



Supporting Online Material for

Enriched Pt-Re-Os Isotope Systematics in Plume Lavas Explained by Metasomatic Sulfides

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Supplementary Online Material

Samples

The Beni Bousera massif (Rif mountains, Morocco) is part of the Betic-Rif orogenic belt and comprises both peridotites and pyroxenites. Pyroxenites intruded the peridotites during a 1.2 Ga melting event during which peridotites were isolated from the asthenospheric mantle (*S1*). The 11 Beni Bousera pyroxenites presented here are mostly garnet-clinopyroxenites and websterites equilibrated in the diamond-stability field (*S2*), GP 137 is an orthopyroxenite margin that formed from the reaction between the highly reactive pyroxenite/eclogite melt with the peridotite. All the pyroxenites have been interpreted as the result of high-pressure crystal fractionation (*S1-S2*). Their varied O and S isotopic systematics demonstrate their derivation from oceanic crust protoliths (*S1*).

Analytical Methods

Whole-rock HSE concentrations were determined by isotopic dilution and inductively coupled plasma mass spectrometry (ICP-MS). Briefly, 1 g of sample powder was spiked with ^{190}Os , ^{191}Ir , ^{99}Ru , ^{194}Pt , ^{106}Pd and ^{185}Re ; and was dissolved with aqua regia (5mL HNO_3 , 2.5 mL HCl) in Carius Tubes at 220°C overnight. Osmium was extracted using the carbon-tetrachloride solvent extraction technique and purified by microdistillation. Os concentration were determined by negative thermal ionisation mass spectrometry (N-TIMS) using the secondary electron multiplier (SEM) detector. Once the remaining aqua-regia fraction was dried down, HSE were recovered using an anion-exchange resin separation procedure and analysed by Element2 ICP-MS. Sulfide analyses differ slightly from the whole-rock method regarding the digestion which only comprises the microdistillation step. The weight range of the sulfide grains analysed is 0.05-4.5 mg. Further details of the analytical method are provided in (*S3*). Procedural blanks (N=7) of the whole-rock pyroxenite chemistry are on average 0.4 ppt Os, 0.5 ppt Re and 1 ppt for Pt. The procedural blanks for the sulfide chemistry (N=2 for Os and 4 for Re and Pt) are 40 fg Os, 31 fg Re and 20 pg Pt and are insignificant for all samples.

For the high precision measurements of Os isotopes, sample digestion procedures are similar except that the samples were not spiked and that digestions were performed in an Anton-Paar HP-asher at 300°C and 130 bars for 16 hours. Up to 120 g of sample in total were dissolved for the whole-rock pyroxenites. Our average total Os blank for the HP-asher digestion is 1.3 pg for 120g of sample and is 0.5 pg for 1 g of sample for the carius-tube digestion. Blank corrections for both methods are thus insignificant. The high-precision measurements of the Os isotopic composition were performed by NTIMS in static mode using a 7-faraday collector Thermo Finnigan Triton at the North East Center for Isotopic and Elemental Tracing (NCIET) at the University of Durham. Measurement procedure and interference correction method have been described in extensive details in (*S4*). They are briefly summarised here. Signals of >150mV on masses 234 ($^{186}\text{OsO}_3^-$) and 235 ($^{187}\text{OsO}_3^-$) are generated for 270 ratios. GP 251 was only measured for 110 ratios because of the small beam size. Mass fractionation was corrected using an exponential law and $^{192}\text{Os}/^{188}\text{Os}$ ratio=3.083. O isotopes were measured in-run to allow very precise oxide interference corrections. In addition, masses 228, 229, 231 and 233 were monitored using the SEM detector before and after the high-precision Faraday measurements in order to detect potential $^{196}\text{PtO}_2^-$, $^{198}\text{PtO}_2^-$, $^{183}\text{WO}_3^-$, $^{185}\text{ReO}_3^-$ interferences. Interferences were corrected if detected. Despite our interference corrections, we observed for the international standard solutions UMD (University of Maryland solution provided by R.J.Walker) and DTM (Department of Terrestrial Magnetism, Carnegie Institution of Washington, R.W.Carlson) residual correlation between $^{184}\text{Os}/^{188}\text{Os}$ and both $^{186}\text{Os}/^{187}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios. These correlations likely reflect an additional interference that we did not correct for rather than a residual mass fractionation (*S4*). In order to correct for such a correlation, we normalised our data to $^{184}\text{Os}/^{188}\text{Os}=0.001300$ which is our average value for PtO_2^- corrected runs and also the average $^{184}\text{Os}/^{188}\text{Os}$ ratio obtained on the Thermo-Finnigan Neptune Multi-collector (MC)-ICPMS of the NCIET (*S5*). The average values for 33 UMD analyses over the measurement period (January to Dec

