Atypically depleted upper mantle component revealed by Hf isotopes at Lucky Strike segment

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Abstract:

The Earth's upper mantle is commonly depicted as a “marble cake” assemblage of a refractory component mingled with varying amounts of geochemically diverse enriched components. This depleted component controls the major element composition of Mid-Oceanic Ridge Basalts (MORBs). It has long been considered a fairly uniform reservoir, depleted by early melting and well homogenized by subsequent convective stirring. We present new Hf, Nd, Pb and Sr isotopes and trace element data for basalts from the center of the Lucky Strike segment of the Mid-Atlantic Ridge (MAR). Despite the limited size of our sampling area (1.6 km along-axis by 5 km across), these data show a large range of isotopic compositions (similar to that of the whole MAR). It has recently been shown that part of the reason for not observing more segments with correlated Hf–Nd isotope systematics may be the lack of fine-scale sampling. Our data confirm this idea and show strong correlations between all isotope ratios. The systematics of Hf–Nd isotopes in Lucky Strike basalts define an atypical correlation, distinct from the global mantle array, with an anomalously high ϵ_{Hf} for a given ϵ_{Nd} . We illustrate that this atypical trend is the signature of an ancient refractory mantle rather than the product of kinetic processes during the melting event. The existence of this mantle component at Lucky Strike allows us to discuss the structure of the upper mantle around the Azores.

Highlights

► High spatial resolution sampling of MAR segment shows small scale mantle heterogeneity. ► Samples define an atypical Hf–Nd isotope correlation, distinct from the mantle array. ► Upper mantle near the Azores hotspot contains different refractory components.

Keywords: Oceanic basalts ; Mid-Atlantic Ridge ; Lucky Strike ; Mantle heterogeneity ; Hf isotopes

26 **1. Introduction**

27 It is now well established that the upper mantle is heterogeneous (Hofmann et al., 2003). This
28 geochemical heterogeneity is evidenced by the composition of basalts which erupted along mid-
29 oceanic ridges, which reveals the existence of broad mantle isotopic domains (e.g., the DUPAL
30 anomaly (Dupré and Allègre, 1983)). Each mantle domain is characterized by its intrinsic lithological
31 and geochemical heterogeneity, suggesting different convective histories (Hamelin et al., 2011;
32 Hanan et al., 2004; Meyzen et al., 2007; Vlastelic et al., 1999). At a local scale, basalt geochemical
33 variations are interpreted toto resultfrom partial melting of a marble-cake upper mantle (Allègre et
34 al., 1984; Morgan and Morgan, 1999; Stracke et al., 2005). This geochemical heterogeneity of ridge
35 basalts has been explained by the addition of various amounts of the FOZO component (Hanan and
36 Graham, 1996; Hart et al., 1992; Stracke et al., 2005) to a uniformly depleted source (Depleted
37 MORB Mantle, DMM). This second asthenospheric component is commonly inferred to have been
38 depleted by previous melting events but subsequently homogenized by convective stirring (Zindler
39 and Hart, 1986). However, recent studies of abyssal peridotites have revealed thatdistinct ancient
40 depletion signals may still be identified in refractory mantle domains (Harvey et al., 2006; Liu et al.,
41 2008; Salters and Dick, 2002; Seyler et al., 2003; Stracke et al., 2011). This observation adds a new
42 level of complexityto the interpretation of MORB data and emphasizes the heterogeneous nature of
43 the depleted mantle.

44 Lu–Hf and Sm–Nd isotope systems have proven to be useful in tracking the signatures of ancient
45 mantle depletion (e.g., Andres et al., 2004; Graham et al., 2006; Salters et al.; Stracke et al., 2011).
46 Their parent/daughter ratios are higher in the residue than in the melt, thus developing a radiogenic
47 signature in time. The similar behavior of these two radiogenic isotope systems during mantle
48 melting results in strongly correlated $^{177}\text{Hf}/^{176}\text{Hf} - ^{143}\text{Nd}/^{144}\text{Nd}$ in oceanic basalts, the so-called

“mantle array” (Patchett and Tatsumoto, 1980). However, deviations from this basic model have long been documented, in particular for mid-oceanic ridge samples (Chauvel and Blichert-Toft, 2001; Debaille et al., 2006; Patchett and Tatsumoto, 1980; Salters and White, 1998). For example, a lack of correlation between these two systems characterizes MORBs collected between 22°N and 35°N (Debaille et al., 2006). Anomalously high values of $^{177}\text{Hf}/^{176}\text{Hf}$ for a given $^{143}\text{Nd}/^{144}\text{Nd}$ have also been measured along Mohs ridge (Blichert-Toft et al., 2005). These deviations from the mantle array model were initially interpreted as the result of isotopic disequilibrium between melts and their mantle source across the garnet-spinel transition beneath the mid-oceanic ridge (Blichert-Toft et al., 2005; Debaille et al., 2006). More recently, a systematic study of Hf-Nd isotopes in oceanic basalts has shown an array of parallel trends on a global scale (Salters et al., 2011). These authors attributed these sub-parallel arrays to the involvement of varying amounts of highly residual peridotites within the upper mantle. According to this model, the non-uniformity of the depleted component together with the lack of fine-scale sampling could explain the lack of correlation between ϵHf and ϵNd along the global mid-oceanic ridge system.

In the central part of the Lucky Strike ridge segment along the Mid-Atlantic Ridge (MAR), the exceptional sampling resolution gives an opportunity to examine the different hypotheses for Lu-Hf and Sm-Nd isotope systematics in the mid-oceanic ridge environment at a local scale. A recently published petrogenetic model for this area has shown the existence of significant geochemical variations in the Lucky Strike segment mantle source (Gale et al., 2011). Based on this study, we have selected a suite of representative samples spanning the whole range of geochemical variation and located within an 8km^2 in the central portion of the segment. The Lucky Strike segment is also proximal to, and influenced by the Azores hotspot (Dosso et al., 1999; Langmuir et al., 1997; Schilling, 1975). Therefore, our new sample collection can also provide new constraints on the origin of the geochemical anomaly associated with the Azores hot spot-MAR interaction.

