Evaluation of the effects of alteration and leaching on Sm-Nd and Lu-Hf systematics in submarine mafic rocks

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Abstract

Nd and Hf isotope systematics of oceanic basaltic rocks are often assumed to be largely immune to the effects of hydrothermal alteration. We have tested this assumption by comparing Nd and Hf isotope data for acid-leached Cretaceous oceanic basalts from Gorgona and DSDP Leg 15 with unleached data on the same rocks. Hf isotope values and Lu/Hf ratios are relatively unaffected by leaching, but $^{143}Nd/^{144}Nd$ values of leached samples are significantly higher than those of unleached fractions of the same sample in most cases. Furthermore, the Sm/Nd ratios of the majority of leached samples are 10–40% greater than those of unleached samples. X-ray diffraction studies indicate that selective removal of secondary minerals, such as smectite, during the acid leaching process is responsible for the fractionation of Sm/Nd ratios. These results have implications for interpretation of the Hf-Nd isotope systematics of ancient submarine rocks (older than ~50 Ma), as (1) the age corrected $^{143}Nd/^{144}Nd$ ratio may not be representative of the primary magmatic signature and (2) the uncertainty of the age corrected εNd value may exceed the assumed analytical precision.

Keywords: Caribbean plateau; neodymium; hafnium; isotope; alteration; leaching.

1. Introduction and background

The effect of seawater alteration on Rb-Sr and U-Pb isotope systematics of submarine basalts is comparatively well established. Many studies suggest that the secondary effect of seawater interaction on Sr and Pb isotope magmatic signatures can be minimised or eliminated by using a

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simple leaching technique (e.g. Cheng, 1987; Mahoney, 1987; Staudigel et al., 1991; 1995), at least for young rocks. This involves leaching rock chips or powder in acid (typically 6N HCl), for a defined time period, with the aim of removing low-temperature secondary minerals that may mask the primary magmatic isotopic signature (e.g. Mahoney, 1997; Castillo et al., 1991; Regelous et al., 2003; Hart and Blusztajn, 2007.). Many studies attest to the effectiveness of this procedure, using the radiogenic isotope signature of minerals, such as clinopyroxene, separated from the whole rock as an independent test of a primary (magmatic), rather than secondary composition (e.g. Holm, 2002; Révillon et al., 2002; Holm and Prægel, 2006).

The Rare Earth Elements (REE), including Nd, are significantly less mobile than Sr and Pb under most geochemical conditions (Brewer and Aitken, 1989; Bau, 1991; Weaver et al., 1990), and it is often assumed that leaching samples prior to Nd isotope analysis is unnecessary. However, it has long been known that REE can be mobilised by low temperature alteration or metamorphic processes (e.g. Seyfried et al., 1978a; Ludden and Thompson, 1978, 1979; Alderton et al., 1980; Gillis et al., 1992; Ward et al., 1992; Pan et al., 1993; German et al., 1995; Staudigel et al., 1995; Smith et al., 2000). Thus, the ^{143}Nd/^{144}Nd values of altered rocks may carry an additional (non-magmatic) signature.

In this study, we compare Nd and Hf isotope data for leached and unleached samples from the ~90 Ma Caribbean plateau. We observe that the ^{143}Nd/^{144}Nd values of leached and unleached fractions of the same sample often show poor correspondence, whilst Hf data remain essentially indistinguishable regardless of whether or not the sample has been leached. Furthermore, our results reveal that whole-rock Sm/Nd ratios, essential for accurate age correction, are significantly fractionated by the leaching process despite the apparently similar geochemical behaviour of the element pair. This fractionation is due to the leaching process selectively dissolving phases with different Sm/Nd ratios to the whole rock value. These factors can affect the calculated ε_{Nd} by up to 2 epsilon units, which is substantially greater than the analytical error commonly reported for Nd isotopes (i.e. <~0.5 epsilon unit). This discrepancy is highly significant, and may impact upon previous interpretations of Nd isotope signatures in pre-Eocene submarine igneous rocks from a variety of tectonic settings.

1.1 Samples included in this study

Samples used in this study are from the Caribbean plateau, drilled during DSDP Leg 15, and from the oceanic plateaux sequences exposed on Gorgona, which has also been linked with the Caribbean plateau (Echeverría, 1980; Kerr et al., 1996; Arndt et al., 1997; Kerr, 2005). Additionally, we present data for a basalt from Site 152 in the Caribbean basin, which is derived from a flow overlying the main plateau (Diebold and Driscoll, 1999; Driscoll and Diebold 1999); this sample is thought to represent melting during a younger rifting event at 81 Ma (Edgar and Saunders, 1971; Sinton et al., 2000). The basalts, komatiites and picrites from Gorgona and basalts from DSDP Sites 146 and 151 are dated at 88–91 Ma (Kerr et al., 1996; Sinton and Duncan, 1997; Walker et al., 1999).

These rocks provide an ideal test of the mobility of Nd during sea floor alteration processes, as they have been in a submarine environment for much of their ~90 Ma history. The Leg 15 rocks currently underlie the Caribbean Sea, and the presence of interbedded marine sediments and associated marine fossils (Edgar and Saunders, 1971) indicates that the rocks were erupted in marine conditions ~90 Ma ago. The Gorgona rocks were also subaqueously emplaced (Echeverría and Aitken, 1986), but according to tectonic reconstructions, they were probably uplifted and accreted in the Mid-to-Late Eocene (Kerr et al., 2002). Nonetheless, they would have been available for interaction with seawater for at least 55 m.y.

The basalts recovered during DSDP Leg 15 are moderately to highly altered, with those from Site 146 being less altered, on average, than those from Sites 151 or 152. The Site 146 basalts consist predominantly of unaltered plagioclase laths partially surrounded by oikocrysts of clinopyroxene. Clinopyroxene is unaltered or slightly altered to Fe-oxyhydroxides along grain margins and cross-cutting fractures. In all cases the groundmass is replaced by brown clays, Fe-oxyhydroxides, and/or green mica. Basalts from Sites 151 and 152 display a greater degree of alteration, and most clinopyroxene is replaced by Fe-oxyhydroxide and brown-green clays. Plagioclase is partly seriticised and chlorite is present as a groundmass-replacing phase. Some basalts from Site 151 and 152 contain limestone inclusions, but care was taken to avoid these during sample preparation and crushing (G. Marriner, pers. com., 2003). Fractures and vesicles in all Leg 15 basalts are infilled with calcite, chalcedony and green mica.

The rocks from Gorgona are generally less altered than the Leg 15 specimens. Basalts are moderately altered, with plagioclase partially replaced by albite and clays, and some clinopyroxene replaced by Fe-oxyhydroxides. Komatiites and picrites are slightly to moderately altered. Some skeletal olivines are altered along grain margins to talc or serpentine, and clinopyroxene is partially altered to Fe-oxyhydroxide, particularly where the crystal habit is more plumose. Plagioclase is also commonly albitised. In all Gorgona rocks, the glassy groundmass is largely replaced by clays.

2. Methodology

Rocks from Gorgona were crushed in a tungsten carbide mill at the University of Leicester; the DSDP Leg 15 samples were crushed in a similar tungsten carbide mill at Royal Holloway, University of London. Where noted, sample powders were leached for one hour in hot 6N HCl, then rinsed in water purified in a Milli-Q reverse osmosis system prior to dissolution and chemical separation. For the Leg 15 samples, leachates were collected (along with the subsequent Milli-Q water rinse) for separate analysis. Nd and Hf isotope ratios were determined at the NERC Isotope Geosciences Laboratory (NIGL) and the data are reported in Table 1. Procedures used in the analysis of Nd and Hf isotopes are given in Royse et al. (1998) and Kempton et al. (2001).

