

Supplemental Information:

Notable Sample Description:

10017: Sample 10017 is a fine-grained vesicular high-Ti-K mare basalt with high modal mesostasis and vesicularity up to 20% (Beaty and Albee, 1978) and consisted of an exterior (10017-405) and interior chip (10017-400). The interior of this sample was measured to have a $\delta^{66}\text{Zn}$ value of -9.6‰ with 5.5 ppm Zn, with an exterior value of -6.42‰ and 6.7 ppm Zn. The $\delta^{37}\text{Cl}_{\text{SBC}}$ of the interior and exterior was 9.23‰ and 12.53, respectively. Compared to other samples, the WSC isotope composition of the interior is anomalously high at 12.63‰. The interior of the sample contained 2500 ppm S with a $\delta^{34}\text{S}$ value of 0.93‰, with an exterior value of 0.39‰ and 1900 ppm S. The interior of this sample contains both lower Zn and Cl isotope values, yet higher S isotope values from the exterior. The abundances of S, Zn, and Cl are comparable in both the exterior and interior sections, and both are enriched in these elements relative to other high-Ti basalts. Lastly, we find it important to note that troilite within high-Ti-K basalts commonly occurs as spherules suggested to reflect sulfide immiscibility, and also occurs as globules within vesicles (Beaty and Albee, 1978).

15016 & 15556: Samples 15016 and 15556 are medium-grained olivine basalts with 1-5 mm vesicles which comprise up to 50% of the samples. The $\delta^{34}\text{S}$ values are comparable at 0.88 and 0.57‰, respectively with differing S contents of 400 and 800 ppm, respectively. In contrast, the $\delta^{66}\text{Zn}$ and $\delta^{37}\text{Cl}_{\text{SBC}}$ values are -1.49 and 1.54, and 2.14 and 10.6‰, respectively. The Cl_{SBC} and F contents of these samples are different at 1.12 and 1.83 ppm, and 11.1 and 15.4 ppm respectively. Goldberg et al. 1976 find F-rich coatings within the vesicles of these samples with 15016 containing 2x more F in the intervesicular region when compared to the vesicles, whereas 15556 is measured to contain similar F contents in both regions.

Samples:

In this work we chose to analyze 19 mare basalts with sample aliquots designated from partnering chips for Cl, Zn and S isotope compositions. Our chosen samples encompass the low-Ti, and high-Ti mare basalt sub-groupings (Neal and Taylor, 1992). We also measured the interiors and exteriors of some notable samples such as 10017 and 12054 to address sample heterogeneity and surface-relate isotopic anomalies. Two Apollo 15 basalts 15016 and 15556 were also measured due to high vesicularity.

Methods:

Chlorine:

Samples for Cl isotope measurements were performed as follows following the method of Sharp et al. (2010): Samples were crushed and leached with deionized water to obtain water-soluble chloride (WSC). Residual leachates were then rinsed again to remove any residual water-soluble chloride fraction, then dried and loaded into quartz tubes. Structurally-bound chloride was then extracted via pyrohydrolysis where the powdered sample was melted in a stream of water vapor, passed through a condensing column and finally collected in the condensed water. The WSC and SBC fractions were processed in the same manner for isotope measurements: Solutions are reacted with 5 mL 50% HNO₃ for 24 hours to degas sulfur, followed by the addition of 1 mL 0.4M AgNO₃ to precipitate AgCl overnight. AgCl is then filtered and loaded into 6mm diameter pyrex tubes. The tubes are evacuated and 10 μ L CH₃I is added prior to flame-sealing. Sealed tubes are then reacted at 80°C for 48 hours to produce CH₃Cl as an analyte. Chlorine isotopes were measured on a Delta^{PLUS}XL in continuous flow mode at the University of New Mexico. Sample reproducibility has been shown to be $\pm 0.25\%$. The isotopic composition of Cl is reported relative to Standard Mean Ocean Chloride (SMOC)

$$\delta^{37}\text{Cl}(\text{‰}) = \left(\frac{\frac{^{37}\text{Cl}}{^{35}\text{Cl}}_{\text{Sample}}}{\frac{^{37}\text{Cl}}{^{35}\text{Cl}}_{\text{SMOC}}} - 1 \right) * 1000$$

Zinc:

Zn isotope measurements were performed at the University of Oxford by S. Hopkins and A. Halliday. Samples were transferred to metal-free centrifuge tubes and cleaned with DI water for 2 hours. Samples were then dried and powdered in an agate mortar. Powder aliquots were then measured to obtain approximately 0.25 ug Zn (around 20-140 mg of sample). Hotplate dissolution was then performed using HF-HNO₃ and HCl over multiple days. Sample dissolution was complete when no undissolved components remained. Small aliquots of each sample dissolution was then weighed and mixed with a ⁶⁴Zn-⁶⁷Zn double spike (5.10025 ppm, (Arnold et al., 2010)) and equilibrated over 48 hours at 60°C. Solutions were then passed through an anion-exchange column before analysis by MC-ICPMS to determine the Zn concentrations. These concentrations were then used to calculate the appropriate mass ratios of spike/sample solution. Appropriated spiked samples were then passed through the anion-exchange column twice to purify Zn from interfering elements. Zn isotope compositions were then measured using a *Nu instruments* Plasma HR mass spectrometer. Masses 62, 64, 66, 67, 67.5, and 68 were measured simultaneously. Masses 62 and 67.5 were used for ⁶⁴Ni⁺ and Ba²⁺ corrections. Exterior sample washes typically had negligible Zn contents (<0.2 ng). USGS reference materials BCR2, BHVO2, and BIR1a were prepared in the same manner as the lunar samples. The isotopic composition of Zn is reported relative to JMC-Lyon

$$\delta^{66}\text{Zn}(\text{‰}) = \left(\frac{\frac{^{66}\text{Zn}}{^{64}\text{Zn}}_{\text{Sample}}}{\frac{^{66}\text{Zn}}{^{64}\text{Zn}}_{\text{JMC-Lyon}}} - 1 \right) * 1000$$

Sulfur:

Sulfur isotopes were measured at the University of Maryland by J. Dottin and J. Farquhar. Samples were firstly coarsely crushed in a steel mortar and pestle and subsequently powdered in an agate mortar using <5mL ethanol to reduce dust loss. Ethanol-powder slurry was then quantitatively transferred to reactions vessels. Flasks were filled with 20mL 5M HCl and 20mL of Cr(II) Chloride solution and heated to sub boiling temperatures with a continuous flow of N₂ (Canfield et al., 1986). The reaction proceeds for ~3 hours as the release of H₂S that is first carried through a water trap to capture acid vapors and second through an AgNO₃ trap where S is precipitated as Ag₂S. Precipitated Ag₂S was then centrifuged and transferred to 1.5ml Eppendorf tubes and rinsed 6 times with Milli-Q.

After rinsing, samples were dried for ~ 2 hours at 70 degrees C and weighed for extraction yields to estimate S concentrations. The Ag₂S was then transferred into clean aluminum foil, loaded into Ni reaction vessels and reacted with approximately 10x stoichiometric excess of F₂ at 250°C overnight yielding SF₆ as an analyte. Analyte gas was separated from non-condensable gases by liquid-N₂ traps. HF was then separated from SF₆ by an ethanol-liquid N₂ trap. SF₆ was then purified by passing through a 12.5 A Hasep Q gas chromatography column. Purified SF₆ was lastly analyzed in dual inlet mode on a MAT 253 mass spectrometer. The isotopic composition of sulfur is normalized using the same method as Antonelli et al. (2014) and Dottin et al. (2018) where samples are first normalized to bracketed analyses of IAEA-S1 from each analytical session and subsequently normalized to the value IAEA-S1 relative to Canyon Diablo Troilite (CDT) reported in Antonelli et al. (2014) which places IAEA-S1 at $\delta^{33}\text{S} = -0.091$, $\delta^{34}\text{S} = -0.401$, $\delta^{36}\text{S} = -1.558$, $\Delta^{33}\text{S} = 0.116$, $\Delta^{36}\text{S} = -0.796$ (Dottin et al. 2020).

$$\delta^{34}\text{S}(\text{‰}) = \left(\frac{\frac{^{34}\text{S}}{^{32}\text{S}}_{\text{Sample}}}{\frac{^{34}\text{S}}{^{32}\text{S}}_{\text{CDT}}} - 1 \right) * 1000$$