

SULFIDE UNDERSATURATED APOLLO 12 BASALTIC MAGMAS: IMPLICATIONS FOR CHALCOPHILE ELEMENT ABUNDANCE IN THE LUNAR MANTLE. D. J. Bombardieri¹, M. D. Norman^{1,2}, V.S. Kamenetsky¹, L.V. Danyushevsky¹ Centre for Ore Deposit Research, School of Earth Sciences, Univ. of Tasmania, Hobart 7001 Australia (danielb@utas.edu.au), ²Research School of Earth Sciences, The Australian National University, Canberra ACT 0200 Australia (Marc.Norman@anu.edu.au).

Introduction: No direct sample of the lunar mantle has yet been discovered, whether by Apollo astronauts or from recovered meteorites. Therefore, estimates of chalcophile element abundances (e.g., Cu, Ni, PGE) in the lunar mantle must be inferred indirectly from the compositions of erupted mare lavas. By definition, chalcophile elements have a strong affinity for sulfide phases, and the concentrations of these elements in primitive terrestrial basalts are largely controlled by the presence or absence of sulfides in the upper mantle during melting [1]. Despite the potential importance of mantle sulfides for understanding the chalcophile element composition of the Moon, few studies have considered the implications of sulfide saturation in mare basalt source regions [2].

In order to provide better constraints on sulfide saturation in low-Ti mare basalts, we conducted a study of experimentally heated, olivine-hosted melt inclusions (MI's) in Apollo 12 picritic lavas to determine the primary S contents for a suite of cogenetic olivine basalts. These data are used to predict whether Apollo 12 magmas experienced sulfide-saturation in their source region, and to assess the implications for chalcophile element abundances of the lunar mantle.

Melt Inclusions: MI's represent small pockets of melt trapped by growing crystals, and thus provide a "snap shot" of a particular evolutionary phase of a magma as sampled by the growing phenocryst. MI's therefore provide a powerful tool for obtaining direct information about major element, trace element, and volatile contents (e.g., S) of an evolving magma [3]. Experiments have shown that olivine (Fo₇₅) is the first silicate phase to crystallise from Apollo 12 parental magmas [4], and that the Apollo 12 olivine basalt suite can be related by olivine accumulation into a parental melt [5]. Therefore, MI's hosted in near-liquidus olivine should provide improved estimates for the initial S contents of low-TiO₂ magmas compared to whole rock compositions which may have been modified by outgassing during eruption.

Samples and Methods: Olivines containing crystalline MIs were separated from 6 whole rock samples of Apollo 12 olivine basalt (12009, 12075, 12020, 12018, 12040, 12035). Heating experiments were conducted on individual MIs using a high temperature heating stage with purified helium atmosphere and optical control. MI's were heated until all crystalline phases were melted followed by rapid quenching to produce homogenous glass suitable for electron microprobe analysis. S abundance was measured by EMP, integrating the entire S peak in 19 steps across the peak

with 25 sec count times per step. Absolute 2 σ uncertainties are estimated at ± 25 ppm S for the concentrations reported here.

Results: Quenched MI's contain a shrinkage bubble (B), glass (G), and sulfide (S) (Fig. 1). S and FeO* (total Fe as FeO) contents of MI's hosted in near-liquidus olivine (Fo₇₅) vary between 567 – 1053 ppm and 11.23-16.36 wt% respectively. Low FeO contents in the glasses compared to whole rock compositions (21 wt % FeO) are attributed to diffusive loss of Fe from the inclusion to the host olivine during cooling [5]. As FeO is the principal compositional control on sulfur solubility, Fe-loss results in the precipitation of sulfides within the MI, either during primary cooling or during the heating experiments. MI compositions were corrected for Fe-loss [6], and initial S contents were estimated by mass balance from the measured composition of the glass plus sulfide globules. Estimated primary S contents range from 850 – 1100 ppm, compared to whole rock values of 750-890 ppm for Apollo 12 olivine basalts [7]. The range of S contents observed in the MI's and the generally lower S contents of the whole rocks vs. MI's may reflect variable degassing of S from the magma during eruption.

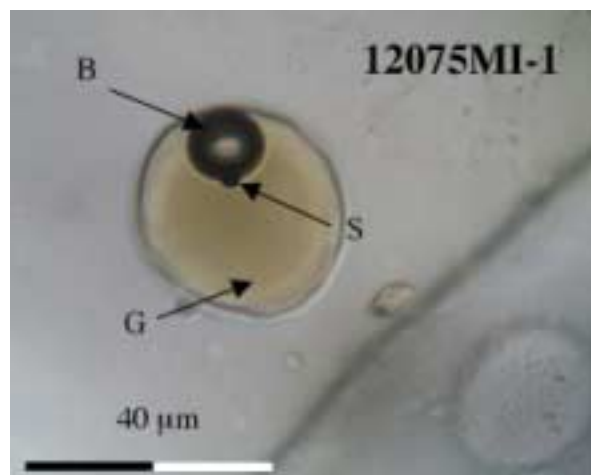


Figure 1.

