

## REDUCED AND OXIDIZED SULFUR COMPOUNDS DETECTED BY EVOLVED GAS ANALYSES OF MATERIALS FROM YELLOWKNIFE BAY, GALE CRATER, MARS.

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**Introduction:** Sulfate minerals have been directly detected or strongly inferred from several Mars datasets and indicate that aqueous alteration of martian surface materials has occurred. Indications of reduced sulfur phases (e.g., sulfides) from orbital and in situ investigations of martian materials have been fewer in number, but these phases are observed in martian meteorites and are likely because they are common minor phases in basaltic rocks. Here we discuss potential sources for the S-bearing compounds detected by the Mars Science Laboratory (MSL) Sample Analysis at Mars (SAM) instrument's evolved gas analysis (EGA) experiments.

**Methods:** Several portions of sample fines from an aeolian bedform termed Rocknest ("RN") and samples drilled from the Sheepbed mudstone at sites named John Klein ("JK") and Cumberland ("CB") were investigated by the MSL SAM and Chemistry and Mineralogy X-ray diffraction/X-ray fluorescence (CheMin) instruments. SAM's EGA detected H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, HCl, NO, OCS, CS<sub>2</sub> and other trace gases. The gases evolved and temperature (T) of evolution can support mineral detection by CheMin and provide information on any trace volatile-bearing phases or amorphous phases which are difficult to characterize with CheMin XRD.

For SAM EGA analyses, delivered sample fines were heated to ~865°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 ~25 mb and the flow rate was ~0.8 standard cubic centimeters per minute. SAM-like EGA laboratory systems were used to characterize analog samples under SAM-like conditions (carrier gas, gas flow and gas pressure conditions, T range and heating ramp rate).

**Results and Discussion:** During EGA, SO<sub>2</sub> and H<sub>2</sub>S were released from the RN [1], JK and CB [2] samples. The JK and CB mudstone samples evolved less SO<sub>2</sub> than RN and exhibited a lower SO<sub>2</sub>/H<sub>2</sub>S ratio [2]. All samples evolved SO<sub>2</sub> and H<sub>2</sub>S over a 500-800°C range, but JK and CB exhibited an additional SO<sub>2</sub> evolution near 300°C (Fig. 1). CheMin analyses revealed ~1 wt% pyrrhotite (and possibly <1 wt % pyrite in JK), and several wt% Ca sulfates (bassanite,

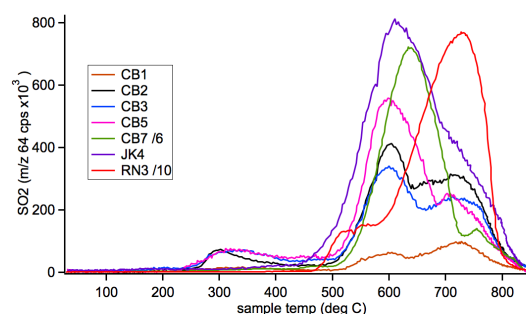


Figure 1. Representative SAM EGA-MS SO<sub>2</sub> traces from RN, JK, and CB subsamples.

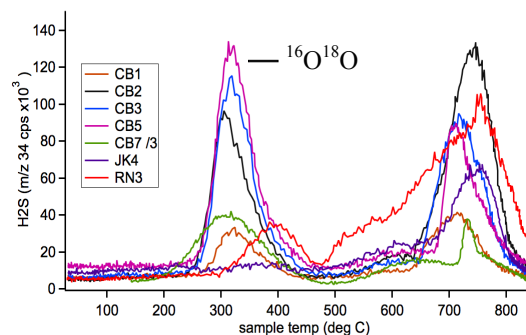


Figure 2. Representative SAM EGA-MS m/z 34 traces attributable to H<sub>2</sub>S from RN, JK and CB at high T. **NOTE:** The ~350°C peak in the m/z 34 traces is coincident with the large O<sub>2</sub> peak evolved from the samples and results from the O<sub>2</sub> isotopologue (<sup>16</sup>O<sup>18</sup>O), not H<sub>2</sub>S.

anhydrite) in CB and JK [3]. In RN, the only S-bearing phase detected by CheMin was anhydrite [4]. Thermal decomposition of Ca-sulfates typically occurs at temperatures above those reached by SAM (>865°C), although it may be possible to release some SO<sub>2</sub> from Ca-sulfates at lower temperatures by reaction with other sample species in the SAM oven during heating. At the time of writing of this abstract this possibility is currently being investigated with laboratory SAM-like EGA studies. Reaction of sulfides with gases evolved from the sample, and/or with other solid sample components, during SAM heating are a likely source of the JK and CB SO<sub>2</sub> (and H<sub>2</sub>S, see below). The CB and JK samples' SO<sub>2</sub> evolution near 300°C is coincident with a major O<sub>2</sub> evolution attributed to the decomposition of an oxychlorine phase [1,5]. This SO<sub>2</sub> likely results

from partial oxidation of the sulfide by the O<sub>2</sub> during heating, and SAM-like EGA-MS of pyrrhotite/Caperchlorate mixtures exhibit both <500°C SO<sub>2</sub> as well as higher T SO<sub>2</sub> generally consistent with the 500-800°C release. Ongoing work with additional sulfides and perchlorate/chlorate phases will be discussed.

