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On the equilibration timescales of isolated trace phases in mantle peridotites: Implications for the interpretation of grain-scale isotope heterogeneity in peridotitic sulfides

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ABSTRACT

Geochemical studies of mid-ocean-ridge basalts (MORB) and mantle peridotites (e.g., abyssal peridotites) provide independent constraints on the composition and evolution of the convecting mantle. Recent studies have revealed systematic differences in the radiogenic isotope compositions of MORB and abyssal peridotites that call into question the complementary nature of these two windows to the upper mantle. The origin of these differences is fundamental to our understanding of MORB petrogenesis and the composition and depletion history of the upper mantle. The use of isotope variations in basalts to probe the composition and evolution of the mantle is predicated on the assumption of local (i.e., grain-scale) isotopic equilibrium during mantle melting. However, several studies have reported Os- and Pb-isotope disequilibrium in distinct populations of peridotite-derived sulfides, with sulfides included within silicate grains typically possessing more "depleted" isotopic compositions than interstitial sulfides. In principle, grain-scale isotopic heterogeneity could reflect variable radiogenic ingrowth in ancient sulfides with variable parent/daughter ratios, or partial re-equilibration of low-Re/Os and U/Pb sulfides with more radiogenic silicate phases along grain boundaries during mantle melting. This would require that sulfides fail to maintain isotopic equilibrium with neighboring phases over geologically long (∼ Ga) time scales. The preservation of Os-isotope disequilibrium in peridotites has been ascribed in several studies to the armoring effect of low-[Os] silicates, which limits diffusive exchange between isolated Os-rich sulfides. This raises the prospect that peridotite-derived melts may not inherit the Os- (or Pb-) isotope composition of their source, which could account for the recently documented systematic differences in the Os- and Pb-isotope compositions of MORB and mantle peridotites.

Although the preservation of isotopic heterogeneity in mantle sulfides is commonly ascribed to the above "armoring effect", the diffusive equilibration timescale of spatially separated sulfides in mantle peridotites has not previously been rigorously estimated. This study examines the parameters that control this equilibration timescale (average sulfide size and spacing, Os and Pb diffusivity in armoring silicate minerals, and element partitioning between silicate and sulfide phases). Equilibration timescale estimates using available constraints on these parameters reveal that most mantle sulfides are expected to isotopically re-equilibrate with neighboring sulfides in less than a few 10 s of Myr at convecting mantle temperatures. Maintenance of isotopic disequilibrium over the ∼ Ga timescales suggested by observed intra-sample Os- and Pb-isotope heterogeneity requires very large sulfides (>100 μm) separated by several mm or diffusion rates ($D < 10^{-18}$ m^2/s), slower than for most elements in olivine. Combined with the observation of intra-sample major element heterogeneity in sulfide Ni and Fe abundances (which should equilibrate quickly in the convecting mantle), these results suggest that the observed isotopic disequilibrium is unlikely to be an ancient feature in mantle peridotites. Instead, recent sulfide metasomatism linked to interaction with melts derived from isotopically enriched eclogite or pyroxenite (or fertile and/or metasomatized peridotite) components is a more likely explanation for observed intra-sample isotopic heterogeneity in peridotites. This interpretation is also consistent with systematic differences between the Nd- and Hf-isotope compositions of MORB and abyssal peridotites. These results further strengthen the proposal that MORB do not accurately reflect the average isotopic composition of the convecting upper mantle, and that upper mantle peridotite is, on average, significantly more depleted and refractory than suggested by MORB-based estimates. The effects of melt generation in a

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heterogeneous marble-cake mantle need to be explicitly considered when using basalt compositions to constrain mantle composition and evolution.

1. Introduction

Mid-ocean ridge basalts and abyssal peridotites provide complementary views into the composition and evolution of the convecting upper mantle. Most studies consider abyssal peridotites to be melt-depleted residues of recent mid-ocean ridge melt extraction, though melt/mantle interactions also affect their compositions (Niu, 1997; Salters and Dick, 2002; Kimura and Sano, 2012). The isotopic compositions of both abyssal peridotites and MORB should thus be representative of the depleted upper mantle. However, several recent studies indicate that abyssal peridotites on average have more depleted isotopic compositions than MORB (e.g., Lassiter et al., 2014; Byerly and Lassiter, 2014). In addition, some highly refractory abyssal peridotites have extremely depleted Os- and Hf-isotope compositions that reflect ancient (>1 Ga) melt extraction (Liu et al., 2008; Stracke et al., 2011). Processes such as melt–rock reaction, though clearly important, cannot account for these systematic isotopic differences.

A second, potentially related observation is that many peridotites from both oceanic and continental settings possess significant isotopic heterogeneity at the grain scale, particularly with respect to mantle sulfides. Alard et al. (2005) noted that magmatic sulfides from abyssal peridotites are shifted to more radiogenic Os-isotope values than included monosulfide solid solution (MSS) phases, and bridge the Os-isotope gap between MORB and bulk abyssal peridotites. Many peridotites appear to contain multiple generations of sulfides, including sulfides with compositions consistent with sulfide melt (usually occurring as interstitial sulfides), and sulfides with residual MSS compositions (most common as inclusions in olivine or other silicate phases) (Harvey et al., 2016). Interstitial sulfides often have more radiogenic ^{187}Os/^{188}Os than included MSS phases (Alard et al., 2005; Harvey et al., 2006). A similar picture is observed for Pb-isotopes. Individual abyssal peridotites contain sulfides with variable Pb-isotope compositions, and included MSS phases often have significantly less radiogenic ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb than either interstitial sulfides or most MORB (Burton et al., 2012; Warren and Shirey, 2012). Significantly, many included MSS grains have Pb-isotope compositions that plot to the left of the geochron. Thus, included sulfides could represent a significant unradiogenic Pb reservoir in the mantle under-sampled during MORB petrogenesis, providing a potential solution for the long-standing "first Pb paradox" (Warren and Shirey, 2012).