2006) are 0.1198425 ± 69 (2SD, 57 ppm) and 0.112787 ± 10 (2SD, 88 ppm) for the $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios respectively.

The 12 detrital Pt-rich alloys from placer deposits on the Pacific coast of California, likely derived from chromitite deposits of the Josephine ophiolite (Oregon) were analysed by laser ablation multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) using a method described in detail in (S6). A new Os isotope reference material (Durham Romil Osmium Standard DROsS) was analysed by solution MC-ICP-MS at the start of each laser analytical session. The average values for 60 DROsS analyses (with an Os concentration of 200ng ml^{-1}) over the period of study (18-10-07 to 25-10-07) are 0.119917 ± 12 (2SD, 99 ppm) and 0.160918 ± 18 (2SD, 113 ppm) for the $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios respectively. These values are indistinguishable to those reported in (S5). External precision for this method has also tested by repeated laser-ablation analyses on 5 different isotopically homogenous Os-rich alloy grains (S6). The 2SD external precision range between 73-314 ppm for $^{187}\text{Os}/^{188}\text{Os}$ and between 74-114 ppm for $^{186}\text{Os}/^{188}\text{Os}$ for the 5 grains. The average internal precision for 40 second analyses at ^{188}Os beam intensities of between 4 and 11V was reported to be between 0.01 and 0.06% (2SE) for the $^{187}\text{Os}/^{188}\text{Os}$ ratio and between 0.01 and 0.03% (2SE) for the $^{186}\text{Os}/^{188}\text{Os}$ ratio. The internal precisions (2SE) obtained for the Pt-rich alloys reported in this study are 0.01-0.8% for $^{186}\text{Os}/^{188}\text{Os}$ and 0.01-1.8% for $^{187}\text{Os}/^{188}\text{Os}$. The poor internal precision for some of the analyses of Pt-rich alloys likely results from their low Os contents in comparison with the Os-rich alloys of (S6) and consequently reflects the relatively small Os signal sizes generated during the analyses of such Pt-rich, Os-poor alloys. Nonetheless, the overall isotopic variation in the alloy grains presented here is substantially greater than the analytical uncertainty of the analyses.

Os isotopic composition calculations.

The $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ can be calculated at a time t for the whole-rock samples and the sulfides using the following equations: $^{187}\text{Os}/^{188}\text{Os}_{(t)} = ^{187}\text{Os}/^{188}\text{Os}_i + ^{187}\text{Re}/^{188}\text{Os}(e^{\lambda t_0} - e^{\lambda t})$ and $^{186}\text{Os}/^{188}\text{Os}_{(t)} = ^{186}\text{Os}/^{188}\text{Os}_i + ^{190}\text{Pt}/^{188}\text{Os}(e^{\lambda t_0} - e^{\lambda t})$, where t_0 is the age (in years) of formation of the sample and t , the age we want the composition to be modelled. The decay constant λ of ^{187}Re and ^{190}Pt are $1.67 \cdot e^{-11} \text{ y}^{-1}$ and $1.417 \cdot e^{-12} \text{ y}^{-1}$, respectively (see S7). $^{187}\text{Os}/^{188}\text{Os}_i$ is the isotopic ratio at the time of formation of the samples, which we assumed to be the mantle isotopic composition at the time of formation. All the Os isotopic ratios have been calculated for an evolution or isotopic ingrowth over 1.2 Ga, comparable to the Beni Bousera massif evolution age (S1). By doing so, we assume that very old (i.e. 1.2 Ga) recycled crustal materials (pyroxenites, eclogites and sulfides) are present in the oceanic mantle. Although ancient, the 1.2 Gy age is somewhat younger than the suggested mean age of recycled oceanic crust residing in the convecting mantle on the basis of Pb isotopes (S8). As such, the ranges of isotopic compositions that we report are likely conservative minima and the modal abundance of bulk pyroxenite or metasomatic sulfides involved in the mantle sources being modelled in order to be able to explain the ^{186}Os - ^{187}Os signatures of oceanic basalts are likely maximum estimates.

