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OSMIUM MASS BALANCE IN PERIDOTITE AND THE EFFECTS OF
MANTLE-DERIVED SULFIDES ON BASALT PETROGENESIS

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ABSTRACT

Analyses of enriched mantle (EM)-basalts, using lithophile element-based isotope systems, have long provided evidence for discrete mantle reservoirs with variable composition. Upon partial melting, the mantle reservoir imparts its isotopic fingerprint upon the partial melt produced. However, it has increasingly been recognised that it may not be simple to delimit these previously well-defined mantle reservoirs; the “mantle zoo” may contain more reservoirs than previously envisaged.

However, here we demonstrate that a simple model with varying contributions from two populations of compositionally distinct mantle sulfides can readily account for the observed heterogeneities in Os isotope systematics of such basalts without additional mantle reservoirs. Osmium elemental and isotopic analyses of individual sulfide grains separated from spinel lherzolites from Kilbourne Hole, New Mexico, USA demonstrate that two discrete populations of mantle sulfide exist in terms of both Re-Os systematics and textural relationship with co-existing silicates. One population, with a rounded morphology, is preserved in silicate grains and typically possesses high [Os] and low [Re] with unradiogenic, typically sub-chondritic $^{187}\text{Os}/^{188}\text{Os}$ attributable to long term isolation in a low-Re environment. By contrast, irregular-shaped sulfides, preserved along silicate grain boundaries, possess low [Os], higher [Re] and a wider range of, but generally supra-chondritic $^{187}\text{Os}/^{188}\text{Os}$ ($[\text{Os}]$ typically $\leq 1$-2 ppm, $^{187}\text{Os}/^{188}\text{Os} \leq 0.3729$; this study). This population is thought to represent metasomatic sulfide.

Uncontaminated silicate phases contain negligible Os (<100 ppt) therefore the Os elemental and isotope composition of basalts is dominated by volumetrically insignificant sulfide ($[\text{Os}] \leq 37$ ppm; this study). During the early stages of partial melting, supra-chondritic interstitial sulfides are mobilized and incorporated into the melt, adding their radiogenic $^{187}\text{Os}/^{188}\text{Os}$ signature. Only when sulfides armoured within silicates are exposed to
the melt through continued partial melting will enclosed sulfides add their high [Os] and unradiogenic $^{187}$Os/$^{188}$Os to the aggregate melt. Platinum-group element data for whole rocks are also consistent with this scenario. The sequence of (i) addition of all of the metasomatic sulfide, followed by (ii) the incorporation of small amounts of armoured sulfide can thus account for the range of both [Os] and $^{187}$Os/$^{188}$Os of EM-basalts worldwide without the need for contributions from additional silicate mantle reservoirs.
1. INTRODUCTION

Peridotite xenoliths are frequently entrained during the eruption of intra-plate magmas. Their utility in investigating mantle composition (e.g. Frey & Green, 1974; Ionov et al., 1993; Wilshire & Shervais, 1975; Stosch & Seck, 1980; Coisy & Nicolas, 1978; Stern et al., 1989) and basalt source reservoirs (e.g. Zindler & Hart, 1986; Hofmann, 1997) has been recognised for several decades. Their geographical dispersion is widespread and their accidental transport to the surface provides a means of sampling the mantle over a range of depths. Xenolith mineralogy, elemental composition, and isotope systematics all suggest that many peridotite xenolith suites have experienced varying degrees of partial melting (e.g. Jagoutz, et al., 1979; Galer & O’Nions, 1988) suggesting that suites of mantle xenoliths may be of particular utility in investigating the long term evolution and history of melt depletion in the mantle (e.g. Ross et al., 1954; Kuno & Aoki, 1970; Carlson & Irving, 1994; Pearson et al., 1995; Pearson, 1999; Griffin et al., 2003; Chu et al., 2009; Harvey et al., 2010).

Similarly, for several decades lithophile element-based isotope systems such as Sm-Nd, and Rb-Sr have been used to fingerprint the variable mantle sources (e.g. Galer & O’Nions, 1989) whose distinctive isotopic flavour is transferred to enriched-mantle (EM) basalts during partial melting. However, recent work involving the Re-Os isotope systematics of EM-basalts (e.g. Class et al., 2009) suggests that it may not be so simple to delimit these previously well defined mantle reservoirs; the “mantle zoo” (Stracke et al., 2005) may contain more reservoirs than previously envisaged. The commonly perceived understanding of how the Re-Os isotope system behaves during mantle melting is that the parent-daughter pair is unique due to the moderately incompatible and compatible nature of rhenium and osmium, respectively, on a bulk-rock scale (Pegram & Allègre, 1992); with rhenium, at least in part, residing within some silicate phases, e.g. garnet, based upon the observation that both Re and Yb concentrations are significantly higher in ocean island basalts (OIB) compared to
mid-ocean ridge basalts (MORB), i.e. $D^{\text{silicate/melt}} \approx Yb$ (Hauri & Hart, 1997; Righter et al., 1998). However, in detail, the bulk-rock budget of Re, Os and the other platinum group elements (PGE), and critically the behaviour of these elements during partial melting, is decoupled from the mechanisms that control lithophile element-based isotope systems. Osmium within the Re-Os isotope system and PGE abundance are controlled, in the main, by volumetrically minor (<0.03 modal %) sulfide (Luguet et al., 2003; 2004).

At least two populations of sulfide are commonly found within peridotite samples from the upper mantle. Sulfide grains wholly enclosed within silicate grains, and effectively shielded from interaction or re-equilibration with metasomatic agents, possess supra-chondritic IPGE (Os, Ir, Ru) abundances, lower PPGE (Pt, Pd, Rh) and Re abundances and often retain sub-chondritic Os isotope ratios attributable to their long-term isolation from the silicate melt from which they immiscibly separated (e.g. Alard et al., 2002, 2005; Griffin et al., 2004; Bockrath et al., 2005; Mungall & Su, 2005; Harvey et al., 2006, 2010). Interstitial, or intergranular sulfides possess supra-chondritic abundances of Re and PPGEs, lower IPGE (Os, Ir, Ru) abundances and variable (sub- to supra-chondritic) Os isotope ratios, (e.g. Burton et al., 1999; Alard et al., 2002; Pearson et al., 2004; Bockrath et al., 2004; Mungall & Su, 2005; Harvey et al., 2006, 2010; Luguet et al., 2008). This population of sulfides has been demonstrated to be highly mobile during metasomatic events (e.g. Harvey et al., 2010), being easily mobilized and redistributed by transient melts and fluids. Hence, in the specific context of PGE distribution between these populations of sulfide and their Re-Os isotope characteristics the sub-oceanic and subcontinental lithospheric mantle (SCLM) are very similar (cf. Alard et al. 2005; Harvey et al., 2006; Liu et al. 2008; Luguet et al. 2008 for sub-oceanic lithospheric mantle and e.g. Burton et al., 1999; Alard et al. 2002; Harvey et al. 2010 for SCLM). It is also the early mobilization of interstitial sulfides during the onset of partial melting to which the apparent “isotopic gap” between mid-oceanic ridge basalts (e.g.,
Gannoun et al., 2004, 2007; Escrig et al., 2005), oceanic basalts (Reisberg et al., 1993; Roy-
Barman & Allègre, 1995; Luguet et al., 2008) and abyssal peridotites (e.g., Alard et al., 2005;
Harvey et al., 2006; Liu et al., 2008) has been attributed; a process that may also occur in
SCLM settings and go at least some way to explaining the notoriously difficult interpretation
of bulk rock rhenium-depletion ($T_{RD}$) ages (Rudnick & Walker, 2009).

This study presents bulk-rock PGE abundances and Re-Os elemental and isotope
analyses of bulk-rock, silicate and spinel mineral separates, and 2 populations of sulfide in a
suite of 28 peridotite xenoliths from Kilbourne Hole, New Mexico, USA. We demonstrate
that the behaviour of the two compositionally and texturally distinct populations of peridotite-hosted sulfide controls the behaviour of Re and Os during partial melting. Moreover, using a
simple two-stage model we demonstrate a means for the generation of the range of Re-Os
elemental and isotopic compositions of worldwide EM-basalts without the need of additional
mantle reservoirs to those proposed by Zindler & Hart (1986) and Hofmann (1997).
2. GEOLOGICAL SETTING, PETROLOGY AND PETROGRAPHY OF SAMPLES

Kilbourne Hole is one of several late Pleistocene volcanic maars situated in the Potrillo volcanic field on the axis of the Rio Grande Rift, an asymmetric system of grabens which extends for over 1000 km north–south through Colorado, New Mexico and Texas in the USA and onwards into Chihuahua, northern Mexico. The petrology and petrography of Kilbourne Hole mantle xenoliths have been the subject of extensive prior study, (e.g. Carter, 1965; Reid & Woods, 1978; Irving, 1979, 1980; Basaltic Volcanism Study Project, 1981; Bussod, 1981; Bussod & Irving, 1981). Mantle and crustal xenoliths are abundant in the lava flows in the Kilbourne Hole area. Dates for the eruption of the host basanite range from 80 Ka ± 10 Ka (Bussod & Williams, 1991; Thompson et al., 2005) to 141 Ka ± 75 Ka (Hoffer, 1976; Dromgoole & Pasteris, 1987) which suggests that any xenoliths exhumed at Kilbourne Hole have been separated from their source for only a relatively short period of geological time and are thus representative of the present-day mantle underlying the south-western USA.

