Lu-Hf and Sm-Nd geochronological constraints on the influence of subduction metamorphism in controlling the Hf-Nd terrestrial array: Evidence from the world’s orogenic belts

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ABSTRACT

To create a better understanding of the influence of subduction metamorphism on the Hf-Nd terrestrial array, this study examines all of the available Lu-Hf and Sm-Nd garnet isochron ages from the world’s orogenic eclogites and amphibolites. The garnet isochron y-intercept values provide a record of each sample’s epsilon Hf (εHf) and Nd (εNd) at the age recorded by the isochron, which in the case of most orogenic eclogites and amphibolites is the time of prograde metamorphism during subduction. It is further possible to assess the extent to which each sample’s Lu-Hf and Sm-Nd isotope systematics have remained undisturbed since the date recorded by the isochron by comparison of the bulk-rock isotope systematics with the isochron initial value. This approach provides a means of understanding the Lu-Hf and Sm-Nd systematics of post-subduction metamorphic oceanic crust. On a global scale, the coupled Lu-Hf and Sm-Nd isotope systematics of this crust closely align with the Hf-Nd terrestrial array and have average 176Lu/177Hf and 147Sm/144Nd ratios within error of the chondritic uniform reservoir values. This is an important finding because it suggests that a reservoir of deeply subducted oceanic crust, possibly residing at the core-mantle boundary, is unlikely to be significantly fractionated from the Hf-Nd terrestrial array. In contrast to the samples of subduction-metamorphosed oceanic crust, metamorphic rocks with a continental crustal protolith demonstrate garnet isochron initial values and bulk-rock Lu-Hf and Sm-Nd isotopic systematics indicating significant decoupling from the Hf-Nd terrestrial array. However, because this material is not readily subducted, this strongly decoupled signature is unlikely to be transferred into deep Earth. Mixing calculations aimed at developing a clearer understanding of what factors control decoupling of a sample’s Lu-Hf and Sm-Nd systematics from the Hf-Nd terrestrial array highlight the complexity of mass-transfer regimes operating in the subduction environment.

INTRODUCTION

At a minimum, oceanic crust equivalent to ~2.2% of Earth’s total mass has been subducted over the last 2.5 b.y. (Rudnick et al., 2000). Although the paradigm is that this crust ultimately gets recycled back into the convecting mantle (Staudacher and Allègre, 1988; Liu et al., 2010; Becker, 2000; Hofmann and White, 1982; Niu and Batiza, 1997; Sobolev et al., 2000; Hoernle et al., 2002; Kellogg et al., 1999; Kelley et al., 2005), there is also ample evidence that a portion of it accumulates at the core-mantle boundary over billion-year time scales (Burke et al., 2008; Hirose et al., 1999; Rao and Kumar, 2014; Spasojevic et al., 2010). Therefore, the geochemical and isotopic signature of this subducted oceanic crustal reservoir must be accounted for during terrestrial-scale geochronological and geochemical mass-balance calculations (Kamber and Collerson, 2000; Sun and McDonough, 1989; Christensen and Hofmann, 1994; Aubach et al., 2008). Two complicating factors are the facts that this reservoir cannot be directly sampled, and that its composition cannot be assumed to equal that of the unsubducted oceanic crust sampleable on the seafloor or in the world’s ophiolite belts. This is because mass is lost from subducting oceanic crust due to devolatilization and partial melting as it undergoes metamorphism, as well as gained from interaction with the subduction-modified mantle wedge, sediments, and other material present in the subduction environment (e.g., Schmidt et al., 2009; Gao et al., 2007; Kessel et al., 2005; Hermann et al., 2006; Stepanov and Hermann, 2013; Xiao et al., 2006; Zack and John, 2007; Feineman et al., 2007).

The effect of mass transfer into the subducting oceanic crust is particularly difficult to quantify on a global scale because the sources of the gained mass vary considerably at all spatial and temporal scales (e.g., Plank and Langmuir, 1998; Ishikawa and Nakamura, 1994; Singer et al., 2007; Peate et al., 1997) in the subduction environment. The presence on the Earth’s surface of (ultra) high-pressure metamorphic rocks with an upper-continental crustal affinity (see recent discussion by Spencer et al., 2017; Wang et al., 2014; Janák et al., 2015; Ingalls et al., 2016) suggests that a portion of the evolved material (e.g., sediments shed off continents, continental margins, and arc terranes) colocated with subducting oceanic crust gets exhumed and does not continue into the deep Earth with the oceanic crust. Therefore, understanding the effect of mass exchange between the subducted oceanic crust and this more evolved material is critically important. Estimating the effects of dehydration and partial melting on subducted oceanic crust by examination of arc magmas (Yogodzinski et al., 2015; Walowski et al., 2015; Harvey et al., 2014) is perhaps more straightforward, but integrating this data stream with the effects of mass transferred...
into the subducted crust from the aforementioned evolved materials, as well as from the modified mantle wedge, is not straightforward. In this regard, the firmest constraints would come from material that is directly representative of the subducted oceanic crust after it has gone through subduction-related phase transformations and mass-balance regimes.