Nd was run as the metal species on double Re-Ta filaments using a Finnigan MAT 262 multicollector mass spectrometer in static mode. The effect of fractionation during the run was eliminated by normalising $^{143}Nd/^{144}Nd$ to a $^{146}Nd/^{144}Nd$ value of 0.7219. Sample values for $^{143}Nd/^{144}Nd$ are reported relative to an accepted value of 0.51186 for the La Jolla Nd standard. Minimum uncertainty is derived from external precision of standard measurements that over the course of analysis average 43 ppm (2σ) for $^{143}Nd/^{144}Nd$. Within-run standard error for Hf isotope measurements is normally less than 22 ppm (2σ). Minimum uncertainties are derived from external precision of standard measurements, which average 44 ppm (2σ). Replicate analysis of our internal rock standard, pk-G-D12, over the course of analysis yielded 0.283050±12 (2σ, n=45), which is indistinguishable from our previously reported value determined by TIMS (0.283046±16, 2 σ, n=9) and PIMMS (0.283049±18, 2 σ, n=27; Kempton et al., 2000). Some of our samples have been run in duplicate or even triplicate, and the data that appear in Table 1 represent averaged analyses. In all cases, within-run precision is less than external reproducibility. The data are corrected for mass fractionation during the run by normalization to $^{179}Hf/^{177}Hf$ of 0.7325 and are reported relative to an accepted value of JMC 475 of 0.282160, as recommended by Nowell et al. (1998). Blanks are < 200 pg for Hf, and <100 pg for Nd.

Sm/Nd and Lu/Hf ratios were obtained both by isotope dilution methods on leached samples and by ICP-MS on a Perkin Elmer Elan 5000 at the University of Cardiff, Wales. For ICP analysis, 0.1g of rock powder was digested in concentrated HF. After evaporation the residue was dissolved with concentrated HNO_3, evaporated again and dissolved in 6 ml of 5M HNO_3. The sample solution was accurately made up to 50 ml with deionised water and a 2 ml aliquot was spiked with a 100 ppb solution of Re and Rh and made up to 10 ml volume. A selection of international standard reference materials was used to calibrate the instrument and W-2 was used as a drift monitor during analysis. The analytical error on both Sm and Nd analysis is likely to be in the order of 1% by ICP-MS and 0.2% by isotope dilution methods.

X-ray diffraction (XRD) analysis was carried out on both leached and unleached fractions of the same fine rock powder. Rock powders were sieved to remove the non-clay (>2µm) fraction and scans were performed on the clay fractions, which were untreated, glycolated and heated to 300° and 550°C.

3. Results

Nd and Hf isotope data for the Caribbean plateau rocks are presented in Table 1 and Figures 1 and 2. The Hf isotope values of leached and unleached samples are indistinguishable within analytical error. In contrast, Nd isotope data for leached and unleached samples display a large variation.

For the DSDP samples, measured $^{143}Nd/^{144}Nd$ isotope ratios of leached samples (filled triangles, Figure 1a) are consistently higher than unleached samples (open triangles), always by a factor well outside analytical error. In contrast, unleached samples and their corresponding leachates (grey shaded triangles) have similar $^{143}Nd/^{144}Nd$ values (Table 1). Sm/Nd ratios of leached and unleached powders from the same samples (Figure 1b) are also markedly different, with leached samples having consistently higher Sm/Nd ratios (20–95%) than unleached samples.

εNd values for these same samples show similar systematics, but the results are complicated by the Sm/Nd ratios used. In the interest of time and cost-effectiveness, it is often assumed that adequate Sm/Nd ratios for age correction of Nd isotopes for petrogenetic studies can be obtained from whole rock ICP-MS analyses, and these are generally prepared from unleached powders or rock chips. If these parent/daughter ratios are used to age correct the isotope data, significantly higher epsilon values (filled squares; Figure 1c) are calculated than when the Sm/Nd ratios are obtained from leached powders (filled triangles).

A similar pattern is seen for the Gorgona dataset. Measured $^{143}Nd/^{144}Nd$ values of leached powders are consistently higher than for unleached powders (Figure 1d), apart from samples 94-32 and 94-38, where the data are indistinguishable within analytical uncertainty. As for the DSDP dataset, it is evident that Sm/Nd ratios obtained on leached powders are typically greater than those obtained on unleached powders. Furthermore, as for the Leg 15 samples, the age-corrected values for unleached powders (open triangles; Figure 1f) show considerable deviation from those obtained on leached powders, particularly where the Sm/Nd ratio is obtained on unleached powders (filled squares, Figure 1f). Greater correspondence is observed between leached and unleached sample results (i.e. filled vs. open triangles) if the epsilon values are calculated using Sm/Nd ratios determined on the same leached powder, although some samples still differ outside of analytical uncertainty (e.g. 94-32, 94-34). Figure 3, a plot of leached and unleached $^{143}Nd/^{144}Nd$ vs. Sm/Nd for Gorgona and Leg 15 samples, clearly illustrates the reason for this: tie lines on this diagram link leached and unleached analyses of the same sample and the generally positive trends of these lines indicate that Sm/Nd values mostly increase concomitantly along with ^{143}Nd/^{144}Nd values as a result of the alteration which has been removed by leaching. Although Figure 3 is essentially an isochron plot we are not using it to determine an age or a geological process. Rather the purpose of this diagram is to illustrate why age correcting leached ^{143}Nd/^{144}Nd values with unleached Sm/Nd ratios will generally result in markedly different ε_{Nd} values than if both leached ^{143}Nd/^{144}Nd and Sm/Nd values are used in the calculation.

4. Mobility of the Rare Earth Elements and effects on ^{143}Nd/^{144}Nd

The REE form trivalent ions that stabilise by preferentially complexing with hard ligands containing highly electronegative donor atoms such as oxygen and fluorine (Wood, 1990). This accounts for their perceived resistance to alteration, metamorphism and weathering processes compared to element groups such as the Large Ion Lithophile Elements (LILE's). However, detailed studies of element profiles from a wide range of hydrothermal alteration zones, ranging from a single mineral to a regional scale, illustrate that REE can be mobilised from the host rock or mineral into the surrounding rock or fluid during hydrothermal alteration (Seyfried et al., 1978a; Ludden and Thompson, 1978, 1979; Alderton et al., 1980; Gillis et al., 1992; Ward et al., 1992; Pan et al., 1993; German et al., 1995; Staudigel et al., 1995; Smith et al., 2000). Whilst the typically low concentrations of the REE, and in particular Nd, present in seawater (i.e. 2.6×10^{-6} ppm; Piepgras et al., 1979) imply that a high water-rock ratio is required in order to create a discernable change in the REE concentration of the rock (Ludden and Thompson, 1979; Michard, 1989; Gillis et al., 1992), the subsequent scavenging of REE by precipitating secondary minerals can modify the distribution of the REE within the whole-rock system and in more extreme cases alter the whole rock REE concentration. In fact, numerous studies suggest that the REE patterns of altered rocks are principally controlled by their secondary mineral assemblages (e.g. Humphris et al., 1978; Humphris, 1984). REE mobilisation can be further enhanced through long periods of seawater exposure (Ludden and Thompson, 1979) and a rock crystallisation history that encourages the development of a glassy mesostasis (Humphris and Thompson, 1978). Perhaps surprisingly, the alteration temperature appears to exert much less control on REE mobilisation than other factors: at temperatures as low as 100°C extensive mobilisation of the REE can occur, depending on water-rock ratio and sea water exposure (Ludden and Thompson, 1979; Michard, 1989; Gillis et al., 1992).

More importantly from a petrogenetic viewpoint, the REE can be fractionated relative to each other during secondary alteration processes (Ludden and Thompson, 1979; Michard, 1989; Terakado et al., 1993; Pan et al., 1993; Poitrasson et al., 1998). This can occur during both the dissolution and the reprecipitation stages of hydrothermal alteration. Seawater typically has a Sm/Nd ratio of 0.2 (Goldberg et al. 1963; Herrmann, 1970), as opposed to 0.32 for MORB (Herrmann, 1970). Therefore, seawater-whole-rock interactions can potentially fractionate the whole-rock Sm/Nd ratio, providing equilibration can occur (Michard, 1989). Low-temperature secondary alteration minerals typically have distinct REE profiles and each will tend to preferentially fractionate different REE (Gillis et al., 1992). For example, celadonite from the Troodos ophiolite displays up to 10-fold chondrite-normalised depletion in the LREE compared to the HREE, whereas chlorite shows moderate relative enrichment in the MREE (Gillis et al., 1992).

