

**SULFUR-BEARING COMPOUNDS DETECTED BY MSL SAM EVOLVED GAS ANALYSIS OF MATERIALS FROM YELLOWKNIFE BAY, GALE CRATER, MARS.** A. C. McAdam<sup>1</sup>, H. B. Franz<sup>1,2</sup>, P. D. Archer, Jr.<sup>3</sup>, B. Sutter<sup>3</sup>, J. L. Eigenbrode<sup>1</sup>, C. Freissinet<sup>1</sup>, S. K. Atreya<sup>4</sup>, D. L. Bish<sup>5</sup>, D. F. Blake<sup>6</sup>, A. Brunner<sup>1</sup>, P. R. Mahaffy<sup>1</sup>, D. W. Ming<sup>3</sup>, R. V. Morris<sup>3</sup>, R. Navarro-Gonzalez<sup>7</sup>, E. B. Rampe<sup>3</sup>, A. Steele<sup>8</sup>, J. J. Wray<sup>9</sup> and the MSL Science Team. <sup>1</sup>NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, <sup>2</sup>Univ. of Maryland, Baltimore, MD 21228, <sup>3</sup>NASA Johnson Space Center, Houston, TX, 77058, <sup>4</sup>Univ. of Michigan, Ann Arbor, MI, <sup>5</sup>Dept. of Geological Sci., Indiana Univ., Bloomington, IN 47405, <sup>6</sup>NASA Ames Research Center, Moffett Field, CA 94035, <sup>7</sup>Universidad Nacional Autónoma de México, México, D.F. 04510, <sup>8</sup>Carnegie Institution of Washington, Washington DC, <sup>9</sup>Georgia Inst. of Tech., GA 30332.

**Introduction:** The Sample Analysis at Mars (SAM) and Chemistry and Mineralogy (CheMin) instruments on the Mars Science Laboratory (MSL) analysed several subsamples of sample fines (<150 µm) from three sites in Yellowknife Bay, an aeolian bedform termed Rocknest (hereafter “RN”) and two samples drilled from the Sheepbed mudstone at sites named John Klein (“JK”) and Cumberland (“CB”). SAM’s evolved gas analysis (EGA) mass spectrometry 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 identity of 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). Here, we focus on potential constraints on phases that evolved SO<sub>2</sub>, H<sub>2</sub>S, OCS, and CS<sub>2</sub> during thermal analysis.

**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 ~0.8 standard cubic centimeters per minute. The SAM breadboard and other SAM-like EGA-MS laboratory systems 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).

**Results and Discussion:** SO<sub>2</sub> and H<sub>2</sub>S were released from the RN (SO<sub>2</sub>: ~3-23 µmol; H<sub>2</sub>S: ~41-109 nmol) [1], JK (SO<sub>2</sub>: ~1.4-2.9 µmol; H<sub>2</sub>S: ~36-95 nmol) and CB (SO<sub>2</sub>: ~0.4-1.4 µmol; H<sub>2</sub>S: ~18-67 nmol) [2] samples during EGA. 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]. Overall, the CB and JK, as well as RN, samples exhibited SO<sub>2</sub> and H<sub>2</sub>S evolution 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 (basanite, anhydrite) in CB and JK [3]. In RN, the only S-bearing phase detected by CheMin was anhydrite [4]. Thermal decomposition of the Ca-sulfates are not likely responsible for evolved SO<sub>2</sub> because they typi-

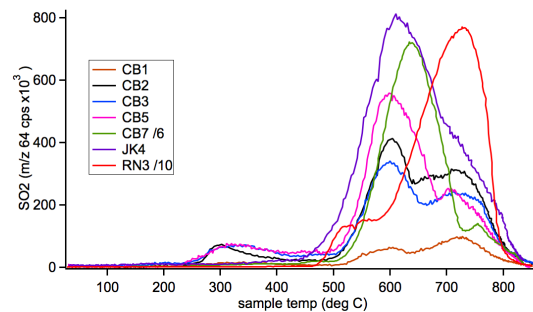


Figure 1. Representative SAM EGA-MS SO<sub>2</sub> traces from RN, JK, and CB subsamples.