Many of the world’s orogenic eclogites and amphibolites (OEs), which can be sampled in a variety of collisional and extensional plate-boundary settings, are fragments of subduction-metamorphosed oceanic crust that have been exhumed from mantle depths. While not all OEs have an oceanic crustal protolith, those that do have the potential to reveal important aspects about the geochemistry of subducted oceanic crust. Indeed, there are many examples in the recent literature (e.g., Zhang et al., 2016; Zirakparvar, 2016; Li et al., 2017; Peters et al., 2017) where OEs have been used for this purpose. One complicating factor in attempting to use an OEs’s geochemistry to understand the chemical consequences of subduction is that it can be difficult to understand when a sample acquired its geochemical characteristics. Fluid circulation and partial melting are well known to occur during the exhumation of formerly subducted terranes (Song et al., 2014; Little et al., 2011) as well as during a sample’s residence in the middle to upper crust of mountain belts (e.g., Miller et al., 1994), which can readily shift a sample’s chemical and/or isotopic composition away from that acquired during subduction metamorphism.

A study by Zirakparvar (2016) took the approach of using garnet Lu-Hf isochron age and initial Hf isotope compositions as means of independently evaluating whether an OEs’s chemical and isotopic systematics had been substantively altered following isotopic closure of the Lu-Hf system through prograde metamorphism. The Zirakparvar (2016) study was focused on understanding the role of subducted oceanic crust in the terrestrial Nb mass balance, but the rationale and approach are applicable to other elemental and isotopic systems. In the present study, published coupled garnet Sm-Nd and Lu-Hf geochronological data (i.e., when both systems are applied to dating garnet in the same sample) are used to understand the HF-Nd systematics of globally subducted oceanic crust. Although coupled Sm-Nd and Lu-Hf garnet geochronology is not as prevalent as instances where only one system has been applied to dating the time of garnet growth during metamorphism, or isotopic closure following garnet growth, coupled Lu-Hf and Sm-Nd garnet geochronological data are available for many of the world’s major orogenic belts. This allows for an empirical assessment of the influence of subduction metamorphism on the HF-Nd terrestrial array (e.g., Vervoort and Blichert-Toft, 1999, and Vervoort et al., 2011).

### Background and Rationale

**Background: Uncertainty over the Role of Subducted Oceanic Crust in Controlling the HF-Nd Terrestrial Array**

The term "terrestrial array," as defined by Vervoort and Blichert-Toft (1999) and Vervoort et al. (2011), refers to the observation that the Hf and Nd isotopic compositions of most terrestrial samples define a single well-correlated linear relationship on a plot of epsilon Hf (εHf) versus epsilon Nd (εNd). The existence of broadly coupled behavior between the Hf and Nd isotopic compositions from individual samples representative of most terrestrial reservoirs, as well as the potential for certain processes to induce significant decoupling, were first recognized during the 1980s and have since been confirmed by numerous studies. For example, it was recognized that the Hf and Nd isotopic compositions of ocean island basalt (OIB) samples are typically internally consistent, whereas those from mid-ocean-ridge basalt (MORB) samples had radiogenic Hf compositions compared to their Nd signatures (e.g., Salters and Hart, 1989, 1991; Patchett and Tastumoto, 1980; Patchett, 1983). This observation led Salters and Hart (1989) to suggest that the presence of residual garnet in the melt generation zone for MORB results in the enrichment of Lu in the residuum, leading to MORB samples that ultimately evolve to lower εNd at a given εHf and a depleted mantle that evolves to higher εNd at a given εHf.

Significant and widespread deviations from the HF-Nd terrestrial array within a particular reservoir require fractionation capable of preferentially decoupling the parent (e.g., 147Sm and 150Nd), daughter (143Nd or 176Hf), or both isotopes of either the Lu-Hf or Sm-Nd isotope system. Well-recognized deviations from the terrestrial array are the behavior of Fe-Mn crusts and nodules (e.g., the seawater array defined by Albarède et al., 1998), eolian dusts (Pettke et al., 2002), and the riverine flux into the oceans (Bayon et al., 2006; Godfrey et al., 2009). A thorough summary of the mechanisms responsible for producing these reservoirs can be found in Vervoort et al. (2011), their section 5.3. While the slope of the terrestrial array is sensitive to the choice of the chondritic uniform reservoir (CHUR) 176Lu/177Hf and 147Sm/144Nd, the Lu and Sm decay constants used, as well as whether initial or present-day εHf or εNd compositions of the individual samples are used, the fact that most terrestrial samples lie along it (regardless of how the aforementioned parameters are chosen) has led to the conclusion that the Lu-Hf and Sm-Nd systematics of the Earth’s crust and mantle have remained coupled over geological time scales (e.g., Vervoort et al., 2011). This is reinforced by the observation that the terrestrial array [εHf = (1.55 x εNd) + 1.21] defined by Vervoort et al. (2011), which includes a large proportion of continental crustal samples, matches the mantle array [εHf = (1.59 x εNd) + 1.28] defined by Chauvel et al. (2008) and is constructed solely using samples produced through mantle melting (e.g., MORB and OIB).

Because the production of MORB involves the generation of a depleted mantle component that evolves to an elevated 147Sm/144Nd ratio (e.g., Vervoort and Blichert-Toft, 1999; Blichert-Toft and Albarède, 1997), it is somewhat surprising that the depleted mantle and terrestrial arrays are not decoupled from one another. Calculations by Chauvel et al. (2008) demonstrate that the Hf and Nd isotope systematics of ocean basaltic (MORB and OIB) can be modulated as mixtures between subducted oceanic crust, depleted mantle, and an oceanic sedimentary component having low εNd yet high εHf, whereas mixing solely between subducted oceanic crust and a depleted mantle component is insufficient to produce the observed MORB-OIB array. However, Chauvel et al. (2008) used the average composition of MORB basalt to approximate the
Lu-Hf and Sm-Nd characteristics of subducted oceanic crust. Because of the growing evidence for high field strength element (HFSE) and rare earth element (REE) mobility within oceanic crust during subduction-zone metamorphism (Münker et al., 2004; White and Patchett, 1984; Pearce et al., 1999; Woodhead et al., 2001; Zack and John, 2007), it is likely that the composition of subducted oceanic crust does not fully mimic that of unsubducted oceanic crust.