It is commonly assumed that Nd isotopes are relatively immune to seawater alteration and even low grade metamorphism (Brewer and Aitken, 1989; Kempton et al., 2002). As such, they are often used as a geochemical tool for establishing the original magmatic signature by "seeing through" these secondary processes. While this may be possible for young rocks, our results (Figure 1) as well as previous studies (Ludden and Thompson, 1979; Michard, 1989; Terakado et al., 1993; Pan et al., 1993; Poitrasson et al., 1998) indicate that both Sm and Nd *are* mobile on a localised scale, and behave differently to one another during certain low-temperature geochemical conditions, which has profound implications for older rocks where age correction is required. This is also borne out by a series of leaching experiments on oceanic plateau basalts reported by Mahoney (1987) who found that while most basalts had the same leached and unleached ε_{Nd} values, one sample, (the most altered) increased its ε_{Nd} value by 1.5 units after leaching. Mahoney (1987) showed that this discrepancy was ultimately due to alteration and suggested this may have been caused by the addition of Nd-bearing fluid from either metalliferous sediments, a fluid contaminant from earlier lava flows or from a sediment between the lavas.

The results from our experiments which show that the Sm/Nd ratio can increase as much as 95% after only 1 hour of acid leaching are particularly surprising, as these elements have similar ionic charge and radii, and display similar behaviour under most geological processes. This implies that much of the Sm and Nd is sited in locations other than the primary rock-forming silicate minerals, such as clinopyroxene, which are resistant to this form of chemical attack. Instead, as we will show below, they appear to be selectively concentrated in low-temperature alteration minerals that have replaced glass and fine-grained minerals of the original mesostatis. These minerals can substantially fractionate the REE with respect to one another (Ludden and Thompson, 1978, 1979;

German et al., 1995; Poitrasson et al., 1995, 1998), and the variation in solubility of the low-T minerals in weak to strong acid means that the acid leachate Sm/Nd ratio will reflect this.

5. Discussion

5.1 Possible causes of Sm/Nd and $^{143}Nd/^{144}Nd$ variation after leaching

Before we can discuss which mineral(s) may be responsible for the observed shift in Sm/Nd and ^{143}Nd/^{144}Nd, we must first rule out anthropogenic factors. Contamination by drilling mud may seem like a plausible explanation for the DSDP basalts, but would obviously not be a viable explanation for the Gorgona rocks which were collected from onland exposures. Similarly, contamination during sample preparation is also an unconvincing explanation, since the initial preparation of the Gorgona and DSDP rocks took place in different laboratories using different crushing equipment. Furthermore, deep-sea manganese coatings or nodule formation can also be ruled out, as such features were not observed petrographically, and neither the Gorgona nor Leg 15 basalts show elevated levels of MnO (Hauff et al., 2000). The deviation observed in ^{143}Nd/^{144}Nd and Sm/Nd ratios is, therefore, much more likely to be attributable to the removal of a secondary mineral phase during the leaching process.

We can gain a further insight into such secondary mineral phases by an X-Ray Diffraction (XRD) analysis of the clay (<2μm) powder fraction of a subset of Leg 15 samples (Table 2; Figure 4). Figures 4a and b show XRD profiles for DSDP sample 15-151-15R-1, 110-113cm, for unleached and leached fractions, respectively. Pronounced peaks corresponding to smectite and illite/montmorillonite are present for the unleached clay fraction, but the smectite peak is completely absent in the leached clay fraction. In this sample the leaching process accounts for 63% weight loss of the <2um fraction (Table 2). A similar, albeit much less pronounced, pattern is displayed by DSDP sample 15-146-43R4, 90-93cm, where kaolinite is present in addition to smectite and illite/montmorillonite in the unleached clay fraction. Both kaolinite and smectite are completely removed by the leaching process, which accounts for 43% weight loss of the <2μm fraction.

Smectite is a common mineral phase associated with the alteration of oceanic floor basalts (Seyfried et al., 1978b; Staudigel and Hart, 1983), and many smectite-group minerals are associated with the weathering of basaltic rocks at ambient seawater temperatures (Seyfried et al., 1978b). Smectite typically forms after palagonitisation and is a common replacement product of basaltic glass. Additionally, its solubility in 6N HCl means that it will be removed during the leaching process. Although there is only very limited data available on the REE profiles of smectite formed by the alteration of basalt, several studies show that smectite is likely to display pronounced LREE enrichment (Salil et al. 1997; Bernotat et al., 2001). Removal of secondary smectite during acid leaching is therefore the most likely explanation for the observed discrepancy in Sm-Nd systematics. This is consistent with the REE data: the increase in Sm/Nd as a consequence of leaching suggests the mineral phase being leached was enriched in LREE relative to the HREE.

The higher $^{143}Nd/^{144}Nd$ ratios observed for the leached, as opposed to the unleached samples imply that the mineral phase(s) removed during the acid leaching process also have a low Nd isotopic ratio relative to the whole rock, thereby increasing the $^{143}Nd/^{144}Nd$ of the leached residue (Table 1, Figure 1). There are two possibilities for the origin of this low radiogenic isotope signature: (1), the fluid that provided the catalyst for the alteration event had a substantially lower $^{143}Nd/^{144}Nd$ isotope signature than the whole rock, or (2) the mineral phase(s) removed by leaching had a sufficiently low Sm/Nd ratio to produce the $^{143}Nd/^{144}Nd$ isotope signatures observed today through radiogenic decay of ^{147}Sm, within a suitable timeframe. The fact that the Hf isotopes are the same within error, and are essentially unaffected by the acid leaching process, suggests that we can rule out the first of these options, because this would imply that the fluids had low Nd without similarly low Hf isotope ratios, which is unlikely, given that most hydrothermal magmatic fluids plot on or close to the mantle array in Hf-Nd isotope space (van de Flierdt et al. 2007).

Modelling calculations (assuming alteration took place shortly after formation, and that this event only reduced the Sm/Nd ratios of the basalts and did not modify the magmatic $^{143}Nd/^{144}Nd$) show that $^{147}Sm/^{144}Nd$ ratios in the secondary clay minerals would have been low enough to generate the present day $^{143}Nd/^{144}Nd$ ratios in the leachates over the 90 m.y. lifetime of the basalts. It thus would appear that the most reasonable explanation for low $^{143}Nd/^{144}Nd$ in these leachates is one which involves a redistribution of Sm and Nd into different secondary phases during alteration within a few m.y. of basalt eruption and not the addition of a low $^{143}Nd/^{144}Nd$ fluid component during later alteration.

5.2 Effect of leaching on the Lutetium-Hafnium isotope system

Hafnium, one of the High Field Strength Elements (HFSE), is regarded to be comparatively immobile in aqueous fluids (e.g. Brenan et al., 1995; Stalder et al., 1998). Thus, hafnium isotope systematics are an ideal tool for characterising rocks that have experienced alteration and low grade metamorphism. By virtue of its perceived resistance to alteration, samples are not usually leached prior to Hf isotopic analysis (e.g. Kempton et al., 2000; 2002; Blichert-Toft et al., 2003; Polat et al., 2003). However, in light of the evidence presented in this study showing the susceptibility of Nd to seafloor alteration, it is important to consider whether Hf shows similar tendencies.

Measured ^{177}Hf/^{176}Hf isotope ratios and εHf for both leached and unleached DSDP Leg 15 samples are shown in Figure 2. Data for leached and unleached powders show a high degree of correspondence and plot within error of each other. This contrasts markedly with similar diagrams for the Nd isotopic system (Figure 1), where measured ^{143}Nd/^{144}Nd isotope ratios of leached samples are consistently higher than unleached samples. Hence it appears that smectite and other alteration phases that can potentially fractionate the Sm/Nd ratio, do not have a similar effect on the magmatic Lu/Hf ratio. This is also suggested by the Gorgona data (Figure 2c-e): Lu/Hf ratios for leached and unleached samples are indistinguishable from one another, and measured ^{177}Hf/^{176}Hf isotope ratios and age-corrected εHf behave in a similar fashion.

