Anomalous ^{33}S in the lunar mantle

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Key Points:

- Orange glass 74002 preserves negative Δ^{33}S values.
- The negative Δ^{33}S associated with orange glass is linked to photochemically processed sulfur in the erupted source.
- Orange and black glass preserve different S isotope compositions that calls into question their genetic relationship.

Abstract

The origin, evolution, and cycling of volatiles on the Moon are established by processes such as the giant moon forming impact, degassing of the lunar magma ocean, degassing during surface eruptions, and lunar surface gardening events. These processes typically induce mass dependent stable isotope fractionations. Mass independent fractionation of stable isotopes has yet to be demonstrated during events that release large volumes of gas on the moon and establish transient lunar atmospheres. We present quadruple sulfur isotope compositions of orange and black glass beads from drive tube 74002/1. The sulfur isotope and concentration data collected on the orange and black glasses confirm a role for magmatic sulfur loss during eruption. The $\Delta^{33}S$ value of the orange glasses is homogenous ($\Delta^{33}S$ = -0.029 ± 0.004 ‰, 2SE) and different from the isotopic composition of lunar basalts ($\Delta^{33}S$ = 0.002 ± 0.004 ‰, 2SE). We link the negative $\Delta^{33}S$ composition of the orange glasses to an anomalous sulfur source in the lunar mantle. The nature of this anomalous sulfur source remains unknown and is either linked to (1) an impactor that delivered anomalous sulfur after late accretion, (2) sulfur that was photochemically processed early in lunar evolution and was transported to the lunar mantle or (3) a primitive sulfur component that survived mantle mixing. The examined black glass preserves a mass-dependent $\Delta^{33}S$ composition (-0.008 ± 0.006 ‰, 2SE). The orange and black glasses are considered genetically related but, the discrepancy in $\Delta^{33}S$ composition among the two samples calls into question their relationship.

Plain Language Summary

Using isotopic compositions measured in volatile elements, we can identify the processes linked to isotopic fractionations and ultimately understand processes involved in a planets' evolution. We present sulfur isotope compositions of lunar glass beads from drive tube 74002/1 and demonstrate that an anomalous sulfur source was erupted from the lunar mantle with the orange glass beads. The observed isotopic anomaly has an unknown origin, but it requires a source of sulfur that was photochemically processed prior to its deliver to the lunar mantle and eruption ~3.6 Ga. Our results suggest that the lunar mantle is not well mixed with respect to sulfur sources and requires future multi-disciplinary investigations to reconcile these important observations.

1 Introduction

The earliest atmospheres on Earth and Mars, received contributions of volatiles from volcanic outgassing, were optically thin, and dominated by ultra-violet (UV) photochemistry of gaseous sulfur bearing molecules that results in mass-independent fractionation of sulfur (MIF-S) (Dottin et al., 2018; Farquhar et al., 2000a, b; Franz et al., 2014). UV photochemistry was a critical component in the cycling of sulfur on these planets. On Earth, MIF was especially important in establishing sulfur budgets available for the preservation of life.

Lunar volcanism, consisting of both effusive and pyroclastic style eruptions, peaked at ~ 3.8 Ga and produced both local and global transient lunar atmospheres (Needham & Kring, 2017;

Saxena et al., 2017). On the Moon, sulfur was consistently contributed to the tenuous atmosphere through magma ocean outgassing and volcanic eruptions (Needham & Kring, 2017; Saxena et al., 2017). Whether or not the Moon shares a similar history with Earth and Mars of sulfur cycling through UV photochemistry in its early evolution remains unknown. Determining a role for UV photochemistry in early lunar atmospheres can shed light on the processes responsible for the distribution of volatiles throughout lunar reservoirs and the establishment of their respective volatile budgets.