Additionally, it is perfectly reasonable to assume that a proportion of oceanic sediments sitting on the subducting slab and having elevated εNd relative to their εNd at the age recorded by the isochron itself. These isochron initial values provide information about the Hf-Nd systematics of oceanic crust that has been subducted and metamorphosed because they

Rationale: Justification for the Use of Orogenic Eclogite and Amphibolite Garnet Isochron Initial Values as a Means of Understanding the Isotopic Composition of Subducted Oceanic Crust

As our understanding of subduction-related metamorphism has grown, so has the realization that this process involves significant mass transfer in and out of the subducting slab (e.g., Münker et al., 2004; White and Patchett, 1984; Pearce et al., 1999; Woodhead et al., 2001; Zack and John, 2007). Oceanic crust that has been subducted and metamorphosed to the eclogite facies and beyond (e.g., Han et al., 2015) is available for direct study in two geodynamic settings: (1) as xenoliths in kimberlite magmas that sample the subcontinental lithospheric mantle (SCLM) and (2) as eclogites and amphibolites in the world’s orogenic belts (the OEs). Although some researchers have had success using the geochemistry of kimberlite eclogite xenoliths to understand the geochemistry of subducted oceanic crust, it is generally recognized that a variety of processes operating with the SCLM itself alter the xenoliths’ chemical composition and mineralogy (e.g., Aulbach et al., 2007; Smid et al., 2014; Smart et al., 2017). In considering that most kimberlite eclogite xenoliths are inferred to have resided in the SCLM over billion-year time scales, it is very difficult to understand which aspects of the eclogites reflect the chemical signature imparted by subduction versus those that have been acquired from the SCLM. Furthermore, because these kimberlites mostly sample ancient cratons (Heaman et al., 2003), any evidence gleaned from their eclogite xenoliths are likely biased toward the older portions of Earth history.

In contrast, OEs occur in mountain belts spanning a wide range of ages and are found on most continents (see the recent review by Brown and Johnson, 2018). Therefore, OEs have the potential to reveal certain aspects about the nature of subducted oceanic crust without the uncertainty imparted to samples that have resided in the SCLM. However, it is still necessary to understand whether an OEs composition fully reflects processes that occurred during subduction-related metamorphism or if it was acquired at a later time (e.g., during exhumation or residence in the middle to upper crust). The Lu-Hf and Sm-Nd systems have been relatively widely applied to dating the timing of garnet growth or isotopic closure following garnet growth in the world’s OEs. Garnet Lu-Hf and Sm-Nd geochronology involves regressing garnet aliquots with other mineral and bulk-rock fractions on isochron diagrams. Depending on which system is used, the y-intercept values from these isochron diagrams is commonly interpreted as either the 176Hf/177Hf or 143Nd/144Nd ratio of the rock at the age recorded by the isochron itself. These isochron initial values provide information about the Hf-Nd systematics of oceanic crust that has been subducted and metamorphosed because they

Regardless of the uncertainty over the composition of subducted sediments, there is a growing consensus that only a small proportion of this sediment is actually transferred into the lower mantle (see discussion by Currie et al., 2007). Therefore, accurately constraining the composition of the subducted oceanic crust itself, which exchanges mass with subducted sediment in the subduction channel, is arguably the most important aspect in trying to understand the effect of subduction on global-scale Hf-Nd systematics. There is ample evidence that subducted oceanic crust exchanges mass with its surroundings during subduction metamorphism (Münker et al., 2004; White and Patchett, 1984; Pearce et al., 1999; Woodhead et al., 2001; Zack and John, 2007; Bebout and Penniston-Dorland, 2016; Spandler and Pirard, 2013; Peters et al., 2017). It is therefore insufficient to use the Sm-Nd and Lu-Hf isotope systematics of unsubducted oceanic crust to model the effect of subduction on the Hf-Nd terrestrial array. In the following section, the rationale for using Sm-Nd and Lu-Hf isotopic data from the world’s OEs as a means of understanding the isotopic systematics of globally subducted oceanic crust is explained. Thereafter, this new source of data is examined within the context of the role of subduction on global-scale Sm-Nd and Lu-Hf isotope systematics.

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are unlikely to have been affected by later disturbances (e.g., Zirakparvar, 2016). This is because major disturbances to the Lu-Hf and Sm-Nd isotope systems would result in a sample that fails to yield an isochron. Additionally, if an OEA’s present-day bulk-rock Lu-Hf and Sm-Nd isotope compositions can be used to calculate initial $^{176}$Hf/$^{177}$Hf and $^{143}$Nd/$^{144}$Nd ratios that overlap those defined by the isochron $y$-intercept, post-subduction metamorphic disturbances to the rocks’ Lu-Hf and Sm-Nd systematics can be further ruled out. In cases where the isochron and calculated bulk-rock initial values agree with one another, it is possible to use the rock’s Lu-Hf and Sm-Nd composition (elemental and isotopic) to calculate how a reservoir of subducted oceanic crust factors into the global Sm-Nd and Lu-Hf mass balance.

