In-situ Pb isotopic analysis of sulfides in abyssal peridotites: New insights into heterogeneity and evolution of the oceanic upper mantle

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ABSTRACT

Abyssal peridotites and mid-oceanic ridge basalts (MORBs) represent complementary residue-liquid products of melting and melt migration in the oceanic mantle. Because MORBs are mixtures of melts from different mantle depths, their isotopic signature does not directly describe the isotopic composition of the mantle source, but instead describes the local average composition of different parts of the mantle. In contrast, abyssal peridotites, the residues of fractional melting and melt-rock reaction, should shed more light on the distribution of isotopic heterogeneities. We analyzed Pb isotopic compositions in sulfide grains from the Southwest Indian Ridge and the Gakkel Ridge (Arctic Ocean) using the high-resolution Cameca 1280 ion microprobe. Sulfide Pb isotope ratios show very large variations, with 16 grains from 1 sample covering ~25% of the entire range observed in the oceanic mantle. Pb isotopes in sulfides preserve a record of mantle compositions not seen in whole-rock MORBs from the same area. Sulfides from the Atlantis II Fracture Zone (Southwest Indian Ridge) confirm the presence of ancient refractory material in the oceanic upper mantle. Gakkel Ridge sulfides define a high degree of isotopic variability, suggesting that oceanic mantle, not subcontinental lithospheric mantle, is the main source of such heterogeneity. Our results confirm that the source of MORBs, as represented by abyssal peridotites, is very heterogeneous and that other mantle end-member components are intimately mixed in. In-situ sulfide analysis is a powerful tool to detect the isotopic diversity of the MORB mantle source.

INTRODUCTION

Isotopic compositions of mid-oceanic ridge basalts (MORBs) are fundamental to understanding the chemical and dynamic evolution of the Earth, as the MORB source mantle is one of its largest reservoirs. It is well established that MORBs can be heterogeneous on a small scale, e.g., among melt inclusions (e.g., Shimizu 1998), or on a very large scale; e.g., MORBs from the Indian Ocean are very different from those from the Atlantic (e.g., Hofmann, 1997). Although N-MORBs (normal MORB not affected by the influence of mantle plumes) are much more homogeneous than ocean island basalts (OIBs), they still have a nontrivial variation of Pb isotopes. Su (2002) estimated the total range of $^{206}$Pb/$^{204}$Pb in N-MORB to be from 17.86 to 18.57. This indicates that the assumption of a single, isotopically uniform depleted MORB mantle (DMM) source is not correct.

Pb isotopes are among the most important of the long-lived radiogenic isotope tracers for mantle geochemistry, due to the production of three members present in abyssal peridotites.

In this study we examine the Pb isotopic composition of the oceanic mantle by analysis of Pb isotopes in peridotite sulfide grains. This study focuses on samples from the Southwest Indian Ridge (SWIR), particularly the oblique segment and the Atlantis II Fracture Zone, and on samples from the Gakkel Ridge in the Arctic Ocean. These locations correspond to ultraslow-spreading ridges, with full spreading rates <20 mm/yr (Dick et al., 2003). Due to on-axis conductive cooling, the expected degree of melting is small and initial (pre-melting) peridotite compositions should be retained (e.g., Bown and White, 1994). The goals of this study are to (1) determine the Pb isotopic variations among populations of sulfide grains, (2) compare those variations with Pb isotopic variations observed in basalts from the same area, and (3) characterize the range of mantle end members present in abyssal peridotites.

METHODS

We analyzed eight samples: RC27–9–6–2, a spinel lherzolite cut by a clinopyroxene vein from the Atlantis II Fracture Zone of the SWIR; spinel lherzolite VAN7–96–28 from the SWIR oblique segment; spinel lherzolites HLY102–29–21A, HLY102–32–64, PS59–246–3, and PS59–238–73 from the Gakkel Ridge; and plagioclase-olivine websterite HLY102–85–4A and plagioclase-harzburgite HLY102–100–79 from the Gakkel Ridge. Samples RC27–9–6–2 and VAN7–96–28 have been studied in detail (Standish et al., 2002; Warren et al., 2009; Warren and Shirey, 2012). A description of the method is given in the GSA Data Repository1.*

1GSA Data Repository item 2014042, Tables DR1 and DR2 and methods, is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
RESULTS

