The compatibility of rhenium and osmium in natural olivine and their behaviour during mantle melting and basalt genesis

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Abstract

Rhenium and osmium (Re–Os) elemental abundances have been obtained for magmatic olivine from a range of host basalt compositions, for mantle olivine and coexisting phases (silicate and sulphide) from a spinel–peridotite, and olivine and Fe–Ni metal from Pallasite meteorites. These data indicate that Re and Os concentrations in olivine are low in both mantle and magmatic environments, and both elements preferentially partition into silicate melt, sulphide or Fe–Ni metal, relative to olivine. For magmatic olivine the partition coefficients for Re and Os correlate with the MgO content of the olivine (like Fe, Mn and Ni), which suggests that the observed partitioning reflects substitution onto crystallographic sites, rather than defects or the presence of included phases. These data indicate that Os is extremely incompatible (that is, excluded from the silicate structure) in magmatic olivine, which suggests that olivine crystallisation alone cannot be responsible for the low Os contents of some oceanic basalts. Rather, olivine crystallisation is itself responsible for sulphide precipitation (in which Os is highly compatible), by producing sulphur saturation of the melt, and it is the coupled crystallisation of these phases that effects the Os–Mg–Ni co-variations observed in oceanic basalts. Rhenium is also incompatible in magmatic olivine but the data suggest that for Fe-rich olivine compositions Re may become compatible, which may explain, at least in part, the compatible behaviour of this element during basalt petrogenesis on other planetary bodies, such as Mars and the Moon. Preliminary data for mantle olivine, not demonstrably contaminated by included phases, suggest that the high Os concentrations (relative to magmatic olivine) relate to partitioning with a sulphide, rather than silicate melt. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The fractionation of Re and Os during basalt genesis is one of the key processes governing the

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distribution of these elements between the Earth's crust and mantle. The low Os concentration of many oceanic basalts is attributed, in part, to Os preferentially partitioning into sulphide in the mantle residue during melting [1–3] but also, in part, to Os partitioning into an unknown phase during magmatic fractional crystallisation [2,4,5]. Some have argued for control by olivine, consistent with Os–Mg–Ni co-variations in oceanic basalts (e.g. [2,4]), and direct measurements of natural olivine [2]. However, others have argued for Os scavenging by immiscible sulphides (e.g. [5]).

Determining partition coefficients for the highly siderophile elements (HSEs, that is, the platinum group elements+Au+Re) into magmatic olivine has been fraught with difficulty, largely because of the problems associated with the measurement of these elements at extremely low levels in silicate material. Following the pioneering study of Mitchell and Keays [6] it is now well established that amongst mantle minerals olivine has low concentrations of both Re and Os. This observation might be taken to indicate that Os is incompatible in olivine relative to a coexisting melt. However, it is difficult to infer Os compatibility in mantle rocks, firstly, because coexisting melt is either absent or not present in sufficient quantity for measurement (i.e. as melt inclusions) and secondly, in the presence of sulphide (which will be a melt at mantle temperatures [7]) Os partitioning will be dominated by this phase rather than a silicate melt. Thus, it has even been argued that, provided that Henry's law is obeyed, the ppt (parts-per-trillion) concentrations seen in mantle olivine can be taken to imply that ppb levels of Os in olivine could exist in equilibrium with a sulphide containing several hundred ppm of Os [8], well below the saturation level in sulphide (expected to be close to the weight percent level [9]).

For magmatic rocks Ross and Keays [10] found high concentrations of Ir (and by inference Os) in olivine from a sulphide-poor komatiite. The same olivine had a low Pd concentration, considered at the time to indicate that sulphide contamination was unlikely. This observation has been taken by many to indicate that crystallisation of olivine would remove Os from the melt, and fractionate Re from Os, consistent with the observed MgO–Os–Ni variations observed in both komatiite and basalt whole-rock suites (e.g. [4,11]). However, it is now known that, in particular, monosulphide solid solution, possesses high Os and Ir concentrations, but low Pd contents (e.g. [12]), hence, for the study of Ross and Keays sulphide contamination remains a distinct possibility. More recently the apparent compatible behaviour of Os in olivine was confirmed by direct measurement and a best estimate of 20 ± 5 was obtained for partitioning between olivine and a basalt melt [2]. However, the Os concentrations measured for olivine in the latter study were not reproducible, and it has been suggested that the high Os concentrations are due to the presence of trace quantities of enclosed sulphide [5]. This may have arisen as a consequence of the large sample sizes, usually greater than 1 g, necessitated by the relatively large Os blanks of between 1 and 18 pg. Indeed, other direct measurements of olivine in both komatiite [13] and basaltic lavas [14] indicate that Os is incompatible in olivine, and preliminary experimental work suggests that both Re and Os may be extremely incompatible [15].

This study presents Re and Os data for magmatic olivines from a diverse range of basalt compositions, olivine and coexisting phases (silicate and sulphide) from a spinel–peridotite xenolith, and olivine and Fe–Ni metal from Pallasite meteorites. Chemical separation was achieved using an ultra low blank solvent extraction technique [16] with an associated Os blank of between 0.006 and 0.033 pg (at least 30 times lower than techniques previously used). This technique allows the analysis of small quantities of high-purity olivine, which in turn enables a precise estimate of partition coefficients for Re and Os in olivine. These results, taken with recent data for magmatic sulphide [5], enable an assessment of the role of olivine and sulphide crystallisation in producing the observed Os abundances in oceanic basalts. Furthermore, preliminary data for mantle olivine provides some insights into the controls on Re and Os partitioning during mantle melting.