The samples examined during the course of this study (n = 28) are Cr-diopside spinel lherzolites and spinel harzburgites with protogranular textures. A single sample (KH03-21) has a texture transitional between protogranular and porphyroclastic. Grain size is therefore generally greater than 1 mm and the samples are almost exclusively coarse grained. Porphyroclastic and granular xenoliths have also been reported at Kilbourne Hole. Although other petrographic textures have been observed (mosaic-porphyroclastic, tabular granular; Dromgoole & Pasteris, 1987; Kil & Wendlandt, 2004) textures other than protogranular are in fact rare at this locality and protogranular xenoliths are most representative of those recovered from Kilbourne Hole (Kil & Wendlandt, 2004).

Large (>1 kg) xenoliths were preferentially selected so that host basalt could be trimmed and the possible effects of host infiltration minimised while still retaining sufficient
material (>500 g) to represent a homogenous sample at the bulk-rock scale. The samples for this study were also selected so as to represent a wide range of clinopyroxene modal abundance, estimated visually in the field and subsequently calculated using a least squares regression method (Tarantola & Valette, 1982). Chrome-diopside modal abundance ranges from 3.3% to 17.2% (±1.6). No discrete metasomatic phases (e.g., phlogopite, amphibole, apatite) were detected during this study, or any prior study of this locality.

In addition to the silicate phases and spinel, which account for in excess of 99.97% of the volume of the samples, individual sulfide grains (n = 33) with bulk compositions broadly equivalent to pentlandite-rich and pentlandite-poor monosulfide solid solution (Luguet et al., 2003, 2004) were also analysed for major element abundances, Os abundances and Os isotopes.
3. ANALYTICAL METHODS

Samples were cut and washed to remove host basalt, surface alteration and contamination and rinsed in ultra-pure (>18 MΩ reverse osmosis scrubbed) water. Samples selected for bulk-rock analysis were dried and then powdered in an agate mortar. For the bulk-rock Re-Os measurements ~2 g of peridotite was dissolved in inverse aqua regia (3 mL 12M HCl / 9 mL 16M HNO₃) in sealed Carius tubes at 230°C for 7 days (Shirey & Walker, 1995). A spike solution, enriched in 185Re and 190Os, was added immediately before the addition of the acids. Osmium was purified using CCl₄, leaving Re in the inverse aqua regia fraction (Cohen & Waters, 1996). The Os was subsequently recovered from the CCl₄ in HBr, microdistilled for 3 h at 90 °C (Birck et al., 1997) and dried down. Rhenium was extracted by drying down the inverse aqua regia and redissolving the residue in 2M Teflon-distilled HNO₃. The Re was recovered in iso-amylol (Birck et al., 1997), cleaned in a wash of 2M HNO₃ and finally extracted in ultrapure water. The reference material UB-N, a serpentinised peridotite, was digested numerous times (n = 6) to assess the efficacy of the Carius tube dissolution method for bulk-rock peridotite. Meisel et al. (2003) questioned “traditional” methods (i.e. low temperature acid attack; Carius tubes) for peridotite dissolution, citing resistant phases remaining undissolved which, in turn, led to poor reproducibility of Os concentrations and Os isotope ratios. Osmium concentrations of UB-N (3.4 to 4.2 ppb, n = 6) were indistinguishable from those obtained by high-pressure asher (e.g. Meisel et al., 2003), although the values obtained for the Os isotope ratio of UB-N were somewhat variable (187Os/188Os = 0.1250 ± 2 to 0.1279 ± 1). However, repeat digestions of Kilbourne Hole bulk-rock samples (KH03-6, KH03-21 & KH03-25) by Carius tubes performed during this study demonstrate excellent reproducibility for both osmium concentrations and Os isotope ratios (e.g. KH03-06: [Os] = 1.54 ± 0.10 (2 sd); 187Os/188Os = 0.1269 ± 4 (2sd); n = 4). This suggests that the variability in the Os isotope measurements for UB-N obtained during this
study are more likely attributable to heterogeneity in the reference material, i.e. a nugget effect at the 2 g sample size, rather than artefacts attributable to incomplete digestion. Notwithstanding the possibility of either incomplete digestion or a nugget effect in the analysis of UB-N, neither of these factors appear to affect repeat analyses of Kilbourne Hole xenoliths. Reproducibility of Re concentrations in duplicate analyses is comparable to that achieved on corresponding Os measurements (KH03-21 [Re] = 0.08 ± 0.3 (2 s.d.) n = 4; KH03-10 [Re] = 0.23 ± 0.10 (2 s.d.) n = 2); KH03-6 [Re] = 0.07 ± 0.02 (2 s.d.) n = 4). Repeat digestions of reference material UB-N (n = 6) yielded Re concentrations of 0.184 ± 0.071 ppb, slightly below the preferred value of Meisel et al. (2003) which ranges from 0.201 to 0.241 ppb, although as stated above this likely reflects the heterogeneity of the reference material rather than inaccuracy of the measured concentration of a particular digestion. Reproducibility of Os isotope ratios in Kilbourne Hole bulk-rock peridotites is good. For example, repeat analyses of KH03-6 (n = 4) and KH03-21 (n = 3) differed by 0.14 % and 0.09 % respectively. Total procedural blanks for bulk-rock Os measurements during the course of this study were 3.85 ± 3.0 pg, $^{187}$Os/$^{188}$Os = 0.170 ± 0.031, and for Re 1.85 ± 2.15 pg.

Aggregates of optically pure olivine, orthopyroxene, clinopyroxene and spinel were handpicked under a binocular microscope to ensure that both visible inclusions and surficial adherents were absent. The aggregates were repeatedly rinsed in analytical grade acetone and ultra-pure water before being powdered in an agate pestle and mortar. The powdered aggregates were then digested and Os and Re purified and recovered by low temperature acid attack, closely following the method described by Birck et al. (1997) and previously employed by Burton et al. (1999) and Harvey et al. (2010) on mineral phases from similar xenolithic material.
Rhenium–osmium chemistry for individual hand-picked sulfide grains was achieved using a modified microdistillation technique that closely follows previously reported procedures (Pearson et al., 1998). The total procedural blanks for Os in individual sulfides were $0.10 \pm 0.06$ pg, $^{187}\text{Os}/^{188}\text{Os} = 0.36 \pm 0.50$, and for Re $3.14 \pm 0.61$ pg. Both Re and Os samples were analysed on platinum filaments using negative thermal ionisation mass spectrometry (N-TIMS) (Volkening et al., 1991; Creaser et al., 1991) using a ThermoScientific Triton at The Open University, collecting individual masses by peak jumping on a secondary electron multiplier. Long term accuracy of a Johnson Matthey standard solution (14 pg to 8 ng; $n = 85$) is generally within 0.1% of the recommended values for $^{187}\text{Os}/^{188}\text{Os}$. Typical signal intensities of $^{190}\text{Os}$ were in excess of 250,000 cps.

Bulk-rock PGE abundances of 6 peridotite xenoliths and the host basalt were determined using the anion-exchange column procedures of Pearson & Woodland (2000) and Dale et al. (2008). Bulk-rock powders were digested, together with a mixed PGE spike, in inverse aqua regia (2.5 mL 12M HCl, 5 mL 16M HNO$_3$) in an Anton Paar high-pressure asher. Following Os extraction by CCl$_4$, the inverse aqua regia was dried, refluxed in 12M HCl and dried again. Chrome in its oxidised form (Cr$^{6+}$) can be present after aqua regia digestion and behaves similarly to PGE on the anion exchange resin and hence can be eluted with the PGE, causing polyatomic isobaric interferences on isotopes of Ru (Meisel et al., 2008). Therefore, any Cr$^{6+}$ present was reduced by the addition of H$_2$O$_2$, which was then dried and the residue taken up in 10 mL of 0.5M HCl and loaded onto a column containing AG1X-8 (100–200#) anion-exchange resin. The sample matrix was eluted with 10 mL of 1M HF/1M HCl and 0.8M HNO$_3$ before Ir, Ru, Pt and Re were collected in 10 mL of 13.5M HNO$_3$. Palladium was collected in 20 mL of 9M HCl after further elution of Zr using 1M HF/1M HCl. Both the Ir–Pt–Ru–Re and the Pd cuts were dried down and taken up in 1 mL of 0.5M HCl for analysis using the ThermoScientific Element2 ICP-MS at Durham University.
Details of mass spectrometry procedures are given in Dale et al. (2008). The reproducibility of Ir, Pt and Pd abundances in the peridotite reference material GP13 is ~10% RSD, whereas Re has an uncertainty of 3% RSD. Reproducibility of IPGE, based upon multiple Os analyses of the peridotite samples is a maximum of ± 6% (2σ).
4. RESULTS

4.1 Bulk rock Re and Os elemental and isotope measurements.

Bulk-rock Re concentrations ([Re]) range from 0.007 ppb to 0.693 ppb, with a mean concentration of 0.094 ppb (Table 1). The range of [Re] obtained during this study is much larger than that of Meisel et al. (2001) whose whole rock [Re] of samples from the same locality range from 0.053 ppb to 0.432 ppb. The mean [Re] from this study, like the mean Os concentration ([Os]), is significantly lower than the average mantle composition of 0.35 ppb (Becker et al., 2006) (Figure 1). Bulk-rock [Os] from this study (0.802 to 3.544 ppb, mean = 1.828; Table 1) are similar to previous studies of this locality (Morgan, 1986; Burton et al., 1999; Meisel et al., 2001) and studies of other peridotite suites from similar non-cratonic settings (e.g. Alard, 2002; Meisel et al., 2001; Liu et al., 2008; Ackerman et al., 2009; Harvey et al., 2010; Wittig et al., 2010) but are significantly lower than the mantle average (Becker et al., 2006).