Data are presented for 30 sulfides from 6 Gakkel peridotites, and 6 sulfides from 2 SWIR peridotites (Table DR1 in the Data Repository). Sulfides in our samples vary in size from 10 to 100 µm, occurring as inclusions inside clinopyroxene and orthopyroxene grains, and also as interstitial grains. They are all pentlandites, with Fe/Ni ratios between 0.6 and 1.7, except for one VAN7–96–28 sulfide and all the RC27–9–6–2 sulfides, which are chalcopyrites (Table DR2). Based on comparison with the standard and the concentration work in Warren and Shirey (2012), we estimate that only sulfide grains with Pb contents >1 ppm yielded data by in-situ analysis. Unfortunately, such high Pb content grains are very rare and the many sulfides with Pb contents below the detection limit are not reported in Table DR1. In some samples (e.g., PS59–246–3 and PS59–238–73) we managed to analyze only two grains. However, sample HLY102–85–4A was extremely rich in high Pb sulfides and we analyzed 16 grains in this sample. In total, sulfides were analyzed from 15 samples, but sulfides in 7 samples did not yield enough Pb for measurement of their isotopic ratios.

The compositional range of the mantle, defined by the compositional range of MORBs and OIBs, forms a “mantle trapezium” in plots of $^{207}\text{Pb} / ^{206}\text{Pb}$ versus $^{208}\text{Pb} / ^{206}\text{Pb}$. The corners of this trapezium are defined by the four mantle end members: HIMU (high µ), EMI (enriched mantle I), EMII (enriched mantle II), and DMM (DMMs–1–3). Atlantis II Fracture Zone sulfides extend from compositions close to DMM at $^{207}\text{Pb} / ^{206}\text{Pb} = 2.06$ to $^{208}\text{Pb} / ^{206}\text{Pb} = 2.14$, larger than the range of associated Atlantis II Fracture Zone basalts (Fig. 2). The two sulfides from the oblique segment of the SWIR have a limited Pb isotope range, but when combined with other oblique segment sulfides (Warren and Shirey, 2012), they cover a larger range than associated basalts. Gakkel sulfides also cover a larger range of compositions than associated basalts (Fig. 3), similar to the observation of Warren and Shirey (2012). Our data show that sulfide populations from some individual samples have large isotopic variations. This observation is significant, as Warren and Shirey (2012) had very few samples for which they analyzed multiple grains. Sulfides in this study also extend to relatively enriched (low $^{208}\text{Pb} / ^{206}\text{Pb}$ and $^{207}\text{Pb} / ^{206}\text{Pb}$) compositions. Our data set may be biased toward more enriched samples, as the in-situ secondary ion mass spectrometry technique requires relatively high Pb concentrations (>1 ppm) to yield Pb isotopic data.

For samples RC27–9–6–2 and VAN7–96–28, sulfide data are similar to the Pb isotopic composition of clinopyroxenes (Warren et al., 2009) that were separated from the same samples (Figs. 1 and 2). The data for VAN7–96–28 are also similar to previous IMS 1270 ion microprobe measurements of sulfides (Warren et al., 2009) and to thermal ionization mass spectrometry measurements of other sulfides from this sample (Warren and Shirey, 2012). Results from this study give $^{207}\text{Pb} / ^{206}\text{Pb} = 0.784$ and 0.791 and $^{208}\text{Pb} / ^{206}\text{Pb} = 1.997$ and 1.998, while the two bulk sulfide analyses in Warren and Shirey (2012) were $^{207}\text{Pb} / ^{206}\text{Pb} = 0.794$ and 0.797 and $^{208}\text{Pb} / ^{206}\text{Pb} = 1.996$ and 1.997.

DISCUSSION

Most abyssal peridotites are altered by various degrees by the processes of serpentinization and weathering by seawater (e.g., Snow et al., 1994; Luguet et al., 2003). There is plenty of evidence that these processes shift Sr isotopic values in abyssal peridotites to more radiogenic seawater ratios (e.g., Snow et al., 1994). However, the Nd isotopic system in abyssal peridotites is much less susceptible to the influence of seawater (e.g., Warren et al., 2009) due to the low Nd content in seawater, ~2–4 ppm. The Pb content of seawater is similar to the Nd content, which suggests that the influence of seawater on sulfide Pb isotopes should be rather limited, although sulfides are susceptible to low-temperature recrystallization and exchange processes (e.g., Klein and Bach, 2009). Studies of sulfides from black smoker chimneys and hydrothermal vent fluids display Pb isotope compositions indistinguishable from that of local basalts (e.g., German et al., 1993). These studies have concluded that the Pb source of hydrothermal sulfides and fluids is basalt dominated, rather than seawater dominated. In addition, sulfides from sample VAN7–96–28 have Pb isotopic compositions that are within error of carefully picked and leached clinopyroxenes grains, suggesting that seawater alteration does not influence sulfide isotopic compositions.
sulfides from the SWIR oblique segment. Other Gakkel sulfides have \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios that are similar to samples from the Fifteen Twenty Fracture Zone. Additionally, Gakkel basalts have Pb isotopic compositions in the range of \(^{206}\text{Pb}/^{207}\text{Pb}\) = 0.7 to 1.0, which is similar to that of MORBs.

