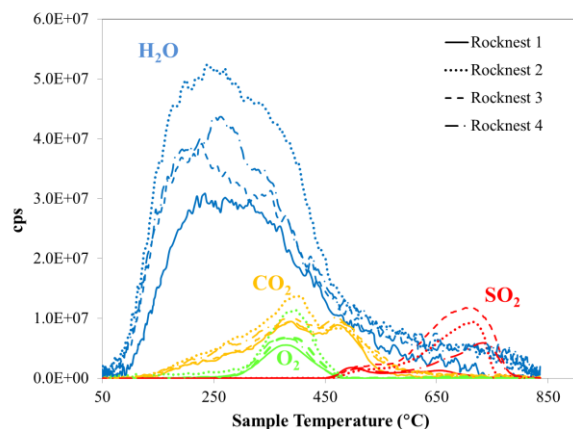


**ABUNDANCES OF VOLATILE-BEARING SPECIES FROM EVOLVED GAS ANALYSIS OF SAMPLES FROM THE ROCKNEST AEOLIAN BEDFORM IN GALE CRATER.** P. D. Archer, Jr.<sup>1</sup>, H. B. Franz<sup>2,3</sup>, B. Sutter<sup>4</sup>, A. McAdam<sup>2</sup>, D. W. Ming<sup>1</sup>, R. V. Morris<sup>1</sup>, P. R. Mahaffy<sup>2</sup>, and the MSL Science Team <sup>1</sup>NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, [doug.archer@gmail.com](mailto:doug.archer@gmail.com) <sup>2</sup>NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, <sup>3</sup>University of Maryland, Baltimore County, Baltimore, MD 21228, <sup>4</sup>Jacobs-ESCG, Houston, TX 77058.

**Introduction:** The Sample Analysis at Mars (SAM) instrument suite on board the Mars Science Laboratory (MSL) recently ran four samples from an aeolian bedform named Rocknest. SAM detected the evolution of H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>, and SO<sub>2</sub>, indicative of the presence of multiple volatile bearing species (Fig 1). The Rocknest bedform is a windblown deposit selected as representative of both the windblown material in Gale crater as well as the globally-distributed martian dust. Four samples of Rocknest material were analyzed by SAM, all from the fifth scoop taken at this location. The material delivered to SAM passed through a 150 μm sieve and is assumed to have been well mixed during the sample acquisition/preparation/handoff process.

SAM heated the Rocknest samples to ~835 °C at a ramp rate of 35 °C/min with a He carrier gas flow rate of ~1.5 standard cubic centimeters per minute and at an oven pressure of ~30 mbar [1]. Evolved gases were detected by a quadrupole mass spectrometer (QMS). This abstract presents the molar abundances of H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>, and SO<sub>2</sub> as well as their concentration in rocknest samples using an estimated sample mass.



**Figure 1** – Major molecular ions of the most abundant gases evolved from rocknest samples. Plot by H. Franz.

**Methods:** Molar abundances were computed in two ways: first, by reference to runs during SAM calibration of known amounts of sample or equimolar gas mixes; and second, by using *in situ* pressure and abundance data measured by the Tunable Laser Spectrometer (TLS) instrument, part of the SAM instrument suite. Abundances of all four gases mentioned were calculated by referring to pre-launch calibration runs. H<sub>2</sub>O,

O<sub>2</sub>, and CO<sub>2</sub> abundances were also calculated based on TLS measurements on Mars.

