Isotopic evidence of sulphur photochemistry during lunar regolith formation

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Abstract

Lunar gardening results in volatile mobilization and stable isotopic fractionations that are mass-dependent. A role for mass-independent fractionation (MIF), such as that produced by photochemistry, has not been demonstrated on the Moon. We observe MIF for sulphur isotopes in lunar soil 75081, 690 while MIF is not observed in soil 74241, 204. The MIF is likely generated after sulphur is volatilized 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 sulphur 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 sulphur bearing gaseous molecules and penetration of ultra-violet (UV) light that generated mass-independent fractionation of sulphur (MIF-S) isotopes (e.g., Farquhar et al., 2000; Franz et al., 2014). These sulphur isotope records shed light on the geochemical conditions involving sulphur 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., Needham & Kring, 2017; Prem et al., 2015) 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 sulphur isotope compositions and sulphur 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 S1). These analyses provide insight into the late-stage lunar volatile cycle during surface gardening and the evolution of sulphur isotope compositions of soils of varying maturity.

Methods

74241, 204 and 75081, 690 were sieved into 9 and 10 grain size fractions, respectively. Sulphur from each sieve fraction was extracted using an HF + $CrCl_2$ digestion method and analyzed as SF_6 using a ThermoFinnigan MAT253 Dual inlet isotope ratio mass spectrometer (see text S1 for details). Isotopic data are reported 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 text S1).

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.

MIF-S in 75081, 690

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 (Aleinov et al., 2019; Head et al., 2020; Needham & Kring, 2017). Due to the thin nature of these atmospheres that allows ultraviolet light to penetrate, one can hypothesize that MIF-S could occur in these environments and impact the sulphur isotope composition observed in the lunar soils. For large-scale transient atmospheres produced by volcanism and impact events, one would expect MIF-S to be ubiquitous among lunar surface materials; however, unambiguous evidence for photochemically derived MIF-S ($\Delta^{33} \neq 0$) has not been observed in any other lunar materials (Thode & Rees, 1979; Wing & Farquhar, 2015). Furthermore, lunar soil production poses a

problem for capturing MIF-S from large scale photochemical events: the isotopic composition should homogenize overtime as gardening occurs (i.e., micrometeorite bombardment and solar wind sputtering). Although both samples share the positive $\delta^{34}S$ signature associated with sulphur loss during gardening (Thode & 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 $\Delta^{33}S$ sulphur to the condensed outer layer material (e.g., Keller & 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 sulphur layer and the indigenous sulphur of the soil grain.

Production of the strongly negative $\Delta^{33}S$ of the outer layer sulphur associated with 75081, 690 requires a process that does not follow canonical mass dependence (i.e., mass-independent). Thus, the associated process is separate from any process associated with sulphur loss during lunar volatilization processes, which are thought to be strictly mass-dependent and only produce variations in $\delta^{34}S$ measurements (e.g., Thode & Rees, 1976). Evidence of such is seen in our analyses of 74241, 240 (immature) that preserves mass-dependent (i.e., near-zero) $\Delta^{33}S$ and $\Delta^{36}S$, but variable $\delta^{34}S$, supporting a strict mass dependent isotope fractionation associated with sulphur loss.

While the exact origin of the variations in $\Delta^{33}S$ and $\Delta^{36}S$ 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_2S, and HS. The components of the soils are ancient (Goswami & 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 sulphur is thought to contribute to the total sulphur observed in soils (Kerridge et al., 1975; Thode & Rees, 1979), our data are not consistent with acquisition of the MIF-S from these sources: the sulphur isotope compositions observed in the meteorite record (Antonelli et al., 2014; Dottin et al., 2018; Labidi et al., 2017; 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 among lunar materials: spallation yields are low and require Fe and low sulphur contents of a metal phase to observe evidence for spallation reactions (Gao & Thiemens, 1991). Thus, we suggest the most parsimonious explanation for acquisition of MIF-S in 75081, is linked to gardening events that volatilizes sulphur that undergoes UV-photochemistry while in the lunar atmosphere (Figure 2).

Assuming the MIF-S observed in 75081, 690 is indeed linked to gardening events, the dichotomy in $\Delta^{33}S$ and $\Delta^{36}S$ between 75081 and 74241 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 volatilized sulphur 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 sulphur species that promote photochemical MIF-S. The production of H-bearing gaseous sulphur 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 & Rees (1979) of size fractions from sample 15021 may also show nonzero $\Delta^{33}S$ (Fig. S6)

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 $\Delta^{33}S$ and $\Delta^{36}S$ between 75081 and 74241 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 sulphur reservoir

$\Delta^{33}S$ in 75081, 690 is consistently negative and presents an issue of mass balance (i.e., a reservoir of sulphur with positive $\Delta^{33}S$). The sulphur with positive $\Delta^{33}S$ 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, $\Delta^{33}S$ 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 $\Delta^{33}S$ from a core collected from a PSR.

