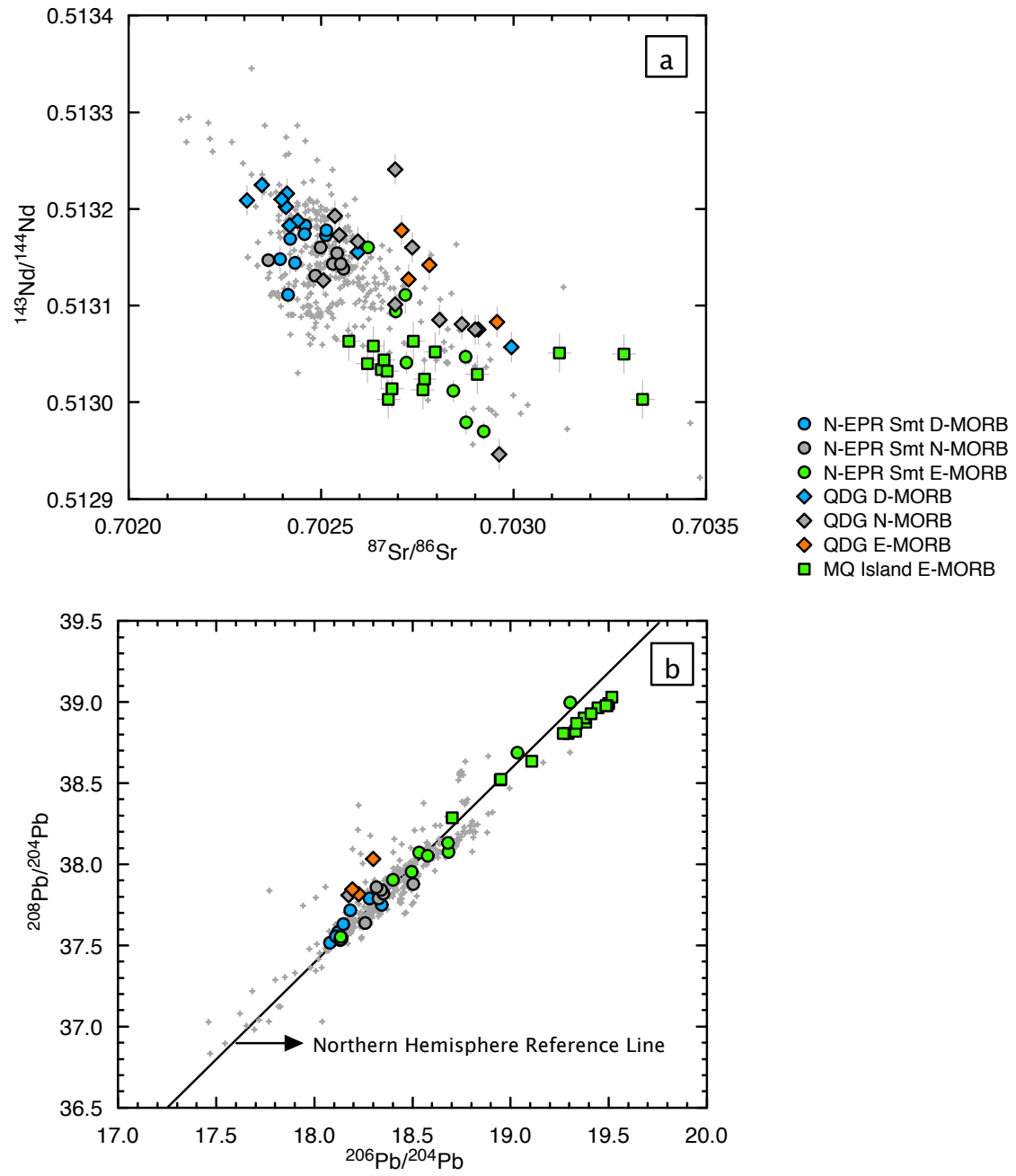


Figure 2-3.

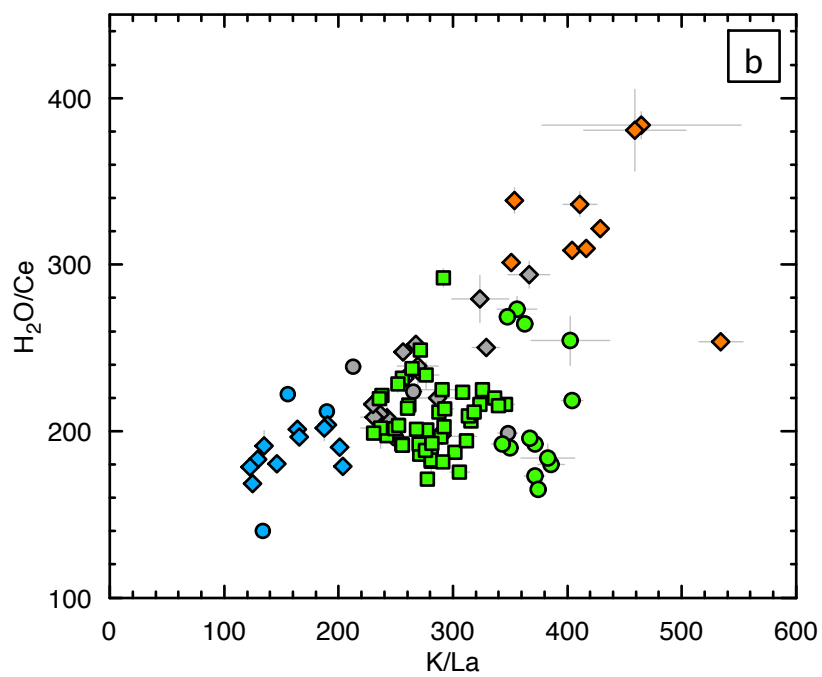
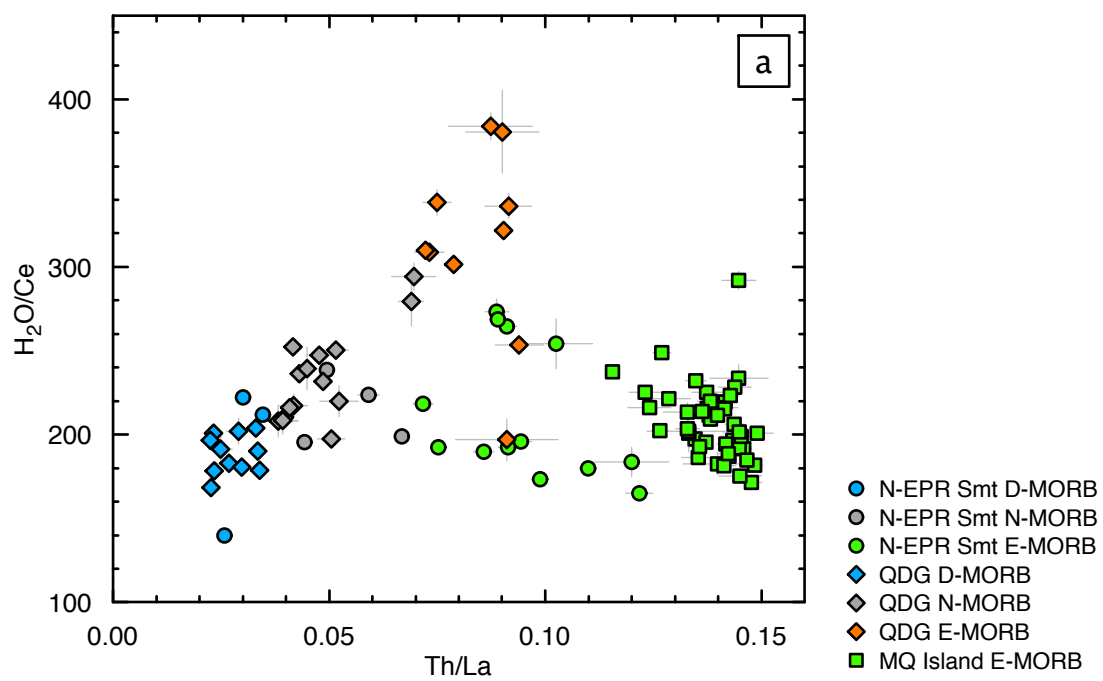


Figure 2-4.

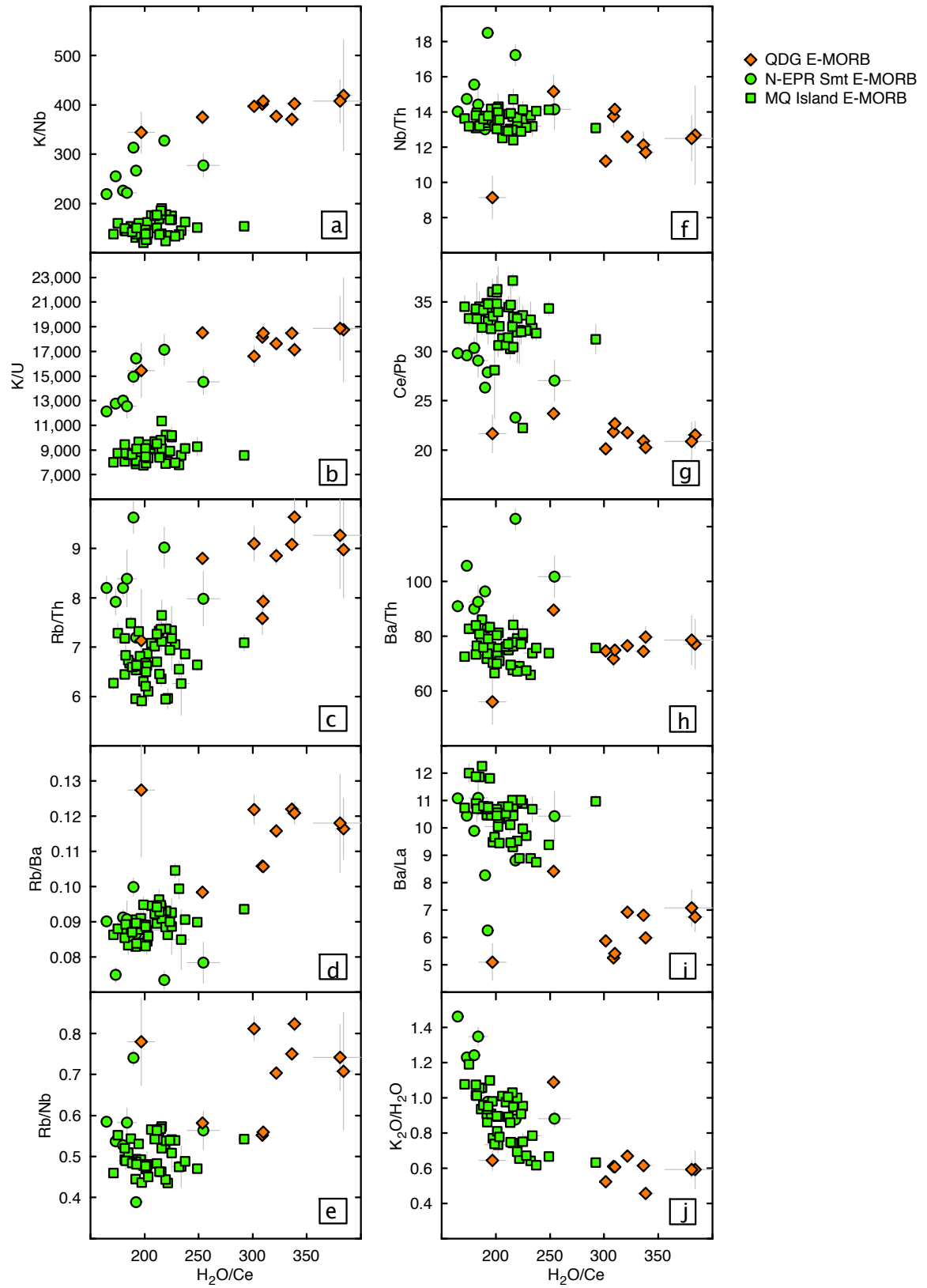


Figure 2-5.

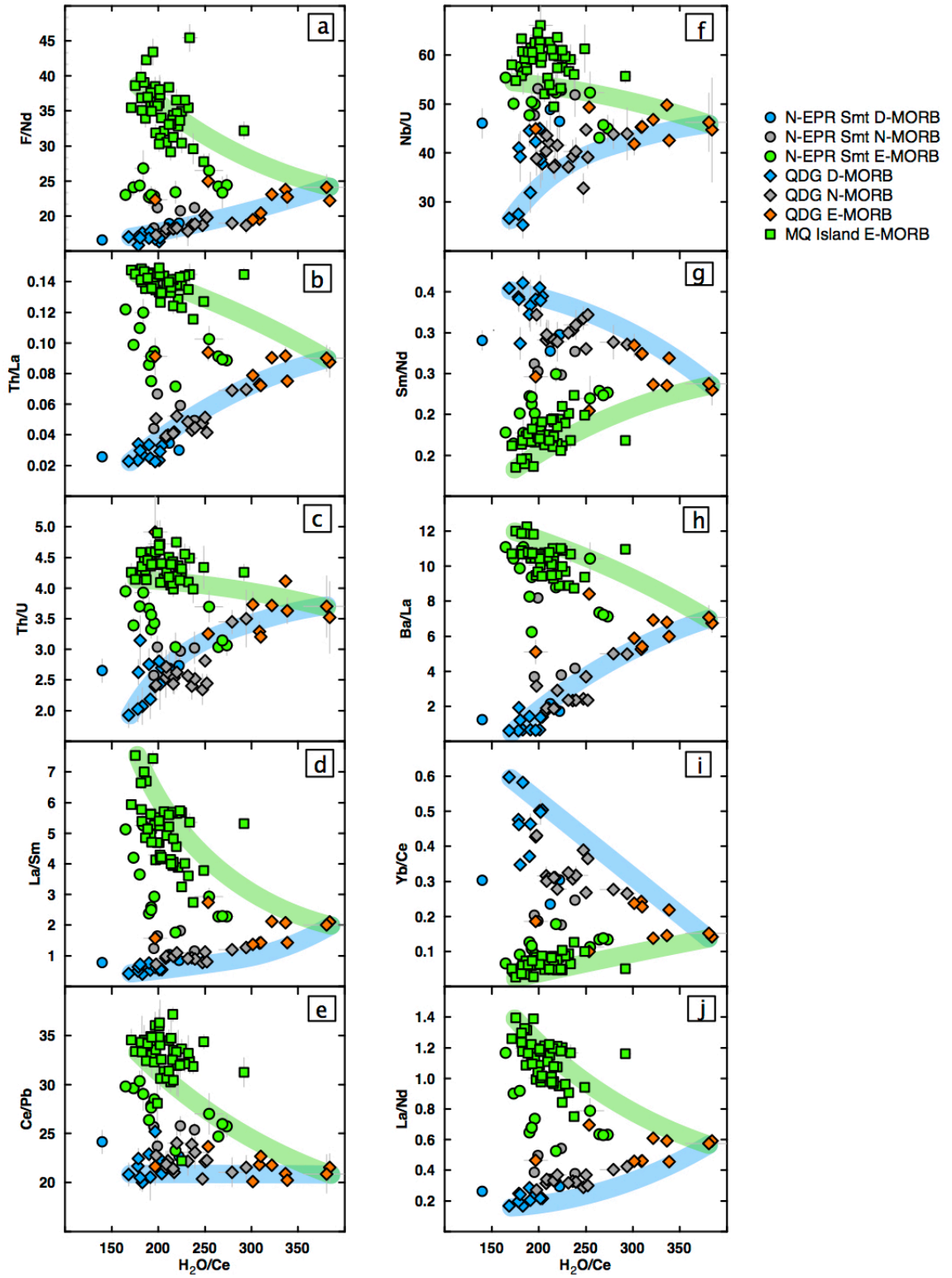


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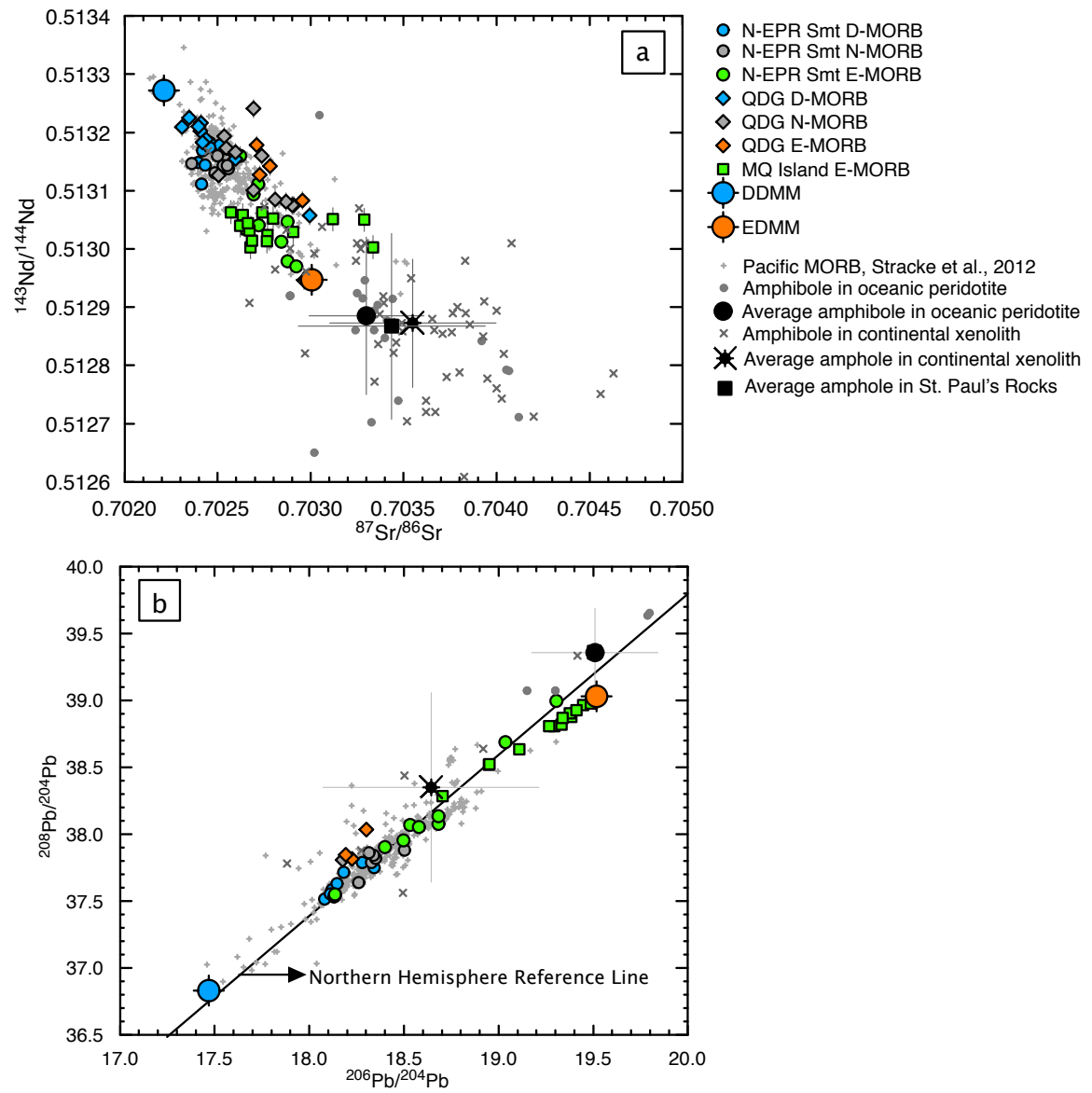


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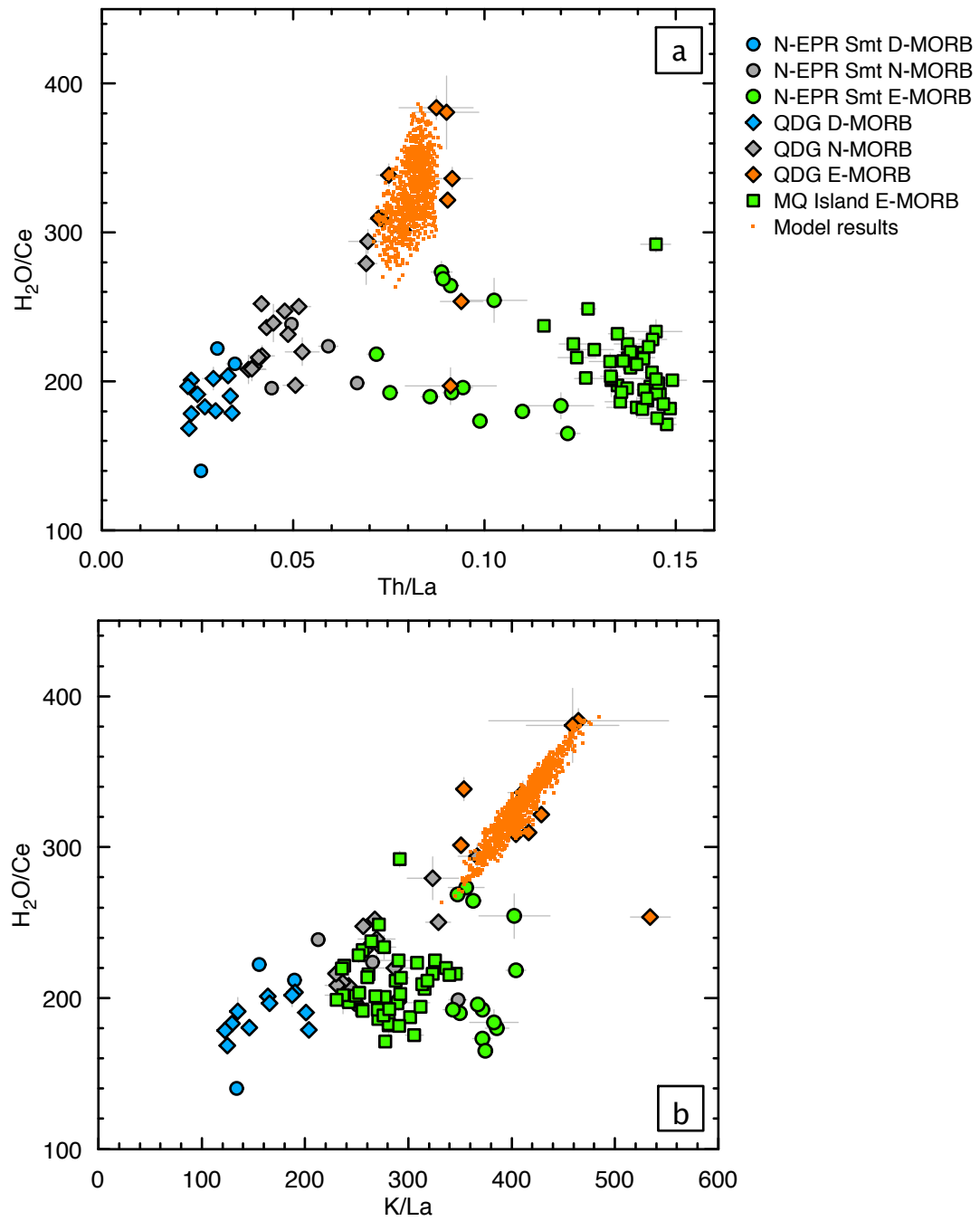


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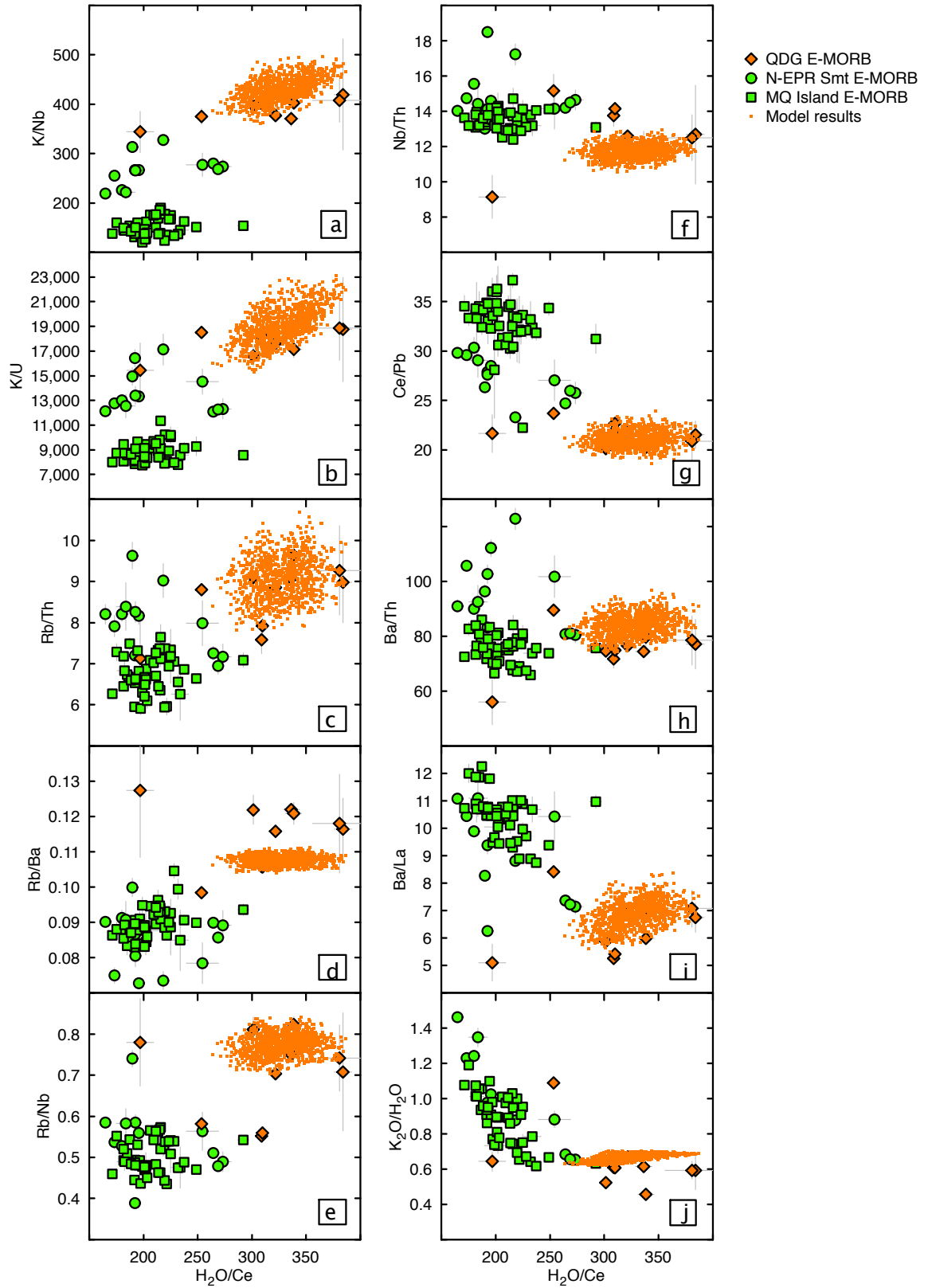


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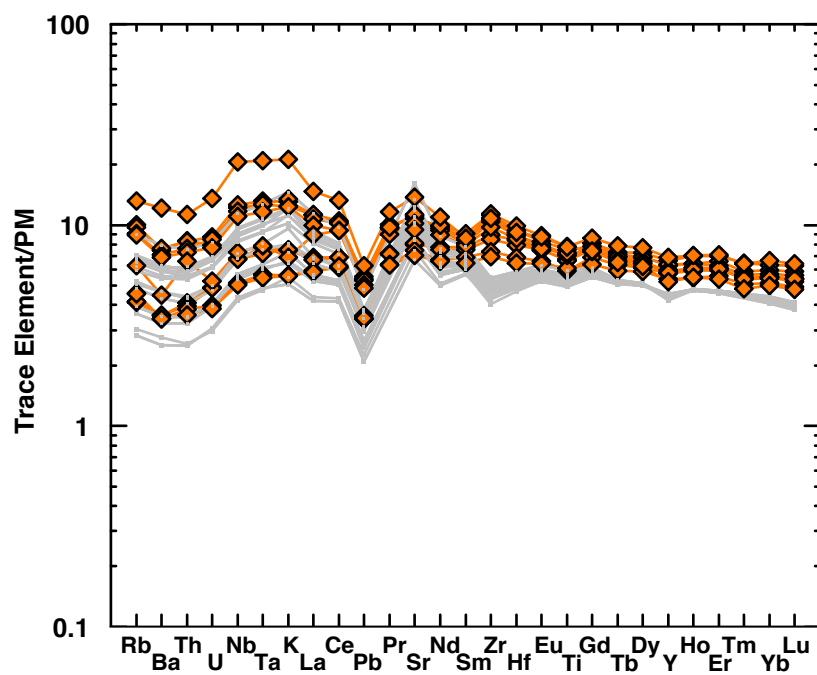


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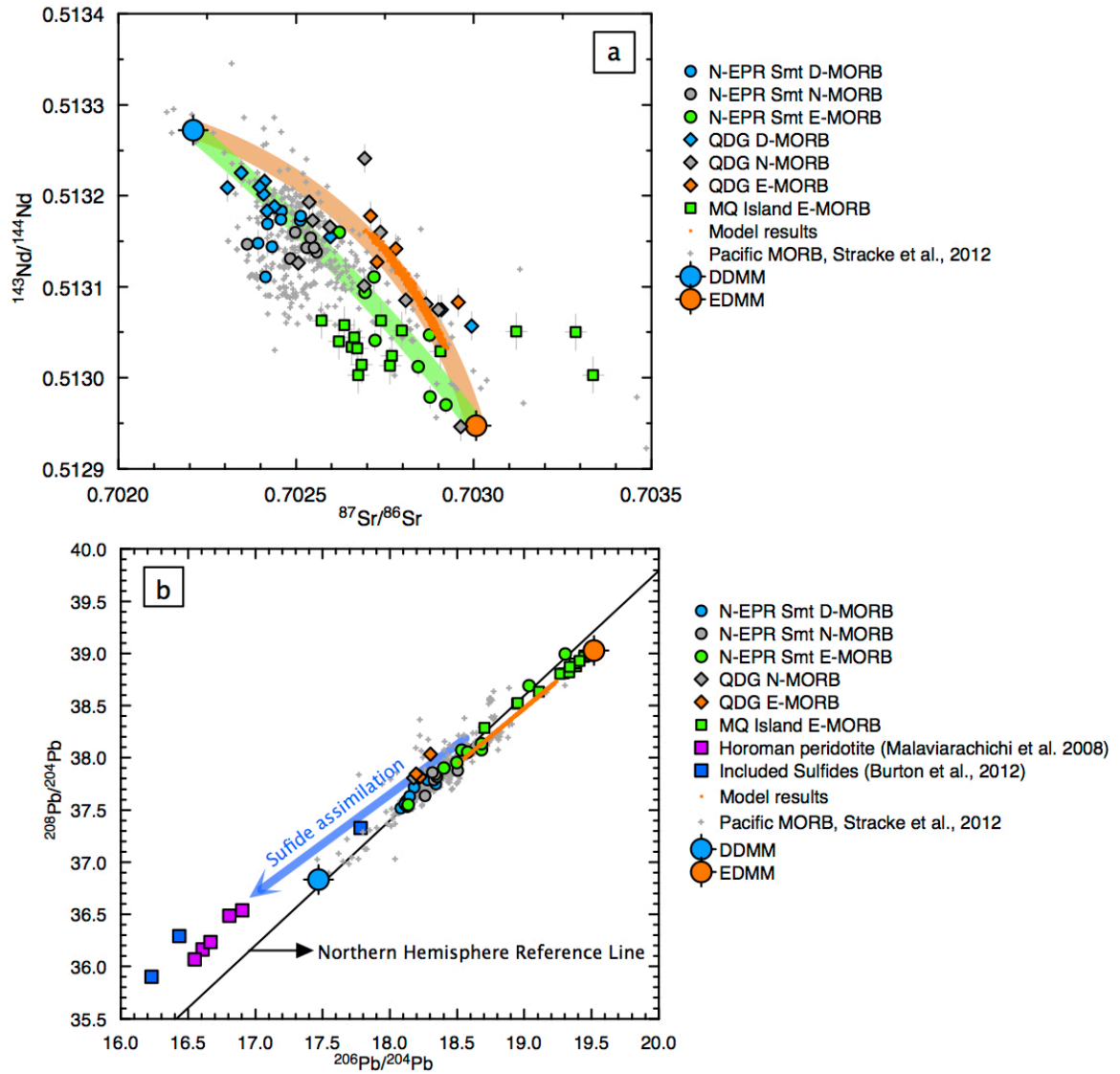


Figure 2-11.