2. Geological setting and small scale sampling

The area studied is located along the MAR, South-West of the Azores triple junction. Geochemical evidence together with geomorphological and geophysical characteristics demonstrate a clear plume-ridge interaction in this region (Asimow et al., 2004; Gale et al., 2011; Gente et al., 2003; Schilling, 1975). In this area, the MAR is characterized by a succession of segments bound by left-lateral, non-transform offsets. The Lucky Strike segment (fig. 1) is 60 km-long and bound by non-transform discontinuities at 37°00'N and 37°35'N. It is a slow ridge segment characterized by a full spreading rate of 21 mm/yr. This segment, located south west of the Azores hotspot, is significantly shallower and volcanically more robust than other MAR segments (Cannat et al., 1999; Escartín et al., 2001). The axial lithospheric structure and composition are typical of slow spreading ridges, characterized by a well-developed, 11-12km-wide axial valley, and a deepening of 1600m of the valley floor towards the segment ends (Detrick et al., 1995) where serpentinized peridotites outcrop (Gràcia et al., 1997). The prominent seamount at the segment center (the Lucky Strike volcano) is 7km wide and 15km along axis. It is underlain by an axial magma chamber 3.4km below the seafloor (Singh et al., 2006) and hosts an active hydrothermal field at its summit (Langmuir et al., 1997). Several volcanic ridges spread north and south from this central volcano suggesting along axis diking, while magnetic data suggest that magmatic accretion in the center of the Lucky Strike segment is presently focused in a narrow graben at the top of the central volcano (Miranda et al., 2005). This area has been well studied since the hydrothermal field discovery in 1992 (Langmuir et al., 1997), with a uniquely dense sampling among slow-spreading segments; more than 200 basaltic samples have been collected with dredges, wax cores, submersibles, and other deep-sea vehicles. Sample distribution along the segment is uneven, with the highest density on the central volcano. We report here new Sr, Nd, Pb and Hf isotopic data for 18 samples collected there during the

Graviluck06 and Bathyluck09 cruises (Table 1), using the Nautilie submersible (IFREMER) and Remotely Operated Vehicles (Victor; Figure 1).

3. Analytical methods

Trace elements were measured using the Brucker 820 ICP-MS quadrupole instrument at the Laboratoire de Planétologie et de Géodynamique in Nantes. Dissolutions were performed on 50 mg of sample at a temperatures of 120°C for 12 hours in 1 mL 8N HNO₃ and 0.5 mL ~23N HF. Samples were evaporated to dryness at 80°C, then re-dissolved in 2mL 8N HNO₃ and re-evaporated. The final dissolution was made in 4 mL 4N HNO₃ before a 1:5000 dilution in 0.3N HNO₃. Ge, Rh, In, Tm and Bi were used for internal standard normalization and the following standards were used for calibration curves: BHVO-2, W2, DNC-1, BIR-1 and the LDEO (Columbia University) in-house standard Mid-Atlantic Ridge basalt MAR. The LDEO in-house standard K1919, collected from the same lava flow as BHVO-1, was also analyzed several times within each analytical run to correct for instrumental drift. The continental basalt reference material BR, from the CRPG Nancy was analyzed several times to test our analytical reproducibility. All data are reported in table 1.

For isotope measurements, powdered samples (400-700 mg) were dissolved in Savillex vials with concentrated HF-HBr ultrapure acids (3:1 in volume). Pb, Hf, Sr and Nd were separated from the same dissolution using four different columns starting with Pb to minimize contamination. The Pb extraction technique used was from (Manhes et al., 1978), using HBr 0.5M and HCl 6M on AG 1-X8 anion resin. Pb blanks measured using this procedure were < 100 pg, and thus are negligible relative to the amount of sample analyzed. The effluent containing Hf, Sr and the rare earths were evaporated and taken up in 6M HCl, evaporated again and taken up in 1 ml of 0.5M HCl/0.15M HF. It was then ready to pass through an AG 50-X8 cation column (microcolumn Savillex, 30 ml, 6.4mm ID x 9.6mm OD x 25 cm). The first 6 mls containing the Hf-Ti fraction were eluted in 0.5M HCl/0.15M

HF. The rest of the elution was completed using 3M HCl to separate Rb from Sr and 4M HNO₃ to separate Ba from rare earths. Nd was separated from Ce and Sm using 0.2M HCl and 0.35M HCl on a 0.8x4cm Biorad column loaded with LN Eichrom resin. The Hf-Ti fraction was evaporated and taken up in 6M HCl with a few µl of H₂O₂. It was loaded on a column made of a pipette tip filled with 100 mg of LN Eichrom resin. Ti was first eluted with 10ml 6M HCl with 50µl of H₂O₂ and Hf was collected in 5 ml of 2M HF.

Sr isotope ratio measurements were carried out by thermal ionization mass spectrometry using a Finnigan Mat26x and a Thermo Finnigan Triton. Compositions were normalized for instrumental mass fractionation relative to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. $^{87}\text{Sr}/^{86}\text{Sr}$ of the NBS987 Sr standard during the course of the analyses yielded 0.710235 ± 45 (n=4, 2σ) for the MAT26x and 0.710255 ± 20 (n=2) for the Triton. Isotopic compositions of Hf and Pb were measured at Ifremer, Brest, using a MC-ICPMS Neptune. Repeat measurements of the Hf isotope standard JMC 475 (Denver) during the course of the analyses yielded $^{176}\text{Hf}/^{177}\text{Hf} = 0.282145 \pm 13$ (n=8, 2σ). The results were normalized to the value of 0.282158 using $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ for mass fractionation correction. The Pb isotope data are reported relative to published values for NBS 981 (Catanzaro et al., 1968). The samples were spiked with thallium to correct for mass fractionation. Based on repeated runs of NBS 981, the estimated external precision for Pb analyses is $\pm 0.02\%$, 2σ for $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ and $\pm 0.03\%$, 2σ for $^{208}\text{Pb}/^{204}\text{Pb}$. During the course of the analyses, 10 replicates of the Pb isotope standard NIST981 gave an average of 16.930 ± 0.003 (2σ) and 15.482 ± 0.003 (2σ) and 36.668 ± 0.008 (2σ) for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ respectively. Isotopic compositions of Nd were measured at Institut Universitaire Européen de la Mer, Brest, using a Thermo Finnigan, Triton. The measurements were carried out in static mode. All Nd data are fractionation corrected to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. During the course of the study, analyses of the La Jolla standard were performed and gave an average of $^{143}\text{Nd}/^{144}\text{Nd} = 0.511843 \pm 4$ (n=4 2σ).

Using the same analytical method, BCR-2 gave values of $^{176}\text{Hf}/^{177}\text{Hf} = 0.282861 \pm 9$, $^{206}\text{Pb}/^{204}\text{Pb} = 18.7496 \pm 7$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.6175 \pm 7$, $^{208}\text{Pb}/^{204}\text{Pb} = 38.7291 \pm 21$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.705008 \pm 8$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.512629 \pm 8$.

