

Experimental and Field Constrains on the Physicochemical Evolution of the Lunar and Terrestrial Mantles

by

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- Dygart**, N., Liang, Y., Hess, P., 2013. The importance of melt TiO₂ in affecting high field strength element partitioning between Fe-Ti oxides and lunar picritic glass melts. *Geochimica et Cosmochimica Acta*, doi:10.1016/j.gca.2012.12.005.
- Wang, C.G., Liang, Y., Xu, W.L., **Dygart**, N., 2013. Interaction between pyroxenite-derived melt and peridotite: laboratory dissolution experiments with applications to mineral compositional variations in mantle xenoliths from the North China Craton. *Contributions to Mineralogy and Petrology*, doi:10.1007/s00410-013-0938-6.

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Introduction

Indistinguishable chromium, titanium, tungsten, and oxygen isotopes suggest the Earth and Moon have a compelling compositional similarity (e.g., Lugmair and Shukolyukov, 1998; Weichert et al., 2001; Touboul et al., 2007; Zhang et al., 2012). The moon cooled relatively quickly never developing plate tectonics (e.g., Carlson and Lugmair, 1988; Alibert et al., 1994; Wieczorek et al., 2006; Wieczorek et al., 2012) and represents a proto-planet that can teach us about the early evolution of terrestrial bodies including earth (e.g., Hostetler and Drake, 1980; Solomatov, 2007). Similarly, study of earth's chemical properties and the physical processes that govern its geologic evolution inform us about the moon, particularly regions that may never be sampled such as its mantle (e.g., Beck et al., 2006; Liang and Hess, 2006).

The moon is thought to have formed in the aftermath of a giant impact between earth and another body that left a deep lunar magma ocean (e.g., Wood et al., 1970; 1975; Warren, 1985). The lunar magma ocean crystallized from the bottom up, leading to gravitationally unstable density stratification (e.g., Snyder et al., 1992; Shearer et al., 2006). Was that instability relieved by solid state flow of dense cumulates near the surface toward the core, a process known as cumulate mantle overturn (e.g., Ringwood and Kesson, 1976; Hess and Parmentier, 1995)? Under what conditions would cumulate overturn occur, and at what scale? Is there geochemical and petrologic evidence for cumulate mantle overturn in lunar basalts?

Lunar and terrestrial basalts share a fascinating property; neither basalt is in chemical equilibrium with mantle rock at low pressures (e.g., Stolper, 1980; Elthon and Scarfe, 1984; Braun and Kelemen, 2002; Grove and Krawczynski, 2009, and references

therein). How can melts percolate through dozens to hundreds of kilometers of mantle and remain chemically insulated? Theory behind melt transport mechanisms is well developed (e.g., Kelemen et al., 1995; Kelemen et al., 1997; Kohlstedt and Holtzman, 2009) but there are surprisingly few field studies that corroborate the theories we often assume to be true. To what extent do melts react with ambient mantle beneath spreading centers on earth and beneath the moon's crust? Does melt-rock reaction affect global geochemical cycling? What can geothermometry teach us about the fundamental differences among the environments where mantle rocks are recovered, and the thermal state of the mantle where melt-rock reaction occurs?

This thesis addresses these questions with a combination of experiments, field studies, and numerical models. The five chapters presented here focus on the geochemistry of the terrestrial and lunar mantles, and the rheology of the lunar mantle. Specifically, they address (1) trace element fractionation during lunar magma ocean crystallization, cumulate overturn, mantle melting, and melt-rock reaction, (2) the effect of ilmenite on lunar cumulate mantle overturn and lunar mantle convection patterns, (3) relationships among mantle melts, dunite channels, host peridotites, and the implications for global geochemical cycles, (4) the unique thermal histories of ophiolitic and abyssal peridotites and what those histories teach us about the dynamics of cooling in distinct tectonic environments in the upper mantle.

The first two chapters are experimental studies that investigate trace element partitioning between Fe-rich lunar basalts, Fe-Ti oxides, and Fe-rich clinopyroxene. In Chapter 1, we explore high field strength element (HFSE), transition metal, and rare earth element (REE) partitioning between ilmenite (FeTiO_3) and armalcolite (FeTi_2O_5) and

high-Ti basaltic melts. Partition coefficients measured by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) are reported for a series of piston-cylinder experiments with a wide range of melt TiO_2 abundances (2.6-28 wt%). A striking correlation between HFSE partition coefficients and melt TiO_2 abundance is noted, and a theoretical framework is developed to interpret the results based on melt structure theory. Partitioning models are parameterized using the measured partition coefficients and applied to lunar magma ocean crystallization (e.g., Snyder et al., 1992) and lunar mantle melting models. The results show that ilmenite and armalcolite fractionate HFSE differently during crystallization and mantle melting. High field strength element compositions of lunar basalts are successfully modeled by both partial melting of an Fe-Ti oxide bearing lunar mantle (e.g., Ringwood and Kesson, 1976; Hess and Parmentier, 1995), and by assimilation of Fe-Ti oxides (i.e., melt-rock reaction) during ascent of lunar basalts to the surface of the moon (e.g., Hubbard and Minear, 1975; Wagner and Grove, 1997). Because the stability of the ilmenite and armalcolite is pressure sensitive (Thacker et al., 2009), distinguishing one phase or the other in the lunar mantle source could provide insight into the dynamics of lunar cumulate mantle overturn. Unfortunately there is not enough high-quality lunar basalt data currently available to make such a distinction.

In Chapter 2 (Dygert et al., 2014), we explore trace element partitioning between Fe-rich clinopyroxene and basaltic melts. This pioneering research focuses on compositions not previously investigated (clinopyroxene Mg# 52-5). The seemingly exotic composition space is actually quite common to planetary bodies throughout the solar system, e.g., Earth (layered intrusions), Mars (nakhlites and basaltic shergottites),

and the angrite parent body (e.g., Wager and Brown, 1967; Papike et al., 1998; Treiman, 2005). Partition coefficients for REE, HFSE, transition metals, and alkali earth elements are measured in piston cylinder experiments analyzed by LA-ICP-MS. The experiments show that partition coefficients for low-Mg systems are quite different than more magnesian systems and the currently available partitioning models fail to predict the experimental results. Applying the method of nonlinear least-squares inversion to the experimental data, we develop lattice strain-based REE and HFSE partitioning models (e.g., Blundy and Wood, 1994, Sun and Liang, 2012) for Fe-rich pyroxene. With the new partitioning models, we investigate lunar magma ocean crystallization (e.g., Snyder et al., 1992), finding that Fe-rich pyroxene fractionate REE less strongly than previously assumed. This result suggests that REE-rich lunar cumulates had to be mixed into the lunar mantle basalt source regions by cumulate overturn. Assimilation of REE-rich cumulates by migrating lunar basalts would lead to relatively flat REE patterns which are not observed in the lunar sample suite.

Chapter 3 (Dygert, Hirth, and Liang, in prep.) is an experimental study of the rheological properties of ilmenite in dislocation creep. A normative ilmenite component is widely observed in lunar basalts (e.g., Papike et al., 1998) suggesting ilmenite is abundant in at least some regions of the lunar mantle. Because the viscosity of ilmenite was previously unknown, efforts to model lunar mantle convection have generally relied on olivine viscosity (e.g., Elkins-Tanton et al., 2002; de Vries et al., 2010), or explored the consequences of different lunar mantle viscosities on mantle convection patterns (e.g., Parmentier et al., 2002; Zhang et al., 2013).

Using axial compression experiments conducted in molten salt assemblies in the Griggs apparatus, we develop a flow law for ilmenite in dislocation creep. Extrapolating the flow law to mantle stresses and temperatures suggests that ilmenite is more than four orders of magnitude weaker than olivine. Preliminary ilmenite-olivine aggregate experiments conducted in shear suggest that the addition of relatively dilute fractions of ilmenite (10%) to olivine can dramatically weaken the viscosity of the aggregate, and that simple mixing models (e.g., Tullis et al., 1991) can be successfully used to predict the viscosity of ilmenite-olivine aggregates. Implications for the dynamic evolution of the lunar mantle are significant. For example, overturned ilmenite-bearing cumulates may be highly stable at the lunar core-mantle boundary (Zhang et al., 2013), and downwelling of large mantle plumes during cumulate overturn may be possible (Parmentier et al., 2002).

Chapter 4 (Dygart and Liang, in prep.) investigates trace element variations across a dunite-harzburgite-lherzolite-plagioclase lherzolite (DHL-PL) sequence at the Trinity ophiolite. Minerals within the dunite, harzburgite, and lherzolite are in equilibrium with a mid ocean ridge basalt-like melt while minerals in the plagioclase lherzolite are in equilibrium with a more ($\sim 30\times$ chondrite) trace element enriched melt. Incompatible trace elements change in unison at the lherzolite-plagioclase lherzolite boundary 9m from the dunite-harzburgite contact. A gradient in Ni is also present but offset several meters toward the dunite (Morgan et al., 2008). The compositional offset suggests chromatographic fractionation of Ni occurred as melt flowed from the dunite into and reacted with plagioclase lherzolite host rock (e.g., Navon and Stolper, 1987; Morgan and Liang, 2005), while the plagioclase lherzolite formed earlier by infiltration of a harzburgitic residue of partial melting (e.g., Nicolas and Dupuy, 1984; Dick, 1989, Saper

and Liang, 2014). Opposite the modern paradigm (e.g., Kelemen et al., 1995; 1997), at this outcrop, dunite is a melt source (rather than a sink) affecting the chemistry of the surrounding rock. Possible explanations relate to corner flow, compaction, or flux of buoyant melt beneath an impermeable boundary. If impregnated peridotites are a common product of dunite-fluxed melt, there may be significantly more enriched lithospheric mantle being subducted than previously estimated.

Chapter 5 (Dygert and Liang, in review) explores the thermal history of ophiolites and abyssal peridotites. We apply the recently developed REE-in-two-pyroxene thermometer of Liang et al., 2013, to 142 orthopyroxene-clinopyroxene pairs. New trace element data and REE temperatures (T_{REE}) are reported for the Josephine ophiolite and the Mariana trench backarc. T_{REE} are also determined for the Trinity ophiolite (Chapter 4) and twelve additional localities from the literature. The closure temperature equation (Dodson, 1973; Ganguly and Tirone, 1999) is used to define cooling curves for the two-pyroxene major element thermometer of Brey and Köhler (1990) and the REE-in-two-pyroxene thermometer (Liang et al., 2013) which overlap the measured closure temperatures and indicate relative cooling rates for each locality and tectonic affinity group. Ophiolites with supra-subduction zone affinity (and many with mid-ocean ridge affinity) appear to cool more slowly than abyssal peridotites. Mid-ocean ridge ophiolites from Corsica and Oman appear to cool as quickly as abyssal peridotites from slow and ultra-slow spreading centers, suggesting the cooling rates of peridotites from mid-ocean ridges are independent of spreading rate and instead controlled by hydrothermal circulation or unroofing.

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CHAPTER 1

The Importance of Melt TiO_2 in Affecting Major and Trace Element Partitioning between Fe-Ti Oxides and Lunar Picritic Glass Melts

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Abstract

Lunar mare basalts and picritic glasses have TiO_2 abundances ranging from less than 1 wt% to over 16%. Any high-Ti mare basalt or picritic glass petrogenetic model must include Fe-Ti oxides in the mantle source or invoke Fe-Ti oxide assimilation during magma ascent to the lunar surface. We conducted partitioning experiments to investigate high field strength element (HFSE), rare earth element (REE), and transition metal distribution between Fe-Ti oxides and lunar picritic glass melts over a range of melt compositions. Our results suggest that ilmenite-melt and armalcolite-melt HFSE, Cr, and V partition coefficients (D_{HFSE} , D_{Cr} , D_{V}) are strongly dependent on melt TiO_2 content, whereas ilmenite-melt REE partition coefficients appear to be insensitive to melt composition. As TiO_2 increases in picritic glass melts, HFSE, Cr, and V activities in melt also increase and Fe-Ti oxide-melt D_{HFSE} , D_{Cr} and D_{V} decrease. The effect of Ti on partitioning behavior can be attributed to the formation of Fe-O-Ti melt species in high-Ti melts. Ilmenite D_{HFSE} range from compatible in oxides in equilibrium with low-Ti melts to incompatible in oxides in equilibrium with depolymerized high-Ti picritic glass melts. D_{HFSE} are inversely correlated with TiO_2 abundance in the melt and become nearly constant for melts with more than 6.8% TiO_2 . We present simple partitioning models that utilize the solubility of ilmenite and armalcolite in melt to effectively predict HFSE partition coefficients across a wide range of picritic glass melt compositions. The HFSE budget of ilmenite cumulates that crystallize from the lunar magma ocean strongly depends on the composition of the magma ocean. Low-Ti and high-Ti lunar basalts can be produced by an ilmenite or armalcolite bearing hybridized mantle source, or by assimilation of late-stage magma ocean cumulates. The dependence of D_{HFSE} and D_{Cr} on

melt TiO_2 is consistent with the formation of lunar Type 1 armalcolite from high TiO_2 picritic glass melt, however, lunar Type 2 and 3 armalcolite have a more complicated (yet undetermined) history of formation.

1. Introduction

Two types of basalts are observed on the moon, picritic glasses which have relatively high MgO , and mare basalts which are more volumetrically abundant and appear to be more fractionated than the picritic glasses (e.g., Papike et al., 1998; Shearer et al., 2006). Perhaps the most striking feature of the mare basalts and picritic glasses is their variable TiO_2 abundance, which ranges from very low values (0.2 wt%) to more than 16% (Fig. 1, Delano, 1986; Papike et al., 1998). Mare basalts and picritic glasses are often classified by their TiO_2 content into three groups: very low-Ti (VLT, $< 1\%$ TiO_2), low-Ti (LT, $< 1\sim 5\%$ TiO_2), and high-Ti (HT, $> 8\%$ TiO_2) (e.g., Binder, 1982; Neal and Taylor, 1992). In many cases, trace element abundances (e.g., REE and HFSE) and isotopic ratios (e.g., Nd, Hf, O, Fe) are correlated with TiO_2 content (e.g., Beard et al., 1998; Hagerty et al., 2006; Shearer et al., 2006; Brandon et al., 2009; Hallis et al., 2010; Liu et al., 2010), suggesting distinct mantle source regions. Picritic glass melts are multiply saturated with olivine and orthopyroxene under lunar mantle conditions (e.g., Grove and Krawczynski, 2009 and references therein). Petrogenetic models of the picritic glasses account for their elevated Ti abundances by invoking a hybrid cumulate mantle produced by the addition of late-stage ilmenite-bearing mafic cumulates of the lunar magma ocean to the early harzburgite cumulates during cumulate mantle overturn (Ringwood and Kesson, 1976; Hess and Parmentier, 1995) or by the assimilation of Fe-Ti

oxides in picritic glass melts as they migrated to the lunar surface (e.g., Hubbard and Minear, 1975; Wagner and Grove, 1997; Elkins Tanton et al., 2002; Liang and Hess, 2006).

It is well known that Fe-Mg partitioning between olivine and basaltic melts is strongly correlated with TiO_2 abundance in melt (Longhi et al., 1978; Delano, 1980; Jones, 1988; Longhi, 1992; Wagner and Grove, 1997; Xirouchakis et al., 2001). As TiO_2 abundance in melt increases, olivine-melt Fe-Mg K_D $[(\text{Fe}/\text{Mg})_{\text{olivine}}/(\text{Fe}/\text{Mg})_{\text{melt}}$, in moles] decreases. This phenomenon has been attributed to a combination of effects related to melt structure and composition. Longhi et al. (1978) argued that Ti destabilizes Al and Si tetrahedra in melt, affecting the mixing properties of Fe and Mg, presumably because Al-Si melt species which bridge with Fe are affected by the formation of Fe-Ti melt species. They noted that Ti may exert an unspecified “intrinsic effect” on Fe-Mg partitioning. Jones (1988) suggested that high TiO_2 abundance in melt leads to the formation of ferropseudobrookite (FeTi_2O_5) melt species which have greater affinity for Fe than coexisting silicate minerals and therefore decrease the olivine-melt Fe-Mg K_D . Xirouchakis et al. (2001) reached a similar conclusion, arguing that increasing TiO_2 content in melt leads to an increase in Q^4 structural units because of the affinity of Ti-O polymers for “network cations.” While the details of these interpretations differ, they are (to first order) consistent with each other. Interestingly, Longhi et al. (1978) predicted that the melt compositional effect on Fe-Mg partitioning would probably affect the mixing properties (and partition coefficients) of other elements as well, particularly of trace elements. One might expect elements that have charges and ionic radii similar to

those of Ti, such as the HFSE, selected transition metals, and perhaps even REE to be most strongly affected by melt Ti content.

A number of ilmenite-melt trace element partitioning studies are reported in the literature. Most of the early studies investigated partitioning between ilmenite and moderate to high-Ti lunar type melts and all obtained similar partition coefficients for HFSE (D_{HFSE}) (e.g., Palme and Wlotzka, 1977; Irving et al., 1978; McCallum and Charette, 1978; Fujimaki et al., 1984; McKay and Wagstaff, 1984; McKay and Wagstaff, 1985; Nakamura et al., 1985; McKay et al., 1986; Nakamura et al., 1986). Palme and Wlotzka (1977) analyzed mineral separates from a lunar basalt (~9.5% TiO₂), while McCallum and Charette (1978) conducted platinum wire loop experiments on high-Ti synthetic basalt (11.4% TiO₂) at a range of temperatures (1105-1128°C). McKay and coworkers ran experiments on synthetic lunar basalts with 8-10% TiO₂ at atmospheric pressure and 1122-1150°C. These three research groups report consistent D_{Zr} (0.2-0.33) and D_{Hf} (0.2-0.41). In contrast, Fujimaki and Tatsumoto (1984) report D_{HFSE} an order of magnitude higher (D_{Zr} 3.0 and D_{Hf} 1.8) for mineral separates from a low-Ti alkali basalt (1.7% TiO₂).

Zack and Brumm (1998) measured trace elements in clinopyroxene and ilmenite in garnet pyroxenites and used known clinopyroxene-melt partition coefficients to determine ilmenite-melt partition coefficients. Klemme et al. (2006) produced a large set of partition coefficients for ilmenite, armalcolite, and ulvöspinel at lower TiO₂ abundances (2.8-7.2% TiO₂ and one high-Ti experiment) and temperatures of 1150-1250°C (Fig. 1e). Their measured D_{HFSE} are between the high values reported in Fujimaki and Tatsumoto (1984) and the lower values of the high-Ti experiments, however their

melt compositions have total alkali $> 3\%$ and silica contents more consistent with rhyolites than lunar basalts (Figs. 1a and 1c). van Kan Parker et al. (2011) reported partition coefficients for ilmenite and armalcolite from two high-Ti experiments (20 and 22.6% TiO_2) at $\sim 1300^\circ\text{C}$ and 1.1 to 1.7 GPa. The D_{HFSE} they report are consistent with earlier work on high-Ti basalts. Figure 1 compares major element compositions of the melt reported in the aforementioned partitioning studies with those observed in the lunar picritic glass melts (Delano, 1986; Papike et al., 1998). The experimental melt compositions appear to deviate from the lunar trends when the TiO_2 abundance in the melt is less than 7%.

In this study, we systematically investigate the effects of melt TiO_2 content on the partitioning of major and trace elements between Fe-Ti oxides and lunar picritic glass melts. In sections 2 – 4, we first report results from an experimental study of trace element partitioning between Fe-Ti oxides and lunar picritic glass melts for a wide range of TiO_2 content in the melt ($\text{TiO}_2 = 2.6\text{-}28\%$) at pressures of 1-2 GPa and temperatures of 1050 to 1350 $^\circ\text{C}$. We show that Fe-Mg, HFSE, Cr, and V partition coefficients for Fe-Ti oxides are inversely correlated with TiO_2 abundance in the melt and discuss this observation in terms of the formation of Fe-Ti melt species with changing melt TiO_2 and structure. In section 5, we present a lattice strain model for REE partitioning in ilmenite and solubility-weighted partitioning models for HFSE distribution between Fe-Ti oxides and a wide range of melt compositions. In section 6, we discuss the variations of HFSE as a function of melt TiO_2 abundance, and compare with trends produced by ilmenite and armalcolite fractionation from a crystallizing lunar magma ocean. We then compare lunar basalt petrogenetic models, and discuss equilibrium melt compositions for lunar

armalcolites and demonstrate that their formation mechanisms need to be reevaluated. Preliminary results from this study were presented in Dygert et al. (2011 and 2012).

2. Methods

2.1 Experimental Preparation and Procedures

We conducted ilmenite-melt and armalcolite-melt partitioning experiments at pressures of 1-2 GPa and temperatures of 1050-1350°C using a 19.1 mm piston cylinder apparatus. Our experimental assembly consisted of a salt-Pyrex[®] sleeve, straight-walled graphite furnace, and internal spacers of crushable MgO with a graphite or graphite lined molybdenum capsule. A total of ten experiments are reported in this study (Table 1). All but one experiment (NJD-2) was conducted with a molybdenum outer capsule (Fig. 2) to maintain reducing conditions similar to those on the moon ($fO_2 \sim IW-1$). NJD-2 was conducted in a graphite capsule and buffered at fO_2 near C-CO. Each experiment utilized a different starting composition (except NJD-18M which replicates NJD-15M) in order to produce different Fe-Ti oxides and coexisting melt compositions with a range of TiO₂ contents (Table 1, for mineral compositions see Supplementary Table ST1). These starting compositions include mixtures of ilmenite and harzburgite, ilmenite and lherzolite, ilmenite and a synthetic Apollo 15 Red Glass (A15-RG, similar in composition to those reported in Delano, 1980), and A15-RG alone. Additionally, four experiments were conducted with an ilmenite saturated low-Ti melt (FR-1290, after Longhi, 2003) with varying amounts of added ilmenite. Samples A15-RG and FR-1290 were prepared using reagent grade oxide and carbonate powders of appropriate proportion. After an initial mixing of 20 minutes in an agate mortar in ethanol, the mixtures were dried and placed in a platinum crucible to decarbonate in an 800°C furnace overnight. The powders

were then mixed in an agate mortar in ethanol for 8 hours. A mixture of REE and HFSE oxides (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Yb, Lu, Y, Zr, Hf, Nb, Ta, and W) was prepared to dope the starting compositions and thus reduce analytical uncertainty during data collection. After weighing, the REE+HFSE oxide powder was mixed in ethanol in a corundum mortar for 8 hours. The A15-RG and REE+HFSE oxide powders were reduced in a 900°C H₂-CO mixed gas furnace for at least 4 hours at $f_{O_2} \sim$ iron-wüstite, while FR-1290 was reduced at 800°C for 7.5 hours to prevent melting. Finally, mixtures of REE+HFSE powder and the starting composition (A15-RG or FR-1290) were ground in ethanol in a cleaned agate mortar for 4 hours at a mass ratio of $\sim$ 1:49.

Peridotite powders were prepared from optically clean minerals picked from a spinel lherzolite xenolith from Kilbourne Hole, NM as described in Thacker et al. (2009). Ilmenite powder was prepared from a sample obtained from Ward's Natural Science and added to these starting compositions in proportions reported in Table 1. All sample charges were placed in a 200°C vacuum oven for at least 8 hours prior to running. Experimental run durations were 46 hours or longer in order to approach chemical equilibrium as well as to ensure adequate crystal growth for chemical analysis.

Partitioning experiments were conducted using the hot-piston in technique; after initially pressurizing to approximately 75% of the target pressure, temperature was increased at a rate of 75°C per minute until the desired temperature was attained. The target pressure was reached through a combination of thermal expansion during heating and additional pressurization. The three experiments with peridotitic starting compositions (NJD-2, 7M, and 10M) were taken directly to their target temperatures and maintained there for the duration of the experiment. The other experiments (NJD-8M,

15M, 16M, 17M, 18M, 19M, and 22M) were heated above their estimated liquidus temperatures (to 1350-1500°C), and then cooled to their target temperatures at rates of 0.1 to 1°C per minute to encourage larger crystal growth. Durations reported in Table 1 are dwell times that were maintained after the final target temperature was reached. Temperatures were measured using a W₉₇Re₃–W₇₅Re₂₅ thermocouple. Uncertainties in temperature measurements are about ±10°C. Experiments were quenched to room temperature by shutting off the power supply to the furnace. No pressure correction was applied to the measured electromotive force and the nominal pressure was not corrected for friction.

2.2 Analytical Techniques

Major element compositions of quenched charges were analyzed using a Cameca SX 100 electron microprobe at Brown University. Analytical conditions are an accelerating voltage of 20 kV and a beam current of 25 nA for all runs except NJD-22 that was analyzed at 20 kV and 15 nA. Fe-Ti oxides were analyzed using a focused beam, while quenched melt was analyzed with a 10 µm defocused beam. Natural and synthetic standards were used for calibration and the ZAF matrix correction was applied. Trace element concentrations in Fe-Ti oxides and melt were obtained using LA-ICP-MS at the Graduate School of Oceanography at the University of Rhode Island (URI) using methods similar to those described in Kelley et al. (2003). One sample (NJD-2) was also analyzed at the Plasma Mass Spectrometry Laboratory at the University of Maryland (UMD) using methods similar to those described in Aravelo and McDonough (2008). A suite of nine well-characterized natural and synthetic glass standards were used to

calibrate the analyses conducted at URI, while two similar standards were analyzed for calibration at UMD. Trace element abundances in NJD-2 measured at the two labs were nearly identical.

Care was taken to select an appropriate normalizing element during data processing. TiO_2 is abundant in Fe-Ti oxides and melt in all runs and averaged microprobe analyses for TiO_2 have relatively low standard deviations (Table 2), making Ti a good candidate for use as a normalizing element. However, the Ti abundance in the glass standards for LA-ICP-MS analysis is much lower than in our melts and Fe-Ti oxides which could introduce errors to measured trace element abundances. As a precaution, we processed our data for 3 experiments using both Mn (which has abundances in minerals and melt consistent with the standards but higher analytical uncertainty in the microprobe data) and Ti as normalizing elements and obtained practically identical results both ways (Supplementary Figure S1). Analytical uncertainties were slightly smaller with Ti, probably owing to the better quality of the microprobe data for TiO_2 . The partition coefficients we report here were processed using Ti as the normalizing element. Ti was previously used as a normalizing element in other Fe-Ti oxide-melt partitioning studies conducted with LA-ICP-MS (Klemme et al., 2006; van Kan Parker et al., 2011).

Because quench growth in low viscosity high-Ti melts is ubiquitous (Fig. 2b), we used 20-60 μm diameter laser spot sizes when analyzing melt, while spot sizes for Fe-Ti oxides ranged from 12-40 μm depending on crystal size. Ilmenite grains in low-Ti experiments tend to be elongated and narrow (Fig. 2c). In order to collect a consistent and sufficiently lengthy analytical signal we did line traverses across clean ilmenite surfaces

in runs NJD-15M, 18M, 19M and 22M. Ilmenite grains were sufficiently large in the other experiments to conduct spot analyses. In all cases, data affected by the intersection of the laser with melt inclusions or undesired phases was discarded. Such affected data is easily identifiable as a spike or decline in analytical signal for particular elements.

3. Results

Table 1 summarizes run conditions and run products for the ten experiments reported in this study. Figure 2 shows a reflected light micrograph and back scattered electron images of two runs representative of high-Ti (Figs. 2a and 2b) and low-Ti (Fig. 2c) ilmenite-melt partitioning experiments. In general, very high-Ti experiments ($\geq 19.1\%$ TiO₂) exhibit extensive quench growth of Fe-Ti oxides and silicates (Figs. 2a and 2b), while melts of lower TiO₂ abundance appear to have quenched as glasses (Fig. 2c). Silicate minerals that crystallized in the high-Ti experiments include olivine and in NJD-10M, our only armalcolite saturated experiment, orthopyroxene. As is well known (e.g., Delano, 1990; Circone and Agee, 1996), high- and very high-Ti melts are denser than olivine and orthopyroxene at pressures relevant to the lunar mantle. In our high-Ti runs, silicate minerals tend to float, while ilmenite, which is denser than high-Ti melts, tends to sink (Figs. 2a and 2b). Our low-Ti experiments were saturated with a wide range of minerals including ilmenite, plagioclase, hedenbergite, quartz, and possibly trace amounts of phosphates (Fig. 2c). The presence or absence of these minerals, however, was highly variable and dependent on the pressure, temperature, and bulk composition of the experiment. In most experiments (high-Ti and low-Ti), trace amounts of chrome spinel are present. Although every effort was made to grow crystals as large as possible

for LA-ICP-MS analysis, ilmenites in low-Ti melts were always small, with the largest ilmenite grains in our lowest TiO_2 experiments approximately 20 μm wide (Fig. 2c). Placing a sufficiently large laser spot (12 μm) on such small mineral grains is difficult, and uncertainties in our measured partition coefficient are generally larger for the low TiO_2 experiments. However, analyses of these small grains are reproducible for abundant elements such as HFSE in Fe-Ti oxides.

Melt compositions are reported in Table 2 and selected major element abundances in melt and experimental temperatures are plotted against TiO_2 in Fig. 1. Note the large range of TiO_2 abundance in melts used in this study (2.6-28.0%, yellow stars), which complement previous partitioning studies. With the exception of those of McKay et al. (1985), Nakamura et al. (1986), and van Kan Parker et al. (2011), SiO_2 , Al_2O_3 , and total alkali abundances in earlier experimental studies are often much higher than, while $\text{Mg\#}$ [$100\text{MgO}/(\text{MgO}+\text{FeO})$, in molar fraction] are much lower than, those in the lunar picritic glasses (Delano, 1986; Papike et al., 1998). Importantly, our high-Ti melt compositions generally fall on the high-Ti extensions of the lunar picritic glass trends in oxide vs. TiO_2 space, particularly for SiO_2 , Al_2O_3 , and $\text{Mg\#}$ (Figs. 1a and 1b). Our low-Ti experiments fall off the lunar picritic glass trends in $\text{Mg\#}$ (and for two experiments, total alkali), however these low-Ti compositions approximate an ilmenite saturated residual melt of the lunar magma ocean calculated by Snyder (1992) and Longhi (2003) (Figs. 1c and 1d). The near linear correlation between melt TiO_2 and experimental temperature is presented in Fig. 1e.

Our measured trace element partition coefficients are listed in Table 3. Figure 3 compares our measured D for ilmenite and armalcolite with those from the literature

(Fujimaki et al., 1984; McKay and Wagstaff, 1984; McKay and Wagstaff, 1985; Nakamura et al., 1985; McKay et al., 1986; Nakamura et al., 1986; Zack and Brumm, 1998; Klemme et al., 2006; van Kan Parker et al., 2011). Partition coefficients for transition metals, middle to heavy REE, and Y are consistent with the literature data, except abnormally high D_{Cu} from run NJD-22M. The cause for the latter is unknown. Mo is moderately compatible in ilmenite and D_{Mo} shows no correlation with melt TiO_2 (Table 3). Mo partitioning is likely affected by the element's heterovalent nature at experimental oxygen fugacities (Danielson et al., 2011). W is highly incompatible in ilmenite and nearly constant across a range of melt TiO_2 . Partition coefficients for HFSE are plotted as a function of melt TiO_2 content in Fig. 4.

In general, partition coefficients of HFSE in ilmenite or armalcolite are negatively correlated with TiO_2 abundance in melt and exhibit striking bimodality (Fig. 4). Between 6% and 7% TiO_2 , the slope of the negative correlation appears to moderate significantly in the high-Ti melt. With the exception of Ta in armalcolite (which is slightly compatible in our high-Ti experiment), all HFSE are moderately to slightly incompatible in ilmenite and armalcolite at high melt TiO_2 . Nb and Ta in ilmenite transition from incompatible at high TiO_2 to compatible somewhere near 5% TiO_2 . In ilmenite, D_{Nb} and D_{Ta} vary by nearly an order of magnitude between low- and high-Ti melts. Zr and Hf remain incompatible at all TiO_2 abundances with their partition coefficients approaching unity in our lowest Ti experiment (2.6% TiO_2). In general, D_{HFSE} in our high-Ti experiments are lower than values previously reported (McCallum and Charette, 1978; Fujimaki et al., 1984; McKay and Wagstaff, 1984; McKay and Wagstaff, 1985; McKay et al., 1986; Nakamura et al., 1985; Nakamura et al., 1986; Zack and Brumm, 1998; Klemme et al.,

2006), but consistent with those from a recent study (van Kan Parker et al., 2011). Ilmenite Fe-Mg K_D [(FeO/MgO)_{ilmenite}/(FeO/MgO)_{melt}, in moles] and selected major element partition coefficients are displayed as a function of melt TiO₂ in Fig. 5, and transition metal partition coefficients are plotted in Fig. 6. REE partition coefficients are plotted as a function of ionic radius in Fig. 7. Although LREE abundances were too low for accurate measurement, our ilmenite D_{REE} fall on a parabola when plotted against ionic radius, suggesting our ilmenites are relatively free of melt inclusions and that D_{REE} are high quality. A diagram displaying D_{REE} as a function of melt TiO₂ is presented in Supplementary Figure S2. Additional information regarding major and trace element abundances in Fe-Ti oxides and melt can be found in Supplementary Tables ST2 and ST3.

4. Discussion

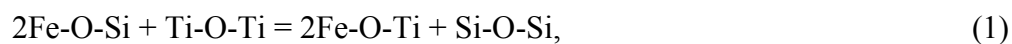
The ability of a trace element to substitute into a crystal is largely determined by its ionic radius and charge disparity (or lack thereof) between the major element normally occupying the site and the trace element (Wood and Blundy, 1997). Only elements with radii similar to that of a major element will be able to substitute into its lattice site, and any charge imbalance between the major and trace element must be compensated. Ilmenite possesses two octahedrally coordinated M sites, with one normally occupied by Fe²⁺ or Mg²⁺ and another occupied by Ti⁴⁺. Armalcolite has one M site occupied by Fe²⁺ or Mg²⁺ and twice as many M sites normally occupied by Ti⁴⁺ (e.g., Lindsley, 1975). Charge disparities can be balanced by several mechanisms including vacancies and coupled substitution. In Fe-Ti oxides, charge imbalances of pentavalent cations, for

example, are probably relieved by coupled substitution of trivalent cations (such as Al^{3+}) for Ti^{4+} (e.g., Horng and Hess, 1999). When substituting into melts, trace elements must satisfy charge and size requirements as well, though the size constraint is significantly relaxed. In this way, melt composition and structure can exert secondary but significant control on trace element partitioning.

4.1 Melt Structure Effects

Ilmenite forms solid solution with geikielite (MgTiO_3), and the FeO/MgO ratio of an ilmenite depends on the composition of coexisting melt. In our experiments, ilmenite-melt FeO-MgO K_D ranges from > 2.5 at low TiO_2 to unity at high TiO_2 (Fig. 5a), suggesting that the dominant control on ilmenite-melt K_D is the TiO_2 content of the melt. Because melt TiO_2 exerts such strong effect on major element partitioning, it follows that the TiO_2 content plays a significant role in trace element partitioning as well, as suggested by Longhi et al. (1978). Indeed, there is a strong inverse correlation between D_{HFSE} and melt TiO_2 abundance (Fig. 4). We attribute the dependence of major and trace element partitioning on melt TiO_2 abundance to the formation of Fe-Ti melt species at elevated melt TiO_2 . Such melt species may be similar to the ferropseudobrookite complexes suggested by Jones (1988).

To further conceptualize the effect of melt structure and TiO_2 content on partitioning behavior, we envision a simple equilibrium between hypothetical melt species,



where Fe-O-Si and Si-O-Si represent nonbridging and bridging oxygen and Fe-O-Ti and Ti-O-Ti are comparable species in TiO₂-rich melts. Based on electronegativity differences (Hess, 1995b), it appears that the right hand side of reaction (1) is more favored. In effect the addition of TiO₂ to a silicate melt leads to the formation of regions enriched in Fe-O-Ti complexes. While the partitioning of certain elements between crystalline Fe-Ti oxides and liquid Fe-Ti complexes will be driven by enthalpic and entropic effects, the structure of the molten Fe-O-Ti phase is not constrained by a crystal lattice and elements of varied sizes and charges can more easily be accommodated by the melt. In this way, as TiO₂ abundance in melt increases, the activity coefficients of HFSE in the melt decrease, and the mineral-melt D_{HFSE} decreases.

Equation 1 predicts that increasing the TiO₂ content of a melt should lead to the formation of more highly polymerized melts. However, we observe ubiquitous quench modification in very high-Ti melts (Figs. 2a and 2b) and very little quench modification in lower Ti melts (Fig. 2c). Because quench growth is indicative of low melt viscosities associated with depolymerized melts, Eq. 1 appears inconsistent with this observation. This can be partly attributed to experimental temperatures. Our low Ti experiments were conducted at lower temperatures than high and very high-Ti experiments (Fig. 1e); lack of quench growth in the colder runs can be partially attributed to the dependence of viscosity on temperature. Another contributing factor is dilution. While adding Ti to a melt may lead to the formation of an increasing number of Si-O-Si melt species, Fe-O-Ti species increase in number more quickly, effectively depolymerizing the melt.

Low TiO₂ melts will contain relatively more abundant bridging Si-O tetrahedra, into which the HFSE are unable to substitute because of the small ionic radius of Si. At

low melt TiO_2 , the combined effects of a higher proportion of network forming to network modifying cations and low TiO_2 abundance drive elements with high affinity for Ti to partition into crystalline Fe-Ti oxides, elevating D_{HFSE} . We infer that the negative D_{HFSE} vs. TiO_2 correlation (Fig. 4) moderates when Si-O-Si melt species become effectively isolated (Eq. 1 is driven to the right), and Fe-O-Ti species are more dominant. The very slight decrease in D_{HFSE} with increasing TiO_2 at abundances $> 6.8\%$ is therefore primarily a mass effect, controlled by the available number of sites in Fe-O-Ti species in melt, though this effect is so slight high-Ti D_{HFSE} are effectively constant.

4.2 Major Element Partitioning

Because the Ti content of an Fe-Ti oxide is approximately constant, the negative correlation between D_{TiO_2} and melt TiO_2 (Fig. 5b) can be attributed to melt TiO_2 abundance, and is a measure of the solubility of Fe-Ti oxide in a given melt. In contrast, Al_2O_3 exhibits a positive correlation with TiO_2 (Fig. 5c), which may be related to the exclusion of Al^{3+} from Fe-O-Ti melt complexes which are more abundant at higher TiO_2 . Although some of the difference between our data and the literature in Fig. 5c could be attributable to Ti^{3+} generated by our experimental methods, previous work has shown that the ratio of Ti^{3+} to Ti^{4+} is less than 0.05 in melt at the iron-wüstite buffer (Schreiber, 1977). This is consistent with our chemical formulas calculated for ilmenite and armalcolite on a 3 and 5 oxygen basis, respectively (Supplementary Table ST2). CaO partitioning shows no dependence on melt TiO_2 (Table 2).

Similar to TiO_2 dependences of FeO-MgO partitioning between olivine and basalts (Longhi et al., 1978; Jones, 1988; Longhi, 1992; Xirouchakis et al., 2001),

ilmenite-melt Fe-Mg K_D are negatively correlated with melt TiO_2 (Fig. 5a). Thacker et al. (2009) showed that FeO-MgO distribution coefficient between olivine and either ilmenite or armalcolite to be effectively independent of temperature with average values of 0.179 ± 0.008 for olivine/ilmenite and 0.319 ± 0.021 for olivine/armalcolite. Taken collectively, results from these earlier and present studies suggest the importance of TiO_2 content and melt structure in controlling FeO-MgO partitioning between mineral and melt in the system Fe-Ti oxides – olivine – basalts.

4.3 Other Trace Elements

The melt structure control on D_{HFSE} should affect Fe-Ti oxide-melt partitioning for any element which substitutes into the Ti site of Fe-Ti oxides. FeO-MgO K_D trends in Fig. 5a suggest elements with size and charge similar to Fe^{2+} could be affected by Fe-O-Ti melt species formation. However, the partition coefficients of Sc (Fig. 6c), Mn (Fig. 6d), Zn, Co and Cu (Table 2), which all have size and/or charge more similar to Fe^{2+} than Ti^{4+} , show no systematic variations in partitioning behavior across the range of TiO_2 investigated. Similarly, REE and Y (Supplementary Figure S2) show no dependence on melt TiO_2 . We infer that only partition coefficients for elements with high affinity for Ti sites in Fe-Ti oxides are affected by melt species formation.

Cr and V are both inversely correlated with TiO_2 (Figs. 6a and 6b) suggesting they may at least partially substitute into Ti sites in Fe-Ti oxides. At the iron-wüstite buffer, V in melt is thought to be predominantly in a 3+ oxidation state (e.g., Sutton et al., 2005), while Cr is probably at 2+ and 3+ valence states in a proportion of ~4:1 (Schreiber, 1977). However, at high melt TiO_2 , D_{Cr} is half its value at low melt TiO_2 (Fig.

6a)! A simple calculation reveals that if Fe-O-Ti melt species sequester all the trivalent Cr from an ilmenite with a partition coefficient of 20 at iron-wüstite buffer, D_{Cr} would decrease to ~ 3 . We argue that only trivalent Cr and V are affected by the formation of Fe-O-Ti melt species. The consistent, negative D_V vs. melt TiO_2 correlation provides qualitative evidence that our fO_2 is consistent among experiments.

5. Quantitative Partitioning Models

Partition coefficients of FeO/MgO, V, Cr, and HFSE in ilmenite and armalcolite are strongly dependent on TiO_2 abundance in the melt, whereas partition coefficients of REE, Y, and Sc in ilmenite appear to be insensitive to melt TiO_2 for lunar relevant melt compositions. The correlations between D_{Cr} and melt TiO_2 and D_V and melt TiO_2 (Figs. 6a and 6b) are approximately linear and interpolation of these trends should provide reasonable ilmenite-picritic glass melt partition coefficients within the range of TiO_2 abundances investigated here. In this section, we present simple models for REE and HFSE partitioning in ilmenite and armalcolite.

5.1 REE Partitioning in Ilmenite

The partitioning of REE, Y, and Sc between ilmenite and lunar picritic melts can be quantified by the lattice strain model (Brice, 1975; Blundy and Wood, 1994; Wood and Blundy, 1997):

$$D_i^{oxide-melt} = D_0 \exp\left(\frac{-4\pi EN_A}{RT} \left(\frac{r_0}{2}(r_0 - r_i)^2 - \frac{1}{3}(r_0 - r_i)^3 \right)\right), \quad (2a)$$

where D_0 is the ilmenite-melt partition coefficient for strain-free substitution; r_0 is the ideal radius for the lattice site; r_i is the ionic radius of REE, Y, and Sc (six-fold, Shannon, 1976); E is the effective Young's modulus of the lattice site; R is the gas constant; N_A is Avogadro's number; and T is temperature. The parameters of the lattice strain model (D_0 , E , and r_0) are typically estimated by non-linear least squares regression analysis of the measured data. Sun and Liang (2012) demonstrated through Monte Carlo simulations that the inverted E and r_0 are highly correlated in regression analysis. Given the limited partitioning data for ilmenite, we set the effective Young's modulus E to 300 GPa in the nonlinear least squares fit to all of our measured REE, Y, and Sc data listed in Table 3 simultaneously using Eq. 2a. The estimated lattice strain parameters are

$$D_0 = 0.61 \pm 0.19 \text{ and } r_0 = 0.688 \pm 0.010 \text{ \AA}, \quad (2b)$$

where errors are estimated 2σ uncertainties. Figure 7 shows the very good agreement between the measured and predicted REE and Y partition coefficients calculated using the lattice strain model. It is interesting to note that middle to heavy REE partition coefficients in ilmenite are the same order of magnitude as those in orthopyroxene (e.g., Sun et al., 2011; Yao et al., 2012), therefore ilmenite could represent a significant proportion of the REE budget of an ilmenite-bearing harzburgitic lunar mantle.

Application of the lattice strain model to HFSE partitioning in ilmenite or armalcolite is considerably more challenging in part because of the limited number of isovalent trace element available for constraining the lattice strain parameters in regression analysis (for a detailed discussion, see Appendix A). Here we take an alternative approach and model ilmenite and armalcolite-melt HFSE partitioning as a function of temperature and solubility of the Fe-Ti oxide in melt.

5.2 Ilmenite-Melt HFSE Partitioning

Since the TiO_2 abundance in ilmenite is approximately constant and the chemical behaviors of Zr and Hf are similar to that of Ti, we can parameterize D_{Zr} and D_{Hf} as a function of the solubility of ilmenite. Fits of the measured partitioning data excluding one outlying experiment from Klemme et al. (2006, their run HD37) are described by the following expressions:

$$\ln(D_{\text{Zr}}^{\text{ilm}}) = 3.87(\pm 1.12) - 1.02(\pm 0.19) \times \frac{10000}{T} + 1.16(\pm 0.13) \times \ln(D_{\text{Ti}}), \quad (3)$$

$$\ln(D_{\text{Hf}}^{\text{ilm}}) = 5.21(\pm 1.16) - 1.17(\pm 0.20) \times \frac{10000}{T} + 1.14(\pm 0.14) \times \ln(D_{\text{Ti}}), \quad (4)$$

where numbers in parentheses are estimated 2σ uncertainties. In a similar way, we can parameterize D_{Nb} and D_{Ta} as a function of temperature and ilmenite solubility while excluding two outlying experiments from Klemme et al. (2006, their runs HD37 and MHD19_3),

$$\ln(D_{\text{Nb}}^{\text{ilm}}) = 6.62(\pm 2.68) - 1.42(\pm 0.47) \times \frac{10000}{T} + 1.64(\pm 0.31) \times \ln(D_{\text{Ti}}), \quad (5)$$

$$\ln(D_{\text{Ta}}^{\text{ilm}}) = 7.73(\pm 2.27) - 1.50(\pm 0.39) \times \frac{10000}{T} + 1.54(\pm 0.27) \times \ln(D_{\text{Ti}}). \quad (6)$$

Figures 8a and 8c show that the models presented in Eqs. 3-6 do an excellent job reproducing the experimental results. Comparison of the second and third coefficients in Eqs. 3 and 4 and Eqs. 5 and 6 reveal that they are identical within the uncertainty. This suggests that the ratio of the partition coefficients ($D_{\text{Hf}}/D_{\text{Zr}}$ or $D_{\text{Ta}}/D_{\text{Nb}}$) is approximately constant across the wide range of melt compositions, pressures, and temperatures reported here and in the literature. Indeed, Figures 9a and 9c demonstrate that $D_{\text{Hf}}/D_{\text{Zr}} \sim 1.27$ and $D_{\text{Ta}}/D_{\text{Nb}} \sim 1.30$ for the reported data.

5.3 Armalcolite-Melt HFSE Partitioning

Although the dataset for armalcolite-melt partitioning is much more limited, models similar to those outlined above were developed for armalcolite D_{HFSE} . Excluding one outlying experiment from Klemme et al. (2006, their run MHD13_1), we have:

$$\ln(D_{Zr}^{arm}) = -0.42(\pm 0.056) \times \frac{10000}{T} + 0.99(\pm 0.12) \times \ln(D_{Ti}) + 0.0090(\pm 0.0028) \times Mg\#_{Melt}, \quad (7)$$

$$\ln(D_{Hf}^{arm}) = -0.34(\pm 0.040) \times \frac{10000}{T} + 0.91(\pm 0.089) \times \ln(D_{Ti}) + 0.0093(\pm 0.0020) \times Mg\#_{Melt}, \quad (8)$$

$$\ln(D_{Nb}^{arm}) = 7.13(\pm 2.45) - 1.40(\pm 0.41) \times \frac{10000}{T} + 1.10(\pm 0.17) \times \ln(D_{Ti}), \quad (9)$$

$$\ln(D_{Ta}^{arm}) = 3.97(\pm 2.61) - 0.80(\pm 0.44) \times \frac{10000}{T} + 0.89(\pm 0.18) \times \ln(D_{Ti}), \quad (10)$$

where numbers in parentheses are estimated 2σ uncertainties. Note the constant term is omitted in Eqs. 7 and 8, as it is statistically insignificant. An additional term incorporating the effect of Mg# in melt on armalcolite D_{HFSE}^{4+} was added, which leads to a significant improvement in the quality of the fit. However, Mg# in the melt does not appear to affect D_{Nb} and D_{Ta} in armalcolite, at least for the limited data examined in this study. Figures 8b and 8d demonstrate the very good agreement between the measured and predicted HFSE partition coefficients calculated using Eqs. 7-10. Similar to those in ilmenite, we observe that ratios of the partition coefficients are approximately constant across the wide range of melt compositions, pressures, and temperatures reported here and in the literature ($D_{Hf}/D_{Zr} \sim 1.31$ and $D_{Ta}/D_{Nb} \sim 1.42$, Figs. 9b and 9d). It is interesting to note that D_{Ta}/D_{Nb} (~ 1.42) for armalcolite is (slightly) different from the other ratios which all are about 1.3, suggesting that armalcolite and ilmenite will fractionate Nb and

Ta differently but Zr and Hf similarly (Fig. 10a). We will demonstrate this point in the next section.

In summary, given their solubilities in silicate melts, it is possible to make accurate estimate of the partition coefficients of Zr, Hf, Nb, and Ta in ilmenite and armalcolite over a wide range of temperatures, pressures, and melt compositions. Solubility-weighted partitioning is consistent with the concept of melt structure effects on HFSE partition coefficients discussed in section 4, and the observation that D_{Ti} plotted at or very close to the apex of the lattice strain parabolas for Ti, Zr, and Hf (Supplementary Figures S4a and S6).

6. Lunar Applications

The fickle partitioning behavior of HFSE has interesting implications. Constant D_{HFSE} should be suitable for modeling trace element partitioning between high-Ti picritic glass melts or mare basalts and Fe-Ti oxides. In contrast, low Ti picritic glass melt or mare basalt petrogenetic modeling will be case-dependent, and selecting appropriate D_{HFSE} for the melt compositions investigated is vital for reaching meaningful results. In this section, we consider four lunar applications.

6.1 HFSE Abundances in Late Lunar Magma Ocean Cumulates

The dependence of Fe-Ti oxide partition coefficients on melt TiO_2 is important during end-stage crystallization of the lunar magma ocean. A solidifying lunar magma ocean is thought to reach ilmenite saturation after ~95% crystallization, when the TiO_2 content of the liquid is roughly 5% (Snyder et al., 1992). As ilmenite continues to

precipitate from the melt during the final 5% of magma ocean crystallization, TiO_2 in the melt will decrease with a corresponding increase in D_{Ti} and the compatibility of HFSE in ilmenite will increase (Fig. 4 and Eqs. 3-10). If the HFSE abundance, major element composition, and mineral fractionation sequence of the lunar magma ocean are known, an estimate of the HFSE budget of an ilmenite-bearing lunar cumulate mantle can be made (Fig. 10b).

We reproduced the lunar magma ocean crystallization model of Snyder et al. (1992) using modifications in the bulk moon composition and phase proportions made by Münker (2010) and our new partitioning data, and compared the compositions of Fe-Ti oxide cumulates to high-quality HFSE measurements of KREEP basalts, picritic glasses, and mare basalts (Wänke et al., 1975; Münker et al., 2003; Münker, 2010). The mare basalts and picritic glasses fall into two groups in Nb/Ta vs. Hf/Ta space. High-Ti basalts have the lowest Nb/Ta and Zr/Hf ratios, low-Ti basalts generally have higher ratios with some overlap, and interestingly KREEP basalts have the highest ratios, plotting far from high-Ti basalts (Fig. 10b). Simulations assuming the magma ocean is armalcolite saturated fall on the margin of lunar basalt data (Supplementary Figure S3), while models assuming ilmenite is the relevant oxide phase plot directly on the data (Fig. 10b). For comparison with the natural samples we plot calculated compositions of ilmenite bearing cumulate (a mixture of anorthite, clinopyroxene, pigeonite, ilmenite, and trapped melt; see caption to Fig. 10 for phase proportions) for three models. Two assume constant partition coefficients. Model 1 uses our average high-Ti melt D_{HFSE} (cyan square, D_{Zr} 0.30, D_{Hf} 0.43, D_{Nb} 0.53, D_{Ta} 0.84), Model 2 uses our average low-Ti melt D_{HFSE} (purple square, D_{Zr} 0.66, D_{Hf} 0.76, D_{Nb} 2.17, D_{Ta} 2.46), and Model 3 uses the composition

dependent partition coefficients according to Eqs. 3-6. Note that cumulate compositions evolve as the magma ocean crystallizes and Fig. 10b shows average cumulate layer compositions for Models 1 and 2, while the evolving compositions at 0.5% crystallization intervals are shown for Model 3. For Model 3, two compositions are plotted, one is the trace element abundance of the bulk ilmenite-bearing cumulate (blue crosses joined by a line) and the other is the ilmenite in the cumulate (black open circles joined by a line). The numbers refer to the percent of magma ocean crystallized.

According to the model of Snyder et al. (1992), the lunar magma ocean becomes ilmenite saturated at 5% TiO_2 and the TiO_2 content of the melt decreases until the magma ocean is completely crystallized. Assuming the bulk composition of the ilmenite saturated magma ocean is reasonable, the partition coefficients used in Models 2 and 3 are more realistic, however these cumulate compositions fall between the low-Ti and high-Ti basalts. Because ilmenite contains almost all of the lunar HFSE, a melt that assimilates even a small amount of cumulate ilmenite will inherit the HFSE ratios of the cumulate. Partition coefficients for the high-Ti melt used in Model 1 better reproduce the low Zr/Hf and Nb/Ta ratios of the high-Ti basalts. Lunar basalt source compositions near the Model 1 cumulates can easily form low-Ti basalts by melting, assimilation of KREEP, or possibly reaction with an early mafic cumulate. Some of these ideas are explored in the next section.

6.2 Melting of a Hybrid Cumulate Lunar Mantle

The dependence of Fe-Ti oxide partition coefficients on melt TiO_2 is also important during melting of an ilmenite or armalcolite bearing cumulate mantle.

Although some work has been done on the solidus temperature and melting reactions of Fe-Ti oxide bearing lithologies (Wyatt, 1977; Van Orman and Grove, 2000; Xirouchakis, 2007; Singletary and Grove, 2008; Thacker et al., 2009), more work remains. If Fe-Ti oxides exist in the picritic glass melt source, oxide-melt D_{HFSE} could vary by over an order of magnitude (Fig. 4 and Table 3) depending on the TiO_2 content of the melt, which is primarily a function of temperature (Fig. 1e) and melting reactions.

One class of picritic glass petrogenetic models accounts for their elevated TiO_2 abundances by invoking an Fe-Ti oxide bearing hybrid cumulate mantle formed by the addition of late-stage magma ocean cumulates to the early harzburgite cumulates during lunar mantle overturn (e.g., Ringwood and Kesson, 1976; Hess and Parmentier, 1995). The stability of ilmenite and armalcolite in a harzburgitic lunar cumulate mantle is known to be pressure dependent (Thacker et al., 2009), with ilmenite stable at pressures above 1.4 GPa and armalcolite stable at pressures below 1.4 GPa in a harzburgite. Therefore, distinguishing between the two minerals in the picritic glass melts could provide important information about the nature of the lunar mantle and picritic glass melt petrogenesis. We model HFSE fractionation during melting of ilmenite- and armalcolite-bearing lunar cumulate mantles (Figs. 11a and 11b, respectively) using HFSE partitioning models obtained in this study. For both models, we added 50-50 mixtures of ilmenite-clinopyroxene cumulates from the ilmenite saturated crystallizing magma ocean (Model 1 in the previous section) to a harzburgite composed of olivine and orthopyroxene cumulates from early stages of magma ocean crystallization. Based on laboratory experiments (Ringwood and Kesson, 1976; Thacker et al., 2009), we assume the

ilmenite-clinopyroxene cumulates react with the harzburgite, forming an ilmenite- or armalcolite-bearing harzburgite (depending on pressure).

By varying degree of melting and selecting appropriate partition coefficients for the high-Ti and low-Ti melts, we are able to reproduce the HFSE abundances in the high-Ti and low-Ti lunar basalts using a single ilmenite bearing source (77.5% olivine, 20% orthopyroxene, 2.5% ilmenite) and perfect fractional melting model (Fig. 11a). Furthermore, by varying degree of melting and the oxide proportion in the mantle source, we are also able to reproduce the HFSE abundances in the high-Ti and low-Ti lunar basalts using an armalcolite-bearing mantle source (Fig. 11b, see figure caption for phase proportions). This is due to the fact that the difference between low-Ti and high-Ti armalcolite partition coefficients is smaller than the difference between low-Ti and high-Ti ilmenite partition coefficients (Figs. 4 and 10b). Distinguishing which oxide phase is present in the source region may require other geochemical proxies.

6.3 Ilmenite-Bearing Cumulate Assimilation

Another class of petrogenetic models accounts for lunar basalt compositions by invoking assimilation of ilmenite in picritic glass melts as they migrated to the lunar surface (e.g., Hubbard and Minear, 1975; Wagner and Grove, 1997; Elkins Tanton et al., 2002; Liang and Hess, 2006). We ran a mixing model assuming a 50-50 mixture of ilmenite-clinopyroxene late stage cumulate is assimilated by an aggregated fractional melt produced by 15% melting of an ilmenite-free harzburgite of early lunar magma ocean cumulate (red line in Fig. 11c). This model successfully reproduces the high-Ti lunar basalts by mixing 20-60% of ilmenite-clinopyroxene cumulates into a harzburgitic

melt. The HFSE abundances are consistent with the TiO_2 content of the generated basalts. However, this model may not appropriately reproduce the low-Ti basalts, which show a different slope than high-Ti basalts. Nonetheless, given the enormous breadth in possible late cumulate compositions, it is likely that a similar mechanism could reproduce the low-Ti basalts (e.g., KREEP assimilation).

6.4 Trace Element Abundances in Lunar Armalcolite

Lunar armalcolites have been divided into three distinct compositional groups: Type 1, 2 and 3 (Haggerty, 1973; see also Papike et al., 1998). Type 1 armalcolite is usually reported to have crystallized from high- TiO_2 mare basalts, with less than 0.5% CaO, 1-2% Cr_2O_3 , and trace HFSE abundances. Type 2 armalcolite have ZrO_2 contents of 3.8-6.2%, Cr_2O_3 contents of 4.3-11.5%, and CaO contents between 3% and 3.5%. Type 3 armalcolites have ZrO_2 contents of 2.0-4.4%, Nb_2O_5 contents of 0.26-0.65%, and Y_2O_3 contents of 0.15-0.53% (Haggerty 1973). Type 2 and 3 armalcolites are interpreted to have crystallized from non-mare feldspathic (high- Al_2O_3) basalts due to their common association with maskelynite. However, they are small grains present in lunar regolith [e.g., in the study of Haggerty (1973), all Type 2 armalcolites are less than $25\mu\text{m}$] and conclusively determining a host melt is difficult. Using Eqs. 7-10, and appropriate D_{Cr} , D_{CaO} , and D_{Y} , we are able to calculate melts in equilibrium with lunar armalcolite.

Assuming that a representative Type 1 armalcolite (Haggerty, 1973) crystallized from picritic glass melt with 20% TiO_2 , we found an equilibrium melt with ~775 ppm Cr and ~7% CaO, consistent with a high-Ti picritic glass melt with fractionated Cr. A KREEP basalt (Mg# of 56.6, 2.14% TiO_2 , Papike et al., 1998) in equilibrium with a

representative Type 2 armalcolite (9.67% Cr_2O_3 , 3.72% CaO , 4.4% ZrO_2) would have ~1600 ppm Cr, ~9580 ppm Zr, and a physically impossible CaO content (>100%)! The same KREEP basalt in equilibrium with a representative Type 3 armalcolite (1.46% Cr_2O_3 , 0.35% CaO , 3.76% ZrO_2 , 0.65% Nb_2O_5 , and 0.53% Y_2O_3) would have 240 ppm Cr, 8200 ppm Zr, 860 ppm Nb, 10.4% Y, and 17.5% CaO . Type 2 armalcolite has exceptionally high CaO and ZrO_2 , possibly owing to impact generated mixing between armalcolite, anorthite, and zircon or baddeleyite present in lunar regolith, or exsolution from more typical Type 1 armalcolite. Type 3 armalcolite has a non-KREEPy Zr/Nb (~9.5) and an astronomical Y abundance. It too may be the product of exsolution from Type 1 armalcolite, or Type 2 and 3 armalcolite may be produced by another unidentified process. The equilibrium melt compositions calculated for Type 2 and 3 armalcolites demonstrate the origins of these lunar minerals should be reexamined.

7. Summary and Conclusions

This study investigated the effect of melt TiO_2 content on the partitioning of major and trace elements between Fe-Ti oxides and picritic glass melts. We observed strong Fe-Mg partitioning dependence on melt TiO_2 , and elements with ionic radii and charges similar to Ti such as HFSE, V, and Cr have partition coefficients strongly affected by melt TiO_2 . Correlations between D_{HFSE} and melt TiO_2 are negative below 6.8% TiO_2 but nearly constant above 6.8%. Cr and V partitioning is inversely correlated with increasing melt TiO_2 across the entire range of compositions investigated. We attribute the effect of melt TiO_2 on D_{HFSE} , D_V , and D_{Cr} on the formation of Fe-O-Ti melt species at elevated TiO_2 . Trace elements that substitute into the Ti site in Fe-O-Ti melt

species are subject to charge balancing requirements, however, Fe-O-Ti melt species are more structurally relaxed than their crystalline counterparts and can accommodate cations slightly larger or smaller than Ti more easily than crystalline Fe-Ti oxides. Partition coefficients for elements which are too large (e.g., Sc, REE) or possessing an oxidation state unsuitable for substitution into a Ti site (e.g., Co, Cu, Zn, Ca, Mn) in Fe-Ti oxides are unaffected by the formation of Fe-O-Ti melt species.

We showed that ilmenite and armalcolite D_{HFSE} can be modeled using simple solubility-weighted partitioning models. The partitioning behavior observed in this study has important implications for HFSE fractionation during lunar magma evolution. Variable HFSE fractionation will occur during melting of an Fe-Ti oxide bearing source depending on the TiO_2 abundance of the melt, and beforehand as Fe-Ti oxides crystallize from a cooling lunar magma ocean. Our results demonstrate the importance of better constraining the possible end-stage lunar magma ocean compositions and the saturation of Fe-Ti oxides in those liquids. If the bulk composition and crystallization sequence of Snyder et al. (1992) is accurate, bulk moon HFSE abundances may need to be reevaluated. Nevertheless, we successfully used the calculated magma ocean cumulates to form hybridized ilmenite and armalcolite bearing sources that can produce low and high-Ti lunar basalt compositions. Finally, HFSE abundances observed in Type 1 armalcolite are consistent with crystallization from a picritic glass type melt. Melts in equilibrium with Type 2 and 3 lunar armalcolite do not resemble KREEP basalt, suggesting these armalcolites have an unknown petrogenetic history.

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10. Figure Captions

Figure 1. Variations of selected major element abundances (in wt%) as a function of TiO_2 for picritic glass melts and Fe-Ti oxide-melt partitioning experiments (a-d). Blue circles are representative picritic glass melts (Delano, 1986; Papike et al., 1998), yellow stars are melt compositions in our partitioning experiments, magenta triangles are melt compositions of McKay and Wagstaff (1985), McKay et al. (1986), Nakamura et al. (1985), Nakamura et al. (1986), Klemme et al. (2006), and black squares are those of van Kan-Parker et al. (2011). Cyan diamond (Longhi, 2003) and red cross (Snyder et al., 1992) symbols represent the composition of a 97% crystallized ilmenite-saturated magma ocean. Note that our melt compositions generally fall on the picritic glass trends, although several experiments ($< 7\%$ TiO_2 , Fig. 1d) approximate a lunar magma ocean composition calculated by Longhi (2003) and fall off the picritic glass trend. Variations of TiO_2 in melt as a function experimental temperature (e). Low TiO_2 literature data that fall off the trend are 1 atm experiments. The correlation illustrates the difficulty in deconvolving the effects of temperature and melt TiO_2 on trace element partitioning, and also the strong dependence of melt TiO_2 on temperature.

Figure 2. (a) Reflected light micrograph of a typical high-Ti run (NJD-7M). Molybdenum capsule is lined with graphite. Note that ilmenite (bright phases) are denser than melt, while silicates (olivine, light gray phases) are less dense than melt. Black circles within experimental charge are laser ablation pits. (b) Backscatter electron image (BSE) of detail within NJD-7M. Note the ubiquitous quench growth in melt. Large laser spot diameters were used to obtain representative composition. (c) BSE image of a low-

Ti experiment (NJD-18M). Ilmenites are long, narrow, bright phases. Hedenbergite is light gray and quartz is black while melt is dark gray. The grain size of the ilmenites in this charge is typical of the low-Ti experiments and their short axes approach the minimum width necessary for LA-ICP-MS analysis of abundant trace elements in ilmenite.

Figure 3. Spider diagram displaying measured ilmenite-melt and armalcolite-melt partition coefficients for transition metals, REE, and HFSE. Cyan and peach fields represent literature data for ilmenite and armalcolite, respectively (Irving et al., 1978; McCallum and Charette, 1978; McKay and Wagstaff, 1984; McKay and Wagstaff, 1985; McKay et al., 1986; Nakamura et al., 1985; Nakamura et al., 1986; Zack and Brumm, 1998; Klemme et al., 2006; van Kan Parker et al., 2011).

Figure 4. Variations of D_{HFSE} as a function of melt TiO_2 (wt%). Diamonds represent experiments conducted by van Kan Parker et al. (2011), while literature data includes partitioning studies cited in Fig. 3.

Figure 5. Variations of ilmenite-melt Fe-Mg K_D (a), D_{TiO_2} (b), and $D_{Al_2O_3}$ (c) as a function of melt TiO_2 (wt%). The negative correlation is consistent with the effect of increasing melt TiO_2 on olivine Fe-Mg K_D (Longhi et al., 1978). Because the TiO_2 content of an Fe-Ti oxide is relatively constant, D_{TiO_2} reflects the solubility of an Fe-Ti oxide in melt. The ilmenite data point deviating from the trend (NJD-8M, 19.1% TiO_2) is our only 2 GPa experiment.

Figure 6. Variations of selected ilmenite-melt partition coefficients for transition metals as a function of melt TiO_2 (wt%). Literature data includes partitioning studies cited in Fig. 3, as well as that of Irving et al. (1978).

Figure 7. Onuma diagram showing the measured ilmenite-melt REE, Y, and Sc partition coefficients as a function of ionic radii (six-fold, Shannon, 1976). Blue diamonds are higher temperature experiments (NJD-7M; 1325°C, NJD-8M; 1320°C) while red diamonds are 1100°C experiments (NJD-19M, 17M, 22M). Data from van Kan Parker et al. (2011) are shown in gray for reference. van Kan Parker et al. (2011) attribute deviation of their LREE partition coefficients to glass contamination of Fe-Ti oxide analyses. Our data are near parabolic suggesting negligible melt contamination. Coefficients in the lattice strain model (Eq. 2b) were inverted from our measured D_{REE} , D_Y and D_{Sc} and are used to plot parabolas (solid lines).

Figure 8. Comparison between model predicted and experimentally measured ilmenite (a, c) and armalcolite (b, d) D_{HFSE} . Dotted lines define 1:2 and 2:1 values while the solid line defines 1:1 values. The predicted values were calculated using Eqs. 2-9. Squares are our experiments, stars are those of Klemme et al. (2006); triangles are those of McKay and Wagstaff (1985); circles are those of Nakamura et al. (1986); and diamonds are those of van Kan Parker et al. (2011). Data omitted from the inversions are circled (see text for specific samples).

Figure 9. Correlations of measured D_{Hf} and D_{Zr} and D_{Nb} and D_{Ta} for ilmenite (a, c) and armalcolite (b, d). Note the approximately constant ratios for charge pairs in the two minerals. Least squares fits to the data are provided. Data omitted from the inversions are included.

Figure 10. Predicted D_{HFSE} ratios plotted as a function of TiO_2 in melt (a) and lunar magma ocean crystallization models (b). In (a), note that ilmenite and armalcolite D_{Zr}/D_{Hf} are approximately parallel, but armalcolite D_{Nb}/D_{Ta} slope changes sign at 7% TiO_2 . (b) Variations of Nb/Ta and Zr/Hf ratios in lunar low-Ti basalts (green circles), high-Ti basalts (red circles), and KREEP basalts (white triangles). Superimposed over the lunar data are calculated cumulate compositions produced by crystallization of the lunar magma ocean (LMO) (Snyder et al., 1992) with modifications in starting composition and phase proportions made by Münker (2010). Three models are presented. In Model 1 (cyan square), constant high-Ti D_{HFSE} are used (D_{Zr} 0.30, D_{Hf} 0.43, D_{Nb} 0.53, D_{Ta} 0.84). In Model 2 (purple square), constant low-Ti D_{HFSE} are used (D_{Zr} 0.66 D_{Hf} 0.76, D_{Nb} 2.17, D_{Ta} 2.46). In Model 3, variable D_{HFSE} calculated using Eqs. 2-5 are used (blue crosses and black circles joined by solid lines). The squares (and blue crosses for Model 3) represent compositions of ilmenite bearing cumulates (in proportions of 46% pigeonite, 2% plagioclase, 33% clinopyroxene, 15% ilmenite, and 3% trapped liquid) formed between 95% and 99.5% crystallization of LMO. Squares are averages for Models 1 and 2. Black open circles are ilmenite compositions at 0.5% crystallization intervals.

Figure 11. Abundances of chondrite (CI) normalized HFSE in lunar basalts and in model derived melts calculated using perfect fractional melting and assimilation models. (a) Melting of a hybridized lunar mantle composed of early and late-stage magma ocean cumulates (75.5% olivine, 20% orthopyroxene, 2.5% ilmenite, blue line). Gray field shows 2-8% melting produced using high-Ti partition coefficients (20% TiO₂, Eqs. 3-6). Cyan field shows 8-18% melting calculated using low-Ti partition coefficients (2.5% TiO₂, Eqs. 3-6). (b) Melting of a hybrid lunar mantle. In this case, early and late cumulates have reacted to form armalcolite-bearing harzburgites with two different modal abundances. Gray field shows 3-13% melting produced using partition coefficients from run NJD-10M (source 75% olivine, 20% orthopyroxene, 5% armalcolite, red line). Cyan field shows 5-20% melts produced using low-Ti partition coefficients (2.5% TiO₂, Eqs. 7-10) and a source with less armalcolite (77.5% olivine, 20% orthopyroxene, 2.5% armalcolite, blue line). (c) Mixing models of an aggregated fractional melt of early magma ocean cumulates (80% olivine, 20% orthopyroxene, 15% melting, red line) and 50-50 ilmenite-clinopyroxene cumulates from late stage LMO crystallization. Heavy black line shows composition of ilmenite-clinopyroxene cumulate while magenta line shows pure ilmenite component. Thin black lines represent different mixing proportions with fraction of cumulate assimilated on right and resulting TiO₂ content on left (wt%). High-Ti basalts are easily reproduced but low-Ti basalts may be better modeled by assimilation of KREEP basalt. Lunar basalt data is from Wänke et al. (1975), Münker et al. (2003), and Münker (2010).

Figure 1.

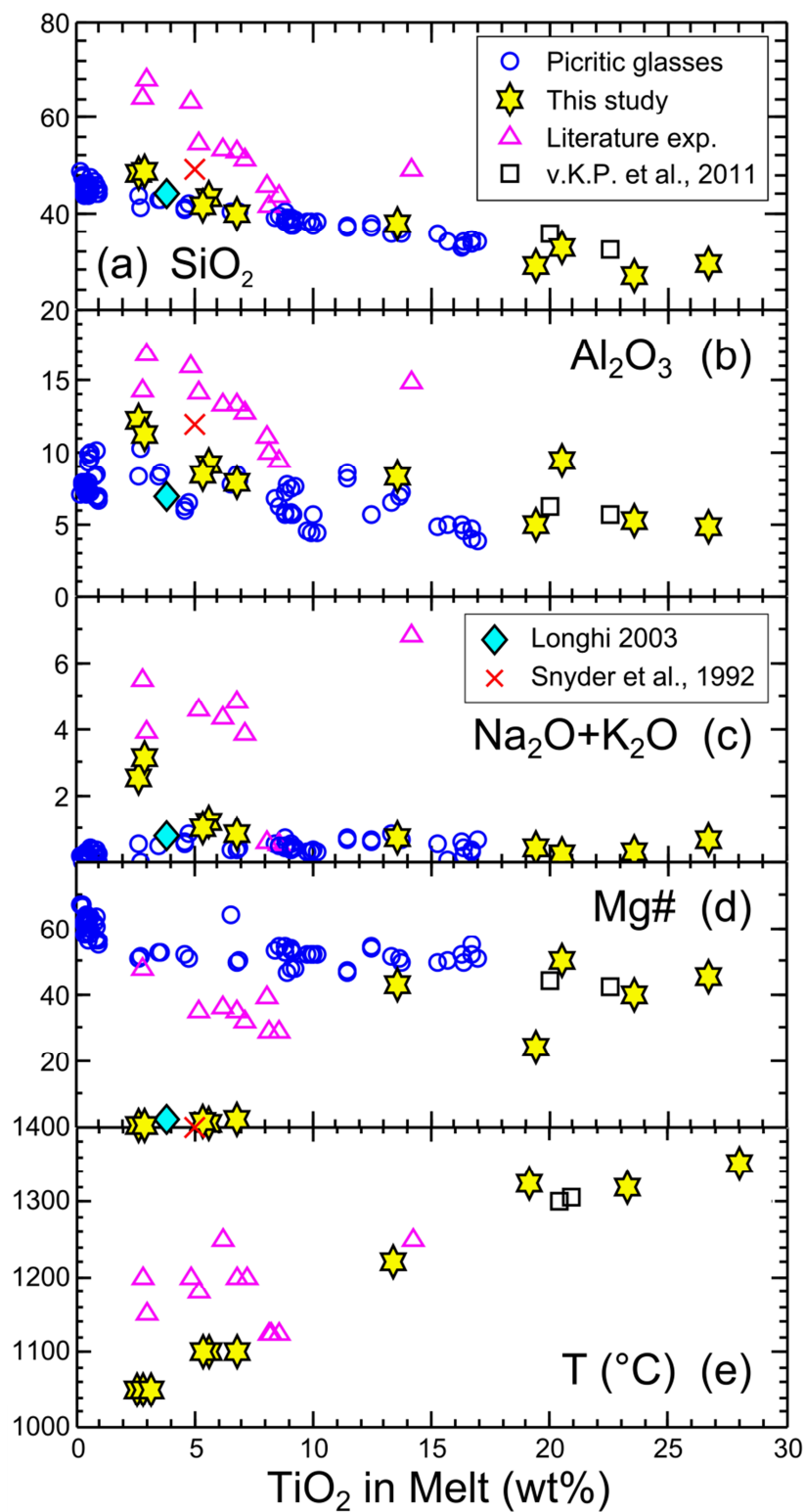


Figure 2.

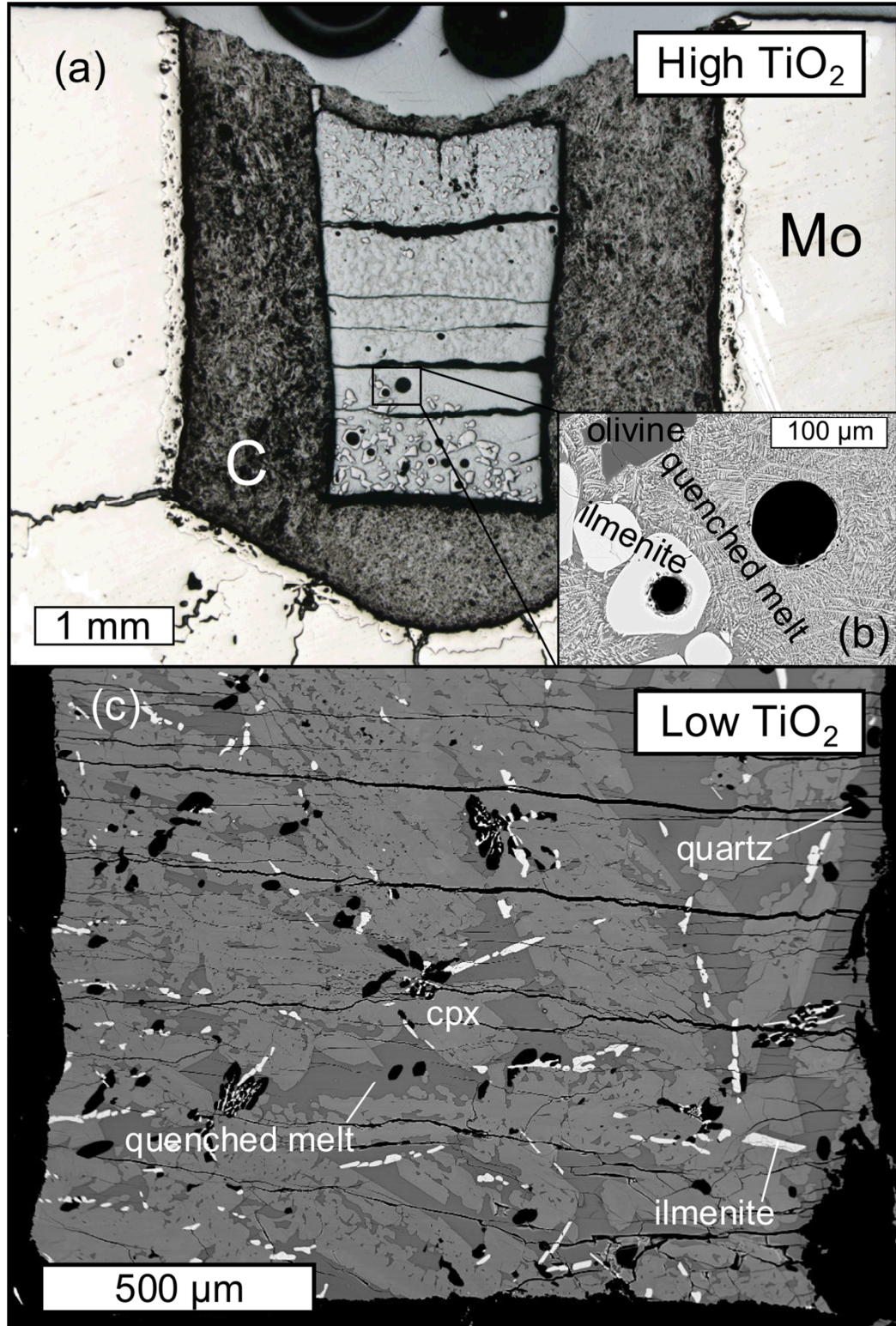


Figure 3.

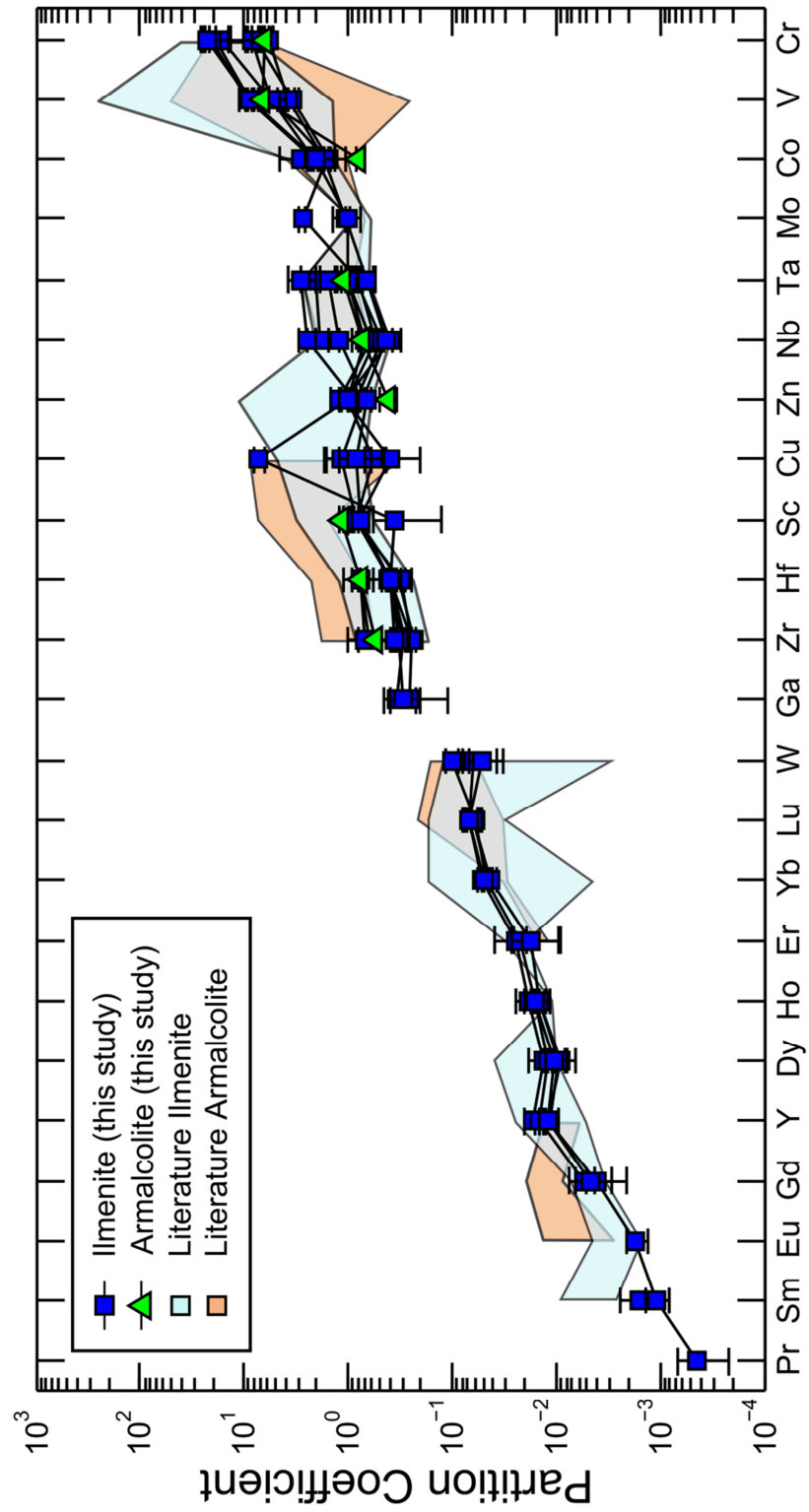


Figure 4.

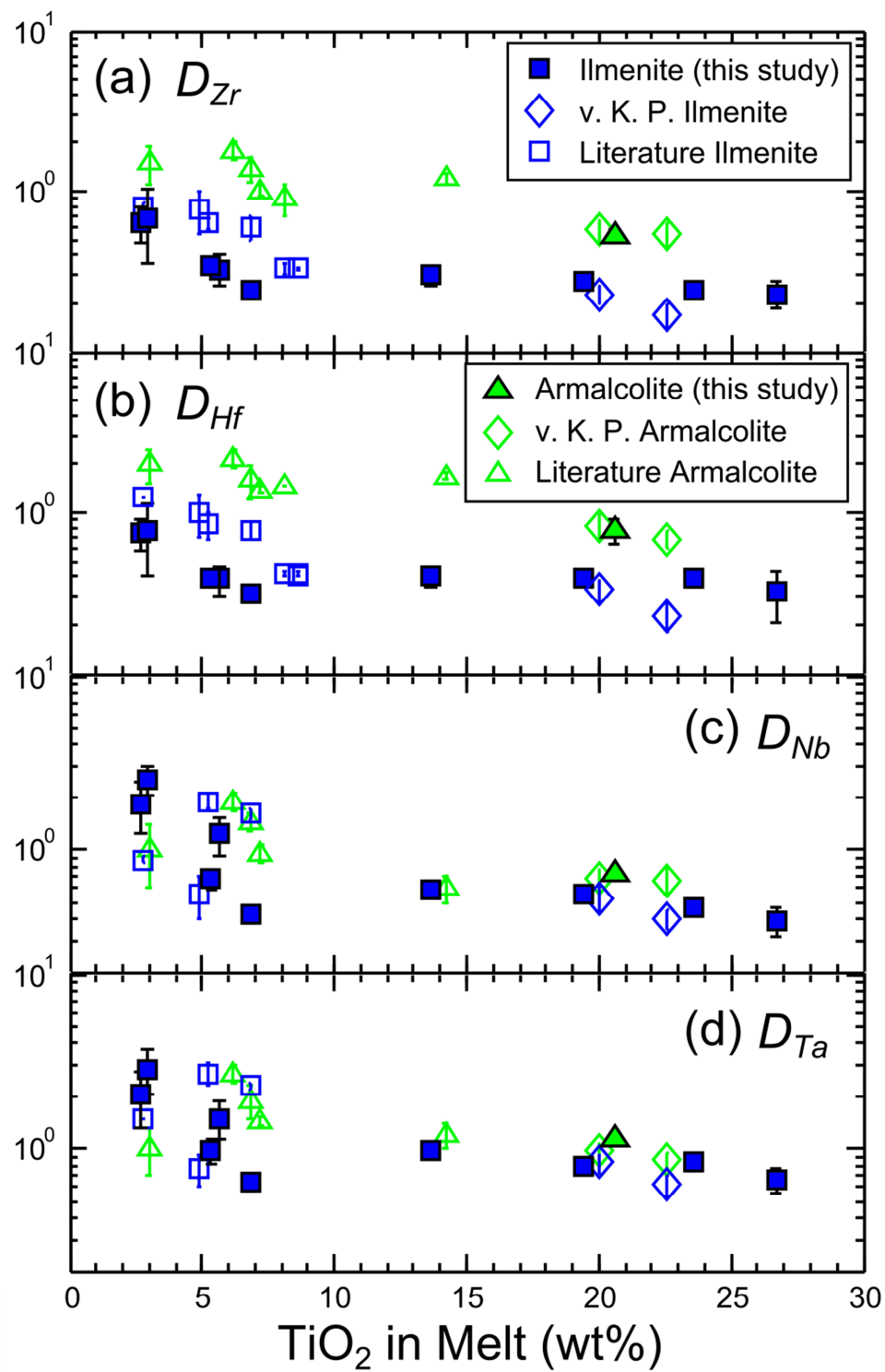


Figure 5.

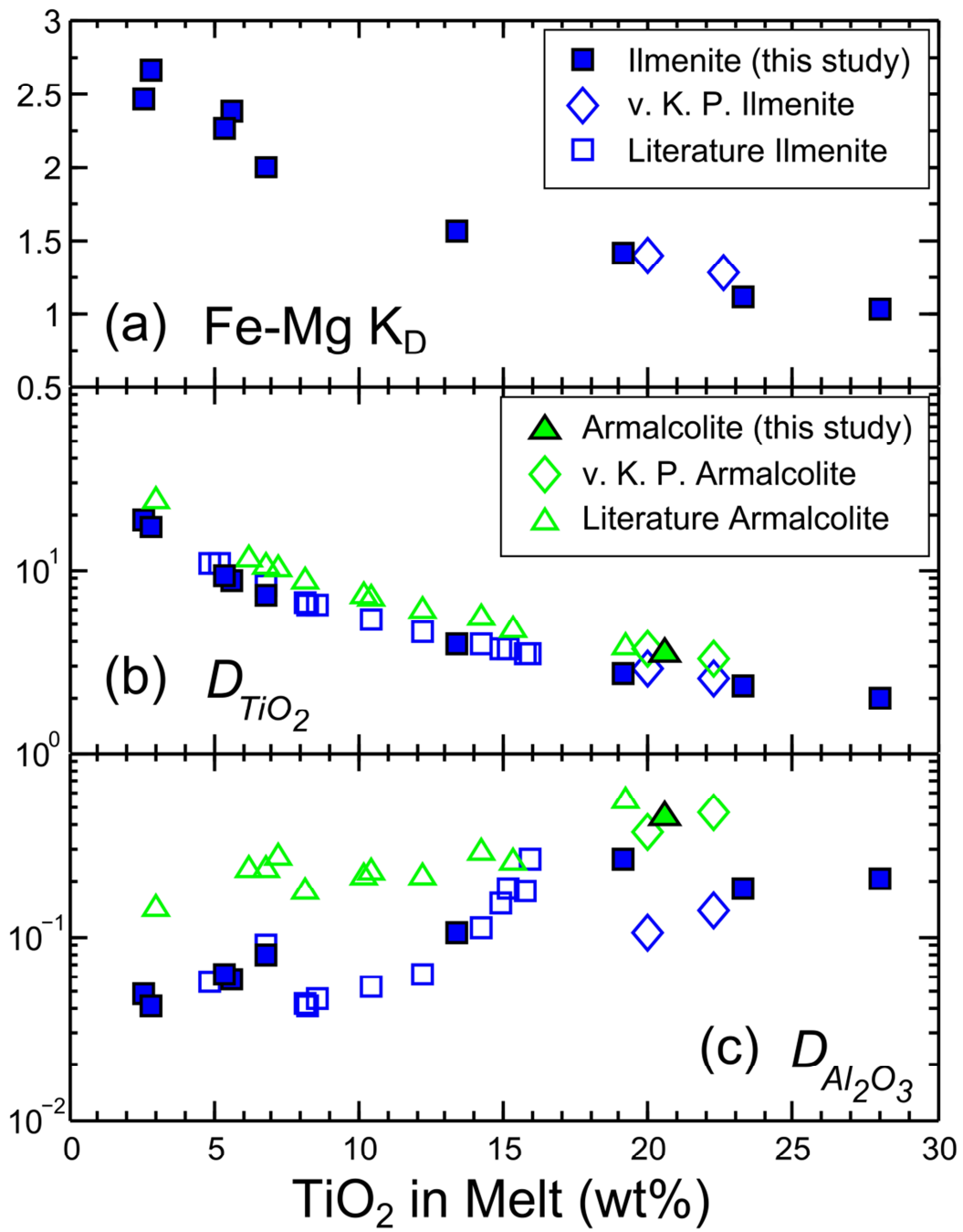


Figure 6.

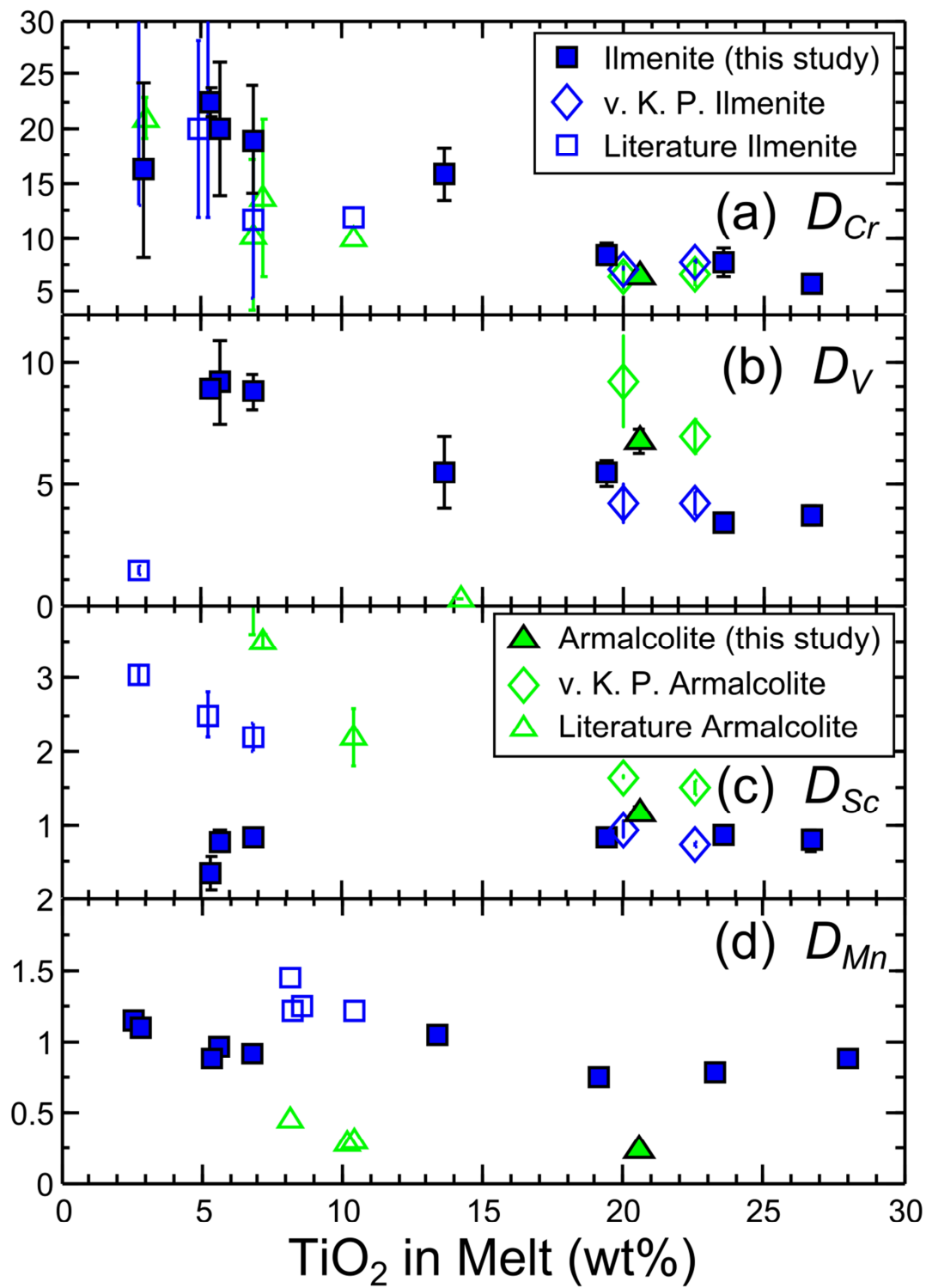


Figure 7.

