

SULFUR-BEARING COMPOUNDS DETECTED BY MSL SAM EVOLVED GAS ANALYSIS OF MATERIALS FROM YELLOWKNIFE BAY, GALE CRATER, MARS. A. C. McAdam¹, H. B. Franz^{1,2}, P. D. Archer, Jr.³, B. Sutter³, J. L. Eigenbrode¹, C. Freissinet¹, S. K. Atreya⁴, D. L. Bish⁵, D. F. Blake⁶, A. Brunner¹, P. R. Mahaffy¹, D. W. Ming³, R. V. Morris³, R. Navarro-Gonzalez⁷, E. B. Rampe³, A. Steele⁸, J. J. Wray⁹ and the MSL Science Team. ¹NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, ²Univ. of Maryland, Baltimore, MD 21228, ³NASA Johnson Space Center, Houston, TX, 77058, ⁴Univ. of Michigan, Ann Arbor, MI, ⁵Dept. of Geological Sci., Indiana Univ., Bloomington, IN 47405, ⁶NASA Ames Research Center, Moffett Field, CA 94035, ⁷Universidad Nacional Autónoma de México, México, D.F. 04510, ⁸Carnegie Institution of Washington, Washington DC, ⁹Georgia 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 bed-form 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 H₂O, CO₂, O₂, H₂, SO₂, H₂S, HCl, NO, OCS, CS₂ 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 SO₂, H₂S, OCS, and CS₂ 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: SO₂ and H₂S were released from the RN (SO₂: ~3-23 µmol; H₂S: ~41-109 nmol) [1], JK (SO₂: ~1.4-2.9 µmol; H₂S: ~36-95 nmol) and CB (SO₂: ~0.4-1.4 µmol; H₂S: ~18-67 nmol) [2] samples during EGA. The JK and CB mudstone samples evolved less SO₂ than RN and exhibited a lower SO₂/H₂S ratio [2]. Overall, the CB and JK, as well as RN, samples exhibited SO₂ and H₂S evolution over a 500-800 °C range, but JK and CB exhibited an additional SO₂ 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 SO₂ because they typi-

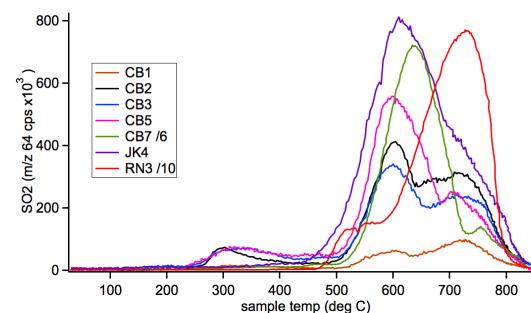


Figure 1. Representative SAM EGA-MS SO₂ traces from RN, JK, and CB subsamples.

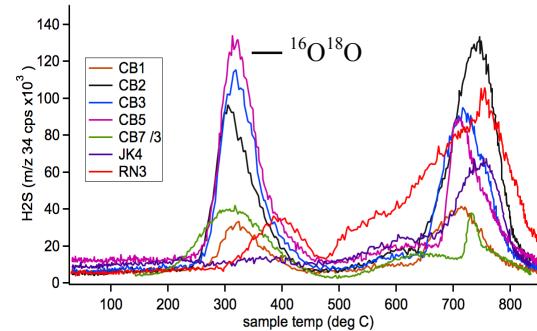


Figure 2. Representative SAM EGA-MS m/z 34 traces attributable to H₂S from RN, JK and CB at high T.

NOTE: The ~350 °C peak in the m/z 34 traces is coincident with the large O₂ peak evolved from the samples and results from the O₂ isotopologue (¹⁶O¹⁸O), not H₂S.

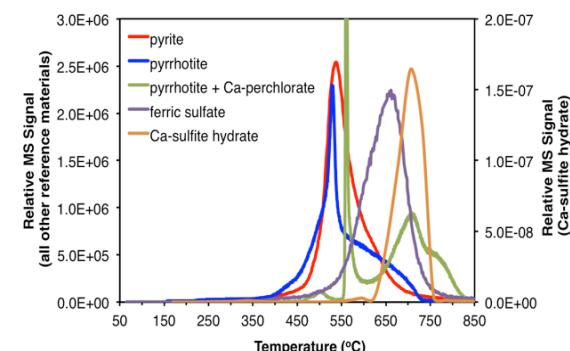


Figure 3. SAM-like EGA-MS SO₂ traces from S-phase reference materials and S-phase containing mixtures.

cally decompose at temperatures above those reached by SAM (>835 °C). The sulfides, however, are a likely source of the JK and CB SO₂ (and H₂S, see below).

The CB and JK samples' SO₂ evolution near 300 °C is coincident with a major O₂ evolution from the samples attributed to the breakdown of an oxychlorine phase [1,5]. This SO₂ likely results from partial oxidation of the sulfide by the O₂ during heating, and SAM-like EGA-MS of pyrrhotite/Ca-perchlorate mixtures exhibit both <500 °C SO₂ as well as higher T SO₂ generally consistent with the 500-800 °C release. The lower T SO₂ 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 O₂ 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 O₂ release.

Although all the CB and JK samples evolve SO₂ from 500-800 °C, there are generally two wide peaks, one near 600 °C and one near 700-750 °C. CB and JK H₂S traces exhibit these two peaks as well, but the ~600 °C peak is much lower intensity than the ~700-750 °C peak (Fig. 2). H₂S is likely produced from the interaction of evolved H₂O, H₂ and/or HCl with the reduced sulfur phases in the SAM oven, and/or produced from the reaction of SO₂ and H₂. The larger 700-750 °C H₂S peaks are coincident with the high T H₂O evolution from the dehydroxylation of CB and JK smectites [2] and the high T H₂ evolved from CB and JK [2,7]. Also, ~700 °C evolution of H₂S has been observed from SAM-like EGA of sulfide/smectite mixtures coincident with high T dehydroxylation H₂O evolution (data not shown). The reaction of H₂ with SO₂ 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 CS₂, are also evolved from CB and JK (and RN) samples at high T, approximately coincident with the ~700-750 °C evolution of H₂S. OCS and CS₂ are probably products of reactions involving a carbon source such as CO₂, CO or reduced carbon and reduced sulfur at high temperature. CO₂ or CO could originate from decomposition of trace calcite and CO₂, 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 SO₂ + H₂S) 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 SO₂ 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 SO₂ 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 SO₃ abundances (JK: ~0.4 wt%; CB: ~0.2 wt% [2]) and CheMin-derived SO₃ abundances [3] (JK: ~3.4 wt%; CB: ~1.8 wt%) are subtracted from APXS-derived bulk SO₃ 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 SO₄²⁻adsorbed allophane and npOx samples by Rampe and Morris [in prep] which has shown that SO₂ 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 CS₂ 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.