INSIGHTS INTO THE SULFUR MINERALOGY OF MARTIAN SOIL AT ROCKNEST, GALE CRATER, ENABLED BY EVOLVED GAS ANALYSES.

A. McAdam[1], H. Franz[1,2], P. Archer, Jr.[3], C. Freissinet[1], B. Sutter[3], D. Glavin[1], J. Eigenbrode[1], H. Bower[1,4], J. Stern[1], P. Mahaffy[1], R. Morris[3], D. Ming[3] , E. Rampe[3], A. Brunner[1], A. Steele[5], R. Navarro-Gonzalez[6], D. Bish[7], D. Blake[8], J. Wray[9,] J. Grotzinger[10], and the MSL Science Team. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, [2]Univ. of Maryland, Baltimore, MD 21228, [3]NASA Johnson Space Center, Houston, TX, 77058, [4]Univ. of Maryland, Baltimore County, Baltimore, MD 21228, [5]Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., Washington, DC 20015, [6]Universidad Nacional Autónoma de México, México, D.F. 04510, [7]Dept. of Geological Sci., Indiana Univ., Bloomington, IN 47405, [8]NASA Ames Research Center, Moffett Field, CA 94035, [9]Georgia Inst. of Tech., GA 30332, [10]Div. Geology and Planetary Sci., Caltech, Pasadena, CA 91125.

Introduction: The first solid samples analysed by the Chemistry and Mineralogy (CheMin) instrument and Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) consisted of < 150 µm fines sieved from aeolian bedform material at a site named Rocknest. All four samples of this material analyzed by SAM's evolved gas analysis mass spectrometry (EGA-MS) released H_2O, CO_2, O_2, and SO_2 (Fig. 1), as well as H_2S and possibly NO. This is the first time evolved SO_2 (and evolved H_2S) has been detected from thermal analysis of martian materials. The identity of these evolved gases and temperature (T) of evolution can support mineral detection by CheMin and place constraints on trace volatile-bearing phases present below the CheMin detection limit or difficult to characterize with XRD (e.g., X-ray amorphous phases). Constraints on phases responsible for evolved CO_2 and O_2 are detailed elsewhere [1,2,3]. Here, we focus on potential constraints on phases that evolved SO_2, H_2S, and H_2O during thermal analysis.

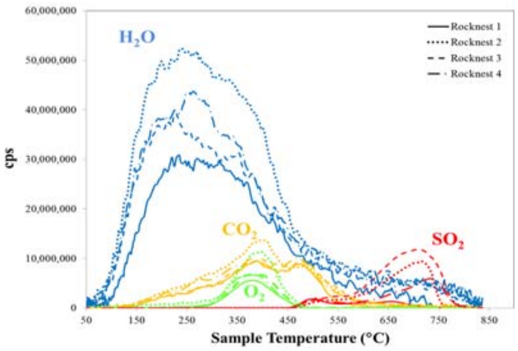

Figure 1. Major gases evolved from Rocknest soil fines during MSL SAM EGA-MS. Lines are plots of MS signal vs. temperature for the major molecular ion for a given compound. Figure by H. Franz.

Methods: For SAM EGA-MS analyses, delivered sample fines were heated to ~835°C at 35°C/min. Evolved gases were carried through manifold lines to the SAM QMS by a He carrier gas. The pressure of He in the oven was ~30 mb and the flow rate was ~1.4 cc/min. The SAM breadboard and other SAM-like EGA teststands at GSFC and JSC were used to characterize analog samples under SAM-like conditions (flight SAM-like carrier gas, gas flow and gas pressure conditions, T range and heating ramp rate). Several milligrams of <150 µm samples were analyzed.