Although all the CB and JK samples evolve SO<sub>2</sub> from 500-800°C, there are generally two wide peaks, one near 600°C and one near 700-750°C. CB and JK H<sub>2</sub>S traces exhibit these two peaks as well, but the ~600°C peak is much lower intensity than the ~700-750°C peak (Fig. 2). H<sub>2</sub>S is likely produced from the interaction of evolved H<sub>2</sub>O, H<sub>2</sub> and/or HCl with reduced sulfur phases in the SAM oven, and/or produced from the reaction of SO<sub>2</sub> and H<sub>2</sub>. The larger 700-750°C H<sub>2</sub>S peaks are coincident with the high T H<sub>2</sub>O evolution from the dehydroxylation of CB and JK smectites [2] and the high T H<sub>2</sub> evolved from CB and JK [2,7]. SAM-like EGA of some sulfide/smectite mixtures exhibit ~700°C evolution of H<sub>2</sub>S coincident with high T dehydroxylation H<sub>2</sub>O evolution. SAM-like EGA studies of additional sulfide/smectite mixtures, and mixtures of sulfides and Cl sources (e.g., chlorides, akaganite), will be reported.

At high T, very small abundances (nmol to sub-nmol levels) of OCS, and in some cases CS<sub>2</sub>, are also evolved from all samples, approximately coincident with H<sub>2</sub>S evolution at ~700-750°C. OCS and CS<sub>2</sub> are probably produced by reactions of CO<sub>2</sub>, CO or reduced carbon and reduced sulfur at high temperature. CO<sub>2</sub> or CO could originate from decomposition of trace calcite and CO<sub>2</sub>, CO or reduced C could result from partial decomposition of organic compounds [8] from meteoritic, or possibly from indigenous martian, sources [10].

If all sulfur evolved from CB and JK (in SO<sub>2</sub> + H<sub>2</sub>S) is assumed to originate from pyrrhotite, the amount of pyrrhotite calculated (assuming a 50 mg SAM sample [1]), is ~0.1-0.4 wt%. This is less than the ~1 wt% estimated from CheMin analyses [3], which may indicate only partial oxidation/reaction of sulfides to produce the evolved S-compounds observed in EGA runs. An experiment in which SAM reheated a previously heated CB subsample is also consistent with this. On initial heating, the S-compound evolution observed was as discussed earlier. On reheat, the only major volatiles evolved were SO<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub> suggesting that some sample sulfur compounds remained after the first heating. While their EGA traces did not display distinct peaks, H<sub>2</sub>O and HCl were also present at significant background levels with a slight decrease in this background at high temperatures.

Several Fe-sulfates evolve SO<sub>2</sub> in a 500-800°C T range (e.g., ferric sulfate), but the implied acidic formation conditions are generally inconsistent with the

circumneutral pH formation/post-formation environments indicated by the mudstone mineralogy. Some sulfites are consistent with the 500-800°C SO<sub>2</sub> evolution and with near neutral pH conditions.

As in RN fines [9], there is evidence that a fraction of JK and CB sulfur is associated with an X-ray amorphous phase that does not decompose in the SAM T range. If SAM-derived SO<sub>3</sub> abundances (JK: ~0.4 wt%; CB: ~0.2 wt% [2]) and CheMin-derived SO<sub>3</sub> abundances [3] (JK: ~3.4 wt%; CB: ~1.8 wt%) are subtracted from APXS-derived bulk SO<sub>3</sub> abundances (JK: ~5.94 wt%; CB: ~2.57 wt% [10]), ~2.1 wt% and 0.6 wt% remain for JK and CB respectively. This is consistent with the ~30 wt% amorphous material detected in JK and CB by CheMin [3] and with preliminary SAM-like EGA of synthetic SO<sub>4</sub><sup>2-</sup>adsorbed allophane and npOx samples by Rampe and Morris [in prep] which has shown that SO<sub>2</sub> can evolve over a range of high temperatures >865°C. It is also supported by the adsorption of sulfate onto iron oxides and other soil phases observed in terrestrial environments [e.g., 11]. The S-rich alteration environment [e.g., 12] and widespread fine-grained Fe-rich material on Mars may facilitate the adsorption of S-anions onto soil materials.

**Implications:** SAM EGA data from JK and CB are consistent with a significant amount of the evolved S-species being derived from oxidation/reaction of sulfides, though some likely derive from more oxidized S-compounds such as sulfates or sulfites, and analysis of relevant analogs in SAM-like systems is currently underway. In addition, mass balance calculations between APXS, CheMin and SAM data suggest that some S is associated with the ~30 wt% X-ray amorphous material. Although Ca sulfates in veins in the Sheepbed mudstone were likely precipitated from more oxidizing diagenetic fluids, the presence of sulfides (and also magnetite) indicate that the bulk rock remained relatively reduced. Reducing environments are generally favorable for organic preservation, and an organic C source of some of the C in OCS and CS<sub>2</sub> released from JK and CB cannot be ruled out.

**References:** [1] Leshin L.A. et al. (2013) *Science*, 341(6153), doi:10.1126/science.1238937. [2] Ming D.W. et al. (2013) *Science*, doi:10.1126/science.1245267. [3] Vaniman D.T. et al. (2013) *Science*, doi: 10.1126/science.1243480. [4] Bish D.L. et al. (2013) *Science*, 341(6153), doi:10.1126/science.1238932. [5] Glavin D.P. et al. (2013) *JGR*, 118, 1955. [6] Bruck et al. (2014) *LPS XLV*. [7] Brunner A. et al. (2014) *LPS XLV*. [8] Eigenbrode et al. (2014) *LPS XLV*. [9] McAdam A.C. et al. (2013) *JGR*, 119, doi:10.1002/2013JE004518. [10] McLennan S.M. et al. (2013) *Science*, doi: 10.1126/science.1244734. [11] Aylmore, L.A.G. et al. (1967) *Soil Science*, 103, 10. [12] McLennan, S.M. and Grotzinger, J.P. (2008) Cambridge Univ. Press, pp. 541-577.