

NEW CONSTRAINTS ON THE ORIGIN OF THE HIGHLY SIDEROPHILE ELEMENTS IN THE EARTH'S UPPER MANTLE.

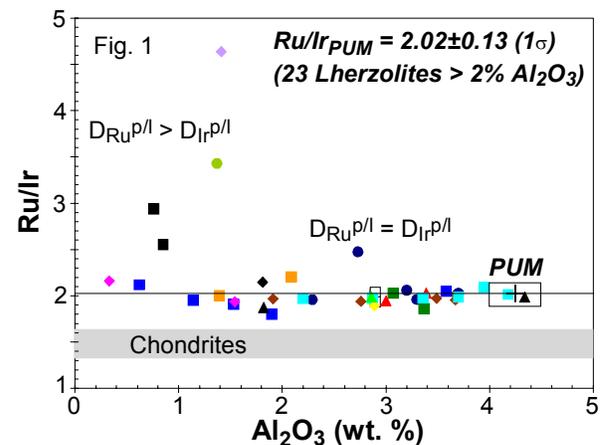
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Introduction: The origin of the highly siderophile elements (HSE) Re, Os, Ir, Ru, Pt, Rh, Pd and Au in the Earth's mantle remains a contentious topic. Relatively high abundances of these elements in the mantle suggest that mantle and core are not in equilibrium regarding the HSE. Hypotheses proposed to explain the HSE excess and near-chondritic HSE ratios in the mantle include: (1) Late accretion of 0.1-1 mass % chondritic material after core formation (Late veneer hypothesis [1-3]). (2) Decrease of metal-silicate partition coefficients at high pressures and metal-silicate equilibration at the bottom of a magma ocean [4]. (3) Incomplete metal-silicate separation during core formation [5]. (4) Contamination of the mantle with outer core material [6]. Each of these models has its problems. More precise estimates of the HSE composition of the primitive upper mantle (PUM) may provide further clues. Here, we present new high-precision data for Re, Os, Ir, Ru, Pt and Pd in mantle peridotites, using improved analytical techniques. New estimates for the HSE in PUM are obtained and the results compared with new high-precision data for HSE in chondrites [7] and in lunar impact melt breccias [8].

Samples: Types of samples analyzed include lherzolite and harzburgite xenoliths from post-Archean and Archean continental lithosphere, samples from ultramafic massifs, ophiolites, and other samples of oceanic mantle.

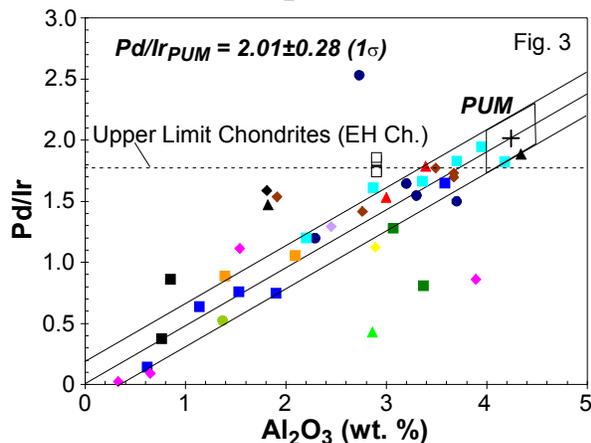
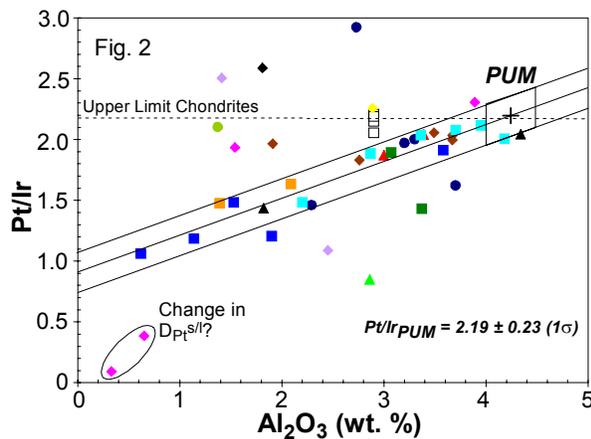
Analytical Techniques: The main problem associated with the determination of HSE abundances in peridotites has been the difficult digestion of refractory phases such as spinel and PGE alloys. This may result in poor yields or incomplete sample-spike equilibration. Recent studies showed encouraging results for the reproducibility and accuracy of HSE abundances in lherzolites using HP ashers at 300-320°C [9, 10]. These studies also suggest that techniques based on NiS fire assay and Carius tubes at 220-240°C, may not always result in complete digestion. For these reasons, we have employed a modified closed-system digestion technique using reverse *aqua regia* and quartz Carius tubes at 345°C. HSE abundances were determined by isotope dilution, with Os and other HSE separated by solvent extraction and anion exchange chromatography. Isotopic ratios were measured by N-TIMS (Sector 54) and ICPMS (Element 2). Sample size was typically

3 g. Blank corrections were negligible or minor, except for Pt, Pd and Re in some highly depleted harzburgites. Accuracy and reproducibility (2-5 %) were tested using the lherzolite reference material UB-N [9, 10]. HSE ratios are reproducible to 2-7 %. Most of this variability reflects sample heterogeneity.