Rocknest evolved SO_2: The intensity and shape of traces attributable to SO_2 (Fig. 1) vary substantially between the Rocknest samples. This likely indicates heterogeneity in sulfur minerals or phases which can evolve SO_2 or their abundances, as well as possibly differences in other sample components that play a role in oven reactions that can produce SO_2. Overall, however, SO_2 traces have a hump indicating SO_2 evolving from ~450 to ~800°C. Within this, at least two "peaks" can be deconvolved, one with peak Ts at ~500-550°C, and one with peak Ts at ~700-750°C (Fig. 1).

Evolved SO_2 could result from a range of potential sources. It could result from S anions adsorbed onto sample materials, or thermal decomposition of S-bearing mineral phases including sulfides, sulfates, and/or sulfites. Data from SAM-like EGA-MS analyses of several S-bearing phase reference materials are shown in Fig. 2 for preliminary comparisons to Rocknest data, although work to build SAM-like EGA-MS reference libraries is ongoing. As shown in Fig. 2, Mg- and Ca-sulfates have SO_2 evolution Ts which are probably too high to be responsible for Rocknest SO_2 (Ca-sulfates evolve SO_2 at >1000 °C). Heating of a reduced S phase in the presence of an oxidant (e.g., CO_2, O_2), and/or SO_2 from other reactions between S-phases and other sample volatile-bearing phases during heating are another possibility. In addition, differences in SO_2 evolution Ts due to particle size differences in S-bearing phases, and other sources which remain to be determined, are potential contributions.

It is also relevant to note that more than one SO_2 peak may result even from only one sulfide mineral in a sample, depending on which other gases are in the oven and how reducing or oxidizing the oven atmosphere is at certain Ts. To investigate this idea, mixtures of minor pyrite in calcite were prepared, and then analyzed in SAM-like EGA lab setups. Several of these analyses produced SO_2 traces with two peaks. A mixture of minor pyrite in nontronite showed similar features, and future work is planned with other mineral mixtures. We hypothesize that some SO_2 is from partial oxidation of the pyrite-hosted reduced S, and then remaining reduced S, possibly in a pyrrhotite reaction product, is then oxidized at the higher Ts by CO_2 or H_2O in the oven at that T. EGA analyses of the minor pyrite mixtures also show a peak in the 60 Da trace, which can be attributed to OCS. Reaction of CO_2 with a reduced S phase can result in an OCS product [4].

In Rocknest data, there is a 60 Da peak that correlates with the higher T SO_2 release (Fig. 3). There is no large CO_2 release at that T, but some residual CO_2 is present. There is also evolution of species at 34, (Fig. 3), 35, and 36 Da (not shown) contemporaneous but not exactly correlated with the higher T SO_2 peak (Fig. 3). We hypothesize that these high T species are due to H_2S release, and SAM GCMS data from several Rocknest samples indicates H_2S. The 34 Da peak at lower T can be primarily attributed to an isotopologue of O_2 (Fig. 1), though GCMS data indicates that minor H_2S must also be present at the lower T and work is on going. Species at 76 Da contemporaneous with the higher T SO_2 may indicate CS_2 evolution (not shown). CS_2, like OCS, may also be a reaction product of a reduced S phase and oven volatiles. The presence of H_2S supports the idea that reduced S was still present in the sample at the time of the highest T SO_2 peak.

Rocknest evolved H_2O: The shape of the H_2O traces are similar between the Rocknest samples (Fig. 1), though the intensity of the low T H_2O hump varies. There are many possible sources of the relatively large amount of water released at <500°C, as well as for the lower H_2O signal at higher Ts. Adsorbed H_2O, H_2O bound to x-ray amorphous phases (e.g., amorphous aluminosilicate materials, nanophase ferric oxides/oxyhydroxides) or interlayer H_2O from expandable phyllosilicates, could contribute to the lower T water, as could the dehydration of several salts (e.g. sulfate phases (Fig. 4)), though the lack of CheMin detection of phyllosilicates or hydrated sulfates suggests that any water from those potential sources is comparatively minor. Higher T H_2O could be due to more tightly bound structural H_2O and OH in minor minerals present below the CheMin detection limit (e.g., from some phyllosilicates), as well as H_2O occluded in minerals (e.g., fluid inclusions in sulfate salts).

