

CARBON AND SULFUR ISOTOPIC COMPOSITION OF ROCKNEST SOIL AS DETERMINED WITH THE SAMPLE ANALYSIS AT MARS (SAM) QUADRUPOLE MASS SPECTROMETER. H. B. Franz^{1,2}, A. C. McAdam¹, J. C. Stern¹, P. D. Archer, Jr.³, B. Sutter³, J. P. Grotzinger⁴, J. H. Jones³, L. A. Leshin⁵, P. R. Mahaffy¹, D. W. Ming³, R. V. Morris³, P. B. Niles³, T. C. Owen⁶, E. Raaen¹, A. Steele⁷, C. R. Webster⁸, and the MSL Science Team. ¹NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, Heather.B.Franz@nasa.gov, ²University of Maryland Baltimore County, Baltimore, MD 21228, ³NASA Johnson Space Center, Houston, TX, 77058, ⁴California Institute of Technology, Pasadena, CA 91125, ⁵Rensselaer Polytechnic Institute, Troy, NY, 12180, ⁶University of Hawaii, Honolulu, HI, 96822, ⁷Carnegie Institute of Washington, Washington, DC, 20015, ⁸Jet Propulsion Laboratory, Pasadena, CA 91009.

Introduction: The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) “Curiosity” rover got its first taste of solid Mars in the form of loose, unconsolidated materials (“soil”) acquired from an aeolian bedform designated Rocknest. Evolved gas analysis (EGA) revealed the presence of H₂O as well as O-, C- and S-bearing phases in these samples. CheMin did not detect crystalline phases containing these gaseous species but did detect the presence of X-ray amorphous materials. In the absence of definitive mineralogical identification by CheMin, SAM EGA data can provide clues to the nature and/or mineralogy of volatile-bearing phases through examination of temperatures at which gases are evolved from solid samples. In addition, the isotopic composition of these gases, particularly when multiple sources contribute to a given EGA curve, may be used to identify possible formation scenarios and relationships between phases. Here we report C and S isotope ratios for CO₂ and SO₂ evolved from Rocknest soil samples as measured with SAM’s quadrupole mass spectrometer (QMS).

Experimental Methods: In EGA experiments, solid samples are heated in one of SAM’s pyrolysis ovens to release volatiles, while the QMS continuously samples the outflow from the oven [1-4, 6]. SAM analyzed four aliquots of Rocknest soil from the same scoop sample. Integration of the QMS signal over time for particular m/z allows quantitative estimates of chemical and isotopic abundance. A portion of the gas stream, parameterized by a desired range of sample temperature, was also collected during each run for isotopic and abundance analysis of CO₂ and H₂O by the SAM tunable laser spectrometer (TLS).

Rocknest EGA Results: All four Rocknest soil samples released H₂O, O₂, CO₂ and SO₂, as shown in Figure 1. This figure shows the major molecular ion for each species to compare approximate relative abundances. In cases where the major molecular ion saturated the QMS detector, its value was estimated based on other isotopologues of that species. The volatile of greatest abundance in these samples was H₂O, followed by CO₂ and SO₂. The possible minerals that may have been present in the samples and their relative abundances as suggested by these data are discussed in oth-

er abstracts at this meeting [1-4].

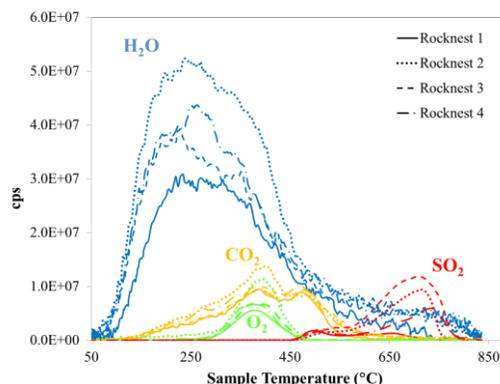


Figure 1. Major volatiles released from Rocknest soil.

Carbon isotope ratios: The compound peak shapes of the CO₂ EGA traces shown in Figure 1 suggest contributions from multiple carbon sources. Candidates for these carbon sources are currently being investigated, but evolution temperatures are most consistent with adsorbed CO₂, Fe- or Mg-bearing carbonates, or combustion of organic compounds that may be of terrestrial origin [2]. Knowledge of the isotopic composition of the various peaks could be helpful in determining relationships between phases. A different temperature cut was directed to the TLS for each Rocknest soil experiment, allowing high-precision characterization of the $\delta^{13}\text{C}$ of various portions of the gas stream over multiple runs. However, the TLS can only sample a single region in each run. Estimating $\delta^{13}\text{C}$ from QMS EGA data can help fill in the gaps and enhance our understanding of the carbon sources.

Interference from other compounds at m/z 12 and 13 and detector saturation at the major molecular CO₂ ion of m/z 44 precluded the use of these m/z values in determining $\delta^{13}\text{C}$ (with respect to V-PDB), which was instead computed from m/z 45 and 46. These calculations require assumptions about the CO₂ oxygen isotopic composition. For the analysis discussed here, oxygen isotope ratios were based on TLS results for $\delta^{18}\text{O}$ of this sample, with an assumed $\Delta^{17}\text{O}$ of 0.32‰. For a known oxygen composition, uncertainties on $\delta^{13}\text{C}$ are currently estimated at $\pm 10\%$, based on repeated laboratory EGA analyses [5].