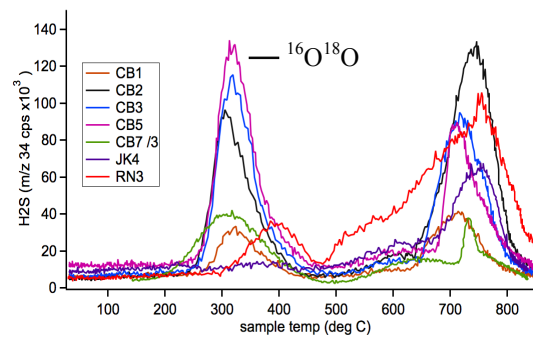


Figure 2. Representative SAM EGA-MS m/z 34 traces attributable to H<sub>2</sub>S from RN, JK and CB at high T. **NOTE:** The ~350 °C peak in the m/z 34 traces is coincident with the large O<sub>2</sub> peak evolved from the samples and results from the O<sub>2</sub> isotopologue (<sup>16</sup>O<sup>18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

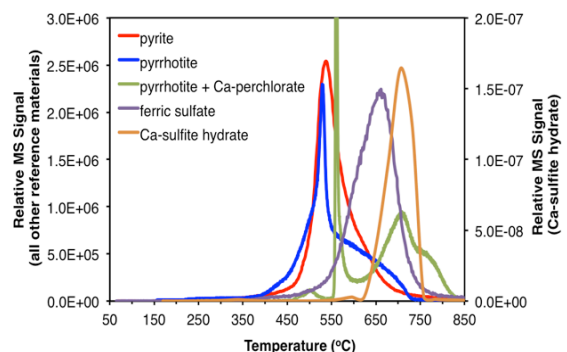


Figure 3. SAM-like EGA-MS SO<sub>2</sub> traces from S-phase reference materials and S-phase containing mixtures.

cally decompose at temperatures above those reached by SAM (>835 °C). The sulfides, however, 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 from the samples attributed to the breakdown 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/Ca-perchlorate 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. The lower T SO<sub>2</sub> was released from the analog mixtures at a higher T (~450 °C) than CB and JK (~300 °C) and this is likely due to a different oxychlorine phase in the martian samples which evolves O<sub>2</sub> at a lower T or reactions occurring within the SAM oven with other samples phases (e.g., Fe-oxide phases [6]) which result in a lower T O<sub>2</sub> release.

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 the 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]. Also, ~700 °C evolution of H<sub>2</sub>S has been observed from SAM-like EGA of sulfide/smectite mixtures coincident with high T dehydroxylation H<sub>2</sub>O evolution (data not shown). The reaction of H<sub>2</sub> with SO<sub>2</sub> is generally favored at high T [e.g., 8], as well.

Very small abundances (nmol to sub-nmol levels) of OCS, and in some cases CS<sub>2</sub>, are also evolved from CB and JK (and RN) samples at high T, approximately coincident with the ~700-750 °C evolution of H<sub>2</sub>S. OCS and CS<sub>2</sub> are probably products of reactions involving a carbon source such as 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 [9] 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, which may indicate only partial oxidation/reaction of sulfides to produce the evolved S-compounds. It also indicates that contributions to the S-volatiles evolved in the SAM T range from other sample sulfur phases are likely very minor. Several Fe-sulfates evolve SO<sub>2</sub> in a 500-800 °C T range (e.g., ferric sulfate (Fig. 3)), but

the implied acidic formation conditions are generally inconsistent with the rest of the mudstone mineral assemblage that indicates circumneutral pH formation/post-formation environments. Some sulfites are consistent with the 500-800 °C SO<sub>2</sub> evolution (e.g., Ca-sulfite, Fig. 3) and with near neutral pH conditions.

As in RN fines [10], 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% [11]), ~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 >835 °C. It is also supported by the commonly observed adsorption of sulfate onto iron oxides and other soil phases in terrestrial environments [e.g., 12]. The proposed S-rich alteration environment [e.g., 13] and ubiquitous fine-grained Fe-rich material on Mars may be comparatively more likely to have S-anions adsorbed onto soil materials.

**Implications:** SAM EGA data from JK and CB are consistent with evolved S-species derived dominantly from sulfides, although mass balance calculations between APXS, CheMin and SAM data suggest that some S is associated with the ~30 wt% X-ray amorphous material detected by CheMin. Although more oxidizing diagenetic fluids were likely responsible for the precipitation of Ca-sulfates in veins in the Sheepbed mudstone, 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 during pyrolysis of 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] Arutyunov, V.S. et al. (1991) *Kinetics and Catalysis*, 32, 1112. [9] Eigenbrode et al. (2014) *LPS XLV*. [10] McAdam A.C. et al. (2013) *JGR*, in revision. [11] McLennan S.M. et al. (2013) *Science*, doi: 10.1126/science.1244734. [12] Aylmore, L.A.G. et al. (1967) *Soil Science*, 103, 10. [13] McLennan, S.M. and Grotzinger, J.P. (2008) Cambridge Univ. Press, pp. 541-577.