*Abundances based on pre-launch data.* During the development/testing phase for the SAM instrument, samples of measured amounts of calcite (CaCO<sub>3</sub>) and a hydrated iron sulfate (FeSO<sub>4</sub>·4H<sub>2</sub>O) were run in SAM. If we assume that thermal decomposition of both of these species is complete by 835 °C (a good assumption supported by laboratory experiments that measure mass loss vs. temperature), then we know the total number of moles evolved for each sample. Integrating under the QMS curves for each gas release can give a value of counts/mole for different mass/charge (*m/z*) numbers. Under nominal SAM operating conditions, the most abundant ion of major species often saturates the detector (given a fixed detector range, this makes the instrument more sensitive to low-abundance materials). Doubly ionized molecules, ion fragments, and isotopes can be used to reconstruct the shape of the major molecular ion by using calibration data or measurements taken of the species in question at lower abundances. For example, *m/z* 44 (CO<sub>2</sub>) is saturated for most of the run because of the amount of CO<sub>2</sub> evolved. To measure the abundance of CO<sub>2</sub>, *m/z* 12 (carbon, an ionization product of CO<sub>2</sub> formed in the detector), *m/z* 22 (doubly ionized 44, *m*=44 *z*=2), and *m/z* 45 and 46 (isotopologues of CO<sub>2</sub>) are used instead of *m/z* 44. The counts/mole ratio was calculated for each of these *m/z* values in calibration runs. The number of moles of CO<sub>2</sub> evolved from Rocknest samples is determined by taking an average of the totals calculated for each *m/z*, with the error being the standard deviation of the average. For H<sub>2</sub>O, *m/z* 19 and 20 were used because *m/z* 17 and 18 are saturated, as was the case in calibration runs. To calculate SO<sub>2</sub> abundances, *m/z* 66 and 50 were used (isotopologues of SO<sub>2</sub> and SO) because 64 and 48 saturated in calibration runs.

Oxygen counts/mole values were computed in a slightly different way because none of the minerals run pre-launch released oxygen. However, another pre-launch characterization run was done using an equimolar mix of O<sub>2</sub>, CO<sub>2</sub>, Ar, and N<sub>2</sub>. From this, we find a value for relative ionization rates for O<sub>2</sub> and CO<sub>2</sub> at similar abundances. This can also be done for the ion fragments/isotopologues of each species so we can retrieve *m/z* 32:12 or 32:45 ratios (among others). The integrated *m/z* 32 counts are multiplied by these ratios

to get to equivalent counts for m/z 12 or 45, for which counts/mole numbers are known.

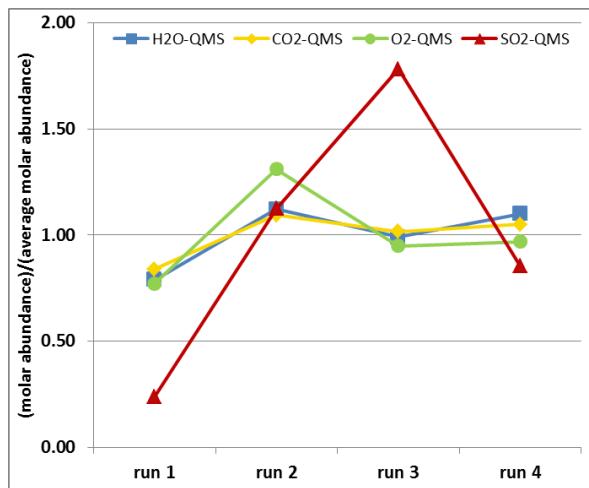
The second method used to calculate abundances of H<sub>2</sub>O and CO<sub>2</sub> is more direct. During thermal analysis, evolved gases were directed to either a hydrocarbon trap, the TLS, or vented to Mars (only a small fraction of the total gas is sent to the QMS). The TLS has the ability to measure internal cell pressure and the mixing ratio for H<sub>2</sub>O and CO<sub>2</sub>. Given a TLS volume of 410 cm<sup>3</sup>, we can compute the number of moles of these gases inside TLS. By integrating under the QMS signal for each gas over the time the valves to the TLS were open and then over the entire gas release, we calculate the fraction of gas sent to the TLS. The total moles evolved can then be calculated (total moles evolved=moles gas in TLS/fraction sent to TLS). At present, the TLS numbers are close to the QMS/pre-launch calculated values but the trends in the numbers do not match what is seen in the QMS. The differences in abundances and the discrepancy in trends in the QMS vs. TLS data is still under investigation.

