**Seawater-derived rare earth element addition to abyssal peridotites during
serpentinization**

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20 **Abstract**

21 Serpentinized abyssal peridotites are evidence for active communication between the
22 Earth's hydrosphere and the upper mantle, where exchange and retention of both major
23 and trace elements occur. Bulk rock Nd isotopes in serpentinized abyssal peridotites
24 imply interaction of seawater with the peridotite. In contrast, the Nd isotopes of
25 clinopyroxenes from serpentinized abyssal peridotites retain their primary magmatic
26 signature. It is currently unclear if, how and where seawater-derived Nd and other REE
27 are being added or exchanged with the mantle peridotite minerals during serpentinization.
28 To remedy this knowledge gap, we present in situ trace and major element
29 concentrations, bulk rock and sequential leaching experiment trace element
30 concentrations as well as Nd, Sr isotope data on refertilized and depleted serpentinized
31 abyssal peridotites from the Southwest Indian Ridge. The secondary serpentine matrix
32 and magnetite veins in these peridotites have elevated LREE concentrations, with
33 variable negative Ce anomalies and large Rb, Sr, Pb and U enrichments that resemble
34 seawater trace element patterns. The LREE concentrations in the serpentine phase are
35 higher than those expected for the primary mantle mineralogy (olivine, orthopyroxene)
36 based on data from relic clinopyroxenes and equilibrium partition coefficients. These data
37 are consistent with seawater-derived REE addition to the peridotite during
38 serpentinization. The bulk rocks have more radiogenic Sr and more unradiogenic Nd
39 isotopes than their clinopyroxene (up to 8 ϵ_{Nd} units lower than clinopyroxene).
40 Sequential leaching experiments designed to mobilize secondary carbonates and Fe-
41 oxides show even more unradiogenic Nd isotope ratios in the leachates than the bulk rock
42 and clinopyroxene, approaching seawater compositions (up to 15 ϵ_{Nd} units lower than

clinopyroxene). Mass balance calculations using trace elements or Nd isotopes suggest that up to 30% of the bulk peridotite Nd budget is of seawater origin and was added to the peridotite, as opposed to being exchanged. These data allows for more accurate constraints of the water/rock mass exchange ratios during serpentinization in these rocks (~1000 to 17000) that are at least an order of magnitude lower than using typical mantle and seawater endmembers. These data provide strong evidence that serpentinization may also be a sink for the light REE, with implications for the refertilization of the peridotite during serpentinization, and the cycling of these elements through the subduction system and into the upper mantle.

Keywords

Serpentinization; abyssal peridotite; rare earth elements; negative Ce anomaly; Sr-isotopes; Nd-isotopes; Laser ablation ICP-MS; sequential leaching.

1.0 Introduction

Submarine peridotite- hosted hydrothermal systems are the interface between the Earth's oceans and the mantle, where significant elemental exchange takes place during the serpentinization of peridotitic rocks. Serpentinization leads to the uptake of H₂O into the peridotite, the redistribution of major cations (i.e. Mg, Ca, Si, Fe and C) among the newly formed secondary minerals (serpentine, magnetite, and brucite), addition of fluid-mobile elements (e.g. B, Cs, I, Sr, U) and the generation of Mg poor, CH₄- and H₂- rich, alkaline hydrothermal fluids (Allen and Seyfried, 2003; Synder et al., 2004; Paulick et al., 2006; Savov et al., 2007; Beard et al., 2009; Bach and Früh-Green, 2010; Deschamps et al., 2013).

Whether rare earth elements (REE) and high field strength elements (HSFE; Nb, Ta, Zr, Hf, Ti) are mobilized or fractionated during serpentinization is unclear. On one hand, the positive correlations of REE concentrations with highly immobile incompatible elements like Th was taken as evidence that serpentinized peridotites preserve their primary magmatic (high temperature) REE systematics (Niu, 2004; Paulick et al., 2006) and that the REE can be used to constrain the primary mineralogy and magmatic history of the peridotite prior to alteration (e.g., Deschamps et al., 2010). Light REE enrichments in the bulk rock serpentinized peridotites relative to the fresh clinopyroxene in the same samples (Niu, 2004) imply some decoupling of REE within these rocks. This decoupling is generally attributed to transient melt infiltration in the peridotite, where a melt percolated and perhaps “froze” along grain boundaries and where the clinopyroxene did not significantly react with that melt (Niu, 2004).

77 In contrast, experimental work suggests REE mobilization into the hydrothermal
78 fluid during serpentinization (Allen and Seyfried, 2005), suggesting that REE may be
79 mobile during alteration. A similar inference was made based on some bulk rock
80 serpentinite compositions from IODP Leg 209, subject to high water / rock ratio reaction
81 (Paulick et al., 2006; Jöns et al., 2010). Furthermore, Sr, Nd isotopic evidence show
82 higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower ϵ_{Nd} for serpentinized abyssal peridotites exposed on the
83 seafloor near spreading centers (McCulloch et al., 1980; Menzies et al., 1993; Snow and
84 Reisberg, 1995; Delacour et al., 2008; Harvey et al., 2014) relative to typical mantle
85 values recorded in abyssal peridotite clinopyroxenes (Salters and Dick, 2002; Ciprianni et
86 al., 2004; Warren et al., 2009; Mallick et al., 2014), and with isotope compositions that
87 approach that of seawater. These data imply isotopic disequilibrium between bulk rock
88 peridotite and clinopyroxenes isotope ratios, although to our knowledge there has not
89 been any systematic work to assess clinopyroxene and bulk rock Sr and Nd isotope
90 compositions in the same sample. From the coupled Sr, Nd isotope systematics of bulk
91 rock peridotites, water / rock mass ratio have been inferred to understand serpentinization
92 and examine mass exchange between seawater and the Earth's upper mantle (Foustoukos
93 et al., 2007; Delacour et al., 2008). As a result of this apparent disequilibrium it is
94 currently unclear if and to what extent the REE budget of peridotites can be affected by
95 serpentinization and seafloor weathering reactions.

96 Here we present a detailed investigation of *in situ* (laser ablation ICP-MS) and
97 bulk major and trace element concentrations, as well as solution Sr and Nd isotopic
98 compositions by MC-ICP-MS on primary and secondary mineralogy (through sequential
99 leaching experiments) of six serpentinized abyssal peridotites from the Southwest Indian

Ridge. The selected samples have preserved primary clinopyroxene and occasionally orthopyroxene while most of olivine has been altered to serpentine. The relic clinopyroxenes preserve the original mantle signature and have been previously characterized for their magmatic elemental and Sr, Nd, Hf compositions (Mallick et al., 2014; Mallick et al., 2015). The detailed elemental and isotope comparison between bulk rock (altered) and clinopyroxene (magmatic) signatures allows to constrain whether REE have been added or exchanged between the reactant seawater and peridotite during serpentinization. We show that the secondary mineralogy (especially serpentine after olivine and orthopyroxene) has a strong seawater – like signature with negative Ce anomalies and Sr, Nd isotopes approaching seawater. This data allows us to reevaluate the utility of Sr-Nd isotope systematics as tracers of water rock ratios, the residence of trace elements in secondary minerals in serpentinized peridotites and the extent of REE exchange between mantle and seawater.

2.0 Sample Description

The analyzed abyssal peridotites are from two on-ridge locations along the Southwest Indian Ridge (SWIR: Dick et al., 2003; Standish et al., 2008) on opposite sides of the 16°E discontinuity (Supplementary Figure 1). Peridotites from 15.23°E (axial trough, subsequently labeled VAN 7-85 samples) sit on an oblique segment of the spreading ridge, while those from the 16.64°E location (fault scarp, subsequently labeled VAN 7-78 samples) are from the orthogonal segment of the spreading ridge as defined by the angle between the spreading direction and the ridge axis (see Dick et al., 2003; Standish et al., 2008 for geodynamic details). These samples have been studied in detail for petrography, major, trace element, Sr, Nd and Hf isotope compositions in

clinopyroxene and major element compositions in spinel (Warren et al., 2009; Mallick et al., 2014; Mallick et al., 2015). Clinopyroxenes from the 15.23°E peridotites have low TiO₂ (≤ 0.24 wt%) and Na₂O (≤ 0.52 wt%), sub-chondritic LREE/HREE ratios and spinels with low TiO₂ (≤ 0.11 wt%). These data suggest minimal interaction with a melt and the 15.23°E peridotites are interpreted as nearly pure melt residues of ~8% melt depletion from a DMM source (Mallick et al., 2014). Peridotites from 16.64°E are interpreted as re-fertilized peridotites due to the frequent presence of plagioclase, high TiO₂ (up to 0.53 wt%) and Na₂O (up to 1.57 wt%) along with often super-chondritic LREE/HREE ratios in clinopyroxene, and spinels with high TiO₂ (up to 0.46 wt%; Warren et al., 2009; Mallick et al., 2014; Mallick et al., 2015). Based on the Hf, Nd isotope compositions of the clinopyroxene from the SWIR peridotites and co-located basalts, Mallick et al. (2015) concluded that the depletion (for 15.23°E peridotites) and post-melting enrichment (for 16.64°E peridotites) processes are related to recent processes beneath the ridge and where the 15.23°E peridotites are consistent with a local depleted endmember of the MORB source mantle.

Common textural features of serpentinization in these samples are shown in SEM images (Fig. 1). Samples are dominated by a serpentine matrix ranging from black (VAN 7-78-36H and VAN 7-78-41) to a yellow-green (VAN 7-78-39 and VAN 7-85 samples) in appearance, with crosscutting fibrous veins of magnetite centrally aligned within the serpentine veins. Notably, magnetite is isolated from the primary minerals (Figs. 1A, 1B, 1C). These features are consistent with the “type-2” veins described by Beard et al., (2009), of magnesian serpentine - magnetite associations in a fluid-dominated system. Transect analyses by SEM across the magnetite veins show a decrease in Fe

concentration and increase in Mg# in the serpentine towards the magnetite vein, also similar to the “type-2” veins of Beard et al. (2009). These observations imply that magnetite is not precipitating directly out of olivine but formed likely as a reaction between pre-existing serpentine-brucite assemblage and fluid (Beard et al., 2009). In general, magnetite in the VAN 7-78 samples is distributed throughout the serpentine matrix with typical widths of 30-80µm. In the VAN 7-85 samples magnetite veins are more abundant in the serpentine matrix with typically smaller vein sizes of 10-40µm.

Tan, fibrous serpentine polymorphs (bastites) of primary minerals, after orthopyroxene and olivine, are found within the VAN 7-78-39 and VAN 7-85- samples. At the mineral boundaries between orthopyroxene / serpentine and olivine / serpentine we observe dissolution features appearing as irregular undulating grain boundaries (Fig 1E, 1F). Orthopyroxene lamellae exsolved in clinopyroxene show preferential replacement by serpentine relative to clinopyroxene (Fig. 1D). Flow structures are seen in the serpentine recording localized stresses, and sometime crosscut by secondary Fe depleted serpentine veins (Figs. 1E, 1F). Our laser ablation investigation is focused on the elemental systematics of these type -2 serpentine veins, which dominate the matrix of these samples.

3.0 Methods

All chemical analyses and measurements were performed at the Center for Elemental Mass Spectrometry, Department of Earth and Ocean Sciences, University of South Carolina. All acids used were produced in-house by single (HF and HNO₃) or double sub-boiling distillation (HCl). 18MΩ water was produced through a Millipore Super-Q system. All sample handling and acid dispensing was in a metal-free clean lab.

All dry downs were performed in custom-made double-HEPA filtered forced air hot plates. All bulk rock concentration analyses were performed on a Thermo ELEMENT 2 HR-ICPMS, using Indium as internal standard, and standardized against the BHVO-2 USGS rock material using the preferred concentrations from the GEOROC database.

