

ON THE POSSIBILITY OF RESIDUAL METAL OR SULFIDE IN MARE BASALT SOURCE REGIONS.

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Introduction: An underlying concern when using mare basalts to determine the highly siderophile element (HSE) abundances of the bulk silicate Moon (BSM) is that regression methods, similar to those used to determine the bulk silicate Earth (BSE) composition, might not be effective due to different oxygen (fO_2) and sulfur (fS_2) fugacities for the two planetary bodies. It has been constrained that the Moon's mantle has a low fO_2 , at around one log unit below the iron-wüstite (IW) buffer (e.g., [1]), whereas Earth's mantle has greater than four orders of magnitude higher oxygen activity, at the fayalite-magnetite-quartz (FMQ) buffer [2]. For this reason, it is possible that metal is stable and residual within mare basalt source regions after partial melting. Equally, with low fO_2 , S contents in mare basalt sources might lead to residual sulfide and decreased sulfide concentration at sulfide saturation (SCSS) [3]. The term SCSS represents the maximum amount of sulfur a melt can dissolve at certain a fO_2 condition, and provides an upper boundary to S concentrations found in melts at reduced fO_2 .

Metal in mare basalt source regions: Previously, Day & Walker [4] showed that W, U and Th are not strongly fractionated in Apollo 12 mare basalts, indicating no residual metal existed in their sources after partial melt extraction. The choice of investigating W, U and Th is that these elements behave similarly during partial melting and fractional crystallization, but that W is a moderately siderophile element and U and Th are strongly incompatible lithophile trace elements. Any residual metal in the source after mare basalt partial melt extraction should lead to retention of W, but effective removal of Th and U. A lack of residual metal would show that all three elements behave as highly incompatible lithophile trace elements.

To evaluate this possibility, data are reported for the Apollo 12 mare basalts presented in [4], and for four mare basalt meteorites (MIL 05035, LAP 02205, NWA 4734 and Dho 287) which, except for NWA 4734, have previously been measured for HSE abundances and Os isotopes. In a plot of W versus U, residual metal in the source after mare basalt melt extraction would be expected to lead to low W abundances for a given U content. As with the Apollo 12 mare basalts, the mare basalt meteorites fall along a linear correlation for W and U, and all samples have similar Th/U (4.2 ± 0.6) (Fig. 1). This result suggests that neither Apollo 12 mare basalts nor mare basalt meteorites came from lunar sources that contained residual metal after melt extraction. Published data for

W and U contents are also available for the Apollo 11, 12, 15 and 17 mare basalts and have generally high W for a given U content, implying lack of residual metal during melt extraction.

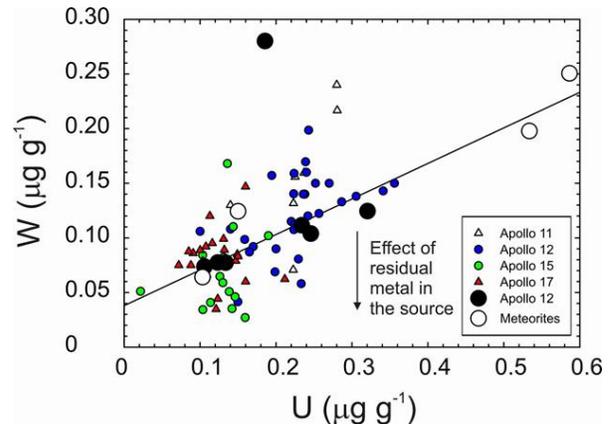


Figure 1: Uranium versus W concentrations in mare basalts from the Apollo 12 site [4] and low-Ti mare basalt meteorites (Meteorites) and published Apollo 11, 12, 15 and 17 mare basalt data.

A collateral consequence of residual metal in the source of mare basalts would be to strongly fractionate the HSE in partial melts that leave metal in the residue, due to the variable but high metal-silicate partition coefficients for the different HSE (e.g., [5]). Strong fractionations of the HSE are not observed in the primitive high-MgO mare basalts, and HSE patterns of low-MgO basalts can be entirely accounted for by near-surface crystal-liquid fractionation [4].

Sulfur contents of mare basalt source regions: It is possible that residual sulfide can occur in mare basalt source regions due to extremely low fO_2 . To understand mare basalt petrogenesis, two key questions need to be addressed: (1) how much S is likely to be in mare basalt sources and, (2) at what point did the parental magmas become saturated in S? Sulfur is a chalcophile and volatile element and is depleted in the Moon, relative to Earth, due to volatile depletion [6]. Based on current estimates, this depletion is between three times to ten times greater than in the BSM relative to BSE [7]. A conservative BSM S estimate is between 25 and 75 ppm, using a BSE S content of 250 ppm [8].

Sulfide saturation is dependent on the major-element composition of the magma, the composition of the immiscible sulfide, and the temperature and pres-

sure, with FeO content having a dominant control on SCSS (e.g., [9]). Recently, Brenan et al. [3] have reported evidence that SCSS falls rapidly as fO_2 approaches metal saturation, resulting in an S-saturated source. So long as metal saturation is not reached, then even mare basalt olivine melt inclusions with between 15 to 25 wt.% FeO would be close to the S-saturation curve. Consequently, sulfide-melt partitioning of 1000-10000, such as that used in [4], would be too low by a factor of ~ 100 to 1000. Furthermore, mare basalt sources could have significantly higher HSE contents than those currently estimated for the BSM.