To date, quadruple S-isotope measurements on materials from the peak of volcanism on the moon only exist on lunar basalts and show no clear evidence of MIF-S. The sulfur isotope composition of lunar basalts $\delta^{34}S = 0.62 \pm 0.20$ ‰, $\Delta^{33}S = 0.002 \pm 0.010$ ‰, $\Delta^{36}S = 0.030 \pm 0.13$ ‰ (Gargano et al., 2022; Kaplan et al., 1970; Kaplan & Petrowski, 1971; Rees & Thode, 1972, 1974; Thode & Rees, 1971, 1972; Wing & Farquhar, 2015). These data have been used to argue the lunar (upper) mantle is well-mixed. However, the data exhibit more variability than what would be expected for a homogenous population given the analytical uncertainties, and suggests there may be previously unidentified processes involved in establishing the S-isotope composition of the lunar basalts. Other materials erupted during the same period, such as lunar glass beads, have not yet been analyzed for quadruple sulfur isotopes. Lunar volcanic glasses are thought to be products of pyroclastic eruptions on the Moon (Heiken et al., 1974) and they contain a surface coating rich in volatiles associated with condensed gas from the volcanic cloud (Weitz et al., 1999). Sulfur is a major component of these surface coatings (Weitz et al., 1999) and it is possible that the sulfur not only retains geochemical information associated with how it was processed while in the volcanic plume, but also provides direct evidence of UV photochemistry that occurred in the volcanic cloud prior to vapor condensation on the glass beads. Furthermore, sulfur also exists within the glass beads (dissolved into the glass and within melt inclusions) (Saal et al., 2008; Saal & Hauri, 2021) This sulfur is likely to retain geochemical information related to the composition of the melt, providing insight into potential sulfur heterogeneity among multiple mantle sources and sulfur behavior during eruption.

Here, we present sulfur isotope data on sieved fractions of lunar volcanic glass beads from drive tube 74002/1. Each sample was sieved into nine grain size fractions and each fraction was processed using the HF + $CrCl_2$ acid digestion technique (see methods for details) to efficiently digest the glassy materials. Using this technique, we were able to extract sulfur trapped within the interior of the glass beads and sulfur coated on the surface of the glass beads. This method is different from the HCl digestion technique that (Ding et al., 1983) used on samples from the same drive tube that likely only extracted sulfur from the grain surfaces. With our new sulfur isotope measurements, we aim to (1) determine any compositional differences between sulfur captured within the glass and condensed on the glass surface and (2) constrain the origin and evolution of sulfur in the lunar mantle.

2 Materials and Methods

2.1 Acid Digestion

Glass beads from drive tube 74002/1 (74002, 2221 and 74001, 2206) were picked for impurities and sieved into a variety of grain size fractions. Sample 74001, 2206 was sieved as two stacks (Stack A and B). Sample 74002, 2221 is from the horizon that is dominated by orange glass (> 90 %) from a depth of 11.000-11.500 cm. Sample 74001, 2206 is from a horizon that is dominated by black glass (90 %) from a depth of 37.500-38.000 cm. The reduced sulfur components (i.e., S^{2-} containing compounds) of 74002, 2221 and 74001, 2206-Stack B was extracted using the HF + $CrCl_2$ digestion method. Each sieved sample was placed into a Teflon reaction vessel with a stir bar and attached to a water trap and an $AgNO_3$ trap. This set-up was purged for 10-15 minutes prior to injection of 20 ml of an acidic Chromium (II) Chloride Solution, 10 ml of Hydrochloric Acid, and 10 ml of Hydrofluoric Acid. The sample + acid bath was then heated to ~70 °C and stirred while allowing N_2 to continuously flow through the set-up. Sulfur was released from the sample as H_2S and first carried through the water trap (to trap acid) and subsequently into the $AgNO_3$ trap, where sulfur was precipitated as Ag_2S. We allowed this reaction to run for ~2.5 to 3 hours.

