1 **Hf – Nd isotope decoupling in bulk abyssal peridotites due to serpentinization.**

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12 **Abstract**

13 Serpentinized abyssal peridotites are the product of the chemical interaction
14 between the Earth's oceans and the peridotitic upper mantle. This reaction is dominated
15 by the addition of water and fluid mobile elements to the peridotite, with implications on
16 the cycling of water and fluid mobile elements in subduction zones. Rare earth elements
17 (REE) were generally thought as immobile during serpentinization. However the
18 identification of Nd (and Sr) isotopic disequilibrium between fresh clinopyroxene and
19 their host bulk serpentinized peridotite suggest addition of Nd and other light REE to the
20 peridotite during serpentinization (Frisby et al., 2016). As with the REE, the high-field
21 strength elements (HFSE) have also been considered immobile and non reactive during
22 serpentinization. However, this has yet to be explicitly tested. Here we present a
23 modified dissolution and extraction method that improves on the yields of REE and
24 HFSE from highly depleted ultramafic rocks (peridotites) through the use of $B(OH)_3$
25 during digestion dry-down steps, Fe-precipitation for REE-HFSE sequestration, and
26 liquid-liquid exchange for Fe removal. Using this method we report on the Nd and Hf
27 isotope compositions of bulk rock serpentinized abyssal peridotites from the South-West
28 Indian Ridge (SWIR), Mid-Atlantic Ridge (MIR) and Mid-Caymen Rise (MCR) and on
29 samples where their clinopyroxene Hf-Nd isotopes were previously reported. The bulk
30 rock Hf isotopes are equal to clinopyroxene to within 1 ϵ_{Hf} , while Nd isotopes in the bulk
31 peridotite are up to 8 ϵ_{Nd} units less radiogenic than their clinopyroxene. Melt-rock
32 reaction between the depleted peridotite endmember and local enriched lavas cannot
33 generate the observed decoupling between Hf and Nd isotopes. Our data is instead
34 consistent with seawater – peridotite interaction as this results in significant shift in Nd

isotopes with little to no change in Hf isotopes until extremely high water / rock mass ratios of $>100,000$. Our data shows that Hf isotopes are not affected by serpentinization and that Hf isotopes in bulk peridotites better record the magmatic composition of peridotites than Nd or Sr. The largest Nd isotopic difference between clinopyroxene and bulk peridotite is observed in the most LREE-depleted samples, while refertilized samples show little change. Based on the bulk rock (serpentinized) and clinopyroxene (magmatic value) Nd isotope compositions we estimate that 1-34% of the bulk rock Nd budget is seawater derived, but only 1-6% of Sm and $<2\%$ of Lu and Hf in these samples. Therefore serpentinization will lower Sm/Nd relative to Lu/Hf ratio in a peridotite and this may lead to decoupling between Hf and Nd isotopes upon recycling and aging, assuming no additional fractionation of these elements during the subduction process. Alternatively, if Nd becomes fluid-mobile upon dehydration during subduction then the excess Nd in the serpentinized peridotites may become an additional reservoir for Nd in arc volcanism.

HIGHLIGHTS

Improved method for REE, HFSE extraction from depleted rocks

Hf isotopes are not affected by serpentinization

Hf concentrations are a reliable tracer of magmatic processes in peridotites

1.0 Introduction:

Serpentinization of mantle peridotite results in both mineralogical (e.g. formation of serpentine group minerals at the expense of primary mantle minerals; Bach et al., 2006; Jöns et al., 2010) and chemical changes, dominated by the addition of water (several wt%) and fluid mobile elements (e.g. B, Li, Cl, U, Sr, Cs, Rb: Paulick et al., 2006; Kodolányi et al., 2012; Deschamps et al., 2013 and references therein) to the protolith. In turn, rare earth element (REE) and high field strength element (HFSE: Nb, Ta, Hf, Zr, Ti) concentrations of mantle peridotite are thought to be relatively insensitive to serpentinization. In a comprehensive study of trace element systematics of bulk abyssal peridotites, Niu (2004) argued that the high degree of correlation between the concentrations of REE and the HFSE is evidence for magmatic (i.e., melting and/or melt rock reaction) control, and that serpentinization has a minor, if any, effect on bulk rock budget of these elements. In contrast, Paulick et al. (2006) attributed enrichment in the LREE concentrations of some highly serpentinized peridotites to hydrothermal alteration, consistent with experimental data that has shown increase in REE concentration in fluids during fluid-serpentinized peridotite reaction (Allen and Seyfried, 2005). More recently, Frisby et al. (2016) showed that bulk rock abyssal peridotites often have more unradiogenic ϵ_{Nd} values than their clinopyroxenes. Through detailed leaching experiments and in situ analyses the authors concluded that an unradiogenic Nd component is mostly hosted in the secondary minerals serpentine and magnetite, and is accompanied with seawater-like trace element systematics, particularly large Ce-negative anomalies and large U/Th ratios. Based on mass balance calculations Frisby et al. (2016) concluded that seawater-derived Nd has been added to the bulk peridotite during

77 serpentization, and in disequilibrium with the clinopyroxene, as the fresh clinopyroxene
78 still retains its high temperature (magmatic) Nd isotope composition and trace element
79 systematics. The addition, as opposed to exchange, of Nd to peridotite during
80 serpentization has implications on water / rock mass ratio calculations and possible
81 parent / daughter fractionation in the oceanic lithosphere beyond those imposed by
82 magmatic processes (Frisby et al., 2016).

83 Frequently observed in mantle peridotites is the decoupling of Hf from Nd
84 isotopes, often with relatively more radiogenic Hf for a given Nd (Salters and Zindler,
85 1995; Bizimis et al., 2004; Stracke et al., 2011). This has been explained by the relative
86 resistance of Hf over Nd, to metasomatic processes (Bizimis et al., 2004; Stracke et al.,
87 2011), which in turn is attributed to the greater compatibility of Hf than Nd in the upper
88 mantle mineralogy (e.g. Salters et al., 2002). As such, Hf isotopes may better preserve
89 information about the time-integrated parent-daughter fractionation of a peridotite than
90 Nd isotopes as shown, for example, in the Hawaiian lithosphere (Bizimis et al., 2004;
91 Bizimis et al., 2007) and the Gakkel ridge mantle (Stracke et al., 2011; Salters et al.,
92 2012). Yet, in light of the evidence for modification of Nd isotopes and REE in
93 peridotites by serpentization cited above, a first order question is whether the bulk
94 peridotite Hf – isotopes are also modified during serpentization. This question stems
95 from the observations and calculations of Stracke et al. (2011) who demonstrated that in a
96 typical upper mantle depleted peridotite a larger proportion of Hf over Nd is hosted in the
97 orthopyroxene and olivine part of the peridotite than clinopyroxene, due to the higher
98 partition coefficients of Hf over Nd for orthopyroxene and olivine (e.g. Salters et al.,
99 2002; McDade et al., 2003). If the non-clinopyroxene part of the peridotite is susceptible

to change in its Nd isotope composition (Frisby et al., 2016), then the effect of alteration may be even greater for Hf. The present study is designed to test this hypothesis.

This study is a continuation of the Frisby et al., (2016) study, and addresses the behavior of HFSE during serpentinization through a comparison of the coupled Hf-Nd isotope systematics of bulk rock serpentinized abyssal peridotites with those of their clinopyroxenes (Mallick et al., 2014; Mallick et al., 2015). We present the first (to our knowledge) Hf isotope data on bulk rock abyssal peridotites from the South West Indian Ridge, two peridotites from Mid-Cayman Rise and the Kane Fracture Zone, and the PCC-1 USGS rock reference material. By comparing the Nd and Hf isotopic composition of the bulk rock with that of the clinopyroxene (i.e. magmatic value) we demonstrate that, unlike Nd, bulk rock Hf isotopes are not affected by serpentinization as the bulk rock Hf isotopes are within error identical to that of their clinopyroxene. Our data demonstrates that bulk rock peridotite Hf isotopes and concentrations are a reliable tracer of high temperature mantle processes and not affected by serpentinization. In addition, we present an updated method for the preconcentration of Hf, Nd, and other HFSE and REE from large amounts (>1 gram) of incompatible trace element depleted ultramafic samples. This method overcomes previous yield problems when processing large amounts of sample and can be used for the Hf and Nd isotope characterization of increasingly more depleted peridotites, those with low or absent clinopyroxene, or orthopyroxene-rich fractions.

