

EVOLVED GAS ANALYSES OF THE MURRAY FORMATION IN GALE CRATER, MARS: RESULTS OF THE CURIOSITY ROVER'S SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT. B. Sutter^{1,2}, A.C. McAdam³, E.B. Rampe², L.M. Thompson⁴, D.W. Ming², P.R. Mahaffy³, R. Navarro-Gonzalez⁵, 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 13 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) [1-6]. The objectives of this work are to 1) Characterize recent evolved SO₂, CO₂, O₂, and NO gas traces of the Murray formation mudstone, 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 geological history of Gale Crater.

Materials & Methods: The Murray formation is a lacustrine mudstone and the basal layer of Aeolis Mons (informally known as Mt. Sharp). Mudstone samples drilled and delivered to SAM include: Confidence Hills (CH, -4461 m elevation), Mojave (MJ, -4459 m), Telegraph Peak (TP, -4453 m), high-silica containing Buckskin (BK, -4447 m), Oudam (OU, -4436 m) a cross-stratified, potentially fluvial interval in Murray, and Marimba (MB, -4410 m). All samples were sieved to less than 150 μm before analysis by SAM. Samples were heated in the SAM oven (~35 °C min⁻¹) from ambient to ~870 °C where 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., SO₂, CO₂, etc.) released at characteristic temperatures from volatile bearing phases were used to identify mineral and/or organic phases.

Results/Discussion: SO₂ - The broad temperature (500-825 °C) of SO₂ release in CH, MJ, TP, and BK is consistent with Fe- and/or Mg-sulfates (Fig. 1) [6]. Some SO₂ evolved from CH, MJ, TP, and MB is attributed to the thermal decomposition of jarosite detected by CheMin [7]. Jarosite cannot account for all of the evolved SO₂; thus, the remaining SO₂ is consistent with amorphous Fe/Mg sulfates or a mixture of crystalline Fe/Mg-sulfates below the CheMin detection limits. The SO₂ release temperatures suggests that OU sulfur is dominated by Fe-sulfate while MB is dominated by Mg-sulfate (Fig. 1).

The Fe/Mg sulfate contents decrease upsection from CH to TP as indicated by the SAM-SO₃ contents (Fig. 1). The Ca-sulfate content increases upsection is indicated by the SAM-SO₃ contents being much lower than the APXS-SO₃ contents in OU and MB (Fig. 1). This demonstrates the dominance of Ca-SO₄ in OU and MB as Ca-SO₄ cannot be detected by SAM which is

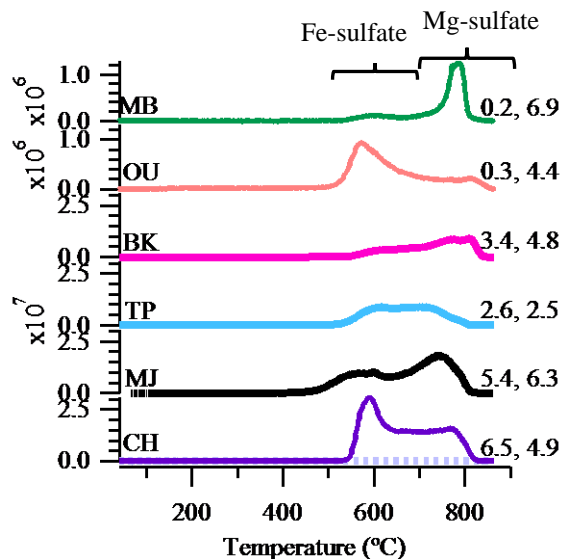


Fig. 1. Evolved SO₂ detected by SAM-EGA. wt. % SO₃ measured by SAM (left) and APXS (right) are indicated on right.