4. Results, geochemical variations in Lucky Strike basalts

The Lucky Strike segment contributes to the definition of the general geochemical gradient South of the Azores (Dosso et al., 1999; Gale et al., 2011; Langmuir et al., 1997; Schilling, 1975). Samples from this area have long been characterized as enriched in incompatible elements compared to normal-MORB with $\text{La}_\text{N}/\text{Sm}_\text{N}$ and $\text{K}_2\text{O}/\text{TiO}_2$ ratios higher than 1.25 and 0.11 respectively. Our data are in good agreement with this first order observation. Lucky Strike samples show varying levels of incompatible element enrichment, with a bi-modal distribution of $\text{K}_2\text{O}/\text{TiO}_2$ ratios (Fig. 2a). We have defined two different groups named “transitional-MORB” ($0.11 < \text{K}_2\text{O}/\text{TiO}_2 < 0.25$) and “enriched-MORB” ($\text{K}_2\text{O}/\text{TiO}_2 > 0.25$), consistent with the definitions in Gale et al. (2011). These two groups also show different petrographic characteristics: transitional-MORB samples are fresh aphyric basalts, whereas enriched-MORB samples are slightly altered vesicular basalts with plagioclase (0-20%) and olivine (0-3%) phenocrysts. Groundmass textures are microcrystalline for E-MORB samples and vary from microcrystalline to glassy for T-MORB samples.

Basalts from the transitional group are found throughout the segment whereas enriched basalts are found almost exclusively in the center. Our samples were recovered solely in the central part of the segment within an area of less than 8 km^2 . They display $1.25 < \text{La}_\text{N}/\text{Sm}_\text{N} < 2$ typical of transitional MORB (9 samples) and $\text{La}_\text{N}/\text{Sm}_\text{N} > 2$ typical of enriched MORB (9 samples) showing therefore the entire range in incompatible element enrichment previously reported for the whole Lucky Strike segment (Gale et al., 2011) (Fig. 2a). Figure 2b presents the REE patterns normalized to chondritic CI values for both groups of samples. Transitional samples are characterized by relatively flat REE

patterns with slight enrichments in light REE, whereas enriched samples have marked enrichments in light REE (60-70x chondrites) and show slight fractionations between middle and heavy REE. It is worth noting that samples from the Eastern slopes of the central volcano and from the Eastern axial valley wall (named GRA-Nxx) show the same range of variation as that from samples collected exclusively on the summit of the Lucky Strike volcano (named B09-ROCxx). This indicates that the patterns described here do not reflect a temporal variability of basalt compositions at time scales of about 500 ka (spreading age of the sample furthest from the axis) or less. Sr, Nd and Pb isotopes show variations that are in good agreement with previous data from this ridge segment (Gale et al., 2011). The most enriched samples exhibit coherent, more radiogenic Pb, Sr and less radiogenic Nd than the intermediate group (fig. 4). In binary isotope diagrams, Lucky Strike samples plot along mixing lines between a depleted mantle component and an enriched component attributed to the Azores hotspot. In these isotopic dimensions, even the less enriched samples from Lucky Strike are significantly more enriched than the DMM, which agrees with their major and trace element compositions. A simple mixing model between the DMM (Salters and Stracke, 2004) and the Azores mantle (Beier et al., 2007) reproduces the variations in $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$ and ϵNd , $^{87}\text{Sr}/^{86}\text{Sr}$.

Our new dataset shows a range of values from $\epsilon\text{Hf} = +14.3$ to $+22.1$, comparable to values previously reported in ridge segments immediately South and North of Lucky Strike (Agranier et al., 2005; Chauvel and Blichert-Toft, 2001). Despite the limited spatial extent of our sampling area, the new data show a range of variation that is of the same order of magnitude as that reported for the entire MAR (Agranier et al., 2005; Andres et al., 2004; Debaille et al., 2006). It is worth noting that the transitional group extends towards a more radiogenic ϵHf end-member in the Hf-Nd isotopic diagram and therefore plots above the mantle array. In contrast, in the same diagram, the enriched group extends toward a lower ϵHf end-member and plots near the Azores isotopic field, below the mantle array (fig. 5). The positive correlation between ϵHf and ϵNd agrees with the expected

coherence of Sm-Nd and Lu-Hf isotopic systems during magmatic processes, albeit with an unusual slope compared to that of the mantle array (Fig. 5). Compared to other isotopic systems, the systematics of Hf isotopes in this region of the MAR are still poorly known (fig. 3), and the Hf isotopic ratios reported here are the first for the Lucky Strike segment. Basalts collected along the MAR between 46° to 35°N reveal a comparable slope, however, (Agranier et al., 2005; Chauvel and Blichert-Toft, 2001; Dosso et al., 1999; Salters et al., 2011; Yu et al., 1997) which is strikingly different from the Nd-Hf correlation observed along other regions of the MAR (Fig. 5). The Hf versus Sr isotope diagram shows a similar abnormal correlation compared to the rest of the MAR. We additionally observe that the Lucky Strike transitional end-member seems relatively radiogenic in Pb isotopes ($^{206}\text{Pb}/^{204}\text{Pb} > 19.35$) compared to the classical depleted mantle (Salters and Stracke, 2004) ($^{206}\text{Pb}/^{204}\text{Pb} \approx 18.20$) (Fig. 5a).

This unusual isotopic signature is however not unique in MORB, having been detected, for example, in basalts from Mohns Ridge (fig. 6). The most depleted samples from this northern Atlantic ridge show values of ϵHf for a given ϵNd to be very similar to those of Lucky Strike samples (Blichert-Toft et al., 2005) (Fig. 6). However, important differences exist between the two zones: (i) Mohns Ridge samples define a hyperbolic ϵHf - ϵNd array instead of the linear Lucky Strike trend (Blichert-Toft et al., 2005), (ii) values of Pb isotopic ratios in depleted Mohns Ridge samples are unradiogenic ($^{206}\text{Pb}/^{204}\text{Pb} \approx 17.95$) and (iii) a geographical trend is present along Mohns Ridge, whereas the Lucky Strike variability is observed within a small ($< 8 \text{ km}^2$) area on axis, and reproduced in basalts from other segments in the 45-35°N MAR region near the Azores.