This decoupled behaviour of Sm/Nd relative to Lu/Hf may result from a combination of factors: the concentration of Hf (and Lu) in seawater is even lower than that of Nd (Hf = 8×10^{-6} ppm; Erlank et al., 1978) and thus any phases formed during alteration are not likely to significantly alter the magmatic Lu/Hf ratio. Additionally, Hf may be located in minor accessory minerals, rather than glass, where Nd is primarily located, and thus remain unaffected by smectite mineralisation and alteration. The fact that both Lu and Hf are less incompatible than Sm and Nd may also be a factor. Thus, we consider that the hafnium isotope system remains unaffected by seawater alteration, and leaching of submarine mafic rocks prior to Hf isotope analysis is probably unnecessary unless the rocks show evidence of Mn coatings.

5.3 Implications for interpretation of Hf-Nd isotope data

The observed dependency of the Nd isotopic ratio on the leaching technique employed can have a major effect on the interpretation of Hf-Nd isotope systematics, particularly for systems where the interpretation relies on comparatively subtle variations in ε_{Hf} vs. ε_{Nd}. One such area of research is that associated with mantle plumes, i.e. the origin of their source material and the implications for mantle geodynamics. For example, Kempton et al. (2000) showed that samples from Iceland and adjacent portions of the Mid-Atlantic Ridge define a field, on a plot of ^{176}Hf/^{177}Hf vs. ^{143}Nd/^{144}Nd, that is oblique to the main ocean-island basalt array and extends towards a long-term depleted, high-^{143}Nd/^{144}Nd component with higher ^{176}Hf/^{177}Hf than the N-MORB source (see Figure 5). This observation was interpreted as evidence for a depleted component that is intrinsic to the plume, i.e. not derived by interaction between the plume and the MORB-source mantle through which the plume ascended, and is consistent with other geochemical characteristics of Icelandic basalts (Fitton et al., 2003). Clearly, whether or not depleted material occurs deep within the mantle (i.e. below the MORB asthenospheric reservoir) is of importance for geodynamic models of the Earth, so it is essential that we understand the uncertainties associated with the geochemical tools we use to make this interpretation.

In common with Iceland, the Caribbean plateau is thought to represent the magmatism associated with a mantle plume (e.g. Duncan and Hargraves, 1984; Kerr, 1996, 2002; Sinton et al., 1998), and several studies have recently applied Nd-Hf isotope systematics to unravelling their petrogenesis (Geldmacher et al., 2003; Thompson et al., 2004a). In contrast to Iceland, however, the Caribbean plateau is ~90 Ma and Caribbean plateau data thus require age correction. Accordingly, Nd-Hf isotope systematics must be considered in the context of uncertainties that may be introduced by modification of the Sm/Nd ratio during seawater alteration (and subsequent sample preparation).

The Caribbean Leg 15 Hf-Nd isotope data are shown on Figure 5, and compared with a variety of MORB and OIB-related data. All three datasets, i.e. (i) both isotopes and parent daughter ratio obtained on leached powders, (ii) both isotopes and parent daughter ratios obtained on unleached powders and (iii) isotopes on leached powders but parent/daughter ratios on unleached powders, form arrays with slopes that are considerably shallower than the crust-mantle array, but the three datasets are offset from one another (Figure 5a). Whilst the data for leached and unleached powders have approximately parallel trends and display a degree of overlap, both with each other and with the mantle array, the isotopic data obtained on leached powders and age-corrected using Sm/Nd ratios from unleached powders (filled squares in Figure 5) extends to much higher εNd for a given εHf.

Depending on which dataset is used, different interpretations are possible. For the dataset in which both isotopes and Sm/Nd ratio are determined on leached powders (i.e. field surrounded by solid line in Figure 5a), the Caribbean plateau array can be interpreted as the product of binary mixing between an “enriched” plume component (C1) and a more “depleted” component (C2, Thompson et al., 2004a). This depleted end member lies within the confines of both the OIB and Iceland arrays and, thus, based solely on its Hf-Nd isotope characteristics, it cannot be unambiguously established whether it is intrinsic to the plume or derived by interaction with shallow MORB-source mantle. However, Nd isotope ratios measured on leached powder and age corrected using Sm/Nd ratios determined on unleached powders, form an array that extends into the MORB field, consistent with a MORB origin for the depleted end member. We must, therefore, conclude that for the Leg 15 data, an unambiguous solution is not possible from Nd-Hf isotope systematics alone.

The Gorgona data show similar variations (Figure 5b). Using the dataset obtained on leached samples (i.e. the field surrounded by solid line in Figure 5b), the Gorgona depleted rocks have been interpreted as evidence for the involvement of a high ε_{Hf} depleted component intrinsic to the plume, due to the lack of overlap with the Pacific MORB field (Thompson et al., 2004a). Data for unleached powders yield similar interpretations. However, if Sm/Nd ratios obtained on unleached powders (open triangles, Figure 5b) are used to age correct the isotope data, a number of the samples plot within the Pacific MORB field, giving the appearance that a MORB origin for the Gorgona rocks is likely. However, the latter is inconsistent with geological and geochemical data for these rocks, e.g. high ^{3}He, high Nb/Y for a given Zr/Y and high inferred mantle temperatures. (For detailed arguments on the plume origin of Gorgona, see Arndt et al., 1997; Walker et al., 1999; Thompson et al., 2004a; Kerr, 2005).

Thus, combining isotope data from leached powders with Sm/Nd data on unleached powders can lead to erroneous interpretations of the Nd-Hf isotope systematics of *old* submarine basaltic rocks, particularly for those with more depleted compositions. The results of our study clearly show that an internally consistent dataset where all analyses are obtained on leached sample material will be most representative of initial magmatic composition. Alternatively, obtaining all data on unleached sample powders will be similarly accurate in most cases (see Figure 5), but may yield inaccurate results for some depleted compositions (see, for example, data for sample 15-152-24R-2, 22-25 cm, Figure 5a). A possible reason for these inaccuracies may be that in a depleted sample most of the REE will initially be in interstitial glass and low-T crystallizing phases, i.e. materials that are more easily altered. For less depleted samples, more of the REE are likely to be locked up in the primary phases, like clinopyroxene, which are more resistant to alteration.

We should however emphasise that this is not a problem for young basaltic rocks where ^{143}Nd/^{144}Nd isotope ratios are not substantially affected by age correction and where Sm/Nd ratios, which have been fractionated by alteration, have not had time to significantly influence ^{143}Nd/^{144}Nd ratios. Furthermore, the fact that similar Nd-Hf systematics are observed for leached and unleached samples (when Sm/Nd is by the same method) indicates that the whole rock system is not strongly disturbed, i.e. it is almost a closed system. The problem stems from the distribution of the REE among the mineral phases within the rock sample and how sample preparation techniques can introduce a bias.

It is also important to note that if we see this sort of discrepancy for Nd isotope systematics, the problem will also exist for Rb-Sr and U-Pb, since the parent and daughter elements will also fractionate significantly into different mineral phases which may alter differently. Furthermore, the difference in mobility may be even greater, so producing accurate parent/daughter ratios may be impossible.