### DATA COLLECTION, PROCESSING, AND RESULTS

#### Data Collection and Processing

The geological literature was surveyed, and data from those studies presenting coupled (i.e., applied to the same rock) Lu-Hf and Sm-Nd ages for metamorphic garnet were compiled into Table 1. A major division in Table 1 delineates (1) Lu-Hf and Sm-Nd ages from metamorphic garnets in rocks of an inferred oceanic crustal provenance (the OEA’s) from (2) those of a continental crustal origin (mostly metagranitoids and meta pelites). Uncertainties on the isochron ages, initial isotope compositions ($^{176}$Hf/$^{177}$Hf and $^{143}$Nd/$^{144}$Nd ratios), and present-day bulk-rock Lu-Hf and Sm-Nd elemental and isotope compositions are reported at the $2\sigma$ level and are taken directly from the data tables provided in the respective studies. In contrast, uncertainty associated with the isochron’s initial $\varepsilon_{Hf}$ and $\varepsilon_{Nd}$ values considers the uncertainty of the CHUR value induced by the isochron’s $2\sigma$ age uncertainty as well as the $2\sigma$ uncertainty of the isochron $y$-intercept value itself. This total uncertainty is tabulated by quadratic addition of both sources of uncertainty. For the bulk-rock initial values (calculated at the isochron age), the total uncertainty is calculated by quadratic addition of the $2\sigma$ uncertainty associated with the isochron age, the present-day bulk-rock $^{176}$Hf/$^{177}$Hf or $^{143}$Nd/$^{144}$Nd ratios, and parent-daughter ratios (in cases where no uncertainty is reported on the bulk-rock $^{176}$Lu/$^{177}$Hf or $^{152}$Sm/$^{144}$Nd ratios, an uncertainty value of 0.5% was applied).

### Results

The literature search resulted in coupled Lu-Hf and Sm-Nd garnet geochronological data for 51 individual samples spread across 22 separate studies (Table 1). Of these 51 samples, 31 are classified as OEA’s with a presumed oceanic crustal provenance in their respective studies, whereas the remaining 20 are classified as other lithologies (mostly pelitic schists and metagranitoids). The lithology column in Table 1 includes the sample description taken directly from the study. To exclude samples whose Lu-Hf and Sm-Nd systematics (both elemental and isotopic) have potentially experienced post-metamorphic disturbance, the degree of concordance between the isochron initial $\varepsilon_{Hf}$ or $\varepsilon_{Nd}$ and bulk-rock initial $\varepsilon_{Hf}$ or $\varepsilon_{Nd}$ calculated at the isochron age (an approach described in the rationale above) was examined. In cases where there was a discrepancy of more than three $\varepsilon_{Hf}$ or $\varepsilon_{Nd}$ units in either the Sm-Nd or Lu-Hf data, the bulk-rock data from that sample was excluded from consideration.

In Table 1, data from these samples are provided in gray font. This treatment resulted in the bulk-rock data from three OEA and two continental crustal samples being removed from consideration. For these five samples with potentially disturbed bulk-rock Lu-Hf or Sm-Nd systematics, the isochron age and initial values are still regarded as robust. As previously explained, this is because the ability to generate an isochron with reasonable regression statistics (see Table 1) necessitates the existence of a closed system, therefore the processes that led to the disturbed bulk-rock systematics in these five samples appear to have been insufficient to disrupt the isochron systematics. As a result, the isochron initial values from these samples should still provide a representation of the Hf and Nd isotope composition of the sample at the age recorded by the isochron. A conceptual flow diagram illustrating the data selection and evaluation process is provided in Figure 1.

Data from the literature survey was used in six plots. In Figure 2, the garnet Lu-Hf isochron age is plotted as a function of the Sm-Nd age from each sample to illustrate the relationship between the dates derived from these two systems. In Figure 3, the isochron initial $\varepsilon_{Hf}$ is plotted as a function of the isochron initial $\varepsilon_{Nd}$ for each sample. The only data excluded from this plot are those from two metagranitoid samples from Seth et al. (2008), which have extreme isochron initial $\varepsilon_{Nd}$ values of $-672 \pm 17$ and $63.8 \pm 2.8$, which stand in contrast to the more...
<table>
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<th>Sample Name</th>
<th>Age (Ma)</th>
<th>Error (Ma)</th>
<th>Sm/Nd</th>
<th>Initial εNd</th>
<th>Hf Age (Ma)</th>
<th>Error (Ma)</th>
<th>Initial εHf</th>
<th>Error (Ma)</th>
<th>Sm Grade</th>
<th>Nd Grade</th>
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**Research Paper**

±Isochron MSWD: Isochron phases. Bulk-rock Sm/Nd ± 2

**Table 1: Compilation of Sm-Nd and Hf isotopic data for eclogites from the Huwan shear zone (China)**

**Results:**

- **Sm-Nd:**
  - Initial εNd ranges from -7.0 to 2.7.
  - Hf Age ranges from 3.8 to 26.76.
  - Initial εHf ranges from -0.3 to 15.6.

- **Hf:**
  - Initial εHf ranges from -7.0 to 2.7.
  - Hf Age ranges from 3.8 to 26.76.