5. Discussion

5.1 Significant geochemical variations in basalts at local scale.

5.1.1. Small scale mantle heterogeneities or disequilibrium melting?

At this fine sampling scale, it is important to investigate whether the geochemical variations observed in basalts are the result of mantle heterogeneity or if they are produced by kinetic processes during melting. Early studies have commonly observed a wide range of ϵ_{Hf} in MORB for a given ϵ_{Nd} , leading to the hypothesis that melts may not be isotopically equilibrated with their peridotitic sources (Blichert-Toft et al., 2005; Debaille et al., 2006). According to this hypothesis, a highly variable Hf isotope dataset may result from the disequilibrium melting of a garnet-bearing peridotite in which the individual mineral phases are not in isotopic equilibrium (Blichert-Toft et al., 2005; Debaille et al., 2006). Because garnet incorporates Lu preferentially over Hf, it could develop a time-integrated signature with elevated ϵ_{Hf} values. Preferential melting of garnet would therefore likely produce highly radiogenic Hf values in basalts. Hf^{4+} is expected to possess a lower diffusion coefficient than Pb^{2+} and Nd^{3+} , which could explain why this element would be more sensitive to this kinetic process. If the isotopic composition of a particular mineral phase dominates the isotopic composition of the generated melt, variable ϵ_{Hf} compositions in MORB may be generated from a single mantle domain during the current melting event below the present-day ridge. In this hypothesis, the local depleted mantle identified on ϵ_{Hf} diagrams (fig. 5) may not correspond to a real end-member, but may instead result from a deviation toward radiogenic ϵ_{Hf} values due to kinetic processes during mantle melting. This disequilibrium melting hypothesis has been proposed to explain the high ϵ_{Hf} component found along Mohs and Knipovich ridges (Blichert-Toft et al., 2005) (fig. 6), and to explain the lack of correlation between ϵ_{Hf} and other isotopes systems along the MAR between 22 and 35°N (Debaille et al., 2006).

Several arguments lead us to rule out this kinetic hypothesis as the cause of observed ϵ_{Hf} variations at Lucky Strike. A primary line of evidence stems from the good correlation between ϵ_{Hf} and other isotopic systems, which is not expected if kinetic processes influenced this isotopic ratio. An assumption of the disequilibrium melting hypothesis is that partial melting takes place in presence of garnet, which is irreconcilable with geochemical characteristics of the Lucky Strike transitional basalts that do not show any fractionation between medium REE and heavy REE as would be expected if melting occurs in the garnet stability field (Fig. 2b). This conclusion is in good agreement with a recent petrogenetic model of melt supply to the Lucky Strike segment based on basalt geochemistry, indicating that melting is controlled by spinel peridotite for the transitional group (Gale et al., 2011). As recently demonstrated by Salters et al., (2011), a second line of argument against disequilibrium melting is based on experimental studies of diffusion coefficients in garnet. In this particular mineral, Dy diffusively equilibrates over 1 mm in 100,000 years at 1400°C (Van Orman et al., 2002). Even if we consider a diffusion coefficient 10 times slower for Hf^{4+} , centimeter-scale isotopic equilibrium at mantle temperatures is expected to take place over one or two million years. This equilibration time is orders of magnitude shorter than the time needed to build up a radiogenic Hf signature. Disequilibrium melting is thus not a plausible hypothesis to explain the unusually radiogenic Hf characteristic of the most depleted component along Lucky Strike.

If melting takes place at isotopic equilibrium, the Hf isotope composition of the melt is controlled by the whole rock composition of the peridotite. The presence or absence of garnet in the residual assemblage of the current melting event is therefore irrelevant and the source itself must have an anomalous isotopic signature.

5.1.2. Small scale mantle heterogeneity and efficiency of magma mixing.

Our study of a high spatial resolution dataset (<5 km) reveals the existence of incompletely mixed coexisting primary magmas in the erupted material, despite the melt lens imaged at 3.4 km below the seafloor (Singh et al., 2006). At first glance, the large variations measured in lithophile element isotopic systems are in conflict with the lack of variation in He and Ne isotopes measured on samples from the same cruises (Moreira et al., 2011). Because noble gas analyses require perfectly fresh glass, He and Ne measurements have been conducted on a slightly different subset of Gravituck06 and Bathyluck09 sampling, excluding samples from the more enriched group. This sampling bias can partly explain the observed discrepancy. However, even within the transitional group of Lucky Strike samples, Sr, Nd, Pb and Hf isotopes illustrate small variations that are not seen in He isotopes. We propose that this difference is explained by the difference of diffusivity in melt between heavy radiogenic isotopes and noble gases. The small-scale geochemical variations of trace elements and Sr, Nd, Pb and Hf isotopes indicate that neither the magma chamber nor the magmatic plumbing system totally homogenize the melts, therefore preserving, at least partially, the local mantle heterogeneity signal. These compositionally distinct liquids can be produced simultaneously if the scales of geochemical heterogeneities in a marble-cake assemblage are smaller than the melting zone. Beneath the Lucky Strike central volcano, we know that the melting column extends 80 km below the seafloor. In addition, geophysical evidence has shown that the focusing of melts toward the centers of segments is common along slow-spreading segments (Detrick et al., 1995), and thus sampling at the segment center can reflect mantle composition at a larger scale. Depending on the efficiency of along-axis melt migration, the volume of mantle tapped by the magmatic body could extend up to the whole ridge segment (70 km at Lucky Strike). This length-scale represents, therefore, an upper limit for the size of geochemical heterogeneities in the marble-cake assemblage. Within the compositional heterogeneity of the Lucky Strike dataset, the atypical Hf isotopic signature is only shown by the transitional group. This observation suggests that this mantle signature is carried by the local, more refractory, mantle component. This high ϵ_{Hf} signature is absent in Azores' islands basalts, most

likely due to the difference of lithospheric thickness between the two geological settings (> 50 km beneath São Miguel and $\approx$ 10 km beneath the ridge); continuation of melting to shallower levels beneath a thin lithosphere allows for a higher degree of melting and thus allows for a greater proportion of melts to derive from the more refractory mantle component. Our study also implies that interpretation of large-scale sampling of mantle domains using inadequate sample spacing should be approached with caution. As shown recently by Salters et al. (2011), the long believed lack of correlation between ϵHf and other isotope systems along mid-oceanic ridges is likely the result of a sampling bias and scarcity of data at a fine scale.

5.2 Origin of the mantle component with anomalous high ϵHf .

According to a recent petrogenetic model based on major and trace element compositions and Sr, Nd and Pb isotopes, the source of Lucky Strike transitional basalts (called “local DM” in figures 5, 6 and 7) results from a mixing between a DMM-like end member and a metasomatized mantle with an isotopic composition similar to Azores mantle (Gale et al., 2011). However, since the Azores lavas have a ϵHf - ϵNd composition below the mantle array, simple mixing cannot account for the high ϵHf values (+24) and relatively low ϵNd values (+10) measured in the transitional group (fig. 5).