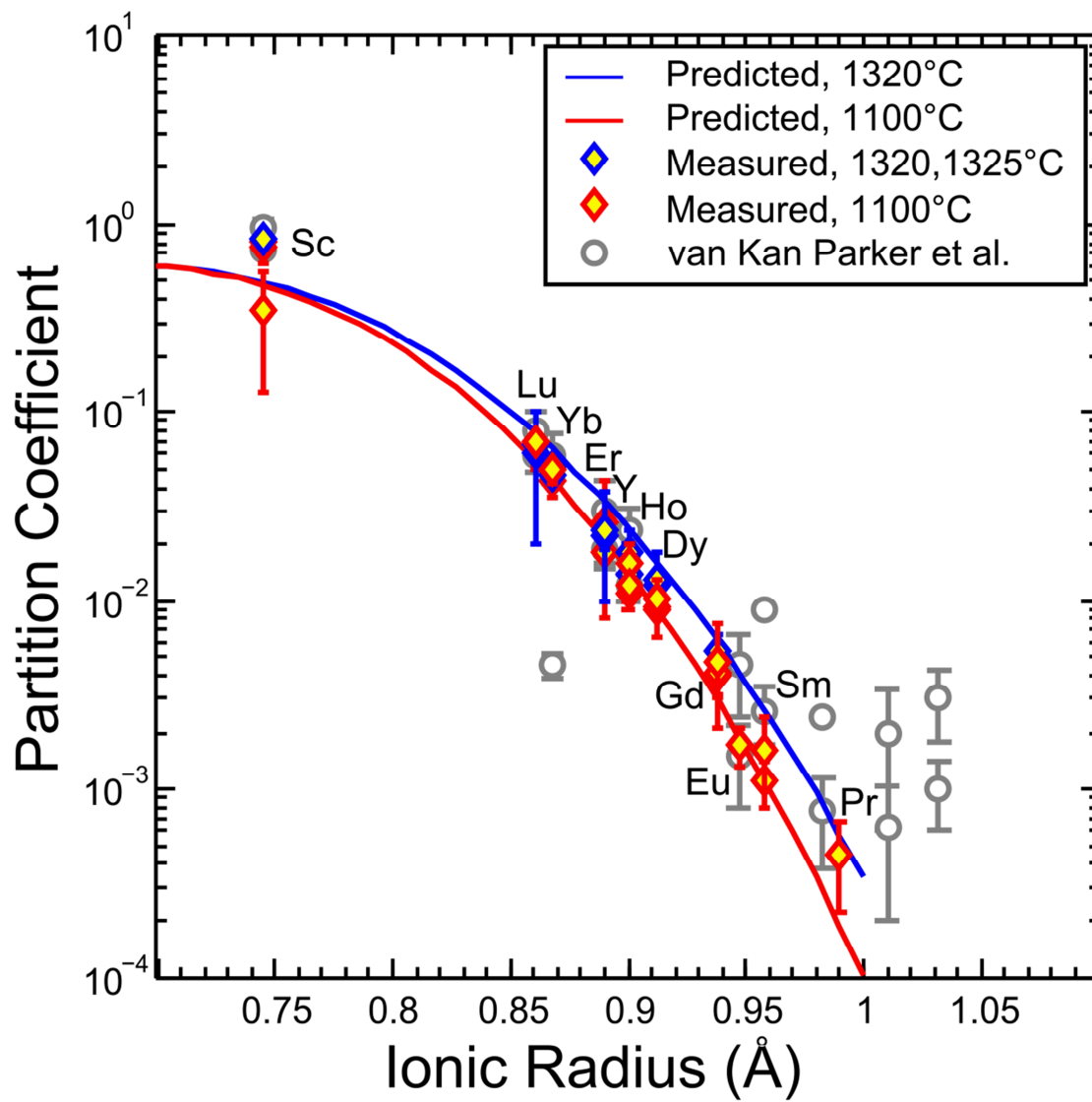


Figure 8.

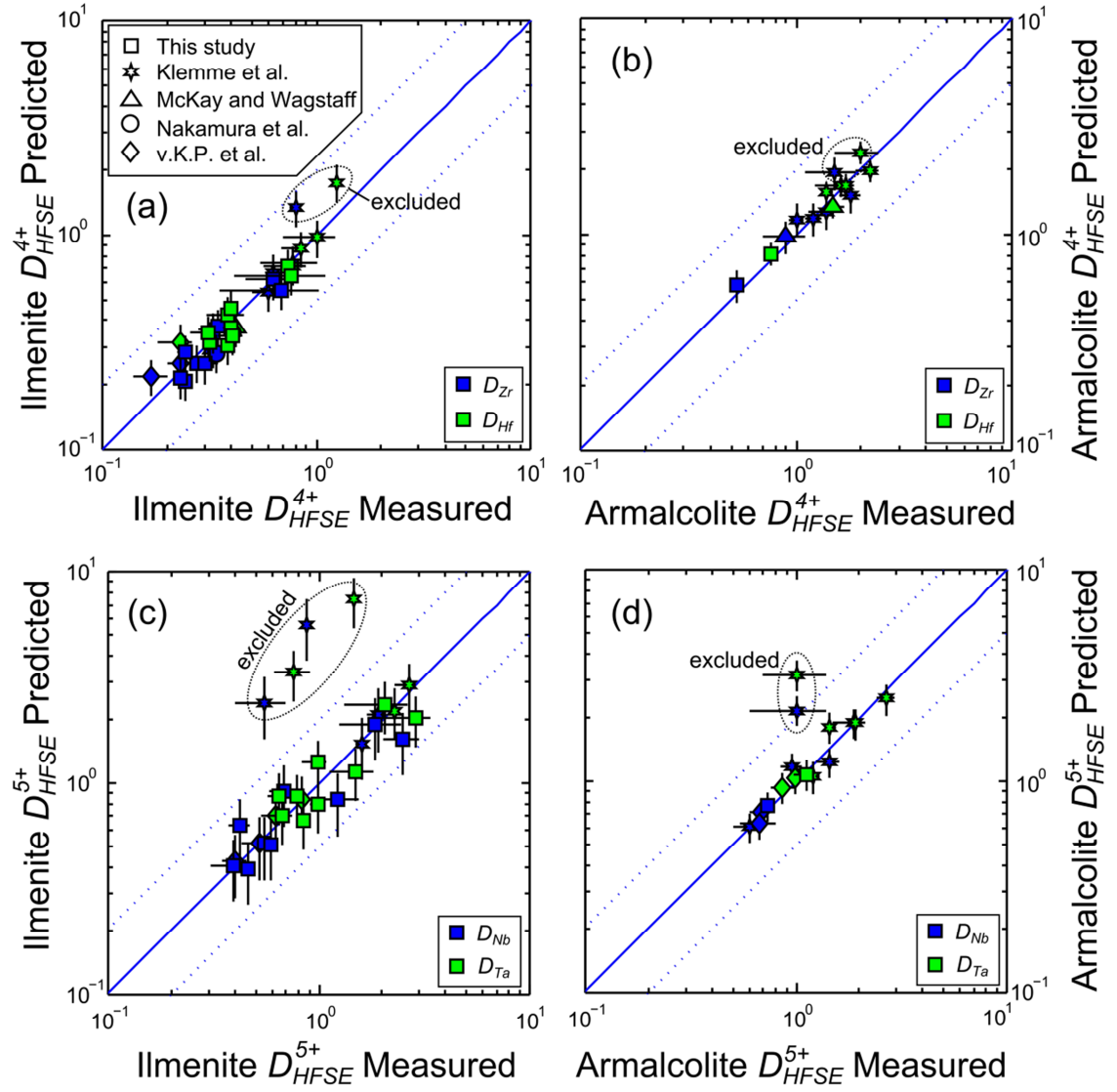


Figure 9.

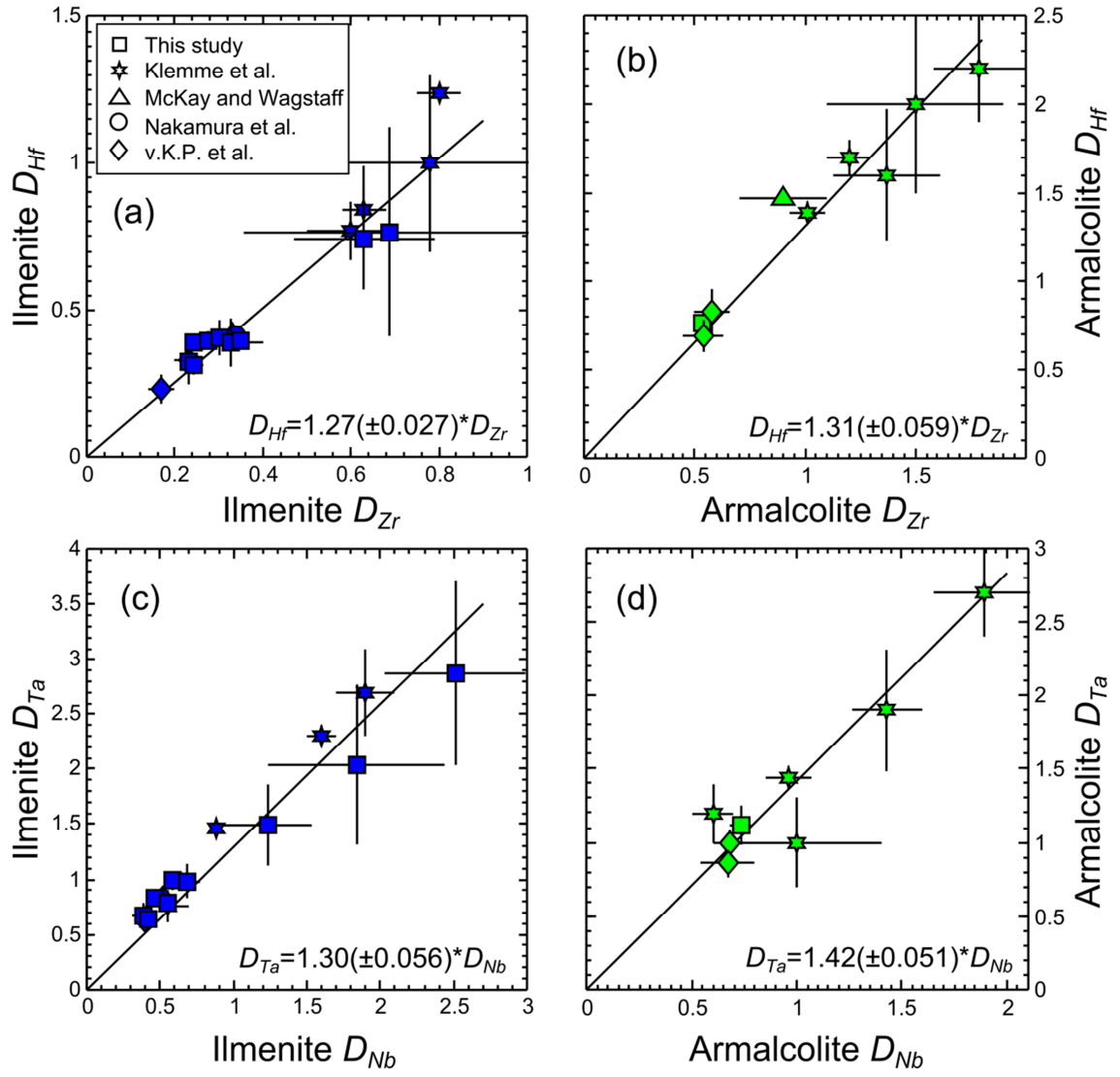


Figure 10.

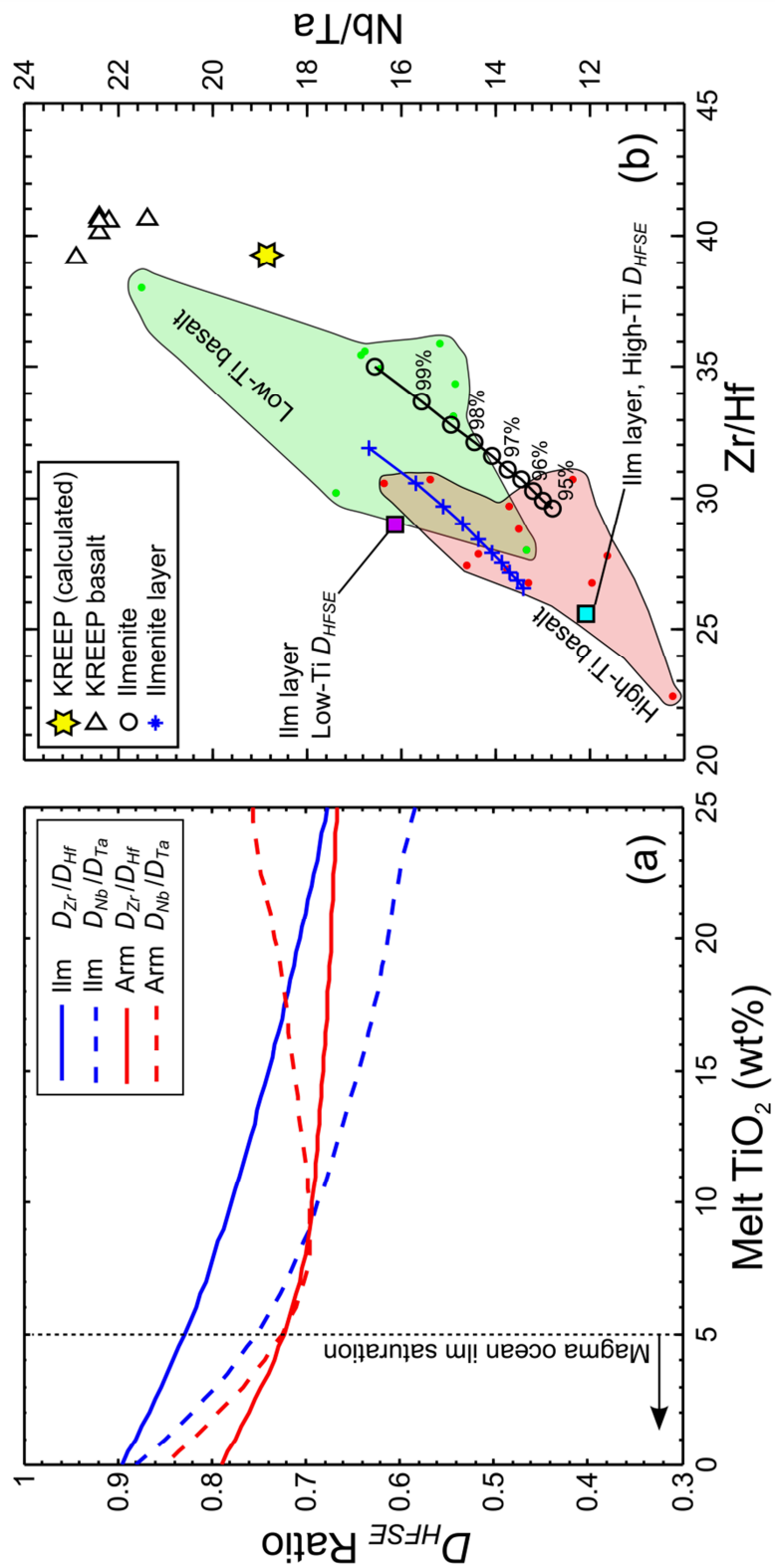


Figure 11.

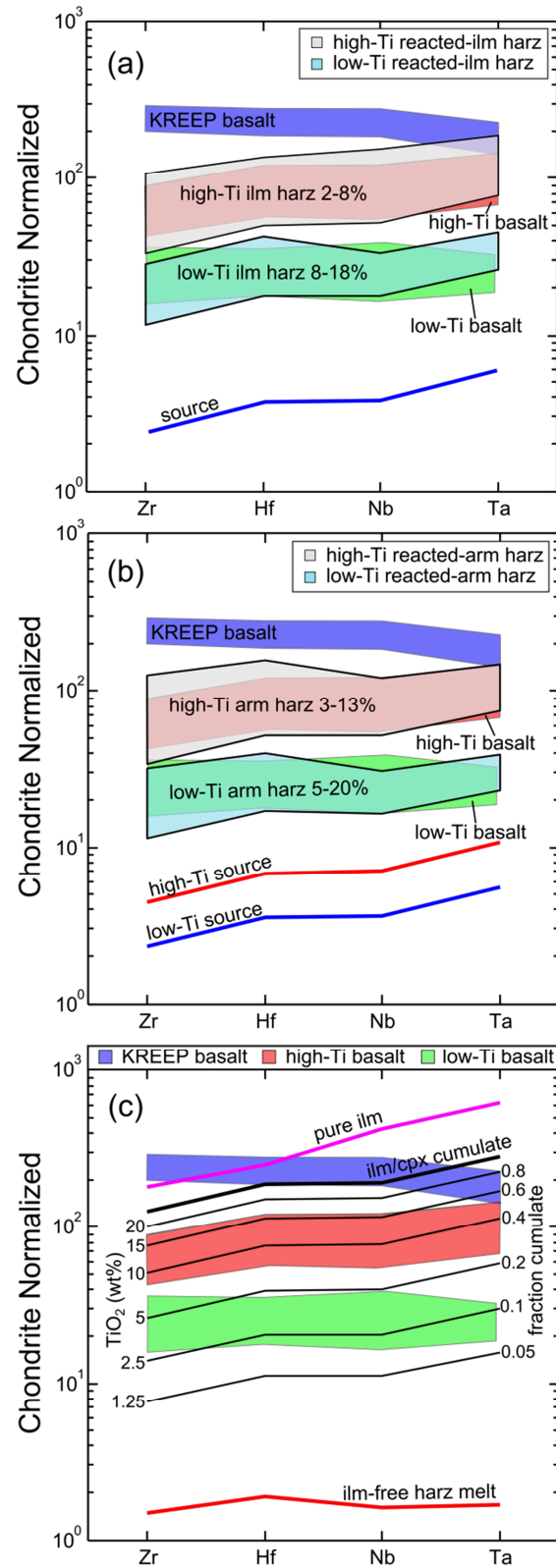


Table 1.

Summary of experimental runs.					
Experiment	Pressure (GPa)	T (°C)	Duration (h)	Starting Composition	Run Products ^a
NJD-2	1.2	1350	48	30% Ilm + 70% Lhz ^b Mixture	Ilm + Silicates + Melt
NJD-7M ^d	1.0	1320	48	17.5% Ilm + 52.5% Hrz ^c + 30% A15 RG	Ilm + Silicates + Melt
NJD-8M	2.0	1325	46	50% Ilm + 50% A15 RG	Ilm + Melt
NJD-10M	1.0	1320	46.5	25% Ilm + 75% Hrz Mixture	Arm + Silicates + Melt
NJD-15M	1.5	1050	47.5	FR-1290	Ilm + Silicates + Melt
NJD-16M	1.4	1220	58.5	A15 RG	Ilm + Silicates + Melt
NJD-17M	1.5	1100	60	17% Ilm + 83% FR-1290	Ilm + Silicates + Melt
NJD-18M	1.5	1050	48.5	FR-1290	Ilm + Silicates + Melt
NJD-19M	1.5	1100	57	9% Ilm + 91% FR-1290	Ilm + Silicates + Melt
NJD-22M	1.5	1100	48	21% Ilm + 79% FR-1290	Ilm + Silicates + Melt
Ilm, Ilmenite; Arm, Armalcolite; Lhz, Lherzolite; Hrz, Harzburgite; A15 RG, Synthetic Apollo 15 red glass; FR-1290, FR-1290 (Longhi 2003).					

Ilm, Ilmenite; Arm, Armalcolite; Lhz, Lherzolite; Hrz, Harzburgite; A15 RG, Synthetic Apollo 15 red glass; FR-1290, FR-1290 (Longhi 2003).

(a) Trace amounts of chrome spinel are present in most runs, however it is difficult to distinguish from Fe-Ti oxides optically and is not reported here for individual experiments.

(b) Lherzolite Composition: 49% Olivine, 33% Orthopyroxene, 18% Clinopyroxene.

(c) Harzburgite Composition: 67% Olivine, 33% Orthopyroxene.

(d) M denotes graphite lined molybdenum capsule.

Table 2.

Average electron microprobe analyses of Fe-Ti oxides, melt, and olivine.

Experiment	n ^b	Phase	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO
NJD-2	23	Ilm	0.1 (1)	55.9 (5)	1.00 (8)	1.74 (4)	27.0 (4)
	6	Melt	28.9 (10)	28.0 (14)	4.7 (6)	0.26 (4)	21.7 (3)
	13	Olivine	38.9 (5)	0.3 (2)	0.07 (4)	0.08 (2)	17.7 (2)
NJD-7M ^a	13	Ilm	-	54.04 (7)	0.97 (7)	1.18 (6)	31.24 (4)
	6	Melt	27.1 (18)	23.3 (15)	5.4 (6)	0.13 (2)	27.7 (8)
	5	Olivine	38.5 (3)	0.3 (1)	0.06 (3)	0.04 (1)	21.9 (3)
NJD-8M	7	Ilm	0.05 (3)	51.7 (2)	1.29 (9)	0.89 (3)	39.7 (2)
	9	Melt	28.8 (14)	19.1 (14)	4.9 (4)	0.08 (3)	31.9 (7)
NJD-10M	10	Arm	-	73.0 (3)	3.5 (1)	0.90 (2)	13.1 (1)
	8	Melt	32.3 (15)	20.4 (28)	9.3 (8)	0.12 (3)	21.7 (25)
NJD-15M	9	Ilm	-	49.3 (4)	0.53 (9)	0.17 (7)	48.8 (2)
	8	Melt	47.1 (7)	2.6 (1)	11.9 (4)	-	23.1 (3)
NJD-16M	14	Ilm	-	54.5 (5)	0.9 (4)	3.5 (3)	33.1 (2)
	10	Melt	37.3 (5)	13.4 (2)	8.2 (2)	0.21 (3)	20.5 (3)
NJD-17M	10	Ilm	-	51.5 (3)	0.7 (2)	0.18 (1)	46.7 (2)
	8	Melt	39.3 (4)	6.8 (5)	7.7 (1)	-	31.3 (3)
NJD-18M	13	Ilm	-	50.6 (4)	0.6 (2)	0.26 (2)	47.6 (2)
	9	Melt	47.1 (7)	2.79 (7)	10.9 (2)	-	23.1 (4)
NJD-19M	12	Ilm	-	50.6 (3)	0.6 (1)	0.26 (2)	47.6 (1)
	14	Melt	42.4 (4)	5.6 (3)	9.0 (2)	-	29.2 (5)
NJD-22M	10	Ilm	-	49.2 (6)	0.53 (2)	0.13 (4)	46.6 (7)
	10	Melt	41.6 (3)	5.3 (2)	8.5 (1)	-	28.9 (4)

Oxide abundances reported in wt %.

Numbers in parantheses indicate two sigma standard deviation of replicate analyses in terms of last significant numbers.

(a) M denotes graphite lined molybdenum capsule.

(b) Number of averaged analyses.

(c) Sum of HFSE+REE+transition metals measured by LA-ICP-MS calculated as oxides.

Table 2 (continued).

Experiment	Phase	MgO	MnO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Spec ^c	Total	Mg #
NJD-2	Ilm	12.1 (4)	1.13 (6)	0.05 (3)	-	-	-	0.32	99.3	44.4
	Melt	9.7 (21)	1.34 (6)	5.9 (6)	0.64 (9)	-	-	0.26	101.4	44.2
	Olivine	41.7 (8)	0.91 (4)	0.14 (3)	-	-	-	-	99.8	80.7
NJD-7M ^a	Ilm	10.5 (2)	1.13 (6)	-	-	-	-	0.37	99.4	37.4
	Melt	10.3 (20)	1.47 (9)	4.0 (6)	0.3 (2)	0.02 (2)	-	1.30	101.0	39.8
	Olivine	39.1 (2)	1.02 (4)	0.11 (2)	-	-	-	-	101.0	76.1
NJD-8M	Ilm	4.96 (7)	1.37 (4)	-	-	-	-	0.42	99.9	18.2
	Melt	5.7 (5)	1.81 (4)	6.2 (5)	0.36 (5)	-	-	2.18	101.0	24.2
	Arm	10.28 (7)	0.31 (3)	-	-	-	-	0.30	101.4	58.3
NJD-10M	Melt	12.2 (18)	1.4 (2)	1.2 (6)	0.2 (1)	-	-	0.31	99.1	50.1
	Ilm	0.05 (1)	0.71 (8)	-	-	-	-	1.36	100.9	0.19
	Melt	0.07 (1)	0.65 (3)	8.2 (2)	1.25 (5)	1.2 (1)	1.1 (2)	1.67	98.9	0.53
NJD-16M	Ilm	8.8 (2)	0.41 (3)	-	-	-	-	0.14	101.4	32.1
	Melt	8.5 (1)	0.40 (3)	8.4 (1)	0.53 (3)	0.17 (3)	0.05 (2)	0.88	99.4	42.9
	Ilm	0.29 (2)	1.82 (6)	-	-	-	-	0.21	101.4	1.1
NJD-17M	Melt	0.39 (4)	1.99 (7)	9.8 (1)	0.47 (3)	0.31 (2)	0.33 (5)	0.79	99.2	2.2
	Ilm	0.13 (1)	1.25 (5)	-	-	-	-	1.11	101.5	0.49
	Melt	0.05 (2)	0.54 (5)	7.7 (1)	1.32 (6)	1.71 (9)	1.2 (1)	1.65	98.0	0.40
NJD-19M	Ilm	0.13 (1)	1.25 (5)	-	-	-	-	0.29	100.7	0.49
	Melt	0.19 (2)	1.34 (5)	9.0 (2)	0.63 (4)	0.52 (7)	0.5 (1)	0.97	99.4	1.2
	Ilm	0.20 (2)	1.7 (1)	-	-	-	-	0.29	98.6	0.75
NJD-22M	Melt	0.28 (1)	1.98 (7)	9.46 (9)	0.6 (1)	0.41 (1)	0.37 (4)	0.80	98.2	1.7

Table 3.

Mineral-melt partition coefficients for Fe-Ti oxides.						
	NJD-10M ^a		NJD-2		NJD-7M	
	Arm/Melt		Ilm/Melt		Ilm/Melt	
Sc	1.16	(8)	0.79	(15)	0.85	(5)
V	6.7	(5)	3.7	(4)	3.4	(4)
Cr	6.4	(5)	5.9	(6)	7.7	(1.4)
Co	0.78	(6)	1.7	(2)	1.5	(2)
Cu	-		0.40	(20)	-	
Zn	0.41	(7)	1.1	(1)	0.84	(16)
Ga	-		-		-	
Mo	-		1.06	(32)	-	
Pr	-		-		-	
Sm	-		-		-	
Eu	-		-		-	
Gd	-		-		0.0054	(12)
Dy	-		-		0.013	(5)
Ho	-		-		0.018	(6)
Er	-		-		0.024	(14)
Yb	-		-		0.051	(7)
Lu	-		-		0.067	(10)
Y	-		0.014	(2)	0.016	(4)
Zr	0.53	(5)	0.23	(8)	0.24	(2)
Nb	0.73	(3)	0.42	(6)	0.46	(3)
Hf	0.76	(14)	0.32	(12)	0.38	(4)
Ta	1.12	(8)	0.67	(10)	0.84	(8)
W	-		-		0.062	(25)
TiO ₂ in melt (wt%)	20.4		28.0		23.3	
n ^b Oxide	5		4		7	
n Melt	2		4		6	

Numbers in parantheses indicate two sigma standard deviation of replicate analyses in terms of last significant numbers.

Ilm, Ilmenite; Arm, Armalcolite.

(a) M denotes graphite lined molybdenum capsule.

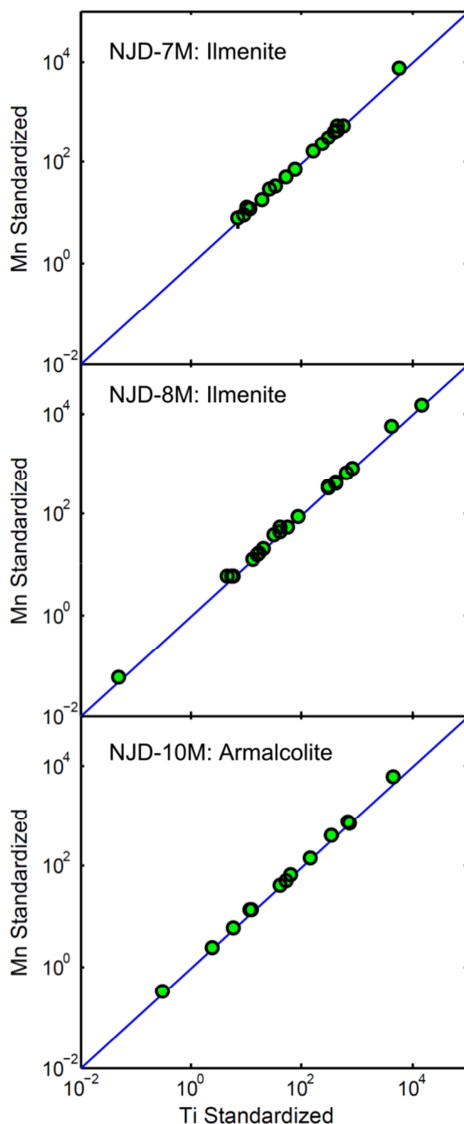
(b) Number of averaged analyses.

Table 3 (continued).

	NJD-16M	NJD-17M	NJD-18M	NJD-19M	NJD-22M
	Ilm/Melt	Ilm/Melt	Ilm/Melt	Ilm/Melt	Ilm/Melt
Sc	-	0.82 (10)	-	0.77 (15)	0.35 (22)
V	5.5 (15)	8.8 (7)	-	9.2 (17)	8.9 (4)
Cr	15.8 (25)	19.0 (49)	16 (8)	20 (6)	22.4 (13)
Co	2.2 (2)	2.0 (2)	-	2.2 (3)	2.0 (3)
Cu	-	1.15 (48)	-	0.8 (4)	7.23 (85)
Zn	1.19 (25)	0.72 (13)	0.9 (3)	0.67 (7)	1.02 (17)
Ga	0.34 (12)	0.25 (14)	-	0.30 (10)	-
Mo	-	-	-	-	1.02 (4)
Pr	-	-	-	0.00044 (22)	-
Sm	-	0.0016 (8)	-	0.0011 (3)	-
Eu	-	-	-	0.0017 (4)	-
Gd	-	0.0041 (9)	-	0.004 (1)	0.0048 (27)
Dy	-	0.0094 (10)	-	0.0091 (27)	0.0104 (24)
Ho	-	0.014 (2)	-	0.014 (2)	0.016 (4)
Er	-	0.026 (18)	-	0.018 (8)	-
Yb	0.07 (3)	0.046 (6)	-	0.043 (7)	0.049 (7)
Lu	0.41 (6)	0.062 (8)	-	0.06 (1)	0.070 (5)
Y	-	0.011 (2)	-	0.012 (2)	0.012 (3)
Zr	0.30 (5)	0.24 (2)	0.69 (33)	0.33 (7)	0.35 (2)
Nb	0.59 (4)	0.42 (5)	2.5 (5)	1.23 (30)	0.68 (9)
Hf	0.41 (6)	0.31 (3)	0.77 (35)	0.38 (8)	0.40 (1)
Ta	0.99 (8)	0.65 (8)	2.87 (84)	1.5 (4)	0.98 (16)
W	-	-	-	-	0.051 (19)
TiO ₂ in melt (wt%)	13.4	6.8	2.8	5.6	5.3
n ^b Oxide	4	8	4	3	4
n Melt	5	10	4	4	4

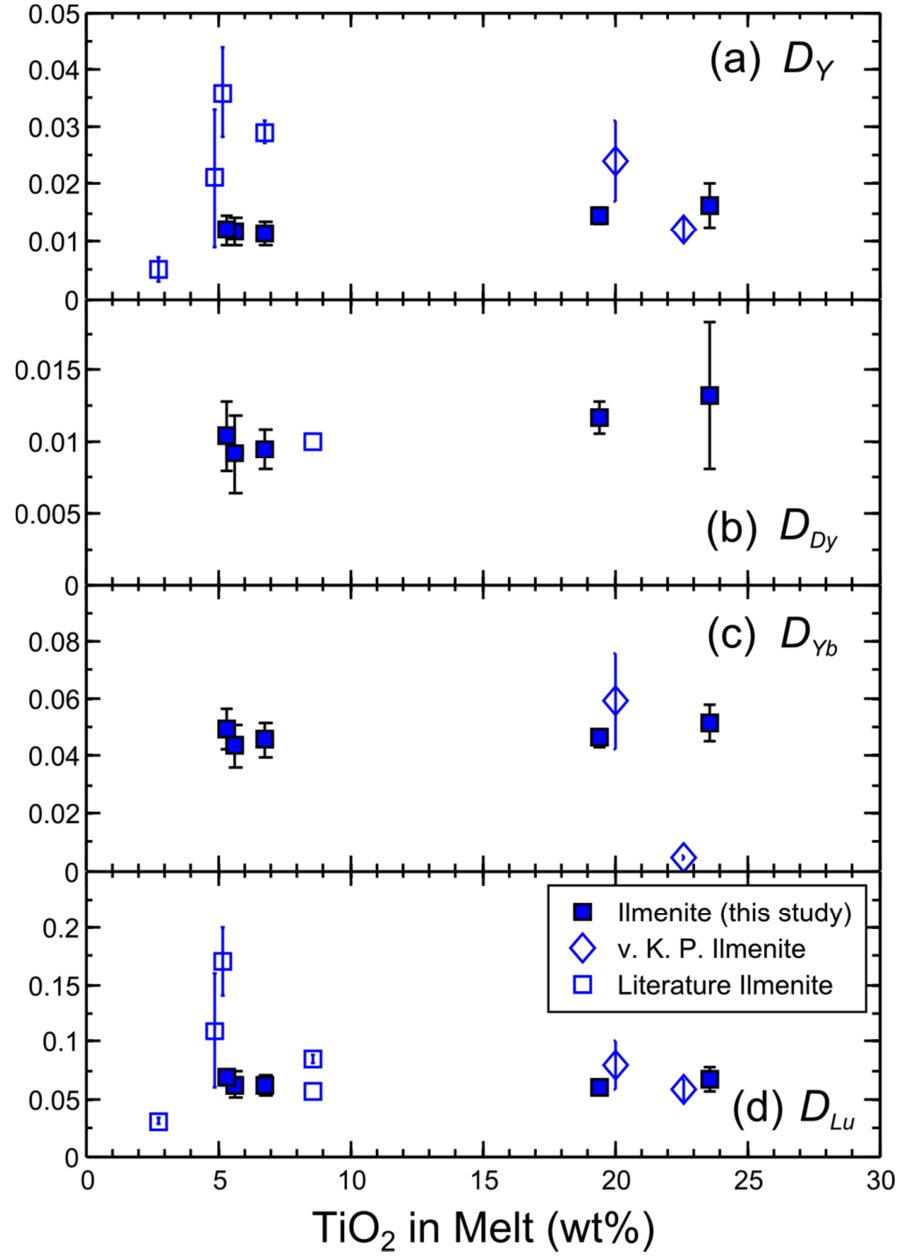
Supplementary Material

Figure S1.



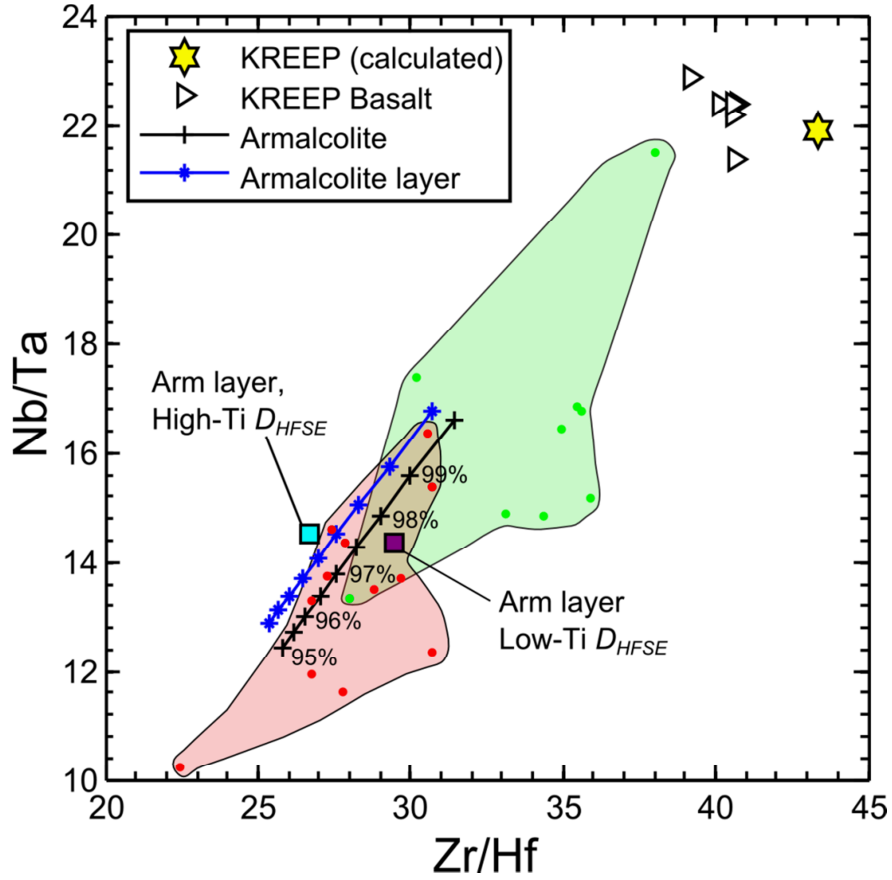
Comparison between Mn and Ti standardized trace element concentrations for Fe-Ti oxides from three runs. Data falls along the 1:1 lines (blue) suggesting that either element is an appropriate calibration analyte. The error bars on the analyses are almost all smaller than the symbols. Ti was used in data processing for partition coefficients reported here because microprobe analyses of Ti, which is much more abundant than Mn, have smaller uncertainties.

Figure S2.



Variations of Y and middle to heavy REE partition coefficients for ilmenite-melt as a function of melt TiO_2 . Literature data includes the studies of McKay and Wagstaff (1985), Nakamura et al. (1986), Klemme et al. (2006), and van Kan Parker et al. (2011).

Figure S3.



Variations of Nb/Ta and Zr/Hf ratios in lunar low-Ti basalts (green circles), high-Ti basalts (red circles), and KREEP basalts (white triangles). Superimposed over the lunar data are calculated cumulate compositions produced by crystallization of the lunar magma ocean (LMO) (Snyder et al., 1992) with modifications in starting composition and phase proportions made by Münker (2010) and assuming armalcolite is the crystallizing Fe-Ti oxide phase. Three models are presented. In Model 1 (cyan square), constant high-Ti D_{HFSE} from NJD-10M (D_{Zr} 0.53, D_{Hf} 0.76, D_{Nb} 0.73, D_{Ta} 1.12) are used. In Model 2 (purple square), average low-Ti D_{HFSE} from four experiments (3.0-7.2% TiO_2 , Klemme et al., 2006) are used (D_{Zr} 1.42 D_{Hf} 1.80, D_{Nb} 1.32, D_{Ta} 1.76). In Model 3,

variable D_{HFSE} calculated using Eqs. 7-10 are used (blue and black crosses joined by solid lines). The squares (and blue crosses for Model 3) represent compositions of armalcolite bearing cumulates (in proportions of 46% pigeonite, 2% plagioclase, 33% clinopyroxene, 15% armalcolite, and 3% trapped liquid) formed between 95% and 99.5% crystallization of LMO. Black crosses are pure armalcolite compositions at 0.5% crystallization intervals. Assuming Model 3 best predicts D_{HFSE} for an armalcolite saturated magma ocean, ilmenite-bearing cumulates (Figure 10b) better match the lunar basalts than the armalcolite-bearing cumulates presented in in this figure. Armalcolite low-Ti and high-Ti partition coefficients (Models 1 and 2) produce armalcolite cumulate compositions similar to Model 3. Melting, KREEP assimilation, or reaction of armalcolite with early mafic cumulates could produce the low-Ti (and much of the high-Ti) data. The result presented here does not rule out armalcolite as an important component of a crystallizing LMO.

Table S1.

Major element compositions of peridotite and ilmenite starting materials				
	Olivine	Opx	Cpx	Ilmenite
SiO ₂	41.02 (13)	55.40 (25)	52.22 (23)	-
TiO ₂	-	0.10 (1)	0.36 (4)	49.5
Al ₂ O ₃	-	4.47 (62)	6.73 (45)	-
Cr ₂ O ₃	0.12 (1)	0.62 (12)	0.98 (7)	-
FeO	8.66 (7)	5.85 (47)	3.23 (39)	45.2
NiO	0.34 (2)	-	-	-
MnO	0.14 (1)	0.13 (2)	0.06 (2)	3.5
MgO	50.13 (14)	32.43 (50)	17.54 (100)	0.3
CaO	0.31 (3)	1.71 (71)	18.98 (98)	-
Na ₂ O	-	0.06 (1)	0.69 (23)	-
K ₂ O	-	-	-	-
P ₂ O ₅	-	-	-	-
Total	100.72	100.76	100.78	98.5
Mg#	91.16	90.81	90.63	1.17
n ^a	23	12	33	

Concentrations reported in weight %.

Number in parantheses is 1 sigma standard deviation of least significant figures.

(a) Number of averaged analyses.

Table S2

Ilmenite chemical formulas calculated on a 3 oxygen basis.

NJD-2									
Oxide	Weight %	Moles Oxide	Moles Cation	Oxygens	Species	Cation Proportion			
TiO ₂	55.72	0.70	0.70	1.40	Ti ⁴⁺	0.97			
Al ₂ O ₃	0.99	0.01	0.02	0.03	Al ³⁺	0.03			
Cr ₂ O ₃	1.73	0.01	0.02	0.03	Cr ³⁺	0.03			
FeO	27.04	0.38	0.38	0.38	Fe ²⁺	0.52			
MgO	12.07	0.30	0.30	0.30	Mg ²⁺	0.42			
MnO	1.14	0.02	0.02	0.02	Mn ²⁺	0.02			
Total	98.70		Sum oxygens: Oxygen factor:	2.15 1.39	Chemical Formula:				
					Fe,Mg,Mn	0.97	Ti	0.97	Cr,Al 0.06 O 3

NJD-7M									
Oxide	Weight %	Moles Oxide	Moles Cation	Oxygens	Species	Cation Proportion			
TiO ₂	54.04	0.68	0.68	1.35	Ti ⁴⁺	0.96			
Al ₂ O ₃	0.97	0.01	0.02	0.03	Al ³⁺	0.03			
Cr ₂ O ₃	1.18	0.01	0.02	0.02	Cr ³⁺	0.02			
FeO	31.24	0.43	0.43	0.43	Fe ²⁺	0.62			
MgO	10.46	0.26	0.26	0.26	Mg ²⁺	0.37			
MnO	1.13	0.02	0.02	0.02	Mn ²⁺	0.02			
Total	99.01		Sum oxygens: Oxygen factor:	2.12 1.42	Chemical Formula:				
					Fe,Mg,Mn	1.01	Ti	0.96	Cr,Al 0.05 O 3

NJD-8M									
Oxide	Weight %	Moles Oxide	Moles Cation	Oxygens	Species	Cation Proportion			
TiO ₂	50.12	0.63	0.63	1.26	Ti ⁴⁺	0.95			
Al ₂ O ₃	1.25	0.01	0.02	0.04	Al ³⁺	0.04			
Cr ₂ O ₃	0.86	0.01	0.01	0.02	Cr ³⁺	0.02			
FeO	38.51	0.54	0.54	0.54	Fe ²⁺	0.81			
MgO	4.81	0.12	0.12	0.12	Mg ²⁺	0.18			
MnO	1.33	0.02	0.02	0.02	Mn ²⁺	0.03			
Total	96.89		Sum oxygens: Oxygen factor:	1.98 1.51	Chemical Formula:				
					Fe,Mg,Mn	1.02	Ti	0.95	Cr,Al 0.05 O 3

Table S2 continued.

NJD-15M						
Oxide	Weight %	Moles Oxide	Moles Cation	Oxygens	Species	Cation Proportion
TiO ₂	46.84	0.59	0.59	1.17	Ti ⁴⁺	0.94
Al ₂ O ₃	0.58	0.01	0.01	0.02	Al ³⁺	0.02
Cr ₂ O ₃	0.19	0.00	0.00	0.00	Cr ³⁺	0.00
FeO	48.54	0.68	0.68	0.68	Fe ²⁺	1.08
MgO	0.06	0.00	0.00	0.00	Mg ²⁺	0.00
MnO	0.73	0.01	0.01	0.01	Mn ²⁺	0.02
Total	96.95		Sum oxygens: 1.59	1.88	Chemical Formula:	
			Oxygen factor:	1.59	Fe,Mg,Mn 1.10	Ti 0.94 Cr,Al 0.02 O 3
NJD-16M						
Oxide	Weight %	Moles Oxide	Moles Cation	Oxygens	Species	Cation Proportion
TiO ₂	51.91	0.65	0.65	1.30	Ti ⁴⁺	0.94
Al ₂ O ₃	0.86	0.01	0.02	0.03	Al ³⁺	0.02
Cr ₂ O ₃	3.43	0.02	0.05	0.07	Cr ³⁺	0.07
FeO	32.92	0.46	0.46	0.46	Fe ²⁺	0.66
MgO	8.79	0.22	0.22	0.22	Mg ²⁺	0.32
MnO	0.41	0.01	0.01	0.01	Mn ²⁺	0.01
Total	98.32		Sum oxygens: 1.45	2.08	Chemical Formula:	
			Oxygen factor:	1.45	Fe,Mg,Mn 0.99	Ti 0.94 Cr,Al 0.09 O 3
NJD-17M						
Oxide	Weight %	Moles Oxide	Moles Cation	Oxygens	Species	Cation Proportion
TiO ₂	51.50	0.64	0.64	1.29	Ti ⁴⁺	0.97
Al ₂ O ₃	0.70	0.01	0.01	0.02	Al ³⁺	0.02
Cr ₂ O ₃	0.18	0.00	0.00	0.00	Cr ³⁺	0.00
FeO	46.70	0.65	0.65	0.65	Fe ²⁺	0.98
MgO	0.29	0.01	0.01	0.01	Mg ²⁺	0.01
MnO	1.82	0.03	0.03	0.03	Mn ²⁺	0.04
Total	101.19		Sum oxygens: 1.50	2.00	Chemical Formula:	
			Oxygen factor:	1.50	Fe,Mg,Mn 1.03	Ti 0.97 Cr,Al 0.02 O 3

Table S2 continued.

NJD-18M						
Oxide	Weight %	Moles Oxide	Moles Cation	Oxygens	Species	Cation Proportion
TiO ₂	46.40	0.58	0.58	1.16	Ti ⁴⁺	0.93
Al ₂ O ₃	0.45	0.00	0.01	0.01	Al ³⁺	0.01
Cr ₂ O ₃	0.03	0.00	0.00	0.00	Cr ³⁺	0.00
FeO	49.18	0.68	0.68	0.68	Fe ²⁺	1.10
MgO	0.04	0.00	0.00	0.00	Mg ²⁺	0.00
MnO	0.60	0.01	0.01	0.01	Mn ²⁺	0.01
Total	96.71		Sum oxygens:	1.87	Chemical Formula:	
			Oxygen factor:	1.60	Fe,Mg,Mn	1.11 Ti 0.93 Cr,Al 0.01 O 3
NJD-19M						
Oxide	Weight %	Moles Oxide	Moles Cation	Oxygens	Species	Cation Proportion
TiO ₂	47.94	0.60	0.60	1.20	Ti ⁴⁺	0.95
Al ₂ O ₃	0.51	0.01	0.01	0.02	Al ³⁺	0.02
Cr ₂ O ₃	0.25	0.00	0.00	0.00	Cr ³⁺	0.01
FeO	47.40	0.66	0.66	0.66	Fe ²⁺	1.04
MgO	0.13	0.00	0.00	0.00	Mg ²⁺	0.01
MnO	1.27	0.02	0.02	0.02	Mn ²⁺	0.03
Total	97.50		Sum oxygens:	1.90	Chemical Formula:	
			Oxygen factor:	1.58	Fe,Mg,Mn	1.07 Ti 0.95 Cr,Al 0.02 O 3
Ilmenite chemical formula calculated on a 3 oxygen basis.						
NJD-22M						
Oxide	Weight %	Moles Oxide	Moles Cation	Oxygens	Species	Cation Proportion
TiO ₂	49.20	0.62	0.62	1.23	Ti ⁴⁺	0.93
Al ₂ O ₃	0.53	0.01	0.01	0.02	Al ³⁺	0.01
Cr ₂ O ₃	0.13	0.00	0.00	0.00	Cr ³⁺	0.00
FeO	46.56	0.65	0.65	0.65	Fe ²⁺	0.92
MgO	0.20	0.00	0.00	0.00	Mg ²⁺	0.00
MnO	1.74	0.02	0.02	0.02	Mn ²⁺	0.03
Total	98.32		Sum oxygens:	1.93	Chemical Formula:	
			Oxygen factor:	1.56	Fe,Mg,Mn	0.97 Ti 0.93 Cr,Al 0.02 O 3

Table S2 continued.

Armalcolite chemical formula calculated on a 5 oxygen basis.						
NJD-10M						
Oxide	Weight %	Moles Oxide	Moles Cation	Oxygens	Species	Cation Proportion
TiO ₂	73.00	0.91	0.91	1.83	Ti ⁴⁺	1.91
Al ₂ O ₃	3.50	0.03	0.07	0.10	Al ³⁺	0.14
Cr ₂ O ₃	0.90	0.01	0.01	0.02	Cr ³⁺	0.02
FeO	13.10	0.18	0.18	0.18	Fe ²⁺	0.38
MgO	10.28	0.26	0.26	0.26	Mg ²⁺	0.53
MnO	0.31	0.00	0.00	0.00	Mn ²⁺	0.01
Total	101.09		Sum oxygens:	2.39	Chemical Formula:	
			Oxygen factor:	2.09	Fe,Mg,Mn	0.92 Ti 1.91 Cr,Al 0.17 O 5

Table S3.

Trace element abundances, minerals and melt.														
	NJD-2			NJD-7M ^a				NJD-8M						
	Ilm		Melt		Ilm		Melt		Olivine		Ilm		Melt	
n ^b	4		4		7		6		3		4		4	
Sc	34	(6)	42	(2)	13	(2)	22	(1)	3.7	(3)	16.8	(9)	20.3	(5)
V	757	(83)	206	(8)	-		124	(10)	10.5	(5)	357	(15)	66	(6)
Cr	-		1720	(17)	419	(38)	972	(128)	298	(21)	5566	(126)	658	(79)
Co	86	(5)	52	(4)	30	(2)	49	(4)	75.7	(9)	43.4	(8)	26.8	(9)
Ni	708	(143)	245	(50)	74	(5)	217	(26)	924	(74)	54	(2)	22	(2)
Cu	14	(7)	35	(4)	-		25	(3)			6	(1)	11	(2)
Zn	334	(39)	311	(17)	306	(23)	362	(61)	309	(5)	439	(55)	431	(23)
Ga	-		-		-		-		-		-		-	
Y	-		18	(1)	9	(2)	575	(54)	6	(1)	16	(1)	1090	(70)
Zr	16	(6)	71	(4)	168	(7)	693	(46)	5.4	(9)	324	(7)	1179	(68)
Nb	328	(62)	843	(47)	549	(31)	1182	(31)	13	(3)	818	(19)	1485	(74)
Mo	3.0	(9)	2.8	(2)	-		1572	(321)	35.7	(2)	15356	(237)	5632	(392)
La	-		6.5	(4)	-		526	(55)	-		-		994	(110)
Ce	-		22	(1)	-		511	(48)	-		-		927	(125)
Pr	-		1.4	(1)	-		457	(50)	-		-		869	(94)
Nd	-		5.6	(4)	-		457	(42)	-		-		866	(66)
Sm	-		1.6	(2)	-		503	(50)	-		-		962	(80)
Eu	-		0.50	(3)	-		555	(56)	-		-		1053	(90)
Tb	-		0.48	(2)	-		0.26	(2)	-		-		0.36	(2)
Gd	-		2.3	(2)	-		593	(51)	-		6	(1)	1132	(67)
Dy	-		4.2	(3)	8	(3)	590	(55)	-		13	(1)	1120	(61)
Ho	-		1.06	(7)	12	(3)	654	(82)	-		20	(1)	1265	(87)
Er	-		3.5	(1)	0.04	(3)	1.8	(2)	-		0.06	(1)	2.5	(2)
Tm	-		0.57	(1)	-		0.32	(5)	-		-		0.42	(4)
Yb	-		3.9	(3)	33	(3)	652	(56)	-		57	(2)	1227	(70)
Lu	-		0.45	(3)	53	(4)	783	(100)	-		90	(3)	1486	(85)
Hf	0.6	(2)	1.9	(3)	234	(15)	605	(42)	5	(1)	412	(10)	1040	(44)
Ta	3.3	(5)	4.9	(2)	438	(36)	524	(25)	5	(2)	661	(15)	838	(39)
W	-		-		33	(12)	537	(67)	-		95	(5)	973	(174)

Ilm, Ilmenite; Arm, Armalcolite.

Concentrations reported in ppm. Number in parantheses is 2 sigma standard deviation of least significant figures.

(a) M denotes graphite lined molybdenum capsule.

(b) Number of averaged analyses.

Table S3 continued.

	NJD-10M				NJD-15M				NJD-16M			
	Arm		Melt		Ilm		Melt		Ilm		Melt	
n ^b	4		3		3		7		4		5	
Sc	41	(2)	35	(2)	-		4	(1)	-		2.6	(5)
V	765	(38)	114	(6)	-		-		16	(2)	2.9	(7)
Cr	6018	(164)	947	(66)	1211	(362)	-		19095	(1635)	1206	(160)
Co	50	(2)	64	(4)	9	(7)	2.8	(7)	11.8	(7)	5.4	(3)
Ni	413	(27)	372	(28)	39	(23)	5.5	(39)	64	(2)	16	(2)
Cu	-		80	(18)	14	(5)	15	(3)	-		12	(1)
Zn	147	(25)	357	(15)	47	(13)	38	(9)	30	(6)	25	(2)
Ga	-		-		-		-		0.65	(21)	1.9	(2)
Y	-		14	(3)	-		822	(84)	-		413	(24)
Zr	68	(4)	128	(8)	567	(133)	873	(97)	119	(16)	396	(29)
Nb	724	(23)	990	(22)	599	(113)	825	(122)	189	(12)	320	(12)
Mo	-		3261	(230)	-		-		-		-	
La	-		15	(4)	-		1098	(179)	-		328	(14)
Ce	-		32	(12)	-		946	(111)	-		298	(6)
Pr	-		1.9	(6)	-		1012	(156)	-		314	(11)
Nd	-		7	(3)	-		851	(104)	-		301	(14)
Sm	-		2	(1)	-		797	(59)	-		325	(18)
Eu	-		0.9	(1)	-		806	(53)	-		312	(10)
Tb	-		0.3	(2)	-		-		-		0.08	(2)
Gd	-		1.7	(8)	-		859	(92)	-		388	(19)
Dy	-		3.2	(2)	-		841	(90)	-		419	(25)
Ho	-		0.89	(8)	-		799	(118)	-		393	(25)
Er	-		2.4	(3)	-		-		-		0.19	(2)
Tm	-		0.6	(1)	-		-		-		0.015	(4)
Yb	-		3.5	(3)	-		770	(129)	24	(12)	374	(18)
Lu	-		0.5	(1)	-		847	(97)	40	(15)	465	(28)
Hf	2.4	(3)	3.2	(5)	598	(113)	825	(123)	155	(20)	383	(25)
Ta	6.0	(4)	5.3	(2)	1964	(108)	892	(127)	370	(20)	375	(23)
W	-		-		-		-		-		-	

Table S3 continued.

	NJD-17M				NJD-18M				NJD-19M			
	Ilm		Melt		Ilm		Melt		Ilm		Melt	
n ^b	8		10		4		4		3		4	
Sc	14	(2)	16.7	(8)	-		4.1	(5)	7.1	(13)	9.2	(3)
V	315	(14)	36	(3)	-		-		191	(21)	21	(3)
Cr	938	(92)	49	(12)	158	(63)	9.8	(27)	1452	(248)	73	(19)
Co	45	(3)	23	(1)	7.9	(4.8)	2.8	(4)	27	(3)	12.5	(4)
Ni	60	(8)	15	(2)	21	(11)	3.2	(9)	57	(5)	13.2	(7)
Cu	9	(3)	7.6	(1.4)	-		15.9	(8)	12	(5)	14	(2)
Zn	310	(49)	431	(38)	39	(9)	44	(10)	178	(18)	263	(13)
Ga	0.7	(3)	2.9	(12)	-		3.6	(4)	0.79	(26)	2.7	(3)
Y	4.3	(7)	380	(26)	-		692	(69)	5.7	(8)	490	(74)
Zr	82	(5)	334	(16)	621	(293)	904	(95)	146	(10)	447	(94)
Nb	404	(41)	956	(54)	1913	(336)	763	(57)	808	(163)	656	(95)
Mo	-		-		-		-		-		-	
La	-		315	(27)	-		1183	(119)	-		481	(89)
Ce	-		290	(29)	-		1054	(91)	-		437	(57)
Pr	-		303	(22)	-		1108	(94)	0.20	(9)	460	(69)
Nd	-		275	(14)	-		937	(69)	-		429	(75)
Sm	0.47	(2)	291	(17)	-		840	(49)	0.49	(14)	446	(66)
Eu	0.54	(36)	289	(18)	-		830	(38)	0.75	(16)	449	(57)
Tb	-		-		-		0.31	(4)	-		0.29	(4)
Gd	1.4	(3)	350	(23)	-		810	(61)	2.0	(4)	506	(83)
Dy	3.5	(5)	377	(25)	-		724	(68)	4.6	(1.2)	507	(77)
Ho	5.0	(5)	354	(24)	-		723	(77)	7.5	(1)	513	(71)
Er	0.07	(5)	2.7	(2)	-		0.5	(1)	0.025	(12)	1.5	(2)
Tm	-		0.49	(7)	-		0.024	(8)	-		0.23	(2)
Yb	16	(1)	355	(39)	-		666	(87)	22	(2)	503	(64)
Lu	25	(2)	397	(35)	-		691	(86)	32	(3)	512	(77)
Hf	96	(6)	305	(28)	695	(313)	908	(96)	174	(5)	452	(95)
Ta	136	(14)	210	(13)	2501	(678)	870	(96)	466	(69)	311	(61)
W	-		-		-		-		-		-	

Table S3 continued.

	NJD-22M	
	Ilm	Melt
n ^b	4	4
Sc	6.7 (43)	19 (1)
V	284 (10)	32 (1)
Cr	813 (40)	36 (1)
Co	44 (5)	22 (1)
Ni	52 (12)	12 (2)
Cu	184 (21)	25 (1)
Zn	461 (74)	452 (16)
Ga	-	-
Y	4.5 (10)	374 (9)
Zr	110 (4)	315 (6)
Nb	612 (83)	903 (10)
Mo	708 (18)	697 (17)
La	-	337 (7)
Ce	-	352 (2)
Pr	-	346 (4)
Nd	-	321 (5)
Sm	-	334 (10)
Eu	-	321 (7)
Tb	-	0.53 (8)
Gd	1.8 (10)	369 (13)
Dy	3.9 (9)	383 (8)
Ho	5.9 (15)	378 (10)
Er	-	2.9 (2)
Tm	-	0.46 (3)
Yb	19 (3)	378 (6)
Lu	26 (2)	370 (11)
Hf	114 (2)	288 (5)
Ta	185 (29)	188 (3)
W	13 (5)	251 (9)

Appendix A: A Solubility-Weighted Lattice Strain Model for Ti, Zr, and Hf

Partitioning in Ilmenite: Promise and Pitfalls

For silicate and oxide minerals, mineral-melt trace element partitioning can be parameterized using the lattice strain model (Brice, 1975; Blundy and Wood, 1994; Wood and Blundy, 1997):

$$D_i^{oxide-melt} = D_0 \exp\left(\frac{-4\pi EN_A}{RT} \left(\frac{r_0}{2}(r_0 - r_i)^2 - \frac{1}{3}(r_0 - r_i)^3 \right)\right) \quad (A1)$$

where D_0 is the mineral-melt partition coefficient for strain-free substitution; r_0 is the ideal radius for the lattice site of interest; r_i is the ionic radius of the element of interest; E is the effective Young's modulus of the lattice site; R is the gas constant; N_A is Avogadro's number; and T is temperature. The parameters of the lattice strain model (D_0 , E , r_0) are typically estimated by non-linear least squares regression of a set of experimentally determined partition coefficients for a group of elements, which form a parabola when plotted against ionic radius. Because D_0 , E , and r_0 are also dependent on the charge of the element of interest and the physical properties of the lattice site on which it substitutes, only elements of the same charge can be used to construct a parabola to estimate these parameters. More elements provide more statistically significant approximations of D_0 , E , and r_0 .

Useable 4+ cations in ilmenite or armalcolite include Ti, Zr, Hf, and perhaps Th, U, Mo, Si, and W. Even at fO_2 well below iron-wüstite buffer, Zr and Hf retain their 4+ valence states, and at the same fO_2 only a very small fraction of Ti (~ 5%) is reduced to Ti^{3+} in the melt (Schreiber, 1977) (this is supported by calculations of the chemical

formulas of our Fe-Ti oxides, Supplementary Table S2), therefore Ti, Zr, and Hf should reliably define a lattice strain parabola for the 4+ cations. In contrast, U and Th have very large ionic radii relative to Ti and D_U and D_{Th} reported in the literature have correspondingly large uncertainties. They tend to fall above parabolas defined by more “trustworthy” 4+ cations. Other 4+ cation partition coefficients are infrequently reported (Mo, Si) and may be of poor quality due to the lack of an appropriate standard reference material (Si), or complicated by their heterovalent nature (W, Mo). Research suggests that at the iron-wüstite buffer, Mo is divided between 3+ and 4+ valence (Danielson et al., 2011), so we excluded Mo from our parabolas. W is almost exclusively at 6+ valence at the iron-wüstite buffer (O’Neill et al., 2008) and was also excluded. The consequence of such a limited number of useable 4+ cations is that the regression analysis of the lattice strain model for these trace elements in ilmenite is underdetermined, i.e., three elements for three variables.

This obstacle may be overcome for D_{HFSE}^{4+} by making two simple but reasonable assumptions: (1) the ideal ionic radius of a 4+ cation substituting into an Fe-Ti oxide in the lattice strain model is that of Ti (i.e., $r_0 = r_{Ti}$); and (2) the strain-free partition coefficient of a 4+ cation in an Fe-Ti oxide (D_0) is equivalent to ilmenite-melt D_{Ti} . The lattice strain model for D_{HFSE}^{4+} in ilmenite or armalcolite then takes the simple form:

$$D_i^{oxide-melt} = D_{Ti} \exp\left(\frac{-4\pi EN_A}{RT} \left(\frac{r_{Ti}}{2} (r_{Ti} - r_i)^2 - \frac{1}{3} (r_{Ti} - r_i)^3 \right)\right) \quad (A2)$$

Implicit in these assumptions are that 4+ cations exclusively substitute onto the Ti site, and that the ideal ionic radius of this site is fixed by Ti. Figures S4a and S6 show that D_{Ti}

is indeed at the apex of lattice strain parabolas defined by $HFSE^{4+}$, justifying the two assumptions made in the simplification of the lattice strain model (Eq. A2).

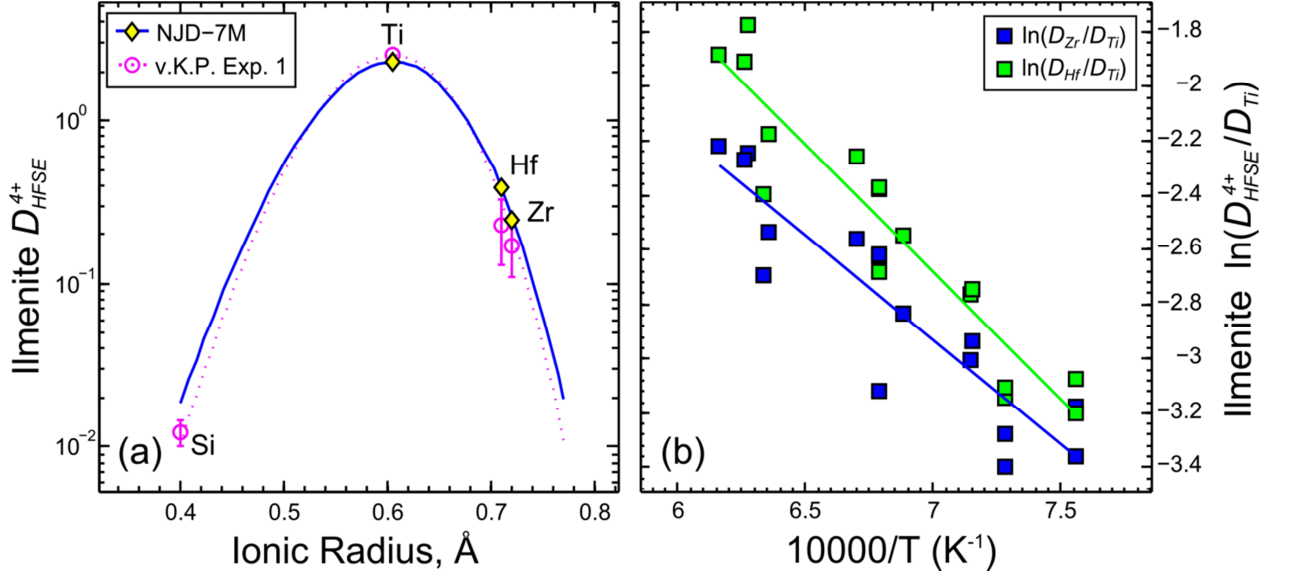


Figure S4. (a) Partition coefficients of 4+ cations in ilmenite for NJD-7M and Exp. 1 from van Kan Parker et al. (2011) define lattice strain parabolas with D_{Ti} at their apexes. (b) Variations of solubility weighted D_{HFSE}^{4+} as a function of inverse temperature. Data includes our results as well as partitioning studies cited in Figure 1 from the main text. Solid lines show linear fits of the data for Zr (blue) and Hf (green).

Because the Ti content of an Fe-Ti oxide is essentially fixed, oxide-melt D_{Ti} is simply a measure of the Ti content of a melt (Figure 5b). In other words, D_{Ti} represents the solubility of an Fe-Ti oxide in a melt at a particular temperature (T), pressure (P), and composition (X). Since D_{Ti} decreases with the increase of TiO_2 abundance in the melt

(Figure 5b), Eq. A2 helps to explain the inverse correlation between D_{HFSE} and melt TiO_2 (Figure 5b).

By fixing D_0 at D_{Ti} and r_0 at r_{Ti} , Eq. A2 can be manipulated to provide what we define as the solubility weighted partition coefficient for a given 4+ element as a function of T and E :

$$\ln\left(\frac{D_i^{oxide-melt}}{D_{Ti}}\right) = \frac{-4\pi EN_A}{RT} \left(\frac{r_{Ti}}{2}(r_{Ti} - r_i)^2 - \frac{1}{3}(r_{Ti} - r_i)^3 \right) \quad (\text{A3})$$

According to Eq. A3, solubility weighted partition coefficients should be linearly correlated with inverse temperature when plotted on a logarithmic scale, with the slope of the correlation representing E . Figure S4b demonstrates that this is indeed the case for D_{Zr} and D_{Hf} in ilmenite, giving confidence to the application of Eq. A3 which reduces the number of fitting parameters from three (Eq. A1) to one (E). Scatter in Figure S4b suggests possible contributions from other factors (e.g., composition) may cause some variability in E .

Application to ilmenite-melt HFSE partitioning

By fitting Eq. A3 for ilmenite (E^{ilm}) using D_{Ti} , D_{Zr} , and D_{Hf} for individual partitioning experiments, we investigated the effects of temperature (T), pressure (P), and mineral and melt composition (X) and determined that the fraction of Al in the structural formula of ilmenite (X_{Al}) is the most important variable affecting E^{ilm} variation. We then fit E^{ilm} as a function of X_{Al} using Eq. A3 and all the partitioning data for D_{Ti} and D_{HFSE}^{4+} through a global or simultaneous non-linear least squares inversion following the

regression procedure detailed in Sun and Liang (2012). The composition dependent E^{ilm} is given by the linear relationship

$$E^{ilm} = 1.169(\pm 0.075) \times 10^3 - 6.813(\pm 3.50) \times 10^3 X_{Al}, \quad (\text{A4})$$

where E^{ilm} is in GPa and numbers in parenthesis are 2σ errors estimated directly from the global inversion. Although the uncertainty in the X_{Al} fitting parameter is somewhat large, the term is significant. A comparison between predicted and measured partition coefficients for 4^+ cations (Zr, Hf) demonstrates good agreement (Figure S5), however careful inspection of the Figure S5 reveals that D_{Hf} are consistently overestimated for our low-Ti experiments and several others from the literature, with no overlap of their uncertainties and the solid blue 1:1 line.

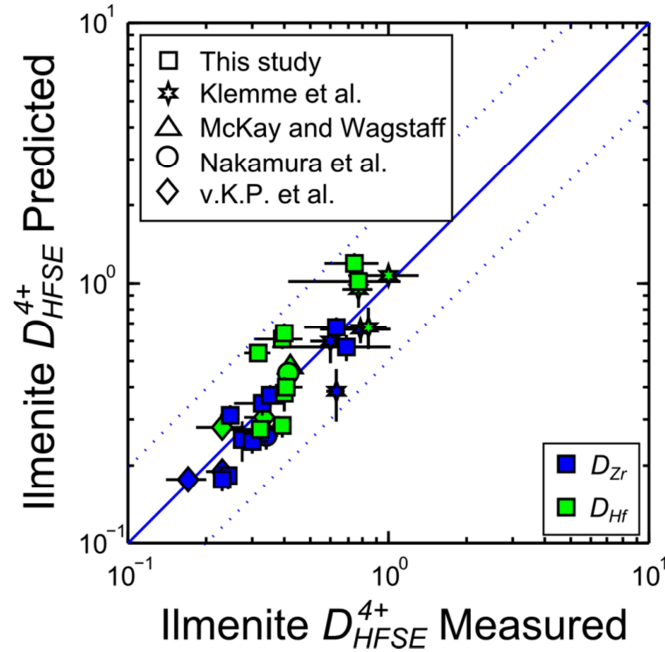


Figure S5. Comparison between predicted vs. measured ilmenite D_{HFSE}^{4+} . Blue dashed lines define 1:2 and 2:1 values while the blue solid line defines 1:1 values. Blue symbols are D_{Zr} , green symbols are D_{Hf} . Squares are our experiments, stars are those of Klemme

et al. (2006); triangles are those of McKay and Wagstaff (1985); circles are those of Nakamura et al. (1986); and diamonds are those of van Kan Parker et al. (2011). Note D_{Hf} is overestimated by this model for our low-Ti experiments and several from the literature. See also Figure 8a in the main text.

Although the predicted Hf partition coefficients are systematically overestimated by Eq. A3, we can still compare the predictive ability of the model to Eqs. 3 and 4 in the main text using the Pearson's Chi-square

$$\chi_P^2 = \sum_{j=1}^N \frac{(D_j - D_j^m)^2}{D_j} \quad (\text{A5})$$

where D_j is the partition coefficient predicted by Eqs. A3 and A4 for element j and D_j^m is the measured value. A more accurate predictive model should produce partition coefficients close to the measured values and therefore lower χ_P^2 . The $\chi_P^2 = 0.99$ for the solubility-weighted lattice strain model (Eqs. A3 and A4), while $\chi_P^2 = 0.22$ for the solubility-weighted empirical model presented in the main text (Eqs. 3 and 4) for the same experimental datasets (cf. Figs. 8a and S5). This demonstrates that the simple partitioning models in the main text better predict the absolute values of the partition coefficients, but more importantly, those models show no systematic deviation from the measured values. In contrast, Eqs. A3 and A4 underestimate D_{Zr}/D_{Hf} for low TiO_2 experiments (Figure S4), which is significant in lunar applications.

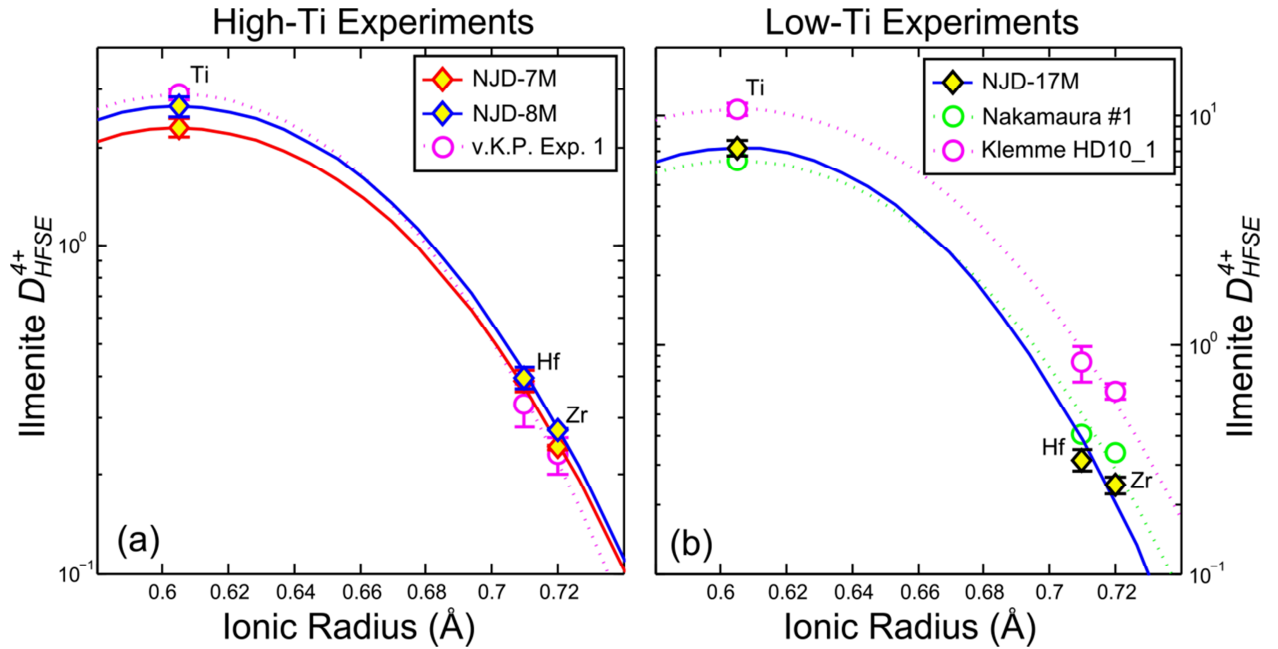


Figure S6. Lattice strain parabolas generated with D_0 , r_0 , and E terms inverted from individual experiments for HFSE^{4+} from this study and the literature (Nakamura et al., 1986; Klemme et al., 2006; van Kan Parker et al., 2011). High-Ti experiments are shown in (a) and low-Ti experiments shown in (b). Lattice strain parabolas fit the high-Ti experimental data very well (a), but fall between the measured values for the low-Ti experiments (b), demonstrating that the low-Ti partition coefficients cannot be accurately modeled with Eqs. A3 and A4.

The cause of the systematic deviation for the low-Ti experiments is unknown. One possible explanation is that the ionic radii of Zr and Hf reported in Shannon (1976) are not suitable for ilmenite. Alternatively, the sluggish kinetics of the lower temperature (low-Ti) experiments may affect the quality of the data. The consistency of HFSE

partitioning among studies that all used different cooling rates and experimental methods (Figure S6b) argues against that hypothesis. A third possibility is that the lattice strain model does not incorporate all the relevant physics of HFSE substitution into ilmenite and armalcolite, such as the different molecular electronic polarizabilities of HFSE and their correspondingly different interactions with Fe-Ti oxide crystal structure (Horng and Hess, 2000). Whatever the cause, it is worth noting that the D_{Ti} coefficients differ slightly between Eqs. 3 and 4 (and between Eqs. 7 and 8), suggesting that the ilmenite solubility effect on D_0 may slightly differ between Zr and Hf. Perhaps with a larger experimental dataset, lattice strain models for 4+ cations can be reinvestigated and refined using a similar approach.

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CHAPTER 2

An Experimental Study of Trace Element Partitioning between Augite and Fe-Rich Basalts

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Abstract

Aluminous titanium-rich hedenbergite and Fe-rich augite were experimentally produced at 1050-1220°C and 0.8-2.2 GPa. Major element compositions are analogous to clinopyroxene from layered intrusions, angrites, nakhlites, and late-stage lunar magma ocean cumulates. Trace element concentrations in pyroxene and coexisting melt were measured by laser ablation inductively coupled plasma mass spectrometry for rare earth elements (REE), high field strength elements (HFSE), transition metals, and large-ion lithophile elements. REE, HFSE, and transition metal partition coefficients (Ds) are tightly correlated with the cation abundance of Fe on the pyroxene M1 site (X_{Fe}^{M1}), and also correlated with Al on the tetrahedral site (X_{Al}^T). Parameterized lattice-strain models were developed to predict REE and HFSE partition coefficients as functions of temperature and pyroxene composition (X_{Al}^T or X_{Fe}^{M1}). The parameterized models can be used to calculate REE and HFSE partition coefficients for Fe-rich high-Ca pyroxene. We calculated partition coefficients for clinopyroxene derived from modeled end-stage lunar magma ocean cumulate compositions and observe a factor of 3 variation in clinopyroxene-melt REE partition coefficients. Using representative nakhlite clinopyroxene core and rim compositions we calculated partition coefficients and observed a factor of 4 variability in clinopyroxene-melt REE partition coefficients. HFSE partition coefficients are even more sensitive to composition, showing variations of a factor of 4 for lunar late cumulates and an order of magnitude for nakhlites. The strong dependence of REE and HFSE partitioning on composition necessitates careful selection of appropriate partition coefficients for Fe-rich systems.

1. Introduction

Mineral-melt trace element partition coefficients (D s) are important parameters in the interpretation of igneous rocks. Significant progress has been made in characterizing and understanding trace element partitioning between major rock-forming minerals such as pyroxene and basaltic melts (e.g., Wood and Blundy, 2003; Sun and Liang, 2013a, and references therein), although most of the studies published to date focus on mafic and ultramafic systems relevant to the Earth's upper mantle. Recent research focused on developing a robust theoretical framework to predict partition coefficients (e.g., Blundy and Wood, 1994; Sun and Liang, 2013a) and applying it to natural systems, while earlier studies focused on understanding fundamental compositional controls of trace element partitioning. Nakamura et al. (1982) noted a correlation between clinopyroxene Fe/(Fe+Mg) ratio and rare earth element (REE) partition coefficients available at that time, generating an Fe-based partitioning model to predict partition coefficients for nakhlites. McKay et al. (1986) argued that REE partitioning in pyroxene is primarily controlled by its wollastonite content and that partitioning is insensitive to the Fe/Mg ratio of the system. Gallahan and Nielsen (1992) obtained consistent results, proposing that the primary crystal-chemical control on partitioning is Ca but that partitioning is also sensitive to the Al content of coexisting melt. Later experimental studies (e.g., Gaetani and Grove, 1995; Lundstrom et al., 1998; Hill et al., 2000) convincingly demonstrated the dependence of REE and high field strength element (HFSE) partitioning on the abundance of tetrahedral Al (X_{Al}^T) in magnesian clinopyroxene. Most recently, Sun and Liang (2012) found the cation fractions of Mg on the pyroxene M2 site (X_{Mg}^{M2}) and Al on

the tetrahedral (X_{Al}^T) and M1 (X_{Al}^{M1}) sites and temperature are the primary factors controlling REE partitioning in clinopyroxene.

Considerably fewer mineral-melt trace element partitioning studies have been done on more Fe-rich systems which are also important to magmatic differentiation in the Earth and planetary bodies. The present study focuses on trace element partitioning between augite and nominally anhydrous Fe-rich basalts, quantifying the relationship between REE and HFSE partition coefficients in Fe-rich augite as a function of composition and temperature. While pure hedenbergite ($\text{CaFeSi}_2\text{O}_6$) and Fe-rich augite are relatively rare, they crystallize at end-stage solidification of magma oceans and layered intrusions, and from evolved igneous melts on bodies throughout the solar system. Examples of Fe-rich pyroxene in natural rocks are presented in Figure 1 and include layered intrusions such as Skaergaard and the Bushveld Complex (blue and red lines, Figure 1a, Wager and Brown, 1967), selected ferroan calc-alkaline systems (e.g., white diamonds, Figure 1b, Olin and Wolff, 2010), angrites (salmon field, Figure 1a, Kuehner et al., 2006), the Martian nakhlites (yellow and green fields, Figure 1a, see figure caption for references), lunar alkali suite rocks (pink diamonds, Figure 1a, Shervais and McGee 1999), and MAGFOX calculated lunar magma ocean cumulates (green dots, Figure 1a,) [MAGFOX is an experimentally calibrated lunar magma ocean crystallization model developed by Dr. John Longhi (1991)].

Studies investigating trace element partition coefficients between clinopyroxene and basaltic melt for Fe-rich systems are rather limited. Two recent experimental studies investigated clinopyroxene-melt partitioning at intermediate Mg#s [$=100 \times \text{MgO}/(\text{MgO} + \text{FeO})$, in moles], but both use somewhat exotic bulk compositions.

Wood and Triglia (2001) report partition coefficients for aluminous clinopyroxene (up to 12 wt% Al_2O_3) with Mg#s of 54-69 in hydrous alkali-rich melts (up to 3 wt% initial H_2O). Their REE partitioning data is included in the study of Sun and Liang (2012) who developed a parameterized lattice strain model for clinopyroxene-melt REE partitioning (see below). Pertermann and Hirschmann (2002) measured clinopyroxene-melt partition coefficients in anhydrous experiments with bulk compositions representing partial melts of a quartz-bearing eclogite ($\text{SiO}_2 \sim 57\text{wt}\%$). Pyroxenes in their study have Mg#s of 57-60 and exceptionally high Al_2O_3 abundances (up to 17wt%). Partitioning behavior in these systems is very different than in anhydrous ferro-basalts and we were unable to develop a generalized model to predict partition coefficients of Wood and Triglia (2001), Pertermann and Hirschmann (2001), and our experimental results (see section 4.1). These studies will not be discussed further.

Very few additional experimental studies exist for trace element partitioning in Fe-rich basaltic systems. Oe et al. (2001) report REE partition coefficients for nakhlite analogue experiments with intermediate Mg#s (green circles in Figure 1b, green line in Figure 2a) and noted a correlation between REE partition coefficients and Al_2O_3 in pyroxene. These partition coefficients were calculated from electron microprobe analyses of heavily doped experiments conducted at atmospheric pressure. Because the pyroxene compositions in Oe et al. (2001) closely match those of nakhlite cores (Figure 1), the partition coefficients were extensively used in petrogenetic modeling of the nakhlites (e.g., Wadhwa et al., 2004; Day et al., 2006; Udry et al., 2012). The number of elements reported in Oe et al. (2001) is limited, however interpolation between mid and heavy

REE shows a flat pattern (green line in Figure 2a). Major element compositions for the study of Oe et al. (2001) were not reported.

Working on natural samples in a more silicic system (58.6-77.2% SiO₂), Olin and Wolff (2010) report partition coefficients for Fe-rich clinopyroxene (Mg# 59-10, white diamonds, Figure 1b) that crystallized in two rhyolitic tuffs and a phonolite. They calculated partition coefficients using data obtained from laser ablation inductively coupled mass spectrometry (LA-ICP-MS) analyses of pyroxenes and host glasses, and solution ICP-MS analyses of the glasses. The REE partition coefficients reported in their study range from ~1 to 10 and are not relevant to basaltic systems, but examination of these partition coefficients (solid brown lines in Figure 2a) reveals two interesting observations. First, the partition coefficients have very high absolute values. Should this be attributed to the highly silicic host melts, or could it also be a function of the very low Mg#? Second, the REE partition coefficients increase with decreasing ionic radii for heavy-REE (HREE), leading to significant concave-up curvature between Er and Lu. The latter was not observed in the partitioning data of Oe et al. (2001).

In a recent study, Sun and Liang (2012) developed a parameterized lattice strain model for clinopyroxene-melt REE partitioning as functions of temperature and composition using 43 high-quality partitioning experiments from the literature (light blue field, Figure 1b). The model was mostly calibrated with pyroxene with Mg#>60 (in one experiment by Wood and Triglia, 2001, Mg#=54). According to their model, cation fractions of Mg on the pyroxene M2 site (X_{Mg}^{M2}) and Al on the tetrahedral (X_{Al}^T) and M1 (X_{Al}^{M1}) sites are primary composition factors controlling REE partitioning in clinopyroxene. Sun and Liang's model does an excellent job predicting clinopyroxene-

melt REE partition coefficients for mafic and ultramafic systems but fails to predict the measured REE partition coefficients for more Fe-rich systems (Figure 2b).

The purpose of the present study is to generate an experimental dataset of high-quality partition coefficients for Fe-rich augite and hedenbergite (Figure 1), and to quantify REE and HFSE partitioning in Fe-rich clinopyroxene as functions of temperature, and pyroxene and melt compositions. In the next section we describe methods we used to determine trace element partition coefficients in piston cylinder experiments at a range of pyroxene compositions (Mg# 4.5-52.2). In Section 3, we report measured partition coefficients for REE, HFSE, transition metals, and large-ion lithophile elements (LILE). Crystal-chemical controls on trace element partition coefficients are discussed in Section 4, and parameterized lattice strain models that predict REE and HFSE partition coefficients as a function of pyroxene composition and temperature are also presented. Finally, the partitioning models are applied to lunar magma ocean crystallization and nakhlite petrogenesis in Section 5.

2. Methods

2.1 Experimental Preparation and Procedures

We conducted pyroxene-melt trace element partitioning experiments at pressures of 0.8-2.2 GPa and temperatures of 1050-1220°C using a 19.1 mm piston cylinder apparatus following methods similar to those described in Dygert et al. (2013). Experimental assemblies consist of a salt-Pyrex[®] sleeve, straight-walled graphite furnace, and internal spacers of crushable MgO with a graphite-lined molybdenum capsule. Experiments were conducted with Mo outer capsules to maintain reducing conditions

($fO_2 \sim \text{iron-wüstite-1}$) and minimize thermal gradients around the sample charge. Compositions of starting materials are presented in Table 1 and their proportions in each experiment are presented in Table 2. As a base starting material, all runs utilized an Fe-rich synthetic lunar basalt analogue ($Mg\# = 1.5$) similar in composition to sample FR-1290 of Longhi (2003). FR-1290 is intended to represent liquid present at end-stage solidification of the lunar magma ocean. Three experiments were run with pure FR-1290 at a range of temperatures and pressures. In an additional experiment, a layer of ilmenite powder (from Wards Natural Science) was placed beneath a thicker layer of FR-1290, and in final three experiments, layers of augite powder ($Mg\# = 82$) were placed beneath thicker layers of FR-1290 to produce a range of pyroxene and melt compositions (red circles in Figure 1b). This method has the added benefit of seeding a few large crystals.

FR-1290 was prepared using reagent grade oxide and carbonate powders of appropriate proportion. After an initial grinding of 20 minutes in an agate mortar in ethanol, the mixtures were dried and placed in a platinum crucible to decarbonate in an 800°C furnace overnight. The powders were then mixed in an agate mortar in ethanol for 8 hours. A mixture of REE and HFSE oxides (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Yb, Lu, Y, Zr, Hf, Nb, Ta, and W) was prepared to dope FR-1290 and thus reduce analytical uncertainty during data collection. After weighing, the REE+HFSE oxide powder was ground in ethanol in a corundum mortar for 8 hours. The REE+HFSE oxide powders were reduced in a 900°C H_2 -CO mixed gas furnace for at least 4 hours at $fO_2 \sim \text{iron-wüstite}$, while FR-1290 was reduced at 800°C for 7.5 hours to prevent melting. Finally, mixtures of REE+HFSE powder and FR-1290 were ground in ethanol in a cleaned agate mortar for 4 hours at a mass ratio of $\sim 1:49$.

Partitioning experiments were conducted using the hot-piston in technique; after initially pressurizing to approximately 85% of the target pressure, temperature was increased at a rate of 75°C per minute until the desired temperature was attained. The target pressure was reached through a combination of thermal expansion during heating and additional pressurization. Pressure was monitored and maintained during cooling intervals. Runs were heated above their estimated liquidus temperatures (to 1400°C) and held there for 8-24 hours before cooling to target temperatures at rates of 0.1-0.2°C per minute to encourage larger crystal growth and homogeneity. Four of the seven experiments had an intermediate cooling interval (Table 2), with faster cooling rates between the super-liquidus and intermediate temperatures (1-0.5°/min). This was done to reduce total run durations, nevertheless they range from 71 to 119 hours. Temperatures were measured using W₉₇Re₃-W₇₅Re₂₅ thermocouples. Uncertainties in temperature measurements are about ±10°C. Experiments were quenched to room temperature by shutting off the power supply to the furnace while maintaining approximate run pressure. No pressure correction was applied to the measured electromotive force and the nominal pressure was not corrected for friction.

2.2 Analytical Techniques

Major element compositions of quenched charges were analyzed using a Cameca SX 100 electron microprobe at Brown University. Analytical conditions are an accelerating voltage of 20 kV and a beam current of 15 nA. Pyroxenes were analyzed using a focused beam, while quenched melt was analyzed with a 10 µm defocused beam. Natural and synthetic standards were used for calibration. Trace element concentrations

in pyroxene and melt were measured by LA-ICP-MS at the Graduate School of Oceanography at the University of Rhode Island using methods similar to those described in Kelley et al. (2003). A suite of nine well-characterized natural and synthetic glass standards was used to calibrate the trace element analyses. Because of its similar abundance in pyroxene, melt, and trace element standards and excellent reproducibility in microprobe analyses (Table 3), Ca was selected as the normalizing element.

We used 40-60 μm diameter laser spot sizes when analyzing melt, and 30-40 μm spot sizes for pyroxene. Care was taken to place laser spots near pyroxene rims in experiments HB-5 and HB-7, which exhibit core to rim zoning in Mg# (varying by about 20 units between rim and core, Fig. 3b and Supplementary Figures S4 and S7), and in minor (e.g., Al_2O_3 , TiO_2) and trace elements. Major and trace element compositions reported for those experiments are rim compositions, and trace element analyses from grain cores in HB-5 and HB-7 were excluded when calculating partition coefficients. In the other experiments, major and trace elements are generally uniform with respect to spot position indicating homogeneity (Supplementary Figures S1-S3, S6). Nevertheless, partition coefficients were calculated using pyroxene rim compositions when possible. Major and trace element analyses (Table 3 and Supplementary Table S1) suggest quenched melt is homogeneous in all experiments and no quench growth was observed except immediately adjacent to pyroxene grains. In all cases, data affected by the intersection of the laser with melt inclusions was discarded. Such affected data is easily identifiable as a spike or decline in analytical signal for particular elements.

3. Results

A total of seven experiments are reported (Table 2). Trace element partition coefficients are shown in Figure 2, and representative backscatter and reflected light micrographs are shown in Figure 3. All experiments contain a few large (hundreds of μm) clinopyroxene crystals and melt with or without trace abundances of spinel and quartz (Table 2). Clinopyroxenes are ferroan augite (runs HB-5, HB-6, HB-7) and aluminous titanium-rich hedenbergite (NJD-20, NJD-22, HB-1, HB-4) with relatively constant Ca (red circles, Figure 1b). Their Mg#s range from 4.5 to 52.2, while the cation abundance of tetrahedral Al (X_{Al}^T , per six oxygen) ranges from 0.07-0.24 (Figure 4). Temperature, X_{Al}^T , Mg#, and the cation fraction of Fe on the M1 site (X_{Fe}^{M1}) in clinopyroxenes are strongly correlated with each other (Figure 4). These chemical trends overlap those observed in clinopyroxene from Nakhilites and MAGFOX calculations. The SiO_2 content of the experimental basaltic melts is low (41.6-46.0 wt%) owing to their richness in FeO (24.9-29.7 wt%). For reference, pyroxene compositions are reported in cations calculated on a six-oxygen basis in Supplementary Table S2.

Small standard deviations in averaged major and trace element analyses demonstrate excellent analytical reproducibility (Table 3 and Supplementary Table S1, Supplementary Figures S1-S4, S6, S7). Uncertainties for REE partition coefficients are generally less than 10% of the reported values (2σ , Table 4, Figure 2). The partition coefficients show nearly flat middle-HREE patterns (solid blue, red, and black lines, Figures 2a,c). Some low Mg# experiments exhibit negative Eu anomalies, while higher Mg# experiments (solid red lines, Figure 2a) have muted or nonexistent anomalies. This observation is addressed in Section 4.4. Figures 5a and 5d display variations of selected

REE partition coefficients as functions of X_{Fe}^{M1} and X_{Al}^T . Within our dataset, high Fe (low Mg#) experiments have higher REE partition coefficients. This observation is also apparent in Figure 2a (compare blue and red lines). Rare earth element partition coefficients are positively correlated with X_{Al}^T , however the trend is scattered among four experiments at high X_{Al}^T (Figure 5d). The measured partition coefficients are below or at the low end of partition coefficients from Mg rich (Mg# > 54) experiments from the literature (Supplementary Figure S8). To investigate the effect of zoning on partition coefficients, trace element compositions in experiment HB-5 were extrapolated to grain rims (Supplementary Figure S4) and partition coefficients were recalculated using the extrapolated compositions. The difference between the measured and extrapolated partition coefficients is within measurement error (Supplementary Figure S5).

High field strength element partition coefficients vary by almost an order of magnitude among the experiments, with higher values in Fe-rich experiments (Figure 5a). The HFSE are systematically correlated with Fe, and like the REE, also exhibit a positive correlation with X_{Al}^T though the data is scattered at high Al. W, Ga, and Mo are highly to moderately incompatible in our experiments while the other transition metals are moderately to highly compatible. Heterovalent trace element partition coefficients are systematically correlated with X_{Fe}^{M1} among the experiments (e.g., V and Cr, Figures 5b,e), which suggests fO_2 conditions are similar among the experiments. In general, transition metal partition coefficients are positively correlated with X_{Fe}^{M1} (Figure 5b), however the positive correlation is more systematic with X_{Al} for certain elements (Ga, Mn, Cu, Zn, Supplementary Figure S9). Because LILE have very low partition coefficients they could not be reported for all experiments, but we note Na, Li, and K partition coefficients

generally decrease with increasing Mg# (Table 4), consistent with REE, HFSE, and transition metals. In addition to X_{Fe}^{M1} and X_{Al}^T , REE, HFSE, and transition metal partition coefficients are correlated with other compositional parameters (X_{Al} , Mg#) and/or T , consistent with the major element correlations presented in Figure 4. For reference, REE, HFSE, and transition metal D s are plotted as functions of X_{Al} , T , and Mg# in Supplementary Figures S9-S11.

4. Discussion

Clinopyroxene-melt partition coefficients in magnesian systems are positively correlated with X_{Al}^T and X_{Fe}^{M1} and our results are consistent (Supplementary Figure S8), however the systematics of HREE partitioning and partition coefficient values at a given X_{Al}^T or X_{Fe}^{M1} are different in Fe-rich systems. Accordingly, the partitioning model of Sun and Liang (2012) overestimates REE partition coefficients reported in the present study and fails to predict appropriate curvature for the partition coefficient patterns (note upward swing of red, blue, and black lines for HREE, Figure 2b). We also note the model of Wood and Blundy (1997) overestimates the measured partition coefficients by up to a factor of 3. Different partitioning behavior in Fe-rich and Fe-poor systems merits new predictive partitioning models that are specific to Fe-rich systems. In the following sections we assess the potential effects of T , X_{Al}^T , and X_{Fe}^{M1} on clinopyroxene-melt partitioning in Fe-rich systems by developing and comparing predictive trace element partitioning models.