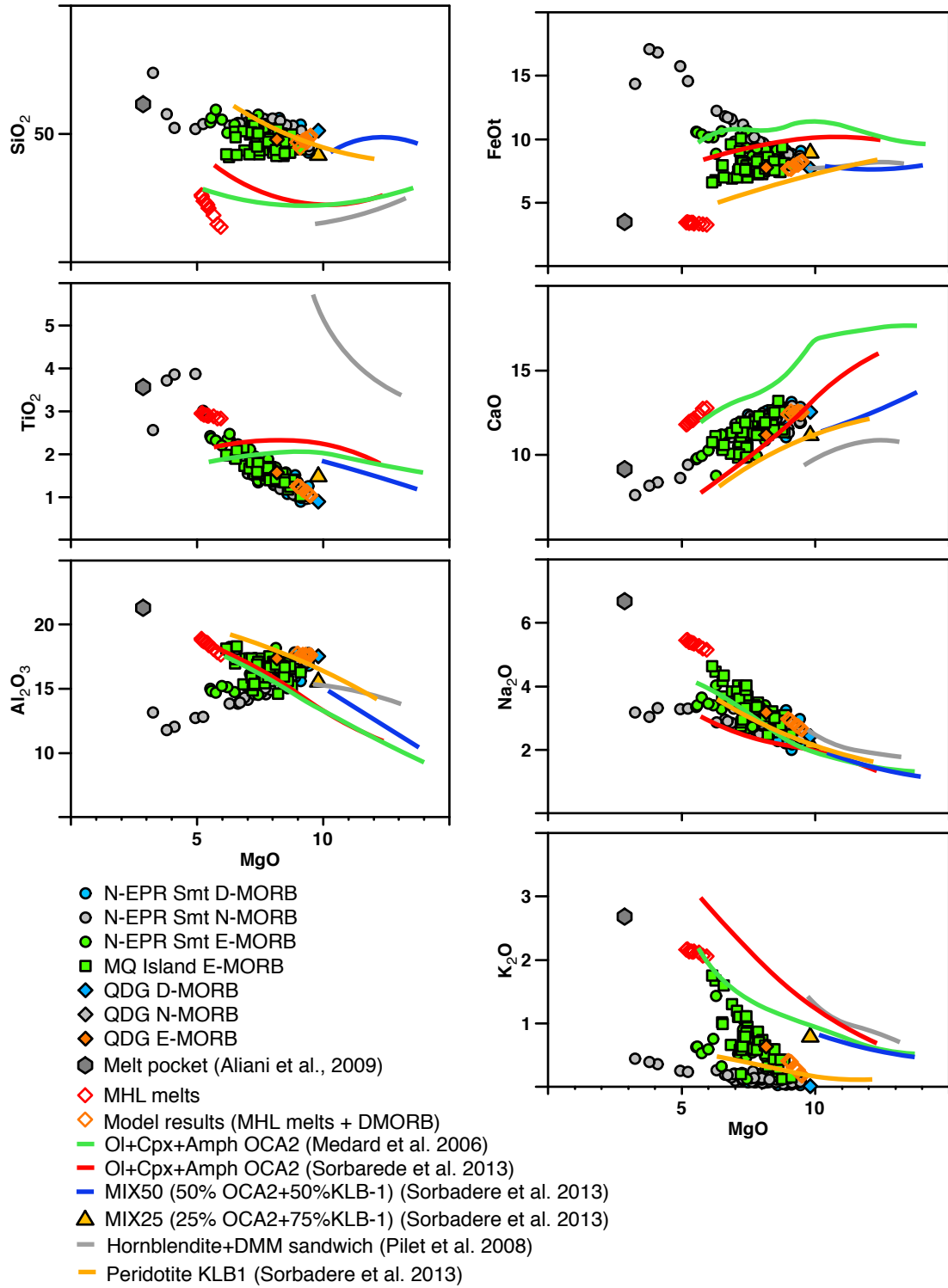


Figure 2-12.

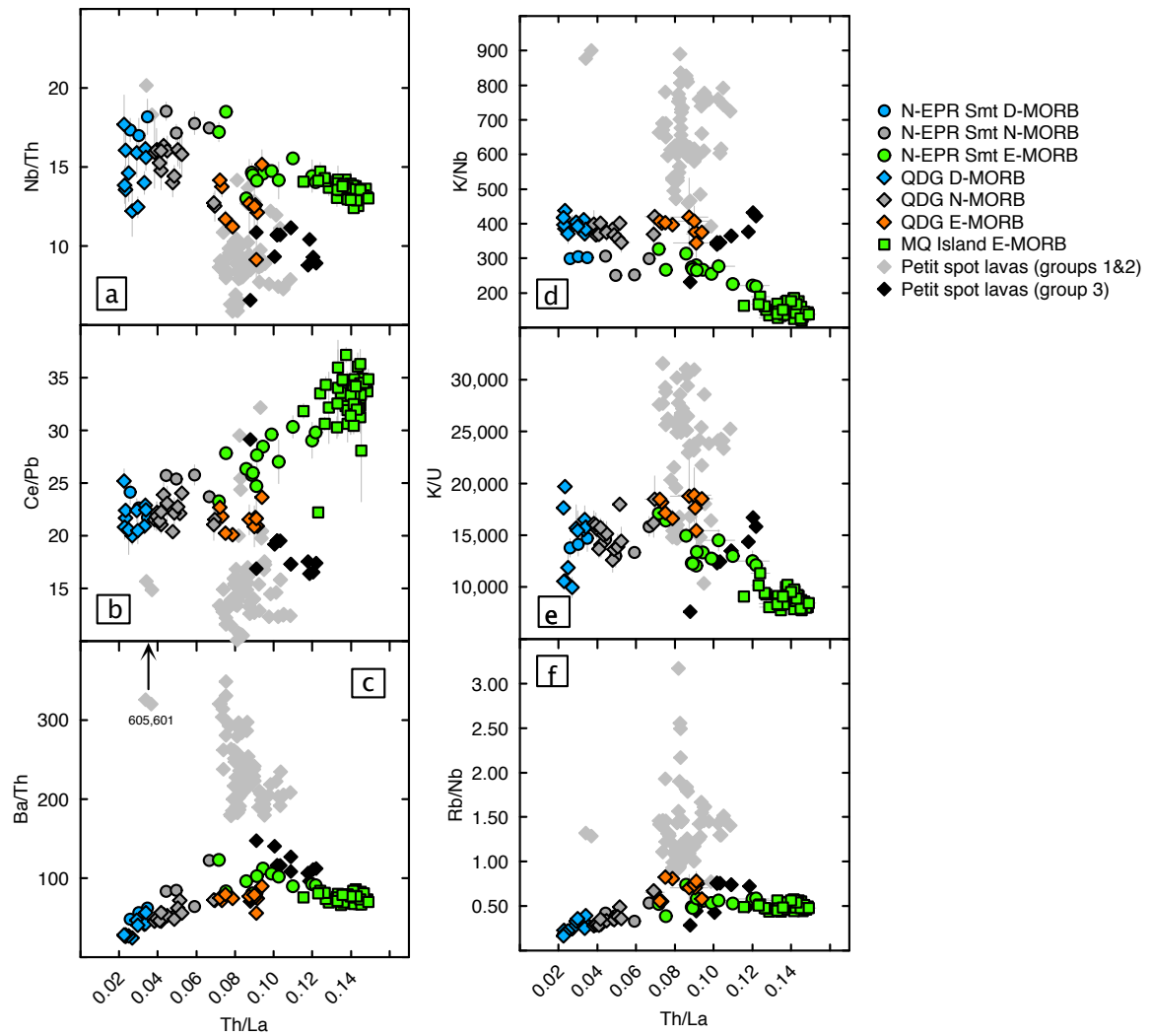


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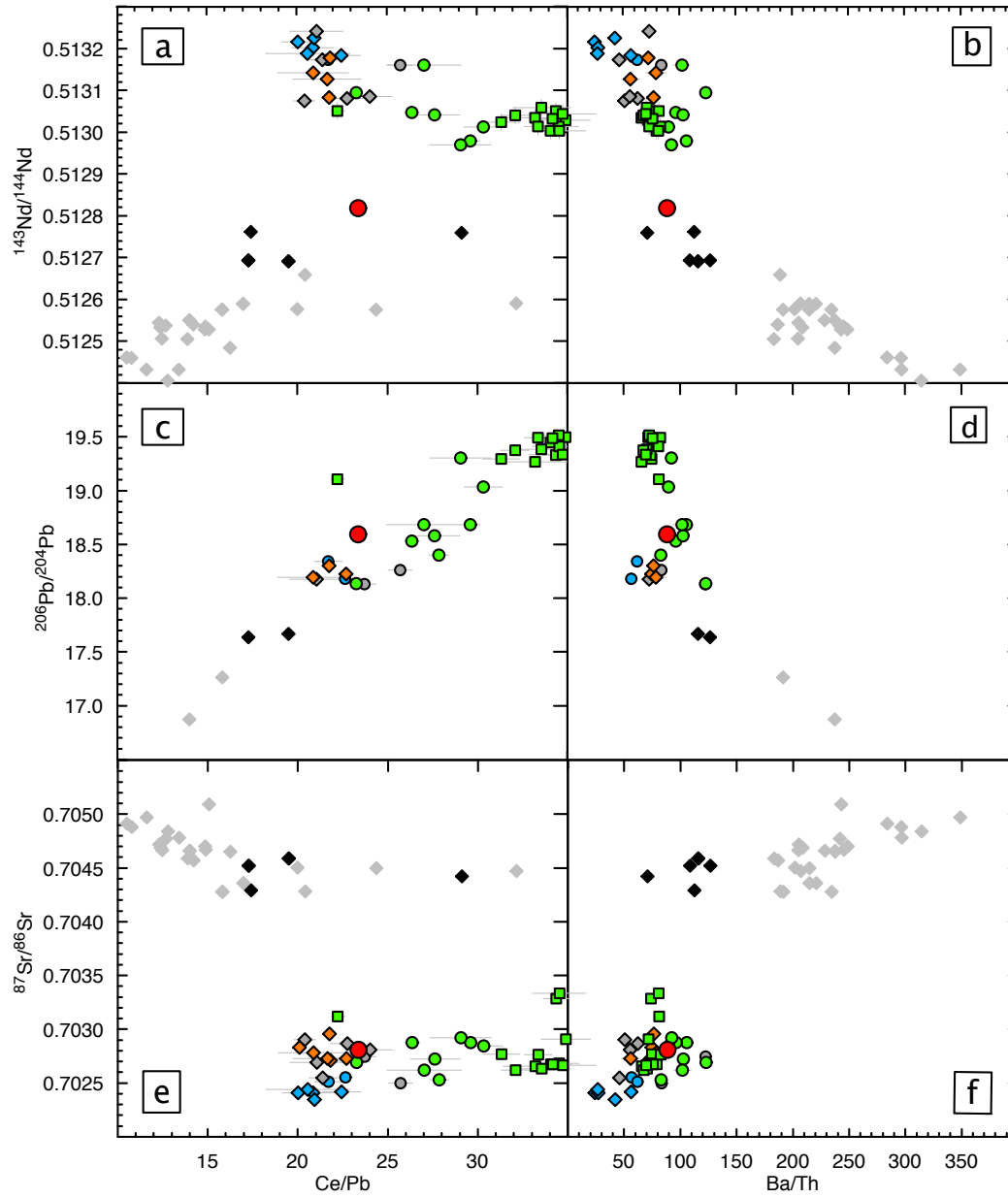


Figure 2-S1.

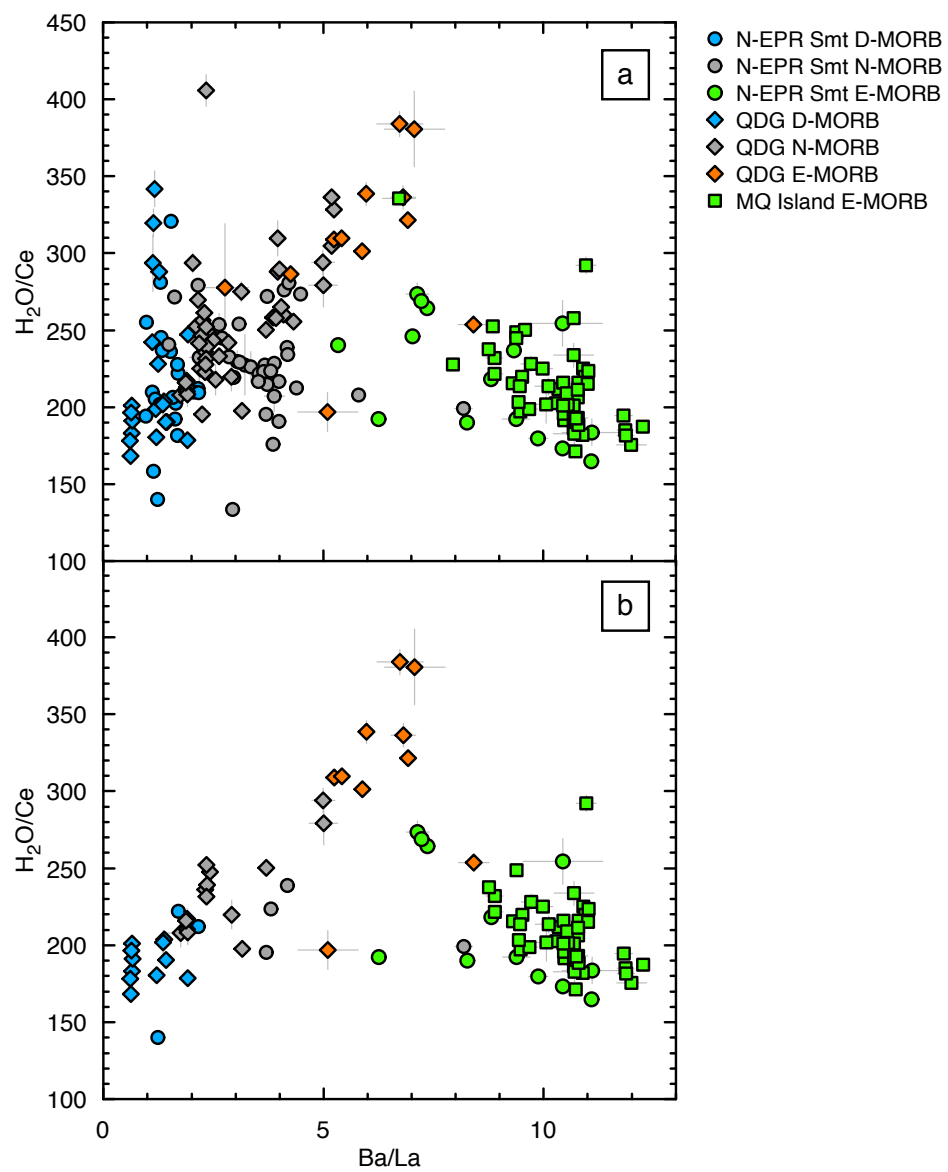


Figure 2-S2

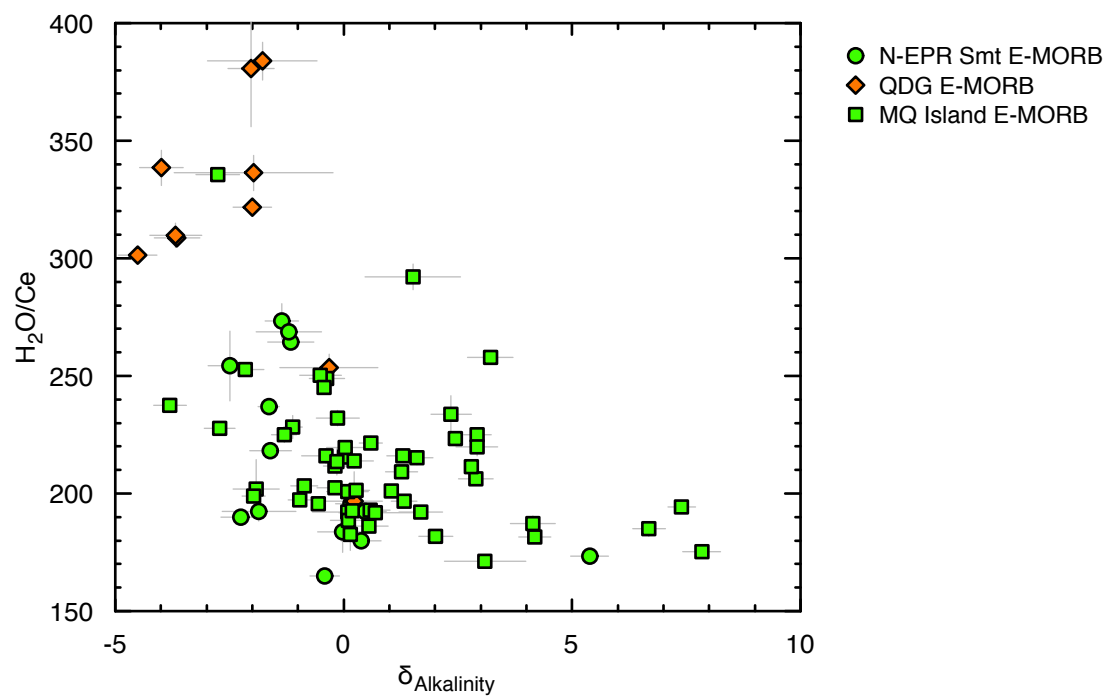
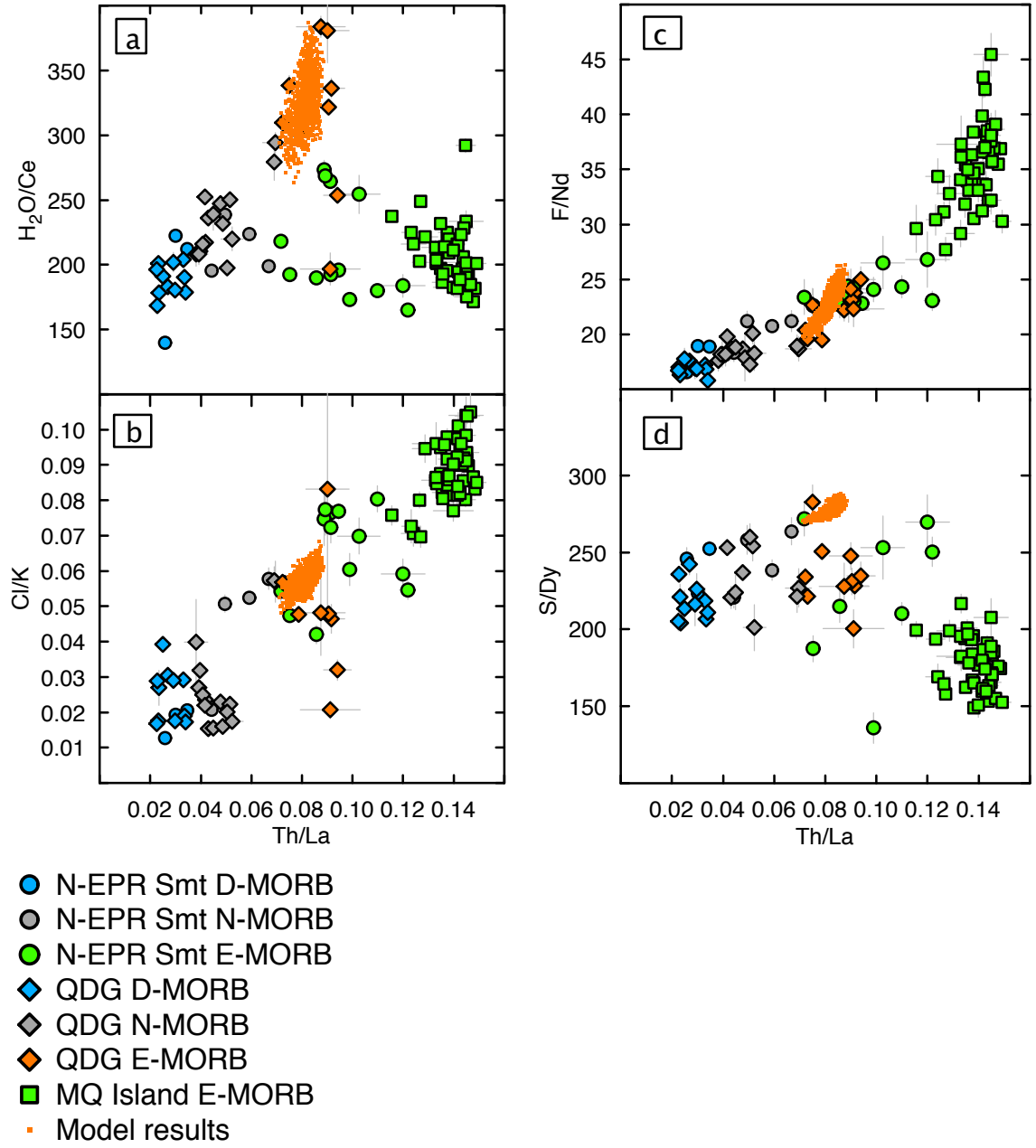


Figure 2-S3.



Tables

Table 2-1. Parameters used in the mantle metasomatism model based on the model of Pilet et al. 2011.

Parameter	Description
F	Initial degree of melting of the EDMM
fL1	Mass fraction of melt left after the anhydrous fractional crystallization
Anhydrous fractional crystallization mineral proportions	Clinopyroxene, orthopyroxene, garnet, trapped liquid
f	Mass fraction of melt left after the first hydrous fractional crystallization (f is constant and set to 0.4)
First hydrous fractional crystallization mineral proportions	Clinopyroxene, garnet, amphibole, phlogopite, plagioclase, ilmenite, titanite, apatite, rutile, allanite, sulfide, carbonate
fL2	Mass fraction of melt left after the second hydrous fractional crystallization
Second hydrous fractional crystallization mineral proportions	Clinopyroxene, orthopyroxene, garnet, amphibole, phlogopite, plagioclase, ilmenite, titanite, apatite, zircon, rutile, allanite, sulfide, carbonate
fmax	Hydrous cumulates formed between fmax and fL2 are combined with residual liquid composition at fL2 to form the MHL (amount of residual liquid up to 30% of MHL)
F_end	Degree of melting of the metasomatised hydrous lithosphere (MHL)

Table 2-2. Range of parameters required to reproduce the QDG E-MORB

Parameters	Min	Max
F	0.014	0.017
fL1	0.529	0.647
fL2	0.309	0.378
fmax	0.533	0.652
F_end	0.415	0.507
<i>Anhydrous fractional crystallization mineral proportions</i>		
Clinopyroxene	0.691	0.845
Orthopyroxene	0.003	0.003
Garnet	0.202	0.246
trapped liquid	0.005	0.006
<i>First hydrous fractional crystallization mineral proportions</i>		
Clinopyroxene	0.117	0.143
Garnet	0.0018	0.0022
Amphibole	0.672	0.821
Phlogopite	0.0018	0.0021
Plagioclase	0.0289	0.0354
Ilmenite	0.00089	0.00108
Titanite	0.00028	0.00034
Apatite	0.00759	0.00928
Rutile	0.00001	0.00002
Allanite	0.00008	0.00009
Sulfide	0.0086	0.0105
Carbonate	0.0612	0.0748
<i>Second hydrous fractional crystallization mineral proportions</i>		
Clinopyroxene	0.0173	0.0211
Orthopyroxene	0.0041	0.0050
Amphibole	0.728	0.890
Phlogopite	0.0160	0.0196
Plagioclase	0.0093	0.0114
Ilmenite	0.00088	0.00108
Titanite	0.000035	0.000043
Apatite	0.00809	0.00989
Zircon	0.00006	0.00007
Rutile	0.00002	0.00002
Allanite	0.00004	0.00005
Sulfide	0.014	0.017
Carbonate	0.102	0.125

Table S2-1. Mineral-liquid partition coefficient used in the model

	Rb	Ba	Th	U	Nb	Ta ^a	K ₂ O	La	Ce	Pb	Pr
Olivine ^a	0.0003	0.000000001	0.000000001	0.000000001	0.001	0.001	0.000000001	0.000007	0.00001	0.00001	0.00004
Clinopyroxene ^a	0.0009	0.00068	0.01	0.003	0.0077	0.0077	0.007	0.0536	0.0858	0.072	0.13
Orthopyroxene ^a	0.0002	0.00001	0.00001	0.00001	0.0029	0.0029	0.00001	0.001	0.003	0.003	0.006
Garnet ^d	0.00001	0.00001	0.001	0.005	0.013	0.013	0.00001	0.001	0.008	0.0005	0.033
Amphibole ^b	0.21	0.16	0.018	0.016	0.14	0.18	1.5 wt%	0.06	0.11	0.096	0.16
Phlogopite ^c	6.41	3.57	0.01	0.01	0.0832	0.1023	9 wt%	0.05	0.055	0.2	0.06
Plagioclase ^d	0.031	0.389	0.07	0.073	0.05	0.05	0.154	0.256	0.159	0.36	0.146
Ilmenite ^{e,f,g}	0.004	0.007	0.008	0.027	13.3	13.3	0	0.01	0.013	0.93	0.02
Titanite ^{e,f,g}	0.0014	0.0024	10	6.6	20	20	0	10.6	15.9	0.1	25
Apatite ^{e,h}	0.006	0.021	11.25	12	0.05	0.05	0	16.9	20.8	0.13	22
Zircon ^{e,g,i}	0.006	0.004	44	250	230	230	0	0.2	1	0.1	2.5
Rutile ^{e,f,g}	0.01	0.01	0.5	0.5	83.4	83.4	0	0.3	0.25	0.22	0.2
Allanite ^{e,g}	0.01	0.01	803	56.3	0.2	0.2	0	1598	1278	2.8	1200
Sulfide ^{j,k}	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0	0.0001	0.0001	50	0.0001
Carbonate ^{l,m}	0.010	0.085	0.012	0.400	0.024	0.024	0	0.100	0.054	0.069	0.044

	Sr	Nd	Sm	Zr	Hf	Eu	Ti	Gd	Tb	Dy	Ho
Olivine ^a	0.00001	0.00007	0.0007	0.004	0.004	0.00095	0.015	0.0012	0.0026	0.004	0.007
Clinopyroxene ^a	0.1283	0.1873	0.291	0.1234	0.256	0.33	0.4	0.37	0.41	0.442	0.43
Orthopyroxene ^a	0.003	0.009	0.02	0.04	0.04	0.03	0.15	0.04	0.05	0.06	0.065
Garnet ^d	0.007	0.057	0.217	0.5	0.5	0.45	0.6	0.9	1.5	2	2.8
Amphibole ^b	0.22	0.22	0.32	0.24	0.42	0.32	2 wt%	0.33	0.33	0.33	0.32
Phlogopite ^c	0.167	0.065	0.07	0.08	0.08	0.09	3 wt%	0.095	0.1	0.1	0.1
Plagioclase ^d	3.17	0.123	0.098	0.0044	0.03	0.148	0.0891	0.0461	0.06	0.032	0.048
Ilmenite ^{e,f,g}	0.04	0.03	0.06	0.02	0.08	0.14	50 wt%	0.14	0.14	0.19	0.16
Titanite ^{e,f,g}	0.35	33.9	48	4.5	7.3	44.2	39.5 wt%	55	50	48.4	45
Apatite ^{e,h}	5.3	25.1	28.3	0.02	0.02	17	0.02	21.3	20.4	19.5	18.7
Zircon ^{e,g,i}	0.03	0.6	3	65 wt%	1 wt%	3	0.1	6.5	26	45	70
Rutile ^{e,f,g}	0.15	0.1	0.08	5.95	7.08	0.05	98.5 wt%	0.04	0.035	0.028	0.022
Allanite ^{e,g}	0.6	1115	746	0.1	0.2	507	2.8	200	150	100	70
Sulfide ^{j,k}	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Carbonate ^{l,m}	10.549	0.043	0.278	0.003	0.025	0.158	0.000	0.133	0.000	0.040	0.030

	Y	Er	Yb	Lu	H ₂ O	CO ₂	F	Cl	S
Olivine ^a	0.023	0.009	0.023	0.03	0.002	0.0007	0.003	0	0.01611111
Clinopyroxene ^a	0.467	0.43	0.43	0.433	0.018	0.0005	0.046	0.00068	0.03925
Orthopyroxene ^a	0.1	0.09	0.1	0.12	0.019	0.0003	0.027	0.00001	0.0304
Garnet ^d	7	3.5	7	9	0.004	0.0001	0.006	0.00001	0.02833333
Amphibole ^b	0.35	0.34	0.35	0.35	2.2 wt%	0	0.5	0.38	0
Phlogopite ^c	0.1	0.1	0.1	0.1	4.3 wt%	0	1.2	0.1	0
Plagioclase ^d	0.0289	0.0185	0.031	0.00687	0.004	0	0.098	0.0014	0
Ilmenite ^{e,f,g}	0.14	0.27	0.19	0.18	0	0	0	0	0
Titanite ^{e,f,g}	43	37.4	30.3	22.8	0	0	0	0	0
Apatite ^{e,h}	16.9	13.8	8.5	7.8	0.4	0	3.4	0.8	0
Zircon ^{e,g,i}	80	90	100	110	0	0	0	0	0
Rutile ^{e,f,g}	0.018	0.015	0.012	0.01	0	0	0	0	0
Allanite ^{e,g}	50	45	30	20	0	0	0	0	0
Sulfide ^{j,k}	0.0001	0.0001	0.0001	0.0001	0	0	0	34 wt%	0
Carbonate ^{l,m}	0.027	0.025	0.020	0.029	0	50 wt%	0	0	0

^aRefractory trace elements (RTE) from a compilation of Kelemen et al. 2003. H₂O, Cl, F, and S from Hauri et al. 2006 and CO₂ from Rosenthal et al. 2015.^bRTE except REE from Dalpé and Baker, 2000 (Experiment FM10). REE from Shimizu et al., 2016 (1100°C). F and Cl from Dalou et al. 2011. TiO₂, K₂O and H₂O treated as major elements.^cRTE from Foley et al. 1996 (Experiment Phl-4). F and Cl from Dalou et al. 2011. TiO₂, K₂O and H₂O treated as major elements.^dRTE from Bideman and Davis, 2000 (Experiment 99-1). H₂O from Johnson, 2005. F and Cl from Dalou et al. 2012. S assumed perfectly incompatible due to lack of experimental^eRTE from Pilet et al. 2011.^fTiO₂ treated as major element following Pilet et al. 2011.^gVolatile elements assumed to be perfectly incompatible.^hH₂O, F, and Cl from Mathez and Webster, 2005. S assumed perfectly incompatible.ⁱZr and Hf treated as major element following Pilet et al. 2011.^jRTE from Pilet et al. 2011, except for Pb D of 50 (within range of experimental and natural observation such as Wood et al., 2008, Lagos et al., 2008, Li and Audétat 2012, Patten et al., 2013, Hart and Gaetani 2016)^kS treated as a major element.^lRTE calculated using apparent cdt/melt D from Ionov et al. 1998 (sample 4-36-9). Ba and U partition coefficients were decreased and increased by factor of 10 respectively to better reproduce natural carbonate RTE content.^mCO₂ treated as a major element.ⁿD values assumed same as Nb partition coefficient for certain phases due to lack of measurements.

CHAPTER 3

Parameterized lattice strain models for REE partitioning between amphibole and silicate melt

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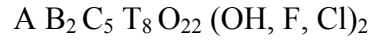
Abstract

The distribution of rare earth elements (REE) between amphibole and silicate melt is important for understanding a wide variety of igneous and metamorphic processes in the lithosphere. In this study, we used published experimental REE and Y partitioning data between amphibole and silicate melt, the lattice strain model, and non-linear least squares regression method to parameterize key parameters in the lattice strain model (D_0 , r_0 , and E) as a function of pressure, temperature, and both amphibole and melt compositions. Two models, which give nearly identical results, are obtained in this study. In the first model, D_0 depends on temperature and amphibole composition: it positively correlates with Ti content, and negative correlates with temperature and Mg, Na, and K contents in the amphibole. In the second model, D_0 depends solely on the melt composition: it positively correlates with Si content, and negatively correlates with Mg, and Ca contents in the melt. In both the mineral and melt composition models, r_0 negatively correlates with the ferromagnesian content in the M4 site of the amphibole and E is a constant. The very similar coefficients in the equations for r_0 and best-fit values for E in the two models allow us to connect the two models through amphibole-melt phase equilibria. An application of our model to amphiboles in mantle xenoliths shows that observed major element compositional variations in amphibole alone can give rise to an order of magnitude variations in amphibole-melt REE partition coefficients. Also our models and experimental data simulating fractional crystallization of arc magmas suggests that (1) REE partition coefficients between amphibole and melt can vary by an order of magnitude during arc magma crystallization due to variation in the temperature and

composition of the amphibole and melt, and that (2) amphibole fractional crystallization plays a key role in depleting the MREE relative to HREE and LREE in arc magmas.

1. Introduction

Amphibole is ubiquitous in the Earth's lithosphere, occurring in a wide variety of igneous and metamorphic rocks. As a member of inosilicate, amphibole has three main structure sites (A, M4, and M1-M3) that can accommodate cations of a range of size and charge. The general chemical formula of amphiboles may be described by the formula



where A = Na, K, or vacant ($\square$) in A site; B = Ca, Na, Mn, Fe^{2+} , Mg in M4 site; C = Fe^{2+} , Fe^{3+} , Mg, Al, Mn, Ti, Cr, in M1, M2, and M3 sites; T = Si, Al in tetrahedral site (Hawthorne, 1983). The smaller M1-M3 sites are in 6-fold coordination, while the larger M4 site is in 8-fold coordination. The latter can accommodate larger cations such as the trivalent rare earth elements (REE) and Y (ionic radii 0.977–1.16 Å, 8-fold coordination, Shannon (1976)), while the smaller M1-M3 sites can accommodate smaller cations such as high-field strength elements.