1.0. Sample description and previous work

Samples for this investigation are from the Southwest Indian Ridge (SWIR), Mid-Cayman Rise and the Kane Fracture Zone (MAR). These samples were analyzed for Nd

and Sr isotopes in their clinopyroxene by Warren et al. (2009); Mallick et al. (2014), and the SWIR samples for Hf isotopes in clinopyroxene in Mallick et al. (2015). Some of the SWIR samples reported here were subject to a detailed Sr, Nd isotope, laser-ablation and sequential leaching study (Frisby et al., 2016) to constrain the residence of REE in serpentinized peridotites. Data from that study is reported here as necessary for data completeness. Further details for locations, sample descriptions, and previous work are highlighted in following paragraphs.

1.1. Southwest Indian Ridge

Southwest Indian Ridge (SWIR) is an ultra-slow spreading ridge segment (full spreading rate 14-15 mm/yr) that extends ~7700 km from Bouvet Island in the west to the Rodrigues triple junction in the east. Two near-ridge hot spots (Bouvet and Marion islands) locally contribute along a large section of the ridge to the geochemical and physical features (transform faulting) of crustal formation along the ridge. The 9-25°E segment of the ridge is bounded by Du Toit Fracture zone in the east and by Shaka Fracture Zone in the west. The ridge spreading direction between 9-16°E segment is at ~57° angle with the ridge axis and is referred to as the oblique segment, with decreased melt production rate per unit of ridge length (Dick et al., 2003; Standish et al., 2008). This part of the ridge consists of linked magmatic and amagmatic segments; mantle peridotites are dominantly dredged from the amagmatic segment. The eastern part of the ridge segment (16-25°E) spreads sub-perpendicular to the ridge axis and referred to as orthogonal segment and consists of short en echelon second-order magmatic ridges that lie sub-perpendicular to spreading direction separated by non-transform offsets (Dick et al., 2003; Standish et al., 2008). The samples analyzed in this study are dredged from

three on-ridge locations: 9.98°E (inside corner high), 15.23°E (axial trough), 16.68°E (fault scarp). Further details on the geodynamic description of this ridge can be found in le Roex et al. (1989); Mahoney et al. (1989); le Roex et al. (1992); Dick et al. (2003); Meyzen et al. (2005); Montési and Behn (2007); Standish et al. (2008); Zhou and Dick (2013).

Dredge VAN7-78 at 16.64°E recovered plagioclase-bearing peridotites between two magmatic segments on a small nontransform offset. These samples have plagioclase present, 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%) and have been interpreted as re-fertilized peridotites (Mallick et al., 2014; Mallick et al., 2015). We analyzed one harzburgite and three lherzolites from this dredge. Clinopyroxene separates were analyzed for trace elements concentrations and Sr, Nd isotopes by Mallick et al. (2014).

Dredge VAN7-85 at 15.23°E are spinel peridotites that were recovered from a ~70 km long oblique amagmatic segment. Clinopyroxenes from these 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%) suggesting minimal interactions with infiltrating melt and are interpreted as nearly pure melt residues of ~8% melt depletion from a DMM source (Mallick et al., 2014). We analyzed five lherzolites from this dredge. Clinopyroxene separates were analyzed for trace elements concentrations and Sr, Nd, Hf isotopes by Mallick et al. (2014); Mallick et al. (2015).

Dredge VAN7-96 is located at 9.98°E on the eastern inside-corner high of the 195 km offset Shaka Fracture Zone. This dredge typically recovered lherzolites with

atypically abundant websterite veins. These peridotites are chemically similar to those recovered from dredge VAN7-78 with cpx having 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 spinel with high TiO₂ (up to 0.46 wt%) and have been interpreted as re-fertilized peridotites (Warren et al., 2009; Mallick et al., 2014; Mallick et al., 2015). We analyzed one lherzolite from this dredge. Clinopyroxene separates were analyzed for trace elements concentrations and Sr, Nd, Hf isotopes by Mallick et al. (2014); Mallick et al. (2015)

1.2. Mid-Cayman Rise

The Mid-Cayman Rise (MCR) is an ~110 km long ultraslow-spreading center (20 mm/yr full spreading rate) with a valley floor 1-2 km deeper than most spreading centers bounded by steep fault scarps exposing a variety of rocks including gabbro and peridotite (Macdonald and Holcombe, 1978; Thompson et al., 1980; White et al., 2001). We analyzed one plagioclase harzburgite (OCE-23-14-2) from the eastern wall of the rift valley floor located near the segment center (Dick et al., 1984). Based on petrography and somewhat elevated LREE/HREE this sample was interpreted as a melt impregnated peridotite (Mallick et al., 2014).

1.3. Mid-Atlantic Ridge

We analyzed one spinel harzburgite (AII-60-9-74) from the middle of the ~100 km long 22°S Fracture Zone from the Mid-Atlantic Ridge. Clinopyroxene from this sample show a LREE depleted pattern with overall lower abundance of MREE and HREE compared to SWIR and MCR low TiO₂ in spinel (0.06 wt.%; Mallick et al., 2014).

2.0 Analytical methods

All chemical separations and mass spectrometry were performed at the Center for Elemental Mass Spectrometry, Department of Earth and Ocean Sciences, University of South Carolina. All chemical separations took place in a metal-free HEPA filtered air clean lab. All digestions and dry downs were performed in custom-made Teflon covered hotplates with double-HEPA filtered forced air.

2.1 Reagents and Materials

HCl, HF, HNO₃ acids were purified in-house with custom made sub-boiling PFA stills (HF and HNO₃) and a quartz double-still (HCl) from reagent grade acids. Dilutions were performed using 18 MΩ purified H₂O from a Millipore Super-Q system. Diethyl ether (ACS grade) and Optima® grade NH₄OH were obtained from Fisher Scientific. Boric acid (Puratronic® 99.9995%), ascorbic acid (ACS grade 99%+), and citric acid (99.5%+) were obtained as powders from Alfa Aesar and were dissolved with 18 MΩ water in precleaned Teflon bottles.

Sample digestions were performed in 60 ml PFA jars. These jars and all other PFA vials were thoroughly cleaned using a multi-step procedure: fluxing closed with a mixture of 1:1 50% HCl (v/v) : 50% HNO₃ (v/v) at ~100°C for ~12-24 hours, followed by a 3:1 concentrated HCl:HNO₃ bath (24 h) and then in hot 50% HNO₃ v/v bath (24 hours minimum), rinsing several times with 18 MΩ water between each step. Before use, the jars were fluxed closed with a sub-boiled distilled 3:1 HF: HNO₃ mixture overnight, identical to that used for sample dissolution. This last step was found to be critical for reproducible low Hf blanks. Columns used for the chemical separation were custom-

made from PFA parts or shrinkable teflon with porous polyethylene frits. All centrifuge tubes, pipette tips and LDPE bottles were cleaned by soaking in a 50% HNO₃ v/v bath at room temperature overnight and thoroughly rinsing with the 18 MΩ water. pH was determined with a ROSS micropH electrode, calibrated daily with stock 4, 7 and 10 pH solutions.

2.2 Previous methods, motivation, and method overview

There are numerous published protocols for Hf and Nd separation. The digestion methods are based either on hydrofluoric acid or flux fusion (Patchett and Tatsumoto, 1980; Salters, 1994; Blichert-Toft et al., 1997; Münker et al., 2001; Bizzarro et al., 2003; Connelly et al., 2006; Pourmand and Dauphas, 2010; Cheng et al., 2014). The flux fusion technique allows for rapid and complete sample dissolution. However, the flux fusion blanks are highly dependent on obtaining low-blank fluxing agents that are not always available or are complicated to produce (Pourmand and Dauphas, 2010). To our knowledge this technique has not been demonstrated for large (>1 gr) samples.