The bulk-rock $^{187}\text{Os}/^{188}\text{Os}$ ratios of the samples range from 0.1159 to 0.1339 with a mean of 0.1256 (Table 1). All but 3 of the 28 xenoliths analysed have $^{187}\text{Os}/^{188}\text{Os}$ ratios <0.1296, the maximum present day estimate of the primitive upper mantle (PUM) of Meisel et al. (1996; 2001) and more than two thirds of the samples (n = 23) have sub-chondritic $^{187}\text{Os}/^{188}\text{Os}$ i.e. < 0.1270 (Walker & Morgan, 1989; Luck & Allègre, 1993). The values obtained in this study are similar to those from previous studies of this locality (Burton et al., 1999; Meisel et al., 2001) i.e. $^{187}\text{Os}/^{188}\text{Os} = 0.117$ to 0.130, mean 0.1257, (n = 17). Whole rock $^{187}\text{Re}/^{188}\text{Os}$ ratios range from 0.009 to 1.35 with a mean of 0.222. However, only 3 samples, KH96-8, KH96-20 and KH96-24, have suprachondritic ratios (i.e. >0.4) and excluding these 3 samples gives a much narrower range of $^{187}\text{Re}/^{188}\text{Os}$ ratios (0.009 to 0.306,
mean = 0.156). This differs somewhat from previous work on xenoliths from the same locality (Burton et al., 1999; Meisel et al., 2001) where the range of $^{187}\text{Re}/^{188}\text{Os}$ values was 0.228 to 0.781 and the mean much higher (0.395), i.e. near chondritic.

Figure 2a is a Re-Os isotope evolution diagram for the 28 bulk-rock peridotites from this study. There is a broad positive co-variation between $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ and the best fit line coincides with a calculated isochron age of 2.3 ± 0.7 Ga, but the relationship cannot be described as convincingly isochronous despite, superficially at least, being in good agreement with the ages derived from Sr isotope ratios of Roden et al. (1988) of 2.5 Ga ± 0.2 Ga for the SCLM beneath the south-western USA. On a bulk-rock scale Re has been described as a moderately incompatible element during partial melting, contrasting with the compatible bulk-rock behaviour of Os during melt depletion (Hart & Ravizza, 1996).

However, Re is mobile under a wide range of conditions (Meisel et al., 1996, 2001; Sun et al., 2004), and the large degree of scatter on bulk-rock Re-Os isotope evolution diagrams can be attributed, at least in part, to rhenium mobility. The best fit line in Figure 2a does not pass through the estimated composition for PUM (Meisel et al., 2001) and the suite of samples from this study appears displaced to a lower $^{187}\text{Re}/^{188}\text{Os}$ composition than those of Meisel et al. (2001) supporting the notion that bulk rock Re may not behave in a systematic manner and may be heterogeneous over spatially restricted areas.

A number of proxies for $^{187}\text{Re}/^{188}\text{Os}$ have therefore been sought amongst elements that are not only moderately incompatible but also immobile and unaffected by secondary processes not related to melt depletion. For example, Al, S and Yb (Reisberg et al., 2005; Hauri & Hart, 1997; Burnham et al., 1998 respectively) are all believed to have similar bulk partition coefficients to Re during partial melting but are generally considered to be immobile at sub-magma generating temperatures. Figure 2b illustrates a much reduced degree of scattering ($R^2 = 0.89$) between $^{187}\text{Os}/^{188}\text{Os}$ and $\text{Al}_2\text{O}_3$ and yields an “aluminachron” age.
(Reisberg & Lorand, 1995) of 2.4 Ga, in good agreement with the best fit line through the Re-
Os isotope evolution diagram in Figure 2a and the Sr isotope age of Roden et al. (1988). We
expand on the subject of Re mobility below in the discussion of metasomatic sulfides and
their mobility.

4.2 Bulk-rock PGE measurements

Six peridotite xenoliths (KH03-10, KH03-15, KH03-16, KH03-18, KH03-21 &
KH03-24) that have experienced a wide range of melt depletion (1.1 to 4.4 wt.% bulk-rock
Al₂O₃) were selected for bulk-rock platinum-group element (PGE) measurements. In
addition, PGE abundances were also obtained for the host basalt. Bulk-rock PGE abundances
(Figure 3) are similar to those obtained elsewhere for non-cratonic lherzolites and
harzburgites (e.g. Lorand & Alard, 2001; Lorand et al., 2003; Wittig et al., 2010) but also
overlap with the lower end of PGE concentrations obtained from bulk-rock cratonic
peridotites (e.g. Pearson et al., 2004; Ivanov et al., 2008), orogenic massifs (e.g. van Acken et
al., 2010) and ophiolitic peridotite (Hanghøj et al., 2010). Osmium, iridium and ruthenium
(IPGE) abundances vary comparatively little within the samples analysed ([Os] = 1.39 to 3.36
ppb; [Ir] = 2.81 to 4.19 ppb; [Ru] = 4.77 to 7.47 ppb; Table 4) whereas Pt and Pd (PPGE),
along with Re, show much greater variability in elemental abundance ([Pt] = 3.35 to 6.58
ppb; [Pd] = 0.55 to 5.58 ppb; [Re] = 0.002 to 0.265 ppb; Table 4). While there is no strong
co-variation between indices of melt depletion (e.g. bulk-rock MgO or Al₂O₃) and PGE
abundance the more fertile peridotites do tend to contain higher abundances of PPGE than
less fertile samples, i.e. the fractionation of IPGE from PPGE appears, in general, to be most
pronounced in the most depleted peridotites, with Re being the most strongly fractionated
from the IPGEs.
4.3 Re-Os abundance and isotope ratios of silicate minerals and spinel

Optically pure mineral separates of olivine, orthopyroxene and clinopyroxene, spinel and individual sulfide grains were handpicked from 4 xenoliths, KH03-15, KH03-16, KH03-21 and KH03-24. These samples were selected on the basis of their wide range of modal abundance of clinopyroxene (2.5 to 17.5 modal %). Osmium concentrations of the silicate phases are presented in Table 2. The high [Os] of clinopyroxene from KH03-16 is probably derived from contamination from one or more microscopic sulfide grains enclosed within the clinopyroxene (surficial contamination, if unobservable during the picking, would probably have been removed during the cleaning process). Osmium concentrations in spinel are up to an order of magnitude more Os than many of the co-existing silicate phases. It is difficult to assess the origin of the high [Os] of spinel as its opaque nature makes it impossible to guarantee that handpicked grains are free from sulfide inclusions. With the exception of presumably contaminated clinopyroxene from KH03-16, [Os] increases in the following manner: olivine < orthopyroxene < clinopyroxene < spinel.

Rhenium concentrations of the same silicates are also presented in Table 2. Spinel tends to have higher [Re] than the silicate phases (47.1 ppt to 818 ppt) (Table 2). While spinel invariably contains the greatest [Re], the distribution of Re amongst the silicate phases is not as clear as the relationship shown for [Os] above. Olivine has the lowest [Re] in all 4 of the samples and the two pyroxenes have a lower [Re] than spinel (other than clinopyroxene from KH03-16, which may be contaminated by sulfide). Although the experimental results of Mallmann & O'Neill (2007) and Righter et al. (2004) suggest that Re does partition into clinopyroxene to a certain extent, the relative partitioning of Re between the pyroxenes in this study is not systematic. The Os isotope ratios and $^{187}$Re/$^{188}$Os ratios for silicate mineral
separates are presented in Table 2. In all cases Os isotope ratios of mineral separates are higher than the corresponding bulk-rock values. Because of the large uncertainties on the mineral Re-Os isochrons no meaningful age information is preserved in the silicate phases alone.

The presence of contamination from included sulfide grains in clinopyroxene from KH03-16 raises the question of whether all of the [Re] and [Os] for mineral separates from this study can be accounted for by varying degrees of sulfide contamination. Burton et al. (1999) demonstrated the effect of included sulfides upon the Os elemental and isotope ratio of a mineral separate. In their study, minerals with sulfide contamination have elevated [Os] (an order of magnitude greater than their clean mineral separates) and Os isotope ratios were indistinguishable from the bulk-rock value. Osmium concentrations of clean mineral separates from this study are similar to those obtained by Burton et al. (1999). The probability of the same degree of sulfide contamination in mineral separates from independent studies is very small. Similarly, the sequential increase in concentration from olivine, through orthopyroxene and clinopyroxene to spinel from all 4 samples from this study (with the exception of KH03-16 clinopyroxene) is difficult to account for with the [Os] being solely attributed to contamination from sulfide inclusions.

4.4. Major element abundances, Re-Os concentration and isotope systematics of individual sulfide grains.

4.4.1 Major element abundances of individual sulfide grains

Based upon the relative proportions of Ni, Fe and Cu, three populations of sulfide have been identified in the Kilbourne Hole xenoliths from this study (Figure 4). Two of the
populations have low Cu abundance (0.08 to 4.68 wt %) and are defined by either a high or
low Fe:Ni ratio. Major element abundances of 57 sulfides derived by electron microprobe are
given in Table 3. These two populations are broadly equivalent to pentlandite-rich and
pentlandite-poor monosulfide solid solution (MSS) sulfides (Luguet et al., 2003, 2004). Within the MSS sulfides analysed there is a broad inverse co-variation between Ni and Fe abundances. The third population of sulfide is characterised by a significantly higher Cu abundance, analogous to chalcopyrite rich sulfides from previous studies (Dromgoole & Pasteris, 1987; Luguet et al., 2003, 2004).