5.4 Implications for interpreting isotopic signatures in island arc rocks

Nd mobilisation through alteration may also be problematic for the study of island arc rocks. Coupled Hf-Nd isotope systematics are a relatively new petrogenetic tool used to investigate ancient island arc signatures, and was developed specifically because of their apparently conservative behaviour during aqueous fluid-dominated subduction zone processes (e.g. Pearce et al., 1999). Additionally, the low mobility of Hf in aqueous fluids means that Hf isotopes provide a compositional window into the mantle wedge, with minimal complications from subduction zone processes (e.g. Pearce et al., 1999, Thompson et al., 2004b). The only exception to this occurs under conditions where slab-derived sediments melt (e.g. Tatsumi, 2001). In contrast, subtle variations in the Nd isotopic signature may reflect small changes in the amount of subduction component involved (Pearce et al., 2002; Thompson et al., 2004b; see Figure 5). As this study has illustrated, however, uncertainties in the appropriate Sm/Nd ratio can lead to significant shifts in the calculated ε_{Nd}, rendering the subduction input (which primarily affects the ε_{Nd}) difficult to quantify. Fortunately, this problem may only be significant for older rocks, where uncertainties in the appropriate Sm/Nd ratio lead to greater errors in the age-corrected ^{143}Nd/^{144}Nd. Thus, we recommend that ancient and visibly altered island arc rocks intended for Nd isotope analysis are subjected to the same sample preparation procedures throughout: both isotopes and parent/daughter ratios should be obtained on either leached or unleached material, but not a mixture of both. As this study suggests that the Lu-Hf system is not susceptible to sea floor alteration processes, leaching of samples intended for Hf isotope analysis is probably unnecessary.

6. Conclusions

1. Caribbean basin basalts and Gorgona mafic rocks leached in hot 6N HCl for one hour prior to dissolution and isotopic analysis have consistently higher ^{143}Nd/^{144}Nd values and Sm/Nd ratios than those that are left unleached.
2. Consequently, age-corrected εNd values are higher for leached samples than for unleached samples. Significantly, for more enriched samples when the Sm/Nd values used to compute the epsilon values are also derived from leached samples, this difference is virtually eliminated, however, the discrepancy remains for more depleted rocks.
3. This discrepancy is likely due to the breakdown and removal of smectite, a groundmass-replacing phase that can preferentially host Nd compared to Sm.
4. ^{177}Hf/^{176}Hf isotope and Lu/Hf ratios appear unaffected by similar acid leaching procedures, and so leaching of samples for Hf isotope analysis is probably unnecessary. Hf isotopes may

therefore be more robust indicators of the primary magmatic signatures of older basaltic rocks than Nd.

5. As a consequence of this study, we recommend that all highly and moderately depleted submarine mafic rocks older than ~50 m.y., that are intended for Nd isotopic analysis, are first subjected to a 6N HCl leaching technique and that Sm/Nd ratios used to compute εNd values, are obtained on the same leached samples.

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Figure captions

Figure 1. Variation in (a) measured $^{143}Nd/^{144}Nd$, (b) Sm/Nd and (c) ε_{Nd} in leached and unleached Caribbean basin basalts from DSDP Leg 15, and (d) measured $^{143}Nd/^{144}Nd$, (e) Sm/Nd and (f) ε_{Nd} in leached and unleached basalts, picrites and komatiites from Gorgona. Note that Sm/Nd values for leached powders are unavailable for samples 94-37 and 94-38.

Figure 2. Variation in (a) measured $^{177}Hf/^{176}Hf$, (b) ε_{Hf} for leached and unleached Caribbean basin basalts from DSDP Leg 15, and (c) measured $^{177}Hf/^{176}Hf$, (d) Lu/Hf and (e) ε_{Hf} for leached and unleached basalts, picrites and komatiites from Gorgona. Note that DSDP Leg 15 leached ε_{Hf} values were computed using unleached Lu/Hf ratios, as insufficient sample material was available to reanalyse them as leached fractions.

Figure 3. Plot of Sm/Nd vs. measured $^{143}Nd/^{144}Nd$ for leached and unleached samples from Gorgona and DSDP Leg 15. Tie lines connect leached and unleached analyses for the same sample.

Figure 4. Results of X-Ray diffraction analysis for <2mm fraction of two basalts from Leg 15. Key: S - smectite, I - illite, M - montmorillonite, K - kaolinite. Note that all phases except illite/montmorillonite are removed by leaching**.**

Figure 5. Initial ε_{Nd} vs. ε_{Hf} for (a) Leg 15 and (b) Gorgona rocks compared with Galápagos (Blichert-Toft et al., 2003), ODP Hole 504B (Thompson et al., 2004a), Iceland (Kempton et al., 2000) and Pacific MORB (Chauvel and Blichert-Toft, 2001; Sims et al., 2002; Kempton et al., 2002). Solid line encloses leached data (using *leached* Sm/Nd ratios), long-dashed line encloses leached data (using *unleached*) Sm/Nd ratios and short-dashed line encloses unleached data. Mantle array from Vervoort and Blichert-Toft (1999).

Fig. 1

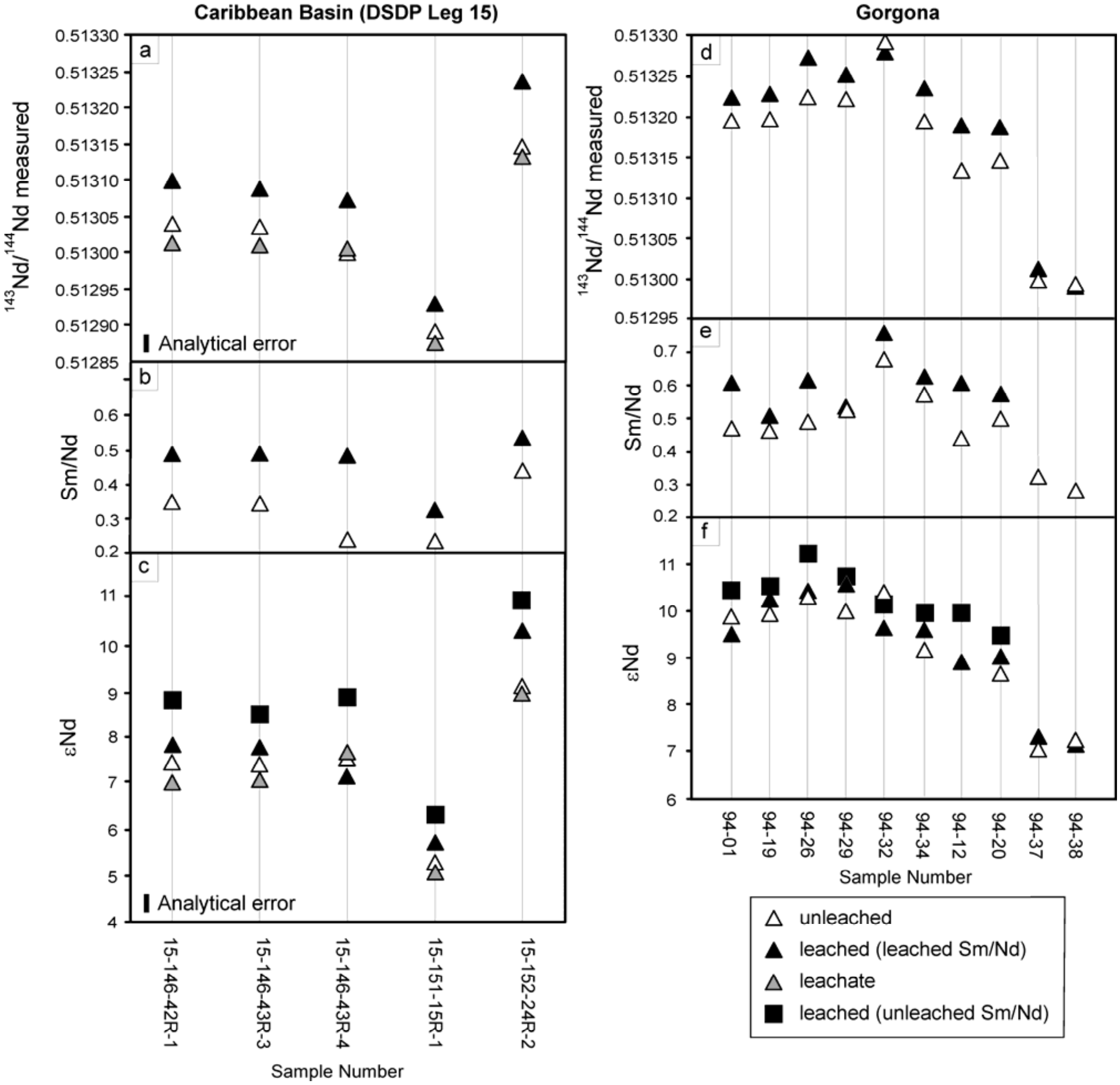

Caribbean Basin (DSDP Leg 15)
Gorgona
a
b
c
d
e
f
^{143}Nd/^{144}Nd measured
Sm/Nd
εNd
0.51330
0.51325
0.51320
0.51315
0.51310
0.51305
0.51300
0.51295
0.51290
0.51285
0.7
0.6
0.5
0.4
0.3
0.2
11
10
9
8
7
6
5
4
Analytical error
Analytical error
15-146-42R-1
15-146-43R-3
15-146-43R-4
15-151-15R-1
15-152-24R-2
94-01
94-19
94-26
94-29
94-32
94-34
94-12
94-20
94-37
94-38
Sample Number
Sample Number
△ unleached
▲ leached (leached Sm/Nd)
▲ leachate
■ leached (unleached Sm/Nd)

