PGE Fractionation Between Sulfide-Bearing Mantle and Basaltic Melt During Partial Melting and Melt Segregation

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The distribution of PGEs between mantle and primitive basaltic melts is well known but poorly understood. The fertile mantle has PGE concentrations of about 0.7 percent of the chondritic values, and the PGE ratios are chondritic (McDonough and Sun 1995). In primitive basalts the PGEs are strongly fractionated from each other such that the refractory elements (Os, Ir, Ru) are depleted relative to the less refractory PGEs (Pt, Pd; Fig. 1). The magnitude of PGE fractionation correlates broadly with depth and degree of melting, in Fig. 1 reflected by normative olivine contents (Ballhaus 1995).

Conventionally, it is thought that absolute and relative PGE concentrations in primitive basaltic melts are controlled by exchange equilibria between a monosulfide liquid solution and silicate melt in the mantle source. If during partial melting sulfide remains as a residual phase in the mantle, the resulting basalt should be low in absolute PGEs owing to the large sulfide/silicate partition coefficients (i.e. MORB). If, on the other hand, the sulfide phase is eliminated, i. e. dissolved in the silicate melt during partial melting, the resulting basalt is thought to have higher PGE concentrations (OIB, komatiites). Despite a wide choice of experimentally determined sulfide/silicate partition coefficients, little progress has been made in modelling convincingly the fractionation of PGEs between mantle and basalt (cf. Fig. 1) by sulfide/silicate exchange equilibria. Observations such as absolute Pd concentrations in basalts similar to primitive mantle (Fig. 2) would rather suggest that sulfide can never be residual. A basalt whose Pd content was controlled by sulfide/silicate exchange equilibria with a residual sulfide phase in the mantle source would have Pd concentrations in the low ppt range.

We report here experiments to understand the physical behavior of sulfide during partial mantle melting. We show that neither the absolute nor the relative PGE abundances in basalts are governed by sulfide/silicate partition coefficients. The absolute PGE concentrations in primitive basalts (Fig. 2), i.e. unmodified by low-pressure fractionation, reflect the proportion of mantle sulfide that was washed out of the crystalline mantle matrix during melt segregation as an "accidental sulfide fraction". The relative PGE abundances (cf. Fig. 1) are a consequence of sulfide dissolution and resulting PGE fractionation during decompression of the basalt to the Earth´s surface.
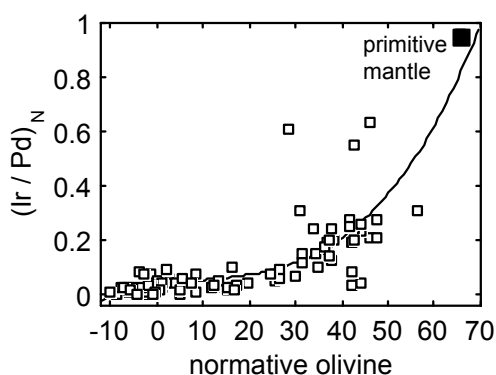

Figure 1. *(Ir/Pd)$_N$ ratios in primitive mantle melts in exchange equilibrium with Fo$_{90}$ as a function of normative olivine content (various sources from the literature). For primitive melts the normative olivine content is a parameter that reflects depth and degree of melting.*
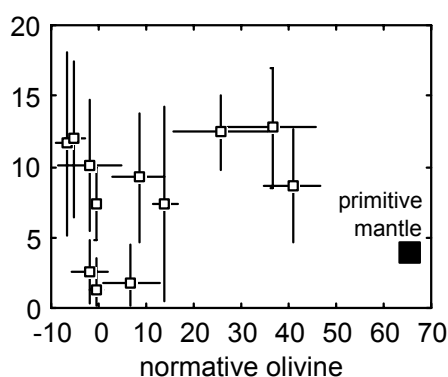

Figure 2. *Average Pd concentrations in a range of primitive mantle melts against normative olivine content (1 sigma). Note that Pd in basalts does not differ fundamentally from the Pd content of primitive mantle; variations are too small to be explained by the presence or absence of a residual sulfide melt.*

Fertile mantle material (i.e., 60 percent olivine, 20 percent orthopyroxene, 20 percent chrome diopside, and 5 percent Al-spinel) was prepared from finely ground natural mineral separates, doped with 0.2 to 2 weight percent Fe-Ni-Cu sulfide (MS 11 in Ballhaus et al. 2001), and melted in a piston cylinder press at 1350°C and 0.5 GPa. All experiments were carried out in open graphite capsules. Oxygen and sulfur fugacity conditions imposed by the container and the metal/S ratio of the sulfide phase are unquantified but within the stability field of a monosulfide liquid solution. The results are summarized as follows:

- The stable sulfide phase in convecting upper mantle is a monosulfide liquid solution.
- Nearly all sulfide collects as droplets immersed in interstitial silicate melt pockets at grain boundaries (Fig. 3). The proportion of sulfide trapped by silicate minerals is negligible.
- Silicate melt wets crystalline silicate phases more efficiently than sulfide melt (cf. Rose and Brenan 2001). As a consequence, all sulfide droplets were found isolated from silicate minerals by thin films of silicate melt.
- No correlation exists between the amount of sulfide added to a charge (0.2 to 2 weight percent) and average sulfide droplet diameter (Fig. 4). The amount of sulfide only controls the number of sulfide droplets exposed per surface unit.
- In static experiments, there is no tendency of sulfide melt to coalesce with time to larger aggregates (cf. Bremond d´Ars et al. 2001), regardless of run time (4 to 22 hours).
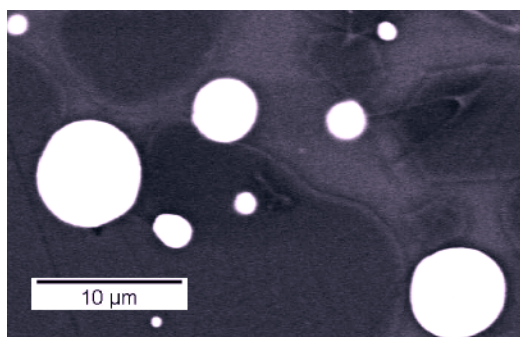
The experiments are applicable to natural systems and can explain both the absolute and relative PGE concentrations in mantle melts. When sulfide-bearing mantle is subjected to partial melting, the sulfide phase will obviously distribute along grain boundaries and will reside quantitatively in silicate melt pockets (Fig. 3). As partial melting ensues, some sulfide will dissolve in the silicate melt, the proportion of which will depend upon sulfide concentration in the source, sulfur solubility in the silicate melt, degree of partial melting, and pressure. That sulfide fraction that cannot dissolve due to oversaturation will remain immersed in silicate melt, in accordance with Fig. 3. Droplet sizes are small enough to be washed out of the matrix as "accidental sulfide fraction" when the silicate melt eventually segregates from the matrix. It is the PGE budget of this accidental sulfide fraction that later dominates the PGE content of a basalt at the surface.

The fractionation of the PGEs relative to each other, reflected by CI-normalized Ir/Pd ratios (Fig. 1), probably occurs during melt decompression to the Earth´s surface. There is growing experimental evidence that sulfur solubility in silicate melt increases markedly with decreasing pressure (Mavrogenes and O´Neill 1999, Holzheid and Groves 2002), so any "accidental sulfide fraction" that may have become entrained during segregation at high pressure has a good chance to become dissolved during decompression. At this point the PGE spectrum of the basalt - undersaturated with respect to sulfide at shallow depth - will be controlled by the relative PGE solubilities in silicate melt (Borisov and Palme 2000 and refs. therein). The most soluble PGEs,
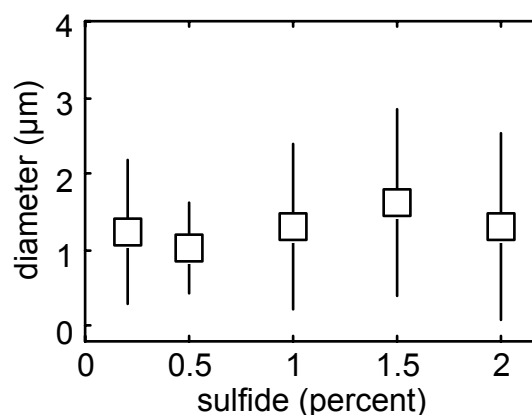

Figure 3. *Backscatter image of silicate melt pools (dark grey) in partially melted mantle matrix (largely olivine) with dispersed sulfide droplets (bright).*

Figure 4. *Average diameters of sulfide droplets as a function of sulfide added to an experimental charge (1 sigma).*

presumably represented by Pd, will dissolve in the silicate melt as oxide complexes and will largely remain in solution. The least soluble, refractory PGEs, i.e. those with the highest melting points (Os, Ir, Ru), will aggregate to discrete alloy nuggets and may thus be fractionated from Pd along with olivine and chromite. As a result, Ir/Pd bulk ratios with fall when the normative olivine content of a primitive melt falls by decompression within the mantle.

According to this model we cannot expect a systematic relationship between PGE sulfide/ silicate partition coefficients, retention of PGEs in residual sulfide, and PGE abundances in basalts. On the contrary: Basalts from sulfide-rich, fertile sources are more likely to be more PGE enriched than basalts from more refractory mantle (sulfide-poor) sources if PGE abundances in the mantle source correlate with total sulfide. Absolute PGE abundances in a basalt cannot be used to speculate on the presence or absence of residual sulfide in the mantle source (Hamlyn 1986), nor is the degree of sulfide saturation at the surface a useful parameter to assess the potential of a basaltic melt to produce a magmatic sulfide-PGE deposit.

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