Stack A underwent a sequential extraction of Acid Volatile Sulfur (AVS), Chromium Reducible Sulfur (CRS), and Thode extraction, to potentially identify and analyze multiple pools of sulfur. This technique was used to attempt extracting mono sulfides (AVS), polysulfides (CRS) and acid soluble sulfate (Thode) from the lunar glasses. We highlight that this extraction occurred in 2008 and there have been advances in the knowledge of sequential sulfur extractions that have led us to only include the results from the Acid Volatile Sulfur fraction. We interpret the results from the AVS fraction from this stack (Stack A) to best represent the reduced sulfur fraction extracted from the surface of the glass beads. To extract AVS, the sieved soil was placed into a glass boiling flask that was connected to a water trap and an $AgNO_3$ trap and purged with N_2 for ~15 minutes. After purging, 25 ml of 5N HCl that was separately purged with N_2, was injected into the boiling flask and was heated to ~ 70 °C. Sulfur was released as H_2S and trapped as Ag_2S in the $AgNO_3$ after passing through the water trap. This reaction was allowed to proceed for ~3.5 hours. For the sequential extraction, the $AgNO_3$ trap was replaced with a new trap and Thode solution was injected in the boiling flask and allowed to react for 3 hours at slightly hotter temperature (to bring the solution to a boil). After 3 hours, the $AgNO_3$ trap was, again, replaced with a new trap and CRS solution was injected into the boiling flask and allowed to react for three hours at a sub-boiling (~70 °C) temperature. Finally, residues were rinsed with Milli-Q water, centrifuged, and saved for later work. For samples that yielded measurable sulfur during the AVS step, we subjected the residues to the HF + $CrCl_2$ acid digestion technique and extracted additional sulfur in this step.

2.2 Mass Spectrometry

All samples, with the exception of 74001, 2206 20-45 µm Stack A, 74001, 2206 45-90 µm Stack A 74001, 2206 20-45µm Stack A Residue and 74001, 2206 45-90µm Stack A Residue are bracketed by analyses of standard gas of international standard IAEA-S1. Analyses of IAEA-S1 were performed at the beginning and end of analytical sessions for 74001, 2206 20-45 µm Stack A, 74001, 2206 45-90 µm Stack A 74001, 2206 20-45µm Stack A Residue and 74001, 2206 45-90µm Stack A. All data are first normalized to analyses of IAEA-S1 performed during the analytical sessions and subsequently to our accepted value of IAEA-S1 relative to Canyon Diablo Troilite measurements performed at UMD ($\delta^{34}S$ = -0.401 ‰, $\Delta^{33}S$ = 0.116 ‰, $\Delta^{36}S$ = -0.796 ‰ (Antonelli et al., 2014). Uncertainties on $\delta^{34}S$ and $\delta^{36}S$ of 0.3 ‰ reflect the long-term uncertainty on repeated measurements of IAEA-S1. Uncertainty on $\Delta^{33}S$ reflects mass spectrometry uncertainty associated with counts on ^{33}S. Samples analyzed 3 times as 8-26 second cycles on the reference and sample have been attributed an uncertainty (2σ) of ±0.016 and samples analyzed 9 times as 8-26 second cycles on the reference and sample have been attributed an uncertainty (2σ) of ±0.008 (Dottin III, et al., 2020). The sulfur isotope data are reported using the following notation:

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

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

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

3 Results

Sulfur isotope compositions and concentrations measured in 74002, 2221 and 74001, 2206 from eight sieved grain size fractions can be found in Table 1. In 74002, 2221, S concentrations range from 231 ppm to 596 ppm. $\delta^{34}S$ value ranges -1.15 to +0.80 ‰, $\Delta^{33}S$ ranges from to -0.036 to -0.014 ‰, and $\Delta^{36}S$ ranges from -0.15 to 1.10 ‰. AVS from 74001, 2206 Stack A exhibit S concentrations ranging from 183 to 26 ppm, $\delta^{34}S$= -3.11 and -2.64 ‰ for the 20-45 μm and 45-90 μm fraction respectively, $\Delta^{33}S$= 0.001 and 0.006 ‰ for the 20-45 μm and 45-90 μm fraction respectively, and $\Delta^{36}S$= -0.16 and -0.01 for the 20-45 μm and 45-90 μm fraction, respectively. Stack A residues yielded S concentrations ranging from 109 to 131 ppm, $\delta^{34}S$= -0.60 and -1.34 ‰, $\Delta^{33}S$= -0.015 and -0.011 ‰, and $\Delta^{36}S$= 0.66 and 0.37 ‰ for the 20-45 μm and 45-90 μm fraction respectively (Table 1). Sulfur from 74001, 2206 stack B was extracted from 6 sieve fractions ranging from 10-20 μm to 150-250 μm and S concentrations ranged from 244 to 100 ppm, respectively. We were able to reliably analyze S from fractions ranging from 10-20 μm to 75-95 μm and observe $\delta^{34}S$ = -2.11 to -1.71 ‰, $\Delta^{33}S$ = -0.019 to 0.003 ‰, and $\Delta^{36}S$ = 0.52 to 2.17 ‰.