**Table 1** – molar abundances (μmoles) of H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, and O<sub>2</sub> and wt% for CO<sub>3</sub><sup>2-</sup>, SO<sub>3</sub>, H<sub>2</sub>O, and ClO<sub>4</sub><sup>-</sup> assuming a 20 mg sample mass. Error for molar abundances is the standard deviation of the average abundances computed using different m/z values and error for wt % is based on a sample size range of ~15-40 mg

|                       | run 1                    | run 2       | run 3       | run 4       |
|-----------------------|--------------------------|-------------|-------------|-------------|
| gas                   | molar abundance (μmoles) |             |             |             |
| H <sub>2</sub> O(QMS) | 92.6 ± 15.7              | 131 ± 21.0  | 116 ± 12.1  | 129 ± 29.7  |
| H <sub>2</sub> O(TLS) | 25.7                     | 50.5        | 75.7        | 75.2        |
| CO <sub>2</sub> (QMS) | 8.32 ± 0.99              | 10.8 ± 1.28 | 10.1 ± 1.22 | 10.4 ± 1.27 |
| CO <sub>2</sub> (TLS) | 18.8 ± 2.43              | 12.5 ± 0.22 | 9.48 ± 2.54 | 10.1 ± 3.38 |
| SO <sub>2</sub> (QMS) | 2.13 ± 0.08              | 14.7 ± 1.02 | 23.3 ± 1.57 | 11.2 ± 0.72 |
| O <sub>2</sub> (QMS)  | 2.98 ± 0.18              | 5.06 ± 0.31 | 3.67 ± 3.35 | 3.74 ± 0.23 |

**Results:** Table 1 lists the molar abundances calculated for the four major inorganic gases released. Figure 3 clearly shows how H<sub>2</sub>O and CO<sub>2</sub> abundances are relatively consistent run to run and track each other well. O<sub>2</sub> is slightly less consistent but follows the same trend. SO<sub>2</sub> is highly variable run to run for unknown reasons. As mentioned previously, all four samples came from the same scoop, represent the < 150 μm size fraction, and should be fairly homogenous. The similar concentrations run to run of the other three evolved gases seem to rule out differences in sample size as the cause of the SO<sub>2</sub> heterogeneity.

The sources of the gas releases will be discussed in detail elsewhere, but current best candidates are perchlorates (H<sub>2</sub>O and O<sub>2</sub> [2]), sulfates or sulfides (H<sub>2</sub>O and SO<sub>2</sub> [3,4]), and carbonates and combusted organic material (CO<sub>2</sub> [4,5]).



**Figure 2** – Molar abundance for each run divided by the average abundance over all four runs (QMS data only).

**Sample Mass Uncertainty.** Volatile abundances in weight % are not given because the mass of sample analyzed by SAM currently has large uncertainties (this does not affect the reported molar abundances). The MSL Sample Acquisition, Sample Processing and Handling system moved Rocknest material sieved to <150 μm into a 75 mm<sup>3</sup> portion tube [6]. One portion was delivered to SAM per sample analysis. Although the portion tube volume is known, the density of the material in the portion tube is sample-dependent and the amount delivered also depends on wind conditions at the time of delivery. Work is currently underway to reduce the uncertainty in delivered sample mass in order to calculate accurate weight % of volatiles in Rocknest material.

**Conclusion:** These results are broadly consistent with data from other instruments on MSL (i.e., CheMin and APXS). CheMin analysis of a different portion of the same sample indicate a large quantity of X-ray amorphous material [7]. Based on the composition of the crystalline component of the sample determined by X-ray diffraction, volatiles are concentrated primarily in the amorphous phase. The amount of SO<sub>3</sub> detected is broadly consistent with APXS measurements of a bulk soil sample of Rocknest [8]. The high water content is still under investigation.

**References:** [1] Mahaffy P. R. et al., (2012) *Space Sci Rev*,170, 401-478. [2] Sutter B. et al., (2013) *this conference*. [3] McAdam A. et al, (2013) *this conference*. [4] Franz H. B. et al., (2013) *this conference*. [5] Sutter B. et al., (2013) *this conference*. [6] Anderson R. C. et al., (2012) *Space Sci Rev*,170, 57-75. [7] Bish D. et al, *this conference*. [8] Gellert R. et al., (2013) *this conference*.