For the HF-assisted digestions (e.g. HF:HNO₃, HF:HClO₄ or similar mixtures) very clean acids can be obtained by repeated distillation, which allows better control of the blank, and this is the method we used here. In HF-assisted digestions the resulting insoluble Ca-Mg-fluoride digest is typically either leached with repeated amounts of HF to complex and preconcentrate Hf in the supernate solution (Salters, 1994; Blichert-Toft et al. 1997), or the fluorides are repeatedly attacked with combinations of HCl, HNO₃ or HClO₄ to dissolve the fluoride digest and complex Hf with chlorides (Scherer et al., 1997; Münker et al., 2001). However, Hf yields are increasingly low for samples with high Ca and Mg concentrations or where large amounts of sample are needed, due to the

apparent scavenging of Hf from the precipitating insoluble Ca, Mg fluorides (Salters, 1994; Blichert-Toft, 2001; Bizimis et al., 2003). As typical upper mantle peridotites have MgO > 38 %wt (Niu, 2004; Canil et al., 2006) this makes them highly prone to formation of significant amounts of insoluble fluorides. Our preliminary digestion tests on >500mg peridotite and orthopyroxene concentrates with the often used HF:HNO₃ (3:1) acid mixture resulted in very low and inconsistent Hf and Nd (as well as other REE) yields. Repeated dry downs with HCl or HNO₃ mixtures improve the yields, but not consistently. Ironically, the poor yields affect proportionally more the most Hf and Nd depleted samples, exactly where yields need to be highest for successful analyses. Below we present a modification of the HF:HNO₃ acid digestion method that improves Hf, Nd yields from bulk peridotite digestion. Briefly, it includes the use of orthoboric acid to minimize formation of the insoluble fluorides (Koornneef et al., 2010), Fe- Al hydroxide precipitation to scavenge REE and HFSE from solution (Sharma and Wasserburg, 1996; Stichel et al., 2012), and HCl-diethyl ether liquid – liquid exchange to remove Fe from solution (Stichel et al., 2012). The method was first optimized for Hf and Nd, and subsequently applied to a combined Pb, Hf, Sr, Nd separation method as Pb and Sr are also preconcentrated with this technique. A schematic flow chart of the separation is shown in figure 1 and details are presented below.

2.2.1 Sample dissolution

Rock powders were prepared in an agate ball mill or by hand in a Al-ceramic mortar and pestle, from previously cut rock billets that were polished with Al-oxide abrasive papers to remove possible surface contamination and saw marks. 1-2gr of peridotite powder was initially reacted with 15 ml 6N HCl overnight at ~100°C. The

supernate was removed with a pipette and kept in a separate PFA beaker. Using Mg and Ni concentrations in the supernate we estimate that 20-30% of the bulk rock was dissolved during this HCl step, dominantly olivine or serpentine after olivine. This process is advantageous because it effectively dissolves a large part of sample in a fluoride – free form and removes a significant part of Mg, as well it seemed to enhance subsequent dissolution of the remaining material. The residue was then digested with 10ml HF:HNO₃ (3:1), capped, at 100°C for 3-4 days. The samples are then dried slowly at 80°C as this slow dry-down seemed to minimize the formation of insoluble fluorides. Once dry, the previously removed part of the digest in 6N HCl was added back to the primary digestion beaker together with 8ml 0.9M H₃BO₃ in 10N HCl. The jar was then closed, heated at 80°C for 3h, opened and dried down at 80°C. Boron strongly complexes F⁻ and volatilizes, thereby preventing the formation of insoluble fluorides. Once dry, 10ml of 7N HNO₃ was added to the jar, closed, and returned to the hotplate for about an hour and then dried at 80°C until incipient dryness.

2.2.2 Al, Fe-precipitation for REE, HFSE preconcentration

Iron and Al have extremely low solubilities around neutral pH, while Mg and Ca remain soluble. Rare earth elements (REE) and high field strength elements (HFSE) as well as other elements are highly reactive and co-precipitate with Fe and Al-hydroxides (Gammons et al., 2005; Quinn et al., 2006; Quinn et al., 2007). We use this principle to quantitatively remove REE and HFSE on Fe and Al-hydroxides that precipitate from the bulk rock solution while leaving the bulk of Mg, Ca, and Ni in solution (Sharma and Wasserburg, 1996; Stichel et al., 2012).

281 The digested rock is redissolved in 100ml of 0.5N HNO₃ (we did not further
282 investigate the effects of different dilution factors on the precipitation). Ammonia
283 hydroxide (NH₄OH; pH~13) was added to the bulk rock solution in a stepwise fashion
284 until a pH of ~7-7.8 (roughly ~2 ml of NH₄OH). An initial Al-, Fe-rich precipitant forms
285 at pH~2-3, depending on the concentration of these elements in solution. After this point,
286 pH changes rapidly, and care should be taken not to overshoot the pH to >8.5 or Mg
287 begins to precipitate (in that case, few drops of HNO₃ can be added to reduce the pH,
288 redissolve Mg and continue with the addition of NH₄OH to pH~7).

289 Repeated tests with different peridotite samples and multi element solutions
290 showed that at pH ~ 4 nearly 100% of Al and ~40-60% of Fe are removed from the bulk
291 rock solution as orange-brown precipitates. At this pH, the REE are also quantitatively
292 (>98%) removed with the Al -Fe precipitant, but curiously only 10-15% of Hf and Zr.
293 The remaining Hf and Zr are removed when the remaining Fe fraction precipitates around
294 pH=7. The different reactivity of Hf, Zr from REE does not appear to be related to
295 selective complexation of these elements with residual fluoride ligands, as tests with F-
296 free elemental solutions showed the same behavior. The different behavior of REE vs.
297 HFSE is likely related to the relative speciation of these elements in the 0.5N HNO₃
298 solution as a function of pH, but the detailed speciation analyses or the mechanism of
299 adsorption on the Al, Fe precipitant were not further explored. Lead removal from
300 solution closely follows that of Fe. In contrast, Mg, Ca, Mn, Co, Ni, Rb quantitatively
301 and ~50% of Sr remain in the supernate at pH ~ 7-7.5.

302 If only REE are of interest, pH ~ 4 is adequate to quantitatively scavenge REE on
303 Al-Fe hydroxides, but to quantitatively scavenge Hf, a pH of 7 must be reached, at least

in rock solutions with high Al and Fe contents. It is also possible to separate both a low pH (~4), Nd (REE)-rich precipitant and a higher pH (~7) a Hf, Zr-rich precipitant, but with lower Hf and Zr yields (70-80%), which may be advantageous in cases where enough Hf for an isotope analyses can be collected thereby simplifying the subsequent chemistry with separate Nd and Hf – rich aliquots.

Once pH = 7-7.5 was achieved, the solution was centrifuged to isolate the Al-Fe hydroxides from the supernate. The Al-Fe oxides are rinsed with 18MΩ water buffered with NH₃OH at pH~7 to remove residual Mg, Ca, Ni that were accumulated with the Al-Fe residue, and centrifuged again. At this point, the Fe-Al precipitant effectively contains only ~10 wt% of the initial digested major cation load with ~ 100% recovery of REE and HFSE, i.e. a reduction of sample size by 90% without column chemistry.

2.2.3 Fe removal by solvent extraction

Iron can be isolated from Hf and the REE using cation resin (Cheng et al., 2014). Our tests however showed that the relatively large quantities of Fe recovered from the precipitation after dissolving 1 -2 gr peridotite or orthopyroxene (in the range of 80-160 mg Fe) make subsequent chromatographic separations unpredictable. This was both due to the formation of gel-like substances on cation resin columns in 2.5 N HCl, or the need to add large amounts of ascorbic acid to reduce all Fe⁺³ to Fe²⁺ as the former outcompetes Hf and REE in the Ln resin (Pin and Zalduegui, 1997; Münker et al., 2001). We therefore removed Fe from the matrix by solvent extraction in di-ethyl ether (Diamond and Tuck, 1960; Stichel et al., 2012). In an HCl media and at less than 8N HCl, Fe (as well as Tl, Au, Sn and Mo in our experiments) is extracted to the diethyl ether while

REE, HFSE and other metals remain quantitatively in the acid. The Al-Fe precipitant is dissolved in 10ml 6N HCl and 10ml of purified diethyl ether is added to the sample using a separatory funnel (diethyl ether was previously cleaned by exchanging it with 6N HCl and then with 0.25 N HCl). The rock acid – ether solution is mixed gently by pumping the mixed solution with a pipette. After the solution settles the ether is removed from the top of the acid – ether mixture with a pipette. Our tests showed that >90% of the Fe is removed from the acid to the ether in the first exchange. We typically exchanged the ether twice. The remaining 6 N HCl solution now contains ~100% of the bulk rock REE, HFSE and Al budgets but effectively < 5% of the original cation load, as the major cations Mg, Ca, Fe, Ni, Si have been removed. From this point on, the sample can be processed with any different number of published separation protocols.