4 Discussion

Previous work that determines the $\delta^{34}S$ values and sulfur concentrations of lunar glass beads has demonstrated that $\delta^{34}S$ values and sulfur concentrations associated with lunar glasses are variable and can be readily linked to processes of sulfur degassing during eruption (Ding et al., 1983; Saal & Hauri, 2021). Similarly, we also observed variable $\delta^{34}S$ values and sulfur concentrations that are associated with sulfur degassing (see supplementary information for detailed discussion). However, unlike previous studies, we have measured the minor stable isotopes of sulfur (^{33}S and ^{36}S) that allow for additional constraints on the nature and origin of sulfur erupted with the pyroclastic glass beads from 74002/1.

4.1 Negative Δ^{33}S measured in orange glass beads

Although there is variability in δ^{34}S values of glasses measured in the glass beads, the Δ^{33}S values among orange and black glasses are homogenous yet distinct from one another. The black glass beads preserve strictly mass dependent Δ^{33}S ($\Delta^{33}S = -0.008 \pm 0.006$ ‰, 2SE), whereas the orange glass beads preserve a mass-independent signature ($\Delta^{33}S = -0.029 \pm 0.004$ ‰, 2SE), that is different from the isotopic composition measured among mare basalts ($\Delta^{33}S = 0.002 \pm 0.004$ ‰, 2SE). Our observation of negative Δ^{33}S in the orange glass beads is unusual. In lunar environments, production of Δ^{33}S variability requires a process that is mass-independent. Mass-dependent processes that may alter the 0.515 power law and induce Δ^{33}S variability, such as S degassing likely did not produce the observed negative Δ^{33}S: the data from the orange glasses require a slope of 0.505 to fit the data, which is outside of the high-temperature limit of 0.513 to 0.516 (Cao & Liu, 2011) and lunar soils with condensed S that experienced fractionation due to atmospheric escape show no associated Δ^{33}S variability (Dottin III et al., 2022). We also exclude MIF-S acquisition from cosmic ray spallation for two reasons: (1) to observe a spallation reaction, this needs to occur in a metal phase with Fe and low S concentrations (Gao & Thiemens, 1991) and (2) the ^{40}Ar/^{36}Ar for these samples is between 4.7 and 10.8, with model ages between 2.6 and 3.6 Ga (Fagan et al., 2014), suggesting there was not much exposure at the surface (consistent with their "immature" classification (I_s/FeO of 0.2-2.5) (Morris, 1978). Thus, there are two possibilities for the observation of negative ^{33}S associated with the orange glass beads. The first possibility is that the negative Δ^{33}S may have been captured upon condensation of a photolytic component in the volcanic cloud. It is possible that this photochemistry occurred as Lyman-alpha photolysis, a process that has been linked to early solar nebula chemistry that results in small Δ^{33}S variation in differentiated meteoritic materials (Antonelli et al., 2014; Dottin et al., 2018; Rai et al., 2005; Wu et al., 2018). The second possibility is that we are observing mantle heterogeneity.