Melting models can reproduce primary partial melt characteristics and Ir contents measured in primitive mare basalts with sulfide-melt partition coefficients of between 1000 and 10000. However, when higher sulfide-melt partition coefficients are used (100000 to 1000000), as would be expected from low SCSS, the compositions of mare basalts cannot be reproduced (Fig. 2). Instead, Brenan et al. [3] proposed that low SCSS requires mare basalt mantle sources with HSE contents within around four times of BSE. The models highlight several important issues for mare basalt petrogenesis. In the first instance, with more extreme sulfide-melt partition coefficients, the likelihood for inter-element fractionation becomes greater. A firm constraint on viable models for partial melting of mare basalt sources in the presence of residual sulfide is that the melting results in chondrite-relative abundances of the HSE and long-term Re/Os within a few percent of chondrites to satisfy primitive mare basalt compositions. Second, melting intervals required to explain mare basalt compositions from a source with low SCSS and HSE contents only ~ 4 times lower than in the BSE are restricted.

Discussion: Presence of residual metal or sulfide in the sources of mare basalts would lead to the inevitable underestimation of HSE contents for the BSM. Currently, there is no strong geochemical evidence for residual metal or sulfide after mare basalt partial melt extraction. Low S contents (25-75 ppm) are likely in the BSM, considering the evidence for loss of moderately volatile elements including Cl, S, K, Zn and Rb during formation and differentiation of the Moon [6], further limiting the likelihood for residual sulfide in mare basalt sources. Potential draw-down of S into a lunar core has not been accounted for, but would lead to the inevitable conclusion that the S contents of the BSM are >4 times lower than in the BSE. Melting models for the HSE support lower sulfide-melt partitioning to account for the chondrite-relative abundances of the HSE and near-chondritic measured $^{187}\text{Os}/^{188}\text{Os}$ in primitive mare basalts from the Apollo 12, 15 and 17 sites. The low ($0.00023 \pm 2 \times \text{CI}$ chon-

drite) and chondritic relative composition of the BSM [4] remains a robust constraint on the quantity of late accretion materials present in mare basalt sources. This suggests that the Moon experienced limited and disproportional late accretion compared to Earth and that S and other volatile elements were not added in significant quantity by this event.

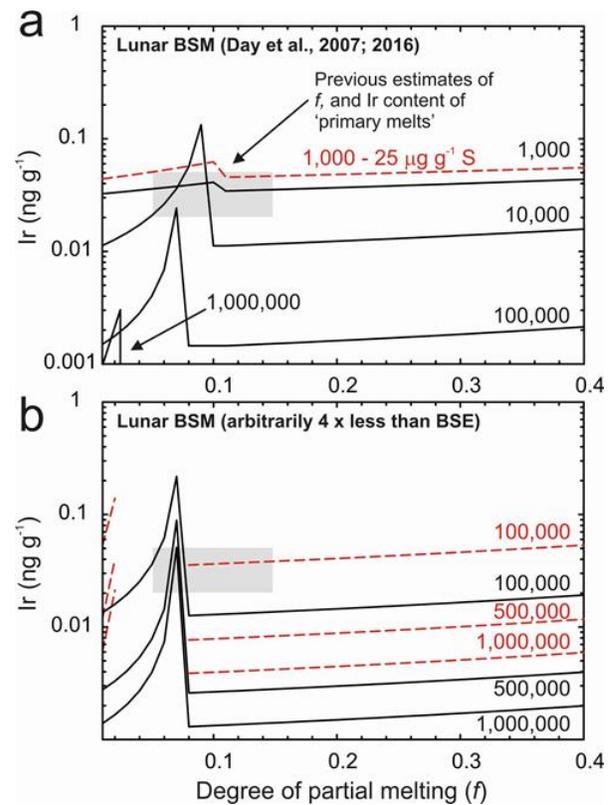


Figure 2: Melting models for Ir content as a function of partial melting for (a) different sulfide-melt partitioning in a columnar melting regime, assuming 75 ppm S in the source (black lines), 1050 ppm S in the melt and a BSM HSE composition and estimates of partial melting from prior studies [4]. 25 ppm S in the source is shown in red; (b) sulfide-melt partitioning assuming low SCSS and a BSM with four times lower HSE than BSE [3].

References: [1] Wadhwa, M. (2008) *RIMG*, **68**, 493; [2] Cottrell, E., Kelley, K.A. (2013) *Science*, **340**, 1314; [3] Brenan J. et al. (2016) 4th HSE Workshop, p.35; [4] Day, J.M.D., Walker, R.J. (2015) *EPSL*, **423**, 114; [5] Mann, U. et al. (2012) *GCA*, **84**, 593; [6] Day, J.M.D., Moynier, F. (2014) *PTRSA*, 20130259; [7] Bombardieri, D. et al. (2005) *M&PS*, **40**, 659; [9] McDonough W.F., Sun, S.-S. (1995) *Chem. Geol.* **120**, 223; [10] O'Neill, H.S.C., Mavrogenes (2001) *J. Pet.* **43**, 1049.