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FELLOWSHIP FINAL REPORT

Tracing sulfur isotopes during iron sulfide melt formation in Lunar basalts

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REPORT INFO

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ABSTRACT

The Moon is a cornerstone for understanding the early history (origin, budget and timing) of volatile elements (H, C, F, S, Cl) delivered to all terrestrial planets. The volatile study of lunar magmatism is the most direct way to reconstruct the volatile budget of the Moon's interior. However, this reconstruction is compromised by magmatic processes that modify the initial compositions of the lunar magmas. The final goal of our work is to determine how sulfide saturation and segregation in all the compositional range of lunar lavas have affected the sulfur isotopic composition of the magmas. The determined sulfur isotopic fractionation between lunar silicate melts and immiscible sulfide blebs will allow us to directly unravel the sulfur isotopic composition of the heterogeneous reservoirs forming the Moon's interior, and therefore, provide fundamental information on the early evolution of sulfur isotopes of the Earth's satellite.

1- Introduction

Establishing the origin of volatile elements, and how and when the budgets of these elements were set in planetary bodies during the earliest stages of Solar System evolution has important implications for understanding the genesis and evolution of the terrestrial planets. Therefore, unraveling this history is a fundamental step to elucidate the mechanisms of planetary formation and differentiation.

The Moon, in contrast to Earth, provides a frozen record of the first few hundred million years of Solar System evolution, becoming a cornerstone for understanding the early history (origin, budget and timing) of volatile elements (H, C, F, S, Cl) delivery to all terrestrial planets. Among these volatile elements, the sulfur contents and isotopes of lunar samples are a powerful geochemical tool to provide information on the conditions of the Moon formation, differentiation and evolution (see Wing and Farquhar, 2015; Saal and Hauri, 2021 and reference therein).

The sulfur isotopic composition of the Moon's interior is most directly reconstructed from the record preserved in the lunar magmatism. However, this reconstruction is compromised by magmatic processes that modify the initial compositions of the magmas, such as magma degassing, as well as sulfide saturation and segregation during melting, melt transport and eruption. Only after those processes have been accounted for by detailed petrological experiments and geochemical studies, the sulfur isotopes of the source regions of the lunar basalts can be inferred, providing key information on the origin and early evolution of the Moon.

Motivated by the work of Brenan et al. (2019), who demonstrated for first time the saturation of sulfides with variable Fe/S ratios in low-titanium Lunar magmas, we decided to extend

the sulfide saturation experiments considering all the compositional range of Lunar magmas. Lunar basalts define a significant compositional range from high-Ti, to low-Ti to very low-Ti magmas pointing to the early evolution of the Moon and the generation of the heterogeneous reservoirs responsible for the compositionally diverse lunar volcanism. We are performing experiments of sulfide saturation in silicate melts at conditions relevant to the Lunar basalts. The resulting immiscible sulfide and silicate glass phases from the experiments are being analyze for sulfur isotopes to determine the sulfur isotopes fractionation. This is a fundamental piece of information that will allow us to understand the evolution of sulfur isotopes in lunar magmas from their generation until eruption. These results will provide the primitive sulfur isotopes of the heterogeneous reservoirs responsible for the Lunar magmatism.

2- Experimental and Analytical details

Starting material. The silicate melts used in the sulfur solubility and isotope fractionation experiments were modelled after the lunar mare basalt 12009 (low Ti) and lunar volcanic glasses 74220 (high Ti) and 15426/7 (very low Ti) considered to be primitive melt composition.

The synthesis involved the initial calcining of a powdered, high purity oxide mix, then fusion at 1,470 °C for 60 min in a Fe crucible in a gas-mixing furnace at an fO_2 approximate to the IW buffer. The glass was then grounded under ethanol to limit the introduction of ferric iron into the subsequent experiments.

The sulfide melt used in the solubility experiments was of FeS stoichiometry, synthesized from high-purity sulfur and iron, encapsulated in a vacuum-sealed silica ampoule and sintered at 600 °C for 9 h and then at 900 °C for 3 h, followed by cooling in air.

The sulfide starting materials were subsequently ground under ethanol, dried and stored in a desiccator. The starting materials contained excess Fe to ensure saturation in both the metal and sulfide melt phases.

Sulfur solubility experiments. The synthetic lunar basalt and stoichiometric FeS, in approximately equal proportions by weight, were encapsulated in Fe100 or an Fe–Ir alloy. The fO_2 of the experiment was calculated relative to the IW heterogeneous equilibrium according to equation (1).

$$\Delta IW = 2 (\log a^{FeO}_{silicate} - \log a^{Fe}_{metal}) \quad (1)$$

The activity of Fe in the metal phase was calculated using the thermodynamic data summarized in Woodland and O'Neill (1997). The activity of FeO in the silicate melt was calculated from the measured mole fraction of FeO (X_{FeO}) using the expression

$a^{FeO}_{silicate} = 1.7X_{FeO}$ (Holzheid, et al., 1997).

Variation in the metal composition, by the addition of Ir, serves to change the fO_2 of the experiment. Capsule compositions spanned the range from Fe100 to Fe96Ir4 (at%). Fe100 capsules were fabricated from a pure Fe rod. Fe96Ir4 capsules were synthesized by sintering pressed powders under reducing conditions. For a melt with ~ 20 wt% FeO, this range in capsule composition defines the fO_2 of ~IW–1. Experiments were done over the pressure of 0.1 MPa. Experiments were contained in fused silica ampoules, in which ~200 mg of a Fe–FeS buffer powder was loaded at the bottom, followed by a thin silica spacer, the Fe100 capsule and then a silica spacer. The loaded silica tube was then evacuated for at least 30 min and finally fused shut with an oxyacetylene torch. Samples were placed upright on the hearth plate of a glass-melting furnace and held at 1,400 °C for varying durations. Experiments were terminated by dropping the sample into a water–ice bath.