2. Sample petrography

2.1. Magmatic olivine

The studied samples range from picritic lavas (MgO = 15.93%) at Bandama, Grand Canaria to less MgO rich basalts from Mt. Maletto (MgO = 7.09%) and Mt. Silvestri (MgO = 5.73%) on Mt. Etna, Italy. The Quaternary volcanics at Bandama in Grand Canaria (Canary Islands) comprise a sequence of pyroclastic rocks and lava flows of alkali basanite composition (Table 1). In the sample studied here olivine, clinopyroxene, spinel and magnetite occur as phenocrysts in a fine-grained groundmass. Olivine is the most abundant mineral, and occurs as large, ≥ 1 cm, crystals which preserve major element compositional zoning with increasing Mg (Fig. 1) and Ni, and decreasing Fe, from core (Fo ≈ 86.8) to rim (Fo ≈ 88.2) (where Fo refers to the forsterite content of olivine %Fo (= 100 Mg/(Mg+Fe)) and a high Ca content (∼ 0.20 wt% CaO). The lavas at Mt. Maletto (≤ 14 000 kyr) [17] and historic lavas at Mt. Silvestri [18] form part of a trachybasaltic suite considered to result partly from low-pressure crystal fractionation and partly as a consequence of mixing of distinct mantle sources (e.g. [17–20]). The sample from Mt. Maletto is a glomeroporphyritic basalt with a fine-grained
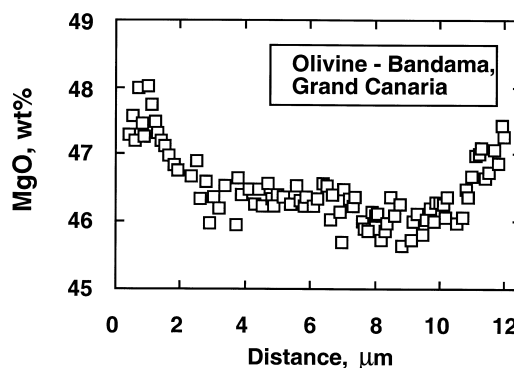

Fig. 1. Mg zonation (MgO, wt%) across the olivine megacryst from Bandama, Gran Canaria, used in this study (see Table 1 for complete representative analysis).

groundmass of plagioclase, clinopyroxene and magnetite, with olivine and clinopyroxene phenocrysts. The olivine phenocrysts are up to 2 mm in diameter, and are the most primitive (Mg-rich) to have been found on Mt. Etna (Fo ≈ 83–90). The lavas from Mt. Silvestri are more evolved than those from Mt. Maletto (Table 1) and contain phenocrysts of olivine (Fo ≈ 77.5), clinopyroxene, plagioclase and magnetite in a fine-grained groundmass.

In all of the samples analysed here the olivine crystals contain primary melt inclusions (i.e. trapped during the growth of their host phase)

Table 1
Representative olivine and host basalt compositions

	Bandama, Grand Canaria				Maletto, Mt. Etna		Silvestri, Mt. Etna	
	olivine rim	core	groundmass	melt-inclusion in olivine core	olivine	groundmass	olivine	groundmass
SiO_2	40.44	40.18	41.94	39.65	40.30	47.29	38.27	49.48
Al_2O_3	0.06	0.09	10.33	11.35	0.06	15.34	0.02	15.48
TiO_2	0.04	0.00	3.40	3.70	0.05	1.49	0.05	1.71
Fe_2O_3	–	–	–	–	–	11.78	–	–
FeO	11.29	12.58	8.90	11.35	14.75	–	21.17	9.96
MnO	0.14	0.17	0.17	0.17	0.20	0.18	0.46	0.18
MgO	47.49	46.53	15.93	12.91	44.75	7.09	39.89	5.73
CaO	0.19	0.18	11.79	11.62	0.24	12.13	0.24	10.74
Na_2O	–	–	2.86	3.16	–	2.78	–	3.55
K_2O	–	–	0.96	1.66	–	1.32	–	1.55
P_2O_5	–	–	0.64	0.85	–	0.46	–	–
Ni (ppm)	2890	2594	492	–	1740	166	1280	67

Each reported mineral analysis is the average of at least 10 measurements. Extended count times of 240 s were used for CaO and Ni. Analytical errors (in rel. %) for CaO were ∼ 2.5% and for Ni were ∼ 12%.

which preserve aliquots of their parental magmas. The melt inclusion compositions are similar to the groundmass, which, when taken with the high CaO contents of the olivine host (Table 1), suggest that all the olivines studied here crystallised from the host lava in a low-pressure environment (i.e. are phenocrystic) rather than being derived from a peridotite mantle source (i.e. xenocrystic) [18–20]. For the olivines from Bandama, Fe–Mg distribution between the olivine core and melt inclusions (Table 1) indicates a Fe–Mg $K_D = 0.30$. The higher K_D of 0.42 between the olivine rim and groundmass probably reflects the presence of a high Fe/Mg residual liquid in the groundmass, rather than disequilibrium growth. Olivine from Mt. Silvestri yields a Fe–Mg $K_D = 0.30$ (olivine from Mt. Maletto possesses a range of compositions). These data suggest that, at least for Bandama and Silvestri, the olivine crystallised in chemical equilibrium with the host lava.