2.3 Chromatographic column separations

Following ether exchange the solution is dried down with concentrated HBr to complex Pb, and processed in Teflon micro-columns (~100ul) filled with anion resin using HBr and HNO₃ acids (Manhès et al., 1984; Lugmair and Galer, 1992; Abouchami et al., 1999). The bulk of the sample containing Hf, Nd and Sr is eluted from the column and the Pb cut is processed once more for purification. Note that this step is used only when a Pb cut is needed, otherwise the separation can begin in the next step.

The Hf, Nd, Sr cut from the Pb columns is loaded on PFA columns loaded with 4 ml cation resin in ~0.5-1 ml 2.5N HCl /0.1 N HF acid. Hafnium, Zr, Ti and most of the Al is eluted right away in 5 ml 2.5N HCl as the presence of F⁻ prevents HFSE from complexing with the cation resin (Salters, 1994). The remaining alkali metals are eluted with another 15 ml 2.5N HCl, and a Sr-rich cut is collected in 8 ml 2.5 N HCl. The

LREE-rich cut is collected next in 10 ml 6N HCl. The advantage of this separation is that it creates individual Hf, Sr, REE rich cuts that can be subsequently purified, while it further enhances the separation Hf from Yb and Lu, which cause isobaric interferences on ^{176}Hf .

The Sr cut is further purified with the Sr-spec resin (Eichrom) in 125ul Teflon micro-columns, by loading in 3.5 N HNO_3 , eluting the impurities in 2 ml 3.5N HNO_3 , and collecting the purified Sr in 1.5 ml 0.001N HNO_3 . Neodymium is purified using the Ln Resin (Eichrom; Pin and Zalduegui, 1997) in ~100ul micro-columns, using 0.2N HCl to remove the bulk of Ba, La, Ce, Pr and collect in ~0.5 ml 0.25N HCl. If needed, Sm is subsequently mobilized in 0.5 ml of 0.6 N HCl.

Hafnium is purified following the protocol of Münker et al., (2001), including removal of the bulk of Zr using 6N HCl / 0.06N HF, prior to collecting Hf in 6N HCL/0.2N HF. Our tests showed that for small amounts of Hf (5ng or less), the purity of the Hf cut is important in getting precise and accurate $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratios by monitoring the stable ratios $^{178}\text{Hf}/^{177}\text{Hf}$ and $^{174}\text{Hf}/^{177}\text{Hf}$ ratios and ensuring that they are within the values of the standard.

Digestion, ether exchange and column blanks for Hf were ~ 50 pg, less than 10 pg for Nd and 20-56 pg for Pb. The Nd sample-to-blank ratio is typically over 1000, and over 150 for Hf, for the analyzed samples here. We could not determine the Fe precipitation part of the blank, as there was no Fe to precipitate.

2.4 Mass spectrometry

All elemental concentrations were determined on an ELEMENT 2 HR-ICPMS following established protocols in our lab (Sen et al., 2011; Frisby et al., 2016). All isotope ratios were determined on a THERMO NEPTUNE MC-ICPMS, equipped with the PLUS upgrade, a high sensitivity option that uses a larger interface pump and a JET-sampler and X-skimmer cone configuration. Sample introduction was with an APEX-Q introduction system and a 100 μ l/minute PFA nebulizer (~120-150 μ l/minute actual uptake). Amplifier gain calibration was performed daily. Baseline was determined by beam deflection. Typical runs consisted of 35-40 8.3 second integrations. During the course of this study the JMC-475 Hf standard was determined at $^{176}\text{Hf}/^{177}\text{Hf} = 0.282141 \pm 0.000012$ for ~30ng runs (2 standard deviations: 2stdev, n= 23), using $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ for fractionation correction. The reproducibility for 3ng runs was worse but the ratio was within error the same (0.282131 ± 0.000034 , 2stdev, n=5). Typical sensitivity was ~1000V/ppm for Hf. All data is reported relative to the JMC-475 value of $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$.

The LaJolla Nd standard was determined at $^{143}\text{Nd}/^{144}\text{Nd} = 0.511856 \pm 0.000007$, (2stdev, n=19, ~25ng runs), using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ for fractionation correction, and ~1500V/ppm typical sensitivity. The NBS 987 Sr standard was determined at 0.710307 ± 0.000007 , (2stdev, n=11, ~20ng runs with 1500V/ppm typical signal) and the values are reported relative to 0.710250. Krypton interference on ^{86}Sr was corrected online by the instrument software and no attempt was made to further correct it (Jackson and Hart, 2006).

3.0. Results

3.1 PCC-1 peridotite

Table 1 reports the Hf, Nd isotope compositions of the USGS reference material PCC-1, a variably serpentinized depleted peridotite with low Hf and Nd concentrations of ~ 5 ppb and 25 ppb, respectively; (Eggins et al., 1997; Willbold and Jochum, 2005) and BIR-1, a relatively depleted Icelandic tholeiite with 0.56ppm Hf and 2.4 ppm Nd (Eggins et al., 1997; Willbold and Jochum, 2005). The three PCC-1 determinations agree within error with average $^{176}\text{Hf}/^{177}\text{Hf} = 0.283389 \pm 0.000017$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512234 \pm 0.000017$. To our knowledge these are the first reported Hf isotope ratios for PCC-1 while the Nd isotope ratios agree with the previously published values obtained by TIMS corrected to the same La Jolla value ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512229$; Chu et al., 2009; 0.512237 ± 0.000018 ; Shibata and Yoshikawa, 2004). Assuming an age of 160Ma for the Cedars Ultramafic unit where PCC-1 was sourced from (Blake et al., 2012), similar to other coastal range ophiolites (Shervais et al., 2005; Blake et al., 2012), and parent - daughter ratios calculated from the Sm, Nd, Lu, Hf (Willbold and Jochum, 2005), leads to initial isotope compositions of $\epsilon_{\text{Nd}160\text{Ma}} = -7.5$ and $\epsilon_{\text{Hf}160\text{Ma}} = +10$. The initial Hf isotope composition of PCC-1 is consistent with derivation from the depleted upper mantle and within the calculated age of a Pacific MORB mantle source at ~160 Ma (Choi et al., 2008). However, initial Nd isotope composition is too unradiogenic for a given Hf isotope composition, so that PCC-1 falls above the terrestrial array in Hf-Nd space and above the seawater array as defined by Albarède et al. (1998) (Fig. 2). Clinopyroxenes from other Coastal range peridotites have relatively radiogenic Nd and Hf isotopes that plot close to the terrestrial array (Choi et al., 2008). This decoupling of Hf from Nd

isotopes between bulk rock PCC-1 and clinopyroxenes from similar peridotites in the Coastal range ophiolite may result from preferential addition of Nd from crustal fluids, or from seawater during serpentinization (Frisby et al., 2016). Strontium isotopes for PCC-1 are highly radiogenic at $^{87}\text{Sr}/^{86}\text{Sr} = 0.711067 \pm 0.000005$ ($^{87}\text{Sr}/^{86}\text{Sr}_{160\text{Ma}} = 0.70992$, calculated using PCC-1 Rb, Sr concentrations from Eggins et al., 1997), higher than the seawater Sr isotope composition in late Jurassic of $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.707$, which implies instead interaction with crustal fluids. We are unaware of other Sr isotope determinations of PCC-1. The BIR-1 Hf and Nd isotope compositions acquired with this method fall within previously published values (Bizzarro et al., 2003; Le Fevre and Pin, 2005; Chu et al., 2009; Hoffmann et al., 2010; Fourny et al., 2016).

3.2 Abyssal Peridotites

Some of the abyssal peridotite samples were originally processed with the conventional HF:HNO₃ digestion method followed by repeated HCl dry downs. Some of those analyses yielded successful Hf-Nd isotope determinations and that data is reported along with the data generated with our new method. In every case, the new method resulted in higher yields and higher signal intensities during the isotope ratio analyses than the conventional method. Some of the samples were first leached with 6N HCl for two hours to remove easily leached seawater alteration, and the residues were also analyzed for Hf-Nd isotopes to track the affect of seawater alteration on the Hf-Nd systematics. Table 1 reports all available Hf, Nd isotope data for these samples, including previously published clinopyroxene Hf, Nd data (for Sr and Nd: from Mallick et al, 2014; for Hf: from Mallick et al, 2015) and bulk rock Nd, Sr data (from Frisby et al, 2016) for completeness and meaningful comparison.