Fig. 2

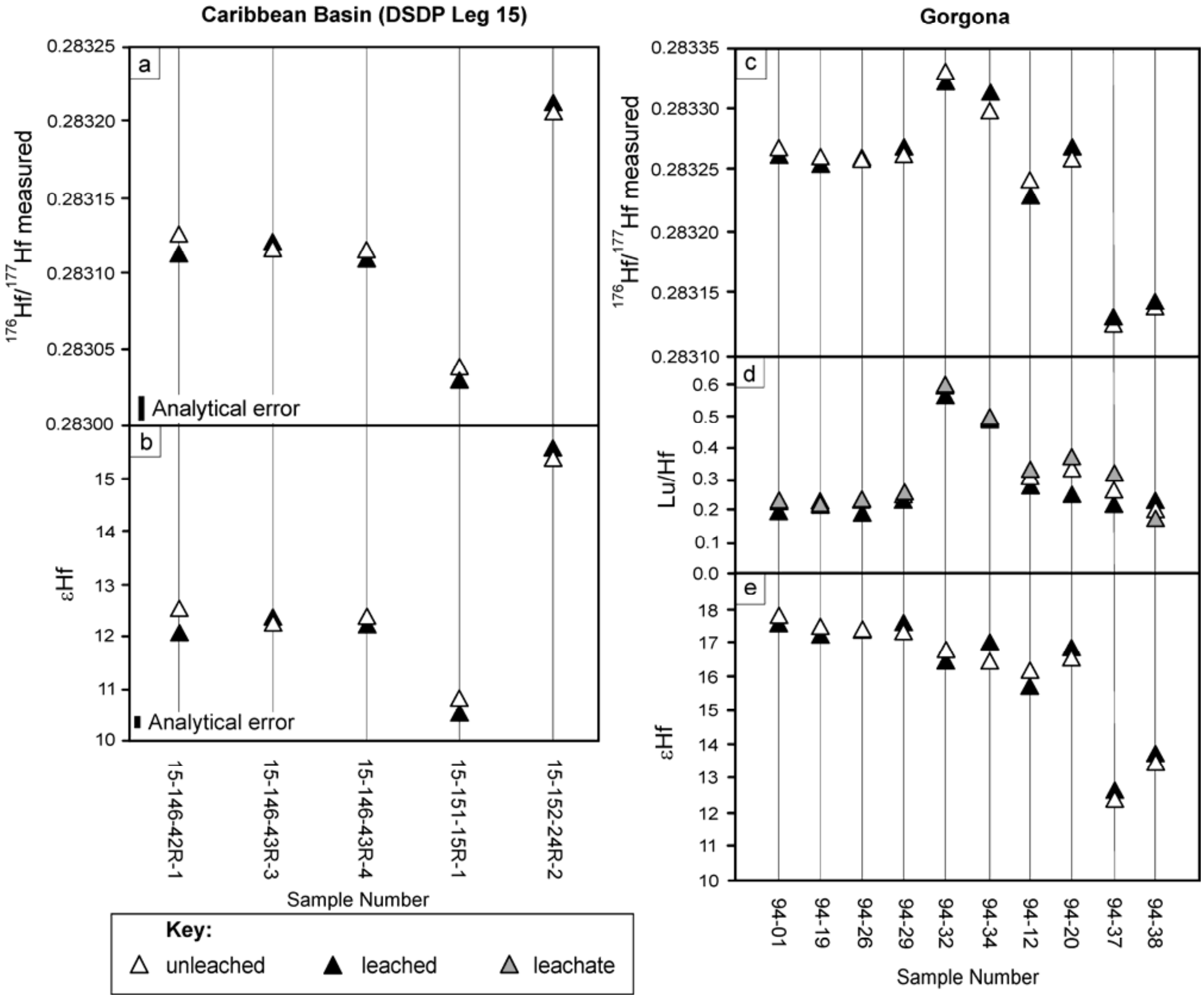

Caribbean Basin (DSDP Leg 15)
Gorgona
a
b
c
d
e
^{176}Hf/^{177}Hf measured
εHf
Lu/Hf
0.28325
0.28320
0.28315
0.28310
0.28305
0.28300
15
14
13
12
11
10
0.28335
0.28330
0.28325
0.28320
0.28315
0.28310
0.6
0.5
0.4
0.3
0.2
0.1
0.0
18
17
16
15
14
13
12
11
10
Analytical error
Analytical error
15-146-42R-1
15-146-43R-3
15-146-43R-4
15-151-15R-1
15-152-24R-2
94-01
94-19
94-26
94-29
94-32
94-34
94-12
94-20
94-37
94-38
Sample Number
Sample Number
Key:
△ unleached
▲ leached
▲ leachate

Fig. 3

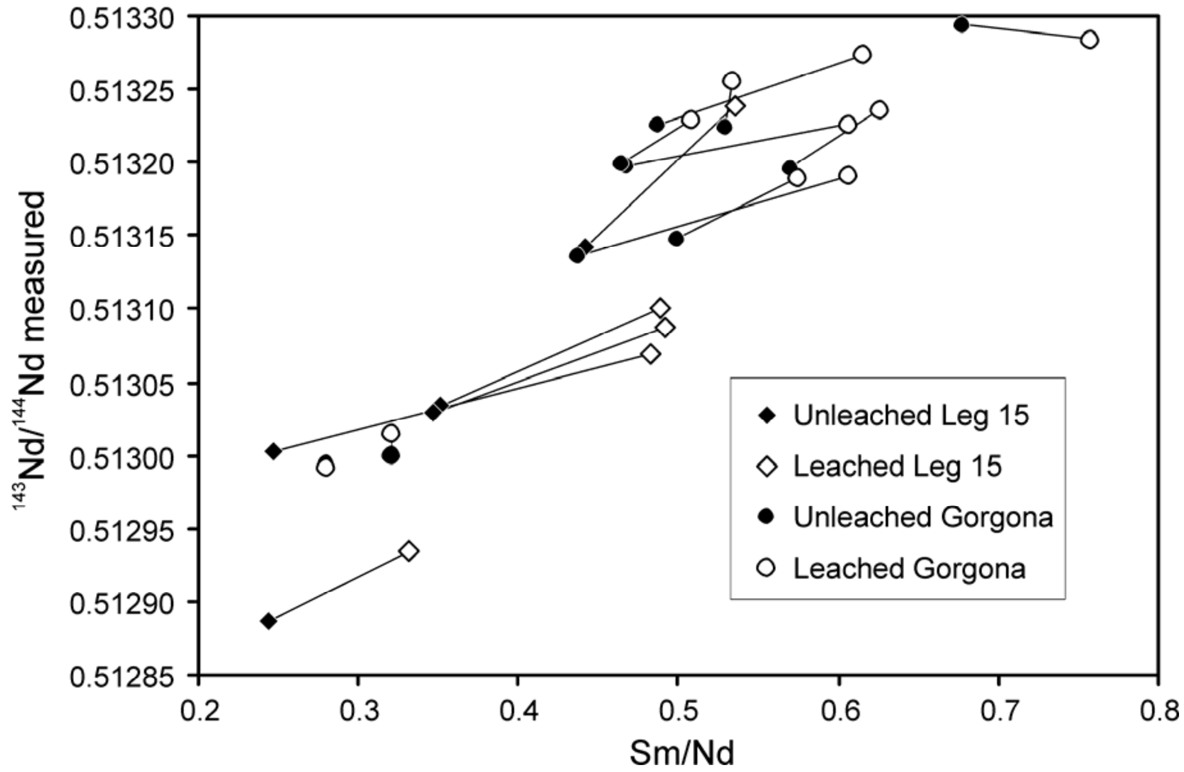

0.51330
0.51325
0.51320
0.51315
0.51310
0.51305
0.51300
0.51295
0.51290
0.51285
^{143}Nd/^{144}Nd measured
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Sm/Nd
◆ Unleached Leg 15
◇ Leached Leg 15
● Unleached Gorgona
○ Leached Gorgona