The subject of the present study is REE partitioning between amphibole and silicate melt, which is important to understand the generation and differentiation of hydrous magma. According to the lattice strain model (Blundy and Wood, 1994; Brice, 1975; Wood and Blundy, 1997), the partition coefficients of trivalent REE between amphibole and silicate melt vary systematically with their ionic radii:

$$D_j^{\text{amph-melt}} = D_0 \exp \left[-\frac{4\pi EN_A}{RT} \left(\frac{r_0}{2} (r_0 - r_j)^2 - \frac{1}{3} (r_0 - r_j)^3 \right) \right], \quad (1)$$

where D_0 is the amphibole-melt partition coefficient for the strain-free substitution; r_0 is the radius of a hypothetical cation that substitutes into the site with zero strain; r_j is the ionic radius of the element of interest; E is the effective Young's modulus for the lattice site; N_A is Avogadro's number; R ($= 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$) is the gas constant; and T is temperature in Kelvin. The lattice strain parameters (D_0 , r_0 , E) are, in general, a function of pressure (P), temperature (T), and composition (X).

Amphibole-melt REE partition coefficients have been shown to negatively correlate with T (Green and Pearson, 1985; Klein et al., 1997; Nicholls and Harris, 1980) and P (Adam and Green, 1994; Adam and Green, 2003; Dalpé and Baker, 2000; Green and Pearson, 1985), and positively correlate with the degree of melt polymerization (Green and Pearson, 1985; Klein et al., 1997; Nicholls and Harris, 1980; Tiepolo et al., 2007; Tiepolo et al., 2000). The effect of amphibole crystal chemistry on amphibole-melt REE partition coefficients has also been observed in previous studies. For example, greater occupation of the A site by Na and K were shown to decrease the partition coefficients, presumably suggesting substitution of REE in place of Na and Ca in the M4 site charge compensated by a vacancy in the A site (e.g., $\text{Ca}_{M4}^{2+} \text{K}_A^{1+} \Leftrightarrow \text{REE}_{M4}^{3+} \square_A$) (Brenan et al., 1995; Green and Pearson, 1985; Nicholls and Harris, 1980). Also, amphibole-melt REE partition coefficients have been demonstrated to correlate with the amphibole-melt partition coefficient of Ca (Hilyard et al., 2000; Klein et al., 1997; Sisson, 1994). These correlations have been used to build empirical predictive models of amphibole-melt REE partition coefficients (Sisson, 1994; Tiepolo et al., 2007; Tiepolo et al., 2000). These previous models are useful for predicting the REE and Y partition coefficients when the equilibrium melt composition (Sisson, 1994; Tiepolo et al., 2007;

Tiepolo et al., 2000) or amphibole-melt major element partition coefficients (Hilyard et al., 2000) are available. These are difficult to constrain, however, for natural amphiboles such as those found in cumulates and xenoliths. Further, previous models parameterized partition coefficient for individual element independently, so each element requires a different set of model coefficients. This makes it difficult to understand the general behavior of REE partitioning in amphibole and to develop accurate models for elements with sparse partitioning data (such as Gd and Tm). In addition these empirical models require a large number of coefficients to describe the partitioning of all the REE and Y.

In this study, we present the first parameterized lattice strain models for REE and Y partitioning between amphibole and silicate melt for a range of P , T , melt and amphibole compositions. These models were developed following a new protocol that has been successfully used to develop parameterized lattice models for REE and Y partitioning between mantle minerals (clinopyroxene, orthopyroxene, and garnet) and basaltic melts (Dygert et al., 2014; Sun and Liang, 2012; Sun and Liang, 2013a; Sun and Liang, 2013b; Yao et al., 2012). We develop two parameterized lattice strain models, one of which is described by T and mineral composition, and the other is fully captured by melt composition. We reconcile the two models through amphibole-melt equilibria, and, as a byproduct, developed a new thermometer for calculating amphibole liquidus. As geochemical applications of our models, we (1) evaluate the ranges of amphibole-melt REE partition coefficients in mantle amphiboles using observed amphibole compositions in mantle xenoliths, and (2) calculate the REE concentration in experimental melts that simulate fractional crystallization of arc magmas to evaluate the effect of amphibole fractional crystallization on the REE concentration in arc magmas.

2. Method

2.1. Data compilation

REE and Y partitioning data for amphibole and silicate melts were compiled from published experimental studies. The data was filtered on the basis of attainment of equilibrium (e.g., absence of core to rim variation, sector zoning in major elements, absence of melt inclusions in the analyzed volume, and run duration), misfit or outlier with reference to the lattice strain model (e.g., Eu anomaly), following the procedure established in the previous studies (Dygert et al., 2014; Sun and Liang, 2012; Sun and Liang, 2013b; Yao et al., 2012). Experimental data that were analyzed using an ion probe and laser ablation inductively couple mass spectrometry (LA-ICP-MS) were inspected for their quality by plotting the partition coefficients of similarly incompatible element pairs (e.g., La-Ce and Lu-Yb). In these plots, most partitioning data follow a well-defined correlation suggesting high quality and internally consistent analysis while some partitioning data significantly deviate off the trend. The off-trend partitioning data were excluded as they suggest either poorly equilibrated experiments or low quality analysis. This method could not be used to inspect the quality of highly doped experiments analyzed using an electron microprobe (EMP) as they often contain fewer than 3 elements far from each other in incompatibility. Furthermore, the studies of Adam and Green (1994) and Klein et al. (1997) showed evidence of Henry's law behavior of REE in their doped experiment by running an undoped experiment at the same P - T - X conditions, while the study of Hilyard et al. (2000) did not show an evidence for this. As shown later in this study, however, their partitioning data follow our partitioning models in the same

manner as other partitioning data suggesting the Henry's law behavior of REE in their experiments. Hence, we included the partitioning data from the Hilyard et al. (2000) study in our dataset. We obtained 458 partitioning data from 92 experiments reported in 8 studies (Adam and Green, 1994; Adam and Green, 2003; Adam and Green, 2006; Dalpé and Baker, 2000; Hilyard et al., 2000; Klein et al., 1997; LaTourrette et al., 1995; Tiepolo et al., 2000).

Table 1 summarizes the filtered partitioning studies that were used to calibrate the model described below. The selected 92 experiments were conducted at 800–1100°C and 0.2–2.5 GPa. These experiments produced calcic amphiboles and melts with large variations in composition (e.g., Si = 5.72–6.59 a.p.f.u in amphibole, Mg# = 36.5–100 in amphibole, Mg# = 1.9–100 in melt, SiO₂ = 34.14–68.7 wt% in melt; see Fig. 1 and Table 1 for details) and partition coefficients (e.g., D_{La} = 0.03–0.59, D_{Sm} = 0.27–3.58, D_{Lu} = 0.28–2.07) (Fig. 2). The compositional variations in the experimental amphiboles and melts cover a large portion of those in natural samples from arc and intraplate settings and mantle xenoliths (Figs. 1a–f).

2.2. Parameterization method

To develop a parameterized model for trivalent REE and Y partitioning between amphibole and silicate melt, we conducted a multivariable nonlinear least squares analysis. Following the procedure of recent studies on mineral-melt REE partitioning (Dygert et al., 2014; Sun and Liang, 2012; Sun and Liang, 2013a; Yao et al., 2012), we conduct the least squares analysis in two steps: (1) identification of key variables that affect D_0 , r_0 , and E in the lattice strain model through least squares analysis of individual

experiments, and (2) simultaneous inversion of all the filtered experimental data using the primary variables identified in step (1). An important advantage of step (2) is that it allows us to include experiments that reported only one or two trace elements and hence they can be used to calibrate the three-parameter lattice strain model in step (1) (see Supplementary Fig. S1 and S2 for experiments from the Hilyard et al. (2000) and Klein et al. (1997) studies). We assume that REE and Y enters the M4 site in amphibole, and use eightfold coordinated ionic radii from Shannon (1976). We did not distinguish between the M4 and M4' sites (Bottazzi et al., 1999) given the lack of evidence of the two-site occupancy of the REE in amphibole. We assumed that D_0 in the lattice strain model has the simple form

$$\ln D_0 = a_0 + \frac{a_1}{RT} + f\left(X, \frac{P}{T}\right), \quad (2)$$

where a_0 and a_1 are constants to be determined, and f is a function of mineral and melt composition and P/T . The r_0 correlates well with the amphibole composition, while E does not show a correlation with r_0 or amphibole composition.

Through an extensive search of various permutations of the composition variables, we found that D_0 can be described as a function of melt Si, Mg and Ca contents or as a function of T and Ti, Mg, Na and K contents in amphibole. For convenience of description, we refer to the latter as the mineral composition model and the former as the melt composition model. In both models, ferromagnesian (sum of Mg, Fe^{2+} , and Mn^{2+}) content in the M4 site of the amphibole (designated as Fm hereafter) is the main factor affecting r_0 , while E is a constant. For the melt composition model, the lattice strain parameters D_0 , r_0 , and E take on the following expressions:

$$\ln D_0^{\text{amph}} = a_0 + a_1 \ln(X_{\text{Si}}^{\text{melt}}) + a_2 \ln(X_{\text{Mg}}^{\text{melt}}) + a_3 \ln(X_{\text{Ca}}^{\text{melt}}), \quad (3)$$

$$r_0^{\text{amph}} = a_4 + a_5 X_{\text{Fm}}^{\text{amph}}, \quad (4)$$

$$E^{\text{amph}} = a_6. \quad (5)$$

For the mineral composition model, we have

$$\ln D_0^{\text{amph}} = b_0 + \frac{b_1}{RT} + b_2 X_{\text{Ti}}^{\text{amph}} + b_3 X_{\text{Mg}}^{\text{amph}} + b_4 X_{\text{Na}}^{\text{amph}} + b_5 X_{\text{K}}^{\text{amph}}, \quad (6)$$

$$r_0^{\text{amph}} = b_6 + b_7 X_{\text{Fm}}^{\text{amph}}, \quad (7)$$

$$E^{\text{amph}} = b_8, \quad (8)$$

where $a_0, a_1, \dots, a_6$ and $b_0, b_1, \dots, b_8$ in Eqs. (3)–(8) are constants determined by stepwise multiple linear regression analyses of the lattice strain parameters (D_0 , r_0 , and E); $X_{\text{Ti}}^{\text{amph}}$,

$X_{\text{Mg}}^{\text{amph}}$, $X_{\text{Na}}^{\text{amph}}$, and $X_{\text{K}}^{\text{amph}}$ are cation numbers (per 23 oxygen) and $X_{\text{Fm}}^{\text{amph}}$ is the $\text{Fe}^{2+} +$

$\text{Mn}^{2+} + \text{Mg}$ content in the M4 site assuming all iron is present as ferrous iron; and $X_{\text{Si}}^{\text{melt}}$,

$X_{\text{Mg}}^{\text{melt}}$, and $X_{\text{Ca}}^{\text{melt}}$ are mole fractions of cations in the melt calculated on anhydrous basis.

We used anhydrous basis for the melt because some H_2O contents in the melt are calculated according to mass balance, which may introduce large uncertainties. Also, Na occupies both the M4 and A sites in amphibole, but we use the total Na content for the mineral composition model. We attempted using Na in the M4 and A sites as separate variables, but the coefficients for the two variables are nearly identical, leading us to use total Na content instead.

To further improve the fit to the measured partitioning data and better assess the uncertainties for the fitting coefficients, we performed global least squares analyses for

the melt composition and mineral composition models by substituting equations (3)–(5) and (6)–(8) into Eq. (1), respectively. For the melt composition model (Eqs. (1), (3)–(5)), we inverted the 6 coefficients ($a_0, a_1, \dots, a_6$) simultaneously through a global inversion of the 458 filtered partitioning data. For the mineral composition model (Eqs. (1), (6)–(8)), we inverted the 8 coefficients ($b_0, b_1, \dots, b_8$) simultaneously through a global inversion of the same data used for the mineral composition model. To carry out the global inversions, we used the coefficients from the stepwise multiple linear regression as initial values in the nonlinear least squares analysis and minimize the Chi-square as defined below:

$$\chi_p^2 = \sum_{j=1}^N \left(\ln D_j - \ln D_j^m \right)^2, \quad (9)$$

where D_j is defined by Eq. (1) for element j , D_j^m is the measured amphibole-melt partition coefficient for element j , and N ($= 458$) is the total number of measured partitioning data used in this study. Although convenient in nonlinear regression analysis, the absolute values of the Chi-square defined by Eq. (9) depend on the number of data used in the inversion. To assess the goodness of fit in a simple way, we calculated the Pearson's Chi-square (χ_p^2) after the inversion using the expression

$$\chi_p^2 = \sum_{j=1}^N \frac{\left(D_j - D_j^m \right)^2}{D_j}. \quad (10)$$

A better predictive model should provide partition coefficients closer to measured values and hence has a smaller χ_p^2 . The results are shown in Fig. 3 and discussed below.

3. Results

The global fit to the 458 partitioning data from the 92 experiments produces two sets of expressions for the lattice strain parameters for REE and Y partitioning in amphibole. For the melt composition model, we have:

$$\ln D_0^{\text{amph}} = -1.89(\pm 0.41) + 1.01(\pm 0.30) \ln(X_{\text{Si}}^{\text{melt}}) - 0.15(\pm 0.03) \ln(X_{\text{Mg}}^{\text{melt}}) - 0.80(\pm 0.07) \ln(X_{\text{Ca}}^{\text{melt}}), \quad (11)$$

$$r_0^{\text{amph}} = 1.045(\pm 0.003) - 0.049(\pm 0.014) X_{\text{Fm}}^{\text{amph}}, \quad (12)$$

$$E^{\text{amph}} = 338(\pm 19), \quad (13)$$

where r_0 is in Å; and E is in GPa; and numbers in parentheses are 2σ uncertainties estimated directly from the simultaneous inversion. As D_0 defines the peak value of the parabola in the lattice strain model (Eq. (1)), the melt composition model indicates REE partition coefficients in amphibole increase with the increase of Si content in the melt and decrease with the increase of Ca and Mg content in the melt. Figs. 4a–c shows that amphibole-melt Sm partition coefficient positively correlates with Si and negatively correlates with Ca and Mg contents in the melt. The Si, Ca, and Mg contents in the experimental melts are comparable to those in the natural melts saturated in amphibole (Si = 0.37–0.75, Ca = 0–0.17, Mg = 0–0.15, data source in Fig. 1).

For the mineral composition model, we have

$$\ln D_0^{\text{amph}} = -3.19(\pm 1.42) + \frac{5.82(\pm 1.06) \times 10^4}{RT} + 1.20(\pm 0.26) X_{\text{Ti}}^{\text{amph}} - 0.45(\pm 0.07) X_{\text{Mg}}^{\text{amph}} - 1.17(\pm 0.35) X_{\text{Na}}^{\text{amph}} - 2.09(\pm 0.39) X_{\text{K}}^{\text{amph}}, \quad (14)$$

$$r_0^{\text{amph}} = 1.044(\pm 0.004) - 0.045(\pm 0.018) X_{\text{Fm}}^{\text{amph}}, \quad (15)$$

$$E^{\text{amph}} = 331(\pm 24). \quad (16)$$

The mineral composition model indicates REE partition coefficients in amphibole increase with the increase of Ti content and decrease with the increase of T and Mg, Na, and K contents in the amphibole. Fig. 4d shows a negative correlation between amphibole-melt Sm partition coefficient and T that is consistent with the expression for D_0 in the mineral composition model (Eq. (14)). In order to highlight the effect of amphibole composition, we subtract the effect of T on the amphibole-melt Sm partition coefficient using the following expression

$$\overline{D_{\text{Sm}}^{\text{amph-melt}}} = D_{\text{Sm}}^{\text{amph-melt}} \exp \left[\frac{4\pi EN_A}{RT} \left(\frac{r_0}{2} (r_0 - r_{\text{Sm}})^2 - \frac{1}{3} (r_0 - r_{\text{Sm}})^3 \right) - \frac{5.82 \times 10^4}{RT} \right], \quad (17)$$

where $\overline{D_{\text{Sm}}^{\text{amph-melt}}}$ is the normalized amphibole-melt Sm partition coefficient; r_0 is calculated using Eq. (15) and E is that in Eq. (16). Figs. 4e, 4f, and S3 show that, to the first order, normalized amphibole-melt Sm partition coefficient positively correlates with Ti content, and negatively correlates with Mg and K contents in the amphibole, consistent with Eq. (14). The negative correlation with Na contents in amphibole is less clear (Fig. S3a), but it is more clear when other compositional effects are subtracted from the normalized amphibole-melt Sm partition coefficient (not shown). The Ti, Mg, Na, and K contents in the experimental amphiboles are comparable to those in natural amphiboles (Ti = 0.02–0.77, Mg = 0.5–4.1, Na = 0.33–1.2, and K = 0–0.47, data source in Fig. 1).

In both the mineral and melt composition models, r_0 decreases with increasing Fm content of the M4 site in the amphibole. We interpret this to indicate that the ideal radius of the M4 site decreases with increasing occupancy by elements with relatively small ionic radius such as Mg, Fe^{2+} , and Mn^{2+} . The range in Fm content of the M4 site in the experimental amphibole is 0–0.39, which is comparable to 0–0.47 observed in the

compilation of natural amphiboles (data source in Fig. 1). This range in Fm content of the M4 site in the compilation of natural amphiboles translates to a small range in r_0 of 1.022–1.045 Å which is consistent with the subparallel parabola defined by the REE + Y partitioning data (Fig. 2). Further, the proximity of r_0 to MREE such as Dy (1.027 Å) and Tb (1.04 Å) also explains why fractional crystallization of amphibole can produce depletion in MREE relative to HREE and LREE in the magma (Davidson et al., 2007; Davidson et al., 2013).

4. Discussion

Our mineral composition and melt composition models reproduce the 458 partitioning data from the 92 partitioning experiments (fits to the individual experiments are shown in Supplementary Fig. S1 and S2). Figs. 3a and 3b show that the partition coefficients predicted by the mineral composition model and the melt composition model both follow the 1:1 correlation line when plotted against the measured values and generally fall between the 1:2 and 2:1 correlation lines. Hence to the first approximation, both models equally describe the variability of partition coefficients. In detail, the melt composition model ($\chi_p^2 = 17.5$) performs slightly better than the mineral composition model ($\chi_p^2 = 45.9$), especially for cases when measured $D > 1$.

4.1. Comparison with the empirical model of Tiepolo et al. (2007)

Our new melt composition model has 4 variables and 7 coefficients for the 15 elements (REE+Y), whereas the melt composition model of Tiepolo et al. (2007), which is a linear fit to one composition variable, has 8 coefficients for 4 elements (La, Dy, Y,

and Yb). In terms of reproducing measured partitioning data for these 4 elements, the Pearson's Chi-square for the original model of Tiepolo et al. (2007) (8.45) is larger than our melt model (5.84). To further compare with the model of Tiepolo et al. (2007), we recalibrated their equations for the 15 elements (REE+Y) using our compiled database (Table S1 provides the new coefficients). The updated model has a χ_p^2 value of 21.6, which is still larger than that for our melt model (17.5). Therefore, our melt composition model has a better reproducibility and a smaller number of coefficients to describe the REE partitioning between amphibole and silicate melt. This further underscores the advantage and importance of the lattice strain model in quantifying REE partitioning in amphibole. In addition, as shown later in this study, our mineral composition model provides an understanding of the REE substitution mechanism in amphibole, and it has an advantage that of being applicable to natural samples without the knowledge of the melt composition.

4.2. Relation between the mineral and melt compositions models

The connection between the mineral and melt compositions models can be understood in terms of amphibole-melt phase equilibria. To within estimated uncertainties, the coefficients in the equations for r_0 and best-fit values for E are identical between the melt and mineral composition models (Eqs. (12) vs. (15); Eqs. (13) vs. (16)). This implies that D_0 between the two models are the same, given the two models are equivalent in terms of reproducing measured REE partitioning data (Figs. 3a and 3b). Equating Eqs. (11) and (14), we have the following expression relating amphibole composition to coexisting melt composition,

$$-1.89 + 1.01 \ln(X_{\text{Si}}^{\text{melt}}) - 0.15 \ln(X_{\text{Mg}}^{\text{melt}}) - 0.80 \ln(X_{\text{Ca}}^{\text{melt}}) = -3.19 + \frac{5.82 \times 10^4}{RT} + 1.20 X_{\text{Ti}}^{\text{amph}} - 0.45 X_{\text{Mg}}^{\text{amph}} - 1.17 X_{\text{Na}}^{\text{amph}} - 2.09 X_{\text{K}}^{\text{amph}} \quad (18)$$

Eq. (18), in effect, describes the liquidus of amphibole, and hence can be taken as a thermometer for amphibole-melt equilibria, viz.,

$$T = \frac{6.99 \times 10^4}{1.30 - 1.20 X_{\text{Ti}}^{\text{amph}} + 0.45 X_{\text{Mg}}^{\text{amph}} + 1.17 X_{\text{Na}}^{\text{amph}} + 2.09 X_{\text{K}}^{\text{amph}} + 1.01 \ln(X_{\text{Si}}^{\text{melt}}) - 0.15 \ln(X_{\text{Mg}}^{\text{melt}}) - 0.80 \ln(X_{\text{Ca}}^{\text{melt}})} \quad (19)$$

This thermometer provides an opportunity to independently test our melt composition model (Eqs. (1) and (11)–(13)) and mineral composition model (Eqs. (1) and (14)–(16)) as discussed below.

There are a large number of amphibole-melt phase equilibria studies reported in the literature. Here we use Eq. (19) to calculate the temperatures of 185 amphibole-melt phase equilibrium experiments from 16 studies (Alonso-Perez et al., 2009; Blatter et al., 2013; Costa et al., 2004; Foden and Green, 1992; Gardner et al., 1995; Grove et al., 1997; Grove et al., 2003; Holtz et al., 2004; Kawamoto, 1996; Moore and Carmichael, 1998; Nandedkar et al., 2014; Nekvasil et al., 2004; Pichavant et al., 2002; Pilet et al., 2010; Prouteau and Scaillet, 2003; Sato et al., 2005). These experiments were conducted at 730–1130°C and 0.1–1.5 GPa, generally at lower P - T conditions compared to the REE partitioning experiments. Despite some overlap in composition, these experiments produced calcic amphiboles generally higher in Si and lower in alkalis, and melt with higher SiO₂ content compared to those in the REE partitioning experiments (Fig. 1). The temperatures of these experiments calculated using our thermometer (Eq. (19)) and the measured temperatures generally follow the 1:1 correlation line to within 100°C of the

measured temperature with a precision of 87°C (RMSE) (Fig. 5), which is an independent verification of our amphibole-melt thermometer (Eq. 19) and hence our mineral composition and melt composition models. Furthermore, the validity of our thermometer to lower P - T conditions and more evolved amphibole and melt composition compared to the REE partitioning experiments suggests the applicability of our models at these conditions.

Our thermometer for amphibole-melt equilibria (Eq. 19) show similarities to a recent amphibole-melt thermometer of Molina et al. (2015):

$$T(^{\circ}\text{C}) = \frac{71975 - 11896 \ln \left[X_{\text{Ca}}^{\text{melt}} / (X_{\text{Ca}}^{\text{melt}} + X_{\text{Al}}^{\text{melt}}) \right]}{8.3144 \ln D_{\text{Mg}}^{\text{amph-melt}} + 58} - 273 \quad (20)$$

where $X_{\text{Ca}}^{\text{melt}}$ and $X_{\text{Al}}^{\text{melt}}$ are mole fractions of Ca and Al in the melt, and $D_{\text{Mg}}^{\text{amph-melt}}$ is the molar partition coefficient of Mg between amphibole and melt. This thermometer and our thermometer both involve the temperature dependence of Mg partitioning between the amphibole and melt as well as Ca content in the melt. The thermometer of Molina et al. (2015) has a better precision (49°C) than our thermometer (87°C) based on the same data set as in Fig. 6, but they are surprisingly comparable especially given that our models are calibrated to predict REE partitioning between amphibole and melt and not temperatures. Therefore, our thermometer captures the essential parameters required in a thermometer for amphibole-melt equilibria.

4.3. Substitution mechanism

The mineral composition model may provide insights to the REE substitution mechanism in amphibole. According to the mineral composition model, D_0 positively

correlates with Ti and negatively with Mg. Hence REE substitution is related to the Ti–Al^{iv} substitution in the M1,2,3 and tetrahedral sites. Furthermore, the model may suggest that REE substitution for Na in the M4 site is charge compensated by vacancies in the A site, given the negative correlation between Na and K contents in amphibole and D_0 . Taken together, the mineral composition model suggests the following substitution mechanism of REE in amphibole,



According to this substitution mechanism, REE partition coefficient should positively correlate with Al^T similar to that observed in clinopyroxene (e.g. Gaetani and Grove, 1995; Hill et al., 2000; Lundstrom et al., 1998; Wood and Blundy, 1997). There is a weak positive correlation between Al^T and amphibole-melt Sm partition coefficient (Fig. S3c), and its scatter may be due to the effect of T and other mineral compositions similar to that observed for Na content in the mineral composition model (Fig. S3a). A mineral composition model with Al^T, Mg, Na, and K contents in the amphibole as compositional variables for D_0 has a Pearson's Chi-square of 50.6, which is higher than our preferred mineral composition model (45.9). Although Al^T plays an important role in REE substitution in amphibole, in practice, our mineral composition model performs slightly better when we use Ti rather than Al^T as a compositional variable.

5. Applications

5.1. Melting of amphiboles in the mantle

Amphibole is often observed in mantle xenoliths brought to surface by basalt volcanism, suggesting the presence of hydrated and metasomatized mantle lithosphere

(e.g. Boettcher and O'Neil, 1980; Chazot et al., 1996; Ionov and Hofmann, 1995). Partial melting of such mantle can give rise to melts with a range of compositions (e.g., alkali basalts to nephelinites) (e.g. Médard et al., 2006; Pilet et al., 2008; Sorbadere et al., 2013). In general, major element compositions in mantle amphiboles vary considerably (Figs. 1d–f). According to the data compiled from 10 studies shown in Fig. 1, Ti in amphiboles found in mantle xenoliths varies from 0.02 to 0.65 (per 23 oxygen), Mg from 2.25 to 4.08, Na from 0.65 to 1.22, and K from 0 to 0.38. Based on our mineral model, we expect considerable variability in amphibole-melt REE partition coefficient. For purpose of demonstration, we calculated the amphibole-melt REE partition coefficients in amphiboles found in mantle xenoliths from the 10 studies using the mineral composition model for a temperature of 1000°C. As shown in Fig. 6, amphibole-melt REE partition coefficients in amphiboles found in xenoliths vary by nearly an order of magnitude purely due to their compositional variation. Further, the REE partition coefficients decrease more than 20% when the temperature is increased to 1100°C (cf. heavy blue and red lines in Fig. 6). This simple example demonstrates the importance of composition and temperature dependent amphibole-melt REE partition coefficients to geochemical modeling of melting of an amphibole-bearing lithology in the mantle. For convenience, we list in Table 2 the average, maximum, and minimum REE partition coefficients between amphiboles in mantle xenoliths and melt calculated using the mineral composition model at four selected temperatures.

5.2. Fractional crystallization of arc magmas

Fractional crystallization of amphibole and clinopyroxene in arc magmas have

been postulated to cause the decrease in Dy/Yb and Dy/Dy* $\left(\text{Dy}_N / \left(\text{La}_N^{4/13} \text{Yb}_N^{9/13} \right) \right)$ ratios (i.e. depletion in MREE relative to HREE and LREE) with increase in SiO₂ observed in rock samples from single arc volcanoes (Davidson et al., 2007; Davidson et al., 2013). However, given the large range in published mineral-melt partition coefficients, the relative importance of amphibole and clinopyroxene in producing the low Dy/Yb and Dy/Dy* ratios in arc magmas is not clear. In order to better understand this, we use REE partitioning models and mass balance calculations to estimate and compare the effects of amphibole and clinopyroxene fractional crystallization on the REE pattern of experimental arc melts (Nandedkar, 2014; Nandedkar et al., 2014). The experiments of Nandedkar et al. (2014) and Nandedkar (2014) simulate fractional crystallization of the same initial starting material at pressures of 0.7 GPa and 0.4 GPa, respectively. (Hereafter we refer to the experiments of Nandedkar et al. (2014) as the 0.7 GPa experiments and those of Nandedkar (2014) as the 0.4 GPa experiments.) The initial starting material in these experiments is an olivine-tholeiite with an Mg# of 73 and H₂O content of 3 wt%, and both experiments were run at an oxygen fugacity of Ni-NiO. The experimental temperatures of the 0.7 GPa and 0.4 GPa experiments range from 1170 to 700°C and 1110 to 920°C, respectively. The final amounts of fractional crystallization are 85 wt% for the 0.7 GPa experiments and 76 wt% for the 0.4 GPa experiments. Both experiments crystallized clinopyroxene, olivine, plagioclase, and magnetite, but the 0.7 GPa experiment also crystallized amphibole with less plagioclase. This may be due to the greater stability of amphibole and the lesser stability of plagioclase at high pressure (Allen and Boettcher, 1983; Nandedkar, 2014; Spulber and Rutherford, 1983). Hence, the comparison between the model REE patterns and abundances in the melts of these

experiments using REE partitioning models and mass balance calculations provide an insight into the effect of fractional crystallization on the REE pattern of arc magmas under different P - T conditions and crystallizing phases. Particularly interesting is the effect of amphibole fractional crystallization, which may play a key role in the depletion of MREE relative to HREE in arc magmas (Davidson et al., 2007; Davidson et al., 2013).

We used the temperature, mineral and melt composition in the 0.7 GPa and 0.4 GPa experiments to calculate the amphibole-melt and clinopyroxene-melt REE partition coefficients using the melt composition model of this study and the model of Sun and Liang (2012). The calculated amphibole-melt MREE and HREE partition coefficients in the 0.7 GPa experiments increases by approximately an order of magnitude from the highest to lowest temperature experiment due to the increase in Si, and decrease in Ca and Mg content in the melt (Fig. 7a). In contrast to the MREE and HREE, the LREE partition coefficients do not vary significantly because elements with larger ionic radius relative to r_0 becomes more incompatible with decreasing temperature (Eq. 1), and this counteracts the increase in D_0 . A calculation using the mineral composition model from this study also predicts an increase in the MREE and HREE partition coefficient with progressive fractional crystallization largely due to the decrease in temperature, but also due to decrease in Na and K content in the amphibole. However, the increase of partition coefficients is a factor of 2 smaller than that predicted by the melt composition model at 730°C. The disagreement between the models is likely due to the low crystallization temperature (730°C), which is below the model calibration range (800–1100°C). (We suspect kinetics may also play a role in controlling major element compositions in amphiboles at lower temperatures.) Hence caution should be exercised when

extrapolating our models to T - X conditions outside the calibration range (Table 1). At temperatures higher than 730°C, the differences between the amphibole-melt REE partition coefficients predicted by the two models are all within 31%, and the results discussed in the rest of this section are not model dependent. The range in clinopyroxene-melt REE partition coefficients in the 0.7 GPa and 0.4 GPa experiments are similar to each other except for the high Al clinopyroxene found in the 0.7 GPa experiment at 1040°C. The olivine-melt, opx-melt, and plagioclase-melt REE partition coefficients are calculated using the models of Sun and Liang (2013b), Yao et al. (2012), and Bédard (2006) respectively. The spinel-melt REE partition coefficients are from Kelemen et al. (2003).

The partition coefficients and the phase proportions in the 0.7 GPa and 0.4 GPa experiments (Nandedkar, 2014; Nandedkar et al., 2014) were used to model the REE abundances in the melts during fractional crystallization. The model results are shown in in Figs. 7b, c, and d. The Dy/Dy* and Dy/Yb ratios of the 0.7 GPa melt decreases significantly more than those of the 0.4 GPa melt during fractional crystallization (Fig. 7b). Furthermore, the 0.7 GPa melts are more depleted in MREE and HREE compared to the 0.4 GPa melts for a given degree of fractional crystallization (Figs. 7c and d). These differences are due to fractional crystallization of amphibole in the 0.7 GPa melts. As shown in the results section, amphibole fractional crystallization decreases the Dy/Dy* and Dy/Yb ratios in the melt due to the affinity of amphibole for MREE over HREE and LREE (i.e. similarity between r_0 of the amphibole and ionic radius of MREE) (Fig. 7a). In addition, amphibole fractional crystallization moderates the MREE and HREE concentration in the melt since they behave compatibly in amphiboles, especially in those

crystallizing from more evolved melts (i.e., high Si) at lower temperatures (Fig. 7a). In contrast, the Dy/Dy* and Dy/Yb ratios do not decrease as much and the MREE and HREE concentrations are significantly higher in the 0.4 GPa melts than the 0.7 GPa melts since they do not crystallize amphibole (Fig. 7b). To some extent, the Dy/Dy* and Dy/Yb ratios in the 0.4 GPa melts decreases due to clinopyroxene fractional crystallization (Fig. 7b), but by much less than the 0.7 GPa melts since REE are incompatible in the crystallizing clinopyroxenes especially at high temperatures (Fig. 7a). In contrast, amphibole can significantly fractionate the REE pattern of the 0.7 GPa melts due to the lower crystallization temperatures in the 0.7 GPa melts compared to the 0.4 GPa melts for a given degree of fractional crystallization, perhaps due to the larger temperature difference between the solidus and liquidus at higher pressure.