3.2.1 Peridotite trace element systematics

The trace element systematics of the analyzed abyssal peridotites are compared with the abyssal peridotite compilation of Niu (2004) and depleted MORB source mantle (DMM: Salters and Stracke, 2004; Workman and Hart, 2005). The samples overlap with the global abyssal peridotite compilation with positive Sr, Pb and U spikes and lower HREE than DMM (Fig. 3). Samples that are strongly LREE depleted (all VAN7-85 peridotites and OCE23-14-2) also show a strong negative Ce anomaly with enrichments in La and Pr over Ce. The bulk rock Hf concentrations range from 0.017 to 0.1 ppm. The peridotites with the highest Hf concentrations (VAN7-96-29, VAN7-76-36H) have flatter bulk rock REE systematics and have been interpreted previously as melt impregnated (Mallick et al. 2014), while the samples with lowest Hf concentrations are the LREE depleted.

3.2.2 Hf-Nd isotope systematics

We see no significant difference in the Hf-Nd isotope systematics between the conventional bulk rock digestion (whenever that was possible) and our new method (Table 1) with the Hf and Nd isotope data being identical within error. For the rest of the discussion we use the bulk rock Hf, Nd isotope data from the new digestion method, as those signals during mass spectrometry were always higher and presumably more precise.

The bulk rock ϵ_{Hf} isotopes are within 1-1.5 ϵ_{Hf} units identical to that of their clinopyroxene (Table 1), while the bulk rock ϵ_{Nd} values are often lower than the clinopyroxene by up to 8 ϵ_{Nd} units. As a result, on a ϵ_{Hf} vs. ϵ_{Nd} plot (Fig. 2) some of the analyzed bulk abyssal peridotite compositions show a characteristic near-horizontal offset

towards lower $^{143}\text{Nd}/^{144}\text{Nd}$ relative to their clinopyroxene. Importantly, the largest shift in Nd isotopes is seen in the rocks with the most radiogenic Hf isotopes (dredge VAN7-85- samples), which are also the most trace element depleted (Fig. 3). The leached residues of the analyzed peridotites for the most part overlap with their bulk rock isotope value (e.g. VAN7-85-44, VAN7-96-29) or are shifted towards more radiogenic Nd, towards the clinopyroxene values, with essentially no change in their Hf isotopes (Fig. 4).

Bulk peridotite samples VAN7-85-47 and VAN7-85-39 show a correlated shift towards less radiogenic Hf and Nd isotopes than their cpx, while sample VAN7-85-44 has bulk rock Hf isotopes more radiogenic than cpx, yet in both cases the Hf isotope shifts are within 1.5 ϵ_{Hf} units and just outside the overall analytical uncertainties of the pyroxenes and bulk rock (Fig. 3). It is difficult to assign too much significance in these minor shifts in Hf isotopes, especially when they are dwarfed by the Nd isotope shifts in the most depleted samples. The combined Hf-Nd bulk rock data of the SWIR peridotites confirms the conclusions of Mallick et al., (2015) in that peridotites from the 15.23°E (VAN7-85 samples) have more radiogenic Hf isotopes than their local SWIR basalts, while peridotites from 9.98°E and 16.64°E have Hf isotopes that largely overlap their eruptive counterparts (Fig. 2). The bulk rock Hf-Nd isotope composition for the AII-60-9-74 peridotite from the Kane FZ approximately overlaps the nearby basalt compositions (Agranier et al., 2005), while the OCE23-14-2 sample from MCR has more radiogenic Hf and Nd isotopes than the collocated MCR basalts (Mallick et al., 2014), plotting close to the VAN7-85 dredge samples from SWIR, but still within the MORB field.

3.2.2 $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} data

The abyssal peridotite bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} are plotted on Fig. 5, along with their clinopyroxene compositions. Clinopyroxenes have presumably retained their magmatic mantle signature and plot within the MORB field (Salters and Dick, 2002; Cipriani et al., 2004; Warren et al., 2009; Mallick et al., 2014). In contrast, the bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} are variably shifted to higher and lower values, respectively, than the corresponding clinopyroxene. The more depleted VAN7-85-, OCE23-14-2 samples show a shift in both $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} compared to their clinopyroxene, with their bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ near identical to that of modern seawater ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70916$), and ϵ_{Nd} up to 8 units lower than clinopyroxene as discussed above. The refertilized VAN7-78, VAN7-96-29 and AII-60-9-74 samples show a shift in $^{87}\text{Sr}/^{86}\text{Sr}$ towards seawater but not as extreme as the VAN7-85- samples, with little change in ϵ_{Nd} .

4.0 Discussion

The central observation in our study is that while bulk rock Nd and / or Sr are isotopically shifted to more enriched compositions in bulk rock serpentinized abyssal peridotites than their clinopyroxene, the Hf isotopes remain largely identical to their clinopyroxene. In the following we explore in more detail the Hf-Nd isotope systematics between the bulk rock and clinopyroxene to assess the effects of melt metasomatism and serpentization of the Hf-Nd isotope systematics of the analyzed bulk abyssal peridotites.

4.1. Melt infiltration?

In a detailed modeling assessment of REE and Hf distribution in melt-residual peridotites Stracke et al. (2011) showed that a larger percentage of the bulk rock Nd budget is residing in clinopyroxene than Hf, due to a higher partition coefficient of Hf in olivine and orthopyroxene than Nd (e.g. Salters et al., 2002). For example, in a depleted peridotite with ~ 5% modal residual clinopyroxene, 70 to 80% of the bulk rock Nd is in the clinopyroxene vs. 60-70% for Hf (Stracke et al., 2011, their Figure 2). This is consistent with the Hf concentrations measured in the olivine, orthopyroxene and clinopyroxene in some of the SWIR peridotites analyzed here (Frisby et al., 2016). As the peridotites analyzed here retain unaltered clinopyroxene (Mallick et al., 2014; Mallick et al., 2015; Frisby et al., 2016), their corresponding bulk rock Hf budget may be more susceptible to alteration than Nd as there is proportionally less Hf over Nd bound in alteration resistant clinopyroxene. The lack of significant Hf isotope shift between bulk rock and clinopyroxene (Fig. 3,) shows that this is not the case and Hf concentrations appear more resilient during serpentinization than Nd.

All else being equal, the shift in Nd but not Hf isotopes in bulk rock over the clinopyroxene requires that the Nd/Hf ratio of the agent responsible for that shift is greater than the Nd/Hf ratio of the peridotite. As Nd is more incompatible in mantle mineralogy than Hf, a mantle melt will typically have a higher Nd/Hf ratio than a melt-residual peridotite, satisfying the above constrain. Mixing of an enriched melt with relatively unradiogenic Hf and Nd isotopes with a depleted peridotite with radiogenic Hf and Nd isotopes will then generate concave down curves on a Hf vs. Nd isotope plot (e.g., Bizimis et al., 2004; Bizimis et al., 2005; Salters et al., 2006; Salters et al., 2011; Mallick

et al., 2015). If there was transient melt infiltration in these abyssal peridotites (perhaps as a late stage melt while they were being emplaced at the ridge) and that melt did not equilibrate with the clinopyroxene (e.g. Niu, 2004), then the bulk peridotite Hf-Nd isotope composition should lie on a mixing line between the isotope composition of the clinopyroxene and that of the infiltrating melt. We examine this model for the most depleted VAN7-85 samples, as those show the largest shift in Nd isotopes. Mallick et al. (2015) suggested that the VAN7-85 dredge peridotites with the most radiogenic Hf and Nd isotopes in their clinopyroxene likely represent the local depleted mantle endmember in this SWIR segment, consistent with their LREE depleted trace element patterns (Fig. 3). Mixing calculations between the average VAN7-85 depleted peridotite and the most isotopically and trace element enriched melts found locally at the “Narrowgate” segment (e.g. Standish et al., 2008; Mallick et al., 2015) will generate concave-down curves (Fig. 2; see Table 2 for modeling parameters). Because of the highly enriched nature of the melt, the isotope composition of the bulk peridotite becomes extremely sensitive to very small melt additions. For example, 0.1% melt addition results in a shift of $\sim 1.3 \epsilon_{\text{Hf}}$ and $\sim 4 \epsilon_{\text{Nd}}$ units in the bulk peridotite compositions. However, such a mixing model does not generate the near- horizontal shift in Nd isotopes seen in the VAN7-85 peridotites. Simply put, the ratio of $(\text{Nd}/\text{Hf})_{\text{melt}}/(\text{Nd}/\text{Hf})_{\text{peridotite}}$ (~ 5.6) is not high enough, and the isotopic difference between melt and peridotite is not large enough to generate the observed near – horizontal decoupling between clinopyroxene and bulk rock. It can be also readily deduced from Figure 2 that mixing between this peridotite and any other SWIR basalt composition will generate even smaller decoupling in the Hf-Nd systematics of the metasomatized peridotite. We surmise that while melt addition could explain part

of the shift in Nd isotopes, it cannot explain all of it, not without also significantly changing the Hf isotopes.