3.1 Laser Ablation:

Fragments of the samples were mounted in epoxy, polished to 1µm with Al₂O₃ powder and characterized and imaged with a reflected light petrographic microscope and a Tescan Vega3 SBU Variable Pressure SEM equipped with an EDX system for composition determinations, at the Electron Microscopy Center, University of South Carolina. In situ mineral major (²³Na, ²⁹Si, ²⁷Al, ²⁵Mg, ⁴⁴Ca, ⁴⁷Ti, ⁵³Cr, ⁵⁷Fe, ⁵⁵Mn, ⁶⁰Ni) and trace (⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁹Sm, ¹⁵⁷Gd, ¹⁶³Dy, ¹⁶⁷Er, ¹⁷³Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ²⁰⁸Pb, ²³²Th, ²³⁸U) element concentrations were determined using a Photon Machines UV-Eximer 193nm laser ablation system with a HELIX 2 sample cell in He-atmosphere, coupled to a Thermo ELEMENT 2 HR-ICP-MS. Concentrations were determined by spot ablation with an 110µm spot at 8Hz with ~ 11 J/cm² fluence. Additional laser settings can be found in Table 1. Due to the size of the laser beam and potential fine scale heterogeneity of serpentine (e.g. Frost and Beard, 2007; Frost et al., 2013) and orthopyroxene due to exsolutions, we determined the major element compositions of each spot following the method of Humayun et al. (2010) where background corrected peak intensities are converted to oxide concentration ratio with respect to silica using relative sensitivity factors (RSF) defined as:

$$RSF = (C_i/C_{SiO_2}) / (I_i/I_{29Si}) \quad (1)$$

where C_i is the concentration of element or oxide i , and I_i is the intensity of the element or oxide peak. Relative sensitivity factors were obtained from multiple analyses of the glass reference materials NIST 612 and BHVO-2G, BIR-1G.

Application of the RSFs required the SiO_2 content to be determined using the equation:

$$\text{SiO}_2 = 100 / \sum (x_i / \text{SiO}_2) \quad (2)$$

where x_i are the major oxides MgO, FeO, CaO, TiO_2 , MnO, Al_2O_3 , NiO_2 , SiO_2 and H_2O .

When serpentine was ablated we assumed 13wt% H_2O , otherwise it was set to 0. Trace element concentrations were then determined from equation (1) using SiO_2 concentrations determined from equation (2). Analyses of magnetite always overlapped with serpentine matrix due to the fine nature of those veins, so we used the determined SiO_2 of the composite spot as an internal standard. The validity of this method is shown in Supplementary Table 2 by the good stoichiometry of the average measured serpentine to the formula $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$ and in Table 2 by comparing the clinopyroxene major element concentrations determined here against electron microprobe clinopyroxene data for these samples reported elsewhere (Warren et al., 2009; Mallick et al., 2014; Mallick et al., 2015). For SiO_2 , which we use as our LA-ICMPS internal standard, the variance between the two methods is ~ 6% relative, or less. Based on this and the inherited uncertainty in assuming the water concentration of the serpentine at 13wt%, we estimate that the in situ trace element concentrations of the serpentine are accurate to within 10-15% relative. Average trace element concentrations are reported in Table 3 and all individual spot analyses are reported in Supplementary Table 1.

3.2 Sequential Leaching Experiments.

Interior pieces of the peridotites were powdered with an agate ball mill. The bulk rock was digested for trace element and isotope analyses. A second fraction (~ 1 gram) was taken through a sequential leaching procedure following a modified technique after Chester and Hughes (1967) shown schematically in Supplementary figure 2. The leaching steps were: first, an H₂O leach for removal of any readily exchangeable metals; second, a buffered (pH=5) sodium acetate solution (NaOAc) for the selective removal of carbonates; third, a buffered (pH=4) hydroxylamine hydroxide (HH) solution for the preferential removal of Fe-oxide and Fe-oxyhydroxides and fourth, cold leach with 6N HCl for the removal of surface bound trace elements at mineral grain boundaries and removal of easily dissolvable mineral fractions (alteration). The leached residues were also dissolved and an aliquot of each fraction was taken for trace element analyses. The trace element and Sr, Nd isotopes of the leachates and the residual rock were then compared to those of the bulk (unleached) rock. See Supplementary text material for additional details on the leaching protocol.

3.3. Sr, Nd Isotopes

We analyzed the bulk rock, the combined NaOAc and HH leachates, 6N HCl leachate, and the residual rock for Sr, Nd isotopes. The clinopyroxene Sr and Nd isotope compositions are taken from Mallick et al., (2014). Separation of REE from Sr was performed using cation exchange resin (Eichrom 50W-X8). Sr was purified on micro-columns with Sr-Spec resin. Nd was purified from the other REE on micro-columns with LN spec resin. Sr and Nd isotope ratios were measured on a Thermo NEPTUNE MC-ICPMS. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are normalized for fractionation to $^{86}\text{Sr}/^{88}\text{Sr} =$

0.1194 and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively. During these analyses the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the NISTSRM-987 was measured at 0.710306 ± 17 (2σ , $n = 7$) and $^{143}\text{Nd}/^{144}\text{Nd}$ of LaJolla at 0.511839 ± 10 (2σ , $n = 20$), typical to other studies from our lab (Mazza et al., 2014; Whalen et al., 2015). The isotope ratios are corrected for instrument bias to $^{87}\text{Sr}/^{86}\text{Sr} = 0.710250$ for the NISTSRM-987 (Weis et al, 2005), and $^{143}\text{Nd}/^{144}\text{Nd} = 0.511858$ for La Jolla (O’Nions et al., 1977).

4.0 Results

4.1 Major element compositions

Average major element data for primary and secondary (serpentine, iron oxides) minerals are reported in Table 2. For sample VAN 7-78-36H we use the clinopyroxene data reported in Mallick et al. (2014). In short the major element compositions of clinopyroxene from these two locations (VAN7-78 and VAN7-85) display in general modest variation considering the variability of cpx from other ridge locations. Based on a somewhat larger dataset reported by Mallick et al. (2014) the VAN7-85 sample suites are characterized by restricted and depleted character e.g., low Na_2O (0.37 - 0.52 wt.%), TiO_2 (0.17 - 0.24 wt.%) content consistent with the harzburgitic composition. VAN7-78 clinopyroxene have Na_2O content similar to VAN7-85 samples, but are characterized by a high and large range of TiO_2 (0.23 to 0.53 wt.%) content, which seems consistent with the presence of frequent plagioclase in VAN7-78 peridotites mineral assemblage. Further details on the clinopyroxene major element systematics can be found in Mallick et al. (2015) and are not further discussed here, as our focus is the trace element systematics related to serpentinization.

Olivine was variably altered, from cloudy partially serpentinized grains to serpentine with variable extents of alteration based on the MgO/SiO₂ ratios acquired with SEM-EDX at multiple spots of the sample. The serpentine stoichiometry from LA-ICPMS serpentine analyses is (Mg+Fe)/Si ~ 1.3 to 1.55 in cation moles and straddles the ideal serpentine (lizardite) mineral stoichiometry of (Mg,Fe)₃Si₂O₅(OH)₄ (see Supplementary Table 2, e.g., Frost and Beard, 2007). Consistency of serpentine stoichiometry was found among all serpentine phases despite the nature of the primary minerals they are replacing (olivine, orthopyroxene). Serpentine after orthopyroxene was found to have elevated concentrations of trace metals (Ti, Sc, Zr, REE, Hf) compared to serpentine after olivine (see Supplementary Table 1), consistent with the higher partition coefficients of these elements in orthopyroxene over olivine. We used these trace element characteristics along with (Mg+Fe)/Si ratios and the Al concentrations to identify the protolith mineral of the serpentine, i.e. olivine vs. orthopyroxene (Supplementary Table 2) and to calculate the average serpentine after olivine in Tables 2 and 3. We did not identify brucite (Mg,Fe)OH₂ with the SEM analyses in any sample. We also performed XRD analyses on samples VAN7-78-39 and VAN7-85-42 using a Shimadzu LabX XRD-6000 (at USC) but again no brucite was identified. Nevertheless brucite may still be present in minor and disseminated within the serpentine (e.g. Frost and Beard, 2007), which may explain some of the (Mg+Fe)/Si variance.

Orthopyroxene has (Mg+Fe)/Si ~0.9 – 1.1 that straddles stoichiometric orthopyroxene (Mg,Fe)SiO₃ and co-varies strongly with the Mg content as a result of partial overlap with serpentine or replacement by serpentine in some cases (Figure 1D).

Magnetite (identified by the Fe_3O_4 stoichiometry from SEM analyses) is found widespread in these rocks, typically as disseminated veinlets in the serpentine (Fig. 1A, 1B). Due to their small size compared to our laser beam size, the magnetite analyses overlapped with the matrix (always serpentine), as can be seen by the significant MgO and SiO_2 in their totals and the Si/Mg cation ratios (Table 2). Nevertheless, as the signal is dominated by the magnetite (spot analyses $\text{FeO}_{(\text{T})} > 60 \text{ wt\%}$) these magnetite data are informative in constraining the trace element systematics of these magnetite veins.

4.2. Trace element systematics of the bulk rock and minerals

4.2.1 Bulk Rock

Bulk rock REE patterns for the 6 peridotites are shown in Figure 2. Both groups of peridotites have roughly similar HREE concentrations that are lower than primitive mantle (Fig. 2A), consistent with being residues of melt extraction at a mid oceanic ridge setting. The VAN 7-78 samples have higher LREE/HREE ratios than the VAN 7-85 samples with concave up REE patterns from La to Dy. The VAN 7-85 samples have a strongly depleted LREE to HREE pattern from Nd to Lu, but show a prominent negative Ce anomaly relative to La and Pr. The extended bulk rock trace element patterns show strong positive U, Pb and Sr anomalies (Fig. 2B), as typically found in other abyssal peridotites (Niu, 2004; Paulick et al., 2006; Delacour et al., 2008; Jöns et al., 2010, Kodolányi et al., 2012; Deschamps et al., 2013), and usually attributed to interaction with seawater. The higher concentrations in the LREE-MREE and Hf, Zr, Ti of the VAN 7-78 over the VAN 7-85 samples are consistent with the refertilized nature of the former (e.g. Mallick et al., 2014; Mallick et al., 2015) as also identified in their clinopyroxene concentrations (see below).

4.2.2 Clinopyroxene

Clinopyroxene in the three VAN 7-85 peridotites and the VAN 7-78-39 show strong LREE depletions over the HREE. Most importantly, they lack the large negative Ce anomaly identified in the bulk rock patterns (compare Figs. 2A and 3). The VAN 7-78-36H and VAN 7-78-41 clinopyroxenes show relative flatter REE patterns consistent with refertilization by melt-rock reaction (Mallick et al., 2015).

Extended trace element patterns for the clinopyroxene show similar patterns for both sample suites with enrichments in U over the LREE and Th, strong depletions in Sr and to a lesser extent Zr, Hf, Ti over the adjacent REE (compare Figs 2B and 4) and unlike the bulk rock concentrations. Clinopyroxenes from VAN 7-78-36H and VAN 7-78-41 show a flatter pattern with over two orders of magnitude higher LREE, Th and Ba than the other samples, consistent with refertilization and also seen in their bulk rock trace element systematics.

4.2.3 Orthopyroxene

The orthopyroxene HREE concentrations are similar in the two rock suites and roughly a factor of 4 lower than the corresponding clinopyroxene, generally consistent with experimental partitioning data (e.g. Salters et al., 2002; McDade et al., 2003). Orthopyroxenes in the VAN 7-78 samples have higher LREE contents than the VAN 7-85 samples, consistent with these enrichments in the bulk rock and clinopyroxene systematics discussed above. The samples with the greatest LREE depletions display a distinct uptick in La over Ce that is not observed in the corresponding clinopyroxene (compare Figures. 2A and 3), and opposite to what is predicted from the partitioning systematics where LREE become increasingly more incompatible in the pyroxenes with

decreasing atomic number and increasing coordination size (Hauri et al., 1994; Wood and Blundy, 1997; Salters et al., 2002; McDade et al., 2003).

The extended trace element patterns of the orthopyroxene are roughly similar for the two suites with positive U and Pb spikes over the LREE and highly variable Sr concentrations. The positive Hf, Zr, Ti spikes compared to the REE is consistent with higher partition of these elements over the adjacent REE in a compatibility diagram in orthopyroxene (e.g. Salters et al., 2002, compare Figures 2B and 4)

4.2.4 Serpentine / matrix

Serpentine concentrations (Fig. 3, 4) are variable and a significant part of their variance depends on their proto-mineral (orthopyroxene or olivine). As discussed in section 4.1 the proto-mineral of the serpentines were distinguished by their trace element characteristics along with (Mg+Fe)/Si ratios and the Al concentrations. For the average serpentine composition reported in Tables 2 and 3 only the serpentine after olivine was used. Overall, the HREE concentrations of the serpentine after olivine are 10-20 times lower than the corresponding clinopyroxene, roughly consistent with the partitioning of these elements between olivine and clinopyroxene (e.g. Salters et al., 2002; McDade et al., 2003) and where the LREE are depleted with respect to HREE. Serpentine after orthopyroxene typically has HREE concentrations similar to 5 times lower than that of fresh orthopyroxene while LREE concentrations are often 10-20 times greater with a negative Ce anomaly (Fig. 3). Serpentine in the VAN 7-85 and VAN 7-78-39 samples with the largest depletion in their LREE over HREE show characteristic negative Ce anomalies compared to La and Pr, as also observed in the bulk rock trace element systematics (compare Figures 2A and 3) but also have elevated LREE compared to the

fresh primary mineral (Fig. 3). The extended trace element patterns for these serpentines show strong positive U, Pb, and Sr anomalies together with negative anomalies in Th, Ce and Zr, mirroring those of the bulk rock trace element patterns (compare Figures 2B and 4).