**Variations in Pb Isotopic Composition of Gakkel Sulfides**

Peridotite sulfides from the Gakkel Ridge (Fig. 3) show a very large spread in Pb isotopic compositions, whereas Gakkel basalts have a limited range of Pb isotopic compositions. Many Gakkel sulfides have Pb isotopic ratios similar to those of peridotite sulfides from the SWIR oblique segment. Other Gakkel sulfides have \(^{206}\text{Pb}/^{207}\text{Pb}\) and \(^{208}\text{Pb}/^{206}\text{Pb}\) ratios that are unique among all samples in this study, and suggest mixing between HIMU and DMM.

Our results show larger variations and more enriched compositions compared to sulfides from the Gakkel Ridge analyzed by Warren and Shirey (2012). The greater abundance of more enriched compositions in this study may reflect a sampling bias, as sulfides with high Pb concentrations are necessary for ion probe in-situ analysis. In contrast, one of the sulfides analyzed by Warren and Shirey (2012) has extremely high \(^{206}\text{Pb}/^{207}\text{Pb}\) and \(^{208}\text{Pb}/^{206}\text{Pb}\) ratios, which corresponds to a very unradiogenic composition.

Sulfides from a single sample, HLY102–85–4A, cover ~25% of the global range of Pb isotopic compositions observed in OIB and MORB. This sample is a plagioclase-olivine websterite, which either formed by melting or refertilization of a residual peridotite or as a cumulate. The range of sulfide isotopic compositions in this sample probably reflects hybrid compositions formed during melt-rock interaction. Results from this sample confirm that abyssal peridotites are not always simple melt extraction residues, and they show signs of interacting with melts with diverse isotopic compositions. This means that on length scales within a melting region beneath a ridge, isotopic (and chemical) variabilities of melt fractions can be large, much larger than MORB would indicate, and interaction between these melts and wall-rock peridotites leaves records of isotopic and chemical heterogeneities in abyssal peridotites.

There is no clear distinction between sulfides from the western volcanic zone and sparsely magmatic zone, in contrast to the observation by Goldstein et al. (2008) of a change in Pb isotopic composition among basalts. Based on basalt trace element and isotopic results, Goldstein et al. (2008) suggested that the SCLM, as represented by basalts from Spitsbergen, is involved in the generation of western volcanic zone basalts. However, the very unradiogenic Os isotopic compositions among Gakkel Ridge
abyssal peridotites caused Liu et al. (2008) to suggest that old refractory domains are dispersed in the mantle beneath the Gakkel Ridge. A similar conclusion was reached by Stracke et al. (2011) based on very depleted Hf isotope ratios in Gakkel peridotites. The evidence for ancient depleted samples in these two studies was used to argue for dispersed reservoirs in the oceanic mantle, not for pieces of SCLM in the mantle beneath the Gakkel Ridge. The most relevant SCLM samples for this area are peridotite xenoliths from Spitsbergen, which is ~600 km from the Gakkel Ridge. These peridotites have $^{206}\text{Pb}/^{204}\text{Pb}=0.82–0.86$ and $^{207}\text{Pb}/^{204}\text{Pb}=2.05–2.11$ (Ionov et al., 2002). These values overlap the isotopic range of Spitsbergen and Gakkel basalts, but are distinct from the Gakkel peridotite sulfide data. It is clear that some material in the upper mantle is to a large extent not involved in the genesis of the Gakkel basalts or is volumetrically limited.

**CONCLUSIONS**

Sulfides from abyssal peridotites collected at the SWIR and Gakkel Ridge include residual sulfides and those crystallized from melt percolating through peridotite matrix. They show that in some cases a clear distinction exists between the Pb isotopic compositions of peridotites and basalts from the same area. In addition, sulfides confirm the presence of both unradiogenic and radiogenic materials in the mantle that are not always recognized in basalts. The occurrence of isotopically variable sulfides within individual samples suggests the existence of significant compositional heterogeneity in the upper mantle at relatively small length scales, which is averaged out when melts form to produce basalts. In-situ Pb isotopic data in sulfides thus provide a powerful tool for detecting the distribution, composition, and length scale of mantle heterogeneities.

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**REFERENCES CITED**