Fig. 4

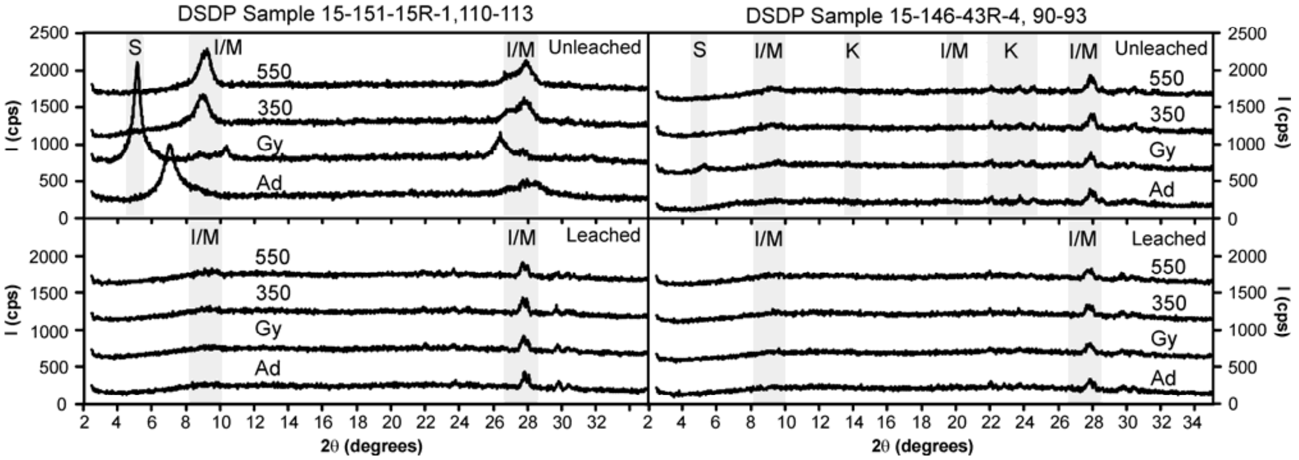
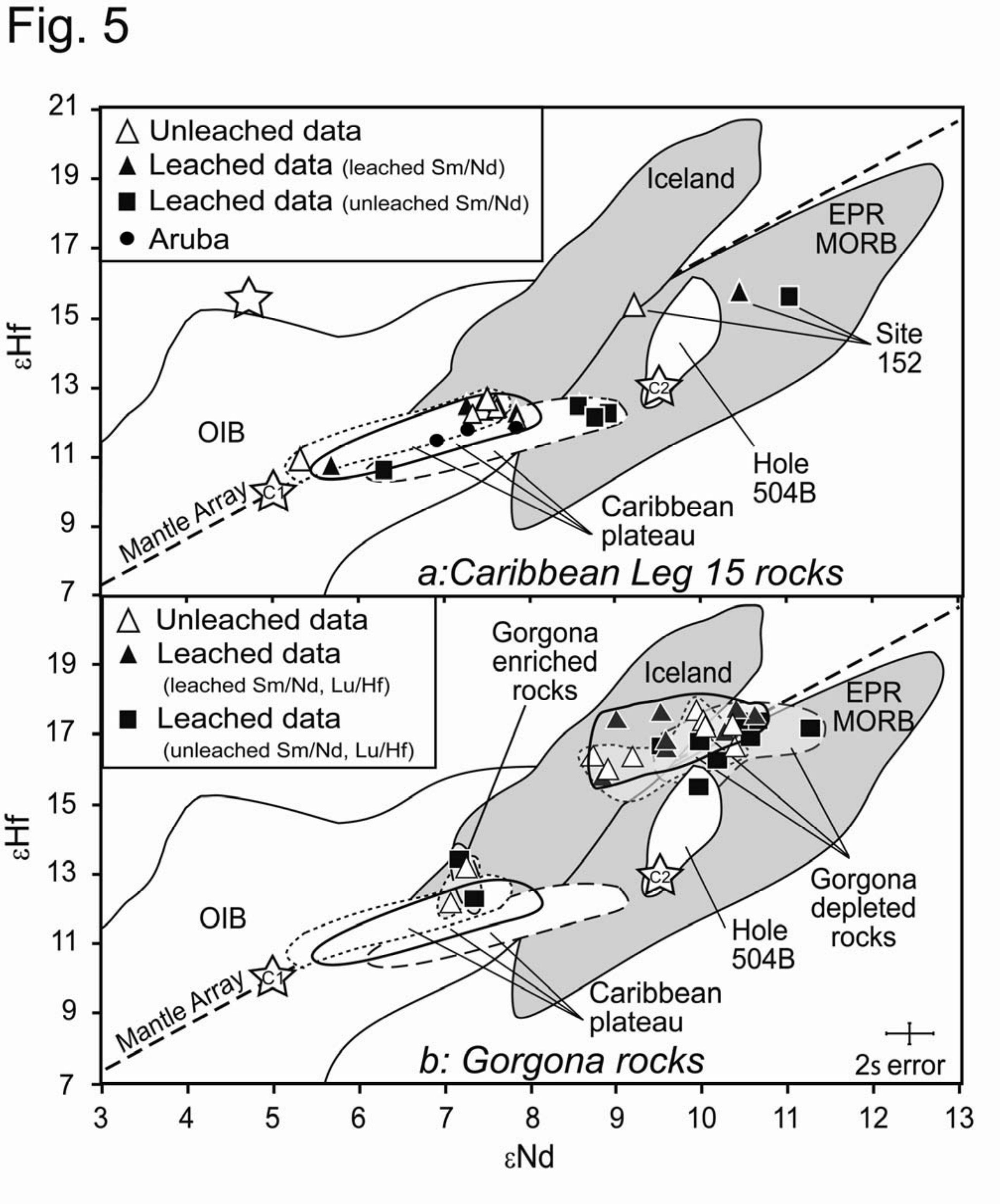

DSDP Sample 15-151-15R-1,110-113
DSDP Sample 15-146-43R-4, 90-93
S
I/M
K
Unleached
Leached
550
350
Gy
Ad
I (cps)
2θ (degrees)
0
500
1000
1500
2000
2500
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34

Fig. 5


△ Unleached data
▲ Leached data (leached Sm/Nd)
■ Leached data (unleached Sm/Nd)
● Aruba
Iceland
EPR MORB
Site 152
C2
Hole 504B
OIB
C1
Mantle Array
Caribbean plateau
a:Caribbean Leg 15 rocks
△ Unleached data
▲ Leached data (leached Sm/Nd, Lu/Hf)
■ Leached data (unleached Sm/Nd, Lu/Hf)
Gorgona enriched rocks
Iceland
EPR MORB
Gorgona depleted rocks
Hole 504B
OIB
C1
C2
Mantle Array
Caribbean plateau
b: Gorgona rocks
2s error
εHf
7
9
11
13
15
17
19
21
εNd
3
4
5
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10
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12
13

Table 1. Nd and Hf isotope and trace element data for the Caribbean plateau, showing leached, unleached and leachate data.