2.2. Mantle olivine

The sample studied is an anhydrous spinel–lherzolite (VNP1) from Vietnam in which silicate minerals have homogeneous major element compositions (Table 2) and display protogranular to porphyroclastic textures. Olivine and orthopyroxene occur as large crystals (up to 5 mm across) often showing kink banding and deformation lamellae. Spinel occurs as large, irregular grains (up to 5 mm across) intergrown with orthopyroxene and clinopyroxene. Sulphide occurs as both inter-

stitial and included grains. Olivine and ortho- and clinopyroxene contain secondary melt inclusions, which occur along healed fracture planes. These silica-rich melt inclusions are considered to represent high-pressure near-solidus melts in equilibrium with a peridotitic assemblage [21,22].

2.3. Pallasite olivine

Two samples have been analysed, Eagle Station and Marjalahti, chosen for their range in olivine composition. Eagle Station contains highly angular olivine (Fo $\approx$ 81), many grains of which possess rims consisting of intergrowths of ortho- and clinopyroxene, troilite, whitlockite and stanfieldite (cf. [23,24]), set in Fe–Ni metal (Ni $\approx$ 15.4 wt% [25]). Marjalahti contains mixed angular olivine grains (Fo $\sim$ 88) [23] and chromite set in Fe–Ni metal (Ni $\approx$ 9.2 wt% [25]).

3. Analytical techniques

All of the samples (basalt, xenolith and Pallasite) were selected on the basis of the high degree of optical purity of the olivine. For Bandama, five different fractions from a single olivine crystal (including rim and core, and three 'bulk' separates) and the host basalt were analysed. For Mt. Silvestri and Mt. Maletto, olivine and host basalt (groundmass) were analysed. For the spinel–lherzolite from Vietnam, Re–Os isotope and elemental data have been obtained for all the major silicate

Table 2
Representative mineral compositions for the spinel–peridotite, Vietnam

	Olivine	Orthopyroxene	Clinopyroxene	Spinel
SiO$_2$	40.84	55.80	52.87	0.06
Al$_2$O$_3$	0.00	3.79	4.35	48.42
TiO$_2$	0.02	0.04	0.14	0.07
Cr$_2$0$_3$	0.02	0.58	1.02	20.69
FeO	9.28	5.78	2.47	11.34
NiO	0.40	0.09	0.06	0.33
MnO	0.11	0.12	0.09	0.06
MgO	49.10	33.52	16.19	19.76
CaO	0.07	0.78	22.11	0.01
Na$_2$O	0.00	0.07	0.76	0.00
K$_2$O	0.00	0.00	0.02	0.00
Total	99.84	100.57	100.08	100.74

phases, sulphide and the bulk xenolith. For the Pallasite meteorites, silicate and metal were separated by crushing. For each sample silicate minerals were hand-picked and cleaned in ethanol, water and dilute HCl. Following separation all minerals (including spinel) were powdered in agate, and dissolved in HBr+HF in a PFA pressure vial heated at 145°C for at least 24 h [16]. Os and Re separation was achieved using a solvent extraction technique [16] and mass spectrometric techniques closely following those described previously [16,26,27]. Total procedural blanks for Os during the course of this study were 0.021 ± 0.010 pg/g, $^{187}Os/^{188}Os = 0.331 \pm 0.054$, and for Re were 1.3 ± 0.4 pg/g ($n = 24$). The short-term reproducibility of the Os blank was usually $\pm 10\%$ or better, but the absolute values varied between each batch of prepared reagent (see legend to Table 3). The minerals from the spinel–lherzolite were analysed during the period September 1996 to February 1997, whereas the Bandama and Silvestri samples were analysed between July 1998 and December 1998 and Mt. Maletto during December 1999. Consequently, the blank corrections use the mean values obtained for those periods (Table 2) rather than the overall mean value given above.

4. Results

4.1. Magmatic olivine

The Os concentrations in magmatic olivine are low (Table 3) and for the phenocryst from Bandama exceptionally so, ranging from 0.083 ppt for the olivine core to 0.009 ppt for the olivine rim. The concentrations of Re and Os in olivine from Maletto and Silvestri are somewhat higher than those from Bandama. Nevertheless, for all samples studied here the concentrations of both of these elements in olivine are lower than those of the host basalt matrix, and much lower than those previously obtained (e.g. [2]). At first sight the derived partition coefficient (D_{Os}) olivine/basalt (groundmass) appear to be highly variable, ranging from 0.0004 to 0.061, which might be attributed to defects or inclusions of other phases. Similarly, it might be argued that the groundmass

Table 3
Re–Os elemental data for magmatic olivine and host basalt

Olivine/basalt	Sample wt (mg)	Re	Os
Bandama, Grand Canaria			
Host basalt	217.22	629.4	22.43
	197.34	633.8	21.24
Olivine[a] 1 core	209.29	39.90	0.083
2	240.53	24.43	0.066
3	207.08	23.80	0.039
4	212.93	17.39	0.038
5 rim	185.16	14.36	0.009
Maletto, Mt. Etna			
Host basalt	160.72	837.7	188.5
Olivine	17.93	165.3	5.56
Silvestri, Mt, Etna			
Host basalt	21.78	668.9	1.981
Olivine	19.74	229.7	0.121