Consistent with equilibrium, the sulfur content of run-product glasses was homogeneous in terms of the relatively small standard deviation in electron microprobe analyses and lack of any systemic zonation within run products. Also, the sulfur content of the experiments was reproducible for experiments done at different range in time.

Analysis of run products. Run products were mounted in epoxy and polished with 240 grits SiC, followed by 600 grits SiC and then 1 µm diamond. The major element composition of the run-product phases was determined using the Cameca SX50 electron microprobe at the Institut des Sciences de la Terre d'Orléans. Silicate melt analyses were done using an accelerating voltage of 15 kV, a beam current of 10 nA and a 10–30 µm defocused beam to limit the glass damage. Sulfide analyses were done using a 20 kV accelerating voltage and a 30 nA beam, which was defocused for sulfide analyses. Count times were 10–20 s for most elements. For all the analyses, raw count rates were converted into concentrations using the ZAF data-reduction scheme.

Sulfur is extracted for isotopic analysis via wet chemistry at Institut de Physique du Globe de Paris following the technique reported in Labidi et al. (2012). Briefly, pieces of glassy basalts and sulfides were chosen, cleaned and crushed to a grain size < 63 microns separately. The samples were digested in 20 mL of 2.1 M $CrCl_2$ solution with 5 ml of 12 M HCl and 5 ml of 29 M HF (for glass) and 12 M HCl (for sulfide) in a Teflon vessel under continuous flushing of pure N_2. Reduced sulfur was extracted as H_2S, bubbled through a water trap and subsequently into a sulfide trap filled with $AgNO_3$ (0.3 M) where H_2S reacted to precipitate Ag_2S. Sulfate occurrence was not anticipated for the conditions of lunar basalts. Here, bulk sulfur concentrations are estimated with an electron microprobe, while reduced sulfur is quantified with the wet chemistry protocol (Labidi et al., 2012). Any sulfates potentially present in glasses remained in the digestion solution (Labidi et al., 2012). We infer the S^{2-}/S_{tot} ratios by mass balance, with a relative uncertainty of ~10%.

The sulfur isotope measurements were performed using a dual inlet MAT 253 gas-source mass spectrometer. Once $\delta^n S$ are determined (n = 33, 34, 36), $\Delta^{33}S$ and $\Delta^{36}S$ are calculated ($\Delta^{33}S = \delta^{33}S - 1000((\delta^{34}S/1000 + 1)^{0.515} - 1)$ and ($\Delta^{36}S = \delta^{36}S - 1000((\delta^{34}S/1000 + 1)^{1.90} - 1)$)). Aliquots of Canyon Diablo Troilite (CDT) analyzed relative to the IPGP reference gas give average $\Delta^{33}S$ and $\Delta^{36}S$ values of −0.024±0.004‰ and −0.13±0.04‰ (1σ, n=11). Repeated analyses of IAEA-S1 versus the IPGP in-house SF_6 tank give $\Delta^{33}S$ = +0.082±0.004‰, $\Delta^{36}S$ = −0.91±0.11‰ (all 1σ, n=43, S_{S1} is fixed at -0.30‰ and hereafter defines the V-CDT scale). All $\delta^{34}S$ are reported against V-CDT and all $\Delta^{33}S$ and $\Delta^{36}S$ values are anchored on the CDT scale. The silicate glass and immiscible sulfide separated from the experiments are being analyzed for S isotopes. We expect precision in $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ values of ~ 0.1, 0.012, and 0.1‰ respectively (1σ), similar to the uncertainty obtained on basalt standards (Labidi et al., 2012).

3- Results and discussion

The results for the first sulfur saturation experiments on low Ti lunar basalts were already published in Brenan et al. (2019). The authors presented clear evidence of equilibrium between silicate glasses and immiscible sulfide, reporting the major element compositions for both phases. Form those experiments we selected 12 experimental charges all at fO_2 ~IW-1. We are in the process of separating the silicate glass and immiscible sulfide phases for S isotopes wet chemistry analysis at Institut de Physique du Globe de Paris. In the meantime, we continue performing sulfide saturation experiments on high Ti and very low Ti lunar magma compositions. At this point we do not have results to present and discuss.

4- Conclusion

We do not have results yet for the sulfur isotope experimental study.

5- Perspectives of future collaborations with the host laboratory

Over the 3 months of residence as a fellow at LE STUDIUM Institute for Advanced Studies, Saal started a collaboration with faculty at ISTO. Prof. Koga is recruiting a MSc student to complete the necessary experiments. The expectation id for Saal to write an Advanced ERC Grants on the study of lunar volatiles in

magmatic systems, The deadline for the proposal submission is August 27, 2026.

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7- References

J. M. Brenan, J. E. Mungall, N. R. Bennett, Abundance of highly siderophile elements in lunar basalts controlled by iron sulfide melt. Nat. Geosci. 12, 701–706 (2019).

J. Labidi, P. Cartigny, J. L. Birck, N. Assayag, J. J. Bourrand, Determination of multiple sulfur isotopes in glasses: A reappraisal of the MORB δ34S. Chemical Geology 334, 189–198 (2012)

A. E. Saal and E. H. Hauri, Large sulfur isotope fractionation in lunar volcanic glasses reveals the magmatic differentiation and degassing of the Moon. Sci. Adv. 2021; 7: eabe4641 (2021)

B. A. Wing, J. Farquhar, Sulfur isotope homogeneity of lunar mare basalts. Geochim. Cosmochim. Acta 170, 266–280 (2015).