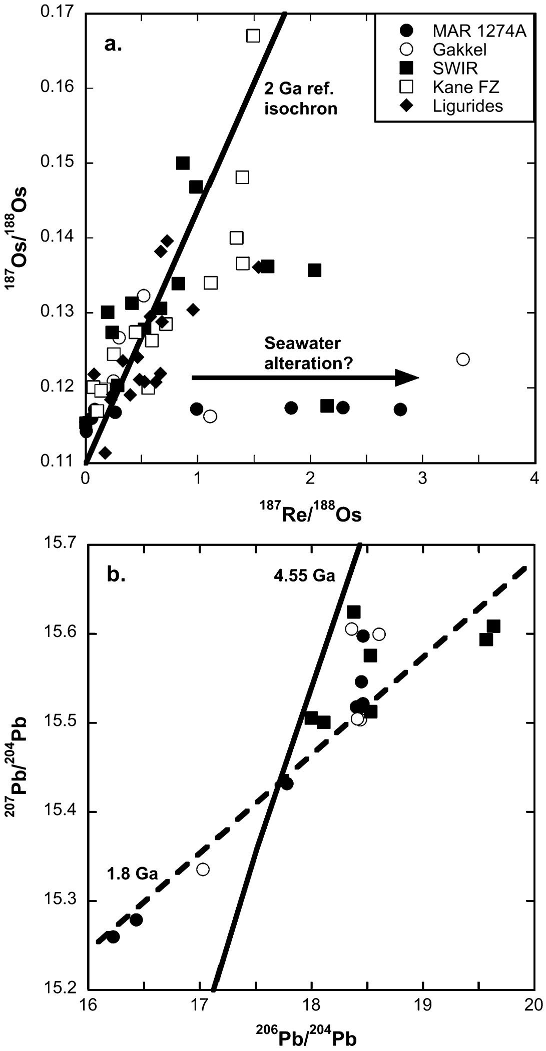

Fig. 1. a. ^{187}Os/^{188}Os variations in individual sulfides from MAR, SWIR, and Gakkel ridge abyssal peridotites as well as from the Liguride ophiolites. b. ^{206}Pb/^{204}Pb–^{207}Pb/^{204}Pb variations in peridotite sulfides (data from Alard et al., 2005; Harvey et al., 2006; Burton et al., 2012, and Warren and Shirey, 2012). 2.0 and 1.8 Ga isochrones shown for reference. Sulfides from multiple localities fall along similar Re/Os–^{187}Os/^{188}Os and ^{206}Pb–^{207}Pb trends which can be interpreted either as isochrons or as mixing trends. See text for details.

The hand-sample-scale heterogeneity in interstitial and included sulfide Pb- and Os-isotopes in abyssal peridotites presents a "chicken or the egg" problem whose solution is critical for the interpretation of isotopic variations in both MORB and abyssal peridotites. Previous studies have suggested that because sulfides have much higher [Os] and [Pb] than the major silicate phases in peridotites, isotopic heterogeneity can be preserved for geologically long periods of time due to the "armoring effect" of low-[Os], low-[Pb] phases that physically separate sulfides. This armoring effect slows diffusive exchange between neighboring sulfides, so that the equilibration timescale is much longer than the diffusive timescale suggested by sulfide spacing. Burton et al. (2012) and Harvey et al. (2006) suggested that ^{206}Pb–^{207}Pb and ^{187}Re/^{188}Os–^{187}Os/^{188}Os correlations observed in peridotite sulfides represent internal isochrons, with ages of ~1.8–2.1 Ga (Fig. 1). If spatially separated sulfides can preserve Os- and Pb-isotope variations for geologically long periods, then it is possible that mantle melting preferentially samples Os and Pb contained in (radiogenic) sulfides present along grain boundaries, but under-samples the less radiogenic sulfides present as inclusions in silicate phases (Alard et al., 2005). Although this model does not explain the different Nd- or Hf-isotope signatures of MORB and abyssal peridotites (Byerly and Lassiter, 2014), it could explain the overlap between MORB and interstitial sulfide Os-isotopes. Alternatively, if such heterogeneities cannot be preserved for geologically long periods, then the observed heterogeneity would suggest that many peridotites have experienced recent enrichment via melt/rock reaction, most likely associated with melt production beneath the modern mid-ocean ridge, with the isotopically "enriched" melts responsible for this refertilization potentially generated by melting of pyroxenitic or eclogitic components in the convecting upper mantle. Thus, the origin of grain-scale isotopic heterogeneity in abyssal peridotites has fundamental implications for the processes of MORB generation and the composition and evolution of the convecting upper mantle.

The very high sulfide/silicate partition coefficients typical for Os (and to a lesser extent Pb) results in a "moat" of low-Os (and Pb) material separating discrete sulfide phases. This slows, but does not prevent, isotopic equilibration of distinct generations of sulfides. Numerous studies have appealed to this "moat effect" to explain the preservation of grain-scale isotopic heterogeneity in mantle sulfides (Burton et al., 1999; Harvey et al., 2011). However, previous studies have not examined in detail the parameters that control the isotopic equilibration timescale for physically separated phases. In the following discussion, I evaluate the parameters that control this timescale to provide estimates of reasonable equilibration timescales. These estimates show that grain-scale isotopic heterogeneity in mantle peridotites is more reasonably explained by recent metasomatic enrichment via melt/rock reaction rather than preservation of ancient heterogeneities. The systematically "enriched" nature of the inferred metasomatic component suggests a role for pyroxenite or eclogite melting and melt/mantle reaction beneath ocean ridges (see e.g., Fig. 9 of Lambart et al., 2012) and may also explain the systematic isotopic differences between MORB and abyssal peridotites. The following discussion is limited to the effects of diffusion on hand-sample-scale isotopic equilibration. Other processes, such as mixing via mantle strain or chemical reactions associate with phase transitions (e.g., from garnet to spinel peridotite) are likely to further reduce isotopic equilibration timescales at this scale. The implications for this model for the composition and evolution of the bulk upper mantle are investigated.

2. Background

Isotopic and trace element variations in basalts from different tectonic settings are routinely used as probes to study mantle compositional variations, which in turn provide insight into processes ranging from long-term melt depletion to crustal recycling via subduction (see review by Hofmann, 1997). The use of isotope variations in basalts to probe the composition and evolution of the mantle is predicated on the assumption of local (i.e., grain-scale) isotopic equilibrium during mantle melting (Hofmann and Hart, 1978). For most traditional lithophile elements this assumption is likely robust. Most incompatible trace elements are hosted primarily within clinopyroxene, which is directly involved in melting reactions, or along grain boundaries. In addition, once melt generation initiates, diffusion in grain-boundary-wetting silicate melts is much more rapid than in solid peridotite, facilitating the rapid destruction of small-scale heterogeneities (cf., Hoffmann and Hart, 1978; Hart, 1993). Therefore, the assumption of local equilibrium during partial melting appears well founded for most isotopic and trace element systems.

