

EVOLVED GAS ANALYSES OF SEDIMENTARY MATERIALS IN GALE CRATER, MARS: RESULTS OF THE CURIOSITY ROVER'S SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT FROM YELLOWKNIFE BAY TO THE STIMSON FORMATION. B. Sutter^{1,2}, A.C. McAdam³, E.B. Rampe^{1,2}, D.W. Ming², P.R. Mahaffy³, R. Navarro-Gonzalez⁴, J.C. Stern³, J.L. Eigenbrode³, P.D. Archer^{1,2}. ¹Jacobs, Houston, TX 77058, brad.sutter-2@nasa.gov, ²NASA/JSC Houston, TX 77058, ³NASA/GFSC, Greenbelt, MD 20771. ⁴Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico

Introduction: The Sample Analysis at Mars (SAM) instrument aboard the Mars Science Laboratory rover has analyzed 10 samples from Gale Crater. All SAM-evolved gas analyses have yielded a multitude of volatiles (e.g. H₂O, SO₂, H₂S, CO₂, CO, NO, O₂, HCl) [1,2,3,4,5]. The objectives of this work are to 1) Characterize the evolved H₂O, SO₂, CO₂, and O₂ gas traces of sediments analyzed by SAM through sol 1178, 2) Constrain sediment mineralogy/composition based on SAM evolved gas analysis (SAM-EGA), and 3) Discuss the implications of these results relative to understanding the geochemical history of Gale Crater.

Materials & Methods: Rocknest (RN) is an eolian drift material that occurs 50 m from the John Klein (JK) and Cumberland (CB) lacustrine mudstones. Windjana (WJ) is a fluvial sandstone stratigraphically higher and located 4 km to the SW of JK and CB. The Confidence Hills (CH), Mojave (MJ), Telegraph Peak (TP), and Buckskin (BK) fluvial/lacustrine mudstones occur above WJ near the base of Mt. Sharp. The unaltered Big Sky (BY) and altered Greenhorn (GH) materials are eolian sandstones that are above BK (Fig. 1). Rocknest was acquired with a scoop while the other samples were drilled (1.6 cm diameter x 6 cm deep) from sedimentary rock. All analyzed samples were sieved to less than 150 μm.

Samples delivered to the SAM oven were heated (~35 °C min⁻¹) from ambient to ~860°C. The evolved gases were swept from the oven by a He stream (~0.8 sccm; 25 mbar) to a quadrupole mass spectrometer (QMS) for identification. Evolved gases (e.g., H₂O, CO₂, etc.) released at characteristic temperatures from volatile bearing phases were used to identify mineral or organic phases.

Results/Discussion: Water – All samples contain H₂O (~1-2 wt.%, Fig. 1) and have releases <~450°C that can be attributed to atmospherically adsorbed water, structural water in amorphous phases, phyllosilicate interlayer H₂O, hydrated salts (e.g. bassanite, perchlorate, chlorate,), and/or akaganeite dehydroxylation [1]. The 450-500°C peaks in the CH, MJ, and TP traces can be attributed to H₂O from dehydroxylation of jarosite detected by CHEMIN [7]. The 750-800°C peaks in CB, JK, and MJ traces result from smectite dehydroxylation [2]. The wide >~500°C peak in BK, BY, and GH can be attributed to glass matrix, vesicle, and/or trapped magmatic water in x-ray amorphous phases (e.g., volcanic

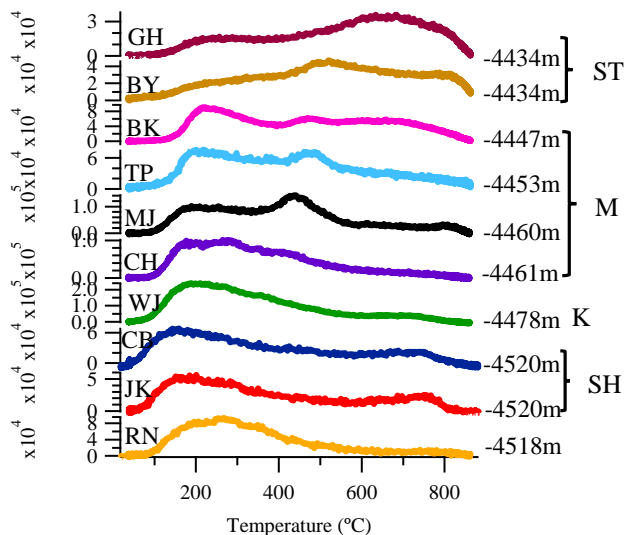


Figure 1. Evolved water detected by SAM-EGA. Elevation and sedimentary rock units are designated: Sheepbed mudstone (SH), Kimberly sandstone (K), Murray mudstone (M), Stimson sandstone (ST).

glass) [8].