Applying the present REE partitioning model to the 0.7 GPa experiments by Nandedkar et al. (2014) suggests that the amphibole-melt REE partition coefficient may vary by an order to magnitude during fractional crystallization of an arc magma due to changes in T , and the melt and amphibole compositions. This demonstrates the importance of composition and temperature dependent REE partition coefficients in geochemical modeling of amphibole-melt fractionation. For convenience, we list the amphibole-melt REE partition coefficients for amphiboles in the 0.7 GPa experiments calculated using the melt composition model (Table 3). Our modeling results suggest that fractional crystallization of amphibole plays a key role in decreasing the Dy/Yb and Dy/Dy* ratios and also in moderating the MREE and HREE concentrations in arc magmas. Fractional crystallization of clinopyroxene can also decrease the Dy/Yb and Dy/Dy* ratios in the arc magmas, although much less efficiently. The pressure of

fractional crystallization affects the crystallization temperature of the melt and stability of amphibole (Allen and Boettcher, 1983; Nandedkar, 2014; Spulber and Rutherford, 1983), so it is also a key factor that controls the behavior of REE in solidifying magmas.

6. Summary and Further Discussion

We developed two parameterized lattice strain models for REE and Y partitioning between amphibole and silicate melt over a large range of P - T - X using published partitioning data between amphibole and silicate melt and non-linear least squares regression method. The melt composition model suggests that REE and Y partition coefficients in amphibole positively correlate with Si content and negatively correlate with Ca and Mg contents in the melt. The mineral composition model suggests that REE and Y partition coefficients in amphibole negatively correlate with T and Mg, Na, and K contents and positively correlate with Ti content in amphibole. In both the mineral and melt composition models, r_0 negatively correlates with the Fm content in the M4 site of amphibole and E is a constant. The very similar coefficients of the equations for r_0 and best-fit values for E in the two models suggest that the D_0 in the two models are equivalent. Hence there are considerable trade-offs between major element compositions of coexisting amphibole and melt in the parameterized lattice strain models for REE partitioning in amphibole. The connection is the liquidus surface of amphibole. To further demonstrate this point, we developed a hybrid model for amphibole-melt REE partitioning using a combination of amphibole and melt compositions and the results are summarized in Appendix A. The hybrid model, which performs slightly better than the melt and mineral compositions models, can be used to predict REE partition coefficients

if major element compositions of both amphibole and melt are available. Application of our model to amphiboles found in mantle xenoliths suggests an order of magnitude variation in the amphibole-melt REE partition coefficients purely due to compositional variation. During arc magma crystallization, REE partition coefficients between amphibole and melt can increase by an order of magnitude due to decrease in T and effects of amphibole (e.g. decrease in Na and K) and melt composition (e.g. increase in Si). In contrast, r_0 of the crystallizing amphiboles do not change significantly and remain similar to the ionic radius of MREE such as Dy and Tb. Therefore, fractional crystallization of amphibole has a strong leverage on the REE concentrations in arc magmas and likely plays a key role in depleting its MREE relative to HREE and LREE.

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Appendix A. A Hybrid Model for Amphibole-Melt REE Partitioning

Following the same procedure outlined in the parameterization method, we found a hybrid model in which parameters D_0 , r_0 , and E take on the following expressions:

$$\ln D_0^{amph} = -3.27(\pm 0.26) + 1.28(\pm 0.17)X_{\text{Ti}}^{amph} - 1.24(\pm 0.21)X_{\text{Na}}^{amph} - 0.65(\pm 0.24)X_{\text{K}}^{amph} - 0.40(\pm 0.05)\ln(X_{\text{Ti}}^{melt}) - 0.79(\pm 0.08)\ln(X_{\text{Ca}}^{melt}), \quad (\text{A1})$$

$$r_0^{amph} = 1.045(\pm 0.002) - 0.047(\pm 0.011)X_{\text{Fm}}^{amph}, \quad (\text{A2})$$

$$E^{amph} = 337(\pm 14), \quad (\text{A3})$$

where r_0 is in Å; and E is in GPa; and numbers in parentheses are 2σ uncertainties

estimated directly from the simultaneous inversion. The hybrid model has 9 fitting parameters and provides an improved fit ($\chi_p^2 = 11.8$) over the melt (7 fitting parameters) and mineral composition (9 fitting parameters) models presented in the main text. It can be used to predict REE partition coefficients if major element compositions of both amphibole and melt composition are available.

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Figure captions

Figure 3-1. Compositions of melt and amphibole in phase equilibrium experiments (gray dots) and partitioning experiments (yellow dots). Also shown are compositions of lavas and amphiboles in intraplate and arc settings (orange crosses) and xenoliths (red plus signs). The structural formula of amphiboles were calculated using the method of 13 cations excluding Ca, Na, and K described by Leake et al. (1997). The partitioning data are from the compiled experiments in Table 1. Phase equilibrium data from 16 studies (Alonso-Perez et al., 2009; Blatter et al., 2013; Costa et al., 2004; Foden and Green, 1992; Gardner et al., 1995; Grove et al., 1997; Grove et al., 2003; Holtz et al., 2004; Kawamoto, 1996; Moore and Carmichael, 1998; Nandedkar et al., 2014; Nekvasil et al., 2004; Pichavant et al., 2002; Pilet et al., 2010; Prouteau and Scaillet, 2003; Sato et al., 2005). Lavas and amphiboles in intraplate and arc settings from 20 studies (Bernard et al., 1996; Buckley et al., 2006; Costa and Chakraborty, 2004; Demény et al., 2004; Gourgaud et al., 1989; Grove et al., 2005; Heliker, 1995; Mayer et al., 2013; Mortazavi and Sparks, 2004; Neumann et al., 1999; Nye and Turner, 1990; Pallister et al., 1996; Pallister et al., 2008; Pichavant et al., 2002; Reubi and Nicholls, 2004; Ridolfi et al., 2008; Samaniego et al., 2005; Shane et al., 2005; Tappe et al., 2007; Toya et al., 2005) and xenoliths from 10 studies (Chazot et al., 2005; Chazot et al., 1996; Grégoire et al., 2000; Ionov and Hofmann, 1995; Moine et al., 2001; Vannucci et al., 1995; Vaselli et al., 1995; Witt-Eickschen et al., 2003; Wulff-Pedersen et al., 1996; Zanetti et al., 1996).

Figure 3-2. Onuma diagram showing the REE and Y partition coefficients between amphibole and silicate melt measured in the partitioning studies listed in Table 1 (yellow

dots). The orange lines are the best-fit parabolas to the trivalent REE and Y using the lattice strain model (Blundy and Wood, 1994; Brice, 1975; Wood and Blundy, 1997) for experiments in which there are more than 3 partitioning data.

Figure 3-3. Comparison between the experimentally measured partition coefficients to those predicted using (a) the melt composition model (Eqs. (1), (11)–(13)) and (b) the mineral composition model (Eqs. (1), (14)–(16)). Observed values are from partitioning studies listed in Table 1. The solid line represents 1:1 ratio, and dashed lines represent 2:1 and 1:2 ratios, respectively. χ_p^2 is the Pearson's Chi-square calculated according to Eq. (10).

Figure 3-4. Plots of amphibole-melt Sm partition coefficient against mole fractions of (a) Si, (b) Ca, and (c) Mg in the melt and (d) *T*, (e) Ti, and (f) Mg content in the amphibole. The partition coefficients of Sm in (e) and (f) are normalized using Eq. (17). The partitioning data are from the compiled experiments in Table 1.

Figure 3-5. Comparison between observed temperatures in phase equilibrium experiments to those predicted using the thermometer for amphibole-melt equilibria (Eq. 19). Open symbols are experiments containing melts with composition beyond the calibration range of our melt and mineral composition models (SiO₂ higher than 68.7 wt%). Source of data: (1) Alonso-Perez et al. (2009), (2) Blatter et al. (2013), (3) Costa et al. (2004), (4) Foden and Green (1992), (5) Gardner et al. (1995), (6) Grove et al. (1997), (7) Grove et al. (2003), (8) Holtz et al. (2004), (9) Kawamoto (1996), (10) Moore and

Carmichael (1998), (11) Nandedkar et al. (2014), (12) Pilet et al. (2010), (13) Pichavant et al. (2002), (14) Nekvasil et al. (2004), (15) Sato et al. (2005), and (16) Prouteau and Scaillet (2003).

Figure 3-6. Amphibole-melt REE partition coefficients calculated using the mineral composition model (Eqs. (1), (14)–(16)) and compositions of for amphiboles found in mantle xenoliths. All except the red curve labeled 1100°C were calculated assuming a temperature of 1000°C. The general effects of T and amphibole and melt composition on the amphibole-melt REE partition coefficients are also shown. Data source are the same as those in Fig. 1.

Figure 3-7. (a) Predicted amphibole-melt (blue lines) and clinopyroxene-melt (red and green lines) REE partition coefficients for mineral and melt compositions reported in the studies of Nandedkar et al. (2014) (0.7 GPa experiments, blue and red lines) and Nandedkar (2014) (0.4 GPa experiments, green lines), calculated using the melt composition model for amphibole-melt and the model of Sun and Liang (2012) for the clinopyroxene-melt. The dotted red line is the clinopyroxene-melt REE partition coefficient for a high Al clinopyroxene found in the 0.7 GPa experiment at 1040°C. Numbers on the right are crystallization temperatures in °C. (b) Dy/Dy* vs. Dy/Yb ratios (Davidson et al., 2013) and (c)-(d) REE concentrations in the 0.7 GPa and 0.4 GPa melts normalized to those in the initial melt. They are calculated using the mineral-melt partition coefficients and consideration of mass balance. In (a), the red circles are 0.7 GPa melts saturated in clinopyroxene, the blue circles are those saturated in amphibole,

and the green circles are the 0.4 GPa melts. For (c) and (d) the numbers associated with each circles correspond to crystallization temperatures in °C, and the percentage of the melt that has not been crystallized.

Figure 3-S1. Comparisons of measured amphibole-melt partitioning data (yellow circles) and those predicted by the melt composition model (Eqs. (1, (11)–(13))). Dashed lines are the 95% confidence interval of the predicted partition coefficients.

Figure 3-S2. Comparisons of measured amphibole-melt partitioning data (yellow circles) and those predicted by the mineral composition model (Eqs. (1, (14)–(16))). Dashed lines are the 95% confidence interval of the predicted partition coefficients.

Figure 3-S3. Plots of amphibole-melt Sm partition coefficient against (a) Na, (b) K, and (c) tetrahedrally coordinated Al^T in the amphibole. The partition coefficients of Sm in (a) and (b) are normalized using Eq. (17). The partitioning data are from the compiled experiments in Table 1.

Table headings

Table 3-1. Data sources and experimental run conditions.

Table 3-2. List of recommended amphibole-melt REE and Y partition coefficients for amphiboles found in xenoliths.

Table 3-3. List of recommended amphibole-melt REE and Y partition coefficients for arc magma environment.

Table footnotes

Table 3-1. ^an represents the number of experiments. ^bm represents the number of partitioning data. ^cMelt H₂O content shown when reported in the study. It was measured using SIMS by Tiepolo et al. (2000) and LaTourrette et al. (1995) and calculated using mass balance by Adam and Green (2003) and Adam and Green (2006).

Table 3-2. Note: Calculated at different temperatures using the mineral composition model of this study and compositions of for amphiboles found in mantle xenoliths (Data source in Fig. 1). The composition of amphiboles is kept constant for the calculation at different temperatures.

Table 3-3. Note: Calculated using the melt composition model and the composition of amphiboles in the 0.7 GPa experiments of Nandedkar et al. (2014). *The set of partition coefficient at 730°C should be used with caution since the temperature is significantly below the calibration range of our model.

Figures

Figure 3-1.

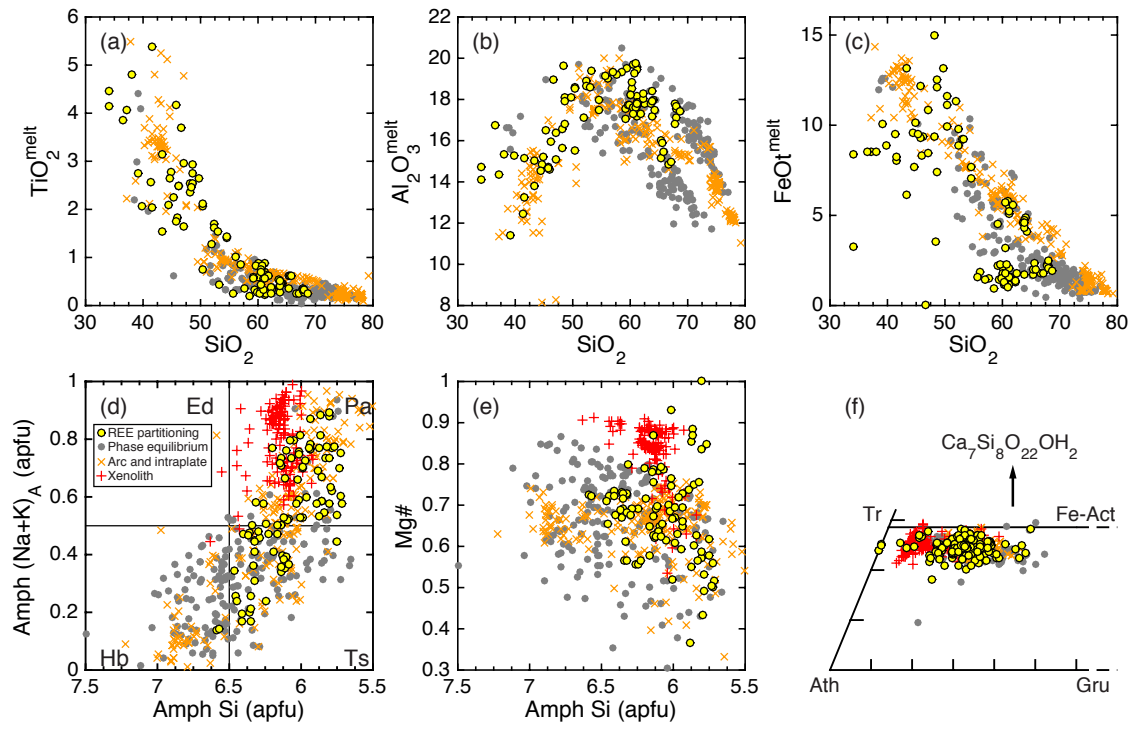


Figure 3-2.

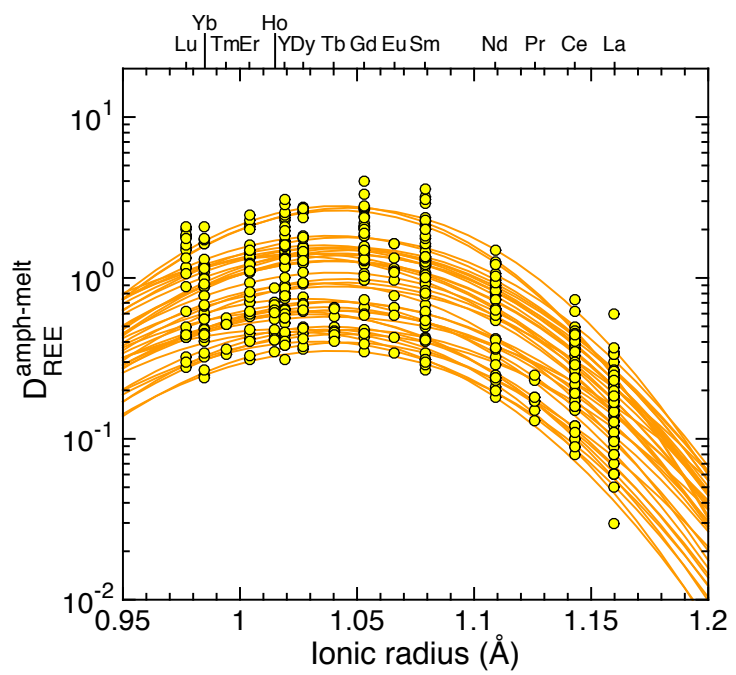


Figure 3-3.

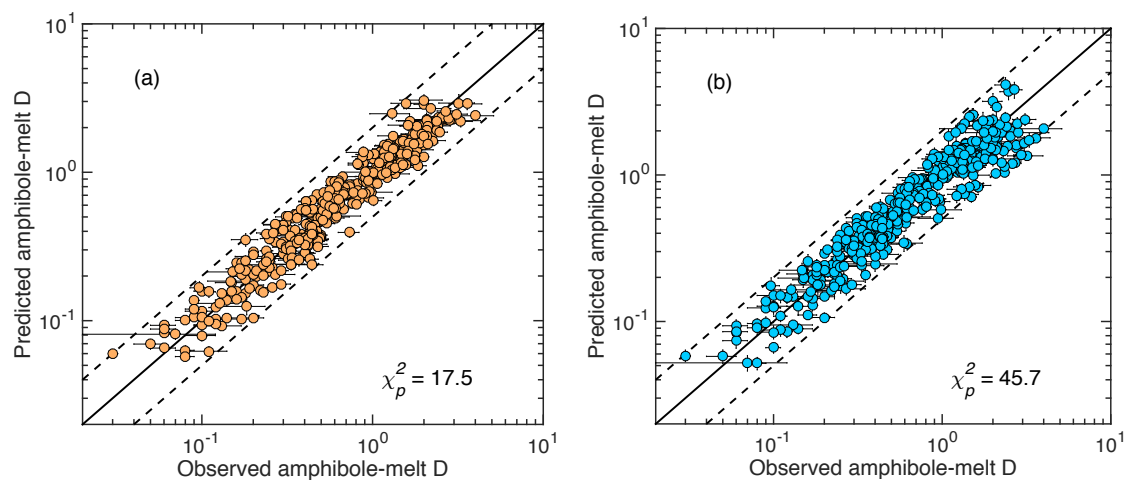


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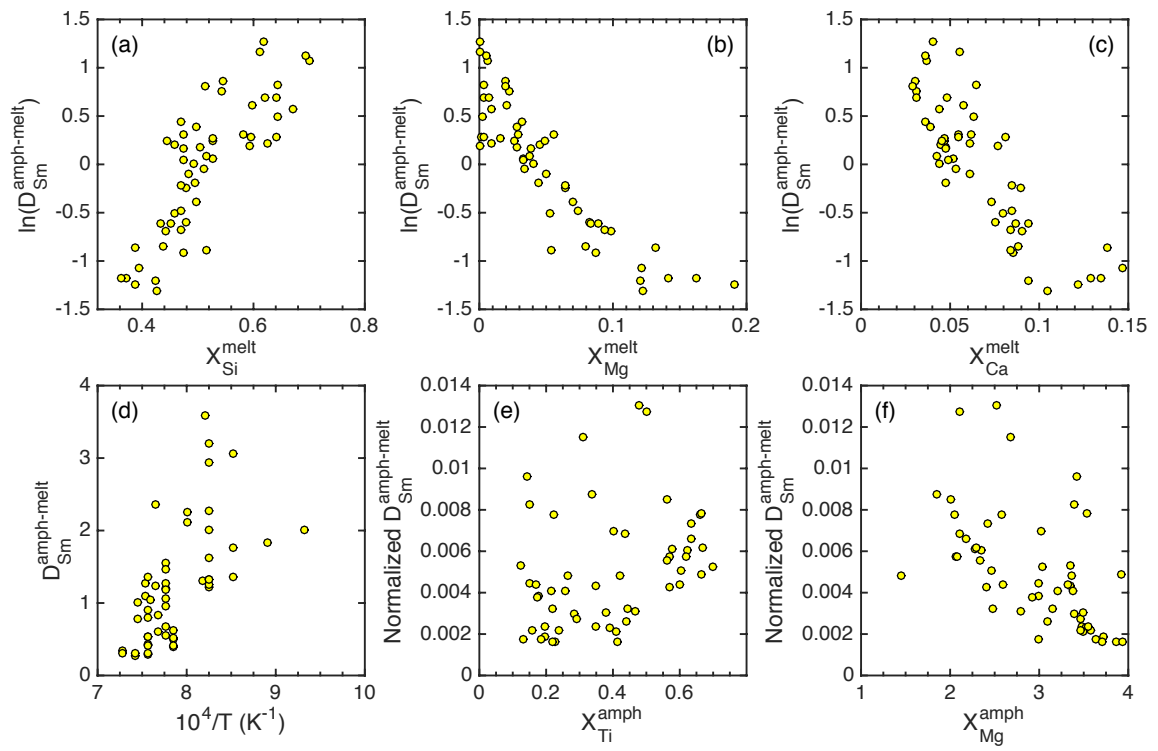


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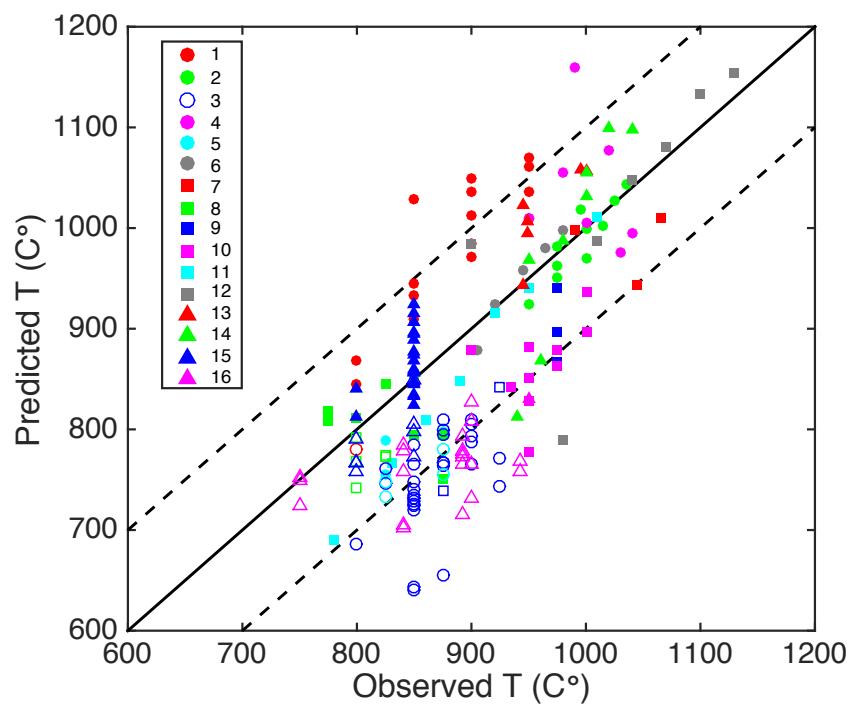


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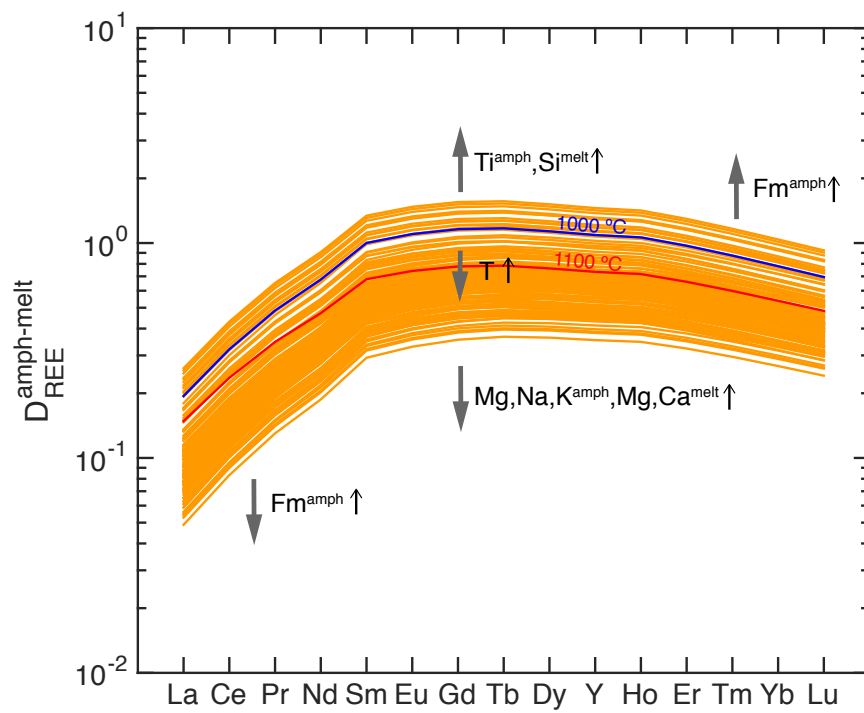


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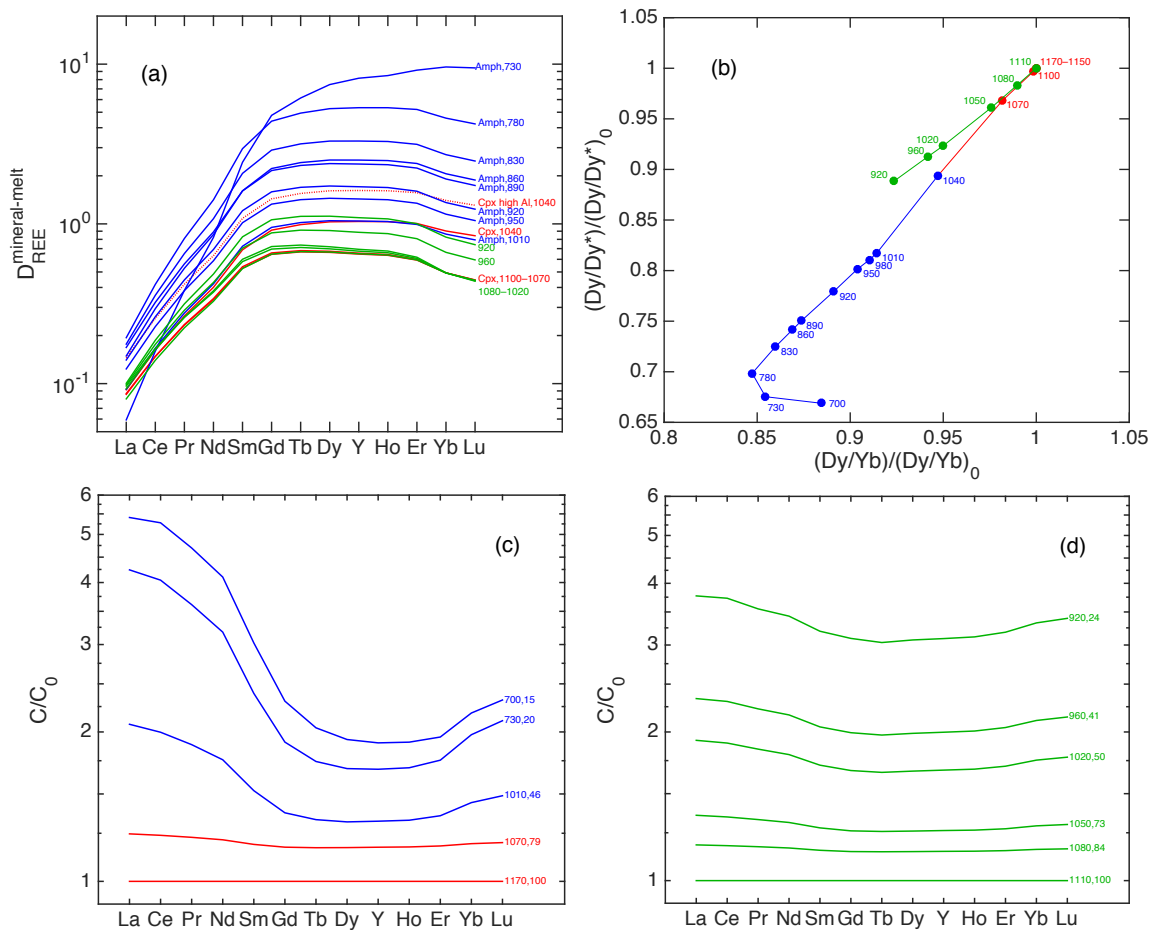


Figure 3-S1

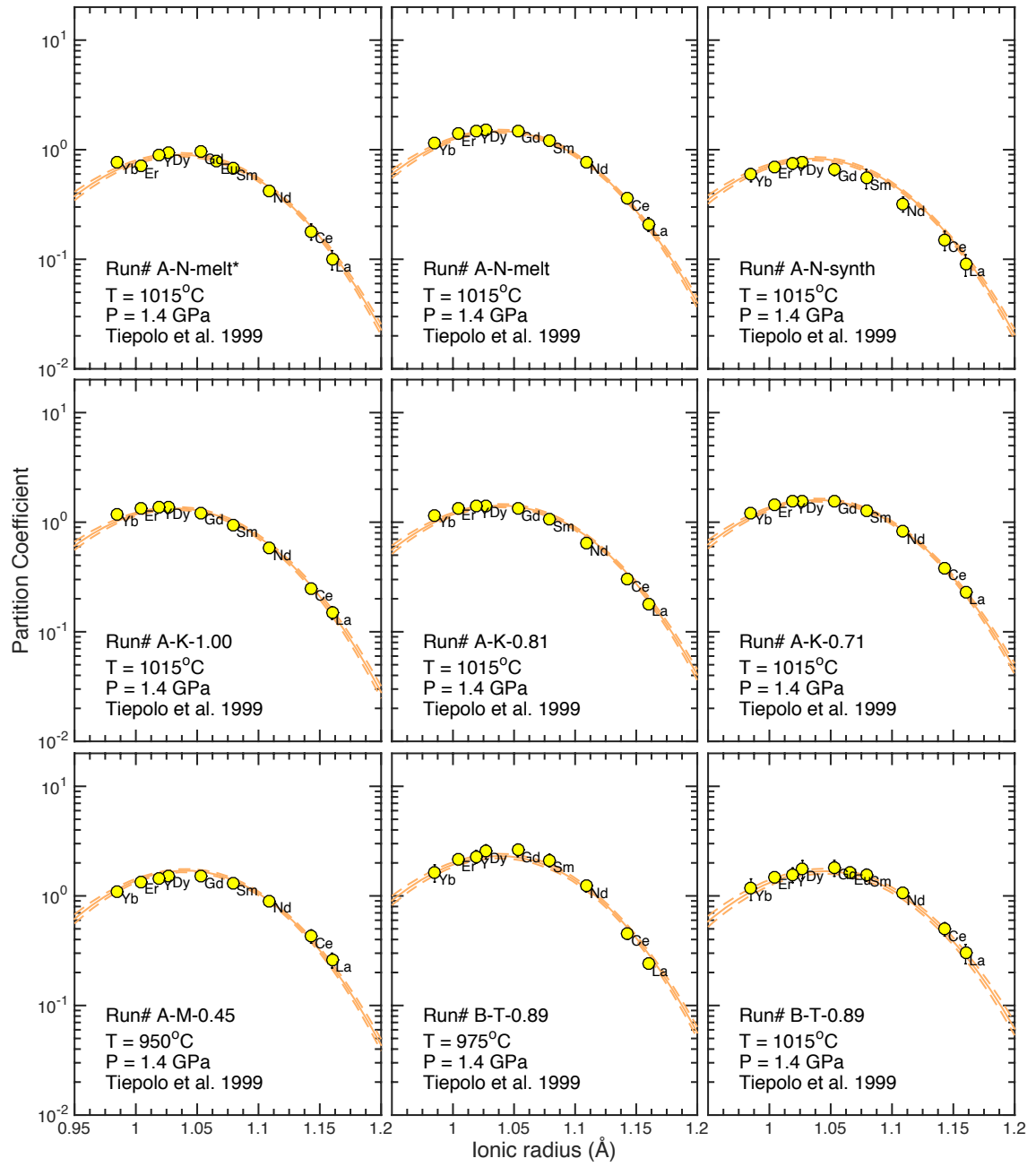


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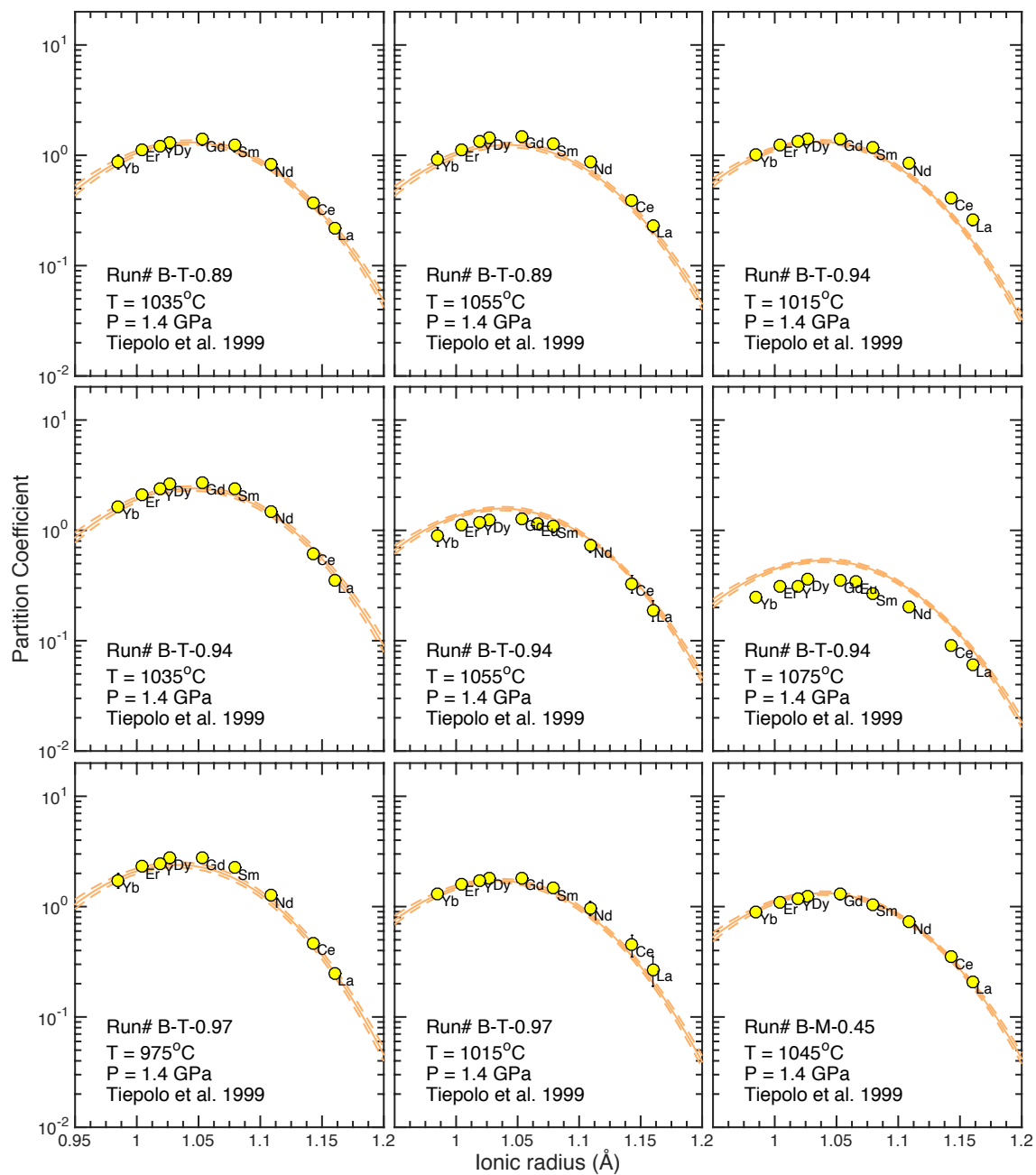