4.1 Trace Element Partitioning Models

For silicate and oxide minerals, mineral-melt trace element partition coefficients from a given partitioning experiment vary systematically as functions of ionic radius (Onuma et al., 1968) and can be described by the lattice strain model (Brice, 1975; Blundy and Wood, 1994; Wood and Blundy, 1997):

$$D_i^{augite-melt} = D_0 \exp \left(\frac{-4\pi E N_A}{RT} \left(\frac{r_0}{2} (r_0 - r_i)^2 - \frac{1}{3} (r_0 - r_i)^3 \right) \right), \quad (1)$$

where D_0 is the mineral-melt partition coefficient for strain-free substitution; r_0 is the ideal radius for the lattice site of interest; r_i is the ionic radius of the element of interest; E is the effective Young's modulus of the lattice site; R is the gas constant ($=8.31$ J/mol/K); N_A is Avogadro's number; and T is temperature in K. The parameters in the lattice strain model (D_0 , E , r_0) are typically estimated by non-linear least squares regression of a set of experimentally determined partition coefficients for a group of isovalent cations, which form a parabola when plotted against ionic radii (referred to as Onuma diagram hereafter). Because D_0 , E , and r_0 are also dependent on the charge of the element of interest and the physical properties of the lattice site on which it substitutes, only elements of the same charge can be used to construct a parabola to estimate these parameters. More elements provide more statistically significant estimates of D_0 , E , and r_0 .

Lattice strain parabolas inverted from measured partition coefficients by nonlinear least squares regression for four individual experiments are shown in Figure 6 (remaining experiments are shown in Supplementary Figure S12), and corresponding D_0 , E , and r_0 terms are presented in Table 5. Sufficient partition coefficient data exist to define

parabolas for cations with the following charges: 1+, 2+, 4+, and 3+ on the M1 (Al, Sc, Cr) and M2 (REE, Y) sites separately. The highly parabolic nature of the partition coefficients in Onuma diagrams (Figure 6) demonstrates the quality of our data. Though parabolas for LILE, HFSE, and 3+ cations on the M1 site are defined by just three elements they are systematic and consistent among the experiments. Cr may be divided between 2+ and 3+ valence states at our experimental fO_2 (Schreiber, 1977), but its partitioning behavior is most consistent with substitution as a 3+ cation on the M1 site and we chose to group it with Al and Sc to define that parabola (green lines, Figure 6). In agreement with Wood and Blundy (2003), we observe strong dependence of the elastic properties of the lattice site on cation charge, with higher cation charges yielding larger effective Young's moduli (Table 5, Figure 7). Interestingly the effective Young's moduli for 2+ cations (122-139 GPa) are very close to the measured bulk modulus of end-member hedenbergite (120 GPa, Kandelin and Weidner, 1988).

Key parameters in the lattice strain model (D_0 , r_0 , E) from the parabolas presented in Figure 6 were compared to P , T , and X terms for pyroxene and melt and correlations were noted (e.g., Figures 5c,f). Finally, D_0 , E and r_0 were parameterized as functions of T and crystal composition by simultaneous inversion of all of our experimental data for the REE and HFSE following the method described in Sun and Liang (2012). The advantage of this method is its potential to isolate convoluted P - T - X effects on trace element partitioning provided a dataset exists with a sufficient number of experiments and variation in the control parameters. However, because of systematic covariation of compositional parameters in our limited data (e.g., Figure 4), we were not able to deconvolve the effects of Al and Fe with confidence. Based on charge balancing

arguments and our current understanding of REE substitution in clinopyroxene, we choose to present Al-based models below. Fe-based models similar in form are presented in the supplementary material.

4.1.1 Rare Earth Element Partitioning Model

Informed by the positive correlation of REE partition coefficients with Al on the tetrahedral site (Figure 5d) and correlation of T with the D_0 term from individual parabola inversions (Supplementary Figure S10), we found, through a global inversion of the seven experiments reported in this study (a total of 92 observations), that

$$\ln(D_0) = -11.04(\pm 0.54) + 10.83(\pm 0.68) \times \frac{10^4}{RT} + 0.97(\pm 0.32) \times X_{Al}^T, \quad (2)$$

$$E = 2.06(\pm 0.13) \times 10^2, \quad (3)$$

$$r_0 = 1.00(\pm 0.005). \quad (4)$$

where r_0 is in Å, E is in GPa, and X_{Al}^T is the tetrahedral Al cation abundance calculated assuming any deficit in Si is relieved by Al. Coefficient uncertainties are 1σ . A comparison of predicted and measured partition coefficients (yellow circles, Figure 8) shows that this model does an excellent job reproducing the experimentally determined partition coefficients. The quality of the prediction can be slightly improved by including additional fitting parameters, but we believe the simple model presented here is superior for several reasons. It successfully predicts experimentally determined partition coefficients, is simple to use and physically reasonable, and is consistent with previous studies (e.g., Gallahan and Nielsen, 1992; Gaetani and Grove, 1995; Lundstrom et al., 1998; Hill et al., 2000; Sun and Liang, 2012).

4.1.2 High Field Strength Element Partitioning Model for 4+ Cations

Taking a similar approach, we found that HFSE partitioning in Fe-rich clinopyroxene can be parameterized as a function of T and the cation abundance of Al on the tetrahedral site. Coefficients in the lattice strain model (Eq. 1) are parameterized in the following form:

$$\ln(D_0) = -15.16(\pm 1.50) + 16.90(\pm 1.90) \times \frac{10^4}{RT} + 2.64(\pm 0.88) \times X_{Al}^T, \quad (5)$$

$$E = 2.22(\pm 0.38) \times 10^3, \quad (6)$$

$$r_0 = 0.655(\pm 0.002), \quad (7)$$

where r_0 is in Å and E is in GPa. A comparison of predicted and measured partition coefficients is shown in Figure 8 (green circles). Again, the quality of the fit can be slightly improved by including additional composition terms, but as for the REE, the simplicity and generality of this model are assets. The absolute values of the effective Young's moduli obtained from the Al and Fe based models are identical for both REE and HFSE, as are the r_0 terms. Finally, we note that the HFSE partitioning model of Hill et al. (2011) fails to reproduce the experimentally measured partition coefficients (Supplementary Figure S13).

4.2 Transition Metal Partitioning

Zn, Mn, Sc, and Cr plot on parabolas for trace elements of their charge group (Figure 6). Other transition metals (Ni, Cu, Co, V, Mo) fall off the appropriate parabolas. This can be attributed to their heterovalent nature and/or incomplete d-orbital electron shells which are known to violate the assumptions of the lattice strain model by

promoting ionic polarization (e.g., Wood and Blundy, 2003). Nevertheless, Cr, V, Ni, and Co are well correlated with X_{Fe}^{M1} (Figure 5b), which may be expected given their similar ionic radii and charge to Fe. Other transition metals with similarly favorable ionic radii and charge (Mn, Zn, also Cu, Ga) are better correlated with X_{Al} (Supplementary Figure S9). Sc partitioning is relatively constant and is best correlated with T (Supplementary Figure S10). These observations further demonstrate that the convolution of pyroxene composition and temperature-pressure conditions make uniquely determining controls on trace element partitioning difficult with a limited dataset.

4.3 Crystal-Chemical Controls of Trace Element Partitioning in Fe-Rich Pyroxene

REE and HFSE partition coefficients are systematically correlated with X_{Fe}^{M1} , but it is difficult to envision a physical mechanism by which Fe controls their partitioning behavior. The high-spin ionic radius of Fe^{2+} is larger than Mg^{2+} in VI coordination (0.78 and 0.72Å respectively, Shannon, 1976), whereas the low-spin ionic radius of Fe^{2+} (0.61Å) is much smaller than Mg^{2+} . Because Fe has a partition coefficient of about 1 in our pyroxene (Table 3), the 2+ lattice strain parabolas (purple lines, Figure 6) show that Fe is most likely in high-spin state. As the Fe content of pyroxene increases and Mg correspondingly decreases, the M2 site may become larger and more accommodating to REE. Consistent with this logic, Rutstein and Yund (1969) observed a positive correlation of unit cell volume with hedenbergite content in synthetic clinopyroxene. However, our Fe and Al based partitioning models both fix r_0 at constant values for REE and HFSE. Charge balancing due to substitution of trivalent Fe could increase partition

coefficients, but the low $f\text{O}_2$ imposed by the graphite-lined molybdenum capsules in our experiments should preclude the presence of significant Fe^{3+} from the system.

Tetrahedrally coordinated Al in pyroxene has been argued to increase partition coefficients of trivalent and tetravalent cations in pyroxene by providing a charge balancing mechanism for their substitution into M sites (e. g., Colson et al., 1989, Gaetani and Grove, 1995; Lundstrom et al., 1998; Hill et al., 2000). The abundance of X_{Al}^T exceeds trace element concentrations in most pyroxene. Tetrahedral Al can directly charge balance REE, decreasing REE activity coefficients and increasing partition coefficients, but how does tetrahedral Al balance tetravalent and pentavalent cations? Coupled substitution (e.g., tetrahedral Al and M-site vacancies or LILE) is required. Because the Al based partitioning models provide slightly better predictions and have smaller coefficient uncertainties than the Fe based models, we suggest that T and X_{Al}^T may be the dominant factors controlling REE and HFSE partitioning within Fe-rich basaltic systems. The fact that our partition coefficients are lower than those found in the high Mg# experiments while X_{Al}^T and T are consistent with high Mg# experiments (Supplementary Figure S8) suggests Fe must also play a role in partitioning systematics at some scale. Conclusively determining the importance of Fe requires further exploration in composition space as we cannot isolate the effect of Fe from that of Al within our limited dataset.

4.4 Eu Anomalies

Differing Eu anomalies apparent in Figure 2 are a consequence of crystal-chemical effects on partitioning, not variable $f\text{O}_2$. The 2+ parabolas inverted from the

experimental data include Eu^{2+} and the goodness of the fit suggests Eu substitution is dominantly if not completely as $2+$. Because Eu^{2+} has a much larger ionic radius than Eu^{3+} (Shannon, 1976) it may be more incompatible in pyroxene than interpolation between its nearest neighbors on a spider diagram would predict. However, under specific conditions it is possible for the M2 site in pyroxene to be hospitable to Eu^{2+} so that no Eu anomaly is observed. This concept has been demonstrated by Sun and Liang (2013b) for REE partitioning between low-Ca pyroxene and lunar picritic melts. If the $2+$ and $3+$ M2 parabolas are positioned such that they predict equivalent partition coefficients at the appropriate ionic radii, no Eu anomaly will be evident. Eu partition coefficients are plotted in Figure 6 using both $2+$ and $3+$ ionic radii (cyan diamonds and circles). Experiments HB-4, NJD-20, and NJD-22 exhibit moderate Eu anomalies (Figure 2a, also see Table 4) owing to the relative positions of their $2+$ and $3+$ parabolas (Figures 5c,f). The relative positions of the $2+$ and $3+$ parabolas can be partly attributed to differing pyroxene compositions; experiments with the most pronounced anomalies have lower Mg#s.

4.5 Heavy Rare Earth Element Partitioning

Olin and Wolff (2010) observed significant concave-up curvature for Er to Lu partition coefficients in their Fe-rich pyroxene and attribute it to substitution of HREE onto M1 and M2 sites of pyroxene. They modeled HREE (Er to Lu) partition coefficients using the lattice strain model assuming partition coefficients are the sum of M1 and M2 site substitution, and estimated properties of the M1 site assuming 8-fold coordination and using Sc to anchor the parabolas. Because we did not dope our experiments with Er

or Tm the curvature of our REE spidergrams is somewhat obscured by interpolation. However, our ferroan augite experiments contain enough Er and Tb to report and Figure 2a (red lines) shows subtle concave up curvature of Tm to Lu. Although the upward curvature is within the analytical uncertainty, we estimated parameters in the lattice strain model for individual experiments using La to Lu and La to Tm separately to determine the significance of the curvature. Figure 9 compares parabolas inverted from all REE (solid lines) and La to Tm (dotted gray lines). The La to Lu inversion slightly overestimates Tm and Er partition coefficients but reproduces them within the experimental uncertainty and successfully models Lu and Yb. The La to Tm inversion underestimates Lu D s by about 10% but does a slightly better job estimating lighter REE. There is probably limited substitution of HREE onto the M1 site in our pyroxene, but the subtlety of the HREE curvature does not merit parameterizing M1 and M2 partitioning separately. The success of Eqs. 1-4 in predicting all REE partition coefficients (Figure 8) warrants its use for the basaltic systems considered here.

5. Applications

To demonstrate the importance of pyroxene composition on trace element partition coefficients we apply our partitioning models to two planetary systems, the Martian nakhlites and the late lunar magma ocean cumulates.

5.1 Partition Coefficients for Lunar Magma Ocean Cumulates

The moon is thought to have formed in a giant impact that left a deep lunar magma ocean (LMO). As the LMO crystallized the liquid evolved from pyrolytic to

basaltic (e.g. Snyder et al., 1992; Elkins-Tanton et al., 2011), and it is thought that in the last 15% crystallization the residual liquid Mg# plummeted from about 55 to 0 (Snyder et al., 1992). Models of LMO crystallization predict clinopyroxene saturation after 80-85% solidification; it follows that the Fe (and X_{Al}^T , Figure 4b) content of LMO cumulate clinopyroxene increased significantly as solidification proceeded. REE and HFSE partition coefficient variation during LMO crystallization can be investigated using the MAGFOX model. Assuming an initial magma ocean depth of ~400 km, we used MAGFOX to calculate end-stage (93-96% LMO crystallization) cumulate clinopyroxene compositions (green circles joined by black line, Figure 1a). Conveniently, our partitioning models are pressure insensitive and MAGFOX outputs temperature. Predicted REE and HFSE⁴⁺ partition coefficients are shown in Figure 10a with color representing pyroxene Mg#, and selected partition coefficients are also reported in Table 6. For the compositions investigated, REE partition coefficients vary by a factor of 4.6 while HFSE partition coefficients, which show more dependence on X_{Al}^T (compare terms in Equations 5 and 2), vary by a factor of 10. Partition coefficient variation of this magnitude in a crystallizing magma ocean will affect trace element concentrations in clinopyroxene and other late stage LMO cumulates (e.g., plagioclase, Fe-Ti oxides, phosphates) as well as coevolving residual liquid.

To better understand the evolution of REE concentrations in a crystallizing lunar magma ocean, we ran a non-modal LMO crystallization model based on Snyder et al. (1992), incorporating modifications made by Münker (2010) and Dygert et al., (2013) (Figure 10b). The model assumes a sequence of five different crystallization lithologies; olivine ($F = 0-40\%$, where F is the degree of crystallization), orthopyroxene ($F = 40-$

78%), olivine-pigeonite-plagioclase ($F = 78-86\%$), pigeonite-clinopyroxene-plagioclase ($F = 86-95\%$), and finally pigeonite-clinopyroxene-plagioclase-ilmenite ($F = 95-100\%$), see figure caption for phase proportions. Batch crystallization ($F = 0-78\%$) is followed by fractional crystallization, and each cumulate pile consists of 3% trapped melt as in previous studies (Münker, 2010; Dygert et al., 2013). Because REE and HFSE partition coefficients are composition dependent, LMO crystallization models that track trace element behavior must simultaneously budget major element compositions of fractionating minerals and host liquid. To calculate clinopyroxene partition coefficients we used MAGFOX output (Figure 10a). Because the MAGFOX crystallization sequence differs from Snyder et al. (1992), we use the first and last calculated MAGFOX clinopyroxene compositions (Table 6) as end members and assume linear partition coefficient variation between them for each crystallization step (0.05%). This is obviously a crude approximation as current LMO crystallization models cannot make accurate predictions of mineral compositional variations.

For plagioclase, orthopyroxene, and ilmenite, we used new experimentally determined lunar-relevant partition coefficients (Dygert et al., 2013; Graff et al., 2013; Sun and Liang, 2013b), and calculated olivine and pigeonite partition coefficients (Sun and Liang 2013a; Yao et al., 2012) for major element compositions from experimental work by Dygert et al. (2013) (olivine) and a lunar pigeonite from KREEP basalt 15386 (Takeda et al., 1978). The model results are shown in Figure 10b as solid black lines. The field defined by KREEP basalts (Papike, 1998) is shown in green for comparison. We ran a similar model with constant clinopyroxene partition coefficients (red lines, Figure 10b) from McDade et al. (2003; heavy black line, Figure 10a), which were used previously by

Münker (2010). Other partition coefficients (olivine, orthopyroxene, pigeonite, plagioclase, and ilmenite) are the same in both models. Comparison of the red and black lines in Figure 10b shows the two models have similar LREE abundances at each crystallization interval while mid-heavy REE concentrations are initially similar but diverge as F approaches 99.5%, with the constant partition coefficient model generating lower mid-heavy REE abundances than the variable partitioning model. The variable partitioning model has lower bulk mid-heavy REE partition coefficients and correspondingly higher REE concentrations in calculated residual liquids (Black lines, Figure 10b). Equations 1-4 predict increasing partition coefficients as LMO crystallization proceeds, however the partition coefficient values never reach those of McDade et al. (2003) (Figure 10a) so the models diverge. Abundances of La, Ce, and Pr in residual melts in the two models are approximately equal because partition coefficients for those elements are higher in plagioclase than hedenbergite, pigeonite, and ilmenite (e.g., $D_{\text{La}} = 0.058$ for anorthite, Graff et al., 2013). The consequence of these two effects is a difference in slope for the REE pattern, with the variable partition coefficient model exhibiting a shallower slope. The constant partition coefficient model does a slightly better job matching the REE pattern expressed by KREEP basalts, which are thought to be derivative of late-stage LMO cumulates. This could be attributed to several different factors, such as incorrect crystallization sequence and phase proportions in the Snyder et al. (1992) model. Incorporation of composition dependent partition coefficients for all relevant minerals could improve the model prediction. The discrepancy could also be due to melting processes, for example, melts of LMO cumulates could produce a steeper REE pattern consistent with the KREEP basalts. To better constrain cumulate compositions a

new magma ocean crystallization model is needed, and the phase equilibrium data and partitioning models of this study will support future efforts to model LMO crystallization.

5.2 Partition Coefficients for Nakhrites

The nakhrites are a suite of Martian meteorites consisting of olivine-bearing clinopyroxenites. They are thought to have originated from a single lava flow (e.g., Wadhwa and Crozaz, 1995; Treiman, 2005). Nakhrites have zoned clinopyroxene with cores of near uniform composition (Mg# ~62, X_{Al}^T 0.010-0.048) but widely varying rim compositions (Mg# 19-53, X_{Al}^T 0.026-0.145), suggesting they came from distinct stratigraphic horizons in a fractionating cumulate pile (e.g., Day et al., 2006; Udury et al., 2012). Recent attempts at inverting parent melt compositions apply partition coefficients reported in McKay et al. (1994) and Oe et al. (2001) (e.g., sample NJ-4, heavy black line, Figure 10c) to nakhrite cores (e.g., Wadhwa and Crozaz, 1995; Day et al., 2006; Udry et al., 2012). Here, we calculate partition coefficients for representative nakhrite rim and core compositions to demonstrate the dependence of REE and HFSE partitioning on X_{Al}^T , and to compare with NJ-4. Partition coefficients for representative rim and core compositions from most nakhrites (Nakhla, Governador Valdaferes, Lafayette, NWA 817, NWA 998, Yamato Y000593, Yamato 000749, MIL 03346, MIL 090030, MIL 090032, MIL 090136, see figure caption for references) are presented in Figure 10c (colored lines). Averaged partition coefficients calculated for nakhrite rims and cores are also listed in Table 6. In the calculation, we assume cores crystallized at 1160°C (Oe et al., 2001) and rims crystallized at 1000°C. Nakhrite cores (dashed lines, Figure 10c) have near uniform partition coefficients while rims (solid lines) have more widely varying

partition coefficients. Core-to-rim partition coefficient variations are more than a factor of 3 for REE and 5 for HFSE. Predicted nakhlite core partition coefficients are calculated at the experimental temperature of NJ-4 (1160°C, Oe et al., 2001) and approximate the measured values (compare heavy black line and dashed lines, Figure 10c). Nakhlite cores (circled in Figure 4) are slightly less Ca, Fe, and Al rich than our experiments (about 10 Mg# units higher and 0.03 X_{Al}^T units lower), demonstrating the Al based partitioning models can be extrapolated within Fe-rich basaltic systems. As a further test of our Al based model, we compared REE partition coefficients calculated using Equations 1-4 at 1000°C to partition coefficients calculated from SIMS analyses of pyroxene rims and mesostasis in MIL 03346 and NWA817 (Day et al., 2006; Wadhwa et al., 2004). Results are presented in Figure 10d, with D_s calculated using the partitioning model shown as solid lines and D_s from SIMS analyses shown as dashed lines. For both meteorites the model predictions match the curvature of the partition coefficients as well as the absolute values. These exercises demonstrate the applicability of Equations 1-4 to the nakhlites, and provide evidence that Al based models better predict REE partitioning in Fe-rich basaltic systems.

In general as a clinopyroxene-bearing liquid crystallizes its Fe and Al content increases, leading to enrichment in X_{Al}^T and X_{Fe}^{M1} in clinopyroxene rims (e.g., Figure 4b). Temperature concomitantly decreases so both composition and temperature work to increase REE and HFSE partition coefficients from a clinopyroxene core to its rim (e.g., Figure 10b). These variations in partition coefficients will introduce zoning independent of changes in REE and HFSE concentrations in the host liquid. Interpretations of grain

scale concentration variations in pyroxene with evolved rim compositions must take this into account or the compositional evolution of host melt may be overestimated.

6. Summary and Conclusions

Fe-rich clinopyroxene often occurs at late stage differentiation of mafic magmas from Earth, the Moon, Mars, angrite parent bodies, and elsewhere. Trace element clinopyroxene-melt partitioning in Mg-rich systems is well characterized while Fe-rich basaltic systems are understudied. We measured trace element partition coefficients for Fe-rich augite and hedenbergite at temperatures of 1050-1220°C and pressures of 0.8-2.2 GPa. Partition coefficients are reported for 37 elements. We observe strong correlations of REE and HFSE partition coefficients with the cation abundance of Fe on the pyroxene M1 site and Al on the tetrahedral site. We developed simple parameterized lattice-strain models that quantify REE and HFSE partition coefficients as functions of T and X_{Al}^T or X_{Fe}^{M1} . Consistent with crystal-chemical arguments and previous studies, model predictions and coefficient uncertainties suggest that Al is a better predictor of partition coefficients within Fe-rich basaltic systems. Partitioning models were applied to lunar magma ocean cumulate compositions calculated by MAGFOX and revealed a factor of 4.6 variation for REE and a factor of 10 variation for HFSE. Representative nakhlite clinopyroxene cores and rims were similarly investigated, and REE partition coefficients vary by a factor of 3 while HFSE partition coefficients vary by a factor of five. Experimental data and partitioning models reported here are significant improvements over what was available previously. They could be used to invert parent magma compositions, model the

petrogenesis of Fe-rich basaltic rocks, or be incorporated into improved magma ocean crystallization models.

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9. Figure Captions

Figure 1. Examples of naturally occurring Fe-rich pyroxene (a), and pyroxene compositions in selected trace element partitioning studies (b). Fe-rich pyroxene is observed in nakhlite meteorites from Mars (yellow and green fields), the angrite parent body (salmon field), terrestrial layered intrusions (red and blue lines), the lunar alkali suite (pink diamonds), and MAGFOX calculated lunar magma ocean cumulates (green circles joined by black line). Blue field in (b) denotes pyroxene compositions in laboratory trace element partitioning studies that were included in the parameterized lattice strain model of Sun and Liang (2012). White diamonds are clinopyroxene from natural rocks (tuff and phonolite), green circles are nakhlite analogue experiments, and large red circles are from this study. Data used to define nakhlite fields is from Wadhwa and Crozaz (1995), Wadhwa et al. (2004), Day et al. (2006), and Udury et al. (2012).

Figure 2. (a) REE partition coefficients from the literature (brown and green lines) and this study (red, black, and blue lines, see legend in 2b). Partition coefficients of Olin and Wolff (2010) (brown lines) show significant upward HREE curvature and high absolute values. Note the nakhlite analogue experiment of Oe et al. (2001) (green line) plots between our FR-1290+Augite experiments and experiments with lower Mg#s (blue and black lines). (b) Ratio of measured vs. predicted partition coefficients using the parameterized partitioning model of Sun and Liang (2012). The model underestimates HREE partition coefficients for Olin and Wolff (2010) and significantly overestimates partition coefficients reported in this study. (c) Partition coefficients reported for our experiments grouped by element affinity. Error-bars are 2σ .

Figure 3. Reflected light micrograph (a) and backscatter electron image (b) of two partitioning experiments (HB-4 and HB-5, respectively). The crystal sizes and lack of quench modification are typical of the experimental suite. Note the presence of ulvöspinel along edges of the charge in (a). Core-rim zoning is evident in (b) and also present in HB-7. Zoning is minimal in other experiments. Ablation pits (black circles) are indicated in (b).

Figure 4. Temperature (a) and compositional parameters (b, c) with potential to affect trace element partitioning in pyroxene plotted against tetrahedrally coordinated Al in pyroxene (X_{Al}^T). The correlations make isolating the effect of individual parameters on trace element partitioning impossible with the current dataset. Note the nakhlites (yellow circles) and MAGFOX calculated magma ocean cumulates (red circles) overlap our experimental results in X_{Fe}^{M1} vs. X_{Al}^T (b) and Mg# vs X_{Al}^T (c). Nakhlite cores are circled, remaining nakhlite data are rims.

Figure 5. Partition coefficients plotted against X_{Fe}^{M1} (a, b) and X_{Al}^T (d, e), and D_0 terms in the lattice strain model obtained by inverting our measured partitioning data plotted against X_{Fe}^{M1} (c) and X_{Al}^T (e). Note the systematic positive correlation of partition coefficients with X_{Fe}^{M1} for almost all elements, with the possible exception of some transition metals (Ga, Sc, Co, Mn, Zn) at high X_{Fe}^{M1} . Partition coefficients are also positively correlated with X_{Al}^T , though the data is scattered at high X_{Al}^T .

Figure 6. Onuma diagrams showing variations of measured trace element partition coefficients as a function of ionic radius for 1+ cations (black lines), 2+ cations (violet lines), 3+ cations with smaller ionic radii (green lines), REE+Y (red lines) and 4+ cations (blue lines) for four experiments (see supplementary Figure S12 for the three remaining experiments). Eu is plotted against its two and three plus ionic radii (cyan circle and diamond respectively). Lattice strain parabolas inverted from experimental data are shown as color-coded curves. Parabolas for 2+ cations were inverted from measured partition coefficients including Eu.

Figure 7. Variation of effective Young's moduli (E) inverted from individual partitioning experiments (Figure 6, Supplementary Figure S12, Table 4) as a function of ionic charge for 1+ to 4+ cations.

Figure 8. Measured REE (yellow) and HFSE (green) partition coefficients plotted against X_{Al}^T -based model predictions. Uncertainties in the predicted and measured values are 2σ . Solid blue line is 1:1 and dotted lines are 1:2 and 2:1.

Figure 9. Onuma diagrams comparing lattice strain parabolas inverted from REE+Y from individual experiments (solid lines) to parabolas inverted from Tm-La (gray dotted lines). Tm-La parabolas better model Tm and Er, but La-Lu parabolas better model all REE.

Figure 10. Partition coefficients calculated from MAGFOX output for lunar magma ocean (LMO) clinopyroxene cumulates compared to those from McDade et al. (2003) (a),

calculated liquid compositions for lunar magma ocean crystallization models (b), partition coefficients calculated for representative nakhlite compositions (rims are dotted lines, cores are solid lines) compared to NJ-4 from Oe et al. (2001) (c), and comparison of nakhlite rim partition coefficients calculated from SIMS analyses (dashed lines) and Equations 1-4 (solid lines) (d). Line color in (a) and (c) corresponds to Mg# as defined by the scale in (c). Major element data used in (c) is from Wadhwa and Crozaz (1995), Wadhwa et al. (2004), Day et al. (2006), and Udury et al. (2012). Phase proportions for LMO crystallization model are the following: (1) 97% olivine, 3% trapped liquid (2) 97% orthopyroxene, 3% trapped liquid (3) 24% olivine, 21% pigeonite, 51% plagioclase, 3% trapped liquid (4) 25% pigeonite, 37% clinopyroxene, 35% plagioclase, 3% trapped liquid and (5) 33% pigeonite, 23% clinopyroxene, 30%, plagioclase, 11% ilmenite, and 3% trapped liquid. Data used to produce (d) is from Wadhwa et al. (2004), and Day et al. (2006).

Figure 1.

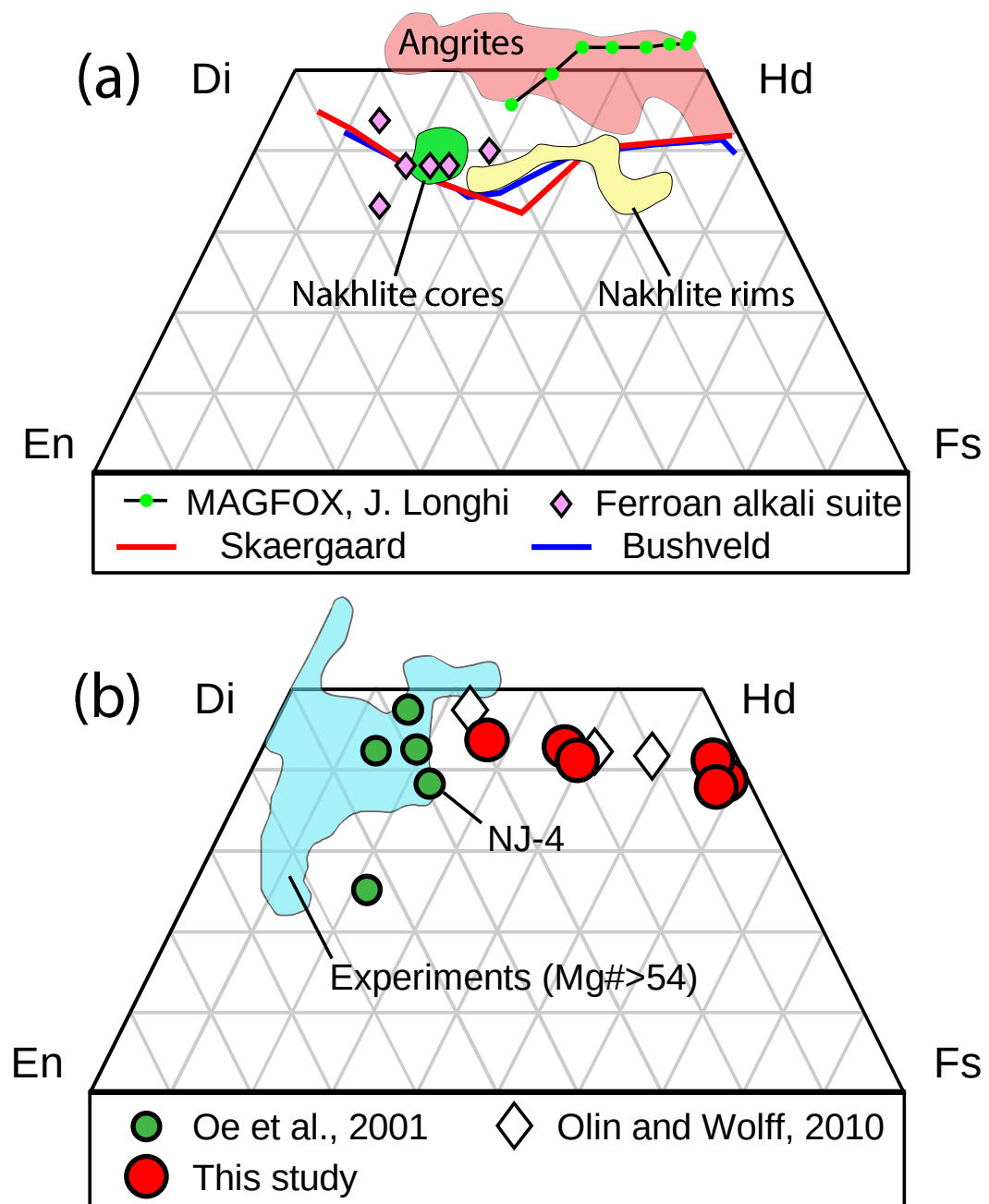


Figure 2.

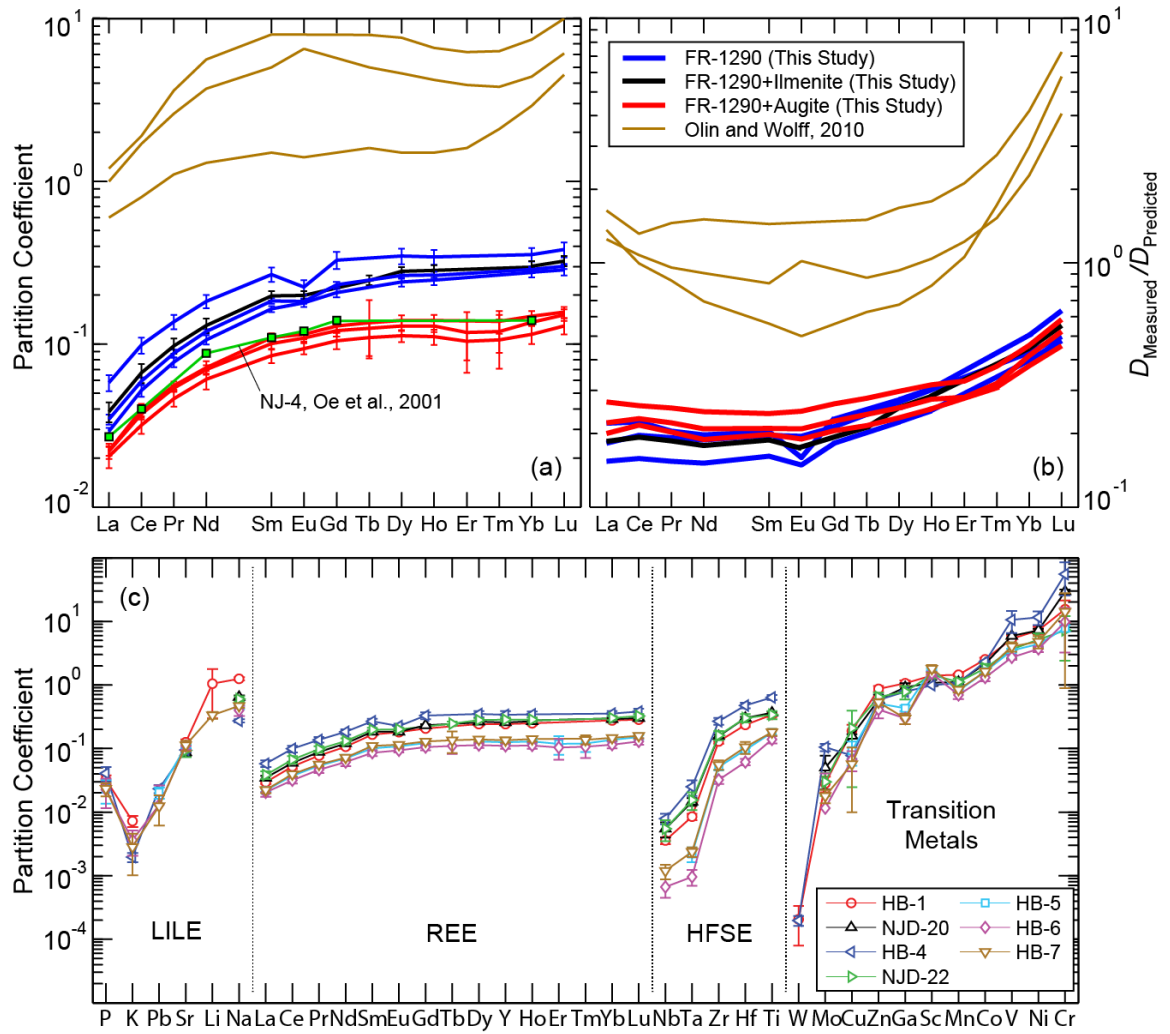


Figure 3.

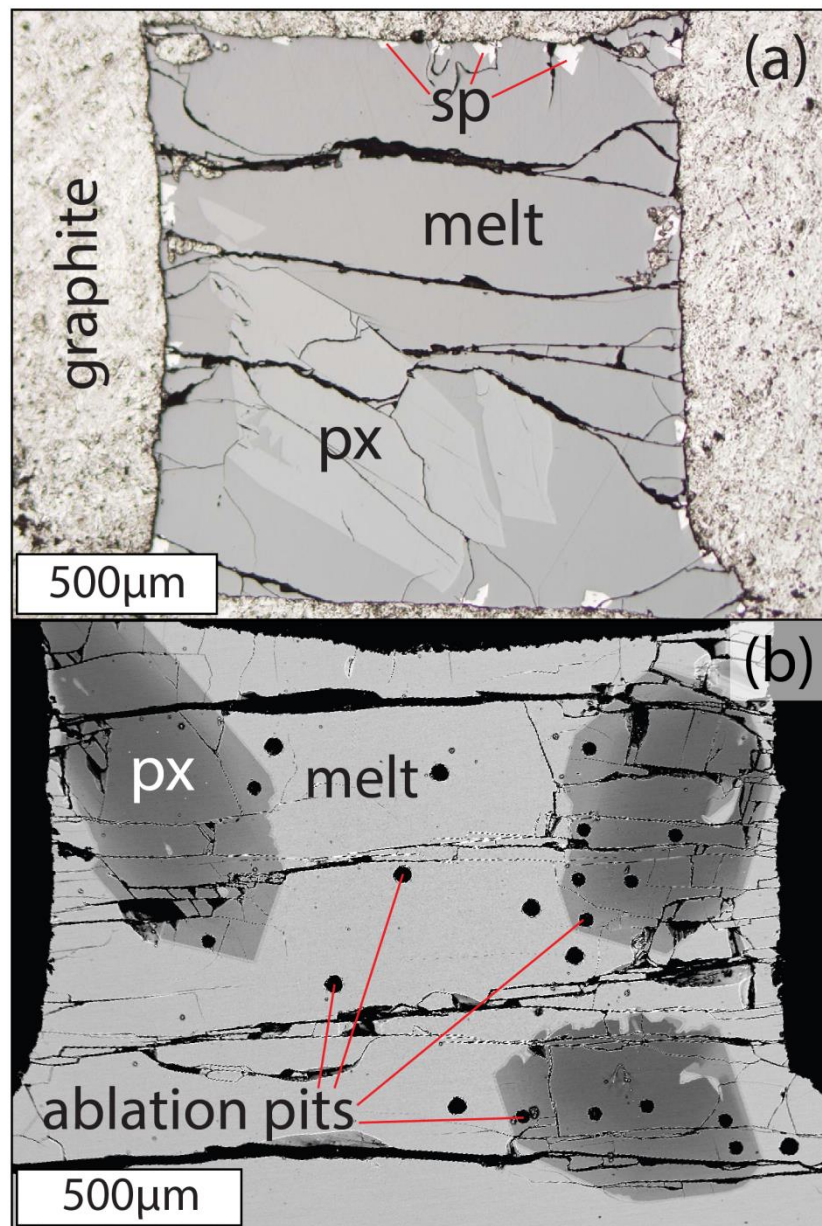


Figure 4.

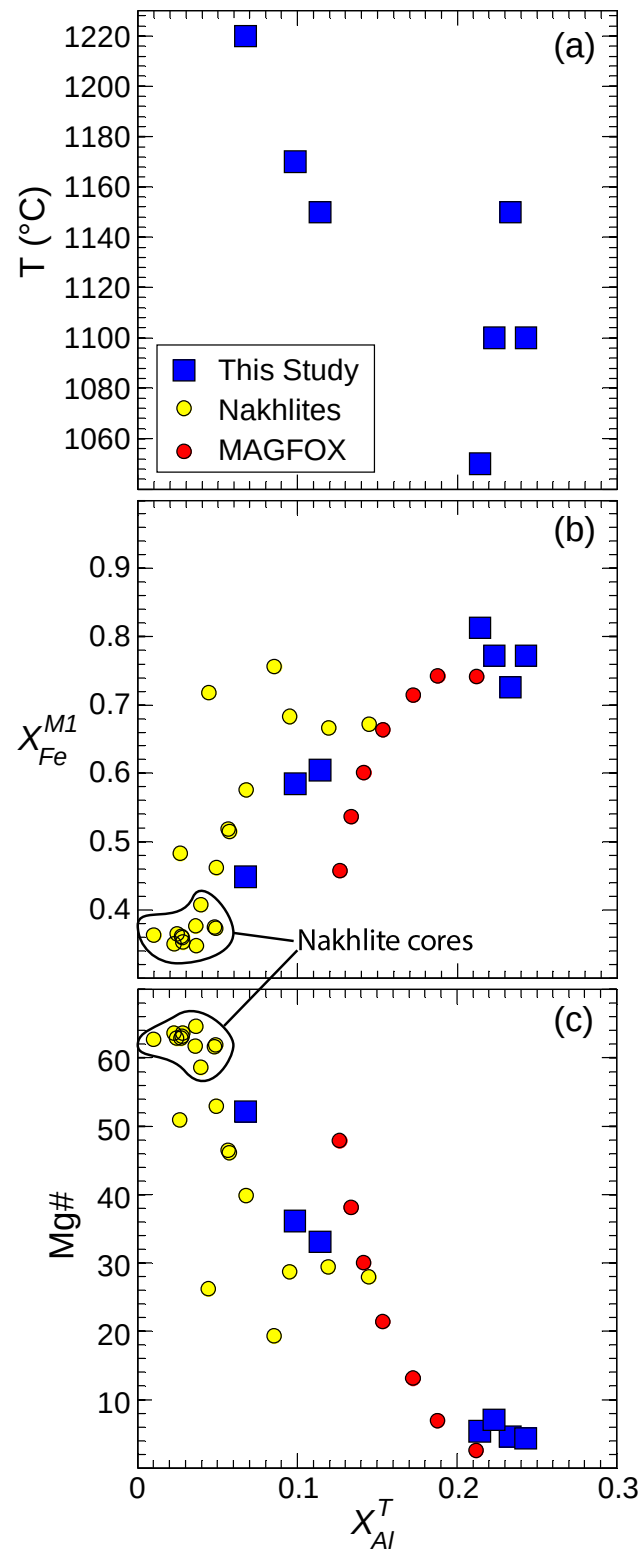


Figure 5.

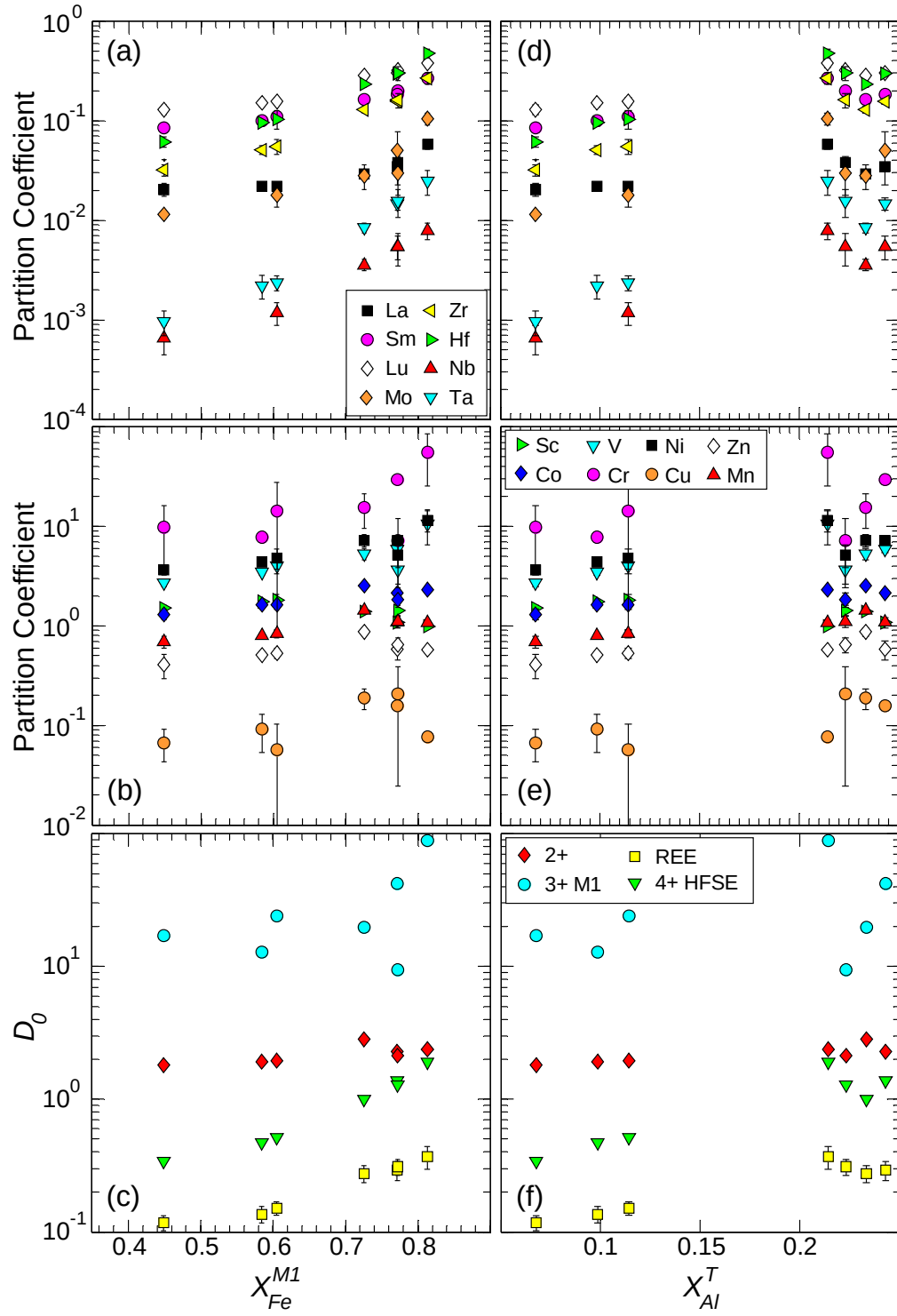


Figure 6.

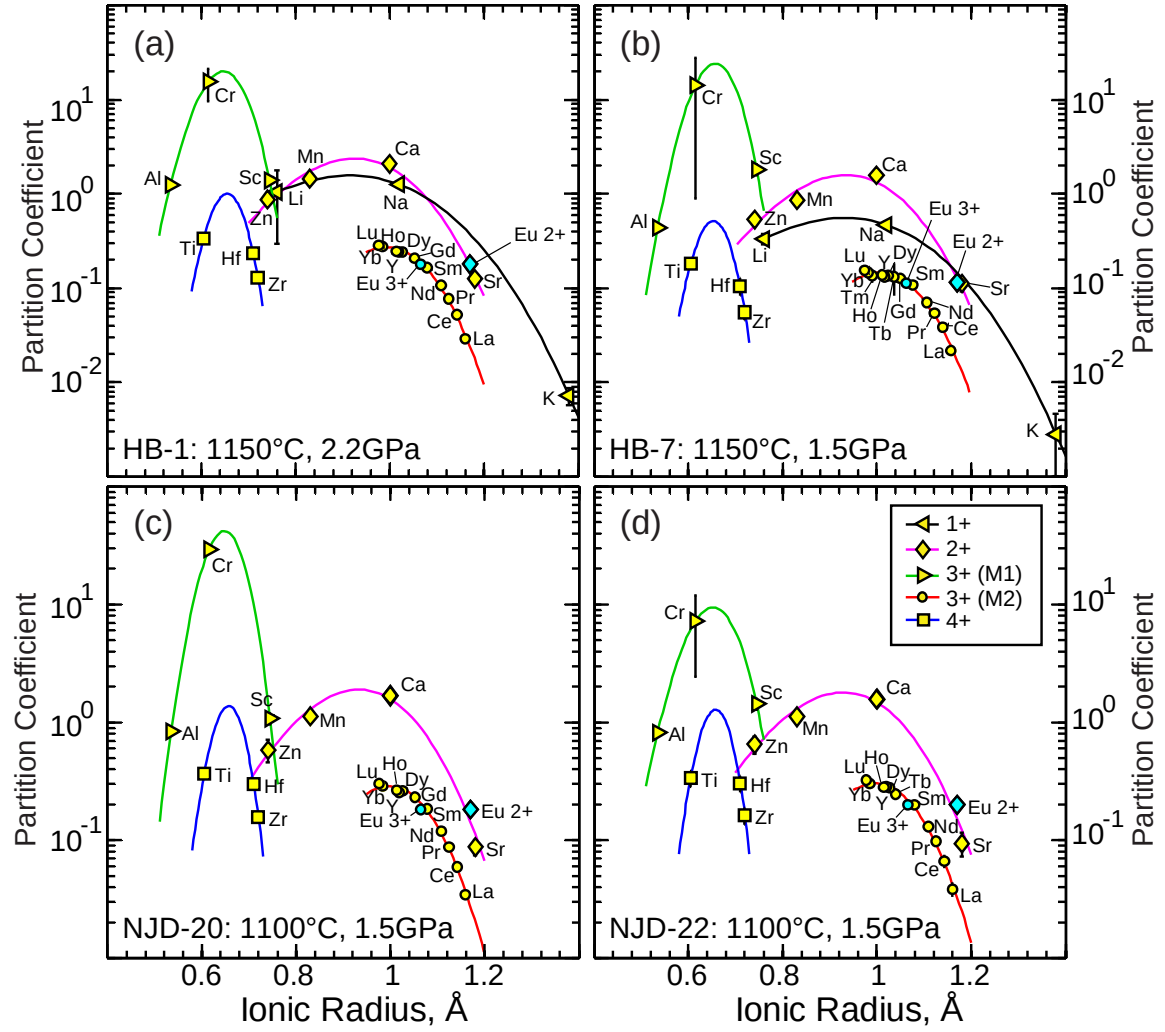


Figure 7.

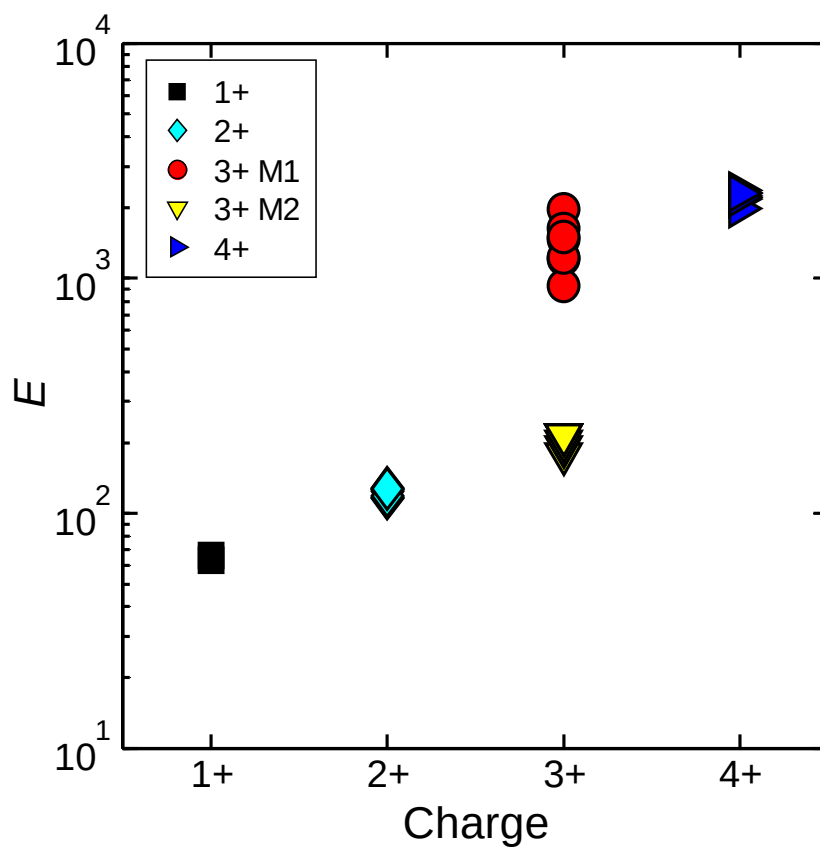


Figure 8.

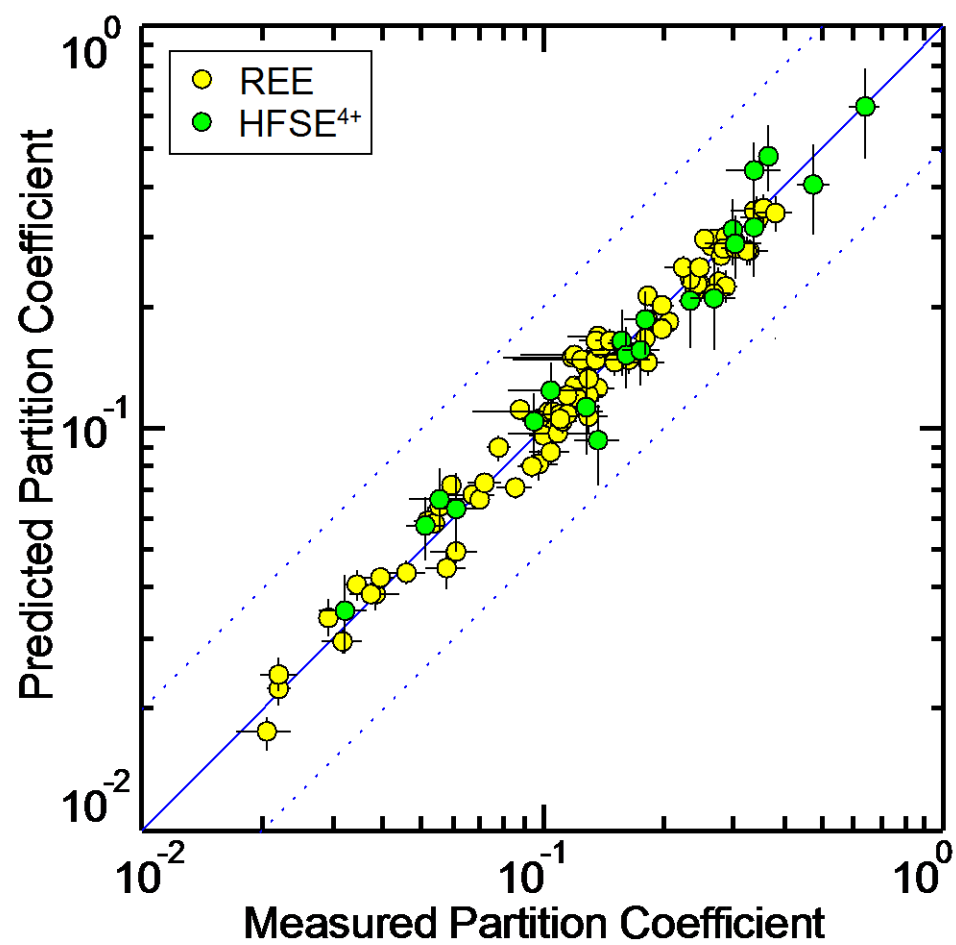


Figure 9.

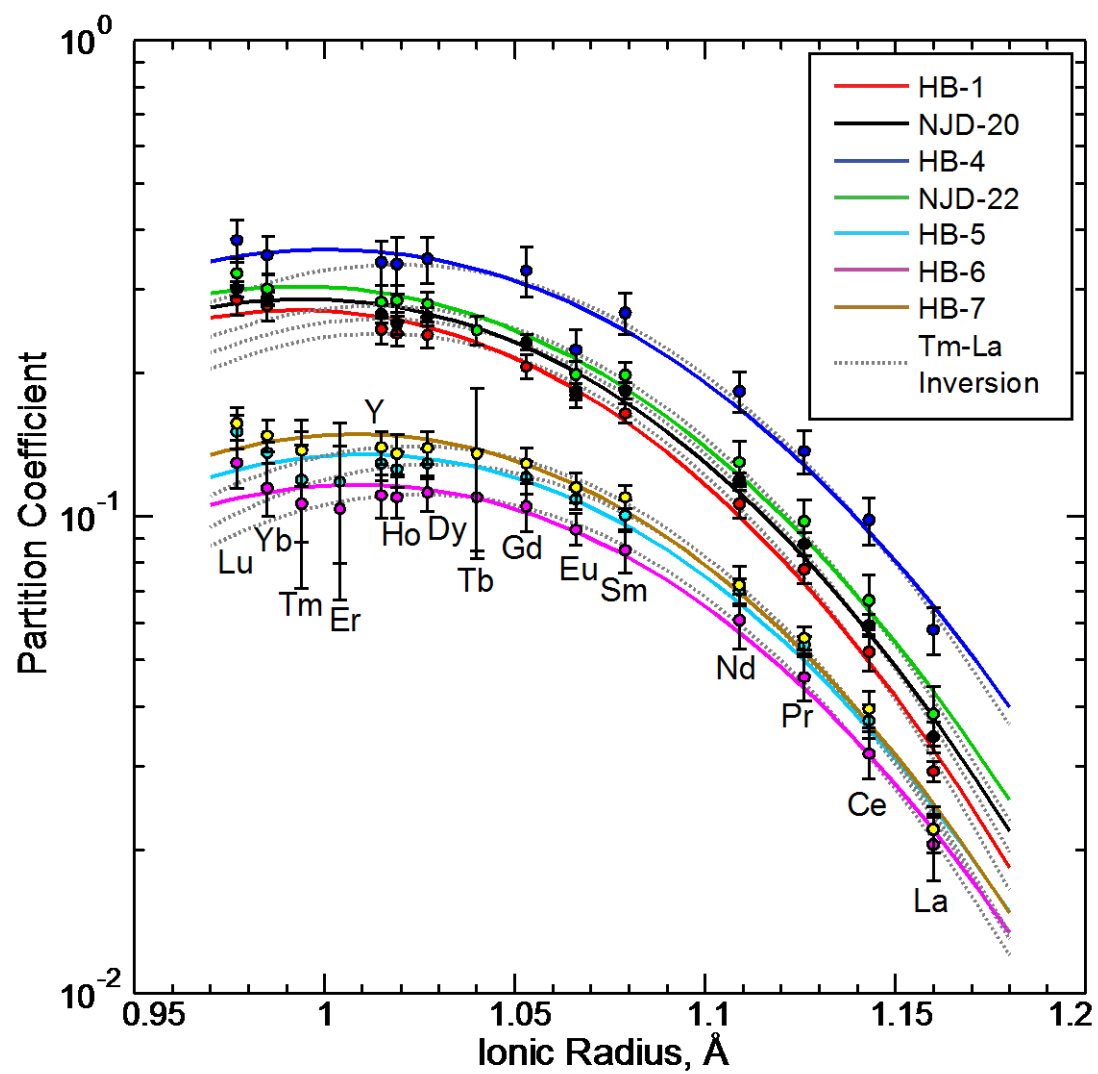


Figure 10.

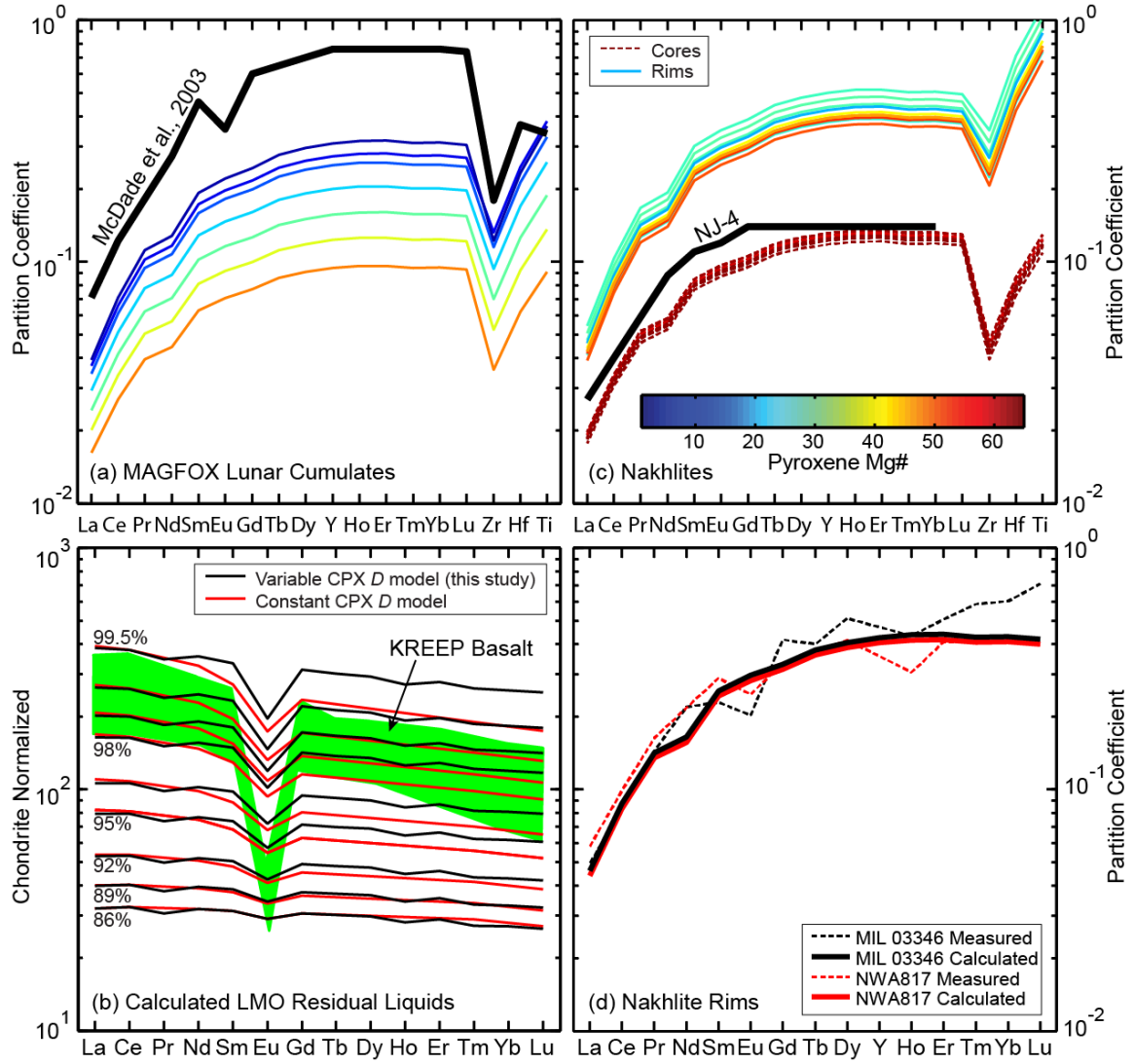


Table 1.

Composition of Starting Materials												
Material	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MgO	MnO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total Mg#
FR-1290 ^a	44.16	4.05	8.67	0.11	29.86	0.26	0.70	10.89	0.50	0.36	0.40	100.0
Ilmenite ^b	-	49.50	-	-	45.20	0.30	3.50	-	-	-	-	98.5
Harcourt Augite ^c	53.98	0.10	0.77	-	6.05	15.84	-	21.04	1.22	-	-	99.0

^aMajor element composition of our FR-1290 starting material (as reported by Longhi, 2003), not including added mixture of REE+HFSE oxides.

^bAnalysis reported by Thacker et al. (2009).

^cAnalysis reported by Hoch et al. (1996).

Table 2.

Starting Materials and Run Conditions							
Experiment	Starting Material	P (Gpa)	T(°C)	Target dwell (h)	Total duration (h)	Temperature Path (°C) ^a	Run Products ^b
NJD-20	FR-1290	1.5	1100	59	97	1400° (8h) → 1250° @ 0.5°/min → 1100° @ 0.1°/min	Px + Sp + Qtz + Melt
	83% FR-1290 + 17% Ilm					1400° (8h) → 1250° @ 0.5°/min → 1100° @ 0.1°/min	
NJD-22	Ilm	1.5	1100	48	86		Px + Ilm + Melt
HB-1	FR-1290	2.2	1150	50	71	1400° (8h) → 1150° @ 0.2°/min	Px + Qtz + Melt
	1400° (8h) → 1200° @ 0.5°/min → 1050° @ 0.1°/min						
HB-4	FR-1290	0.8	1050	48	88	1400° (24h) → 1300° @ 1.0°/min → 1170° @ 0.1°/min	Px + Sp + Melt
	80% FR-1290 + 20% Augite						
HB-5	80% FR-1290 + 20% Augite	1.5	1170	50	97		Px + Melt
HB-6	Augite	1.5	1220	65	119	1400° (24h) → 1220° @ 0.1°/min	Px + Melt
HB-7	89% FR-1290 + 11% Augite	1.5	1150	46	96	1400° (8h) → 1150° @ 0.1°/min	Px + Melt

^aTemperature path with superliquidus dwell time in parentheses. Arrows (→) signify a temperature decrease with cooling rates in °C/min following @

^aTemperature path with superliquidus dwell time in parentheses. Arrows (→) signify a temperature decrease with cooling rates in °C/min following @ symbols.

^bPx = pyroxene, Sp = spinel, Qtz = quartz, Ilm = ilmenite

Table 3.

Table 3: Major element compositions of pyroxene and melt

Pyroxene		HB-1		HB-4		NJD-22		NJD-20		HB-7 Rim		HB-5 Rim		HB-6 Rim	
n ^a	15	2σ	8	2σ	18	2σ	9	2σ	8	2σ	10	2σ	6	2σ	
SiO ₂	43.12	0.48	42.60	0.59	43.02	0.62	42.49	0.24	47.25	0.37	47.82	0.23	49.71	0.64	
TiO ₂	1.24	0.12	2.11	0.33	1.80	0.36	1.81	0.19	0.81	0.06	0.74	0.05	0.49	0.07	
Al ₂ O ₃	8.70	0.61	5.85	0.73	6.92	0.85	7.50	0.44	3.87	0.34	3.37	0.28	2.34	0.30	
Cr ₂ O ₃	0.46	0.16	-	-	-	-	0.46	0.21	0.12	0.05	0.08	0.03	0.23	0.10	
FeO	28.72	0.55	28.92	1.01	29.23	0.67	29.83	0.70	21.60	0.72	20.45	0.30	15.79	1.72	
MgO	0.77	0.10	0.92	0.13	1.24	0.14	0.76	0.06	5.99	0.52	6.50	0.14	9.67	1.18	
MnO	0.86	0.03	0.87	0.05	2.11	0.10	0.99	0.06	0.64	0.05	0.60	0.05	0.46	0.03	
CaO	14.96	0.21	16.76	0.65	14.85	0.55	15.32	0.26	18.49	0.44	19.13	0.21	20.07	0.31	
Na ₂ O	0.52	0.08	0.19	0.04	0.32	0.07	0.31	0.08	0.29	0.16	0.27	0.04	0.28	0.04	
Spec ^a	0.47		0.34		0.22		0.49		0.11		0.15		0.30		
Total	99.82		98.55		99.70		99.94		99.17		99.12		99.34		
Mg#	4.5		5.3		7.0		13.5		33.1		36.2		52.2		

Table 3 continued.

<u>Melt</u>	HB-1		HB-4		NJD-22		NJD-20		HB-7		HB-5		HB-6	
	10	2 σ	7	2 σ	10	2 σ	10	2 σ	12	2 σ	13	2 σ	11	2 σ
n	43.13	0.27	45.03	0.53	41.62	0.27	42.61	0.18	44.40	0.30	43.91	0.42	45.97	0.36
SiO ₂	4.65	0.09	3.85	0.37	5.34	0.17	5.12	0.04	3.83	0.14	3.81	0.09	3.27	0.08
TiO ₂	8.84	0.13	9.47	0.57	8.47	0.14	9.10	0.13	8.10	0.12	7.94	0.10	7.29	0.14
Al ₂ O ₃	29.27	0.62	27.96	1.45	28.90	0.40	29.69	0.58	26.69	0.12	25.43	0.30	24.88	0.29
FeO	0.18	0.01	0.12	0.02	0.28	0.01	0.12	0.01	1.43	0.02	1.63	0.06	2.47	0.04
MgO	0.81	0.07	0.82	0.07	1.98	0.07	0.91	0.05	0.74	0.03	0.73	0.05	0.69	0.06
MnO	9.71	0.26	9.37	0.23	9.46	0.09	9.13	0.24	11.87	0.18	12.39	0.16	13.49	0.12
CaO	0.55	0.10	0.67	0.06	0.59	0.12	0.66	0.07	0.60	0.07	0.70	0.09	0.68	0.09
Na ₂ O	0.44	0.05	0.45	0.08	0.41	0.01	0.48	0.03	0.35	0.02	0.36	0.01	0.33	0.01
K ₂ O	0.45	0.11	0.53	0.15	-	-	0.47	0.11	0.40	0.04	-	-	0.33	0.05
P ₂ O ₅	0.84		0.82		0.83		0.81		1.46		0.66		1.06	
Spec ¹	98.87		99.09		97.88		99.10		99.88		97.55		100.46	
Total	1.1		0.8		1.7		0.7		8.7		10.2		15.0	
Mg#														

^aNumber of averaged analyses.^bSum of trace element concentrations measured by LA-ICPMS reported as oxides.

Table 4.**Pyroxene-melt trace element partition coefficients**

Experiment	HB-1		HB-4		NJD-22		NJD-20	
Element	<i>D</i>	2 σ	<i>D</i>	2 σ	<i>D</i>	2 σ	<i>D</i>	2 σ
Li	0.76	0.56	-	-	-	-	-	-
Na	0.93	0.06	0.27	0.01	0.60	0.06	0.64	0.04
P	0.025	0.006	0.041	0.011	-	-	-	-
K	0.0054	0.0012	0.0020	0.0003	-	-	-	-
Sc	1.03	0.09	0.99	0.04	1.43	0.16	1.08	0.12
Ti	0.25	0.02	0.64	0.06	0.34	0.05	0.37	0.01
V	3.9	0.5	10.6	4.0	3.6	1.0	5.9	0.4
Cr	11.2	5.2	55.2	29.8	7.2	4.8	29.4	2.1
Mn	1.06	0.05	1.08	0.07	1.11	0.15	1.10	0.04
Co	1.86	0.10	2.32	0.07	1.83	0.31	2.13	0.14
Ni	5.3	0.7	11.5	2.8	5.2	1.3	7.2	0.4
Cu	0.14	0.03	0.077	0.008	-	-	0.16	0.01
Zn	0.64	0.05	0.58	0.03	0.65	0.11	0.58	0.13
Ga	0.78	0.09	0.78	0.04	0.78	0.19	0.91	0.15
Sr	0.094	0.011	0.094	0.007	0.094	0.022	0.087	0.013
Y	0.181	0.018	0.339	0.046	0.284	0.020	0.255	0.014
Zr	0.096	0.012	0.268	0.034	0.162	0.027	0.157	0.010
Nb	0.0027	0.0004	0.0079	0.0015	0.0054	0.0020	0.0054	0.0015
Mo	0.021	0.006	0.105	0.014	0.030	0.012	0.050	0.027
La	0.022	0.001	0.058	0.007	0.038	0.005	0.035	0.003
Ce	0.038	0.003	0.099	0.011	0.067	0.009	0.059	0.003
Pr	0.057	0.005	0.137	0.014	0.098	0.011	0.088	0.005
Nd	0.079	0.007	0.183	0.017	0.130	0.014	0.120	0.004
Sm	0.123	0.010	0.268	0.027	0.198	0.013	0.184	0.007
Eu	0.134	0.011	0.224	0.023	0.199	0.013	0.183	0.007
Gd	0.155	0.016	0.328	0.039	0.246	0.017	0.232	0.008
Tb	-	-	-	-	-	-	-	-
Dy	0.180	0.018	0.348	0.039	0.280	0.016	0.264	0.012
Ho	0.185	0.019	0.342	0.036	0.283	0.021	0.267	0.012
Er	-	-	-	-	-	-	-	-
Tm	-	-	-	-	-	-	-	-
Yb	0.206	0.020	0.355	0.033	0.301	0.023	0.288	0.011
Lu	0.213	0.022	0.381	0.039	0.324	0.024	0.301	0.011
Hf	0.175	0.020	0.476	0.047	0.303	0.048	0.300	0.014
Ta	0.0062	0.0008	0.0248	0.0070	0.0155	0.0048	0.0147	0.0020
W	0.00015	0.00009	0.00020	0.00003	-	-	-	-
Pb	-	-	0.023	0.003	-	-	-	-
n_{pyroxene}^a	6		3		5		5	
n_{melt}	10		4		4		8	
$\text{Mg\#}_{\text{pyroxene}}$	4.5		5.3		7.0		13.5	

^aNumber of averaged analyses.

Table 4 continued.

Experiment Element	HB-7 Rim		HB-5 Rim		HB-6 Rim	
	<i>D</i>	2σ	<i>D</i>	2σ	<i>D</i>	2σ
Li	0.331652	0.041068	-	-	-	-
Na	0.47	0.04	0.45	0.03	0.40	0.07
P	0.023	0.006	0.023	0.009	0.023	0.011
K	-	-	-	-	0.0036	0.0016
Sc	1.81	0.25	1.76	0.07	1.51	0.12
Ti	0.18	0.02	0.18	0.02	0.14	0.02
V	4.0	0.7	3.5	0.2	2.7	0.2
Cr	-	-	7.8	0.9	9.78	6.54
Mn	0.84	0.08	0.81	0.04	0.69	0.09
Co	1.63	0.17	1.63	0.13	1.31	0.16
Ni	4.8	1.1	4.4	0.4	3.7	0.4
Cu	-	-	0.092	0.038	0.07	0.02
Zn	0.53	0.06	0.51	0.04	0.41	0.11
Ga	-	-	0.43	0.04	0.30	0.06
Sr	0.112	0.021	0.108	0.006	0.110	0.016
Y	0.136	0.013	0.126	0.011	0.110	0.011
Zr	0.055	0.009	0.051	0.005	0.032	0.004
Nb	0.0012	0.0003	-	-	0.0007	0.0002
Mo	0.018	0.004	-	-	-	-
La	0.022	0.002	0.022	0.001	0.020	0.003
Ce	0.039	0.003	0.037	0.003	0.032	0.004
Pr	0.056	0.003	0.054	0.002	0.046	0.005
Nd	0.072	0.007	0.070	0.004	0.061	0.008
Sm	0.110	0.006	0.101	0.008	0.085	0.009
Eu	0.115	0.008	0.109	0.005	0.094	0.007
Gd	0.130	0.010	0.121	0.010	0.105	0.012
Tb	0.135	0.051	-	-	0.110	0.028
Dy	0.139	0.011	0.129	0.009	0.112	0.010
Ho	0.140	0.011	0.129	0.010	0.111	0.012
Er	-	-	0.118	0.039	0.104	0.037
Tm	0.138	0.022	0.120	0.031	0.106	0.035
Yb	0.148	0.012	0.136	0.007	0.115	0.015
Lu	0.157	0.012	0.151	0.012	0.130	0.015
Hf	0.104	0.022	0.095	0.007	0.061	0.007
Ta	0.0024	0.0004	0.0022	0.0006	0.0010	0.0003
W	-	-	-	-	-	-
Pb	0.012	0.006	0.020	0.004	-	-
n_{pyroxene}^a	3		3		7	
n_{melt}	5		6		8	
$\text{Mg\#}_{\text{pyroxene}}$	33.1		36.2		52.2	

Table 5.

Lattice strain parameters from individual experiments							
Run	HB-1	HB-4	NJD-22	NJD-20	HB-7	HB-5	HB-6
<u>M2 (1+)</u>							
D_0	1.15	-	-	-	0.55	-	-
r_0 (Å)	0.92	-	-	-	0.93	-	-
E (GPa)	64	-	-	-	66	-	-
<u>M2 (2+)</u>							
D_0	1.73	1.96	1.79	1.89	1.58	1.54	1.44
r_0 (Å)	0.925	0.937	0.928	0.933	0.933	0.934	0.941
E (GPa)	125	122	117	127	127	131	142
<u>M1 (3+)</u>							
D_0	14.2	89.0	9.44	42.0	24.0	12.9	17.1
r_0 (Å)	0.647	0.649	0.652	0.648	0.657	0.660	0.659
E (GPa)	1191	1969	929	1630	1461	1229	1503
<u>M2 (3+)</u>							
D_0	0.205	0.364	0.304	0.287	0.152	0.135	0.117
r_0 (Å)	0.991	1.001	0.993	0.995	1.006	1.010	1.009
E (GPa)	213	179	192	202	215	216	215
<u>M1 (4+)</u>							
D_0	0.75	1.90	1.29	1.37	0.513	0.468	0.34
r_0 (Å)	0.655	0.656	0.660	0.657	0.653	0.653	0.651
E (GPa)	2193	1975	2316	2363	2240	2205	2298
$Mg^{\#}_{\text{pyroxene}}$	4.5	5.3	7.0	13.5	33.1	36.2	52.2

Table 6.

Calculated LMO and Nakhlite Partition Coefficients					
	First LMO clinopyroxene ^a	Last LMO clinopyroxene ^b	Average LMO clinopyroxene ^c	Nakhlite Rims	Nakhlite Cores
La	0.016	0.056	0.032	0.063	0.024
Ce	0.022	0.084	0.048	0.097	0.036
Pr	0.031	0.121	0.068	0.142	0.050
Nd	0.040	0.166	0.091	0.196	0.066
Sm	0.058	0.256	0.138	0.306	0.098
Eu	0.065	0.294	0.157	0.354	0.112
Gd	0.072	0.330	0.175	0.398	0.124
Tb	0.077	0.359	0.190	0.435	0.135
Dy	0.081	0.382	0.201	0.463	0.142
Y	0.083	0.391	0.206	0.475	0.146
Ho	0.084	0.395	0.208	0.479	0.147
Er	0.085	0.400	0.210	0.485	0.148
Tm	0.084	0.398	0.210	0.483	0.148
Yb	0.083	0.392	0.206	0.475	0.146
Lu	0.081	0.383	0.202	0.464	0.143
Zr	0.027	0.241	0.104	0.260	0.051
Hf	0.048	0.468	0.196	0.516	0.093
Ti	0.070	0.732	0.300	0.819	0.140

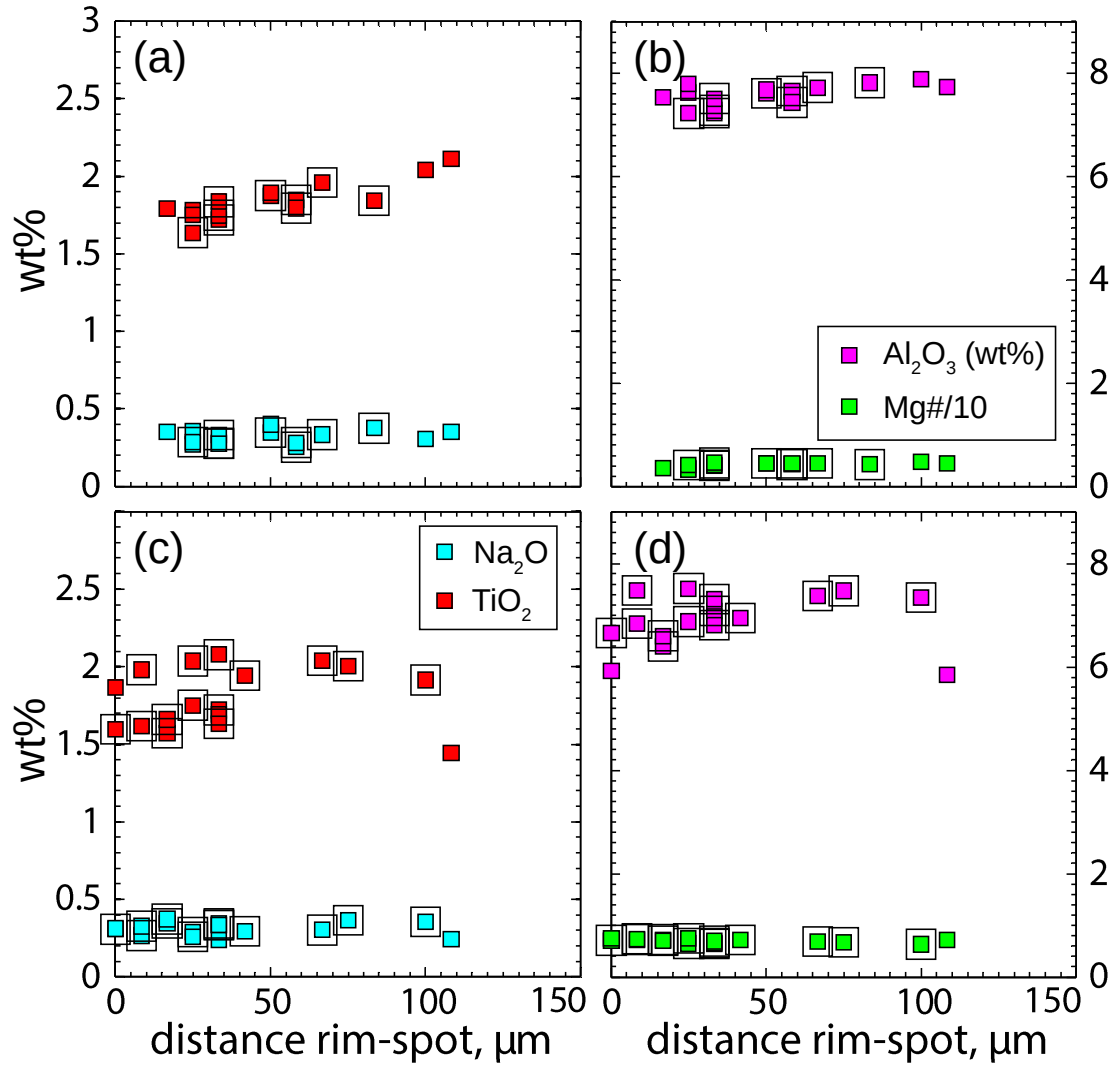
^aCalculated from MAGFOX output at clinopyroxene saturation.

^bCalculated from the last MAGFOX output.

^cAveraged from MAGFOX output at 7 crystallization intervals.

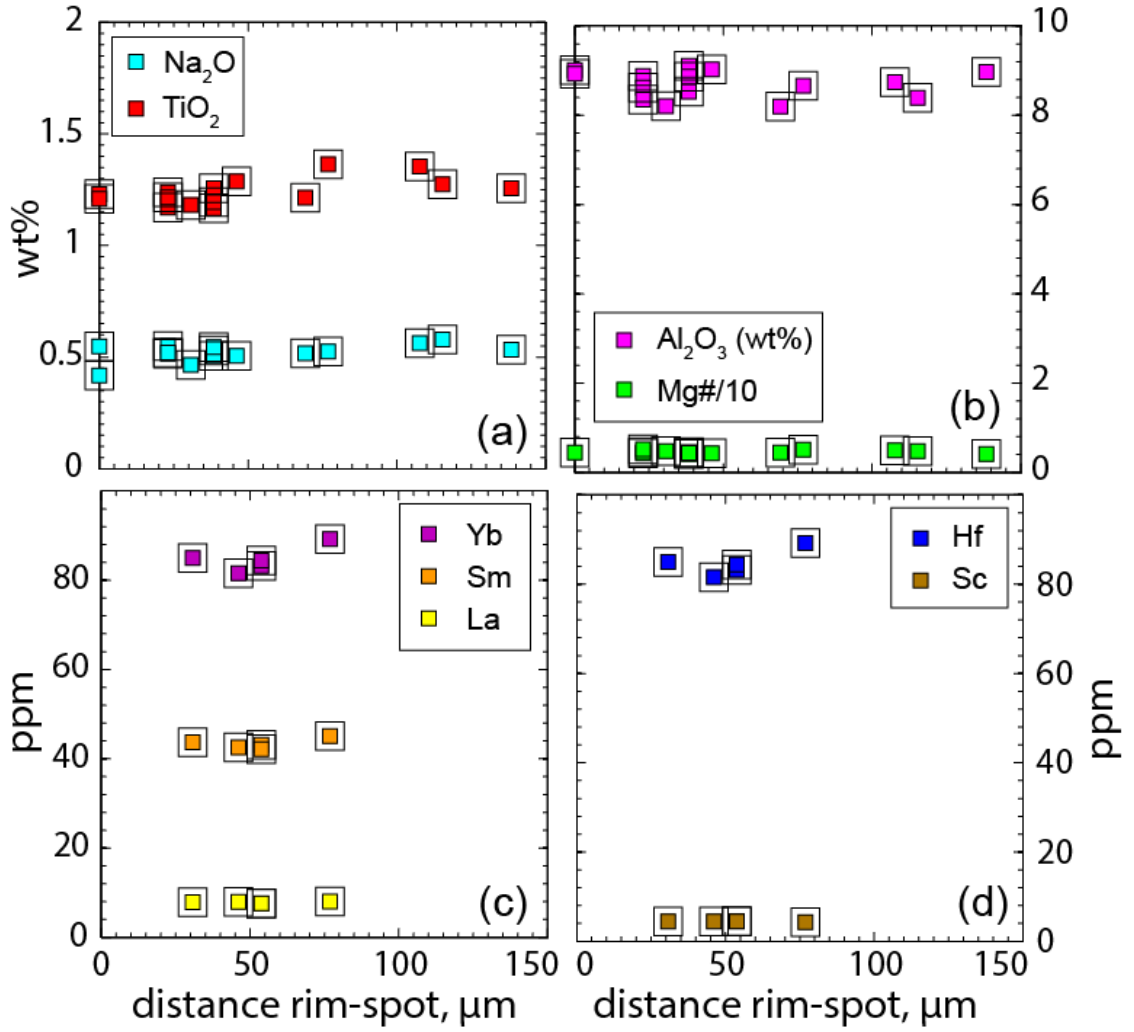
Supplementary Material

Figure S1.



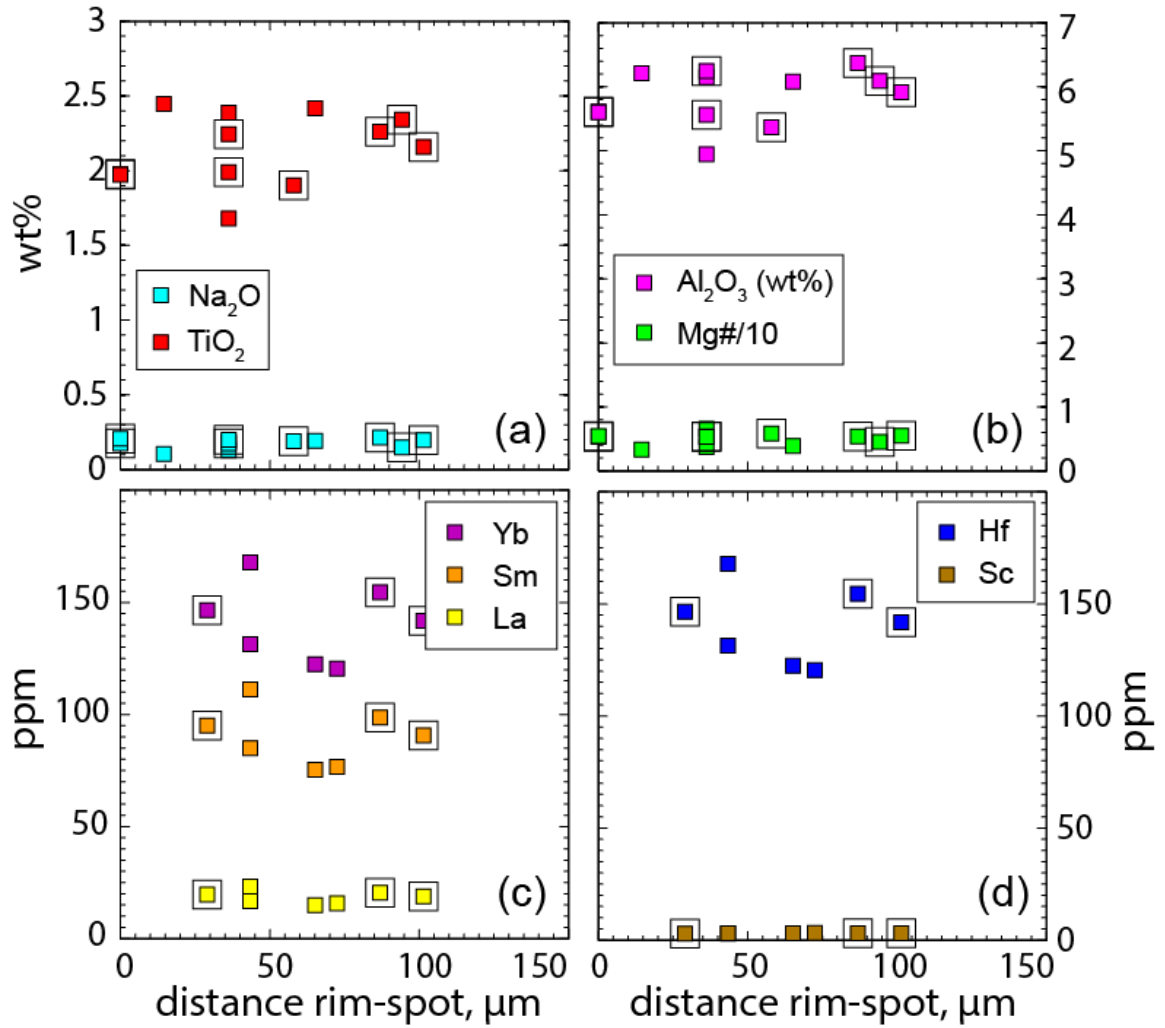
Selected major element compositions from experiments NJD-20 (a,b) and NJD-22 (c,d) plotted against approximate distance from spot center to crystal rim. Colored squares are individual spot analyses, larger black open squares show spots that were averaged in data reported in the main text. Data used for averaging was selected based on microprobe totals and scatter relative to all data. NJD-22 exhibits no observable zoning and zoning in NJD-20, if present, is within the analytical uncertainty.

Figure S2.



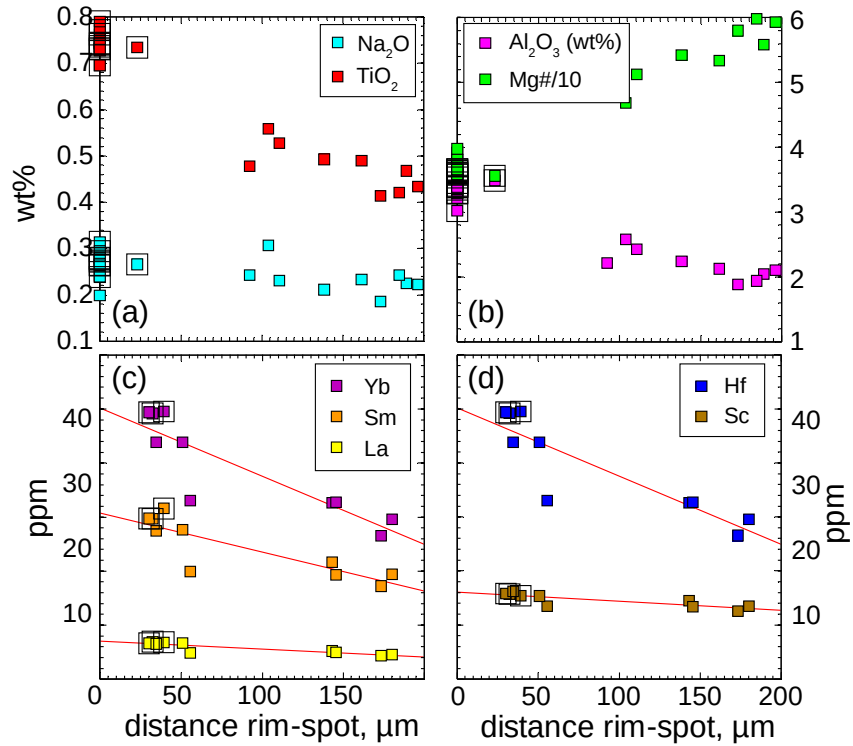
Selected major (a, b) and trace (c, d) element compositions from experiment HB-1 plotted against approximate distance from spot center to crystal rim. HB-1 exhibits no observable zoning and all measured data was averaged to report in the main text.

Figure S3.



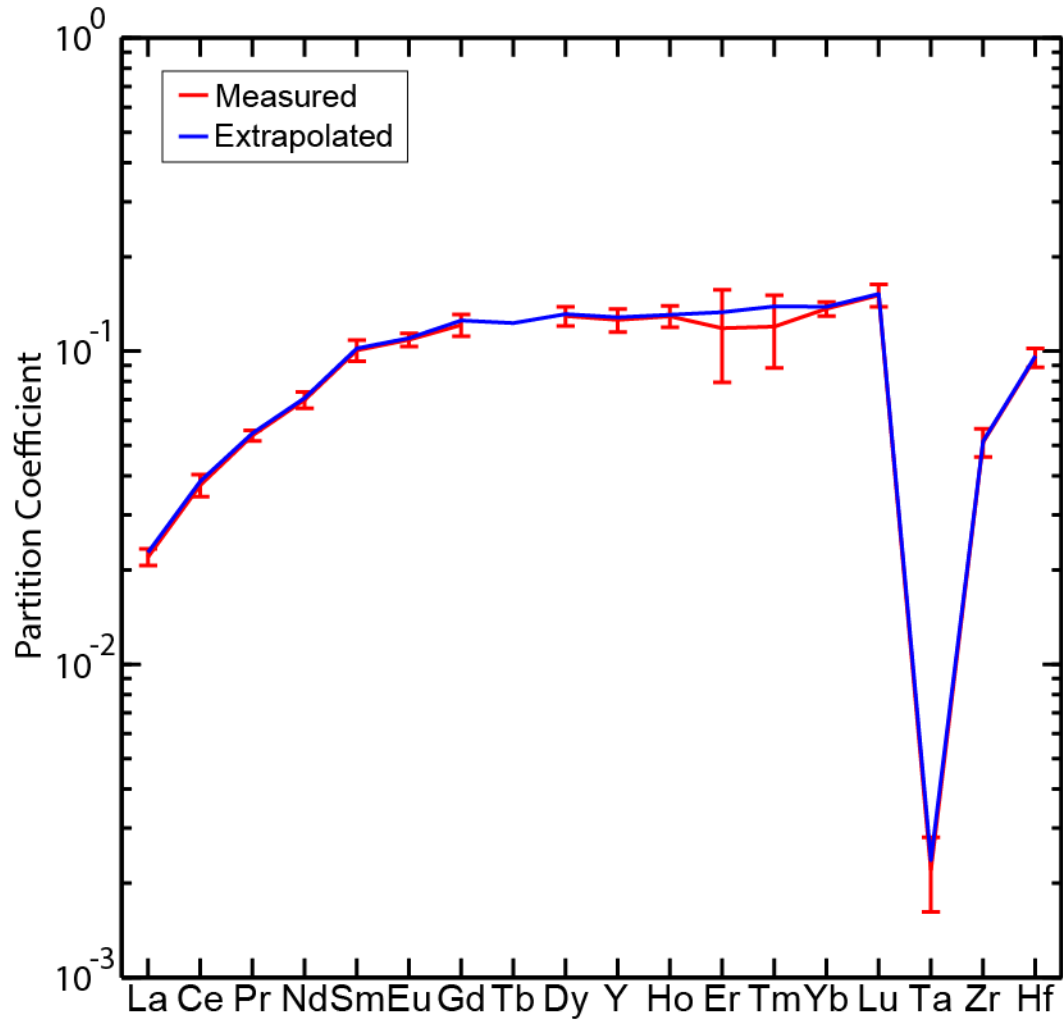
Selected major (a, b) and trace (c, d) element compositions from experiment HB-4 plotted against approximate distance from spot center to crystal rim. Colored squares are individual spot analyses, larger black open squares show spots that were averaged in the reported data. Data was selected for averaging based on microprobe totals and/or elemental scatter relative to all data. HB-4 exhibits no observable zoning.