High-Cu sulfides from this study have very high Fe:Ni ratios and plot significantly
below the array of the monosulfide solid solution samples. The relative proportion of Ni, Fe, and Cu in sulfides has implications for the capacity of a sulfide to host Os. Monosulfide solid solution with higher Ni content has a greater proportion of octahedral sites in which Os is commonly hosted (Mackovicky et al., 1986; Cabri, 1999; Ballhaus et al., 1999). A single sulfide with a composition similar to that of the basalt hosted sulfide of Burton et al. (1999) is also illustrated in Figure 4. However, in this instance the sulfide is located within a peridotite xenolith (KH03-23) rather than the host basalt suggesting that some degree of infiltration of and interaction with the host lava itself has occurred (Hammond et al., 2010).

4.4.2. Re-Os concentration and isotope systematics of individual sulfide grains

Individual sulfide grains have by far the highest Os content of any of the constituent phases of mantle xenoliths. All of the xenoliths from which mineral separates were picked contain sulfides with [Os] several orders of magnitude greater than any of the co-existing silicates or spinel. A total of 33 individual sulfide grains were analysed: KH03-15 (n = 7), KH03-16 (n = 7), KH03-21 (n = 10) and KH03-24 (n = 9). Their [Os] vary from 0.001 ppm
to 36.85 ppm (Table 5). Rhenium concentrations of the sulfide grains are also high and, in
general, orders of magnitude greater than the silicate phases and spinel. Rhenium
concentrations for 19 sulfide grains were obtained during this study (KH03-15, n = 4; KH03-
16, n = 5; KH03-21, n = 4; KH03-24, n = 6) which range from 0.002 ppm to 138.9 ppm
(Figure 6). Curiously, sulfide grains from relatively fertile samples (KH03-21 and KH03-24)
have a narrow range of [Os] but a wide range of [Re] and sulfide grains from depleted,
metasomatised samples (KH03-15 and KH03-16) show the opposite i.e. a wide range of [Os]
but a restricted range of [Re].

The morphology of each individual grain was assessed in an attempt to determine the
textural location of the sulfide prior to disaggregation of the xenolith and hand-picking of the
grain. The separated grains were categorised as either euhedral / rounded / subrounded, or
anhedral / subhedral / irregular. The former were inferred to have originated as grains
armoured within individual silicate grains while the latter were ascribed to an interstitial
origin (Alard et al., 2002). Euhedral / rounded / subrounded grains tend to have high Os
concentration and low Re concentrations while the converse is generally true in the anhedral /
subhedral / irregular grains.

The 33 individual sulfide grains have Os isotope ratios ranging from 0.1185 to
0.3729. Sulfides from individual xenoliths also have a wide range of $^{187}\text{Os}/^{188}\text{Os}$ ratios (Table
5). Within the entire sulfide population there is a broad inverse trend between Os isotope ratio
and [Os], i.e. grains with the highest [Os] are frequently the least radiogenic and vice versa
(Figure 5). Although the trend as a whole is less clear in the bulk-rock measurements, Figure
5b illustrates that the samples with the highest bulk-rock [Os] also tend towards the lower Os
isotope ratios. Enclosed sulfide grains, which are often rounded, subrounded or euhedral in
shape, have uniformly low $^{187}\text{Os}/^{188}\text{Os}$ values that are slightly below or indistinguishable
from the bulk-rock Os isotope ratio (Figure 5b) and commonly have the highest [Os] and low
[Re]. Interstitial sulfide grains are often anhedral, irregular or subangular shaped and, like the silicate and spinel mineral separates, are characterised by Os isotope ratios that exceed those of the corresponding bulk-rock value. They have much lower [Os] and higher [Re] than the other sulfide population. That the silicate minerals and interstitial sulfides in many cases yield similar Os isotope compositions for a range of Re/Os ratios suggests a degree of recently attained isotopic equilibrium (cf. Burton et al., 1999).
5. DISCUSSION

5.1. Bulk rock Re-Os isotope systematics during partial melting.

The commonly held perception of the behaviour of Re and Os on a bulk-rock scale is that Os behaves as a compatible element during partial melting of the mantle. This contrasts with Re which behaves as a moderately incompatible element (e.g. $D_{\text{Re} \text{opt/melt}} = 0.013$, $D_{\text{Re cpx/melt}} = 0.18–0.21$; Righter et al., 2004). A first order prediction therefore would be that this will result in a residue that, after melt extraction, retains a moderately high Os content yet is significantly depleted in Re; almost complete exhaustion of Re can be expected with continued melt depletion. In the absence of subsequent metasomatism, evidence for prior melt depletion should therefore be preserved within, for example, peridotite xenoliths and will be characterized by unradiogenic, i.e. sub-chondritic Os isotope ratios ($^{187}\text{Os}/^{188}\text{Os} <0.1270$; Luck & Allègre 1983; Walker & Morgan, 1989). However, metasomatism occurring after melt depletion has the effect of obscuring the primary Os isotope signature of ancient melt depletion. This may take the form of addition of $^{187}\text{Os}$ from material recycled back into the asthenosphere or by adding metasomatic Re which, over time, will generate radiogenic $^{187}\text{Os}$, thus shifting bulk-rock $^{187}\text{Os}/^{188}\text{Os}$ to higher values.

Conversely, enriched-mantle (EM) basalts produced by the partial melting of peridotite generally contain significantly less Os than peridotite (often < 10 ppt, average $[\text{Os}] = 428$ ppt; Reisberg et al., 1993; Roy-Barman & Allègre, 1995; Martin et al., 1994; Bennett et al., 1996; Hauri & Kurz, 1996; Hauri et al., 1996; Lassiter & Hauri, 1998; Widom et al., 1999; Brandon et al., 1999, 2007; Lassiter et al., 2000, 2003; Skovgaard et al., 2001; Eisele et al., 2002; Workmann et al., 2004; Gaffney et al., 2005; Jamais et al., 2008; Debaille et al., 2009; Day et al., 2009; Class et al., 2009), but occasionally extend to values comparable with those of peridotite samples (e.g. >4.4 ppb; Ireland et al., 2009). Although isolated EM-basalts...
have relatively unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ (e.g. as low as 0.1212; Debaille et al., 2009) in
general EM-basalts have radiogenic Os isotope ratios, extending to $^{187}\text{Os}/^{188}\text{Os} = 0.2621$
(Ireland et al., 2009). All of these observations are consistent with, on a bulk-rock scale, Os
behaving as a compatible element during partial melting and the moderately incompatible
nature of Re. When plotted against a reliable index of melt depletion, e.g. bulk-rock Al$_2$O$_3$
wt%, peridotite Os isotope ratios seem to co-vary with the effects of the extraction of
increasing amounts of basaltic melt (e.g. Reisberg & Lorand, 1995). Lower Os isotope ratios
coupled with low Al$_2$O$_3$ wt% would seem consistent with the early and efficient removal of
Re during melt depletion and a lack then of radiogenic ingrowth of $^{187}\text{Os}$ – a process masked
in Figure 2a by the subsequent addition of metasomatic Re but seemingly stripped away by
using a suitable proxy for melt depletion in Figure 2b.

However in detail, Os elemental abundances of, in particular, non-cratonic xenoliths
such as those from this study, and other non-cratonic xenolith localities worldwide, are
simply not consistent with the notion that on a bulk-rock scale Os behaves as a compatible
element during partial melting. What is inconsistent with this hypothesis is that only 1 sample
from this study and 3 samples in total, from 42 samples in 4 separate studies of this locality
(Morgan, 1986; Burton et al., 1999; Meisel et al., 2001; this study) have [Os] that are higher
than a nominally fertile mantle – a characteristic that should be the norm rather than the
exception if Os behaves compatibly on a bulk-rock scale during partial melting. In effect,
there is a significant deficiency of [Os] in bulk-rock peridotite if Os behaves in a compatible
manner during melt depletion and if this is the main control on the behaviour of this element.
5.2 Osmium mass balance in peridotites