Serpentines in samples VAN 7-78-36H and VAN 7-78-41 show flatter REE patterns with higher LREE concentrations than the other samples and no obvious negative Ce anomaly, also consistent with their bulk rock trace element systematics. The extended trace element pattern for samples VAN 7-78-36H and VAN 7-78-41 is elevated compared to the VAN 7-85 and VAN 7-78-39 samples, with positive anomalies for U, Pb, and Sr but no distinct negative anomalies in Zr (compare Figs. 2B and 4).

4.2.5 Plagioclase

Plagioclase was found in the VAN 7-78 samples, as veins generally smaller than 100 μ m in width. Laser ablation data of Plagioclase on samples VAN 7-78-36H and VAN 7-78-41 was acquired on the largest minerals found. The REE pattern shows a LREE enriched pattern with the distinct positive Eu anomaly typical of plagioclase. The HREE concentrations are lower than the serpentine matrix, but the LREE are higher (compare Figs. 3 and 5A). Extended trace element patterns show the strong positive Sr anomaly and higher Ba than the matrix serpentine, and characteristic large depletions in the HFSE compared to the REE (compare Figures 4 and 5B).

4.2.6 Magnetite

Magnetites in the VAN 7-78 samples have slight LREE depleted patterns with small negative Ce anomalies. Their REE concentrations are roughly a factor of 5 lower than the corresponding serpentine (compare Figs. 3 and 5C). In contrast, magnetite in

sample VAN 7-85-42 has a flat REE pattern with up to 100 times higher LREE concentrations than corresponding serpentine and again with a distinct negative Ce anomaly. The extended trace element patterns are quite variable, with strong positive U, Pb, Sr spikes similar to serpentine concentrations (compare Figures 4 and 5D). The HFSE are far more variable with both positive and negative Ti anomalies, but with a dominant negative Th, Zr, and Hf anomalies, particularly pronounced in sample VAN 7-85-42 with the high REE concentrations.

4.2.7 Modal Abundances and Bulk Rock Reconstruction Model

We used the average laser ablation mineral concentration data above to estimate the modal abundance of the analyzed phases (Tables 2 and 3: spots used to determine mineral concentration averages are identified in Supplementary Table 1). We then use these modal abundances to reconstruct the bulk rock trace element composition and compare in detail the measured vs. reconstructed trace element systematics. This exercise, although somewhat circular, allows to better assess the main hosts for different trace elements between primary and secondary phases. Mineral modes were determined empirically by minimizing the average difference between modeled REE concentrations and measured bulk rock REE patterns from solution chemistry. In order to avoid spurious results we constrained the modal abundance to less than 2% modal magnetite and plagioclase (where present), less than 10% clinopyroxene and a maximum serpentine to orthopyroxene ratio of 30. In cases of poor overall match, we attempted to fit the HREE concentrations only. The determined modal abundances are reported on Table 2. The best-fit reconstructions have 1 to 8 % modal clinopyroxene, 3 to 25% orthopyroxene

and up to 90% serpentine. Importantly, 0.5 to 2% modal magnetite was always found necessary to best reconstruct the bulk rock concentration patterns (Figures 6 and 7).

The VAN 7-85 samples have the best overall fits between measured and reconstructed compositions, with less than 15% average difference across the REE. This suggests that our laser investigation identified all major REE reservoirs in the rock and that the calculated modal abundances are reasonable (Table 2). The VAN 7-78 samples were harder to fit, particularly for the LREE (La, Ce, Pr, Nd) where the model concentrations are significantly lower than the measured. The REE reconstruction is particularly poor for sample VAN 7-78-41 as the HREE concentrations of clinopyroxene, orthopyroxene and serpentine are higher than the measured bulk rock, leading to steeper LREE/HREE ratios and crossing patterns for the modeled vs. measured bulk, and unreasonably low clinopyroxene mode (negative). In this case it appears that there is small-scale sample heterogeneity between the aliquot used for trace elements and for laser and modal abundances cannot be reasonably estimated for this sample with this method. For sample VAN 7-78-39, the most LREE depleted of this suite, the HREE can be modeled well but the LREE fit is poor and highly sensitive to small changes of either the clinopyroxene or plagioclase modes. The mismatch between measured and model trace element concentrations in the VAN 7-78 samples can be explained if our laser investigation “missed” a relatively LREE enriched component in these peridotites. As these samples are considered refertilized by a LREE enriched melt (Mallick et al., 2014; Mallick et al., 2015) perhaps there are components in the matrix related to this refertilization (trapped melt along grain boundaries, or perhaps other minor phases) that evaded our ablation investigation.

4.3 Trace element systematics of leachate experiments

4.3.1 H₂O Leach

The H₂O leachates have about 2 orders of magnitude lower REE concentrations than the bulk rock, but with REE patterns that closely mimic that of the bulk rock including Ce depletion in the VAN 7-85 samples (Fig. 8). The extended trace element patterns show larger positive U and Sr anomalies than those of the bulk rock (Fig. 9), with or without Pb spikes (VAN 7-85-42, 85-47). These large U and Sr enrichments in the H₂O leachates closely resemble that of average seawater (Fig. 9, lower right hand corner).

4.3.2 Na-Acetate leach

The NaOAc leach REE pattern mirrors that of the bulk rock for all samples. The VAN 7-78 samples have concave up patterns with only a slight negative Ce anomaly and the VAN 7-85 samples have a distinct negative Ce anomaly. Overall, the REE concentrations are roughly a factor of 20 lower than the bulk rock (Fig. 8). The extended trace element patterns again show strong positive anomalies for Sr and U, although the U enrichment is proportionally greater than the Sr compared to the bulk rock, suggesting stronger U mobilization in this leachate (Fig. 9). Characteristic is also the greater Ba/Th than all other fractions and the bulk rock, which we speculate is related to the affinity of Ba to substitute Ca in carbonate. Importantly, all NaOAc leachate patterns overall resemble that of seawater but with higher HFSE depletions relative to the REE than average seawater. This implies that the phase mobilized by this leachate carried REE, Sr and U preferentially over the HFSE.

4.3.3 Hydroxylamine Hydroxide Leach

The HH leach pattern generally mirrors the REE pattern of the bulk rock with concave up patterns for the VAN 7-78 samples and LREE depleted patterns with a distinct negative Ce anomaly in the VAN 7-85 samples. Importantly, the HH leachate has higher LREE/HREE ratios than NaOAc leachate in the VAN 7-85 samples as seen by their crossing REE patterns (Fig. 8). The extended trace element patterns show distinct positive Sr, Pb and U anomalies with pronounced negative Ti, Zr, and Hf anomalies for all samples (Fig. 9). This is evidence for strong REE-HFSE fractionation during Fe-oxide and magnetite precipitation.

4.3.4 6N HCl Leach

The 6N HCl leachate REE are 3-5 times lower in concentration than the bulk rock, but with higher LREE/HREE than the bulk rock (Fig. 8). The extended trace element patterns show the prominent positive U spike, as in the other leachates, while the Sr spike is now largely absent (Fig. 9). Negative Zr, Hf, and Th anomalies relative to the REE persist, while Ti depletions that were observed in the other leachates are absent.

4.3.5 Residual Rock

The residual rock after all leaching steps has a REE pattern that parallels the original bulk rock pattern at 2 to 4 times lower concentration (Fig. 8). The extended trace element patterns lack the Sr peak observed in the bulk and the H₂O, NaOAc, HH leachates. The U enrichment is now also lower and in some cases small positive Zr and Hf peaks are present, which is consistent with the presence of residual orthopyroxene (Fig. 9).

Overall, with sequential leaching there is progressive removal of the fluid mobile elements (Ba, Sr, Th and U) with 45-98% of the bulk rock budget mobilized by leaching (Supplementary Figure 3). Between 20% and 60% of the REE budget are mobilized from the bulk rock during total leaching while only up to 10% of the Hf and Zr bulk rock budget was been mobilized (Supplementary Figure 3). The percent distribution of trace elements in the different leachate fractions is show schematically in the Supplementary Figures 3. The sum of trace element concentrations in the leachate and residual fractions matches the bulk rock well, confirming that all elemental reservoirs have been accounted for during the sequential leaching (Figure 10).

4.4. Sr and Nd isotope data

$^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} values for the bulk rock and leachates are reported in Table 5 and plotted on a Sr-Nd anticorrelation isotope diagram (Figure 11) along with the clinopyroxene compositions from these samples from Mallick et al., (2014). The clinopyroxenes from these peridotites appear to have retained their magmatic mantle signature and plot within the MORB field (Warren et al., 2009; Mallick et al., 2014). In contrast, the bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} data are shifted to higher and lower values respectively than clinopyroxene. The more depleted VAN 7-85 samples show a shift in both $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} compared to their clinopyroxene, with their bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ essentially identical to that of modern seawater ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70916$), and ϵ_{Nd} up to 8 units lower than clinopyroxene (e.g., sample VAN 7-85-43, Table 5). The refertilized VAN 7-78 samples show a shift in $^{87}\text{Sr}/^{86}\text{Sr}$ towards seawater but not as extreme as the VAN 7-85 samples, and with little change in ϵ_{Nd} .

The leached rock ϵ_{Nd} values fall between the clinopyroxene and the bulk rock for both sample suites. This shift in Sr isotopes in serpentinized peridotites during leaching is also consistent with the observations of Harvey et al., (2014) on serpentinites from the 15°20'N fracture zone, Mid Atlantic ridge. For samples VAN 7-85-47 and VAN 7-85-42, their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increased after leaching to values higher than seawater. This peculiar observation was previously described as “orphan” ^{87}Sr , possibly the result of incorporation of Sr of crustal origin as clays within the rock structure, which was not removed during leaching (Snow et al., 1993) and our experiments seem to confirm such a component in these peridotites.

The combined NaOAc and HH leachates invariably have higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower ϵ_{Nd} than the bulk rock (with ϵ_{Nd} as low as - 2.8 for Van 7-85-47; Table 5). Even for the VAN 7-78 samples that show little change in the bulk rock vs. clinopyroxene Nd isotopes, the NaOAc + HH leachate has lower ϵ_{Nd} than the bulk rock. The 6N HCl leachates have higher ϵ_{Nd} than the NaOAc + HH leachates, approaching the leached rock composition. This indicates that the enriched Nd isotopes are preferentially concentrated in a relatively easily mobile phase, yet some persist in the leached bulk rock.

5.0 Discussion

The key observations from the data presented above are summarized as follows:

1. U, Sr, Ba, Pb positive spikes and negative Ce anomalies are observed in situ in the serpentine fraction of altered peridotites, and in magnetite associated with veins within serpentine.

2. These anomalies are also observed both in the easily mobile phases as demonstrated by the leaching experiments, suggesting that they are dominantly hosted in secondary phases.

3. The lack of negative Ce anomalies in the relic clinopyroxene is evidence for disequilibrium reactions in the serpentinized peridotites where the negative Ce anomalies are imprinted to the bulk rock at lower temperatures than magmatic conditions.

4. $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} isotopes in the bulk rock and leached fractions of these peridotites are higher and lower, respectively, than their clinopyroxene and approach the composition of seawater, linking directly the observed U, Sr, Pb spikes and negative Ce concentration anomalies in these fractions to seawater input.

5. The Sr, Nd isotope shifts between clinopyroxene and bulk rock, as well as the magnitude of Ce anomalies in the serpentine are more evident in the depleted peridotites from the VAN 7-85 dredge than the refertilized peridotites from the VAN 7-78 dredge.