Figure S4.



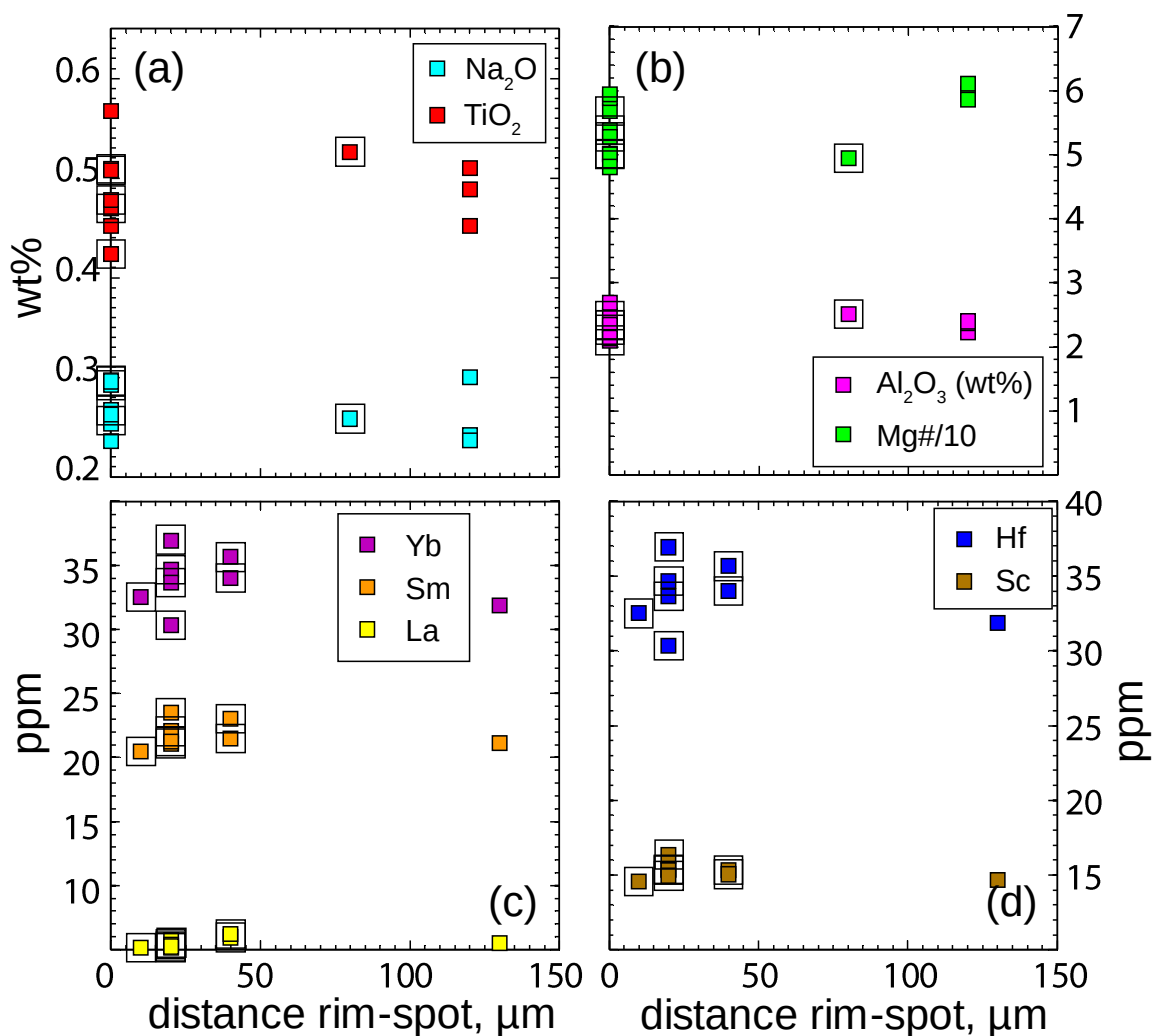
Selected major (a, b) and trace (c, d) element compositions from experiment HB-5 plotted against approximate distance from spot center to crystal rim. Spots are from all three pyroxene grains (see Figure 3b). Colored squares are individual spot analyses, larger black open squares show spots that were averaged in the reported data. Note the consistency of open square compositions. Their proximity to grain rims suggests they should be well equilibrated with melt. Elements with partition coefficients close to one are homogeneous throughout the crystals (Sc) while incompatible elements (e.g. REE, Hf) show the most significant gradients. Compatible elements also show zoning, note the significant gradient in Mg# (green squares). Red lines in (c) and (d) show linear compositional extrapolation to grain rims using all the measurements. Partition coefficients calculated using the extrapolations are within the analytical uncertainty of the measured values and typically differ by < 3% (Supplementary Figure S5).

Figure S5.



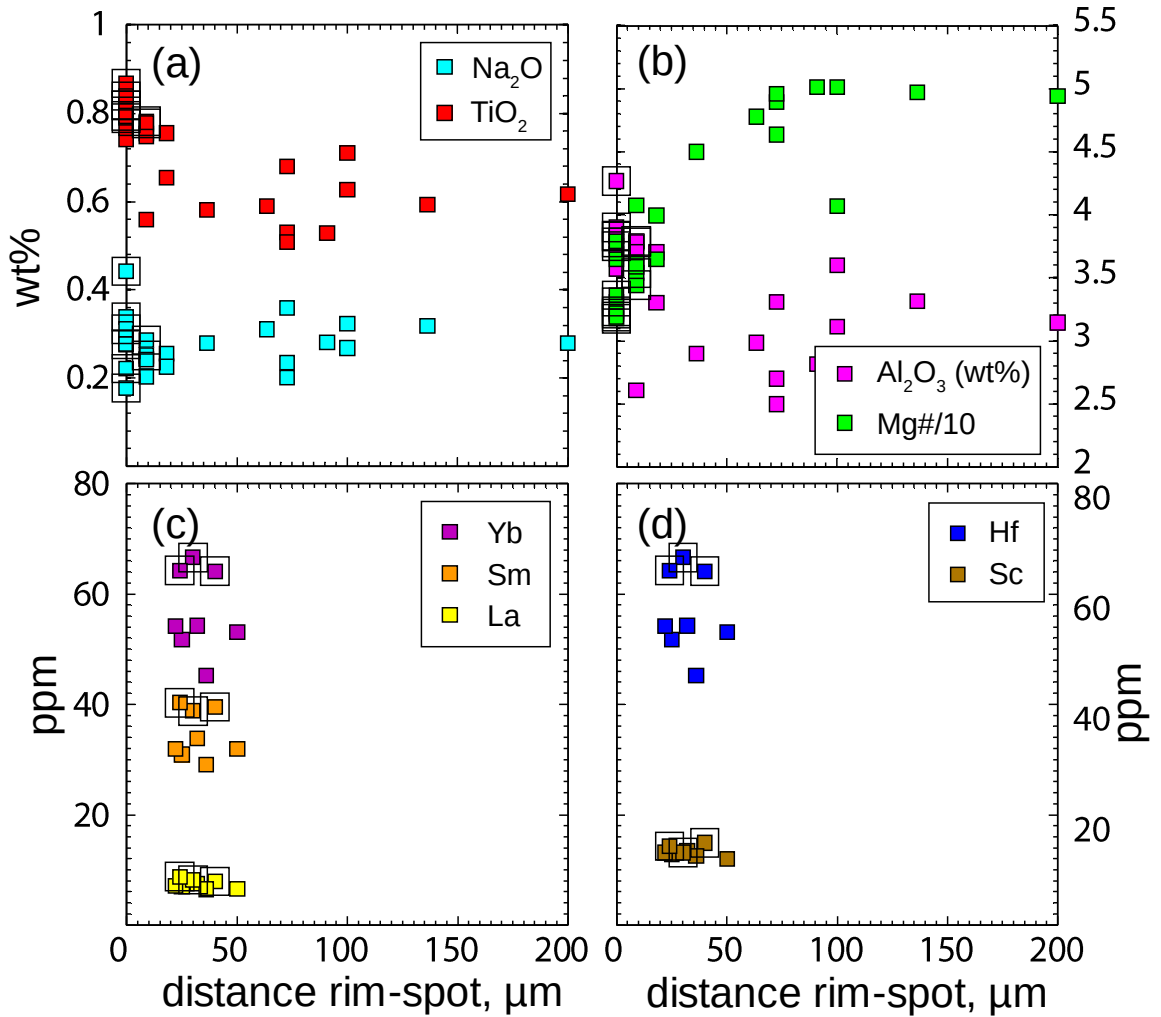
Rare earth and HFSE partition coefficients from experiment HB-5 calculated using measured rim compositions (red line with error bars, open squares in Supplementary Figure S4c, d) and extrapolated rim compositions (blue line, red lines in Supplementary Figure S4c, d). The difference between measured and extrapolated partition coefficients is within measurement error.

Figure S6.



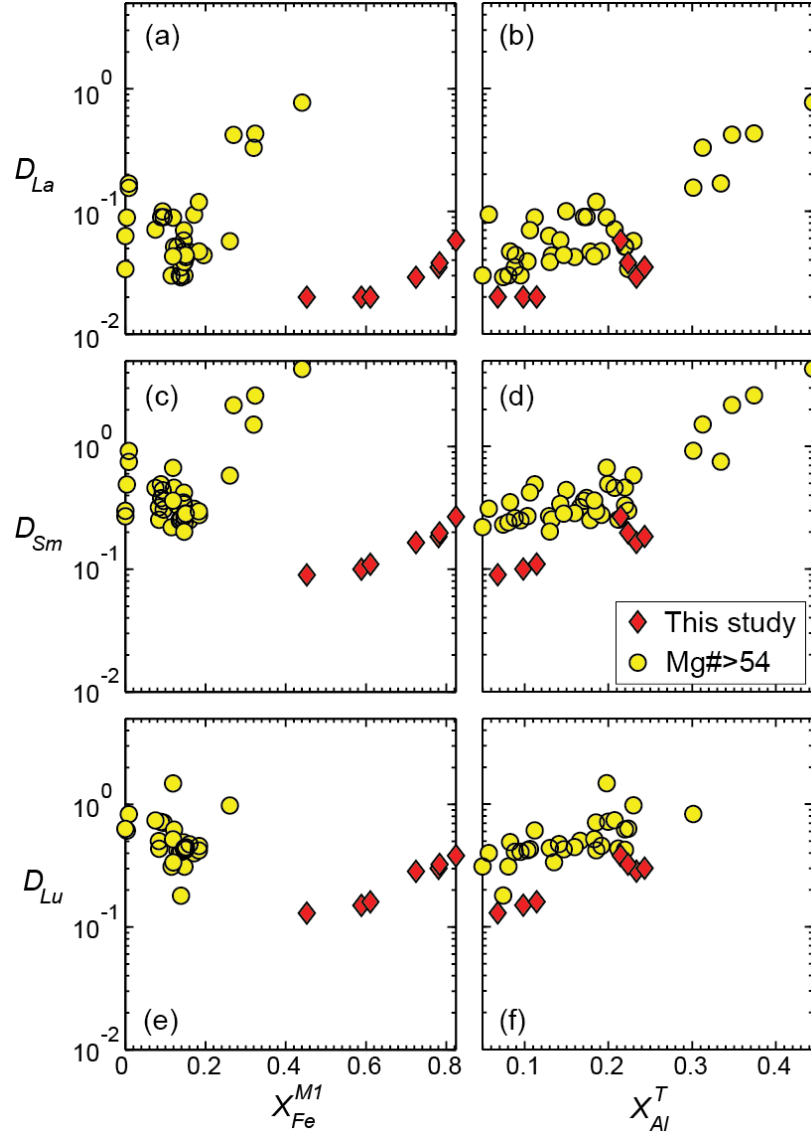
Selected major (a, b) and trace (c, d) element compositions from experiment HB-6 plotted against approximate distance from spot center to crystal rim. Colored squares are individual spot analyses, larger black open squares show spots that were averaged in the reported data. Presumably this experiment is more well-equilibrated throughout crystal interiors than HB-5 (Supplementary Figure S4) or HB-7 (Supplementary Figure S7) owing to the relatively long experimental duration and higher temperature.

Figure S7.



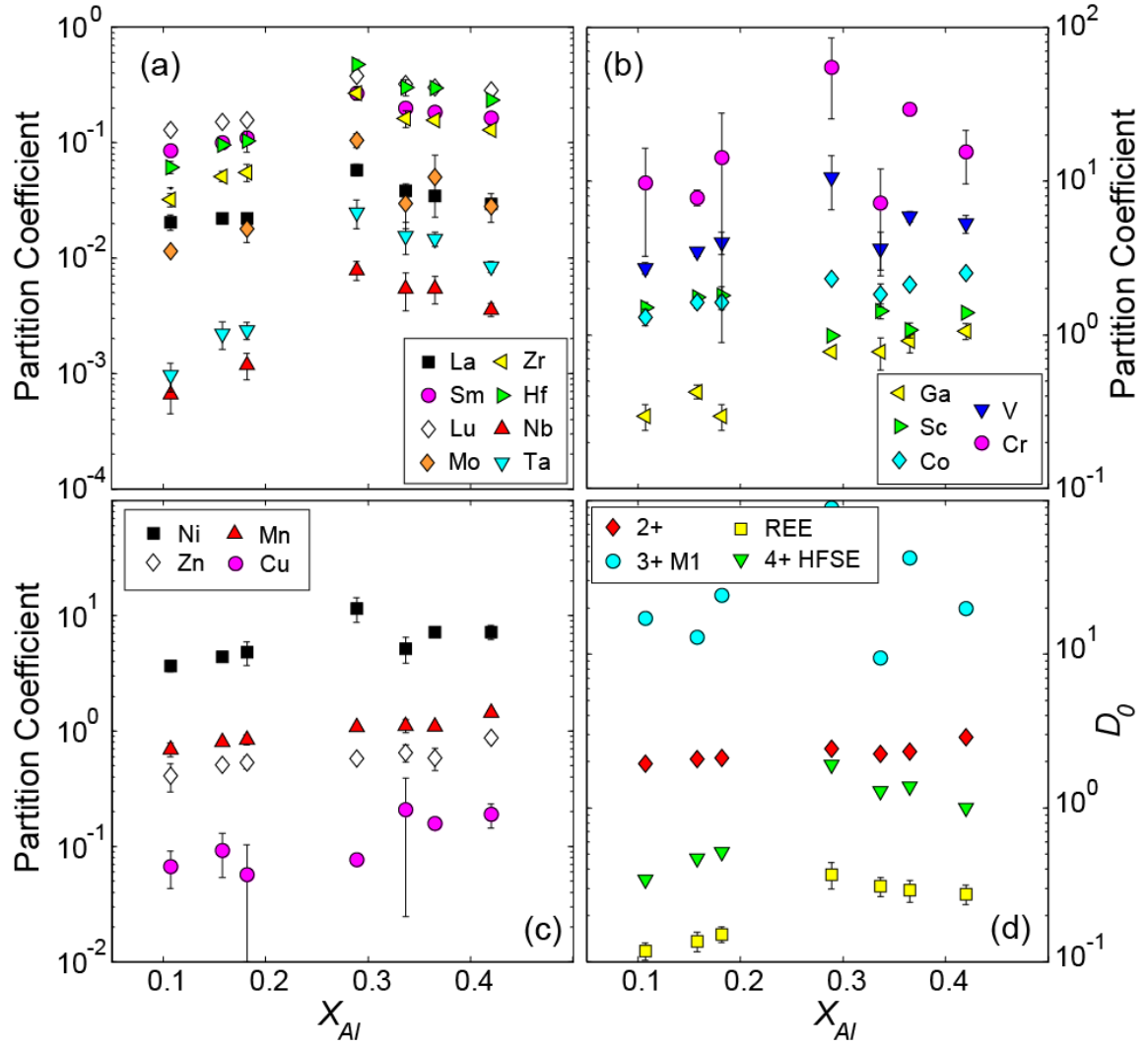
Selected major (a, b) and trace (c, d) element compositions from experiment HB-7 plotted against approximate distance from spot center to crystal rim. Colored squares are individual spot analyses, larger black open squares show spots that were averaged in the reported data. Because no trace element data was measured for grain interiors, the three most consistent measurements (which also have the highest incompatible trace element concentrations) were selected as representative rim compositions.

Figure S8.



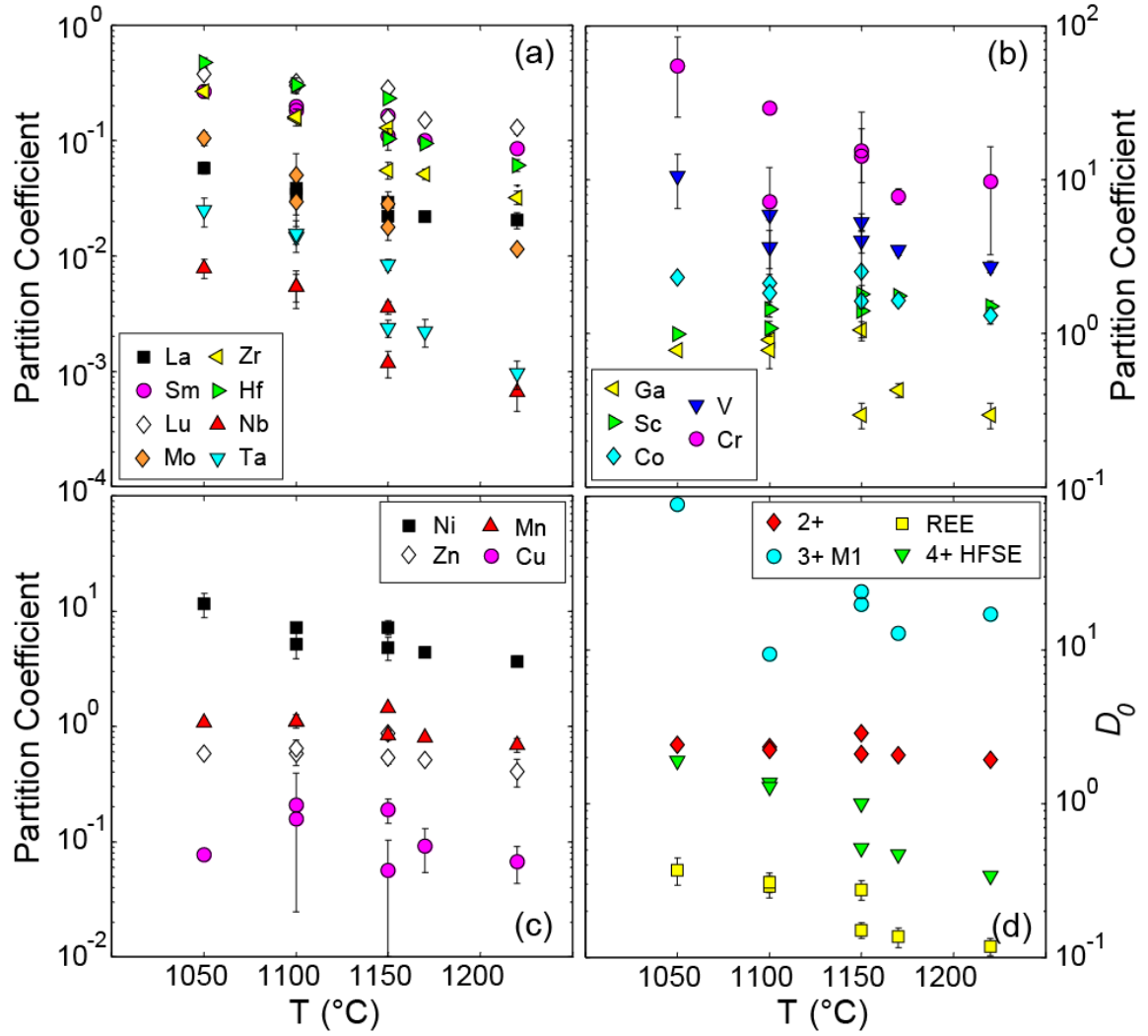
La, Sm, and Yb partition coefficients from this study (red diamonds) and from experiments with $Mg\# > 54$ (yellow circles) plotted against compositional parameters (X_{Al}^T , X_{Fe}^{M1}). Note the correlations are generally consistent but experiments from this study are below or at the low end of high Mg experiments. Literature data are from experiments with T varying from 1042-1470°C and SiO_2 in melt from 42.1-56.8 wt% (from Table 1 in Sun and Liang, 2012).

Figure S9.



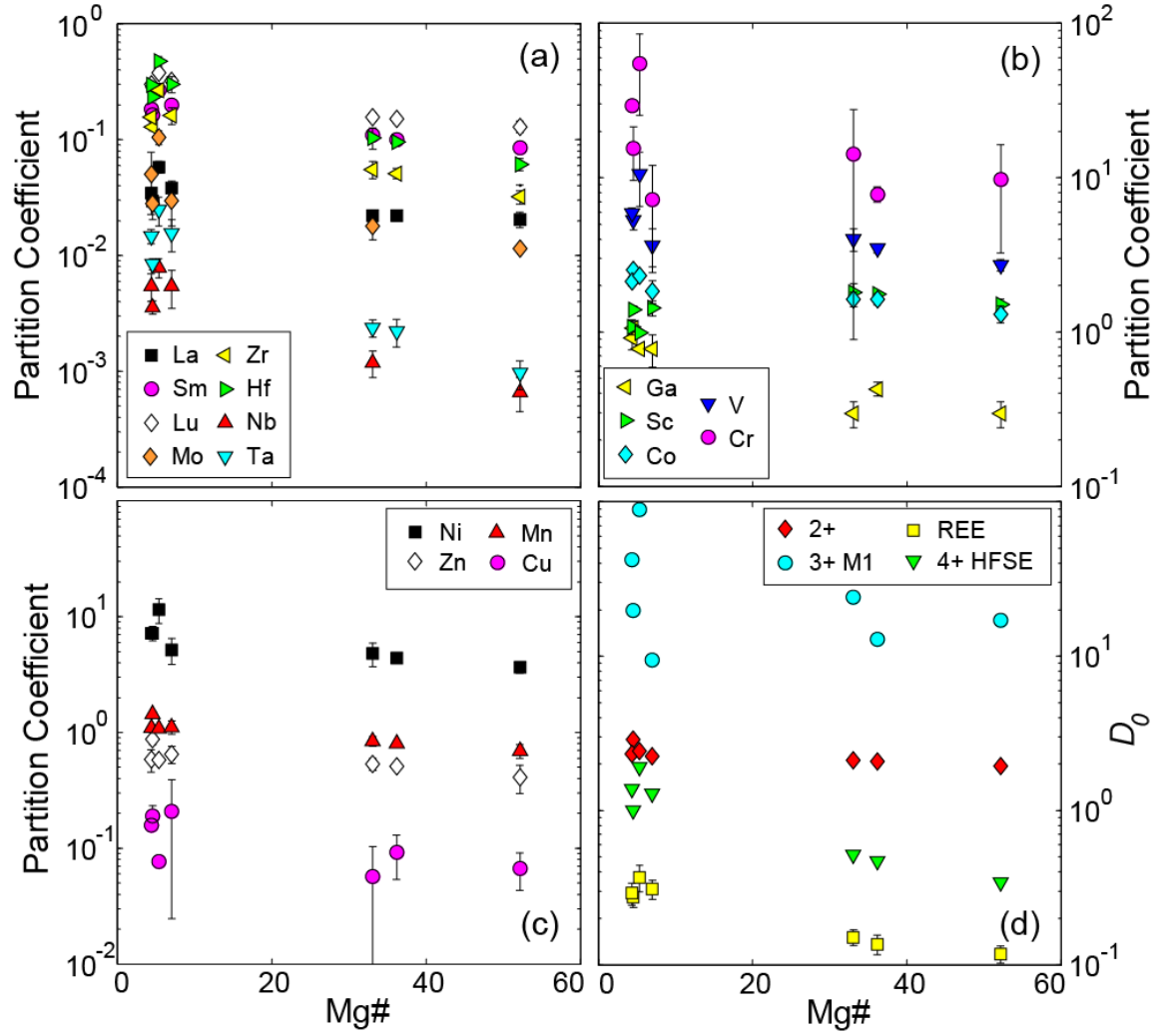
Variations of measured partition coefficients (a-c) and the lattice strain parameter D_0 defined in Eq. 1 in the main text (d) as a function of total Al in pyroxene (X_{Al}). (a) REE, HFSE, and Mo, (b) divalent and trivalent transition metals, (c) divalent and/or monovalent transition metals.

Figure S10.



Variations of measured partition coefficients (a-c) and the lattice strain parameter D_0 defined in Eq. 1 in the main text (d) as a function of temperature T . (a) REE, HFSE, and Mo, (b) divalent and trivalent transition metals, (c) divalent and/or monovalent transition metals.

Figure S11.



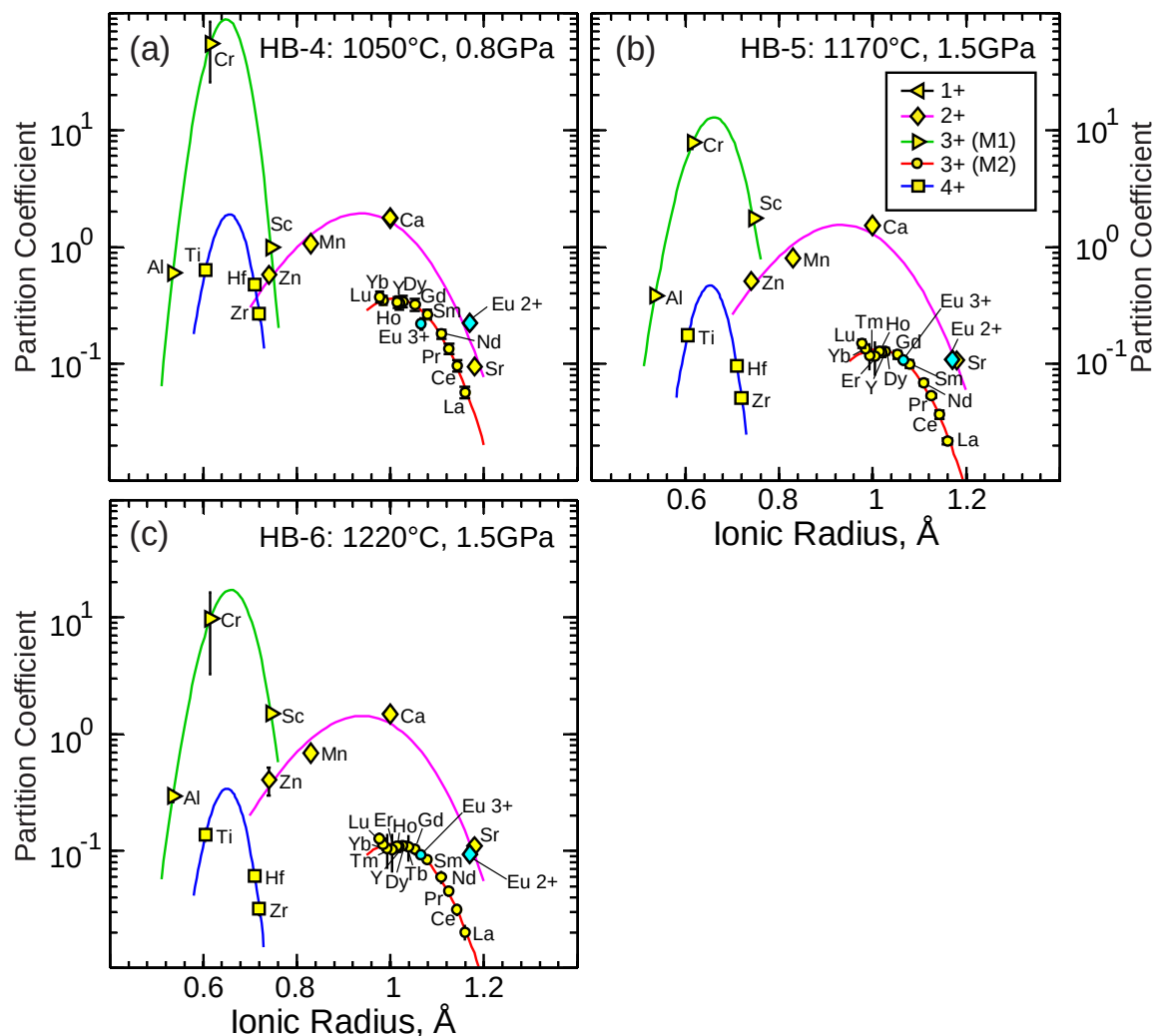
Variations of measured partition coefficients (a-c) and the lattice strain parameter

D_0 defined in Eq. 1 in the main text (d) as a function of Mg# in pyroxene. (a) REE,

HFSE, and Mo, (b) divalent and trivalent transition metals, (c) divalent and/or

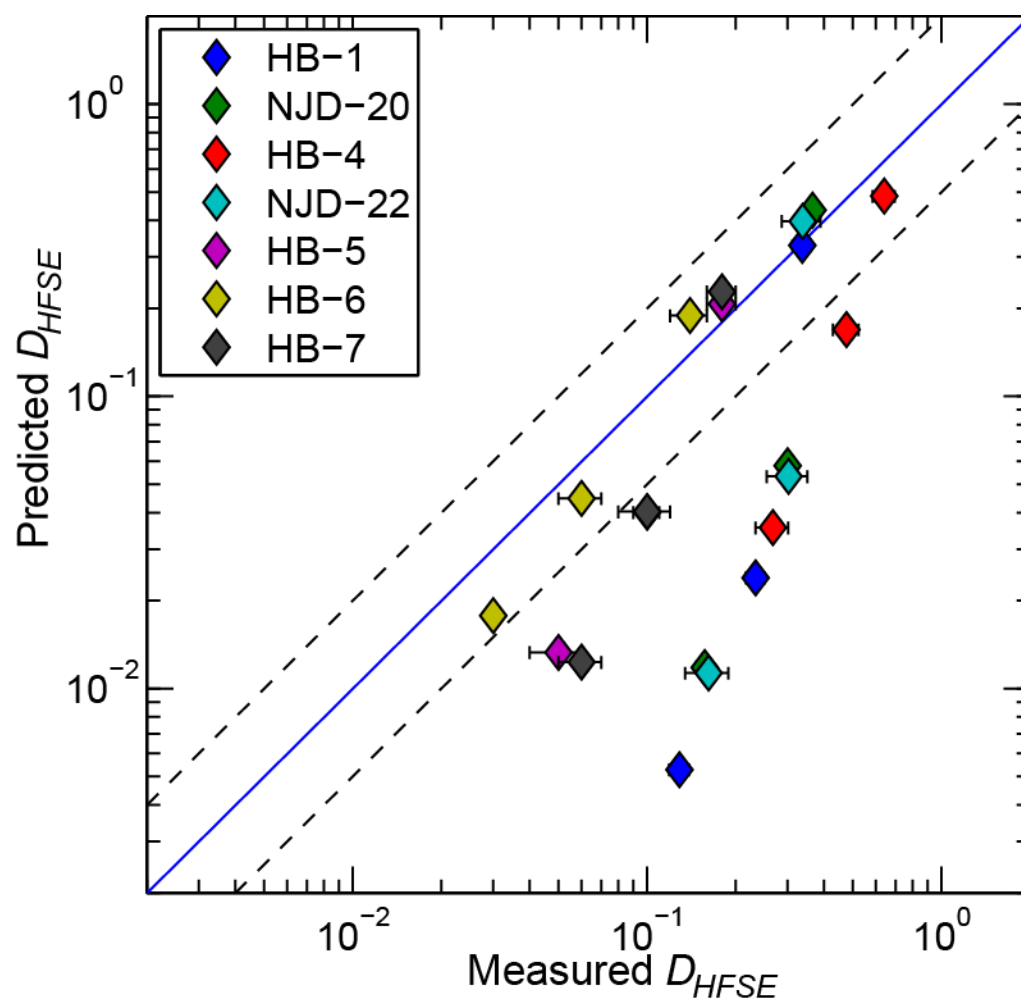
monovalent transition metals.

Figure S12.



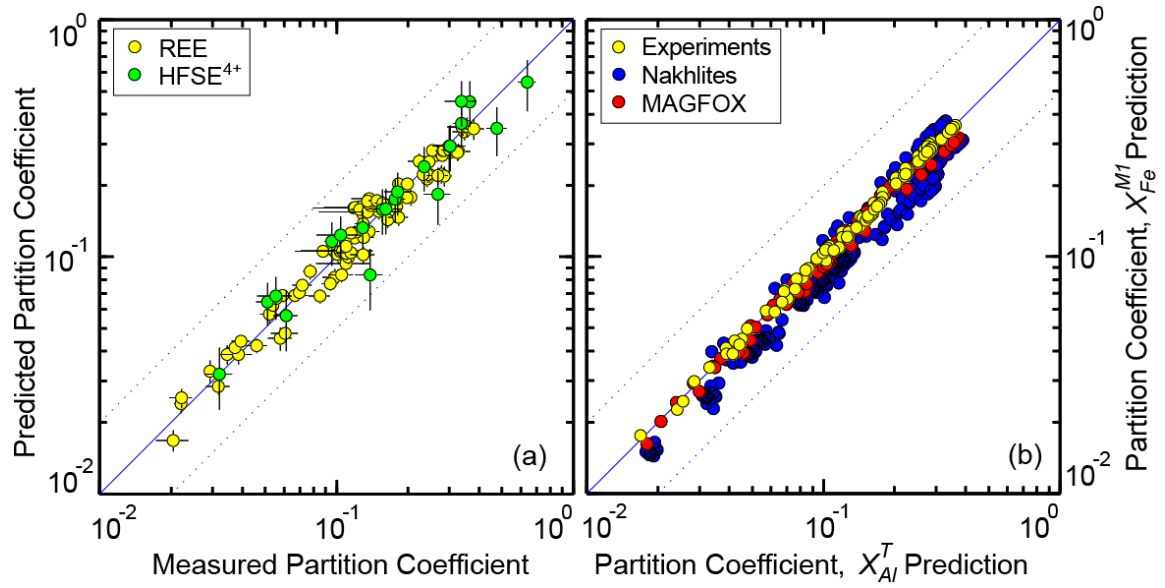
Onuma diagrams showing variations of measured trace element partition coefficients as a function of ionic radius for 2+ cations (violet lines), 3+ cations with smaller ionic radii (green lines), REE+Y (red lines) and 4+ cations (blue lines) for experiments HB-4, HB-5, and HB-6. The Eu partition coefficient is plotted against ionic radii of Eu^{2+} and Eu^{3+} (cyan diamond and circle, respectively). Parabolas for 2+ cations were inverted from measured partition coefficients including Eu.

Figure S13.



Measured HFSE partition coefficients plotted against partition coefficients predicted by the model of Hill et al. (2011). Solid blue line is 1:1 and dashed lines are 1:2 and 2:1.

Figure S14.



(a) Measured partition coefficients plotted against partition coefficients predicted by the Fe-based partitioning models (Equations S1-S6). Dotted lines are 1:2 and 2:1, solid blue line is 1:1. (b) A comparison of REE partition coefficients calculated for experiments (this study), nakhilites, and MAGFOX cumulates using the Al-based partitioning models (Equations 1-4, main text) and the Fe-based models (Equations S1-S3) assuming $T = 1160^{\circ}\text{C}$ for nakhlite cores and $T = 1000^{\circ}\text{C}$ for nakhlite rims. The models appear to be self-consistent in basaltic systems.

Table S1.**Trace element concentrations in pyroxene and melt analyzed by LA-ICPMS****Pyroxene**

Experiment:	HB-1		HB-4		NJD-22		NJD-20	
n^a	6	2σ	3	2σ	5	2σ	5	2σ
Li	0.39	0.25	-	-	-	-	-	-
Sc	4.4	0.2	3.0	0.1	27.0	2.5	14.3	1.5
V	6.1	0.8	6.1	1.4	92.8	23.5	9.8	0.4
Cr	2504	1091	971	493	245	148	2324	128
Mn	5802	200	5937	350	15174	1880	6628	253
Co	9.0	0.4	8.8	0.2	35.5	4.8	12.4	0.8
Ni	104	14	51	12	64	14	29	1
Cu	1.0	0.2	0.5	0.1	6.7	0.7	9.8	0.6
Zn	20.4	1.3	16.1	0.4	289.5	33.7	46.3	10.0
Ga	1.72	0.19	2.85	0.05	2.11	0.39	2.69	0.42
Sr	0.95	0.10	0.92	0.05	1.08	0.24	0.92	0.14
Y	71	6	132	16	103	4	104	4
Zr	35	4	92	5	50	7	59	3
Nb	0.89	0.12	2.43	0.42	4.47	1.52	1.97	0.52
Mo	2.2	0.6	42.4	4.2	17.3	3.7	1.0	0.5
La	7.8	0.4	19.7	1.7	12.7	1.6	12.7	0.7
Ce	12.7	1.0	31.6	3.1	21.9	1.9	20.4	0.5
Pr	21.1	1.5	49.9	4.6	32.7	2.4	33.3	1.4
Nd	26.7	2.0	60.8	4.7	41.1	3.0	42.8	0.6
Sm	43.8	3.2	94.7	8.0	66.7	2.2	69.1	2.2
Eu	51.0	3.8	83.9	7.6	68.7	1.5	71.5	1.8
Gd	65.0	5.9	130.8	13.2	-	-	98.5	2.7
Tb	-	-	-	-	0.098	0.037	-	-
Dy	76.4	6.9	140.6	13.0	107.9	2.9	116.6	4.2
Ho	79.1	7.3	143.5	12.2	109.2	6.2	119.4	4.3
Er	-	-	-	-	-	-	-	-
Tm	-	-	-	-	-	-	-	-
Yb	85.6	7.0	147.6	12.9	116.2	7.0	131.6	4.5
Lu	94.5	8.5	170.0	14.3	121.5	5.4	136.1	3.8
Hf	75.8	7.0	189.0	12.4	91.4	12.5	130.0	4.8
Ta	2.48	0.29	9.61	2.36	2.83	0.84	6.06	0.80
W	0.046	0.028	0.056	0.009	-	-	-	-
Pb	-	-	0.013	0.002	-	-	-	-

^aNumber of averaged spot analyses.

Table S1 continued.

Pyroxene						
Experiment:	HB-7 Rim		HB-5 Rim		HB-6 Rim	
n^a	3	2σ	3	2σ	7	2σ
Li	4.94	0.55	-	-	-	-
Sc	14.1	1.8	15.7	0.4	15.3	1.1
V	72.3	11.4	80.7	3.9	94.6	7.9
Cr	-	-	414	27	1534	1024
Mn	3901	360	3963	84	3277	433
Co	13.6	1.3	17.3	0.7	15.6	1.9
Ni	36	8	49	2	65	6
Cu	-	-	0.5	0.2	0.3	0.1
Zn	39.4	4.2	54.9	0.9	44.7	11.8
Ga	-	-	2.77	0.19	1.78	0.33
Sr	3.57	0.67	4.45	0.22	4.34	0.60
Y	65	2	43	2	32	3
Zr	25	4	16	1	9	1
Nb	0.33	0.08	-	-	0.15	0.05
Mo	78.9	17.9	-	-	-	-
La	8.3	0.8	6.8	0.3	5.6	0.9
Ce	12.3	1.0	10.8	0.3	8.2	0.9
Pr	19.2	0.9	16.5	0.2	12.3	1.3
Nd	24.1	2.1	20.3	1.0	15.1	1.9
Sm	39.5	1.5	30.3	2.2	21.8	2.2
Eu	39.0	2.7	34.1	1.1	25.5	1.8
Gd	59.3	1.3	41.4	2.1	30.1	3.4
Tb	0.031	0.012	-	-	0.027	0.006
Dy	64.8	2.0	45.3	1.3	32.9	2.7
Ho	66.9	1.7	45.5	2.0	32.2	3.3
Er	-	-	0.151	0.048	0.119	0.042
Tm	0.032	0.003	0.031	0.008	0.025	0.008
Yb	65.0	2.8	49.3	0.3	34.0	4.3
Lu	78.1	0.6	56.4	1.9	39.5	4.4
Hf	52.1	10.3	34.6	1.0	18.1	2.0
Ta	0.99	0.16	0.71	0.19	0.25	0.07
W	-	-	-	-	-	-
Pb	0.054	0.027	0.056	0.010	-	-

Table S1 continued.

Trace element concentrations in pyroxene and melt analyzed by LA-ICPMS

Melt

Experiment:	HB-1		HB-4		NJD-22		NJD-20	
n	10	2 σ	4	2 σ	4	2 σ	8	2 σ
Li	0.51	0.19	-	-	-	-	-	-
Sc	4.3	0.3	3.0	0.1	18.8	1.1	13.2	0.4
V	1.6	0.1	0.6	0.2	25.5	2.9	1.7	0.1
Cr	224	39	18	3	34	9	79	4
Mn	5454	173	5502	185	7632	367	6016	74
Co	4.8	0.2	3.8	0.1	19.4	1.9	5.8	0.2
Ni	19.8	0.4	4.4	0.2	12.5	1.6	4.0	0.2
Cu	7.1	0.7	6.7	0.2	-	-	61.9	1.0
Zn	32	2	28	1	447	54	80	2
Ga	2.2	0.1	3.6	0.2	2.7	0.4	3.0	0.1
Sr	10.2	0.4	9.8	0.5	11.5	0.8	10.6	0.3
Y	394	21	388	25	362	21	409	14
Zr	368	21	344	39	312	23	377	16
Nb	336	18	309	25	822	97	361	17
Mo	103	7	405	36	583	195	19	1
La	363	13	340	26	329	23	369	19
Ce	331	16	321	18	328	34	345	16
Pr	368	15	363	18	335	26	381	13
Nd	339	15	332	18	315	23	358	11
Sm	358	15	353	18	336	19	375	9
Eu	382	15	375	19	346	21	390	10
Gd	419	22	398	26	-	-	424	10
Tb	0.19	0.03	0.10	0.02	0.54	0.03	0.37	0.02
Dy	424	19	404	25	386	20	442	11
Ho	428	22	419	26	386	20	448	11
Er	0.30	0.06	0.18	0.03	2.80	0.22	1.00	0.04
Tm	0.02	0.00	0.01	0.01	0.46	0.04	0.10	0.01
Yb	416	22	416	14	386	18	457	9
Lu	443	23	446	26	375	22	453	10
Hf	433	28	397	29	302	24	434	12
Ta	397	27	387	52	183	17	414	16
W	310	21	282	19	-	-	-	-
Pb	-	-	0.57	0.01	-	-	-	-

^aNumber of averaged spot analyses.

Table S1 continued.

Experiment:	HB-7 Rim		HB-5 Rim		HB-6 Rim	
n	5	2 σ	6	2 σ	8	2 σ
Li	14.90	0.84	-	-	-	-
Sc	7.8	0.4	8.9	0.3	10.1	0.3
V	18.1	0.9	23.3	1.1	34.9	0.8
Cr	-	-	53	5	157	6
Mn	4656	157	4912	197	4752	115
Co	8.4	0.4	10.6	0.7	11.9	0.2
Ni	7.4	0.5	11.2	0.7	17.7	0.8
Cu	9.1	0.7	5.5	0.8	4.9	0.5
Zn	74	4	108	8	110	7
Ga	-	-	6.5	0.5	6.0	0.2
Sr	31.8	0.9	41.3	1.4	39.4	1.3
Y	478	42	340	23	290	7
Zr	445	38	317	18	274	8
Nb	278	12	251	16	221	8
Mo	4414	308	26	3	3199	86
La	375	19	308	11	272	8
Ce	312	12	289	22	257	8
Pr	346	9	307	11	267	7
Nd	335	12	291	10	249	6
Sm	359	15	301	9	257	7
Eu	339	6	314	11	271	7
Gd	458	33	342	21	287	7
Tb	0.23	0.01	0.28	0.04	0.24	0.02
Dy	465	33	350	23	293	8
Ho	478	36	352	23	291	7
Er	1.12	0.15	1.28	0.11	1.15	0.05
Tm	0.24	0.03	0.26	0.02	0.23	0.02
Yb	439	29	362	19	296	9
Lu	497	39	374	28	305	10
Hf	499	37	363	23	295	11
Ta	417	24	321	14	261	9
W	-	-	-	-	-	-
Pb	4.41	0.25	2.75	0.21	-	-

Table S2.

Pyroxene Compositions in Cations^a							
	HB-1	HB-4	NJD-22	NJD-20	HB-7	HB-5	HB-6
Si	1.77	1.79	1.78	1.76	1.89	1.89	1.93
Ti	0.038	0.066	0.056	0.056	0.024	0.022	0.014
Al	0.42	0.29	0.34	0.37	0.18	0.16	0.11
Al _T ^b	0.23	0.21	0.22	0.24	0.11	0.11	0.07
Al _{M1}	0.19	0.07	0.11	0.12	0.07	0.06	0.04
Cr	0.015	-	-	0.015	0.004	0.002	0.007
Fe	0.98	1.01	1.01	1.03	0.72	0.69	0.51
Fe _{M1} ^c	0.73	0.81	0.77	0.77	0.60	0.59	0.45
Fe _{M2} ^c	0.290	0.221	0.300	0.286	0.132	0.111	0.076
Mg	0.047	0.057	0.076	0.047	0.356	0.385	0.560
Mg _{M1} ^c	0.035	0.046	0.058	0.035	0.299	0.329	0.490
Mg _{M2} ^c	0.012	0.011	0.017	0.011	0.055	0.051	0.067
Mn	0.030	0.031	0.074	0.035	0.022	0.020	0.015
Ca	0.66	0.75	0.66	0.68	0.79	0.81	0.84
Na	0.041	0.015	0.026	0.025	0.022	0.025	0.021
Sum	4.00	4.01	4.01	4.01	4.01	4.01	4.01

^aCalculated on a six oxygen basis.

^bTetrahedral aluminum = 2-Si.

^cCalculated assuming random distribution of Fe and Mg between the M sites.

Appendix A. REE and HFSE Partitioning Models Based on Fe Abundance in Pyroxene

Rare Earth Elements

Taking the approach described in Section 4.1 of the main text but considering covariation of partition coefficients with Fe instead of Al, we found the terms in the lattice strain model (Equation 1, main text) can be parameterized in the following form:

$$\ln(D_0) = -11.25(\pm 0.84) + 10.94(\pm 1.20) \times \frac{10^4}{RT} + 0.42(\pm 0.31) \times X_{Fe}^{M1}, \quad (S1)$$

$$E = 2.06(\pm 0.14) \times 10^2, \quad (S2)$$

$$r_0 = 1.00(\pm 0.005), \quad (S3)$$

where r_0 is in Å, E is in GPa, R is the gas constant, X_{Fe}^{M1} is the cation fraction of Fe on the pyroxene M1 site calculated assuming random distribution of Fe among the M1 and M2 sites. Coefficient uncertainties are 1σ .

Predicted partition coefficients are plotted against measured partition coefficients in Supplementary Figure S14a on the next page (yellow circles), showing Equations S1-S3 do an excellent job reproducing the experimentally determined values listed in Table 3. Model predictions of Equations 1-4 and S1-S3 are reasonably self-consistent for nakhlites and MAGFOX calculated lunar magma ocean cumulates (Supplementary Figure S14b), however, we note that Equations 1-4 do a better job reproducing partition coefficients measured by Oe et al. (2001), suggesting that Equations 1-4 may be more extrapolatable beyond the compositions investigated in this study. We caution that neither model should be extrapolated beyond Fe-rich basaltic systems until partitioning in more silicic systems is better understood.

High Field Strength Elements

Following the same method, we found that the cation fraction of Fe on the pyroxene M1 site can be used to predict measured HFSE⁴⁺ partition coefficients when unknowns in the lattice strain model are parameterized in the following form:

$$\ln(D_0) = -13.62(\pm 2.41) + 14.06(\pm 3.47) \times \frac{10^4}{RT} + 2.01(\pm 0.89) \times X_{Fe}^{M1}, \quad (S4)$$

$$E = 2.22(\pm 0.41) \times 10^3, \quad (S5)$$

$$r_0 = 0.655(\pm 0.002), \quad (S6)$$

where r_0 is in Å and E is in GPa. A comparison of predicted and measured partition coefficients is shown in Supplementary Figure S14a (green circles). Again, the Al based model is preferred owing to smaller uncertainties in the model predictions (compare Figure 7 and Supplementary Figure S14a).

CHAPTER 3

A Flow Law for Ilmenite in Dislocation Creep and Implications for Lunar Cumulate Mantle Overturn

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Abstract

A unique feature of basalts from the Moon is their extraordinary range in TiO_2 abundance, ranging from terrestrial values to 16 wt%. To account for the elevated TiO_2 , lunar basalt petrogenetic models invoke melting of an ilmenite-bearing lunar mantle, or assimilation of ilmenite by lunar mantle melts as they migrated to the surface of the Moon. These models suggest ilmenite is a relatively abundant component of the lunar basalt source region. The viscosity of ilmenite and its effect on the rheology of the lunar mantle were previously unknown. Here we present an experimentally determined flow law for pure synthetic ilmenite deformed in axial compression. Experiments were conducted in molten salt assemblies in a Griggs apparatus at strain rates of 1×10^{-6} to 1×10^{-4} and temperatures of 900-1100°C. The strain rate stepping experiments exhibit a stress exponent of 2.96 ± 0.20 and an activation energy of 290 ± 28 kJ/mol. Lower temperature experiments have smaller average grain sizes and textures indicative of dynamic recrystallization suggesting deformation in the dislocation creep regime. The ilmenite flow law predicts a viscosity more than four orders of magnitude lower than dry olivine at mantle stresses and temperatures. Aggregate viscosity predictions made using end-member flow laws suggest small amounts of ilmenite can significantly weaken an aggregate composed mostly of a stronger phase. These predictions are corroborated by experiments conducted in shear on ilmenite-olivine aggregates. Just 5 volume % ilmenite in a harzburgitic lunar mantle may halve the viscosity of the aggregate, making long wavelength cumulate mantle overturn more likely. The presence of overturned ilmenite around the lunar core can explain an ultralow viscosity zone that may surround the core. Ilmenite makes transport of pyroxene-hosted heat producing elements to the core easier,

providing a mechanism for partial melting of lowermost mantle which can explain a zone of seismic attenuation there. Recently published numerical simulations suggest that because of their low viscosity, overturned ilmenite bearing cumulates in the lunar interior may be highly stable around the core, and that the formation of upwelling diapirs of overturned ilmenite rich material is highly unlikely. Thus, the petrogenesis of high-Ti lunar basalts requires entrainment of overturned ilmenite bearing cumulates by convecting overlying harzburgite, or incomplete or inefficient cumulate mantle overturn.

1. Introduction

Lunar basalts have TiO_2 abundances that range from terrestrial values (<1 wt%) to >16 wt%. Spectroscopic investigations of basalts exposed on the lunar surface [e.g., *Lucey et al.*, 1998; *Giguere et al.*, 2000] and chemical analyses of samples returned by the Apollo missions [e.g., *Delano*, 1986] suggest a significant proportion of the lunar basalts have $>8\%$ TiO_2 . Lunar petrologists have argued that such basalts can be produced by (1) melting an ilmenite (FeTiO_3) bearing lunar mantle [e.g., *Ringwood and Kesson*, 1976], or (2) partial melting of the lunar mantle followed by assimilation of ilmenite as the melt migrated to the lunar surface [e.g., *Hubbard and Minear*, 1975]. In either scenario, ilmenite is an important component of the lunar basalt source region.

Lunar basalt petrogenetic models have been used to make inferences about the dynamic evolution of the lunar mantle [e.g., *Ringwood and Kesson*, 1976]. Currently favored models of lunar formation propose the Moon originated from a giant impact between the Earth and another large body [e.g., *Wood et al.*, 1970; *Warren*, 1985; *Canup*, 2012; *Ćuk and Stewart*, 2012] that left a deep magma ocean on the nascent Moon. The

magma ocean crystallized from the bottom up, causing its composition to evolve from Fe and Ti poor to Fe and Ti rich [e.g., *Snyder et al.*, 1992]. Estimates of the bulk composition of the Moon suggest that after about 95% solidification, the lunar magma ocean reached ilmenite saturation, resulting in the precipitation of ilmenite and Fe-rich clinopyroxene enriched in incompatible trace elements (K, P, and rare earth elements, commonly referred to as KREEP) beneath an anorthositic flotation crust [*Snyder et al.*, 1992; *Hess and Parmentier*, 1995]. Instead of forming a uniform layer, these cumulates may have sank into underlying olivine rich cumulates as they crystallized, forming a thicker layer of ilmenite-bearing cumulates (IBC) [*Hess and Parmentier*, 1995; *Parmentier et al.*, 2002]. The ilmenite bearing magma ocean cumulates were denser than the early mafic cumulates (predominantly magnesian olivine and orthopyroxene), and the resulting unstable density stratification may have been relieved by solid state cumulate mantle overturn [e.g., *Ringwood and Kesson*, 1976; *Hess and Parmentier*, 1995]. The cumulate overturn model proposes that dense late stage cumulates formed a downwelling diapir or diapirs that displaced less dense cumulates closer to the lunar core. The ilmenite-bearing cumulates eventually melted, possibly forming the high-Ti lunar basalts found on the lunar surface.

Because the viscosity of ilmenite and ilmenite-bearing lunar mantle cumulates was previously unknown, efforts to model lunar cumulate mantle overturn and its aftermath have relied on olivine viscosity [*Elkins Tanton et al.*, 2002; *de Vries et al.*, 2010], or explored the effects of different viscosities on lunar mantle convection patterns during or after cumulate overturn [*Hess and Parmentier*, 1995; *Zhong et al.*, 2000; *Parmentier et al.*, 2002; *Zhang et al.*, 2013a]. *Hess and Parmentier* [1995] proposed that

ilmenite bearing cumulates mix with underlying harzburgites which then flow to the center of the Moon, producing a hybrid cumulate mantle by subsequent melting and mixing with overlying cumulates. *Elkins Tanton et al.* [2002] proposed that ilmenite bearing cumulates are too viscous to overturn as solids and instead may melt where they crystallized beneath the anorthositic crust. *de Vries et al.* [2010] found the ilmenite bearing cumulates rapidly flow to the lunar core and may be stable there, forming an ilmenite core or outer core.

Lunar basalts are almost exclusively concentrated on the Moon's nearside in a large basin known as the Procellarum KREEP terrane. A series of studies explored the possibility of a convection-related origin for this concentration [*Zhong et al.*, 2000; *Parmentier et al.*, 2002; *Zhang et al.*, 2013a]. Using Rayleigh-Taylor stability analysis, *Zhong et al.* [2000] investigated whether spherical harmonic degree-one upwelling of previously overturned ilmenite bearing cumulates at the lunar core could concentrate ilmenite bearing cumulates beneath Procellarum. They found models where the cumulates are more viscous than overlying mantle are most likely to form a single large upwelling plume, and models where the ilmenite-bearing cumulates are more likely to form multiple smaller plumes. *Zhang et al.* [2013a] investigated the thermochemical evolution of the lunar mantle and core after cumulate overturn with a wide range of temperature dependent cumulate viscosities. They observed that a weaker ilmenite layer surrounding the lunar core tends to form multiple upwelling plumes, and that very weak ilmenite-bearing cumulate layers are highly stable (i.e., internally convecting but stationary) at the core to the present day. *Parmentier et al.* [2002] investigated whether degree-one downwelling could lead to the spatial concentration of the basalt-forming

lunar cumulates. Assuming a scenario where a layer of ilmenite bearing material overlies a thicker layer of ultramafic (olivine and orthopyroxene rich) cumulates, they found that low viscosity ilmenite bearing cumulate layers are capable of generating degree-one downwelling plumes. The wide range of outcomes from these models demonstrates the importance of constraining the viscosity of the ilmenite bearing cumulates for understanding the physicochemical evolution of the Moon.

Here, we present an experimentally determined flow law for pure ilmenite deformed in axial compression in dislocation creep. The flow law predicts that ilmenite is more than four orders of magnitude weaker than dry olivine at lunar mantle stresses and temperatures. We use end-member flow laws to make predictions about the viscosity of ilmenite-olivine aggregates which are corroborated by ilmenite-olivine shear experiments. Finally, we make predictions about the effect of ilmenite on the style of convection in the lunar mantle, and about the fate of ilmenite bearing cumulates after cumulate mantle overturn.

2. Methods

2.1 Starting Materials

Synthetic ilmenite (Iron II titanate, Sigma Aldrich) was separated into grain size brackets of 20-30 μ m and 30-50 μ m using Stokes' settling in ethanol. The ilmenite contains trace amounts of rutile (TiO₂) and Fe metal (~1.5 volume % in total, Supplementary Figure S1b). Our starting material also contains trace amounts of K, P, and Si as a result of the flux used in the mineral synthesis (Sigma Aldrich, personal communication, Supplementary Figure S2); ironically these components are similar in

composition to lunar KREEP. After grain size separation, air dried ilmenite powders were baked in a gas mixing furnace at 800 °C and $f_{\text{O}_2} \approx \text{Fe-FeO}$ to drive off any residue of ethanol. The powders were then run through a magnetic separator several times to remove as much of the flux contaminant as possible. Analysis of hot-pressed samples showed up to 1 vol% of a grain boundary phase (Supplementary Figures S1b and S2). After we recognized the presence of the flux components, we washed the starting powders in 1M nitric acid, which decreased the amount of the grain boundary phase down to ~0.5 vol% (Supplementary Figure S2c). Mechanical data from experiment ID-13 (which utilized acid washed ilmenite powder) is consistent with the other experiments.

2.2 Experimental Procedures and Data Analysis

Axial compression experiments were conducted in a Griggs apparatus. Molten salt assemblies were utilized, which employ a eutectic KCl-NaCl mixture as the confining medium in contact with the jacketed sample. The KCl-NaCl mixture is molten or partially molten at the run conditions. Molten salt assemblies minimize thermal gradients and friction in the assembly, thereby maximizing the stress resolution of the deformation apparatus, which we estimate to be about 5 MPa. The assembly designs employed are similar to *Holyoke* [2005]. Oxygen fugacity was buffered at or below Ni-NiO by thick-walled 0.2” ID Ni jackets enclosed in welded or mechanically sealed Pt outer jackets (Supplementary Figure S1a). Confining pressures were nominally 1 GPa, but in several experiments pressure decreased up to 100 MPa owing to Pb loss around the load piston packing ring. Temperatures (measured with Pt-Pt10% Rh thermocouples) were controlled between 900 and 1100°C. Experiments were conducted using 20-30 μm

or 30-50 μ m cold pressed powders, and annealed overnight at run conditions before deformation. In general, samples deformed homogeneously (e.g., Supplementary Figure S1a) and mechanical data were processed assuming constant volume shortening. Force and displacement were corrected to account for apparatus distortion following procedures described in *Stipp and Tullis* [2003] and using the frictional force measured during initial advancement of the load piston.

All experiments were imaged using the Cameca SX-100 electron microprobe at Brown University to check for salt infiltration. A salt leak did occur in experiment ID-3. There is no obvious weakening event in the stress-strain record (Figure 2e) so it is possible the leak occurred during quenching or while the sample was unloaded. Because a repeat experiment (ID-12) shows practically identical stress-strain relations (Figure 2f), we include sample ID-3 in our analysis.

3. Results

The results of six axial compression experiments are presented in Table 1. Reflected light micrographs are shown in Figure 1. Differential stress versus axial strain curves are shown in Figure 2. Total strains range from 22 to 31% and differential stresses range from 29-340 MPa. We conducted one constant strain rate experiment (ID-1) and five strain rate stepping experiments (ID-2, ID-3, ID-5, ID-12, ID-13). Experiments ID-2, ID-3, ID-5, and ID-12 were deformed over four strain rate intervals, experiment ID-13 was deformed over five strain rate intervals. ID-13 demonstrated strain weakening over the first strain rate step, so the mechanical data from that step was excluded from the flow

law determination. We note that including or excluding data from the first step results in stress exponents within error of each other (3.1 ± 0.8 vs. 2.5 ± 1).

3.1 Microstructures

Reflected light micrographs show that experiments deformed at lower temperatures have smaller average grain sizes than higher temperature experiments (compare Figures 1e and 1a). Twinning is present in the sample deformed at the lowest temperature (ID-5, Figure 1e). With the exception of experiment ID-1 (which was deformed at a relatively high temperature and slow strain rate), the experiments exhibit curved and interpenetrated grain boundaries characteristic of grain boundary migration (Figures 1b-1e). In contrast, ID-1 has polygonal grains, straight grain boundaries, 120° triple junctions, and larger grain size (e.g., compare Figures 1a and 1b).

4. Discussion

4.1 Deformation Mechanisms

The textures and grain size reduction in the strain rate stepping experiments are indicative of dynamic recrystallization. Consistent with the microstructures (Figures 1b-1e), the strain rate stepping experiments exhibit non-Newtonian stress-strain rate relations with stress exponents for individual experiments ranging from 2.8 ± 0.2 to 3.4 ± 1.0 (Table 1, Figure 3a). Collectively, these observations support deformation in dislocation creep.

In contrast, the equilibrium texture of experiment ID-1 supports diffusion creep as the dominant deformation mechanism. This is further supported by its weak rheology relative to ID-12 which has abundant microstructural evidence of dynamic

recrystallization (Figure 1b). Although they deformed at the same temperature, experiments ID-1 and ID-12 have different textures probably owing to their different strain rate paths (compare Figures 2d and 2f). ID-12 had initially coarser starting material than ID-1, but dynamic recrystallization led to formation of the microstructures which are visible after quenching (i.e., in Figure 1b).

4.2 Flow Law

For the reasons described in the previous section (i.e., microstructures and mechanical evidence) we choose to exclude two data points from our determination of a flow law for ilmenite in dislocation creep. One is experiment ID-1, the other is the first strain rate step from experiment ID-3 which was deformed at an identical strain rate and temperature using the same starting material. We include the first strain rate step from ID-12 (which was also deformed at 1100°C and 1×10^{-5}) because that experiment utilized a coarser starting material and the mechanical data is consistent with a stress exponent of 3.4 (Figure 3a). Data from strain rate steps we assume to represent dislocation creep are normalized to 100 MPa and plotted against $10000/T$ in the inset in Figure 3b. The slope of the strength-temperature relation gives an activation energy of 302 ± 13 kJ/mole (2σ), slightly higher than values determined for magnetite (264 kJ/mol, *Crouch and Robertson* [1990]) and hematite (225 ± 10 kJ/mol, *Siemes et al.* [2003]).

A flow law for ilmenite in dislocation creep was parameterized in the standard form using the experimental observations presented in Figure 3b. Unknowns in the flow law were estimated by simultaneous nonlinear inversion. Excluding the data we assume to be in diffusion creep, we find that

$$\dot{\epsilon} = 12.30(\pm 16.16) \sigma^{2.96(\pm 0.20)} e^{\frac{-290(\pm 28)}{RT}}, \quad (1)$$

where σ is in MPa, activation energy in kJ/mol, $R=8.31 \text{ J/mol}\times\text{K}$, the preexponential term is in $\text{MPa}^{-n}\text{s}^{-1}$, and coefficient uncertainties are 1σ . Flow law predictions are shown by the black lines in Figure 3b and are consistent with the experimental data.

We are not aware of any earlier experimental studies on ilmenite, but hematite [e.g., *Crouch*, 1972; *Siemes et al.*, 2003], magnetite [e.g., *Crouch and Robertson*, 1990; *Gómez-García et al.*, 2002], and other Fe-oxide minerals have been investigated previously (see *Siemes et al.* [2003] and *Till and Moskowitz* [2013] for summaries). Hematite and ilmenite have the same crystal structure and form a complete solid solution at high temperature. *Crouch* [1972] deformed porous synthetic hematite compacts in four-point bending experiments and found an activation energy of 335 kJ/mol for diffusion creep and stress exponents of 3.2-3.5 for dislocation creep. *Siemes et al.* [2003] investigated the rheology and fabric development of hematite ores deformed in axial compression in a Paterson apparatus. They parameterized a flow law for dislocation creep with stress exponent of 4.0 ± 0.3 and activation energy of $225\pm 20 \text{ kJ/mol}$. Scaling the hematite flow law of *Siemes et al.* [2003] to the lower melting temperature of ilmenite, *Till and Moskowitz* [2013] estimated an ilmenite flow law that predicts a slightly weaker rheology (Supplementary Figure S3).

4.3 Comparison to Other Minerals

It has been argued that magnetite creep is rate limited by oxygen diffusion (e.g., *Gómez-García et al.* [2002]) and that oxygen diffusion should therefore control the temperature dependence of magnetite creep [*Till and Moskowitz*, 2013]. Experimentally

measured activation energies for ^{18}O diffusion in magnetite (e.g., 188 kJ/mol, *Giletti and Hess* [1988]) are significantly lower than the one determined from creep experiments of *Crouch and Robertson* [1990] (264 kJ/mol). A different rate limiting mechanism (e.g., oxygen vacancy diffusion [*Crouch and Robertson*, 1990]) may be more important. Oxygen diffusion has not been measured in ilmenite or other minerals with ilmenite structure; such studies are needed to better understand the physical significance of the activation energy in Equation 1. The magnetite flow law of *Till and Moskowitz* [2013] is parameterized using the activation energy from *Giletti and Hess* [1988] and therefore may underestimate the temperature sensitivity of magnetite creep.

The rheology of ilmenite is compared to other oxides and silicates in Figures 4a-c using published flow laws (*Hirth and Kohlstedt* [1996]; *Rybacki and Dresen* [2000]; *Siemes et al.* [2003]; *Till and Moskowitz* [2013]) and Equation 1. Magnetite is weaker than ilmenite at geologically relevant stresses and temperatures. Consistent with its lower melting temperature than hematite, ilmenite is slightly weaker than hematite at most geologically relevant stresses and temperatures. Ilmenite viscosity is underestimated by the hematite-based ilmenite flow law presented by *Till and Moskowitz* [2013] at temperatures $<1000^\circ\text{C}$ (Supplementary Figure S3). Dry olivine is about 4 orders of magnitude more viscous than ilmenite at 1300°C and the difference in viscosity increases significantly at lower temperatures owing to the larger activation energy of olivine (Figure 4c).

Dry anorthite and ilmenite have similar viscosity at $\sim 1300^\circ\text{C}$ but ilmenite's lower temperature sensitivity suggests it is dramatically weaker under crustal conditions. This is corroborated by field observations. Ilmenite has been observed intermingling with

cataclastically deformed silicates in gabbroic shear zones at ophiolites [Hopkinson and Roberts, 1995] and in oceanic drill cores from several localities [e.g., Agar and Lloyd, 1997; Dick *et al.*, 2000]. The ilmenite often possesses evidence of crystal plastic deformation. Geochemical and textural relationships led authors in the aforementioned studies to argue the ilmenite is not native to the gabbros, but that it crystallized during synkinematic infiltration of fractured gabbro by ilmenite saturated melts. The melts may have originated from magma chambers directly plumbed to the shear zones by listric normal faults [Dick *et al.*, 1991; Hopkinson and Roberts, 1995] or be late-stage fractionation products squeezed from olivine gabbros deeper in the crust [Dick *et al.*, 2000]. The role of ilmenite in the initiation of shear localization in gabbros may be secondary to fracturing, but textures in natural gabbro-hosted ilmenite led Agar and Lloyd [1997] to propose that a weak ilmenite-rich layer in a shear zone could accommodate aseismic creep at low temperatures (200-400°C). We do not have low-temperature experimental data to fully vet this hypothesis, but Equation 1 does predict that ilmenite is exceptionally weak relative to plagioclase and olivine at low temperature (Figure 4c).

4.4 Aggregate Viscosities

Ilmenite is often a minor phase in natural rocks so determining the effect of low modal abundance on aggregate viscosities is critical. In Figure 5 we show modeled ilmenite-olivine aggregate rheologies calculated using the mixing model of Tullis *et al.* [1991], which parameterizes a volume-weighted aggregate flow law based on end member flow laws (solid lines). Also shown are isostrain and isostress (i.e., Voigt and

Reuss) bounds (thin dashed and dash-dotted lines, respectively) that are rigorous upper and lower limits for the rheology of the aggregate. The mixing model of *Tullis et al.* [1991] has been shown to be remarkably accurate at predicting the strength of experimentally deformed two-phase aggregates (e.g. *Dimanov and Dresen* [2005]). However, in situations where strain is accommodated on interconnected layers of a weak phase, the isostress bound may be more appropriate, similarly, isolated weak inclusions may have little effect on the rheology of an aggregate composed mostly of a stronger phase [e.g., *Handy*, 1990; 1994].

Initial results of ilmenite-olivine aggregate experiments (9 parts San Carlos olivine, 1 part ilmenite; 1 part olivine, 1 part ilmenite) conducted in shear show high peak stresses followed by long and significant decreases in viscosity which may be attributed to textures that develop at strains >1 (Appendix A, Supplementary Figure S5). Measured viscosities are intermediate to the isostress (Reuss, i.e. low viscosity) bound and the model of *Tullis et al.* [1991] suggesting ilmenite can significantly weaken an aggregate composed mostly of a stronger phase (Supplementary Figure S6). However, Fe-Mg exchange between ilmenite and olivine prior to and during deformation complicates interpretation of these results. Ilmenite forms a solid solution with geikielite (MgTiO_3) and exchanges Fe for Mg with olivine until the equilibrium K_D ($(\text{FeO/MgO})_{\text{ol}}/(\text{FeO/MgO})_{\text{ilmenite}}$) of 0.18 is attained (*Thacker et al.* [2009]). Olivine viscosity is sensitive to Mg# ($\text{Mg}/[\text{Mg}+\text{Fe}]$, in moles), decreasing as Mg# decreases (*Zhao et al.* [2009]). Geikielite has a melting temperature $\sim 200^\circ\text{C}$ higher than ilmenite (*Johnson et al.* [1971]) and is therefore probably stronger than pure ilmenite. Consequently, the greater the ilmenite:olivine ratio in an aggregate, the weaker the

olivine and the stronger the ilmenite-geikielite solid solution will be, i.e., in Figure 5 the “ilmenite” end member will move to higher viscosities and the olivine end member will move to lower viscosities. Because Fe-Mg exchange will affect aggregate viscosity in the lunar mantle as well as the laboratory, for the sake of discussion here we assume the maximum viscosity of lunar ilmenite-olivine aggregates follows the *Tullis et al.* [1991] models.

5. Implications

The role of ilmenite in the physicochemical evolution of the Moon can be considered in three separate stages, (1) solidification of the ilmenite bearing cumulate layer during lunar magma ocean crystallization and the immediate aftermath, (2) downwelling of ilmenite bearing cumulates during cumulate mantle overturn, (3) upwelling of ilmenite bearing cumulates after cumulate mantle overturn. Here we discuss each stage in turn.

5.1 Solidification of the Lunar Magma Ocean

The magma ocean becomes ilmenite saturated while anorthite and Fe-rich pyroxene are actively crystallizing [e.g., *Snyder et al.*, 1992]. Because at that time an anorthositic carapace has already formed on the magma ocean surface, latent heat from ilmenite layer crystallization (which occurs at $\sim 1100^{\circ}\text{C}$) is conductively dissipated and the layer solidifies over ~ 100 Myr [*Hess and Parmentier*, 1995]. Given the low viscosity of the ilmenite, the large density contrast between anorthite ($\rho \sim 2.8$ g/cc) and ilmenite ($\rho \sim 4.7$ g/cc), and the timescale of solidification, we expect effective separation of

plagioclase from ilmenite, leaving behind a cumulate layer of ilmenite and Fe-rich pyroxene in volume proportions $\sim 15:85$ [e.g., *Hess and Parmentier*, 1995]. The dense ilmenite-pyroxene cumulates will begin downwelling before solidification of the cumulate layer is complete, mixing into underlying peridotitic cumulates [*Hess and Parmentier*, 1995]. The number of downwelling ilmenite-pyroxene plumes that form is proportional to the relative viscosities of the ilmenite-pyroxene cumulates and underlying peridotites. Under certain textural conditions the ilmenite-pyroxene aggregate viscosity could approach that of pure ilmenite which will promote the formation of a smaller number of large downwelling plumes that rapidly sink into the lunar mantle. Alternatively, if the viscosity contrast between the cumulate layers is small, the number of diapirs that form will be greater, promoting efficient mixing of crystallizing ilmenite and pyroxene cumulates and underlying peridotitic cumulates. In that scenario, a layer of ilmenite-bearing cumulate harzburgite with a thickness on the order of 100 km would form beneath the lunar crust [*Hess and Parmentier*, 1995; *Parmentier et al.*, 2002]. In the following discussion on the scale of cumulate overturn, we assume the existence of this type of well-mixed ilmenite-bearing cumulate layer.

5.2 Cumulate Mantle Overturn

Lunar cumulate mantle overturn will occur at a scale that depends on the viscosity contrast between the newly formed ilmenite bearing peridotite cumulates and underlying ilmenite-free harzburgites. Lower viscosity ilmenite-bearing cumulate layers favor longer wavelength instabilities. *Parmentier et al.* [2002] argued that it is possible to form degree-one downwelling plumes if the viscosity contrast between the ilmenite-bearing

cumulates and underlying harzburgites is 10^4 . *Parmentier and Hess* [1995] estimated the ilmenite bearing cumulates have about 5% ilmenite. According to viscosity models presented in Figure 5, adding 5 volume % ilmenite to a harzburgitic lunar mantle will at minimum halve the viscosity of the aggregate, but the ilmenite-olivine aggregate experiments conducted in shear suggest the weakening effect could be much greater (Supplementary Figure S6). This reduction in viscosity improves the chances of forming long wavelength downwelling instabilities [*Parmentier et al.*, 2002], but additional weakening (for example by partial melting) may be required to form degree-one downwelling instabilities.

5.3 Upwelling of Ilmenite Bearing Cumulates (IBC)

Now we turn to upwelling of overturned IBC. Numerical models investigating the stability of overturned IBC in the lunar interior found that upwelling plumes develop when heating of the IBC by radioactive decay causes thermal expansion and the IBC become positively buoyant [*Zhong et al.*, 2000; *Zhang et al.*, 2013a; *Zhang et al.*, 2013b]. The development of upwelling plumes depends on the viscosity of the IBC. *Zhang et al.* [2013a] found that highly temperature sensitive IBC viscosities prevent formation upwelling plumes. When the viscosity of the IBC decreases through heating, convection in the IBC layer efficiently dissipates heat into the overlying harzburgitic cumulates and thermal buoyancy is unable to offset the high density of the IBC [*Zhang et al.*, 2013a]. The same thing will happen if the viscosity of the IBC is low regardless of its temperature sensitivity. In that case, ilmenite-bearing cumulates that sink to the lunar core-mantle boundary will not form upwelling plumes and may instead form stable (i.e., internally

convecting but stationary) layers around the core [e.g., *de Vries et al.*, 2010; *Zhang et al.*, 2013a].

Reanalysis of seismograms collected by the seismic network of the Apollo program led *Weber et al.* [2011] to propose that the Moon has a solid inner core and fluid outer core surrounded by a partially molten silicate layer. Recently, a lunar viscosity model was developed to understand the tidal dissipation of the Moon [*Harada et al.*, 2014] that also predicts a layer surrounding the lunar outer core with an exceedingly low viscosity of $2 \cdot 10^{-16}$ Pa·s. This viscosity is consistent with viscosities predicted by our mixing models for ilmenite-olivine aggregates with ilmenite fractions relevant to IBC (e.g., red line, Figure 5) at the estimated temperature of the lunar core-mantle boundary (~ 1200 - 1400°C , see Figure 9 in *Zhang et al.* [2013a] for a summary of estimates). Partial melting of overturned IBC at the core-mantle boundary would further reduce the viscosity of the IBC layer. A deep low viscosity layer coincides with the zone of possible seismic attenuation around the lunar core through which no moonquakes have been observed [e.g., *Nakamura et al.*, 1973; *Wieczorek et al.*, 2006; *Wieczorek*, 2009; *Weber et al.*, 2011]. The low viscosity and seismic attenuation zones can both be explained by the presence of a stable, partially molten ilmenite-bearing cumulate layer surrounding the lunar core. The low viscosity of ilmenite helps carry heat producing elements (which mostly reside in Fe-rich clinopyroxene that crystallized with the ilmenite) to the core-mantle boundary during cumulate overturn. A hot stable blanket of IBC around the lunar core may cause negative heat flux at the core-mantle boundary suppressing convection in the core and the development of a convection-driven core dynamo [*Zhang et al.*, 2013a].

The probable stability of ilmenite bearing cumulates around the lunar core has important implications for lunar basalt petrogenesis. The high-Ti basalts require an ilmenite component in their source. Overturned IBC may be entrained by convecting harzburgite above the stable IBC layer. If such entrainment is inefficient, cumulate mantle overturn must have been incomplete. Ilmenite beneath the lunar crust that failed to overturn could have been assimilated by upwelling melts to form the high-Ti basalts [e.g., *Hubbard and Minear, 1975; Wagner and Grove, 1997; Elkins Tanton et al., 2002; Dygert et al., 2013*]. Alternatively, the ilmenite fraction in the IBC may have been locally low enough to prevent significant viscosity reduction and density increase of the IBC, preventing downwelling. This could occur by dilution of IBC by underlying harzburgites during cumulate mantle overturn, or if initial mixing of ilmenite-pyroxene magma ocean cumulates and underlying peridotites was spatially and volumetrically heterogeneous. Efficient heat conduction from a stable (convecting) layer of IBC into the overlying harzburgites provides a long-term heating mechanism for generation of low and high-Ti lunar basalts.

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8. Figure Captions

Figure 1. Contrast enhanced reflected light micrographs of experiments ID-1 (a), ID-12 (b), ID-2 (c), ID-13 (d) and ID-5 (e). The scale bars are 40 μ m. Experiments are shown in order of descending temperature. Note the contrasting textures in ID-1 (a) and ID-12 (b). ID-1 shows polygonal grain boundaries indicating textural equilibrium while ID-12 shows smaller grains along irregular grain boundaries, suggesting grain boundary migration. Twinning is visible in experiment ID-5 (e).

Figure 2. Differential stress-strain paths for experiments reported in this study.

Figure 3. (a) Differential stress-strain rate relations for individual experiments. (b) Data used in the flow law determination plotted against the natural logarithm of strain rate and 10000/T (K). Symbols are the same as those shown in (a). Numbers next to the data points indicate measured differential stresses (MPa) at the strain rate-temperature condition. Data points with multiple stresses are repeat measurements. The black lines are flow law predictions at a series of differential stresses. Inset shows experimental data normalized to 100MPa ($n=2.96\pm0.20$) plotted against 10000/T (K).

Figure 4. Stress-strain rate (a), temperature-strain rate (b), and temperature-viscosity (c) relations predicted by Equation 1 (thick red line) and flow laws reported in the literature. Silicates are dashed lines and oxides are solid lines.

Figure 5. Viscosity of ilmenite-olivine aggregates calculated using the model of *Tullis et al.* [1991] (solid lines) for Equation 1 and the flow law for dry olivine from *Hirth and Kohlstedt* [1996]. Dashed lines are isostrain bounds and dash-dotted lines are isostress bounds. Data from ID-2 extrapolated to 3MPa (yellow and magenta squares) are plotted on the flow law predictions.

Figure 1.

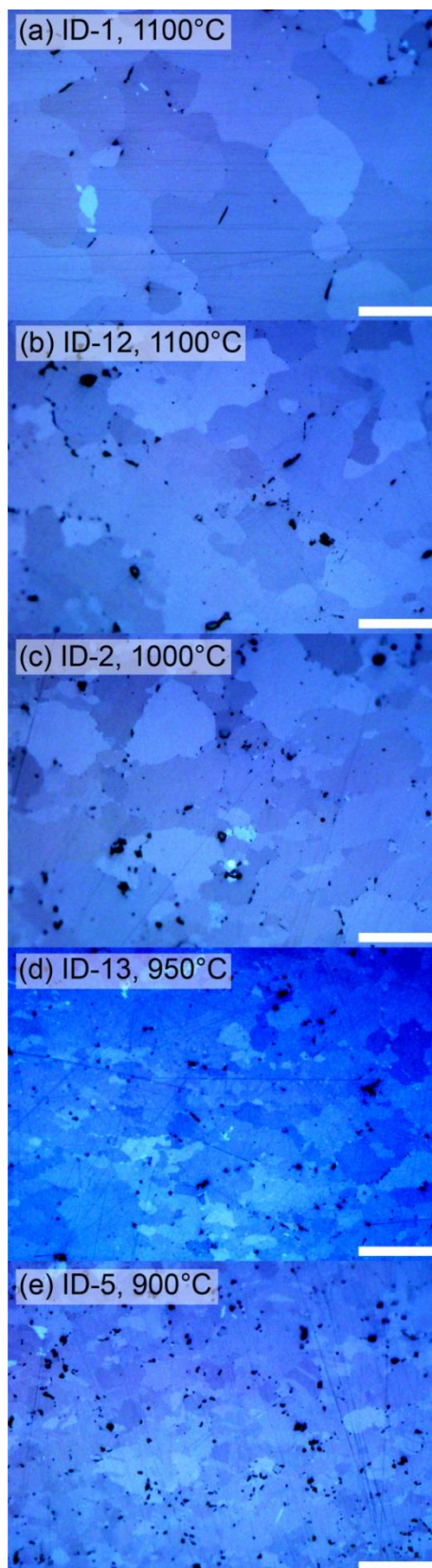


Figure 2.

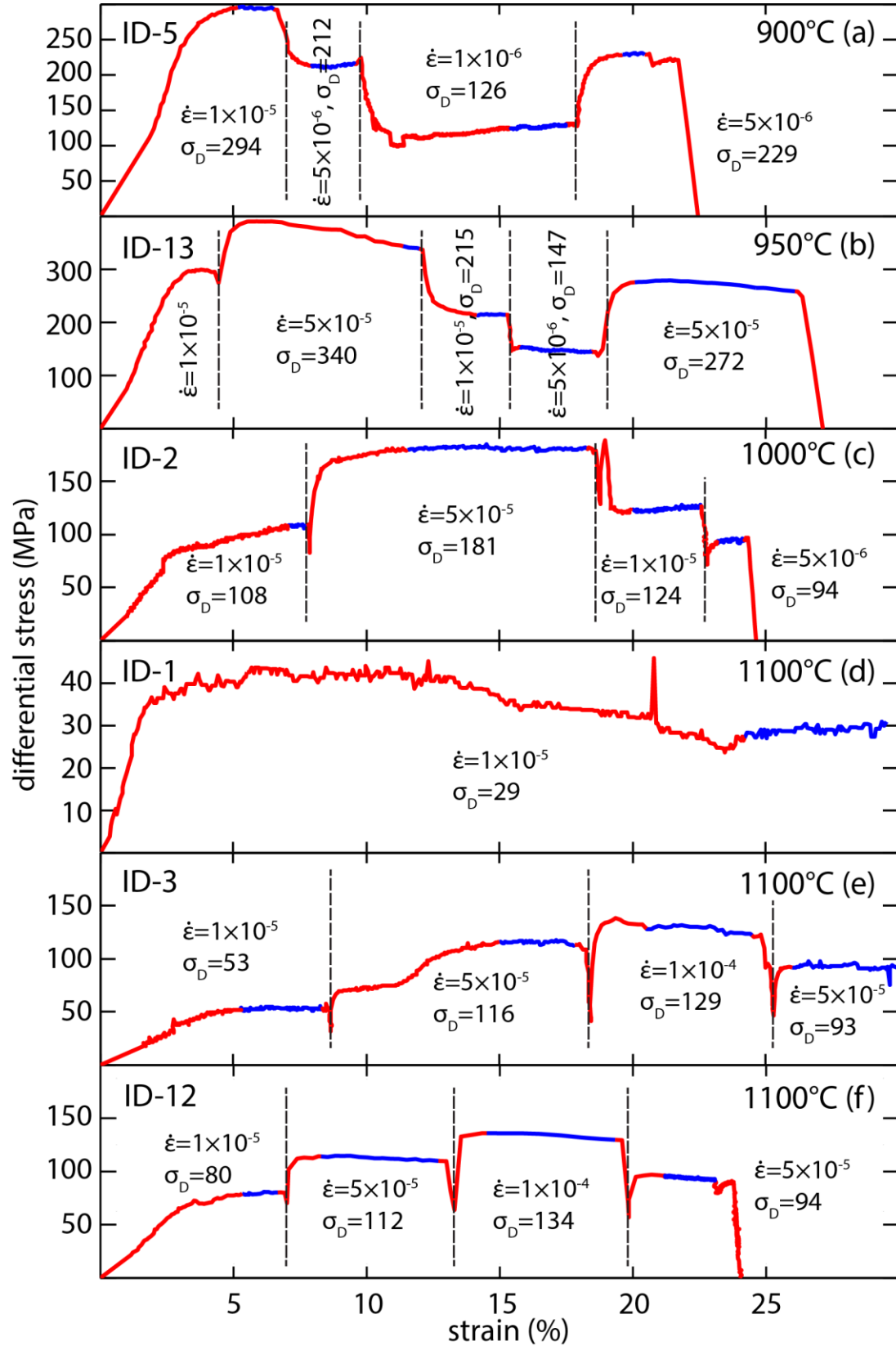


Figure 3.

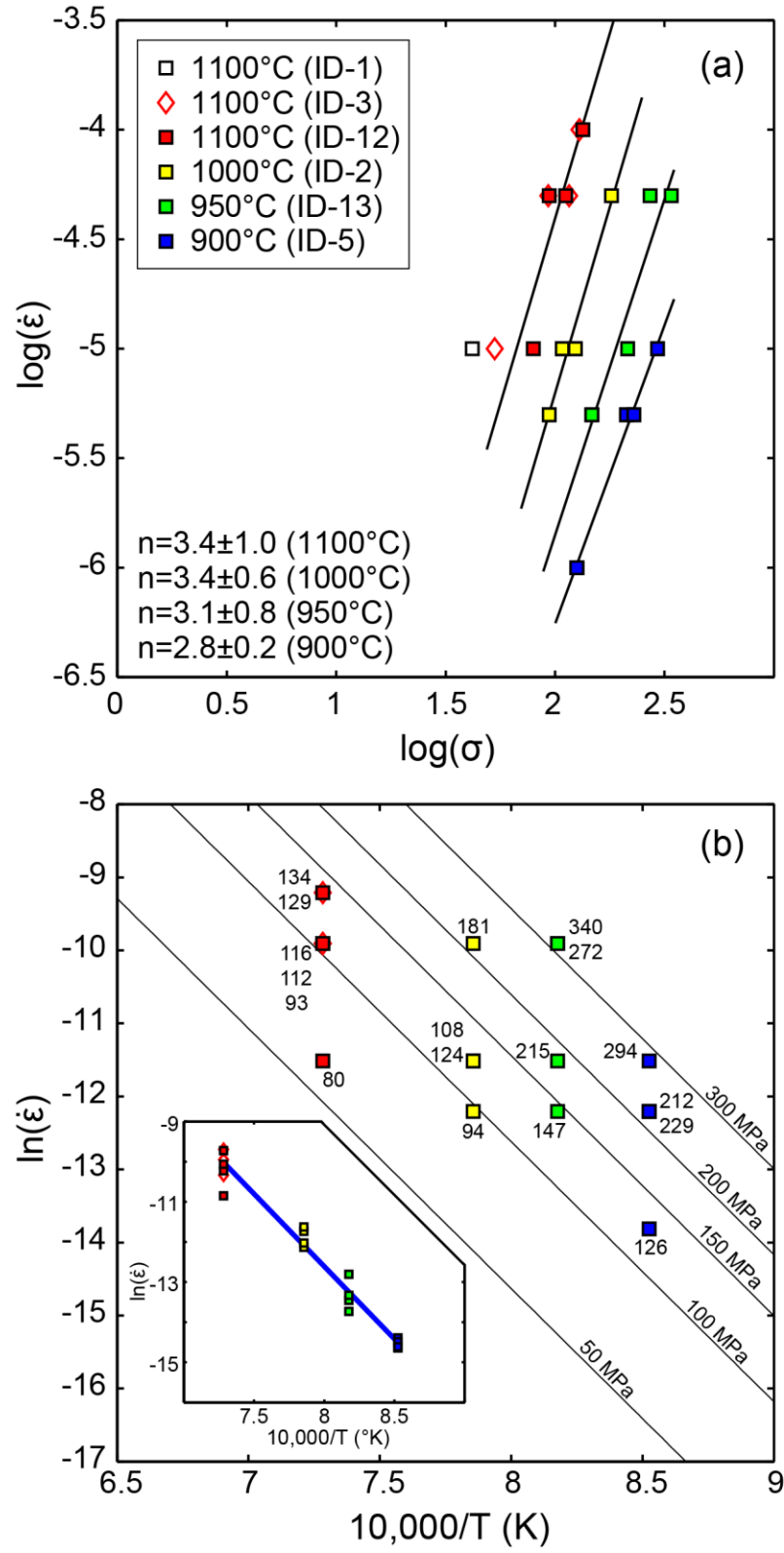


Figure 4.

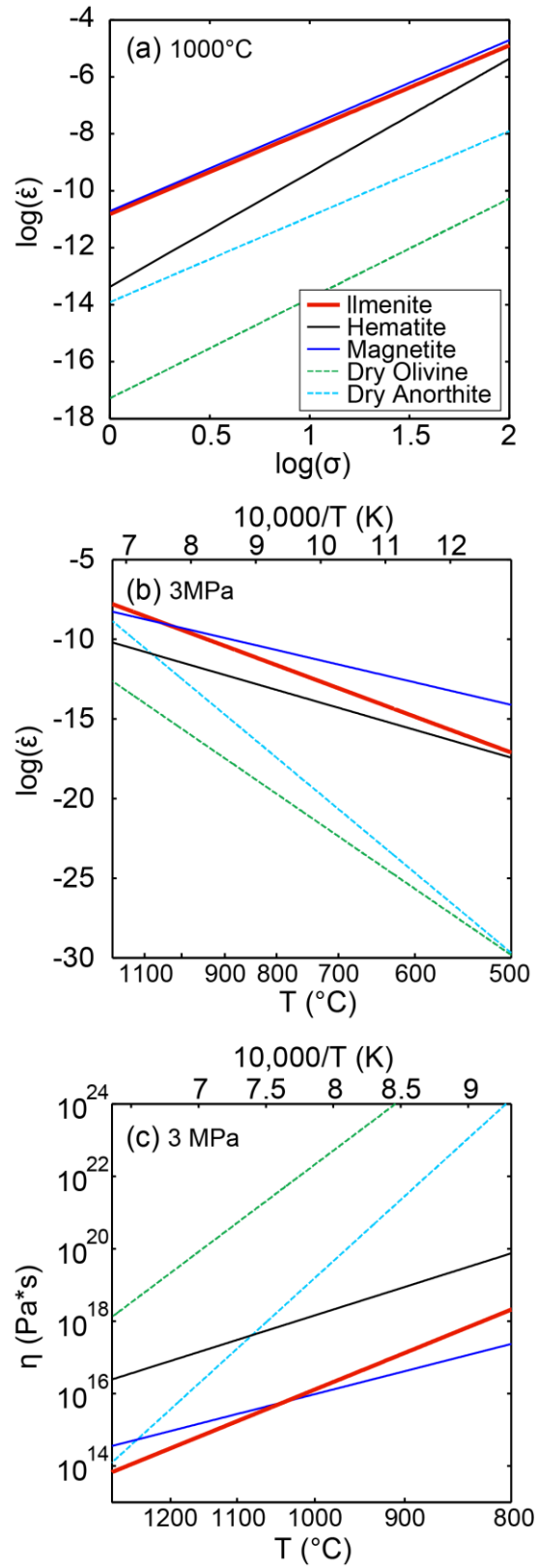


Figure 5.

