

## COMPARISON OF HIGHLY SIDEROPHILE ELEMENTS BETWEEN EARTH AND MARS

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**Introduction:** The highly siderophile elements (HSE: Re, Os, Ir, Ru, Rh, Pt, Pd, Au) with very high metal-silicate distribution coefficients  $D_{\text{met/sil}} > 10^4$  (e.g., [1], [2], [3]) should have stripped from the silicate mantle into the FeNi-rich metallic core during differentiation of the Earth. The modest levels of depletion and the approximately cosmic relative abundances of some HSE (Os, Ir, Pd) led to the hypothesis that these elements were added to the accreting Earth by a late bombardment after core formation (e.g., [4], [5], [6], [7]). The question whether or not HSE are fractionated in the Earth's mantle and crust is particularly interesting. The answer may contribute to the understanding of the processes involved in the formation of planetary bodies, and the late accretionary history of planets.

### HSE in Earth mantle:

The past twelve years we have measured the HSE in many mantle suites of the Earth by neutron activation. Estimates of Rh/Ir, Ru/Ir, Pd/Ir, and Pt/Os derived from most mantle suites indicates modestly supra-chondritic compositions for average primitive upper mantle (PUM). The enigmatical mantle Ru/Ir ratio of  $2.01 \pm 0.12$  [8] in comparison of  $1.51 \pm 0.04$  of the known different chondrite groups has been observed by other groups as well [9], [10]. During basalt petrogenesis Os, Ir, and Ru behave highly compatibly and are retained in the source, whereas Re, Pd and Pt act moderately to highly incompatibly and are concentrated in the liquid [11]. The behavior of Rh is known with much less certainty. However, based on data from many mantle samples, it appears that Rh has compatibilities to those of Os, Ir, and Ru. From highly melt depleted peridotites [11] and metasomatized mantle xenoliths [12] we conclude that processes such as melt depletion, refertilization and metasomatism can be excluded in establishing the elemental pattern in PUM. However, the Os, Ir, Ru, Pt, and Pd pattern on PUM perfectly match IVA iron meteorite data (Charlotte) recently derived by Walker et al. [13]. One of the major processes in producing siderophile element fractionations in iron meteorites is fractional crystallisation of a liquid iron core in the parent meteorite bodies with elements concentrating preferentially in the liquid or solid phase (e.g. [14]).

The question raises if HSE in PUM are added to the accreting Earth by a late bombardment of (a) iron meteorites, (b) some unsampled inner solar system materials (more highly fractionated than enstatite chondrites), or (c) excess Rh, Ru, Pt, and Pd in the depleted mantle may have predated the late veneer, or

(d) added by crustal recycling [15], or (e) HSE are mixed from the differentiated outer core into the mantle after core formation [16]?

### HSE in Mars mantle:

Martian meteorites (SNC meteorites) can be accommodated in terms of three endmembers: primitive (in terms of mantle derivation), have nearly chondritic Re/Au ratios, evolved and highly evolved (have lower than chondritic Re/Au ratios) [17]. Jones et al. [17] noted that there are at least two distinct siderophile element signatures in the SNC meteorites. In the case of Re there is some analytical problem [17], such that all Walker group Re analyses were high by a factor of 3 [18]. However as noted by Jones et al. [17], the disagreements between Re analyses of SNCs between different research groups are qualitatively very similar to disagreements between Re analyses of terrestrial mantle xenoliths. For example, Meisel et al. [19] have shown that Re analyses of the Basaltic Volcanism Ultramafic Suite by the Walker group are, on average, a factor of 3 higher (possible terrestrial Re contamination) than those of Morgan and co-workers who analyzed them by RNAA [20]. Whole rock samples from our terrestrial suites have Re concentrations in the range of 0.09 to 0.23 ng/g; the mean is  $0.16 \pm 0.05$  (1s) ng/g [8], in good agreement with recent estimates of Re in the depleted MORB mantle (DMM) [21]. Similar to earlier studies, Au shows a wide scatter. For reasons given above and because Au and Re abundances in peridotites are more susceptible to alteration than other HSE both elements were excluded from interpretations ([15], [22], [23], [12], [8]). For comparison with PUM I have chosen Dar al Gani 476, ALH 77005 and EET 79001A which seem most primitive, and Nakhla, Shergotty and Zagami as highly evolved compositions.