4.2. Mantle –seawater interaction

The relatively radiogenic Sr isotope compositions of many abyssal peridotites (Fig. 5) and the Sr isotopic difference between abyssal peridotite clinopyroxenes and bulk rock is typically attributed to seawater interaction (Snow et al., 1994; Boschi et al., 2006; Harvey et al., 2006; Delacour et al., 2008; Harvey et al., 2014; Frisby et al., 2016). This is generally understood by the high Sr concentration in seawater compared to mantle peridotite and addition or exchange of seawater-derived Sr with the rock. Some serpentinized peridotites also have Nd isotope compositions that approach that of seawater (Fig. 5). This shift in Nd isotopes has been previously used to calculate water / rock ratios during serpentinization (Delacour et al., 2008), particularly for rocks where their bulk rock Sr isotopes are similar to seawater. Such water / rock ratio calculations assume closed system interaction, where the bulk rock (fresh) peridotite and seawater Nd concentrations do not change, but rock and seawater exchange isotopically. We apply this model to the bulk peridotite compositions reported here using the seawater-rock interaction equations described by Delacour et al., (2008). The seawater Nd, Hf concentration and isotope composition is taken from deep waters in the southern ocean (Stichel et al., 2012) and the local peridotite mantle is taken as the average depleted VAN7-85 peridotite (see Table 2 endmember compositions). In $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$ space, the peridotite - seawater interaction generates a highly concave-down curve, similar to that seen in Sr-Nd space (compare Fig. 2 and Fig. 5). With increasing water / rock mass ratio there is a large shift in Nd isotopes for near constant Hf isotopes (e.g. 11 ϵ_{Nd} units for ~

0.6 ϵ_{Hf} units change, at a water / rock mass ratio of 10,000). This large shift in the Nd isotopes is consistent with what is observed for the VAN7-85 clinopyroxene – bulk rock pairs. This shift is because the $(\text{Nd}/\text{Hf})_{\text{seawater}}/(\text{Nd}/\text{Hf})_{\text{peridotite}}$ (~21), is large and because the Hf isotopic composition of seawater is more radiogenic than the terrestrial array at a given Nd isotope ratio (e.g. Albarède et al., 1998; Chauvel et al., 2008). To a first order, these calculations demonstrate that the Hf isotope composition of a peridotite is more resistant to serpentinization and seawater interaction than the Nd isotopes.

4.3 Nd vs. Hf seawater contribution and protolith dependence

While the above calculation clearly illustrate the potential decoupling of Hf from Nd isotopes during serpentinization, it also assumes that the entire rock participates in the exchange with seawater. The decoupling of Nd-Sr and Nd-Hf isotope pairs between bulk rock and clinopyroxene (Fig. 3, Fig. 5) instead suggests that only part of the rock must participate in such exchange. Frisby et al., (2016) showed that the shift in Nd isotopes between clinopyroxene and bulk rock in serpentinized peridotites (some of which are discussed here) is the result of seawater- derived Nd addition to the rock, as opposed to exchange. This addition appears largely restricted in the secondary alteration phases (serpentine, magnetite) while the clinopyroxene still records the original (magmatic) isotope and trace element composition of the rock. We can approximate the amount of seawater-derived Nd added to the bulk peridotite relative to the magmatic Nd budget by assuming that the shift in Nd isotopes is due to Nd addition from seawater, and that other processes, like melt infiltration, were insignificant. This seawater-derived Nd, or %Nd_{SW} is calculated by mass balance as:

$$\%Nd_{SW} = \frac{^{143}\text{Nd}/^{144}\text{Nd}_{BR} - ^{143}\text{Nd}/^{144}\text{Nd}_{Cpx}}{^{143}\text{Nd}/^{144}\text{Nd}_{SW} - ^{143}\text{Nd}/^{144}\text{Nd}_{Cpx}}$$

where $^{143}\text{Nd}/^{144}\text{Nd}_{BR}$ is the measured bulk rock $^{143}\text{Nd}/^{144}\text{Nd}$, $^{143}\text{Nd}/^{144}\text{Nd}_{Cpx}$ is the
 clinopyroxene composition and $^{143}\text{Nd}/^{144}\text{Nd}_{SW}$ is the Nd isotope composition of seawater
 (data from Table 1 and Table 2). The calculated %Nd_{SW} ranges from ~ 1% to 34%
 (Table 3) in these peridotites. If Nd and Hf are removed from seawater and added to the
 rock at a similar proportion to their seawater abundance, then we can use the %Nd_{SW} to
 calculate %Hf_{SW}, or the relative amount of seawater-derived Hf added to the rock. Based
 on this reasoning we find that the largest %Hf_{SW} is 1.9% in the analyzed samples (Table
 3). This value is largely within error of typical ICPMS concentration analyses, especially
 at these low concentrations. While these numbers depend somewhat on the choice of the
 seawater endmember they nevertheless show that Hf addition to the peridotite during
 seawater alteration and serpentinization will be much smaller than that of Nd. This
 calculation is independent of the Hf isotope measurements and provides additional
 support to our inferences from the Hf isotopes above that during peridotite - seawater
 interaction Hf isotopes are more resistant to alteration than Nd.

The above conclusions demonstrate that bulk peridotite Hf concentrations are
 insensitive to serpentinization and can be used as a reliable tracer of the magmatic
 composition of serpentinites. We take advantage of this to further investigate the extent
 of Nd addition on these peridotites during serpentinization. Figure 6 plots %Nd_{SW}
 against 1/Hf of the peridotites. The peridotites with the greatest %Nd_{SW} are the most
 depleted samples (highest 1/Hf; Fig. 6A). Therefore, the most depleted peridotites are
 more likely to have their bulk rock Nd budget significantly affected by serpentinization
 than the more enriched ones.

The extent of Nd addition from seawater is also reflected on the U/Th systematics of these peridotites. The peridotites with the highest %Nd_{SW} also have the highest U/Th ratios (Fig. 6B). The ubiquitous U enrichment in serpentinized peridotites is attributed to U addition from seawater (e.g. Deschamps et al., 2011; Kodolányi et al., 2012; Deschamps et al., 2013), and the correlation between U and %Nd_{SW} provides an independent constrain that Nd has been added to these rocks by seawater.

Finally, the %Nd_{SW} can be converted to water / rock ratio if we assume that the added amount of Nd is the result of quantitative removal of Nd from seawater during rock – fluid reaction, which is a reasonable assumption as REE are highly particle reactive (e.g., Frisby et al., 2016 and discussion therein). The %Nd_{SW} is converted to amount of added Nd per gram of rock, which is then converted to mass of water using the seawater Nd concentration in Table 2. The resultant water / rock mass ratios range from ~130 to ~6000. These water / rock ratios do not correlate either with depletion (e.g. Hf concentrations) or possible seawater interaction indicators (U/Th of %Nd_{SW}). This is not unreasonable as the extent of serpentinization and water / rock ratio should vary independently to the type and fertility of the protolith and is likely the product of local faulting or other tectonics at the ridge.

4.4. Implications on the Hf-Nd isotope systematics in the mantle

The Hf-Nd isotope systematics of mantle peridotites provide important constraints on the composition and chemical heterogeneity of the mantle and the time –integrated fractionation processes that takes place during melting and post-melting metasomatism (Salters and Zindler, 1995; Blichert-Toft et al., 2000; Bizimis et al., 2004; Ionov et al., 2005; Bizimis et al., 2007; Stracke et al., 2011; Mallick et al., 2015; Warren, 2016). As

Hf is resistant to serpentinization, bulk rock Hf isotopes of peridotites can also be used to infer mantle processes, as do the clinopyroxenes. In case of serpentinized rocks, bulk rock Hf isotopes will be more robust proxies of the protolith than Nd. Using again the depleted VAN7-85 samples as an example, their bulk rock Nd isotopes overlap their local basalts, but the Hf isotopes are more radiogenic than the later. If the Nd and Hf isotope compositions were considered separate from each other, the peridotite-basalt comparison would result in two completely different conclusions as to the relationship of peridotite to their host basalt. In all, our data confirms that abyssal peridotites and oceanic peridotite mantle xenoliths, on average, overlap or extend towards more radiogenic Hf and/or Nd compositions than their proximal lavas (Salters and Dick, 2002; Bizimis et al., 2004; Cipriani et al., 2004; Bizimis et al., 2007; Warren et al., 2009; Stracke et al., 2011; Byerly and Lassiter, 2014; Mallick et al., 2015), implying the presence of additional (and presumably more fertile) components in the mantle source of magmas.