6. The combination of radiogenic Sr and unradiogenic Nd isotopes that approach the composition of seawater, together with U, Sr, Pb enrichments and negative Ce anomalies in the leaching experiments, suggests that seawater-derived Nd (and by inference other REE) has been incorporated into these peridotites during serpentinization.

These data is strong evidence that in addition to the typical enrichments in fluid mobile elements seen in serpentinized peridotites (B, Cl, Sr, Rb, Cs, Li, C, S; e.g.,

Scambeluri et al., 2004; Alt et al., 2013; Deschamps et al., 2013, for detailed literature reviews), the REE systematics of peridotites can also be affected by seawater interaction.

5.1 Nd-isotope mass balance between peridotite and seawater

Assuming that the shift in bulk rock Nd isotopes in these peridotites, from their mantle isotope composition recorded in the clinopyroxene towards more enriched compositions, is entirely due to seawater interaction, we can determine the proportion of the bulk rock Nd that is seawater-derived. This is calculated by mass balance using the Nd-isotope compositions of clinopyroxene (i.e., the mantle value) and seawater as end members, and that of the measured bulk rock as the mixture (eq. 3).

$$\%Nd_{SW} = (^{143}Nd/^{144}Nd_{BR} - ^{143}Nd/^{144}Nd_{Cpx}) / (^{143}Nd/^{144}Nd_{SW} - ^{143}Nd/^{144}Nd_{Cpx}) \quad (3)$$

where $^{143}Nd/^{144}Nd_{BR}$ is the measured bulk rock $^{143}Nd/^{144}Nd$, $^{143}Nd/^{144}Nd_{Cpx}$ is the measured clinopyroxene and $^{143}Nd/^{144}Nd_{SW}$ is the measured $^{143}Nd/^{144}Nd$ of average seawater from near the SWIR (see Table 5: Stichel et al., 2012). The calculated range of seawater-derived Nd ranges from 3% for VAN 7-78-36H to 31% for VAN 7-85-43 of the bulk rock Nd budget (Table 5). The more depleted VAN 7-85-dredge samples record a greater proportion of seawater-derived Nd than the refertilized 78-dredge samples. To a first approximation, this implies that depleted peridotites with low REE contents are more susceptible to a seawater influence and changes in their REE budget than more fertile ones.

While this calculation is informative in terms of the impact of serpentinization on the bulk rock Nd budget, it does not reveal whether there was REE exchange between

seawater and peridotite or seawater addition, or how the negative Ce anomaly developed. In the following we discuss: 1) the origin of the negative Ce anomaly in the bulk rock and serpentine, 2) the evidence for LREE addition within the secondary mineralogy, and 3) whether serpentinization acts as a sink for REE from seawater, or whether REE are exchanged between the ocean and the peridotite.

5.2 LREE addition or exchange?

5.2.1 Origin of the negative Ce anomalies

One possible explanation for the negative Ce anomalies is preferential mobilization of Ce from the rock while all other REE are retained. In principle, this is unlikely as we are not aware of any process that will make Ce more mobile, or soluble, than the other LREE. Instead, Ce^{+3} can be preferentially oxidized to Ce^{+4} , which is less soluble and less mobile than the other REE. We can nevertheless test this hypothesis by calculating the hypothetical magmatic concentrations of the unaltered orthopyroxene and olivine in these peridotites using the REE concentrations of the fresh clinopyroxene and published mineral-mineral partition coefficients values (e.g. McDade et al., 2003; Bizimis et al., 2004; Kelemen et al., 2004; Sun and Liang, 2014; see Supplementary Table 3). From these concentrations and the modal abundances determined by the laser-ablation reconstruction (section 4.2.7) and assuming that the serpentine modal abundance equals that of the precursor olivine we reconstruct the REE concentrations of the primary peridotite (Fig. 12). If preferential mobilization of Ce out of the rock was the reason for the Ce depletions, then the reconstructed LREE concentrations (except Ce) should match that of the measured bulk rock. We test this on the more depleted VAN 7-85 samples, as those have simpler REE patterns and are less affected by melt refertilization. For the

VAN 7-85 samples, the HREE concentrations between measured and calculated bulk rocks match well, suggesting that the calculated modal abundances are reasonable (despite the volume increase of serpentine relative to olivine). Yet, the calculated LREE are lower than the measured bulk rock, with no Ce anomaly. As the partition coefficient between pyroxenes and olivine lack a Ce anomaly, even small errors in the modal abundances of any of these minerals cannot account for the Ce anomaly. These data point to addition of (at least) La and Pr but not Ce to the rock, rather than selective Ce mobilization out of the rock.

U and Th are both highly incompatible in the peridotite mineralogy (e.g., Salters et al., 2002), so their relative fractionation in the abyssal peridotites (Fig. 2B) is largely controlled by a strong U addition that has been attributed to seawater (e.g. Niu, 2004; Deschamps et al., 2013) as U is generally a conservative element in seawater (Chen et al., 1986). With increasing U/Th ratio and increasing seawater influence on the bulk rock U budget, the magnitude of the Ce anomaly increases (Fig. 13). This indirectly implies that the La and Pr addition over Ce must also be controlled to some extent by seawater, which has a distinct negative Ce anomaly due to oxidation of Ce^{3+} to Ce^{+4} and its preferential scavenging over the other REE (Elderfield et al, 1982; Piegras et al, 1992; Alibo and Nozaki, 1999). As this U/Th vs. Ce anomaly correlation is dominant feature in the global abyssal peridotite compositions (Fig. 13), it implies that the process of LREE addition by seawater might be also wide spread in abyssal peridotites in general and not only confined in the SWIR peridotites.

5.2.2 Nd isotopes and LREE addition

Using the same bulk rock reconstruction from clinopyroxene as above (Section 5.2.1), we compare the calculated Nd concentration of the primary peridotite (Nd_{PR}) to that of the measured bulk rock (Nd_{BR}), their difference being potentially an estimate of the amount of Nd that was added to the rock during serpentinization. In this calculation the amount of added Nd to the Nd_{PR} here ranges from 17% to 70%. For samples VAN 7-85-42, and VAN 7-85-43 there is a striking similarity (<5% difference) between the excess Nd calculated from the measured vs. modeled bulk rock, and the seawater-derived Nd from the Nd-isotope mass balance approach (Table 6). This implies that addition of seawater-derived Nd alone can reasonably account for the unradiogenic Nd isotopes and the excess Nd in these rocks.

For the VAN 7-78 samples, we find greater amount of excess Nd in the bulk rock than the calculated seawater-derived Nd from the isotope mass balance. This discrepancy can be explained by transient metasomatism of the VAN 7-78 samples by a melt prior to serpentinization. If the infiltrating melt did not equilibrate with clinopyroxene, then the clinopyroxene concentrations will not be representative of the bulk rock and will lead to lower calculated bulk rock Nd concentrations than those measured. In this case, the amount of seawater-derived Nd can best be calculated from the isotope mass balance, assuming that the infiltrating melt had a similar (i.e., relatively radiogenic) Nd isotopic composition to the primary clinopyroxene. The studies of Mallick et al., (2014) and Mallick et al., (2015) have shown that clinopyroxene in these peridotites have similar Nd and Hf isotope compositions as their proximal lavas, providing support for this scenario.

5.2.3 LREE addition and HFSE depletions in the secondary mineral phases

A key observation is that magnetite has negative Ce anomalies, as does the serpentine (Figs. 3, 5C). Magnetite also has flatter REE patterns than those observed in both the primary and secondary silicate minerals and similar to seawater pattern. Kodolányi et al. (2012) made similar observations in forearc serpentinites, where serpentine + magnetite veins have higher LREE contents than serpentine alone. The presence of an Fe-oxide phase with flat REE patterns and Ce-anomaly is also inferred by the strong negative Ce anomalies in the HH leachates (Fig. 8). In the VAN-7-85-42 and VAN-7-85-43 samples the HH leachates have flatter REE patterns and larger Ce-anomalies than their bulk rock (Fig. 8). This indicates that a portion of the LREE bulk rock budget (except Ce) is hosted in the secondary phases, consistent with both the REE modeling (section 5.2.1) and the Nd isotopes (section 5.2.2) arguments above. As we discussed earlier (Section 2), the presence of magnetite within serpentine veins and away from relic olivine is explained by high fluid flux during the main stage of serpentinization (Beard et al., 2009). The petrologic observation for high fluid and the Ce anomalies in magnetite imply that the source of these LREE enrichments is likely seawater-derived fluid.

In contrast to the LREE element enrichments, negative Zr and Hf anomalies in both the magnetite (Fig. 5D) and the HH leachate fractions (Fig. 9) compared to the REE implies that the HFSE budget is less sensitive to serpentinization than the REE and must be dominated by the silicate minerals in the protolith. This conclusion is further supported by comparing the bulk rock and leachate fractions Hf vs. Ti to that of Nd vs. Ti concentrations (Fig. 14). Hf and Ti are coupled and show a tight correlation, where as

the NaOAc + HH and the 6N HCl leachates have preferential enrichment for the REE over Ti with nearly 2 orders higher Nd concentrations for a given Ti (Fig. 14). Therefore Nd is enriched in the easily mobilized phases, but not Hf. This supports previous inferences that HFSE are a more faithful recorder of bulk rock magmatic processes (e.g. Niu, 2004; Lapen et al., 2005; Bizimis et al., 2007; Stracke et al., 2011) than LREE in peridotites. In addition to those studies however, here we present strong evidence that serpentinization may also be responsible for the decoupling of LREE from the HFSE in serpentinized abyssal peridotites.

5.2.4 Nd Isotopic disequilibrium within the peridotites

The above evidence points to addition of a seawater-derived LREE component to peridotites during serpentinization. It is unclear however whether the REE hosted within the secondary phases (i.e., those mobilized from the NaOAc and HH) are exclusively from seawater or are a mixture of both seawater and of primary magmatic origin, that were mobilized during alteration. Insight on this can be gained by the Nd isotope compositions of the leachate and bulk rock fractions. For our samples, Sr is less useful in deciphering rock vs. seawater contributions, as the leachate Sr isotope composition is dominated by a seawater signal that does not vary significantly (Fig. 11).

Figure 11 compares the Nd and Sr isotope composition of the clinopyroxene (i.e., representing the primary mantle signature) with that of the bulk rock, the combined NaOAc + HH leachates, the 6N HCl leachate, and the residual rock after leaching. The leachate NaOAc + HH fractions have highly radiogenic seawater-like $^{87}\text{Sr}/^{86}\text{Sr}$ and lower ϵNd than the bulk rocks, up to the highly unradiogenic value of $\epsilon\text{Nd} = -2.8$ for sample VAN-7-85-47. Despite their unradiogenic values, these leachate fractions do not have a

pure seawater Nd isotope signature ($\epsilon_{\text{Nd}} \sim -9.7$), but rather a mixture of rock and seawater composition. This implies that the Nd budget (and by inference the other LREE, besides Ce) in the secondary phases is not exclusively derived from seawater, but some of the LREE are redistributed from the primary minerals to the alteration phases. This inference is similar to that of Berndt et al., (1988) for Sr, where during hydrothermal alteration of mid ocean ridge basalts, Sr is thought to be released from the primary rock and then reincorporated in the alteration phases. Here we infer that the process of release and re-incorporation likely takes place during serpentinization. Finally, the leached rock Nd-Sr isotope compositions plot invariably between that of the clinopyroxene and the bulk rock (Fig. 11), indicating that the seawater signature is pervasive within the residual silicate fractions, and which probably include significant amounts of secondary serpentine, although we cannot directly confirm this by the solution chemistry.

6.0 Summary and Implications

The Nd isotope data reveals strong isotopic disequilibrium in the various fractions of these serpentinized peridotites, with compositions approaching seawater in the secondary phases, pervasive alteration in the silicates, but preservation of the mantle values in the clinopyroxene (and possibly orthopyroxene; Warren et al, 2009). Combined with the enrichments in LREE along with the fluid mobile elements like Ba, U, Sr, and Pb in the serpentine and secondary minerals, we conclude that these data provide strong evidence LREE addition to the peridotite during serpentinization, and where the precipitation of secondary phases, like magnetite, appears to play a significant role in hosting the added LREE budget. Note that our data cannot easily constrain any HREE addition that might also be taking place, due to the higher HREE concentrations in all

primary silicate minerals over LREE, and the relatively flatter REE pattern of seawater compared to those silicates, making LREE addition from seawater more prevalent and obvious than HREE addition. We also emphasize that these rocks still preserve relic high temperature mineral phases and as such they are not completely serpentinized.