In Fig. 1 and 2 the SNCs highly siderophile elements are plotted, using the preferred values from Jones et al. [17]. It was proposed by many authors (e.g., [24], [3], [18]) that highly siderophile elements exist at or near chondritic relative abundances in the martian mantle. Compared to the martian meteorite ALH 77005 (olivine cumulate classified as a lherzolite), Ru and Pt are slightly elevated and Os and Ir are somewhat lower in PUM (Fig. 1). Rhodium and Pd cluster near the ALH 77005 line. In Dar al Gani 476 (basalt with some cumulus olivine) Os and Ir are significantly depleted and Rh and Pd are significantly enriched relative to PUM. In EET 79001A (basalt with ultramafic xenoliths) Os, Ir and Ru are significantly depleted and Rh and Pd cluster near the PUM line.

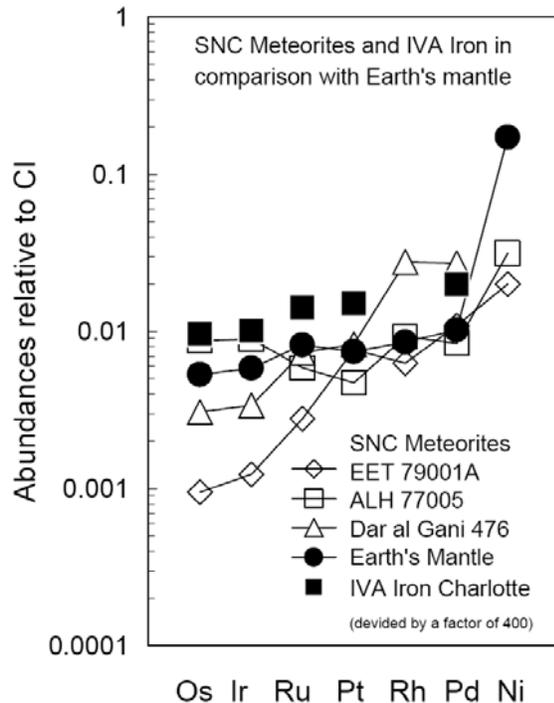


Fig. 1. CI-normalized concentrations of siderophiles in EET 79001A (basalt with ultramafic xenoliths) – ALH 77005 (olivine cumulate classified as a Iherzolite) – Dar al Gani 476 (basalt with some cumulus olivine) [17] – IVA Iron meteorite Charlotte [13] (Charlotte data divided by a factor of 400 for comparison) and the Earth's upper continental crust. Errors are smaller than the symbols. Chondrite normalizations in this paper were taken from [25]. As can be seen from the figure Charlotte and the Earth's mantle have very similar siderophile signatures. Dar al Gani 476 forms a smooth, fractionated pattern that is depleted in Os and Ir, enriched in Rh and Pd, and whose Ru and Pt concentrations are largely unchanged from those of the Earth's mantle. However, there are no Martian meteorite data that match the mantle siderophile element pattern in detail. Closest to the mantle pattern of the Earth is ALH 77005.

However, Fig. 1 shows that there is generally good agreement among the IVA iron meteorite Charlotte and PUM. However, the total variation observed in the analyses of ALH 77005 (in terms of their HSE element signatures the less fractionated from all martian meteorites) is modest with negative anomalies for Re and Au (not shown) [17]. Some process has fractionated Ru from Pd and Rh, but these authors could not explain the less than CI Ru/Pd ratios in SNCs? Jones et al. [17] noted that Ru and Pd do not readily fractionate during martian igneous processes, otherwise the Ru/Pd ratio would not be so constant. However, some un-

grouped IVA Iron meteorites do have similar less Ru/Pd ratios [13] than SNC meteorites. These observations strengthen the suggestion that the martian mantle has probably iron meteorite relative abundances instead of CI relative abundances of the highly siderophile elements. The fractionated Ru/Pd is probably the result of a late bombardment of iron meteorites or some unsampled inner solar system materials after core formation.

#### HSE in Earth crust:

In contrast to the mantle, the HSE and Ni pattern of the Earth's upper continental crust (UCC) is strongly fractionated. Osmium and Ir behave very similarly (Fig. 2) and both elements can become strongly decoupled from the other siderophile elements Ru, Pt, Rh, Pd and Ni. The highly fractionated Ru/Ir ratio preserved in the Earth's UCC is unparalleled in terrestrial magmatic systems. It seems unlikely that sulfide fractionation would cause Os and Ir to decrease, while leaving Ru, Rh, Pt and Pt essentially unchanged. Also these depletions in Os and Ir are unlikely to be caused by spinel and/or chromite fractionation [17], [26], [27]. Spinel as a host for Os and Ir has been documented in terrestrial samples [26], [27] but not in SNC spinels [28].

In fact, the HSE and Ni systematics of the UCC closely resembles IIIAB iron meteorites, pallasites, as well as the SNC meteorites Nakhla, Shergotty and Zagami, probably an indication that the UCC preserves an imprint of some of the major fractionation processes which have occurred in such meteorites.