However, numerous studies have documented significant grain-scale Os- and Pb-isotope heterogeneity within mantle peridotites from both continental and oceanic settings (e.g., Burton et al., 1999; Harvey et al., 2011; Warren et al., 2012). In particular, systematic differences have been noted in the Pb- and Os-isotope compositions of included, MSS-type sulfides and interstitial sulfides that commonly have compositions more typical of sulfide melt. For example, MSS-type sulfides from Mid-Atlantic Ridge peridotites define ^{187}Re–^{187}Os and ^{207}Pb/^{204}Pb–^{206} Pb/^{204}Pb correlations that, if interpreted as isochrons, define "ages" of $\sim$ 2.06 and 1.83 Ga, respectively (Harvey et al., 2006; Burton et al., 2012). In these and other examples, both interstitial sulfides and bulk peridotites typically have more radiogenic ^{187}Os/^{188}Os than included sulfides. Several interpretations of this intra-sample heterogeneity have been proposed. Burton et al. (1999) noted that silicate phases may host a significant fraction of a bulk peridotite's Re, whereas almost all Os is hosted in sulfide phases. As a result, silicates evolve with higher Re/Os than coexisting sulfides. During peridotite ascent, decompression melting may facilitate re-equilibration of silicate phases and interstitial sulfides, while included sulfides retain their original composition ("self-metasomatism"). Alternatively, different generations of sulfides with different Re/Os and/or initial ^{187}Os/^{188}Os (or U/Pb, ^{206}Pb/^{204}Pb) may preserve their isotopic identity for geologically long periods due to the "moat effect". In this case, the observed ^{187}Re–^{187}Os and ^{207}Pb/^{204}Pb–^{206}Pb/^{204}Pb correlations may have true age significance, recording distinct episodes of melt depletion and/or metasomatism. Finally, the observed isotopic disequilibrium in mantle peridotites could be generated by recent introduction of an externally-derived (as opposed to in-situ) melt or fluid. In this case, the included sulfides, which are wholly or partially shielded from this metasomatic agent, most accurately record the isotopic composition of the bulk peridotite prior to recent melt/mantle or fluid/mantle interaction.

A fundamental constraint on these models is the timescale over which distinct silicate and sulfide phases can maintain isotopic disequilibrium at convecting mantle conditions. It has long been recognized that the high sulfide/silicate K_d values for Os (and Pb) reduce the diffusive flux between separated sulfide phases and thus increase the equilibration timescales (e.g., Burton et al., 1999). However, few previous studies have attempted to quantify this effect. Burton et al. (1999) suggested that the high sulfide/silicate K_d(Os) has the effect of shortening the effective diffusive length-scale by a factor proportional to this partition coefficient. This treatment has been adopted in several subsequent studies (e.g., Harvey et al., 2016). However, as discussed below, this inference is incorrect and also does not capture the full set of parameters that control the effective equilibration timescale for two physically separated phases. The following discussion examines this equilibration problem and its implications for the interpretation of grain-scale isotopic heterogeneity in the mantle. The following discussion focuses on the case of Os-isotope heterogeneity in mantle sulfides, but is readily applicable to other systems.

3. Controls on equilibration timescales

3.1. Sulfide size and spacing

The question of whether the mantle can maintain local isotopic disequilibrium over geologically long periods is hardly new. Hofmann and Hart (1978) examined the potential for development of cm-scale isotopic heterogeneity in mantle peridotites, and concluded that in the absence of grain-boundary melt or fluid, isotopic heterogeneity could be preserved for $\sim 10^8$–10^9 yr timescales. Other studies have examined the equilibration of olivine-hosted melt inclusions with surrounding melt after entrapment (e.g., Gaetani and Watson, 2000; Cottrell et al., 2002; Spandler et al., 2007). In these and many other systems, the "armoring" of discrete phases with high concentrations of a given element by other phases with much lower concentrations acts to slow equilibration of neighboring but spatially separated phases due to the low diffusive flux through the armoring phase. The equilibration timescale for nearest neighbor phases in the above scenario is controlled by the mean size and spacing of the "enriched" phases (e.g., sulfides for the cases of Os and Pb or clinopyroxene for Nd and Sr), element diffusivity within the armoring phase, and the partition coefficient between the "enriched" and armoring phase. In general, the higher the partition coefficient between the enriched and armoring phase, the longer the equilibration timescale.

Conceptually, equilibration of two physically separated enriched phases is similar to the classic problem of the equilibration of water levels in two buckets connected by a narrow-gage hose. This

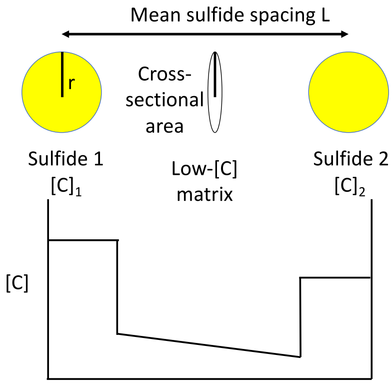

Fig. 2. Schematic representation of the diffusive equilibration problem. For elements where sulfide/silicate $K_d >> 1$, $t_{eq} >> t_{diff}$ and the concentration gradient at any time in the silicate separating the sulfide phases approximates a straight line. The sulfide equilibration timescale is then a function of sulfide mass and elemental flux, which is itself a function of sulfide spacing, diameter, sulfide/silicate K_d, and element diffusivity in the silicate. See section 3.2 for more detailed discussion of t_{diff} and t_{eq}.

problem is essentially an application of Torricelli's Law – the velocity of water through the hose connecting the two buckets is a function of the difference in head (chemical potential), but the total flux is a function of both the difference in head and the hose diameter (element concentration in armoring phase). The higher the partition coefficient between sulfide and silicate or oxide phases, the narrower the hose and lower the flux, resulting in longer equilibration timescales. For simplicity, I consider equilibration of two sulfides of equal size in the discussion below. The basic relevant parameters for this problem are illustrated in Fig. 2.

The size and separation distance (spacing) of sulfides in mantle peridotites have a strong control on equilibration timescales. All else being equal, small sulfides spaced close together will more readily equilibrate with neighboring sulfides than large sulfides spaced further apart. In practice, these two parameters are not mutually independent. The mean spacing of sulfides in mantle peridotites is a function of total sulfur content and mean sulfide size. If we assume that all sulfur in the mantle is contained in sulfides, then sulfide modal abundance correlates directly with mantle sulfur abundance. Estimates of sulfur concentration in typical peridotites range from ~250 ppm for primitive mantle (McDonough and Sun, 1995) to ~100 ppm for depleted MORB-source mantle (Salters and Stracke, 2004), although some peridotites have higher sulfide abundances reflecting metasomatic sulfide addition (e.g., Luguet et al., 2003). The modal abundance of sulfide (M_s) in peridotite is proportional to the sulfur concentration:

$$M_s = V_s/V_p = X_s/x_s * \rho_p/\rho_s \qquad (1)$$

where V_s and V_p are the total volume of peridotite (including sulfide phases) and sulfide phases within the peridotite, X_s and x_s are the sulfur concentration in the bulk peridotite and in the sulfide phase, respectively, and ρ_p and ρ_s are the density of the bulk peridotite (~3300 kg/m^3) and the sulfide phases. For bulk metal sulfide compositions (~35 wt.% S) and densities (~4600 kg/m^3) typical of peridotitic sulfides, sulfur abundances of 100–250 ppm correspond to sulfide modal abundances ranging from ~0.02–0.05%. These estimates are consistent with modal determinations based on thin section analysis. For example, abyssal peridotites have average modal sulfide abundances of ~0.02% (Luguet et al., 2001, 2003), consistent with DMM sulfur abundance estimate of Salters and Stracke (2004).