6.1 Water / rock ratio modeling

The Sr-Nd isotope systematics of serpentinized peridotites have been used to assess the integrated water/rock (W/R) ratio during serpentinization (e.g. Snow et al., 1994; Delacour et al., 2008), a key parameter that allows to place constraints on pH, hydrogen generation, seawater-rock exchange as well as heat generation in hydrothermal systems (e.g. Foustoukos et al., 2008). These calculations typically assume either closed (bulk exchange) or open (incremental reaction) system water/rock reaction (see Delacour et al., 2008 for details in the equations used here), Sr and Nd concentrations of the end member fluid and rock that remain unchanged during reaction, and that the fluid and rock are in equilibrium (e.g. Delacour et al., 2008). Indeed, if rock or fluid concentrations are also free variables, these types of calculations cannot be solved explicitly and would require a range of solutions for a range of compositions. The isotopic disequilibrium between the different parts of these serpentinized peridotites (Fig. 11) and the preferential addition of LREE in the alteration phases shown here, raise questions as to the validity of the assumptions used in those calculations, and to the calculated water / rock ratios. In light of these data, we explore the results of these W/R calculations on these peridotites, assuming either the bulk rock or parts of the bulk rock (effectively bulk peridotite minus clinopyroxene) reacted with seawater. Compared to other literature efforts, here we know explicitly the primary magmatic isotopic composition of each sample from the

clinopyroxene Sr and Nd isotopes, as well as the bulk rock Sr and Nd concentrations which to a first approximation we take to represent the protolith. In the VAN 7-78 samples ϵ_{Nd} varies less than half ϵ_{Nd} unit and do not provide enough resolution to use the ϵ_{Nd} as a tracer of W/R ratios for these samples. As the Nd isotopic composition of global seawater varies in the different ocean basins (e.g., Piepgras et al., 1979), we use seawater Nd isotope and concentration data from that available closest to the South West Indian ridge (Stichel et al., 2012).

From the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the bulk peridotites and using either open or closed system water / rock reactions equations (Delacour et al., 2008) we calculate a W/R ratio for the VAN 7-78 samples in the range of $\sim 0.6 - 40$. For the VAN 7-85 samples using the Nd-isotopes we calculate a range of $\sim 1070 - 8500$ (Table 6). Due to the low W/R determined in the VAN 7-78 samples and no variability in the Nd concentrations, and our primary focus being on potential LREE addition to the samples we will only focus on the VAN 7-85 samples in the following discussion.

As the relic clinopyroxene has retained its mantle value concentration and isotope composition, we can assume that only the Nd in bulk rock minus the Nd in the clinopyroxene exchanged with the seawater during serpentinization. We calculate the Nd concentration of the orthopyroxene + olivine fraction of the rock by subtracting the amount of Nd locked in the clinopyroxene, using the clinopyroxene modal abundance from the modeling above and its measured concentration (Table 3). We assume that the primary peridotite orthopyroxene + olivine fraction must have had the same Nd isotope composition as the clinopyroxene, as these rocks were until very recently under high temperature conditions in the upper mantle (1 to 2 My; Warren et al., 2009) and this is

not enough time for significant (within one $\epsilon_{\square\square}$ unit) change in Nd isotopes. We then calculate the Nd isotope composition of the “altered” orthopyroxene + olivine rock by subtracting the amount of radiogenic Nd locked in the clinopyroxene from the bulk rock Nd budget (Table 6). In every case, the new water / rock ratio (without the clinopyroxene) is only marginally higher in all samples except VAN 7-85-43 which doubled from ~8000 to ~17800 for a closed system (Table 6) and ~6500 to 9200 for open system. This is due to a large proportion of the bulk rock Nd residing in the clinopyroxene, which results in highly unradiogenic Nd in the orthopyroxene + olivine fraction and high W/R ratios.

Note that if an average depleted mantle Nd concentration is assumed (e.g., 0.7 ppm Salters and Stracke, 2004; 0.48 ppm, Workman and Hart, 2005) for the peridotite protoliths, the calculated W/R ratios would increase by at least ten-fold, to over 170,000. This is because these peridotites have far lower bulk rock Nd concentrations than depleted or primitive mantle (Table 2), requiring less reaction (by mass) with seawater to change their Nd isotope composition. This explains why our calculated W/ R ratios are at least an order of magnitude lower than those reported by Delacour et al. (2008) for serpentinites from the Atlantis Massif, despite those samples having similar Nd isotopes to the SWIR peridotites reported here. This demonstrates the need to use the actual peridotite concentrations to more accurately assess the W/R ratios from radiogenic isotopes.

An alternative method to estimate W/R is to assume that the proportion of seawater-derived Nd in the bulk rock (Section 5.2) originated by complete scavenging of Nd from the seawater / fluid to the rock during serpentinization. Qualitatively this is

consistent with the high reactivity of REE for mineral surfaces e.g., adsorption of REE on marine particulates (De Baar et al., 1985a; De Baar et al., 1985b; Elderfield et al., 1990; Erel and Morgan, 1991; Sholkovitz et al., 1994), aquifer sands (Duncan and Shaw, 2003; Tang and Johannesson, 2005), mineral surfaces (variety of surface types, Byrne and Kim, 1990; silica beads, Schijf and Marshall, 2011; clays, Coppin et al, 2002; Fe-hydroxides Quinn et al., 2006a; 2006b; 2007) and organic macromolecules (Sonke and Salters, 2006; Stern et al., 2007; Stern et al., 2014) as well as our own experiments on olivine reacting with seawater (Frisby et al., 2011; 2013). Assuming a closed system reaction, the relative mass of seawater required to react with the peridotite ranges from 1000-5400, lower but remarkably similar to the W/R ratios by Nd isotope exchange calculated above using the measured bulk rock concentrations. These calculations are again consistent with Nd addition rather than exchange during serpentinization. We emphasize that the sensitivity of the Nd-isotopes to infer water-rock ratios also depends on the Nd concentration and therefore fertility of the protolith. Depleted and non-refertilized peridotites with low Nd concentrations will be more sensitive to change in their LREE concentrations and Nd isotopes than fertile or metasomatized ones. In other words, it is more likely that low water rock ratios will be evidenced in depleted samples, while for fertile samples higher water rock ratios are needed to shift the Nd isotope enough to be resolved. Additional detailed analyses of this kind are needed to assess the effects of increasing degrees of serpentinization on the REE elements of peridotites of variable initial composition.

6.2 REE sink and impact on mantle reservoirs

It has been suggested that the bulk rock REE systematics of serpentinized peridotites are controlled by depletion and melt addition (Niu, 2004), or redistribution

and reequilibration during serpentinization (Allen and Seyfried, 2003; Deschamps et al., 2012; Deschamps et al., 2013; Lafay et al., 2013). Here, we further postulate that significant addition of LREE also occurs during serpentinization of peridotites. Such preferential addition of LREE will fractionate both the REE and HFSE/REE systematics in the serpentinized peridotites, leading to lower Sm/Nd (and possibly higher Lu/Hf ratios if HREE are also being significantly added) than unaltered peridotites. Subduction of serpentinized oceanic lithosphere is thought as a key mechanism of transferring water and fluid mobile elements (e.g. As, Sb, B, Li, Cs, Pb, U, Ba, Sr) into the mantle wedge beneath arc systems (Tatsumi et al., 1986; Kessel et al., 2005; Kessel et al., 2015; Cannat et al., 1995; Carlson, 2001; Mével, 2003; Scambelluri et al., 2004; Savov et al., 2007, Cannat et al., 2010; Deschamps et al., 2011). The limited available experimental data shows that during dehydration melting of peridotite (Tatsumi et al., 1986; Kessel et al., 2005; Spandler et al., 2014; Kessel et al., 2015), the LREE will preferentially partition to the fluid/melt over the HREE. The excess LREE in serpentinized peridotites shown here coupled with their preferential mobility could then result in a high LREE/HREE and possibly high REE/HFSE ratio flux from the serpentinized peridotite to the mantle wedge during dehydration melting, along with the fluid mobile elements.

Alternatively, if REE are retained within the serpentinized peridotite, past the subduction factory and into the upper mantle, the fractionated Sm/Nd and possibly Lu/Hf ratios will persist in the peridotite leading to decoupled Nd and Hf isotope systematics in the recycled altered lithosphere over time. Lower Sm/Nd ratios and possibly higher Lu/Hf ratios will result in relatively less radiogenic Nd isotopes for a given Hf isotopes, as frequently observed in oceanic peridotites (Bizimis et al., 2003; Bizimis et al., 2007;

Stracke et al., 2011). Detailed experimental data on the mobility of REE out of serpentinites during dehydration are critically needed to further test this hypothesis.

7.0 Conclusions

The combined in situ trace element determinations, and sequential leaching experiments in serpentinitized abyssal peridotites reveal that a seawater trace element signature is primarily confined within the secondary minerals of serpentine and magnetite. The Nd isotopic shifts between clinopyroxene, bulk rock and leachates, together with the high LREE/HFSE ratios and negative Ce-anomalies are all consistent with LREE addition to the peridotite during serpentinization, as opposed to exchange. An accurate assessment of the water / rock mass ratios during serpentinization requires knowledge of the primary (mantle) isotopic composition of the rock (usually through clinopyroxene analysis) and the trace element systematics of the rock. Modification of the LREE and LREE/HFSE ratios during serpentinization has implications for the trace element budget and possibly Nd and Hf isotope systematics of recycled lithosphere and as a function of the mobility of these elements during dehydration of the serpentinitized lithosphere within the subduction factory. Finally, based on the preferential addition of LREE compared to HFSE, we can surmise that HFSE are potentially a better recorder of primary magmatic processes in serpentinitized peridotites.

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Figure Captions

Figure 1: Typical and common morphological features in the analyzed samples observed by SEM: A) Magnetite veins (bright features) in VAN 7-78-41 with feathery structures within serpentine. Note the predominance of magnetite at the center of the veined serpentine. Qualitative SEM data shows decreasing Fe content near the magnetite vein, as described by Beard et al. (2009). B) Olivine replacement by serpentine in VAN 7-78-39 with vein and pseudomorphic texture. Different contrast areas are all variably altered olivine with often but not always slightly different Fe/Mg ratios. Note magnetite is never found in contact with preserved olivine. D) Replacement of opx exsolution lamellae in cpx by serpentine (VAN 7-85-42). Note cross-cutting fractures through the lamellae are also serpentinized. Opx is preserved in the exsolutions at the bottom right of the figure. E) Flow structure preserved in serpentine with cross-cutting serpentine vein with preserved cpx and opx relics. Note the jagged edges of orthopyroxene on the right (VAN 7-85-47). F) Detail of serpentine after olivine structure (VAN 7-85-47). Note the symmetric shading along the center of the veins where darker shades have lower Fe contents.

Figure 2: A) Primitive mantle normalized Rare Earth Element patterns, and B) extended trace element patterns of the bulk rock peridotites, determined by dissolution chemistry. VAN 7-78 samples are shown in dashed lines and VAN 7-85 samples in solid lines. Grey lines are serpentinized abyssal peridotites from Niu (2004), and Deschamps et al (2013).

1112 Figure 3: REE patterns for cpx (blue), opx (orange), all serpentine (grey), modeled
1113 primary OPX (orange dashed) and modeled primary olivine (green dashed) (see text for
1114 details). LREE enrichment is noted in the fresh cpx for samples VAN 7-78-36H and
1115 VAN 7-78-41. A negative Ce anomaly is observed in the serpentine of sample VAN 7-
1116 78-39 and all VAN 7-85 samples.

1117

1118 Figure 4: Extended trace element patterns for cpx (Blue), opx (orange), serpentine
1119 (grey), modeled primary opx (orange dashed) and modeled primary olivine (green
1120 dashed). General flatter pattern is noted in primary CPX for VAN 7-78-36H and VAN
1121 7-78-41. Serpentine phases have strong positive U, Pb and Sr anomalies, higher
1122 LREE/HREE, and often Ti depletions compared to modeled concentration patterns.

1123

1124 Figure 5: Primitive mantle-normalized plagioclase and magnetite concentration patterns.
1125 A) Plagioclase REE, B) Plagioclase extended trace element patterns, C) magnetite REE
1126 and, D) magnetite extended trace element patterns.