5.2.1 Ancient, residual mantle component.

It has long been suggested that Hf-Nd isotope decoupling in the mantle source can be produced by an ancient melting event involving garnet fractionation, and subsequent melting of the resulting mantle residue (Blichert-Toft and Albarede, 1997; Chauvel and Blichert-Toft, 2001; Salters and Hart, 1989; Salters and Zindler, 1995). Because the ratio of Lu and Hf partition coefficients between garnet and a basaltic liquid ($K_{D_{\text{Grt-liq}}}^{\text{Lu}}/K_{D_{\text{Grt-liq}}}^{\text{Hf}}$) is very high (> 30), mantle residues produced by melt extraction at great depth would likely be HREE-enriched relative to Hf. An ancient partial melting event in the garnet stability field should yield a high $^{177}\text{Hf}/^{176}\text{Hf}$ signal in the residue, and the

amplitude of this signal should increase with the time elapsed since the melting event. In contrast, Sm and Nd have similar partition coefficients in garnet and spinel peridotite and ϵ_{Nd} is therefore expected to remain almost unaffected by the two different types of melting events. Given a sufficient length of time (1-2 Ga), the residual garnet peridotite should therefore develop an isotopic signature characterized by a steeper slope in ϵ_{Hf} versus ϵ_{Nd} diagram. This interpretation is consistent with the mixtures of variously-depleted mantle model proposed by Salters et al. (2011) to explain the array of sub-parallel trends of Hf-Nd isotope ratios in oceanic basalts on a global scale. According to this model, ancient residual oceanic lithosphere (ReLish, Salters et al., 2011), produced by the extraction of the crust, is recycled and mingled into the MORB and/or OIB mantle sources. Is the ReLish a possible component of the Lucky Strike mantle assemblage?

As mentioned earlier, the recently published petrogenetic model for Lucky Strike basalts (Gale et al., 2011) does not fit the unusual ϵ_{Hf} - ϵ_{Nd} correlation obtained for our samples. This model can briefly be summarized by a 2-step geochemical history: i) mixing between the DMM (90%) and the Azores mantle (10%), and ii) metasomatism by low-degree melts produced in the garnet stability field in the Azores mantle. The first step defines the regional gradient along the MAR South of the Azores, whereas the second step generates the local variability shown by transitional and enriched groups. We attempted to adjust this petrogenetic model and we replaced the DMM component with a mixture between DMM and ReLish. This latter component is highly depleted and almost completely exhausted of incompatible elements, and its signatures can easily be overpowered by a small addition of enriched components. This could explain why the influence of the ReLish component is not observed on highly incompatible isotopes system (Rb-Sr, U,Th-Pb). We have modeled the trace elements (REE+Hf) together with the Sr-Nd-Pb-Hf isotope compositions of Lucky Strike basalts. The details of the melting models are in the supplementary material and results can be seen on figure 5, 6 and 7. In this model, the ReLish component was produced 1.2 Ga ago, by a 6% melting event in the

garnet stability field, from a MORB source that has been isolated from the bulk silicate Earth reservoir for 2 Ga. We are able to reproduce the trace element and isotopic systematics of Lucky Strike basalts by a two-steps model: i) mixing of 20% of the ReLish component to a mantle assemblage of DMM (70%) and Azores mantle (10%), and ii) a metasomatism of this local Lucky Strike mantle by low-F melts produced in presence of garnet from the Azores mantle. This solution is not unique and it is possible to fit the data with a different set of parameters. For example, the mass fraction of the ReLish component is inversely proportional to its formation age: a more recent ReLish would simply imply a greater proportion in the mantle assemblage. Our goal is therefore not to quantify these melting events accurately, but rather to show that the presence of a ReLish component in the source of Lucky Strike basalts is able to produce the atypical high ϵ_{Hf} end-member (Fig. 6). The presence of such refractory component could also explain the relatively low degree of melting (7%) calculated by Gale et al. (2011) for the present day melting beneath the ridge. Although residual oceanic lithosphere material is probably a ubiquitous mantle component, due to its refractory properties, it is expected to contribute little to the observed global MORB variations.

5.2.2 Sub-continental lithospheric mantle.

A second potential candidate for the atypical source signature in Lucky Strike transitional basalts is the Sub-Continental Lithospheric Mantle (SCLM). Compositions of the SCLM are primarily based on xenolith and xenocryst samples. These samples show a large range of Hf isotopic compositions up to very radiogenic values (Simon et al., 2007). This variability in Hf isotopes is associated with less variable and less radiogenic Nd isotopic compositions. The SCLM consists mainly of ultramafic rocks, ranging from lherzolites to dunites. Despite the observed petrological diversity of this reservoir, a recent tomographic study has suggested that most Archean sub-continental lithospheric mantle originally consisted of depleted dunites and harzburgites (Griffin et al., 2009). In intraplate volcanic areas, these refractory peridotites are subsequently metasomatized and refertilized.

In xenolith datasets, the decoupling between Hf and Nd isotopes in this subcontinental reservoir has been interpreted as a result of depletion events followed by carbonatite-type metasomatism (Simon et al., 2007). This process is expected to link very radiogenic ϵHf values with relatively less radiogenic Nd and enrichment in highly incompatible trace elements, consistent with the geochemical characteristics of the transitional Lucky Strike basalts (Fig. 5).

Several studies have argued for contamination of the MORB source by either the crustal or the mantle part of the continental lithosphere (e.g. Hanan et al., 2004; Janney et al., 2005). Because the Rb/Sr ratio is very high in the continental crust, addition of this material to the depleted mantle would dramatically increase $^{87}\text{Sr}/^{86}\text{Sr}$ values. In contrast, the mantle portion of the continental lithosphere is not expected to have an exceptionally high Rb/Sr ratio and is therefore a more likely component. The presence of relics of SCLM preserved in the upper mantle in the North-central Atlantic area has been a matter of debate for the last 15 years. For example, SCLM is suspected to explain the distinctive metasomatic parageneses and garnet signature in spinel-peridotite xenoliths from Cape Verde Archipelago (Bonadiman et al., 2005). Similarly, the enriched component in the lavas from São Miguel has been inferred to contain a contribution from localized pieces of SCLM material (Madureira et al., 2011; Moreira et al., 1999; Widom et al., 1997). According to these studies, this sub-continental lithospheric mantle originally resided beneath North-western Africa or Iberia and was delaminated during rifting upon the opening of the Atlantic Ocean basin. However, based on the low ϵHf measured in lavas from Azorean islands, other studies have argued against this hypothesis (Beier et al., 2007; Elliott et al., 2007). In contrast to these studies, we propose that SCLM material is a potential candidate for the origin of the transitional group basalts, and should be seen as a possible refractory component of the mantle rather than the source of the enriched basalts. As previously discussed in §5.1.2, this is in good agreement with the fact that this signature is exclusively observed

at the ridge axis, where the shallower melting compared to Azores islands allows more refractory material to melt.