Several earlier studies (Hart & Ravizza, 1996; Burton et al., 1999; Harvey et al., 2010) have demonstrated that the contribution to the [Os] of bulk-rock peridotites derived from the major rock-forming minerals (olivine, orthopyroxene, clinopyroxene, spinel) is negligible. In optically pure hand-picked aggregates of these minerals from this study no more than 5% of bulk-rock Os can be accounted for from these phases. This is consistent with previous experimental studies (e.g. Fleet et al., 1991, 1996, Brenan et al., 2003, 2005) which determined the relative affinities of Os and the other PGE between sulfide and silicate assemblages. The experimentally derived partition coefficients for Os between sulfide and silicate liquids \( D_{\text{Os}}^{\text{sulfide/silicate}} \) of \( 10^4 \) to \( 10^6 \) are supported by the [Os] measured in optically pure silicate phases and hand-picked individual sulfide grains of this study (Table 5). Thus, volumetrically insignificant sulfides account for >95% of the Os mass balance of peridotite xenoliths. It is the behaviour of sulfide during melt depletion that will determine the Os abundance and isotope systematics of a basalt formed by the partial melting of a predominantly silicate pre-cursor source rock. However, compositional heterogeneity exists within mantle sulfide populations; Alard et al. (2002) and Pearson et al. (2002) identified two distinct sulfide populations based upon their morphology, [Os], \(^{187}\text{Os}/^{188}\text{Os}, [\text{Re}]\) and textural constraints. Sulfides that appear to be entirely enclosed within silicate grains, and thus protected from any subsequent interaction with melts or fluids tend to be rounded to sub-rounded, have high Os concentration ([Os] = 10s ppm), unradiogenic (sub-chondritic) \(^{187}\text{Os}/^{188}\text{Os}\) and low [Re], thus reflecting a long term evolution in a low-Re environment and probably representing the separation of an immiscible sulfide liquid during a previous melt depletion event (e.g. Holzheid, 2010). This is consistent with the findings of Bockrath et al. (2004) and Mungall & Su (2005) where Os-Ir-Ru rich sulfides remained in a peridotite
residue because of their tendency to adhere to silicate grains. This also supports the notion that enclosed sulfides are the result of an immiscible sulfide liquid that separated from a co-existing silicate liquid during fractional crystallisation of an early melt; the sulfides being preserved within early forming silicate phases. In contrast, a second population of sulfides occupies interstitial and intergranular locations within the peridotite. Their composition is somewhat different to the first population; [Os] is frequently at the sub-ppm level, [Re] is higher and more variable than enclosed sulfides and consequently $^{187}\text{Os}/^{188}\text{Os}$ of these sulfides is more radiogenic, i.e. variable and supra-chondritic, even within a population recovered from a single xenolith (Table 5). The textural relationship of these sulfides with silicate phases suggests that this population of sulfides are secondary and most likely derived from a metasomatic event subsequent to melt depletion. While sulfides entirely enclosed within silicate grains tend to evolve under closed system conditions, interstitial sulfides, by virtue of their textural location in the peridotite, experience open system behaviour and are prone to melting, dissolution or physical displacement by any transient melt or fluid. As such, their composition can be modified by mixing of interstitial sulfides of different ages and/or Re/Os ratios, possibly accounting for the wide range of Re/Os ratios in interstitial sulfides. This is notwithstanding the possible additions to the Re and Os budget of interstitial sulfides from Re and/or radiogenic Os fluxed from basaltic material mixed back into the convecting mantle, although the relative quantity of these elements in interstitial sulfides from this source is difficult to quantify. The logical extension of these observations is that bulk-rock Re-Os systematics of peridotite xenoliths will therefore be governed by the relative proportions of these two sulfide populations; the exact nature of an individual xenolith being determined by the abundance of each sulfide population. Figure 6 demonstrates the contribution of these two populations of sulfide in four samples from this study. Mass balance calculations show that in most cases the difference in [Os] between sulfide populations is sufficiently high that,
assuming similar abundances of each population, the contribution from low concentration, interstitial (i.e. metasomatic) sulfide is small and does not markedly affect the whole rock Os isotope ratio. Figure 6 also confirms that the proportion of whole rock Os that can be accounted for by the contributions of olivine, orthopyroxene, clinopyroxene and spinel in 4 samples from this study is <5% of the whole rock Os budget and in the case of KH03-21 as little as 2.4%.

While a simple mass balance calculation reveals that KH03-24 does not require a contribution from interstitial sulfides to account for its measured bulk-rock Os abundance and isotope ratio, radiogenic interstitial sulfides with low [Os], high [Re], were sampled from this xenolith (Table 5). Consequently, this suggests that the significantly greater [Os] of enclosed sulfides vastly outweighs the contribution to the Os budget of the interstitial grains. The majority of the sulfide grains analysed from KH03-16 are interstitial (see Table 5). However, to balance the bulk-rock Os isotope ratio of KH03-16 an unradiogenic component is required. Bulk-rock S analyses, which limit the amount of sulfide available for mass balance calculations, suggests that as little as 0.02 wt% of typical enclosed sulfide would balance the whole rock Os isotope ratio and Os concentration of xenolith KH03-16. However the most unradiogenic enclosed sulfides, which must be present, were not recovered from this xenolith. Therefore, the contribution to the bulk rock Os budget from each population of sulfide can only be estimated for KH03-16. In order to balance the whole rock Os isotope ratio the interstitial sulfides cannot contribute more than 17.5% of the whole rock budget, but with the knowledge of the [Os] of enclosed sulfides from other Kilbourne Hole xenoliths the contribution from interstitial sulfides is probably significantly less. The Os isotope ratio of KH03-15 is too radiogenic be accounted for by the sum of the contributions from the silicates and spinel plus an overwhelming contribution from enclosed sulfides alone. A relative contribution of 3.5% from interstitial sulfide is sufficient to balance the bulk-rock Os isotope
ratio and bulk-rock [Os]. A similar calculation to that of KH03-15 is required for KH03-21, except a greater contribution (<17.5 %) must come from interstitial sulfides to balance the whole rock Os systematics. When metasomatic, interstitial sulfide is present in these quantities bulk-rock \(^{187}\text{Os}/^{188}\text{Os}\) will deviate significantly from the Os isotope signature of a xenolith whose [Os] is dominated by enclosed sulfides.

With the exception of KH03-21, the effects of metasomatic, interstitial sulfide on the Os isotope ratio of the whole rock are of little consequence. Only in samples where the abundance of radiogenic, low [Os], interstitial sulfide is so great as to skew the whole rock Os isotope ratio are whole rock \(^{187}\text{Os}/^{188}\text{Os}\) ratios unrepresentative of their enclosed sulfides. Nevertheless, in peridotites xenoliths elsewhere, when the abundance of interstitial metasomatic sulfides is higher, an early melt depletion signature may easily be obscured and bulk-rock Re-Os systematics will only describe a mixture of metasomatic sulfide and earlier melt depletion-related sulfides, thus yielding nothing more than a meaningless “average” Os isotope ratio. For example, bulk-rock \(T_{\text{RD}}\) can vastly underestimate the timing of melt depletion by up to 0.5 Ga (e.g. Harvey et al., 2006). Figure 7 illustrates the relationship between bulk-rock Re-Os systematics of KH03-15, KH03-16, KH03-21 and KH03-24 and their constituent components. In all cases the bulk-rock \(^{187}\text{Os}/^{188}\text{Os}\) appears to be strongly controlled by enclosed sulfides, mainly as a result of their high [Os] (Table 5). In general, the xenoliths appear to have at least one silicate phase that resembles the \(^{187}\text{Os}/^{188}\text{Os}\) of the bulk-rock. However the [Os] of these phases (Table 3 and Figure 7) is insufficient to exert a significant control on bulk rock [Os] and therefore bulk-rock \(^{187}\text{Os}/^{188}\text{Os}\). Consequently, in peridotite xenoliths in general, bulk-rock \(T_{\text{RD}}\) ages are often unlikely to reflect an early melt depletion event, especially when a large proportion of the peridotite sulfide budget comes from the interstitial, secondary or metasomatic population. A more accurate appraisal of early melt depletion is more likely derived from the analysis of individual enclosed sulfide grains.
that have been protected from subsequent metasomatism. For example, the bulk-rock $T_{RD}$ age of KH03-15 (Table 1) underestimates the age of the oldest sulfide analysed from the same bulk-rock sample by >400 Ma. Similarly, the bulk-rock $T_{RD}$ age of KH03-24 is 150 Ma younger than the oldest enclosed sulfide recovered from that xenolith.

The low sulphur concentrations of the Kilbourne Hole xenoliths of this study suggests that a large proportion of their original sulphur has been lost prior to transport to the surface in the host basalt. Sulphur concentrations for KH03-15, KH03-16, KH03-21 and KH03-24 are all below 50 ppm (KH03-16 [S] <10 ppm), significantly below that expected for fertile mantle ([S] = 200 ± 40 ppm, O’Neil, 1991). Consequently, as sulfide is likely the dominant phase for [S] in peridotite this implies that a significant proportion of sulfide has also been lost, which may, at least in part, account for the low [Os] when compared to the primitive mantle. However, low [S] is not ubiquitous in sub-continental lithospheric mantle xenoliths and therefore this mechanism is unlikely to be universal (e.g. Reisberg et al., 2005). Moreover, the interstitial nature of one of the populations of sulfide suggests that it is more likely to be mobile and prone to alteration under a wide range of circumstances, e.g. supergene weathering (e.g. Lorand et al., 2003), melt depletion and / or metasomatism (e.g. Handler et al., 1999) than those sulfides enclosed within a host silicate grain with no exposure to grain boundary processes.

5.3 Control of HSE abundances by multiple sulfide populations during partial melting

5.3.1 Osmium concentrations and $^{187}Os/^{188}Os$ in EM-basalts

The generation of basaltic magma requires partial melting of a peridotite precursor material, the exact melt composition being dependent upon the pressure, temperature, $fO_2$ and
the composition of the source reservoir. It is, for instance, the variability in the composition
of EM-basalts that has often been attributed to the variability in the source material; their
heterogeneity being ascribed to various discrete, yet compositionally distinct mantle
reservoirs variously refertilised or enriched with recycled basaltic and/or sedimentary
material as a result of ongoing subduction and mixing (Zindler & Hart, 1986; Hofmann
1997). The contrasting physical properties of these re-introduced components has been
suggested to be responsible for their resistance to complete re-mixing back into the
asthenospheric mantle to produce a single homogeneous reservoir from which subsequent
basalt can be extracted (e.g. Allège & Turcotte, 1986; Hart, 1988; Manga, 1996). It has long
been accepted that the re-melting of these recycled components generates the distinctive
isotopic flavour of the various EM-basalts; their Sr-Nd-Pb isotope composition being
geographically restricted and reflecting the mixture of melt derived from asthenospheric
mantle and its enriched sub-reservoirs. While this explanation of EM-basalt heterogeneity is
robust for isotope systems that are reliant upon lithophile elements (Rb-Sr, Sm-Nd, Pb-Pb,
etc.) it has recently been suggested that in order to account for the wide range of Re-Os
isotope heterogeneity in EM-basalts, and Grande Comore EM-basalts in particular (e.g. Class
et al., 2009), additional enriched mantle reservoirs are required.