1127

1128 Figure 6: Bulk rock REE reconstructed concentrations (dotted lines) from laser ablation
1129 data compared to bulk rock patterns determined via traditional dissolution chemistry.
1130 Samples VAN 7-78 (dashed lines) fits well for HREE, but the reconstructed REE are
1131 typically lower than measured. Samples Van 7-85 (solid lines) measured and modeled
1132 patterns fit well. For further description see text.

1133

Figure 7: Primitive mantle-normalized bulk rock extended trace element reconstructed concentration patterns (dotted lines) from laser ablation data compared to bulk rock patterns determined via traditional dissolution chemistry. Sample VAN 7-78-39 has a poorer fit to measured concentrations than VAN 7-78-36H and VAN 7-78-41 and the VAN 7-85 samples (solid lines), for which the patterns match well. For further discussion see text.

Figure 8: Primitive mantle-normalized REE patterns for bulk rock (black line), H₂O-leachate (red line), NaOAc-leachate (green line), HH-leachate (purple line), 6N HCL-leachate (blues line), residual (leached) rock (orange line) and average seawater (grey dash-dot line; bottom right panel). Leachates mostly follow bulk rock patterns, but in the VAN 7-85 samples the NaOAc and HH leachates have flatter REE pattern than the bulk rock (see text for further discussion).

Figure 9: Primitive mantle-normalized extended trace element patterns for bulk rock, leachates and residual rock shown in figure 10. Note the characteristic depletions in Hf, Zr, Ti relative to the REE in the NaOAc and HH leachates, implying excess REE addition during alteration. Also note the decrease in the Sr enrichment with progressive leaching (see text for further discussion).

Figure 10: Comparison of extended trace element patterns between measured (dashed lines) and reconstructed bulk rock using the leachate data (dotted line).

Figure 11: $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd values for primary cpx (blue dot), bulk rock (orange triangle), leached rock (green square), NaOAc + HH leachate (red square), and 6N HCl leachate (red diamond) for each of the peridotites analyzed. Samples are compared to the MORB-OIB field and a rock-seawater interaction model using the equations given in Delacour et al. (2008). The model assumes isotopic equilibrium between seawater and bulk rock and no change in their respective concentrations (i.e., pure element and isotope exchange). Here we use the Nd –isotope compositions of cpx for these peridotites reported in Mallick et al. (2014) and the measured bulk rock Nd concentration as the rock end-member. This assumes no change in the Nd concentrations of the peridotites during exchange. The Nd concentration and isotopic composition for seawater near the Southwest Indian Ridge is taken from Stichel et al., 2012 (SW). Tick marks along the lines show water/ rock mass ratios. The primary cpx falls within the MORB-OIB field while bulk rock falls closer to seawater, having more radiogenic Sr and less radiogenic Nd than the cpx. The leached peridotites plot closer to their respective cpx. The combined NaOAc+HH leachates plot closer to seawater, while the 6N HCl leachate plots close to bulk rock for VAN 7-78 samples, and between bulk and leached rock for VAN 7-85 samples.

Figure 12: Peridotite protolith REE reconstructed composition (blue lines) using determined modal abundances from bulk rock reconstruction models, where serpentine = olivine (see table 2), and cpx partition coefficients compared to measured bulk rock. For details see text.

1180 Figure 13: Ce/Ce^* (Ce anomaly) vs. U/Th where all ratios are determined from
1181 concentrations and Ce/Ce^* is calculated as $Ce/((La+Pr)/2)$. Where with increasing U/Th
1182 there is an increase in seawater influence due to the addition of U and subsequently a
1183 decreasing Ce/Ce^* due to the addition of Pr and La to the peridotite.

1184

1185 Figure 14: Bulk Rock and leachate Ti vs. Nd (A) and Hf vs. Ti (B) where Hf for a given
1186 Ti has a tighter correlation in the bulk rock. NaOAc+HH leachates for a given Ti falls
1187 closer to the linear trend observed for Hf than that of Nd, which has a higher overall
1188 concentration.

1189

Figure 1

FIGURES

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Table 1: LA-ICP-MS Settings

RF Power (W)	1200
Ar Nebulizer flow (L/min)	0.6-0.8
Ar Auxiliary gas (L/min)	0.7
Ar cooling gas (L/min)	15
He Carrier Gas (L/min)	0.3-0.7
ThO ⁺ /Th ⁺ (%)	<2
Laser-repetition rate (Hz)	8
Spot size (μm)	110
Energy Density (J/cm ²)	Matrix -Dependent (4.5-11)

Table 2

Table 2: Average mineral phase major element concentrations from laser-ablation ICP-MS

Sample ID	Modal Reconstruction (%)	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO(t)	MnO	NiO	MgO	CaO	Na ₂ O	H ₂ O (Assumed)	Total	MgO/SiO ₂
		wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%		
VAN 7-78-36H	Clinopyroxene [@]	6	53.93	0.29	2.04	0.70	2.23	0.08	0.00	16.92	24.18	0.26	100.63	0.31
	St. Dev.													
	Orthopyroxene (n=1)	15	56.93		3.87	1.53	6.58	0.36	0.00	29.49	1.24		100.00	0.52
	St. Dev.		0.26		0.12	0.11	0.41	0.13	0.00	0.22	0.16			
	Serpentine (n=12)	75	42.51	0.02	0.57		3.81	0.06	0.26	39.73	0.03	13.00	100.38	0.94
	St. Dev.		0.92	0.08	0.51		1.18	0.05	0.05	0.89	0.02			
	Fe-Oxide [Ⓕ] (n=1)	2	20.89	0.03	1.20	1.77	60.93	0.08	0.13	14.94	0.02		100.00	
	St. Dev.													
	Plagioclase (n=2)	2	43.57	0.05	23.98		0.16	0.03	0.00	0.24	31.92	0.05	100.00	0.01
	St. Dev.		2.56	0.00	1.24		0.09	0.03	0.00	0.18	1.04	0.01		
	Reconstructed Bulk Rock		43.80	0.05	1.78	0.29	5.58	0.13	0.21	35.53	1.48	0.01	9.93	98.81 0.81
VAN 7-78-39	Clinopyroxene [@]		52.54	0.28	3.07	1.09	2.53	0.08		16.00	23.10	0.48		
	Clinopyroxene (n=4)	7	51.11	0.15	5.02		3.93	0.10	0.08	20.54	19.08		100.00	0.40
	St. Dev.		0.66	0.01	0.93		0.76	0.01	0.03	4.38	4.00			
	Orthopyroxene (n=4)	25	55.27	0.07	4.74		6.49	0.14	0.09	31.41	1.78		100.00	0.57
	St. Dev.		1.23	0.01	0.37		0.08	0.00	0.00	0.80	0.22			
	Serpentine (n=6)	65	42.87	0.01	0.39		7.54	0.08	0.33	37.59	0.04	13.00	100.38	0.89
	St. Dev.		1.21	0.02	0.14		1.41	0.03	0.04	1.09	0.01			
	Fe-Oxide (n=2)	1	16.99	0.00	0.15		68.18	0.58	0.13	13.93	0.03	0.00	100.00	
	St. Dev.		3.95	0.00	0.02		5.41	0.04	0.02	1.46	0.00	0.00		
	Plagioclase* (n=2)	1	43.57	0.05	23.98		0.16	0.03	0.00	0.24	31.92	0.05	100.00	0.01

	St. Dev.		2.56	0.00	1.24	0.00	0.09	0.03	0.00	0.18	1.04	0.01			
	Reconstructed Bulk Rock		45.65	0.04	1.94	0.00	7.62	0.10	0.24	33.95	2.20	0.00	8.51	100.25	0.74
VAN 7-78-41	Clinopyroxene [@]		52.87	0.22	4.22	1.08	2.62	0.13		15.45	23.09	0.33			
	Clinopyroxene (n=2)	1	49.40	0.19	2.53		2.84	0.10	0.04	17.06	27.67			99.84	0.35
	St. Dev.		0.05	0.03	0.50		0.03	0.01	0.00	0.59	0.00				
	Orthopyroxene (n=3)	19	54.69	0.08	2.20		6.81	0.16	0.08	31.03	1.50			96.56	0.57
	St. Dev.		2.82	0.00	0.59		0.64	0.02	0.01	2.24	0.52				
	Serpentine (n=6)	77	42.57	0.00	0.50		2.72	0.06	0.35	40.76	0.03		13.00	100.76	0.91
	St. Dev.		2.73	0.09	0.97		2.34	0.09	0.13	3.85	0.33				
	Fe-Oxide (n=1)	2	20.89	0.03	1.20	1.77	60.93	0.08	0.13	14.94	0.02			100.00	
	St. Dev.														
	Plagioclase (n=2)	1	40.00	0.00	27.48		0.78	0.13	0.01	2.70	28.89			100.00	0.07
	St. Dev.		1.03	0.00	4.10		0.55	0.10	0.01	0.62	4.36				
	Reconstructed Bulk Rock		43.72	0.07	1.99	0.63	6.04	0.13	0.19	35.91	0.98	0.02	10.39	100.06	0.82
VAN 7-85-42	Clinopyroxene [§] (n=5)	5	51.65	0.22	6.28	1.08	3.27	0.10		17.06	21.09	0.36		101.11	0.33
	St. Dev.		0.38	0.03	0.40	0.11	0.14	0.01		0.35	0.57	0.01			
	Orthopyroxene [§] (n=3)	25	55.08	0.08	5.20	0.72	6.23	0.12		31.50	2.03	0.03		100.98	0.57
	St. Dev.		0.18	0.00	0.10	0.01	0.09	0.02		0.33	0.27	0.01			
	Serpentine (n=7)	69	41.48	0.01	0.40		7.34	0.07	0.32	37.33	0.05		13.00	100.41	0.86
	St. Dev.		2.64	0.04	1.32		4.35	0.06	0.08	2.48	0.20				
	Fe-Oxide [#]	1	16.37	0.00	0.47		65.82	1.68	0.36	15.24	0.07			100.00	
	St. Dev.														
	Reconstructed Bulk Rock		43.69	0.05	2.13	0.16	8.62	0.12	0.20	33.82	1.48	0.02	10.23	100.53	0.77

VAN 7-85-43	Clinopyroxene [§] (n=4)	8	51.79	0.17	6.33	1.13	2.97	0.11		16.68	21.03	0.40		100.61	0.32
	St. Dev.														
	Orthopyroxene (n=1)	25	54.86		7.20	1.22	6.13	0.14	0.16	28.34	1.92			99.97	0.52
	Serpentine (n=11)	66	41.13	0.00	0.43		7.22	0.06	0.33	37.80	0.03		13.00	100.33	0.92
	St. Dev.		0.54	0.00	0.13	0.00	0.83	0.01	0.02	0.41	0.00				
	Fe-Oxide (n=1)	1	16.37	0.00	0.47		65.82	1.68	0.36	15.24	0.07			100.00	
	Reconstructed Bulk Rock		45.01	0.02	2.31	0.37	7.34	0.10	0.27	33.85	2.07	0.03	8.90	100.27	0.75
VAN 7-85-47	Clinopyroxene [§]		51.54	0.22	6.31	1.07	3.21	0.10		17.08	20.88	0.37			
	Clinopyroxene (n=6)	5	51.17	0.16	5.76		3.54	0.11	0.05	18.25	20.64			99.69	0.36
	St. Dev.		1.15	0.01	0.42		2.37	0.00	0.00	0.92	1.45				
	Orthopyroxene (n=1)	16	56.09	0.07	4.69		6.18	0.14	0.09	30.93	1.80			100.00	0.55
	Serpentine (n=6)	78	42.46	0.01	1.16		7.99	0.09	0.27	34.76	0.26		13.00	100.38	0.84
	St. Dev.		2.21	0.01	1.16		2.37	0.02	0.06	1.49	0.34				
	Fe-Oxide [#]	1	16.37	0.00	0.47		65.82	1.68	0.36	15.24	0.07			100.00	
	Reconstructed Bulk Rock		44.61	0.03	1.69	0.00	8.33	0.11	0.24	33.45	1.63	0.00	10.19	100.28	0.75

"n" equals the number of spots determined.

⌘ Assumed magnetite from VAN 7-78-41.

Assumed magnetite from VAN 7-85-43.

* Assumed plagioclase from VAN 7-78-36H.

@ Major element data from Mallick et al., (2014).

§ Major element data from Warren et al., (2009).