4.1.1 Evidence against a condensed photochemical component

Sulfur photochemistry is known to have occurred on early Earth and Mars through the interaction of Ultraviolet (UV) light with gaseous sulfur compounds from volcanic eruptions (Farquhar et al., 2000a, b) and is an analogue for the expected behavior of volatile elements on the Moon. Thus, when searching for evidence of sulfur photochemistry on the moon, it is most logical to investigate materials that have surface coatings condensed from the eruptive cloud, such as glass beads from 74002/1. To produce Δ^{33}S variability during photochemistry, UV light needs to be able to penetrate the gas from the eruptive cloud and ultimately interact with gaseous sulfur compounds. The hypothesis for the origin of 74002/1 glass beads is that they originated from a fire-fountain event(s), where the more degassed black glass erupted as a columnar jet and was recycled through the jet through multiple events (Heiken et al., 1974) and the orange glass quenched on the exterior of the broader portions of the eruptive cloud (Heiken et al., 1974; Weitz et al., 1999). When considering the distribution of the orange and black glass in the volcanic cloud, it is possible that the orange glass captured a photochemical component simply because it was at the edge of the plume and the black glass did not capture MIF-S because the UV rays could not penetrate deep enough to affect the isotopic compositions. However, for this to occur, the orange glass melt globules would need to experience in-gassing of photochemically processed sulfur prior to quenching. In sulfur concentration profiles of orange glass beads, the profiles strictly demonstrate sulfur loss and no evidence of sulfur in-gassing (Saal et al., 2008). Furthermore, our data do not support a condensed photochemical component associated with the glass bead coatings. Assuming that the sulfur isotope composition of sulfur within the glass was similar to lunar basalts and given surface/volume ratios of condensed vapor to grain sizes (i.e., condensed vapor component dominates as grain size decreases), we would expect to see a linear mixing relationship (extending from the composition of mare basalts to the smallest grain fraction from orange glass beads) between the largest and smallest sieve fractions of the orange glass beads if a photochemical component was added to the glass beads. This is not observed, and we instead observe a consistently negative $\Delta^{33}S$ value across all grain sizes which suggests a singular composition was erupted (Table 1 and Figure 1). Although MIF readily occurred on Earth and Mars (Dottin et al., 2018; Farquhar et al., 2000a, b; Franz et al., 2014), it does not seem to have occurred during the fire-fountain eruption(s) associated with the 74002/1 glass beads.

4.1.2 Establishing Lunar mantle heterogeneity

Considering any added anomalous component would result in a mixing relationship in isotopic space among the largest and the smallest grain sizes, our isotopic observations instead suggests that the $\Delta^{33}S$ value of S associated with the orange glasses is in equilibrium with sulfur within the glass and condensed on the exterior of the glass beads. Thus, any process that strictly affects grain exteriors, such as solar wind sputtering, can be ruled out as the cause of negative $\Delta^{33}S$. As a result, the observed negative $\Delta^{33}S$ value is best reconciled as a signature associated with atmospheric UV photochemistry and this requires the S to have been photochemically processed prior to its transport to the lunar mantle. There are three possible hypotheses to establish the source of negative $\Delta^{33}S$ in the lunar mantle that we admittedly cannot rule out at this time: (1) the sulfur with negative $\Delta^{33}S$ was delivered to the mantle by a large impactor with anomalous ^{33}S; (2)

anomalous sulfur, which was photochemically processed early in an early formed lunar atmosphere, was transported to the mantle; or (3) the $\Delta^{33}S$ signature is associated with a primitive sulfur component that survived late accretion and mantle mixing.

Hypothesis 1 – an impactor injected anomalous sulfur into the lunar mantle

It is conceivable that the exogenous S was delivered by a meteoritic component, such as a carbonaceous chondrite source. Carbonaceous chondrite delivery has been used to explain the water contents of the lunar mantle (Hauri et al., 2015) and could possibly explain the sulfur isotope compositions as sulfur was likely also delivered with the carbonaceous chondrite materials. With this mechanism, carbonaceous chondrite sulfur would be injected into the lunar mantle. Carbonaceous chondrites are often sulfur rich (Labidi et al. 2017) with bulk sulfur contents that can exceed > 21,000 ppm. Carbonaceous chondrites also often preserve negative $\Delta^{33}S$ values (e.g., LEW 85312 bulk $\Delta^{33}S$ of -0.058 ‰). Given the high S concentration of these materials, delivery of carbonaceous chondrite material to the lunar mantle post core formation and late accretion can readily overprint the isotopic composition of the lunar mantle, particularly if lunar mantle mixing and homogenization was not efficient.

Hypothesis 2-Sulfur processed in an early formed atmosphere and transferred to the mantle

The sulfur erupted with the orange glasses may have been photochemically processed early in lunar evolution (Saxena et al., 2017) and delivered to the lunar mantle by a process associated with early lunar mantle evolution (Zhong et al., 2000) and crust formation (Prissel & Gross, 2020). At this time, we are not able to identify a mechanism that could be responsible for the transport of sulfur from the lunar surface into the lunar mantle. Although on Earth plate tectonics is primarily responsible for the transfer of surface materials into the mantle, the Moon does not have plate tectonics. However, our data may indicate either a high Rayleigh number convection during the existence of a lunar magma ocean (Shearer et al., 2006) or long-wavelength (‘degree one’) convection during a later mantle overturn event (Zhong et al., 2000) may have transferred the sulfur from an early proto-lunar atmosphere to the surface through condensation, and lastly into the lunar mantle. Such a process may also explain some of the variability in the lunar basalt data.