It is important to note that the geochemical composition of the SCLM remains poorly constrained. It is therefore difficult to produce an incontrovertible mixing model involving this reservoir. SCLM samples show highly heterogeneous isotopic signatures, which seems to be inconsistent with the tightly defined nature of the more depleted Lucky Strike end-member. However, based on our present day knowledge of the Hf-Nd isotope characteristics of SCLM xenoliths, the addition of this type of material to the Lucky Strike upper mantle could account for the abnormal isotopic signature of the local depleted end-member.

Distinguishing whether the abnormal Hf-Nd isotopic signature is the result of the presence of residual oceanic lithosphere previously melted in the garnet stability field (*i.e.* ReLish) (§5.2.1) or the contribution of sub-continental lithospheric mantle (§5.2.2), is not straightforward. Very ancient depleted signatures in Os isotopes have long been suggested as a characteristic of subcontinental lithospheric mantle. But recent studies of abyssal peridotites have shown a wide range of $^{187}\text{Os}/^{188}\text{Os}$ ratios at slow mid-oceanic ridge settings extending to very unradiogenic values (Liu et al., 2008). If highly depleted Os isotope signatures are not unique to the SCLM, there are no isotopic or chemical signatures that unambiguously distinguish the two proposed hypotheses.

5.3. Geodynamical implications.

We have shown that the unusual Hf isotope signature in basalts from Lucky Strike is best explained by the melting of a refractory component in the mantle near the Azores rather than by a kinetic effect during the current melting event. Even if we cannot specify whether this refractory component is a ReLish or a SCLM, we have shown that this component is mixed with the depleted mantle and the Azores mantle prior to the addition of the metasomatic agent (low-F melts derived

from the Azores; Gale et al., 2011). The existence of this component and its mixing relationship raise the question of the structure of the upper mantle around the Azores.

Since only limited data are available for Hf isotopes compared to other isotope systems, it is not possible to map precisely the extent of the particular Hf signature recognized in our local scale study. However, the Nd vs. Hf isotopes of segments North and South of the Lucky Strike segment show a similar correlation (fig. 5). The latitudinal extension of this atypical correlation is therefore at least between 46°N to 35°N, and centered at the latitude of the Azores hotspot. This along-axis extension is significantly shorter than the regional gradients defined by Sr isotopes or La/Sm ratios (Dosso et al., 1999; Gale et al., 2011; Langmuir et al., 1997; Schilling, 1975). By analogy to observations along the MAR near Ascension Island (Paulick et al., 2010), the hypothesis involving mixing between one enriched component and two different depleted components (DMM and ReLish/SCLM) is expected to produce a cloud or two different trends in Nd-Hf isotope diagrams. Since only one trend is seen from 46°N to 35°N (Agranier et al., 2005; Chauvel and Blichert-Toft, 2001; Dosso et al., 1999; Yu et al., 1997) (fig. 4), we can infer that the depleted components in the system are well homogenized.

A first possible model for the upper mantle structure in the Lucky Strike and Azores domain is that the refractory mantle component is a primary constituent of the Azores hotspot, mixing with the regional mantle (fig. 8A). In this hypothesis, this refractory component has been recycled in the asthenosphere and brought back to the surface by the hotspot. The initial depletion event could either be the result of deep ancient melting in an oceanic domain (ReLish) or of some mantle material from the base of the continental lithosphere (SCLM) which was recycled deep in the mantle.

An alternative model is an upper mantle constituted of different coexisting refractory materials prior to the arrival of the Azores plume (fig. 8B). In this hypothesis, the atypical depleted component could be a ubiquitous residual mantle component (*i.e.* ReLish) or relics of the SCLM left behind by

the North-East drifting of the African continent (fig. 8B). The presence of the particular isotopic signature in the transitional Lucky Strike samples could be the result of a change of the melting regime near the Azores (Asimow et al., 2004; Schilling, 1975). Between 46°N and 35°N, the thin lithosphere and the local increase of mantle potential temperature (Asimow et al., 2004; Schilling, 1975) (+ 35°C) associated with the thermal influence of the Azores enhances mantle melting. These pressure and temperature conditions would allow melting of the more refractory mantle identified around the Azores region. Future Hf-Nd studies along segments near Lucky Strike will provide constraints on the geographical extension of this refractory component and allow study of the along-axis evolution of its mixing proportions with the ambient mantle.

6. Conclusion

We report a strong correlation between Hf and Nd isotopic systems from MORBs within the Lucky Strike segment along the MAR, which is contrary to the commonly accepted decoupling of these systems. In good agreement with recent results by Salters et al. (2011), our results suggest that the lack of correlation between ϵHf and other isotope systems along the global mid-oceanic ridge system is the result of sampling bias. Part of the reason for not observing more segments with correlated Hf-Nd isotope systematics may be the lack of fine-scale, dense sampling. In order to discuss the origin and significance of large-scale mantle composition, alternative solutions are (i) high spatial resolution sampling of the ridge or (ii) statistical techniques such as spectral analyses (Agranier et al., 2005), where the dataset interpretation is weighted by the sampling density.

The Hf-Nd isotope correlation seen in Lucky Strike samples is significantly different from the global mantle array defined by MORB and OIB, and is characterized by an unusually high ϵHf values for a given ϵNd . In every binary isotopic plot, Lucky Strike basalts define a trend from this atypical radiogenic Hf mantle component toward the Azores enriched mantle. We have shown that kinetic

effects cannot account for the observed Hf-Nd systematics in Lucky Strike basalts and that this trend is best explained by mixing enriched and depleted components in the local mantle. If the origin of the enriched component is clearly related to the Azores hotspot, the origin of the depleted mantle source is more controversial. We propose that this unusual end-member could either indicate the presence of some residual oceanic lithosphere or some sub-continental lithospheric mantle left behind by the drifting of the African continent. At Lucky Strike, enhanced melting conditions associated with the Azores plume allow us to detect this refractory component within basalts erupted on-axis. This observation points towards the existence in the mantle of domains of refractory material that do not melt in normal mid-oceanic ridge conditions, thus contributing little to the global MORB compositions. This study emphasizes the heterogeneous nature of the depleted mantle long considered the archetype of a homogeneous mantle domain.

