

HIGHLY SIDEPHILE ELEMENT ABUNDANCE CONSTRAINTS ON THE NATURE OF THE LATE ACCRETIONARY HISTORIES OF EARTH, MOON AND MARS. R.J. Walker¹, I.S. Puchtel¹, A.D. Brandon², M.F. Horan³ and O.B. James⁴, ¹Department of Geology, University of Maryland, College Park, MD 20742 (rjwalker@geol.umd.edu), ²NASA, JSC, Houston, TX 77058, USA, ³Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd., Washington DC 20015, ⁴U.S. Geological Survey, 926A National Center, Reston, VA 20192.

Introduction. The highly siderophile elements (HSE) include Re, Os, Ir, Ru, Pt and Pd. These elements are initially nearly-quantitatively stripped from planetary silicate mantles during core segregation. They then may be re-enriched in mantles via continued accretion *sans* continued core segregation [1]. This suite of elements and its included long-lived radiogenic isotopes systems ($^{187}\text{Re} \rightarrow ^{187}\text{Os}$; $^{190}\text{Pt} \rightarrow ^{186}\text{Os}$) can potentially be used to “fingerprint” the characteristics of late accreted materials. The fingerprints may ultimately be useful to constrain the prior nebular history of the dominant late accreted materials, and to compare the proportion and genesis of late accretionary materials added to the inner planets.

The past ten years have seen considerable accumulation of isotopic and compositional data for HSE present in the Earth’s mantle, lunar mantle and impact melt breccias, and Martian meteorites. Here we review some of these data and consider the broader implications of the compiled data.

Earth. Of perhaps greatest importance to humans is the late accretionary history of the Earth. In addition to the fact that you can still get hit on the head by late accreted materials, it has also been widely suggested that late additions to Earth could have provided the planet with much of its water and with organic matter. Studies of the Os isotopic compositions of terrestrial peridotites that have been long isolated from convection in the upper mantle (e.g. ancient subcontinental lithospheric mantle) led to the conclusion that: a) important constraints can be placed on the Os isotopic composition of the Primitive Upper Mantle (mantle unmodified by melt depletion or enrichment), and 2) the inferred $^{187}\text{Os}/^{188}\text{Os}$ of Earth’s dominant late accreted materials matches that of enstatite/ordinary chondrites, not the more volatile rich carbonaceous chondrites [2].

Recent attempts to constrain the absolute and relative HSE budget of the PUM have led to recognition that there are some discrepancies between PUM and chondrites. For various suites of peridotites (including continental mantle, orogenic lherzolites and abyssal peridotites), HSE were recently correlated with melt depletion/enrichment indicators and extrapolated to an estimate of the PUM [3]. For most HSE, abundances in PUM are similar to earlier estimates. However, estimates of Ru/Ir and Pd/Ir derived from most suites indicates modestly suprachondritic compositions for average

PUM. This has been observed by other groups as well [4-5], although the effects of melt depletion can now be discounted. Thus, although HSE in the terrestrial PUM can be placed in a broad “chondritic” family, it is not a perfect match to any one chondrite group that exists in our collections. This can be interpreted in one of several ways. First, the dominant late accreted materials may have had a somewhat different nebular history compared to the chondrites in our collections. This would not be surprising. Nebular, and perhaps subsequent processing on parent bodies has been shown to result in considerable fractionation of HSE [6]. Second, the deviation from chondritic ratios could be an indication that processes other than, or in addition to late accretion controlled HSE abundances in the mantle. For example, many workers have experimentally explored the possibility that the comparatively high abundances of HSE in the mantle are a result of relatively low metal-silicate bulk partitioning at the base of a deep magma ocean [7]. This is an unlikely explanation for the Os isotopic systematics, given the close adherence of $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ to chondritic (which allows us to constrain Re/Os and Pt/Os in the PUM better than any other HSE ratios). Retention of precisely chondritic Pt/Re/Os is an unlikely result of metal-silicate partitioning. Nonetheless, this possibility begs future experimental consideration. Also, retention of excess Ru and Pd in the silicate Earth following metal segregation, relative to other HSE, could result in suprachondritic ratios involving these elements, allowing the possibility of a hybrid model for generating HSE abundances. Finally, it may be that mantle processes (melt removal & refertilization, crustal recycling) have complicated the HSE budget of the mantle beyond our current capability to deconvolute them and obtain an accurate estimate of the PUM.

Moon. We recently completed a study of the Os isotopic and HSE concentration systematics of lunar picritic orange and green glasses with the intent of constraining Os concentration in the lunar mantle sources of these relatively high MgO melts [8]. We discovered that residues of leached glass spherules contained more radiogenic Os than the leachates, but lower Os abundances, suggesting the presence of at least two Os (and likely other HSE) components. The presumed radiogenic indigenous component has much lower Os and HSE concentrations than had been previously presumed for lunar glasses. This may be a re-

flection of the mantle sources of the glasses containing low concentrations of these elements.