#### HSE in Martian crust:

The martian crust formed at about 4.55 by [29]. As pointed out by [17] Nakhla, Shergotty and Zagami have very similar siderophile signatures (Fig. 2) but extremely different Sr and Nd isotopic characteristics. Highly siderophile element signatures are highly independent of lithologic type and petrologic history. These meteorites are probably most representative of the martian crust. The observations suggest that the siderophile signatures of SNCs were acquired recently and are strongly decoupled from lithophile element fractionations. The abundances of the highly siderophile elements in the martian mantle and the martian crust may therefore have been established by a late veneer, as is inferred for the Earth mantle and crust [30]. Zagami and Nakhla, with relatively evolved compositions, forms smooth, fractionated pattern that are strongly depleted in Os and Ir, modestly depleted in Ru, Rh, Pd, Ni, and whose Pt concentrations are slightly enriched from those of the Earth crust. IIIAB iron meteorites, for example Grant and the pallasites Brenham, Giroux, Sommervell County, and South Bend generally show similar fractionated element patterns with low Os and Ir, and high Ru, Pt, Rh, and Pd

than the pattern derived for the martian crust (Figs. 3-4). Additionally, the Ni/Ir ratio of the martian crust is not distinguishable from the Ni/Ir ratios found in magmatic iron meteorites and pallasites. The similarity in HSE ratios and the very systematic compatible-incompatible element behaviour of IIIAB irons, pallasitic metal and the martian crust strongly supports a genetic link between these meteorites and the HSE component of the martian crust. A possible interpretation is that the HSE in the martian crust may have been introduced by impacts of magmatic iron meteorites and/or pallasites as it is supposed for the Earth crust [30]. In fact the first meteorite of any type ever identified on another planet by NASA's Mars Exploration Rover Opportunity was an iron meteorite.

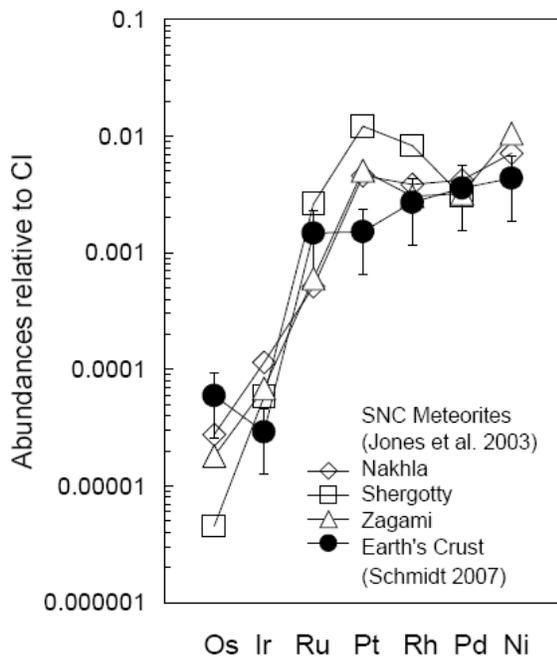


Fig. 2. CI-normalized concentrations of siderophiles in Nakhla (augite cumulate) – Shergotty (basalt with some cumulus pyroxene) – Zagami (basalt with some cumulus pyroxene) [19] and the Earth's crust. Chondrite normalizations in this paper were taken from [25]. Nakhla, Shergotty and Zagami have very similar siderophile signatures. The figure compares the Nakhla – Shergotty – Zagami pattern to that of the Earth's crust. Errors for SNC analyses are smaller than the symbols. Except for the Shergotty Os, Pt, and Rh analysis, the Nakhla – Shergotty – Zagami data match those of the Earth's crust pattern quite well. Shergotty, a relatively evolved composition, forms a smooth, fractionated pattern that is strongly depleted in Os and Ir, modestly depleted in Ru, Rh and Pd, and whose Pt and Ni concentrations are largely unchanged from those of the Earth's crust.