Links among $\delta^{34}S$, sulphur concentration, and grain size

Successfully linking the observed MIF-S to UV photolysis of volatiles during lunar gardening events is contingent upon a model that can also explain the observed $\delta^{34}S$ and sulphur concentrations of various grains size fractions from 74241, 204 and 75081, 690.

The $\delta^{34}S$ and sulphur concentrations of various grains size fractions could be explained by a grain margin subject to diffusive sulphur 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 text 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 text 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 sulphur (e.g., Clayton et al., 1974; Ding et al., 1983; Kerridge & Kaplan, 1978), given the observed MIF-S in 75081, 690, the most parsimonious explanation is linked to condensed sulphur fractionated by atmospheric escape (e.g., Clayton et al., 1974; Switkowski et al., 1977, see text S-2)).

Conclusion

We present isotopic evidence that mass-independently fractionated sulphur condensed onto lunar soil grains associated with 75081, 690. As illustrated in figure 2, we hypothesize that sulphur from both soils underwent atmospheric escape to space, producing ^{34}S enrichments. Although 75081, 690 and 74241, 240 share ^{34}S enrichments, the same mass-independent signal is not observed in 74241, 240. We suggest that sulphur with MIF, later condensed on 75081, 690, was produced during UV photochemistry in the tenuous lunar atmosphere after sulphur without MIF was volatilized during gardening events. The lack of MIF-S in 74241, 240 may be linked to (1) lower amounts of solar wind implanted hydrogen that can be readily available to form H-bearing sulphur species that undergo photochemistry and/or (2), processing in a shaded environment.

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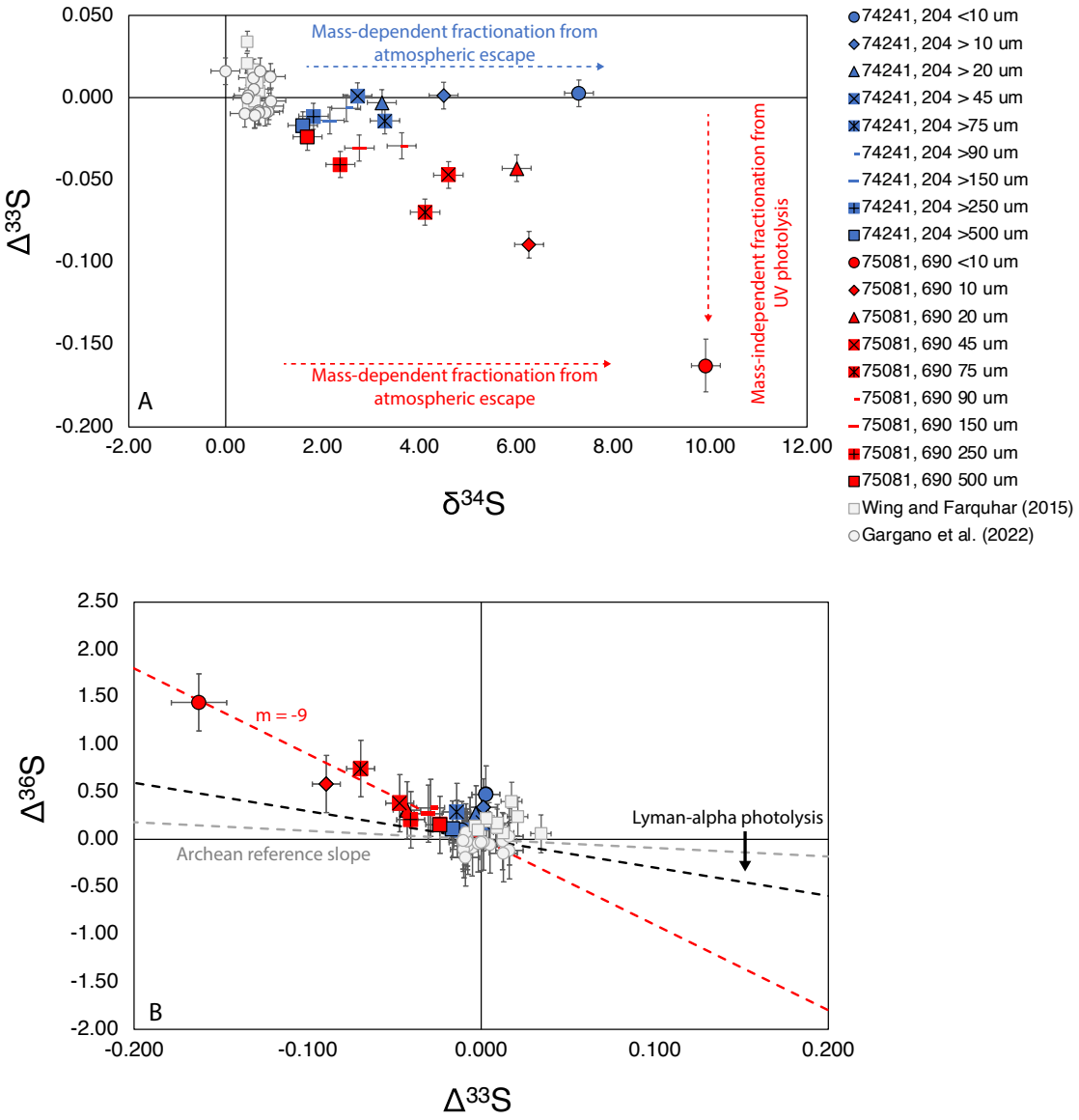