We showed above that Hf concentrations in these peridotites are little (if any) changed by the serpentinization processes compared to Nd (Table 3). We use the same arguments as above to calculate the effect of serpentinization on the Sm and Lu bulk peridotite concentrations, assuming again that the shift in Nd isotopes between clinopyroxene and bulk rock is due to addition of Nd from seawater. These calculations (Table 3) show that for a 1 to 34% change in the Nd bulk rock budget due to serpentinization, the bulk rock Sm budget will change by 1 to 6%, while Lu mimics Hf with up to 1.9% change. These data imply that seawater interaction will decrease the Sm/Nd ratio of the bulk peridotite while Lu/Hf ratio will be largely unaffected. If these lower Sm/Nd ratios of the serpentinized peridotite survive the subduction dehydration

process and pass into the upper mantle, they can contribute to mantle heterogeneity by decreasing Sm/Nd relative to Lu/Hf ratio of the recycled lithosphere which will generate less radiogenic Nd isotopes for a given Hf isotopes over time. This decoupling is illustrated by an example, using peridotite VAN7-85-43 with the largest calculated seawater-derived Nd addition (34%, Table 3). Assuming that this peridotite originated 1 Ga ago from a MORB source (values from Khanna et al., 2014) and was serpentinized leading to its measured Sm/Nd and Lu/Hf ratios (Supplementary Table 1), it would evolve to present day $\epsilon_{\text{Hf}} = 150$ and $\epsilon_{\text{Nd}} = 66$, falling above the extension of the mantle array with a slope of 1.59 (Chauvel et al., 2008). If the excess seawater-derived Nd and Sm calculated in Table 3 are removed from the rock (i.e. no serpentinization), then this peridotite would evolve to present day $\epsilon_{\text{Hf}} = 150$ and $\epsilon_{\text{Nd}} = 102$, i.e. with nearly 40 ϵ_{Nd} units more radiogenic Nd, and would plot along the extension of the mantle array in radiogenic ϵ_{Hf} and ϵ_{Nd} space. As the contribution of recycled oceanic lithosphere to oceanic volcanism is increasingly debated (e.g. Workman et al., 2004; Bizimis et al., 2005; Bizimis et al., 2013; Salters et al., 2011; Williams and Bizimis, 2014), modification of the peridotitic lithosphere by serpentinization is an additional mechanism of heterogeneity and variability in recycled oceanic lithosphere, albeit more pronounced in the most depleted peridotites (e.g. Figure 6).

Alternatively, limited experimental data on serpentinite dehydration (Tatsumi et al., 1986; Kessel et al., 2005; Spandler et al., 2014; Kessel et al., 2015) suggests that LREE may be preferentially mobilized to the fluid / melt over the HREE and HFSE. It is then conceivable that upon dehydration of serpentinized peridotite during subduction, the excess seawater-derived Nd that is hosted within alteration phases (Frisby et al., 2016)

might be preferentially released to the mantle wedge over along with other fluid mobile elements (e.g. As, Sb, B, Li, Cs, Pb, U, Ba, Sr) (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) thereby further contributing to the Nd budget of arc lavas (the low Nd concentrations of peridotites notwithstanding). Additional experimental data on the coupled mobility of REE and HFSE with fluid mobile elements during dehydration of the oceanic lithosphere is needed to evaluate the above models.

5.0 Conclusions

We present a method for the efficient preconcentration of REE and HFSE out of >1 gram of ultramafic rock material, using a combination of Fe-Al co-precipitation and ether exchange. This method can be applied for the analyses of depleted samples such as harzburgites or lherzolites, where enough clinopyroxene may be difficult to separate, or for analyzing orthopyroxenes, which are the second largest reservoir of Nd and Hf in peridotites. Here we use this method to determine the bulk rock Hf and Nd isotope compositions of serpentinized abyssal peridotites as well as Nd and Hf isotope data for the USGS rock reference material PCC-1. These data show that serpentinized abyssal peridotites have bulk rock Hf isotopes that are within error identical to those of their clinopyroxene, while Nd and Sr isotopes are shifted towards more seawater-like isotope ratios. These data show that the bulk rock Hf budget and Hf isotopes remain unaffected during serpentinization and record the magmatic high temperature value of the rock, while Nd appears to have been added to the peridotite during serpentinization. Therefore, Hf isotopes in bulk rock serpentinized peridotites can be used to trace the

magmatic history of the rock more reliably than Nd isotopes, and Hf concentrations are now a demonstrated reliable tracer of the magmatic history of serpentinized peridotite. These data also demonstrate that the most trace element depleted peridotites are more susceptible to having their bulk rock Nd isotopes and Nd budget affected by serpentinization than the more fertile ones. The demonstrated fractionation of the peridotite Sm/Nd and Lu/Hf ratios by serpentinization has implications for both being an additional agent of heterogeneity in the mantle upon recycling and aging of the serpentinized lithosphere, or as an additional reservoir for fluxing Nd to the subarc mantle along with the fluid mobile elements.

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Figure Captions

Figure 1:

Schematic diagram of the described analytical protocol, including digestion, REE and HFSE preconcentration, Fe separation and column chromatography.

Figure 2:

ϵ_{Hf} vs. ϵ_{Nd} isotope plot of bulk rock abyssal peridotites (circles, this study) compared to their clinopyroxene (diamonds), local basalt and the MORB –OIB fields. Seawater array from Albarede et al., (1998) and terrestrial array from Chauvel et al. (2008). Green dashed line shows closed system exchange between seawater and the depleted VAN7-85 peridotites (endmember data from Table 2). Red dashed line shows melt addition of most trace elements and isotopically enriched local basalts from the Narrowgate segment to the depleted VAN7-85 peridotites (endmember data from Table 2). The seawater - peridotite mixing model produces a more strongly concave curve than the melt-peridotite mixing model with greater change in Nd isotopes for a given Hf isotopes at the initial stages of seawater or melt-peridotite reaction, and better fits the observed shift in Nd isotopes between bulk rock and corresponding clinopyroxenes.

Figure 3:

Primitive mantle normalized bulk rock trace element systematics for the peridotites reported here (data in Supplementary Table 1), compared with abyssal peridotite data from the literature (Niu, 2004). Our data largely overlaps the global peridotite data with characteristic positive U, Pb, and Sr anomalies and variable flat to

1018 depleted LREE / HREE ratios. DMM from Workman and Hart (2005) and Salters and
1019 Stracke (2004).

1020 **Figure 4:**

1021 ϵ_{Hf} and ϵ_{Nd} isotope diagram showing the composition of coexisting clinopyroxene
1022 (colored diamonds), leached bulk rock (colored squares) and bulk rock (colored circles).
1023 Tie lines connect fractions of the same sample. The most LREE depleted samples
1024 (VAN7-85) show little change in ϵ_{Hf} while ϵ_{Nd} shifts from mantle values (clinopyroxene)
1025 toward that of seawater. LREE enriched peridotites (VAN7-78, VAN7-96-29) have all
1026 their components fall within or close to the SWIR basalt field.

1027 **Figure 5:**

1028 $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} values for primary clinopyroxene (colored diamonds) and bulk
1029 rock (colored circles) for the analyzed peridotites. The clinopyroxenes falls within the
1030 MORB-OIB field while bulk rock falls closer to seawater, having more radiogenic Sr and
1031 less radiogenic Nd than the clinopyroxene. The samples are compared to the MORB-
1032 OIB field and a rock-seawater interaction model using the equations given in Delacour et
1033 al. (2008), with peridotite and seawater endmember compositions from Table 2. The
1034 model assumes isotopic equilibrium between seawater and bulk rock and no change in
1035 their respective concentrations (i.e. only element and isotope exchange). Tick marks
1036 along the line show water/ rock mass ratios. Other bulk rock and clinopyroxene abyssal
1037 peridotite data is from Roden et al. (1984); Brueckner et al. (1988); Snow et al. (1994);
1038 Snow and Reisberg (1995); Delacour et al. (2008) and clinopyroxene data Salters and

Dick (2002); Cipriani et al. (2004); Warren et al., (2009); Mallick et al. (2014). The abyssal peridotite compilation data plotted here is given in the Supplementary Table 2.