SO₂ - Sulfur dioxide was mostly released above 500°C (Fig. 2). More SO₂ evolved from WJ, Murray Formation (CH, MJ, TP, BK), and altered Stimson (GH) (2.6 to 6.5 wt.% SO₃) than Sheepbed Mudstone (CB, JK) and less altered Stimson (BY) (0.2-0.7 wt.% SO₃) samples.. The SO₂ release temperatures are consistent with Fe- or Al-sulfates but the non-detection of Fe or Al sulfates by CheMin in RN, WJ, BY, and GH suggest that these sediments contain amorphous or trace crystalline Fe and/or Al sulfate or adsorbed sulfate [3,9,10]. CheMin detection of sulfides in JK and CB suggest that partial Fe-sulfide oxidation to Fe-sulfate may have released SO₂. Some SO₂ evolved from in CH, MJ, and TP is attributed to the thermal decomposition of jarosite detected by CheMin [7]. Jarosite cannot account for all of the evolved SO₂; thus some SO₂ could be derived from amorphous Fe/Al sulfates. CB exhibited a low SO₂ release at ~300°C (Fig. 2), which is coincident with O₂ evolution from oxychlorine thermal decomposition (not shown) and likely resulted from sulfide oxidation directly to SO₂. Another possible source of evolved SO₂ in some sediments (e.g., RN, JK, CB, GH) could be

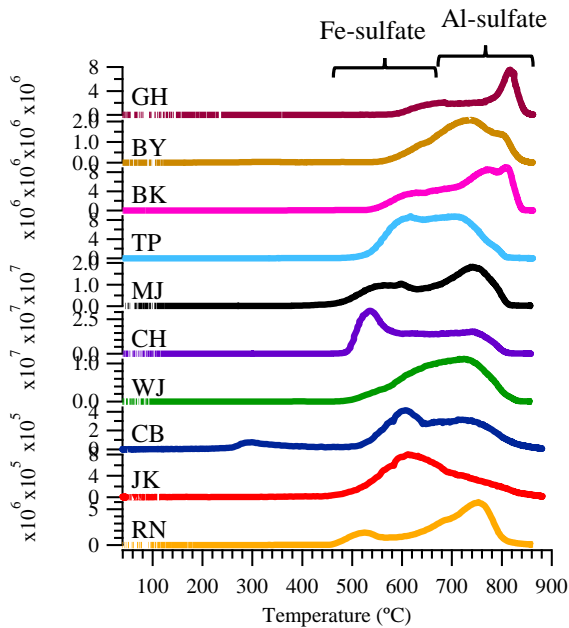


Fig. 2. Evolved SO_2 detected by SAM-EGA.

through catalytic reactions of Ca- and/or Mg-sulfate with other minerals in Gale Crater sediments [11].

CO₂ – CO₂ releases have been detected over the entire SAM temperature range (Fig. 3). Atmospherically adsorbed CO₂ and SAM background decomposition products are candidates for CO₂ evolved at <200°C. All samples exhibit CO₂ releases between 200 and 450°C which could be contributions from SAM background and/or martian organics. However, oxalate derived from meteoritic sources could also evolve CO₂ between 200 and 700°C [12]. CO₂ releases between 500 and 700°C are also consistent with carbonates in RN, TP, and GH. Subtle CO₂ releases >700°C are candidates for a refractory organic source in RN, CH, MJ, BK, BY, and GH [13].

O₂ – All samples evolve O₂ below 550°C with three sediments (CH, MJ, BK) yielding O₂ releases above 600°C (Fig.4). All O₂ releases below 550°C are attributed to oxychlorine (e.g., chlorate/perchlorate) decomposition while sulfate thermal decomposition is likely providing O₂ above 600°C. The variation of O₂ release temperatures below 500°C is likely caused by variation in oxychlorine cations and/or variation in mineral species that catalyzed oxychlorine thermal decomposition.

