

HIGHLY SIDEROPHILE ELEMENT ABUNDANCES IN MARE BASALTS REFLECT LATE ACCRETION TO THE MOON'S INTERIOR

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Introduction: Highly siderophile element abundances (HSE: Au, Re, Pd, Pt, Rh, Ru, Ir, Os) estimated for lunar reservoirs are a key constraint on the formation of the Moon, and for models of late accretion (e.g., [1-4]) and planetary volatile inventories (e.g., [5]). Lunar mantle HSE abundances are estimated on the basis of HSE contents and $^{187}\text{Os}/^{188}\text{Os}$ for mare basalts [6,7], where it has been shown that there was an absence of residual sulfide or metal after partial melting [8]. Neglecting these lines of evidence, Brenan et al. [9] suggested, based on experiments, that the source of mare basalts is likely to be saturated in an S-poor, Fe-rich sulfide melt that “concentrated some HSE more than others”. To explain the higher-than-expected HSE contents of mare basalts from their model, they then suggested “mixing between primary sulfide-saturated melts and minute (<1%) amounts of lunar regolith that contain impact debris”, casting doubt on the validity of using lunar basalts to estimate HSE inventories in the Moon. Here we present laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses of metals, sulfides, silicates and oxides in mare basalts (Fig. 1), along with model calculations, to reinforce that contamination of mare basalts cannot explain the HSE abundances measured within them. Instead, we demonstrate that HSE abundances in mare basalts reflect fractional crystallization processes, and that estimates of lunar mantle HSE content from mare basalts remain a robust means for estimating late accretion to the Moon’s interior.

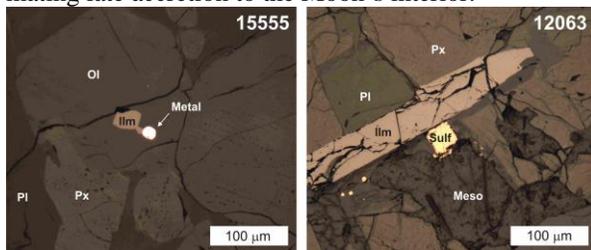


Figure 1: Reflected light images of metal and sulfide in 15555 and 12063.

Methods: LA-ICP-MS was used to measure >130 metal and sulfide grains, as well as silicate phases (clinopyroxene, plagioclase, olivine, glass and ilmenite) for five polished sections of mare basalts (ilmenite basalt 12063, olivine-normative basalt 15555, and mare basalt meteorites Dhofar [Dho] 287, La Paz Icefield [LAP] 02205, and Miller Range [MIL] 05035) that span a range of bulk rock MgO contents (13.2-6.3 wt.%). Analyses were done using a *New Wave Re-*

search UP213 (213 nm) laser ablation system coupled to a *Thermo Scientific* iCAP Qc ICPMS, as described in [10]. Where sulfide or metal grains were smaller than the laser beam diameter, a background subtraction of silicate composition was performed.

Discussion: Measurements were done on metal - and some sulfide - grains occurring in early crystallized silicate phases (olivine, pyroxene) in mare basalts, as well as in the mesostasis. Sulfide grains typically occur as interstitial phases, or associated with oxide phases (spinel, ilmenite). Average silicate and oxide grains for 12063, 15555 and Dho 287 have low HSE contents, typically below detection limits, whereas metal (M) and sulfide (S) grains have elevated HSE contents, typically $>0.1 \times \text{CI}$ chondrite, with elevated Au+Re+Pt+Pd relative to Rh+Ru+Ir+Os, and notably high Pd contents (Fig. 2).

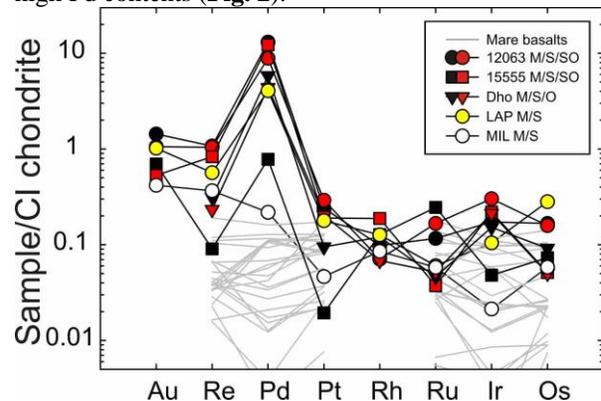


Figure 2: CI chondrite normalized average HSE patterns for metal (M) and sulfide (S) grains from mare basalts (12063, 15555) and mare basalt meteorites (Dho 287, LAP 02205, MIL 05035). Shown in grey are the compositions of mare basalts and mare basalt meteorite whole rocks ($\times 1000$) from [6,7].