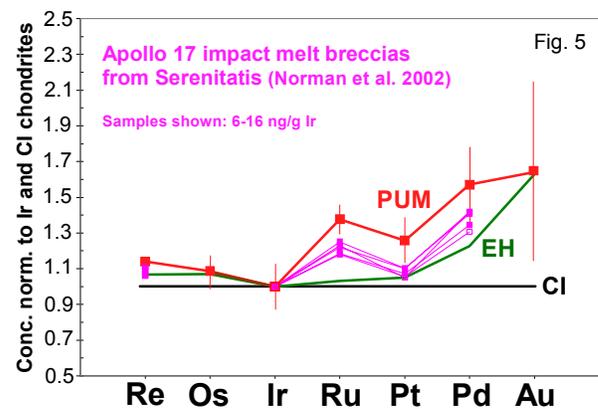
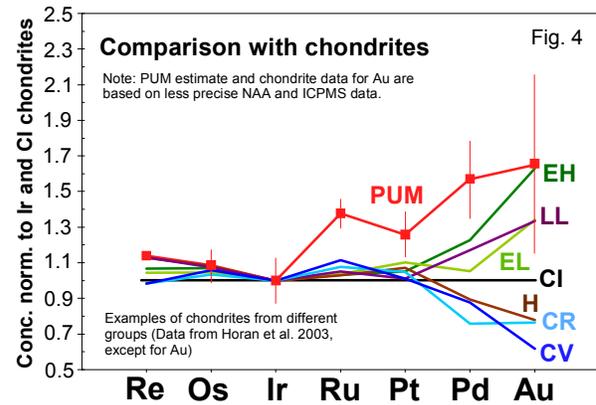
Results: Iridium, Os and Ru concentrations show increasing variability from lherzolitic to harzburgitic compositions. The mean Ir concentration of 23 lherzolites with > 2% Al₂O₃ is Ir_{PUM} = 3.5±0.4 ng/g (1σ), similar to previous estimates for PUM based on fertile lherzolites (e. g., [3]). Os/Ir and Ru/Ir (Fig. 1) are constant over a wide range of compositions (1-4.5 wt. % Al₂O₃) but increase substantially in some harzburgites, indicating an increase in the harzburgite-melt partition coefficients of Os and Ru relative to Ir. While Os/Ir_{PUM} is chondritic (1.12±0.09, 1σ), Ru/Ir_{PUM} (Fig. 1) is evidently suprachondritic (2.02±0.13, 1σ). These ratios in combination with Ir_{PUM}, yield Os_{PUM} = 3.9±0.6 ng/g (1σ), and Ru_{PUM} = 7.0±1.0 ng/g (1σ), respectively. ¹⁸⁷Os/¹⁸⁸Os in most peridotites correlates well with Al₂O₃, with the slopes of different suites of samples depending on the age of melt extraction. Some depleted samples, however, plot off these correlations, indicating addition of radiogenic Os. Using ¹⁸⁷Os/¹⁸⁸Os_{PUM} (0.1296±0.0008, [11]), we obtain Re/Os_{PUM} = 0.090±0.002 and Re_{PUM} = 0.35±0.06 ng/g. Pt/Ir (Fig. 2) and Pd/Ir (Fig. 3) also correlate well with Al₂O₃. Some samples show deviations from these cor-

relations that might be caused by secondary processes such as melt percolation. Assuming $Al_2O_{3PUM} = 4.0-4.5$ wt. % [12], the correlations yield chondritic to slightly suprachondritic $Pt/Ir_{PUM} = 2.19 \pm 0.23$ (1σ), slightly suprachondritic $Pd/Ir_{PUM} = 2.01 \pm 0.28$ (1σ), $Pt_{PUM} = 8.5 \pm 1.4$ ng/g (1σ), and $Pd_{PUM} = 7.0 \pm 1.3$ ng/g (1σ). Due to the improved digestion technique and the use of isotope dilution, the overall scatter of the data is lower, and our new estimates for Ru, Pt, Pd and Re in PUM are significantly higher than previous estimates that were based on data of variable quality [3].



Discussion: PUM shows a stronger enrichment of the volatile HSE than chondrites (Fig. 4). None of the chondrites analyzed so far provides a good match for the PUM pattern. EH chondrites do not show Ru enrichment, are less enriched in Pd, and have lower Re/Os than PUM. The best match to the HSE pattern of PUM comes from 3.9 Ga lunar impact melt breccias from the Serenitatis impact basin (Fig. 5, [8]). The HSE patterns of the breccias shown in Fig. 5 are dominated by contributions from the impactor, and their similarities with PUM strengthens the case that the HSE inventory of PUM may have been produced by late accretion 4.5-3.8 Ga ago. The non-chondritic

HSE pattern of the lunar impact melt breccias suggests a temporal change in HSE character of impactor materials after the accretion of the Earth and Moon. More HSE analyses of ancient lunar impact rocks are necessary to better constrain the compositional range of the impactors.



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