Mean sulfide spacing can be readily approximated for a given sulfide size and modal abundance. Although sulfide shapes vary, one can consider sulfides as having an "effective radius" equal to the radius of a sphere with a volume equal to the sulfide volume. For equally spaced sulfides, one can then consider every sulfide as the sole sulfide occupying the center of a cubic reference volume with a modal sulfide abundance equal to that of the bulk peridotite. The volume of this cube is then given by:

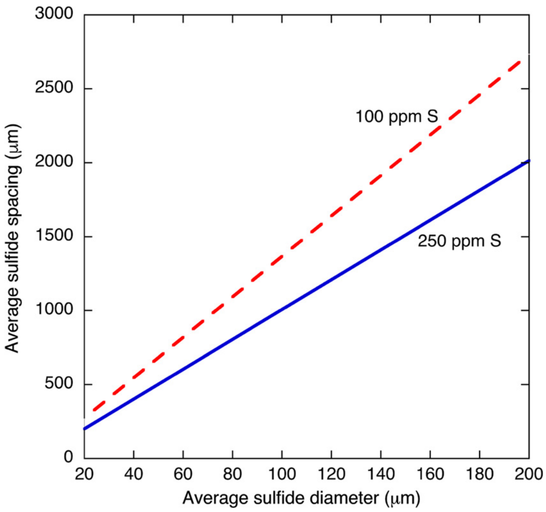

Fig. 3. Calculated mean sulfide spacing as a function of sulfide size for different mantle sulfur abundances. See text for details.

$$V_r = V_s/M_s, \quad \text{or} \quad V_r = \left(4/3\pi * r_s^3\right)/M_s, \qquad (2)$$

where V_r is the reference volume, V_s is the sulfide volume, and r_s is the sulfide effective radius.

The mean spacing between sulfides is then the distance between the center of adjacent reference volumes, which is simply the length of the cube:

$$L_s = \left(V_r^{1/3}\right) = \left[\left(4/3\pi * r_s^3\right)/M_s\right]^{1/3}. \qquad (3)$$

Although estimates of sulfide abundance in mantle peridotites vary considerably, the effect on mean sulfide spacing is modest as spacing is proportional to the cube root of modal abundance.

Fig. 3 shows the calculated mean spacing of sulfides as a function of size for different mantle sulfur contents, assuming uniform size and distribution. Sulfide spacing varies linearly with mean size. For mantle with 250 ppm sulfur, estimated sulfide spacing ranges from ~200 μm (for 20 μm diameter sulfides) up to ~2 mm (for 200 μm diameter sulfides). Because sulfide size and spacing are interrelated, the overall sulfur abundance allows an estimation of sulfide spacing for a given sulfide size, and in most peridotites neighboring sulfides are predicted to be separated by no more than ~10–15 times their diameter.

Natural sulfides in mantle peridotites vary greatly in size, from <10 μm to several mm (e.g., Burton et al., 1999). However, most are less than a few hundred μm in diameter, although detailed statistical analyses of sulfide size, shape, and spatial distributions in natural samples are lacking. Studies examining Os- and Pb-isotopes in individual sulfides have by necessity concentrated on larger sulfides. Warren and Shirey (2012) analyzed Pb- and Os-isotopes in individual sulfides from Gakkel Ridge abyssal peridotites that ranged from 3–285 μg in mass, which translates to sulfide effective radii of ~50–250 μm. Harvey et al. (2006) and Burton et al. (2012) also analyzed sulfides with masses equivalent to effective radii of 1–200 μm. In all of these studies, however, there is likely a selective bias towards larger sulfides due to analytical constraints. For these sulfide sizes and normal mantle sulfur abundances, the nearest-neighbor spacing will typically be much less than 1 cm and often <1 mm.

3.2. Sulfide/silicate partitioning and silicate diffusivity

For elements present in higher concentrations in sulfide phases than in armoring silicate or oxide phases, the armoring phase slows chemical or isotopic equilibration of neighboring sulfides, much as trace element equilibration of olivine-hosted melt inclusions with surrounding melt is slowed by the low trace element abundances in olivine (e.g., Cottrell et al., 2002). It is the elemental flux, and not the diffusivity, that controls how rapidly two phases can equilibrate. As a result, the equilibration timescale will typically be much greater than the diffusive timescale (t_{diff}; $\sim L^2/D$, where L is the characteristic separation distance and D is the diffusivity for a given element in the intervening medium). In this case a nearly linear potential gradient is established in the medium separating the sulfide (or other trace) phases, and we can consider the elemental flux between the two sulfides to be in quasi-steady state. Note that although a high sulfide/silicate K_d value reduces the flux though the silicate medium, the diffusive length-scale depends only on the diffusivity in the medium and on time, and is independent of K_d. Previous studies suggested that high K_d values had the effect of shortening the effective diffusive length-scale (e.g., Burton et al., 1999; Harvey et al., 2016). This is incorrect, as discussed in more detail in a later section.

Consider two sulfides with Os concentrations C_1 and C_2 where $\Delta C = C_1 - C_2$. For $t >> t_{diff}$, the elemental flux F is given by:

$$F = \rho_p * D * A * \left[(C_1 - C_2)/K_d\right]/L_s,$$
$$\text{or } \Delta C * \left[\rho_p * D * A/(L_s * K_d)\right]; \qquad (4)$$

where D is the diffusivity of Os in silicate matrix phase(s), K_d is the sulfide/silicate partition coefficient for Os, and A is the cross-sectional area of the sulfides, given by πr_s^2.

The flux is proportional to the compositional difference between the two phases, ΔC. The change in ΔC over time is a function of the elemental flux and the volume of the sulfides:

$$d\Delta C/dt = -2F/m_s,$$
$$\text{where } m_s \text{ is the mass of the sulfide given by } V_s * \rho_s. \qquad (5)$$

Sulfide disequilibrium therefore evolves in a fashion analogous to radioactive decay:

$$\Delta C_t = \Delta C_i * e^{-\lambda t};$$
$$\text{where } \lambda = (3/2) * (\rho_p/\rho_s) * D/(K_D * L_S * r_s) \qquad (6)$$

The characteristic equilibration timescale required for an initial normalized $\Delta C = 1$ to decay to $1/e$ is simply $1/\lambda$. Thus, the equilibration timescale is proportional to the sulfide/silicate K_d, as noted in previous studies (e.g., Burton et al., 2012), and inversely proportional to diffusivity. Note that this approximation considers the simple case of two sulfides diffusively communicating only with one another. In the more realistic case of sulfides present in a 3-D matrix with multiple close neighbors, the equilibration timescale is approximately $1/(4\lambda)$.