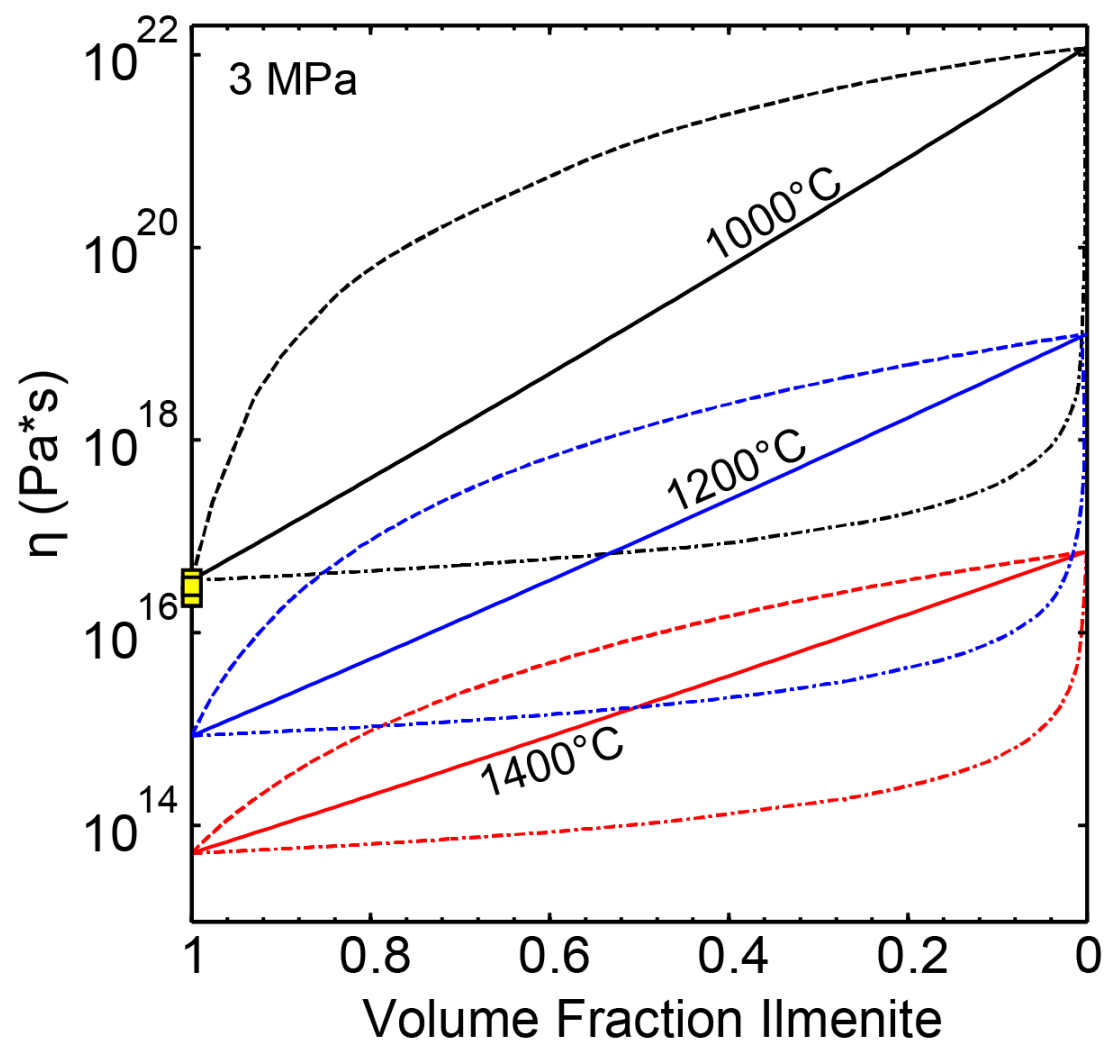


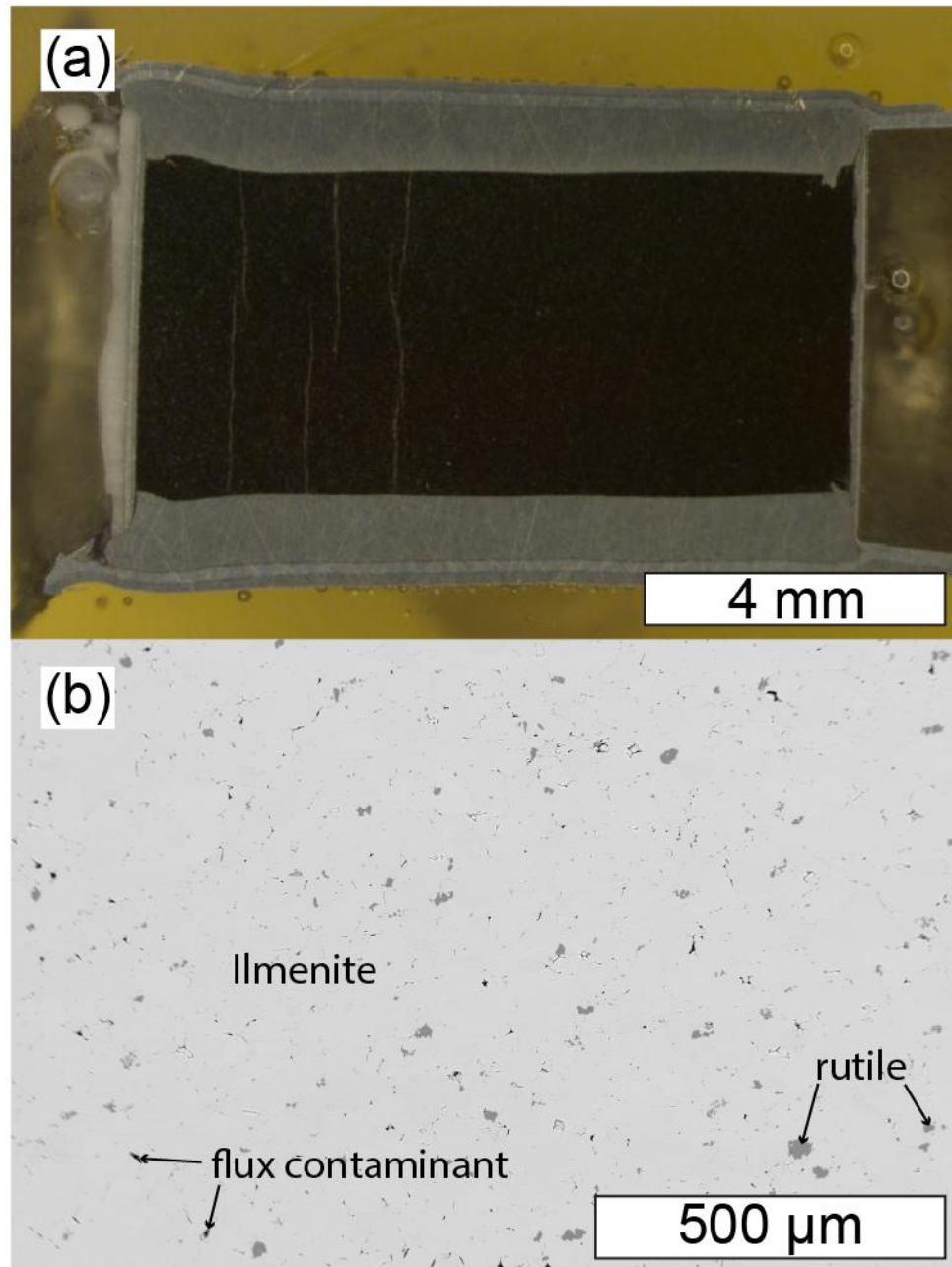
Table 1.

Table 1. Summary of experimental conditions and results.						
Run Name	T (°C)	d ^a (μm)	ε	σ _D (MPa)	Σε (%)	n (2σ)
ID-1	1100	20-30	1×10 ⁻⁵	29	30	-
ID-3	1100	20-30	1×10 ⁻⁵ , 5×10 ⁻⁵ , 1×10 ⁻⁴ , 5×10 ⁻⁵	53, 116, 130, 93	31	3.4±1.0
ID-12	1100	30-50	1×10 ⁻⁵ , 5×10 ⁻⁵ , 1×10 ⁻⁴ , 5×10 ⁻⁵	80, 111, 130, 93	24	3.4±1.0
ID-2	1000	20-30	1×10 ⁻⁵ , 5×10 ⁻⁵ , 1×10 ⁻⁵ , 5×10 ⁻⁶	108, 181, 125, 94	24	3.4±0.6
ID-13	950	30-50	5×10 ⁻⁵ , 1×10 ⁻⁵ , 5×10 ⁻⁶ , 5×10 ⁻⁵	340, 215, 148, 276	26	3.1±0.8
ID-5	900	20-30	1×10 ⁻⁵ , 5×10 ⁻⁶ , 1×10 ⁻⁶ , 5×10 ⁻⁶	294, 214, 127, 229	22	2.8±0.2

^a Approximate grain size of starting material before cold pressing.

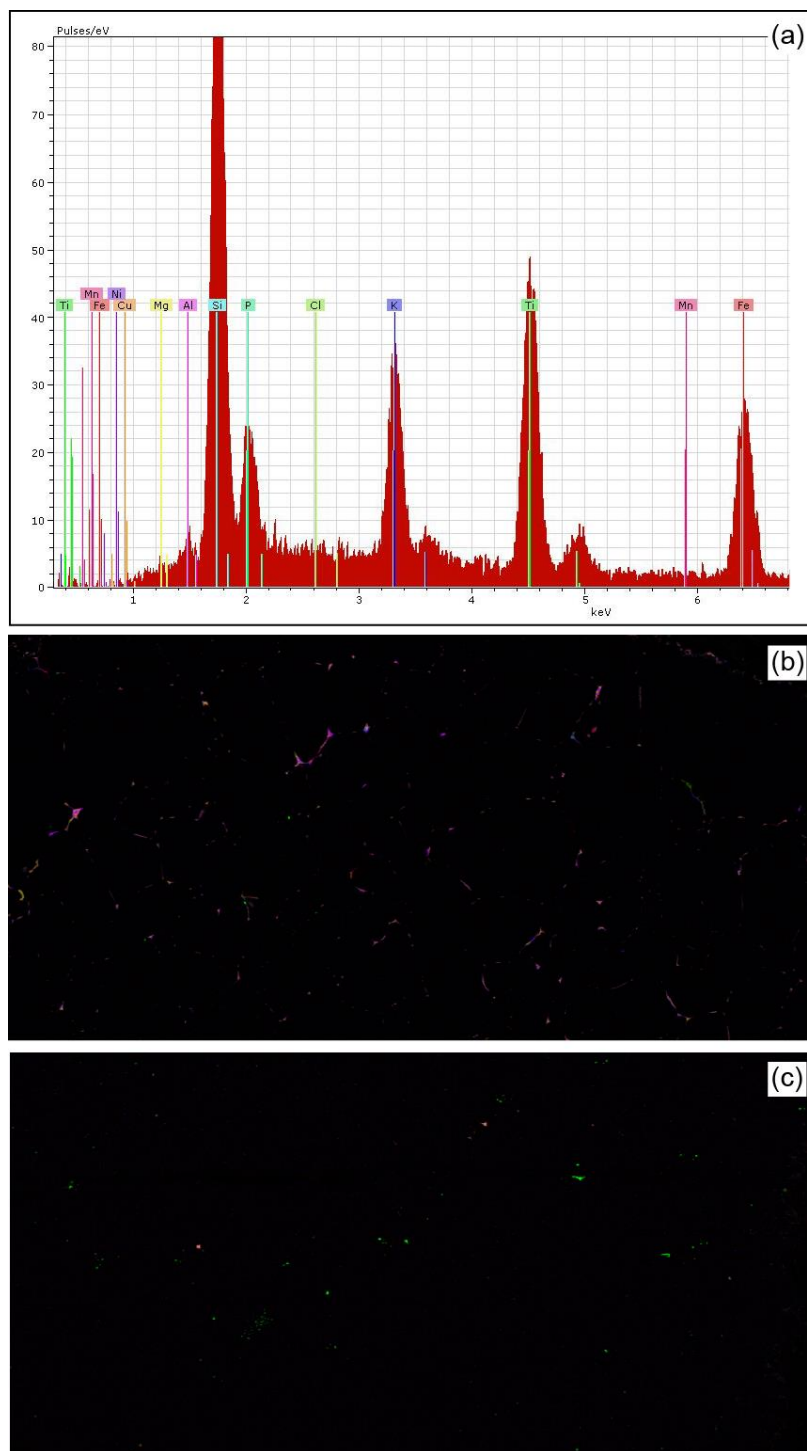
Supplementary Material

Figure S1.



(a) Example of a deformed experimental charge. (b) Backscatter electron micrograph of experiment ID-1. The light gray phase is ilmenite and the dark gray phase is rutile. Isolated black pockets are quenched melt from flux contaminant in the starting material.

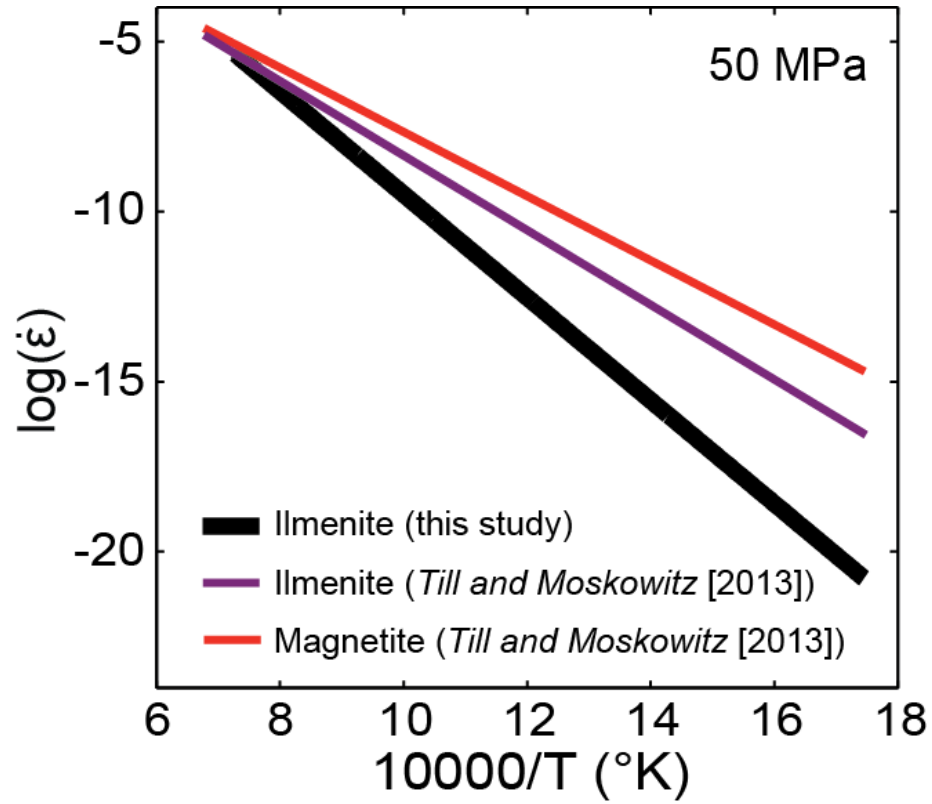
Figure S2.



(a) Representative EDS spectra of an area of flux contamination in experiment ID-1. (b) Three element false color X-ray map of annealed starting material that was not

acid washed. Three separate element maps were assigned a color (red=K, green=Si, blue=P) and the maps were superimposed on each other. The black background is ilmenite. The image covers an area 0.5 mm tall by 1 mm wide. 1.16% of the pixels show some contamination. (c) Three element false color X-ray map of annealed starting material that was acid washed. 0.55% of the pixels show some contamination.

Figure S3.



Flow laws for ilmenite and magnetite from *Till and Moskowitz* [2013] compared to Equation 1. Equation 1 predicts higher viscosity than the flow law from *Till and Moskowitz* [2013], which was estimated by “adjusting” a flow law for hematite (that of *Siemes et al.* [2003]) to the lower melting temperature of ilmenite.

Appendix A. Ilmenite-Olivine Aggregate Experiments

Methods

Ilmenite-olivine aggregates were deformed in shear in a Griggs apparatus in molten salt assemblies. The experiments utilize 10-20 μ m San Carlos olivine powder that was grain size separated using Stokes' settling. Mixtures of 10-20 μ m ilmenite and 10-20 μ m olivine were prepared by mechanically stirring ilmenite and olivine powders in 1M nitric acid in volume fractions of 1:1 and 1:9 (ilmenite to olivine). The mixtures were washed in deionized water, dried, and stored in an oven prior to jacketing.

Ilmenite-olivine aggregates were deformed at 1000°C with 45° alumina pistons. All the experiments employed an axial strain rate of 10^{-5} . Experiments W1866 and W1867 were annealed at the run conditions for >60 hours, experiment W1870 was annealed for 14 hours. W1866 utilized a 1:1 mixture of ilmenite and olivine, W1867 and W1870 utilized a 1:9 mixture of ilmenite and olivine. The starting material for experiment W1867 was contaminated by alumina chips from a cracked shear piston that was replaced before cold sealing the jacket. Based on visual inspection the alumina appears to constitute <5% of the deformed sample.

Mechanical data were processed using a MATLAB program similar to “rig” (Pec, 2012, <https://sites.google.com/site/rigprogram/>) which corrects for apparatus distortion, friction, and changes in confining pressure. Bulging of deformed material around the edges of the alumina pistons was minimal so in data processing we assumed no thinning of the deforming layer.

Results

A summary of experimental conditions and results are presented in Supplementary Table 1. Backscatter electron micrographs are presented in Supplementary Figure S4. The deformed aggregates are generally well mixed though isolated pockets of more abundant olivine or ilmenite can occasionally be observed. W1867 and W1870 appear to contain limited porosity. In all of the experiments, olivine have core-rim Mg# gradients that depend on the proximity of the spot to an ilmenite grain. Mg# gradients are most severe in W1866 (cores are 92 and rims are ~75) because the equilibrium olivine composition is far from the initial condition. Experiment W1867 has core-rim olivine Mg# gradients of 90 to 85, and W1870 has core-rim Mg# gradients of 91 to 85. Ilmenite grains are effectively homogeneous in composition. The backscatter micrographs show elongated ilmenite and/or olivine grains at an ~25° angle to the shear direction. In experiment W1866 ilmenite appear to form an interconnected layer, ilmenite grains are mostly isolated from one another in W1867 and W1870.

Shear stress-shear strain relations and axial equivalent viscosities are presented in Supplementary Figure S5. None of the experiments reached a steady-state condition at quenching but they appear to be approaching lower steady-state viscosities. The experiments show high peak stresses followed by long and significant decreases in viscosity which may be attributable to textures that develop at shear strains >1. W1866 and W1867 have approximately the same viscosity at any strain which is surprising as the starting materials vary greatly in ilmenite abundance. W1870 has significantly higher viscosity than W1867 which may be attributable to its shorter anneal time.

Mixing Models

In Supplementary Figure S6, axial equivalent viscosities measured in the shear experiments are compared to predictions of ilmenite-olivine aggregate viscosities. The viscosity predictions were made using the model of *Tullis et al.* [1991] for end-member flow laws (this study and Hirth and Kohlstedt [1996]). Isostress (lower) and isostrain (upper) bounds are also presented (dash-dotted and dashed lines respectively) which should be robust upper and lower limits for the aggregate viscosity. All of the measured viscosities are intermediate to the prediction of *Tullis et al.* [1991] and the lower viscosity isostress bound. The experiments suggest that addition of small amounts of ilmenite to a dunite (or harzburgite) will significantly lower the viscosity of the aggregate.

Reference

Peč, M. (2012), Experimental investigation on the rheology of fault rocks. PhD Thesis, University of Basel.

Table S1.

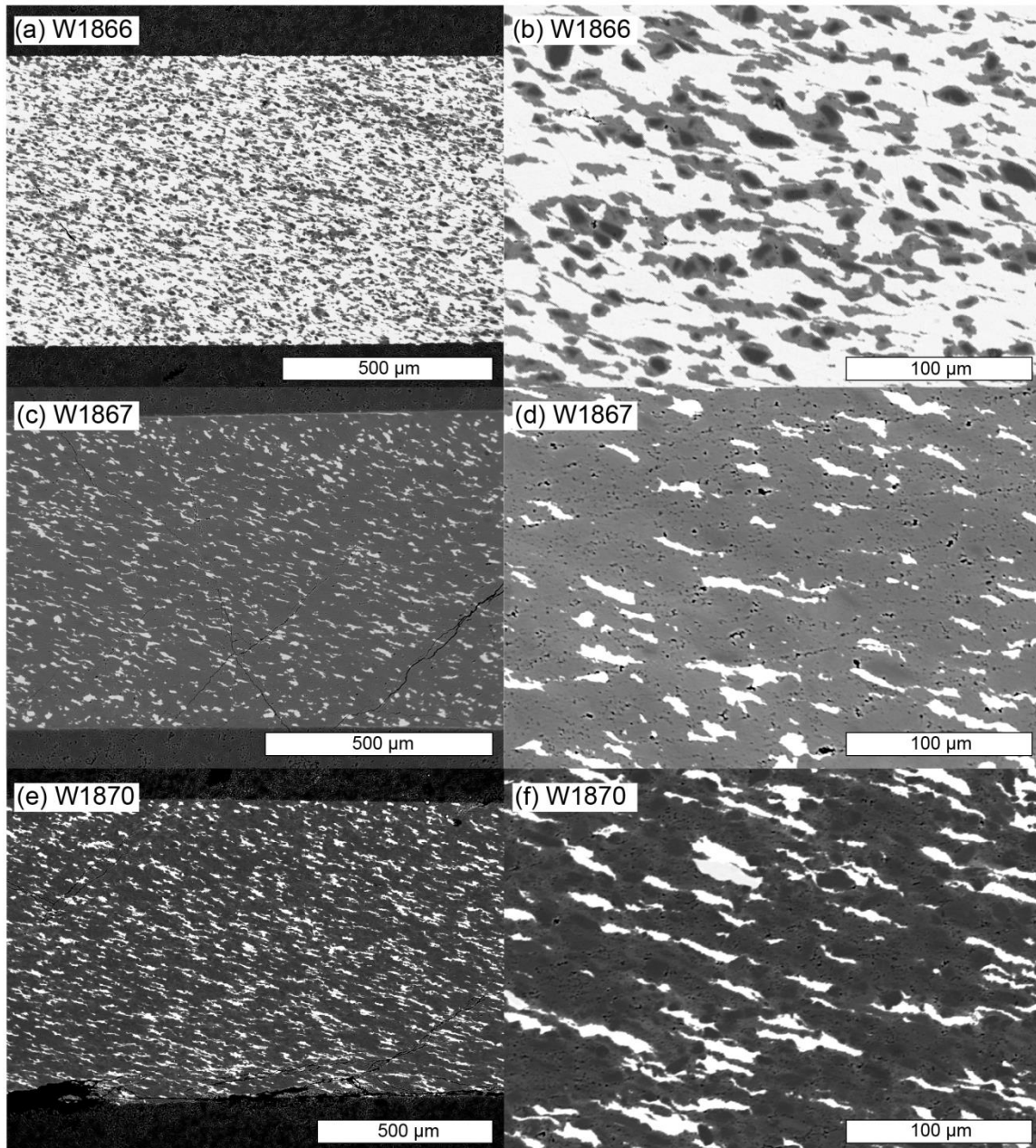
Summary of experimental conditions and results for ilmenite-olivine aggregates deformed in shear.

Run Name	T (°C)	Composition	Anneal	d ^a (μm)	ε	τ (MPa)	Σε (%)
W1866	1000	0.5 Ilm : 0.5 Ol	69h	10-20	1×10 ⁻⁵ (axial)	466 ^b	225
W1867	1000	0.1 Ilm : 0.9 Ol	63h	10-20	1×10 ⁻⁵ (axial)	363	289
W1870	1000	0.1 Ilm : 0.9 Ol	14h	10-20	1×10 ⁻⁵ (axial)	697	269

^a Approximate grain size of starting material before cold pressing.

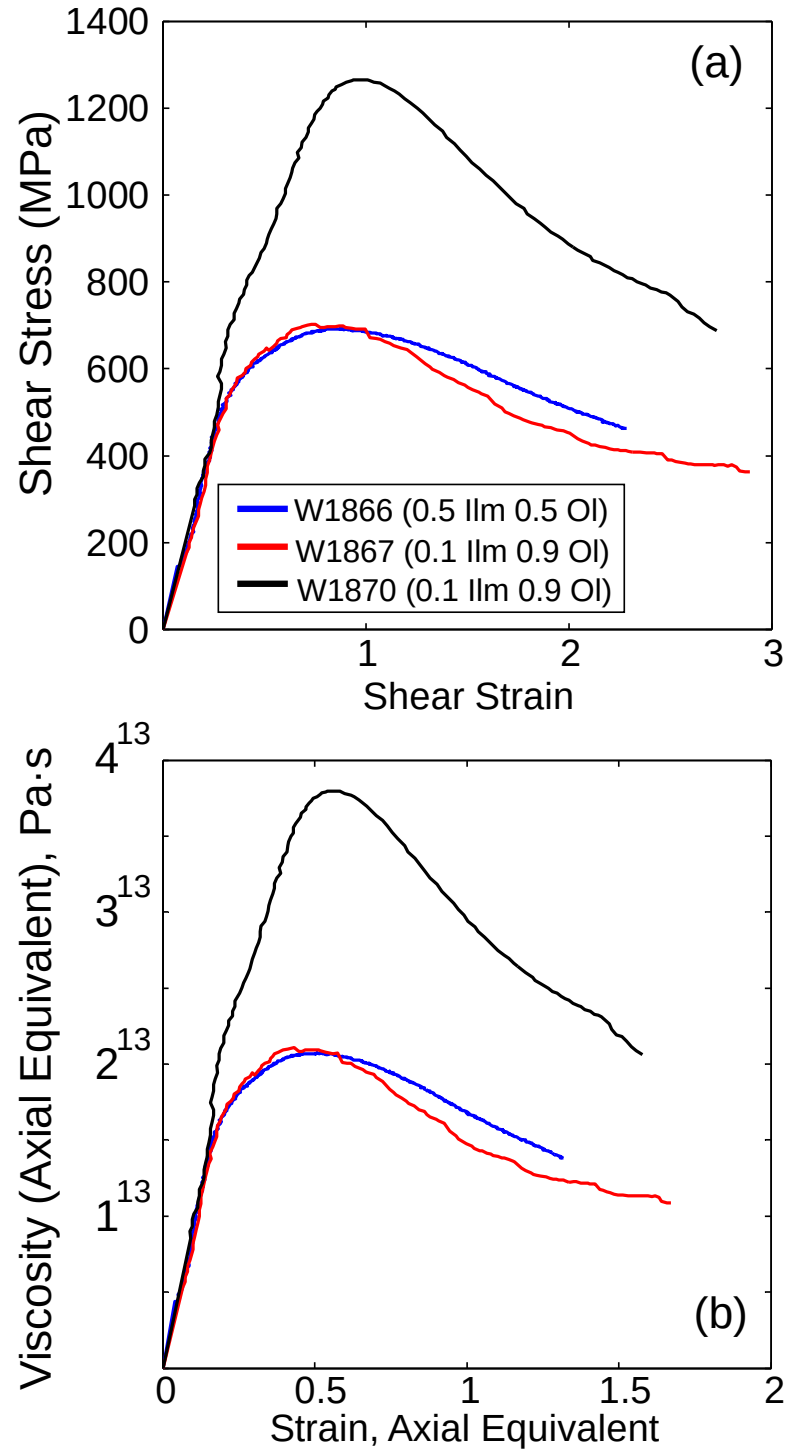
^b Differential stress at quench. None of the shear experiments reached a steady state differential stress.

Figure S4.



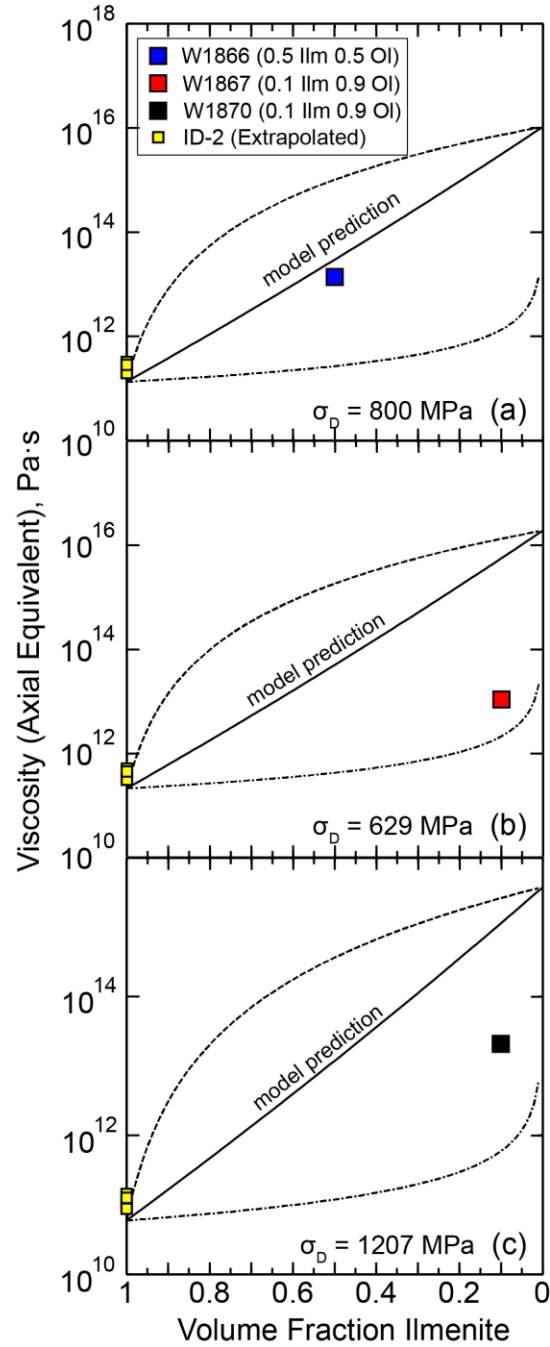
Backscatter electron micrographs of shear experiments. Experiment W1866 utilized a 50-50 mixture of ilmenite and olivine, experiments W1867 and W1870 utilized a 90 olivine 10 ilmenite mixture (by volume). W1866 and W1867 were annealed for approximately three days before deformation; W1870 was annealed overnight before deformation. For all images the shear direction is left lateral parallel to the long axis of image. Micrographs in (a), (c), and (e) show the alumina pistons bounding the deformed sample. Differences in contrast within olivine in (b), (d), and (f) are principally Mg# variations. The small black spots in (d) and (f) are probably porosity.

Figure S5.



Shear stress plotted against shear strain (a), and axial equivalent viscosity plotted against axial equivalent strain (b).

Figure S6.



Mixing models [Tullis *et al.*, 1991] calculated for ilmenite and olivine end-member flow laws (this study, Hirth and Kohlstedt, 1996) compared to the measured viscosities (blue, red, and black squares). Also shown are data from ID-2 extrapolated to the axial equivalent differential stress of the shear experiment (yellow squares). Dashed line is the isostrain bound and dash-dotted line is the isostress bound.

CHAPTER 4

Trace Element Fractionation during Melt Percolation and Melt-Rock Reaction in the Mantle: an Example from a Dunite-Harzburgite- Lherzolite-Plagioclase Lherzolite Sequence from Trinity Ophiolite

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In Preparation for **Journal of Petrology**.

Abstract

Trace elements were analyzed in clinopyroxene and orthopyroxene across an ~20 m long dunite-harzburgite-lherzolite-plagioclase lherzolite (DHL-PL) sequence at the Trinity Ophiolite by laser ablation inductively coupled plasma mass spectrometry. Rare earth element (REE) and high field strength element concentrations increase in unison about 9 m from the dunite-harzburgite contact. A previous investigation of major elements at the transect (Morgan *et al.*, 2008) observed that minor elements in clinopyroxene also increase ~9 m from the dunite-harzburgite contact, and that NiO in olivine increases from lower to higher values ~3 m from the dunite-harzburgite contact. Clinopyroxene grains in plagioclase lherzolite samples farthest from the dunite-harzburgite contact exhibit core-rim variations in minor and trace elements that mimic the outcrop scale element trends. Collectively, the lithological sequence and major and trace element concentration gradients suggest a two stage history of evolution is preserved at Trinity. In the first stage, basaltic melt infiltrated a harzburgitic residue of partial melting, precipitating plagioclase and pyroxene and forming plagioclase lherzolite. In the second stage, a trace element depleted pyroxene and plagioclase undersaturated melt migrated from a dunite channel into the plagioclase lherzolite, forming a hybridized composition owing to reaction with plagioclase lherzolite. Orthopyroxene saturated hybridized melt precipitated new clinopyroxene with depleted major and trace element compositions as it cooled. Because Ni is relatively fast diffusing in olivine, it was chromatographically fractionated from trace elements in the infiltration event. Chromatographic fractionation among incompatible trace elements in plagioclase lherzolite is not observed because they experienced disequilibrium transport owing to their sluggish diffusivity in pyroxene. REE

abundances of melts in equilibrium with pyroxene in the dunite, harzburgite, and lherzolite are similar to boninitic dikes that cut crustal units at Trinity and may be genetically related. Dunite-harzburgite-lherzolite-plagioclase lherzolite sequences from Trinity and other peridotites (e.g., Horoman, Ronda, Lanzo) likely formed by the similar processes. The infiltration of dunite-hosted melts into peridotitic host rock may be common, providing an explanation for the wide array of melt-peridotite interactions observed in abyssal peridotites and some ophiolites.

1. Introduction

A number of physical and chemical processes are involved in the segregation of partial melts from the asthenospheric mantle. Chief among them are buoyancy driven porous flow in a deformable solid matrix and chemical potential driven melt-rock reaction in regions above initial melting (e.g., McKenzie, 1984; Stevenson, 1986; 1989; Kelemen *et al.*, 1997; Holtzman *et al.*, 2003; Kholstedt & Holtzman, 2009). Mechanisms of melt segregation are still not fully understood. They include grain scale porous flow, focused flow along high porosity channels, and possibly hydrofractures (Nicolas, 1989; Sleep, 1988; Spiegelman & Kenyon, 1992; Kelemen *et al.*, 1995a, Kelemen *et al.*, 1997; Holtzman *et al.*, 2003). Such mechanisms are necessary to explain (and were largely developed to rationalize) the observation that least fractionated mid-oceanic basalts (MORB) are multiply saturated with olivine and orthopyroxene at pressures greater than 1 GPa (e.g., O'Hara 1965; Stolper, 1980; Elthon & Scarfe, 1984; Braun & Kelemen, 2002). Further evidence that efficient melt extraction processes are required came with analysis of trace element compositions in clinopyroxene grains in abyssal peridotites

(Johnson *et al.*, 1990) and in ultra-depleted olivine hosted melt inclusions (e.g., Sobolev & Shimizu, 1993; Shimizu, 1998), which display compositional systematics characteristic of near-fractional melting. Additionally, long lived isotopic ratios (e.g., Salters & Hart, 1989) and U-series disequilibria (e.g. Beattie, 1993) consistent with mantle melting in the garnet stability field was observed, requiring some type of channelized flow of melts to the seafloor.

Melt migration through tabular dunites (i.e., dunite channels) is currently the transport mechanism favored by many mantle geochemists because it is consistent with laboratory and field observations. As envisioned by Kelemen *et al.* (1995a, 1997), the mantle undergoes decompression melting beneath a spreading center and the melt buoyantly percolates toward the seafloor. Assuming a lherzolitic mantle, the melt is initially saturated with olivine, orthopyroxene, and clinopyroxene. The stability of pyroxene in a basaltic melt is a function of pressure (e.g., O'Hara 1965; Shibata, 1976; Stolper 1980; Elthon & Scarfe, 1984). As the melt migrates upward and pressure decreases, the olivine-pyroxene peritectic shifts toward orthopyroxene, expanding the olivine stability field (e.g., O'Hara, 1968; Shibata, 1976; Walker *et al.*, 1977; Quick, 1981a) and making the basalt pyroxene undersaturated. Melt rock-reaction experiments have established that pyroxene undersaturated basalts react with harzburgite or lherzolite to form melt-bearing dunite (e.g., Daines & Kohlstedt, 1994; Morgan & Liang, 2003, 2005; Van den Bleeken *et al.*, 2010). Morgan & Liang (2005) further demonstrated that pyroxene dissolution is concomitant to olivine precipitation, so olivine grains in the reacting peridotite coarsen. Because permeability scales as the product of grain size squared and porosity cubed (e.g., Wark & Watson, 1998), harzburgite or lherzolite hosted

dunites that form by melt-rock reaction are more permeable than pyroxene-bearing peridotite. Consequently, local pressure gradients will drive partial melts from harzburgite and lherzolite into dunite, developing reactive infiltration instabilities (e.g., Ortoleva *et al.*, 1987; Steefel & Lasaga, 1990; Kelemen *et al.*, 1995b; Spiegelman *et al.*, 2001) that form a network of tabular dunites (dunite channels). Because olivine-melt partition coefficients are generally very low for incompatible trace elements (e.g., Beattie *et al.*, 1991; Evans *et al.*, 2008; Mallmann & O'Neill, 2010; Sun & Liang, 2013), melts migrating in dunite channels will retain the geochemical signature of their source regions. Dunite-hosted melts transported from depth will also be olivine saturated and pyroxene undersaturated, consistent with magnesium-rich oceanic basalts (e.g., Braun & Kelemen, 2002).

The chemical evolution of peridotite is determined by the combined effects of melt extraction and melt-rock interactions. There is considerable outcrop and grain-scale evidence suggesting migrating melts interact with and impose their chemical signatures on mantle harzburgite and lherzolite (e.g., Dick, 1989; Bodinier *et al.*, 1990; Elthon, 1992; Garrido & Bodinier, 1999; Niu, 2004; Warren & Shimizu, 2010). For example, many plagioclase bearing peridotites are thought to have formed by impregnation of refractory peridotite by basaltic melts, and the resultant rocks have dramatically different major and trace elements compositions than the original rocks (e.g., Nicolas & Dupuy, 1984; Dick, 1989; Rampone *et al.*, 1997; Tartarotti *et al.*, 2002; Piccardo *et al.*, 2007; Müntener *et al.*, 2010).

Because melt migration processes are highly localized, field investigations require good spatial and geochemical information. Of the numerous geochemical studies of

mantle ophiolites, a minority report integrated spatial-geochemical information. Examples include Quick (1981a), Obata & Nagahara (1987), Kelemen *et al.* (1992), Takahashi (1992), Takazawa *et al.*, (1992), Varfalvy *et al.* (1996), Kubo (2002), Suhr *et al.* (2003), Braun (2004), Lundstrom *et al.* (2005), Maaløe (2005), Zhou *et al.* (2005), Morgan *et al.* (2008), and Pagé *et al.* (2008). These authors propose different origins of the geochemical variations they report, but observations common to all of the studies are statistically significant gradients in major and trace element geochemistry across and/or beyond dunite-harzburgite contacts. These observations beg the following questions: Do tabular dunites always drain host lherzolite and harzburgite, or can they also act as pathways that facilitate melt-rock interaction? If so, under what conditions should we expect dunites to assume these roles and how do the functions of tabular dunites evolve during mantle upwelling and corner flow? Are there petrologic and geochemical trends common to multiple localities that reflect dunite facilitated melt infiltration? To address these questions, here we undertake a geochemical field investigation of a dunite-harzburgite-lherzolite-plagioclase lherzolite (DHL-PL) sequence at the Trinity Ophiolite (Figure 1).

1.1 A Brief Description of Trinity Ophiolite

Trinity ophiolite occupies an approximately 50×75 km section of the Klamath Mountains, northern California. It is a lherzolite-subtype ophiolite (Boudier & Nicolas, 1985) with a relatively thin (~2 km), poorly developed crustal section mostly comprised of gabbroic plutons (e.g., Lindsley-Griffin, 1977). Aside from small volumes of pyroxenitic and gabbroic dikes, the ultramafic section is dunite (15-20%), harzburgite

and lherzolite (60-70%), and plagioclase bearing harzburgite and lherzolite (~15%) (Quick, 1981a, 1981b). Characteristic of the dunites in the plagioclase lherzolite bearing sections are dunite-harzburgite-lherzolite-plagioclase lherzolite sequences which surround the tabular dunites (e.g., Figure 1).

Trinity is thought to have formed at a slow spreading center (e.g., Boudier *et al.*, 1989) proximal to a subduction zone (e.g., Quick, 1981a, Metcalf *et al.*, 2000). These arguments are based on observation of negative high field strength element (HFSE) anomalies and large ion lithophile element (LILE) enrichment in Trinity gabbros and basaltic dikes, and the facts that Trinity has a relatively thin crustal section and poorly developed sheeted dike complex as well as subduction-related metavolcanics and trench related sedimentary basins (Quick, 1981a; Wallin & Metcalf, 1998). Sm-Nd dating gives ages of 402 and 472 Ma for gabbros and plagioclase lherzolite respectively (Gruau *et al.*, 1995; Jacobsen *et al.*, 1984), while U/Pb dating of zircons in Trinity gabbros gives ages of 404 to 431 Ma (Wallin & Metcalf, 1998).

1.2 Previous Research on Trinity Ophiolite

Trinity is an important field area in the historical and ongoing study of ophiolites and melt migration theory. Quick (1981a) investigated the formation mechanisms of tabular dunites at Trinity using major element compositional profiles across a DHL-PL sequence and was among the first to propose a reactive origin for dunite formation. While he observed significant concentration gradients in selected elements, particularly TiO₂ in clinopyroxene, Quick's interpretation was based on observations that the dunite was plastically deformed and therefore had to form at high temperatures, that it contained

clinopyroxene oikocrysts, plagioclase, and Cr-spinel which are common basaltic cumulates, that Trinity dunites resemble tabular dunites from other ophiolites thought to have an igneous origin, and that Trinity clinopyroxene oikocrysts have $\delta^{18}\text{O}$ of 6.0 ± 0.2 , consistent with a mantle origin. Quick (1981b) argued that the formation of dunites by basalt-peridotite reaction suggests basalts are inherently picritic at low pressure, and that basaltic melts in equilibrium with dunite would retain their high-pressure multiple saturation depths.

Informed by thermodynamic models, experimental work, field observations, and spatial-geochemical data from Trinity, Kelemen *et al.* (1992) argued that massif and xenolith peridotites have an overabundance of orthopyroxene and that their mineralogies are generally controlled by melt-rock reaction rather than partial melting. The first rare earth element (REE) concentration profiles (Nd) from Trinity were published for three transects, two extending from tabular dunites and one extending from a pyroxenite into host rock. All three transects show increasing clinopyroxene Nd concentrations away from the dunite or pyroxenite into host peridotite with chondrite normalized values ≤ 1 in the dikes and values of 5-12 in host peridotite. Kelemen *et al.* (1992) suggested that melt fluxing out of Trinity dunites into host rock is responsible for generation of the lithological sequences and major and trace element signatures.

Lundstrom *et al.* (2005) analyzed three transects across dunite-harzburgite contacts at Trinity, including an ~20 m long DHL-PL sequence at Vicki's Bluff (7 samples from TP90-20, originally sampled by Kelemen *et al.*, 1992) for Li, B, Nd, Sr, and Li isotopic abundances. Aside from a spike at a late-stage pyroxenite vein within the dunite, near the dunite-harzburgite contact, Lundstrom *et al.* (2000) observed lower $\delta^7\text{Li}$,

Li, and B concentrations (~2.5‰, 1, and 0.11 ppm, respectively) in dunite and harzburgite which increase to more elevated values in lherzolite (~12‰, 2.4, and 0.4ppm), consistent with the observations of Kelemen *et al.* (1992). Lundstrom *et al.* (2005) proposed a diffusive infiltration model for generation of the observed chemical gradients. In their model, alkali elements in melt fluxing through the dunite diffusively interact with surrounding host peridotite, causing partial melting within a few meters of the dunite and concomitant melt suction into the dunite. By including melt suction, the model successfully reproduced observed Li isotopic gradients. However, Li is an extremely fast diffusing element and no effort was made to correct for subsolidus reequilibration, which was shown to strongly affect slower diffusing Ca in another study of the same traverse (Morgan *et al.*, 2008).

Morgan *et al.* (2008) conducted high-resolution sampling across the ~20 m wide DHL-PL sequence at Vicki's Bluff (Figure 1) and reported major element abundances in clinopyroxene, orthopyroxene, olivine, and spinel in 44 peridotite samples. They observed concentration gradients in TiO₂, Al₂O₃, Cr₂O₃, and Na₂O in clinopyroxene along the DHL-PL sequence (e.g., Figure 5a, also see Figure 14 in Morgan *et al.*, 2008), with more elevated concentrations in the plagioclase lherzolite and nearly constant, lower concentrations within the dunite, harzburgite, and lherzolite. A gradient in Ni in olivine offset toward the dunite relative to other major elements was also observed (Figure 4b). Ni in olivine and Ti in clinopyroxene gradients were shown to be statistically significant after correction for subsolidus reequilibration. Informed by the results of a series of simple numerical models that investigated concentration gradients generated by melt flow (1) into dunite from host harzburgite, (2) into host harzburgite from dunite, or (3) with no

lateral advection into dunite or host harzburgite, Morgan *et al.* (2008) argued the gradient could only be produced by the migration of a plagioclase and pyroxene undersaturated melt from dunite into host plagioclase lherzolite.

Motivated by the DHL-PL sequence at the Trinity ophiolite, Morgan & Liang (2005) conducted lherzolite reactive dissolution experiments using basaltic andesite and alkali basalt at 1 GPa. They showed that reaction of lherzolite with basaltic andesite produces a dunite-free harzburgite-lherzolite sequence and that reaction of lherzolite with alkali basalt produces a dunite-harzburgite-lherzolite sequence. Compositions of olivine and melt vary gradually across the experimental charges in contrast to the lithological boundaries which are sharp. Morgan & Liang (2005) proposed that the DHL-PL sequence at Trinity could be produced by reaction of olivine saturated melt with plagioclase lherzolite. The degree of undersaturation of the dissolving phases in reacting melt is greatest for plagioclase, followed by clinopyroxene and then orthopyroxene.

In order to better understand melt flow and melt-rock reaction processes at Trinity, we examined spatial variations of rare earth element (REE), high field strength element (HFSE), alkali element, and transition metal abundances in clinopyroxene and orthopyroxene in selected samples from the DHL-PL sequence studied by Morgan *et al.* (2008). Because of their differing diffusivities and partition coefficients many of these trace elements are more sensitive to melt migration and melt-rock reaction processes than major elements and thus enable us to better understand the origins of the DHL-PL sequence.

2. Methods

Clinopyroxene and orthopyroxene in samples distributed across the transect were analyzed for Na, K, Sc, V, Cr, Co, Ni, Sr, REE, Y, Ti, Zr, Nb, Hf, Ta, and Pb. Clinopyroxene was analyzed in 22 samples and orthopyroxene was analyzed in 13 samples. A complimentary major element dataset is presented in Morgan *et al.*, 2008. To measure trace element abundances in minerals using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), we analyzed thick thin sections (approximately 60 μm) prepared from 1" drill cores used in the study of Morgan *et al.* (2008). Drill core spacing is at the cm scale within the dunite and near the dunite-harzburgite contact but widens away from the contact to approximately one sample every meter in the plagioclase lherzolite. Only moderately serpentinized samples were analyzed. Clinopyroxene porphyroclasts are present in the lherzolite and plagioclase lherzolite, but in the dunite (and to a lesser extent, in the harzburgite) smaller clinopyroxene grains ($\sim 100\ \mu\text{m}$ in diameter, e.g., Figure 2a) are present. These grains were difficult to identify optically so each thin section was mapped using the Cameca SX-100 microprobe at Brown University. Trace element analyses were conducted on a Thermo X-series quadrupole ICP-MS coupled with a New Wave 213 nm laser ablation system at the Plasma Mass Spectrometry Laboratory, Graduate School of Oceanography, University of Rhode Island using methods similar to those described in Kelley *et al.* (2003). Natural and synthetic glass standards (ATHO, BCR, BIR, BHVO, GOR 132, KL2, ML3B, St. Helens Basalt, T1) were measured at the beginning and end of each analytical session. Mg was used as the calibration analyte for most clinopyroxene and orthopyroxene analyses, however some clinopyroxene were processed using Ca. A range of spot sizes (40 to 120 μm) were used depending on grain size and anticipated trace element

abundance in the mineral. However, the majority of the analyses were conducted with 40 or 60 μ m spots. Most pyroxenes within and near the dunite are only large enough for a single analysis, however, they reach diameters of several millimeters in the plagioclase lherzolite (e.g., Figure 2f) and for those larger grains care was taken to place the laser spot as close as possible to the rim and at a range of distances from the grain rim. Because of the inherently three-dimensional nature of laser ablation analysis, serpentinized regions and/or phases other than those intended for analysis were occasionally intersected by the laser beam beneath the mineral surface exposed on the thin section. These compositional anomalies are clearly visible as sudden spikes or dips in trace element signal and all affected data was excluded during data processing.

3. Results

3.1 Sample Description and Petrography

Here we briefly discuss the physical characteristics and textures of pyroxene as a function of distance from the dunite-harzburgite contact (additional sample description is provided in Morgan, 2006, and the Supplementary Material of Morgan *et al.*, 2008). Backscatter electron micrographs of representative pyroxene are presented in Figure 2. Clinopyroxene are extremely isolated in the interior of the dunite but become less scarce near the boundary with harzburgite, reaching a maximum of several grains per thin section at the lithological boundary. Dunite clinopyroxene are barely large enough to analyze by LA-ICP-MS given their trace element concentrations (i.e., $\sim 100\ \mu$ m in diameter, Figure 2a). Clinopyroxene in the harzburgite are considerably more abundant than in the dunite (1-5 volume %) and have larger grain sizes ranging from 100 μ m to

1mm in diameter (Figures 2b-2d). The maximum clinopyroxene grain size increases across the transect; grain diameters in plagioclase lherzolite can be 2mm or more (Figures 2e, 2f). These larger grains display orthopyroxene exsolution lamellae which are often serpentinized (e.g., Figures 2e, 2f). Across the transect, large clinopyroxene grains display lobate olivine embayments which may be indicative of melt rock reaction (e.g., Figures 2d, 2f). Smaller clinopyroxene have tortuous grain boundaries and tend to be interstitial to larger olivine and orthopyroxene grains (e.g., Figures 2a, 2b, 2c).

In general, orthopyroxene have larger grain sizes than clinopyroxene; within the harzburgite they are commonly 1-2 mm in diameter (Figures 2b-2d). Like clinopyroxene they increase in size across the transect reaching diameters of up to 4 mm in the plagioclase lherzolite. They usually have unaltered clinopyroxene exsolution lamellae (e.g., Figures 2b-2d). Orthopyroxenes are more serpentinized than clinopyroxene, especially at their rims which appear “scooped out” in the backscatter electron micrographs. In contrast to clinopyroxene, orthopyroxenes generally have coherent gradually curving or straight grain boundaries (Figures 2b-d), though lobate olivine embayments can occasionally be observed.

3.2 Trace Element Concentrations

Sample averaged trace element abundances in clinopyroxene and orthopyroxene are presented in Tables 1 and 2, and pyroxene rim and core analyses are presented in Supplementary Table S1. Primitive mantle normalized concentrations of REE, Y, HFSE, and selected transition metals are shown in Figure 3a where each line represents an average of multiple (core and rim) spot analyses for a thin section. In general the patterns

are smooth and standard deviations are small for clinopyroxene indicating good reproducibility (larger uncertainties for orthopyroxene are omitted from the figure for clarity but presented in Table 2 and Figure 3b). Samples are distinguished by their distance from the dunite-harzburgite contact and fall into one of two groups, more depleted samples < 9 m from the dunite harzburgite contact (red and black lines), and more enriched samples > 9 m from the dunite harzburgite contact (blue and magenta lines). Clinopyroxene in samples > 9 m from the dunite-harzburgite contact have pronounced negative Sr and notable Eu anomalies possibly owing to the higher partition coefficients for those elements in plagioclase than in pyroxene (e.g., Blundy & Wood, 1994; Bindeman *et al.*, 1998; Wood & Blundy, 2003). Negative high field strength element anomalies are present in all clinopyroxene, but large positive HFSE anomalies are present in orthopyroxene. Calculated bulk rock compositions presented in Supplementary Figure S1 (for samples Z26 and Z24, both harzburgites) show that the bulk rocks do not exhibit HFSE anomalies.

Trace element patterns can inform us about the position of the boundary between lherzolite and plagioclase lherzolite which is difficult to distinguish in the field and in thin section because plagioclase in our samples is completely altered. Based on the position of the Sr and Eu anomalies, here we place the lherzolite-plagioclase lherzolite boundary 9 m from the dunite-harzburgite contact. [The boundary was assumed to be ~ 6 m from the contact in Morgan *et al.* (2008)].

Figure 3b shows chondrite normalized REE in pyroxene. All clinopyroxene have light rare earth element (LREE) depletion, but samples in the plagioclase lherzolite have steeper LREE anomalies. Orthopyroxene have REE patterns with fairly constant slopes,

but LREE are somewhat scattered owing to larger analytical uncertainty for these elements which have low abundances. Figure 3c compares our analytical results to previous analyses of Trinity samples collected at or near the traverse discussed in this study. The light blue field is unpublished plagioclase lherzolite data (Lo Cascio, 2008), the green field is data from Kelemen *et al.* (1992), and the brown field is from Morgan *et al.* (2008). Collectively, the data show lower REE concentrations in Trinity dunite, harzburgite, and lherzolite, and higher concentrations in lherzolite and plagioclase lherzolite.

3.3 Spatial-Geochemical Variations

Minor elements, Cr_2O_3 , Al_2O_3 , REE, and HFSE in clinopyroxene are plotted as a function of distance from the dunite-harzburgite contact in Figure 4. Additional trace elements (Sr, Sc, V, Co, Zn) are shown in Supplementary Figure S2. Cr_2O_3 and Al_2O_3 in clinopyroxene are positively correlated with each other and increase from constant values within the dunite and harzburgite-lherzolite to more elevated values in the far-field plagioclase lherzolite (Figure 4a). Grain scale concentration gradients (indicated by the arrow) are present in the far-field samples which have enriched cores that trend toward compositions similar to clinopyroxene in the dunite, harzburgite, and lherzolite at the rims (also see Figure 5a). NiO in olivine (Figure 4b) increases from lower to higher values between 2.2 and 3.6 m from the dunite-harzburgite contact. In contrast, incompatible trace elements analyzed by LA-ICP-MS (REE, Y, Zr, Ti, Figures 4c and 4d) monotonically increase between 8.5 and 9.5 m from the dunite-harzburgite contact. The same is true of V (Supplementary Figure S2c). Importantly, there is no spatial offset

between light and heavy REE concentrations along the transect (Figure 4c), i.e. La and Lu all increase from low to high values the same distance from the dunite-harzburgite contact, similar to HFSE (Figure 4d).

Core-to-rim minor element concentration variations in far-field plagioclase lherzolite samples are shown in Figure 5a (also see Figure 14 in Morgan *et al.*, 2008). In general, plagioclase lherzolite clinopyroxene have lower TiO_2 , Al_2O_3 , Cr_2O_3 , and Na_2O rim concentrations than core concentrations. These grain scale concentration gradients mimic the meter-scale gradients observed by Morgan *et al.* (2008) in that plagioclase lherzolite clinopyroxene rims trend toward compositions of the harzburgitic pyroxene. Clinopyroxene neoblasts in the plagioclase lherzolite have also minor element concentrations like harzburgite clinopyroxene (Lo Cascio and Liang, unpublished data). Consistent with grain scale minor element variations, trace elements in plagioclase lherzolite samples vary from core to rim, and grain rims are more depleted than cores (Figure 5b). The scale of the core to rim variations is on the order of tens of μm which is difficult to resolve with the spot sizes utilized in this study. However, mean trace element concentrations in clinopyroxene rims are >5% lower than cores, and orthopyroxene in far field samples show similar gradients.

4. Discussion

4.1 Origin of the Plagioclase Lherzolite

Plagioclase bearing peridotite is commonly observed in ophiolites (e.g., Menzies & Allen, 1974; Quick, 1981a; Nicolas & Dupuy, 1984; Takazawa *et al.*, 1992; Borghini *et al.*, 2007; Piccardo *et al.*, 2007; Rampone *et al.*, 2008; Liu *et al.*, 2010) and dredged

abyssal peridotites from slow spreading centers and fracture zones (e.g., Dick, 1989; Elthon, 1992; Tartarotti *et al.*, 2002; Brunelli *et al.*, 2006; Warren *et al.*, 2009; Brunelli & Seyler, 2010). Plagioclase peridotites from these tectonic settings have refractory major element compositions (e.g., high Mg# and NiO olivine), elevated incompatible element concentrations, and textures consistent with melt impregnation processes. The formation of ophiolitic plagioclase peridotite was originally ascribed to in-situ crystallization of plagioclase in undepleted peridotites that experienced limited partial melting (e.g., Menzies & Allen, 1974; Spray, 1982). More recently, it has been attributed to infiltration of depleted partial melting residues by basaltic melts which crystallize plagioclase and trace element enriched pyroxene (e.g., Nicolas & Dupuy, 1984; Dick, 1989; Elthon, 1992; Niu & Hékinian, 1997; Tartarotti *et al.*, 2002; Borghini *et al.*, 2007; Piccardo *et al.*, 2007; Rampone *et al.*, 2008; Müntener *et al.*, 2010; Saper & Liang, 2014).

REE in Trinity plagioclase lherzolite are compared to plagioclase-free abyssal peridotites in Figure 6a. REE concentrations in Trinity clinopyroxene are a factor of two greater than enriched plagioclase-free abyssal peridotites. The evolution of Trinity in a supra-subduction environment where high degrees of melting are expected is inconsistent with primary REE-enriched plagioclase lherzolite and Trinity plagioclase lherzolite must have formed by basaltic melt impregnation.

Trinity REE concentrations and LREE depletion are very similar to ophiolitic plagioclase peridotites from the literature (Figure 6b). Their strong LREE depletion can be attributed to relatively high plagioclase partition coefficients for LREE (e.g., Bindeman *et al.*, 1998), and the degree of LREE depletion in the impregnating melts that formed the plagioclase peridotites. Clinopyroxene from abyssal plagioclase peridotites

are compared to Trinity in Figure 6c. The data is limited, but Trinity plagioclase lherzolites show steep LREE depletion not exhibited by some of the abyssal peridotites. Variable LREE enrichment and large core-to-rim trace element concentration gradients in the literature data (e.g., Warren *et al.*, 2009; Brunelli & Seyler, 2010) suggest that the abyssal peridotites experienced melt infiltration followed by cooling at rates above which plagioclase, orthopyroxene, and clinopyroxene could establish chemical equilibrium. In contrast, ophiolitic plagioclase peridotites (Figure 6b) show compositional homogeneity (at a given locality) suggesting melt infiltration was followed by reequilibration over longer periods of time. This observation is consistent with cooling rate systematics observed by Dygert and Liang (2014) for abyssal peridotites and ophiolites.

Trinity plagioclase lherzolite clinopyroxene (and clinopyroxene in ophiolitic plagioclase peridotites in general) are more middle and heavy-REE enriched than abyssal plagioclase peridotites (Figures 6c, 6b). A possible explanation is differences in the extent of depletion in plagioclase peridotite forming impregnating melts, with ophiolitic melts being less depleted than abyssal melts. This could be attributed to the melting of a more enriched mantle source in ophiolitic tectonic environments, or differences in degree of melting between abyssal and ophiolitic tectonic settings.

Because plagioclase lherzolites are formed by melt infiltration and melt-rock reaction, melts in equilibrium with plagioclase lherzolite clinopyroxene are not representative of the infiltrating melt. However, trace elements in plagioclase lherzolite pyroxene are useful for constraining the infiltrating melt composition. Orthopyroxene have strong positive HFSE anomalies complementary to negative anomalies in clinopyroxene (compare red and black lines, Figure 3a). The bulk composition of the

plagioclase lherzolite is unknown, but Trinity harzburgites show HFSE anomalies similar in magnitude to the plagioclase lherzolites (Figure 3a), and have bulk rock compositions lacking HFSE anomalies (Supplementary Figure S1) suggesting the source of the infiltrating melt is not depleted in HFSE. The steep LREE depletion in plagioclase lherzolite clinopyroxene also suggests the infiltrating melt was highly LREE depleted.

Taking these factors into consideration, we modeled formation of the plagioclase lherzolite by assuming mixing of an instantaneous fractional melt of a depleted MORB mantle (DMM) source (Workman & Hart, 2005, degree of melting = 7%) and a depleted harzburgite. Major element compositions of the infiltrating melt were calculated using alphaMELTS (Smith & Asimow, 2005) along an adiabat with a potential temperature of 1300°C. Major and trace element data for Trinity refractory harzburgites is unavailable. For the purpose of illustration we used a depleted melting residue (whose composition was also calculated using alphaMELTS) assuming fractional melting of a DMM source with a potential temperature of 1300°C (degree of melting = 19%). This “sample” was carefully selected for its low bulk Al_2O_3 and CaO, which are important for forming a mineralogy and composition consistent with plagioclase lherzolites from Trinity (Table 3).

Models with three different melt:rock ratios are presented in Figure 7 (dashed black lines, 5% melt and 95% harzburgite, 7.5% melt and 92.5% harzburgite, 10% melt and 90% harzburgite), two additional models (20% melt and 80% harzburgite, 30% melt and 70% harzburgite) are presented in Table 3. The success of the models was judged on the consistency of bulk rock major element compositions with published values for Trinity plagioclase lherzolites, and the consistency of trace element concentrations and

patterns with those we measured in Trinity clinopyroxene. After calculating the bulk composition of the melt-peridotite mixture, alphaMELTS (Asimow & Ghiorso, 1998) was used to estimate the mineralogy of the melt-rock mixture at 1000°C and 0.3 GPa. Trace element abundances in olivine, orthopyroxene, clinopyroxene, and feldspar were calculated using the bulk trace element abundance and the mineral proportions from the alphaMELTS output. Specifics of the model inputs and results are presented in Table 3.

Modeled clinopyroxene REE are highly consistent with measured plagioclase lherzolite clinopyroxene REE (compare red and black dashed lines, Figure 7). The 7.5% melt model does the best job matching the heavy REE concentrations and the LREE depletion. Major element bulk compositions of the model results approximate Trinity plagioclase lherzolite well, especially in their CaO and Al₂O₃ abundances (Table 3). However, the model results are less orthopyroxene normative than Trinity plagioclase lherzolite reported by Quick (1981b). This may suggest the protolith of Trinity plagioclase lherzolite had a high initial orthopyroxene content, consistent with arguments made by Kelemen *et al.* (1992).

The melt:rock ratios we use are lower than those used in several previous studies that modeled plagioclase lherzolite formation, which range from 10% to greater than 30% (e.g., Dick, 1989; Piccardo *et al.*, 2007; Müntener *et al.*, 2010; Dick *et al.*, 2013). These studies focus on the trace or minor element abundances of the plagioclase lherzolite, and assume the mineralogy of the peridotite-melt mixture varies as a function of the plagioclase and pyroxene content of the infiltrating melt based on normative chemistry, petrography, or the best fit to the trace element data. However, the modal abundance of the resulting plagioclase lherzolites was not carefully considered. Saper and Liang (2014)

demonstrated that high melt:rock ratios lead to the formation of wehrlites as opposed to plagioclase lherzolites because high proportions of infiltrating basalt lead to crystallization of abundant pyroxene. The model with 30% melt and 70% harzburgite results in a peridotite bordering on websterite rather than plagioclase lherzolite. In many cases melt:rock ratios $\lesssim 10\%$ may be most appropriate for modeling the formation of plagioclase peridotites (e.g., Elthon, 1992; Rampone *et al.*, 2008, Saper & Liang, 2014).

The mineralogy of the melt-peridotite mixture has important implications for trace element distribution within the plagioclase lherzolite. Higher melt:rock ratios increase the REE content of the bulk rock, but they also increase the pyroxene abundance. Our models show that crystallization of additional clinopyroxene buffers the REE concentrations in clinopyroxene so that they become less sensitive to the melt:rock ratio at higher melt fractions (Table 3). To achieve physically meaningful results, future efforts to model plagioclase lherzolite formation should take major element compositions and mineralogy into consideration.

4.2 Formation of the Distinct Lithologies and Trace Element Patterns

How can the variation in rock type and trace element composition expressed at Trinity be explained? Partial melting that varies in extent across the transect is an obvious mechanism to consider, but can be rejected on physical grounds. The thermal gradient necessary to form dunite by melting and still preserve residual plagioclase lherzolite is unsustainable at geologic timescales. Lundstrom *et al.* (2005) proposed that diffusive interaction of alkali elements and plagioclase lherzolite adjacent to the dunite lowers the solidus temperature of mantle around the dunite leading to a gradient in degree of

melting. However, melting the plagioclase lherzolite would cause increasingly large degrees of LREE depletion not exhibited by clinopyroxene in the dunite, harzburgite, and lherzolite (compare red and blue lines, Figure 3c). We propose the lithological sequence and trace element patterns originate from a two-stage melt-rock reaction process. As discussed in the preceding section, in the first stage, extensive infiltration of mantle peridotite by basaltic melt followed by cooling resulted in the formation of plagioclase lherzolite. In the second stage, pyroxene and plagioclase undersaturated melt from a distinct mantle source flowed from a tabular dunite into the plagioclase lherzolite, forming the DHL-PL sequence (Morgan *et al.*, 2008). Stage two requires the presence of a dunite channel which may have formed during or prior to the second melt infiltration event. Here, we focus on melt infiltration rather than speculating on the timing of dunite channel formation. We note that to establish grain-scale porous flow, the plagioclase lherzolite must have been partially molten. First we consider what the trace element compositions of pyroxene can tell us about the infiltrating melt.

4.3 Characteristics and Origin of the Infiltrating Melt

Clinopyroxene in Trinity dunite, harzburgite, and lherzolite are compared to abyssal peridotites in Figure 8a, and have similar LREE depletion and REE concentrations. Clinopyroxene in the dunite (green lines) have slightly lower concentrations than those in the harzburgite and lherzolite (blue lines), which may be attributable to subsolidus REE redistribution between orthopyroxene and clinopyroxene (see Appendix A). However, we note the REE-in-two-pyroxene thermometer of Liang *et al.* (2013) gives near solidus temperatures for samples in the harzburgite, lherzolite, and

plagioclase lherzolite (Supplementary Figure S5; Appendix B), suggesting subsolidus redistribution between pyroxene was minimal. Indeed, dunite, harzburgite, and lherzolite hosted clinopyroxene have similar compositions (compare green and blue lines, Figure 8). Trinity clinopyroxene are compared to those in peridotites from supra-subduction environments in Figure 8b. Samples from the Polar Urals (gray field) are very similar to Trinity. These samples were interpreted to be residues of partial melting that experienced a late-stage infiltration of high-Ca boninitic melts (Batanova *et al.*, 2011). Samples from supra-subduction zone tectonic settings that experienced high degrees of melting and more limited melt infiltration (Hellenic ophiolites, Bizimis *et al.*, 2000) have much lower REE concentrations than Trinity (blue field, Figure 8b).

In Figure 9 we present calculated equilibrium melt compositions for clinopyroxene in the dunite, harzburgite, and lherzolite. Primitive normal mid-ocean ridge basalt (N-MORB, $Mg\# > 60$, chondrite normalized $La/Nd < 0.7$) has trace element concentrations slightly higher than DHL equilibrium melts but shows less LREE depletion and a shallower mid-heavy REE slope (Figure 9a). Equilibrium melt trace element concentrations are compared to rocks from the crustal section of Trinity in Figure 9b. Basalts and dikes have REE abundances comparable to melts in equilibrium with DHL samples. Four mafic dikes from the crustal section of Trinity (Metcalf *et al.*, 2000) have REE abundances and LREE depletion similar to the DHL equilibrium melts (orange lines, Figure 9c). These mafic dikes (samples 978-9, 978-11, P987-47, 986-5) cut intrusive crustal complexes at three different localities (Bonanza King, Craggy Peak, and Porcupine Lake) and according Metcalf *et al.* (2000), have boninitic major element compositions. Some are amphibole bearing, and all have elevated LILE/HFSE ratios.

Metcalf *et al.* (2000) argued the dikes have major and trace element compositions suggesting a depleted MORB-type mantle source enriched by subduction-related fluids. Because the dikes cross-cut intrusive crustal rocks they must have formed late in the evolutionary history of the ophiolite, perhaps contemporaneous to crystallization of the last dunite-hosted melts in the mantle section. It is tempting to speculate that these dikes are related to melts that crystallized clinopyroxene in the dunite, harzburgite, and lherzolite, though such a connection cannot be confirmed by trace element patterns alone. Indeed, the similarity between olivine-hosted melt inclusions from the Mid-Atlantic Ridge and dunite-harzburgite-lherzolite clinopyroxene equilibrium melts (Figure 9a) suggests the trace element patterns are common to ordinary near-fractional melts of the MORB mantle. These trace element patterns are also very similar to boninite-derived dunite-hosted clinopyroxene in the Voykar ophiolite (gray field, Figure 8b). In summary, the trace element patterns in Figures 8 and 9 place little constraint on the infiltrating melt composition, but suggest a possible connection to dikes in the crustal section of Trinity. If there is such a genetic relationship, the similarity of dikes to DHL equilibrium melts suggests the dikes escaped significant crystal fractionation and melt-rock reaction on their way to the crust.

Could the infiltrating melt which formed the plagioclase lherzolite and the DHL-forming melt have originated from a common evolving source; e.g., an initially fertile region of the mantle wedge that became depleted owing to extensive hydrous melting? Figure 9c compares the melt from our plagioclase lherzolite formation model (purple line) to Trinity dunite-harzburgite-lherzolite equilibrium melts (green and blue lines). Because the plagioclase lherzolite infiltrating melt is more LREE depleted than the

dunite-harzburgite-lherzolite equilibrium melt, no batch or fractional melt of a source that generated the plagioclase lherzolite infiltrating melt is capable of producing LREE concentrations consistent with dunite-harzburgite-lherzolite equilibrium melts at higher extents of melting. The slope of the plagioclase lherzolite infiltrating melt trace element pattern is model dependent but it should be a good approximation. Thus, the two melts probably originated from unique sources.

The isotopic composition of Trinity plagioclase lherzolites (initial $\epsilon_{\text{Nd}}=+9.6$ to $+10.4$; Jacobsen *et al.*, 1984) differs from most Trinity crustal rocks (initial ϵ_{Nd} of 0 to $+7.5$, Jacobsen *et al.*, 1984; Brouxel & Lapierre, 1988; Gruau *et al.*, 1995). If the melt that produced Trinity dunite-harzburgite-lherzolite clinopyroxene is related to these crustal rocks the differing isotopic compositions suggest distinct mantle sources for the plagioclase lherzolite and dunite-harzburgite-lherzolite forming melts. Gruau *et al.* (1995) made a similar argument to explain a large isotopic compositional gradient they observed in Trinity lherzolite (7 ϵ_{Nd} units across 20 m of peridotite around a gabbroic dike). They argued that the most plausible way to produce such a large isotopic variation over such a short distance is by reaction of basaltic melt (low ϵ_{Nd}) with preexisting plagioclase lherzolite ($\epsilon_{\text{Nd}} \approx +10$).

A particularly effective way to deliver melts from distinct sources to nominally stationary regions of the mantle may be nonlinear porosity waves which are predicted to develop during melt migration beneath spreading centers owing to feedbacks among dissolution, compaction and upwelling (Liang *et al.*, 2011; Hesse *et al.*, 2011). In the numerical simulations in which they were observed, these compaction-dissolution waves develop a significant component of lateral melt transport and rapidly migrate across the

simulation domain. Thus, melts sourced from disparate regions of the mantle may percolate through a single parcel of mantle near the surface. However, the age relationships of Trinity crustal rocks and plagioclase lherzolites suggest that invoking such melt transport mechanisms may not be necessary, as Trinity gabbros are tens of millions of years younger than plagioclase lherzolite (see Introduction). In the dynamic environment of the mantle proximal to a subduction zone over that length of time, the delivery of a diverse array of components (e.g., sediments, mantle heterogeneities) to the melt source region may be expected.

4.4 Origin of the Dunite-Harzburgite-Lherzolite Sequence

The formation of dunite-harzburgite and dunite-harzburgite-lherzolite sequences in experiments that juxtapose basalt against partially molten harzburgites or lherzolites is well established (e.g., Daines & Kohlstedt, 1994; Morgan & Liang, 2003, 2005; Van den Bleeken *et al.*, 2010; Wang *et al.*, 2013). In those studies, the lithological sequences formed by diffusion accommodated dissolution of pyroxene into pyroxene undersaturated basalt. Morgan & Liang (2005) and Wang *et al.* (2013) also showed that harzburgite-lherzolite sequences form by juxtaposition of partially molten lherzolites against basaltic andesites, i.e., melts that are less orthopyroxene undersaturated. These results suggest that the lithology and thickness of the distinct mineralogical layers depends on the initial undersaturation of reacting phases in the melt, and the composition of the hybridized melt after melt-rock reaction occurs. Harzburgites produced in the aforementioned melt-rock reaction studies are clinopyroxene free. Tursack & Liang (2011) formed clinopyroxene-bearing dunites and harzburgites in step cooled melt-rock reaction experiments by

crystallizing clinopyroxene from small pools of trapped melts in the newly formed peridotites, which is probably how Trinity dunites and harzburgites became clinopyroxene bearing.

The thick chemical boundary layers at Trinity of ~3.5 m for NiO in olivine and ~9 m for REE, HFSE, Sr, and V, strongly suggest that infiltrating melt advected into plagioclase lherzolite (Figure 4, Supplementary Figure S2). Consideration of the mineralogy, grain size, and compositional variations across the DHL-PL sequence can inform us about the nature of melt infiltration and melt rock reaction. In addition to the boundary layer thicknesses, important geochemical information to consider includes (1) the sharp transition from low to high trace element abundances 9 m from the dunite, and (2) grain scale composition gradients that mimic the outcrop scale concentration gradients (Figure 5). Important textural information to consider includes (1) residual textures and large grain size of orthopyroxene across the transect (e.g., Figures 2c and 2d), (2) clinopyroxene that show melt-rock reaction textures in the harzburgite and lherzolite (e.g., Figures 2c and 2d), and (3) the increase in clinopyroxene grain size across the transect (Figure 2). Based on this information, we can envision the following mechanism for forming the DHL-PL sequence.

A plagioclase and pyroxene undersaturated melt migrated from dunite into a partially molten plagioclase lherzolite. As it left the dunite the melt was strongly plagioclase and clinopyroxene undersaturated and it thus dissolved those phases. The melt quickly became orthopyroxene saturated, leaving residual orthopyroxene in place and forming a harzburgite. Orthopyroxene in the harzburgite diffusively reequilibrated with the infiltrating melt so that its major and trace element compositions reflected the

infiltrating melt composition. This is corroborated by calculated equilibrium melt compositions for harzburgite-lherzolite orthopyroxene, which are highly consistent with melts in equilibrium with harzburgite-lherzolite clinopyroxene (Supplementary Figure S3). Owing to clinopyroxene dissolution, the melt became clinopyroxene and plagioclase saturated some distance from the dunite-harzburgite contact where it ceased dissolving those phases. The abrupt geochemical front ca. 9 m from the dunite-harzburgite contact marks the position where residual plagioclase lherzolite clinopyroxene remain. The melt continued percolating past the clinopyroxene saturation front far into the plagioclase lherzolite. It retained the depleted minor and trace element signature of its source and diffusively interacted with plagioclase lherzolite pyroxene, generating the observed core-to-rim element variations in far field samples (Figure 5). Finally, as the peridotite cooled, trapped melts in the harzburgite precipitated new clinopyroxene (cf. Tursack & Liang, 2011) and possibly additional orthopyroxene reflecting the infiltrating melt composition.

4.5 Fractionation of Trace Elements Across the DHL-PL Sequence

The spatial offset between Ni and incompatible trace elements can be attributed to chromatographic fractionation that occurred as melt percolated from the dunite into plagioclase lherzolite (Morgan *et al.*, 2008). Under conditions of equilibrium exchange between liquid and solid, trace elements in a fluid advecting through a porous medium will be fractionated due to solid-liquid exchange when the porous solid and fluid are initially out of chemical equilibrium (e.g., Hofmann 1972; Navon & Stolper 1987; Bodinier *et al.*, 1990). A relatively large proportion of fluid must migrate through a given region of the matrix to equilibrate a compatible element compared to an incompatible

element, which will slow the transport of the compatible element relative to the incompatible element. Ni is very compatible in mantle peridotite owing to its high partition coefficient in olivine (~ 10) and pyroxene (~ 4), but the trace elements shown in Figure 4c and 4d are all incompatible. Thus, it is not surprising that as melt percolated from the dunite into plagioclase lherzolite Ni transport was chromatographically retarded relative to incompatible trace elements.

Chromatographic theory predicts that trace elements should be fractionated from one another owing to their differing compatibilities (e.g., La and Yb have bulk partition coefficients of ~ 0.01 and ~ 0.06 in a lherzolite). In the conceptual description of chromatographic fractionation we assumed instantaneous equilibration between melt and solid, which may not be an unreasonable assumption for fast diffusing major elements (e.g., Ni). In contrast, diffusion rates for REE in pyroxene are more than three orders of magnitude slower than Ni in olivine at mantle temperatures (e.g., Van Orman *et al.*, 2001; Petry *et al.*, 2004; Cherniak & Liang, 2007). Consequently, solid-liquid equilibration of REE may be limited by slow grain scale diffusion in pyroxene if the advection rate of the melt exceeds the rate of diffusion in pyroxene. Figure 5b demonstrates that this condition applies to plagioclase lherzolite hosted pyroxene at Trinity. Under such conditions, REE will advect through the plagioclase lherzolite close to the fluid velocity and no chromatographic fractionation will be observed. Clinopyroxene in Trinity harzburgite crystallized directly from the infiltrating melt during cooling and thus have trace element compositions which were unaffected by chromatographic fractionation.

5. Further Discussion

The concentration gradients we observe (low trace element abundances in dunite grading into higher concentrations in plagioclase lherzolite) are opposite those present in Oman (i.e., low REE concentrations in harzburgite grading into high REE concentrations in dunite, Figure 10) which were interpreted as facilitating near-fractional melt extraction (Kelemen *et al.*, 1995a). This study demonstrates that at least in the observable geologic history of Trinity, dunite channels were a source for local melt infiltration in addition to a melt extraction pathway.

Globally, the formation of DHL-PL lithological sequences has been attributed to variations in partial melting (e.g., Obata & Nagahara, 1987; Takahashi, 1992), melt-rock reaction and partial melting (e.g., Takazawa *et al.*, 1992; Takazawa *et al.*, 2000; Lundstrom *et al.*, 2005), or melt-rock reaction alone (e.g., Piccardo *et al.*, 2007; Morgan *et al.*, 2008; Garrido *et al.*, 2014). We argue that while the details of DHL-PL formation must differ depending on locality (e.g., the plagioclase lherzolite and infiltrating melt compositions), the relatively simple melt-rock reaction formation mechanism proposed here is a physically viable candidate for forming DHL-PL sequences in general. Thus, DHL-PL sequences may be diagnostic of infiltration by dunite hosted pyroxene and plagioclase undersaturated melts. DHL-PL sequences similar to Trinity have been observed at the Lanzo, Horoman and Ronda peridotites (e.g., Takazawa *et al.*, 1992; Piccardo *et al.*, 2007; Garrido *et al.*, 2014) suggesting that such infiltration events can be common. DHL-PL sequences are lithological expressions of dunite-sourced infiltration events. However, numerous geochemical studies of ophiolites and abyssal peridotites propose a multi-stage evolutionary process involving partial melting, refertilization,

and/or metasomatism (e.g., Elthon, 1992; Kelemen *et al.*, 1992; Ozawa & Shimizu, 1995; Niu, 2004; Brunelli *et al.*, 2006; Warren & Shimizu, 2010; Batanova *et al.*, 2011). These infiltration events may be facilitated by melt migration from dunite channels.

What physical mechanisms can cause melt migration from dunite channels into host rock? Morgan *et al.* (2008) pointed out this must occur at the front of a propagating dunite channel, which may develop due to corner flow beneath a spreading center. Any dunite channel network that formed in vertically upwelling mantle beneath a spreading center will ultimately be rotated so that it is sub-parallel to the direction of seafloor spreading. Indeed, field observations show that ophiolitic tabular dunites are often sub-parallel to the Moho (e.g., Kelemen *et al.*, 1995a, Suhr *et al.*, 2003). With a steady supply of melt from below, a dunite channel oriented at an acute angle to the crust will facilitate flow into overlying host rock (e.g., Suhr *et al.*, 2003). However, dunite-harzburgite-lherzolite plagioclase lherzolite sequences are generally symmetric about the dunite (Quick, 1981a; Takazawa *et al.*, 1992; Garrido *et al.*, 2014), suggesting this process may not be relevant to the genesis of most DHL-PL sequences.

Another mechanism capable of facilitating infiltration of host rock by dunite hosted melts relates to buoyancy. If a melt-bearing dunite channel had an impermeable cap, e.g., from in situ crystallization of dunite-hosted melt near the top of the channel, the underlying column of buoyant melt would apply a pressure in all directions proportional to its height and melt would flow laterally into the dunite channel host rock. This process was argued to be capable of nucleating asthenospheric hydrofractures (Nicolas, 1989) but the fracture strength of partially molten peridotite is unknown. Buoyancy-driven dunite channel host rock infiltration could be especially important at slow and ultra-slow

spreading centers which are thought to have a relatively deep conductive thermal regime (e.g., Shen & Forsyth, 1992; Cannat, 1996; Conley & Dunn, 2011).

Recent numerical simulations predict melt focusing along dunite channel-host rock contacts due to feedbacks among melt-rock reaction and compaction (Aharonov *et al.*, 1995; Spiegelman *et al.*, 2001; Spiegelman & Kelemen, 2003; Schiemenz *et al.*, 2010; Liang *et al.*, 2010; Liang *et al.*, 2011). The predictions appear to be corroborated by geochemical concentration gradients observed within some dunite channels, and the crystallization of dunite-channel hosted melt cumulates along some dunite channel walls (e.g., Suhr *et al.*, 2003; Maaløe, 2005; Morgan *et al.*, 2008; Dygert & Liang, 2010; Batanova *et al.*, 2011). Melt focusing within dunites may make buoyant infiltration of host rock easier by positioning melt along the dunite-host rock contact prior to infiltration. Alternatively, late stage compaction of focused melts along dunite channel walls may force the melts into dunite channel host rock. Buoyant infiltration and late stage compaction could operate in tandem.

If extensive infiltration of mantle peridotite by dunite hosted basaltic melts is a commonly occurring process, crystallization of significant volumes of melt directly in the mantle may be expected (e.g., Cannat, 1996; Conley & Dunn, 2011; Sleep & Warren, 2014) and estimates of trace element fluxes at subduction zones need reevaluation. Clinopyroxene in Trinity plagioclase lherzolite have REE abundances $> 20\times$ chondritic values, and DHL clinopyroxene are about $4\times$ chondritic, bracketing REE concentrations in global N-MORB. Although the bulk trace element composition of these peridotites is lower than basalts (ca. $0.5\text{--}2\times$ chondritic, Gruau *et al.*, 1995), oceanic lithosphere is composed of significantly more mantle than crust, especially at slow spreading centers.

The importance of such a process to global geochemical cycles depends on the volume of pervasive mantle infiltration and its frequency in general. Evaluating the impact of this process requires new, large-scale geochemical-spatial investigations of ophiolitic peridotites, and the reevaluation of evolutionary processes at previously studied ophiolites by those who know them well.

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8. Figure Captions

Figure 1. Photograph of the transect investigated in this study. Drill holes from sample collection are visible on the outcrop face. The dunite-harzburgite contact is marked in black. Plagioclase lherzolite is beyond the field of view of this image; the portion of the outcrop visible here is about 10 meters across. A late-stage pyroxenite vein sub-parallel to the dunite-harzburgite contact is marked in green.

Figure 2. Backscatter electron micrographs of representative pyroxene grains at different positions across the transect. (a) Clinopyroxene within the dunite, (b-d) clinopyroxene and orthopyroxene within the harzburgite, (e-f) clinopyroxene within the plagioclase lherzolite.

Figure 3. Trace element concentrations in trinity pyroxene distinguished by their distance from the dunite-harzburgite contact. (a) Primitive mantle normalized clinopyroxene (red and blue lines) and orthopyroxene (black and magenta lines). Error bars are omitted from orthopyroxene data to avoid cluttering the figure, see Table 2 for uncertainties. (b) Chondrite normalized rare earth elements in pyroxene. (c) Chondrite normalized rare earth elements in Trinity clinopyroxene from this study (red and blue lines) compared to ion probe analyses of Trinity clinopyroxene from [1] Lo Cascio, 2008; [2] Kelemen *et al.*, 1992, [3] Morgan *et al.*, 2008.

Figure 4. Concentration gradients plotted as a function of distance from the dunite harzburgite contact. (a) Cr₂O₃ and Al₂O₃ in clinopyroxene (Morgan *et al.*, 2008) a few additional data points are included from LA-ICP-MS analyses, (b) NiO in olivine (Morgan *et al.*, 2008), (c) Yb, Dy, and Ce in clinopyroxene (this study), (d) Ti and Zr in clinopyroxene (this study).

Figure 5. Core-rim minor element concentration gradients in a representative clinopyroxene grain in plagioclase lherzolite (a) (sample TP90_22_8_2_T2, Lo Cascio, 2008), and core-rim gradients in trace elements measured by LA-ICP-MS plotted as a function of distance from the dunite-harzburgite contact (b). The coherence of these trends disappears in samples closer to the dunite, presumably because much lower trace element concentrations near the dunite lessen the quality of the data.

Figure 6. Chondrite normalized REE and Y abundances in Trinity plagioclase lherzolite clinopyroxene compared to spinel bearing abyssal peridotites (a), plagioclase bearing ophiolitic peridotites (b), and (c) abyssal plagioclase peridotites. References are as follows: [1] Barth *et al.*, 2003; [2] Guarnieri *et al.*, 2012; [3] Rampone *et al.*, 2008; [4] Liu *et al.*, 2010; [5] Warren *et al.*, 2009; [6] Brunelli & Seyler, 2010; [7] Brunelli *et al.*, 2006.

Figure 7. Results and inputs of the plagioclase lherzolite formation model. Red and blue lines are Trinity clinopyroxene. Orange line is a harzburgitic melting residue of a DMM source, purple line is a 7% instantaneous fractional melt of the depleted MORB mantle

(Workman & Hart, 2005), and black dashed lines are clinopyroxene compositions calculated for mixtures of different proportions of harzburgite and melt.

Figure 8. Chondrite normalized REE and Y abundances in Trinity dunite harzburgite and lherzolite clinopyroxene compared to abyssal peridotites (a) and peridotites from supra subduction zone tectonic settings (b). References are as follows: [1] Dygert & Liang, 2014; [2] Batanova *et al.*, 2011; [3] Bizimis *et al.*, 2000.

Figure 9. Melt compositions in equilibrium with Trinity clinopyroxene compared to (a) the global N-MORB suite (PetDB) and olivine-hosted melt inclusions from the mid-Atlantic ridge (Shimizu, 1998), (b) dikes and basalts from the crustal section of Trinity (Brouxel & Lapierre, 1988; Metcalf *et al.*, 2000), and (c) four boninitic dikes that cross cut crustal gabbros at Trinity (Metcalf *et al.*, 2000) and the plagioclase lherzolite forming infiltrating melt shown in Figure 7. Equilibrium melt compositions were calculated using the temperature and composition dependent partition coefficient model of Sun & Liang (2012) for REE+Y (at 1200°C), Sr and HFSE were calculated using partition coefficients from Kelemen *et al.* (2003).

Figure 10. Clinopyroxene from Trinity plagioclase lherzolites (red lines) and dunites, harzburgites and lherzolites (red lines) compared to clinopyroxene from Oman (Kelemen *et al.*, 1995a). Note samples from Trinity dunite, harzburgite and lherzolite have lower REE concentrations than Trinity plagioclase lherzolite, opposite the relationship exhibited by samples from Oman.

Figure 1.



Figure 2.

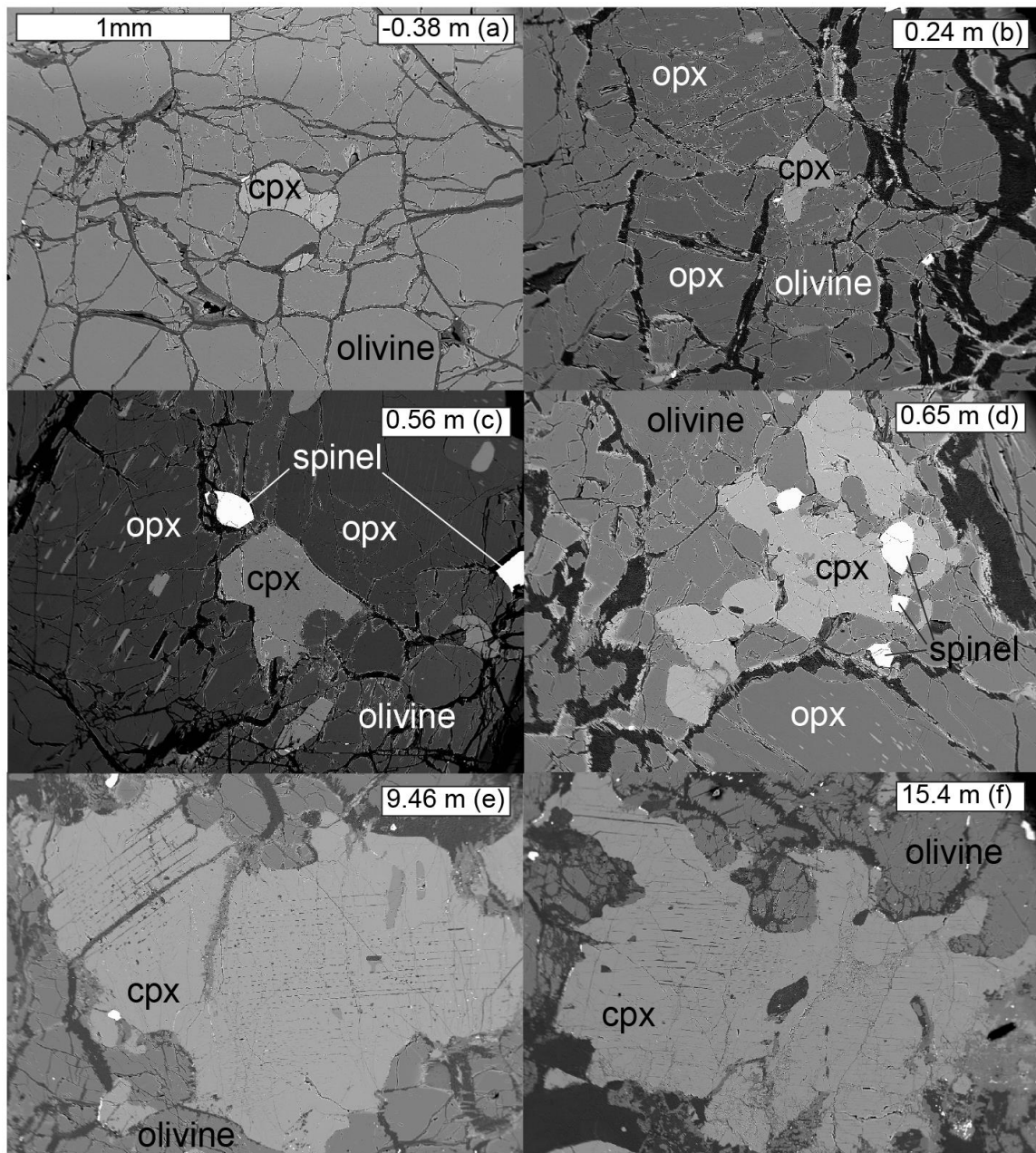


Figure 3.

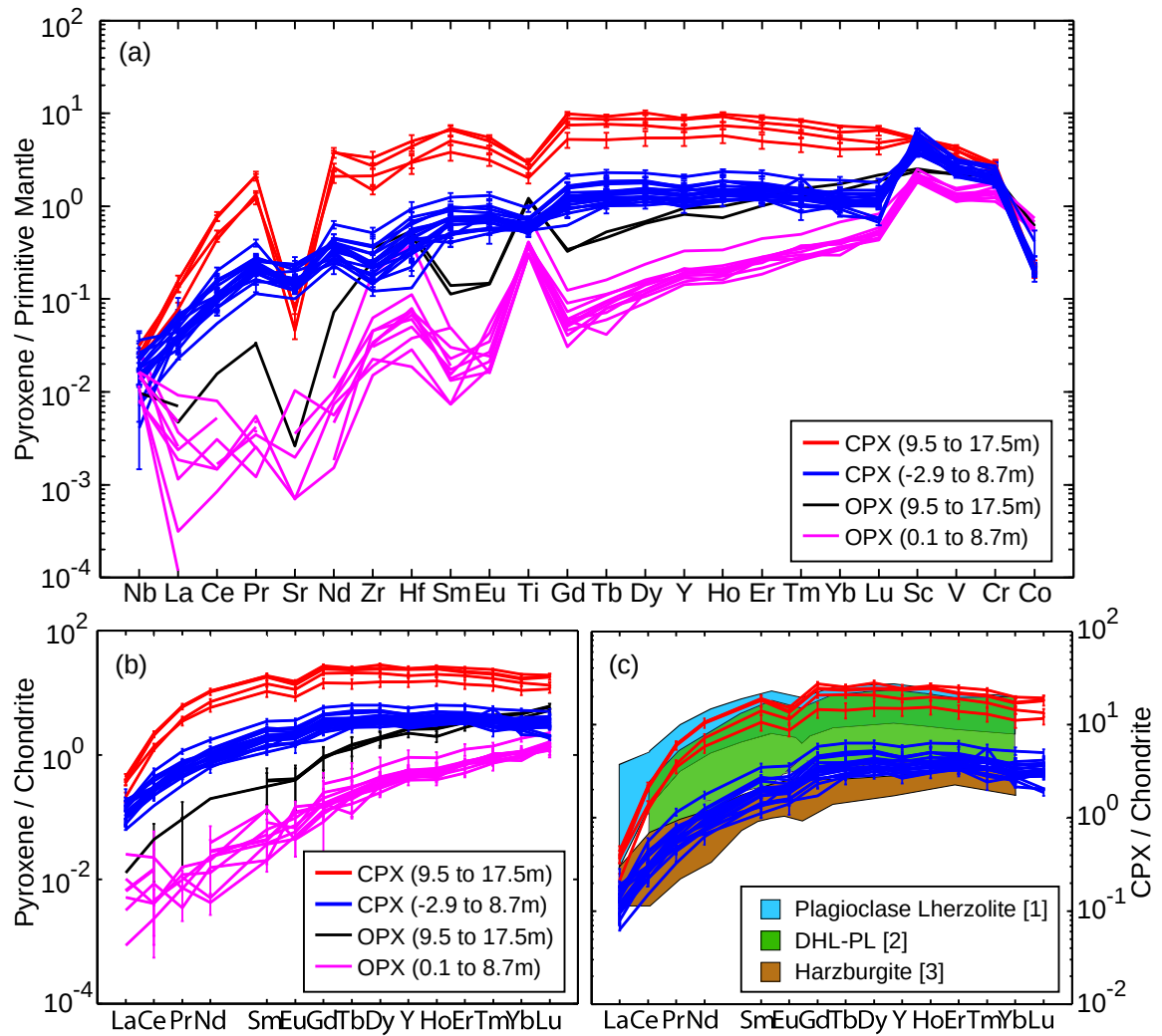


Figure 4.