Implications of metasomatic sulfide addition to the S and highly siderophile element composition of the oceanic mantle and the oceanic basalts.

The effect on HSE abundances in the reacted peridotite after addition of metasomatic BMS is variable. For Os and Re, typical mantle concentrations are maintained (3-4 ppb and 0.7-1.3 ppb, respectively). However, Pt concentrations will increase to 22-30 ppb. S concentrations will range between 116 and 4000 ppm depending on the Os contents of metasomatic BMS involved in the mixing process. Suitable contenders for such metasomatically enriched wall-rocks can be found in massif peridotites as orthopyroxene-rich zones between pyroxenite veins and host peridotite (S9-S10). These rocks may contain up to 0.6 wt.% BMS (≈ 2000 ppm S) and show high Pt contents overlapping our modelling results (18-150 ppb) (S10). Upon melting, these metasomatised peridotites will transfer their radiogenic ^{186}Os - ^{187}Os signature to the resulting partial melts. However, the resulting melts should not inherit elevated S and Pt contents because of the limited S solubility in mantle-derived silicate melts. While S partitions into the melt, its pressure-controlled solubility reaches its maximum

at shallow depth and high temperature (*S11*). Similarly, the solubility of Pt into silicate melt has been estimated at ≈ 8 ppb at 1400°C and FMQ (*S12*), yielding Pt concentrations of the same order as those observed in ^{186}Os -enriched Hawaiian picrites (*S13*), Pyke Hill (*S14*) and Gorgona komatiites (*S15*) (e.g. 2-16 ppb). Moreover, at high degrees of partial melting, Pt is expected to behave compatibly because of the formation of refractory platinum group alloys in response to the complete consumption of BMS (*S16*). These two factors impose a natural limit to the Pt concentration of mantle-derived melts and make it unlikely that melt produced from sulfide-metasomatised peridotites will bear a high-Pt signature. Hence, while the Os isotope systematics of melts produced in the upper mantle will reflect any source enrichment from radiogenic sulfides, their HSE abundance patterns will be decoupled.

Table S1: HSE concentrations, $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ ratios of Beni Bousera pyroxenites, of base-metal sulfides from Beni Bousera pyroxenites, Udachnaya and Mir eclogites and of Pt-rich alloys from Josephine ophiolite (Oregon).