4. Constraints on preservation of grain-scale isotopic disequilibrium in mantle peridotites

The above discussion provides a framework for evaluating the timescales over which grain-scale Pb- and Os-isotope disequilibrium can be preserved in mantle peridotites. The following discussion examines both the potential for sulfide and silicate phases with differing parent/daughter ratios to evolve and preserve distinct isotopic signatures and the potential for different generations of sulfides to maintain their isotopic identity independent of one another.

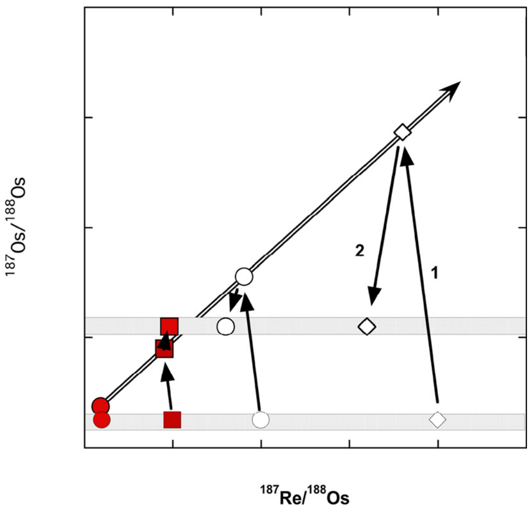

Fig. 4. An intuitive but physically unrealistic model for the Os-isotopic evolution of discrete sulfide (filled symbols) and silicate (open symbols) phases in mantle peridotites. Modified from Harvey et al. (2016) and Burton et al. (1999). During initial melt depletion ($t = 0$), silicate and sulfide phases share a common initial ^{187}Os/^{188}Os but variable Re/Os. Initially, minerals evolve according to their respective mineral Re/Os, not the bulk peridotite Re/Os. This evolution presupposes isotopic closure of individual minerals which, although possible for sulfide phases due to the "moat effect", is unlikely in low-[Os] silicate phases at convecting mantle conditions. Subsequent partial melting or introduction of externally-derived melt results in resetting of silicate and interstitial sulfide phases and/or precipitation of new sulfides along grain boundaries. Included sulfides are protected from this isotopic re-equilibration.

4.1. Silicate–sulfide equilibration

Sulfides are commonly the primary host for Os in mantle peridotites, often accounting for >90% of total Os (e.g., Harvey et al., 2016 and references therein). In contrast, sulfide/silicate K_d values for Re are much lower, and a significant fraction of the rhenium in mantle peridotites is hosted in silicate phases (Burton et al., 1999). As a result, silicate phases in mantle peridotites evolve with higher Re/Os than coexisting sulfide phases. Similarly, because Pb is mildly chalcophilic whereas U is strongly lithophile, silicate phases generally have higher U/Pb than coexisting sulfides. In principle, silicates may therefore evolve distinct, radiogenic Os- and Pb-isotope signatures relative to coexisting sulfides. During partial melting, this radiogenic Os and Pb may be preferentially sequestered into the melt, whereas Os and Pb locked in included sulfides is unable to contribute. This would result in a melt that is isotopically more enriched than the bulk peridotite from which it derives.

This scenario, which has been proposed in several studies (see e.g., Fig. 4, modified from Burton et al., 1999 and Harvey et al., 2016), requires that silicate phases maintain isotopic disequilibrium with coexisting sulfides. Previous studies suggested that high sulfide/silicate K_d(Os) and K_d(Pb) prevent coexisting sulfide and silicate phases from equilibrating with one another via diffusion. However, the "moat effect" does not protect phases with low Os (or Pb) abundance from re-equilibrating with coexisting phases enriched in these elements. In this case, the equilibration timescale for the silicate phase is simply equal to the diffusive timescale, which can be approximated as $\sim L^2/D$, where here L is half the mean spacing distance between sulfides and D is the diffusivity of Os or Pb within the intervening silicate. As discussed above, the mean spacing of sulfides in mantle peridotites is likely on the order of 1 mm or less. For this spacing, development and preservation of isotopic heterogeneities via radiogenic ingrowth in silicate phases with an apparent "age" of ~1 Ga would require diffusivity within the silicate phase of $< 1 \times 10^{-23}$ m^2/s. However, almost

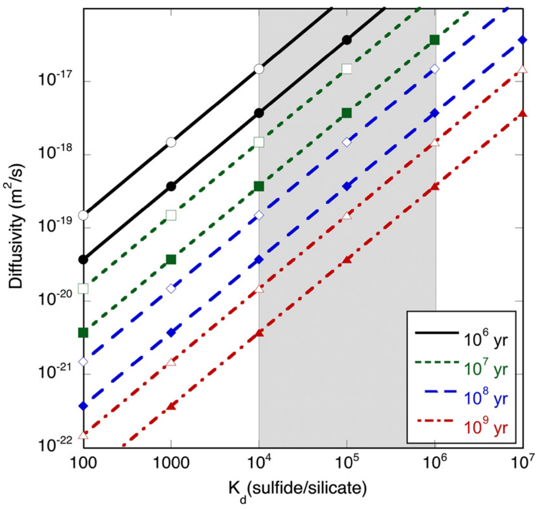

Fig. 5. Calculated sulfide equilibration timescales as a function of diffusivity and sulfide/silicate partition coefficient. Equilibration timescales are calculated for 100 μm diameter sulfides evenly dispersed in a peridotite with 250 ppm bulk sulfur. Open symbols represent the 1-D approximation; solid symbols are for the 3-D approximation. Shaded field represents reasonable range of sulfide/olivine K_d(Os) values, based on literature data (see text for discussion). Preservation of isotopic heterogeneities in discrete sulfide grains for a given timeframe requires the D and K_d values for the element of interest to plot below the line defining the equilibration timescale.