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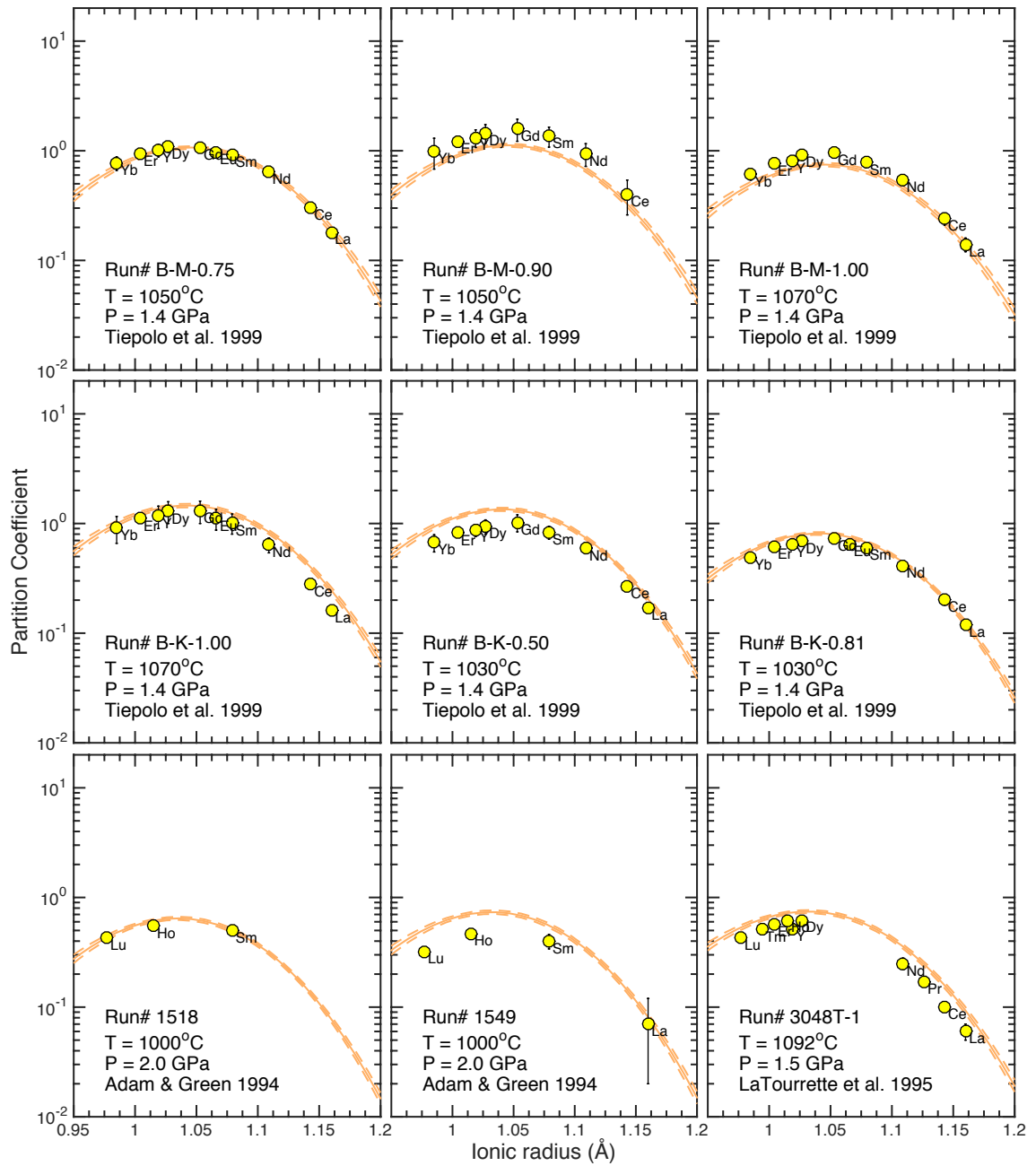


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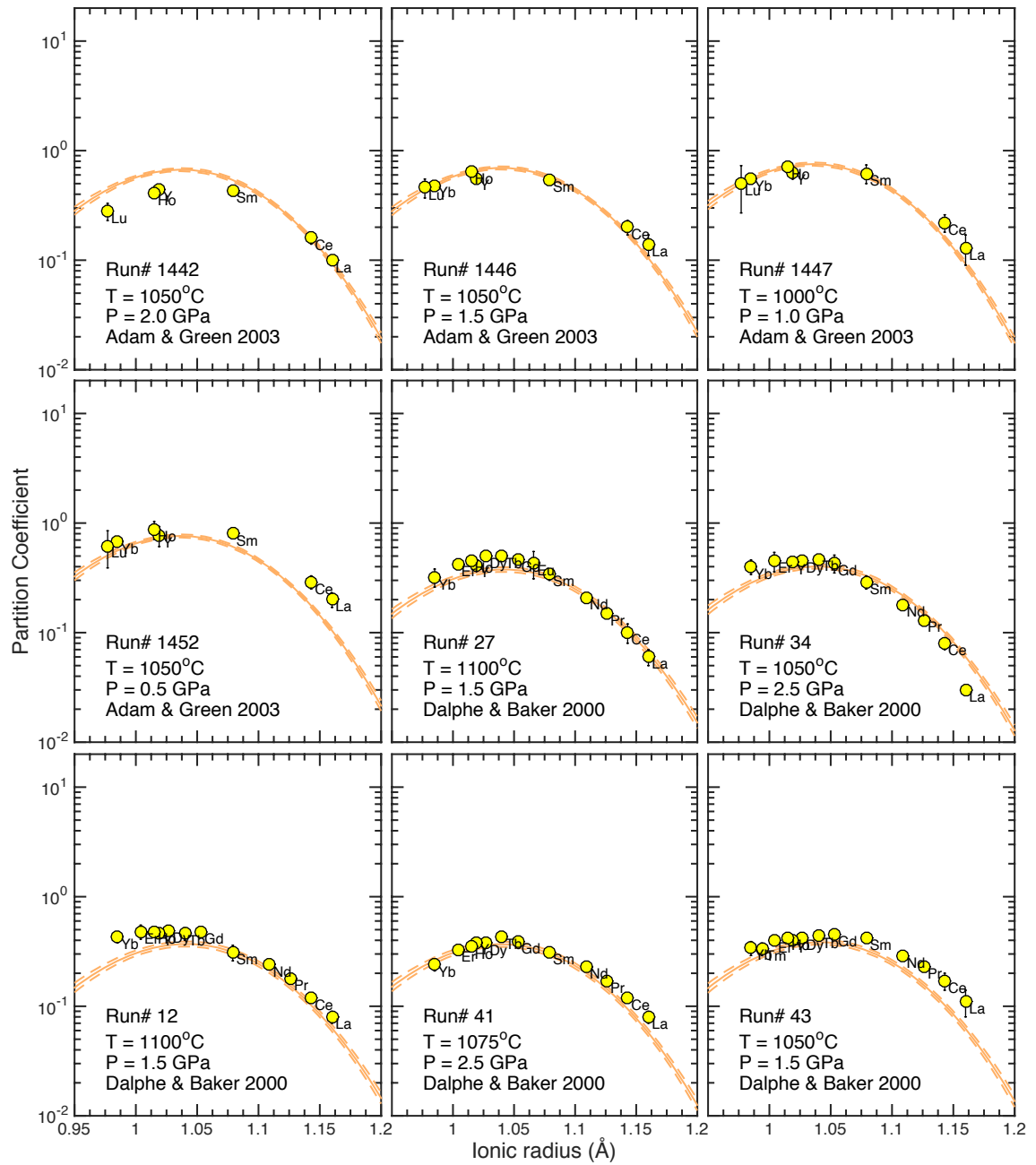


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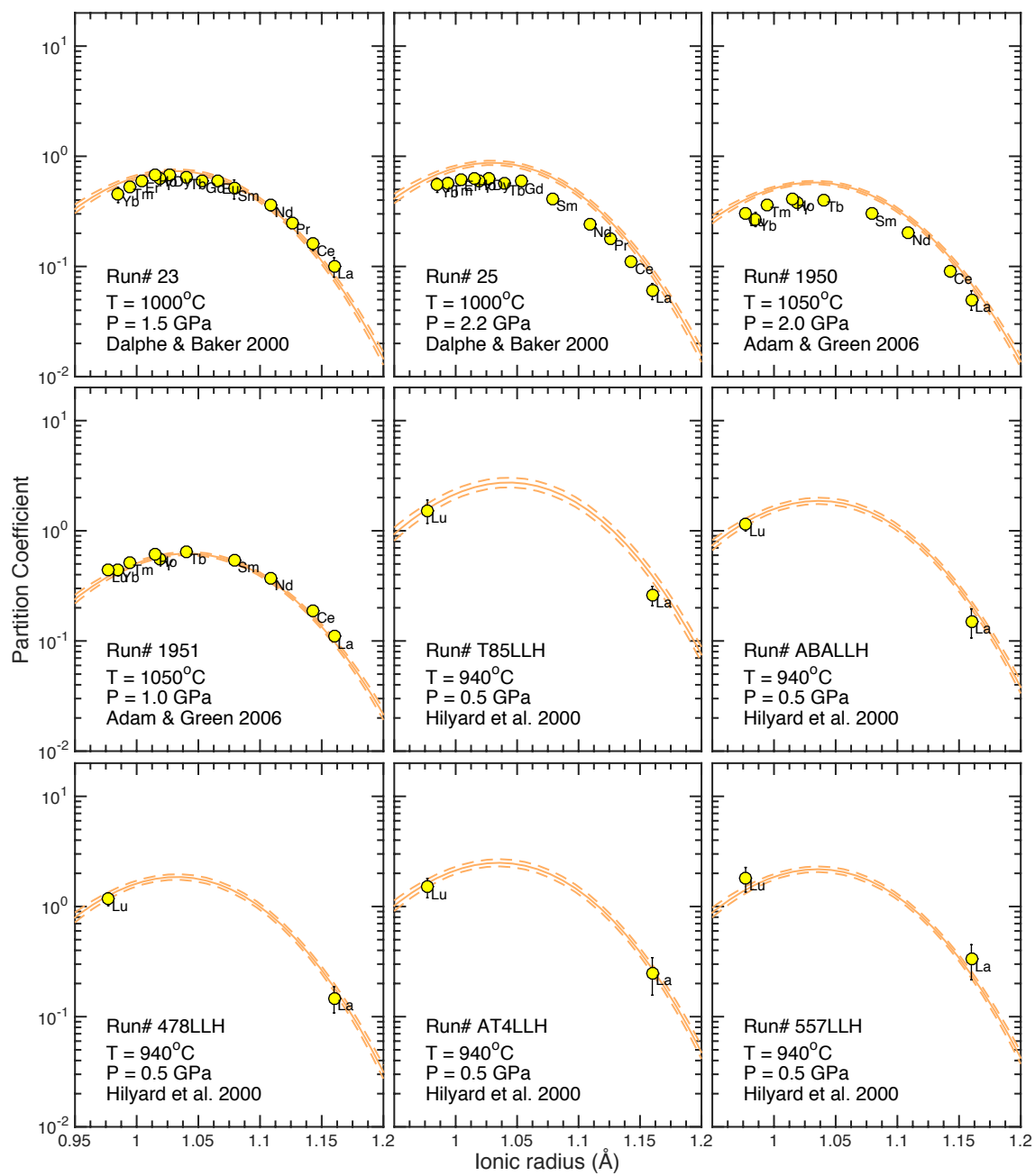


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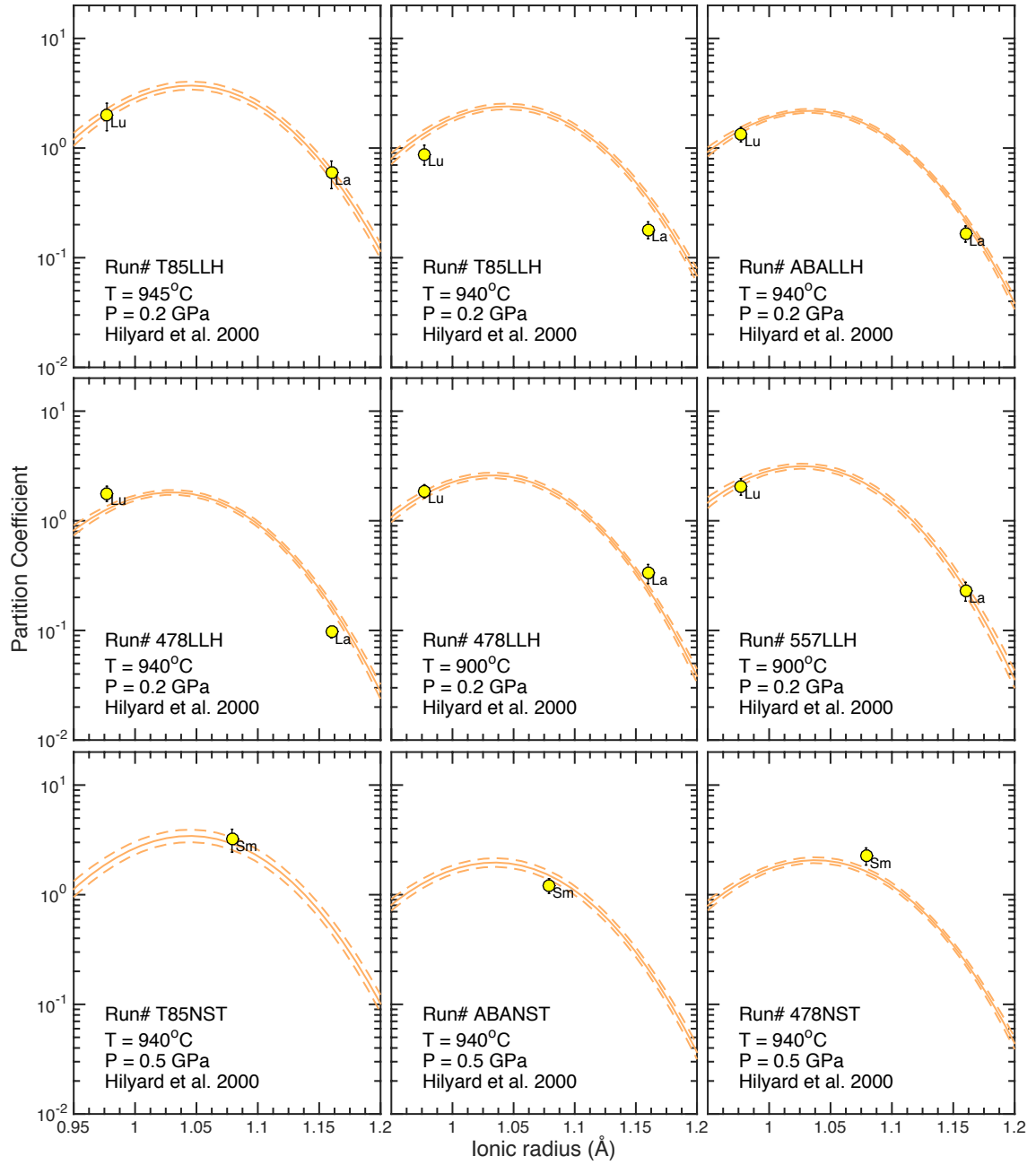


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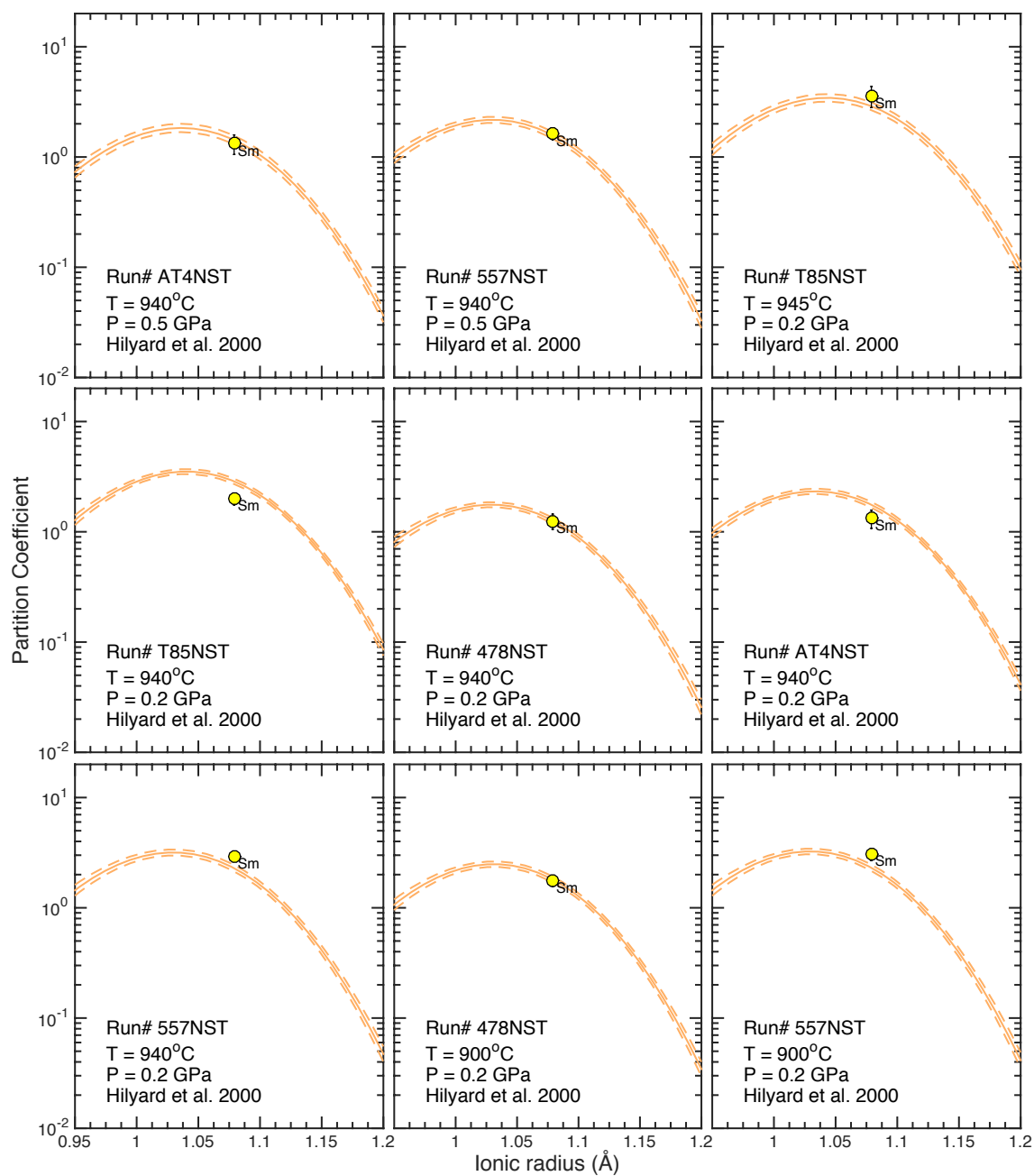


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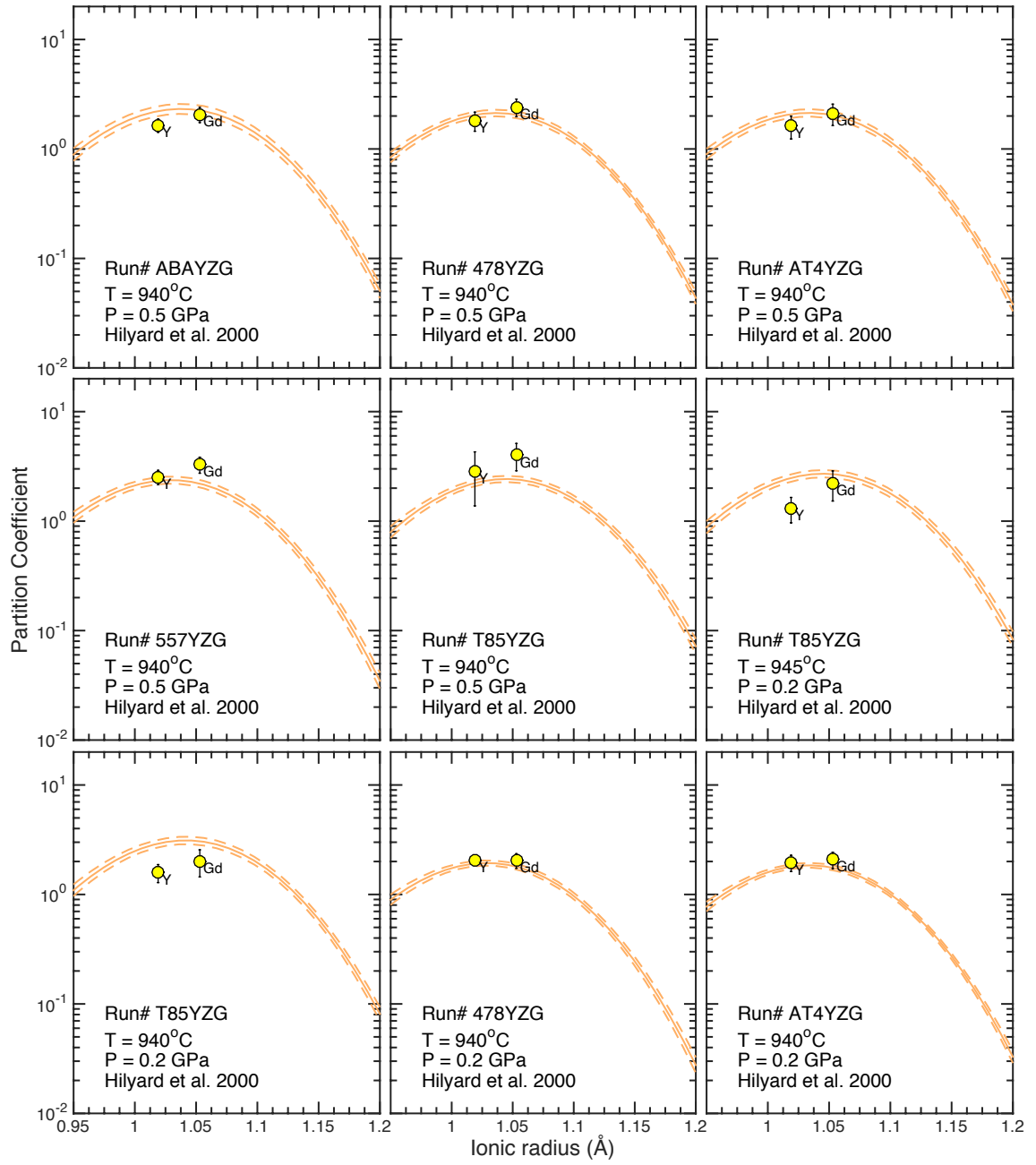


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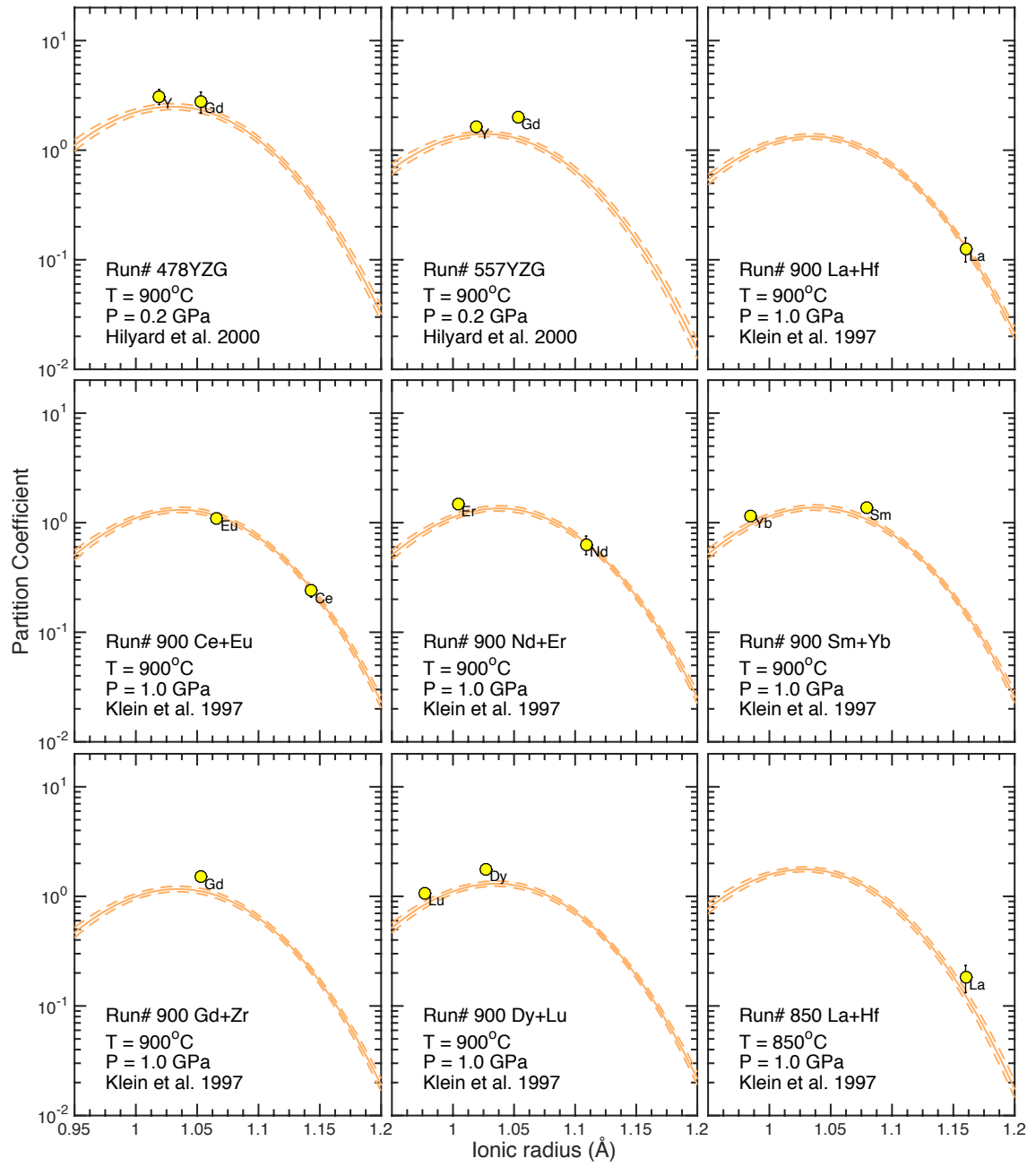


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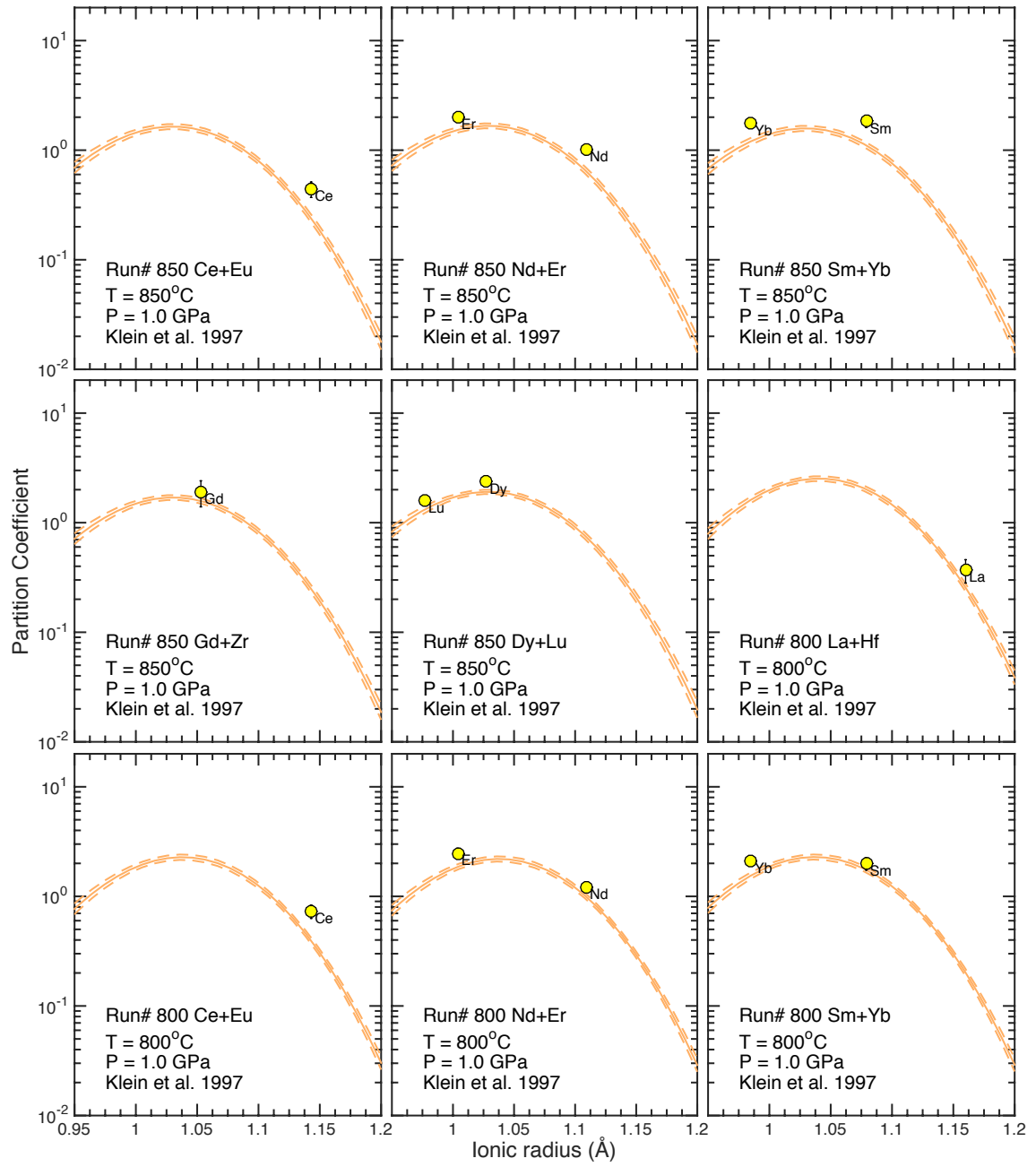


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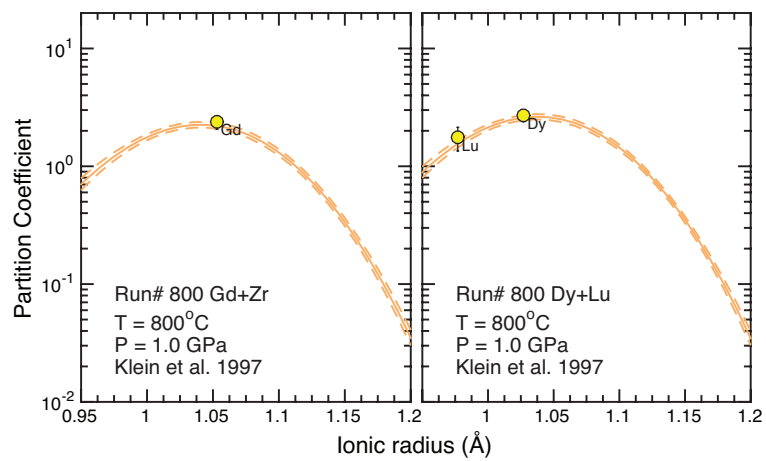