**Discussion:**

- **Sm-Nd:**
  - The initial εNd values are lower than those of the co-existing felsic granulites, suggesting an older, more radiogenic source.
  - The Hf isotopic compositions are more variable, ranging from slightly radiogenic to slightly depleted.

- **Hf:**
  - The initial εHf values are more variable than those of the Sm-Nd system, with some samples showing significant depletion.

**Conclusion:**

- The study provides new insights into the tectonic setting and magma source of the Huwan shear zone, highlighting the complexity of the region's tectonic history.

**Figure:**

- A diagram showing the distribution of initial εNd and εHf values for the eclogites from the Huwan shear zone.

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**Note:**

- The data presented in this table are essential for understanding the tectonic evolution of the Huwan shear zone and the region it represents.

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**References:**

- Cheng et al. (2018); Eclogite from the Huwan shear zone (China)
- Cheng et al. (2013); Eclogite from the Huwan shear zone, Dabie orogen (China)
- Zhuang et al. (2017); Eclogite from the Huwan shear zone, Dabie orogen (China)
- Chen et al. (2016); Eclogite from the Huwan shear zone, Dabie orogen (China)
- Li et al. (2015); Eclogite from the Huwan shear zone, Dabie orogen (China)
Figure 3. Plot of the isochron initial $\epsilon_{\text{Hf}}$ values as a function of $\epsilon_{\text{Nd}}$ for the orogenic eclogite and amphibolite (blue) and continental (yellow) crustal samples. Individual $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ values from each sample are contained in Table 1. Sources of referenced data are indicated in the figure.
Figure 4. Plot of the position of each sample’s isochron initial $\Delta \epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ (expressed as $\Delta \epsilon_{\text{Hf}}$) relative to the terrestrial array as a function of bulk-rock Lu/Hf and Sm/Nd ratios. The $\Delta \epsilon_{\text{Hf}}$ value is calculated according to Vervoort et al. (2011), where $\Delta \epsilon_{\text{Hf}} = \epsilon_{\text{Hf}} - (1.55 \times \epsilon_{\text{Nd}} + 1.21)$. Black dots correspond to data from the orogenic eclogites and amphibolites whereas the gray dots are from continental rocks.

Figure 5. Plots of bulk-rock ratios of Sm/Nd versus Hf, Lu/Hf versus Hf, Sm/Nd versus Nd, and Lu/Hf versus Nd. Note the mixing parabolas between the mantle (M: Sm = 0.27 ppm, Nd = 0.713 ppm, Lu = 0.063 ppm, and Hf = 0.199 ppm; values are from Salters and Stracke [2004] and based on a global mid-ocean-ridge basalt data set) and crustal (C: Sm = 5.32 ppm, Nd = 25.2 ppm, Lu = 0.39 ppm, and Hf = 1.44 ppm; values are from Chauvel et al. [2009] and based on analysis of a subduction trench-bound sedimentary pile) end members with composition fit to the form of the data field defined by the metamorphic rocks. However, a modified set of mantle (M': Sm = 1.2 ppm, Nd = 2 ppm, Lu = 0.8 ppm, Hf = 0.625 ppm) and crustal (C': Sm = 6.56 ppm, Nd = 40 ppm, Lu = 0.4 ppm, Hf = 12.5 ppm) end members must be used to encompass the entire data field. Black dots correspond to data from the orogenic eclogites and amphibolites whereas the gray dots are from continental rocks.
Figure 6. Plots of isochron initial $\varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$ versus bulk-rock Lu/Hf and Sm/Nd ratios. Mixing lines are drawn between the same elemental compositions listed in the caption of Figure 5, whereas the $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the mantle (M) end member are 0.28328 and 0.51531 (from Salters and Stracke 2004), respectively, and are 0.282615 and 0.512336 (from Chauvel et al., 2009), respectively, for the crustal end member (C). For the M′ and C′ compositions, ratios of $^{176}\text{Hf}/^{177}\text{Hf} = 0.283125$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.511314$ were used for M′, and ratios of $^{176}\text{Hf}/^{177}\text{Hf} = 0.282195$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.51186$ were used for C′. Black dots correspond to data from the orogenic eclogites and amphibolites whereas the gray dots are from continental rocks.

Figure 7. Plot of the ratio of Lu-Hf and Sm-Nd garnet ages as a function of garnet Lu relative enrichment factor, calculated as $[({}^{176}\text{Lu}/^{177}\text{Hf})_{\text{ggt}}/({}^{176}\text{Lu}/^{177}\text{Hf})_{\text{source}}] / [({}^{143}\text{Sm}/^{144}\text{Nd})_{\text{ggt}}/({}^{143}\text{Sm}/^{144}\text{Nd})_{\text{source}}]$ where ggt denotes the garnet fraction with the highest observed $^{176}\text{Lu}/^{177}\text{Hf}$ ratio. Black dots correspond to data from the orogenic eclogites and amphibolites whereas the gray dots are from continental rocks.
$^{176}\text{Lu}/^{177}\text{Hf}$ ratio for the eclogites and amphibolites is $0.033 \pm 0.004$, and is $0.004 \pm 0.002$ for the continental rocks. The weighted average $^{147}\text{Sm}/^{144}\text{Nd}$ ratio for the eclogites and amphibolites is $0.18 \pm 0.02$, and is $0.13 \pm 0.01$ for the continental rocks. Note that the bulk-rock isotope compositions excluded from these weighted average calculations, for reasons described in the rationale above, are grayed out in Table 1. All the regressions and weighted averages were calculated using Isoplot version 3.75 (Ludwig, 2012).