Concentrations in ppt (10^{-12} g/g) by weight. Procedural blank for Os $= 0.021 \pm 0.009$ pg; $^{187}Os/^{188}$ Os $= 0.331 \pm 0.054$ and Re $= 1.3 \pm 0.4$ pg for the period July 1996 to December 1999 ($n = 24$). The absolute value of the blank varied between reagent batch, and the short-term reproducability of the Os blank was typically $\pm 10\%$ or better. Consequently, the blank corrections use the mean values obtained for the appropriate short-term periods rather than the overall mean value given above. For the samples from Bandama (analysed between July 1998 and December 1998) this is critical because some concentrations can only be resolved using the blank appropriate to that time interval. July 1996 to August 1996 Os $= 0.034 \pm 0.002$ pg ($n = 4$); September 1996 to February 1997 Os $= 0.022 \pm 0.003$ pg ($n = 6$); March 1997 to June 1997 Os $= 0.016 \pm 0.002$ pg ($n = 4$); July 1997 Os $= 0.033 \pm 0.001$ pg ($n = 2$); July 1998 to December 1998 Os $= 0.008 \pm 0.002$ pg ($n = 4$); August 1999 Os $= 0.025 \pm 0.005$ pg ($n = 2$); December 1999 Os $= 0.019 \pm 0.003$ pg ($n = 2$).
[a] For Bandama five olivine fractions were obtained from the same individual crystal, including core and rim (sample 1 and 5, respectively) and three 'bulk' separates (2–4).

fraction analysed here preferentially sampled sulphide or some other Os-rich phase. However, there are a number of lines of evidence to suggest that this is not the case: Firstly, sulphide is not present in any of the samples studied here, although it is not possible to rule out the presence of Os-rich alloy phases. Secondly, the duplicate measurement of the groundmass from Bandama yields an indistinguishable Re–Os abundance suggesting, in this sample at least, a homogeneous distribution of phases. Thirdly, for Bandama and Silvestri the groundmass yields low Os concentrations and Os–Ni–Mg variations typical of
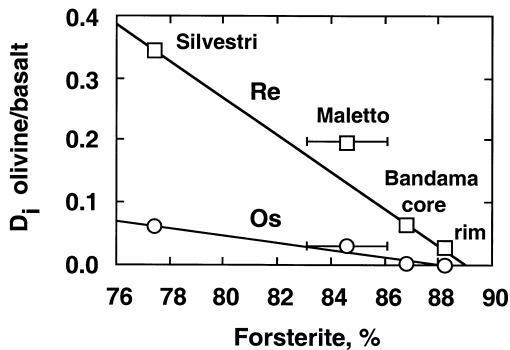
Fig. 2. Partition coefficients (olivine/basalt) for Re and Os shown against the forsterite content of the olivine. These results show that Os is extremely incompatible in magmatic olivine in all of the samples studied here. Moreover, the correlation with major element composition (forsterite content) indicates that the partitioning of these elements occurs by substitution onto crystallographic sites (cf. [28,29]), rather than reflecting the presence of defects or included phases.

those found in oceanic basalts. For Mt. Maletto the high Os concentration of the groundmass is indeed unusual, and might be attributed to the presence of an Os-rich phase. However, for all of the samples (including Mt. Maletto) the measured partition coefficients for both Re and Os show a clear correlation with MgO content of the olivine (Fig. 2) which suggests that partitioning of these elements, like Fe, Mn and Ni (e.g. [28,29]), occurs by substitution onto crystallo-

graphic sites, rather than reflecting the presence of defects or inclusions. Thus, these data demonstrate that the observed partitioning relationships reflect a crystal–chemical control on Re and Os incorporation into olivine, and that Os is extremely incompatible in olivines studied here.

4.2. Mantle olivine

The concentrations of Re and Os in mantle silicates from the Vietnam spinel–lherzolite are low (Table 4), and comparable to those previously measured in spinel–lherzolites from Kilbourne Hole [2,3], and garnet–peridotites from Tanzania [30]. The two olivine fractions yield indistinguishable Re and Os concentrations, which strongly suggests that the olivine is homogeneous with respect to these elements, and that the concentrations have not been significantly affected by the presence of an included phase. The silicate minerals, sulphide and the bulk xenolith samples yield similar $^{187}Os/^{188}Os$ values for a range of $^{187}Re/$ ^{188}Os ratios (Table 4; Fig. 3) which suggests that all the major Re- and Os-bearing phases in this rock, including sulphide, are in Os isotope equilibrium. Consequently, the Re and Os distribution between phases likely represents equilibrium partitioning in this assemblage. Of the phases analysed olivine has the lowest Re and Os concentrations, and accounts for just 2.5% of the Os

Table 4
Re–Os data for spinel–peridotite from Vietnam

Mineral/whole-rock/basalt	sample wt (mg)	$^{187}Os/^{188}Os$[a]	$^{187}Re/^{188}Os$[b]	Re	Os
Spinel–peridotite, Vietnam					
Olivine 1	470.20	0.12171 ± 0.00019	1.190	13.10	52.98
Olivine 2	481.67	0.12280 ± 0.00041	1.229	13.05	51.15
Clinopyroxene	51.21	0.12284 ± 0.00013	1.912	46.0	113.3
Orthopyroxene	403.33	0.12230 ± 0.00044	1.389	41.76	144.8
Spinel	27.61	0.12271 ± 0.00036	0.821	179.9	1056
Sulphide	0.04	0.12234 ± 0.00010	0.380	201.1*	2549*
Bulk xenolith 1	323.98	0.12227 ± 0.00039	0.415	106.6	1236
Bulk xenolith 2	255.99	0.12176 ± 0.00032	0.376	97.76	1253