Figure 3-S2

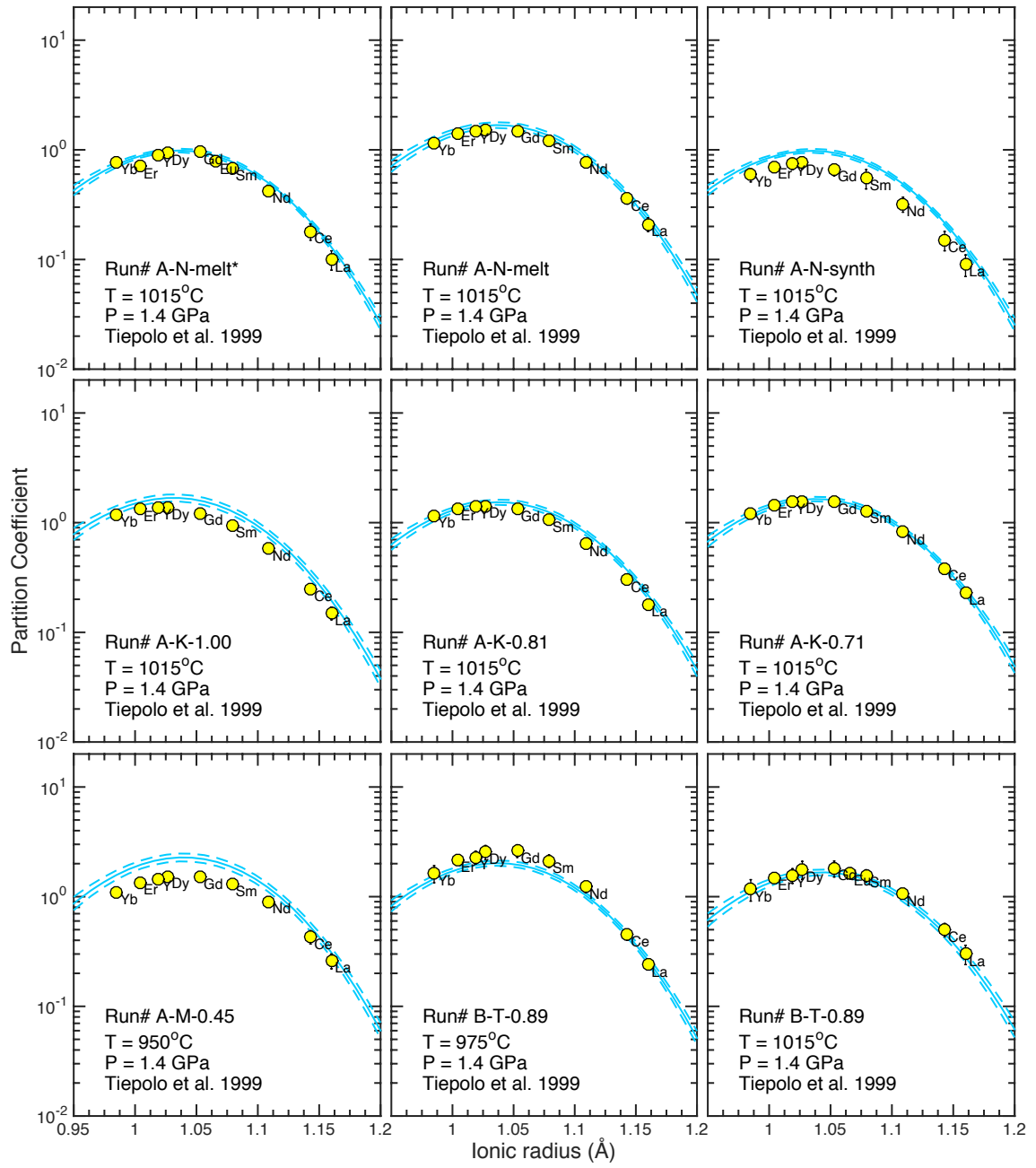


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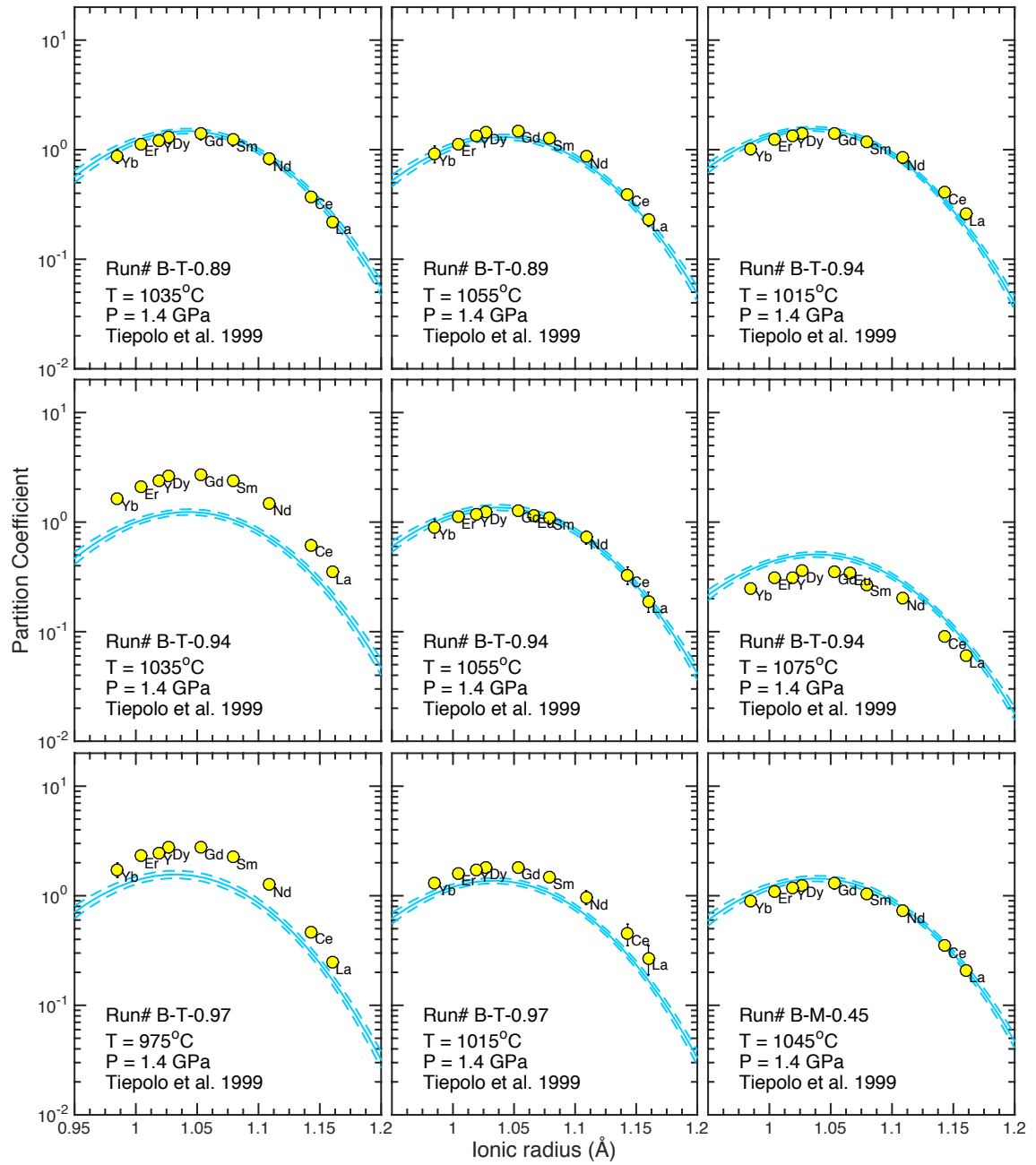


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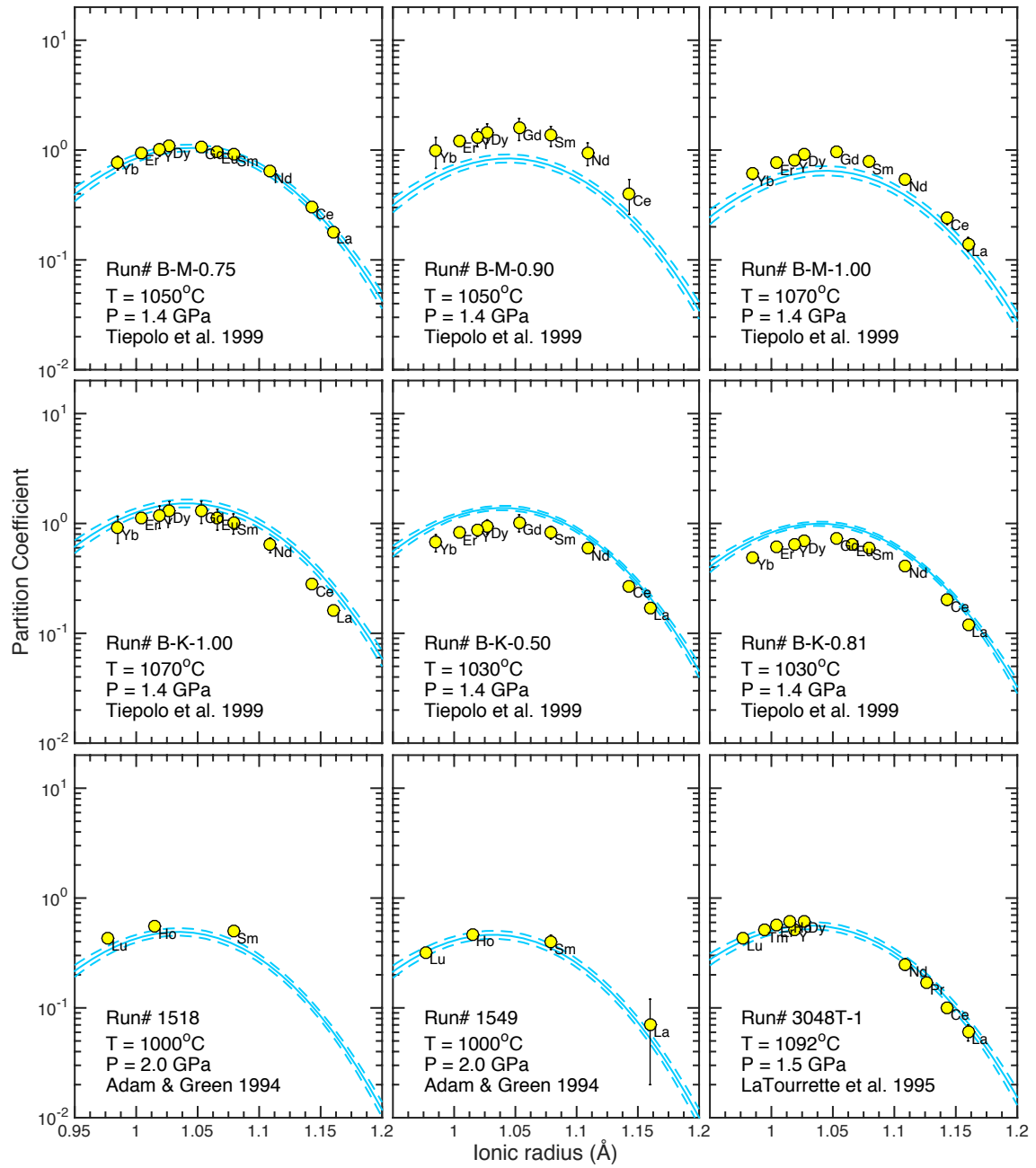


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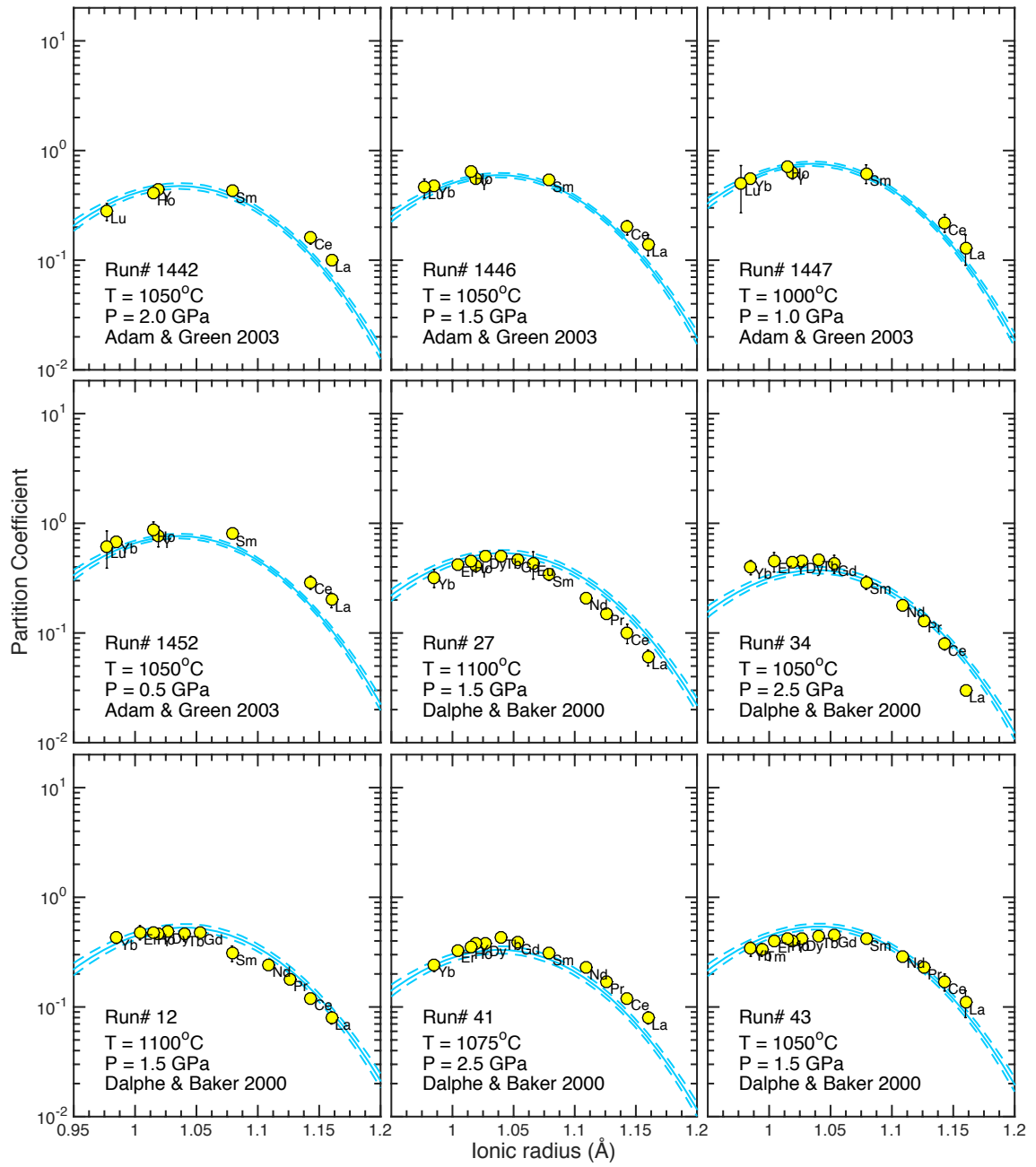


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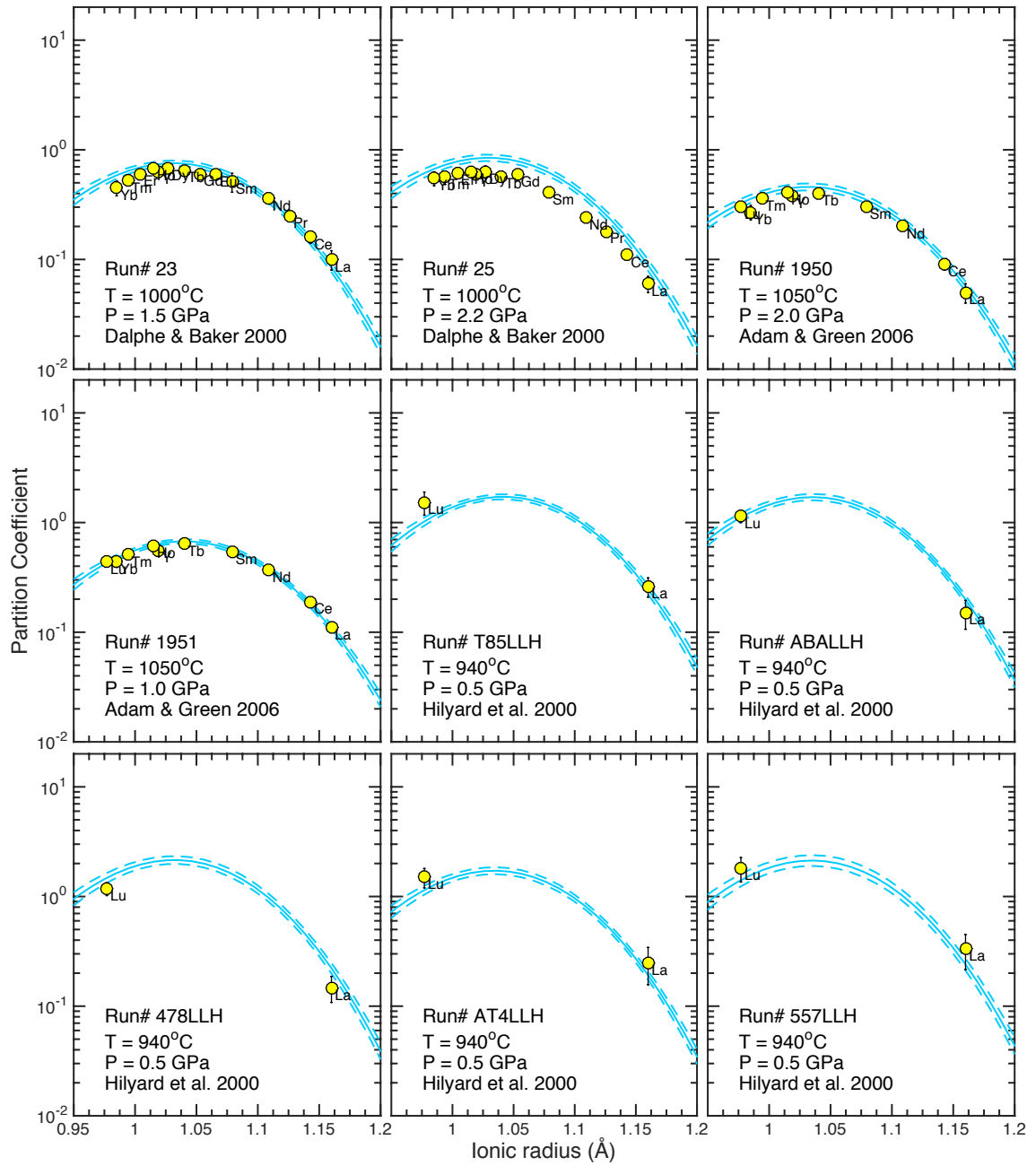


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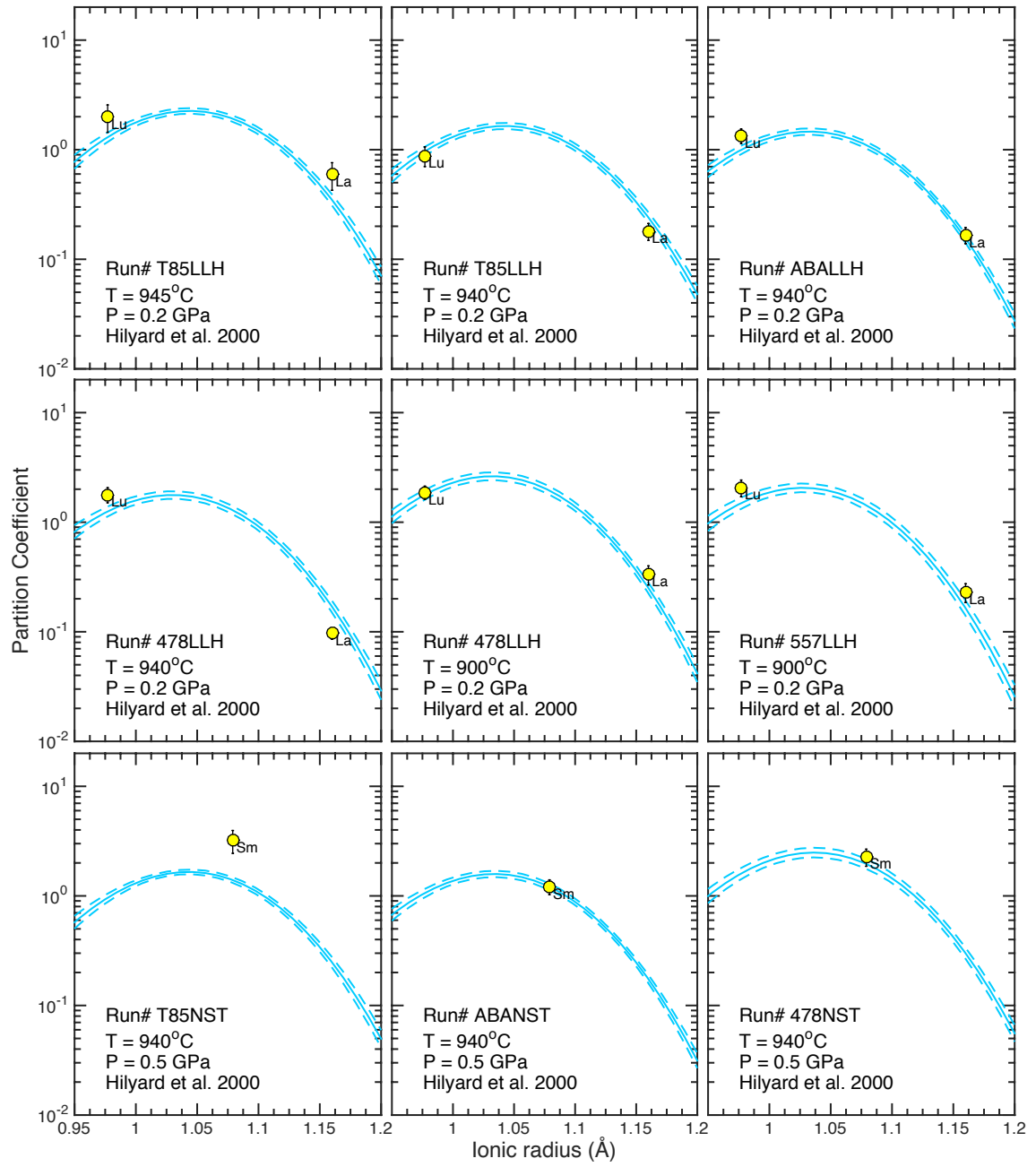


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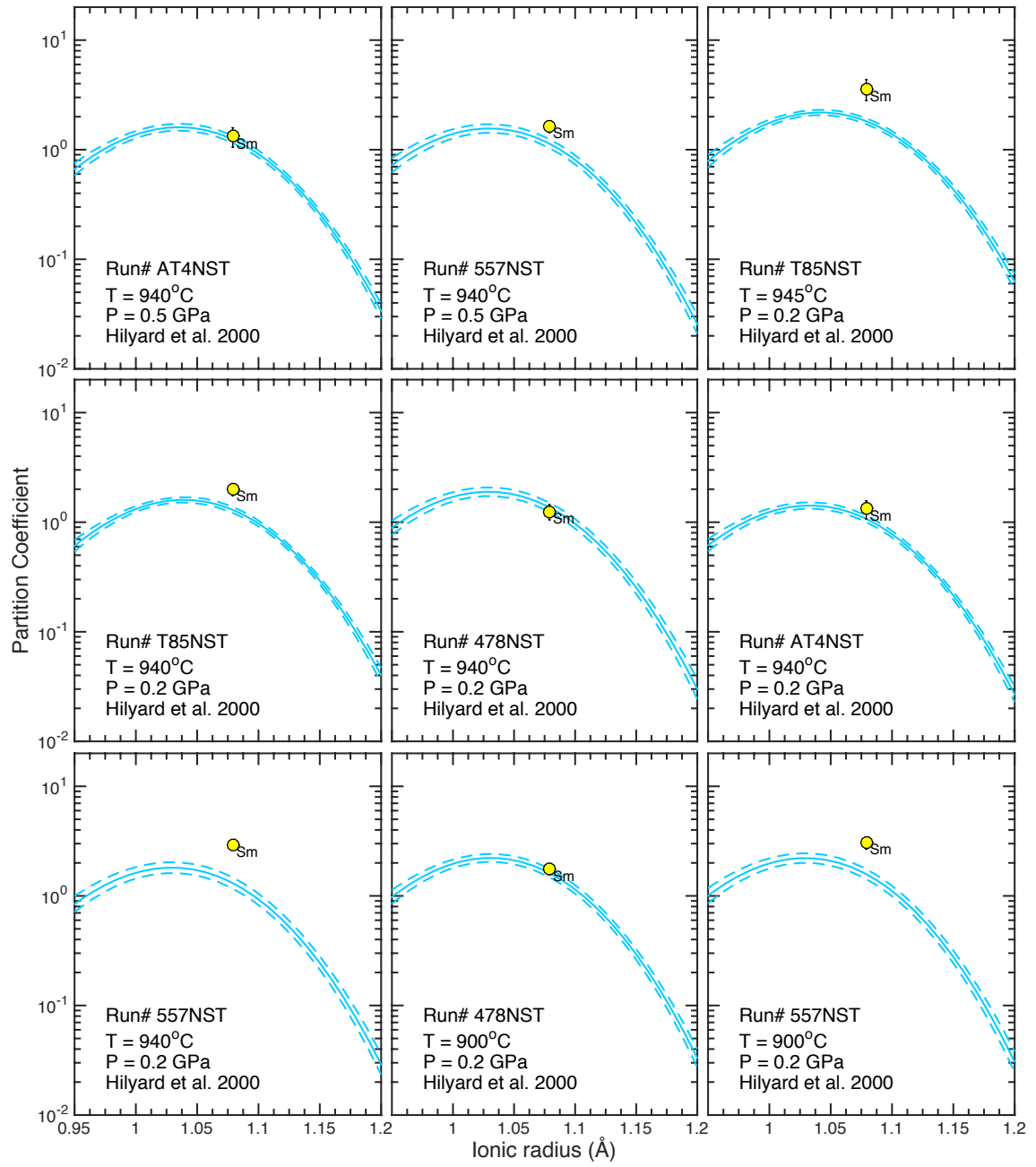


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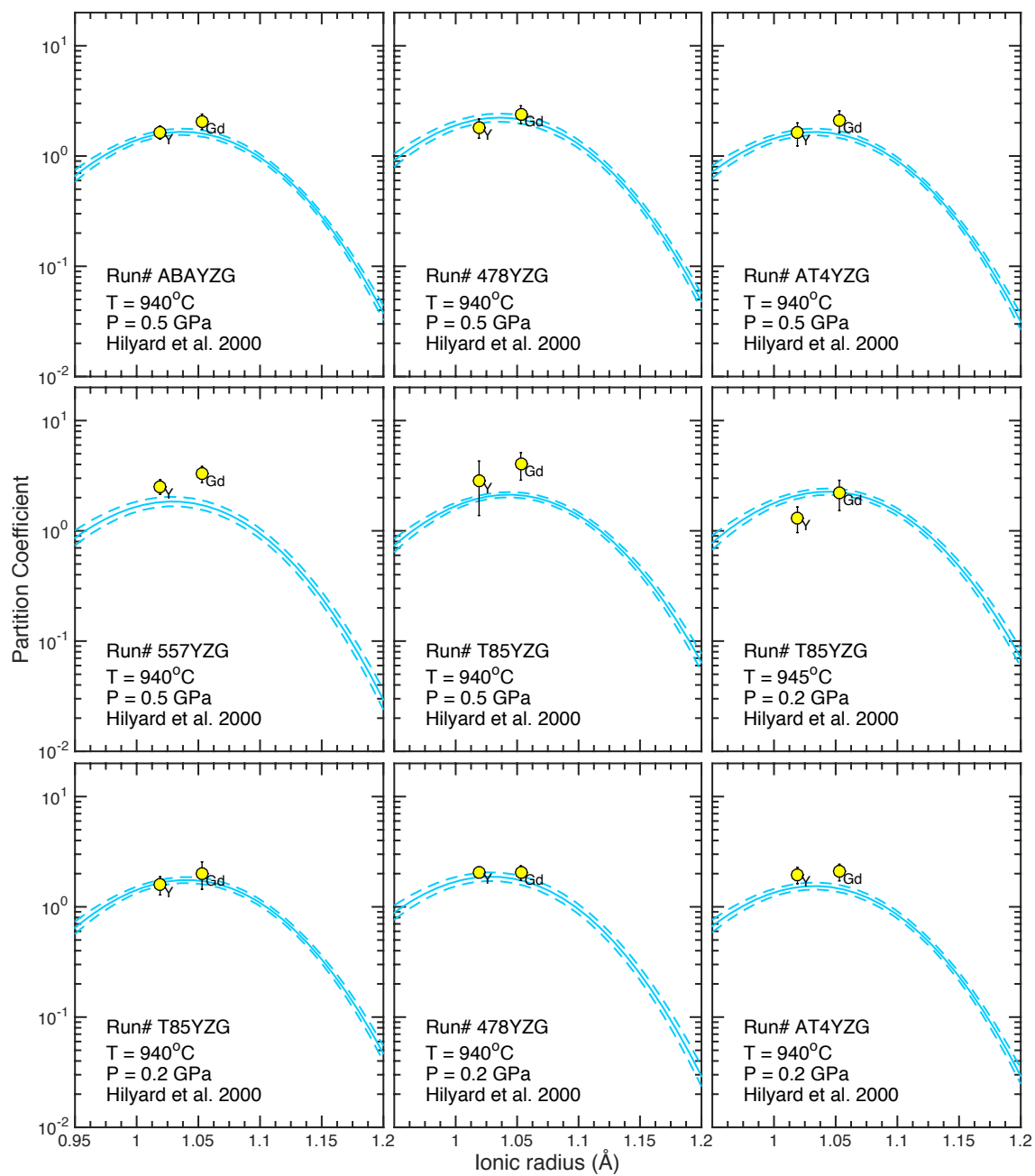


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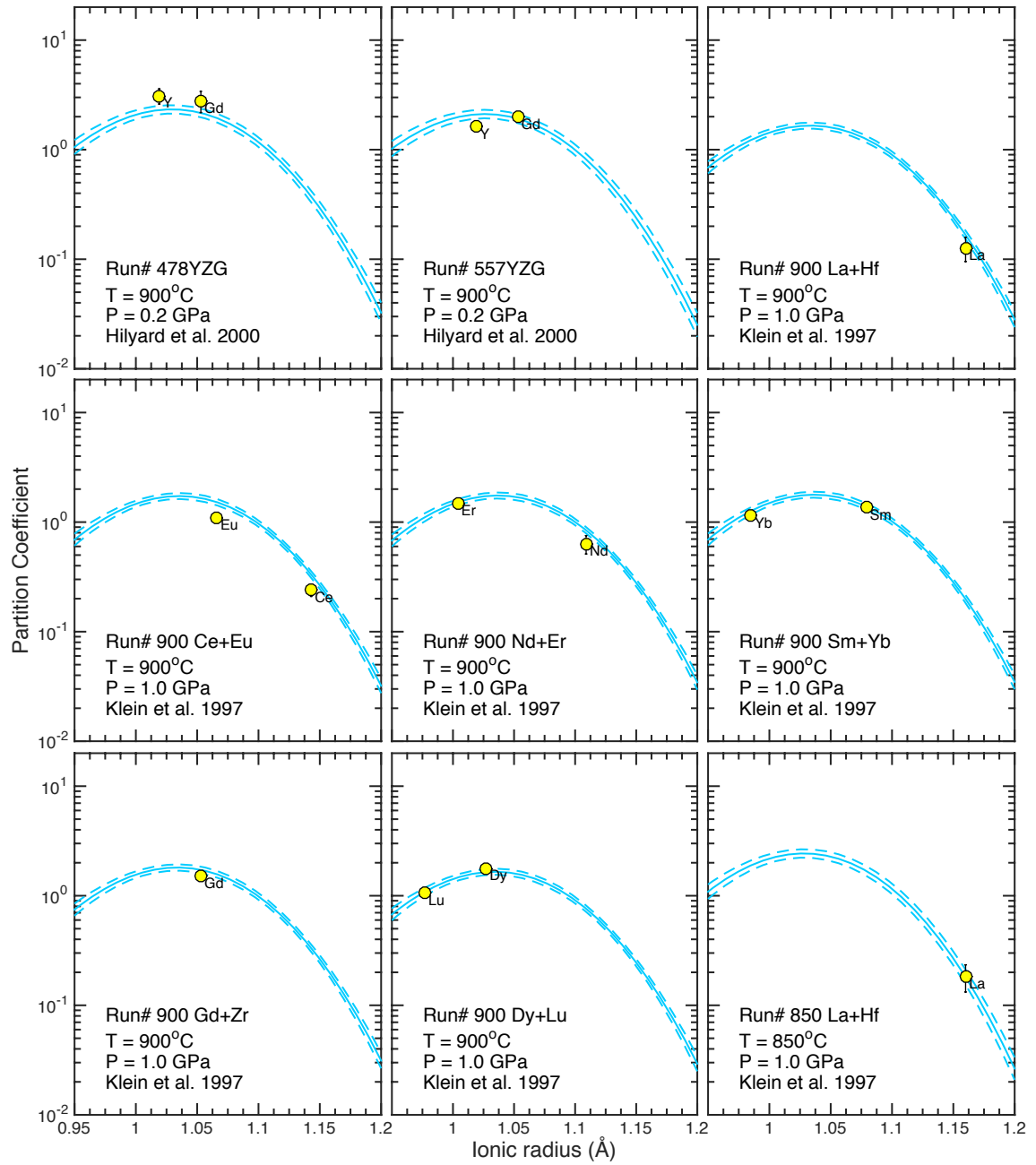