Conclusions: SAM-EGA results demonstrate that Gale Crater sediments have been exposed to alkaline (phyllosilicates, carbonates) and acidic solutions (Fe-/Al-sulfate). Despite the presence of highly oxidized minerals (chlorates/perchlorates), CO₂ evolution temperatures are consistent with the persistence of carbon oxidation states ranging from reduced carbon in Gale Crater sediments though oxidized C (oxalates, carbonates). These results demonstrate that despite oxidizing/acidic geochemistry, the preservation of reduced organic biosignatures on Mars is possible.

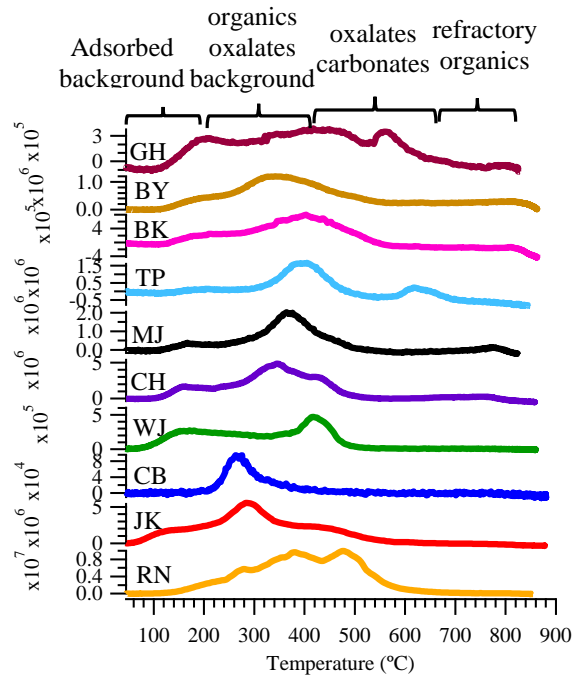


Fig. 3. Evolved CO_2 detected by SAM-EGA.

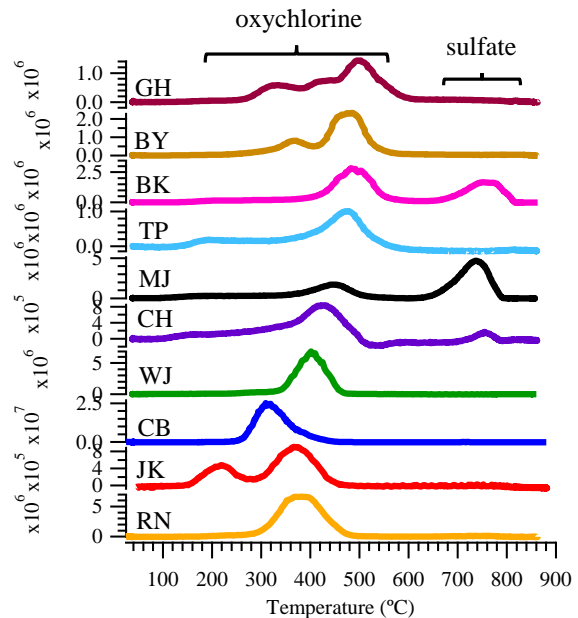


Fig. 4. Evolved O_2 detected by SAM-EGA

References: [1] Leshin, L.A. et al. (2013) *Science* 341. [2] Ming, D.W. et al. (2014) *Science* 343. [3] McAdam, A.C., et al. (2014) *J.G.R. Planet.*, 119, 373. [4] Freissinet, C. et al., (2015) *J.G.R. Planet.*, 120, 495. [5] Stern, J.C. et al. (2015) *PNAS* 112, 4245. [6] Vaniman, D.T. et al., (2014), *Science* 343. [7] Rampe, E.B. et al. (2015), *AGUFall* #2689. [8] Westrich, 1987, *Chem. Geol.* 63, 335. [9] Frost, R.L., et al. 2006, *Thermochim.* 443, 56. [10] Rampe, E.B. et al. (2015), *LPSC* #2689. [11] McAdam, A.C. et al. (2016) *LPSC* this meeting. [12] Eigenbrode, J.L., et al. (2014) *LPSC* #1605. [13] Eigenbrode, J.L. et al. (2015) *AGUFall*