**DISCUSSION**

The Hf-Nd Systematics of Globally Subducted Oceanic Crust: Relationship to the Hf-Nd Terrestrial Array

In Figure 3, several different regressions through the coupled Lu-Hf and Sm-Nd garnet isochron initial $\varepsilon_H$ and $\varepsilon_{Nd}$ values are compared with regressions corresponding to the seawater array defined by Albarède et al. (1998), the first definition of the Hf-Nd terrestrial array by Vervoort and Blichert-Toft (1999), as well as the updated Hf-Nd terrestrial array defined by Vervoort et al. (2011). An important observation is that regression 1 through the garnet Sm-Nd and Lu-Hf isochron initial $\varepsilon_H$ and $\varepsilon_{Nd}$ values closely matches the slope and $y$-intercept value for the most recent definition of the terrestrial Array (Vervoort et al., 2011) whereas regression 2, made using only the OEA data, more closely matches the earlier definition of the terrestrial array by Vervoort and Blichert-Toft (1999). Equally important is the fact that the regression made solely through isochron initial values from the metamorphic rocks with a continental crustal protolith diverges conspicuously from either iteration of the Hf-Nd terrestrial array and instead more closely matches the slope of the seawater array defined by Albarède et al. (1998), albeit with a more unradiogenic $\varepsilon_H$ $y$-intercept. The significance of these observations, as well as the fact that some of the coupled Lu-Hf and Sm-Nd isochron initial values are strongly decoupled from the terrestrial array (Fig. 3), will now be discussed.

Vervoort et al. (2011) attributed the steeper slope and more unradiogenic $y$-intercept $\varepsilon_H$ value of the more recent iteration of the Hf-Nd terrestrial array to the inclusion of samples reflective of modern continental crust as well as the use of present-day $\varepsilon_H$ and $\varepsilon_{Nd}$ values. In contrast, the earlier version of the Hf-Nd terrestrial array (Vervoort and Blichert-Toft, 1999) was constructed using calculated initial $\varepsilon_H$ and $\varepsilon_{Nd}$ values and a data set heavily weighted toward ancient sediments and Precambrian granitoids. The inclusion of the samples with Lu-Hf and Sm-Nd systematics reflecting modern-day zircon-rich continental detritus has the effect of raising the slope while decreasing the $y$-intercept of the terrestrial array because such samples have low Lu/Hf but average Sm/Nd ratios. Therefore, it is unsurprising that the regression through the garnet isochron initial $\varepsilon_H$ and $\varepsilon_{Nd}$ values that include rocks with a continental crustal protolith more closely aligns with the latest iteration of the terrestrial array (Vervoort et al., 2011), whereas the regression through only the OEA data more closely aligns with the earlier definition of the terrestrial array (Vervoort and Blichert-Toft, 1999).

Another observation from Figure 3 is that the regression made solely through the garnet Lu-Hf and Sm-Nd isochron initial $\varepsilon_H$ and $\varepsilon_{Nd}$ values from samples with a continental crustal protolith (regression 3) diverges prominently from the terrestrial array, instead defining a slope mimicking that of the seawater array defined by Albarède et al. (1998). The relatively unradiogenic $y$-intercept $\varepsilon_H$ value defined by the regression through the continental rocks is expected because of the propensity for continental crust to exhibit lower Lu/Hf ratios in comparison to their Sm/Nd ratios on account of the “zircon” effect. However, the shallow slope of the seawater array has been interpreted (e.g., Albarède et al., 1998) to reflect the presence of a zircon-free clayey component with elevated ratios of Lu/Hf compared to Sm/Nd in the nodules themselves. Such a mechanism is unlikely to be the sole cause of the shallow slope for the isochron initial values defined by the continental rocks, but it worth considering that a number of studies have now shown that certain classes of sediments (e.g., aeolian sediments; Pettke et al., 2002) have elevated Lu/Hf ratios. Therefore, it is possible that the shallow slope of the continental isochron initially reflects the addition of a component (e.g., clay) with elevated Lu/Hf ratios, but the unradiogenic $y$-intercept reflects the presence of unradiogenic material that is also characteristic of continental crust.

Another observation about Figure 3 is that some samples exhibit significant decoupling from the Hf-Nd terrestrial array, in some cases falling outside of the data compilation used by Vervoort et al. (2011) to construct the latest Hf-Nd terrestrial array. Such decoupling is equally prevalent in the OEs and continental crustal rocks, and it could reflect open-system behavior during metamorphism. The mechanisms of this fractionation will be explored in more detail in the next subsection. However, the basic observation that the coupled Lu-Hf and Sm-Nd systematics (as recorded in the isochron initial values) collectively behave as expected based on the current understanding of what controls the slope of the terrestrial array and support the validity of the approach taken in this study. It also reinforces previous suggestions (i.e., Chauvel et al., 2008; Vervoort et al., 2011) that the process of subduction itself balances the fractionated Lu-Hf and Sm-Nd isotope systematics that can develop as a result of magmatic, metamorphic, and weathering-related processes near or on the Earth’s surface. At a minimum, the data suggest that subducting oceanic crust is not contributing to the development of a reservoir composed of material that is substantially deviated from the Hf-Nd terrestrial array.