		unleached						leached						(unleached Sm/Nd)	leachate				
Rock	**Sample #**	**age (Ma)**	**Sm**	**Nd**	**Sm/Nd**	**measured $^{143}Nd/^{144}Nd$**	**initial $^{143}Nd/^{144}Nd$**	**εNd**	**Sm ppm**	**Nd ppm**	**Sm/Nd**	**$^{143}Nd/^{144}Nd$**	**εNd**	**initial $^{143}Nd/^{144}Nd$**	**εNd**	**weight loss during leaching**	**calculated Sm/Nd ratio of leachate**	**leachate $^{143}Nd/^{144}Nd$**	**initial $^{143}Nd/^{144}Nd$**	**εNd**
DSDP Site 146 basalt	**15-146-42R-1, 29-32**	88	2.26	6.43	0.35	0.513034	0.512912	7.51	1.32	2.71	0.49	0.513100	7.86	0.512930	8.80	*0.50*	0.21	0.513013	0.512965	8.55
DSDP Site 146 basalt	**15-146-43R-3, 33-36**	88	2.12	6.11	0.35	0.513029	0.512908	7.44	1.22	2.49	0.49	0.513087	7.60	0.512916	8.57	*0.50*	0.20	0.513013	0.512963	8.51
DSDP Site 146 basalt	**15-146-43R-4, 90-93**	88	2.12	8.60	0.25	0.513002	0.512916	7.60	0.92	1.91	0.48	0.513069	7.30	0.512901	8.91	*0.50*	0.01	0.513008	0.512926	7.79
DSDP Site 151 basalt	**15-151-15R-1,110-113**	88	5.94	24.34	0.24	0.512886	0.512801	5.35	2.58	7.79	0.33	0.512935	5.71	0.512820	6.31	*0.50*	0.16	0.512873	0.512843	6.16
DSDP Site 152 basalt	**15-152-24R-2, 22-25**	75	3.05	6.91	0.44	0.513143	0.513012	9.14	1.60	2.98	0.53	0.513239	10.47	0.513080	11.01	*0.50*	0.35	0.513136	0.513108	11.02
Gorgona komatiite	**GOR 94-01**	88	1.38	2.95	0.47	0.513197	0.513034	9.90	0.92	1.51	0.61	0.513226	9.52	0.513015	10.47	0.16	0.44			
Gorgona komatiite	**GOR 94-19**	88	1.22	2.63	0.46	0.513199	0.513037	9.96	1.08	2.12	0.51	0.513229	10.25	0.513052	10.55	0.42	0.43			
Gorgona komatiite	**GOR 94-26**	88	1.19	2.44	0.49	0.513226	0.513056	10.33	0.83	1.34	0.62	0.513274	10.39	0.513059	11.27	0.10	0.47			
Gorgona komatiite	**GOR 94-29**	88	1.26	2.38	0.53	0.513224	0.513040	10.01	1.31	2.45	0.53	0.513255	10.58	0.513069	10.61	0.80	0.51			
Gorgona picrite	**GOR 94-32**	88	0.59	0.87	0.68	0.513294	0.513058	10.36	0.42	0.55	0.76	0.513283	9.61	0.513019	10.15	0.12	0.67			
Gorgona picrite	**GOR 94-34**	88	0.90	1.58	0.57	0.513196	0.512998	9.19	0.41	0.66	0.63	0.513236	9.59	0.513018	9.97	0.20	0.56			
Gorgona depleted basalt	**GOR 92-12**	88	2.31	5.28	0.44	0.513135	0.512983	8.90	1.15	1.89	0.61	0.513191	8.84	0.512980	9.99	0.44	0.31			
Gorgona depleted basalt	**GOR 92-20**	88	1.74	3.49	0.50	0.513147	0.512973	8.71	0.80	1.40	0.57	0.513188	9.00	0.512988	9.51	0.28	0.47			
Gorgona enriched basalt	**GOR 94-37**	88	2.40	7.48	0.32	0.513000	0.512888	7.05	1.38	3.76	0.32	0.513014	7.02	0.513014	7.33	0.48	0.32			
Gorgona enriched basalt	**GOR 94-38**	88	2.17	7.75	0.28	0.512995	0.512898	7.23	1.31	3.59	0.28	0.512992	6.66	0.512992	7.18	0.54	0.28			

		unleached							leached					(unleached Lu/Hf)	leachate	
Rock	**Sample #**	**age (Ma)**	**Lu**	**Hf**	**Lu/Hf**	**measured $^{177}Hf/^{176}Hf$**	**initial $^{177}Hf/^{176}Hf$**	**εHf**	**Lu ppm**	**Hf ppm**	**Lu/Hf**	**measured $^{177}Hf/^{176}Hf$**	**εHf**	**initial $^{177}Hf/^{176}Hf$**	**εHf**	**weight loss during leaching**	**calculated Lu/Hf ratio of leachate**
DSDP Site 146 basalt	**15-146-42R-1, 29-32**	88	0.37	1.63	0.23	0.283126		12.58				0.283113			12.12		
DSDP Site 146 basalt	**15-146-43R-3, 33-36**	88	0.35	1.57	0.22	0.283117		12.30				0.28312			12.41		
DSDP Site 146 basalt	**15-146-43R-4, 90-93**	88	0.31	1.53	0.20	0.283116		12.42				0.283111			12.26		
DSDP Site 151 basalt	**15-151-15R-1,110-113**	88	0.36	5.39	0.07	0.283039		10.88				0.283031			10.59		
DSDP Site 152 basalt	**15-152-24R-2, 22-25**	75	0.55	2.43	0.23	0.283206		15.41				0.283212			15.62		
Gorgona komatiite	**GOR 94-01**	88	0.2	0.92	0.22	0.283268	0.283216	17.69	0.15	0.76	0.20	0.283261	17.60	0.283213	17.44	0.16	0.22
Gorgona komatiite	**GOR 94-19**	88	0.18	0.8	0.23	0.283261	0.283207	17.37	0.19	0.79	0.23	0.283254	17.04	0.283197	17.13	0.42	0.22
Gorgona komatiite	**GOR 94-26**	88	0.22	0.95	0.23	0.283260	0.283204	17.29	0.16	0.83	0.19	0.283261	17.68	0.283215	17.32	0.10	0.24
Gorgona komatiite	**GOR 94-29**	88	0.22	0.89	0.25	0.283262	0.283202	17.21	0.19	0.80	0.24	0.283269	17.57	0.283212	17.47	0.80	0.29
Gorgona picrite	**GOR 94-32**	88	0.24	0.4	0.60	0.283331	0.283186	16.64	0.20	0.34	0.57	0.283322	16.58	0.283184	16.34	0.12	0.60
Gorgona picrite	**GOR 94-34**	88	0.2	0.4	0.50	0.283298	0.283177	16.34	0.20	0.39	0.51	0.283314	16.84	0.283192	16.91	0.20	0.50
Gorgona depleted basalt	**GOR 92-12**	88	0.32	1.06	0.30	0.283241	0.283169	16.02	0.22	0.77	0.28	0.283230	15.80	0.283162	15.62	0.44	0.32
Gorgona depleted basalt	**GOR 92-20**	88	0.35	1.05	0.33	0.283260	0.283179	16.41	0.24	0.95	0.25	0.283269	17.45	0.283209	16.73	0.28	0.37
Gorgona enriched basalt	**GOR 94-37**	88	0.38	1.42	0.27	0.283124	0.283054	12.17	0.31	1.41	0.22	0.283131	12.83	0.283078	12.41	0.48	0.31
Gorgona enriched basalt	**GOR 94-38**	88	0.32	1.61	0.20	0.283139	0.283086	13.28	0.29	1.28	0.22	0.283145	13.28	0.283091	13.50	0.54	0.17

Table 2. Results of X-ray diffraction analysis for both leached and unleached fractions of two samples from DSDP Leg 15.

	15-151-15R-1,110-113	15-146-43R-4, 90-93
Unleached		
wt. % <2μm fraction	11	7
Mineralogy:		
Illite/Montmorillonite	10	57
Smectite	90	37
Kaolinite	0	6
Leached		
wt. % <2μm fraction	3	4
Mineralogy:		
Illite/Montmorillonite	100	100
Smectite	0	0
Kaolinite	0	0