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Figure captions

Figure 1: Bathymetric maps of (A) the Mid-Atlantic Ridge, (B) Lucky Strike segment and (C) Arctic ridges. Locations of our new samples (square symbols) are shown together with published samples: of the entire MAR (gray circles), the Azores geochemical anomaly (yellow circles) and Mohns ridge (green triangles). Symbols are the same in all the figures, published data are from (Agranier et al., 2005), (Andres et al., 2004; Andres et al., 2002), (Blichert-Toft et al., 2005), (Castillo and Batiza, 1989), (Chauvel and Blichert-Toft, 2001), (Debaille et al., 2006), (Dosso et al., 1993; Dosso et al., 1999; Dosso et al., 1991), (Douglass et al., 1999), (Frey et al., 1993), (Fontignie and Schilling, 1996), (Hamelin et al., 1984), (Hanan et al., 1986), (Ito et al., 1987), (Machado et al., 1982), (Nowell et al., 1998), (Paulick et al., 2010), (Salters, 1996), (Schiano et al., 1997), (Schilling et al., 1994), (Shirey et al., 1987), (Yu et al., 1997).

Figure 2: A) histogram showing the bimodal distribution of Lucky Strike samples. Two distinct peaks define the two petrological groups described in this study: “Transitional” if $K_2O/TiO_2 < 0.25$ and “enriched” if $K_2O/TiO_2 > 0.25$. Data are from this study together with unpublished data (Bezou personal communication), Gale et al. (2011) and Ferreira (2006). B) Diagram showing normalized REE concentration of the two groups.

Figure 3: Geochemical gradient south of the Azores. The center of Lucky Strike segment shows a large range of geochemical variation.

Figure 4: Binary isotopic plots showing Lucky Strike data compared to previously published MAR and Azores data. Mixing models between a depleted (DMM, (Salters and Stracke, 2004)) and an enriched (Azores, Gale et al., 2011) components are shown. The chosen Azores mantle composition assumed is that of the least enriched end-member (Sete Cidades samples, Beier et al. (2007)).

Figure 5: Hf isotopes versus other isotopic systems. The model modified from (Gale et al., 2011) is shown as black lines. Small dark squares along these lines represent percentage of low-F melts additions (1% step) to the local Depleted Mantle (Local DM, see text for further explanations). Compare to the mantle array, new data from Lucky Strike segment define a trend with very radiogenic Hf composition for a given ϵNd . The same atypical correlation can be observed along the MAR in samples collected between 46 and 35°N (yellow circles).

Figure 6: Comparison between Lucky Strike data and Mohns ridge sample, previously described as geochemically abnormal with ϵHf for a given ϵNd . The same model shown in figure 5 is reported here, fractions of low-F melts added to the regional mantle are shown in percent.

Figure 7: Hf isotopes versus La/Hf, and Nd isotopes versus La/Nd. Metasomatism of the regional mantle by low-F melts allow to reproduce the geochemical heterogeneity measured at Lucky Strike.

Figure 8: Two different models for the structure of the upper mantle near the Azores. In the left column, the atypical depleted component is a primary constituent of the Azores hotspot. In the right column, this component resides in the upper mantle prior to the plume arrival.

Supplementary figure: Lu/Hf vs Sm/Nd diagram. Green and orange lines represent melting models (batch and fractional) with residual spinel and residual garnet, respectively. The black line represents low-F melts metasomatism model (see text for further explanations). The Lucky Strike abnormally high Lu/Hf ratio for a given Sm/Nd ratio is well explained by the influence of this recent metasomatism event.

Table 1: Major element, trace element and isotopes data for samples collected at Lucky Strike segment center. AII127-D15G has previously been published in Dosso et al. (1999), except new Pb

508 and Hf isotope measurements done on a MC-ICPMS at SDSU in collaboration with Barry Hanan. ^b
509 Sr isotope measured using a Thermo Finnigan Triton. ^c Sr isotope measured using a Finnigan
510 MAT26x.

511

512 **Table 1**
513

Sample	AII127- D15G	B09-ROC01	B09-ROC07	B09-ROC08	B09-ROC11	B09-ROC13
Long. (°)	-32.283	-32.282	-32.282	-32.282	-32.277	-32.276
Lat. (°)	37.291	37.284	37.291	37.291	37.297	37.299
Type	T-MORB	E-MORB	T-MORB	T-MORB	E-MORB	E-MORB
SiO ₂	51.4	49.3	51.4	51.5	48.8	50.1
TiO ₂	1.07	1.08	1.05	1.05	1.28	1.20
Al ₂ O ₃	14.7	17.0	14.8	15.1	16.4	16.7
FeO	9.8	6.4	9.9	9.5	7.5	6.8
MnO	0.18	0.12	0.18	0.19	0.15	0.13
MgO	8.1	9.4	8.0	8.2	8.2	8.5
CaO	12.1	13.9	12.2	12.4	14.1	14.3
Na ₂ O	2.2	2.3	2.3	2.2	2.4	2.3
K ₂ O	0.20	0.46	0.16	0.18	0.60	0.70
P ₂ O ₅	0.14	0.19	0.12	0.13	0.27	0.23
L.O.I.		0.25	-0.63	-0.51	0.97	0.07
Sum	99.9	101.0	100.7	101.0	101.5	102.0
La	12.45	12.45	5.74	5.74	16.59	15.58
Ce	24.49	24.49	12.32	12.32	31.36	29.74
Pr	2.94	2.94	1.71	1.71	3.65	3.49
Nd	12.35	12.35	8.04	8.04	14.99	14.15
Sm	2.75	2.75	2.39	2.39	3.19	3.11
Eu	0.98	0.98	0.89	0.89	1.11	1.07
Gd	3.19	3.19	3.27	3.27	3.70	3.55
Tb	0.50	0.50	0.58	0.58	0.58	0.55
Dy	3.07	3.07	3.88	3.88	3.56	3.41
Ho	0.63	0.63	0.85	0.85	0.75	0.72
Er	1.74	1.74	2.39	2.39	2.08	2.00
Yb	1.62	1.62	2.34	2.34	1.97	1.91
Lu	0.25	0.25	0.36	0.36	0.30	0.29
Hf	1.9	1.87	1.62	1.62	2.05	1.84
⁸⁷ Sr/ ⁸⁶ Sr	0.702945	0.703118 ^b	0.702957 ^b	0.702933 ^c	0.703109 ^b	0.703049 ^c
εNd	8.97	7.04	9.15	9.12	7.18	7.28
²⁰⁶ Pb/ ²⁰⁴ Pb	18.822	19.337	18.886	18.94	19.159	19.219
²⁰⁷ Pb/ ²⁰⁴ Pb	15.538	15.592	15.544	15.546	15.579	15.582
²⁰⁸ Pb/ ²⁰⁴ Pb	38.421	38.898	38.511	38.547	38.773	38.801
εHf	21.38	-	21.65	20.69	14.36	14.76