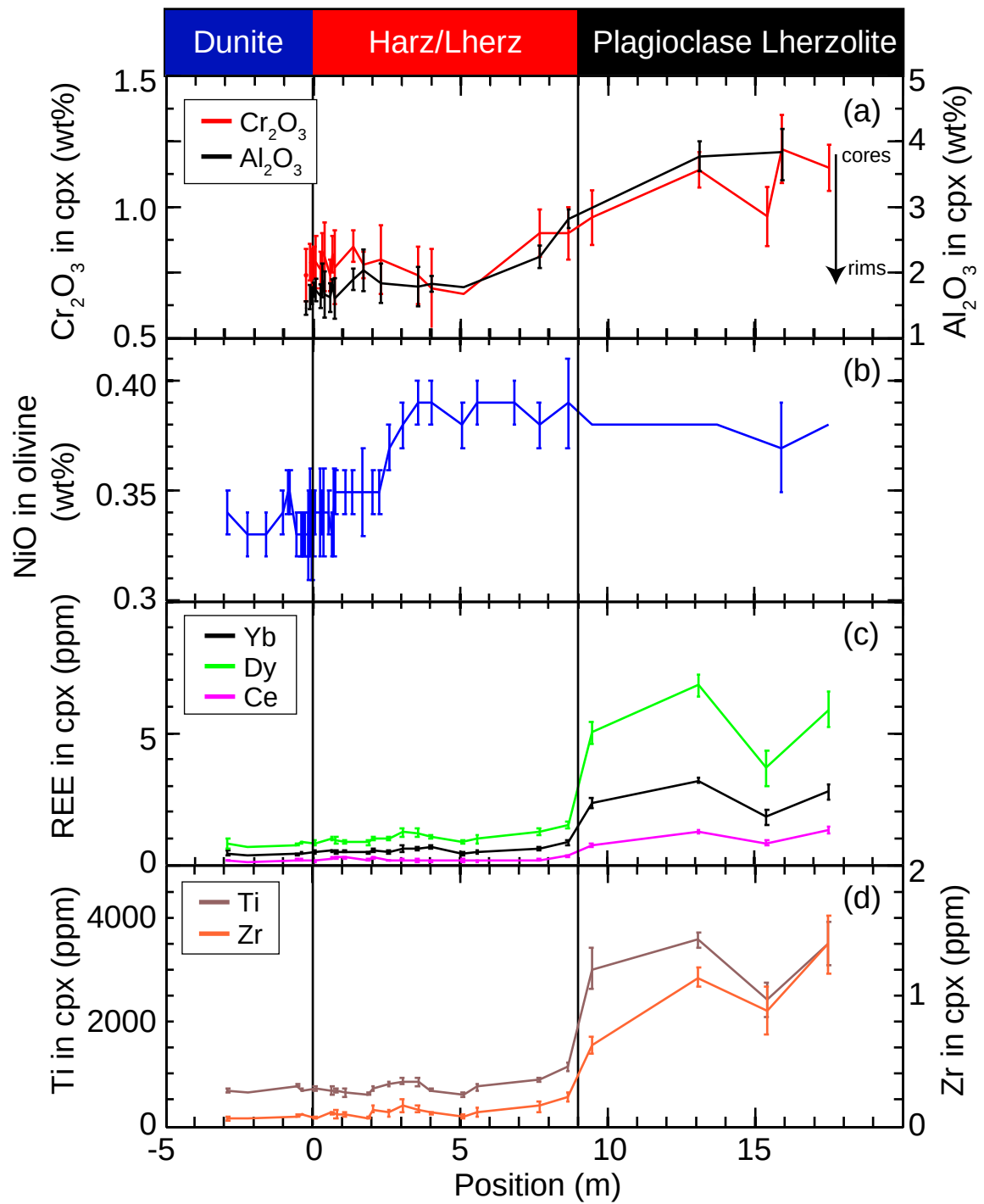


Figure 5.

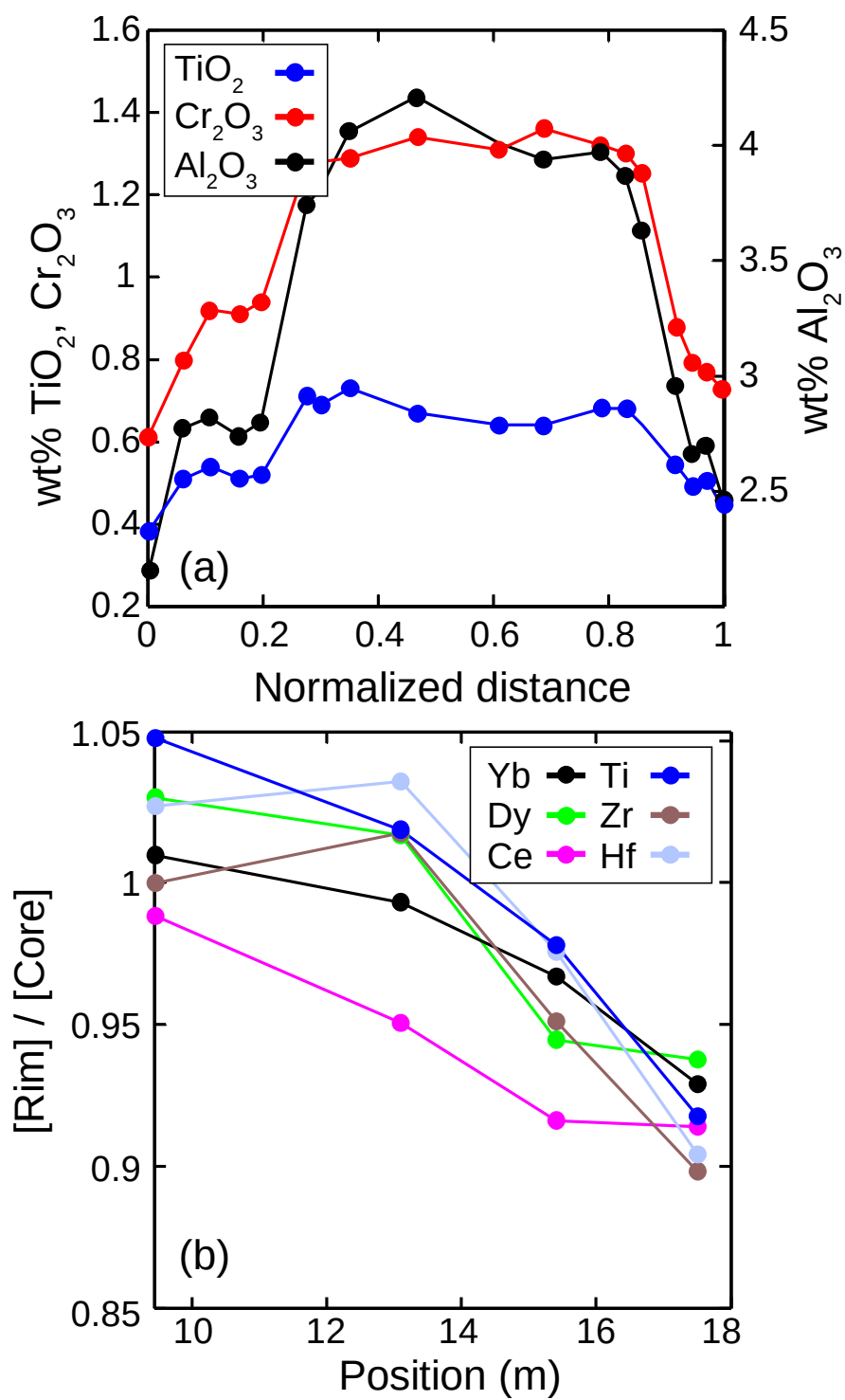


Figure 6.

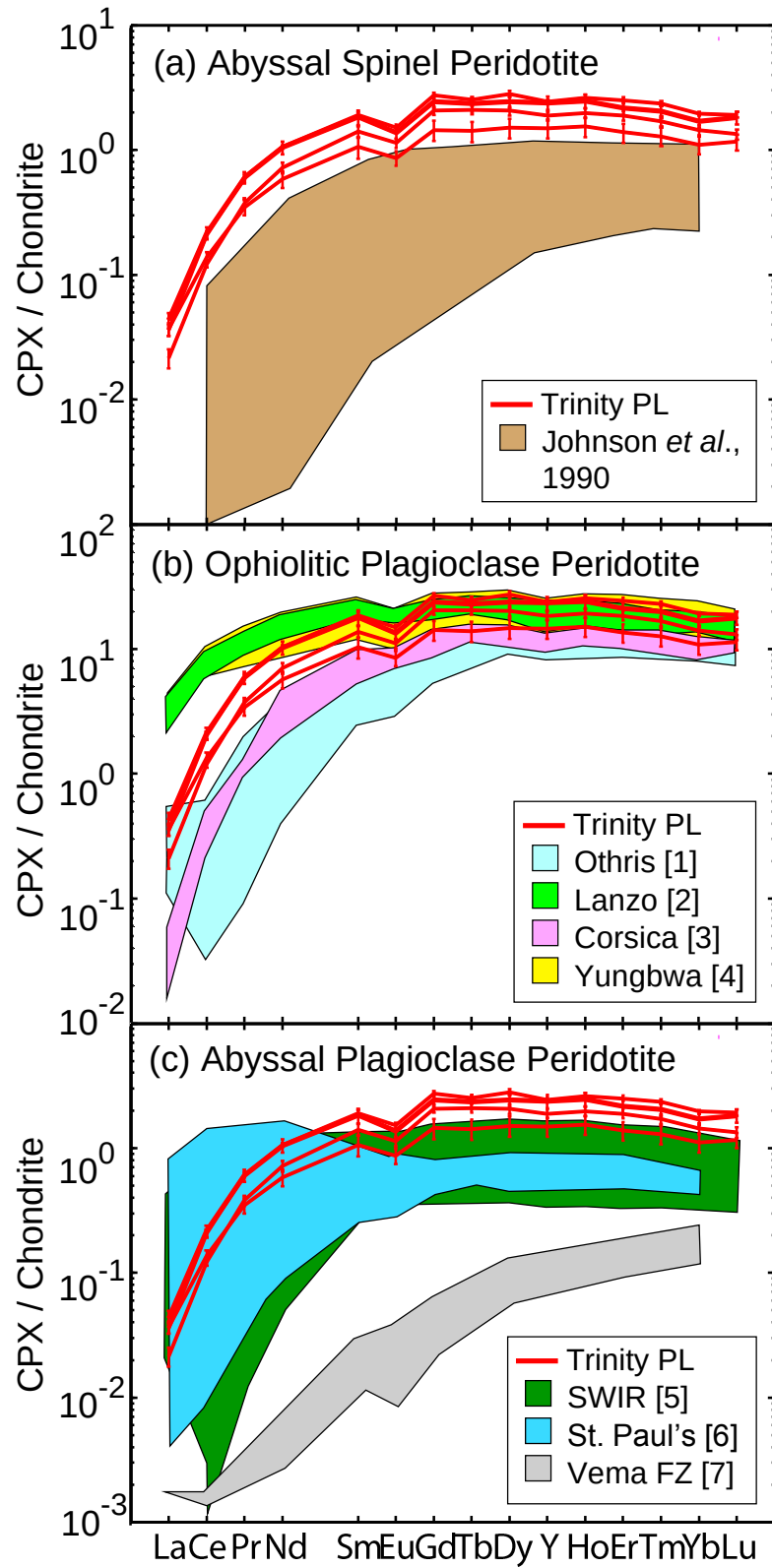


Figure 7.

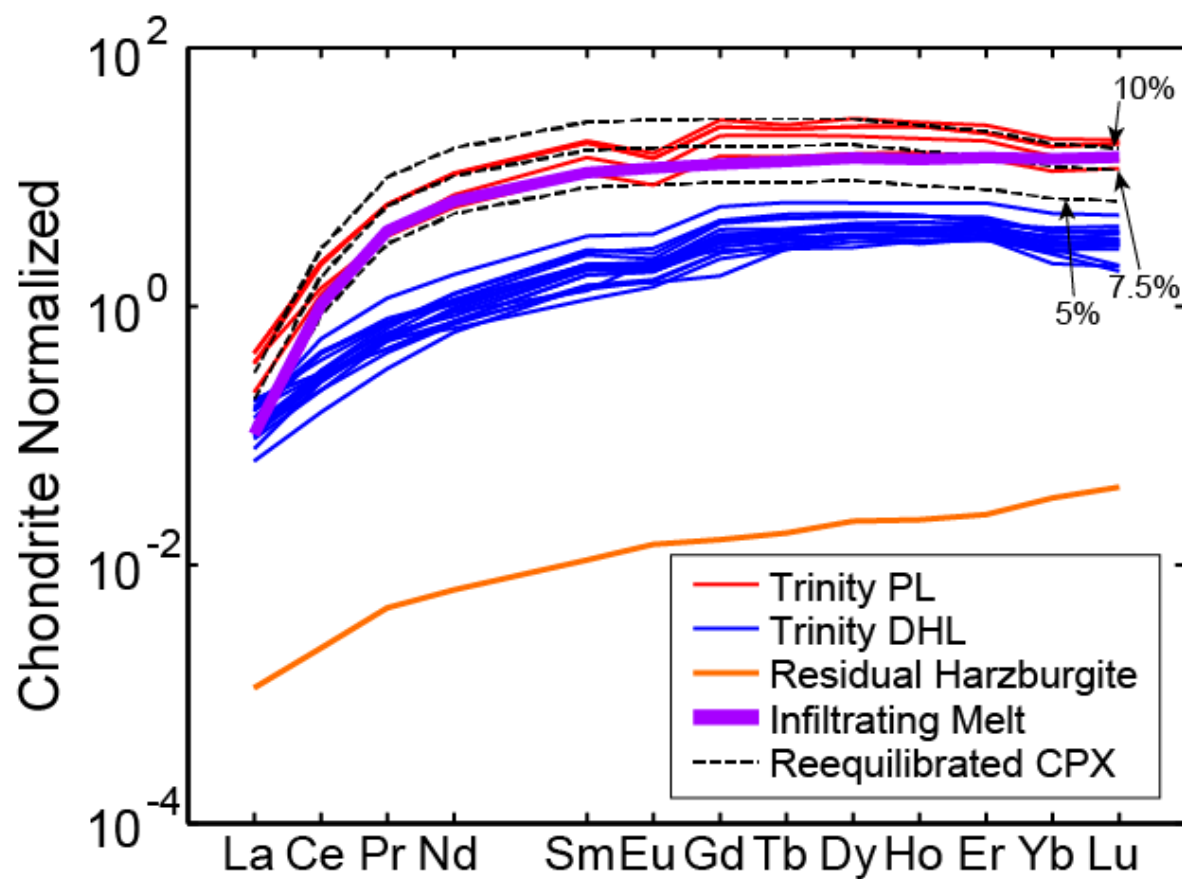


Figure 8.

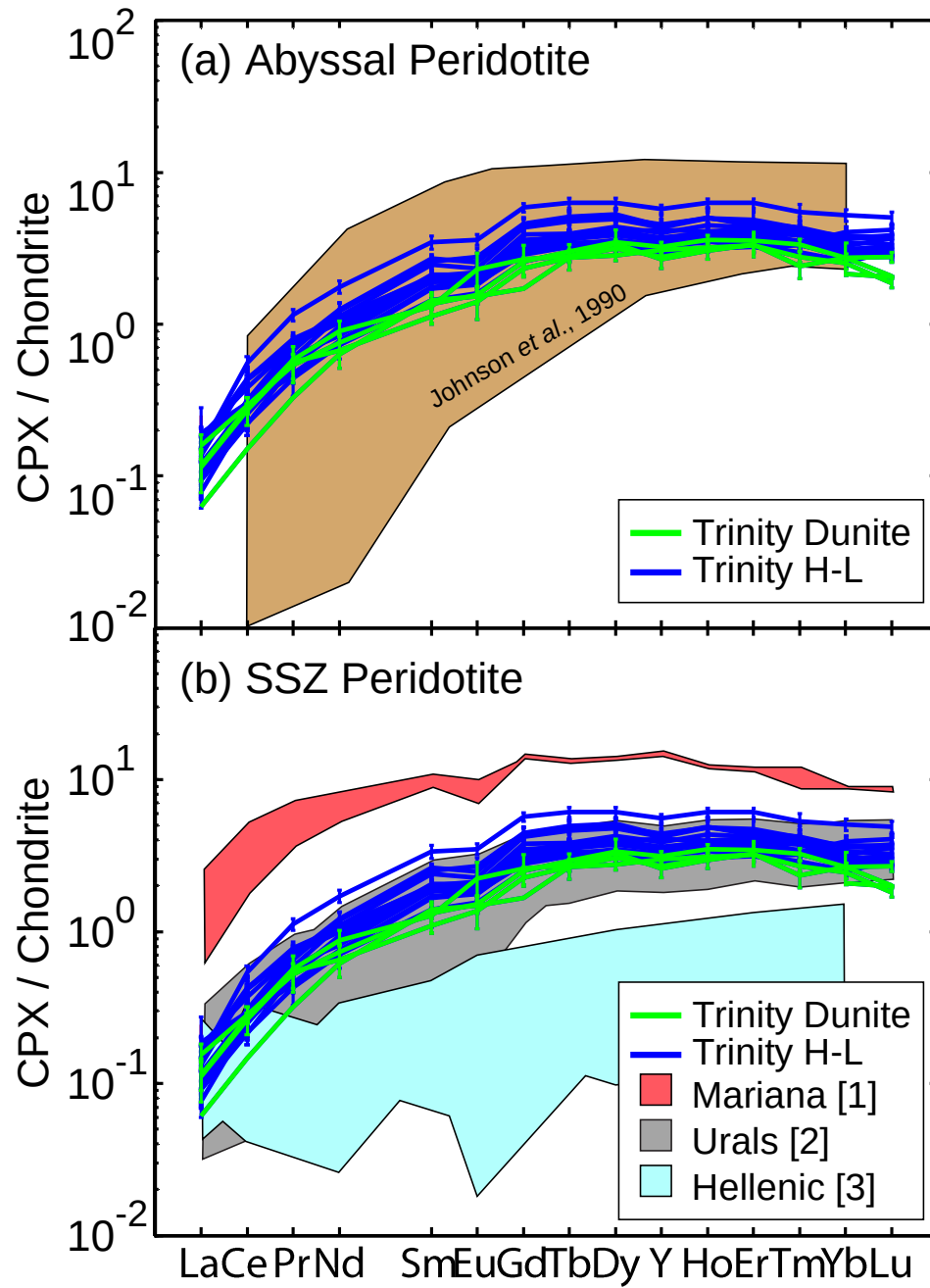


Figure 9.

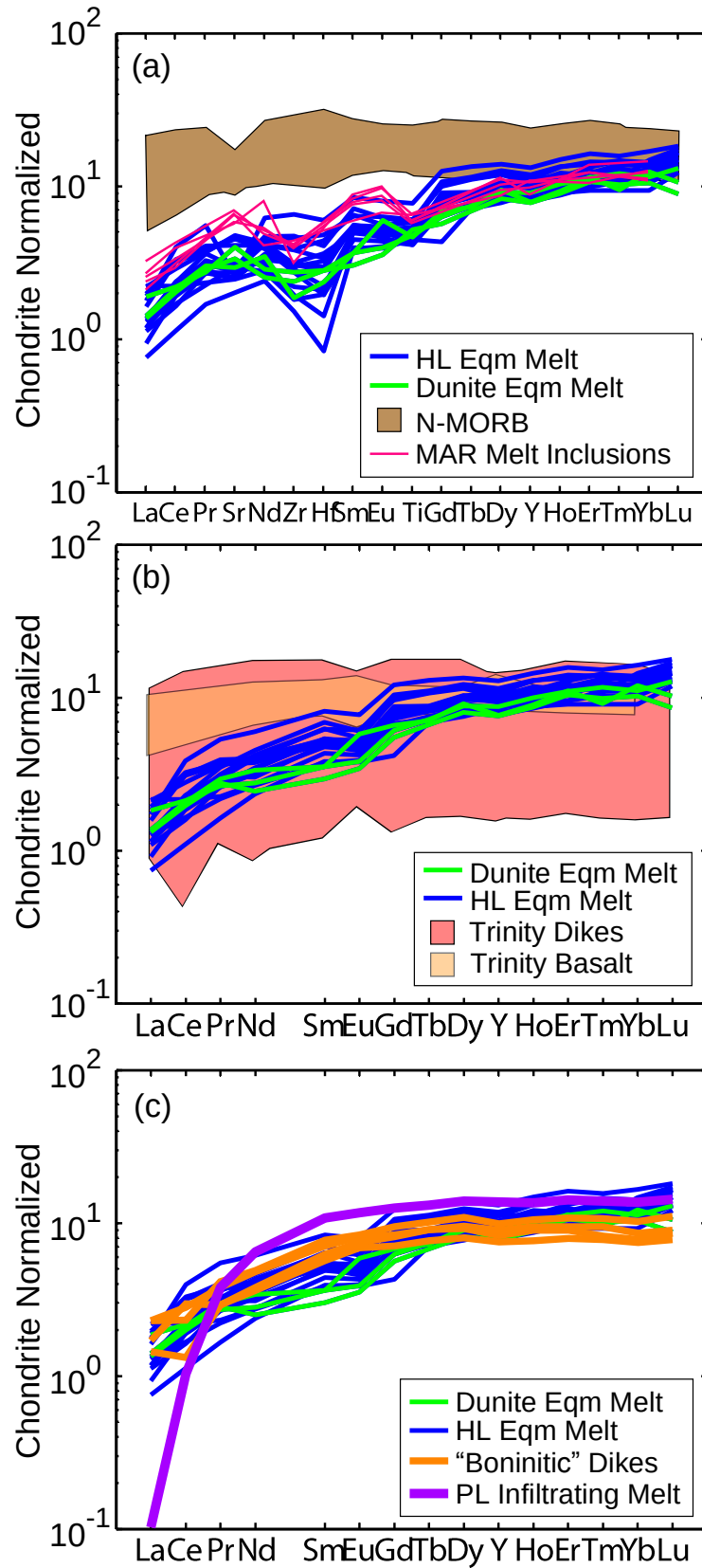


Figure 10.

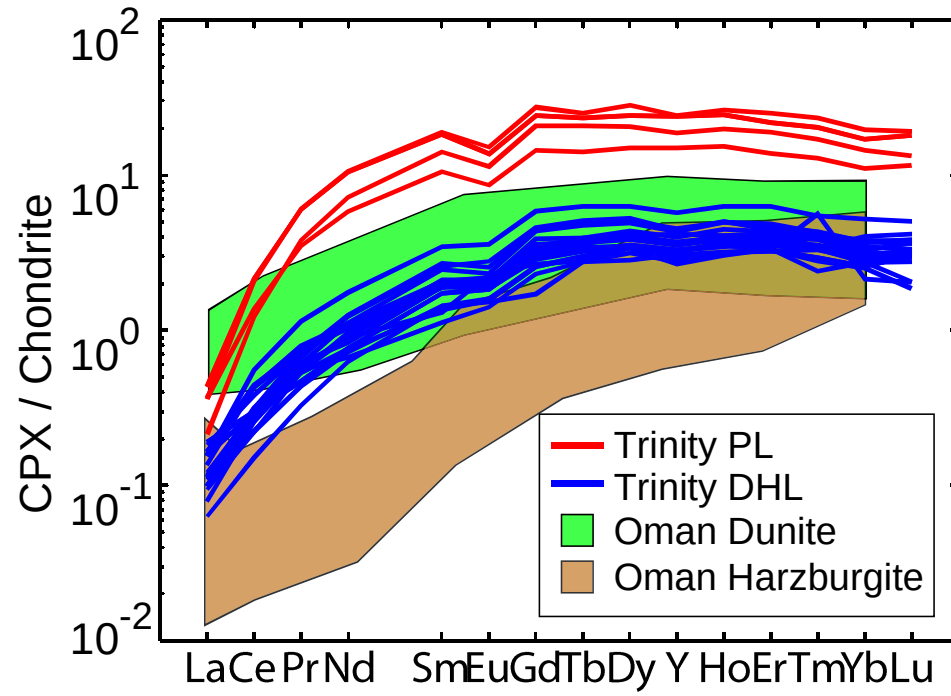


Table 1.

Trace elements in clinopyroxene							
Sample	Z01	1σ	Z02	Z04	1σ	Z06	1σ
Lithology	Dunite		Dunite	Dunite		Dunite	
Position	-2.89		-2.22	-0.53		-0.38	
n Core	2		1	3		5	
n Rim	-		-	-		-	
Li	-	-	-	-	-	-	-
Na₂O	0.148	0.041	0.147	0.205	0.017	0.223	0.050
K₂O	-	-	-	0.00137	0.00043	0.00333	-
Sc	100.1	1.2	94.7	111.3	0.4	93.1	5.0
TiO₂	0.114	0.006	0.110	0.129	0.003	0.117	0.004
V	257	19	179	265	10	227	7
Cr	6519	516	4677	5172	358	4805	630
Co	43.8	13.3	21.6	27.5	2.8	19.1	0.6
Ni	516.0	91.3	294.3	292.8	54.7	249.9	6.3
Sr	2.91	0.29	2.00	3.33	0.21	3.95	0.29
Y	4.2	0.5	4.8	4.4	0.2	5.1	0.3
Zr	1.54	0.41	1.27	1.97	0.17	2.28	0.16
Nb	0.0027	-	0.0048	0.0050	-	0.0046	-
La	0.028	0.006	0.015	0.027	0.009	0.037	0.007
Ce	0.171	0.009	0.091	0.163	0.034	0.177	0.021
Pr	0.052	0.001	0.029	0.050	0.013	0.048	0.009
Nd	0.406	0.066	0.284	0.303	0.070	0.341	0.043
Sm	0.193	0.045	0.211	0.165	0.018	0.199	0.028
Eu	0.128	0.036	0.085	0.079	0.019	0.087	0.012
Gd	0.102	0.019	0.100	0.100	0.007	0.109	0.002
Tb	0.525	0.122	0.337	0.454	0.040	0.505	0.033
Dy	0.820	0.186	0.688	0.759	0.023	0.835	0.035
Ho	0.169	0.020	0.177	0.173	0.006	0.198	0.016
Er	0.530	0.087	0.525	0.527	0.061	0.561	0.080
Tm	0.058	0.010	-	0.067	0.006	0.081	0.008
Yb	0.447	0.105	0.346	0.410	0.038	0.446	0.027
Lu	0.050	0.001	0.049	0.045	0.003	0.067	0.005
Hf	0.104	0.033	0.037	0.124	0.035	0.124	0.020
Ta	-	-	0.00383	0.00146	-	0.00076	-
Pb	0.015	0.010	0.002	0.009	0.006	-	-

Na₂O, K₂O, and TiO₂ are reported in wt. %, all other elements in ppm.

Table 1 continued.

Trace elements in clinopyroxene								
Sample	Z13	1σ	Z18	1σ	Z20	1σ	Z21	1σ
Lithology	Spinel Harz		Spinel Harz		Spinel Harz		Spinel Harz	
Position	0.08		0.65		0.79		1.08	
n Core	12		7		4		4	
n Rim	-		3		-		-	
Li	1.25	-	0.62	0.42	1.00	0.19	1.10	0.37
Na₂O	0.212	0.014	0.210	0.015	0.254	0.045	0.259	0.031
K₂O	-	-	-	-	0.00063	0.00030	-	-
Sc	83.2	6.9	87.7	7.8	74.1	7.4	69.5	9.4
TiO₂	0.120	0.010	0.117	0.014	0.112	0.007	0.105	0.012
V	201	13	204	20	204	26	198	14
Cr	5174	531	5060	302	5181	783	5143	532
Co	22.9	2.6	21.6	1.9	21.3	3.2	21.1	1.5
Ni	289.9	22.3	292.7	27.5	268.9	36.0	276.3	19.9
Sr	2.95	0.43	4.73	0.40	4.54	1.08	4.49	0.25
Y	5.1	0.4	6.5	0.4	5.5	0.7	5.0	0.5
Zr	1.51	0.19	2.57	0.19	2.37	0.80	2.28	0.37
Nb	-	-	0.0243	0.0195	0.0154	0.0144	0.0124	0.0045
La	0.026	0.005	0.043	0.007	0.039	0.009	0.037	0.005
Ce	0.135	0.024	0.230	0.034	0.267	0.049	0.258	0.034
Pr	0.039	0.009	0.064	0.013	0.067	0.008	0.066	0.007
Nd	0.328	0.059	0.507	0.057	0.479	0.062	0.464	0.047
Sm	0.212	0.051	0.297	0.059	0.278	0.032	0.284	0.043
Eu	0.089	0.013	0.110	0.017	0.118	0.013	0.113	0.011
Gd	0.507	0.056	0.668	0.089	0.631	0.065	0.124	0.009
Tb	0.108	0.010	0.133	0.015	0.133	0.020	0.612	0.055
Dy	0.827	0.097	0.989	0.081	0.939	0.120	0.845	0.069
Ho	0.192	0.019	0.225	0.018	0.215	0.028	0.207	0.018
Er	0.581	0.056	0.673	0.082	0.602	0.065	0.555	0.053
Tm	0.084	0.007	0.100	0.008	0.085	0.011	0.085	0.005
Yb	0.498	0.069	0.533	0.033	0.504	0.063	0.507	0.051
Lu	0.078	0.011	0.089	0.015	0.078	0.010	0.071	0.005
Hf	0.087	0.014	0.130	0.020	0.098	0.021	0.086	0.016
Ta	-	-	0.00138	0.00107	-	-	0.00037	-
Pb	0.015	0.011	0.050	0.029	-	-	0.020	0.001

Table 1 continued.

Trace elements in clinopyroxene								
Sample	Z27	1σ	Z23	1σ	Z24	1σ	Z25	1σ
Lithology	Spinel Harz		Spinel Harz		Spinel Harz		Spinel Harz	
Position	1.89		2.04		2.58			
n Core	5		3		4		4	
n Rim	-		-		-		-	
Li	1.19	0.30	0.92	0.18	0.98	0.14	0.91	0.24
Na₂O	0.221	0.025	0.270	0.017	0.184	0.016	0.181	0.030
K₂O	0.00055	0.00029	0.00071	0.00033	0.00035	0.00016	0.00035	0.00015
Sc	70.9	6.0	79.5	9.2	68.8	5.0	74.9	10.5
TiO₂	0.105	0.005	0.122	0.009	0.133	0.007	0.144	0.010
V	199	20	222	13	212	7	205	17
Cr	5734	1226	5264	197	4953	444	4804	658
Co	27.0	9.2	21.9	1.8	21.6	2.4	19.6	3.5
Ni	374.3	142.9	285.9	21.3	299.5	31.3	276.1	39.7
Sr	3.18	0.26	4.07	0.46	2.48	0.20	2.91	0.59
Y	4.9	0.5	5.8	0.6	5.7	0.6	7.1	1.1
Zr	1.71	0.21	3.20	0.65	2.56	0.57	3.92	1.26
Nb	0.0109	0.0062	0.0117	0.0040	0.0106	0.0028	0.0094	0.0020
La	0.026	0.008	0.032	0.011	0.018	0.004	0.023	0.006
Ce	0.191	0.018	0.260	0.019	0.156	0.009	0.190	0.013
Pr	0.055	0.004	0.071	0.004	0.050	0.003	0.064	0.008
Nd	0.397	0.069	0.496	0.046	0.427	0.028	0.568	0.054
Sm	0.281	0.045	0.304	0.014	0.310	0.014	0.399	0.026
Eu	0.105	0.007	0.123	0.008	0.119	0.010	0.143	0.010
Gd	0.578	0.043	0.657	0.047	0.703	0.062	0.175	0.026
Tb	0.120	0.021	0.129	0.008	0.135	0.010	0.894	0.089
Dy	0.869	0.121	0.993	0.078	1.011	0.068	1.224	0.161
Ho	0.182	0.017	0.223	0.022	0.226	0.027	0.277	0.040
Er	0.540	0.075	0.631	0.089	0.634	0.045	0.737	0.125
Tm	0.085	0.014	0.096	0.012	0.093	0.013	0.105	0.018
Yb	0.489	0.058	0.563	0.071	0.502	0.064	0.607	0.101
Lu	0.076	0.011	0.081	0.011	0.076	0.006	0.088	0.016
Hf	0.068	0.016	0.150	0.038	0.125	0.028	0.180	0.065
Ta	0.00033	0.00027	-	-	-	-	0.00010	-
Pb	0.026	0.003	0.022	0.014	0.024	0.009	0.015	0.012

Table 1 continued.

Trace elements in clinopyroxene								
Sample	Z26	1 σ	TP90.11	1 σ	TP90.13	1 σ	TP90.14	1 σ
Lithology	Spinel Harz		Spinel Harz		Spinel Lherz		Spinel Lherz	
Position	3.55		4.01		5.09		5.59	
n Core	6		1		3		7	
n Rim	4		2		3		7	
Li	1.02	0.27	-	-	-	-	-	-
Na ₂ O	0.209	0.024	0.272	0.081	0.249	0.121	0.321	0.170
K ₂ O	0.00113	0.00053	0.00611	0.00496	-	-	0.00825	-
Sc	81.3	14.3	70.5	1.8	59.3	3.0	59.3	4.3
TiO ₂	0.143	0.013	0.116	0.004	0.102	0.007	0.127	0.011
V	202	16	169	4	187	10	222	14
Cr	5214	936	4476	125	5380	387	6069	647
Co	23.2	2.0	21.2	0.6	19.7	1.2	21.4	2.0
Ni	346.9	36.4	300.9	21.4	321.8	26.9	340.3	34.8
Sr	2.75	0.31	2.46	0.12	2.44	0.19	2.72	0.33
Y	6.7	1.0	6.2	0.2	5.2	0.3	5.5	0.6
Zr	3.23	0.62	2.49	0.09	1.82	0.41	2.63	0.74
Nb	0.0102	0.0041	0.0117	0.0037	0.0142	0.0034	0.0174	0.0056
La	0.023	0.006	0.022	0.003	0.044	0.022	0.026	0.009
Ce	0.159	0.039	0.134	0.008	0.181	0.070	0.157	0.032
Pr	0.054	0.009	0.048	0.002	0.042	0.005	0.048	0.008
Nd	0.507	0.043	0.438	0.044	0.345	0.041	0.408	0.048
Sm	0.364	0.039	0.307	0.018	0.256	0.034	0.286	0.047
Eu	0.130	0.019	0.118	0.013	0.103	0.012	0.113	0.012
Gd	0.855	0.115	0.766	0.113	0.606	0.071	0.143	0.020
Tb	0.172	0.022	0.142	0.010	0.118	0.014	0.681	0.106
Dy	1.193	0.165	1.059	0.073	0.862	0.065	0.972	0.155
Ho	0.276	0.045	0.248	0.001	0.196	0.016	0.225	0.033
Er	0.776	0.141	0.689	0.089	0.521	0.047	0.557	0.085
Tm	0.104	0.011	0.082	0.014	0.071	0.004	0.082	0.011
Yb	0.599	0.068	0.652	0.063	0.422	0.039	0.482	0.082
Lu	0.094	0.015	0.101	0.008	0.074	0.004	0.080	0.015
Hf	0.195	0.048	0.143	0.014	0.093	0.036	0.160	0.040
Ta	-	-	0.00121	0.00087	-	-	0.00045	-
Pb	0.055	0.051	0.105	0.056	0.264	0.118	-	-

Table 1 continued.

Trace elements in clinopyroxene								
Sample	TP90.16	1 σ	TP90.17	1 σ	17BK	1 σ	18A	1 σ
Lithology	Spinel Lherz		Spinel Lherz		Plag Lherz		Plag Lherz	
Position	7.68		8.66		9.46		13.1	
n Core	6		5		8		6	
n Rim	3		5		7		6	
Li	-	-	-	-	-	-	-	-
Na₂O	0.370	0.144	0.318	0.096	0.248	0.094	0.388	0.051
K₂O	0.01446	0.01156	-	-	-	-	0.00053	-
Sc	61.6	2.5	68.4	3.8	90.6	9.4	88.0	6.4
TiO₂	0.149	0.008	0.191	0.016	0.506	0.066	0.593	0.025
V	237	15	262	10	334	23	359	14
Cr	7122	672	7118	534	6304	715	7574	468
Co	22.1	1.6	22.2	1.1	-	-	23.4	1.4
Ni	339.9	26.2	366.4	65.1	-	-	322.1	19.1
Sr	2.87	0.38	2.55	0.18	0.95	0.22	-	-
Y	6.9	0.4	9.0	0.5	29.1	2.4	37.9	1.6
Zr	3.81	1.12	5.45	0.76	15.54	1.58	28.49	2.00
Nb	0.0238	0.0044	0.0165	0.0054	0.0168	0.0081	0.0205	-
La	0.029	0.011	0.036	0.006	0.050	0.009	0.084	0.008
Ce	0.180	0.039	0.336	0.032	0.736	0.044	1.253	0.087
Pr	0.060	0.010	0.102	0.009	0.329	0.042	0.542	0.024
Nd	0.555	0.071	0.795	0.074	3.236	0.335	4.805	0.152
Sm	0.380	0.032	0.509	0.053	2.036	0.240	2.790	0.156
Eu	0.156	0.021	0.201	0.017	0.632	0.057	0.849	0.044
Gd	0.902	0.089	1.147	0.076	4.001	0.442	0.914	0.051
Tb	0.185	0.018	0.228	0.017	0.746	0.072	5.382	0.278
Dy	1.273	0.121	1.524	0.120	4.944	0.477	6.813	0.411
Ho	0.280	0.023	0.349	0.024	1.096	0.093	1.456	0.079
Er	0.703	0.058	0.994	0.072	2.961	0.287	3.975	0.223
Tm	0.100	0.013	0.132	0.016	0.407	0.043	0.568	0.026
Yb	0.615	0.069	0.843	0.075	2.350	0.213	3.189	0.089
Lu	0.091	0.005	0.122	0.010	0.332	0.040	0.467	0.026
Hf	0.214	0.054	0.265	0.049	0.844	0.138	1.237	0.131
Ta	0.00085	0.00067	0.00103	0.00054	-	-	0.00082	-
Pb	0.116	0.109	-	-	0.010	0.004	0.007	0.005

Table 1 continued.

Trace elements in clinopyroxene				
Sample	19BK	1σ	19B	1σ
	Plag		Plag	
Lithology	Lherz		Lherz	
Position	15.41		17.51	
n Core	13		15	
n Rim	8		9	
Li	-	-	-	-
Na₂O	0.278	0.025	0.387	0.070
K₂O	0.00030	-	0.00069	0.00042
Sc	84.4	5.8	84.7	6.4
TiO₂	0.403	0.052	0.582	0.071
V	284	14	325	20
Cr	6229	893	7239	1071
Co	20.4	2.3	19.7	2.0
Ni	308.2	43.7	291.5	29.5
Sr	1.58	0.21	1.47	0.36
Y	23.3	4.1	37.2	4.5
Zr	22.17	4.44	34.84	5.51
Nb	0.0147	-	0.0170	0.0066
La	0.086	0.010	0.102	0.015
Ce	0.831	0.080	1.300	0.140
Pr	0.310	0.044	0.537	0.057
Nd	2.631	0.394	4.724	0.560
Sm	1.556	0.300	2.690	0.362
Eu	0.484	0.067	0.772	0.089
Gd	0.515	0.096	4.785	0.590
Tb	2.843	0.522	0.851	0.112
Dy	3.657	0.674	5.896	0.673
Ho	0.857	0.150	1.370	0.167
Er	2.201	0.380	3.450	0.436
Tm	0.311	0.053	0.493	0.060
Yb	1.795	0.292	2.765	0.305
Lu	0.282	0.040	0.441	0.052
Hf	0.835	0.208	1.415	0.232
Ta	0.00094	-	-	-
Pb	0.010	0.005	-	-

Table 2.

Trace elements in orthopyroxene							
Sample	Z13	Z18	1σ	Z20	Z27	1σ	Z23
Lithology	Spinel Harz	Spinel Harz		Spinel Harz	Spinel Harz		Spinel Harz
Position	0.08	0.65		0.79	1.89		2.04
n Core	1	6		1	2		1
n Rim	-	5		-	-		-
Li	1.03	-	-	0.29	0.26	0.02	0.27
Na ₂ O	-	-	-	0.010	0.007	0.001	0.009
K ₂ O	0.00164	-	-	-	0.00032	0.00025	-
Sc	32.9	39.9	3.6	30.4	31.7	0.5	36.4
TiO ₂	0.060	0.083	0.007	0.062	0.060	0.003	0.081
V	100	125	7	97	96	7	101
Cr	4253	4744	462	3656	3233	570	3484
Co	70.8	78.3	1.9	58.1	61.1	1.9	56.4
Ni	738	802	29	584	620	31	556
Sr	-	-	-	-	0.014	0.007	-
Y	0.72	0.92	0.13	0.76	0.61	0.11	0.82
Zr	0.20	0.34	0.17	0.24	0.16	0.03	0.34
Nb	0.0187	0.0120	0.0050	0.0195	0.0070	0.0014	0.0075
La	0.0024	0.0027	0.0015	0.0007	0.00041	-	-
Ce	0.0024	-	-	0.005	0.0014	0.0009	0.003
Pr	0.0014	0.0017	0.0013	0.0003	0.00065	0.00046	0.0009
Nd	0.009	0.014	0.013	0.007	0.0019	0.0007	0.010
Sm	0.020	0.0107	0.0046	0.0030	0.0030	0.0001	0.0056
Eu	0.0025	0.0047	0.0025	0.0083	0.0028	0.0015	0.0033
Gd	0.017	0.033	0.017	0.032	0.0253	0.0049	0.033
Tb	0.0079	0.0096	0.0023	0.0041	0.0059	0.0015	0.0071
Dy	0.077	0.099	0.025	0.078	0.060	0.010	0.085
Ho	0.0239	0.0292	0.0057	0.027	0.0224	0.0043	0.0308
Er	0.117	0.120	0.020	0.115	0.081	0.012	0.108
Tm	0.020	0.0246	0.0036	0.018	0.0179	0.0012	0.025
Yb	0.130	0.185	0.024	0.160	0.1483	0.0058	0.173
Lu	0.035	0.0393	0.0044	0.029	0.0308	0.0018	0.037
Hf	0.011	0.0138	0.0069	0.0053	0.0080	0.0011	0.022
Ta	0.00062	-	-	0.00039	0.000156	0.000083	0.00024
Pb	0.0055	-	-	-	0.028	0.003	0.0051

Na₂O, K₂O, and TiO₂ are reported in wt. %, all other elements in ppm.

Table 2 continued.

Trace elements in orthopyroxene								
Sample	Z24	1 σ	Z26	1 σ	TP90.11	1 σ	TP90.13	1 σ
Lithology	Spinel Harz		Spinel Harz		Spinel Harz		Spinel Lherz	
Position	2.58		3.55		4.01		5.09	
n Core	2		4		4		1	
n Rim	-		2		3		2	
Li	0.23	0.06	-	-	-	-	-	-
Na₂O	0.012	0.005	0.012	0.008	-	-	0.038	0.025
K₂O	-	-	0.00093	0.00037	-	-	0.00358	0.00262
Sc	33.9	2.9	35.1	1.8	29.6	1.0	34.6	2.6
TiO₂	0.0751	0.0003	0.081	0.003	0.062	0.002	0.072	0.002
V	113	5	96	5	92	1	91	1
Cr	3802	687	2933	261	3829	189	3273	95
Co	59.8	0.5	58.9	1.9	59.8	1.0	55.7	0.7
Ni	631	7	691	87	719	8	663	20
Sr	-	-	-	-	-	-	0.070	0.056
Y	0.90	0.19	0.89	0.10	0.66	0.09	0.83	0.04
Zr	0.35	0.13	0.35	0.08	0.47	0.21	0.48	0.24
Nb	0.0072	0.0026	0.0064	0.0032	0.0095	0.0028	0.0052	0.0036
La	-	-	-	-	0.0043	0.0033	0.0046	-
Ce	-	-	0.0024	0.0017	-	-	0.013	0.001
Pr	-	-	0.0013	0.0010	0.0013	0.0007	-	-
Nd	-	-	0.0058	0.0042	0.0053	0.0029	0.0128	0.0067
Sm	0.0122	0.0097	0.0093	0.0043	0.0054	0.0034	0.0094	0.0011
Eu	0.0037	0.0024	0.0054	0.0025	0.0029	0.0022	0.0066	0.0033
Gd	0.049	0.026	0.0399	0.0080	0.0221	0.0051	0.029	0.027
Tb	0.0112	0.0047	0.0109	0.0031	0.0079	0.0042	0.0090	0.0053
Dy	0.102	0.027	0.109	0.020	0.072	0.015	0.084	0.029
Ho	0.032	0.010	0.0340	0.0079	0.0262	0.0062	0.0294	0.0043
Er	0.119	0.020	0.124	0.015	0.095	0.021	0.123	0.013
Tm	0.0245	0.0045	0.0238	0.0032	0.0195	0.0035	0.0219	0.0082
Yb	0.1813	0.0078	0.178	0.018	0.160	0.016	0.184	0.043
Lu	0.0352	0.0022	0.0358	0.0026	0.0303	0.0027	0.033	0.011
Hf	0.021	0.010	0.0190	0.0054	0.021	0.011	0.0171	0.0014
Ta	0.00060	0.00036	0.00112	0.00061	0.00041	0.00026	0.0033	-
Pb	0.0244	0.0006	-	-	0.069	0.050	0.040	0.026

Table 2 continued.

Trace elements in orthopyroxene								
Sample	TP90.16	1σ	TP90.17	1σ	17BK	1σ	19B	1σ
Lithology	Spinel Lherz		Spinel Lherz		Plag Lherz		Plag Lherz	
Position	7.68		8.66		9.46		17.51	
n Core	3		2		3		16	
n Rim	5		3		3		2	
Li	-	-	-	-	-	-	-	-
Na₂O	-	-	-	-	0.016	0.009	0.034	0.016
K₂O	-	-	-	-	-	-	0.00046	0.00033
Sc	32.2	2.1	35.7	3.0	38.8	1.9	40.7	2.4
TiO₂	0.082	0.005	0.158	0.029	0.230	0.014	0.245	0.023
V	109	4	128	7	181	7	180	18
Cr	3637	199	4793	394	5421	500	5649	1139
Co	58.9	2.2	57.4	0.6	64.7	0.7	63.9	4.7
Ni	701	27	682	6	733	15	724	61
Sr	-	-	-	-	0.052	0.035	-	-
Y	0.81	0.14	1.42	0.45	3.49	0.52	4.10	0.73
Zr	0.66	0.37	2.00	0.95	2.69	1.23	3.72	1.08
Nb	0.0107	0.0067	0.0104	0.0060	-	-	0.0101	0.0053
La	0.0096	0.0045	0.0028	0.0042	0.0045	0.0029	0.0062	0.0043
Ce	0.013	0.011	-	-	0.026	0.021	-	-
Pr	0.00072	0.00066	-	-	0.0100	0.0070	0.0085	0.0071
Nd	0.012	0.011	0.018	0.015	0.108	0.086	-	-
Sm	0.0077	0.0082	0.024	0.011	0.046	0.029	0.057	0.034
Eu	-	-	0.0069	0.0075	0.022	0.012	0.023	0.015
Gd	0.031	0.013	0.067	0.033	0.186	0.074	0.176	0.091
Tb	0.0084	0.0050	0.016	0.011	0.046	0.024	0.052	0.018
Dy	0.096	0.018	0.160	0.062	0.44	0.12	0.46	0.13
Ho	0.0298	0.0064	0.050	0.011	0.111	0.021	0.148	0.029
Er	0.119	0.019	0.196	0.042	0.443	0.051	0.53	0.10
Tm	0.0246	0.0063	0.0340	0.0038	0.088	0.024	0.104	0.016
Yb	0.184	0.020	0.299	0.034	0.647	0.076	0.76	0.11
Lu	0.0302	0.0061	0.0555	0.0072	0.1266	0.0091	0.147	0.016
Hf	0.032	0.017	0.111	0.050	0.136	0.053	0.153	0.053
Ta	-	-	-	-	0.00097	0.00057	-	-
Pb	0.106	0.072	0.053	0.047	-	-	-	-

Table 3.

Plagioclase Lherzolite Formation Model					
Description:	Trinity Plagioclase Peridotite ¹			Depleted Melting Residue ²	Infiltrating Melt
Sample:	9W20	8W40D	9W2		
<u>Composition</u>					
SiO ₂	44.14	43.21	43.22	40.97	50.90
TiO ₂	0.02	0.04	0.06	0.01	0.78
Al ₂ O ₃	2.9	2.08	1.68	0.44	17.13
Cr ₂ O ₃	0.36	0.57	0.45	0.71	0.06
Fe ₂ O ₃				0.08	0.47
MgO	42.45	43.77	44.3	47.72	11.04
CaO	1.99	1.77	0.95	0.48	11.82
MnO	0.12	0.12	0.16	0.17	0.01
FeO	7.68	8.12	8.91	9.11	6.04
Na ₂ O	0.1	0.06	0.05	0.00	1.72
				<u>REE</u>	
La	-	-	-	0.00026	0.024
Ce	-	-	-	0.00136	0.62
Pr	-	-	-	0.00041	0.34
Nd	-	-	-	0.00289	2.93
Sm	-	-	-	0.00159	1.58
Eu	-	-	-	0.00080	0.65
Gd	-	-	-	0.00305	2.45
Tb	-	-	-	0.00064	0.48
Dy	-	-	-	0.00524	3.39
Ho	-	-	-	0.00123	0.76
Er	-	-	-	0.00386	2.24
Yb	-	-	-	0.00531	2.23
Lu	-	-	-	0.00096	0.35
<u>Mineralogy</u> ³					
Olivine	0.70	0.76	0.77	0.95	-
Orthopyroxene	0.22	0.17	0.19	0.050	-
Clinopyroxene	0.055	0.066	0.027	-	-
Plagioclase	0.028	0.007	0.006	-	-

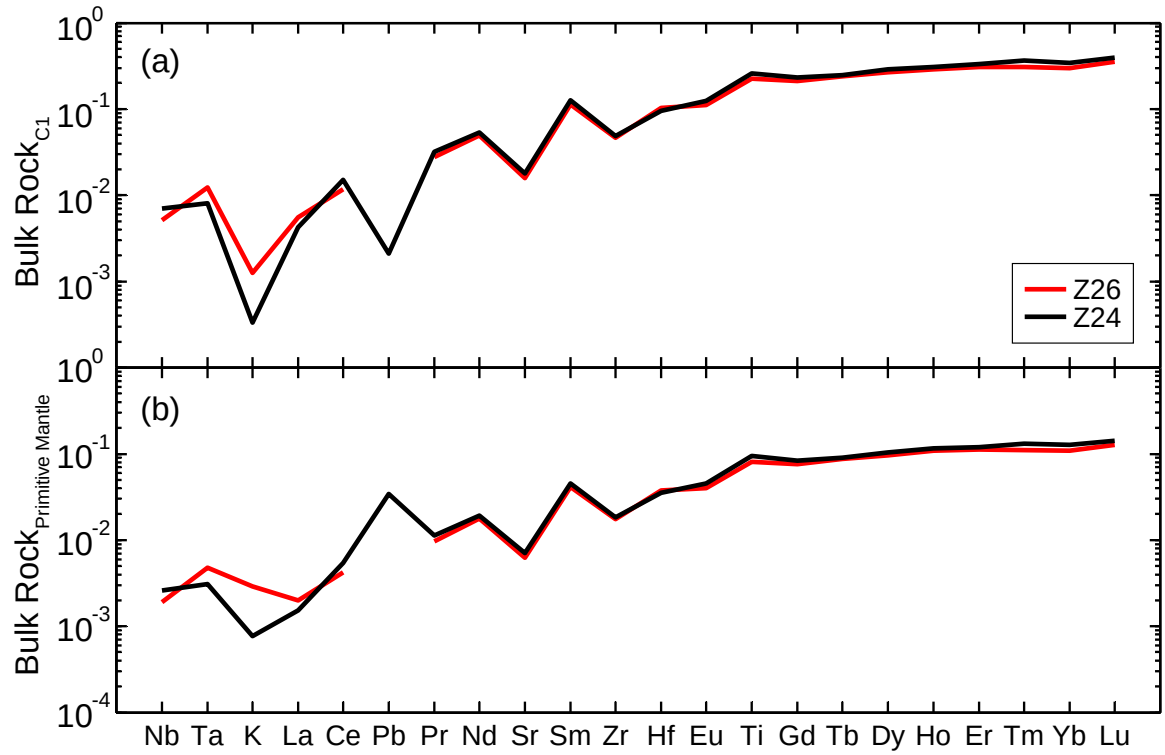
¹Quick, 1981b.²Fractional melting residue of a DMM with a potential temperature of 1300°C.
Extent of melting is 19%.³In weight fraction, calculated using alphaMELTS (Asimow & Ghiorso, 1998;
Smith & Asimow, 2005) at 3kb and reported on a spinel free basis

Table 3 continued.

Description:	5% Melt + 95% Harzburgite Mixture	7.5% Melt + 92.5% Harzburgite Mixture	10% Melt + 90% Harzburgite Mixture	20% Melt + 80% Harzburgite Mixture	30% Melt + 70% Harzburgite Mixture
Sample:					
<u>Composition</u>					
SiO ₂	41.47	41.72	41.96	42.96	43.95
TiO ₂	0.05	0.07	0.09	0.17	0.24
Al ₂ O ₃	1.27	1.69	2.11	3.77	5.44
Cr ₂ O ₃	0.68	0.66	0.65	0.58	0.52
Fe ₂ O ₃	0.10	0.11	0.12	0.16	0.20
MgO	45.88	44.97	44.05	40.38	36.71
CaO	1.05	1.33	1.61	2.75	3.88
MnO	0.16	0.16	0.15	0.14	0.12
FeO	8.96	8.88	8.80	8.50	8.19
Na ₂ O	0.09	0.13	0.17	0.35	0.52
	<u>Calculated REE in Clinopyroxene (ppm)</u>				
La	0.04	0.04	0.05	0.06	0.07
Ce	0.85	1.01	1.12	1.41	1.64
Pr	0.44	0.53	0.59	0.75	0.87
Nd	3.81	4.58	5.10	6.49	7.53
Sm	1.97	2.37	2.65	3.40	3.95
Eu	0.78	0.94	1.06	1.36	1.58
Gd	2.79	3.40	3.82	4.96	5.79
Tb	0.52	0.63	0.71	0.94	1.10
Dy	3.45	4.27	4.85	6.43	7.58
Ho	0.70	0.88	1.01	1.37	1.63
Er	1.82	2.31	2.68	3.70	4.44
Yb	1.50	1.95	2.30	3.31	4.05
Lu	0.21	0.27	0.32	0.47	0.59
<u>Mineralogy</u> ³					
Olivine	0.89	0.87	0.84	0.74	0.64
Orthopyroxene	0.059	0.068	0.078	0.11	0.14
Clinopyroxene	0.036	0.045	0.054	0.085	0.11
Plagioclase	0.011	0.019	0.027	0.065	0.11

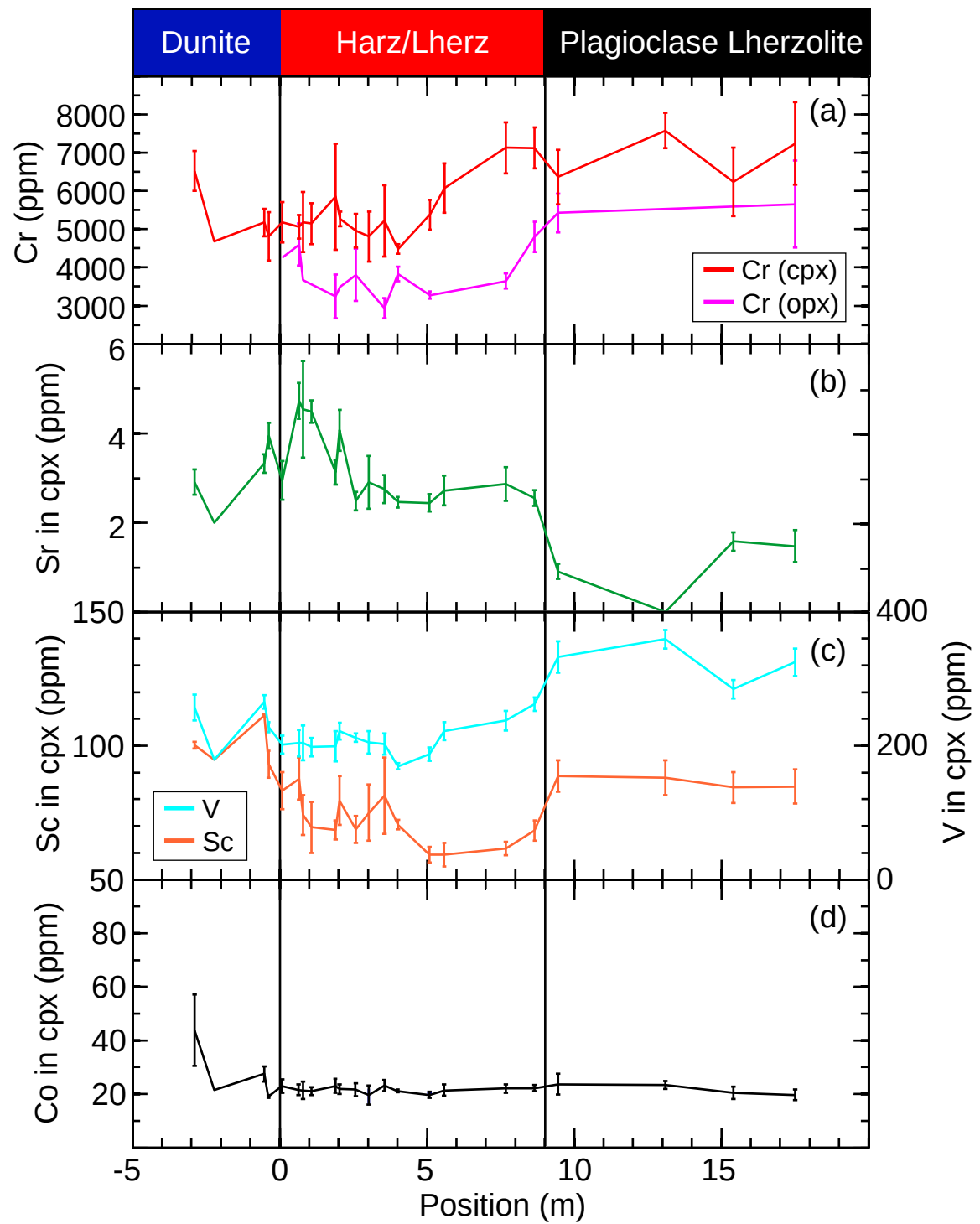
Supplementary Material

Figure S1.



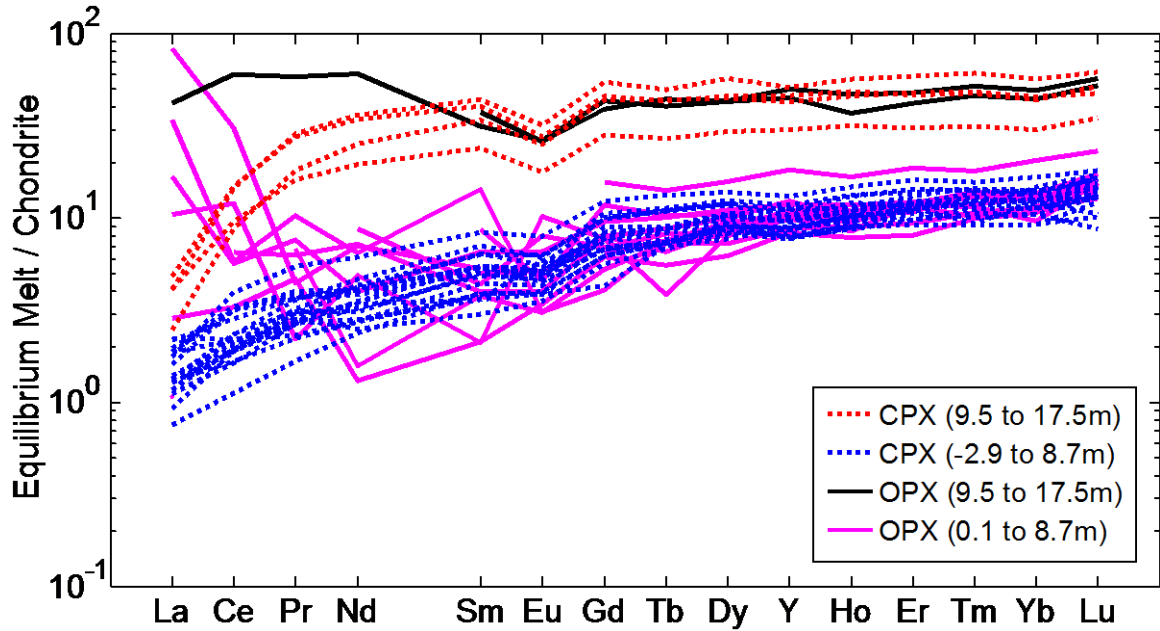
Bulk rock compositions calculated assuming all trace elements are hosted in pyroxene using mineral modes from Morgan *et al.* (2008); (a) is chondrite normalized and (b) is primitive mantle normalized. Note the lack of negative HFSE anomalies.

Figure S2.



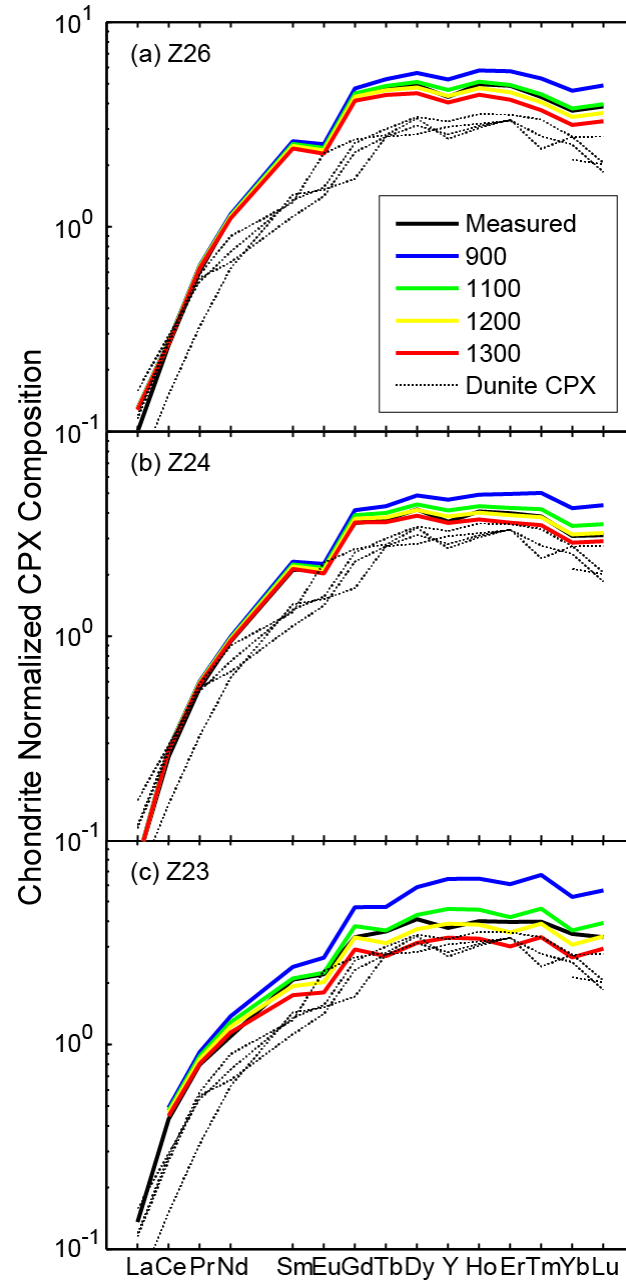
Trace elements concentrations plotted against distance from the dunite-harzburgite contact.

Figure S3.



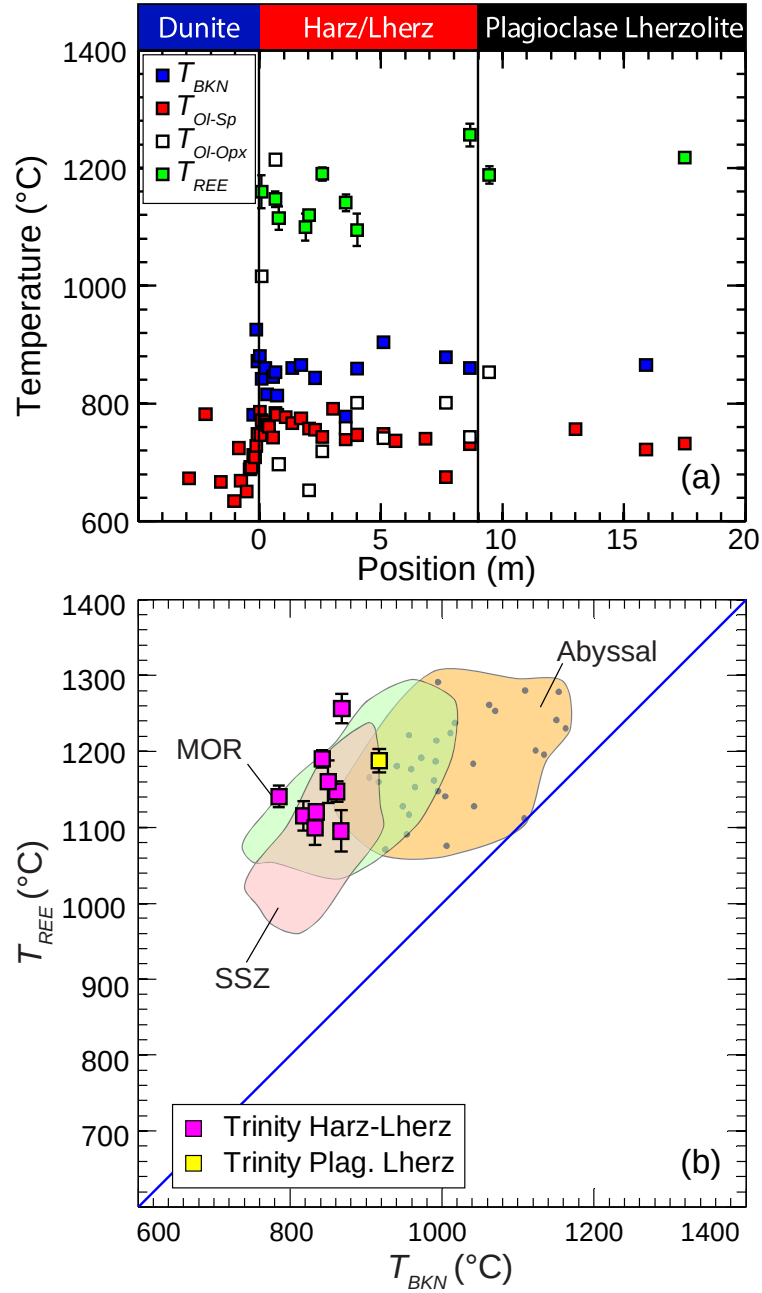
Chondrite normalized melts in equilibrium with clinopyroxene (dotted lines) and orthopyroxene (solid lines) calculated using the partitioning models of Sun & Liang (2012) and Yao *et al.* (2012). Note the consistency of equilibrium melts for clinopyroxene and orthopyroxene suggesting both phases were in equilibrium with the DHL forming infiltrating melt. Low LREE abundances in orthopyroxene makes them difficult to measure resulting in considerable scatter.

Figure S4.



REE+Y in clinopyroxene in three Trinity harzburgites (solid black lines) compared to subsolidus reequilibration corrected concentrations calculated for different temperatures ($^{\circ}\text{C}$) using the method of Sun & Liang (2014) (see Appendix A). Measured REE concentrations fall between compositions calculated for 1100 and 1200 $^{\circ}\text{C}$. Dashed black lines are clinopyroxene in Trinity dunite.

Figure S5.



Temperatures calculated using major element and REE-in-two pyroxene thermometers plotted as a function of distance from the dunite-harzburgite contact (a). Red squares are the olivine-spinel thermometer of Li *et al.*, 1995, blue squares are the two pyroxene thermometer of Brey & Köhler, 1990, white squares are the Ni in olivine

and orthopyroxene thermometer of Kelemen *et al.* (1998), green squares are the thermometer of Liang *et al.*, 2013. (b) REE-in-two-pyroxene temperatures for Trinity samples plotted against temperatures determined using the two pyroxene major element thermometer of Brey & Köhler, 1990. Red field is defined by the global dataset of ophiolites with supra-subduction zone tectonic affinity, green field is from ophiolites with mid-ocean ridge tectonic affinity, the peach field is abyssal peridotites (Dygert *et al.*, 2014).

Table S1.**Core Compositions****Clinopyroxene**

Sample	Z01	1σ	Z04	1σ	Z06	1σ	Z13	1σ
Lithology	Dunite		Dunite		Dunite		Spinel Harz	
Position	-2.89		-0.53		-0.38		0.08	
n Core	2		3		5		12	
Li	-	-	-	-	-	-	-	-
Na₂O	0.148	0.041	0.205	0.017	0.223	0.050	-	-
K₂O	-	-	0.00137	0.00043	-	-	-	-
Sc	100.1	1.2	111.3	0.4	93.1	5.0	83.2	6.9
TiO₂	0.114	0.006	0.129	0.003	0.117	0.004	0.120	0.010
V	257	19	265	10	227	7	201	13
Cr	6519	516	5172	358	4805	630	5174	531
Co	43.8	13.3	27.5	2.8	19.1	0.6	22.9	2.6
Ni	516.0	91.3	292.8	54.7	249.9	6.3	289.9	22.3
Sr	2.91	0.29	3.33	0.21	3.95	0.29	2.95	0.43
Y	4.2	0.5	4.4	0.2	5.1	0.3	5.1	0.4
Zr	1.54	0.41	1.97	0.17	2.28	0.16	1.51	0.19
Nb	-	-	-	-	-	-	-	-
La	0.028	0.006	0.027	0.009	0.037	0.007	0.026	0.005
Ce	0.171	0.009	0.163	0.034	0.177	0.021	0.135	0.024
Pr	0.052	0.001	0.050	0.013	0.048	0.009	0.039	0.009
Nd	0.406	0.066	0.303	0.070	0.341	0.043	0.328	0.059
Sm	0.193	0.045	0.165	0.018	0.199	0.028	0.212	0.051
Eu	0.128	0.036	0.079	0.019	0.087	0.012	0.089	0.013
Gd	0.102	0.019	0.100	0.007	0.109	0.002	0.108	0.010
Tb	0.525	0.122	0.454	0.040	0.505	0.033	0.507	0.056
Dy	0.820	0.186	0.759	0.023	0.835	0.035	0.827	0.097
Ho	0.169	0.020	0.173	0.006	0.198	0.016	0.192	0.019
Er	0.530	0.087	0.527	0.061	0.561	0.080	0.581	0.056
Tm	0.058	0.010	0.067	0.006	0.081	0.008	0.084	0.007
Yb	0.447	0.105	0.410	0.038	0.446	0.027	0.498	0.069
Lu	0.050	0.001	0.045	0.003	0.067	0.005	0.078	0.011
Hf	0.104	0.033	0.124	0.035	0.124	0.020	0.087	0.014
Ta	-	-	-	-	-	-	-	-
Pb	0.015	0.010	0.009	0.006	-	-	0.015	0.011

Na₂O, K₂O, and TiO₂ are reported in wt. %, all other elements in ppm.

Table S1 continued.

Core Compositions								
Clinopyroxene								
Sample	Z18	1σ	Z20	1σ	Z21	1σ	Z27	1σ
Lithology	Spinel Harz		Spinel Harz		Spinel Harz		Spinel Harz	
Position	0.65		0.79		1.08		1.89	
n Core	7		4		4		5	
Li	-	-	1.00	0.19	1.10	0.37	1.17	0.34
Na₂O	-	-	0.254	0.045	0.259	0.031	0.222	0.029
K₂O	-	-	0.00063	0.00030	-	-	0.00055	0.00034
Sc	88.4	7.8	74.1	7.4	69.5	9.4	68.6	3.6
TiO₂	0.116	0.014	0.112	0.007	0.105	0.012	0.103	0.002
V	204	18	204	26	198	14	199	23
Cr	5037	328	5181	783	5143	532	5848	1385
Co	21.6	1.5	21.3	3.2	21.1	1.5	23.0	2.6
Ni	291.7	32.3	268.9	36.0	276.3	19.9	311.8	34.1
Sr	4.67	0.37	4.54	1.08	4.49	0.25	3.14	0.28
Y	6.4	0.4	5.5	0.7	5.0	0.5	4.6	0.3
Zr	2.58	0.17	2.37	0.80	2.28	0.37	1.63	0.10
Nb	-	-	0.0154	0.0144	0.0124	0.0045	0.0100	0.0069
La	0.043	0.008	0.039	0.009	0.037	0.005	0.026	0.010
Ce	0.229	0.040	0.267	0.049	0.258	0.034	0.190	0.020
Pr	0.062	0.015	0.067	0.008	0.066	0.007	0.055	0.004
Nd	0.514	0.067	0.479	0.062	0.464	0.047	0.377	0.060
Sm	0.278	0.053	0.278	0.032	0.284	0.043	0.280	0.052
Eu	0.109	0.020	0.118	0.013	0.113	0.011	0.104	0.007
Gd	0.133	0.017	0.133	0.020	0.124	0.009	0.117	0.023
Tb	0.651	0.101	0.631	0.065	0.612	0.055	0.562	0.027
Dy	1.001	0.095	0.939	0.120	0.845	0.069	0.836	0.111
Ho	0.224	0.020	0.215	0.028	0.207	0.018	0.176	0.011
Er	0.665	0.096	0.602	0.065	0.555	0.053	0.512	0.045
Tm	0.098	0.009	0.085	0.011	0.085	0.005	0.080	0.009
Yb	0.522	0.033	0.504	0.063	0.507	0.051	0.468	0.040
Lu	0.092	0.015	0.078	0.010	0.071	0.005	0.072	0.009
Hf	0.131	0.021	0.098	0.021	0.086	0.016	0.062	0.012
Ta	-	-	-	-	-	-	-	-
Pb	-	-	-	-	0.020	0.001	0.026	0.003

Table S1 continued.

Core Compositions								
Clinopyroxene								
Sample	Z23	1σ	Z24	1σ	Z25	-	Z26	1σ
Lithology	Spinel Harz		Spinel Harz		Spinel Harz		Spinel Harz	
Position	2.04		2.58				3.55	
n Core	3		4		4		6	
Li	0.92	0.18	0.98	0.14	0.91	0.24	-	-
Na₂O	0.270	0.017	0.184	0.016	0.181	0.030	0.213	0.029
K₂O	0.00071	0.00033	0.00035	0.00016	0.00035	0.00015	0.00088	0.00052
Sc	79.5	9.2	68.8	5.0	74.9	10.5	73.0	10.5
TiO₂	0.122	0.009	0.133	0.007	0.144	0.010	0.136	0.010
V	222	13	212	7	205	17	203	18
Cr	5264	197	4953	444	4804	658	5455	1102
Co	21.9	1.8	21.6	2.4	19.6	3.5	22.5	1.8
Ni	285.9	21.3	299.5	31.3	276.1	39.7	327.1	33.1
Sr	4.07	0.46	2.48	0.20	2.91	0.59	2.74	0.41
Y	5.8	0.6	5.7	0.6	7.1	1.1	6.2	0.9
Zr	3.20	0.65	2.56	0.57	3.92	1.26	3.12	0.79
Nb	0.0117	0.0040	0.0106	0.0028	0.0094	0.0020	0.0112	0.0041
La	0.032	0.011	0.018	0.004	0.023	0.006	0.024	0.007
Ce	0.260	0.019	0.156	0.009	0.190	0.013	0.170	0.049
Pr	0.071	0.004	0.050	0.003	0.064	0.008	0.056	0.011
Nd	0.496	0.046	0.427	0.028	0.568	0.054	0.501	0.056
Sm	0.304	0.014	0.310	0.014	0.399	0.026	0.360	0.043
Eu	0.123	0.008	0.119	0.010	0.143	0.010	0.130	0.024
Gd	0.129	0.008	0.135	0.010	0.175	0.026	0.158	0.015
Tb	0.657	0.047	0.703	0.062	0.894	0.089	0.799	0.111
Dy	0.993	0.078	1.011	0.068	1.224	0.161	1.096	0.139
Ho	0.223	0.022	0.226	0.027	0.277	0.040	0.257	0.048
Er	0.631	0.089	0.634	0.045	0.737	0.125	0.692	0.105
Tm	0.096	0.012	0.093	0.013	0.105	0.018	0.099	0.012
Yb	0.563	0.071	0.502	0.064	0.607	0.101	0.566	0.064
Lu	0.081	0.011	0.076	0.006	0.088	0.016	0.083	0.008
Hf	0.150	0.038	0.125	0.028	0.180	0.065	0.164	0.027
Ta	-	-	-	-	-	-	-	-
Pb	0.022	0.014	0.024	0.009	0.015	0.012	-	-

Table S1 continued.

Core Compositions								
Clinopyroxene								
Sample	TP90.13	1σ	TP90.14	1σ	TP90.16	1σ	TP90.17	1σ
Lithology	Spinel Lherz		Spinel Lherz		Plag Lherz		Plag Lherz	
Position	5.09		5.59		7.68		8.66	
n Core	3		7		6		5	
Li	-	-	-	-	-	-	-	-
Na₂O	0.325	0.139	0.364	0.222	0.424	0.150	0.361	0.115
K₂O	0.01086	0.00913	-	-	0.01568	0.01216	0.00796	0.00559
Sc	57.8	1.0	57.8	4.1	60.9	2.7	65.5	1.7
TiO₂	0.099	0.003	0.127	0.012	0.152	0.007	0.178	0.012
V	191	7	228	16	246	7	257	8
Cr	5668	210	6569	323	7395	637	7256	500
Co	20.7	0.6	22.2	2.2	22.3	1.8	22.2	1.5
Ni	345.6	10.5	353.4	37.3	339.9	30.1	352.6	34.0
Sr	2.41	0.27	2.84	0.42	3.01	0.40	2.58	0.20
Y	5.0	0.2	5.5	0.6	7.1	0.3	8.8	0.3
Zr	1.84	0.57	2.69	0.86	4.31	1.06	5.10	0.91
Nb	0.0133	0.0045	0.0206	0.0050	0.0241	0.0049	0.0181	0.0050
La	0.047	0.016	0.029	0.010	0.033	0.010	0.039	0.006
Ce	0.164	0.036	0.159	0.043	0.196	0.039	0.344	0.027
Pr	0.040	0.007	0.049	0.007	0.064	0.010	0.102	0.007
Nd	0.354	0.051	0.420	0.059	0.587	0.061	0.784	0.037
Sm	0.245	0.035	0.310	0.043	0.387	0.038	0.499	0.049
Eu	0.103	0.012	0.113	0.008	0.163	0.023	0.200	0.013
Gd	0.115	0.018	0.145	0.024	0.192	0.017	0.222	0.015
Tb	0.595	0.058	0.682	0.119	0.924	0.104	1.111	0.054
Dy	0.833	0.031	0.986	0.184	1.264	0.141	1.514	0.077
Ho	0.192	0.008	0.230	0.041	0.279	0.025	0.349	0.011
Er	0.500	0.024	0.572	0.104	0.718	0.059	0.983	0.091
Tm	0.074	0.001	0.085	0.011	0.102	0.016	0.133	0.015
Yb	0.415	0.039	0.482	0.096	0.613	0.059	0.838	0.024
Lu	0.074	0.005	0.079	0.017	0.091	0.005	0.123	0.010
Hf	0.066	0.029	0.156	0.029	0.232	0.055	0.249	0.038
Ta	-	-	-	-	-	-	-	-
Pb	0.348	0.075	-	-	0.154	0.114	0.185	0.014

Table S1 continued.

Core Compositions								
Clinopyroxene								
Sample	17BK	1σ	18A	1σ	19BK	1σ	19B	1σ
	Plag		Plag		Plag		Plag	
Lithology	Lherz		Lherz		Lherz		Lherz	
Position	9.46		13.1		15.41		17.51	
n Core	8		6		13		15	
Li	-	-	-	-	-	-	-	-
Na₂O	0.228	0.019	0.402	0.064	0.289	0.021	0.427	0.078
K₂O	-	-	-	-	-	-	0.00069	0.00051
Sc	86.9	4.5	86.3	7.3	82.6	6.0	82.3	7.9
TiO₂	0.491	0.028	0.589	0.021	0.407	0.059	0.608	0.061
V	331	18	359	17	288	13	328	18
Cr	6566	709	7805	464	6598	773	7859	596
Co	24.2	4.9	23.7	1.3	20.8	2.4	20.2	2.2
Ni	375.3	108.5	330.0	17.4	319.4	47.5	296.8	33.7
Sr	0.85	0.06	-	-	1.63	0.20	1.54	0.33
Y	29.1	1.5	37.9	0.9	23.6	4.5	38.5	3.7
Zr	15.64	1.51	28.29	1.85	22.59	4.85	36.77	4.40
Nb	-	-	-	-	-	-	0.0180	0.0067
La	0.050	0.007	0.084	0.010	0.090	0.008	0.106	0.011
Ce	0.740	0.029	1.278	0.099	0.858	0.073	1.361	0.117
Pr	0.339	0.025	0.551	0.023	0.319	0.045	0.566	0.040
Nd	3.192	0.241	4.863	0.130	2.695	0.440	4.965	0.394
Sm	2.006	0.138	2.816	0.110	1.596	0.335	2.846	0.259
Eu	0.625	0.047	0.862	0.035	0.501	0.066	0.811	0.063
Gd	0.743	0.044	0.919	0.031	0.533	0.106	0.889	0.084
Tb	4.055	0.227	5.432	0.236	2.900	0.587	4.997	0.441
Dy	4.945	0.234	6.768	0.371	3.736	0.739	6.092	0.507
Ho	1.096	0.050	1.438	0.054	0.876	0.167	1.427	0.125
Er	2.959	0.189	3.946	0.190	2.243	0.407	3.577	0.341
Tm	0.411	0.028	0.570	0.025	0.316	0.058	0.507	0.052
Yb	2.330	0.149	3.197	0.047	1.818	0.329	2.871	0.241
Lu	0.321	0.032	0.468	0.018	0.290	0.040	0.457	0.036
Hf	0.848	0.112	1.220	0.151	0.843	0.235	1.488	0.204
Ta	-	-	-	-	-	-	-	-
Pb	-	-	0.006	0.003	0.010	0.005	0.013	0.009

Table S1 continued.

Rim Compositions								
Clinopyroxene								
Sample	Z18	1σ	Z26	1σ	TP90.11	1σ	TP90.13	1σ
Lithology	Spinel Harz		Spinel Harz		Spinel Harz		Spinel Lherz	
Position	0.65		3.55		4.01		5.09	
n Rim	3		4		2		3	
Li	-	-	-	-	-	-	-	-
Na₂O	-	-	0.204	0.017	0.236	0.071	0.173	0.015
K₂O	-	-	0.00151	0.00028	0.00360	0.00338	0.00117	0.00022
Sc	86.0	9.2	93.8	9.0	70.6	2.5	60.8	3.8
TiO₂	0.118	0.018	0.153	0.010	0.114	0.004	0.105	0.010
V	204	27	201	16	167	4	183	12
Cr	5114	284	4852	560	4407	53	5091	284
Co	21.5	3.0	24.4	2.0	21.0	0.7	18.6	0.4
Ni	295.1	16.6	376.6	13.8	289.7	12.9	298.1	4.1
Sr	4.87	0.52	2.76	0.12	2.52	0.08	2.48	0.14
Y	6.5	0.3	7.5	0.3	6.3	0.3	5.4	0.2
Zr	2.56	0.28	3.39	0.25	2.50	0.12	1.81	0.31
Nb	-	-	-	-	0.0101	0.0035	0.0151	0.0026
La	0.041	0.002	0.023	0.006	0.022	0.004	0.041	0.030
Ce	0.232	0.019	0.143	0.009	0.131	0.010	0.199	0.101
Pr	0.070	0.010	0.051	0.008	0.047	0.002	0.043	0.003
Nd	0.490	0.027	0.515	0.013	0.412	0.012	0.336	0.037
Sm	0.342	0.054	0.371	0.035	0.300	0.021	0.267	0.035
Eu	0.111	0.008	0.130	0.012	0.120	0.018	0.103	0.015
Gd	0.135	0.010	0.193	0.005	0.139	0.011	0.121	0.012
Tb	0.708	0.032	0.938	0.060	0.731	0.134	0.616	0.095
Dy	0.959	0.025	1.338	0.055	1.082	0.087	0.892	0.083
Ho	0.227	0.019	0.305	0.018	0.248	0.002	0.199	0.024
Er	0.691	0.042	0.902	0.072	0.726	0.087	0.543	0.060
Tm	0.106	0.004	0.111	0.005	0.090	0.004	0.068	0.005
Yb	0.560	0.011	0.650	0.038	0.684	0.043	0.428	0.045
Lu	0.082	0.011	0.110	0.006	0.102	0.010	0.074	0.005
Hf	0.130	0.020	0.240	0.032	0.139	0.018	0.119	0.019
Ta	-	-	-	-	-	-	-	-
Pb	-	-	-	-	0.081	0.054	0.180	0.090

Table S1 continued.

Rim Compositions								
Clinopyroxene								
Sample	TP90.14	1 σ	TP90.16	1 σ	TP90.17	1 σ	17BK	1 σ
			Plag		Plag		Plag	
Lithology	Spinel Lherz		Lherz		Lherz		Lherz	
Position	5.59		7.68		8.66		9.46	
n Rim	7		3		5		7	
Li	-	-	-	-	-	-	-	-
Na ₂ O	0.278	0.097	0.262	0.029	0.276	0.052	0.281	0.147
K ₂ O	0.00507	0.00433	-	-	0.00295	0.00254	-	-
Sc	60.7	4.4	62.9	1.9	71.2	3.1	90.9	7.1
TiO ₂	0.126	0.012	0.142	0.004	0.203	0.008	0.516	0.099
V	215	8	221	8	267	10	334	32
Cr	5570	468	6576	350	6980	587	6086	662
Co	20.6	1.7	21.8	1.2	22.2	0.8	22.9	1.7
Ni	327.2	29.0	340.0	21.7	380.3	88.9	343.3	51.6
Sr	2.60	0.15	2.58	0.01	2.53	0.17	0.99	0.24
Y	5.5	0.7	6.5	0.3	9.1	0.6	29.5	3.3
Zr	2.58	0.66	2.82	0.14	5.80	0.39	15.63	1.85
Nb	0.0143	0.0044	0.0232	0.0043	0.0149	0.0057	0.0155	0.0095
La	0.023	0.008	0.020	0.008	0.033	0.006	0.050	0.012
Ce	0.155	0.018	0.149	0.009	0.327	0.038	0.731	0.064
Pr	0.048	0.010	0.051	0.001	0.102	0.012	0.335	0.039
Nd	0.397	0.036	0.491	0.044	0.805	0.104	3.358	0.428
Sm	0.262	0.039	0.366	0.009	0.518	0.061	2.148	0.286
Eu	0.114	0.016	0.143	0.010	0.202	0.021	0.650	0.072
Gd	0.141	0.016	0.171	0.013	0.234	0.018	0.776	0.073
Tb	0.680	0.100	0.857	0.025	1.184	0.082	4.123	0.425
Dy	0.957	0.134	1.290	0.090	1.535	0.162	5.092	0.613
Ho	0.220	0.026	0.284	0.025	0.350	0.034	1.100	0.144
Er	0.542	0.066	0.674	0.051	1.005	0.057	3.051	0.342
Tm	0.080	0.011	0.095	0.004	0.131	0.018	0.416	0.052
Yb	0.483	0.074	0.619	0.100	0.848	0.109	2.352	0.303
Lu	0.080	0.014	0.092	0.006	0.121	0.011	0.330	0.032
Hf	0.165	0.050	0.177	0.031	0.281	0.058	0.871	0.166
Ta	-	-	-	-	-	-	-	-
Pb	0.065	0.049	-	-	-	-	-	-

Table S1 continued.

Rim Compositions						
Clinopyroxene						
Sample	18A	1σ	19BK	1σ	19B	1σ
	Plag		Plag		Plag	
Lithology	Lherz		Lherz		Lherz	
Position	13.1		15.41		17.51	
n Rim	6		8		9	
Li	-	-	-	-	-	-
Na₂O	0.368	0.012	0.261	0.020	0.349	0.030
K₂O	-	-	-	-	-	-
Sc	90.6	4.6	87.2	4.5	86.9	3.5
TiO₂	0.600	0.032	0.398	0.041	0.558	0.073
V	359	9	278	12	321	22
Cr	7226	172	5630	769	6658	1104
Co	22.9	1.6	19.7	2.1	19.3	1.8
Ni	310.3	16.8	290.1	31.4	286.5	25.1
Sr	-	-	1.51	0.21	1.41	0.38
Y	38.0	2.6	22.7	3.6	35.9	4.8
Zr	28.78	2.48	21.48	3.89	33.03	5.95
Nb	0.0199	0.0069	-	-	-	-
La	0.084	0.006	0.078	0.006	0.098	0.017
Ce	1.215	0.056	0.786	0.074	1.244	0.138
Pr	0.529	0.020	0.295	0.040	0.510	0.059
Nd	4.717	0.157	2.526	0.304	4.498	0.608
Sm	2.751	0.221	1.490	0.237	2.544	0.390
Eu	0.829	0.054	0.456	0.064	0.735	0.096
Gd	0.906	0.079	0.486	0.073	0.814	0.126
Tb	5.306	0.357	2.749	0.416	4.586	0.653
Dy	6.880	0.518	3.529	0.575	5.712	0.769
Ho	1.483	0.110	0.828	0.120	1.316	0.187
Er	4.018	0.292	2.133	0.347	3.331	0.491
Tm	0.565	0.032	0.304	0.046	0.481	0.066
Yb	3.175	0.140	1.758	0.234	2.667	0.332
Lu	0.466	0.038	0.269	0.039	0.426	0.061
Hf	1.263	0.108	0.823	0.169	1.346	0.241
Ta	-	-	-	-	-	-
Pb	0.008	0.007	0.011	0.007	-	-

Table S1 continued.

Core Compositions								
Orthopyroxene								
Sample	Z18	1σ	Z27	1σ	Z24	1σ	Z26	1σ
Lithology	Spinel Harz		Spinel Harz		Spinel Harz		Spinel Harz	
Position	0.65		1.89		2.58		3.55	
n Core	6		2		2		4	
Li	-	-	0.26	0.02	0.23	0.06	-	-
Na₂O	-	-	0.007	0.001	0.012	0.005	0.012	0.009
K₂O	-	-	0.00032	0.00025	-	-	-	-
Sc	39.8	4.3	31.7	0.5	33.9	2.9	34.4	1.7
TiO₂	0.085	0.007	0.060	0.003	0.075	0.000	0.081	0.004
V	123	10	96	7	113	5	96	6
Cr	4702	653	3233	570	3802	687	2897	329
Co	77.8	2.6	61.1	1.9	59.8	0.5	59.7	1.6
Ni	785	65	620	31	631	7	715	102
Sr	-	-	0.014	0.007	-	-	-	-
Y	0.92	0.15	0.61	0.11	0.90	0.19	0.88	0.13
Zr	0.37	0.19	0.16	0.03	0.35	0.13	0.33	0.08
Nb	-	-	0.0070	0.0014	0.0072	0.0026	-	-
La	-	-	-	-	0.0001	0.0001	-	-
Ce	-	-	0.0014	0.0009	-	-	0.0020	0.0020
Pr	-	-	0.0006	0.0005	-	-	-	-
Nd	0.0129	0.0116	0.0019	0.0007	-	-	0.0084	0.0015
Sm	-	-	0.0030	0.0001	0.0122	0.0097	0.0086	0.0044
Eu	-	-	0.0028	0.0015	0.0037	0.0024	0.0051	0.0027
Gd	0.0096	0.0024	0.0059	0.0015	0.0112	0.0047	0.0109	0.0037
Tb	0.0395	0.0163	0.0253	0.0049	0.0491	0.0264	0.0398	0.0101
Dy	0.1037	0.0279	0.0604	0.0098	0.1021	0.0272	0.1063	0.0245
Ho	0.0289	0.0072	0.0224	0.0043	0.0315	0.0103	0.0331	0.0090
Er	0.1245	0.0218	0.0808	0.0117	0.1195	0.0199	0.1311	0.0057
Tm	0.0256	0.0034	0.0179	0.0012	0.0245	0.0045	0.0233	0.0040
Yb	0.1830	0.0255	0.1483	0.0058	0.1813	0.0078	0.1794	0.0231
Lu	0.0388	0.0049	0.0308	0.0018	0.0352	0.0022	0.0366	0.0028
Hf	0.0164	0.0074	0.0080	0.0011	0.0209	0.0095	0.0192	0.0070
Ta	-	-	0.00016	0.00008	0.00060	0.00036	-	-
Pb	-	-	0.0284	0.0032	0.0244	0.0006	-	-

Table S1 continued.

Core Compositions								
Orthopyroxene								
Sample	TP90.11	1σ	TP90.16	1σ	TP90.17	1σ	17BK	1σ
Lithology	Spinel Harz		Plag Lherz		Plag Lherz		Plag Lherz	
Position	4.01		7.68		8.66		9.46	
n Core	4		3		2		3	
Li	-	-	-	-	-	-	-	-
Na₂O	0.050	0.040	0.021	0.009	-	-	0.023	0.005
K₂O	0.00408	0.00348	0.00172	0.00019	-	-	-	-
Sc	30.1	0.7	32.5	1.5	34.2	1.0	40.5	0.4
TiO₂	0.062	0.003	0.081	0.004	0.177	0.018	0.230	0.009
V	91	1	109	5	130	3	187	1
Cr	3869	224	3627	284	5177	147	5801	230
Co	59.3	0.9	58.5	1.8	57.7	0.2	64.9	0.2
Ni	718	10	697	31	685	5	746	7
Sr	0.101	0.061	0.050	0.031	-	-	0.056	0.010
Y	0.72	0.06	0.81	0.12	1.11	0.06	3.92	0.25
Zr	0.60	0.19	0.47	0.07	2.58	1.05	3.69	0.76
Nb	0.0100	0.0020	0.0094	0.0041	0.0122	0.0109	-	-
La	-	-	-	-	-	-	0.0042	0.0035
Ce	0.0119	0.0083	0.0032	0.0013	-	-	0.0451	0.0015
Pr	0.0014	0.0008	0.0003	0.0001	-	-	0.0142	0.0058
Nd	-	-	0.0047	0.0012	0.0090	0.0028	0.1603	0.0642
Sm	0.0060	0.0029	0.0080	0.0061	0.0242	0.0052	0.0637	0.0346
Eu	-	-	0.0039	0.0019	-	-	0.0332	0.0024
Gd	0.0103	0.0039	0.0082	0.0025	0.0076	0.0047	0.0649	0.0165
Tb	0.0246	0.0028	0.0356	0.0115	0.0544	0.0001	0.2514	0.0181
Dy	0.0779	0.0162	0.1033	0.0253	0.1253	0.0066	0.5363	0.0640
Ho	0.0286	0.0073	0.0279	0.0048	0.0456	0.0023	0.1252	0.0130
Er	0.1093	0.0160	0.1223	0.0288	0.1664	0.0206	0.4728	0.0609
Tm	0.0181	0.0041	0.0268	0.0031	0.0324	0.0056	0.1017	0.0277
Yb	0.1595	0.0187	0.1849	0.0064	0.2743	0.0045	0.6948	0.0856
Lu	0.0298	0.0026	0.0303	0.0058	0.0554	0.0090	0.1218	0.0116
Hf	0.0273	0.0109	0.0331	0.0065	0.1472	0.0466	0.1752	0.0404
Ta	-	-	-	-	0.00081	0.00017	-	-
Pb	0.0863	0.0612	0.0267	0.0037	-	-	-	-

Table S1 continued.

Core Compositions		
Orthopyroxene		
Sample	19B	1σ
Lithology	Plag Lherz	
Position	17.51	
n Core	-	
Li	-	-
Na₂O	0.036	0.016
K₂O	-	-
Sc	41.0	2.0
TiO₂	0.244	0.022
V	186	11
Cr	6035	727
Co	64.9	4.5
Ni	742	52
Sr	0.041	0.022
Y	4.21	0.75
Zr	4.00	0.94
Nb	-	-
La	-	-
Ce	-	-
Pr	0.0087	0.0077
Nd	-	-
Sm	0.0602	0.0360
Eu	0.0220	0.0170
Gd	0.0541	0.0194
Tb	0.1810	0.1011
Dy	0.4817	0.1320
Ho	0.1531	0.0296
Er	0.5454	0.1055
Tm	0.1058	0.0168
Yb	0.7672	0.1155
Lu	0.1477	0.0162
Hf	0.1615	0.0542
Ta	-	-
Pb	-	-

Table S1 continued.