### Estimated Mass of Iron Meteorites Contributing to HSE and Ni Inventory of Earth Continental Crust:

IIIAB Iron is a common iron meteorite type and many of the small impact craters on Earth are produced by this type of iron meteorite projectiles (cf. [31] and references therein). An average density of  $2.8 \text{ g cm}^{-3}$  for the Earth crust gives a total crustal mass of  $2.06 \times 10^{25} \text{ g}$  ( $\pm 7\%$ ) [32]. The meteoritic mass (magmatic irons or pallasites, for example Grant with  $92.4 \text{ mg/g Ni}$  [33]) is thus estimated to be  $1.32 \times 10^{22} \text{ g}$ ,

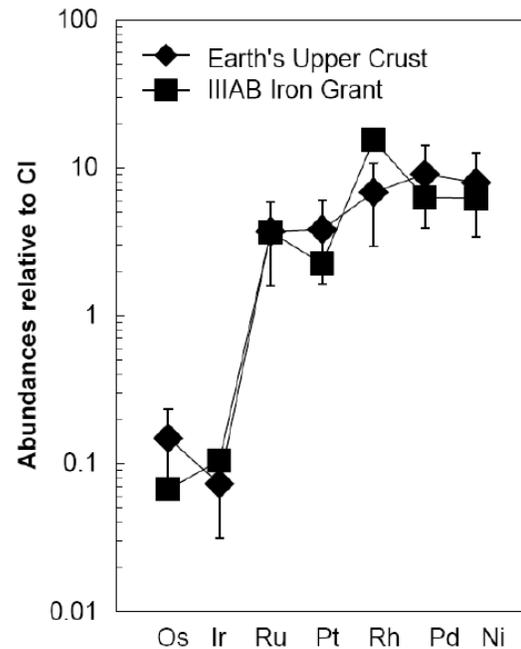


Fig. 3. CI-normalized concentrations of siderophiles in the Earth's upper crust and IIIAB Iron meteorite Grant [37] (crustal data are multiplied by a factor of  $2 \times 10^3$  for comparison). Chondrite normalizations in this paper were taken from [25]. Grant has a very similar siderophile signature than the Earth crust. Grant forms a smooth, fractionated pattern that is strongly depleted in Os and Ir, modestly depleted in Pt, and whose Ni/Ir ratio is unchanged from those of the Earth's crust.

which account for the abundances of Ni and HSE in the Earth continental crust. Assuming a mean density of  $8 \text{ g cm}^{-3}$  for magmatic iron meteorites [34], this corresponds to a volume of  $1.65 \times 10^{21} \text{ cm}^3$  and thus a sphere with a radius of 73 km as an upper limit. Since the mass of the upper continental crust is about half the mass of the total crust [35] and the Ni content of the UCC is  $47 \pm 11 \text{ } \mu\text{g/g}$  (cf. [36]) the addition of less than 0.03 % of a meteoritic (magmatic irons or palla-

sites) component is required. Assuming that (1) bulk Ni in the upper crust is extraterrestrial in origin and (2) the mass of the upper continental crust is about half the mass of the total crust, this corresponds to a volume of  $6.55 \times 10^{20} \text{ cm}^3$  and thus a sphere with a radius of about  $54 \pm 4 \text{ km}$  as an upper limit [30]. Of course these estimates are very rough but not unlikely assuming that more than a single projectile may have hit the Earth upper continental crust since its formation.

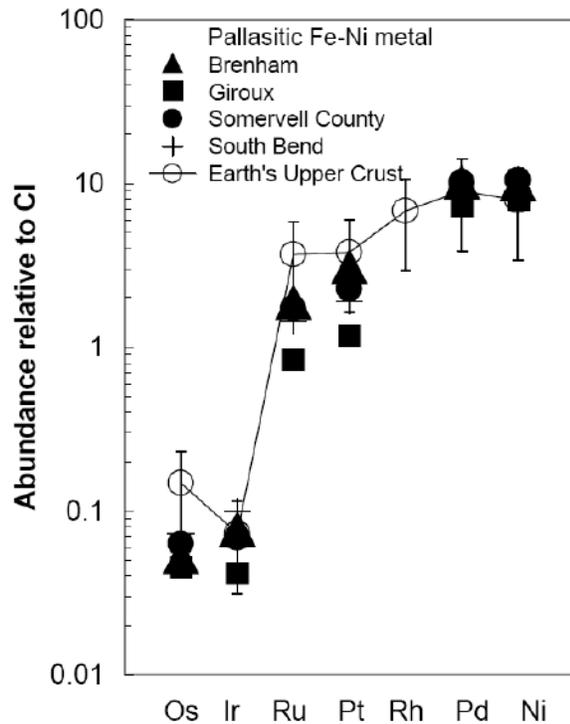


Fig. 4. CI-normalized highly siderophile element and Ni concentrations from pallasites and the upper continental crust. Pallasite data from [38]; data from the Earth's upper crust from this study (multiplied by a factor of  $2.5 \times 10^3$  for comparison). Error-bars are represented by the size of the symbols, if no error-bars indicated. The element pattern of the continental upper crust is similar to those observed in Fe,Ni metal from Brenham, Giroux, Somervell County, and South Bend.

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