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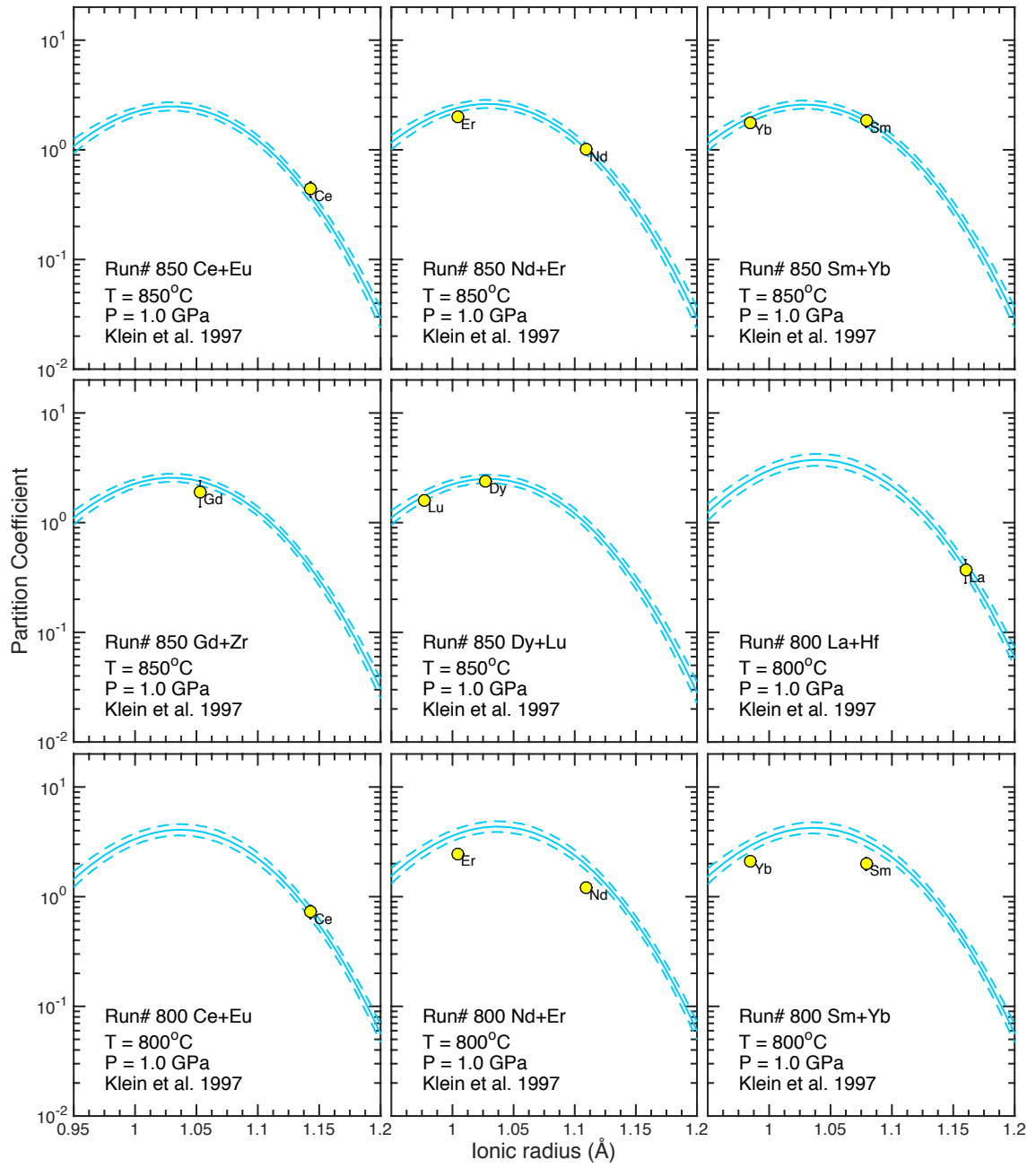


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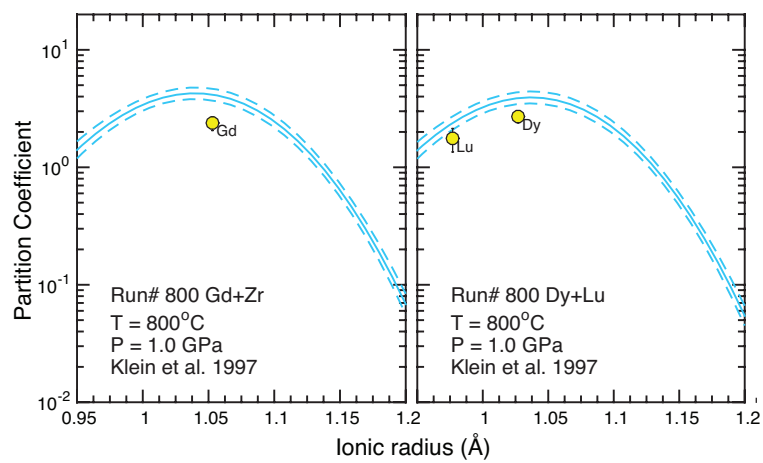


Figure 3-S3.

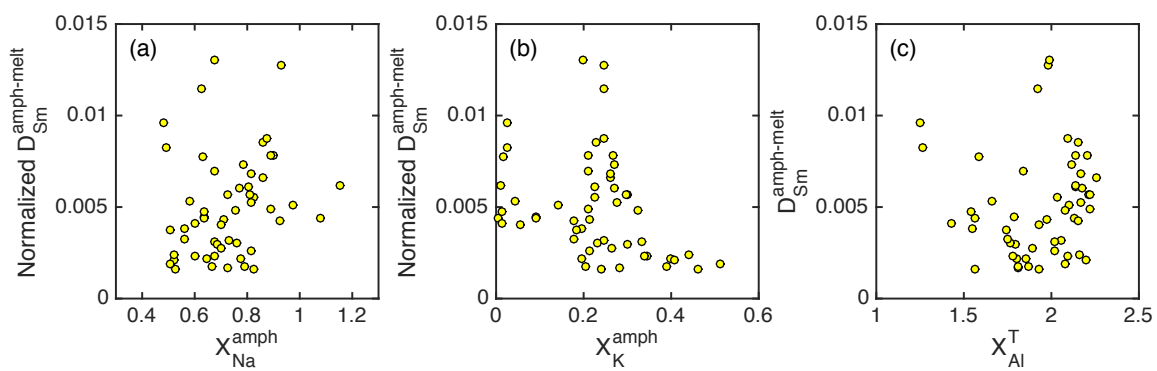


Table 3-1. Data sources and experimental run conditions.

Study	n ^a	m ^b	P (GPa)	T (C°)	Dur (h)	Amph Mg#	Melt Mg#	Melt SiO ₂ (wt%)	Melt H ₂ O (wt%) ^c
Ion probe analysis									
Tiepolo et al., (2000)	24	222	1.4	950–1075	36	36.5–100	15.1–100	41.5–54.6	2.4–6.15
LaTourrette et al., (1995)	1	10	1.5	1092	17.5	79.3	63.2	44.6	4.27
LA-ICP-MS analysis									
Adam and Green (2003)	4	27	0.5–2	1000–1050	24	73.0–78.5	48.1–54.3	39.9–46.0	6.2–13.0
Dalpe and Baker (2000)	7	88	1.5–2.5	1000–1100	24–100	67.0–93.0	46.4–87.3	34.1–47.1	
Adam and Green (2006)	2	20	1.0–2.0	1050	48	78.9–80.0	51.2–56.5	39.1–41.4	10.3–14.1
EMP analysis									
Adam and Green (1994)	2	8	2	1000	24	78.3–78.5	60.4–72.0	41.6–43.3	
Klein et al., (1997)	18	27	1	800–900	58–85	55.5–69.0	21.6–45.1	60.5–68.7	
Hilyard et al., (2000)	34	56	0.2–0.5	900–945	70–100	59.3–75.5	1.9–40.2	55.8–67.0	
Total range	92	458	0.2–2.5	800–1100	17.5–100	36.5–100	1.9–100	34.1–68.7	2.4–14.1

^an represents the number of experiments.
^bm represents the number of partitioning data.

^cMelt H₂O content shown when reported in the study. It was measured using SIMS by Tiepolo et al., (2000) and LaTourrette et al., (1999) and calculated using mass balance by Adam and Green (2003) and Adam and Green (2006).

Table 3-2. List of recommended amphibole-melt REE and Y partition coefficients for amphiboles found in xenoliths.

Temperature (C°)	1100			1000			900			800		
	Min	Average	Max	Min	Average	Max	Min	Average	Max	Min	Average	Max
La	0.044	0.08	0.134	0.052	0.094	0.157	0.064	0.147	0.19	0.082	0.188	0.238
Ce	0.07	0.132	0.222	0.087	0.162	0.271	0.112	0.256	0.343	0.151	0.345	0.453
Pr	0.104	0.201	0.339	0.133	0.255	0.428	0.177	0.405	0.563	0.249	0.57	0.779
Nd	0.142	0.284	0.479	0.187	0.369	0.622	0.256	0.586	0.844	0.373	0.853	1.213
Sm	0.207	0.433	0.733	0.279	0.582	0.984	0.396	0.905	1.389	0.6	1.372	2.09
Eu	0.226	0.485	0.821	0.307	0.657	1.113	0.44	1.007	1.587	0.674	1.542	2.418
Gd	0.238	0.521	0.883	0.325	0.709	1.203	0.467	1.068	1.727	0.719	1.644	2.653
Tb	0.24	0.537	0.912	0.328	0.733	1.246	0.472	1.08	1.794	0.728	1.665	2.765
Dy	0.233	0.532	0.906	0.318	0.727	1.236	0.457	1.044	1.779	0.702	1.604	2.74
Y	0.225	0.52	0.885	0.306	0.708	1.205	0.437	1	1.731	0.669	1.531	2.659
Ho	0.22	0.511	0.87	0.298	0.694	1.183	0.425	0.973	1.696	0.649	1.485	2.601
Er	0.202	0.478	0.815	0.272	0.647	1.103	0.386	0.882	1.572	0.584	1.335	2.393
Tm	0.183	0.44	0.751	0.245	0.591	1.009	0.344	0.786	1.428	0.515	1.177	2.154
Yb	0.165	0.401	0.685	0.218	0.535	0.914	0.304	0.694	1.282	0.449	1.027	1.915
Lu	0.148	0.364	0.622	0.194	0.482	0.824	0.267	0.611	1.146	0.391	0.893	1.694

Note: Calculated at different temperatures using the mineral composition model of this study and compositions of for amphiboles found in mantle xenoliths (Data source in Fig. 1). The composition of amphiboles are kept constant for the calculation at different temperatures.

Table 3-3. List of recommended amphibole-melt REE and Y partition coefficients for arc magma environment.

Temperature (C°)	1010	950	920	890	860	830	780	730*
La	0.092	0.124	0.141	0.168	0.149	0.177	0.194	0.059
Ce	0.167	0.228	0.262	0.323	0.295	0.357	0.418	0.16
Pr	0.277	0.382	0.446	0.562	0.528	0.652	0.81	0.384
Nd	0.421	0.588	0.691	0.89	0.858	1.078	1.415	0.823
Sm	0.725	1.017	1.209	1.608	1.611	2.071	2.958	2.431
Eu	0.849	1.19	1.419	1.909	1.94	2.514	3.706	3.512
Gd	0.951	1.329	1.588	2.157	2.221	2.896	4.395	4.78
Tb	1.019	1.418	1.694	2.322	2.42	3.169	4.938	6.139
Dy	1.047	1.446	1.726	2.385	2.511	3.299	5.264	7.451
Y	1.042	1.432	1.708	2.37	2.509	3.301	5.338	8.165
Ho	1.034	1.417	1.689	2.347	2.491	3.28	5.336	8.481
Er	0.992	1.347	1.601	2.236	2.389	3.148	5.205	9.17
Tm	0.931	1.253	1.486	2.082	2.236	2.946	4.935	9.526
Yb	0.863	1.15	1.36	1.91	2.06	2.712	4.591	9.602
Lu	0.794	1.049	1.236	1.739	1.882	2.475	4.225	9.474

Note: Calculated using the melt composition model and the composition of amphiboles in the 0.7 GPa experiments of Nandedkar et al., (2014). *The set of partition coefficient at 730°C should be used with caution since the temperature is significantly below the calibration range of our model.

Supplementary material

Recalibration of the empirical model of Tiepolo et al. (2007)

We recalibrated the melt composition model of Tiepolo et al. (2007) for 15 elements (REE+Y) using our compiled database. Their model takes on the following expression,

$$\ln D_{\text{REE}}^{\text{amph-melt}} = a + b X_{\text{nf}} / X, \quad (\text{S1})$$

where a and b are constants determined by linear regression analysis of individual amphibole-melt REE+Y partition coefficients; X_{nf} / X is the measure of melt polymerization (mole fractions of Si and Al balanced by alkalis, Nielsen (1985)). The new coefficients obtained from the recalibration are given in Table S1.

Table 3-S1. Coefficients in the regression equations of Tiepolo et al. (2007) recalibrated using the partitioning data compiled in this study (Table 1).

	a	1σ	b	1σ
La	-5.06	0.03	5.3	0.03
Ce	-5.27	0.02	6.72	0.02
Pr	-2.14	0.04	0.89	0.04
Nd	-4.75	0.02	7.18	0.02
Sm	-4.53	0.02	7.48	0.02
Eu	-3.75	0.04	6.19	0.04
Gd	-3.91	0.02	6.91	0.02
Tb	-1.69	0.02	2.11	0.02
Dy	-3.91	0.02	6.9	0.02
Y	-4.11	0.02	7	0.02
Ho	-2.26	0.02	3.19	0.02
Er	-3.93	0.02	6.73	0.02
Tm	-2.94	0.03	4.16	0.03
Yb	-4.24	0.02	6.86	0.02
Lu	-5.44	0.02	8.32	0.02

Note: a and b are coefficients of Eq. (S1).

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CHAPTER 4

A REE-in-amphibole-plagioclase thermometer

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Abstract

A REE-in-amphibole-plagioclase thermometer has been developed for amphibole- and plagioclase-bearing rocks. This new thermometer is based on the temperature-dependent REE partitioning between amphibole and plagioclase, and is calibrated against experimentally determined amphibole-melt and plagioclase-melt partition coefficients. Application of the REE-in-amphibole-plagioclase thermometer to oceanic and continental gabbroic rocks from the Mid-Atlantic Ridge and Sondalo gabbroic complex in Northern Italy shows that temperatures derived from the REE-in-amphibole-plagioclase thermometer are significantly higher than those calculated using major element-based thermometers. Numerical experiments were conducted to test whether REE concentrations in amphibole and plagioclase that crystallized from different melts at different temperatures may record apparent temperatures. Inversion of synthetic REE patterns of amphibole and plagioclase crystallized from two different melts at different temperatures suggests the REE-based temperature may record a temperature between amphibole and plagioclase crystallization that is not physically meaningful. Care must be taken in selecting samples that show evidence of co-crystallization of amphibole and plagioclase. The temperatures of oceanic gabbros recorded in the REE-in-amphibole-plagioclase thermometer agree well with the calculated closure temperature of REE in plagioclase in the oceanic gabbro layer. This may suggest that REE-based thermometer record a higher closure temperature than the major element-based thermometers due to the slower diffusion of REE relative to the major elements. Based on this inference and using the temperature recorded by the REE-in-amphibole-plagioclase thermometer, we estimate the cooling rate of continental gabbros to be 10^2 to 10^5 °C/Myr. Future work to

better understand the physical meaning of the temperatures recorded in the REE-in-amphibole-plagioclase thermometer includes (1) detailed and high quality analysis of gabbroic rocks containing amphibole and plagioclase to produce high quality data, (2) diffusion modeling of amphibole and plagioclase crystallization to evaluate if kinetic effects could cause REE-in-amphibole-plagioclase thermometer to record disequilibrium temperatures, (3) experimental study of REE diffusion in amphibole, and (4) further calibration of the plagioclase-melt REE partitioning model to lower T .

1. Introduction

Amphibole and plagioclase are common rock-forming minerals in igneous and metamorphic rocks, and their equilibrium temperatures and pressures provide important constraints for understanding magmatic and metamorphic processes. Various thermometers and barometers have been developed to quantify amphibole, plagioclase, and amphibole-plagioclase pair equilibrium temperatures and pressures based on empirical and/or thermodynamic relationships among mineral composition, temperature, and pressure (e.g. Faak et al., 2013; Hammarstrom and Zen, 1986; Holland and Blundy, 1994; Johnson and Rutherford, 1989; Putirka, 2016; Ridolfi et al., 2010; Schmidt, 1992). Amphibole-only and amphibole-melt thermometers have been developed utilizing the temperature dependence of amphibole Si content and amphibole-melt Mg partition coefficient (Molina et al., 2015; Putirka, 2016; Ridolfi and Renzulli, 2012; Ridolfi et al., 2010). Thermodynamic relationship between amphibole and plagioclase compositions have been used to develop amphibole-plagioclase thermometer (Blundy and Holland,

1990; Holland and Blundy, 1994). These thermometers may record temperatures affected by subsolidus cooling owing to the fast diffusion of major elements in the minerals.

Recent studies suggest that fractional crystallization of amphibole produces the characteristic depletion in middle rare earth elements (MREE) relative to heavy REE (HREE) and light REE (LREE) observed in arc volcanic rocks (Davidson et al., 2007; Davidson et al., 2013). Our recent work detailed in preceding chapter also suggests that indeed fractional crystallization of amphibole plays a key role in generating the depletion in MREE relative to HREE and LREE pattern in arc magmas. Crystallization temperature of amphiboles in crustal cumulates have been estimated using major element thermometers (e.g. Holland and Blundy, 1994; Putirka, 2016). Although these thermometers provide important information, there are situations where the major elements in minerals may be reset by subsolidus re-equilibration (Blundy and Holland, 1990; Dessimoz et al., 2012; Holland and Blundy, 1994).

The distribution of rare earth elements (REE) between two coexisting minerals depends on temperature, pressure and mineral compositions (Lee et al., 2007; Liang et al., 2013; Seitz et al., 1999; Stosch, 1982; Sun and Liang, 2014; Witt-Eickschen and O'Neill, 2005), and can be used to develop REE-based thermobarometers (Liang et al., 2013; Sun and Liang, 2015). Compared to major element based thermometers, REE-based thermometers may record temperatures closer to the magmatic temperatures owing to the significantly lower diffusion rates of REE relative to those of major elements. In this study, we further expand the idea of REE-based thermometers and develop a REE-in-amphibole-plagioclase thermometer. We show that the new thermometer can be applied to amphiboles and plagioclase in oceanic and crustal cumulates to obtain temperatures,

and we discuss physical meanings of the derived temperatures in terms of magmatic and subsolidus processes.

2. A REE-in-amphibole-plagioclase thermometer

As shown by studies of Liang et al. (2013) and Sun and Liang (2015), REE distribution between two phases α and β can be quantitatively determined by the lattice strain model (Blundy and Wood, 1994),

$$D_{\text{REE}}^{\beta-\alpha} = \frac{D_0^\beta}{D_0^\alpha} \exp \left[-\frac{4\pi N_A E^\beta}{RT} \left(\frac{r_0^\beta}{2} (r_0^\beta - r_{\text{REE}}) \right)^2 - \frac{1}{3} (r_0^\beta - r_{\text{REE}})^3 \right] + \frac{4\pi N_A E^\alpha}{RT} \left(\frac{r_0^\alpha}{2} (r_0^\alpha - r_{\text{REE}}) \right)^2 - \frac{1}{3} (r_0^\alpha - r_{\text{REE}})^3 \right] \quad (1)$$

where D_0 is the mineral-melt partition coefficient for the strain-free substitution; r_0 is the radius of a hypothetical cation that substitutes into the site with zero strain; r_{REE} is the ionic radius of a given REE; E is the effective Young's modulus for the lattice site; N_A is Avogadro's number; R ($= 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$) is the gas constant; and T is temperature in Kelvin. Superscripts α and β refer to minerals α and β respectively.

We have recently developed parameterized lattice strain models for trivalent REE and Y partitioning between amphibole and basaltic melt and between plagioclase and basaltic melt (Shimizu et al., in review; Sun et al., in review). These models were developed following a new protocol that has been successfully used to develop parameterized lattice models for REE and Y partitioning between mantle minerals (clinopyroxene, orthopyroxene, garnet and spinel) and basaltic melts (Dygert et al., 2014; Sun and Liang, 2012; Sun and Liang, 2013a; Sun and Liang, 2013b; Yao et al., 2012). Our database includes 92 amphibole-melt partitioning experiments (800–1100°C, 0.2–

2.5GPa) and 23 plagioclase-melt partitioning experiments (1127–1400°C, 0.6–1GPa). The amphiboles are calcic amphiboles with Mg number ($Mg\# = 100 \times Mg / (Mg + Fe^{2+})$ in mole) of 36.5–100 (assuming all iron in amphibole is present as ferrous iron), and the plagioclases have anorthite content ($An = 100 \times Ca / (Ca + Na + K)$ in mole) of 53–98.

The supplementary material lists the parameterized lattice strain models for REE partitioning between amphibole and basaltic melt and between plagioclase and basaltic melt. In the plagioclase model, D_0 positively correlates with T , and negatively correlates with Ca content in the plagioclase (Eqs. S2a–c). Constant E and r_0 were found to adequately fit the compiled plagioclase partitioning data. In the amphibole mineral composition model, D_0 positively correlates with Ti content, and negatively correlates with T , Mg, Na, and K contents in the amphibole (Eqs. S1a–c). r_0 negatively correlates with the ferromagnesian content ($Fe^{2+} + Mn^{2+} + Mg^{2+}$) in the M4 site of the amphibole. In addition to this mineral composition model, for amphibole, we developed a melt composition model and a hybrid model involving both melt and amphibole compositions. There are considerable trade-offs between major element compositions of coexisting amphibole and melt in the parameterized lattice strain models for REE partitioning in amphibole. Here we focus on the mineral composition model given the purpose of this study.

We can construct an amphibole-plagioclase REE partitioning model using Eq. (1) (α = amphibole and β = plagioclase) and the lattice strain parameters listed in the supplementary material. To examine the effect of temperature and mineral composition, we calculated amphibole-plagioclase REE partition coefficients using Eq (1) and mineral major element composition from a troctolite (153-923A-8R1) from the Mid-Atlantic

Ridge (Coogan et al., 2001) and gabbro-norite (1710A4E) from the Talkeetna arc section (Greene et al., 2006) for three temperatures (800°C, 950°C, and 1100°C). Figure 1 shows that amphibole-plagioclase REE partition coefficients decrease systematically with the ionic radius, temperature, and anorthite content of the plagioclase. As temperature increases from 800°C to 1100°C, REE is preferentially partitioned from plagioclase into amphibole, increasing the D_{REE} by approximately four orders of magnitude. As An increases by 24 unit, the amphibole-plagioclase REE partition coefficients increase by close to two orders of magnitude (Fig. 1). The strong temperature dependence arises primarily from the significantly temperature sensitive plagioclase-melt REE partition coefficients (Sun et al., in review).

Given the strong temperature dependence of amphibole-plagioclase REE partitioning, we can develop a REE-in-amphibole-plagioclase thermometer. Rearranging Eq. (1), we have a linear expression for temperature,

$$B_j = T \left(\ln D_j^{\text{amph-plg}} - A \right), \quad (2a)$$

where the coefficient A depends on the major element composition of amphibole and plagioclase; the coefficient B is a function of mineral major element composition and the ionic radii of REE,

$$A = -16.55 + 1.22 X_{\text{Ti}}^{\text{amph}} - 0.47 X_{\text{Mg}}^{\text{amph}} - 1.39 X_{\text{Na}}^{\text{amph}} - 2.34 X_{\text{K}}^{\text{amph}} + 4.77 \left(X_{\text{Ca}}^{\text{plg}} \right)^3, \quad (2b)$$

$$B_j = 2.81 \times 10^4 + 909.85 G(r_j), \quad (2c)$$

$$G(r_j) = E^{\text{plg}} \left(\frac{r_0^{\text{plg}}}{2} (r_0^{\text{plg}} - r_j)^2 - \frac{1}{3} (r_0^{\text{plg}} - r_j)^3 \right) - E^{\text{amph}} \left(\frac{r_0^{\text{amph}}}{2} (r_0^{\text{amph}} - r_j)^2 - \frac{1}{3} (r_0^{\text{amph}} - r_j)^3 \right). \quad (2d)$$

Following steps similar to those for the REE-in-two-pyroxene thermometer in Liang et al. (2013), we can calculate the temperature for a rock with coexisting amphibole and plagioclase. Here we briefly summarized these steps: (1) visually examine REE patterns of amphibole and plagioclase on a spider diagram; (2) examine amphibole-plagioclase REE partition coefficients in a spider diagram and check if REE define a line passing through the origin in a plot of $(\ln D_j - A)$ vs. B_j (D denotes $D_j^{\text{amph-plg}}$ hereafter); (3) calculate coefficients A and B_j using Eqs. (2b–d) and mineral major element composition; and (4) perform linear least square regression analysis of amphibole-plagioclase REE partition coefficients in the plot of $(\ln D_j - A)$ vs. B_j to determine the slope of the line, i.e., the temperature. The uncertainties of the estimated temperature can be obtained through the linear least squares analysis.

Figures 2a–c show an example of the temperature inversion for a troctolite (SOX/1) from the Sondalo gabbroic complex in Central Alps reported in Tribuzio et al. (1999). In this sample, REE are enriched in amphibole and depleted in plagioclase (Fig. 2a). MREE and HREE are strongly incompatible in plagioclase, and their abundances in this particular plagioclase are close to detection limits. In the temperature inversion diagram or inversion diagram for short (Fig. 2b), REE define a straight line through the origin. Eu was excluded in the temperature inversion because it is mainly divalent in plagioclase and is off the trend defined by the other trivalent elements. The slope of this line gives a temperature of $1073 \pm 6^\circ\text{C}$. This temperature is higher than that calculated using the amphibole-plagioclase thermometer (1024°C , edenite richterite thermometer) of Holland and Blundy (1994) and the amphibole-only thermometer of Putirka (2016) (904°C , eq. 5 in Putirka (2016)).

3. Applications

REE data for coexisting amphibole and plagioclase are limited in the literature. Here we compiled 4 oceanic and 8 continental gabbroic rocks with major elements and REE in amphibole and plagioclase reported in the literature. The oceanic gabbros were collected in the Ocean Drilling Program Hole 923A located on the western flank of the Mid-Atlantic Ridge south of the Kane Fracture Zone (Cannat et al., 1995). The hole penetrated ~70 m into a large gabbroic exposure located ~10 km west of the neo-volcanic ridge and collected ~40 m of gabbroic rocks. The major element and REE composition of the amphiboles ($Mg\# = 91 - 98$) and plagioclases ($An = 57 - 74$) were reported in Coogan et al. (2001) and Coogan et al. (2000) respectively. The continental gabbros are from the Sondalo gabbroic complex in Central Alps (Tribuzio et al., 1999). They are thought to be mafic intrusion into mid-crustal levels (0.3–0.7 GPa) based on the amphibolite facies character of the country rocks and the occurrence of sillimanite in xenoliths and country rocks. Amphibole ($Mg\# = 95 - 97$) and plagioclase ($An = 60 - 73$) in these samples have major element composition within calibration range of our REE-in-amphibole-plagioclase thermometer. We calculated the temperatures of the amphibole and plagioclase in the samples using the REE-in-amphibole-plagioclase thermometer, the amphibole-plagioclase thermometer (edenite richterite thermometer) of Holland and Blundy (1994), and the amphibole only thermometer of Putirka (2016).

The oceanic gabbros are troctolites and olivine gabbros that are plagioclase $\pm$ olivine cumulates enclosed in clinopyroxene $\pm$ olivine oikocrysts (Coogan et al., 2000), and amphibole constitutes <1% of the mode. We used a subset of the gabbros containing

both amphibole and plagioclase major element and REE compositional data. Coogan et al. (2001) demonstrated that certain types of amphiboles (i.e. interstitial and bleb amphiboles) in the samples are magmatic since their trace and volatile element composition lack evidence of a seawater component (i.e. high Nb/La and low Cl/F ratios). Of the magmatic amphiboles, we used the interstitial amphiboles since the bleb amphiboles are enclosed in clinopyroxene, hence, are not in contact with plagioclase (Coogan et al., 2001). The interstitial amphiboles are both subgranular and elongate crystals that appear to wet the grain boundaries and triple junctions. Only one major and REE composition is reported for each amphibole. The plagioclases are zoned with a more anorthitic core ($An = 70 - 74$) than the rim ($An = 57 - 68$), and the core tends to have lower REE and higher Y concentration. The HREE are below detection limit for the plagioclase. Temperatures calculated using the major element compositions of amphibole and plagioclase rims and the two major element thermometers (amphibole-plagioclase (Holland and Blundy, 1994) and amphibole-only thermometer (Putirka, 2016)) are within 34°C of each other and ranging from $939 - 1004^{\circ}\text{C}$ with an average of $977 \pm 36^{\circ}\text{C}$. Using the amphibole-plagioclase cores for the amphibole-plagioclase thermometer results in consistently higher temperature ($+40 \pm 30^{\circ}\text{C}$) compared to the amphibole-only thermometer. Hence, for the oceanic gabbros we focus on the amphibole-plagioclase rim pairs.

The continental gabbros are troctolites and norites mainly consisting of euhedral to subhedral plagioclase, olivine, orthopyroxene, and clinopyroxene with 5–20% amphibole by volume (Tribuzio et al., 1999). The amphiboles are mainly found as discontinuous rim around mafic minerals in the troctolites, while they are poikilitic

enclosing other minerals in the norites. Only one major element composition is reported per sample. Two REE compositions from two amphibole grains are reported for some samples. The two REE compositions are both from the inner part of the amphibole and the maximum difference between them is 33%. We used an average of the amphibole REE compositions. The plagioclase is reversely zoned in the troctolites ($An = 61\text{--}64$) and normally zoned norites ($An = 64\text{--}73$). The core of the plagioclase in the troctolite has lower REE concentration compared to the rim, while the core and rim have similar REE concentrations in norite. Unlike the oceanic gabbros, the core and rim composition are not available for all the plagioclase. Hence, the rim composition is used if available, but the core composition is used for most samples. Temperatures calculated using the mineral major element compositions and the two major element thermometers are higher and less variable for the amphibole only thermometer ($904\text{--}956^\circ\text{C}$, $939 \pm 40^\circ\text{C}$) than the amphibole-plagioclase thermometer ($933\text{--}1024^\circ\text{C}$, $993 \pm 81^\circ\text{C}$).

We used the REE-in-amphibole-plagioclase thermometer (Eqs. 2a–d) and major element and REE composition of the amphibole-plagioclase pairs to invert for temperatures. Figures 2 and 3 shows representative examples of the temperature inversions for the continental and oceanic gabbros, respectively. The ranges in temperatures obtained using the REE-in-amphibole-plagioclase thermometer for the oceanic gabbros are $1049\text{--}1112^\circ\text{C}$ with an average of $1090 \pm 44^\circ\text{C}$ and that for the continental gabbros are $1037\text{--}1137^\circ\text{C}$ with an average of $1085 \pm 82^\circ\text{C}$, both of which are significantly higher than those obtained using the two major element-based thermometers. Below we examine the physical meaning of the inverted temperatures in two scenarios.

3.1 Scenario 1: Initial chemical disequilibrium

One possible explanation for the higher temperature recorded in the REE-in-amphibole-plagioclase thermometer is that the amphibole and plagioclase were never in chemical equilibrium such that they record an apparent or fictitious temperature. Situations such a scenario may arise include (1) amphibole and plagioclase crystallized from two different melts at different temperatures and they did not re-equilibrate due to slow diffusion of REE, and (2) amphibole and plagioclase crystallized from the same melt at the same temperature but their REE abundances are not in equilibrium partitioning as a results of disequilibrium crystallization due again to slow diffusion of REE in the minerals.

In order to evaluate the effects of scenario (1) on the inversion, we conduct forward modeling of REE concentration in the amphibole and plagioclase that crystallized from two different melts and temperatures using the major element composition of the minerals in an oceanic gabbro (153-923A-16R1) and the mineral-melt REE partitioning models for amphibole (Shimizu et al., in review) and plagioclase (Sun et al., in review). We then use these synthetic data to invert for a temperature using the amphibole-plagioclase REE thermometer. We assume that the major element thermometer of Putirka (2016) records the crystallization temperature of amphibole, and that plagioclase crystallized at 1150°C (arbitrarily chosen for the purpose of illustration). We recognize the potentially more complex origin of amphiboles from reaction between hydrous melt, plagioclase, and clinopyroxene as argued by Coogan et al. (2001), but here we assume the amphiboles crystallized from a melt for simplicity and for the purpose of

illustration. Without loss of generality, we assume that amphibole and plagioclase crystallized from melts with the same primitive mantle normalized REE abundances of 10. The temperature inversion is done only using La, Sm, Pr, and Y such that we can make a direct comparison with the inversion results of the natural samples in which HREE in plagioclase were below detection limit. The inverted temperature for a forward model using the mineral major element compositions in sample 153-923A-16R1 is $1112 \pm 2^\circ\text{C}$ (Fig. 4a), which is in between the assumed plagioclase and amphibole crystallization temperatures. Further, the elements fit the temperature inversion line well, so this may lead to the misinterpretation that the amphibole-plagioclase REE thermometer records a meaningful temperature. In reality, however, two individual melts that crystallize amphibole and plagioclase may have different REE abundances.