Rim Compositions								
Orthopyroxene								
Sample	Z18	1σ	Z26	1σ	TP90.11	1σ	TP90.13	1σ
Lithology	Spinel Harz		Spinel Harz		Spinel Harz		Spinel Lherz	
Position	0.65		3.55		4.01		5.09	
n Rim	5		2		3		2	
Li	-	-	-	-	-	-	-	-
Na₂O	0.009	0.003	0.012	0.010	0.006	0.003	-	-
K₂O	-	-	0.00082	0.00055	0.00044	0.00008	-	-
Sc	41.2	1.7	36.6	0.9	28.9	0.9	33.1	0.1
TiO₂	0.079	0.005	0.083	0.001	0.061	0.001	0.071	0.002
V	121	8	98	1	92	2	91	0
Cr	4432	345	3005	35	3775	156	3241	109
Co	77.4	2.2	57.1	1.0	60.5	0.7	55.3	0.3
Ni	782	25	645	4	721	8	671	19
Sr	0.034	0.009	0.033	0.020	0.008	0.004	-	-
Y	0.90	0.07	0.91	0.00	0.58	0.04	0.84	0.06
Zr	0.24	0.04	0.40	0.08	0.31	0.04	0.37	0.22
Nb	0.0115	0.0068	0.0073	0.0060	0.0088	0.0040	-	-
La	-	-	-	-	-	-	-	-
Ce	0.0038	0.0034	0.0033	0.0005	0.0019	0.0014	-	-
Pr	-	-	0.0014	0.0003	-	-	-	-
Nd	-	-	-	-	-	-	0.0099	0.0065
Sm	-	-	0.0108	0.0050	-	-	-	-
Eu	0.0047	0.0025	0.0059	0.0031	0.0015	0.0013	0.0081	0.0030
Gd	0.0090	0.0023	0.0110	0.0028	0.0046	0.0017	0.0082	0.0072
Tb	0.0224	0.0065	0.0400	0.0044	0.0187	0.0061	-	-
Dy	0.0864	0.0135	0.1149	0.0049	0.0634	0.0102	0.0676	0.0121
Ho	0.0276	0.0017	0.0359	0.0074	0.0229	0.0031	0.0289	0.0060
Er	0.1139	0.0131	0.1088	0.0196	0.0760	0.0033	0.1230	0.0188
Tm	0.0233	0.0028	0.0248	0.0007	0.0214	0.0013	0.0189	0.0090
Yb	0.1954	0.0204	0.1757	0.0030	0.1602	0.0146	0.1604	0.0190
Lu	0.0409	0.0034	0.0342	0.0013	0.0309	0.0032	0.0274	0.0061
Hf	0.0105	0.0037	0.0187	0.0007	0.0130	0.0042	0.0173	0.0019
Ta	-	-	0.00146	0.00027	0.00057	0.00021	-	-
Pb	-	-	-	-	0.0466	0.0208	-	-

Table S1 continued.

Rim Compositions								
Orthopyroxene								
Sample	TP90.16	1σ	TP90.17	1σ	17BK	1σ	19B	1σ
Lithology	Plag		Plag		Plag		Plag	
	Lherz		Lherz		Lherz		Lherz	
Position	7.68		8.66		9.46		17.51	
n Rim	5		3		3		-	
Li	-	-	-	-	-	-	-	-
Na₂O	-	-	0.022	0.021	0.008	0.004	0.022	0.007
K₂O	0.00585	0.00582	-	-	0.00065	0.00064	0.00079	0.00039
Sc	32.1	2.6	36.8	3.6	37.1	0.4	39.5	4.8
TiO₂	0.083	0.006	0.145	0.031	0.230	0.020	0.248	0.034
V	108	4	126	9	175	3	152	20
Cr	3644	169	4537	232	5042	374	3912	1166
Co	59.2	2.7	57.3	0.8	64.5	1.0	59.5	3.2
Ni	704	27	680	7	720	3	643	17
Sr	0.115	0.110	-	-	-	-	-	-
Y	0.80	0.16	1.63	0.49	3.06	0.23	3.57	0.46
Zr	0.77	0.44	1.61	0.82	1.69	0.44	2.44	0.83
Nb	0.0116	0.0082	0.0091	0.0027	-	-	-	-
La	0.0096	0.0045	0.0009	0.0004	-	-	-	-
Ce	0.0195	0.0091	-	-	0.0074	0.0030	0.0202	0.0017
Pr	-	-	-	-	-	-	0.0078	0.0054
Nd	-	-	0.0234	0.0179	-	-	0.0535	0.0282
Sm	-	-	-	-	0.0283	0.0034	0.0420	0.0214
Eu	-	-	0.0099	0.0086	0.0114	0.0014	0.0265	0.0064
Gd	0.0085	0.0063	0.0213	0.0115	0.0264	0.0066	0.0436	0.0042
Tb	-	-	0.0760	0.0434	0.1213	0.0240	0.1536	0.0109
Dy	0.0915	0.0145	0.1832	0.0750	0.3410	0.0680	0.3832	0.0710
Ho	0.0310	0.0075	0.0534	0.0144	0.0977	0.0196	0.1249	0.0131
Er	0.1164	0.0153	0.2163	0.0429	0.4137	0.0122	0.4788	0.0916
Tm	0.0233	0.0076	0.0351	0.0031	0.0735	0.0099	0.0962	0.0122
Yb	0.1832	0.0266	0.3152	0.0367	0.5986	0.0091	0.7221	0.0466
Lu	0.0302	0.0070	0.0555	0.0080	0.1315	0.0013	0.1413	0.0159
Hf	0.0307	0.0214	0.0865	0.0405	0.0960	0.0274	0.1139	0.0246
Ta	-	-	-	-	-	-	-	-
Pb	0.1531	0.0388	0.0397	0.0321	-	-	-	-

Table S2.

Thermometry								
Sample	Position	T _{BKN} ¹	T _{Putirka} ²	T _{Wells} ³	T _{Ol-Sp} ⁴	T _{Ol-Opx} ⁵	T _{REE} ⁶	T _{REE} Uncertainty (1 σ)
30Z01	-2.89	-	-	-	673	-	-	-
30Z02	-2.22	-	-	-	782	-	-	-
30Z03	-1.59	-	-	-	667	-	-	-
Z01	-1.04	-	-	-	634	-	-	-
TP90.2	-0.86	-	-	-	724	-	-	-
Z03	-0.76	-	-	-	669	-	-	-
Z04	-0.53	-	-	-	651	-	-	-
Z05	-0.4	-	-	-	688	-	-	-
Z06	-0.38	-	-	-	692	-	-	-
Z07	-0.32	-	-	-	691	-	-	-
Z08	-0.25	781	835	867	713	-	-	-
Z09	-0.18	-	-	-	709	-	-	-
Z10	-0.13	926	939	969	728	-	-	-
TP90.3	-0.07	872	890	929	-	-	-	-
Z11	-0.02	-	-	-	748	-	-	-
TP90.4	0.02	881	896	936	-	-	-	-
Z12	0.03	-	-	-	-	-	-	-
Z13	0.08	842	879	911	786	1016	1160	28
Z14	0.24	860	893	921	747	-	-	-
Z15	0.3	815	870	892	771	-	-	-
Z16	0.38	763	866	853	769	-	-	-
Z17	0.56	846	871	911	764	-	-	-
Z18	0.65	853	888	918	761	1214	1147	13
Z19	0.72	813	847	889	743	-	-	-
Z20	0.79	-	-	-	784	697	1115	20
Z21	1.08	-	-	-	781	-	-	-
TP90.7	1.35	861	873	921	-	-	-	-
Z27	1.08	-	-	-	-	-	1099	23
Z22	1.7	865	898	923	-	-	-	-
Z23	2.04	-	-	-	777	653	1120	5
TP90.9	2.28	844	875	910	767	-	-	-
Z24	2.58	-	-	-	775	719	1190	11

¹Brey & Köhler, 1990.²Putirka, 2008.³Wells, 1977.⁴Li *et al.*, 1995.⁵Kelemen *et al.*, 1998.⁶Liang *et al.*, 2013.

Table S2 continued.

Sample	Position	T_{BKN}¹	T_{Putirka}²	T_{Wells}³	T_{Ol-Sp}⁴	T_{Ol-Opx}⁵	T_{REE}⁶	T_{REE} Uncertainty (1σ)
Z25	3.03	-	-	-	757		-	-
Z26	3.55	778	848	866	756	758	1141	14
TP90.11	4.01	859	877	925	743	801	1095	27
TP90.13	5.09	904	903	956	739	741	-	-
TP90.14	5.59	-	0	-	747	-	-	-
TP90.15	6.38	-	-	-	748	-	-	-
TP90.16	7.68	878	900	932	736	801	-	-
TP90.17	8.66	861	891	919	740	743	1256	19
17BK	9.46	-	-	-	675	853	1188	15
18A	13.1	-	-	-	731	-	-	-
18BK	13.71	-	-	-	757	-	-	-
TP90.19	15.91	866	909	916	722	-	-	-
19B	17.51	-	-	-	732	-	1218	8

Appendix A: Subsolidus Reequilibration

Interpretation of any spatial-geochemical data in mantle samples requires consideration of the effects of diffusive reequilibration at the subsolidus state. Subsolidus reequilibration among minerals can in some cases completely overprint compositional variations generated by magmatic processes. In other cases, the combined effects of lithological variability and subsolidus reequilibration can generate concentration gradients resembling those of magmatic origin that are actually caused by diffusive exchange. Utilizing the concept of mean square diffusive penetration distance, Morgan *et al.* (2008) determined that fast-diffusing cations such as Fe-Mg, Ca, and Li are capable of significant redistribution (e.g., meters to hundreds of meters in olivine) at geologically relevant cooling rates (1-100 °C/Myr) and temperatures, while slower diffusing cations such as REE and HFSE are essentially immobile. In order to interpret the NiO in olivine gradient from the Trinity traverse (Figure 4b), Morgan *et al.* (2008) used modal abundances calculated from bulk rock analyses, bulk NiO content calculated from modal mineralogy data and microprobe analyses, and temperature dependent mineral-mineral partition coefficients (Witt-Eickschen & O'Neill, 2005) to recalculate NiO concentrations in olivine across the transect at an assumed magmatic temperature of 1300°C. The analysis suggests that the NiO gradient in olivine is magmatic in origin and statistically significant.

We observed a gradient in Cr concentrations in pyroxene and spinel (e.g., Supplementary Figure S2a), and taking the approach of Morgan *et al.*, 2008, investigated Cr using temperature-dependent partition coefficients determined from Witt-Eickschen &

O'Neill (2005). Bulk rock data for Cr is limited and we were only able to calculate an equilibrium temperature for one sample (3001Z26, 3.55 m from the dunite-harzburgite contact). The analysis suggests Cr reequilibrated among the minerals to a temperature of ~800°C. The observed Cr gradients may partly reflect magmatic processes, but the significance of the observed gradients cannot be determined with currently available data.

Subsolidus Reequilibration and High Field Strength Element Anomalies

HFSE depletion in extrusive rocks is often used as a proxy for hydrous melting, but subsolidus reequilibration complicates the interpretation of negative HFSE anomalies in melting residues. Orthopyroxene often exhibit positive HFSE anomalies complementary to negative anomalies in clinopyroxene (e.g., Rampone *et al.*, 1991) making it difficult to conclude a sample is depleted in HFSE without bulk rock data or a negative HFSE anomaly in orthopyroxene. Preliminary models of orthopyroxene-clinopyroxene HFSE partitioning show some temperature sensitivity (Sun, 2014). However, orthopyroxene-clinopyroxene REE partition coefficients are known to be highly temperature sensitive, decreasing with decreasing temperature (e.g., Sun & Liang, 2014). Positive HFSE anomalies in orthopyroxene likely develop from subsolidus redistribution of REE around HFSE. An additional contribution to apparent anomalies is the order in which elements are plotted, corresponding to their compatibility in bulk mantle rather than pyroxene. For example, Ti has a partition coefficient closer to Lu than middle-REE in pyroxene (e.g., Dygert *et al.*, 2014b). Calculated bulk rock compositions

for Trinity harzburgites do not have negative HFSE anomalies (Supplementary Figure S1).

Subsolidus Reequilibration and Rare Earth Elements

Orthopyroxene-clinopyroxene partition coefficients for REE are strongly temperature dependent (e.g., Sun & Liang, 2014) and subsolidus exchange of REE between orthopyroxene and clinopyroxene will occur where the two phases coexist. To determine the influence of this process on REE distribution in Trinity harzburgite, we recalculated pyroxene REE abundances as a function of temperature for three samples for which bulk rock data is available (Z26, Z23 and Z24). Using mineral modes from the bulk rock data (Morgan *et al.*, 2008) and assuming olivine and spinel are free of REE, the bulk REE abundance of the rock is calculated. Temperature dependent orthopyroxene-clinopyroxene partition coefficients are calculated using Sun & Liang (2012) and Yao *et al.* (2012) assuming major element compositions do not vary as a function of temperature. Finally, REE concentrations in orthopyroxene and clinopyroxene are calculated as a function of temperature, which are plotted in Supplementary Figure S4. Measured concentrations in clinopyroxene are shown by the solid black lines and calculated compositions for a range of temperatures are shown by the solid colored lines. The measured concentrations fall between the 1100° and 1200° calculated compositions, similar to temperatures given by the REE-in-two pyroxene thermometer (Liang *et al.*, 2013) which are reported in Appendix B.

REE concentrations in dunite clinopyroxene (which should be unaffected by subsolidus reequilibration with orthopyroxene) are shown for comparison with the calculated concentrations. Assuming they crystallized from the same melt as the harzburgite clinopyroxene, the slightly lower concentrations suggest that major element redistribution during cooling may have a small but important effect on orthopyroxene-clinopyroxene partition coefficients. Trace element concentrations in dunite clinopyroxene can be used as most representative of the infiltrating melt composition.

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Appendix B: Major and Trace Element Thermometry

Temperatures determined using major element two pyroxene, olivine-spinel, and olivine-orthopyroxene thermometers (Brey & Köhler, 1990; Li *et al.*, 1995; Kelemen *et al.*, 1998) and the REE-in-two-pyroxene thermometer (Liang *et al.*, 2013) are presented in Supplementary Table S2 and plotted as a function of distance from the dunite-harzburgite contact in Supplementary Figure S5 (temperatures calculated using the thermometers of Wells, 1977 and Putirka, 2008 are also listed in Table S2). There is little variation in two-pyroxene (T_{BKN}) or olivine-spinel (T_{Ol-Sp}) temperatures across the transect (they average $\sim 850^{\circ}\text{C}$ and $\sim 750^{\circ}\text{C}$, respectively) aside from significantly lower T_{Ol-Sp} within the dunite ($\sim 700^{\circ}\text{C}$) which Morgan *et al.* (2008) attributed to smaller spinel grain size within the dunite near the dunite-harzburgite interface. With the exception of two outliers, the Ni in olivine and orthopyroxene thermometer of Kelemen *et al.* (1998, T_{Ol-Opx}) gives temperatures generally consistent with the olivine-spinel thermometer. Scatter in the T_{Ol-Opx} data may be attributed to scatter in LA-ICP-MS analyses which were used to characterize NiO concentrations in orthopyroxene. In general major element-based thermometers give lower subsolidus temperatures than the REE-based two-pyroxene thermometer. This can be attributed to the relatively faster diffusivity of Ca, Fe, Mg, and Ni in mantle minerals at subsolidus conditions (e.g., Cherniak & Dimanov, 2010; Chakraborty, 2010; Van Orman & Crispin, 2010, and references therein). In contrast, REE-in-two-pyroxene temperatures are closer to magmatic temperatures owing to the relatively sluggish diffusion of REE in pyroxene (c.f. Liang *et al.*, 2013). T_{REE} are slightly higher in the plagioclase lherzolite than the harzburgite and lherzolite ($\sim 1200^{\circ}\text{C}$

vs. $\sim 1150^{\circ}\text{C}$). Dygert *et al.* (2014) showed that within the global T_{REE} dataset for ophiolites, plagioclase peridotites have higher temperatures than spinel peridotites. This could be related to the melt impregnation processes that formed the plagioclase peridotites. Alternatively, it could be attributed to the larger grain sizes typical of plagioclase peridotites (e.g., compare Figures 2c and 2d to 2e and 2f), as closure temperature increases as a function of grain size squared (Dodson, 1973).

Samples from Trinity are compared to abyssal peridotites and ophiolitic samples from different tectonic settings in Supplementary Figure S5b. The data plots within the field defined by supra-subduction zone and mid-ocean ridge ophiolites, but at lower T_{BKN} than the abyssal peridotites. These low temperatures may suggest cooling rates slower than those characteristic of mid-ocean ridges (Dygert *et al.*, 2014).

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CHAPTER 5

Temperatures and Cooling Rates Recorded in REE in Coexisting Pyroxenes in Ophiolitic and Abyssal Peridotites

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Abstract

Mantle peridotites from ophiolites are commonly interpreted as having mid-ocean ridge (MOR) or supra-subduction zone (SSZ) affinity. Recently, a REE-in-two-pyroxene thermometer was developed (Liang et al., 2013) that has higher closure temperatures (designated as T_{REE}) than major element based two-pyroxene thermometers for mafic and ultramafic rocks that experienced cooling and has the potential to extract meaningful cooling rates from ophiolitic peridotites and thus shed new light on the thermal history of the different tectonic regimes. We calculated T_{REE} for available literature data from abyssal peridotites, subcontinental (SC) peridotites, and ophiolites around the world (Alps, Coast Range, Corsica, New Caledonia, Oman, Othris, Puerto Rico, Russia, and Turkey), and augmented the data with new measurements for peridotites from the Trinity and Josephine ophiolites and the Mariana trench. T_{REE} are compared to major element based thermometers, including the two-pyroxene thermometer of Brey and Köhler (1990, T_{BKN}). Samples with SC affinity have T_{REE} and T_{BKN} in good agreement. Samples with MOR and SSZ affinity have near-solidus T_{REE} and T_{BKN} hundreds of degrees lower. Closure temperatures for REE and Fe-Mg in pyroxenes were calculated to compare cooling rates among abyssal peridotites, MOR ophiolites, and SSZ ophiolites. Abyssal peridotites appear to cool more rapidly than peridotites from most ophiolites. SSZ ophiolites have lower closure temperatures than abyssal peridotites and many ophiolites with MOR affinity. We propose that these lower temperatures can be attributed to the residence time in the cooling oceanic lithosphere prior to obduction. MOR ophiolites define a continuum spanning cooling rates from SSZ ophiolites to abyssal peridotites. Consistent high closure temperatures for abyssal peridotites and the Oman and Corsica

ophiolites suggests hydrothermal circulation and/or rapid cooling events (e.g., normal faulting, unroofing) control the late thermal histories of peridotites from transform faults and slow and fast spreading centers with or without a crustal section. This study demonstrates the ability of the REE-in-two-pyroxene thermometer to unravel the tectonic history of ultramafic rocks.

1. Introduction

Geothermometers have long been widely used to study the thermal history of mafic and ultramafic rocks (e.g., Boyd, 1973; Wells, 1977; Wood and Banno, 1973). These thermometers are experimentally calibrated and rely on temperature sensitive major element partitioning among a mineral assemblage. One class of thermometers commonly applied to ultramafic rocks uses Ca distribution (e.g., Brey and Köhler, 1990; Lindsley and Andersen, 1983) and/or Fe-Mg exchange (e.g., Putirka, 2008; Wells, 1977) between two pyroxenes to determine temperature. Systematic studies of trace element distribution among mantle minerals have demonstrated that mineral-mineral trace element partition coefficients depend on temperature, pressure, and mineral composition and the functional relationship can be used as a trace element based thermometer or thermobarometer (e.g., Eggins et al. 1998; Hellebrand et al., 2005; Lee et al., 2007; Seitz et al., 1999; Stosch, 1982; Sun and Liang, 2014; Witt-Eickschen et al., 2009; Witt-Eickschen and O'Neill, 2005). One recent example is the REE-in-two-pyroxene thermometer of Liang et al. (2013) which was developed using parameterized lattice-strain models for REE partitioning between clinopyroxene (cpx) and basaltic melt (Sun and Liang, 2012) and orthopyroxene (opx) and basaltic melt (Yao et al., 2012). These

pyroxene-melt partitioning models were calibrated using experimentally determined mineral-melt partitioning data and tested against well-equilibrated spinel lherzolites from cratonic mantle from a number of localities. As an application of their thermometer, Liang et al. (2013) calculated REE-in-two-pyroxene temperatures (designated as T_{REE}) for abyssal peridotites from Gakkel Ridge (Hellebrand et al., 2005), Southwest Indian Ridge (9°E – 16°E, Warren et al., 2009; 52°E – 69°E, Seyler et al., 2011), and the St. Paul region of Central Atlantic Ocean (Brunelli and Seyler, 2010). They showed that abyssal peridotite T_{REE} range from 975 to 1300°C, and the T_{REE} are 50-300°C higher than temperatures derived from the major element based two-pyroxene thermometer of Brey and Köhler (1990). Liang et al. (2013) further suggested that REE-based thermometers may have the capacity to record near-magmatic temperatures and major element thermometers record much lower cooling temperatures, due to differences in closure temperature between the trivalent and divalent cations in pyroxenes.

The purpose of this study is to report the first REE-in-two-pyroxene based thermometry determinations for mantle sections of ophiolites from around the world, and to compare and contrast those results with the abyssal peridotite T_{REE} reported by Liang et al. (2013). Comparative study of the thermal histories of ophiolites and abyssal peridotites can inform us about the similarities and differences among peridotites formed in supra-subduction zone (SSZ), mid-ocean ridge (MOR), and sub-continental (SC) environments. New thermometric data from ophiolites has the potential to improve our understanding of subsolidus processes, cooling rates, tectonics, and physical processes that determine the thermal histories of mantle peridotites.

2. Data Sources

We report new thermometric data for 72 mantle peridotites and six mafic cumulates. Sample lithologies include spinel and plagioclase harzburgite and lherzolite, and cumulate dunite, wehrlite, and websterite. Major and trace element analyses were used from the literature for ophiolites and peridotites from the following regions: the Alps (Lower Platta, Malenco, and Davos, Müntener et al., 2010), Coast Range, California (Jean et al., 2010), Corsica (Rampone et al., 2008), Pyrenees (Lherz, Riches and Rogers, 2011), Oman (lower Wadi Fizh, Takazawa et al., 2003; upper Wadi Fizh, Akizawa et al., 2012; Wadi Sarami, Khedr et al., 2014), Greece (Othris, Barth et al., 2003), New Caledonia (Massif du Sud, Pirard et al., 2013), Russia (the Polar Urals, Batanova et al., 2011), Puerto Rico (Marchesi et al., 2011), and Turkey (Tekirova and Köyceğiz, Aldanmaz, 2012). All the data sources analyzed trace elements in pyroxene using laser ablation inductively coupled mass spectrometry (LA-ICP-MS) except Takazawa et al. (2003), who analyzed mineral separates by solution ICP-MS. Using a variety of geochemical and geologic indicators [e.g., spinel Cr# ($100\text{Cr}/(\text{Cr}+\text{Al})$, in moles), high field strength element (HFSE) anomalies, trace element characteristics, field relationships, tectonic reconstructions], these authors interpreted the ophiolites to have MOR type affinity, SSZ affinity, or SC affinity. Here we defer to the judgment of the authors of the data sources in assigning each sample a tectonic affinity. Although among the data sources similar criteria are used for tectonic affinity assignment, the specific reasoning of each study is unique and described in detail in the Supplementary Appendix.

To augment the published data, we used LA-ICP-MS to analyze 16 peridotite samples from the Trinity and Josephine ophiolites that were collected and described by

Morgan et al. (2008). Based on geologic and geochemical evidence, Trinity and Josephine are thought to have formed in a SSZ tectonic setting (e.g., Kelemen and Dick, 1995; Wallin and Metcalf, 1998). We also analyzed three samples from the Mariana trench collected and described by Michibayashi et al. (2009) (Figure 1). The new measurements yield a total of 16 reliable temperatures (Figure 2a).

3. Analytical Methods and Temperature Inversion

3.1 Sample Preparation and Analysis

Thin sections of samples from the Trinity ophiolite (Morgan et al., 2008) were prepared by Burnham Petrographics from 1” drill cores, while samples from the Mariana Trench (Michibayashi et al., 2009), and the Josephine ophiolite were prepared from billets cut from hand samples at Brown University. Because pyroxenes in mantle peridotite have ppb to ppm level REE abundances we made extra thick thin sections (approximately 70-150 μ m) to maximize collection time during analysis. Major elements in the Trinity and Josephine samples were reported by Morgan et al. (2008). Major elements in the Mariana samples were reported by Michibayashi et al. (2009). Rare earth elements, high field strength elements, and transition metals were analyzed by LA-ICP-MS at the Graduate School of Oceanography at the University of Rhode Island using methods similar to those described in Kelley et al. (2003). Spot sizes ranged from 40-80 μ m depending on REE abundance in pyroxene. Care was taken to place spots at grain cores, rims, and in between, however the ability to measure rim compositions is limited by alteration and relatively large laser spot sizes. Multiple opx and cpx grains were analyzed in each thin section, and serpentinized grains were avoided. Mg was used as our

calibration analyte for trace element data processing because of its abundance in opx and cpx and low analytical uncertainty in microprobe analyses. A limited number of Trinity cpx were processed using Ca. The new data is presented in Supplementary Table S1.

3.2 Temperature Inversion

Temperatures were calculated using representative average mineral compositions from grain core and rim analyses, which generally have small standard deviations (Figure 1, Supplementary Table S1). When rim and core compositions were reported separately in the data sources they were averaged. Temperatures were inverted from the trace element data using methods discussed in Appendix A of Liang et al. (2013). First, chondrite normalized REE abundances were plotted on extended REE diagrams to check data quality. Particular attention was devoted to light REE (LREE) in opx which have very low concentrations in depleted samples. We also looked for LREE enrichment indicative of metasomatism and the smoothness of the trends in general and noted any obvious outlying elements.

Next, opx-cpx REE partition coefficients (D) were plotted on $\ln(D)$ -A vs. B diagrams, where A is a function of major element composition of pyroxene and B is a function of ionic radius of a given element and predicted physical properties of the pyroxene lattice sites (Liang et al., 2013). A best fit line was then plotted through the measured data anchored by the origin (Supplementary Figures S5a-S5h). The slope of the line is the temperature, and it should ideally overlie all the measured data. When analytical data have large uncertainties the measured data often scatter about the regression line, and poor quality data fails to define a line. Often middle and heavy REE

(HREE), which are more easily measurable (and less sensitive to metasomatism), define a linear trend while LREE are scattered. In that case outlying data are excluded and a meaningful temperature is inverted from the linear data. When the two-pyroxene bearing system is perturbed, the measured data define a trend or line that is rotated away from the origin. In that case, a meaningful temperature cannot be determined. Each sample was scrutinized individually before being added to or omitted from a database of approved temperatures. Of 142 investigated temperatures, 78 were accepted based on the criteria outlined above. One sample exhibits a magmatic temperature (MM2_10 from Corsica, Rampone et al., 2008) but the data is highly systematic and we do not wish to reject the sample based on criteria other than input data and inversion quality. Figures generated for the main text of this study only include approved data, which is summarized in Supplementary Tables 2 and 3. Additional filtering (described below) was conducted to generate Figures 5, 9b and 9d. To make direct comparisons among all samples a pressure of 1 GPa was assumed for major element thermobarometers. Assuming a pressure of 0.5 GPa results in systematically lower temperatures (e.g., 8°C lower on average for the two-pyroxene thermometer of Brey and Köhler, 1990) and the assumption of a particular pressure does not affect the results.

4. Results

Calculated T_{REE} and temperatures from the major element based two-pyroxene thermometer of Brey and Köhler (1990, T_{BKN}) are presented in Figure 2a (our data) and Figure 2b (literature data). Several interesting features are apparent in Figure 2. (1) Most samples plot hundreds of degrees above the 1:1 line, but some samples fall along (or

slightly below) the line. (2) Temperatures for a particular location are clustered within a range of a few hundred degrees or less, except samples from the Alps and Turkey which are more scattered. (3) Temperatures vary widely among different ophiolites with a total T_{REE} range of about 600°C (688-1,287°C). (4) Samples from many ophiolites have lower T_{REE} and T_{BKN} than abyssal peridotites, and many ophiolites plot farther from the 1:1 line than abyssal peridotites.

In Figure 3a T_{REE} are plotted against T_{BKN} and distinguished by the presence or absence of plagioclase. Plagioclase-bearing peridotites are surprisingly hotter on average and have a smaller T_{REE} range than spinel-bearing samples (1,051-1,265°C vs. 688-1,287°C). Some spinel peridotites show T_{REE} consistent with T_{BKN} but all of the plagioclase-bearing samples show T_{REE} higher than their T_{BKN} . There are 11 plagioclase-bearing samples from five localities (Trinity, Othris, Mariana, Corsica, and the Alps), so the relatively narrow range of temperatures for plagioclase-bearing samples may be a consequence of the limited data. We note the coldest spinel peridotites all have subcontinental affinity, but plagioclase bearing samples are still hotter than the coldest peridotites from MOR and SSZ-type environments. Figure 3b shows that the entire range of T_{REE} is shared by harzburgites and lherzolites, but many harzburgites have lower T_{BKN} than an average lherzolite.

Figure 4 compares T_{REE} with temperatures derived from the olivine-spinel thermometer of Li et al. (1995, T_{Ol-Sp}) which is an update of Fabriès (1979). Data for abyssal peridotites with T_{REE} is limited, so additional T_{Ol-Sp} determinations were made for data from Hellebrand et al. (2002), Johnson and Dick (1992), and Seyler et al. (2007). The range of abyssal peridotite T_{Ol-Sp} is shown by the rectangle on the x axis. In general,

abyssal peridotite temperatures are more consistent with ophiolites using the olivine-spinel thermometer than the pyroxene-based thermometers. We note that most of the ophiolites with lower T_{Ol-Sp} than the abyssal peridotites have SSZ affinity, and that ophiolites sharing T_{Ol-Sp} space with abyssal peridotites are mostly MOR-type.

Figure 5 shows histograms for T_{REE} and T_{BKN} for samples from each tectonic affinity group (histograms showing T_{Ol-Sp} and T_{REE} are presented in Supplementary Figure S1). The data in Figure 5 is also summarized as averages from each data source and tectonic affinity type in Supplementary Table 4. To establish more meaningful statistics, scattered data (samples from Aldanmaz, 2012; sample To-7 from Müntener et al., 2010; MM2_10 from Rampone et al., 2008) was filtered out, as well as some data from Akizawa et al. (2012) which was clearly disturbed by late-stage melt-rock reaction processes (see Data Quality in the Discussion and Appendix A). Well-equilibrated mantle xenoliths reported by Liang et al. (2013) are shown in Figure 5a, and subcontinental peridotites are shown in Figure 5b. These tectonic affinity groups have consistent major element temperatures and T_{REE} . SSZ ophiolites have lower T_{REE} and T_{BKN} than abyssal peridotites. Many (but not all) MOR ophiolites (Figure 5e) have lower T_{BKN} than abyssal peridotites and there is a larger range of T_{REE} for MOR ophiolites than abyssal peridotites. MOR ophiolites generally have higher T_{REE} than SSZ ophiolites.

Modal abundances and trace and major element compositions of bulk rocks, pyroxene, olivine, plagioclase, and spinel were compared to T_{REE} and are briefly described here (Figures 6 and 7). A positive correlation between T_{REE} and Cr# in spinel may be present (Figure 6a), but Mg# in olivine exhibits no correlation with T_{REE} on a global or local scale (Figure 6b). CaO in opx is positively correlated with T_{REE} reflecting

temperature sensitive Ca partitioning around the enstatite-diopside solvus (Figure 6c). There is no correlation between pyroxene modal abundance and T_{REE} at the global or local scale (Figure 6d). Minor elements thought to indicate extent of melting are plotted against T_{REE} and distinguished by tectonic affinity in Figure 7. Clinopyroxene from ophiolites with SSZ affinity are low in Al_2O_3 relative to MOR ophiolites, and on average, SC ophiolites have the highest Al_2O_3 (Figure 7a). SSZ ophiolites have low TiO_2 in cpx compared to samples with MOR affinity and SC samples (Figure 7b). However, there is no clear correlation between Al_2O_3 or TiO_2 and T_{REE} . We did not observe meaningful correlations of trace element concentrations with T_{REE} , however selected minor and trace element distributions that appear to be controlled by subsolidus reequilibration (e.g., Cr_2O_3 in opx; Ti, Zr, Sc, and V partitioning between opx and cpx) show good correlations with T_{REE} (Supplementary Figures S2 and S3). Plagioclase compositions were reported for only six samples and no correlation of T_{REE} with An# (100Ca/Ca+Na in moles) exists for those samples. Bulk rock major elements show no obvious correlations with T_{REE} .

5. Discussion

5.1 Data Quality

Thermometric determinations are sensitive to data quality. Using Monte Carlo simulations, Liang et al. (2013) showed that uncertainties in T_{REE} calculation are strongly and positively correlated with analytical uncertainties in REE abundance in opx, temperature, and the number of REE used in the inversion. For a $\pm 50^\circ C$ uncertainty in T_{REE} , an analytical uncertainty of 20-30% (relative) for REE in opx is a prerequisite. We note that the T_{REE} for samples from Trinity, Josephine, and Mariana based on the high

quality data reported in this study (Figure 1) are tightly clustered compared to T_{REE} determinations from many literature data (Figure 2).

Some of the T_{REE} scatter for the literature data can be attributed to the geologic histories of the samples. T_{REE} for samples from Akizawa et al. (2012) (white squares, Figure 2b) are scattered because cpx-opx pairs were measured in and around wehrlite and gabbro that intruded depleted harzburgite. Crystallization of infiltrating melt likely resulted in the precipitation of second-generation cpx (e.g., Tursack and Liang, 2012) that failed to equilibrate with primary minerals. Liang et al. (2013) found very high temperatures for abyssal peridotites affected by melt infiltration which were filtered out of the dataset presented here. These examples demonstrate that obtaining meaningful T_{REE} requires representative, high-quality REE analyses of both cpx and opx. Some of the scatter within individual ophiolites in Figures 2b-9 can be attributed to melt-rock reaction processes and data quality issues beyond our control. The impact of a melt infiltration event on T_{REE} depends on the major and trace element composition of the infiltrating melt, and on the temperature at which infiltration occurs. After a melt-rock reaction event pyroxene will re-approach equilibrium, but the reestablishment of equilibrium depends on temperature and the time available.

The formation of exsolution lamellae in pyroxene is temperature dependent and has an inevitable effect on the major and trace element compositions of the host minerals. To our knowledge, most of our data sources analyzed major elements in pyroxene using focused beams which exclude the contribution of exsolution lamellae to the bulk composition of the mineral [Müntener et al. (2010) used 2-10 μ m beams while Akizawa et al. (2012) and Khedr et al. (2014) used a 3 μ m beam]. In contrast, LA-ICP-MS (and

solution ICP-MS) analysis provides representative average trace element compositions of minerals. Liang et al. (2013) investigated the effect of exsolution lamellae on T_{REE} using the dataset of Hellebrand et al. (2005). They compared T_{REE} calculated using major elements measured with a defocused (hence averaging) beam and those measured using focused beams (Figure 6, Liang et al., 2013). T_{REE} obtained using the focused beams are systematically higher than those using the defocused beam (12-88°C), and T_{BKN} are slightly lower using the point beams. Systematic differences of this magnitude will not affect our conclusions.

5.2 T_{REE} and Closure Temperatures of REE in Pyroxenes

Temperatures determined by major and trace element based thermometers can be related to cation diffusion in pyroxene in response to cooling. Cherniak and Liang (2007) modeled diffusive reequilibration of REE between a cpx-opx pair undergoing prescribed cooling with temperature dependent opx-cpx partition coefficients (see their Figure 11). They observed the development of significant REE concentration gradients in opx while cpx compositions remained relatively constant owing to the small and temperature dependent opx-cpx REE partition coefficients and diffusion coefficients. Similar concentration gradients will develop in opx in peridotite experiencing cooling at mantle relevant cooling rates, mineral proportions, and grain sizes. Considering bi-mineralic aggregates more generally, Liang (2014a) showed that diffusive reequilibration rates of REE in opx-cpx systems are largely determined by the “minor’s rule,” which states the mineral with the lesser amount of a trace element in the system dominates the reequilibration timescale. On average, peridotites in this study have ~25% as much cpx as

opx. REE concentrations in cpx are much higher than in opx, ranging from several orders of magnitude for LREE to a factor of a few for HREE (at mantle temperatures). Hence, opx serves as the “minor” component for REE in most peridotites and REE diffusion in opx is rate limiting for most of the samples investigated in this study.

The physical meaning of T_{REE} maybe understood in terms of closure temperature of REE in pyroxene. Closure temperature is the effective temperature at which a mineral ceases diffusive exchange of a chemical species with other phases in a system at a prescribed cooling rate. According to Dodson (1973), closure temperature (T_c) takes the following expression:

$$\frac{E}{RT_c} = \ln \left(\frac{ART_c^2 D_0}{Ea^2 \dot{s}} \right) \quad (1)$$

where E and D_0 are the activation energy and the pre-exponential factor for diffusion; 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. Closure temperature is negatively correlated with diffusion rate, and because diffusion rates of divalent Ca, Mg, and Fe are 2-3 orders of magnitude faster than those of trivalent REE in pyroxene (e.g., Cherniak and Dimanov, 2010 and references therein), major element based thermometers have lower closure temperatures. The effect of cooling on T_{REE} closure temperature was investigated numerically in simulations of diffusive reequilibration of REE between cpx and opx at prescribed cooling rates (Yao and Liang, in review). The simulations suggest that T_{REE} approximate closure temperature of REE diffusion in opx, consistent with the minor’s rule detailed in Liang (2014a). This was further verified mathematically by a closure temperature equation for bi-mineralic systems (Liang, 2014b). We note the dependence

of the REE-in-two-pyroxene thermometer on major elements contributes some uncertainty to T_{REE} determinations, a subject of active research.

Equation 1 shows that closure temperature depends on the product of the cooling rate and the square of effective grain size. Hence Eq. 1 can be used to calculate and directly compare closure temperatures for two elements in the same grain, defining a “closure curve” in the temperature correlation diagram. This is illustrated in Figure 8a, which shows correlations between closure temperatures of REE in opx on the y axis and major elements in pyroxene on the x axis (Ca, Mg, Fe-Mg, Ca-Mg-Fe, and (Fe,Mn)-Mg, see figure caption for sources of diffusion data). The models are encouraging as they overlap at least some of the observed data shown in the background in gray. Dodson’s closure temperature formulation assumes diffusion within a grain is rapid enough for the composition of the core to respond to the changing composition of the rim before closure occurs. This assumption is often violated in circumstances where slow diffusing elements (e.g., REE) are considered, especially in larger grains. Ganguly and Tirone (1999) developed a modified form of Dodson’s equation that calculates closure temperature for cases when this assumption is invalid. The model of Ganguly and Tirone (1999) also considers the initial temperature (T_0) of the system, which is important when T_0 approaches closure temperature (cf. Ehlers and Powell, 1994). The Ganguly and Tirone (1999) model recovers the Dodson (1973) model when cooling rates are sufficiently slow.

Figure 8b shows closure temperatures calculated using the method of Ganguly and Tirone (1999) for a range of initial temperatures (T_0 , 1000-1400°C, indicated right of the solid black 1:1 line). For the purpose of illustration, we used the diffusion data of

Dimanov and Wiedenbeck (2006) for (Fe,Mn)-Mg interdiffusion in diopside to calculate major element closure temperature. Black dots connected by thin black lines correspond to cooling rates (in °C/Myr, indicated by the numbers above the magenta line) for a 5 mm effective grain size. These models qualitatively explain the spread of the data. Assuming they are initially well equilibrated, all samples start somewhere along the 1:1 line, and they move to the left toward the Dodson (1973) model as they cool. Samples that lie to the left of the Dodson (1973) model may be attributed to one or some combination of the following factors or processes: (1) melt-rock reaction; (2) a more complicated thermal history than simple cooling (e.g., early cooling followed by late heating); (3) meaningless temperatures owing to poor data quality. Samples right of the Dodson (1973) model closed at higher temperatures owing to fast cooling, large grain size, or some combination of these effects. Melt-rock reaction may perturb a sample along its closure path, but as it continues to cool after reaction it will move toward the Dodson model.

In some refractory harzburgites with very low cpx abundance (e.g., our Josephine samples, harzburgites from the Urals, Oman, and Corsica), REE diffusion in cpx becomes the rate-limiting factor in controlling the rate of diffusive exchange of REE between opx and cpx (following the minor's rule, see also Fig. 5 in Liang, 2014a, Fig. 2 in Liang, 2014b). Unlike REE diffusion in opx which is thought to be constant among all REE (Cherniak and Liang, 2007), REE diffusion in cpx depends on ionic radius. Under experimental conditions, LREE are $\sim 35\times$ slower diffusing than HREE (Van Orman et al., 2001). Depending on the variability of mineral modal abundance within a group of samples from an individual ophiolite, this could lead to scattered closure temperatures although all the samples experienced the same thermal history. In Figure 8c, we plot

closure temperatures for Yb and La in cpx using the method of Ganguly and Tirone (1999) (green and blue lines, respectively) and compare them to closure temperatures for REE in opx (magenta line). Closure temperatures for La and Yb in cpx bracket closure temperatures for REE in opx, providing robust upper and lower limits. Because samples with low cpx abundance tend to be very depleted in trace elements, T_{REE} are usually calculated with middle to heavy REE and closure temperatures for Yb in cpx and REE in opx are more realistic bounds. However, we note there is no obvious correlation between cpx modal abundance and T_{REE} (Figure 6d), suggesting the effect of low cpx abundance on the systematics of T_{REE} closure temperatures is small, if not negligible. This is partly attributable to the fact that cpx are smaller than opx in most of the samples, which was shown to lessen the effect of low cpx abundance on closure temperatures of cpx-opx aggregates (Liang, 2014b).

6. Geological Implications

Comparison of the temperature distributions and closure temperature models enables us to assess different cooling histories for different tectonic environments. Individual samples are plotted by tectonic affinity in Figure 9a. Figure 9b shows T_{REE} and T_{BKN} averaged by locality, error bars are 1σ standard deviations (also see Supplementary Table 4). A few outlying data points were excluded from the averages as discussed in Section 4. Averaging by locality reduces some of the scatter associated with marginal data quality and modal abundance and grain size variability for a study area. By averaging we implicitly assume all the samples from a reference experienced the same

thermal history. Data selection for this process was made carefully with that in mind (see Appendix A).

Data from Trinity, Josephine, and Mariana are tightly clustered at T_{REE} of 1100-1200°C and T_{BKN} of ~870°C. These peridotites have well established SSZ affinities, T_{REE} consistent with or lower than abyssal peridotites, and significantly lower T_{BKN} than the abyssal peridotites. Other localities with SSZ affinity have similar temperatures (New Caledonia) or significantly lower T_{BKN} and T_{REE} (Urals). Peridotites with MOR affinity show more scatter in their temperatures. Some are highly consistent with the abyssal peridotites (Oman, Corsica) while others (Othris, Puerto Rico, Coast Range) have lower T_{BKN} and T_{REE} . The pink field in Figure 9b highlights localities with SSZ affinity and the light green field highlights localities with MOR affinity. In general, samples with SSZ affinity have lower T_{BKN} and T_{REE} than ophiolitic peridotites with MOR affinity. Samples with SSZ affinity and many samples with MOR affinity have lower temperatures than abyssal peridotites.

SC samples have distinct thermal histories from ophiolitic peridotites (Figure 9a). Based on field relationships, texture and mineralogy, geochemistry, and thermometric data, Müntener et al. (2010) interpreted peridotites from different (but closely located) outcrops in the Alps as forming in separate tectonic regimes, a MOR-like rift regime and a SC regime. With one outlying exception ($T_{BKN} = 571^{\circ}\text{C}$), two-pyroxene major element thermometry shows no distinction between the samples ($T_{BKN} \approx 860 \pm 25^{\circ}\text{C}$). In contrast, T_{REE} are high for two samples with MOR affinity collected at different localities (1074 ± 22 and $1256 \pm 5^{\circ}\text{C}$) and low for the samples with SC affinity ($831\text{-}901^{\circ}\text{C}$) (indicated in Figure 9a). REE-in-two-pyroxene thermometry corroborates the

interpretation of Müntener et al. (2010) and demonstrates the disparate thermal regimes in these two environments.

The closure temperature models shown in Figure 9b (T_{REE} approximated by REE diffusion in orthopyroxene, T_{BKN} approximated by (Fe,Mn)-Mg in clinopyroxene) are overlaid on individual samples (Figure 9c) and averages from each locality (Figure 9d) distinguished by tectonic affinity. For comparison, well-equilibrated mantle xenoliths from Liang et al. (2013, with T_{BKN} calculated at 1.5 GPa) averaged by locality are also shown in Figure 9d, and fall on the 1:1 line demonstrating good agreement between the major and REE-in-two-pyroxene thermometers for rapidly exhumed samples from stable thermal environments. The closure temperature models provide relative cooling rates for the samples with an important caveat. Closure temperature scales with the product of cooling rate and the square of the effective grain size (Eq. 1). Any samples that experienced the same cooling history will plot in different places in Figure 9c if they have different grain size. Grain size does vary among the samples we investigated. According to our observations and the descriptions in the data sources, abyssal peridotites tend to have the largest grains (opx are 10 to 20 mm in diameter), opx from MOR ophiolites range from 1 to ~5 mm, and opx from SSZ ophiolites range from 1 to 10 mm. The different positions of the fields defined by abyssal peridotites and colder ophiolites cannot be attributed to grain size variability of this magnitude, i.e., the closure temperature models suggest there are real differences in cooling rate between many ophiolites and abyssal peridotites (see the figure caption to scale the cooling curves to different grain sizes). Without direct access to the samples in our data sources, assessing the differences between MOR and SSZ ophiolites is more difficult. However, the data

sources report consistent grain sizes among samples in each group, suggesting that, to first order, grain size does not preferentially skew closure temperatures and that SSZ and hot MOR ophiolites experience different thermal histories.

At the tectonic scale, the location of a sample must be an important factor determining its cooling history. Peridotites near ophiolitic soles are probably disturbed by deformation and obduction, which usually occurs at amphibolite grade P - T conditions. This may affect basal peridotites from Oman (yellow triangle, Figure 9b, Khedr et al., 2014) that have relatively low temperatures considering their MOR affinity. [Surprisingly, another sample from the basal section of the Oman ophiolite (brown triangle in Figure 9b, Takazawa et al., 2003) has high T_{REE} and T_{BKN} closure temperatures.] The proximity of a sample to the surface (and its lateral distance from the ridge axis) must also affect its P - T - t path. Samples close to the surface will cool more quickly. This was shown by Hanghøj et al. (2010) who found an $\sim 300^\circ\text{C}$ difference in T_{BKN} across an ~ 10 km transect beneath the Moho at the Oman ophiolite. Hydrothermal circulation could preferentially affect shallower samples. Crustal thickness may be important. Carefully conducted geologic/thermometric investigations of ophiolites are needed to isolate the effects responsible for different cooling histories at the outcrop scale. In this study, we assume the data we have are generally representative of each locality and focus on cooling history as a function of tectonic setting.

Relatively high closure temperatures for abyssal peridotites suggest they cool more rapidly than most ophiolites. The abyssal peridotites in this study are from slow and ultra-slow spreading centers or transform faults, where the conductive cooling regime probably penetrates deeper than at normal spreading centers (e.g., White et al., 2001). A

simple thought experiment helps us consider the dependence of cooling rate on spreading rate. In a scenario where hydrothermal circulation is ignored and all mantle upwelling is in the ductile regime, samples from spreading centers advect through a conductive temperature gradient whose depth depends entirely on spreading rate (e.g., Figure 5 in Shen and Forsyth, 1992). Consequently, samples from slow spreading centers would be expected to cool more slowly than samples from faster spreading centers. How can ophiolites, which come from tectonic settings with a wide range of spreading rates, cool more slowly than abyssal peridotites from ultra-slow spreading centers? If grain size is not an issue, higher closure temperatures for abyssal peridotites suggest that hydrothermal circulation is more important than spreading rate at transform faults and slow and ultra-slow mid-ocean ridges, or that abyssal peridotites are quenched from near-asthenospheric temperatures by faulting or unroofing.

Abyssal peridotites come from localities that often lack overlying crust. Oceanic crust might be expected to act as a thermal insulator for underlying mantle and represent a barrier to seawater infiltration. However, the consistent T_{REE} , T_{BKN} , and T_{Ol-Sp} (see Figure 4) for abyssal peridotites and MOR-type samples from Oman (corroborated by Hanghøj et al., 2010) suggests similar cooling histories among these samples. Because the Oman Ophiolite has a fully developed crustal section, the closure temperature similarity suggests that hydrothermal circulation and/or faulting may determine the cooling history of mantle peridotites from spreading centers regardless of whether a crustal section is present. Furthermore, Oman is thought to have originated from a moderate to fast spreading center (e.g., Hanghøj et al., 2010, and references therein). The apparent similarity in cooling rate between abyssal peridotites (which are from slow and

ultra-slow spreading centers) and Oman suggests that cooling rate is independent of spreading rate. Unfortunately, the lack of REE data for abyssal peridotites from fast spreading mid-ocean ridges precludes comparison between Oman and peridotites from modern fast spreading centers.

In contrast to Oman (and Corsica), SSZ ophiolites have lower closure temperatures than abyssal peridotites suggesting cooling over longer intervals and possibly from lower T_0 . We attribute their longer cooling histories to timescales of residence in forearcs prior to obduction. MOR ophiolites with low T_{REE} and T_{BKN} (e.g., Coast Range, Othris) experienced late thermal histories similar to SSZ ophiolites and may have also formed in arc-related environments. Alternatively, the longer thermal histories of these samples could be a consequence of their proximity to the Moho (c.f. Figure 7, Hanghøj et al., 2010), a spreading center or a fracture zone, or be a remnant of the obduction process.

Previous studies of ophiolite cooling rates that utilized the Ca in olivine-clinopyroxene thermometer of Köhler and Brey (1990) focused on cooling as a function of distance from the crust-mantle boundary at two localities in Oman. Coogan et al. (2002) found cooling rates between 0.1 and 10,000 °C/Myr (depending on the diffusion data used) just above the Moho. VanTongeren et al. (2008) found cooling rates on the order of 10,000 °C/Myr at the Moho, and 0.1 to 10^{-8} °C/Myr for a group of samples from the mantle section ~3 km below the Moho. Our cooling rates for representative samples from Oman (Akizawa et al., 2012; Takazawa et al., 2003) are on the order of 1000 °C/Myr, slower than or consistent with values reported previously for crustal samples at

the Moho, but much faster than the values reported by VanTongeren et al (2008) for a group of samples below Moho.

Better closure temperature models combined with careful field studies could ultimately provide tighter constraints on the dynamics and timescales of mantle lithosphere formation and obduction. The consequences of multi-stage cooling paths and nonlinear cooling rates should be explored in the development of such models. We reiterate that measurement of high quality REE data is essential for obtaining meaningful T_{REE} .

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9. Figure Captions

Figure 1. Chondrite normalized REE + Y abundances in peridotite pyroxenes from the Trinity Ophiolite (a), Josephine Ophiolite (b), and Mariana Trench (c). Opx are in green, cpx are in red. Error bars are 1σ .

Figure 2. Comparison of temperatures derived from the REE-in-two-pyroxene thermometer of Liang et al. (2013) (T_{REE}) and those calculated with the major element based two-pyroxene thermometer of Brey and Köhler (1990) (T_{BKN}) by locality. (a) Temperatures for new trace element analyses reported in this study. (b) Temperatures for literature data. [1] is from Takazawa et al. (2003); [2] is from Akizawa et al. (2012); [3] is from Khedr et al. (2014). See Section 2 for other references. Small circles in the abyssal field are individual abyssal peridotites.

Figure 3. Sample lithology and temperatures derived from the REE-in-two-pyroxene thermometer and the major element based two-pyroxene thermometer of Brey and Köhler (1990, T_{BKN}). (a) Comparison of plagioclase-free and plagioclase-bearing samples. Plagioclase-bearing samples have higher temperatures on average. (b) Comparison of harzburgites and lherzolites.

Figure 4. Comparison of temperatures derived from the REE-in-two-pyroxene thermometer with temperatures from the olivine-spinel thermometer of Li et al. (1995, T_{Ol-Sp}). Abyssal peridotite data with T_{REE} determinations is limited owing to our data sources.

The range of T_{Ol-Sp} for representative abyssal peridotites is shown by the box at the bottom of the figure (Hellebrand et al., 2002; Johnson and Dick, 1992; and Seyler et al., 2007). [1] is from Takazawa et al. (2003); [2] is from Akizawa et al. (2012); [3] is from Khedr et al. (2014).

Figure 5. Histograms for samples with different tectonic affinities showing temperatures calculated using the REE-in-two-pyroxene thermometer (green) and the two-pyroxene major element thermometer of Brey and Köhler (1990) (black diagonal lines).

Figure 6. T_{REE} plotted against commonly used fractionation indices [spinel Cr#, (a); olivine Mg#, (b)], CaO in opx (c), and clinopyroxene mode (d) by locality. Note the lack of global or local correlations in (b) or (d); (a) may show a positive correlation. The strong correlation of T_{REE} and CaO in opx (c) can be attributed to Ca partitioning around the pyroxene solvus.

Figure 7. T_{REE} plotted against major commonly used indices of extent of melting. (a) Al_2O_3 in cpx and (b) TiO_2 in cpx. No obvious correlations are evident. SC samples have the highest TiO_2 and Al_2O_3 , while SSZ samples have the lowest TiO_2 and Al_2O_3 .

Figure 8. Closure curves based on closure temperature models of Dodson (1973) and Ganguly and Tirone (1999). (a) Models are calculated using the Dodson (1973) formulation for a sphere with a 5 mm effective radius at a range of cooling rates. T_{REE} are modeled using REE diffusion in opx (Cherniak and Liang, 2007). T_{BKN} are modeled using

a variety of major element diffusion data in cpx (solid lines) and opx (dotted lines). Sources of diffusion data are the following: [1] Brady and McCallister (1983), [2] Zhang et al. (2010), [3] Müller et al. (2013), [4] Gasc et al. (2006), [5] Dimanov and Wiedenbeck (2006), [6] Schwandt et al. (1998), [7] Ganguly and Tazzoli (1994). (b) Closure temperatures calculated using the method of Ganguly and Tirone (1999), which takes initial temperature into account. T_{BKN} are approximated using (Fe,Mn)-Mg diffusion in cpx from Dimanov and Wiedenbeck (2006). Closure temperature calculations are shown for a range of initial temperatures (T_0 , 1000-1400°C) as indicated right of the solid black 1:1 line. Small black dots connected by thin black lines correspond to cooling rates (°C/Myr) as indicated by the numbers above the magenta line. (c) Same as (b) but for two additional choices of REE diffusion data in pyroxene to model T_{REE} . Blue and green lines are Yb and La in cpx, respectively (Van Orman et al., 2002). Gray symbols and field are T_{REE} and T_{BKN} determined from analytical data.

Figure 9. Variations of T_{REE} and T_{BKN} for samples as a function of their tectonic affinity. (a) Individual data points, (b) averages for each locality, error bars are 1σ standard deviations, (c) and (d) show the same data overlaid by closure curves from Figure 9b. For comparison, well equilibrated mantle xenoliths from Liang et al. (2013) averaged by locality are shown in (d). Cooling rates shown in (c) and (d) can be rescaled for different grain sizes. Because $T_C \propto \text{grain size squared}$, grains twice as large will cool four times faster than indicated.

Figure 1.

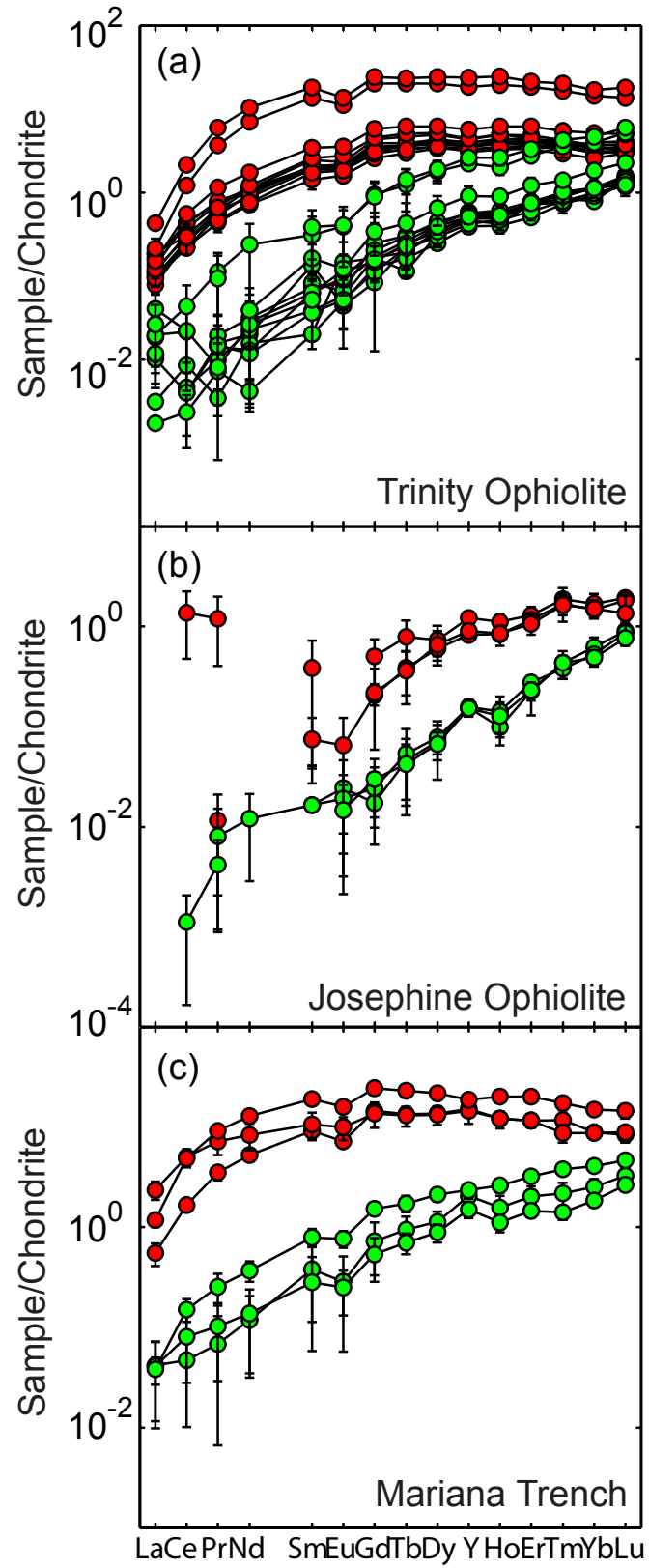


Figure 2.

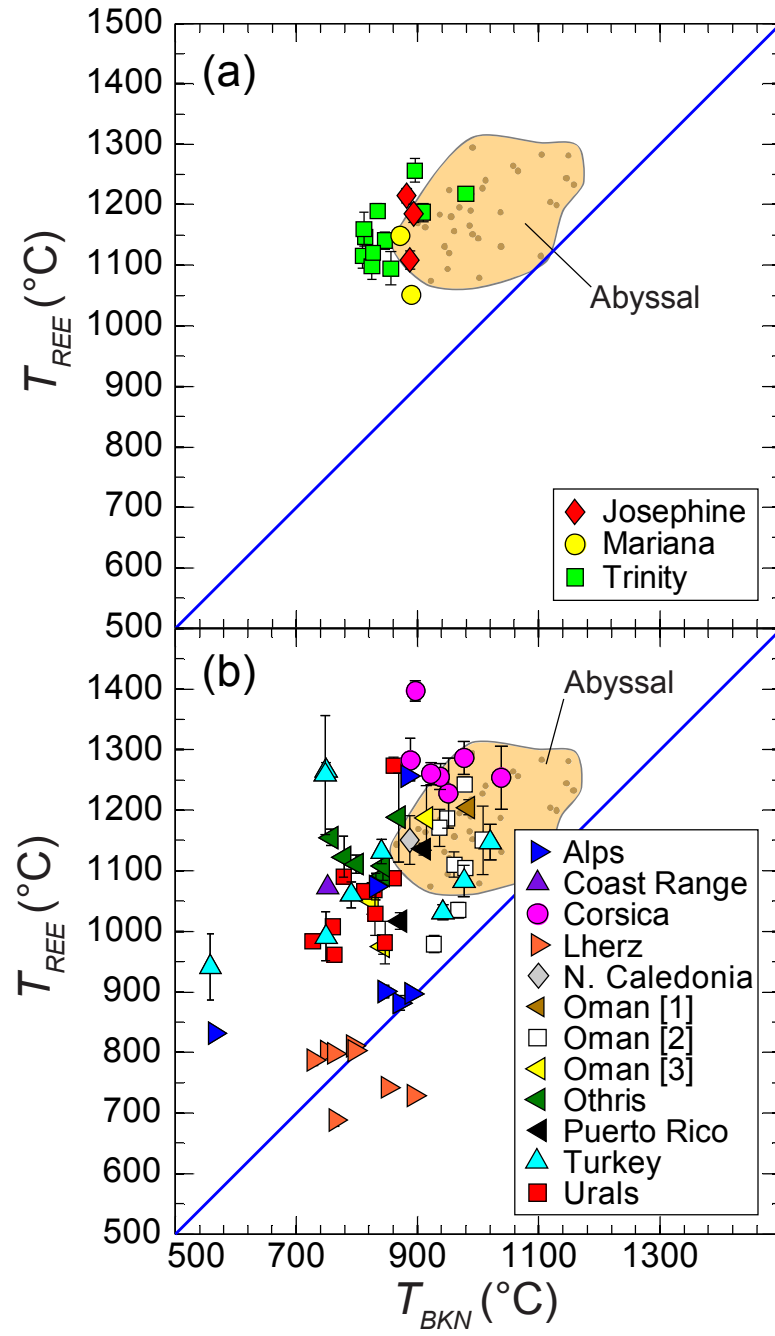


Figure 3.

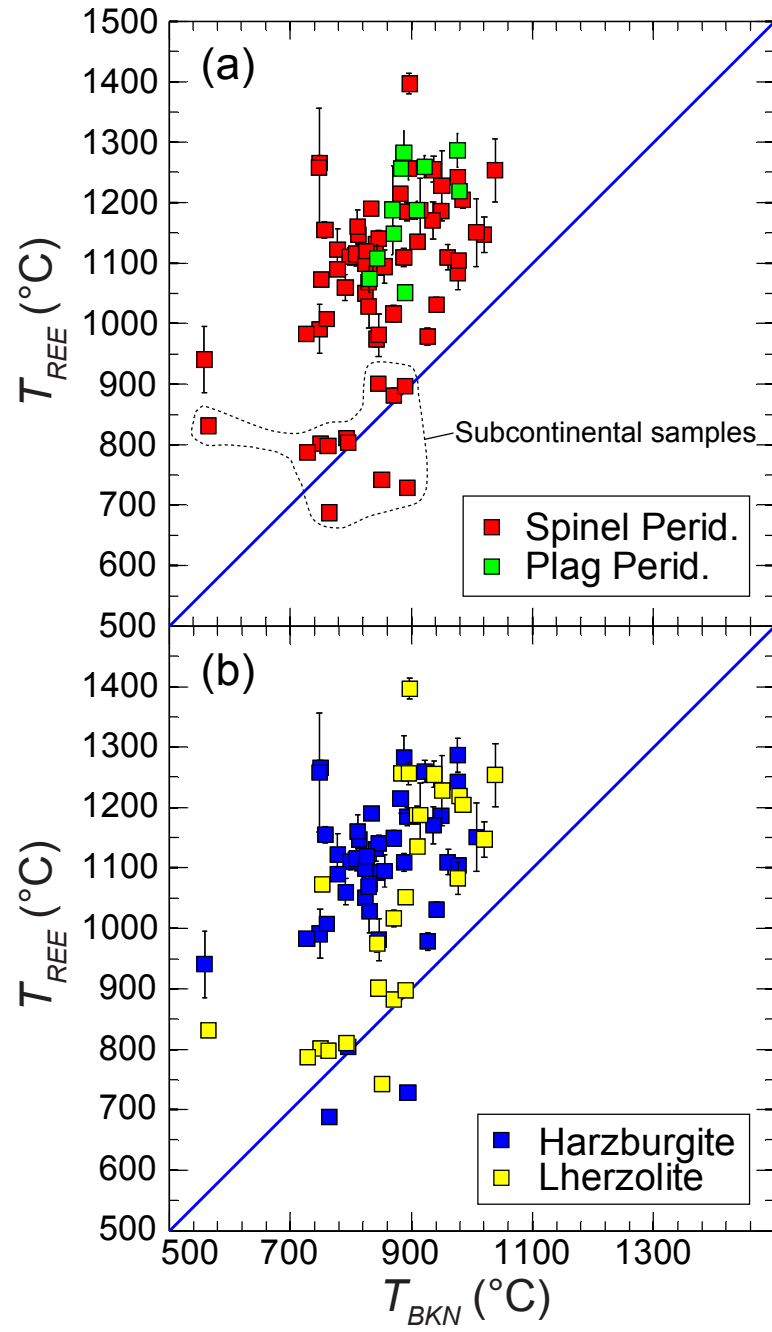


Figure 4.

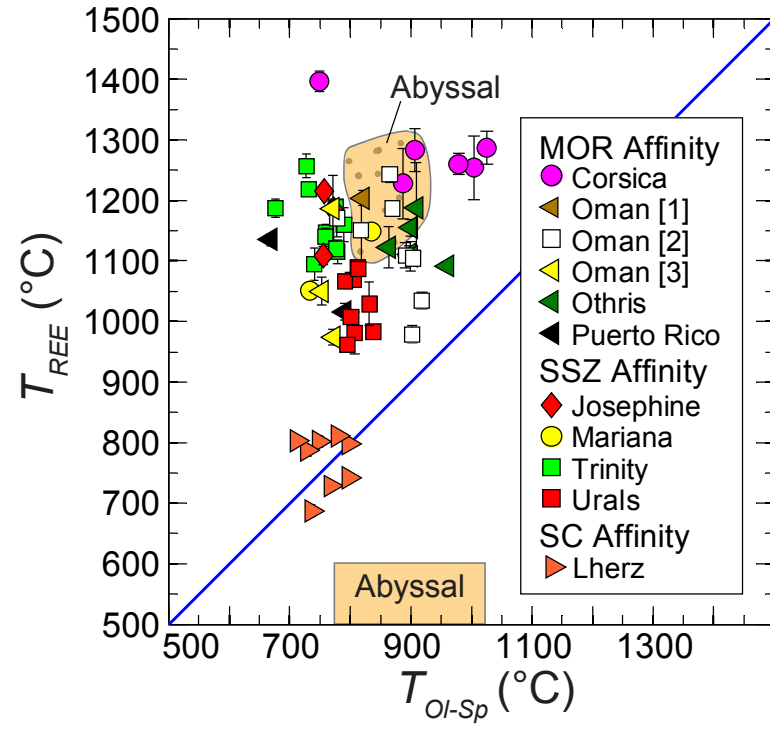


Figure 5.

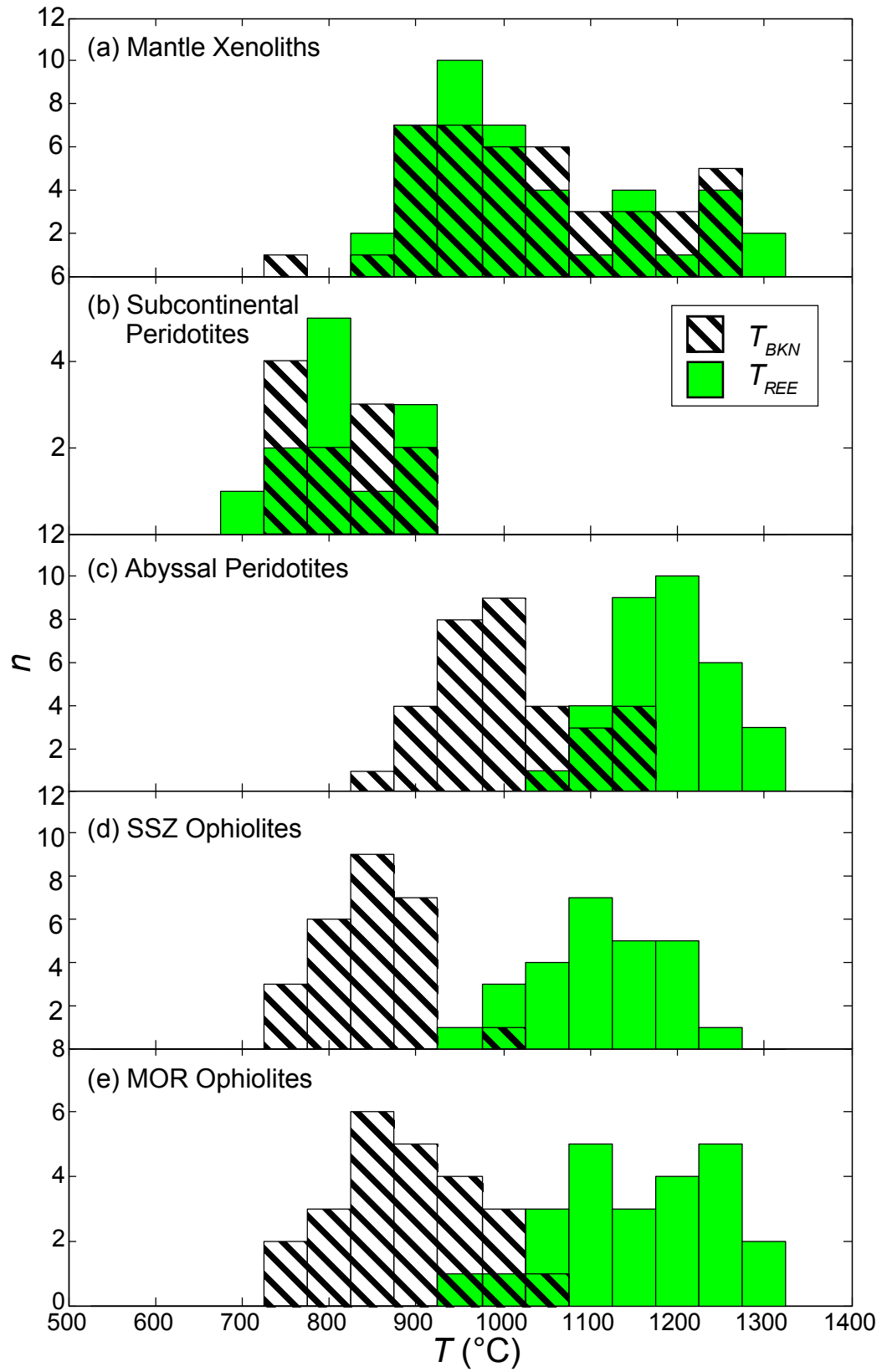


Figure 6.

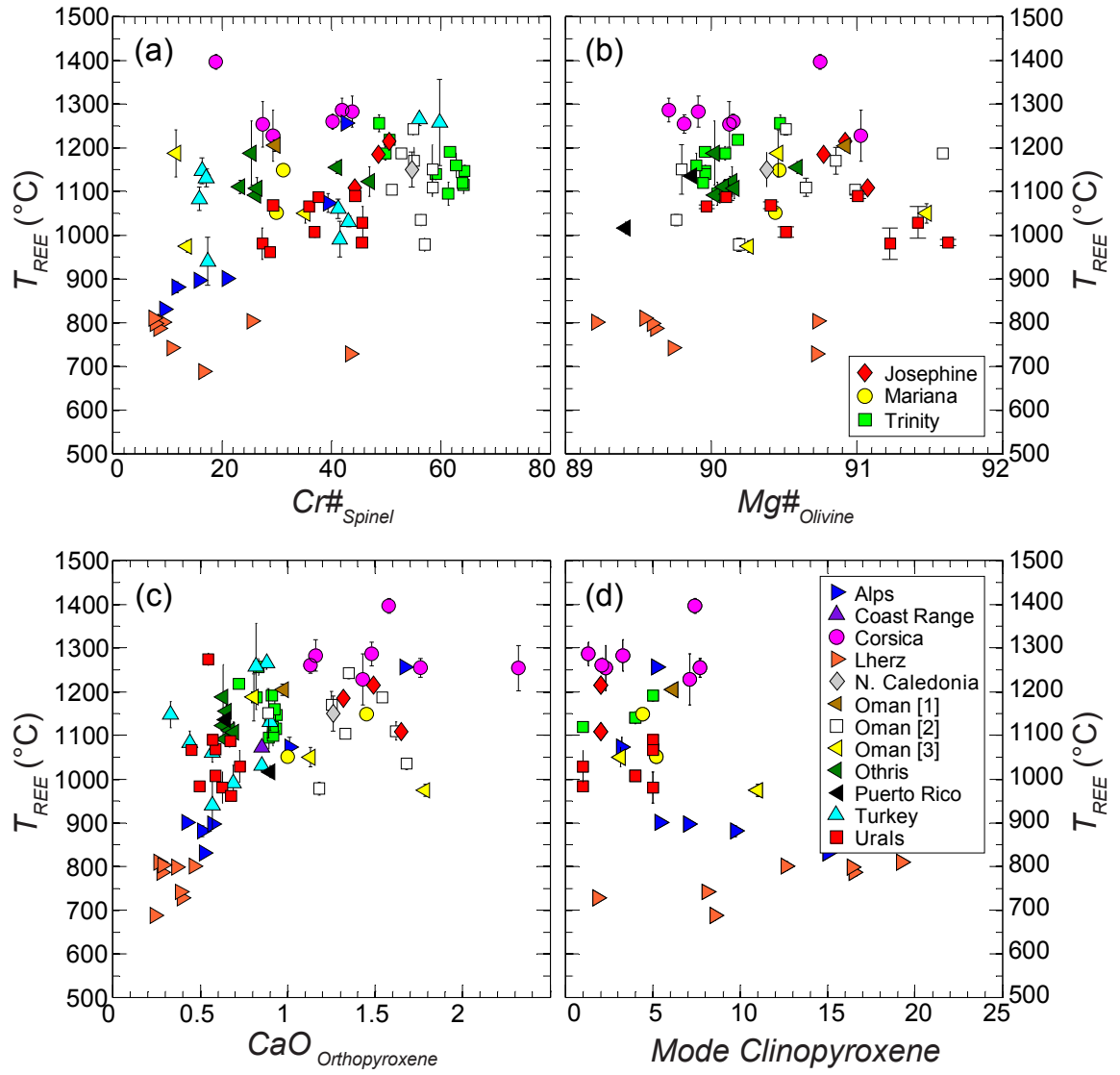


Figure 7.

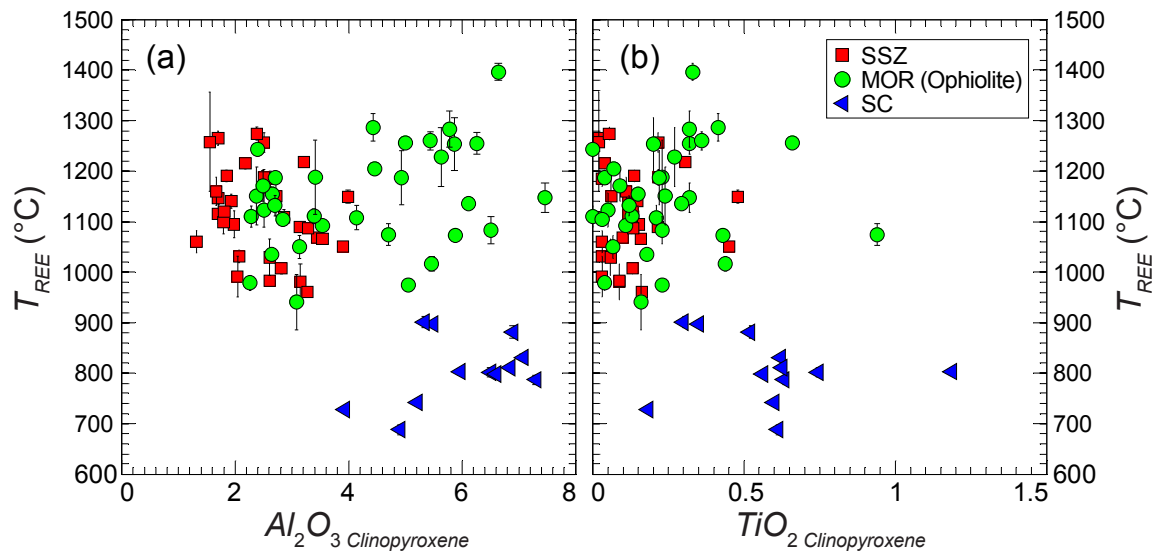


Figure 8.

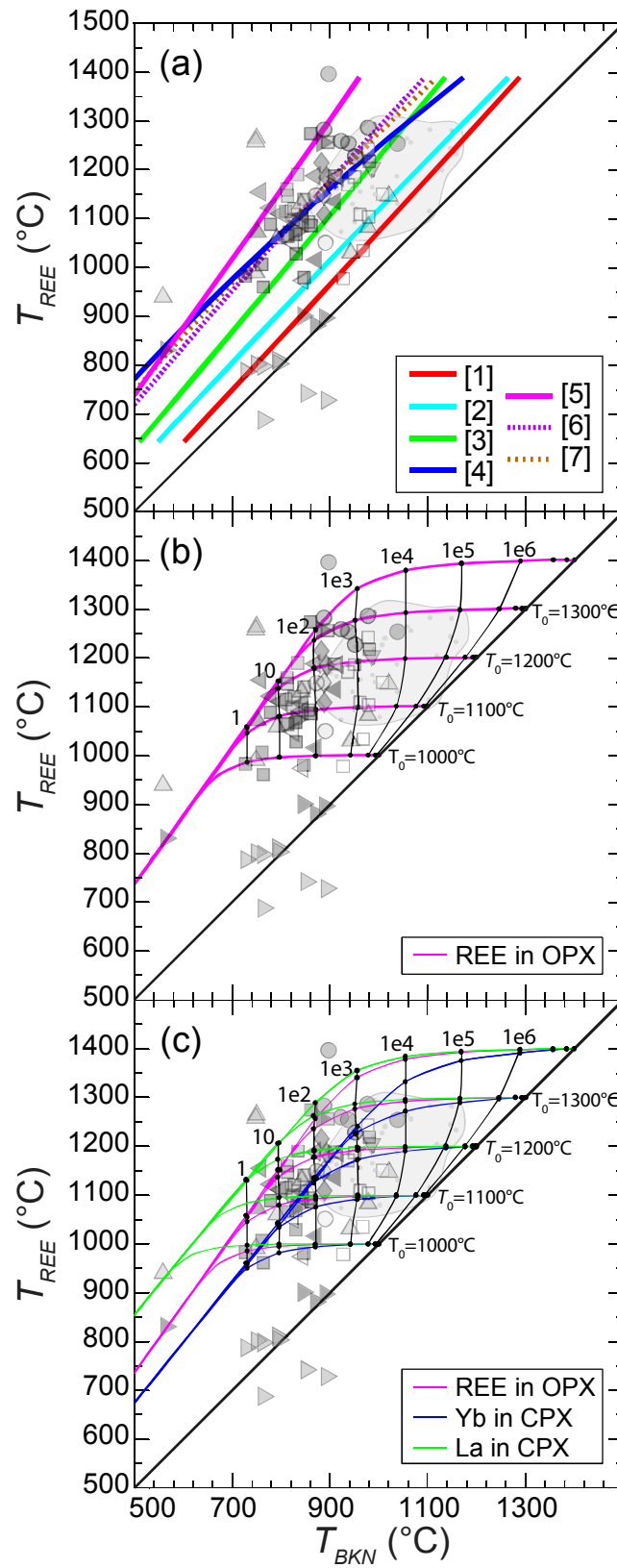
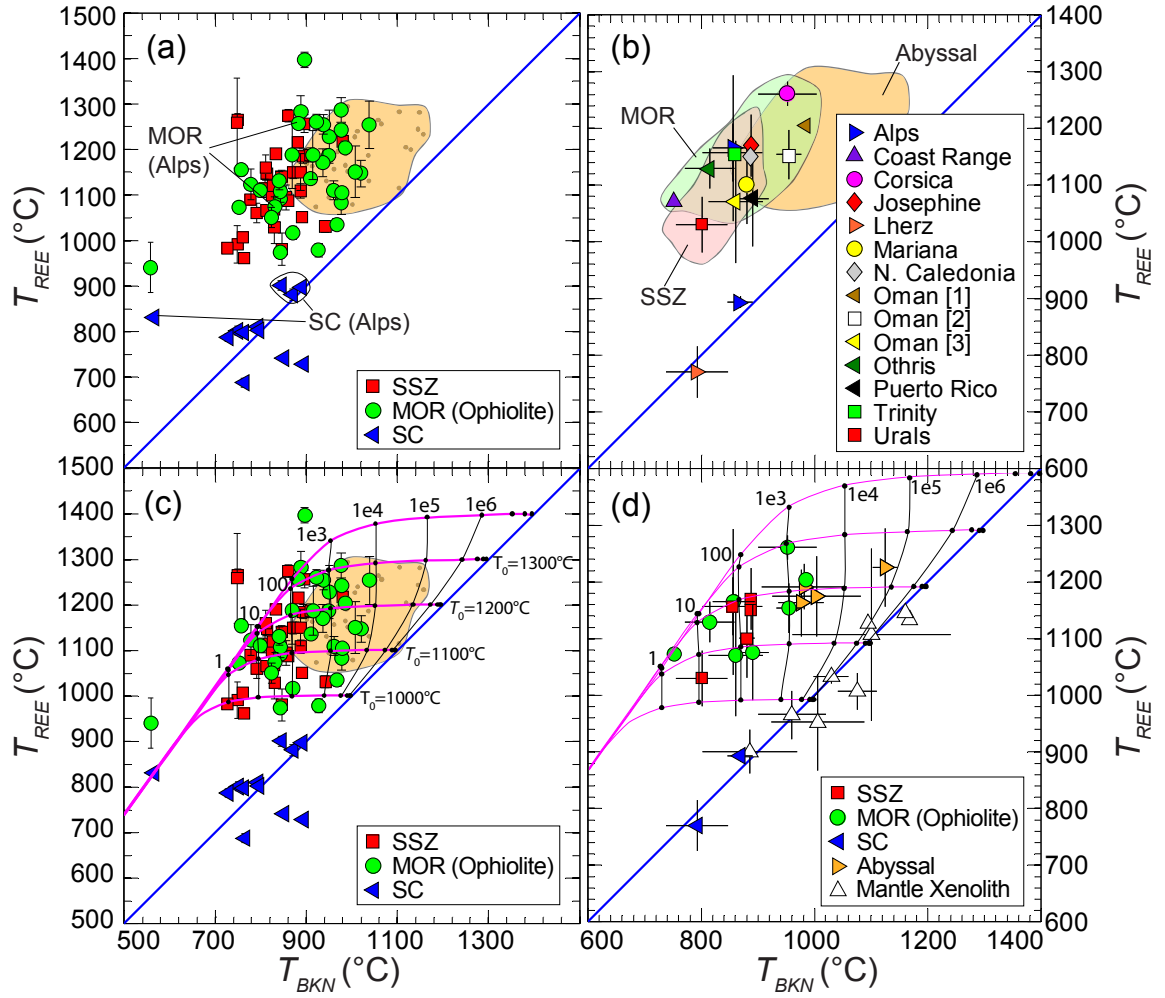
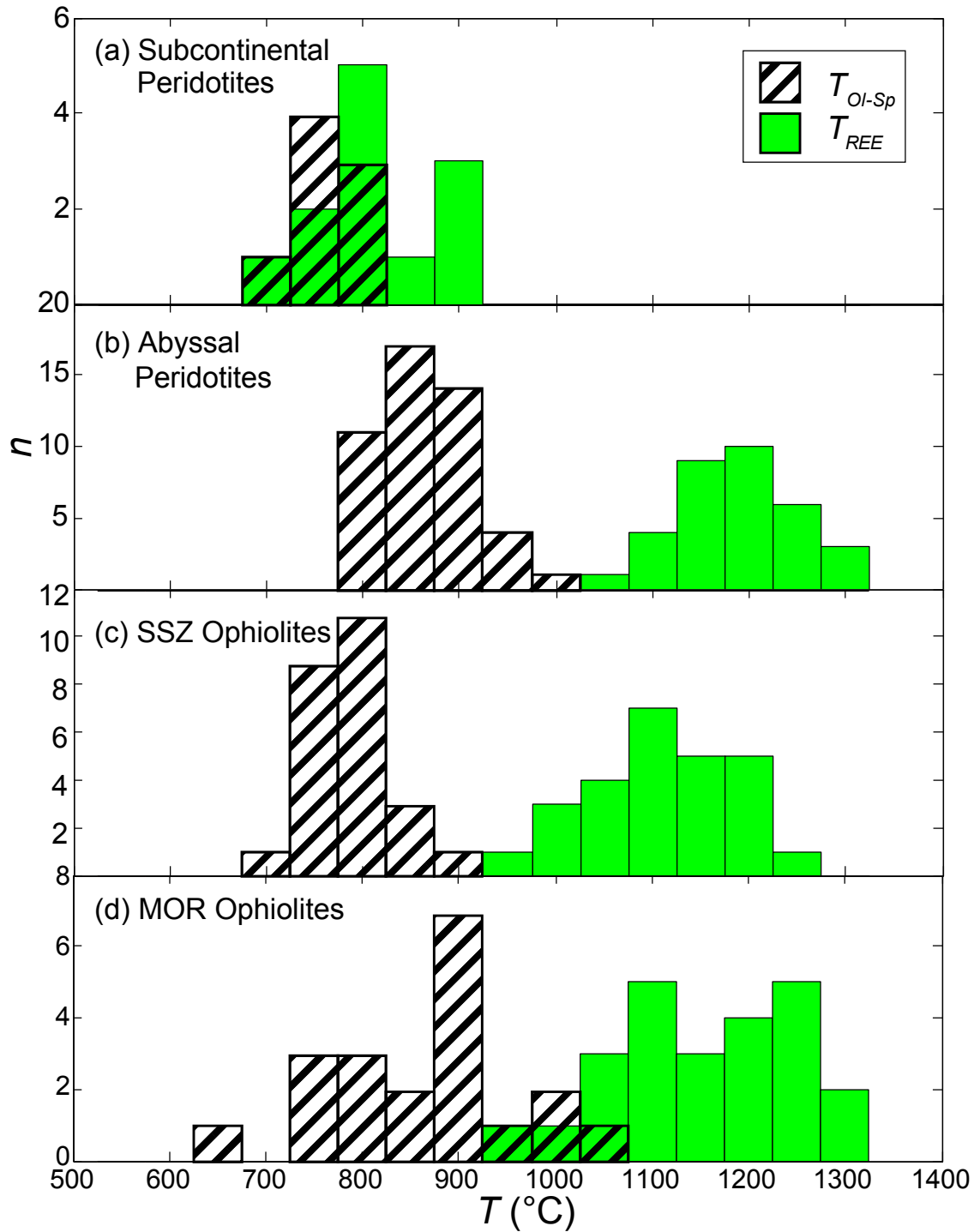


Figure 9.



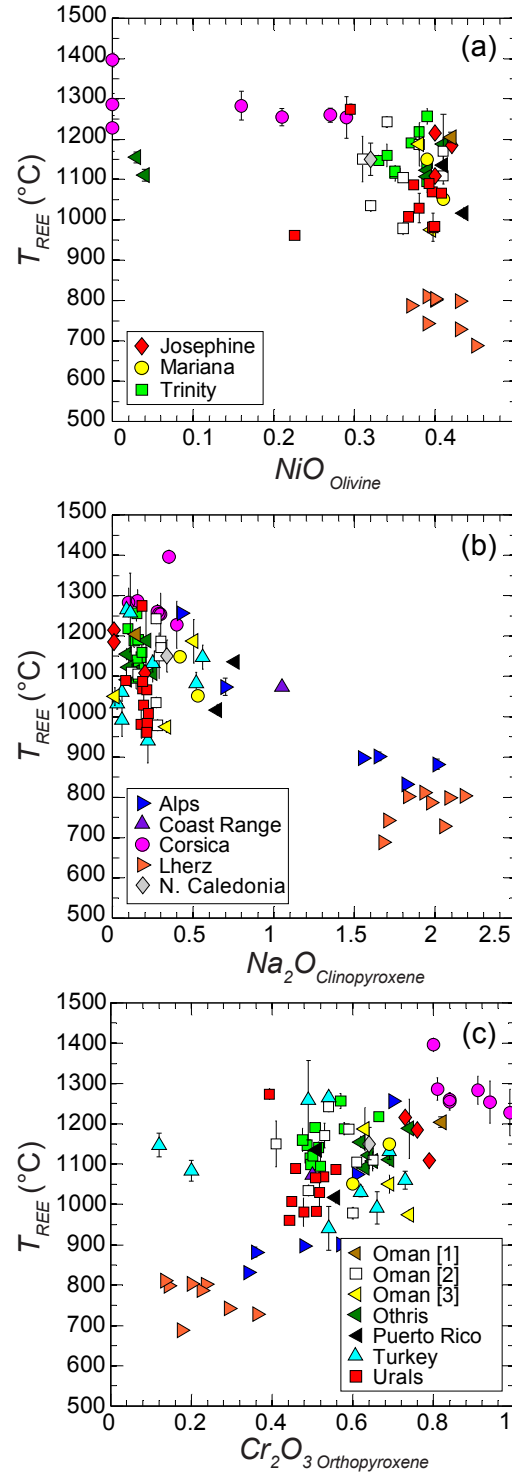
Supplementary Material

Figure S1.



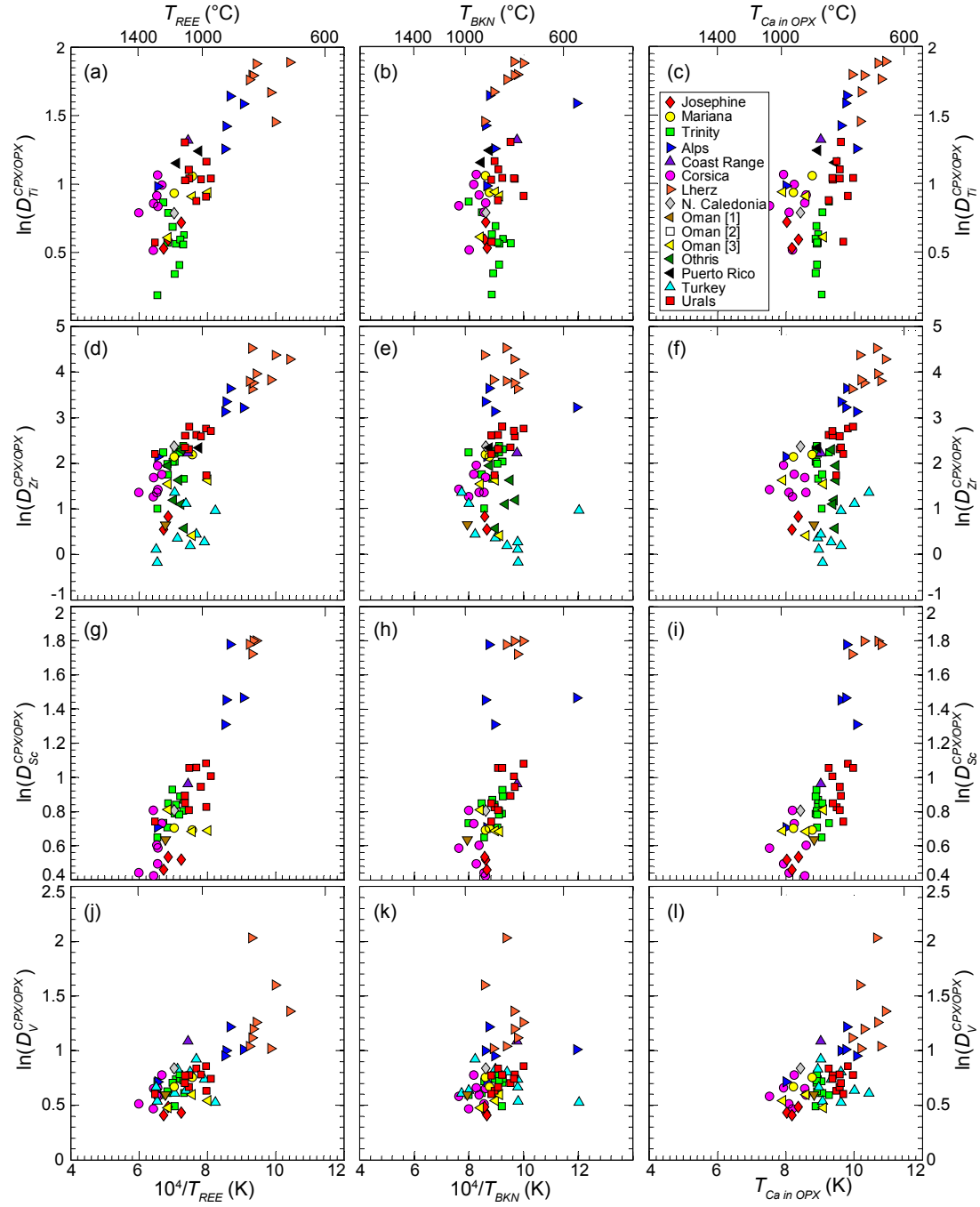
Histograms for samples with different tectonic affinities showing temperatures calculated using the REE-in-two-pyroxene thermometer (green) and the olivine-spinel major element thermometer of Li et al. (1995) (black diagonal lines).

Figure S2.



