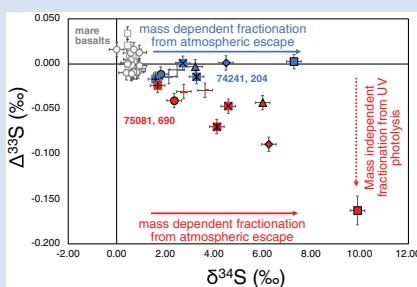# Isotopic evidence of sulfur photochemistry during lunar regolith formation

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Abstract

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Lunar gardening results in volatile mobilisation and stable isotopic fractionations that are mass dependent. An unambiguous role for mass independent fractionation (MIF), such as that produced by photochemistry, has not been demonstrated on the Moon. We observe MIF for sulfur isotopes in lunar soil 75081, 690 while MIF is not observed in soil 74241, 204. The MIF is likely generated after sulfur is volatilised during soil maturation processes. The isotopic discrepancy between 75081, 690 and 74241, 204 may reflect differences in photochemistry, such as illumination or in generation of photochemically active volatile sulfur species, for instance, due to varying H contents from solar wind implantation.

Introduction

The earliest atmospheres on Earth and Mars were optically thin and contained sufficient sulfur-bearing gaseous molecules and penetration of ultraviolet (UV) light that generated mass independent fractionation of sulfur (MIF-S) isotopes (*e.g.*, Farquhar *et al.*, 2000; Franz *et al.*, 2014). These sulfur isotope records shed light on the geochemical conditions involving sulfur and other elements and provide key information about the evolution of these planets' fluid envelopes. The early evolution of the Moon (3.8–3.1 Ga) included pyroclastic and effusive volcanism, and large impact events that provided enough gas to produce optically thin transient atmospheres (*e.g.*, Prem *et al.*, 2015; Needham and Kring, 2017) where UV light can penetrate and produce MIF-S. To date, no unambiguous evidence of this process has been found on the Moon.

We present new analyses of the quadruple sulfur isotope compositions and sulfur concentrations for 9 and 10 size fractions (<10 to >500 μm and >1000 μm) from lunar basaltic regolith samples 74241, 204 (immature, I_s/FeO = 5.1) and 75081, 690 (sub-mature, I_s/FeO = 40) (Morris, 1978) (Table S-1). These analyses provide insight into the late stage lunar volatile cycle during surface gardening and the evolution of sulfur isotope compositions of soils of varying maturity.

Methods

74241, 204 and 75081, 690 were sieved into 9 and 10 grain size fractions, respectively. Sulfur from each sieve fraction was extracted using an HF + $CrCl_2$ digestion method and analysed as SF_6 using a ThermoFinnigan MAT253 Dual Inlet isotope ratio mass spectrometer (see Supplementary Information S-1 for details). Isotopic data are reported in per mil using the following notation:

$$\delta^{34}S = [((^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{reference}) - 1]$$

$$\Delta^{33}S = [((^{33}S/^{32}S)_{sample}/(^{33}S/^{32}S)_{reference}) \\ - (^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{reference})^{0.515}]$$

$$\Delta^{36}S = [((^{36}S/^{32}S)_{sample}/(^{36}S/^{32}S)_{reference}) \\ - (^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{reference})^{1.9}]$$

Uncertainties on $\delta^{34}S$ and $\Delta^{36}S$ (±0.3 ‰) reflect the long term uncertainty on repeated measurements of reference material IAEA-S1. Uncertainty on $\Delta^{33}S$ reflects mass spectrometry uncertainty associated with counts on ^{33}S and is similar to our long term uncertainty estimates (±0.016 ‰ and ±0.008 ‰, for short and long counting sessions, respectively; see Supplementary Information S-1).

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Results and Discussion

We observe non-zero $\Delta^{33}S$ and $\Delta^{36}S$ values in 75081, 690 (Fig. 1). The same non-zero variability is not observed in 74241, 204. The dichotomy in $\Delta^{33}S$ and $\Delta^{36}S$ among 74241, 204 and 75081, 690 is unclear, but indicates that there are processes operating on only some locations of the lunar surface.