In a second forward model, we assume that plagioclase crystallized from a melt with primitive mantle normalized REE abundances of 10 while amphibole crystallized from melt that has a greater abundance of REE with a more depleted REE pattern. Due to this difference in REE abundances in the two melts, REE are slightly rotated relative to the temperature slope in the inversion diagram (Fig. 4e). In fact, this model result matches the deviation of La and Y relative to the slope observed in some natural samples (Fig. 3). Hence, it is possible that some amphibole-plagioclase pairs in oceanic and continental gabbros crystallized from two different melts, and in such case, REE-in-amphibole-plagioclase thermometer does not record a meaningful temperature. If this were the main reason why the REE-in-amphibole-plagioclase thermometer records a higher temperature than the major element thermometer, this would suggest that most amphiboles and plagioclases in oceanic and continental gabbros crystallized from distinct

melts.

The REE-in-amphibole-plagioclase thermometer may not record a meaningful temperature, however, even if amphibole and plagioclase co-crystallized from a single melt. This is because during their co-crystallization, the amphibole-melt and/or plagioclase-melt may not necessarily be in chemical equilibrium in terms of REE. For example, if plagioclase tends to have higher REE concentration than the equilibrium concentration due to sluggish diffusion of REE, this would lead to a lower amphibole-plagioclase REE partition coefficient than the equilibrium partition coefficient. Inversion for temperature using these amphibole-plagioclase pairs would lead to an overestimation of their equilibrium temperatures because amphibole-plagioclase REE partition coefficients are higher at higher temperatures (Fig. 1). If this is the case, it would have broader implications on topics such as the interpretation of REE concentration and pattern in magmas, which are typically made based on the assumption of chemical equilibrium during magma fractional crystallization. A diffusion model can be used to evaluate this assumption, and this will be pursued in a future work.

3.2 Scenario 2: Initial chemical equilibrium and closure temperature

Crystallization of amphibole and plagioclase from different melts can explain some aspects of the temperature inversions with off-trend elements, but those elements may also be affected by analytical uncertainties. Further, it is difficult to explain inversion results in which most elements follow the slope with no evidence of rotation (Fig. 4a) unless individual melts that crystallized amphibole and plagioclase had very similar REE patterns (i.e. forward model 1 in previous section 3.1). An alternative

explanation for the difference in temperatures recorded by the different thermometers is that the REE-in-amphibole-plagioclase thermometer records a higher closure temperature that is closer to the crystallization temperature than the major element thermometer due to the slower diffusion of REE compared to major element. In order to evaluate if this is plausible, we use the expression of closure temperature (T_c) of Dodson (1973);

$$\frac{E}{RT_c} = \ln \left(\frac{ART_c^2 D_0}{Ea^2 \dot{s}} \right) \quad (4)$$

where E and D_0 are the activation energy and the pre-exponential factor for diffusion in a mineral; A is a geometric constant; a is an effective grain size; $\dot{s}$ is the cooling rate at closure temperature; and R is the gas constant. Although diffusivity of REE in amphibole is unknown, closure temperature of REE in plagioclase may closely approximate those in amphibole-plagioclase pair according to the minor's rule (Liang, 2014) since REE is strongly and preferentially partitioned into amphibole relative to plagioclase. However, the modal abundance of the minerals are also important in the minor's rule (Liang, 2014), so the closure temperatures for REE in plagioclase may be different from those of amphibole-plagioclase pair for the oceanic gabbros that have a small amount of amphibole relative to plagioclase. Nonetheless, we calculate the closure temperature of REE in plagioclase using the E and D_0 for La in plagioclase (labradorite, $An = 67$) from Cherniak (2003). We assume an A value for a sphere (55), effective grain size of 500 μm , and a range of cooling rate from 10 to 10^5 $^{\circ}\text{C}/\text{Myr}$. Faak et al. (2015) estimated cooling rates for the oceanic gabbros using the Mg-in-plagioclase geospeedometer. Their reported values range from 10^2 to 10^5 $^{\circ}\text{C}/\text{Myr}$, which leads to an estimated range in closure temperature of REE in plagioclase in oceanic gabbros from 980 $^{\circ}\text{C}$ to 1198 $^{\circ}\text{C}$ (Fig. 5). This

range of estimated closure temperature of REE in plagioclase in the oceanic gabbros brackets those recorded by the REE-in-amphibole-plagioclase thermometer in natural oceanic gabbros (1049 to 1112°C), which may suggest that the REE-based thermometer records the T_c of REE in plagioclase. For the continental gabbros, cooling rate of mafic material injected into the mid-crust is not well constrained, but the average temperature recorded by the REE-in-amphibole-plagioclase thermometer ($1085 \pm 82^\circ\text{C}$) suggests a cooling rate of approximately 10^2 to 10^5 °C/Myr assuming that they have also reached closure temperature. Although this estimate is preliminary and its fundamental aspects are still in question as discussed in section 3.1, a more refined estimate would provide useful constraints to better understand magma emplacement processes and development of large magma chambers in the continental crust (e.g. Annen, 2011).

4. Summary and future work

We developed a REE-in-amphibole-plagioclase thermometer for amphibole- and plagioclase-bearing rocks, and applied it to oceanic and continental gabbroic rocks from the Mid-Atlantic Ridge (Coogan et al., 2000; Coogan et al., 2001) and Sondalo gabbroic complex in Northern Italy (Tribuzio et al., 1999). The temperatures of the gabbroic rocks derived from the REE-in-amphibole-plagioclase thermometer are significantly higher than those calculated using major element-based thermometers (Holland and Blundy, 1994; Putirka, 2016). Initial conditions of amphibole and plagioclase crystallization are important for understanding the physical meaning of the temperature recorded in the REE-in-amphibole-plagioclase thermometer. Two scenarios are discussed and it is difficult to determine whether or not the REE-in-amphibole-plagioclase thermometer

records meaningful temperatures from the results of the present study. In an initial disequilibrium scenario, temperature inversions with off-trend elements may suggest crystallization of amphibole and plagioclase from different melts at different temperatures, in which case the recorded temperatures are not physically meaningful. The off-trend elements, however, may also be affected by the analytical uncertainty. Also REE-in-amphibole-plagioclase thermometer may not record a meaningful temperature due to sluggish REE diffusion during amphibole and plagioclase crystallization from a melt. On the other hand in an initial equilibrium scenario, the REE-in-amphibole-plagioclase thermometer may record the closure temperature of REE in the amphibole-plagioclase pairs since the recorded temperatures in oceanic gabbros agree well with the expected closure temperature of REE in plagioclase in an oceanic gabbro. However, diffusion data in amphibole is not available, and the closure temperature of amphibole-plagioclase pair cannot be fully evaluated without this data. Furthermore, the plagioclase-melt REE partitioning model is not calibrated to low T due to lack of experimental partitioning data. Therefore, future work will involve (1) producing high quality REE partitioning data between amphibole and plagioclase in gabbroic rocks through detailed and high quality analysis, (2) evaluating the kinetic effects on the temperature recorded in the REE-in-amphibole-plagioclase thermometer through diffusion modeling of amphibole and plagioclase crystallization, (3) fully evaluating the closure temperatures of REE in amphibole-plagioclase pair by experimentally measuring diffusion rates of REE in amphibole, and (4) calibrating the plagioclase-melt REE partitioning model to low T by conducting low T REE partitioning experiments between plagioclase and melt. This would provide a better understanding of the meaning of temperatures recorded by the

REE-in-amphibole-plagioclase thermometer, which in turn would provide a constraint on the petrogenesis of amphiboles in gabbroic rocks and potentially provide important constraints for magma emplacement processes in the crust. Finally, understanding the kinetic effects during amphibole and plagioclase crystallization would have broader implications on problems such as the effect of disequilibrium crystallization on the REE abundances of magmas.

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Figure captions

Figure 4-1. Onuma diagrams showing the temperature, pressure and composition dependent amphibole-plagioclase REE partition coefficients. The partition coefficients were calculated using Eq. (2) for three temperatures (1100°C, 950°C, 800°C) and two field samples with different mineral compositions. Red dashed curves represent the calculated partition coefficients for a troctolite (153-923A-8R1) from the Mid-Atlantic Ridge (Coogan et al., 2001) and blue curves show the calculated partition coefficients for a gabbro-norite (1710A4E) from the Talkeetna arc section (Greene et al., 2006).

Figure 4-2. Inversion of temperatures from REE abundances in amphibole and plagioclase for (a–c) troctolite (SOX/1) and (d–f) norite (SO5/11) from the Sondalo gabbroic complex in Central Alps from Tribuzio et al. (1999). (a, d) shows the primitive mantle normalized REE abundance in amphibole (filled black circles) and plagioclase (open squares). Symbols with light blue colors highlight the low quality data for REE and Eu that were excluded in the temperature inversion. The dotted line is a representative detection limit of REE in the LA-ICP-MS at the mass spectrometer analytical facility at Brown University. Primitive mantle compositions are from McDonough and Sun (1995). (b, e) shows inversions of the temperature through linear least squares regression analysis. T_{REE} is the temperature calculated using the REE-in-amphibole-plagioclase thermometer. T_{HB94} is the temperature calculated using the amphibole-plagioclase thermometer of Holland and Blundy (1994). T_{P16} is the temperature calculated using the amphibole-only thermometer of Putirka (2016). (c, f) shows the observed amphibole-plagioclase REE partition coefficients, and the calculated partition coefficients using T_{REE} shown in (b, e).

Figure 4-3. Inversion of temperatures from REE abundances in amphibole and plagioclase for troctolites collected in the Ocean Drilling Program Hole 923A located on the western flank of the Mid-Atlantic Ridge south of the Kane Fracture Zone (Coogan et al., 2000; Coogan et al., 2001). Refer to caption for Fig. 2 for detailed description of the figure.

Figure 4-4. Inversion of temperatures from REE abundances in amphibole and plagioclase for forward models 1 (a–c) and 2 (d–f). Both models were conducted using the major element composition of the minerals in an oceanic gabbro (153-923A-16R1) (Coogan et al., 2000; Coogan et al., 2001). The temperature inversion is done only using La, Sm, Pr, and Y to make a direct comparison with the inversion results of the oceanic gabbro samples in which HREE were below detection limit. Refer to section 3.1 for the details of the model and caption for Fig. 2 for detailed description of the figure.

Figure 4-5. Closure temperature of La in plagioclase for a range of cooling rates calculated using the expression of closure temperature (T_c) of Dodson (1973). We used the E and D_0 for La in labradorite ($An = 67$) from Cherniak (2003). We assume an A value for a sphere (55) and effective grain size of 500 μm .

Figures

Figure 4-1.

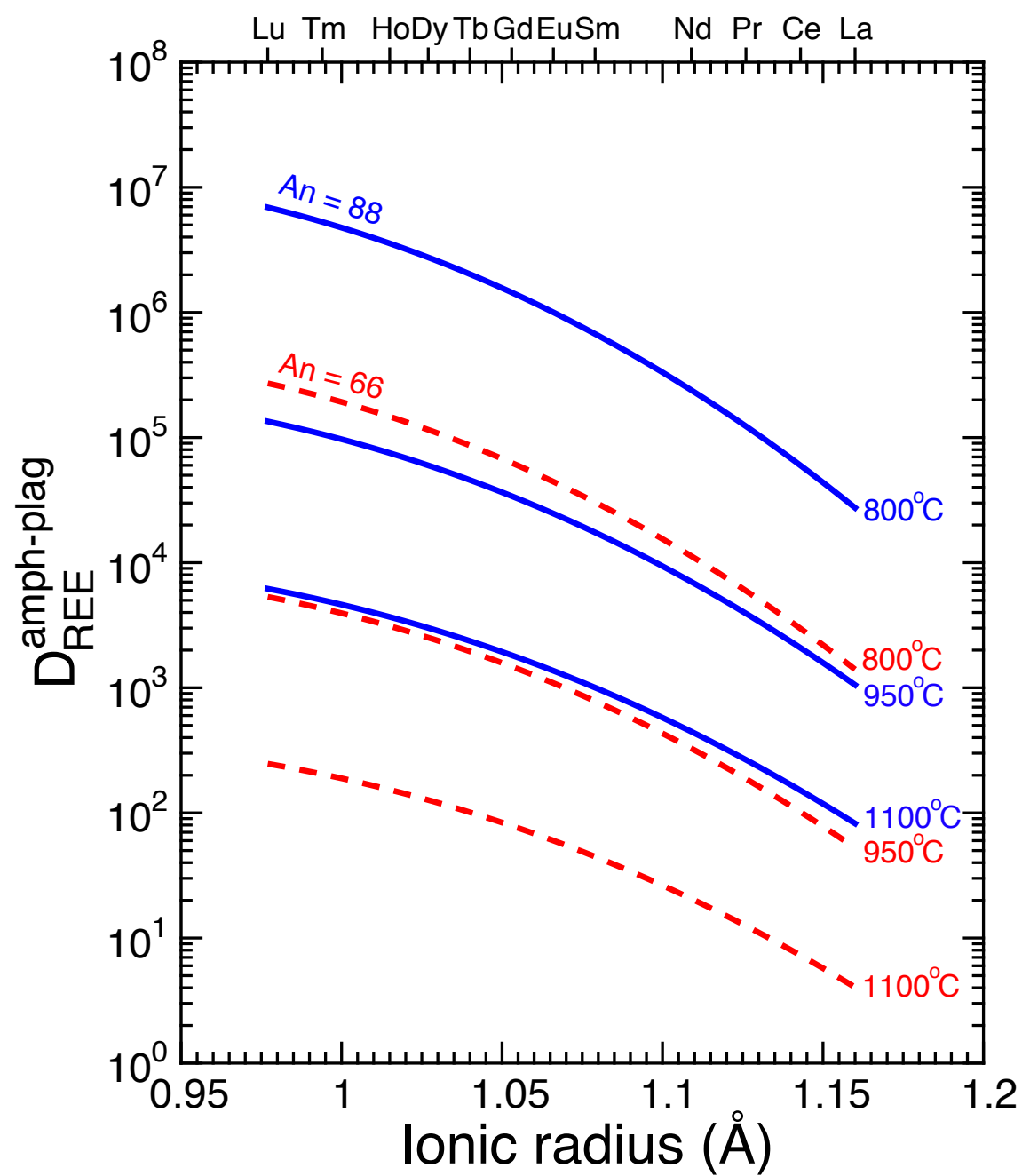


Figure 4-2.

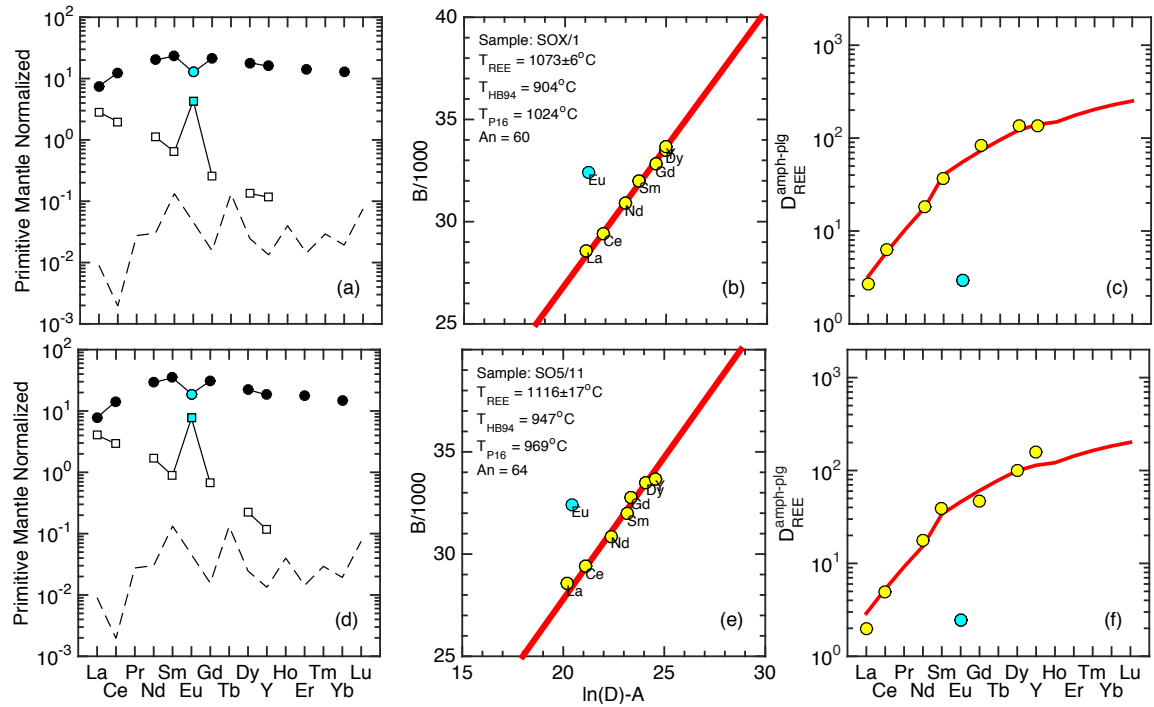


Figure 4-3.

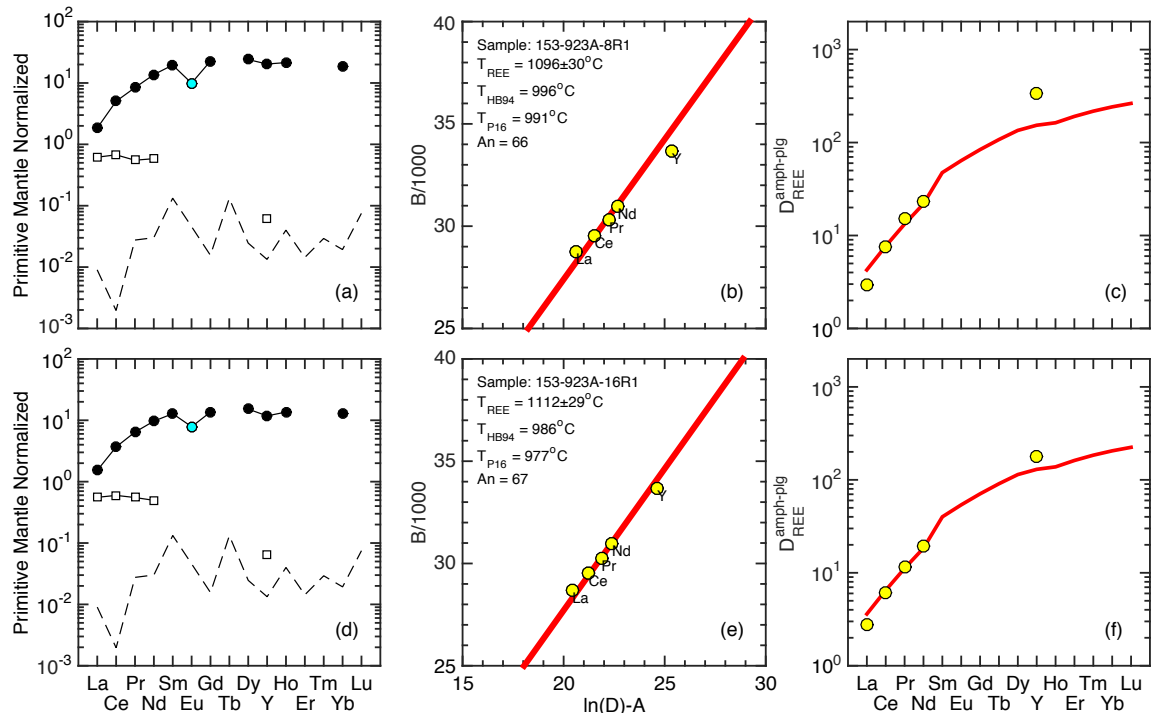


Figure 4-4.

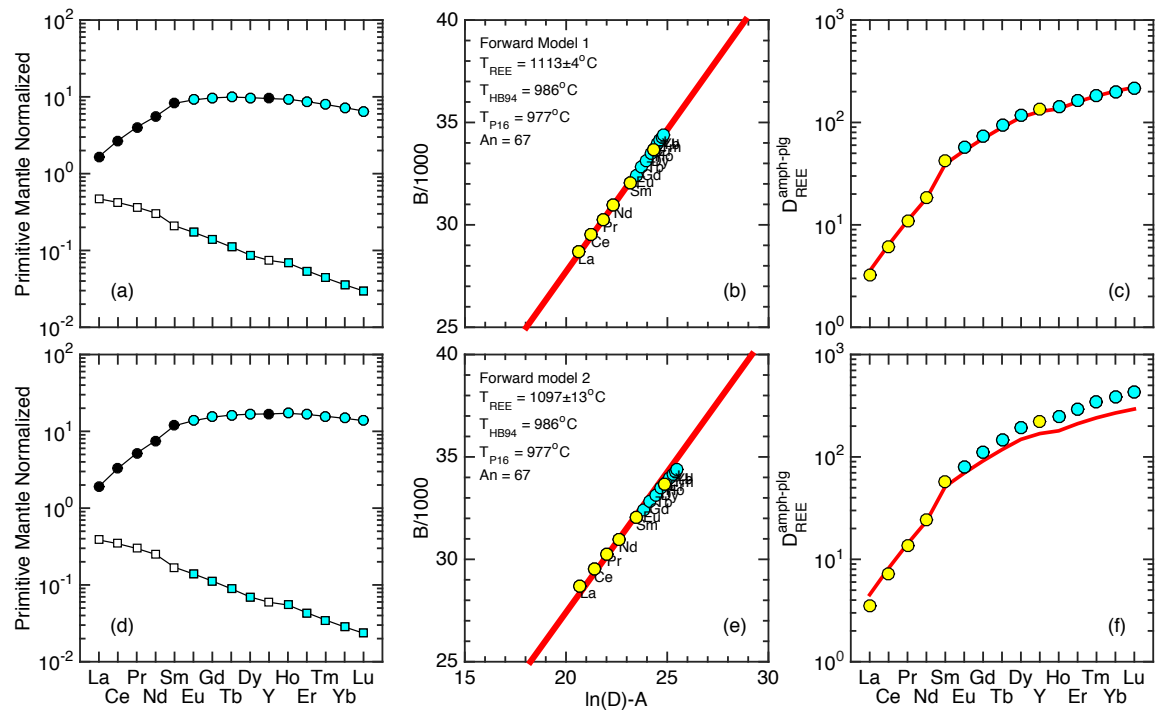
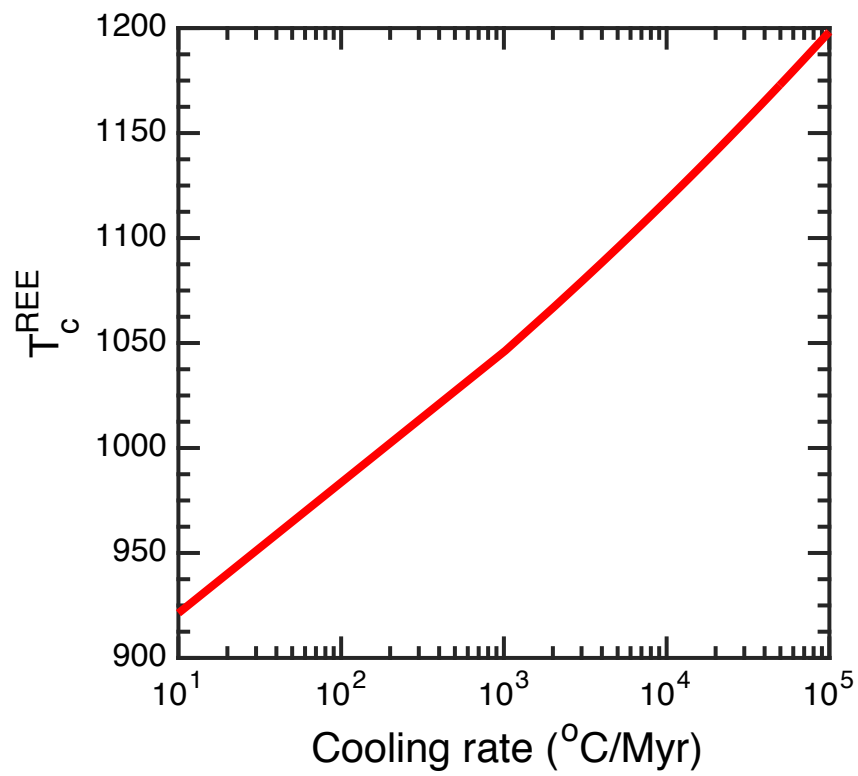


Figure 4-5.



Supplementary material

Parameterized lattice strain models for REE partitioning between amphibole/plagioclase and melt

The following equations summarize the parameters used in the lattice strain models (Eq. 2) for REE partitioning between amphibole/plagioclase and melts:

1. Amphibole model (Shimizu et al., in review)

$$\ln D_0^{\text{amph}} = -3.19(\pm 1.42) + \frac{5.82(\pm 1.06) \times 10^4}{RT} + 1.20(\pm 0.26) X_{\text{Ti}}^{\text{amph}} - 0.45(\pm 0.07) X_{\text{Mg}}^{\text{amph}} - 1.17(\pm 0.35) X_{\text{Na}}^{\text{amph}} - 2.09(\pm 0.39) X_{\text{K}}^{\text{amph}}, \quad (\text{S1a})$$

$$r_0^{\text{amph}} (\text{\AA}) = 1.044(\pm 0.004) - 0.045(\pm 0.018) X_{\text{Fm}}^{\text{amph}}, \quad (\text{S1b})$$

$$E^{\text{amph}} (\text{GPa}) = 331(\pm 24), \quad (\text{S1c})$$

2. Plagioclase model (Sun et al., in review)

$$\ln D_0^{\text{plg}} = 14.03(\pm 1.89) - \frac{17.52(\pm 2.27) \times 10^4}{RT} - 4.77(\pm 0.40) (X_{\text{Ca}}^{\text{plg}})^3, \quad (\text{S2a})$$

$$r_0^{\text{plg}} (\text{\AA}) = 1.235(\pm 0.074), \quad (\text{S2b})$$

$$E^{\text{plg}} (\text{GPa}) = 132(\pm 62), \quad (\text{S2c})$$

In these equations, numbers in parentheses are 2σ uncertainties estimated directly from the simultaneous inversion; D_0 is the partition coefficient for strain-free substitution; r_0 is the ionic radius of the “ideal” cation for the strain-free lattice site; E is the apparent Young’s modulus for the lattice site; P is pressure in GPa; T is temperature in K ; and R is the gas constant ($= 8.3145 \text{ J/mol}^{-1} \text{ K}^{-1}$). In Eq. (1a), $X_{\text{Ti}}^{\text{amph}}$, $X_{\text{Mg}}^{\text{amph}}$, $X_{\text{Na}}^{\text{amph}}$, and $X_{\text{K}}^{\text{amph}}$ are

cation contents in amphibole per-23 oxygen and $X_{\text{Fm}}^{\text{amph}}$ is the $\text{Fe}^{2+} + \text{Mn}^{2+} + \text{Mg}$ content in the M4 site assuming all iron is present as ferrous iron. In Eq. (S2a), $X_{\text{Ca}}^{\text{plg}}$ is the cation content of Ca in plagioclase per 8-oxygen.

Conclusion

In chapter 1, we analyzed 203 mid-ocean ridge basalts (MORB) glass samples from the Northern East Pacific Rise off-axis seamounts, Quebrada-Discovery-GoFar transform fault system, and Macquarie Island for major, trace, volatile (C, H, F, Cl, S) elements, and a subset of samples for Sr-Nd-Pb isotopic composition. From our data and geochemical modeling of a two-component mantle melting mixing process, we concluded that (1) at the time of melt generation, the source that generated the EMORB was essentially peridotitic, (2) the majority of the MORB mantle (~80%) is ultra-depleted (D-DMM) in volatile and refractory incompatible elements while the rest is enriched (E-DMM) and (3) incremental fractional melting of the E-DMM controls most of the chemical variation in MORB; namely we argue that there is no DMM source and that NMORB is the result of a two component mantle melting mixing process. Based on our data, modeling, and after filtering the volatile data for secondary processes (volatile degassing, sulfide saturation, assimilation of seawater-derived component, and fractional crystallization), we estimated of the volatile content of D-DMM ($\text{CO}_2 = 22$ ppm, $\text{H}_2\text{O} = 59$ ppm, $\text{F} = 8$ ppm, $\text{Cl} = 0.4$ ppm, and $\text{S} = 100$ ppm), E-DMM ($\text{CO}_2 = 990$ ppm, $\text{H}_2\text{O} = 660$ ppm, $\text{F} = 31$ ppm, $\text{Cl} = 22$ ppm, and $\text{S} = 165$ ppm), and the Pacific upper mantle (78% D-DMM and 22% E-DMM) ($\text{CO}_2 = 235$ ppm, $\text{H}_2\text{O} = 191$ ppm, $\text{F} = 13$ ppm, $\text{Cl} = 5$ ppm, and $\text{S} = 114$ ppm). Our model suggests that a fraction (~65 to 80%) of the low degree EMORB melts (~1.3%) may escape melt aggregation by freezing at the base of the oceanic lithosphere significantly enriching it in volatile and trace elements to generate the E-DMM. This process of EDMM generation is consistent with the constant CO_2/Cl ratio of $\sim 57 \pm 8$ in D-DMM and E-DMM, and decreasing volatile and refractory ITE

abundances in E-DMM normalized to D-DMM as a function of increasing peridotite-basaltic melt bulk partition coefficient suggesting the two sources can be related by a single melting event. The volatile element budget of the Pacific upper mantle presented in this paper provides a fundamental constraint to establish the origin and evolution of the volatile element budget in the Earth.

In chapter 2, EMORB from QDG transform fault characterized by high H_2O/Ce , K/Nb , Rb/Th ratios and lower Nb/Th , Ce/Pb , Ba/Th are shown to define a different magma component from other EMORB from NEPR seamounts and MQ Island. QDG transform fault EMORB might derive from melting of a metasomatized oceanic lithosphere most likely triggered by formation of intra-transform spreading ridges due to clockwise rotation in Pacific-Nazca plate relative motion. Our geochemical model suggests that re-melting of hydrous cumulates crystallized from low degree melts of the EDMM in the lithosphere can reproduce the composition of EMORB from the QDG transform fault. Geological evidence for metasomatism of the oceanic lithosphere by the EDMM include magmatic amphiboles in peridotites in the St. Paul's Rocks that show evidence of derivation from the EDMM as well as lavas recently erupted (<9.2 Ma) near the Japan Trench that show geochemical signature of re-melted metasomatized oceanic lithosphere. The previously unrecognized effect of re-melting of metasomatized oceanic lithosphere on the chemical composition of MORB suggests that the common assumption for the purely asthenospheric origin of MORB could lead to erroneous estimates of the asthenospheric mantle composition. We also show that amphiboles in oceanic peridotites and off-craton continental xenoliths have average isotopic composition that limits the average age of the metasomatism to within ~ 200 Myrs assuming the amphiboles were

produced from metasomatism by EDMM derived melts. This could suggest a hydration induced weakening of the continental lithospheric mantle by metasomatism, and preferential delamination of the metasomatized continental lithospheric mantle within ~200 Myrs of the metasomatic event.

Chapter 3 presents parameterized lattice strain models for REE partitioning between amphibole and silicate melt developed using published experimental REE and Y partitioning data between amphibole and silicate melt, the lattice strain model and non-linear least squares regression method. We developed a mineral composition model in which D_0 depends on temperature and amphibole composition (Ti, Mg, Na, K), and also a melt composition model in which D_0 depends on the melt composition (Si, Mg, Ca). We show that the two models are connected through amphibole-melt phase equilibria. To further demonstrate this, we developed a hybrid model for amphibole-melt REE partitioning using a combination of amphibole and melt compositions. An application of our models to amphiboles in mantle xenoliths shows that observed major element compositional variations in amphibole alone can give rise to an order of magnitude variations in amphibole-melt REE partition coefficients. Also our models and experimental data simulating fractional crystallization of arc magmas suggests that (1) REE partition coefficients between amphibole and melt can vary by an order of magnitude during arc magma crystallization due to variation in the temperature and composition of the amphibole and melt, and that (2) amphibole fractional crystallization plays a key role in depleting the MREE relative to HREE and LREE in arc magmas.

Chapter 4 presents a REE-in-amphibole-plagioclase thermometer based on the temperature-dependent REE partitioning between amphibole and plagioclase, and is

calibrated against experimentally determined amphibole-melt and plagioclase-melt partition coefficients. Temperatures in oceanic and continental gabbroic rocks derived from the REE-in-amphibole-plagioclase thermometer are significantly higher than those derived from major element-based thermometers. We use numerical experiments to show that the higher temperatures recorded in the REE-based thermometer may be apparent temperatures resulting from amphibole and plagioclase crystallization from different melts at different temperatures (i.e. initial disequilibrium scenario). However, we also show that higher temperatures recorded in the REE-based thermometer may be closure temperatures of REE in amphibole-plagioclase pairs that are higher than those for major elements due to the slower diffusion of REE relative to major elements (i.e. initial equilibrium scenario). Assuming initial equilibrium, we estimate the cooling rate of continental gabbroic rocks gabbros to be 10^2 to 10^5 °C/Myr. Finally, we propose future works to better understand the physical meaning of the temperatures recorded in the REE-in-amphibole-plagioclase thermometer.