All errors are $2\sigma_m$. Concentrations in ppt (10^{-12} g/g) by weight, * except for sulphide in ppb. Procedural blank as for Table 3. Bulk xenolith samples 1 and 2 are replicates of the same powder repeated through chemistry and mass spectrometry.
[a] $^{187}Os/^{188}Os$ normalised to $^{192}Os/^{188}Os = 3.08271$. Given ratios are blank-corrected and corrected using measured $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios of 0.002047 and 0.00037, respectively. IPG-Paris 100 pg internal standard yields 0.17394 ± 17 (2σ; $n = 26$).
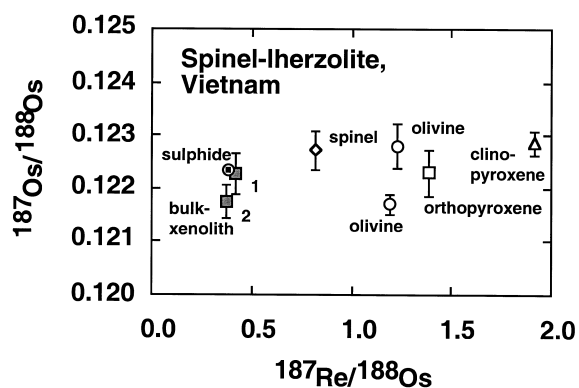[b] $^{187}Re/^{188}Os$ ratio determined to a precision of ± 1.0%.

Fig. 3. ^{187}Re/^{188}Os evolution diagram for silicate and sulphide phases from the spinel–lherzolite studied here. Silicate minerals, sulphide and bulk xenolith yield similar Os isotope compositions for a range of Re/Os ratios, which suggests that for the Re–Os system all these phases are in isotope equilibrium, and that the distribution of Re and Os between phases likely represents equilibrium partitioning in this assemblage.

in the bulk xenolith, despite comprising some 60% of the xenolith by mode. These results confirm those of previous studies, indicating that both Re and Os are incompatible in olivine relative to sulphide. If it is assumed that the sulphide was present as a melt with the coexisting olivine (most sulphides melt at mantle temperatures) then olivine/sulphide partition coefficients of 6.5×10^{-5} and 6.8×10^{-6} are indicated for Re and Os, respectively, similar to those found in previous studies [2,3,30].

4.3. Pallasite olivine

The concentration of Os in the Pallasite olivines

is relatively low, between 16.7 and 42 ppt (Table 5), comparable to that observed in some mantle olivines. In contrast, Re concentrations of over 600 ppt are the highest seen in the olivines studied here. For Eagle Station the metal contains 15.23 ppm Os and 1189 ppb Re. These values are in good agreement with the results of Shen et al. [31] for the same sample; the metal phase of Marjalahti has not been measured here and the data shown in Table 5 are taken from their study. Calculated olivine/metal partition coefficients using these data range from $3–6 \times 10^{-6}$ for Os and 5.3×10^{-4} to 3.12×10^{-3} for Re. These results confirm that both Os and Re preferentially partition into the metal phase relative to olivine. However, the Os isotope composition of the olivines and corresponding metal yield best-fit regression lines corresponding to ages of 32.2 ± 0.9 Myr (Marjalahti) and 10 ± 1 Myr (Eagle Station), respectively, indicating open system behaviour at very recent times. The metal phase for these Pallasites lie on a best-fit regression consistent with type IIA Iron meteorites, suggesting that the Re–Os isotope systematics of the metal is relatively undisturbed [31]. In which case it seems most likely that it is the Re–Os abundances in the olivine that have been perturbed.

5. Discussion

5.1. Magmatic olivine

The data obtained in this study indicate that Os is extremely incompatible in magmatic olivine,

Table 5
Re–Os data for Pallasite olivine and Fe–Ni metal

Olivine/Fe–Ni metal	Sample wt (mg)	^{187}Os/^{188}Os[a]	^{187}Re/^{188}Os[b]	Re	Os
Eagle Station					
Fe–Ni metal (this study)	3.49	0.12446 ± 0.00003	0.3801	1189*	15.23*
Fe–Ni metal [31]	109.00	0.12469 ± 0.00004	0.3708	1172*	15.21*
Olivine	51.19	0.1355 ± 0.0011	63.47	628.3	47.75
Marjalahti					
Fe–Ni metal [31]	184.00	0.12254 ± 0.00004	0.3432	0.1956*	2.74*
Olivine	72.32	0.2180 ± 0.0025	178.1	610.8	16.72

All errors are $2\sigma_m$. Concentrations in ppt (10^{-12} g/g) by weight, * except Re and Os in Fe–Ni metal given in ppm. Procedural blank and footnotes a,b as for Table 3.

contrary to many previous studies (e.g. [2,10,11]), but consistent with direct measurement of komatiite [13] and MORB [14] olivine, and with preliminary experimental results [15]. It has been suggested that the HSE are unlikely to partition into silicates because their high electronegativities will inhibit the formation of ionic bonds required to enter the silicate structure [32]. However, the data presented here, taken with experimental results for spinel and clinopyroxene [33,34], suggest that the HSEs do indeed enter the silicate structure. In principle, prediction of crystal melt partition coefficients for Re and Os in olivine from elastic moduli should be possible (e.g. [35]). However, the oxidation state of Re and Os in the magmatic environment remains poorly constrained. Data for Os in silicate melts [36], Re in magnetite [37], and Ru and Rh in clinopyroxene [34] suggest a likely oxidation state of +4 for Re and Os. For an oxidation state of +4 for six-fold coordination Re and Os possess identical ionic radii (0.77 Å [38]). Yet, the data presented here clearly shows a marked difference in their crystal melt partition coefficients (Fig. 2). However, recent experimental data suggests that Re dissolves in terrestrial magmas predominantly as Re^{+6} [39]. For an oxidation state of +6 Re has an ionic radii of 0.69 Å [38] which may well account for the observed difference in partitioning. Alternatively, Re and Os may be substituted into different lattice sites in olivine, or there may be some error in the given ionic radii (cf. [40]).