Hypothesis 3 – The sulfur isotopes represent a primitive signature

Incorporation of an isotopically fractionated vapor component that was produced either during the early solar nebula (Antonelli et al., 2014) or from the moon forming impact (either through photochemistry of gas released during the impact or the introduction of anomalous S from the moon forming impactor), into a poorly mixed lunar mantle, could generate our observations in the orange glasses. Although there is isotopic similarity in sulfur isotopes among the bulk silicate Earth (Labidi et al., 2013) and lunar basalts (Gargano et al., 2022; Wing & Farquhar, 2015), these estimates may not represent primitive unaltered signatures from accretion of sulfur during Earth and Moon formation as the Earth and Moon’s primitive mantle have been altered. On Earth, processes, such as plate tectonics, differentiation, and late accretion have altered the original sulfur isotopic composition (Dottin III et al., 2021; Dottin III et al., 2020a, b; Labidi et al., 2013; Labidi & Cartigny, 2016; Labidi et al., 2022). Similarly, the Moon’s primitive mantle sulfur isotope composition was likely been altered by differentiation processes (Saal & Hauri, 2021) and late accretion. There are estimates that the Earth’s primordial mantle has a $\Delta^{33}S$ value of 0 ‰ (Dottin III et al., 2020a), but this is a composition that still may have been altered by late accretionary processes, and we still have no robust estimate of the sulfur isotope composition of Earth’s core, which would best represent the primitive sulfur isotope composition of the Earth prior to late accretion.

Considering we are observing an unusual Δ^{33}S value erupted from the lunar mantle, it is possible that this Δ^{33}S value is a representation of the primitive lunar mantle. Primitive anomalous Δ^{33}S within the Moon's (or Earth's) mantle is not completely unexpected given that there are early solar system materials from differentiated meteorites that preserve anomalous Δ^{33}S (Antonelli et al., 2014; Dottin et al., 2018; Rai et al., 2005; Wu et al., 2018). It is possible that the data can be reconciled as representing a poorly mixed lunar mantle composed of primitive and late accreted sulfur. Assuming the Earth and Moon are genetically related in their primitive starting materials (Dauphas et al., 2014; Herwartz et al., 2014), the anomalous ^{33}S for the Earth may still exist, but may have been sequestered to the earth's core during differentiation. What remains to be reconciled is the apparent homogeneity of other genetic tracers like oxygen isotopes (Hallis et al., 2010; Spicuzza et al., 2007; Wiechert et al., 2001; Young et al., 2016). Although oxygen is chemically similar to sulfur and some heterogeneity in Δ^{17}O values have been observed in lunar materials (Cano et al., 2020), similar isotope behavior is not shared between the oxygen and sulfur isotope compositions of lunar basalts (e.g., Gargano et al., 2022; Wing & Farquhar, 2015). From our S isotope data, it is possible that the isotopic composition of lunar glasses are windows into previously unrecognized heterogeneity associated with the building blocks of the Earth and Moon that should be assessed using other genetic tracers.

4.2 Are the orange and black glasses genetically linked?

The homogenous negative Δ^{33}S of the orange glass beads (Δ^{33}S = -0.029 ± 0.004 ‰, 2SE) analyzed indicates that an anomalous source of sulfur was erupted and that this sulfur is of distinct origin from the melts associated with mare basalts (Δ^{33}S = 0.002 ± 0.004 ‰ 2SE) and the black glasses (Δ^{33}S = -0.008 ± 0.006 ‰ 2SE). There are numerous arguments that support a genetic link between the black and orange glasses (i.e., from the same eruption) with their distinction primarily linked to devitrification (Heiken et al., 1974). Upon initial observation, the glass data, including the data from the sequential extraction, hint at a trend that represents mixing among two separate sulfur components. However, the lack of sulfur isotopic similarity between the two glass samples (from bulk glass data) calls into question whether they originate from the same mantle source or if the singular melt source is heterogenous. It is possible that the sulfur isotope data are illustrating that the orange and black glasses are sourced from similar melt compositions and were processed in the mantle (i.e., parental melt generation and volatile loss) identically. These processes would lead to similarities in the mass-dependent tracers for S isotopes ($\delta^{34}S$), which is observed. However, if the melt sources were inherently different relative to the sulfur source, like mantle heterogeneity on Earth (Dottin III et al., 2021; Dottin III et al., 2020a, b; Labidi et al., 2022), then $\Delta^{33}S$ values are expected to be different among different lunar mantle reservoirs. Ultimately, further investigation from other isotope systems is needed to fully deconvolute the potential lack in genetic link among the orange and black glasses.