Figure 6:

A): Plot of $\%Nd_{SW}$ versus $1/Hf$ and, B) $\%Nd_{SW}$ versus U/Th . As Hf is not affected by serpentinization, $1/Hf$ is a reliable proxy of depletion. U/Th is taken here as representative of added seawater due to the excess U found in seawater compared to that of Th. Panel A shows a positive correlation between percent of added seawater-derived Nd and the most depleted of our analyzed samples (VAN7-85). Panel B shows a positive correlation between seawater-derived Nd and high U/Th ratios. These two figures provide evidence that the more depleted the sample the more susceptible it is to record Nd addition from seawater. DMM value from Workman and Hart, (2005).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1

Table 1: Hf, Nd and Sr isotopes of analyzed peridotites

Sample	Latitude (degree)	Longitude (degree)	Lithology	$^{87}\text{Sr}/^{86}\text{Sr}$	2σ	$^{143}\text{Nd}/^{144}\text{Nd}$	2σ	$^{176}\text{Hf}/^{177}\text{Hf}$	2σ	ϵ_{Nd}	ϵ_{Hf}
BIR-1						0.513113	0.000008	0.283278	0.000005	9.27	17.43
BIR-1								0.283278	0.000007		17.43
PCC-1						0.512234	0.000022			-7.88	
PCC-1						0.512219	0.000018	0.283401	0.000018	-8.17	21.78
PCC-1				0.711067	0.000006	0.512245	0.000006	0.283377	0.000014	-7.67	20.92
VAN7-78-36H	52.38S	16.64E	Pl Hz	0.702858	0.000019	0.513044	0.000019	nd		7.92	
CPX [@]				0.708543	0.000005	0.513010	0.000005	0.283114	0.000009	7.26	11.6
Bulk [§]				0.705788	0.000020	0.513048	0.000003	0.283115	0.000008	8.00	11.7
Leached Bulk*											
VAN7-78-39	52.38S	16.64E	Pl Lz	0.702992	0.000007	0.513031	0.000009	0.283082	0.000008	7.67	10.5
CPX [@]				0.707067	0.000007	0.512989	0.000004	0.283060	0.000003	6.85	9.7
Bulk [§]				0.706889	0.000006	0.512968	0.000005	0.283047	0.000007	6.43	9.3
Leached Bulk* [§]											
VAN7-78-41	52.38S	16.64E	Pl Hz	0.702800	0.000007	0.513046	0.000009	0.283035	0.000025	7.96	8.8
CPX [@]				0.708411	0.000007	0.512918	0.000004	0.283066	0.000006	5.46	9.9
Bulk* [§]				0.707895	0.000008	0.512923	0.000021	0.283056	0.000006	5.56	9.6
Leached Bulk [§]											
VAN7-85-30	52.25S	15.4E	Lz	0.704899	0.000049	0.513321	0.000092	0.283281	0.000010	13.32	17.5
CPX [@]				0.708913	0.000005	0.513049	0.000024	0.283310	0.000012	8.02	18.6
Bulk [§]				nd		0.512916	0.000004	0.283304	0.000010	5.42	18.4
Leached Bulk* [§]											
VAN7-85-42	52.25S	15.4E	LZ	0.702440	0.000170	0.513319	0.000014	0.283284	0.000013	13.28	17.6
CPX [@]				0.709175	0.000008	0.513164	0.000009	0.283269	0.000020	10.26	17.1
Bulk* [§]				0.709463	0.000008	0.513181	0.000006	0.283283	0.000010	10.59	17.6
Leached Bulk* [§]											
VAN7-85-43	52.25S	15.4E	Lz	0.702902	0.000147	0.513320	0.000021	0.283314	0.000014	13.30	18.7
CPX [@]				0.709143	0.000008	0.512930	0.000014	0.283272	0.000010	5.70	17.2
Bulk* [§]				0.709044	0.000010	0.513127	0.000069	0.283309	0.000011	9.54	18.5
Leached Bulk* [§]											
VAN7-85-44	52.25S	15.4E	Lz	0.702762	0.000015	0.513269	0.000009	0.283323	0.000011	12.31	19.0
CPX [@]				0.708864	0.000008	0.513146	0.000012	0.283360	0.000010	9.91	20.3
Bulk				nd		0.513153	0.000011	0.283361	0.000007	10.05	20.4
Leached Bulk*											
VAN7-85-47	52.25S	15.4E	LZ	0.702308	0.000013	0.513323	0.000003	0.283296	0.000014	13.36	18.1
CPX [@]				0.709199	0.000008	0.513163	0.000028	nd		10.24	
Bulk [§]				0.709568	0.000007	0.513208	0.000007	0.283259	0.000009	11.12	16.8
Leached Bulk* [§]											
VAN7-96-29	53.14S	9.98E	Sp Lz	0.703041	0.000009	0.512921	0.000009	0.283169	0.000006	5.52	13.6
CPX [@]				0.705077	0.000008	0.512881	0.000008	nd		4.74	
Bulk				nd		0.512906	0.000006	0.283186	0.000012	5.23	14.2
Bulk*				nd		0.512915	0.000004	0.283181	0.000003	5.40	14.0
Leached Bulk*											
AII-60-9-74	21.93S	11.8W	Pl Lz	0.702759		0.513144		nd		9.87	
CPX [@]				0.707825	0.000010	0.513122	0.000006	0.283109	0.000012	9.44	11.5
Bulk						0.513157	0.000006	0.283130	0.000005	10.12	12.2
Bulk*											
OCE23 -14-2	18.21N	81.54W	Pl Hz	0.703350		0.513132		nd		9.64	
CPX [@]				0.709098	0.000009	0.513261	0.000010	0.283259	0.000006	12.15	16.8
Bulk*											

@ Nd and Sr isotopes from Mallick et al. (2014) and Hf isotopes from Mallick et al. (2015). nd: not determined

§ $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ from Frisby et al. (2016).

* Fe-precipitation method

Table 2: Seawater-peridotite and melt-peridotite mixing model parameters

	Abyssal Peridotite*	Melt [§]	Seawater [#]
⁸⁷ Sr/ ⁸⁶ Sr	0.702689		0.70916
¹⁴³ Nd/ ¹⁴⁴ Nd	0.5133	0.51279	0.51216
¹⁷⁶ Hf/ ¹⁷⁷ Hf	0.2833	0.28300	0.28288
Sr (ppm)	6.1		8.00
Nd (ppm)	0.32	25.7	3.2x10 ⁻⁵
Hf (ppm)	0.22	3.15	1.0x10 ⁻⁶

* Average concentration of the depleted abyssal peridotite bulk rocks (dredge VAN7-85). Sr, Nd, Hf isotopes are the magmatic values taken from the clinopyroxene.

[§] Mallick et al. (2015)

[#] Seawater Hf, Nd values from Stichel et al., (2012), average of station 104 depths 2000 and 4440m. Sr from Delacour et al. (2008)

Table 3

Table 3: Relative amount of Nd, Sm, Lu and Hf derived from seawater with corresponding W/R ratios.

Sample	%Nd _{SW}	%Sm _{SW}	%Lu _{SW}	%Hf _{SW}	W/R Closed System	W/R Open System
VAN7-78-36H	4.0	1.6	1.5	0.4	4461	4376
VAN7-78-39	5.0	1.5	0.5	0.4	1951	1904
VAN7-78-41	14.0	4.4	1.4	1.3	4590	4243
VAN7-85-30	23.0	4.6	1.2	0.8	3905	3409
VAN7-85-42	13.0	1.5	0.4	0.3	1167	1085
VAN7-85-43	34.0	5.9	1.9	1.9	8234	6670
VAN7-85-44	11.0	1.9	0.4	0.2	1230	1159
VAN7-85-47	14.0	2.1	0.7	0.7	2261	2098
VAN7-96-29	5.0	1.9	3.9	0.7	10879	10590
AII-60-9-74	2.0	1.1	0.9	0.5	3579	3539