Sample	Os (ppb)	Ir (ppb)	Pt (ppb)	Re (ppb)	Pt/Os	Re/Os	$^{186}\text{Os}/^{188}\text{Os}_{\text{SC}}$	$^{187}\text{Os}/^{188}\text{Os}_{\text{SC}}$	$^{186}\text{Os}/^{188}\text{Os}_{\text{SM}}$	$^{187}\text{Os}/^{188}\text{Os}_{\text{SM}}$
Beni Bousera Pyroxenites										
GP 137	2.78	2.56	5.53	1.95	1.99	0.70	0.1198401	0.18746	0.1198262±11	0.178510±32
GP 139	0.17	0.13	0.85	1.44	4.93	8.43	0.1198449	0.92007		
GP 33B	0.45	0.37	3.21	1.41	7.11	3.13	0.1198485	0.41814		
GP 148	0.30	0.26	0.80	1.03	2.70	3.50	0.1198413	0.45307		
GP 251M	0.41	0.30	6.80	1.05	16.60	2.56	0.1198642	0.36326	0.1198571±60	0.607048±12
GP 253	0.10	0.12	2.25	0.74	23.61	7.79	0.1198757	0.85981		
GP 140	0.30	0.17	0.87	1.68	2.94	5.64	0.1198417	0.65576		
GP 138	0.30	0.24	0.74	1.11	2.46	3.68	0.1198409	0.46966		
GP 87T	0.10	0.16	3.47	0.03	34.36	0.30	0.1198934	0.14893		
GP 28	0.21	0.14	1.70	1.29	8.14	6.18	0.1198502	0.70643		
GP 130	0.53	0.41	4.44	1.13	8.32	2.11	0.1198505	0.32107		
Base-metal sulfides of Udachnaya and Mir eclogites										
U2300-C1	1789.8	316.0	52.8	254.3	0.03	0.14	0.1198369	0.13436		
U2300-C3	6.1	223.1	39.1	355.4	6.41	58.29	0.1198474	5.64773		
U2300-R2	4.2	10.1	2.5	84.0	0.61	20.24	0.1198378	2.03971		
U2300-C2	11307.0	1296.9	861.0	2721.9	0.08	0.24	0.1198369	0.14372		
U2300-R1	486.6	136.8	20.1	125.5	0.04	0.26	0.1198369	0.14534		
U2300-R3	14.9	154.3	77.5	140.3	5.21	9.44	0.1198454	1.01609		
U2371-1	25.7	491.1	1310.4	153.1	51.09	5.97	0.1199209	0.68680		
U2371-5	21.8	1569.7	681.1	75.5	31.30	3.47	0.1198884	0.45007		
U2290-4	8.5	80.0	567.7	105.0	67.02	12.40	0.1199472	1.29642		
U2290-6	40.3	1375.9	2281.8	395.6	56.57	9.81	0.1199300	1.05074		
U2340-6	546.2	798.4	6251.5	1154.8	11.45	2.11	0.1198557	0.32136		
U2288-2	177.6	702.3	642.5	77.1	3.62	0.43	0.1198428	0.16206		

U2288-3	44.5	0.1	1165.7	107.4	26.23	2.42	0.1198800	0.34996
M2015-3	10.1	253.8	1479.4	52.5	146.77	5.21	0.1200785	0.61495
M2015-9	15.8	386.1	1548.3	44.4	97.74	2.80	0.1199978	0.38680

Base-metal sulfides of Beni Bousera pyroxenites

BB Pyr1	360.9	169.9	1373.4	90.0	3.81	0.25	0.1198431	0.14455
BB Pyr2	n.d.	111.1	994.0	90.0	n.d.	n.d.	n.d.	n.d.
BB Pyr3	1101.7	329.2	79.5	101.4	0.07	0.09	0.1198369	0.12962
BB Pyr4	n.d.	284.9	1488.8	72.4	n.d.	n.d.	n.d.	n.d.
BB Pyr5	262.0	168.1	1290.6	65.5	4.93	0.25	0.1198449	0.14458

HSE alloys of Josephine ophiolite (Oregon)

PGA1				3170	0.0024		0.120590±181	0.122230±331
PGA2				5554	0.0024		0.121779±973	0.121449±2151
PGA3				404	0.000021		0.120020±40	0.128443±78
PGA4				3488	0.0024		0.120949±240	0.124623±380
PGA5				146	0.00012		0.120014±66	0.143227±146
PGA6				2725	0.0030		0.120980±290	0.146708±399
PGA7				100	0.000008		0.119858±13	0.126259±22
PGA8				1935	0.0011		0.120281±113	0.125717±238
PGA9				231	0.000024		0.119876±29	0.137079±59
PGA10				777	0.000072		0.119980±66	0.126885±85
PGA11				1362	0.0024		0.120168±109	0.125275±149
PGA12				502	0.000074		0.119956±66	0.134319±155

M : measured Os isotopic compositions by Triton N-TIMS for the whole-rock pyroxenite (S4) and by laser-ablation ICP-MS (S5) for the HSE alloys;

data are reported with 2 SE uncertainty, C : calculated ratios. n.d. : not determined.

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