Finally, it is important to note that magnetite is present in all of the samples studied here. It has been suggested that Re preferentially partitions into this phase ($D_{Re} = 20$–50 [37]), in which case the Re partition coefficient may differ in magnetite-free samples. However, sulphide possesses a similar partition coefficient to magnetite, $D_{Re} \approx 43$ [5], and preliminary data for a sulphide-bearing MORB sample from the Famous region yields olivine (Fo $\approx$ 88)/basalt (groundmass) partition coefficients for Re and Os of 0.316 and 0.006, respectively (K.W. Burton; unpublished data), close to those observed here.

5.2. Mantle olivine

Of the major silicate phases in the spinel–peridotite studied here, olivine has the lowest concentrations of Re and Os, as is the case for most other xenoliths analysed thus far [2,3,30]. Nevertheless, the Os concentrations in olivine from mantle lithologies are significantly higher than those from the basalts analysed in this study. Moreover, comparison with Ni (Table 6; Fig. 4), a compatible element in olivine (e.g. [28]), indicates that for the xenolith olivines there is a positive co-variation between Ni and Os, suggesting that Os is behaving as a compatible element in mantle rocks. Such a contrast in behaviour between the mantle and magmatic environment might be attributed to a change in the oxidation state of Os, related to changing oxygen fugacity, or to systematic changes in the size of crystallographic sites in olivine with increasing pressure, similar to those observed for clinopyroxene [40]. Alternatively, the apparent compatible behaviour of Os in mantle rocks may simply reflect equilibrium with an Os-rich sulphide melt, rather than an Os-poor silicate melt. The variations in Ni in the olivine data presented here lie well within the range documented thus far for mantle [41]. It might be argued that the observed variations could be produced by diffusional exchange or melt/rock reaction, rather than partial melting (e.g. [42]). But, in either case a positive correlation between Ni content of olivine and modal percent orthopyroxene would be anticipated [42]. In contrast, what is actually observed is that the Kilbourne Hole sample KH8312 with the lowest Ni

Table 6
Summary of Re–Os–Ni data for mantle olivine

	Fo (%)	Re (ppt)	Os (ppt)	Ni (ppm)
Kilbourne Hole [2]	89	–	36	2661
Kilbourne Hole [3]	90	15.31[a]	25.5[a]	2200
Vietnam (this study)	90	13.10	52.0	3143
Tanzania BD730 [30]	91	11.29	97.71	3378[b,c]
Tanzania BD738 [30]	90	28.21	152.72	3478[c]

[a] New unpublished data for Kilbourne Hole olivine KH8312 that supersedes that given in [3].
[b,c] Ni data from [22] and [60], respectively.

content in olivine contains ∼ 31.0% orthopyroxene by mode. Whereas, the sample from Tanzania with the highest Ni content (BD730) contains ∼ 20.0% orthopyroxene by mode. Such a relationship is thus consistent with simple models of Ni enrichment in olivine accompanying melt depletion, and the increase in Ni observed in Fig. 4 correlates with increasing depletion of the bulk xenolith. Those samples possessing olivine with low Ni contents are relatively fertile spinel–peridotites from Kilbourne Hole (i.e. $Al_2O_3 \approx 4.0$ wt% [2,3]), whereas those with olivines having higher Ni contents are extremely depleted garnet–peridotites from Tanzania (i.e. $Al_2O_3 = 0.5$ wt% [30]). At mantle temperatures most sulphides will be present as a melt [7]. Thus, if it is assumed that the sulphide in the xenolith were once present as a melt in equilibrium with the coexisting silicates, and that the Os concentration in the sulphide melt was not significantly modified by sulphide crystallisation, then the measured Os in the sulphide gives some indication of the Os concentration of the sulphide melt. The olivine/sulphide melt partition coefficient calculated in this way (from Table 4) yields a value of 2×10^{-5}, much lower than that even for olivine/silicate melt (Fig. 2), reflecting the extreme compatibility of Os in sulphide. Thus, compared to a sulphide melt, Os is incompatible, and the higher concentration in

mantle olivine simply reflects the greater concentration of Os in mantle rocks, and in particular in sulphide. In this case, the trend observed in Fig. 4 may reflect increasing loss of sulphide with higher degrees of melting (due to loss of S in a silicate melt [43]) where the modally decreasing residual sulphide possesses systematically higher Os concentrations, as does, therefore, coexisting olivine. Recent studies have shown that primary mantle sulphide tends to possess relatively low Re concentrations, and that that most of the Re is located in coexisting silicates [3,30]. Given the generally incompatible behaviour of Re it might be expected that this element should also co-vary with Ni and Os in mantle olivine. For the samples analysed thus far, three of the four do indeed show a decrease in Re concentration with Ni content (Fig. 4). Further data are required to confirm if this is general behaviour for Re–Os in mantle olivine. However, the difficulty therein is that any samples that do not lie on these trends may simply reflect the difficulty of separating clean mineral separates. In this respect, many studies have demonstrated the ease with which sulphide inclusions in silicate minerals may dominate the Os chemistry of both host minerals and the whole-rock [2,30,44,45]. The correlation between silicate sample size and Os concentration (degree of sulphide contamination) [30] most likely reflects the difficulty in separating large quantities of sulphide-free silicate, and highlights the need for very low blank Os chemistry for work on mantle silicates. For the large sample sizes demanded by other techniques the chemical and isotopic information obtained from silicates will, at best, reflect the chemistry of the sulphide inclusions, and will, at worst, reflect a mixture of sulphide and silicate, potentially yielding little meaningful age or chemical information.
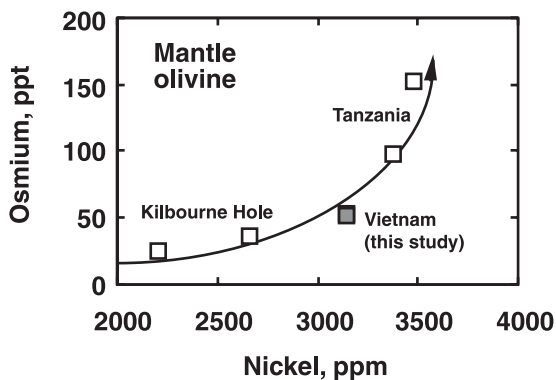
Fig. 4. Osmium (ppt) against nickel (ppm) in mantle olivines. The arrow indicates increasing depletion from fertile spinel–peridotites from Kilbourne Hole ($Al_2O_3 \approx 4.0$ wt% [2,3]) to extremely depleted garnet–peridotites from Tanzania ($Al_2O_3 \leq 0.5$ wt% [30]). Shaded symbol represents the spinel–peridotite from Vietnam studied here (see Section 5.2 for discussion).