5 Conclusions

Our sulfur isotope data indicate that the lunar interior preserves multiple reservoirs of distinct sulfur. The nature and origin of this anomalous sulfur component remains poorly understood and may be linked to (1) an exogenous impactor, (2) photochemically processed sulfur in an early formed lunar atmosphere and its transportation into the lunar mantle, or (3) a primitive sulfur isotope composition of the lunar mantle. If the anomalous S is associated with photochemical processing in an early atmosphere, the data may hint at the first evidence of mantle recycling on the moon. However, to fully understand the mechanism of this process, multiple disciplines within the lunar science community are needed to come together and determine whether this is a viable process on the moon, and whether there are other lines of indirect evidence that indicate there are crustal components that may have been recycled through the lunar mantle. Additional sulfur isotope analyses both as bulk and in-situ measurements on a variety of lunar materials are needed to determine the amount of sulfur isotope heterogeneity that exists among different lunar volatile reservoirs and to establish how the compositions fit within the context of the full lunar volatile cycle. These measurements can also be applied to evaluating the primitive sulfur isotope composition of the lunar mantle.

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Open Research

All sulfur isotope and sulfur concentration data collected for this study are available in the Digital Repository at the University of Maryland (DRUM) http://hdl.handle.net/1903/29502.

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Figure captions and Tables

Figure 1. A.) $\Delta^{33}S$ vs. $\delta^{34}S$ and B.) $\Delta^{36}S$ vs. $\Delta^{33}S$ for lunar glasses (this study) and basalts (Gargano et al., 2022; Wing & Farquhar, 2015).

Table 1. Sulfur isotope compositions and sulfur concentrations for lunar soils and glasses

	Size Fraction	S (ppm)	$\delta^{34}S$ (‰)	$\Delta^{33}S$ (‰)	$\Delta^{36}S$ (‰)
74002, 2221	0-10	596	-1.15	-0.026	0.33
74002, 2221	10-20	355	-0.39	-0.014	-0.15
74002, 2221	20-45	296	-0.04	-0.036	0.05
74002, 2221	45-75	289	0.12	-0.034	0.11

74002, 2221	75-90	313	0.80	-0.029	0.51
74002, 2221	90-150	270	0.30	-0.028	0.12
74002, 2221	150-250	231	0.66	-0.033	0.16
74002, 2221	250-500	294	0.66	-0.031	1.10
74001-2206 stack B	10-20	165	-2.10	-0.019	0.52
74001-2206 stack B	20-45	244	-1.71	-0.018	0.60
74001-2206 stack B	45-75	134	-2.11	0.009	0.95
74001-2206 stack B	75-90	107	-2.01	0.003	2.17
74001-2206 stack B*	90-150	225			
74001-2206 stack B*	150-250	100			
74001-2206 stack B	250-500	n.d			
74001-2206 stack A Res.	20-45	120	-0.60	-0.015	0.66
74001-2206 stack A Res.	45-90	131	-1.34	-0.011	0.37
74001-2206 stack A Res.*	90-150	109			
74001-2206 stack A[†]	20-45	182	-3.01	0.001	-0.29
74001-2206 stack A[†]	45-90	133	-2.54	0.006	-0.14
74001-2206 stack A[†]	90-150	119			
74001-2206 stack A[†]	150-250	94			
74001-2206 stack A[†]	250-500	26			

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*Refers to samples that were too small to measure

[†] Refers to samples that were extracted using AVS technique. See methods for details.

n.d. = not detected