Empirical Constraints on Role of Subducted Oceanic Crust in the Terrestrial Hf-Nd Mass Balance

In Figure 4, the calculated $\Delta\varepsilon_H$ from each sample (see the results above for a description of this calculation) is shown as a function of that sample's bulk-rock Lu/Hf and Sm/Nd ratios. According to Vervoort et al. (2011), samples with positive $\Delta\varepsilon_H$ values can be viewed as being anomalously radiogenic in Hf, whereas a sample with a negative $\Delta\varepsilon_H$ value is anomalously unradiogenic in Hf. In this way, the greater a sample’s deviation from $\Delta\varepsilon_H = 0$ (either in the
positive or negative direction), the more decoupled it is from the terrestrial array. Examination of Figures 4A and 4B reveals that there is no discernible correlation between the degree of decoupling and bulk-rock Lu/Hf or Sm/Nd. A strong relationship between the degree of decoupling and the bulk-rock Lu/Hf or Sm/Nd would indicate that the decoupling mechanisms were related to preferential enrichment of either the parent or daughter element in the Sm-Nd and/or Lu-Hf bulk-rock systematics. For example, a protolith with an abundance of ancient zircon might be expected to have an anomalously unradiogenic Hf signature at the time of metamorphism as well as a low Lu/Hf ratio. The same could be true of a sample that was experiencing mass exchange with a HFSE-enriched fluid during metamorphism—if the source of the fluid is ancient material, the sample could acquire an unradiogenic Hf signature as well as a low Lu/Hf ratio.

The scenarios put forth above are but two geological examples of why a relationship between the degree of decoupling and the bulk-rock Lu/Hf and/or Sm/Nd ratios might be expected. However, the lack of such a relationship does not indicate that the Lu-Hf and Sm-Nd data cannot be explained as a function of processes known to operate during subduction metamorphism. In Figures 5 and 6, the bulk-rock Lu, Hf, Sm, and Nd concentrations as well as the isochron initial ɛ Hf and ɛ Nd values are shown on a variety of plots that also include a series of mixing lines (computed using the two-component mixing equations of Faure and Mensing, 2005) between crustal and mantle end members. One set of end members (values for the end-member compositions are provided in the captions of Figs. 5 and 6) represent the composition of crust (C) and mantle (M) estimated by Salters and Stracke (2004) and Chauvel et al. (2009). The mixing lines drawn between these two end-member compositions do lie within the field defined by the individual data points. However, it is clear from examination of the data set collected in this study that these two end-member compositions do not encompass the broad range of Lu-Hf and Sm-Nd systematics (both elemental and isotopic) displayed by the metamorphic rock samples. Therefore, a hypothetical set of crustal (C′) and mantle (M′) values was devised that satisfies the range of compositions displayed by the samples in this study.

These hypothetical compositions (provided in the captions of Figs. 5 and 6) were chosen to fit the data field defined by the samples considered in this study, but they are still consistent with crustal and mantle components. For example, the hypothetical crustal end member (C′) has an unradiogenic Hf isotope composition, a high Hf concentration, as well as elevated Sm and Nd concentrations. This would be consistent with a clay-rich sedimentary rock that also contains a high proportion of ancient zircon. Although the data points defined by the elemental systematics (Fig. 6) follow the mixing lines between the hypothetical end members, the isotopic systematics (Fig. 6) do not. This is likely the result of the fact that the sources of material from which the samples acquired their Lu-Hf and Sm-Nd isotope compositions at the time of metamorphism (for those samples that have experienced significant open-system behavior) are likely quite variable. Equally variable is the extent to which mass was lost from the sample. Therefore, it is not straightforward to model each sample’s isotopic composition as a function of its Lu/Hf or Sm/Nd. However, the data can still be used to estimate the average 176Lu/177Hf and 147Sm/144Nd ratios of globally subducted oceanic crust, which in turn can be used to understand how the subducted oceanic crust reservoir fits into the global Hf-Nd mass balance.

The weighted average bulk-rock 176Lu/177Hf and 147Sm/144Nd ratios of the OEs (see the results above for the data selection criteria) are 0.033 ± 0.004 and 0.18 ± 0.02, respectively, which are both within error of the CHUR values of 0.0336 ± 0.0001 and 0.1960 ± 0.0004 (Bouvier et al., 2008). Although the precision associated with the OEA-weighted averages is significantly lower than the CHUR value determinations, as would be expected for highly variable Lu-Hf and Sm-Nd systematics, the fact that they do produce average values within error of CHUR suggests that a reservoir composed of deeply subducted oceanic crust residing at the core-mantle boundary may be chondritic overall. As expected, the weighted average 176Lu/177Hf and 147Sm/144Nd ratios of the continental rocks (0.004 ± 0.002 and 0.13 ± 0.01, respectively) are significantly lower than those of the OEs. However, because the manner and extent to which this material gets directly transferred into the deep Earth are not well understood (e.g., by gravitationally driven process versus subduction; see Tang et al., 2015), it is not possible to understand whether it offsets the basic observation that subducted oceanic crustal material is chondritic.