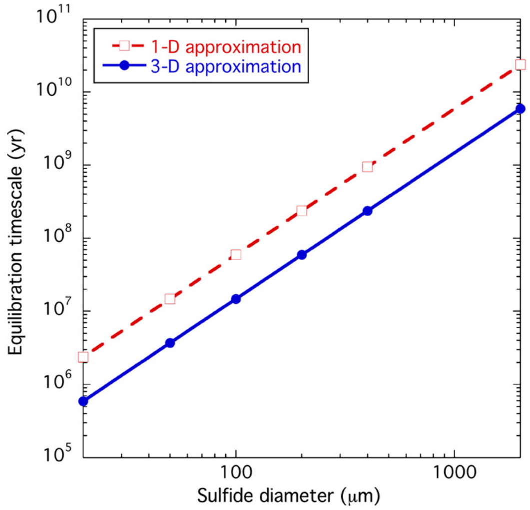

Fig. 6. Representative variation in equilibration timescale as a function of sulfide diameter. Equilibration timescale is proportional to the square of sulfide radius. Calculated timescales are for peridotite with 250 ppm bulk sulfur and assuming Os diffusivity in silicate $D(\mathrm{Os}) = 10^{-16.5}$ m^2/s (Kogiso et al., 2004) and sulfide/silicate $K_d(\mathrm{Os}) = 10^6$. Equilibration timescale for Pb and for major cations (Fe, Ni) would be significantly shorter than for Os. See text for details.

all trace elements have significantly higher diffusivities in olivine at convecting mantle conditions (e.g., $T > 1300\,°\mathrm{C}$) (Chakraborty, 2010). Although no direct measurements of Os diffusivity in silicates have been reported, Kogiso et al. (2004) estimated an Os diffusivity in olivine on the order of $10^{-16.5}$ m^2/s using the elastic strain model of Van Orman et al. (2001). For this diffusivity, even sulfide spacing of ∼1 cm would result in an equilibration timescale in mantle silicates <<1 Ma. Thus, unless Os diffusion in silicates is extremely slow, it appears unlikely that *in situ* ingrowth of ^{187}Os in high-Re/Os silicate phases can generate significantly elevated ^{187}Os/^{188}Os in these phases – silicates are expected to be above the "blocking temperature" for the Re–Os system in the convecting mantle. The "self metasomatism" model illustrated in Fig. 4, though intuitively appealing, is physically unrealistic and cannot account for observed isotopic differences between silicate and sulfide phases in mantle peridotites.

4.2. Sulfide–sulfide equilibration

Although the "self-metasomatism" model described above appears unlikely, the question remains as to whether different generations of sulfides with differing initial isotopic composition and/or parent/daughter ratios can evolve in isolation from one another. In this situation, the "moat effect" does come into play. As discussed previously, sulfide size, spacing, sulfide/silicate partitioning, and diffusivity all influence the equilibration timescale. Due to the relationship between sulfide size and spacing, the equilibration timescale increases linearly with the square of the mean sulfide radius when the dependence of both sulfide spacing and sulfide mass on sulfide radius are considered together. The equilibration timescale also increases linearly with the sulfide/silicate partition coefficient and is inversely proportional to diffusivity. Estimation of Os (and Pb) partitioning and diffusivity thus allows us to examine whether separated sulfides are expected to remain "closed" to one another for ∼ Ga timescales in the mantle.

Fig. 5 shows the equilibration timescales for sulfides with a mean diameter of 100 μm in a peridotite containing 250 ppm bulk S, as a function of partition coefficient and diffusivity. For this case, the mean sulfide spacing is ∼1 mm. The interpretation of Re/Os–^{187}Os/^{188}Os correlations in included sulfides from abyssal peridotites as isochrons with ages of ∼2 Ga (Harvey et al., 2006) would require isotopic closure be preserved for this timescale. Fig. 5 illustrates the range of sulfide/silicate partition coefficients and silicate diffusivity required for this. Sulfide/silicate K_d(Os) can be estimated from measured [Os] in both mantle silicate and sulfide phases. Harvey et al. (2011) reported [Os] in MSS-type peridotite sulfides ranging from ∼1–37 ppm. Osmium concentrations in olivine from the same peridotites ranged from 10–36 ppt. From this, one can infer sulfide/silicate K_d(Os) on the order of 10^4–10^6. For sulfide/silicate K_d(Os) within this range, preservation of isotopic heterogeneities for ∼10^9 yr timescales requires Os to have a diffusivity in olivine less than ∼10^{-19}–10^{-21} m^2/s at convecting mantle temperatures (>1300 °C), which is significantly lower than for most other trace elements.

The above analysis indicates that, given the existing large uncertainties in the diffusivity of Os in silicate phases, it is possible that large individual sulfides could maintain Os-isotope disequilibrium with neighboring sulfides for geologically long (>10^9 yr) periods. However, this would require a combination of unusually low Os diffusivity in silicate phases (<10^{-19} m^2/s), unusually large sulfide grains (>100 μm), and very high silicate/sulfide K_d (>10^5). Although it is possible that the above conditions are met in the convecting mantle, as previously discussed, Kogiso et al. (2004) estimated Os diffusivity in olivine on the order of $10^{-16.5}$ m^2/s using the elastic strain model of Van Orman et al. (2001). If this estimate is accurate, then isotopic re-equilibration of sulfides with a diameter of ∼100 μm is expected to occur in less than a few 10 s of million years even assuming sulfide/silicate $K_d(\mathrm{Os}) = 10^6$. Preservation of sulfide isotopic heterogeneity under these conditions for ∼Ga timescales would require mean sulfide diameters >400 μm, significantly larger than typical in most mantle peridotites (Fig. 6). It should be noted, however, that long-term preservation of isotopic heterogeneity in different populations of sulfides may be possible at the hand-sample scale if the different populations are inhomogeneously distributed throughout the sample (e.g., as veins or clusters).

In contrast to Os, several studies have examined both Pb partitioning and diffusivity in mantle phases. Although Pb is moderately chalcophile, sulfide/silicate melt K_d values are only ∼3 (Warren and Shirey, 2012). Beattie (1993) estimated olivine/basalt K_d(Pb) of ∼7×10^{-5} to 5×10^{-4}. In contrast, Adam and Green (2006) estimated olivine/basanite K_d(Pb) on the order of 10^{-3}. The partition coefficient of Pb in clinopyroxene, as for most other incompatible trace elements, is significantly higher (∼10^{-2}; e.g., Hauri et al., 1994). From these estimates, sulfide/olivine K_d(Pb) is calculated to be in the range of ∼6×10^3 to 4×10^4. Direct measurement of Pb diffusivity in olivine has not been reported. However, comparison with Pb diffusivity in other phases and with diffusivity of other +2 valent cations in olivine (e.g., Sr) can place reasonable constraints on Pb diffusivity in olivine. For example, extrapolation of the diffusion measurements from Cherniak (2000) indicates a diffusivity of Pb in pyroxene at 1300 °C of ∼$10^{-16.5}$ (for augite at QFM) to ∼10^{-18} m^2/s (for Cr-diopside). Pb diffusivity is likely similar to that of Sr, which in olivine at 1300 °C is ∼10^{-18} m^2/s (Cherniak, 2010). This diffusivity is somewhat slower than that estimated by Kogiso et al. (2004) using the elastic strain model of Van Orman et al. (2001), which suggests a Pb diffusivity in olivine at convecting mantle conditions of ∼$10^{-16.6}$ m^2/s.