Despite the apparent incompatibility of Os in silicate minerals, demonstrated both
experimentally (Fleet et al., 1991, 1996; Brenan et al., 2003, 2005) and measured in natural
samples (Hart & Ravizza, 1996; Burton et al., 1999; Harvey et al., 2010; this study) there is
insufficient Os within the silicate phases to produce a significant volume of EM-basalt with
the observed range of [Os], even at very low degrees of partial melting – the meagre Os
budget in the silicate minerals is quickly exhausted and massively diluted during the melting
of the silicate phases. This is in contrast to the lithophile element-based isotope systems
whose parent and daughter elements (e.g. Rb, Sr, Sm, Nd, U, Pb) are present in much greater
abundances within the silicate minerals that produce the basaltic melt. The Os budget of EM-basalts is much more likely derived from mantle sulfide which hosts the vast majority of mantle Os. Mobilisation of this sulfide and its incorporation into a basaltic partial melt is therefore a far more plausible mechanism for producing a wide range of Os isotope ratios in EM-basalts and, moreover, the wide range of [Os] observed worldwide. A simple two stage model demonstrates that the entire range of EM-basalt Os isotope and elemental abundances can be produced by the sequential incorporation of (i) interstitial sulfide with sub ppm [Os] and radiogenic $^{187}$Os/$^{188}$Os followed by (ii) the gradual addition of sulfide grains formerly enclosed within silicate grains which, as melt depletion intensifies, become exposed to the melting process as their host grains themselves start to melt. These formerly enclosed sulfides, randomly oriented within their host grains, then contribute their high [Os] and comparatively unradiogenic $^{187}$Os/$^{188}$Os to the basaltic melt. Figure 8 illustrates this process and demonstrates schematically that with a representative range of mantle sulfides the entire range of both [Os] and Os isotope ratios can be produced from simple batch melting. As discussed above, melting of the silicate minerals can only produce a very limited range of [Os] and will not account for any great variability in $^{187}$Os/$^{188}$Os given a broadly chondritic starting material. The range of melt compositions from the silicate components alone is shown in Figure 10 (white box). This is derived from 1-10 % batch melting of sulfide-free silicates whose compositions were determined in this study, Burton et al. (1999) and Harvey et al. (2010). A very limited range of small volume melts can be produced even when $D_{\text{Os, silicate/melt}}$ is varied by up to an order of magnitude. Interstitial sulfide, with its particularly low melting temperature compared to that of silicate minerals (Hsieh et al., 1987; Eggler and Lorand, 1993), will become mobilized and incorporated into the melt very early in the partial melting process. As soon as melt forms an interconnected network around grain boundaries then the contribution of interstitial sulfide to the Os budget of the basalt can be added
(process 1 on Figure 8). However, this may only occur at higher temperatures than those at
which sulfide would physically melt (e.g. Bockrath et al., 2004; Ballhaus et al. 2006) as
sufficient silicate melting will need to occur before sulfide can be mobilised (the mobility of
interstitial sulfide in silicate melts during partial melting is summarized in Rudnick &
Walker, 2009). With continuing melt depletion enclosed sulfide grains, randomly oriented
with regard to their proximity to silicate grain boundaries, will progressively be exposed and
thus incorporated into the melt, rapidly increasing the basalt [Os] and lowering the overall
\[^{187}\text{Os}/^{188}\text{Os}\] (process 2, Figure 10). For example, using the range of [Os] and \[^{187}\text{Os}/^{188}\text{Os}\] for
Kilbourne Hole interstitial sulfides alone it is possible to produce basalts with a range of Os
isotope ratios between approximately that of primitive upper mantle (PUM \[^{187}\text{Os}/^{188}\text{Os} =
0.130;\) Meisel et al., 2001) and 0.170, and with [Os] of <100 ppt to c. 270 ppt. This is readily
achieved by mixing the results of up to 10% batch melting of a typical PUM silicate
assemblage and adding less than 0.01 modal % of Kilbourne Hole interstitial sulfide, i.e. an
amount of sulfide well within the range of modal abundances measured by e.g. Luguet et al.
(2003). Using the range of cratonic sulfides from Griffin et al., (2004), the full range of Os
elemental and isotope systematics of Comores EM-basalts, the extreme \[^{187}\text{Os}/^{188}\text{Os}\] end-
member of EM-basalt, can be generated with an order of magnitude less sulfide. The range of
higher [Os] and less radiogenic EM-basalts is then easily accommodated by the gradual
addition of formerly enclosed sulfides with high [Os] and generally sub-chondritic
\[^{187}\text{Os}/^{188}\text{Os}\]. Although only two examples are calculated here these two solutions are not
numerically unique and various combinations of geologically reasonable sulfide populations
with both normal [Os] and \[^{187}\text{Os}/^{188}\text{Os}\] allow the Os systematics of the full range of EM-
basalts, and most ocean island basalts (OIB) in general to be generated.

5.3.2 The influence of sulfide on EM-basalt PGE systematics
The early mobilisation of interstitial sulfides followed by the later incorporation of formerly enclosed sulfides is also supported by the observed behaviour of other platinum group elements (PGE). Previous studies of the two discrete populations of mantle sulfides have shown that Os-rich enclosed sulfides are also rich in Ir and Ru (IPGEs) but, compared to interstitial sulfides, are depleted in Pt, Pd (PPGEs) and, as previously discussed, Re (Lorand & Alard, 2001; Aulbach et al., 2004; Bockrath et al., 2004; Mungall & Su, 2005). The early incorporation of PPGEs into MORB has also been demonstrated to be responsible for the apparent PGE and Os-isotopic gap between MORB, ocean island basalts (OIB) and their mantle sources (Alard et al., 2005; Luguet et al., 2008). Consequently, the behaviour of any two IPGE in bulk-rock peridotite during partial melting should be strongly correlated, as should that of any two PPGE as the two populations of sulfide, each with a distinctive composition, contribute to the basaltic melt in a predictable, but different way. Conversely, it would be expected that no significant correlation would be observed between an IPGE and a PPGE in peridotites over an interval of melt depletion. Figure 9a demonstrates an excellent correlation in bulk-rock peridotite abundances of pairs of IPGE, i.e. IrN vs. OsN & (where XN is [X] normalised to the composition of CI chondrite, after Horan et al., 2003) over the range of melt depletion experienced by the peridotites of this study. Similarly PPGE, e.g. PdN vs. PtN, demonstrate a similar behaviour (R^2 > 0.9, with the exclusion of KH03-16), albeit because of the mobilization of a different sulfide population. However, very little co-variation between individual IPGE vs. individual PPGE exists (PtN vs. OsN). This strongly suggests that the behaviour of IPGE and PPGE during melt depletion is controlled by different phases, i.e. the two compositionally distinct populations of interstitial (high PPGE/IPGE) and enclosed (low PPGE/IPGE) sulfide. This observation is not unique to this particular locality and although the co-variation is not as statistically robust when worldwide peridotites are
considered (Figure 9b) the positive co-variation between individual IPGE is still evident in
other non-cratonic peridotite xenoliths (Lorand & Alard, 2001; Lorand et al., 2003; Wittig et
al., 2010), cratonic peridotite xenoliths (Pearson et al., 2004; Ivanov et al., 2008), orogenic
peridotites (e.g. van Acken et al., 2010), abyssal peridotites (e.g. Luguet et al., 2001, 2003,
2004) and ophiolitic peridotite (Hanghøj et al., 2010). The notion that IPGE and PPGE
mobility, and hence their contribution to basaltic magmas during partial melting of peridotite,
is controlled by two separate phases is also supported by the PGE distribution amongst
mantle sulfides themselves. Strong correlations between \( \text{Ir}_N \) vs. \( \text{Os}_N \) (\( R^2 > 0.99 \)) in sulfides
from non-cratonic peridotite (Lorand & Alard, 2001), cratonic peridotite (Aulbach et al.,
2004) and abyssal peridotites (Luguet et al., 2001, 2003, 2004) are evident (Figure 9c) and
demonstrate that sulfide is the primary control on the behaviour of PGE and Re during melt
extraction. Although the co-variation is not as strong between sulfide PPGE, the general trend
is still compelling. The net result of the preferential incorporation initially of interstitial
sulfide followed by the gradual addition of enclosed sulfide with increasing degrees of partial
melting is then clear. The strong correlations between paired IPGE and paired PPGE in
peridotitic sulfide (Figure 9c) and lack of correlation between individual IPGE and PPGE
illustrates that the two populations of sulfide are the main control on PGE abundance in
peridotites not just from this study (Figure 9a) but non-cratonic, cratonic, abyssal and
ophiolitic peridotites worldwide (Figure 9b). Moreover, the consistent and predictable
behaviour of mantle sulfide during partial melting is evident when the PGE composition of
worldwide basalts are examined; the same consistent behaviour of IPGE and PPGE is also
evident in basalts irrespective of tectonic setting (Figure 9d) – the PGE abundances and Os
isotope composition of basaltic magma can be explained simply by the contribution of first
one population of sulfide, with a high PPGE/IPGE, followed by gradual addition of formerly
enclosed sulfide with low PPGE/IPGE controls.
Using continental peridotites to derive the composition of oceanic basalts may not always be appropriate as SCLM has invariably been isolated from the convecting mantle for longer and hence likely experienced more metasomatic input than its sub-oceanic counterpart. However, in the case of the peridotites used for this study the choice of material appears justified. In selecting petrographically and texturally simple peridotites that last equilibrated at or near the local asthenosphere / lithosphere boundary the protogranular lherzolites and harzburgites share a number of features with similar oceanic peridotites. Mean Os isotope ratios for abyssal peridotites ($^{187}\text{Os}/^{188}\text{Os} = 0.1236$; Snow & Reisberg, 1995; Brandon et al., 2000; Harvey et al., 2006; Liu et al., 2008) are similar to the Kilbourne Hole peridotites used here ($^{187}\text{Os}/^{188}\text{Os} = 0.1256$) and when the exceptionally depleted abyssal peridotites of Harvey et al. (2006) are excluded are almost indistinguishable from each other (abyssal peridotite $^{187}\text{Os}/^{188}\text{Os} = 0.1257$; Snow & Reisberg, 1995; Brandon et al., 2000; Liu et al., 2008). Abundances of PGE are also similar in oceanic mantle and SCLM, both in terms of absolute abundances and co-variation of paired IPGE and PPGE in bulk-rock peridotite (Fig 9b) and sulfides derived from them (Fig 9c; cf. Luguet et al., 2001, 2003, 2004) so during melt depletion of both these types of peridotite the redistribution of PGE as a result of sulfide mobility should be comparable. However, caution should be exercised in the choice of material used where for example high S abundances could be the result of large quantities of metasomatic sulfide, in texturally complex peridotites, or where bulk-rock PGE abundances materially differ from those of abyssal peridotites.