75081, 690 preserves a MIF-S signature. Mass independent isotope effects most commonly arise in gas phase reactions in the presence of UV light because the lifetimes of excited state molecules allow for other isotopically selective factors to come into play (Okabe, 1978) and thus, could have occurred in the lunar atmosphere throughout its evolution. Global and local transient lunar atmospheres may have been produced early (prior to 3.0 Ga) in lunar history through volcanic eruptions and large impact events (Needham and Kring, 2017; Aleinov *et al.*, 2019; Head *et al.*, 2020). Due to the thin nature of these atmospheres that allows ultraviolet light to penetrate, one can hypothesise that MIF-S could occur in these environments and impact the sulfur isotope composition observed in the lunar soils. For large scale transient atmospheres produced by volcanism and impact events, one would expect MIF-S signatures to be ubiquitous among lunar surface

materials; however, unambiguous evidence for photochemically derived MIF-S ($\Delta^{33}S \neq 0$) has not been observed in any other lunar materials (Thode and Rees, 1979; Wing and Farquhar, 2015). Furthermore, lunar soil production poses a problem for capturing MIF-S from large scale photochemical events: the isotopic composition should homogenise overtime as gardening occurs (*i.e.* micrometeorite bombardment and solar wind sputtering). Although both samples share the positive $\delta^{34}S$ signature associated with sulfur loss during gardening (Thode and Rees, 1976) (Fig. 1), the MIF signature in 75081, 690 overprints the gardening signature and requires MIF-S to have occurred after or during lunar gardening.

75081, 690 shows a relationship between $\delta^{34}S$ and $\Delta^{33}S$ that links the negative $\Delta^{33}S$ sulfur to the condensed outer layer material (*e.g.*, Keller and McKay, 1997, and references within). Effects related to surface/volume ratios result in the strongest negative $\Delta^{33}S$ signal seen in the smallest grain size (Fig. 1). Therefore, our observed isotopic signatures are a mixture between the condensed sulfur layer and the indigenous sulfur of the soil grain.