Relative to terrestrial rocks with comparable MgO contents, the lunar mantle sources of the orange and green glasses were depleted in the HSE by at least a factor of 20. This observation may indicate that the lunar mantle did not receive a late accretionary component like that suggested to explain the HSE budget of Earth's mantle. The "missing" HSE could reside in the lunar crust, which is both ancient and thick, and may have protected the lunar mantle from much of the putative late influx of material. Alternately, the missing HSE could have been extracted into a small lunar core at the time of its formation, or may even continue to reside in the lunar mantle in residual metallic iron. The latter two hypotheses can be tested, because metal would likely lead to strong fractionation of Re from Os in the silicate mantle. This is because metal has less affinity for Re than Os. Consequently, other materials derived from the lunar mantle, such as basalts, would likely show supra-chondritic Os isotopic compositions at the time of their formation, if metal was responsible for the apparent depletion of HSE in the lunar mantle. Preliminary results show that this is not the case but much additional work will be required.

Potentially direct information regarding the chemical nature of late accreted materials to the Earth-Moon system can be obtained by examining the HSE contained in lunar impact-melt rocks. Our work on lunar impact melt rocks are discussed elsewhere by Puchtel et al. [9].

Mars. Re-Os studies of SNC meteorites indicate that the Martian mantle evolved with a dominantly chondritic Re/Os [10]. As with the terrestrial mantle, this is most easily explained via the addition of a late veneer with chondritic Re/Os subsequent to core formation.

Absolute and relative abundances of HSE in Martian mantle rocks could ultimately provide a useful fingerprint for late accreted materials., however, we currently have no direct samples of the Martian mantle. As noted previously, SNC meteorites have Os concentrations broadly consistent with derivation from mantle sources bearing Os concentrations similar to those present in the terrestrial upper mantle (**Fig. 1**). Nonetheless, as with the production of lunar basalts and picrites, Os may not behave the same during melting of the Martian mantle as during melting of the terrestrial mantle (in the terrestrial mantle it is normally strongly compatible due to retention in sulfides and alloys).

To broaden our understanding of HSE in the Martian mantle, We have begun a more comprehensive analysis of HSE in SNC meteorites. The ten SNC me-

eteorites we analyzed for platinum-group element abundances have Pt and Pd concentrations that range from 1.5 to 7.5 ppb and 1.3 to 6.5 ppb respectively. These concentrations are generally within the lower range of terrestrial samples with comparable MgO (as with Os; **Fig. 1**). Given the typical mantle-melt D values close to unity (for terrestrial systems), these results are more robust indicators than Os concentrations of similarity of HSE abundances in the Martian and terrestrial mantles.

These results suggest that the Martian mantle received a proportionally similar mass of late accreted materials as was added to Earth..

References. [1] Chou (1978) *Proc. 9th Lunar Planet. Sci. Conf.*, 219-230. [2] Meisel et al. (2001) *Geochim. Cosmochim Acta* **65**, 1311. [3] Becker et al. (2006) *Geochim. Cosmochim Acta* **70**, 4528. [4] Pattou et al. (1996) *Nature* **379**, 712. [5] Schmidt (2004) *Met. Planet. Sci.* **39**, 1995. [6] Horan et al. (2003) *Chem. Geol.* **196**, 5. [7] Drake (2000) *Geochim. Cosmochim Acta* **64**, 2363. [8] Walker et al. (2004) *EPSL* **224**, 399. [9] Puchtel et al (2007) *LPSC XXXVIII*. [10] Brandon et al. (2000) *Geochim. Cosmochim Acta* **64**, 4083.

Acknowledgements. This work was supported by NASA grants NNG04GJ49A and NNG04GK52G, and NSF grant EAR0207107.

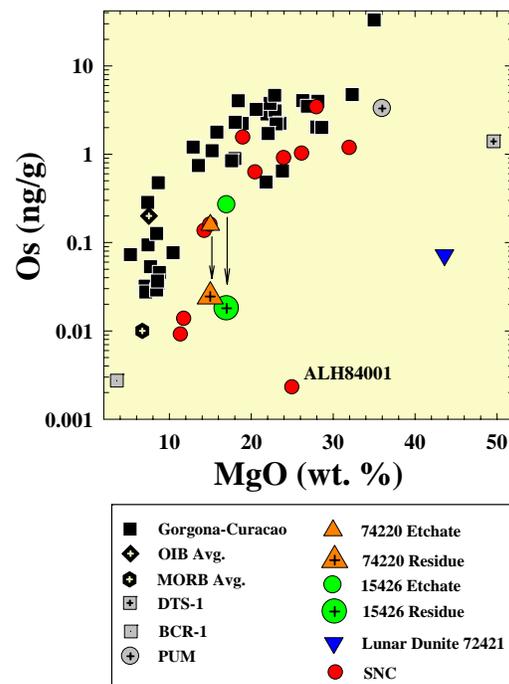


Fig. 1. MgO vs. Os for typical terrestrial rocks, lunar orange and green glasses, and Martian SNC meteorites. Concentrations of etchates and residues of green glass 15426,164 (>200 μm) and orange glass 74220 (74-150 μm) are shown. The Os concentrations of the indigenous components in the lunar glasses (residues) are considerably less than the concentrations in the bulk glasses. SNC meteorites plot at the lower end of the terrestrial array, with ALH84001 plotting well below the Martian trend. Most data from [8 & 10].