A Note on the Petrological Significance of the Relationship between Garnet Sm-Nd and Lu-Hf Ages

While the Lu-Hf and Sm-Nd data in this study were compiled for the primary purpose of understanding the geochemistry of subducted oceanic crust, the data set also has implications for how Lu-Hf and Sm-Nd garnet isochron ages are interpreted. Examination of Figure 2 reveals that Lu-Hf and Sm-Nd ages are well correlated on a global scale. The regression lines through the OEs as well as the continental Lu-Hf and Sm-Nd garnet ages both yield slopes that are within error of 1, suggesting that these two systems tend to produce comparable ages regardless of the host rock’s bulk composition or crustal provenance. This is reinforced by inspection of Figure 7, which illustrates the relationship between the Lu-Hf and Sm-Nd ages as a function of the degree to which 176Lu and 147Sm are enriched in the garnet relative to the bulk rock (this is discussed in more detail in the subsequent paragraph). In Figure 7, it is clear that the majority of the Sm-Nd and Lu-Hf ages are within 10% of each other, with only a marginal number of samples producing Lu-Hf ages that are older than the Sm-Nd ages. The widespread agreement in the ages produced by both systems is likely a testament to the short time scales of garnet growth during subduction-zone metamorphism (see discussion by Dragovic et al., 2012, 2015).

The relationship between garnet Lu-Hf and Sm-Nd ages has been the subject of several studies (e.g., Lapen et al., 2003; Kohn, 2009; Bloch et al., 2015; Bloch and Ganguly, 2015; Ibanez-Mejia et al., 2016; Kylander-Clark et al., 2007), with the primary focus being on trying to understand why Lu-Hf ages are sometimes older than Sm-Nd ages for the same garnet. In these situations
(which appear to be the exception, rather than the norm), the existence of an older Lu-Hf age (relative to the Sm-Nd age) has been interpreted either as reflecting post-metamorphic diffusive equilibration or as an artifact of garnet’s much higher affinity for Lu than Sm, Nd, or Hf. While the majority of garnet Lu-Hf and Sm-Nd ages are in good agreement with one another (Figs. 2 and 7), the significance of the factors possibly responsible for their occasional decoupling can be assessed on a global scale by examination of the data set to understand if there is any systematic shift in the relationship between the Lu-Hf and Sm-Nd ages as a function of the degree to which Lu is enriched (relative to Sm) in the garnet. In practice, this “relative enrichment” factor might be determined by looking at the $^{176}\text{Lu} / ^{177}\text{Hf}$ and $^{147}\text{Sm} / ^{144}\text{Nd}$ ratios of the garnet fraction with the highest $^{176}\text{Lu} / ^{177}\text{Hf}$ ratio in comparison to the bulk-rock ratios of $^{176}\text{Lu} / ^{177}\text{Hf}$ and $^{147}\text{Sm} / ^{144}\text{Nd}$ according to the following formula: $\text{Lu enrichment factor} = \left( \frac{^{176}\text{Lu} / ^{177}\text{Hf}_{\text{bulk-rock}}}{^{176}\text{Lu} / ^{177}\text{Hf}_{\text{garnet}}^*} \right) / \left( \frac{^{147}\text{Sm} / ^{144}\text{Nd}_{\text{bulk-rock}}}{^{147}\text{Sm} / ^{144}\text{Nd}_{\text{garnet}}^*} \right)$, where $gt$ denotes the values from the garnet fraction (in a particular isochron regression) with the highest $^{176}\text{Lu} / ^{177}\text{Hf}$ ratio.

If the predominant cause for the occurrence of Lu-Hf garnet ages that are older than the garnet Sm-Nd ages relates to the existence of central garnet domains that are strongly enriched in Lu relative to Sm (e.g., Lapen et al., 2003; Skora et al., 2006), then there should be a positively sloped trend in Figure 7. However, the data do not appear to exhibit a progression toward comparatively older Lu-Hf ages at increasing Lu enrichment levels. Similarly, if the occurrence of Lu-Hf ages that are older than Sm-Nd ages is due to preferential loss of Lu relative to Hf during post–garnet growth thermal disturbances (as has been suggested by Bloch and Ganguly, 2015), then there should be a negatively sloping trend on Figure 7. However, the data do not display such a trend. Therefore, neither mechanism appears to be globally widespread. This is not to say that situations do not exist where these mechanisms are responsible for age discrepancies between the Lu-Hf and Sm-Nd systems (e.g., Lapen et al., 2003; Kohn, 2009; Bloch et al., 2015; Bloch and Ganguly, 2015; Ibanez-Mejia et al., 2016; Kylander-Clark et al., 2007). Rather, the data suggest that such situations are the exception rather than the rule and that the Lu-Hf and Sm-Nd garnet geochronometers typically yield ages in agreement with one another.

### CONCLUSIONS

Global assessment of coupled Lu-Hf and Sm-Nd garnet isochron initial $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ values in conjunction with bulk-rock Lu-Hf and Sm-Nd elemental and isotopic systematics indicates the following:

1. On a global scale, the isochron initial $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ values from OEs display evidence of open-system behavior during subduction-zone metamorphism. Because of the complex and highly variable nature of the subduction environment, it is difficult to model the extent of this open-system behavior on a global scale.

2. On average, the $^{176}\text{Lu} / ^{177}\text{Hf}$ and $^{147}\text{Sm} / ^{144}\text{Nd}$ ratios of globally subducted oceanic crust are within error of the CHUR values, suggesting that a reservoir of deeply subducted oceanic crust residing at the core-mantle boundary is largely chondritic. This simplifies global mass-balance calculations involving these isotope systems.

3. In contrast to the OEA data, Lu-Hf and Sm-Nd garnet isochron initial $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ values from continental crustal samples are significantly decoupled from the Hf-Nd terrestrial array. However, because only a small proportion of the evolved continental material represented by these samples actually remains in the mantle after subduction, it is argued that this strongly decoupled signature does not get transferred into the deep mantle.

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