Sulfide capacity of Apollo 12 magmas: The correlation between FeO and S content measured in the Apollo 12 MI's define a sulfide-saturation trend (Fig. 2). Sulfide saturation in low-Ti mare basalts appears to occur at lower S contents for a given FeO (between 11 and 16 wt%) compared with terrestrial basalts [8]. Extrapolation of the saturation trend to higher FeO con-

Primary S Contents of APOLLO 12 Olivine Basalts: D. J. Bombardieri, M. D. Norman, V.S Kamenetsky, L.V. Danyushevsky

tents (16 to 21 wt% FeO) would suggest that Apollo 12 low-Ti basaltic magmas with 21 wt % FeO require ≥ 1800 ppm S to achieve sulfide saturation, in agreement with previous experiments [8]. Therefore, Apollo 12 basaltic magmas with primary S contents ~ 1100 ppm would have been undersaturated in sulfide on eruption. The experimentally defined sulfide saturation trend suggests that the Apollo 12 lavas became saturated with sulfide near their solidus (e.g. 1200 ppm S, 17 wt % FeO) (Fig 2), consistent with the occurrence of troilite in the groundmass of these lavas.

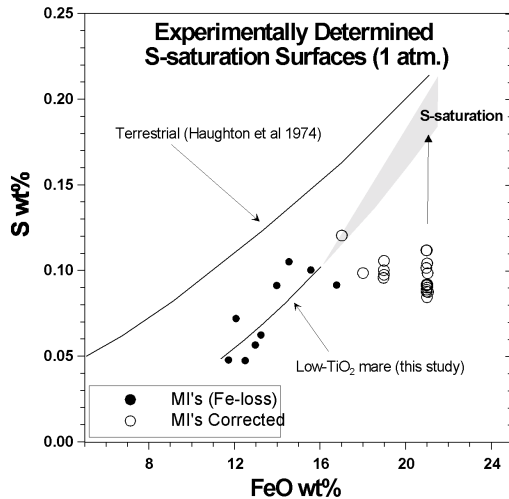


Figure 2.

Sulfide saturation in the lunar mantle: Sulfur solubility is a function of temperature, melt composition, oxygen and sulfur fugacities at low pressure [8]. However the effect of pressure on sulfur solubility is poorly understood. For example, some studies show that the solubility of sulfur in a silicate melt increases with decreasing pressure [10,11], so that a melt becomes further removed from sulfide saturation as it migrates toward the surface. Other investigations have found the opposite effect [12], or suggest that decreasing temperature during magma ascent will negate the effects of pressure on sulfur solubility [13]. Taking into account the low lunar pressure gradient, we conclude that the effect of pressure on sulfur solubility in the Apollo 12 olivine basalts will be minimal, and that these magmas would have required ≥ 1800 ppm to achieve sulfide saturation in their source regions.

Implications for chalcophile elements in mare basalts: Low concentrations of chalcophile elements in MORBs and Hawaiian basalts are attributed to the retention of sulfide in their mantle source regions [1, 14]. Evidence that some MORBs remained sulfide-saturated on eruption is shown by the presence of sulfide globules in pillow rim glasses. Low to moderate degrees of melting in the terrestrial mantle (5 to 20%) produces sulfide-saturated melts that are depleted in chalcophile and siderophile elements due to partition-

ing of these elements into residual mantle sulfide. If the degree of melting is sufficiently large ($>20\%$), sulfide will be exhausted from the source, the silicate melt will be sulfide-undersaturated, and the ascending magma should contain the mantle abundance of chalcophile elements [9].

Our results suggest that the Apollo 12 low-Ti mare basalts were sulfide-undersaturated in their source regions, so that no residual sulfide phase remained in the mantle during melting. In this case the chalcophile element composition of these magmas reflect their abundance in the lunar mantle without modification by partitioning into residual sulfides.

Conclusions: Primary S contents of Apollo 12 magmas are inferred to be ~ 1100 ppm based on the compositions of experimentally heated silicate melt inclusions hosted by olivine phenocrysts. Assuming no pressure effect on sulfur solubility, a minimum of 1800 ppm S would be necessary to achieve sulfide saturation in these magmas during melting. Even if the sulfur capacity of these magmas is reduced by 500 ppm due to a pressure effect, it is still unlikely these melts would have left residual sulfide in their mantle source.

Petrographic evidence for vitrophyre 12009, which best represents the primary magma composition for the Apollo 12 olivine basalt suite, indicates that this lava was not saturated with sulfide on eruption based on the absence of sulfide globules in both the matrix glass and in early-formed olivine phenocrysts ($F_{0.75}$). We conclude that the Apollo 12 olivine basalt magmas did not equilibrate with residual sulfide in their mantle source regions, and they remained undersaturated as they migrated rapidly toward the lunar surface. If this is true, the Apollo 12 olivine basalts may have carried most of the mantle budget of these elements, transferring them to the lunar surface. The low abundances of chalcophile elements in low-Ti mare basalts must be a primary feature of the lunar mantle and not the result of sulfide saturation during melting.

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