5.3. Pallasite olivine

The concentration of both Os and Re in Pallasite olivine is extremely low compared to the coexisting metal phases. For Os the concentrations in olivine are comparable to those seen in mantle olivine (Table 6) whereas Re concentrations are somewhat higher. However, there is a significant

difference in olivine/metal partition coefficients for Re and Os, some two to three orders of magnitude. At first sight this might be taken to indicate that, contrary to the natural variations observed in magmatic iron meteorites [46], metal–silicate separation can produce a significant fractionation of Re/Os. However, as was noted previously (Section 4.3) the Os isotope composition of the olivine suggests very recent open system behaviour, which most probably reflects diffusional exchange between metal and olivine. In this case, the calculated partition coefficients between olivine and metal represent, at best, maximum values.

5.4. Re–Os behaviour in oceanic basalts

The partitioning data obtained here for magmatic olivine can be combined with that for magmatic sulphide [5] to obtain some idea of the consequences of fractional crystallisation of these phases on the chemistry of oceanic basalts. Fractional crystallisation of 30% olivine, while satisfying the observed variations in Mg and Ni, cannot produce the range of Os concentrations (Fig. 5). Conversely, 0.015% sulphide crystallisation can produce the range of Os concentrations but not the variations observed for Mg or Ni (Fig. 4). Preliminary data for clinopyroxene and plagioclase suggest that neither Re or Os are strongly compatible in these phases ([47,48] and K.W. Burton unpublished data). However, both elements are highly compatible in PGE-rich alloys (e.g. [6]) and are also compatible in some spinels [14,33]. Thus, it might be argued that the crystallisation of these or other phases are responsible for the low Os concentration of oceanic basalts, rather than sulphide. Irrespective of the phase controlling Os, the variations in Ni and Mg are primarily controlled by olivine, thus the Os–Mg–Ni co-variations in oceanic basalts demonstrate a relationship between the amount of olivine crystallisation (assuming, to a first approximation, a single parental melt for the trends shown in Fig. 5) and the fraction of Os-rich phase present. For sulphide such a correlation can be simply explained by the fact that olivine crystallisation produces sulphur saturation of the melt, which in many cases will result in sulphide crystallisation
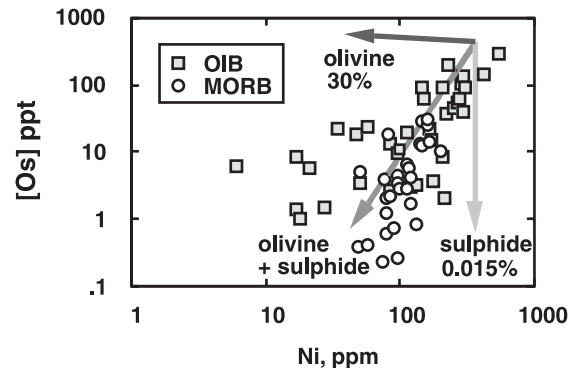

Fig. 5. Osmium (ppt) against nickel (ppm) relationships in oceanic basalts. These data show clear co-variations between Os–Ni for both mid-ocean ridge [55] and ocean island [56,57] basalts. Using the new partition coefficient data for Os in olivine obtained here, fractional crystallisation of 30% olivine, while satisfying the observed variations in Ni cannot produce the range of Os concentrations. Conversely, 0.015% sulphide crystallisation can produce the range of Os concentrations but not the variations observed for Ni. The observed correlation between Os and Ni (and MgO) is most simply explained by the fact that olivine crystallisation produces sulphur saturation of the melt, which in many cases will result in sulphide crystallisation (see Section 5.4). The model trends shown assume a single parental melt composition with 500 ppm Ni and 500 ppt Os (cf. [2]). The model used is a simple olivine crystallisation model, similar to that used in ref. [2] that assumes a starting composition of 15% MgO in the melt, and olivine crystallisation in equilibrium with the melt (K_D Fe–Mg = 0.3). The D_{Ni} for olivine was calculated using the relationship between D_{Ni} and MgO (in the melt) given in ref. [28], and D_{Os} was calculated using the relationship between D_{Os} and MgO (in the olivine) obtained in this study ($D_{Os} \approx 0.51$ ($5.8 \times 10^{-3} \times$ %Fo)). In the absence of more precise estimates for sulphide the D_{Os} value used was that of Roy-Barman et al. [5] ($D_{Os} \approx 4.8 \times 10^4$ [5]) and for D_{Ni} that of Peach and Mathez [50] ($D_{Ni} \approx 575$–836).