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Sample	B09-ROC14	B09-ROC15	B09-ROC20	B09-ROC21	B09-ROC22	B09-ROC23
Long. (°)	-32.276	-32.275	-32.280	-32.280	-32.280	-32.278
Lat. (°)	37.300	37.301	37.291	37.291	37.291	37.290
Type	E-MORB	E-MORB	T-MORB	T-MORB	T-MORB	T-MORB
SiO ₂	-	48.7	51.6	51.8	51.7	51.6
TiO ₂	-	1.01	1.06	1.06	1.05	1.05
Al ₂ O ₃	-	17.9	14.3	15.0	15.0	15.1
FeO	-	6.7	10.3	10.0	9.9	9.5
MnO	-	0.14	0.19	0.19	0.18	0.18
MgO	-	8.7	8.2	8.1	8.1	8.2
CaO	-	14.5	12.3	12.3	12.2	12.5
Na ₂ O	-	2.2	2.3	2.3	2.3	2.2
K ₂ O	-	0.41	0.16	0.16	0.16	0.18
P ₂ O ₅	-	0.18	0.13	0.13	0.12	0.13
L.O.I.	-	0.50	-0.78	-0.77	-0.77	-0.68
Sum	-	101.5	100.8	101.3	101.1	101.0
La	14.03	14.03	4.98	4.98	5.01	5.54
Ce	26.41	26.41	11.25	11.26	11.26	12.15
Pr	3.17	3.17	1.59	1.58	1.59	1.68
Nd	12.85	12.85	7.55	7.57	7.65	7.92
Sm	2.85	2.85	2.34	2.34	2.34	2.37
Eu	1.00	1.00	0.88	0.88	0.88	0.89
Gd	3.29	3.29	3.25	3.26	3.27	3.25
Tb	0.53	0.53	0.59	0.59	0.59	0.58
Dy	3.26	3.26	3.96	3.95	3.93	3.84
Ho	0.68	0.68	0.87	0.87	0.87	0.84
Er	1.90	1.90	2.46	2.47	2.45	2.37
Yb	1.83	1.83	2.45	2.46	2.45	2.34
Lu	0.28	0.28	0.38	0.38	0.38	0.36
Hf	1.69	1.69	1.59	1.59	1.58	1.61
⁸⁷ Sr/ ⁸⁶ Sr	-	0.70304 ^c	0.702915 ^c	0.702926 ^c	0.702921 ^c	0.702962 ^c
εNd	6.10	7.00	9.25	9.40	9.21	9.15
²⁰⁶ Pb/ ²⁰⁴ Pb	19.355	-	18.888	18.884	18.89	18.932
²⁰⁷ Pb/ ²⁰⁴ Pb	15.591	-	15.543	15.545	15.544	15.547
²⁰⁸ Pb/ ²⁰⁴ Pb	38.93	-	38.507	38.513	38.511	38.542
εHf	14.32	14.98	21.97	22.12	21.76	-

Sample	B09-ROC24	GRA N05-1	GRA N06-1	GRA N10-2	GRA N10-3	GRA N12-1
Long. (°)	-32.278	-32.220	-32.275	-32.237	-32.257	-32.235
Lat. (°)	37.290	37.285	37.291	37.280	37.285	37.280
Type	T-MORB	E-MORB	E-MORB	T-MORB	E-MORB	E-MORB
SiO ₂	52.1	50.4	48.1	51.7	51.0	50.3
TiO ₂	1.06	1.1	1.12	1.09	0.97	1.01
Al ₂ O ₃	15.2	18.7	17.5	15.0	16.6	16.2
FeO	9.6	5.9	6.8	9.4	7.5	7.8
MnO	0.18	0.1	0.14	0.17	0.14	0.16
MgO	8.2	6.8	8.2	8.0	8.3	8.8
CaO	12.6	14.4	15.1	12.4	13.4	13.3
Na ₂ O	2.3	2.4	2.0	2.2	2.1	2.1
K ₂ O	0.18	0.3	0.46	0.18	0.41	0.30
P ₂ O ₅	0.13	0.2	0.24	0.14	0.18	0.20
L.O.I.	-0.53	1.2	1.01	-0.26	0.21	0.53
Sum	102.1	102.1	101.5	101.2	101.6	101.5
La	5.60	8.51	14.01	6.08	11.65	8.68
Ce	12.36	16.93	27.49	13.41	22.36	17.54
Pr	1.70	2.19	3.36	1.83	2.68	2.22
Nd	8.03	9.69	13.90	8.39	11.08	9.63
Sm	2.40	2.50	3.15	2.45	2.58	2.38
Eu	0.90	1.02	1.12	0.92	0.92	0.91
Gd	3.27	3.16	3.57	3.29	3.13	2.96
Tb	0.59	0.53	0.57	0.58	0.51	0.50
Dy	3.87	3.38	3.50	3.78	3.23	3.15
Ho	0.85	0.72	0.73	0.82	0.69	0.67
Er	2.38	1.98	2.02	2.32	1.93	1.88
Yb	2.36	1.91	1.92	2.27	1.86	1.85
Lu	0.37	0.30	0.29	0.35	0.29	0.29
Hf	1.62	2.01	2.09	1.66	1.66	1.71
⁸⁷ Sr/ ⁸⁶ Sr	0.702981 ^b	-	-	-	-	0.702978 ^b
εNd	8.97	7.85	-	-	8.07	8.39
²⁰⁶ Pb/ ²⁰⁴ Pb	18.944	-	19.229	19.013	19.238	19.003
²⁰⁷ Pb/ ²⁰⁴ Pb	15.548	-	15.59	15.56	15.583	15.56
²⁰⁸ Pb/ ²⁰⁴ Pb	38.557	-	38.833	38.624	38.807	38.62
εHf	21.04	17.84	14.33	19.89	17.46	20.05

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