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165 **Figure 1. $\Delta^{33}S$ vs. $\delta^{34}S$ (A) and $\Delta^{36}S$ vs. $\Delta^{33}S$ (B) of analyzed lunar soils 75081 (red) and 74241**
166 **(blue) and literature data on from lunar basalts (grey).** In panel B, we highlight that data from
167 75081, 690 indicates the photochemistry occurring is different from that in other planetary
168 environments, such as early-Earth (e.g., Johnston, 2011) - Archean reference slope, grey dotted
169 line) and the early-solar nebula (e.g., Antonelli et al., 2014) -Lyman-alpha photolysis, black dotted
170 line).

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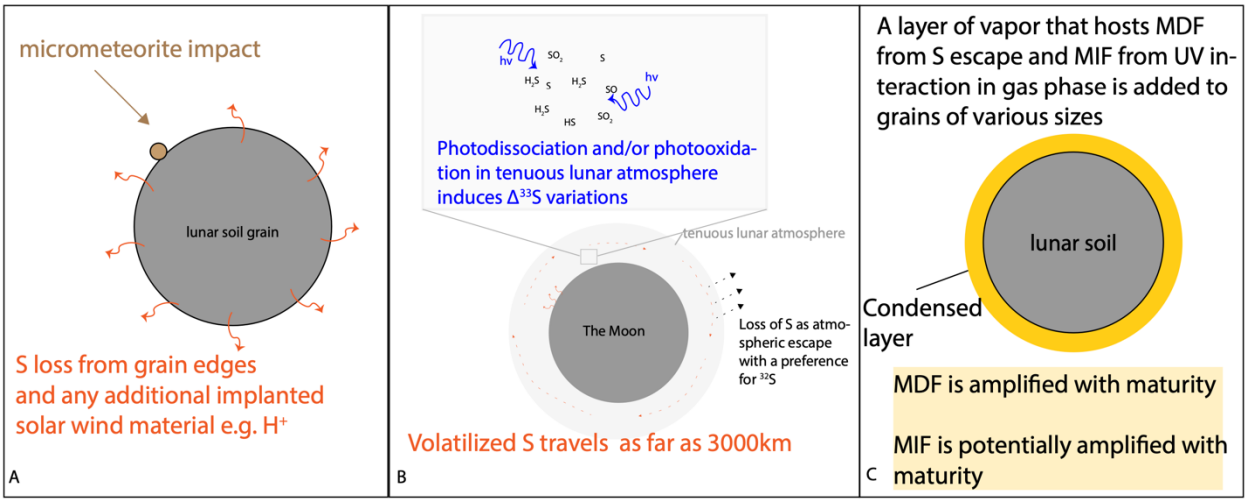

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173 **Figure 2. Hypothesis for the origin of sulphur isotope variations in lunar soils.** (A)
174 Micrometeorite impacts result in volatilization and loss of sulphur at the edge of grains. (B)
175 Vaporized sulphur is added to the tenuous lunar atmosphere and travels up to 3000 km before
176 condensing. Here, gaseous sulphur molecules can escape, which induces mass-dependent ^{34}S
177 enrichments, and they can undergo photolytic reactions, resulting in mass-independent
178 fractionation (MIF) (seen in 75081, 690). (C) Vapor condenses on regolith soil with isotopic
179 evidence of how sample was processed.

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