



Sulfur isotope homogeneity of lunar mare basalts

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Abstract

We present a new set of high precision measurements of relative $^{33}\text{S}/^{32}\text{S}$, $^{34}\text{S}/^{32}\text{S}$, and $^{36}\text{S}/^{32}\text{S}$ values in lunar mare basalts. The measurements are referenced to the Vienna-Canyon Diablo Troilite (V-CDT) scale, on which the international reference material, IAEA-S-1, is characterized by $\delta^{33}\text{S} = -0.061\text{‰}$, $\delta^{34}\text{S} \equiv -0.3\text{‰}$ and $\delta^{36}\text{S} = -1.27\text{‰}$. The present dataset confirms that lunar mare basalts are characterized by a remarkable degree of sulfur isotopic homogeneity, with most new and published SF_6 -based sulfur isotope measurements consistent with a single mass-dependent mean isotopic composition of $\delta^{34}\text{S} = 0.58 \pm 0.05\text{‰}$, $\Delta^{33}\text{S} = 0.008 \pm 0.006\text{‰}$, and $\Delta^{36}\text{S} = 0.2 \pm 0.2\text{‰}$, relative to V-CDT, where the uncertainties are quoted as 99% confidence intervals on the mean. This homogeneity allows identification of a single sample (12022, 281) with an apparent ^{33}S enrichment, possibly reflecting cosmic-ray-induced spallation reactions. It also reveals that some mare basalts have slightly lower $\delta^{34}\text{S}$ values than the population mean, which is consistent with sulfur loss from a reduced basaltic melt prior to eruption at the lunar surface. Both the sulfur isotope homogeneity of the lunar mare basalts and the predicted sensitivity of sulfur isotopes to vaporization-driven fractionation suggest that less than $\approx 1\text{--}10\%$ of lunar sulfur was lost after a potential moon-forming impact event.

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1. INTRODUCTION

Precise stable isotope measurements of lunar samples can potentially constrain important features of the Earth–Moon system; a hypothesized Moon-forming giant impact (e.g., [Wiechert et al., 2001](#); [Herwartz et al., 2014](#)), potential planetary-scale volatilization of elements from lunar melts ([Paniello et al., 2012](#)), and the nature of lunar water ([Sharp et al., 2010](#)) are three examples. Given the sensitivity of stable isotopes to vaporization-driven fractionation ([Humayun and Clayton, 1995](#)) and the proposition that the lunar mantle may have two to three times less sulfur

than the terrestrial mantle ([Bombardieri et al., 2005](#)), sulfur isotope measurements may offer new insight into early events in the Earth–Moon system.

However, it is still unclear how the sulfur isotope composition of the Earth–Moon system compares to that in meteorites, where the observed isotopic variations are small ([MacNamara and Thode, 1950](#); [Hulston and Thode, 1965a, b](#); [Gao and Thiemens, 1991, 1993a, b](#)). Pioneering measurements suggest that lunar basalts may possess homogeneous sulfur isotope compositions that are slightly enriched in ^{34}S relative to the most common composition in the meteoritic record (e.g., [Thode and Rees, 1971](#)), but published compilations document a variability that is of the same magnitude as the potential enrichment (e.g., [Des Marais, 1983](#)). High-precision sulfur isotope measurements of mare basalts are a critical pre-requisite before the sulfur isotope system can add new constraints to the early history of the Earth–Moon system.

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In addition, $^{34}\text{S}/^{32}\text{S}$ values of sulfur extracted from lunar soils correlate positively with different indicators of soil maturity (Kaplan and Smith, 1970; Rees and Thode, 1972, 1974; Kerridge et al., 1975; Thode and Rees, 1976), implying that S isotope measurements may track the interaction of lunar regolith and the space environment, and provide a new record of solar activity through time (Lucey et al., 2006). Simple models can account for this observation by incorporating the preferential removal of ^{32}S during sulfur loss from the lunar surface (e.g., Kerridge et al., 1975; Moynier et al., 2006). This isotope effect appears to be mass dependent (Rees and Thode, 1972), and large (Kerridge et al., 1975). The competing loss processes (sputtering and micrometeorite-induced vaporization; Haff et al., 1977; McEwing et al., 1980) have slightly different dependencies on isotopic mass, raising the possibility that the actual loss process may be identified through a combination of high-precision $\delta^{33}\text{S}$, $\delta^{34}\text{S}$, and $\delta^{36}\text{S}$ measurements and theoretical advances on mass-dependent fractionation (e.g., Farquhar et al., 2003; Farquhar and Wing, 2003; Johnston et al., 2005; Ono et al., 2006, 2007). For this to happen, a precise accounting of the initial sulfur isotope abundances in the parent material for lunar soils is a necessary first step.