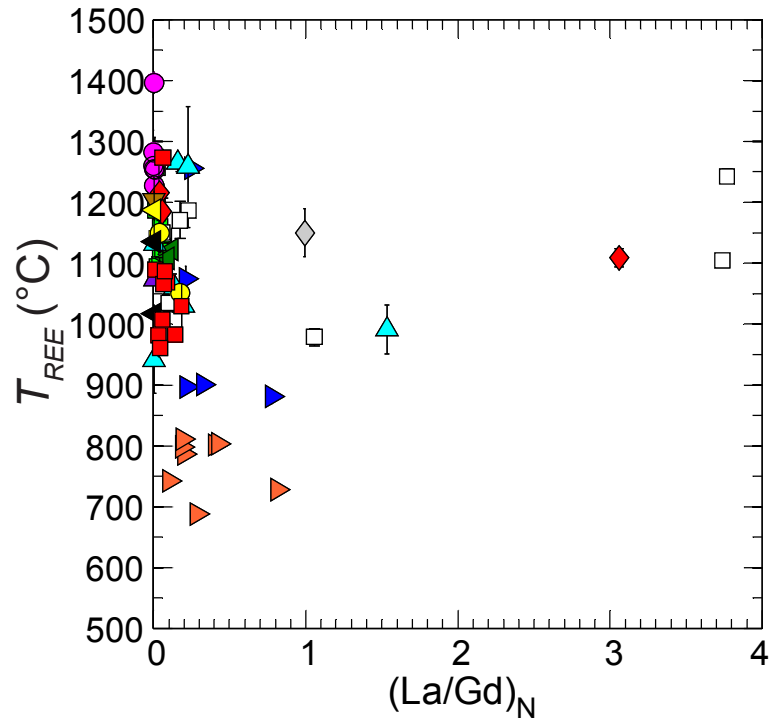
T_{REE} plotted against selected minor elements in minerals (in wt%). The correlations may be attributable to subsolidus equilibration.

Figure S3.



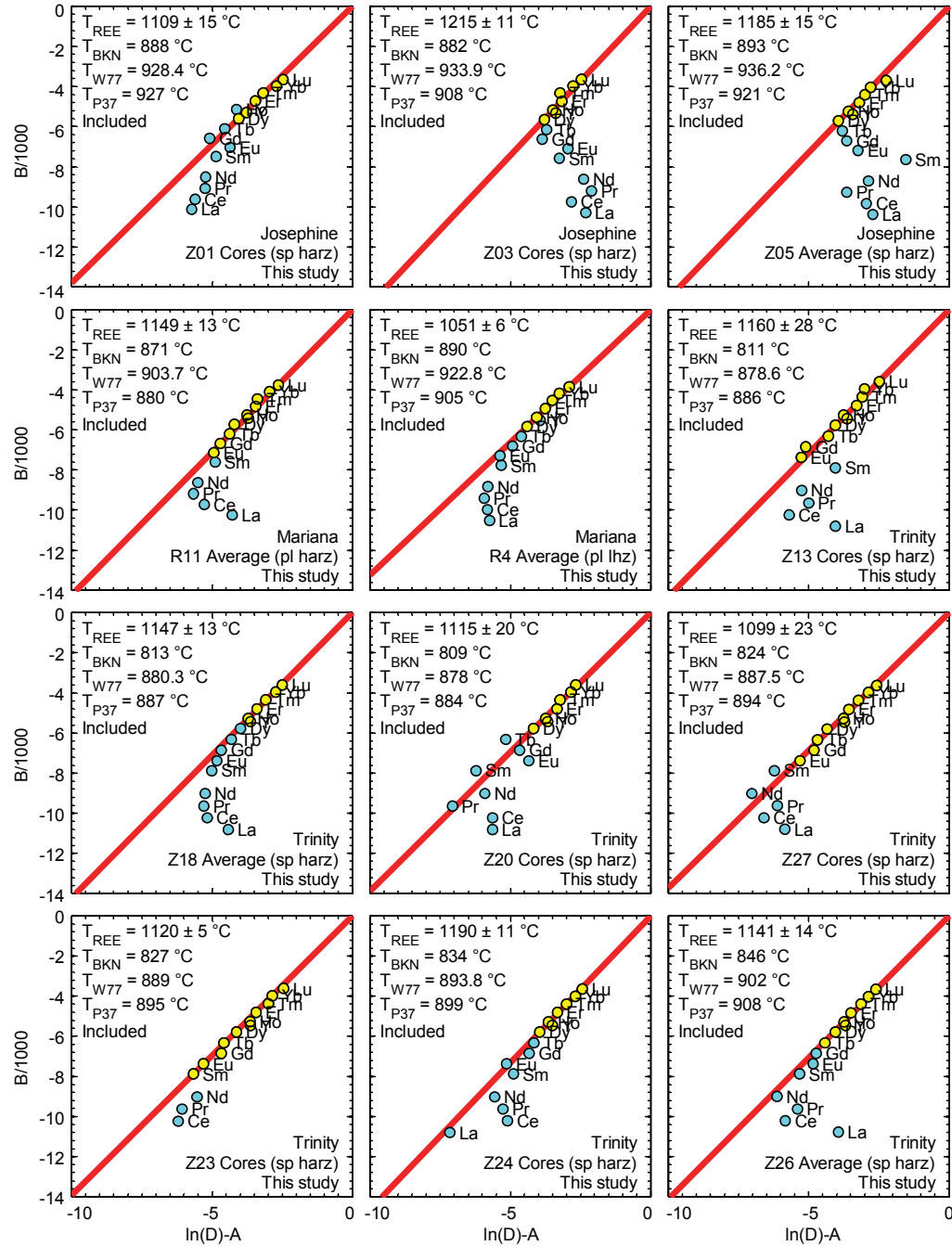
Opx-cpx partitioning for HFSE (a-f), and selected transition metals (g-l) against T_{REE} , T_{BKN} , and the Ca in opx thermometer of Brey and Köhler (1990). Note good correlations for T_{REE} , poor correlations for T_{BKN} , and scattered correlations for Ca in opx. The trends may reflect temperature (and composition) sensitive opx-cpx partitioning.

Figure S4.



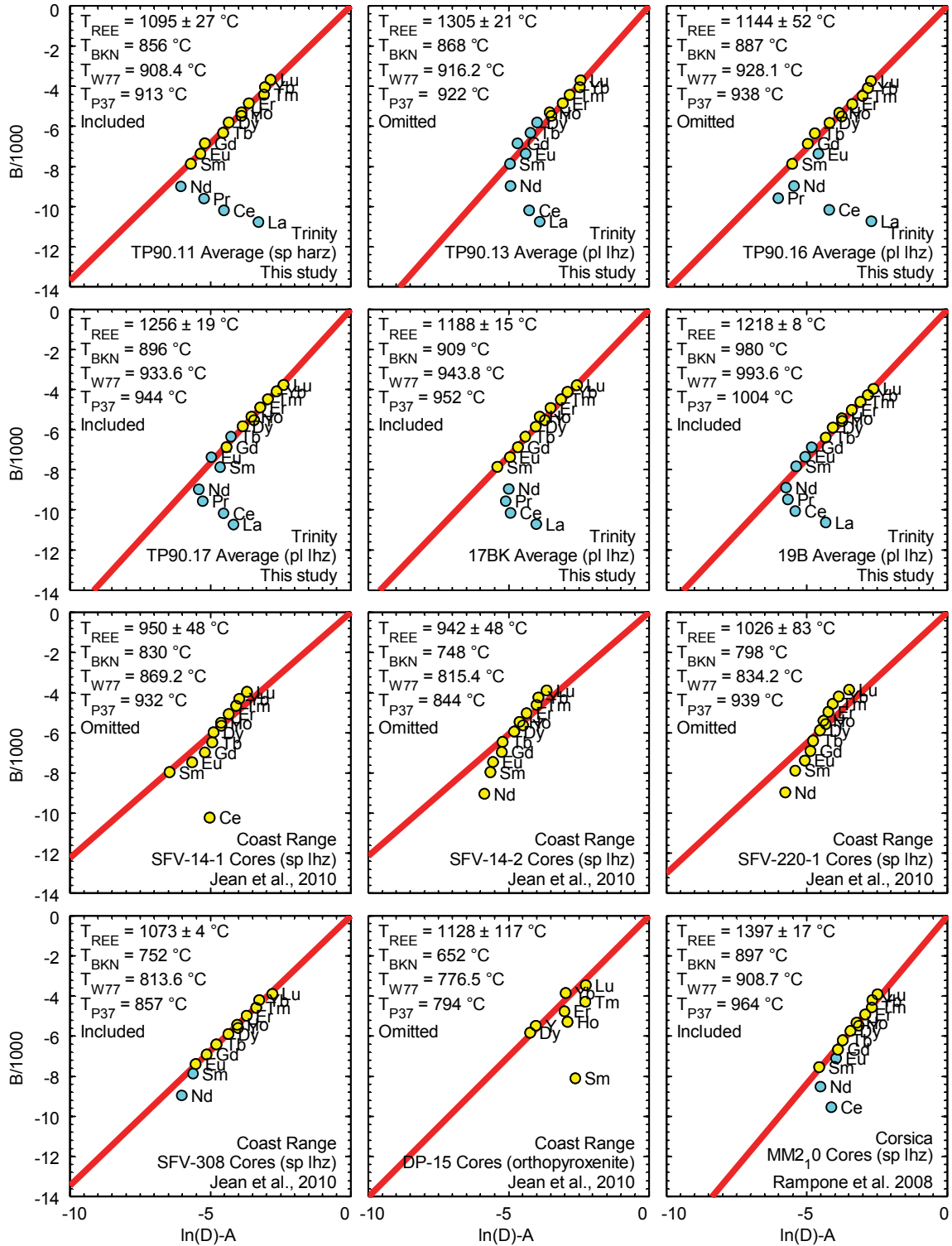
T_{REE} vs. chondrite normalized La/Gd in clinopyroxene. The trend for samples with $(La/Gd)_N > 1$ may reflect reaction of colder depleted melting residues with hotter LREE-enriched melts. The correlation may be skewed by cold peridotites with low La/Gd from Lherz and the Alps. More data is needed to establish a correlation.

Figure S5a.



Inversion diagrams for data from this study. T_{BKN} refers to the two pyroxene thermometer of Brey and Köhler (1990), T_{W77} refers to the two pyroxene thermometer of Wells (1977), and T_{P37} refers to the two pyroxene thermometer of Putirka (2008, his Eq. 37).

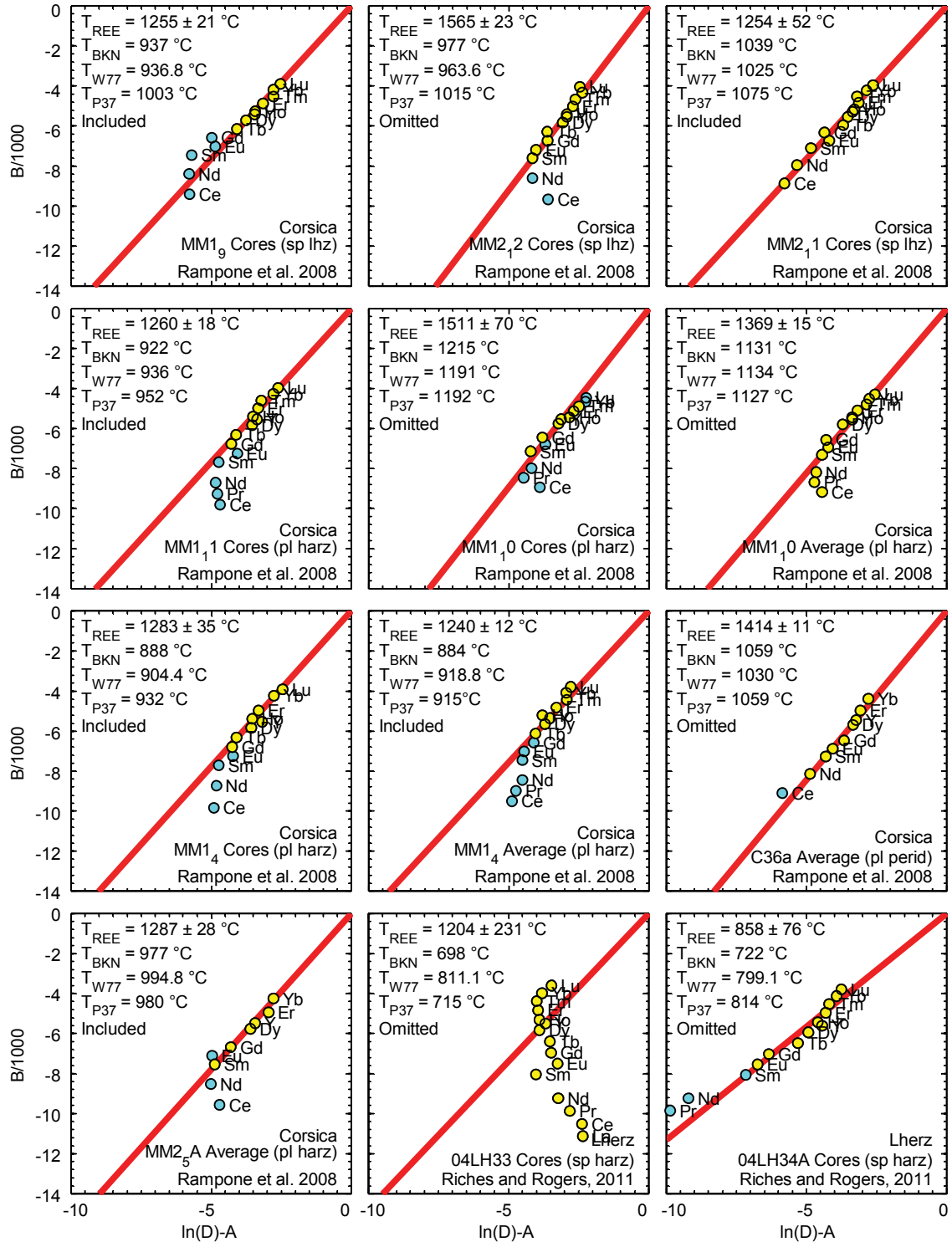
Figure S5b.



Inversion diagrams for data from this study, Jean et al. (2010) and Rampone et al.

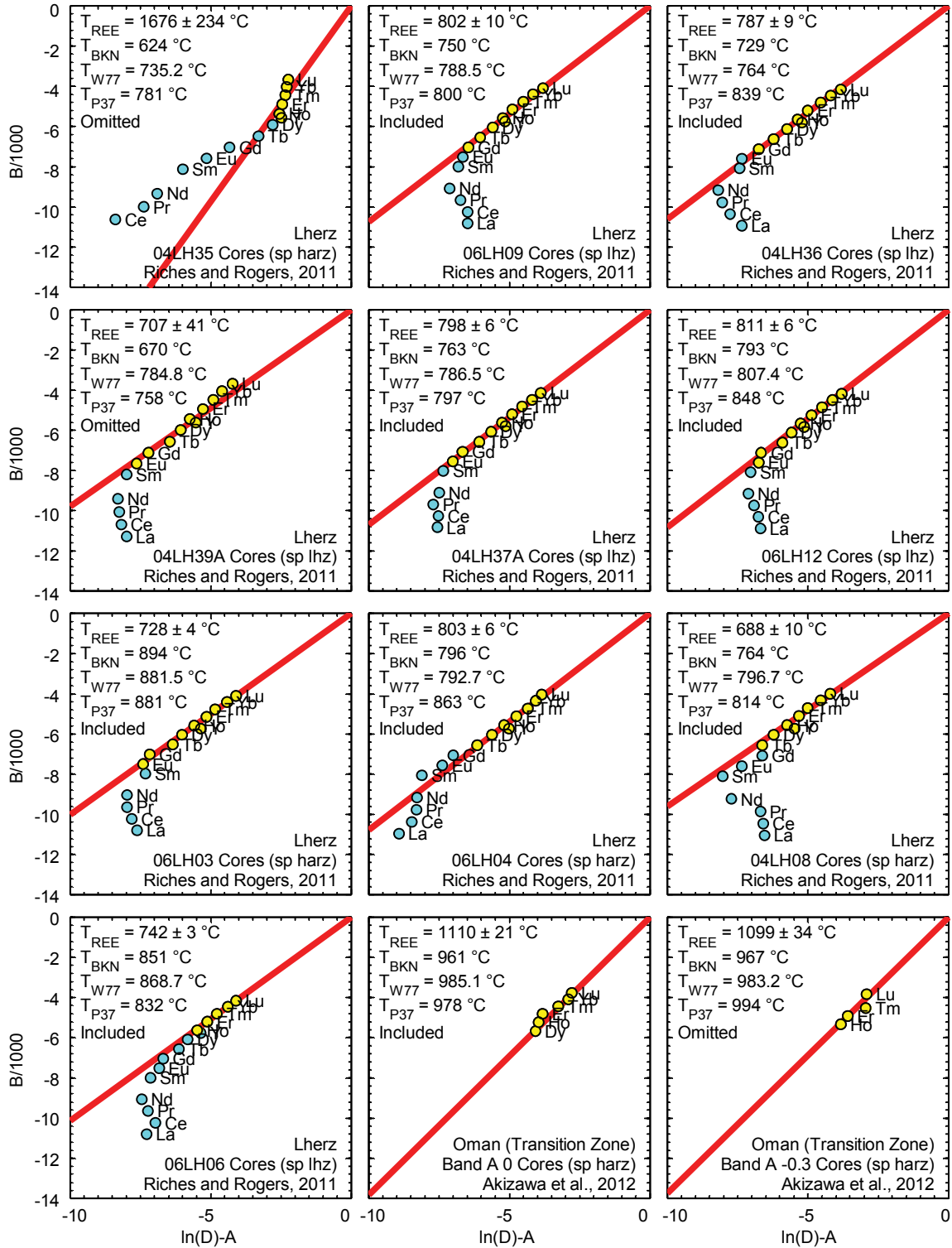
(2008).

Figure S5c.



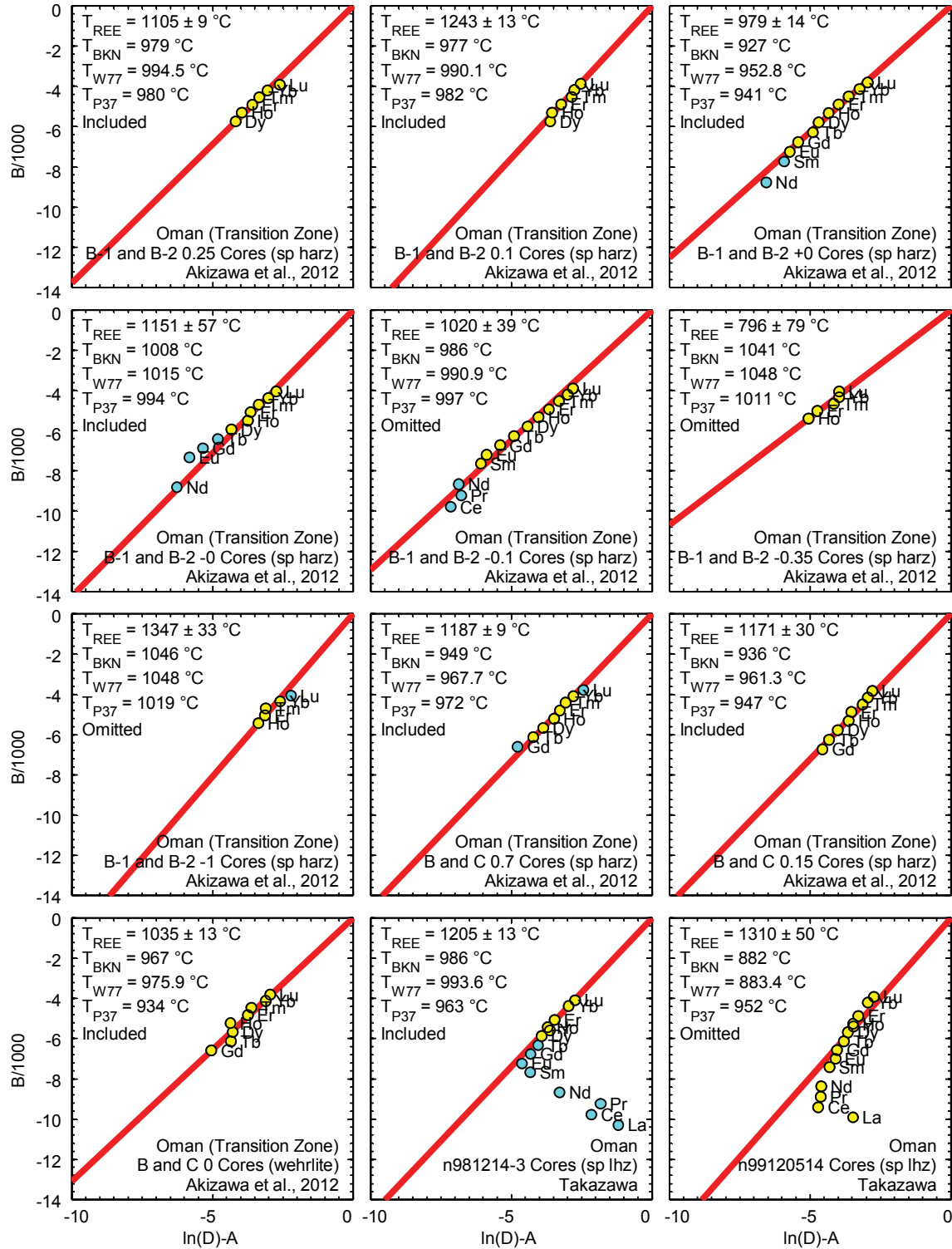
Inversion diagrams for data from Rampone et al. (2008) and Riches and Rogers (2011).

Figure S5d.



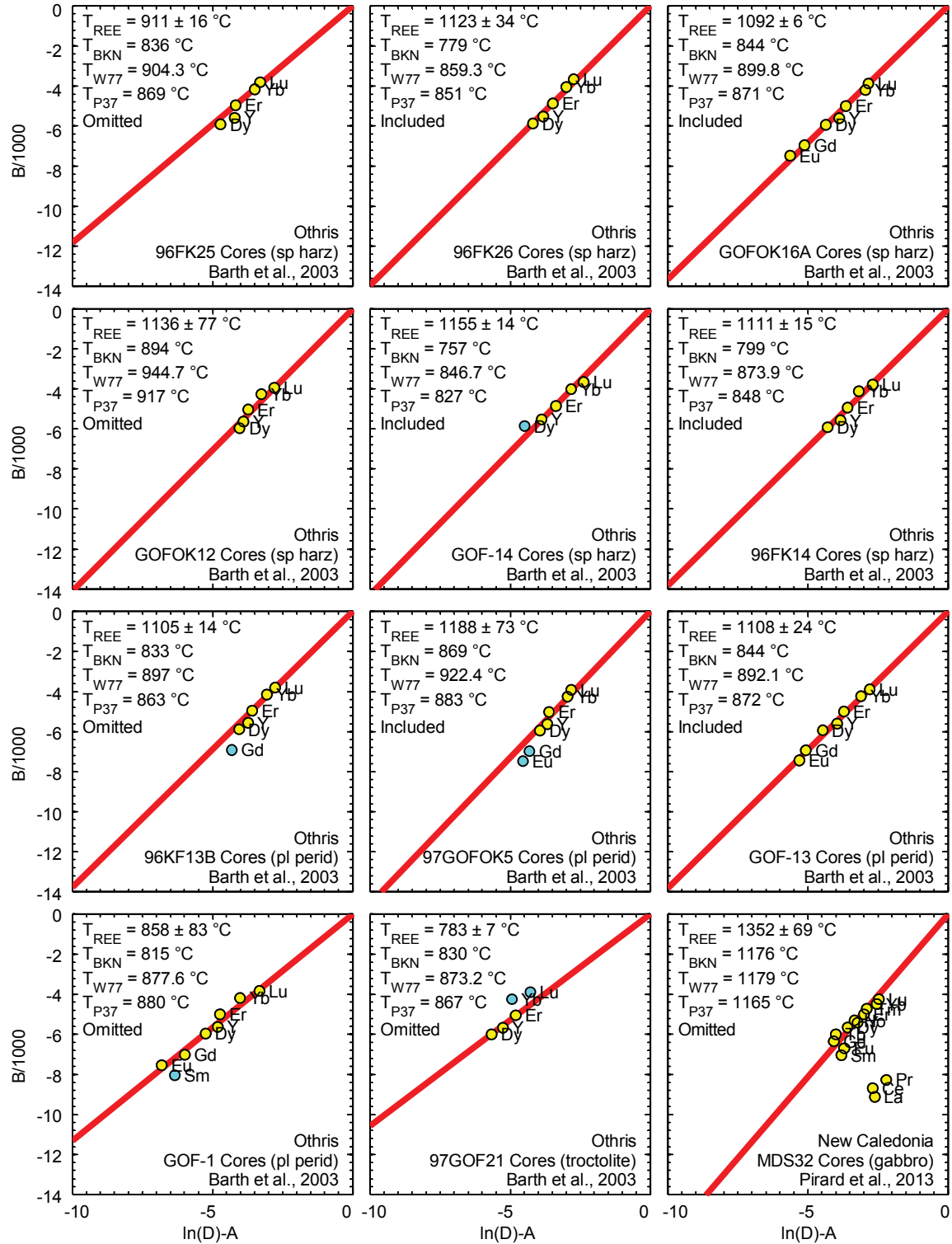
Inversion diagrams for data from Riches and Rogers (2011) and Akizawa et al. (2012).

Figure S5e.



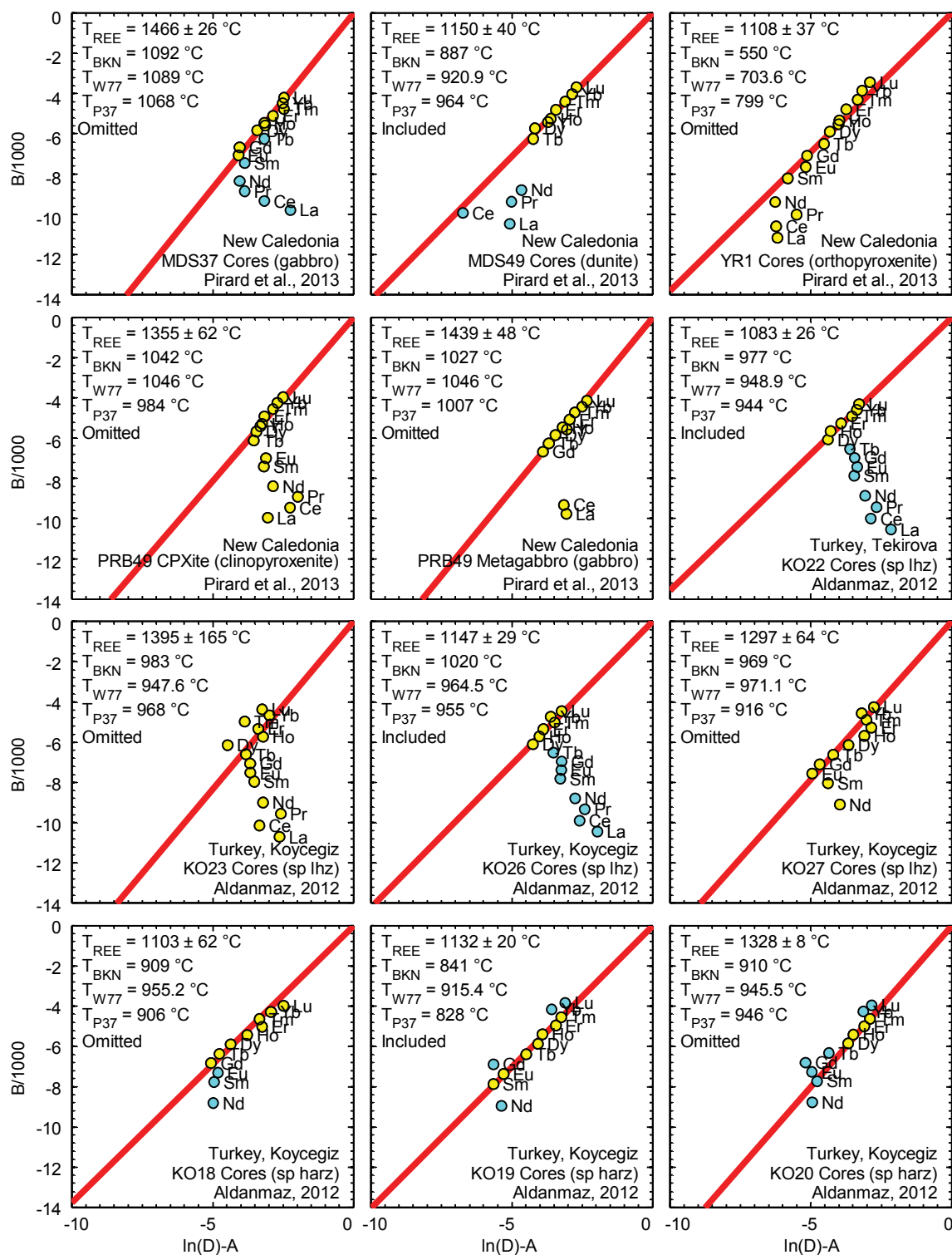
Inversion diagrams for data from Akizawa et al. (2012) and Takazawa et al. (2003).

Figure S5f.



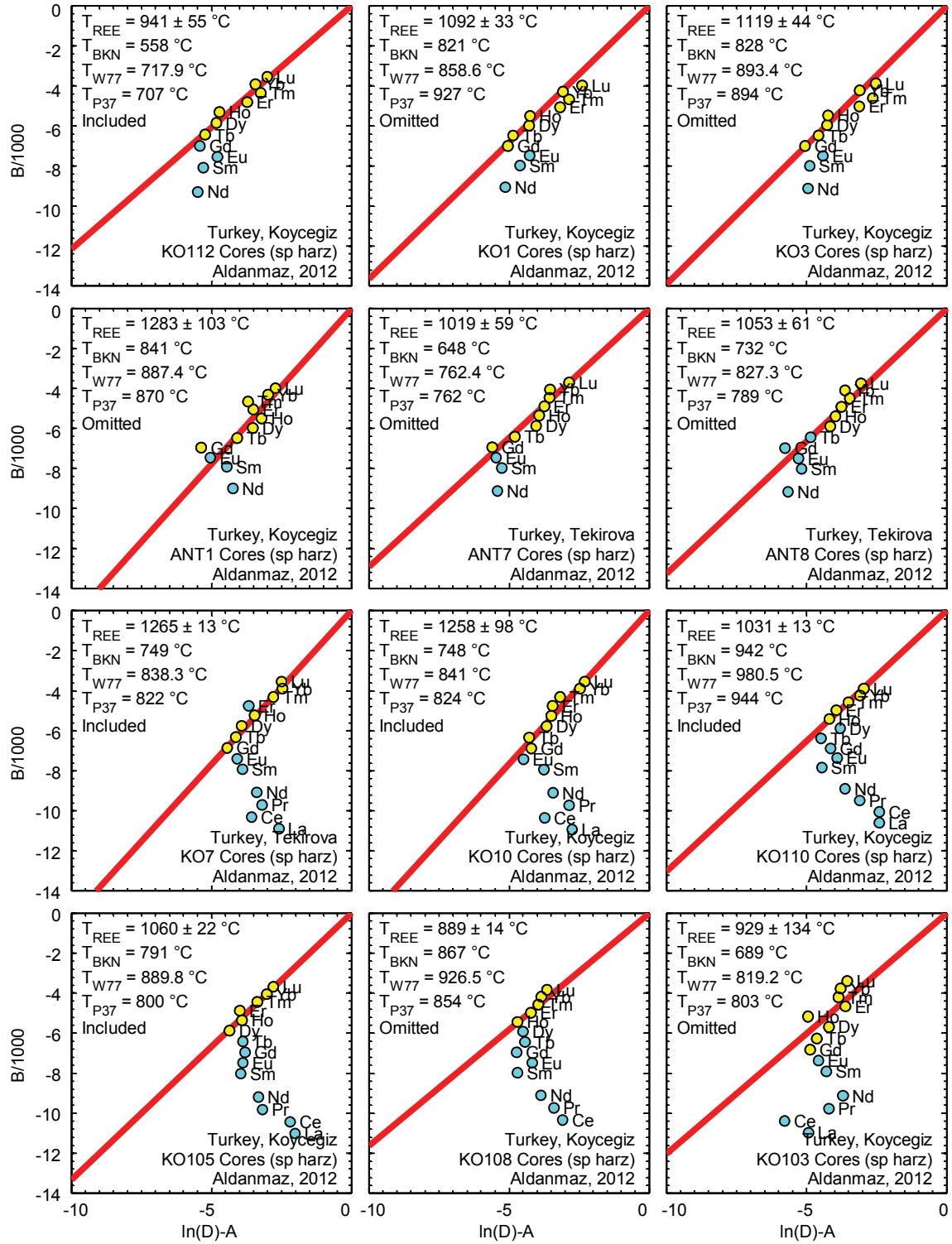
Inversion diagrams for data from Barth et al. (2003) and Pirard et al. (2013).

Figure S5g.



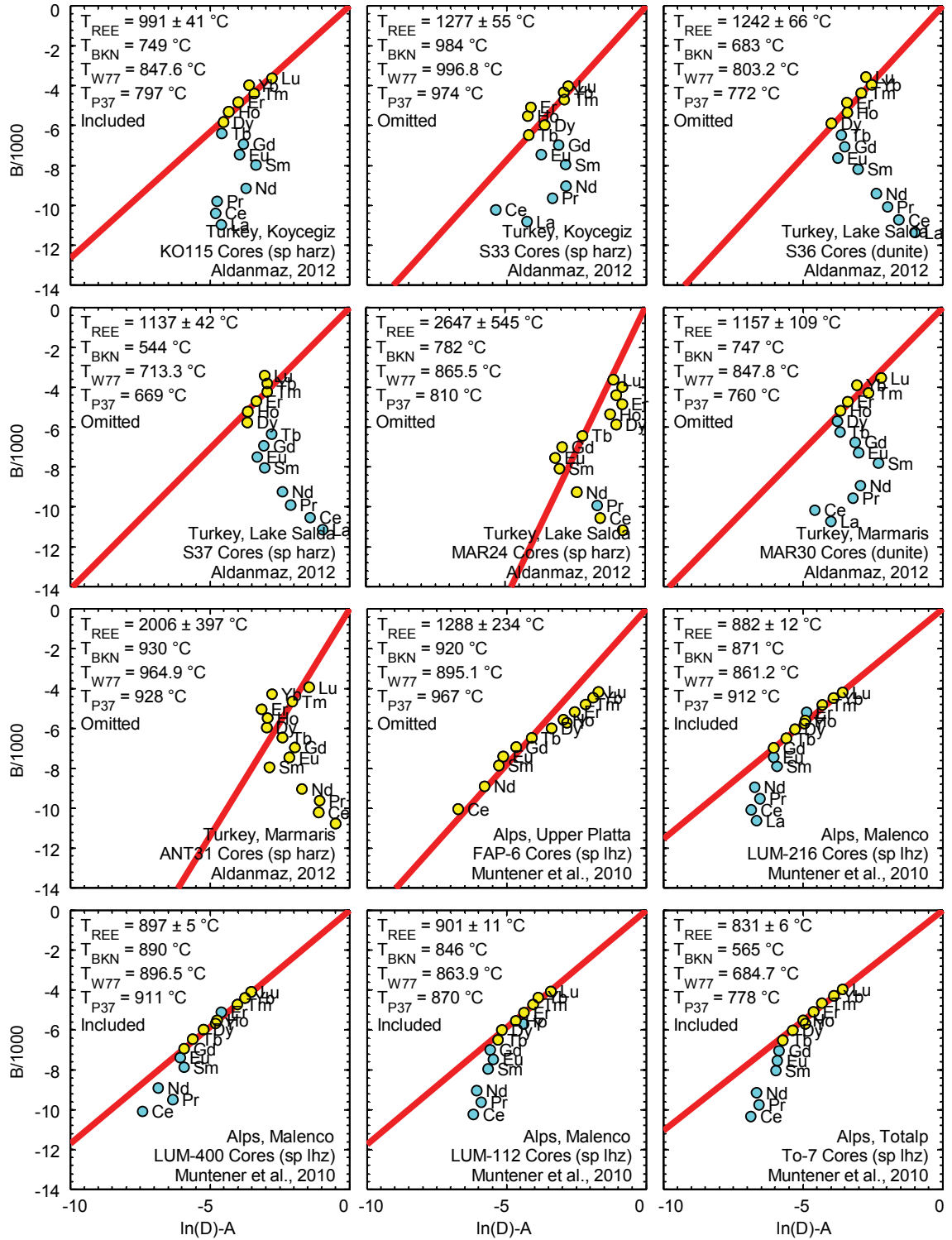
Inversion diagrams for data from Pirard et al. (2013) and Aldanmaz (2012).

Figure S5h.



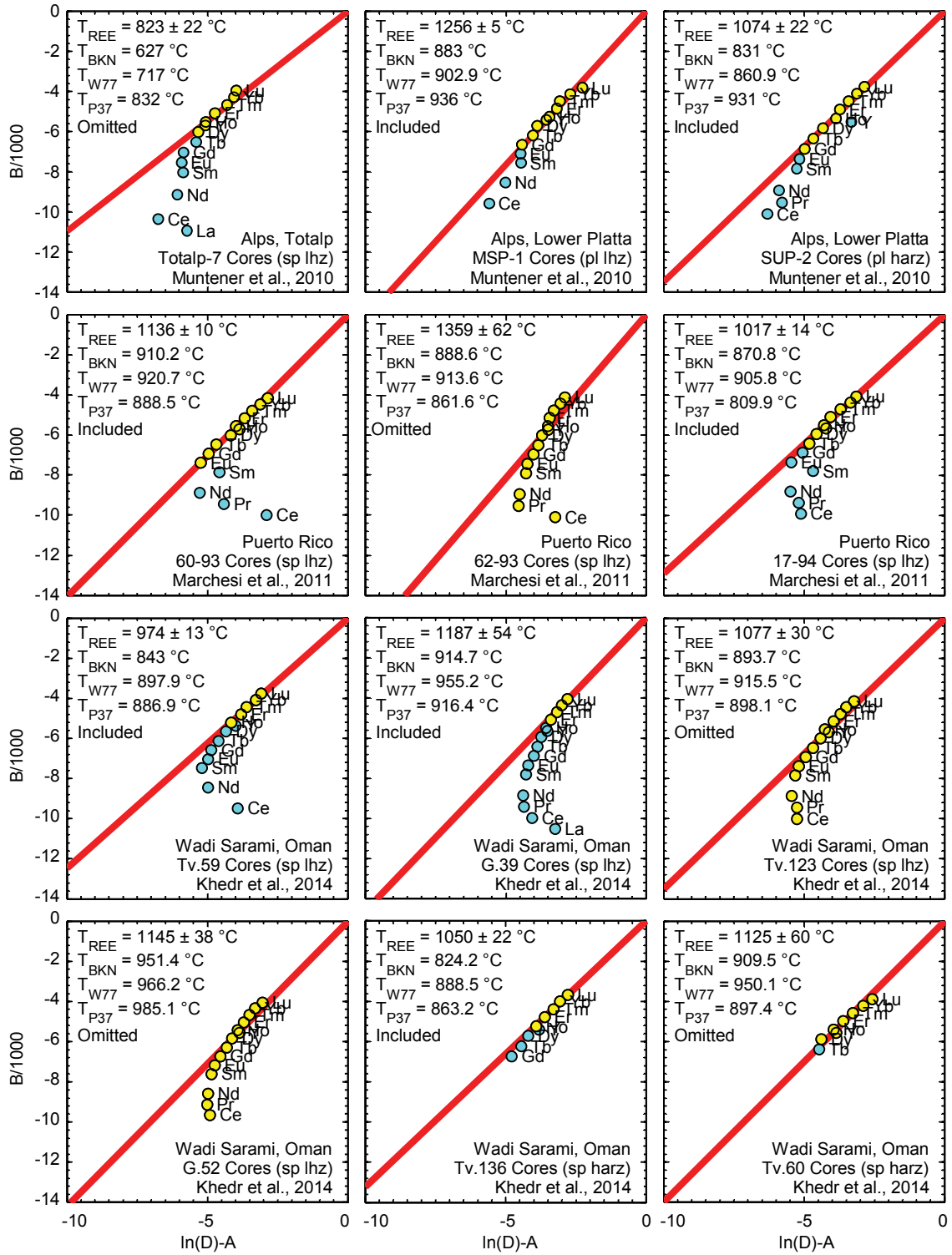
Inversion diagrams for data from Aldanmaz (2012).

Figure S5i.



Inversion diagrams for data from Aldanmaz (2012) and Müntener et al. (2010).

Figure S5j.



Inversion diagrams for data from Müntener et al. (2010), Marchesi et al., 2011, and Khedr et al., 2014.

Figure 10 displays a series of B/1000 vs. $\ln(D)-A$ diagrams for various meteorite samples. The diagrams are arranged in a 4x3 grid, with the last cell containing only one diagram. Each diagram shows a red line representing the theoretical crystallization path and data points for different elements (Dy, Tb, Y, Ho, Er, Tm, Yb, Lu). The y-axis is B/1000 (0 to -14) and the x-axis is $\ln(D)-A$ (-10 to 0). The diagrams are labeled with sample names and core numbers, and each includes calculated temperatures for REE, BKN, W77, and P37, along with a note on whether the sample is 'Included'.

Sample	T_{REE} (°C)	T_{BKN} (°C)	T_{W77} (°C)	T_{P37} (°C)	Included
6 13 Cores (sp harz) Batanova et al., 2011	981 ± 35	846.4	905.7	864.7	Yes
6 24 Cores (sp harz) Batanova et al., 2011	1069 ± 8	829.5	896	875.6	Yes
6 35 ₂ Cores (sp harz) Batanova et al., 2011	1089 ± 5	778	869.3	830	Yes
7 15C6 Cores (sp harz) Batanova et al., 2011	983 ± 7	726.8	825.3	785.6	Yes
7 15C5 Cores (sp harz) Batanova et al., 2011	1029 ± 36	830.3	896.1	851.1	Yes
6 11 ₄ Cores (sp harz) Batanova et al., 2011	1008 ± 11	760.6	845.9	824.1	Yes
6 33 ₂ Cores (websterite) Batanova et al., 2011	1087 ± 7	860.9	913.3	865	Yes
214 ₇ Cores (websterite) Batanova et al., 2011	1274 ± 13	860.6	913.8	894.2	Yes
7 16o Cores (websterite) Batanova et al., 2011	961 ± 7	763.1	846	831	Yes
6 11 _{3c} Cores (websterite) Batanova et al., 2011	1066 ± 5	812.3	872.8	843.7	Yes

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Table S1.

Temperatures, major and trace element data, and representative standard analyses					
Location		Mariana	Mariana	Mariana	Mariana
Sample		R11	R4	R11	R3
Included?		y	y	y	n
Lithology		Plag Harz	Plag Lherz	Plag Harz	Plag Lherz
^a T _{BKN}		871	890	871	855
^b T _{W77}		904	923	904	878
^c T _{P37}		880	905	880	888
^d T _{Ol-Sp}		835	734	835	-
T _{REE}		1149	1051	1177	-
1σ		13	6	18	-
cpx GS (mm)		0.59	0.60	0.59	-
opx GS (mm)		1.93	1.43	1.93	-
n cpx Core		9	13	9	18
n opx Core		19	10	19	11
n cpx Rim		1	4	-	-
n opx Rim		6	0	-	-
SiO ₂	cpx	52.22	52.65	52.22	52.01
TiO ₂	cpx	0.48	0.45	0.48	0.68
Al ₂ O ₃	cpx	3.99	3.90	3.99	3.93
Cr ₂ O ₃	cpx	1.13	0.98	1.13	1.20
FeO	cpx	2.51	2.40	2.51	2.76
MgO	cpx	16.10	16.62	16.10	16.10
MnO	cpx	0.10	0.10	0.10	0.13
CaO	cpx	23.06	22.88	23.06	22.88
Na ₂ O	cpx	0.42	0.53	0.42	0.57
K ₂ O	cpx	0.01	0.01	0.01	0.00
NiO	cpx	0.04	0.06	0.04	0.04
P ₂ O ₅	cpx	0.02	0.02	0.02	0.02
SiO ₂	opx	55.69	55.67	55.69	55.86
TiO ₂	opx	0.16	0.10	0.16	0.19
Al ₂ O ₃	opx	3.39	3.98	3.39	2.47
Cr ₂ O ₃	opx	0.69	0.60	0.69	0.60
FeO	opx	6.16	6.01	6.16	6.35
MgO	opx	33.05	33.48	33.05	33.65
MnO	opx	0.17	0.15	0.17	0.17
CaO	opx	1.45	1.00	1.45	0.88
Na ₂ O	opx	0.03	0.02	0.03	0.03
K ₂ O	opx	0	0	0	0.01
NiO	opx	0.08	0.1	0.08	0.09
P ₂ O ₅	opx	0.01	0	0.01	0.01

Table S1 continued.

Location Sample		Josephine Z01	Josephine Z03	Josephine Z05
Included?		y	y	y
Lithology		Spinel Harz	Spinel Harz	Spinel Harz
^a <i>T</i> _{BKN}		888	882	893
^b <i>T</i> _{W77}		928	934	936
^c <i>T</i> _{P37}		927	908	921
^d <i>T</i> _{Ol-Sp}		756	758	773
<i>T</i> _{REE}		1109	1215	1185
1 σ		15	11	15
cpx GS (mm)		0.23	0.19	0.53
opx GS (mm)		0.85	1.08	0.81
n cpx Core		9	9	1
n opx Core		9	12	20
n cpx Rim		-	-	6
n opx Rim		-	-	0
SiO ₂	cpx	52.81	53.40	53.04
TiO ₂	cpx	0.03	0.04	0.03
Al ₂ O ₃	cpx	2.86	2.18	2.62
Cr ₂ O ₃	cpx	1.11	0.75	1.02
FeO	cpx	2.27	2.25	2.31
MgO	cpx	17.40	17.80	17.60
MnO	cpx	0.08	0.08	0.09
CaO	cpx	23.40	23.80	23.70
Na ₂ O	cpx	0.20	0.01	0.01
K ₂ O	cpx	-	-	-
NiO	cpx	-	-	-
P ₂ O ₅	cpx	-	-	-
SiO ₂	opx	56.13	56.45	56.41
TiO ₂	opx	0.01	0.02	0.02
Al ₂ O ₃	opx	2.42	2.20	2.22
Cr ₂ O ₃	opx	0.79	0.73	0.76
FeO	opx	5.63	5.67	5.86
MgO	opx	33.29	33.38	33.59
MnO	opx	0.14	0.15	0.15
CaO	opx	1.65	1.49	1.32
Na ₂ O	opx	-	-	-
K ₂ O	opx	-	-	-
NiO	opx	-	-	-
P ₂ O ₅	opx	-	-	-

Table S1 continued.

Location		Mariana		Mariana		Mariana	
Sample		R11	1 σ	R4	1 σ	R11	1 σ
Included?		y		y		y	
Lithology		Plag Harz		Plag Lherz		Plag Harz	
Li	cpx	1.29	0.63	0.79	0.58	1.34	0.65
Na ₂ O	cpx	0.428	0.025	0.380	0.060	0.428	0.027
K ₂ O	cpx	0.00100	0.00031	0.00066	0.00038	0.00098	0.00038
Sc	cpx	88.0	6.9	71.3	9.4	87.0	6.6
TiO ₂	cpx	0.477	0.057	0.461	0.113	0.472	0.059
V	cpx	334	20	261	15	334	21
Cr	cpx	8008	643	7070	729	8036	675
Co	cpx	18.3	0.8	19.1	0.9	18.4	0.8
Ni	cpx	298.7	7.7	291.7	19.8	299.6	7.6
Cu	cpx	-	-	-	-	-	-
Sr	cpx	1.44	0.14	6.80	1.11	1.44	0.15
Y	cpx	23.8	1.9	22.5	5.7	23.6	1.9
Zr	cpx	20.34	2.69	28.46	10.26	20.32	2.85
Nb	cpx	0.0127	0.0096	0.0192	0.0128	0.0133	0.0104
La	cpx	0.129	0.033	0.554	0.112	0.127	0.034
Ce	cpx	1.002	0.130	3.033	0.634	0.989	0.130
Pr	cpx	0.314	0.053	0.637	0.164	0.311	0.056
Nd	cpx	2.395	0.270	3.765	1.116	2.411	0.281
Sm	cpx	1.351	0.264	1.577	0.453	1.330	0.271
Eu	cpx	0.404	0.032	0.561	0.145	0.409	0.030
Gd	cpx	2.845	0.333	2.694	0.756	2.841	0.353
Tb	cpx	0.488	0.068	0.474	0.106	0.482	0.070
Dy	cpx	3.342	0.290	3.234	0.691	3.342	0.308
Ho	cpx	0.675	0.086	0.670	0.128	0.681	0.089
Er	cpx	1.839	0.205	1.852	0.294	1.814	0.200
Tm	cpx	0.283	0.041	0.211	0.042	0.280	0.043
Yb	cpx	1.443	0.148	1.433	0.131	1.435	0.154
Lu	cpx	0.204	0.035	0.215	0.027	0.200	0.034
Hf	cpx	0.842	0.129	0.741	0.258	0.831	0.131
Ta	cpx	-	-	0.00464	0.00382	0.00236	0.00253
Pb	cpx	0.011	0.009	-	-	0.010	0.008

Na₂O, K₂O, and TiO₂ are reported in wt. %, all other elements in ppm.

Table S1 continued.

Location		Mariana		Josephine	
Sample		R3	1 σ	Z01	1 σ
Included?		n		y	
Lithology		Plag Lherz		Spinel Harz	
Li	cpx	-	-	2.60	0.62
Na ₂ O	cpx	0.538	0.048	-	-
K ₂ O	cpx	-	-	-	-
Sc	cpx	70.6	9.4	59.5	4.6
TiO ₂	cpx	0.584	0.088	0.034	0.004
V	cpx	297	17	180	30
Cr	cpx	7192	790	4947	1273
Co	cpx	17.7	1.3	17.2	1.8
Ni	cpx	284.9	35.0	261.4	33.1
Cu	cpx	-	-	-	-
Sr	cpx	2.51	0.82	-	-
Y	cpx	29.1	4.0	1.9	0.3
Zr	cpx	43.10	8.62	-	-
Nb	cpx	0.0182	0.0056	-	-
La	cpx	0.276	0.039	-	-
Ce	cpx	2.922	0.308	0.824	0.538
Pr	cpx	0.814	0.081	0.106	0.070
Nd	cpx	5.828	0.765	-	-
Sm	cpx	2.809	0.349	0.056	0.050
Eu	cpx	0.889	0.098	-	-
Gd	cpx	4.796	0.645	0.099	0.047
Tb	cpx	0.839	0.103	0.028	0.013
Dy	cpx	5.253	0.648	0.179	0.069
Ho	cpx	1.124	0.139	0.062	0.012
Er	cpx	3.180	0.372	0.204	0.045
Tm	cpx	0.422	0.062	0.046	0.013
Yb	cpx	2.451	0.321	0.272	0.072
Lu	cpx	0.353	0.058	0.047	0.008
Hf	cpx	1.562	0.347	0.504	0.511
Ta	cpx	0.00513	0.00360	-	-
Pb	cpx	-	-	-	-

Na₂O, K₂O, and TiO₂ are reported in wt. %, all other elements in ppm.

Table S1 continued.

Location		Josephine		Josephine	
Sample		Z03	1 σ	Z05	1 σ
Included?		y		y	
Lithology		Spinel Harz		Spinel Harz	
Li	cpx	3.31	0.62	2.81	0.24
Na ₂ O	cpx	0.023	0.010	0.021	0.006
K ₂ O	cpx	0.00103	0.00074	0.00072	0.00047
Sc	cpx	49.1	3.2	53.2	4.4
TiO ₂	cpx	0.027	0.002	0.033	0.003
V	cpx	153	17	178	16
Cr	cpx	5346	1027	5901	951
Co	cpx	22.9	8.1	19.5	1.9
Ni	cpx	323.6	40.1	310.1	23.0
Cu	cpx	-	-	0.34	0.21
Sr	cpx	0.22	0.09	0.23	0.05
Y	cpx	1.3	0.1	1.4	0.2
Zr	cpx	-	-	-	-
Nb	cpx	0.0126	0.0082	0.0078	0.0056
La	cpx	-	-	-	-
Ce	cpx	-	-	0.002	0.003
Pr	cpx	0.0010	0.0008	-	-
Nd	cpx	-	-	-	-
Sm	cpx	0.011	0.007	-	-
Eu	cpx	0.004	0.003	-	-
Gd	cpx	0.040	0.009	0.043	0.031
Tb	cpx	0.014	0.007	0.013	0.007
Dy	cpx	0.147	0.025	0.159	0.061
Ho	cpx	0.046	0.011	0.048	0.008
Er	cpx	0.183	0.030	0.170	0.040
Tm	cpx	0.041	0.009	0.040	0.013
Yb	cpx	0.241	0.038	0.245	0.051
Lu	cpx	0.044	0.008	0.033	0.016
Hf	cpx	0.0052	0.0044	-	-
Ta	cpx	-	-	-	-
Pb	cpx	-	-	0.009	0.007

Na₂O, K₂O, and TiO₂ are reported in wt. %, all other elements in ppm.

Table S1 continued.

Location		Mariana		Mariana		Mariana	
Sample		R11	1 σ	R4	1 σ	R11	1 σ
Included?		y		y		y	
Lithology		Plag Harz		Plag Lherz		Plag Harz	
Li	opx	0.68	0.49	0.20	0.11	0.74	0.53
Na₂O	opx	0.031	0.013	0.016	0.011	0.034	0.013
K₂O	opx	0.00110	0.00086	0.00038	0.00028	0.00107	0.00093
Sc	opx	43.5	2.9	35.7	1.5	44.5	2.6
TiO₂	opx	0.188	0.012	0.161	0.019	0.187	0.012
V	opx	171	17	122	9	176	15
Cr	opx	5958	808	4640	221	6288	487
Co	opx	56.4	3.5	57.1	0.9	57.0	3.3
Ni	opx	691	53	660	12	705	47
Cu	opx	-	-	-	-	-	-
Sr	opx	0.056	0.043	-	-	0.053	0.045
Y	opx	3.18	0.58	2.35	0.42	3.35	0.54
Zr	opx	2.38	0.73	3.19	0.71	2.62	0.67
Nb	opx	0.0108	0.0063	0.0089	0.0065	0.0120	0.0066
La	opx	0.0098	0.0071	0.0096	0.0073	0.0109	0.0079
Ce	opx	0.028	0.022	0.049	0.032	0.034	0.022
Pr	opx	0.0060	0.0055	0.0091	0.0065	0.0066	0.0056
Nd	opx	0.054	0.040	0.062	0.046	0.059	0.043
Sm	opx	0.056	0.039	0.042	0.033	0.065	0.041
Eu	opx	0.016	0.013	0.0140	0.0066	0.017	0.014
Gd	opx	0.142	0.077	0.105	0.049	0.160	0.077
Tb	opx	0.034	0.012	0.0254	0.0059	0.035	0.013
Dy	opx	0.274	0.077	0.215	0.045	0.291	0.062
Ho	opx	0.087	0.026	0.062	0.012	0.095	0.024
Er	opx	0.321	0.088	0.233	0.032	0.335	0.096
Tm	opx	0.053	0.014	0.0341	0.0057	0.055	0.014
Yb	opx	0.412	0.081	0.301	0.041	0.413	0.078
Lu	opx	0.080	0.018	0.0641	0.0079	0.083	0.017
Hf	opx	0.103	0.061	0.093	0.026	0.106	0.067
Ta	opx	-	-	-	-	-	-
Pb	opx	-	-	0.0056	0.0036	-	-

Na₂O, K₂O, and TiO₂ are reported in wt. %, all other elements in ppm.

Table S1 continued.

Location		Mariana		Josephine	
Sample		R3	1 σ	Z01	1 σ
Included?		n		y	
Lithology		Plag Lherz		Spinel Harz	
Li	opx	0.73	0.45	0.76	0.29
Na₂O	opx	0.070	0.045	0.042	0.082
K₂O	opx	-	-	-	-
Sc	opx	30.8	3.1	35.4	1.6
TiO₂	opx	0.211	0.026	0.017	0.001
V	opx	162	13	117	9
Cr	opx	6066	386	4664	987
Co	opx	56.3	3.7	50.1	3.8
Ni	opx	679	44	583	70
Cu	opx	-	-	0.29	0.19
Sr	opx	0.074	0.038	-	-
Y	opx	3.64	0.64	0.24	0.03
Zr	opx	4.72	0.66	-	-
Nb	opx	0.0114	0.0052	0.0052	0.0026
La	opx	0.0089	0.0027	-	-
Ce	opx	0.091	0.023	0.017	0.020
Pr	opx	0.0226	0.0080	-	-
Nd	opx	0.167	0.037	-	-
Sm	opx	0.116	0.024	0.0024	0.0031
Eu	opx	0.0430	0.0081	0.0014	0.0012
Gd	opx	0.300	0.038	0.0034	0.0021
Tb	opx	0.063	0.012	0.0017	0.0011
Dy	opx	0.511	0.068	0.017	0.010
Ho	opx	0.145	0.022	0.0055	0.0018
Er	opx	0.514	0.074	0.036	0.015
Tm	opx	0.092	0.010	0.0106	0.0019
Yb	opx	0.664	0.069	0.101	0.025
Lu	opx	0.114	0.016	0.0221	0.0047
Hf	opx	0.183	0.025	0.0078	0.0086
Ta	opx	0.00073	0.00058	-	-
Pb	opx	0.0061	0.0051	-	-

Na₂O, K₂O, and TiO₂ are reported in wt. %, all other elements in ppm.

Table S1 continued.

Location		Josephine		Josephine	
Sample		Z03	1σ	Z05	1σ
Included?		y		y	
Lithology		Spinel Harz		Spinel Harz	
Li	opx	1.06	0.47	1.07	0.26
Na₂O	opx	0.0021	0.0005	0.0032	0.0036
K₂O	opx	0.00032	0.00022	-	-
Sc	opx	31.0	1.9	31.2	2.5
TiO₂	opx	0.016	0.001	0.018	0.001
V	opx	101	7	110	9
Cr	opx	5040	795	5040	588
Co	opx	54.7	3.0	55.4	4.8
Ni	opx	657	64	690	68
Cu	opx	-	-	0.24	0.19
Sr	opx	-	-	-	-
Y	opx	0.25	0.04	0.24	0.04
Zr	opx	0.013	0.007	0.008	0.005
Nb	opx	0.0082	0.0031	0.0062	0.0030
La	opx	0.00114	0.00063	-	-
Ce	opx	-	-	0.0007	0.0006
Pr	opx	0.00071	0.00063	0.00037	0.00029
Nd	opx	0.0055	0.0042	-	-
Sm	opx	0.0024	0.0036	-	-
Eu	opx	0.0011	0.0008	0.00082	0.00064
Gd	opx	0.0048	0.0029	0.0059	0.0035
Tb	opx	0.0019	0.0015	0.00154	0.00087
Dy	opx	0.0189	0.0061	0.0162	0.0051
Ho	opx	0.0079	0.0031	0.0070	0.0027
Er	opx	0.0437	0.0075	0.037	0.008
Tm	opx	0.0092	0.0020	0.0105	0.0033
Yb	opx	0.086	0.013	0.079	0.015
Lu	opx	0.0211	0.0029	0.0186	0.0030
Hf	opx	0.0015	0.0012	-	-
Ta	opx	-	-	-	-
Pb	opx	0.0070	0.0054	0.0064	0.0040
Na ₂ O, K ₂ O, and TiO ₂ are reported in wt. %, all other elements in ppm.					

Table S1 continued.

Representative standard analyses				
Standard	BCR	BHVO	BIR	GOR132
Li	8.82	3.62	2.83	9.26
Na₂O	3.15	2.15	1.76	0.85
K₂O	1.75	0.50	0.02	0.03
Sc	36.07	31.84	50.11	35.64
TiO₂	2.46	2.68	1.03	0.28
V	410.54	286.98	299.52	208.60
Cr	20.16	279.55	387.94	2526.97
Co	35.65	39.75	49.37	96.26
Ni	11.28	105.44	160.02	1188.05
Cu	16.77	112.86	112.34	210.12
Sr	362.94	394.36	121.05	14.26
Y	36.21	23.97	17.68	12.92
Zr	195.15	159.85	16.11	9.84
Nb	15.06	19.07	0.58	0.06
La	26.61	14.95	0.69	0.10
Ce	57.82	36.55	1.97	0.36
Pr	6.96	4.87	0.38	0.08
Nd	29.56	22.63	2.60	0.62
Sm	6.73	5.63	1.16	0.54
Eu	2.16	1.88	0.57	0.25
Gd	7.31	6.08	2.47	1.33
Tb	1.09	0.95	0.42	0.29
Dy	6.56	5.01	2.91	1.91
Ho	1.38	0.89	0.66	0.46
Er	3.88	2.28	1.92	1.55
Tm	0.48	0.30	0.28	0.23
Yb	3.39	1.87	1.82	1.49
Lu	0.53	0.26	0.30	0.21
Hf	4.91	4.00	0.59	0.31
Ta	0.93	1.23	0.04	0.02
Pb	11.28	1.66	3.14	20.69

Major elements are reported in wt. %.

Na₂O, K₂O, and TiO₂ are reported in wt. %, all other elements in ppm.

Table S1 continued.

Standard	StHls	ATHO	T1	ML3B	KL2
Li	18.77	40.28	22.41	4.44	6.10
Na₂O	4.43	5.97	3.30	2.26	2.41
K₂O	1.21	3.53	2.06	0.37	0.51
Sc	14.78	12.44	26.70	30.07	27.12
TiO₂	0.75	0.31	0.75	2.01	2.37
V	73.72	4.22	178.82	246.14	302.39
Cr	11.13	8.91	19.20	155.97	302.41
Co	11.34	1.47	17.60	38.25	41.65
Ni	15.86	6.89	8.66	92.77	106.64
Cu	30.95	22.32	17.36	104.13	91.02
Sr	531.04	95.51	290.65	305.26	332.80
Y	13.83	97.37	23.58	22.62	19.26
Zr	140.11	533.53	143.69	114.85	116.34
Nb	7.83	81.22	9.38	8.48	13.93
La	13.64	57.32	68.74	8.46	11.25
Ce	27.06	140.14	126.38	21.75	31.20
Pr	3.36	15.36	12.10	3.16	4.09
Nd	13.78	63.34	40.56	16.19	18.65
Sm	3.28	14.52	6.75	4.69	4.88
Eu	1.08	2.79	1.19	1.66	1.81
Gd	3.45	17.07	5.84	5.37	5.26
Tb	0.48	2.81	0.82	0.84	0.75
Dy	2.62	16.49	4.43	4.56	4.17
Ho	0.51	3.61	0.91	0.92	0.79
Er	1.44	10.33	2.69	2.40	2.09
Tm	0.20	1.63	0.41	0.31	0.27
Yb	1.34	10.47	2.29	1.98	1.57
Lu	0.19	1.64	0.35	0.28	0.21
Hf	3.57	14.18	3.98	3.15	3.05
Ta	0.53	4.71	0.49	0.51	0.85
Pb	9.46	8.13	10.11	1.32	2.06

Major elements are reported in wt. %.

Na₂O, K₂O, and TiO₂ are reported in wt. %, all other elements in ppm.

^aThe two-pyroxene thermometer of Brey and Köhler (1990).

^bThe two-pyroxene thermometer of Wells (1977).

^cThe two-pyroxene thermometer of Putirka (2008).

^dThe olivine-spinel thermometer of Li et al. (1995).

Table S2.

Samples					
Spinel Peridotite	n Samples	n SC ^a	n MOR ^b	n SSZ ^c	Reference
Josephine	3	-	-	3	This study
Trinity	9	-	-	9	This study
Alps	4	4	-	-	Müntener et al. (2010)
Coast Range	1	-	1	-	Jean et al. (2010)
Corsica	4	-	4	-	Rampone et al. (2008)
Oman (Wadi Fizh, lower)	1	-	1	-	Takazawa et al. (2003)
Oman (Wadi Fizh, upper)	7	-	7	-	Akizawa et al. (2012)
Oman (Wadi Sarami)	3	-	3	-	Khedr et al. (2014)
Lherz	8	8	-	-	Riches and Rogers (2011)
Othris	4	-	4	-	Barth et al. (2003)
Puerto Rico	2	-	2	-	Marchesi et al. (2011)
Turkey	9	-	4	5	Aldanmaz (2012)
Urals	6	-	-	6	Batanova et al. (2011)
Total	61	12	26	23	
Plagioclase Peridotite					
Mariana	2	-	-	2	This study
Trinity	2	-	-	2	This study
Alps	2	-	2	-	Müntener et al. (2010)
Corsica	3	-	3	-	Rampone et al. (2008)
Othris	2	-	2	-	Barth et al. (2003)
Total	11	-	7	4	
Cumulates					
Oman (Wehrlite)	1	-	1	-	Akizawa et al. (2012)
New Caledonia (Dunite)	1	-	-	1	Pirard et al. (2013)
Urals (Websterite)	4	-	-	4	Batanova et al. (2011)
Total	6	-	1	5	
Global Dataset	78	12	34	32	

^aNumber of temperatures from samples with subcontinental affinity (reported in original reference).

^bNumber of temperatures from samples with mid-ocean ridge affinity (reported in original reference).

^cNumber of temperatures from samples with supra-subduction zone affinity (reported in original reference).

Table S3.

Temperatures										
Reference	Location	Sample Name	Affinity ^a	Lithology	T_{BKN}	T_{H77}^b	T_{P37}^c	T_{OlSp}	T_{REE}	1σ
This study	Josephine	Z01	SSZ	Spinel Harz	888	928	927	756	1109	± 15
This study	Josephine	Z03	SSZ	Spinel Harz	882	934	908	758	1215	± 11
This study	Josephine	Z05	SSZ	Spinel Harz	893	936	921	773	1185	± 15
This study	Mariana	R11	SSZ	Plag Harz	871	904	880	835	1149	± 13
This study	Mariana	R4	SSZ	Plag Lherz	890	923	905	734	1051	± 6
This study	Trinity	Z18	SSZ	Spinel Harz	813	880	887	760	1147	± 13
This study	Trinity	Z26	SSZ	Spinel Harz	846	902	908	759	1141	± 14
This study	Trinity	TP90.11	SSZ	Spinel Harz	856	908	913	741	1095	± 27
This study	Trinity	TP90.17	SSZ	Plag Lherz	896	934	944	727	1256	± 19
This study	Trinity	17BK	SSZ	Plag Lherz	909	944	952	677	1188	± 15
This study	Trinity	19B	SSZ	Plag Lherz	980	994	1004	732	1218	± 8
This study	Trinity	Z13	SSZ	Spinel Harz	811	879	886	790	1160	± 28
This study	Trinity	Z20	SSZ	Spinel Harz	809	878	884	779	1115	± 20
This study	Trinity	Z27	SSZ	Spinel Harz	824	887	894	-	1099	± 23
This study	Trinity	Z23	SSZ	Spinel Harz	827	889	895	777	1120	± 5
This study	Trinity	Z24	SSZ	Spinel Harz	834	894	899	776	1190	± 11

^aTectonic affinity as reported in original reference.

^bThe two-pyroxene thermometer of Wells, 1977.

^cThe two-pyroxene thermometer of Putirka, 2008.

Table S3 continued.

Reference	Location	Sample Name	Affinity ^a	Lithology	T_{BKN}	T_{W77}^b	T_{P37}^c	T_{OLSp}	T_{REE}	1σ
Muntener et al., 2010	Alps, Malenco	LUM-216	SC	Spinel Lherz	871	861	912	-	882	± 12
Muntener et al., 2010	Alps, Malenco	LUM-400	SC	Spinel Lherz	890	896	911	-	897	± 5
Muntener et al., 2010	Alps, Malenco	LUM-112	SC	Spinel Lherz	846	864	870	-	901	± 11
Muntener et al., 2010	Alps, Totalp Alps, Lower Plattia	To-7	SC	Spinel Lherz	565	685	778	-	831	± 6
Muntener et al., 2010	Alps, Lower Plattia	MSP-1	MOR	Plag Lherz	883	903	936	-	1256	± 5
Muntener et al., 2010	Alps, Lower Plattia	SUP-2	MOR	Plag Harz	831	861	931	-	1074	± 22
Jean et al., 2010	Coast Range	SFV-308	MOR	Spinel Lherz	752	814	857	-	1073	± 4
Rampone et al. 2008	Corsica	MM2_10	MOR	Spinel Lherz	897	909	964	749	1397	± 17
Rampone et al. 2008	Corsica	MM1_5	MOR	Spinel Lherz	950	956	971	887	1228	± 58
Rampone et al. 2008	Corsica	MM1_9	MOR	Spinel Lherz	937	937	1003	-	1255	± 21
Rampone et al. 2008	Corsica	MM2_11	MOR	Spinel Lherz	1039	1025	1075	1004	1254	± 52
Rampone et al. 2008	Corsica	MM1_11	MOR	Plag Harz	922	936	952	979	1260	± 18
Rampone et al. 2008	Corsica	MM1_4	MOR	Plag Harz	888	904	932	907	1283	± 35
Rampone et al. 2008	Corsica	MM2_5A	MOR	Plag Harz	977	995	980	1026	1287	± 28
Riches and Rogers, 2011	Lherz	06LH09	SC	Spinel Lherz	750	789	800	748	802	± 10
Riches and Rogers, 2011	Lherz	04LH36	SC	Spinel Lherz	729	764	839	728	787	± 9
Riches and Rogers, 2011	Lherz	04LH37A	SC	Spinel Lherz	763	786	797	798	798	± 6
Riches and Rogers, 2011	Lherz	06LH12	SC	Spinel Lherz	793	807	848	779	811	± 6

Table S3 continued.

Reference	Location	Sample Name	Affinity ^a	Lithology	T_{BKN}	T_{W77}^b	T_{P37}^c	T_{Ol-Sp}	T_{REE}	1σ
Riches and Rogers, 2011	Lherz	06LH03	SC	Spinel Harz	894	882	881	768	728	± 4
Riches and Rogers, 2011	Lherz	06LH04	SC	Spinel Harz	796	793	863	711	803	± 6
Riches and Rogers, 2011	Lherz	04LH08	SC	Spinel Harz	764	797	813	736	688	± 10
Riches and Rogers, 2011	Lherz	06LH06	SC	Spinel Lherz	851	869	831	797	742	± 3
Pirard et al., 2013	New Caledonia	MDS49	SSZ	Dunite	887	921	964	883	1150	± 40
Takazawa et al., 2003	Oman, Nth. Fizh	981214-3	MOR	Spinel Lherz	985	994	963	822	1205	± 13
Akizawa et al., 2012	Oman, Wadi Fizh	Band A 0	MOR	Spinel Harz	960	985	978	892	1110	± 21
Akizawa et al., 2012	Oman, Wadi Fizh	B-1 and B-2	MOR	Spinel Harz	979	995	980	904	1105	± 9
Akizawa et al., 2012	Oman, Wadi Fizh	0.25	MOR	Spinel Harz	977	990	982	865	1243	± 13
Akizawa et al., 2012	Oman, Wadi Fizh	0.1	MOR	Spinel Harz	927	953	941	902	979	± 14
Akizawa et al., 2012	Oman, Wadi Fizh	B-1 and B-2 +0	MOR	Spinel Harz	1008	1015	994	818	1151	± 57
Akizawa et al., 2012	Oman, Wadi Fizh	B-1 and B-2 -0	MOR	Spinel Harz	949	968	972	870	1187	± 9
Akizawa et al., 2012	Oman, Wadi Fizh	Band C 0.7	MOR	Spinel Harz	936	961	947	778	1171	± 30
Akizawa et al., 2012	Oman, Wadi Fizh	Band C 0.15	MOR	Spinel Harz	967	976	964	918	1035	± 13
Akizawa et al., 2012	Oman, Wadi Fizh	Band C 0	MOR	Wehrlite	843	898	887	772	974	± 13
Khedr et al., 2014	Oman, Wadi Sarami	Tv.59	MOR	Spinel Harz	915	955	916	771	1187	± 54
Khedr et al., 2014	Oman, Wadi Sarami	G.39	MOR	Spinel Harz	824	889	863	753	1050	± 22
Khedr et al., 2014	Oman, Wadi Sarami	Tv.136	MOR	Spinel Harz	778	859	851	864	1123	± 34
Barth et al., 2003	Othris	96FK26	MOR	Spinel Harz						

Table S3 continued.

Reference	Location	Sample Name	Affinity ^a	Lithology	T_{BKN}	T_{W77}^b	T_{P37}^c	T_{ol-sp}	T_{REE}	1σ
Barth et al., 2003	Othris	GOFOK16A	MOR	Spinel Harz	843	900	871	960	1092	± 6
Barth et al., 2003	Othris	GOF-14	MOR	Spinel Harz	757	847	827	900	1155	± 14
Barth et al., 2003	Othris	96FK14	MOR	Spinel Harz	799	874	848	897	1111	± 15
Barth et al., 2003	Othris	97GOFOK5	MOR	Plag Perid	869	922	883	909	1188	± 73
Barth et al., 2003	Othris	GOF-13	MOR	Plag Perid	844	892	872	900	1108	± 24
Marchesi et al., 2011	Puerto Rico	60-93	MOR	Spinel Harz	985	994	963	668	1205	± 13
Marchesi et al., 2011	Puerto Rico	17-94	MOR	Spinel Harz	910	921	888	791	1136	± 10
Aldanmaz, 2012	Turkey, Tekirova	KO22	MOR	Spinel Lherz	977	949	944	-	1083	± 26
Aldanmaz, 2012	Turkey, Köyceğiz	KO26	MOR	Spinel Lherz	1020	965	955	-	1147	± 29
Aldanmaz, 2012	Turkey, Köyceğiz	KO19	MOR	Spinel Harz	841	915	828	-	1132	± 20
Aldanmaz, 2012	Turkey, Köyceğiz	KO112	MOR	Spinel Harz	558	718	707	-	941	± 55
Aldanmaz, 2012	Turkey, Tekirova	KO7	SSZ	Spinel Harz	749	838	822	-	1265	± 13
Aldanmaz, 2012	Turkey, Köyceğiz	KO10	SSZ	Spinel Harz	748	841	824	-	1258	± 98
Aldanmaz, 2012	Turkey, Köyceğiz	KO110	SSZ	Spinel Harz	942	981	944	-	1031	± 13
Aldanmaz, 2012	Turkey, Köyceğiz	KO105	SSZ	Spinel Harz	791	890	800	-	1060	± 22
Aldanmaz, 2012	Turkey, Köyceğiz	KO115	SSZ	Spinel Harz	749	848	797	-	991	± 41

Table S3 continued.

Reference	Location	Sample Name	Affinity ^a	Lithology	T_{BKN}	T_{W77}^b	T_{P37}^c	T_{Ol-Sp}	T_{REE}	1σ
Batanova et al., 2011	Urals	6 13	SSZ	Spinel Harz	846	906	865	807	981	± 35
Batanova et al., 2011	Urals	6 24	SSZ	Spinel Harz	829	896	876	805	1069	± 8
Batanova et al., 2011	Urals	6 35_2	SSZ	Spinel Harz	778	869	830	812	1089	± 5
Batanova et al., 2011	Urals	7 15C6	SSZ	Spinel Harz	727	825	786	839	983	± 7
Batanova et al., 2011	Urals	7 15C5	SSZ	Spinel Harz	830	896	851	831	1029	± 36
Batanova et al., 2011	Urals	6 11_4	SSZ	Spinel Harz	761	846	824	801	1008	± 11
Batanova et al., 2011	Urals	6 11_3c	SSZ	Wehrlite	812	873	844	791	1066	± 5
Batanova et al., 2011	Urals	6 33_2	SSZ	Wehrlite	861	913	865	813	1087	± 7
Batanova et al., 2011	Urals	214_7	SSZ	Wehrlite	861	914	894	-	1274	± 13
Batanova et al., 2011	Urals	7 16o	SSZ	Wehrlite	763	846	831	795	961	± 7
				Maximum ^d	1039	1025	1075	1026	1287	
				Minimum	558	685	707	668	688	

^dExcluding sample MM2_10 from Corsica.

Table S4.

Temperature Averages							
Affinity^a & Locality	n^b	T_{Ol-Sp}	1σ^c	T_{BKN}	1σ^c	T_{REE}	1σ^c
Ophiolite SSZ							
Josephine	3	762	±9	888	±6	1170	±55
Mariana	2	755	±76	881	±14	1100	±69
Trinity	11	752	±34	855	±53	1157	±51
New Caledonia	1	883	-	887	-	1150	-
Urals	9	796	±19	801	±45	1030	±49
Avg Ophiolite SSZ	26	774	±42	843	±54	1110	±78
Ophiolite MOR							
Alps	2	-	-	857	±37	1165	±129
Coast Range	1	-	-	752	-	1073	-
Corsica	6	911	±102	952	±52	1261	±22
Oman [1]	1	822	-	985	-	1205	-
Oman [2]	3	831	±69	955	±22	1154	±44
Oman [3]	3	765	±11	861	±48	1071	±108
Othris	6	883	±25	815	±43	1129	±36
Puerto Rico	2	753	±80	891	±28	1076	±84
Avg Ophiolite MOR	24	848	±82	887	±76	1157	±87
SC							
Alps	3	-	-	869	±22	893	±10
Lherz	8	758	±32	792	±55	770	±45
Avg SC	11	758	±32	813	±47	804	±69
Abyssal^d							
Gakkel	9	-	-	976	±40	1163	±59
Mid Atlantic Ridge	7	878	-	1003	±78	1175	±71
SW Indian Ridge [4]	12	840	±37	982	±75	1192	±40
SW Indian Ridge [5]	5	836	±24	1125	±22	1225	±70
Avg Abyssal	33	842	±32	1006	±79	1185	±58
Avg Mantle Xenolith^d	42	-	-	1033 ^e	±122	1027	±125

^aTectonic affinity as reported in data source.

^bNumber of T_{REE} and T_{BKN} . Many studies have fewer T_{Ol-Sp} .
Obvious outliers and samples with geologic evidence suggesting disequilibrium were excluded from this table.

^c1 σ standard deviation.

^dReported in Liang et al. (2013).

^eCalculated at 1.5GPa.

[1] Takazawa et al. (2003).

[2] Akizawa et al. (2012).

[3] Khedr et al. (2014).

[4] Seyler et al. (2011).

[5] Warren et al. (2009).

Appendix A: T_{REE} in the context of research in data sources

Michibayashi et al. (2009)

Samples from the Mariana Trench (Michibayashi et al., 2009) were collected by manned submersible at ~6000 m depth from a N-S striking left-lateral oblique slip fault southwest of the Santa Rosa Bank. This is a unique tectonic environment where the Mariana Trench curves from an approximate N-S strike to an approximate E-W strike. The samples are talus blocks collected on the fault scarp, some of which contain mylonites. We inverted T_{REE} for an intensely deformed plagioclase lherzolite (R4) and a weakly deformed plagioclase harzburgite (R11). Both have two generations of spinel with disparate Cr#s (one generation with Cr#s ~20, another generation with Cr#s ~45, and a maximum value of 78). Michibayashi et al. (2009) interpreted the different grain sizes and textures in the samples as reflecting asthenospheric flow (dominant in R11) and ductile deformation in cold lithospheric mantle (R4). They argue that all samples likely underwent ductile deformation in the lithospheric mantle, but deformation was inhomogeneous. The samples are generally more enriched (e.g., in bulk Al and Ca) than peridotites typical of the Mariana forearc and the authors argue they formed in a tectonic environment more similar to a backarc. Further, they note the samples were impregnated by melt that precipitated plagioclase and formed the second generation Cr-spinel, so the melting history is difficult to unravel. It seems most likely the samples were depleted by partial melting, then refertilized by impregnating melt. T_{REE} for these samples are consistent with the coldest abyssal peridotites, suggesting the last thermal event the rocks record (possibly the deformation event) occurred at subsolidus temperatures.

Aldanmaz (2012)

Aldanmaz (2012) reported 26 samples from four ultramafic sections of two Tethyan ophiolites located in southwestern Turkey. Here we report temperatures for nine samples from Köyceğiz and Tekirova. Aldanmaz (2012) classified them as having either MOR or SSZ affinity based on major (spinel Cr#, Mg#) and trace element (e.g., REE) abundances, but our investigation shows no discernible difference in T_{REE} between the two groups for this reference. T_{REE} and major element temperatures vary widely at both ophiolites, with some samples plotting near the blue 1:1 major- T_{REE} line in Figure 2b and other samples exhibiting low major element temperatures but elevated T_{REE} . Most of the samples are depleted harzburgites but isolated pods of more cpx-rich rocks are present in the field. The existence of trace-element enriched cpx in otherwise depleted peridotites suggests melt-rock reaction processes affected these samples. LREE enrichment indicative of metasomatism was observed in the most depleted samples (those with SSZ affinity). Low major element temperatures and high T_{REE} suggests that in general the samples were affected by late-stage melt infiltration followed by relatively fast cooling.

Rampone et al. (2008)

Rampone et al. (2008) studied spinel and plagioclase lherzolites and harzburgites from Mt. Maggiore, Corsica. Spinel and plagioclase bearing lithologies show dissolution-precipitation textures indicative of melt-rock reaction, for example, olivine rims on opx, plagioclase/opx intergrowths replacing deformed cpx, and major and trace element zoning. In some samples, trace elements are decoupled from major elements, for example, the most magnesian sample has the highest REE concentrations. Rampone et al.

(2008) applied the V and Sc thermometers of Seitz et al. (1999) and the Ca-in-opx thermometer of Brey and Köhler (1990) to plagioclase peridotites and observed hotter rim (1150-1250°C) than core (1050-1150°C) temperatures. Spinel peridotite porphyroclasts yielded slightly higher temperatures of 1100-1150°C, and two samples have rims with very high temperatures (1200-1300°C). Rampone et al. (2008) argue that a melt-rock reaction event modified (and heated) spinel peridotites when they were in the lithosphere, and that plagioclase peridotite formed in a second melt-rock reaction event that occurred at lower initial temperatures and with a melt of different composition. They argue that to preserve mineral zoning, cooling must have been rapid. T_{REE} (1228-1287°C, with one unusually hot (1397°C) sample) are higher than temperatures reported by Rampone et al. (2008). Plagioclase-bearing samples have temperatures that (when averaged) are indistinguishable from spinel-bearing samples, suggesting a common thermal signature that predates melt impregnation. Spinel and plagioclase bearing samples are hotter than most abyssal peridotites, and the high temperatures suggest the melt-rock reaction events may have occurred in the asthenospheric mantle. Cooling must have been very rapid to preserve such high temperatures.

Riches and Rogers (2011)

Riches and Rogers (2011) studied peridotites at the Lherz massif. They sampled three distinct lithologies at two sample traverses; depleted harzburgites, lherzolites $\pm$ olivine websterites, and late stage hornblende bearing pyroxenites that cross-cut the other lithologies. Trace elements in harzburgites were successfully modeled as residues of fractional melting. LREE enrichment in those samples was attributed to metasomatic

events that postdated partial melting. The lherzolites and olivine websterites are in equilibrium with LREE enriched (“analogous to E-MORB”) melts, and the authors interpreted the presence of amphibole in those lithologies as suggesting formation in a mantle-wedge environment. They argue the harzburgites and lherzolite $\pm$ olivine websterites formed separately, and represent “elongate lithological strips juxtaposed during plastic deformation.” In general, T_{REE} for all samples from Lherz are very low (688-811°C) and agree with major element temperatures (Figure 2b). No significant difference in T_{REE} exists between harzburgites and lherzolites so any thermometric remnants of the formation histories of the two lithologies were lost. Some samples have slightly higher major element temperatures than T_{REE} , they may have experienced late stage heating (rapid enough to reequilibrate major elements but not REE) just prior to exhumation. The very low T_{REE} of the Lherz samples may suggest they cooled in the lithosphere for an extended period prior to exhumation, possibly subsequent to residing in the mantle wedge.

Akizawa et al. (2012)

Akizawa et al. (2012) investigated major and trace elements in sample traverses from the crust-mantle transition zone at the Wadi Fizh section of the Oman ophiolite. They reported REE in two pyroxenes for a subset of samples collected in and around gabbro and wehrlite bands that intruded harzburgites in the mantle section. In two sections (Bands A & B) the host harzburgites are highly depleted (cpx <0.1 vol. %) but in another section the harzburgites are more cpx rich and closer to REE equilibrium with MORB (Band C). Wherlite formation is attributed to pervasive reaction of MORB-like

melts with residual harzburgite at low pressure. For the samples we report, T_{BKN} have a narrow range of 936-1017°C while T_{REE} are more scattered (979-1243°C). T_{REE} recorded in the bands are generally lower than in the host rock. Akizawa et al. (2012) pointed out that MORB-like melts are opx undersaturated at low pressures, so the scattered T_{REE} may be attributable to disequilibrium. In the main text, we use T_{REE} in harzburgites furthest from the bands to calculate average temperature from this reference. These temperatures are consistent with abyssal peridotites.

Takazawa et al. (2003)

Takazawa et al. (2003) investigated major and trace elements in lherzolites from the base of the northern Fizh block, which compliment samples from Akizawa et al. (2012). Takazawa et al. (2013) classified the basal lherzolites as Type I or Type II based on texture (porphyroclastic or mylonitic, respectively) and distinct major and trace element chemistry. Trace element concentrations were analyzed in pyroxene mineral separates by solution ICP-MS. Type II lherzolite is rotated on an $\ln(D)$ -A vs. B inversion diagram (Supplementary Figure S5e) and a meaningful T_{REE} was not determined for that sample. LREE in the Type I lherzolite were affected by a metasomatic event but HREE appear to be well equilibrated. Surprisingly, the T_{REE} ($1205 \pm 13^\circ\text{C}$) and T_{BKN} (994°C) of the Type I basal lherzolite are consistent with abyssal peridotites. Takazawa et al. (2003) proposed that the Type I lherzolites formed by 12-18% melt extraction from a fertile source beneath a failing mid-ocean ridge; the T_{REE} agrees with this hypothesis.

Müntener et al. (2010)

Müntener et al. (2010) investigated spinel- and plagioclase-bearing peridotites from three different ultramafic units in the Alps. Based on field relationships and geochemical arguments, they ascribed spinel-bearing samples to subcontinental lithosphere and plagioclase-bearing samples to rifted mantle that formed in an ocean-continent transition zone. REE concentrations in plagioclase bearing samples were modeled as mixtures of impregnating mantle melts and depleted harzburgite. Nd and Na₂O concentrations in the spinel-bearing samples were modeled as products of fractional melting of a primitive upper mantle source. Müntener et al. (2010) applied the Ca-in-opx thermometer of Brey and Köhler (1990) to the two sample sets and found disparate temperatures of 870-950°C for the spinel peridotites and 1030-1180°C for the plagioclase peridotites, however they made the calculation at different pressures (1.5 and 1.0 GPa, respectively). According to Müntener et al. (2010), the Sc-based thermometer of Seitz et al. (1999) gave a similar temperature for the plagioclase bearing samples. We calculated T_{BKN} for plagioclase and spinel bearing samples at 1.0 GPa and found they have roughly the same major element temperatures (~870°C) with one outlying spinel peridotite having a T_{BKN} of 571°C (Supplementary Table 3). In contrast, T_{REE} are consistent with the Ca-in-opx temperatures reported by Müntener et al. (2010). Plagioclase-bearing samples (collected from the same unit at different locations) have T_{REE} of 1074±22 and 1256±5°C and spinel-bearing samples all have T_{REE} of 831-901°C. These temperatures (and T_{BKN} and T_{REE} discrepancies) are consistent with the hypothesis that spinel-bearing samples equilibrated in the continental lithosphere but plagioclase bearing samples formed or evolved at or near a spreading center.

Jean et al. (2010)

Jean et al. (2010) investigated major and trace element systematics in mantle peridotites from the Coast Range ophiolite to study melting and melt-rock reaction processes and determine whether the rocks have SSZ or MOR affinity. Samples were collected from five localities and are mostly spinel harzburgites, however spinel lherzolites are dominant at one locality (Black Diamond Ridge). Except for one sample from Black Diamond Ridge (SFV-308) that appears to be well equilibrated, the opx-cpx pairs reported by Jean et al. (2010) are scattered on $\ln(D)$ -A vs. B inversion diagrams. REE concentrations in SFV-308 are at the high end of the global dataset of abyssal peridotites, but they have similar light to heavy-REE curvature. Based on the trace element characteristics and low Cr#s the authors classified SFV-308 as having MOR rather than SSZ affinity. In T_{REE} vs. T_{BKN} space (Figure 9b) this sample falls well outside the field defined by abyssal peridotites. It has a low T_{BKN} (759°C) and relatively low T_{REE} (1073±4°C) which place it at the cold end of the data defined MOR-affinity ophiolites, however this sample certainly does not have thermal properties characteristic of SC samples.

Barth et al. (2003)

Barth et al. (2003) investigated major and trace elements in harzburgites and plagioclase peridotites from the Othris ophiolite to determine the origin of the plagioclase, to understand melt extraction and melt-rock interaction at the site, and to constrain the tectonic environment. Pyroxene rims are depleted in Al and Cr relative to cores. The authors argue this is due to reequilibration between pyroxene and spinel (in

the spinel stability field) during cooling. Based on textural evidence and trace element patterns, harzburgites were interpreted as residues of partial melting followed by low degrees of melt infiltration. Plagioclase peridotites were interpreted as forming by similar processes but with larger volumes of infiltrating melt. Barth et al. (2003) note zoning in spinel in plagioclase lherzolite and argue the melt infiltration had to occur at relatively low temperatures to preserve disequilibrium. Based on mineral modes (the presence of plagioclase with little cpx), low Cr# spinel, MORB-like REE patterns in cpx, and a lack of negative HFSE anomalies, the authors argue that Othris formed in a MOR setting rather than a back-arc or island-arc. The T_{REE} and major element temperatures we determined are mostly consistent with that argument although they are on the cold end of MOR-affinity ophiolitic peridotites (Figure 9b). The very close association of boninites and komatiites with the studied outcrops and their low T_{REE} and T_{BKN} may be better evidence for formation in or near a subduction-related environment than the arguments listed previously.

Pirard et al. (2013)

Pirard et al. (2013) conducted a thorough geochemical and petrologic investigation of the Massif du Sud section of New Caledonia. They sampled and analyzed harzburgites, dunites and crustal rocks obtaining a complete picture of ophiolite chemistry. Massif du Sud is exceptionally depleted and no primary cpx is observed beneath the Moho. Based on $\ln(D)$ -A vs. B inversion diagrams, only one sample was found to be in equilibrium, a cumulate dunite (MDS49) collected above the Moho. The authors argue the ophiolite experienced two episodes of melting, one at a spreading

center and a second in an SSZ environment, possibly a forearc. The T_{REE} and T_{BKN} we obtained for this sample are consistent with the global fields for SSZ ophiolites (see Figure 9b).

Khedr et al. (2014)

Khedr et al. (2014) studied harzburgites and lherzolites collected 0-400 m above the metamorphic sole of the Wadi Sarami section of the central Oman ophiolite. Some lherzolites are amphibole bearing. All bulk rock analyses show spoon-shaped REE patterns, but all pyroxene show strongly LREE depleted patterns. Lherzolites have spinel Cr#s ranging from ~5-25, but harzburgites ranging from ~20-54, so the sample suite is consistent with the entire range of abyssal peridotites. Khedr et al. (2014) note the REE patterns in pyroxene are similar to abyssal peridotites. They argue the samples show no textural evidence of melt impregnation, but have elevated concentrations of fluid mobile elements (B, Li, Cs, Rb, Pb) suggesting a late metasomatic event unrelated to infiltration of MORB-like melts. Khedr et al. (2014) propose that lherzolites and harzburgites represent a continuum of samples that experienced different degrees of melting. This hypothesis is supported by major and trace element models that do an excellent job fitting the data. In their petrogenetic model, Khedr et al. (2014) argue more enriched samples are representative of an asthenospheric (mid-ocean ridge type) environment while more depleted samples melted to higher degrees possibly because of their proximity to a nearby dome structure that was interpreted as diapir. We obtained T_{REE} ranging from 974-1187°C for these samples and T_{BKN} ranging from 824-914°C, consistent with other MOR ophiolites but much colder than abyssal peridotites and other samples from Oman. This

suggests the samples have been disturbed by the metasomatic event, or that their observable cooling history is dominated by the obduction process.

Marchesi et al. (2011)

Marchesi et al. (2011) investigated compositions of highly altered peridotites from the Monte del Estado massif, Puerto Rico. Relict minerals (including olivine) are relatively well preserved so that repeat major and trace element analyses are highly consistent. At Monte del Estado, gabbros and pillow basalts are in direct contact with the ultramafic units, which are primarily lherzolites. Harzburgites are also present in lower abundance. Opx occur as large porphyroclasts (up to 5 cm) or smaller (1-4 mm) components of the matrix, and occasionally have lobate embayments suggesting resorption “by olivine.” All of the samples have high olivine Mg# (~90) and low spinel Cr# (<20), similar to abyssal peridotites. REE in cpx fall within the range defined by abyssal peridotites, but bulk rocks show U-shaped REE patterns indicative of melt infiltration. Marchesi et al. (2011) argue the major and trace element characteristics of their samples are consistent with fertile abyssal peridotites, and that the samples are residues after low to moderate extents of partial melting followed by interaction with migrating melts. We obtained meaningful temperatures for a harzburgite (T_{REE} 1136±10 °C, T_{BKN} 910 °C) and lherzolite (T_{REE} 1017±14 °C, T_{BKN} 870 °C) consistent with the field defined by other ophiolites with MOR affinity (Figure 9b). A lherzolite (sample 62-93) reported by Marchesi et al. (2011) appears rotated in a $\ln(D)$ -A vs. B inversion diagram (Supplementary Figure S5j), suggesting REE are perturbed by a melt infiltration event that could also account for its higher cpx abundance.

Batanova et al. (2011)

Batanova et al. (2011) sampled peridotites from the Voykar Ophiolite in the polar Urals. Temperatures were calculated for harzburgites, isolated websterite veins (samples 214/7, 1 16/1o), and websterites that form the boundary between dunites and harzburgites (samples 6 11/3c, 6 33/2). Major and trace elements suggest two distinct episodes of evolution, partial melting with concomitant melt extraction in replacive dunites, and infiltration and reaction of later stage hydrous melts with the melting residues, leading to precipitation of amphibole bearing websterites. Batanova et al. (2011) successfully modeled trace elements in the most depleted harzburgite they found as the product of near fractional melting in the garnet and spinel stability fields. Harzburgites with more enriched trace elements show spatially dependent variations consistent with infiltration by late stage dunite-hosted melts. The absence of feldspar in these plagioclase normative peridotites suggests the last infiltration event occurred at pressures >1 GPa. Based on the stability of amphibole in peridotite and major element thermometry, Batanova et al. (2011) argued the melt infiltration event occurred at temperatures of 1050-1200°C. This is consistent with T_{REE} we obtained for most samples (961-1089 °C). One websteritic vein has a higher temperature ($T_{REE}=1274\pm13^{\circ}\text{C}$) that may suggest a hot late stage intrusion in a cooler environment (i.e., fast cooling). Finally, Batanova et al. (2011) argued the trace element compositions of dunite hosted pyroxenes and late stage pyroxenites are similar to high-Ca boninites from Tonga and the Troodos ophiolite, suggesting they formed in a mantle wedge environment above a subduction zone. The REE and major element

temperatures for this sample suite are at the low end of temperatures we obtained for other SSZ ophiolites.