Mare basalts span a range of relative and absolute HSE abundances, from high MgO rocks (>11wt.%) that have relatively flat CI-chondrite normalized HSE patterns at $\sim 0.0002 \times \text{CI}$, to mare basalts with strongly fractionated HSE patterns and lower total HSE contents ($<0.00001 \times \text{CI}$; e.g., 12038 [7]). These variations have been attributed to lower and more fractionated HSE abundances with decreasing MgO as a function of crystal-liquid fractionation of sulfide and metal [7]. Our new HSE abundance data for sulfides and metals in mare basalts confirm this view, with the strong fractionation of Pd from Pt, or Ir from Os occurring due to the high contents of Pd and Ir in metals and sulfides

(Fig. 2). As noted above, there is petrographic evidence for metal and, occasionally sulfide, trapped in early crystallizing silicate and oxide phases. Removal of minor amounts of such phases during fractional crystallization reproduces HSE patterns of the low MgO mare basalts well.

Due to eruption of mare basalts onto the lunar near-surface or surface environment, they are potentially susceptible to contamination by regolith, which has elevated HSE abundances due to impactor contamination (e.g., [11]). Some mare basalts, especially those with high MgO (>11wt.%) have nearly flat chondrite normalized HSE patterns [6,7]. This has led some to suggest that some mare basalts have experienced limited amounts (<1% by mass) of contamination by the ‘megaregolith’ of the Moon [9]. It is worth noting that only a few mare basalts have previously been suggested to have assimilated limited (<3%) crustal contributions from lithophile incompatible elements [12-14].

Prior study of Apollo 12 basalts showed that contamination by regolith material is inconsistent with the HSE and $^{187}\text{Os}/^{188}\text{Os}$ of samples, and for Ni/Co ratios for mare basalts in particular [7]. This is due to the high Ni/Co in chondrites and in the lunar regolith (Ni/Co > 7) [15]. Bulk rock mare basalts have Ni/Co < 1.7 [7], and the new Ni/Co data for sulfides, metals and silicates in the five mare basalts that we measured, which have no strong evidence for contamination from other proxies, is < 1.2. Furthermore, as also noted by Day & Walker [7] there is no obvious reason why MgO-rich basalts would preferentially assimilate regolith, leading to higher HSE concentrations, compared to more evolved melt products. This is especially true given that contamination is often most effective during later stages of fractional crystallization, enhanced by the latent heat of crystallization. Instead, the observation of sulfide and metal fractionation during fractional crystallization of mare basalts explains their HSE variations with MgO content (Fig. 3).

Performing the same calculations made by [7], but plotting them as a function of CI chondrite normalized HSE patterns (Fig. 3), rather than as plots of Ir versus Pd/Ir, Pt/Ir or Ru/Ir, shows that even the lowest estimated mantle source content of the HSE ($0.00002 \times \text{CI}$ [7]) does not reproduce the patterns of the mare basalts, leading to slightly convex up and HSE-rich patterns, rather than the patterns of generally decreasing Pd and Ir observed in mare basalts.

Sulfide and metal compositions in mare basalts confirm the major control of fractional crystallization – and not contamination – on the compositions of Apollo 12, 15, 17 mare basalts and mare basalt meteorites. Chondritic measured $^{187}\text{Os}/^{188}\text{Os}$, and generally chondrite relative HSE compositions of the most magnesian

mare basalts, reflect the effects of fractionation from their mantle sources, rather than contamination by regolith.

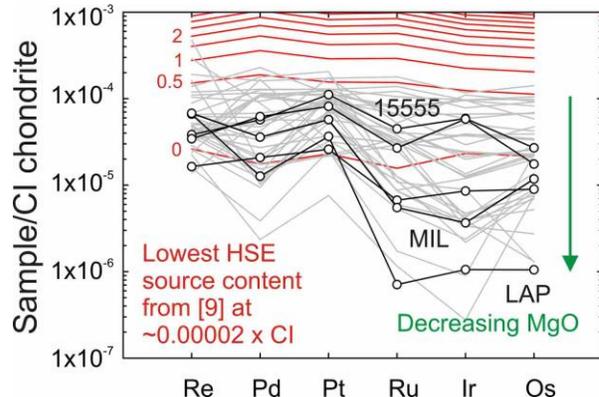


Figure 3: CI-chondrite HSE patterns for mare basalts [6,7] with three of the mare basalts analyzed in this study highlighted, versus the mixing model of [9] between a lunar mantle melt with $0.00002 \times \text{CI}$ and lunar ‘megaregolith’. Note that mare basalts show decreasing and more fractionated HSE contents with decreasing MgO, not higher HSE abundances and enrichment in Pd, as inferred from the model.

The results from this study show that estimates of lunar mantle HSE composition [6] and models relating to disproportional late accretion to the Moon relative to Earth (e.g. [1-4]) remain permissible. Mare basalt petrogenesis implicates partial melting from metal-free, S-poor mantle sources [8] and HSE fractionation by metal and sulfide. The coherent behavior of the HSE into sulfide - but also metal - during fractional crystallization, are consistent with reduced conditions within mare basalt melts during their ascent to the lunar surface. **Acknowledgement:** This work is supported by the NASA Emerging Worlds program.

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