Using the upper bound on the estimated sulfide/olivine K_d(Pb) and the lower bound on Pb diffusivity, one can calculate an upper bound on the equilibration timescale of sulfides embedded in an olivine matrix. For the parameters outlined above, the equilibration timescale is less than a few tens of Myr using the same sulfide size and spacing constraints as above. This timescale is much shorter than the timescale suggested by observed ^{207}Pb/^{204} Pb–^{206}Pb/^{204}Pb correlations. Note that this estimate only considers equilibration of two spatially-separated sulfides with one another. However, clinopyroxene is also a significant Pb host in mantle peridotites (e.g., Warren and Shirey, 2012). Therefore, given the much higher modal abundance of clinopyroxene relative to sulfide in mantle peridotites, it is likely that diffusive equilibration between sulfides and pyroxene is also important and will occur over shorter timescales. In summary, it appears unlikely that ^{207}Pb/^{204}Pb–^{206}Pb/^{204} Pb correlations observed in some peridotite sulfide suites are true isochrons. Instead, these correlations likely reflect recent mixing of Pb from two isotopically distinct reservoirs during reactive melt transport.

One final piece of observational evidence suggests the grain-scale Os- and Pb-isotope heterogeneity discussed above is the result of recent interaction with externally-derived metasomatic agents. The same sulfide suites for which Os- and/or Pb-isotope heterogeneity have been reported also display significant variation in sulfide major element composition (e.g., Burton et al., 1999; Harvey et al., 2011). For example, Ni and Fe concentrations in included, MSS-type sulfides from Kilbourn Hole peridotites are negatively correlated, with Ni concentration ranging from ∼36–20 wt.% and Fe ranging from ∼26–38 wt.%. The Ni–Fe trend defined by these sulfides fall along an extension of the Fe–Ni trend defined by interstitial sulfides, which extend to much lower Ni and higher Fe concentrations similar to the composition of magmatic sulfides in the host basalt.

Peridotite sulfides often contain a complicated array of phases due to sub-solidus exsolution. However, at convecting mantle temperatures, sulfides in equilibrium with mantle peridotite will exist as either a single solid or molten phase or, at pressures between ∼2–4 GPa, as a mixture of sulfide melt and MSS phases (e.g., Bockrath et al., 2004). The wide range of major element compositions reported for sulfides from individual abyssal peridotites therefore indicates that these sulfides are not in chemical equilibrium with one another. In this case, however, the “moat effect” is largely ineffective at preserving chemical heterogeneity for geologically long periods. For example, the major cations in MSS-type sulfides are Ni and Fe. If the cation/sulfur ratio in sulfides is fixed by the local f_{O2} and f_{S2}, then exchange of Ni and Fe between sulfides and surrounding phases will be linked – the sulfides cannot gain Ni without losing a proportionate amount of Fe, and vice versa. In this case, Ni becomes the rate-limiting element, because the ratio of Ni between sulfide and silicate phases (∼10^2) is higher than for Fe (∼4). However, Ni diffusion in olivine is relatively rapid, with D values at convecting mantle conditions $>10^{-16}$ m^2/s (e.g., Chakraborty, 2010). Under these conditions, silicate phases will establish Ni concentrations in equilibrium with one another over lengthscales comparable to the size of a typical hand sample (∼10 cm) in about 3 Myr. Over long periods, therefore, we can assume that Ni:Fe in major phases such as olivine is homogeneous at the hand sample scale. Sulfides must interact with a volume of silicate roughly equal to the sulfide volume times the sulfide/silicate partition coefficient in order to establish equilibrium with surrounding silicates. For a $\mathrm{Ni}_S/\mathrm{Ni}_P$ ratio of ∼100, this then corresponds to a sphere surrounding the sulfide with a radius equal to only ∼4.6× the sulfide effective radius (e.g., 460 μm radius for a 100 μm radius sulfide). Diffusive equilibration over this distance at convecting mantle temperatures is extremely rapid, <100 yr for a 100 μm radius sulfide. In short, major element (e.g., Ni:Fe) heterogeneity cannot be maintained in sulfides from individual hand-sample-sized peridotites for any significant period within the convecting mantle. The observed sulfide heterogeneity requires that sulfide compositions were affected by interaction with metasomatizing silicate or sulfide melts shortly before the peridotites hosting these sulfides were brought to the surface. Finally, although to date studies have not reported major element and Pb- or Os-isotope data for the same sulfides, it is well established that Os-isotopes often correlate with Os concentration in sulfides (e.g., Griffin et al., 2004; Harvey et al., 2016 and references therein), and it is also established that [Os] correlates with sulfide major cation composition (e.g., Alard et al., 2000; Pearson et al., 1998). If sulfide major cation heterogeneity must be relatively young, it seems difficult to escape the conclusion that the correlated isotopic heterogeneity is also young.

This last consideration has implications for the origin of Os- and Pb-isotope heterogeneity in sulfides from sub-continental lithospheric mantle xenoliths. The above discussion considers the likelihood of survival of isotopic heterogeneities in sulfides contained within the convecting mantle, i.e., at temperatures >1300 °C. However, many SCLM xenoliths have equilibration temperatures ranging from 800–1000 °C (e.g., Byerly and Lassiter, 2012), and diffusion of Os and Pb at these temperatures may be sufficiently slow that long-term preservation of isotopic heterogeneities in individual sulfides is possible. However, even at 800 °C, the diffusivity of Fe and Ni in olivine are of the order 10^{-19} to 10^{-20} m^2/s (Chakraborty, 2010), which is sufficiently rapid given the low sulfide/silicate K_d values for these elements to allow chemical equilibration of sulfide phases over geologically short ($<10^6$ yr) periods.

In summary, preservation of Os- and Pb-isotope disequilibrium within different generations of sulfides in mantle peridotites for ∼Ga timescales appears unlikely, and would require a “perfect storm” of large, isolated sulfides and Os and Pb diffusivity in silicate phases significantly lower than for most other cations. Although this scenario cannot be completely ruled out in the case of Os, the preservation of chemical disequilibrium in many suites of mantle sulfides combined with the short equilibration timescales for Fe and Ni indicates that in many cases mantle peridotites have experienced recent metasomatism that resulted in introduction or modification of grain-boundary sulfides and variable and incomplete reequilibration of included sulfides. If this interpretation is correct, then the observed correlations between Re/Os and ^{187}Os/^{188}Os and ^{206}Pb/^{204}Pb–^{207}Pb/^{204}Pb reported for suites of sulfides from individual peridotite samples most likely represent mixing trends rather than isochrons. The implications of this for MORB petrogenesis are examined in the following section.