Production of the strongly negative $\Delta^{33}S$ of the outer layer sulfur associated with 75081, 690 requires a process that does not
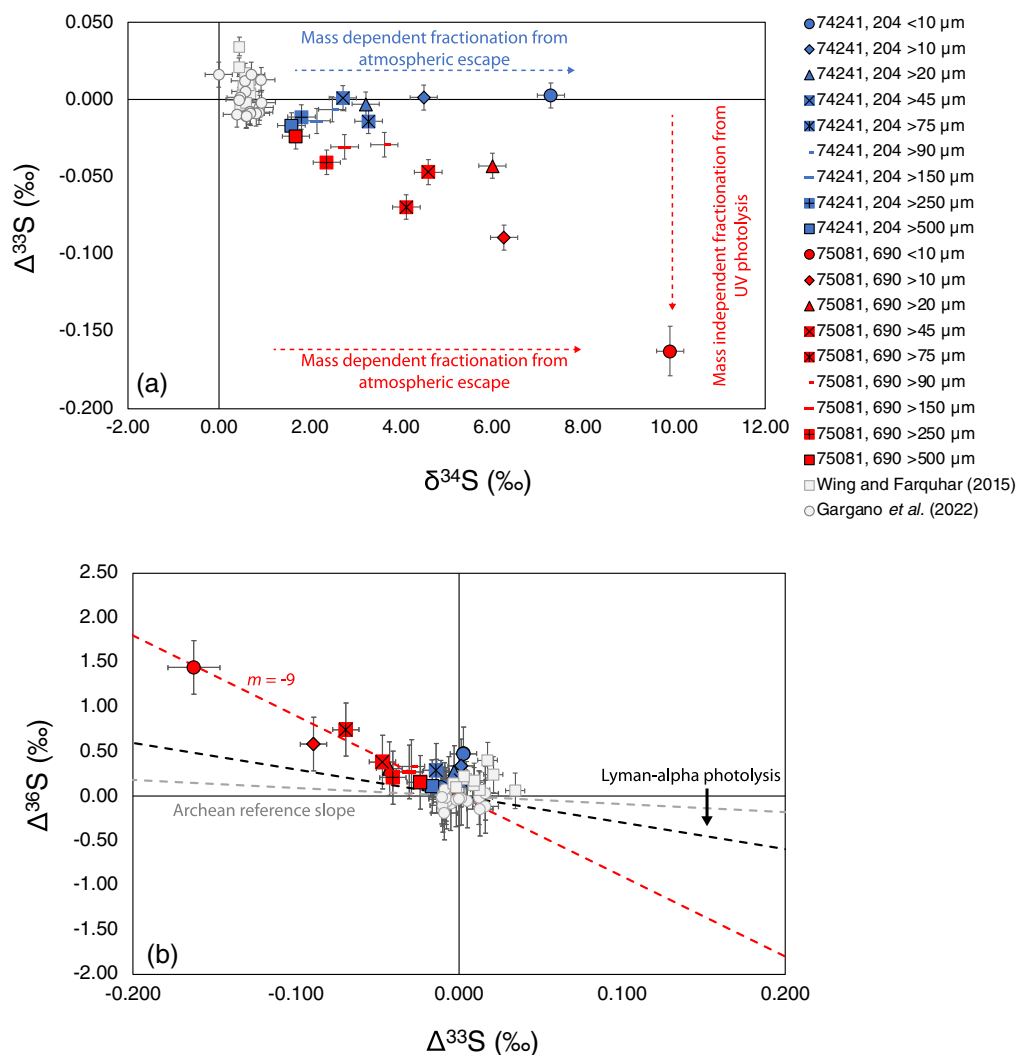
Figure 1 (a) $\Delta^{33}S$ *vs.* $\delta^{34}S$ and (b) $\Delta^{36}S$ *vs.* $\Delta^{33}S$ of analysed lunar soils 75081, 690 (red) and 74241, 204 (blue) and literature data from lunar basalts (grey). In (b), we highlight that data from 75081, 690 indicates the photochemistry occurring is different from that in other planetary environments, such as early Earth (*e.g.*, Johnston, 2011; Archean reference slope, grey dashed line) and the early solar nebula (*e.g.*, Antonelli *et al.*, 2014; Lyman-alpha photolysis, black dashed line).
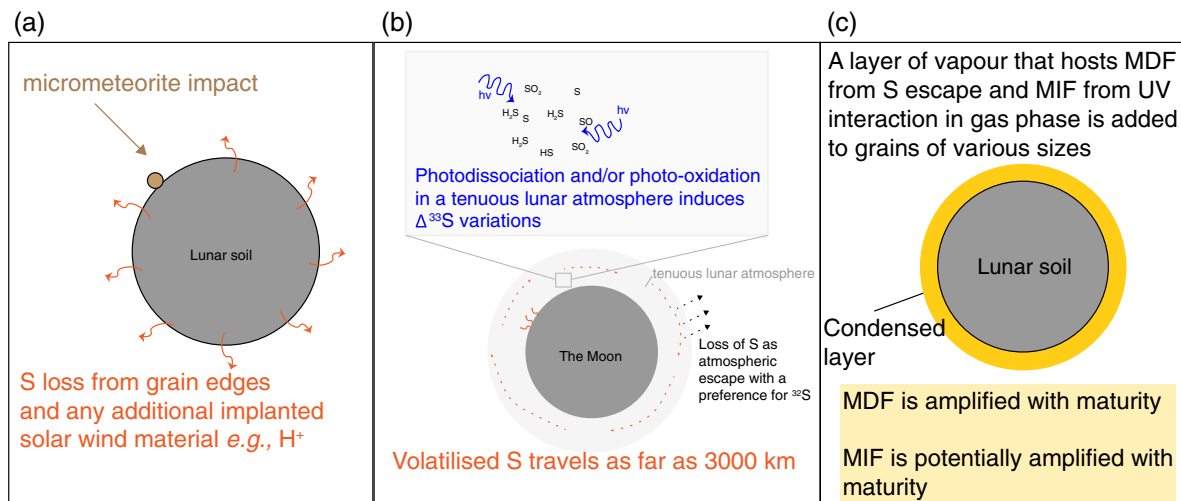
Figure 2 Hypothesis for the origin of sulfur isotope variations in lunar soils. **(a)** Micrometeorite impacts result in volatilisation and loss of sulfur at the edge of grains. **(b)** Vapourised sulfur is added to the tenuous lunar atmosphere and travels up to 3000 km before condensing. Here, gaseous sulfur molecules can escape, which induces mass dependent ^{34}S enrichments, and they can undergo photolytic reactions, resulting in mass independent fractionation (MIF) (seen in 75081, 690). **(c)** Vapour condenses on regolith soil with isotopic evidence of how sample was processed.