Table 3

Table 3: Average mineral phase trace element concentrations from laser-ablation ICP-MS

Sample ID		Ba	Th	U	La	Ce	Pb	Pr	Nd	Sr	Zr	Hf	Sm	Ti	Gd	Dy	Y	Er	Yb	Lu
		(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ug/g)	(ng/g)	(ng/g)	(ng/g)	(ug/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
VAN 7-78-36H	Bulk Rock	580.6	8.12	425.4	101.8	271.2	29.87	42.89	226.6	34.48	1823.6	59.65	95.60	320.5	169.4	248.6	1602	185.7	201.9	32.35
	Clinopyroxene [@]	0.00	7.27	52.89	310.0	1490	59.70	0.00	2200	1.780	14810	480	1020	2093	1940	3090	17180	1930	1710	220.0
	Orthopyroxene (n=2)	0.95	8.02	3.11	3.98	25.10	10.73	5.50	38.63	0.014	2805.5	79.63	22.54	869.6	73.38	230.9	1858	292.6	455.3	79.85
	St. Dev.	4.38	4.47	1.10	3.02	24.51	0.96	5.45	39.50	0.002	2445.9	59.40	17.82	29.09	62.60	137.1	960.3	134.8	136.2	19.55
	Serpentine (n=12)	241.2	3.42	878.7	27.17	64.84	32.63	12.01	68.94	1.491	625.13	16.60	29.24	119.5	51.80	84.44	580.0	73.93	98.85	18.31
	St. Dev.	207.9	1.39	426.9	13.00	52.09	12.76	6.34	41.38	0.370	469	17.69	18.22	63.70	32.6	48.9	285	37.0	32.2	5.3
	Fe-Oxide [Ⓐ] (n=2)	136.8	10.42	208.9	21.64	67.50	38.41	13.07	54.42	0.997	589.80	12.19	21.09	4349	20.70	33.46	162.7	22.13	22.73	5.85
	St. Dev.	544.7	4.82	173.0	9.78	3.78	230.7	7.13	2.39	0.136	44.90	1.65	2.68	0.05	2.78	7.98	94.26	8.07	4.71	1.78
	Plagioclase (n=2)	3423	1.53	13.48	1295	2290	387.1	231.99	785.4	73.79	0.44	2.12	100.5	323.2	79.60	32.98	158.4	12.54	7.31	2.51
	St. Dev.	1179	0.55	7.08	268.7	244.2	11.65	29.81	114.5	19.17	0.00	1.42	9.71	28.38	0.88	1.58	4.81	4.62	1.18	1.84
	Reconstructed Bulk Rock	184.7	4.02	659.9	40.13	143.6	26.61	30.50	191.2	1.239	1788.9	53.59	87.44	350.8	167.8	285.8	1757	216.7	246.5	39.21
VAN 7-78-39	Bulk Rock	407.0	7.27	52.89	51.53	110.4	59.70	16.83	77.49	2.500	729.78	29.73	46.02	262.9	98.96	225.7	1548	194.0	224.3	37.08
	Clinopyroxene (n=4)	64.46	2.88	54.40	4.98	11.35	15.77	14.68	247.1	0.365	495.27	117.9	389.2	945.0	1034	1838	10788	1299	1221	177.9
	St. Dev.	64.30	4.26	75.33	7.71	6.95	18.69	6.56	10.96	0.221	45.95	12.95	7.97	44.59	60.68	32.65	287.9	59.20	21.35	3.93
	Orthopyroxene (n=4)	20.47	0.61	15.84	5.40	3.25	28.19	0.80	9.23	0.148	115.68	23.47	20.37	440.7	68.53	223.9	1795	261.4	385.5	69.56
	St. Dev.	20.68	0.78	20.61	8.41	4.32	15.03	1.69	5.37	0.206	10.02	3.23	5.86	36.07	17.35	18.95	141.3	19.12	28.61	3.00
	Serpentine (n=6)	454.9	1.24	1401	2.79	2.14	59.17	1.38	6.99	2.183	31.19	2.65	9.64	48.89	31.66	63.80	491.5	63.67	81.87	15.96
	St. Dev.	109.6	0.99	1603	3.38	1.89	44.85	1.43	3.38	1.1	14	1.33	6.16	9.41	29.3	60.0	523	68.4	85.0	15.5
	Fe-Oxide (n=2)	1312	4.80	424.7	9.82	15.68	95.99	5.64	17.01	3.630	89.01	7.48	23.34	9.66	48.05	75.42	416.9	61.31	54.83	12.57
	St. Dev.	544.7	4.82	173.0	9.78	3.78	230.7	7.13	2.39	0.136	44.90	1.65	2.68	0.05	2.78	7.98	94.26	8.07	4.71	1.78
	Plagioclase* (n=2)	3423	1.53	13.48	1295	2290	387.2	231.99	785.4	73.79	0.44	2.12	100.5	323.2	79.60	32.98	158.4	12.54	7.31	2.51
	St. Dev.	1179	0.55	7.08	268.7	244.2	11.65	29.81	114.5	19.18	0.00	1.42	9.71	28.38	0.88	1.58	4.81	4.62	1.18	1.84
	Reconstructed Bulk Rock	366.2	1.38	929.9	7.42	7.42	48.43	2.76	26.75	2.085	87.19	16.54	40.85	212.7	115.5	235.4	1577	204.3	241.4	41.28
VAN 7-78-41	Bulk Rock	755.3	4.62	651.7	53.32	81.78	40.65	12.61	53.12	3.110	493.95	19.28	34.35	185.7	71.85	173.1	1271	150.1	169.9	29.79
	Clinopyroxene (n=2)	195.2	39.60	20.06	385.7	1214	18.75	213.17	1167	0.786	6825.3	274.3	764.5	1140	1664	2862	16529	1927	1736	239.0

	St. Dev.	87.26	1.32	0.73	36.40	8.38	0.83	29.45	239.2	0.026	2309.4	56.57	192.7	183.4	330.9	441.7	2737	292.5	282.3	15.61
	Orthopyroxene (n=3)	35.59	24.32	16.34	23.48	50.11	23.51	22.28	46.79	0.124	970.89	55.55	44.79	481.3	110.7	293.4	2395	359.4	542.5	104.9
	St. Dev.	5.82	13.10	9.66	13.05	30.55	12.91	9.25	25.80	0.041	368.69	24.60	19.33	25.30	43.71	61.10	252.0	46.25	50.01	15.15
	Serpentine (n=5)	359.9	7.58	160.7	56.12	59.08	30.33	20.80	53.33	1.205	147.19	9.42	21.19	27.10	34.87	51.93	322.3	48.09	64.84	15.68
	St. Dev.	23.30	3.07	120.4	13.50	38.87	12.69	4.81	18.99	0.2	112	8.69	12.08	14.04	29.4	44.8	278	36.1	30.1	7.9
	Fe-Oxide (n=1)	188.8	12.88	27.19	17.23	37.18	26.82	11.84	8.13	0.585	31.00	3.13	10.51	193.2	9.48	12.32	43.64	13.74	17.50	7.62
	Plagioclase (n=2)	4403	15.35	18.76	376.9	418.9	40.44	50.73	134.9	55.20	11.15	10.01	31.33	24.31	41.96	36.89	162.8	21.04	17.29	8.86
	St. Dev.	2427	18.14	17.02	81.28	96.09	47.53	12.55	32.57	30.01	9.37	5.81	23.98	8.39	36.91	3.23	22.16	1.61	12.47	0.39
	Reconstructed Bulk Rock	333.9	11.30	127.7	56.31	74.28	28.94	23.48	65.25	1.524	377.99	21.14	34.35	129.2	68.07	129.9	898.3	128.1	173.3	34.92
VAN 7-85-42	Bulk Rock	698.7	1.18	745.6	3.39	4.16	3.56	1.21	15.19	143.3	149.77	19.87	26.31	186.6	64.29	160.7	1240	144.1	167.9	29.40
	Clinopyroxene [§] (n=3)	7.63	0.03	6.65	0.20	5.11	13.59	8.85	201.1	0.173	410.01	87.65	344.5	962.8	877.2	1633	9416	1151	1090	156.7
	St. Dev.	6.17	0.00	10.65	0.00	0.16	7.34	0.70	4.07	0.081	14.53	3.56	14.17	23.31	46.49	42.29	269.5	10.96	36.50	4.15
	Orthopyroxene [§] (n=3)	3.46	0.04	0.91	0.30	0.25	8.18	0.08	3.90	0.023	90.80	21.14	13.22	434.8	56.27	181.2	1460	205.5	324.9	58.33
	St. Dev.	3.80	0.05	0.89	0.00	0.18	3.52	0.10	0.74	0.044	7.31	2.10	2.10	9.09	4.89	8.93	64.41	8.57	14.30	3.69
	Serpentine (n=7)	108.5	0.09	1079	0.14	0.28	14.41	0.24	1.90	3.1	30	3.93	5.36	42.82	16.8	38.0	303	36.6	54.4	10.5
	St. Dev.	74.15	0.08	993.9	0.08	0.21	6.31	0.22	2.66	1.9	25	5.90	6.82	55.30	19.1	39.6	275	32.6	48.2	10.2
	Fe-Oxide [#]	9186	2.45	495.1	363.7	352.8	421.7	111.18	429.0	14.89	157.19	1.77	133.3	5.93	166.6	216.9	908.2	141.6	130.6	21.97
	Reconstructed Bulk Rock	157.6	0.10	754.9	3.39	3.60	16.41	1.59	15.55	2.266	64.43	12.14	24.42	183.5	68.46	150.4	1025	132.1	171.3	29.40
VAN 7-85-43	Bulk Rock	374.5	0.48	948.5	17.37	3.51	64.31	3.98	32.73	3.561	149.44	18.41	35.60	179.5	93.57	192.9	1425	163.1	181.7	30.87
	Clinopyroxene [§] (n=4)	2.00	0.00	2.67	0.16	5.69	12.26	10.21	223.2	0.160	356.14	82.04	354.8	847.1	844.4	1551	8896	1083	1059	151.2
	St. Dev.	0.00	0.03	2.96	0.09	0.76	5.71	0.72	10.11	0.008	70.73	5.30	14.70	17.17	23.66	34.92	139.1	17.96	30.58	3.25
	Orthopyroxene (n=3)	12.90	0.02	37.37	1.41	0.65	13.26	0.66	8.31	0.087	100.87	18.71	16.81	383.3	69.13	192.5	1470	214.1	319.0	57.44
	St. Dev.	21.81	0.03	62.95	1.91	0.44	2.30	1.06	4.29	0.149	41.08	3.46	2.87	38.48	18.78	29.26	177.3	21.57	25.97	4.49
	Serpentine (n=11)	107.8	0.23	1094	7.68	0.99	33.96	2.57	11.78	1.895	105.17	3.11	6.76	15.63	17.36	33.57	240.5	30.37	42.15	7.70
	St. Dev.	65.11	0.43	132.9	6.61	2.35	37.04	1.72	7.24	0.4	98	4.03	2.66	17.47	5.8	10.3	67	7.4	12.8	1.9
	Fe-Oxide (n=1)	9186	2.45	495.1	363.7	352.8	421.7	111.18	429.0	14.89	157.19	1.77	133.3	5.93	166.6	216.9	908.2	141.6	130.6	21.97

	Reconstructed Bulk Rock	446.5	0.91	752.3	8.51	4.29	10.94	2.41	28.49	3.835	101.73	13.65	33.53	154.9	89.09	169.9	1189	138.1	158.4	25.67
VAN 7-85-47	Bulk Rock	431.9	1.13	786.8	7.28	4.62	6.53	2.39	25.67	4.039	137.67	16.82	34.95	170.6	79.75	192.9	1447	162.2	177.9	30.93
	Clinopyroxene (n=6)	16.76	2.36	7.93	3.25	9.70	17.74	15.25	273.4	0.263	455.52	112.9	436.2	942.9	1092	1920	11342	1345	1277	183.2
	St. Dev.	16.26	1.33	2.94	1.91	4.12	22.92	2.67	26.18	0.070	31.60	15.60	22.20	65.98	84.28	91.80	614.0	76.09	101.3	12.71
	Orthopyroxene (n=1)	15.80	0.87	7.64	1.36	1.17	6.94	0.82	9.21	0.141	102.05	24.59	16.97	413.1	77.10	202.9	1559	239.0	334.7	54.79
	Serpentine (n=6)	225.7	2.14	1668	1.88	2.22	14.70	1.87	4.99	7.687	48.48	8.61	4.82	88.86	16.66	41.61	323.8	40.09	71.25	13.55
	St. Dev.	82.59	1.31	623.0	1.70	1.29	7.86	1.57	1.25	6.2	21	5.82	2.61	99.68	8.4	24.3	189	23.1	43.9	8.8
	Fe-Oxide [#]	9186	2.45	495.1	363.7	352.8	421.7	111.18	429.0	14.89	157.19	1.77	133.3	5.93	166.6	216.9	908.2	141.6	130.6	21.97
	Reconstructed Bulk Rock	233.1	1.95	1312	3.96	4.48	16.00	3.06	22.60	6.145	79.51	16.72	30.79	185.4	85.17	169.5	1116	142.5	178.1	29.23

"n" equals the number of spots determined.