The possible contribution of PGE from sources other than peridotite-sourced sulfides should also be considered. Many EM-basalts, and OIB in general, are considered to be the product of mixed-source melting with varying proportions being derived from pyroxenite and peridotite (e.g. Hirschmann & Stolper, 1996; Sobolev et al., 2005; 2007). While pyroxenites also contain a significant sulfide fraction it has been demonstrated that in all cases, sulfides...
recovered from pyroxenite xenoliths (e.g. Wang et al., 2009; Sen et al., 2010) and non-xenolithic pyroxenites (e.g. van Acken et al., 2010) contain 1-3 orders of magnitude less PGE than their peridotitic counterparts. Thus it would seem unlikely that even in instances where the production of basaltic melt is dominated by the melting of pyroxenite, the contribution to the basalt PGE budget, and hence Os isotope systematics, will be quickly overprinted by the contribution from peridotite hosted sulfide. A model that accounts for the combined contributions of sulfide from mixed source melting has been proposed by Luguet et al. (2008). Their model suggests that during the melting of a pyroxenite – peridotite source the early melting of pyroxenite results in reaction with the peridotite wall-rock (e.g. Yaxley and Green 1998) creating a source rock containing sulfides from both peridotite and pyroxenite. This reacted wallrock then provides the source for low solidus metasomatic sulfides which are readily incorporated into the basaltic melt; the overall PGE signature being dominated by the contribution from the peridotite source rock. Luguet et al. (2008) also go on to speculate about the possible contribution to basalt PGE and $^{187}$Os/$^{188}$Os systematics from refractory alloy phases. However it seems difficult to reconcile the physical and chemical properties of these phases (i.e. refractory, dense, unreactive) with the incorporation and/or redistribution into a basaltic melt. In summary, based upon the relative PGE budgets of peridotite and pyroxenite, combined with the unfavourable physical and chemical properties of PGE-rich alloys, the Os isotope systematics of EM-basalts in particular and OIB in general are most likely controlled by peridotite-hosted sulfides.
6. CONCLUDING REMARKS

Bulk-rock PGE, Re-Os elemental and isotope systematics of peridotites, and consequently OIB, including EM-basalts, are controlled by volumetrically insignificant sulfides. More than one population of sulfides, which have large compositional differences between the populations in terms of major elements, PGE and Re-Os elemental and isotope systematics, are commonly present in peridotite samples. This means that bulk-rock Re-Os isotope systematics of peridotite are often merely the aggregate signatures of two populations of sulfide, produced at different times and under different conditions, thus rendering bulk-rock Re-Os isotope geochronology extremely difficult to interpret in all but the most straightforward of examples.

The textural characteristics of the two populations of sulfide govern their behaviour during partial melting; interstitial, metasomatic sulfides being liberated from their peridotite host during the early stages of partial melting, whereas sulfides enclosed within silicate grains only becoming exposed to the generated melt as their host grains themselves start to contribute to the production of basalt. The wide range of mantle sulfide compositions present even within a single peridotite xenolith or within a small number of xenoliths from a restricted geographical area can easily account for the Os compositional and isotopic range of EM-basalts. There is therefore no need for additional mantle reservoirs to account for the apparent co-variation of lithophile-element based and siderophile-element based isotope systems in the generation of EM-basalts.
ACKNOWLEDGEMENTS

We would like to thank John Watson for assistance with the XRF measurements and Andy Tindle for his help with the electron microprobe at The Open University. Funding for this research was provided by NERC grant NER/A/S/2001/00538 which has allowed J.H. to undertake the isotope measurements presented here.
REFERENCES


FIGURE CAPTIONS

Figure 1. Rhenium and osmium elemental abundances of 28 spinel lherzolite xenoliths from Kilbourne Hole (this study) and similar samples from the same locality (Morgan, 1986; Burton et al., 1999; Meisel et al., 2001). All concentrations in parts per billion (ppb). Grey square illustrates estimates for [Os] and [Re] of the primitive upper mantle (PUM) of 3.9 ppb and 0.35 ppb respectively (Becker et al., 2006).

Figure 2. (a) Re-Os isotope evolution diagram for the 28 bulk-rock peridotites from this study (Burton et al., 1999 and Meisel et al., 2001 shown for comparison). Scatter between \(^{187}\text{Re}/^{188}\text{Os}\) and \(^{187}\text{Os}/^{188}\text{Os}\) is particularly high amongst the xenoliths from Kilbourne Hole. The best fit line coincides with a calculated isochron age of 2.3 ± 0.7 Ga, but the relationship cannot be described as convincingly isochronous despite agreement with the ages derived from Sr isotope ratios of Roden et al. (1988) of 2.5 Ga ± 0.2 Ga. (b) “Aluminachron” diagram for same samples as (a). Using an immobile melt depletion index, e.g. bulk-rock aluminium abundance reduces the amount of scatter seen in (a) suggesting a certain degree of Re-mobility. Best fit line of 2.4 Ga passes through composition of PUM (Meisel et al., 2001). Dashed lines – calculated Os isotope ratios for different mantle Re-depletion ages \(T_{\text{RD}} = \frac{1}{\lambda} \times \ln \left\{ \left[ \frac{^{187}\text{Os}^{188}\text{Os}_{\text{chon}} - ^{187}\text{Os}^{188}\text{Os}_{\text{sample}}}{^{187}\text{Re}^{188}\text{Os}_{\text{chon}}} \right] + 1 \right\} \) (Shirey & Walker, 1998).

Figure 3. Chondrite-normalized platinum-group element concentrations for 5 bulk-rock Kilbourne Hole peridotites (KH03-10, KH03-15, KH03-16, KH03-21 & KH03-24) and the host basalt (CI chondrite values from Horan et al., 2003). Uncertainties (2 \(\sigma\)) calculated from long-term reproducibility of reference material GP13 and from external reproducibility of repeat measurements on separate aliquots of samples from this study.
Figure 4. Major element abundances of 57 sulfides (see Table 3). Two low-Cu populations (0.08 to 4.68 wt %), defined by either a high or low Fe:Ni ratio, are broadly equivalent to pentlandite rich and pentlandite poor monosulfide solid solution (MSS) sulfides (Luguet et al., 2003, 2004). A third population of sulfide, with higher Cu content, is analogous to chalcopyrite rich sulfides from previous studies (Dromgoole & Pasteris, 1987; Luguet et al., 2003, 2004). Host basalt sulfide from Burton et al. (1999).

Figure 5. (a) Bulk rock peridotite [Os] vs. bulk rock Os isotope ratios. (b) [Os] and \(^{187}\text{Os}/^{188}\text{Os}\) of individual sulfides from KH03-15 (n = 7), KH03-16 (n = 7), KH03-21 (n = 10), and KH03-24 (n = 8). Open circles denote interstitial sulfides, closed circles denote enclosed sulfides. Grey box denotes range of [Os] and \(^{187}\text{Os}/^{188}\text{Os}\) in (a). As in cratonic mantle sulfides (e.g. Griffin et al., 2004), and other non-cratonic sulfides (e.g. Harvey et al., 2006; 2010) the most unradiogenic sulfides possess the greatest [Os]. (c) Sulfide [Re] vs. sulfide [Os] for 7 interstitial and 12 enclosed sulfides from (b). There is no statistically significant co-variation between these variables, however sulfides with high [Re] tend to possess low [Os] and c. 50% of the high-[Os] enclosed have lower [Re] than the interstitial population.