The main theme of this contribution, therefore, is the establishment of an isotopic baseline for sulfur isotope variability in the Earth–Moon system. We present a detailed description of our analytical techniques, and fully characterize the precision of our measurements of sulfur isotope abundances in lunar basalts. The isotopic homogeneity of the new lunar dataset is quantified, compared to existing measurements from the meteorite record, and discussed in terms of implications for the lunar surface environment and mare basaltic volcanism.

2. METHODS

2.1. Analytical procedures

2.1.1. Sulfur extraction

Analyzed samples represent a variety of mare basalts (Table EA-1-1) that likely erupted over a significant portion of the timescale of mare volcanism (Snyder et al., 2000), came from a range of depths in the lunar mantle (Longhi, 1992), and span common (low-Ti) and rare (high-Ti) types of basalt found on the lunar surface (Giguere et al., 2000). Samples were chosen to cover the spectrum of previously measured whole-rock acid-volatile sulfur contents and multiple sulfur isotope compositions (Thode and Rees, 1971, 1972; Rees and Thode, 1972, 1974).

Lunar mare basalts were hand-crushed in a dedicated steel mortar and pestle and powdered in an agate mortar and pestle. Troilite powders from a small chip of Canyon Diablo Troilite (USNM 6725 – US National Meteorite Collection, Department of Mineral Sciences, National Museum of Natural History) were generated with a microsampling drill press and diamond-tipped drill bit. Sulfur was extracted from mineral and rock powders by reaction with 3 M HCl following published techniques (Rees and Thode et al., 1961; Gao and Thiemens, 1993; Farquhar et al., 2000). A detailed description of the extraction procedure

is available in the electronic annex (EA-1). The acidification technique used here quantitatively extracts all sulfur from powdered lunar basalts, as shown by direct comparison of multiple techniques for sulfur determination in lunar basalts (Rees and Thode, 1974). We did not observe any further sulfur release from our samples during additional extraction procedures on residual powders (EA-1), indicating further that our samples did not contain any sulfur beyond that reactive with 3 M HCl.

2.1.2. Sulfur isotope analysis

Sulfur isotope analyses followed published methods (Hulston and Thode, 1965; Gao and Thiemens, 1991; Farquhar et al., 2000; Johnston et al., 2005) as detailed in the electronic annex. We produced SF_6 by reacting Ag_2S powders with pure F_2 gas, and purified the resulting SF_6 cryogenically and chromatographically. Purified SF_6 was introduced to a ThermoFinnigan MAT 253 dual-inlet gas-source mass spectrometer, and sulfur isotope abundances were measured by monitoring the $^{32}\text{SF}_5^+$, $^{33}\text{SF}_5^+$, $^{34}\text{SF}_5^+$, and $^{36}\text{SF}_5^+$ ion beams at $m/z = 127, 128, 129,$ and 131 , respectively.

Sulfur isotope abundances are reported as per mil variations in δ values relative to standard isotopic compositions:

$$\delta^M\text{S}(\text{‰}) = ([^M\text{R} - ^M\text{R}_{\text{standard}}]/^M\text{R}_{\text{standard}}) \times 1000,$$

where M is 33, 34, or 36, and ^MR is $^M\text{S}/^{32}\text{S}$. A single mass spectrometric analysis involved eight comparisons of a reference gas-sample gas pair, and the values reported here are the averages of 3 to 21 such analyses. We use the following definitions for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$:

$$\Delta^{33}\text{S}(\text{‰}) = \delta^{33}\text{S} - ([\delta^{34}\text{S}/1000 + 1]^{0.515} - 1) \times 1000, \quad \text{and,}$$

$$\Delta^{36}\text{S}(\text{‰}) = \delta^{36}\text{S} - ([\delta^{34}\text{S}/1000 + 1]^{1.9} - 1) \times 1000.$$

The exponents in these definitions approximate the relationships for low temperature (0–100 °C) equilibrium isotopic fractionations (Hulston and Thode, 1965a; Farquhar and Wing, 2003; Farquhar et al., 2003).

2.2. Evaluation of isotopic homogeneity

Isotopic homogeneity was evaluated by determining if all values within a given sample population were consistent with a single mean value. Reduced χ^2 values were calculated according to (1),

$$\chi_v^2 \equiv \frac{1}{v-1} \sum_{i=1}^v \left(\frac{x_i - \bar{x}}{\sigma_i} \right)^2, \quad (1)$$

where v is equal to the number of samples in the population, x_i indicates the measured value of the i -th sample, σ_i is the uncertainty associated with that measurement, and the overbar represents the mean of all measurements in the sample population (Bevington and Robinson, 1992). This procedure normalizes χ^2 values to the number of samples in the population, which allows χ^2 values from populations of different sizes to be compared. If the calculated reduced χ^2 value was within the 95% confidence intervals expected for a single population with v samples

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