Figure 2 shows the CO₂ trace at m/z 45 for the fourth Rocknest soil sample, annotated with results for $\delta^{13}\text{C}$. The width of each text box in the figure indicates the temperature range included in the integration for a particular $\delta^{13}\text{C}$ calculation. The upper-most box indicates the temperature cut of gas that was collected in the TLS, 348 – 440 °C. The value for $\delta^{13}\text{C}$ computed from QMS data for that portion of the curve agrees well with the TLS result for this sample, as noted. The $\delta^{13}\text{C}$ determined for the second large peak is indistinguishable from the first peak given the uncertainties, indicating a potential relationship between the carbon sources of these two peaks.

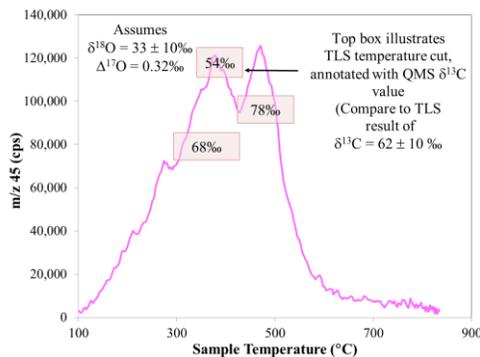


Figure 2. CO₂ released from Rocknest 4 soil sample. QMS results for $\delta^{13}\text{C}$ are shown in pink text boxes. See text for details.

One possibility is that the two peaks derived from a common source and the separate CO₂ releases indicate involvement of a secondary source of oxygen of similar isotopic composition. As Figure 1 shows, the first large CO₂ peak coincided with a significant release of O₂ from another mineral phase, which may have influenced the release of CO₂ [2]. Another possibility is that two C-bearing phases were present that either had similar carbon isotopic compositions initially or have exchanged isotopically at some point. ¹³C-enriched CO₂ has been observed in the atmosphere at Gale Crater with SAM TLS [6] and QMS [7]. The CO₂-bearing phases in Rocknest soil are even more enriched in ¹³C than the atmosphere. Given carbonate-CO₂ carbon isotope fractionation factors [8], this suggests that carbonates formed from the atmospheric CO₂ at low temperature, 0°C or even lower. This supports the idea that the minor amount of carbonates in martian soil could have been derived through atmosphere interaction with soil with only transient water [e.g., 9-10].

Sulfur Isotope Ratios: There are a number of Fe- and S-bearing minerals that release sulfur at temperatures consistent with the Rocknest patterns, but the multiple peaks seen in the SO₂ traces suggest that more than one S-bearing phase was present. Based on the temperatures of sulfur release and the EGA traces of

relevant m/z values, it is possible that these phases include a sulfide and at least one sulfate mineral [1]. Sulfur released from sulfide was presumably oxidized in SAM's pyrolysis oven to form SO₂. Given the coincidence of the first SO₂ peak and the second large CO₂ peak, it seems plausible that the source of oxidant for the sulfide was O₂ formed from CO₂ released from a carbonate mineral. The sulfur isotopic composition of SO₂ released from Rocknest 4 soil was determined from data at m/z 64, 65, and 66, assuming oxygen isotopic composition from TLS measurements. For known oxygen composition, uncertainties in $\delta^{34}\text{S}$ (given with respect to V-CDT) are estimated as $\pm 10\%$, based on repeated laboratory EGA analyses [5].

Figure 3 shows the SO₂ release pattern for the Rocknest 4 sample, annotated with values of $\delta^{34}\text{S}$ computed for the temperature ranges indicated. While there are differences of several per mil in the $\delta^{34}\text{S}$ values computed for the two major SO₂ peaks, the compositions are the same within the uncertainties in the measurements. Both peaks have $\delta^{34}\text{S}$ near zero, consistent with sulfur isotopic compositions measured in martian meteorites [11-13].

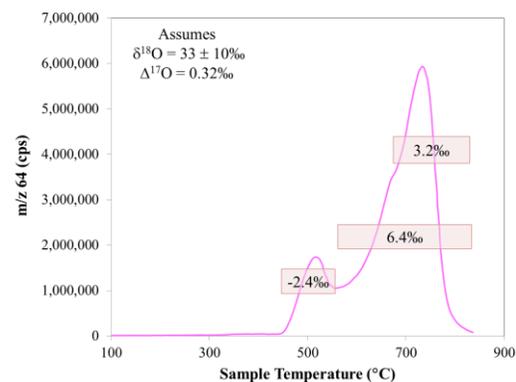


Figure 3. SO₂ released from Rocknest 1 soil sample. QMS results for $\delta^{34}\text{S}$ are shown in pink text boxes. See text for details.

Neither the CO₂ nor SO₂ released from Rocknest 1 soil reveals isotopic evidence suggesting biological activity. The composition of both gases is consistent with products of inorganic geological processes. Refinement of these results and analysis of other Rocknest samples are ongoing.

References: [1] McAdam et al. (2013) LPSC LXIV. [2] Sutter et al. (2013a) LPSC XLIV. [3] Sutter et al. (2013b) LPSC XLIV. [4] Archer et al. (2013) LPSC XLIV. [5] Franz et al. (2008) LPSC XXXIX, #2433. [6] Webster et al. (2013) LPSC XLIV. [7] Franz et al. (2013) LPSC XLIV. [8] Chacko et al. (2008) GCA 72. [9] Bandfield et al. (2003) Science 301. [10] Shaheen et al. (2010) PNAS 107. [11] Franz et al. (2010) LPSC XLI, #2341. [12] Franz et al. (2011) LPSC XLII, #2338. [13] Franz et al. (2012) LPSC XLIII, #2232.