follow canonical mass dependence (*i.e.* mass independent). Thus, the associated process is separate from any process associated with sulfur loss during lunar volatilisation processes, which are thought to be strictly mass dependent and only produce variations in δ^{34}S measurements (*e.g.,* Thode and Rees, 1976). Evidence of such is seen in our analyses of 74241, 204 (immature) that preserve mass dependent (*i.e.* near-zero) Δ^{33}S and Δ^{36}S, but variable δ^{34}S, supporting a strict mass dependent isotope fractionation associated with sulfur loss.

While the exact origin of the variations in Δ^{33}S and Δ^{36}S values in 75081, 690 is not clear, it appears to be different from the shared ^{34}S enrichment with 74241, 204, and likely originates from photolytic reactions of S-bearing gaseous molecular species, such as S, SO, SO$_2$, H$_2$S, and HS. The components of the soils are ancient (Goswami and Lal, 1974), and based on ^{40}Ar/^{36}Ar trapped for 74241 (7.4) compared to 75081 (0.7), 74241 may have last been exposed to space weathering at 3.13 Ga compared to 0.25 Ga for 75081 (*e.g.,* Curran *et al.,* 2020) which suggests either MIF-S is not linked to processes occurring >3.0 Ga or length of exposure to space weathering is critical for MIF-S production. Although extra-lunar sulfur is thought to contribute to the total sulfur observed in soils (Kerridge *et al.,* 1975; Thode and Rees, 1979), our data are not consistent with acquisition of the MIF-S signature from these sources: the sulfur isotope compositions observed in the meteorite record (Antonelli *et al.,* 2014; Labidi *et al.,* 2017; Dottin *et al.,* 2018; Wu *et al.,* 2018, and references within) do not match our observations. We also exclude MIF-S acquisition from large scale transient atmospheres and sputtering due to the ubiquitous lack of MIF-S signatures among lunar materials: spallation yields are low and require Fe and low sulfur contents of a metal phase to observe evidence for spallation reactions (Gao and Thiemens, 1991). Thus, we suggest the most parsimonious explanation for acquisition of MIF-S in 75081, 690 is linked to gardening events that volatilise sulfur that undergoes UV photochemistry while in the lunar atmosphere (Fig. 2).