Discussion: To date, no sulfides or sulfates other than minor anhydrite have been detected by CheMin [5]. This implies their abundance is <1-2 wt. %. Another consideration is that SO_2 could be evolved from X-ray amorphous materials (e.g., sulfate-adsorbed allophane shown in Fig. 2, X-ray amorphous sulfates, etc.). The presence of S-bearing phases is also indicated by APXS analyses of bulk Rocknest soil [6].

Even small amounts of sulfates in soil fines at Gale indicate some aqueous alteration, and could be relevant to the potential for preservation of any organic compounds. Sulfides can be indicative of comparatively reducing conditions, and in general more reducing environments are better for organic preservation. The possibility of both reduced and oxidized sulfur compunds together in the Rocknest soils may play a key part in unraveling the provenance of the soil fines.

References:

[1] Sutter et al. (2013a) *LPSC XLIV*. [2] Sutter et al. (2013b) *LPSC XLIV*. [3] Archer et al. (2013) *LPSC XLIV*. [4] Bhargava et al. (2009) *Fuel*, *88*, 988. [5] Bish et al. (2013) *LPSC XLIV*. [6] Morris et al. (2013) *LPSC XLIV*.

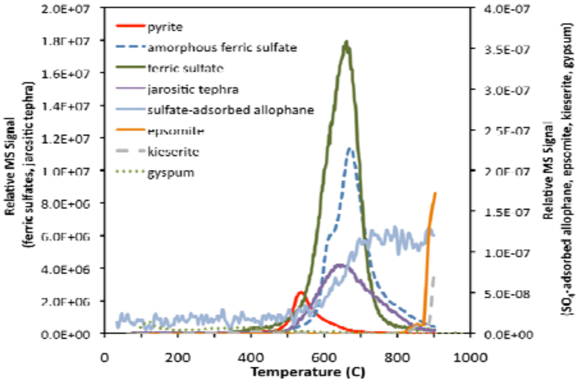

Figure 2. SAM-like EGA-MS SO_2 traces from several sulfur phase reference materials, for comparison with Rocknest data.

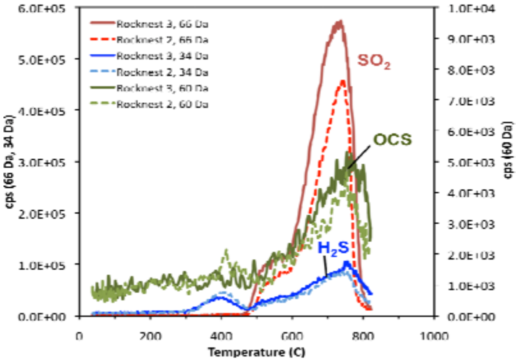

Figure 3. Representative SAM EGA-MS traces attributable to SO_2, H_2S, and OCS from Rocknest sample analyses.

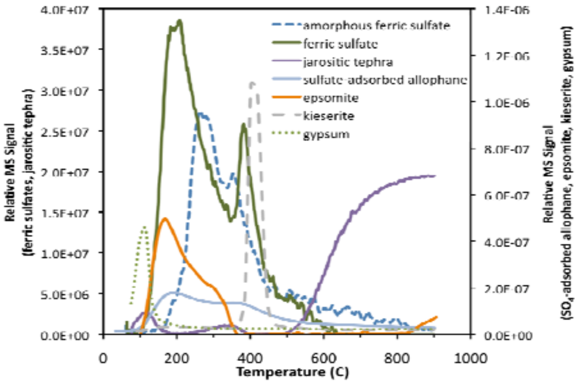

Figure 4. SAM-like EGA-MS H_2O traces from several sulfur phase reference materials, for comparison with Rocknest data.