

PRELIMINARY ESTIMATE OF SULFUR ISOTOPE RATIO PRECISION EXPECTED WITH THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT SUITE OF THE 2009 MARS SCIENCE LABORATORY. H. B. Franz¹, P. R. Mahaffy² and J. Farquhar³, ¹Department of Geology, University of Maryland, College Park, MD 20742 (hfranz@geol.umd.edu), ²NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771 (Paul.R.Mahaffy@nasa.gov), ³Earth System Science Interdisciplinary Center and Department of Geology, University of Maryland, College Park, MD 20742 (jfarquha@essic.umd.edu).

Introduction: A variety of experiments have detected or inferred the presence of sulfates on Mars, including laboratory chemical analyses of martian meteorites [1, 2,] and spacecraft instruments of the Viking Lander [3], Mars Pathfinder [4], MER rover [5, 6, 7], and Mars Express [8] missions. The 2009 Mars Science Laboratory (MSL) [9] is designed to greatly expand our ability to identify minerals on Mars as well as associated organic or inorganic volatiles. The Sample Analysis at Mars (SAM) instrument suite of MSL will measure the chemical and isotopic composition of volatile species. Here we report on preliminary analysis of SAM's ability to measure the sulfur isotope ratios in SO₂, as compared to high-precision results obtained by standard laboratory techniques. Besides being directly applicable to the measurement of sulfur isotope ratios from evolved gas analysis of sulfate minerals, these results may be generalized to approximate the precision anticipated for other isotope ratios obtained by SAM.

Isotope Measurements with SAM: As previously demonstrated [10] in laboratory experiments designed to support first the Mars Polar Lander and later the Phoenix TEGA and MSL/SAM experiments, the evolved gas analysis (EGA) spectra of sulfate compounds can reveal the degree of weathering based on the water structurally incorporated into these materials. As the temperature of the sample is increased, the water of hydration is released first, followed by eventual breakdown of the sulfate to produce SO₂. The degree of incorporation of water into the mineral structure is revealed in the temperature of its release for each sulfate type.

The SAM instrument suite includes an EGA measurement mode in which volatiles released from selected rocks and fines are continuously sampled by a quadrupole mass spectrometer (QMS) or tunable laser spectrometer (TLS) as sample temperature is raised from ambient to 1100 °C. While the TLS is designed to obtain stable isotope ratios of target species with high precision, SAM's present design configuration does not include a TLS channel capable of measuring sulfur isotopes. However, sulfur isotope abundances can be measured with more limited precision via the QMS.

EGA experiments are presently being implemented on a breadboard of the SAM suite to allow characterization of instrument performance and optimization of experimental parameters [Fig. 1]. Measurements of the sulfur isotope ratios in both martian sulfate analogs and SO₂ gas have been performed with the QMS to evaluate the precision obtainable with the EGA experiments. Sulfate analogs include jarositic tephra from Hawaii with different degrees of aqueous alteration. Comparison of these results to those obtained via standard laboratory techniques also provide an estimate of the accuracy of isotope ratios measured with the SAM QMS.

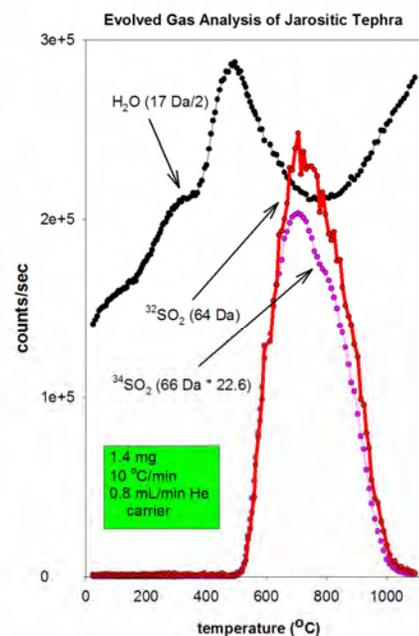


Figure 1. Preliminary EGA Results with Jarositic Tephra

Experimental Methods: To measure sulfur isotope ratios in SO₂ with the SAM breadboard, SO₂ gas was introduced directly into the QMS. Assuming an oxygen isotopic composition of standard mean ocean water (SMOW), sulfur isotope ratios were computed independently from mass spectral peaks of 64-66 for

parent SO₂ molecules and 48-50 for SO fragments. Experimental parameters such as sample pressure and integration period were varied for optimal isotope ratio precision.

For comparison, the sulfur isotopic composition of the same SO₂ was also measured by high-precision laboratory analysis at the University of Maryland. Briefly, the SO₂ was converted to SF₆ through established experimental protocols [11]. The resulting SF₆ was purified cryogenically and chromatographically and input to a ThermoFinnigan MAT 253 mass spectrometer for measurement of sulfur isotopic abundances.

Similar comparative analyses were performed to evaluate the sulfur isotope ratios obtained through SAM EGA experiments. Samples of jarositic tephra were heated in the SAM pyrolysis chamber and sampled with the QMS to measure the SO₂ and SO peaks as described above. Samples of the same material were chemically processed to convert the sulfate to SF₆, whose sulfur isotopic abundances were then precisely measured with the ThermoFinnigan MAT 253.

Results and Future Work: Measurements of sulfur isotope ratios with the EGA experiments and with SO₂ gas yielded promising results for both $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$. The abundance of ^{36}S is below the detection limits of SAM's QMS, so no $\delta^{36}\text{S}$ estimations were included in this analysis. Future work will include additional tests with other martian sulfate analogs, as well as further optimization of experimental parameters to obtain optimal instrument performance.

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