Figure 6. Osmium mass balance for Kilbourne Hole xenoliths. The silicate and oxide phases (olivine, orthopyroxene, clinopyroxene and spinel) account for less than 5% of the whole rock Os budget. Sulfide dominates the Os budget of all of the samples due to exceptionally high sulfide / silicate partition coefficients for Os (e.g. Fleet et al 1991, 1996). At least two populations of sulfide exist, in approximately equal modal abundance not exceeding a total of 0.03 modal% (cf. Luguet et al., 2003; 2004), but their respective contribution to the Os mass...
balance are not equal. In all samples, enclosed sulfides account for the vast majority of Os while the contribution from interstitial sulfide, in the case of KH03-24, is insignificant, and in KH03-15 and KH03-21 account for 3.5 - 17.5 % respectively of the Os present. The relative contributions of the two sulfide populations in KH03-16 is less clear but is probably dominated by the enclosed population. The contribution of the interstitial component in KH03-16 is calculated to be less than 17.5 % of the total. Relative contributions to the osmium budget were calculated on the basis of the [Os] and $^{187}$Os/$^{188}$Os of individual components and the bulk-rock rather than by point counting the two populations of sulfide, which are sparse in thin section.

Figure 7. $^{187}$Re-$^{187}$Os isotope systematics for all mineral components, interstitial and enclosed sulfides and host basalt from KH03-15, KH03-16, KH03-21 & KH03-24. With the exception of KH03-16, all samples show a strong similarity between the $^{187}$Re-$^{187}$Os systematics of enclosed sulfides and the respective bulk-rock. Although no high-[Os] sulfides with particularly unradiogenic ($^{187}$Os/$^{188}$Os < 0.120) were recovered from KH03-16 a high-[Os], unradiogenic component, i.e. enclosed sulfide, must be present in KH03-16 to complete the Os mass balance (see text & Figure 6).

Figure 8. A simple two-stage model for the generation of EM-basalt Os isotope signatures. Black squares denote Os elemental abundance and isotope signature of EM-basalts worldwide (Martin et al., 1994; Bennett et al., 1996; Hauri & Kurz, 1996; Hauri et al., 1996; Lassiter & Hauri, 1998; Widom et al., 1999; Brandon et al., 1999, 2007; Lassiter et al., 2000, 2004; Skovgaard et al., 2001; Eisele et al., 2002; Workmann et al., 2004; Gaffney et al., 2005; Jamais et al., 2008; Debaille et al., 2009; Ireland et al., 2009; Day et al., 2009; Class et al., 2009). Dataset generated using GEOROC and filtered for EM-basalts with [Os] $\geq$ 40 ppt.
to control for the effects of crustal contamination. White bar represents the range of melts produced by melting only silicate components from a fertile mantle precursor ($^{187}\text{Os}/^{188}\text{Os} = 0.130$), [Os] controlled by abundances measured in handpicked silicate aggregates from this study and their approximate modal abundance). $D_{\text{Os}}^{\text{olivine/melt}} = 0.51$ from Burton et al., (2002) but also modelled for $D_{\text{Os}}^{\text{olivine/melt}}$ of up to an order of magnitude greater to account for the full range of PGE $D_{\text{olivine/melt}}$ with decreasing oxygen fugacity of Brenan et al. (2003). The Os elemental abundance and isotope systematics of EM-basalts worldwide can be accounted for by the sequential addition of first interstitial sulfides (1) followed by a contribution from formerly enclosed sulfides (2) as melt depletion in the source peridotite continues (see text).

White circles denote individual Kilbourne Hole sulfides (this study), light- and mid-grey circles are non-cratonic peridotite-derived sulfides from the Mid-Atlantic Ridge and the French Massif Central (Harvey et al., 2006; 2010 respectively) and black circles are cratonic sulfides (e.g. Griffin et al., 2004; Aulbach et al., 2004; Marchesi et al., 2009).

Figure 9. Correlation of paired IPGE and paired PPGE in peridotite, individual peridotite-derived sulfides and basalt. Compositions normalized to CI-chondrite (Horan et al., 2003). (i) Ir$_N$ vs. Os$_N$ for peridotites from this study (a), worldwide peridotites; inset = this study (b), mantle derived sulfides (c), and worldwide basalts (d). (ii) Pd$_N$ vs. Pt$_N$, (iii) Pt$_N$ vs. Os$_N$. The strong correlation of pairs of IPGE (i) and pairs of PPGE (ii), but lack of correlation between IPGE/PPGE pairs (iii) suggests that the two groups behave independently during progressive melt depletion. Key: (a) Yellow discs = this study (b) Yellow discs = this study; red discs = Bene Boussera, dark brown discs = Lesotho, grey discs = Namibia, orange discs = Vitim (Pearson et al., 2004); light blue discs = Oman ophiolite, (Hanghøj et al., 2010); purples discs = Atlas, Morocco (Wittig et al., 2010); pink discs = Massif Central (Lorand et al., 2003). (c) Pink discs = Massif Central (Lorand et al., 2003); Dark green discs = Slave Craton, Canada
(Aulbach et al., 2004); White discs = abyddal peridotite (Luguet et al., 2001, 2003, 2004). (d)
White discs = Kilauea basalts (Pitcher et al., 2009); dark grey discs = Guizhou, China (Qi & Zhou, 2008); light grey discs = Hawaiian picrite (Ireland et al., 2010); black discs =
Philippines Sea (Dale et al., 2008). For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.
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Table 1. Bulk-rock Al$_2$O$_3$/SiO$_2$, Re and Os elemental abundance and Re-Os isotope systematics of 28 peridotite xenoliths from Kilbourne Hole, New Mexico, USA. Al$_2$O$_3$/SiO$_2$ calculated from wt.% of oxides derived by XRF at The Open University. Major element data quality assessed using two rock standards (WS-E and OUG-94). Reproducibility is within 2% of recommended values. Complete major and trace element abundances for all of the samples are the subject of a separate contribution (Hammond et al., 2010). [Re] and [Os] expressed in parts per billion (ppb). Errors shown as 2σ mean. $T_{RD}$ = (minimum) time of rhenium depletion calculated using a mean present-day chondritic value $^{187}$Os/$^{188}$Os = 0.127 (Luck & Allègre, 1983; Walker & Morgan, 1989) and assumes that $^{187}$Re/$^{188}$Os$_{sample}$ = 0. Given isotope ratios blank corrected. $^{187}$Os/$^{188}$Os ratios normalised to $^{192}$Os/$^{188}$Os = 3.08271 and corrected using measured $^{18}$O/$^{16}$O and $^{17}$O/$^{16}$O of 0.002047 and 0.00037, respectively. Johnson Matthey (n = 26) 2.75 ng Os standard $^{187}$Os/$^{188}$Os = 0.17373 ± 12 (2σ). a host lava. b “future” age. c Carius tube digestion. d high pressure asher digestion for PGE concentration measurement. e duplicate measurement.
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Table 2. Re–Os isotope data for mineral separates from KH03-15, KH03-16, KH03-21 & KH03-24. Errors shown are 2σ mean. Re and Os concentrations expressed as parts per trillion (ppt). Standards and corrections for $^{18}$O/$^{16}$O and $^{17}$O/$^{16}$O as in Table 1.
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Table 3. Major element abundances of sulfide grains in peridotite xenoliths from Kilbourne Hole, New Mexico, USA. Repeat analyses of an in-house pentlandite standard yields errors on major elements (S, Fe, Ni) of 2, 5 and 6 % (2σ) respectively, with minor elements (Co, Cu) errors (2σ) of 22% and 70% respectively.
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Table 4. Platinum group element (+ Re) abundances in bulk-rock Kilbourne Hole peridotite xenoliths and host basalt. All concentrations shown in parts per billion (ppb). Precision of [Ir] & [Ru] measurements (± 6%) calculated from the external reproducibility of [Os] on multiple measurements on several powder splits from each xenolith. Precision of [Pd] & [Pt] (± 40%) calculated from the external reproducibility of [Re]. Internal, i.e. within-run precision is more than an order of magnitude better than external precision which is therefore the limiting factor on PGE concentration reproducibility in these samples. a host lava. b duplicate measurement by Carius tube digestion (or some HPA?).
Table 5. Re–Os elemental abundance and isotope data for sulfides from KH03-15, KH03-16, KH03-21 and KH03-24. Errors shown are 2σ mean. Re and Os concentrations expressed as parts per million (ppm). Standards and corrections for ¹⁸O/¹⁶O and ¹⁷O/¹⁶O as in Table 2.

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<th>Sample</th>
<th>Morphology</th>
<th>[Os]</th>
<th>[Re]</th>
<th>¹⁸⁷Os/¹⁸⁸Os</th>
<th>2 s.e.</th>
<th>¹⁸⁷Re/¹⁸⁸Os</th>
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FIGURES

Figure 1
Figure 4
Figure 5

- (a) Bulk rock $^{187}$Os/$^{188}$Os vs. bulk rock Os ppb
- (b) Sulfide $^{187}$Os/$^{188}$Os vs. sulfide Os ppm
- (c) Sulfide [Re] ppm

Graphs showing the distribution and correlation of Os and Re concentrations in bulk rock and sulfide samples.
Figure 6
Figure 7
Figure 8

1. Addition of interstitial sulfides
2. Addition of enclosed sulfides

$^{187}\text{Os}/^{188}\text{Os}$ vs $1/\text{Os}$ plot showing the distribution of interstitial and enclosed sulfides. EM-basalts with $D$ values from 0.5 to 5 are indicated.
Figure 9 a
Figure 9 c & d