(e.g. [49]). Alternatively, crystallisation of spinel with olivine might produce the same trend. In this regard, it is important to note that sulphide is a ubiquitous phase in many oceanic basalts (e.g. [5,49]), and the results presented here suggest that olivine-driven sulphide crystallisation may be a general process.

As noted previously (Section 5.1) Re is also compatible in sulphide (e.g. [5]), consequently fractional crystallisation of this phase is likely to affect Re, as well as Os, contents in the melt. However, although compatible, the partition co-

efficient of Re ($D_{Re} \approx 43$ [5]) is much lower than that of Os ($D_{Os} \approx 4.8 \times 10^4$ [5]) or Ni ($D_{Ni} \approx 575$–836 [50]), hence crystallisation of sulphide will have a much more dramatic affect on the latter elements, which is consistent with the relationship observed in oceanic basalts. For Re the situation is further complicated because variations in Re abundance between Ocean Island basalts (OIB) and MORB are considered to reflect differences in the mineralogy of the residual mantle (e.g. [51]). In particular, the low Re concentrations in OIB relative to MORB have been attributed to the presence of a garnet-bearing residue for OIB [51] (Re being compatible in garnet).

5.5. The behaviour of Re–Os in other planetary bodies

In different planetary bodies (Earth, Mars, Eucrite parent body and the Moon) Os always behaves as a compatible during mantle melting and basalt genesis, whereas Re displays variable behaviour [52–54]. During terrestrial basalt formation Re behaves as a moderately incompatible element and Re/Os fractionation is extreme (e.g. [55–57]). In contrast, for Martian and lunar rocks Re appears to behave as a compatible element,

and lunar rocks in particular show little fractionation from chondritic Re/Os ratios [52–54]. This compatible behaviour of Re might be attributable to contamination by chondritic impact material (e.g. [58]). However, for the lunar samples, relationships indicative of mixing are not evident [52], whereas for the Martian samples this would require that all rock types were related by fractional crystallisation following impact melting, which is considered unlikely [53]. Rather, it has been suggested that the compatible behaviour is due to a difference in the oxidation state of Re because of the lower oxygen fugacity in the mantle source of Martian and lunar basalts [52].

Olivine crystallisation plays an important role in the differentiation of silicate bodies in the solar system, and the results presented here suggest a further possible explanation for the sometimes compatible behaviour of Re. If the linear relationship between partition coefficient and forsterite content holds for all olivine compositions then extrapolation suggests that Re may become compatible in Fe-rich olivine (Fo ≈ 50 or less). Olivine compositions in lunar and Martian rocks are typically Fe-rich compared to most terrestrial basalts and mantle rocks (see [59]), in which case Re may behave as a compatible element during basalt pet-

Table 7
Summary of Re–Os–Ni partition coefficients for natural olivine

	Fo (%)	D_{Re}	D_{Os}	D_{Ni}
Olivine/basalt				
Bandama	88.2	2.3×10^{-2}	3.7×10^{-4}	5.87
Mt. Maletto	~ 86.5	0.197	2.9×10^{-2}	10.48
Mt. Silvestri	77.5	0.343	6.1×10^{-2}	19.10
Olivine/sulphide				
Vietnam (this study)	90.0	6.5×10^{-5}	2.0×10^{-5}	–
Kilbourne Hole [3]	90.0	6.5×10^{-5}	6.8×10^{-6}	8.1×10^{-3a}
Tanzania (BD738) [30]	90.0	8.8×10^{-3}	3.3×10^{-5}	1.4×10^{-2b}
Kilbourne Hole [2]	89.0	–	1.0×10^{-5}	–
Olivine/Fe–Ni metal				
Marjalahti	88.0	3.1×10^{-3c}	6.1×10^{-6c}	1.54×10^{-4d}
Eagle station	81.0	5.3×10^{-4}	3.1×10^{-6}	2.92×10^{-4e}

[a] Calculated assuming interstitial sulphide is in equilibrium with olivine [3].
[b] Calculated assuming included sulphide is in equilibrium with olivine [30].
[c] D_{Re} and D_{Os} calculated using the Fe–Ni metal data for Marjalahti from [31].
[d] Ni contents of olivine and Fe–Ni metal from [59] and [25], respectively.
[e] Ni contents of olivine and Fe–Ni metal from [23] and [25], respectively.

rogenesis. This is supported by the low Re content of the sulphide from Chassigny (ca. 7 ppb, O. Alard, A. Luguet, J.P. Lorand, unpublished data) representing less than 5% of the whole-rock Re budget. This suggests that olivine (Fo = 67.8 ± 0.3), the main rock forming phase (ca. 91%), may have a high Re content.

6. Concluding remarks

The data presented here indicate that both Re and Os are extremely incompatible in olivine relative to a silicate melt, sulphide or Fe–Ni metal (Table 7). For the magmatic environment these results suggest that fractional crystallisation of olivine alone cannot be directly responsible for the low Os contents of oceanic basalts. Nevertheless, the Mg–Ni–Os co-variations observed in oceanic basalts do indicate an intimate role for olivine, and suggest that sulphide precipitation is driven by the crystallisation of olivine. These data also hint at the possibility that the compatible behaviour of Re in other planetary bodies may be due to a compositional dependence of Re partitioning into olivine, where Re becomes compatible in Fe-rich olivine. Finally, preliminary data for mantle olivine, not demonstrably contaminated by included phases, suggests that the high Os concentrations (relative to magmatic olivine) relate to partitioning with a sulphide, rather than silicate melt.

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