5. Implications for MORB petrogenesis and the isotopic composition of the depleted upper mantle

In most of the studies of intra-sample heterogeneity conducted to date, included MSS-type sulfides extend to more depleted (less radiogenic) Os- and/or Pb-isotope compositions than coexisting interstitial sulfides or clinopyroxene. This suggests that the metasomatizing component responsible for producing intra-sample isotopic heterogeneity is enriched relative to typical unmetasomatized peridotite. Thus, the most isotopically depleted (typically included) sulfides in any given peridotite provide the best estimate of the isotopic composition of that peridotite prior to recent melt/mantle interaction beneath the mid-ocean ridge. The inference of Burton et al. (1999), Alard et al. (2005), and others that the "depleted" sulfide isotopic composition reflects long-term preservation of ancient melt-depletion signatures is therefore correct, but it is likely that the entire host peridotite (at the hand-sample scale) shared this depleted signature prior to the most recent episode of melt/mantle reaction associated with its exhumation. Included sulfides therefore do provide a potential means of "seeing through" the effects of recent metasomatism and melt/rock reaction to constrain the original isotopic composition of the peridotite. Note that the above discussion does not preclude significant isotopic heterogeneity in bulk peridotites at the meter scale and above. The characteristic lengthscales of mantle chemical and isotopic heterogeneity in the convecting mantle are largely unconstrained, but could provide an important constraint on the style and vigor of mantle convection. O'Driscoll et al. (2018) recently documented Os-isotope heterogeneity in a suite of xenoliths from a $\sim$45 m^2 peridotite outcrop that spans nearly the entire isotopic range observed globally in abyssal peridotites, demonstrating the preservation of significant mantle isotopic heterogeneity at lengthscales of a few meters. Future studies of spatially correlated samples (and individual grains within samples) may shed significant light on the processes and timescales of isotopic and chemical homogenization in the mantle.

Melts from fertile pyroxenitic and/or eclogitic components within the convecting upper mantle are a potential source of the "enriched" metasomatic component required to account for the above observations, as are unusually fertile and enriched peridotites with high U/Pb and/or Re/Os. Melts from these components may partially overprint the isotopic signatures of depleted peridotites during melt migration through interaction with existing interstitial sulfide (and clinopyroxene) phases or through precipitation of new phases along melt pathways. Because these components typically have lower solidi than mantle peridotites, they are expected to melt deeper and to a greater extent than peridotites in upwelling mantle beneath mid-ocean ridges (e.g., Hirschmann and Stolper, 1996). Numerous studies have reported major and trace element evidence for melt/rock reaction in abyssal peridotites (Niu, 1997; Kimura and Sano, 2012). In particular, many plagioclase-bearing peridotites show petrologic, geochemical, and petrographic evidence for melt/rock reaction (e.g., Yang et al., 2013). Pyroxenites and eclogites (and to a lesser extent peridotites that have experienced melt refertilization or metasomatism) commonly have elevated Re/Os and U/Pb ratios, and will develop radiogenic ^{187}Os/^{188}Os and ^{206}Pb/^{204}Pb over time (e.g., Shirey and Walker, 1998; Becker et al., 2000). Numerous studies have revealed a systematic isotopic mismatch between mid-ocean-ridge basalts and abyssal peridotites or other peridotite samples of the convecting upper mantle (e.g., Cipriani et al., 2004; Warren et al., 2009; Stracke et al., 2011; Byerly and Lassiter, 2014), with peridotites often having more "depleted" Sr-, Nd-, Hf-, or Pb-isotopic compositions than average MORB. This mismatch may reflect preferential sampling of "enriched" and easily fusible components during melt generation (e.g. Byerly and Lassiter, 2014). Thus, intra-sample isotopic heterogeneity within abyssal peridotites may result from the same process that accounts for these systematic differences – melt generation from "enriched" and fertile lithologies within the depleted and refractory peridotite of the convecting upper mantle.

The above discussion further supports the suggestion that MORB do not provide an accurate estimate of the isotopic composition of average upper-mantle peridotites (e.g., Byerly and Lassiter, 2014). Partial melting and melt extraction from heterogeneous mantle inevitably oversamples more fertile and isotopically enriched portions of the mantle. As a result, estimates of mantle composition based in part on inversion of MORB isotopic compositions (e.g., Salters and Stracke, 2004; Workman and Hart, 2005) underestimate the average melt depletion of the upper mantle relative to primitive mantle, with important consequences for estimates of the style and vigor of mantle convection and melt production over time. Analysis of included sulfide phases in abyssal peridotites and mantle xenoliths may provide the most robust means of evaluating isotopic variations in peridotitic portions of the convecting upper mantle. Future isotopic studies of peridotite sulfides, particularly when combined with textural studies that may reveal pathways of melt migration, are likely to provide new insights into the distribution of depleted and enriched components in the mantle and the role of melt/mantle interaction in MORB petrogenesis.

6. Conclusions

Isotopic heterogeneity within populations of sulfide grains in abyssal peridotites and other peridotite samples recently derived from the convecting upper mantle is unlikely to reflect long-term preservation of these heterogeneities at the hand-sample scale. Although high sulfide/silicate K_d values for elements such as Pb and Os significantly reduce the diffusive flux between spatially separated sulfides, the small average spacing of sulfides within peridotites with typical sulfur abundances results in equilibration timescales less than a few 10s of Myr for the Os and Pb isotopic systems for reasonable silicate diffusivities. In addition, major element variations will be destroyed at convecting mantle temperatures over very short timescales. Correlations between sulfide major element compositions and Os- or Pb-isotope composition therefore require that the isotopic heterogeneities are themselves also young.

The presence of grain-scale isotopic heterogeneity therefore requires that many abyssal peridotites are affected by recent melt/mantle or fluid/mantle interaction, with the metasomatic agent consistently more "enriched" than typical upper mantle peridotites. This likely results from early/deep melt generation from fertile pyroxenite or eclogite (or fertile/enriched peridotite) components at the base of the melting region beneath mid-ocean ridges, and suggests a genetic link between abyssal peridotite grain-scale isotopic heterogeneity and systematic isotopic differences observed between abyssal peridotites and MORB. This highlights the importance of melt generation from non-peridotitic components in generating the isotopic and trace element characteristics of modern MORB.

Finally, the most depleted isotopic signatures preserved in included sulfides from any given peridotite sample likely most accurately reflect the composition of that peridotite prior to metasomatism beneath the modern mid-ocean ridge. These signatures commonly include highly unradiogenic Os- and Pb-isotopes, including Pb-isotope values plotting to the left of the geochron. Unmodified upper mantle peridotite may therefore represent a significant reservoir of unradiogenic Pb, providing a potential solution to the long-standing "Pb paradox". The picture that is emerging is that the upper mantle contains significant quantities of refractory and isotopically depleted peridotite with embedded veins of more fertile components. Melt generation inevitably oversamples the fertile and enriched components, so that mantle-derived basalts provide a biased picture of upper mantle composition.

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