⌘ Assumed magnetite from VAN 7-78-41.

Assumed magnetite from VAN 7-85-43.

* Assumed plagioclase from VAN 7-78-36H.

@ Major element data from Mallick et al., (2014).

§ Major element data from Warren et al., (2009).

Table 4

Table 4: Peridotite leachates and residual rock trace element concentrations

Sample ID		Ba	Th	U	La	Ce	Pb	Pr	Nd	Sr	Zr	Hf	Sm	Ti	Gd	Dy	Y	Er	Yb	Lu
		(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)
VAN 7-78-36H	H ₂ O Leach	0.008	0.000	0.006	0.001	0.002	0.001	0.000	0.001	2.296	0.006	0.000	0.001	1.149	0.001	0.002	0.008	0.001	0.001	0.000
	NaOAc Leach	0.248	0.000	0.215	0.017	0.033	0.001	0.005	0.029	17.549	0.000	0.000	0.012	0.039	0.021	0.030	0.164	0.022	0.022	0.003
	HH Leach	0.141	0.001	0.104	0.011	0.026	0.011	0.004	0.018	2.506	0.002	0.000	0.007	0.171	0.012	0.019	0.100	0.014	0.018	0.003
	6N HCl Leach	0.102	0.003	0.075	0.032	0.084	0.006	0.013	0.066	0.757	0.098	0.002	0.027	49.363	0.050	0.074	0.406	0.055	0.061	0.010
	Residual Rock	0.090	0.003	0.028	0.030	0.090	0.015	0.015	0.082	0.365	1.369	0.043	0.036	172.11	0.064	0.098	0.613	0.070	0.073	0.012
VAN 7-78-39	H ₂ O Leach	0.010	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.160	0.002	0.000	0.000	0.635	0.000	0.001	0.005	0.001	0.001	0.000
	NaOAc Leach	0.357	0.000	0.231	0.008	0.007	0.002	0.002	0.008	0.775	0.000	0.000	0.004	0.042	0.008	0.015	0.094	0.012	0.013	0.002
	HH Leach	0.232	0.000	0.106	0.006	0.007	0.010	0.001	0.006	0.340	0.001	0.000	0.003	0.074	0.007	0.011	0.070	0.009	0.013	0.002
	6N HCl Leach	0.060	0.001	0.136	0.013	0.020	0.007	0.003	0.014	0.340	0.026	0.001	0.008	35.400	0.020	0.041	0.248	0.036	0.041	0.007
	Residual Rock	0.138	0.003	0.005	0.025	0.056	0.018	0.008	0.041	0.196	0.527	0.022	0.023	146.02	0.056	0.108	0.719	0.083	0.093	0.016
VAN 7-78-41	H ₂ O Leach	0.005	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.137	0.002	0.000	0.000	0.758	0.000	0.000	0.003	0.000	0.001	0.000
	NaOAc Leach	0.164	0.000	0.025	0.006	0.007	0.001	0.001	0.006	0.433	0.001	0.000	0.003	0.035	0.005	0.010	0.067	0.010	0.012	0.002
	HH Leach	0.071	0.001	0.009	0.005	0.006	0.007	0.001	0.004	0.216	0.000	0.000	0.002	0.155	0.003	0.006	0.035	0.005	0.008	0.001
	6N HCl Leach	0.106	0.002	0.015	0.023	0.044	0.005	0.005	0.023	0.567	0.035	0.001	0.012	41.137	0.029	0.055	0.332	0.046	0.053	0.010
	Residual Rock	0.160	0.003	0.083	0.020	0.032	0.042	0.004	0.021	0.317	0.419	0.016	0.013	96.597	0.031	0.066	0.440	0.054	0.069	0.012
VAN 7-85-42	H ₂ O Leach	0.005	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.246	0.001	0.000	0.000	0.313	0.000	0.000	0.002	0.000	0.000	0.000
	NaOAc Leach	0.398	0.000	0.417	0.001	0.000	0.000	0.000	0.002	70.086	0.001	0.000	0.003	0.067	0.006	0.014	0.093	0.013	0.014	0.003
	HH Leach	0.110	0.000	0.193	0.003	0.001	0.005	0.001	0.003	0.523	0.002	0.000	0.002	0.186	0.004	0.006	0.044	0.006	0.008	0.001
	6N HCl Leach	0.118	0.000	0.068	0.001	0.001	0.001	0.001	0.008	0.277	0.013	0.001	0.011	43.816	0.028	0.056	0.325	0.045	0.046	0.007
	Residual Rock	0.117	0.001	0.015	0.006	0.003	0.015	0.001	0.007	0.356	0.112	0.010	0.013	99.961	0.035	0.080	0.547	0.063	0.082	0.014
VAN 7-85-43	H ₂ O Leach	0.004	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.248	0.001	0.000	0.000	0.484	0.000	0.000	0.003	0.000	0.001	0.000
	NaOAc Leach	0.190	0.000	0.490	0.005	0.000	0.000	0.001	0.005	1.360	0.000	0.000	0.003	0.045	0.009	0.016	0.116	0.015	0.016	0.003
	HH Leach	0.110	0.000	0.221	0.006	0.001	0.007	0.001	0.006	0.411	0.002	0.000	0.004	0.172	0.009	0.017	0.102	0.014	0.019	0.003
	6N HCl Leach	0.058	0.000	0.102	0.002	0.001	0.003	0.001	0.008	0.173	0.007	0.001	0.010	48.134	0.028	0.055	0.328	0.044	0.047	0.008
	Residual Rock	0.083	0.000	0.036	0.005	0.002	0.010	0.001	0.009	0.090	0.076	0.009	0.013	83.144	0.038	0.075	0.519	0.061	0.070	0.013
VAN7-85-47	H ₂ O Leach	0.011	0.000	0.010	0.000	0.000	0.000	0.000	0.000	5.049	0.000	0.000	0.000	0.788	0.000	0.001	0.004	0.001	0.001	0.000
	NaOAc Leach	0.180	0.000	0.430	0.002	0.000	0.002	0.000	0.002	1.512	0.001	0.000	0.001	0.035	0.003	0.007	0.056	0.006	0.007	0.002
	HH Leach	0.148	0.000	0.186	0.001	0.001	0.004	0.000	0.001	11.216	0.002	0.000	0.002	0.155	0.005	0.011	0.074	0.012	0.016	0.003
	6N HCl Leach	0.063	0.000	0.042	0.000	0.001	0.002	0.000	0.003	0.665	0.007	0.001	0.005	37.985	0.012	0.028	0.171	0.025	0.028	0.005
	Residual Rock	0.056	0.001	0.033	0.005	0.002	0.011	0.001	0.012	0.122	0.079	0.011	0.019	146.02	0.047	0.092	0.592	0.073	0.078	0.014

Table 5: $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} Isotopes for Bulk Rock, primary CPX, Leachates and Residual rock.

		$^{87}\text{Sr}/^{86}\text{Sr}$	2σ	ϵ_{Nd}	2σ	% SW Nd contribution [@]
VAN 7-78-36H	Bulk Rock	0.708543	0.000005	7.26	0.10	
	NaOAc + HH Leach	0.709108	0.000004	7.78	0.06	
	6N HCl Leach	N.D.		5.17	1.84	3
	Residual rock	0.705788	0.000020	8.00	0.06	1
	CPX	0.702858	0.000019	7.92	0.37	14
VAN 7-78-39	Bulk Rock	0.707067	0.000007	6.85	0.08	0
	NaOAc + HH Leach	N.D.		3.15	0.23	
	6N HCl Leach	N.D.		5.05	0.08	4
	Residual rock	0.706889	0.000006	6.43	0.10	24
	CPX	0.702992	0.000007	7.67	0.18	14
VAN 7-78-41	Bulk Rock	0.708411	0.000007	5.46	0.08	6
	NaOAc + HH Leach	0.709039	0.000028	2.98	0.14	
	6N HCl Leach	N.D.		6.84	0.10	13
	Residual rock	0.706889	0.000006	5.56	0.10	26
	CPX	0.707895	0.000008	7.96	0.41	6
VAN 7-85-42	Bulk Rock	0.709175	0.000008	10.26	0.18	12
	NaOAc + HH Leach	0.709163	0.000003	6.42	0.25	
	6N HCl Leach	N.D.		11.17	0.24	12
	Residual rock	0.709463	0.000008	10.59	0.12	28
	CPX	0.702440	0.000017	13.28	0.27	9
VAN 7-85-43	Bulk Rock	0.709143	0.000008	5.70	0.27	11
	NaOAc + HH Leach	N.D.		-1.81	0.14	
	6N HCl Leach	N.D.		8.08	1.12	31
	Residual rock	0.709044	0.000010	9.54	1.35	61
	CPX	0.702902	0.000147	13.30	0.41	21
VAN 7-85-47	Bulk Rock	0.709199	0.000008	10.24	0.55	15
	NaOAc + HH Leach	0.709250	0.000009	-2.80	0.22	
	6N HCl Leach	N.D.		10.33	0.11	13
	Residual rock	0.709568	0.000007	11.12	0.14	65
	CPX	0.702308	0.000013	13.36	0.06	12

* From Table 1 Station 101 at 4400m depth in Stichel et al (2012).

@ Calculated from equation 3 using measured bulk rock, CPX and seawater ϵ_{Nd} .

Table 6

Table 6: Water/Rock ratio bulk rock and sans CPX models

	Sr Conc (ppm)	Nd Conc (ppm)	Primary Magmatic $^{87}\text{Sr}/^{86}\text{Sr}^{\S}$	Primary Magmatic $\epsilon_{\text{Nd}}^{\S}$	Bulk Rock $^{87}\text{Sr}/^{86}\text{Sr}$	Bulk Rock ϵ_{Nd}	Closed BR W/R $^{\sim}$	Open BR W/R $^{\sim}$	Closed BR W/R $^{\#}$	Open BR W/R $^{\#}$	Nd addition W/R $^{\text{c}}$
SWIR Seawater*	8	2.00x10 ⁻⁶			0.70916	-9.70					
Van 7-78-36H BR	34.47	0.23	0.702858	7.92	0.708543	7.26	39.72	10.02	-	-	-
Van 7-78-36H BR without CPX	34.26	0.17				7.04	41.02	10.14	-	-	
Van 7-78-39 BR	2.50	0.08	0.702992	7.67	0.707067	6.85	0.61	0.34	-	-	-
Van 7-78-39 BR without CPX	2.45	0.06				6.59	0.63	0.34	-	-	
Van 7-78-41 BR	3.11	0.05	0.702800	5.56	0.708411	5.46	2.91	0.83	-	-	-
Van 7-78-41 BR without CPX	3.11	0.05				5.41	2.92	0.83	-	-	
Van 7-85-42 BR	143.35	0.02	0.702440	13.28	0.709175	10.26	-	-	1150.27	1071.06	927.52
Van 7-85-42 BR without CPX	143.33	0.01				4.99	-	-	1562.87	1239.12	
Van 7-85-43 BR	3.56	0.03	0.702902	13.30	0.709143	5.70	-	-	8085.29	6570.33	5024.71
Van 7-85-43 BR without CPX	3.54	0.02				-2.72	-	-	17829.42	9263.89	
Van 7-85-47 BR	4.04	0.03	0.702308	13.36	0.709199	10.24	-	-	2229.37	2071.21	1790.26
Van 7-85-47 BR without CPX	4.01	0.01				6.88	-	-	2680.59	2262.90	

$\S$ Derived from primary clinopyroxene for each sample.

* From Table 1 Station 101 at 4400m depth in Stichel et al (2012).

$\sim$ W/R determining from Sr isotopes using equations used from Delacour et al (2008).

$\#$ W/R determining from Nd isotopes using equations used from Delacour et al (2008).

c Addition from the determined Nd difference between the measured bulk rock and reconstructed primary peridotite.