Assuming the MIF-S observed in 75081, 690 is indeed linked to gardening events, the dichotomy in Δ^{33}S and Δ^{36}S between 75081, 690 and 74241, 204 may reflect (1) differences in the nature of the target relative to sample maturity (also related to timing of exposure at the lunar surface), and/or

(2) the processing of volatilised sulfur species in regions with or without sunlight. Mature targets that have more implanted hydrogen from solar wind may have a greater chance for formation of H-bearing gaseous sulfur species that promote photochemical MIF-S. The production of H-bearing gaseous sulfur species would require a more local, rather than regional or global, process to generate the variation observed between sites, and the MIF-S likely represents an accumulated fractionation from consistent gardening events. This process would be widespread, and in future measurements of lunar soils, the MIF-S signature should be observed. Literature analyses by Thode and Rees (1979) of size fractions from sample 15021 may also show non-zero Δ^{33}S (Fig. S-6) and be broadly consistent with our results. However, the data have been held up as an example of mass dependent isotope effects due to analytical uncertainty. Processing environment of the soils is important to consider because MIF-S *via* photochemistry requires sunlight. The difference in Δ^{33}S and Δ^{36}S between 75081, 690 and 74241, 204 may reflect processing in sunlit and shadowed parts of the Moon, but such a scenario is difficult to reconcile considering both of our studied sites are on the near side of the Moon and likely share a similar history of illumination.

Missing sulfur reservoir. Δ^{33}S in 75081, 690 is consistently negative and presents an issue of mass balance (*i.e.* a reservoir of sulfur with positive Δ^{33}S is missing). The sulfur with positive Δ^{33}S may have been lost to space, trapped in Permanently Shadowed Regions (PSRs) (Watson *et al.,* 1961), or trapped in micro cold traps of a nearby crater (Hayne *et al.,* 2021). As volatile deposits are identified and explored in the upcoming Artemis missions, Δ^{33}S measurements of returned samples can be potentially used (1) to better understand the volatile cycle on the Moon and the transport of volatiles across the lunar surface, and (2) as a fingerprint for identifying evolving PSRs, such as through measurements of Δ^{33}S from a core collected from a PSR.

Links among δ^{34}S, sulfur concentration, and grain size. Successfully linking the observed MIF-S signature to UV photolysis of volatiles during lunar gardening events is contingent upon a model that can also explain the observed δ^{34}S and sulfur concentrations of various grain size fractions from 74241, 204 and 75081, 690.

The $\delta^{34}S$ values and sulfur concentrations of various grain size fractions could be explained by a grain margin subject to diffusive sulfur loss from the inner grain prior to addition of a condensed layer (Fig. S-7) (Saal *et al.,* 2008). The diffusion model would, however, require diffusion times and/or temperatures that are too long/high to fit the standard understanding of micrometeorite gardening (see Supplementary Information S-2). The data can also be explained with a model involving a degassed melted layer with no isotope fractionation that sits between a homogenous inner grain and an outer isotopically fractionated condensed layer (see Supplementary Information S-2). This model satisfies our observations while relaxing the time/temperature constraints. While various explanations have been proposed to explain the ^{34}S enrichment of the condensed outer layer sulfur (*e.g.,* Clayton *et al.,* 1974; Ding *et al.,* 1983; Kerridge and Kaplan, 1978), given the observed MIF-S in 75081, 690, the most parsimonious explanation is linked to condensed sulfur fractionated by atmospheric escape (*e.g.,* Clayton *et al.,* 1974; Switkowski *et al.,* 1977; see Supplementary Information S-2).

Conclusions

We present isotopic evidence that mass independently fractionated sulfur condensed onto lunar soil grains associated with 75081, 690. As illustrated in Figure 2, we hypothesise that sulfur from both soils underwent atmospheric escape to space, producing ^{34}S enrichments. Although 75081, 690 and 74241, 204 share ^{34}S enrichments, the same mass independent signal is not observed in 74241, 204. We suggest that sulfur with MIF that later condensed on 75081, 690 was produced during UV photochemistry in the tenuous lunar atmosphere after sulfur without MIF was volatilised during gardening events. The lack of MIF-S in 74241, 204 may be linked to (1) lower amounts of solar wind implanted hydrogen that can be readily available to form H-bearing sulfur species that undergo photochemistry, and/or (2) processing in a shaded environment.

Acknowledgments

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Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article2235.

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