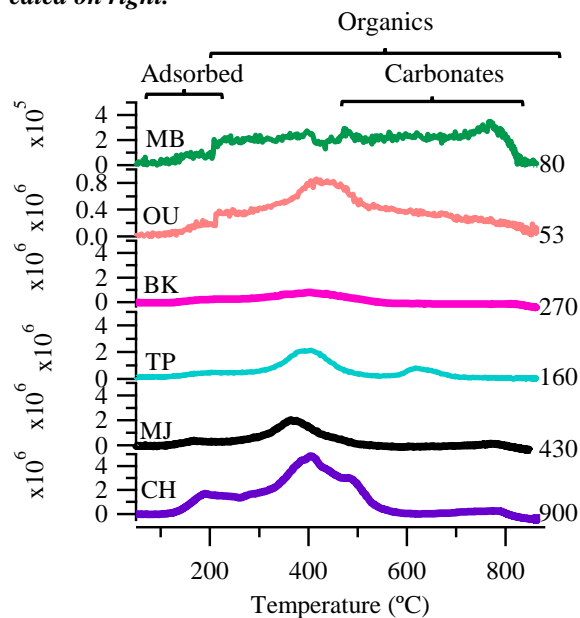


Fig. 2. Evolved CO₂ detected by SAM-EGA. ugC/g indicated along right side.

supported by CheMin detections of Ca-sulfate phases [8]. These results suggest that the diagenetic fluids had shifted from being saturated with respect to Mg/Fe-sulfates in the lower strata (CH, MJ, TP) to being saturated with respect to Ca-sulfate upsection (OU, MB).

CO₂ – CO₂ releases consistent with organic-C and carbonates have been detected over the entire SAM temperature range (Fig. 2). The majority of the CO₂ releases occur below 450°C and are attributed to organic-C sources. Some evolved CO₂ above 450°C is consistent with carbonate especially at 625°C in TP, though organic-C cannot be excluded. The presence of carbonate in TP demonstrates that carbonate was likely added after formation of acidic Fe-sulfate in TP. Similar to SO₂, the CO₂ contents decrease upsection between CH and TP. The CO₂ content, however, does peak in BK while the CO₂ content is the lowest in OU and MB.

NO – Nitrate contents were variable throughout the Murray with the highest content occurring in BK (Fig. 3). The intensity of the BK NO trace is similar to the CH-TP samples up to ~480°C and appears to have an overprinting peak at 525°C. This 525°C peak suggests a later addition of nitrate after BK was deposited. (Fig. 3). Similar to CO₂ contents, OU and MB had the lowest nitrate contents of the measured Murray sediments.

O₂ –All O₂ releases below 550°C are attributed to (per)chlorate decomposition while sulfate thermal decomposition is likely providing O₂ above 600°C in CH, MJ, and BK (Fig. 4). BK had the highest (per)chlorate content in Murray suggesting that like nitrate, additional (per)chlorate could have been added after BK deposition. The non-detection of (per)chlorate in OU and MB suggests as with nitrate, (per)chlorate fluid contents were much lower than what occurred in CH, MJ, TP and BK.

Murray Formation Processes: The SAM-EGA results demonstrate that the Murray samples have undergone complex alteration history. One scenario is that post-depositional downward leaching by fluids affected CH to BK resulted in the observed Fe/Mg sulfate and carbon distributions in CH, MJ, and TP [7]. Such leaching processes removed most of the highly soluble nitrate and (per)chlorate resulting in the observed variable nitrate and (per)chlorate contents. The highest carbon, nitrate and (per)chlorate contents in BK suggest after BK alteration, Greenhorn (GH) alteration fluids could have penetrated down into BK resulting in the addition of these constituents to BK. This is suggested by SAM-EGA similar detections of SO₂, NO, and O₂ in both GH and BK (data not shown). The OU and MB sediments appeared to be derived from sources that differed from the CH, MJ, TP, and BK sources as evidenced by their much lower carbon, nitrate, and (per)chlorate contents. Furthermore, the OU and MB samples were dominated by Ca-sulfate unlike the lower Murray samples which consisted of more Fe/Mg sulfate.

Conclusion: The CH, MJ, TP, and BK samples appear to have under undergone a complex alteration history involving post depositional leaching and addition of salts. The observed geochemical trends in OU and

MB are argued to reflect source mineralogies and depositional solution chemistries that differed from sources and fluids that affected the lower CH to BK sediments.

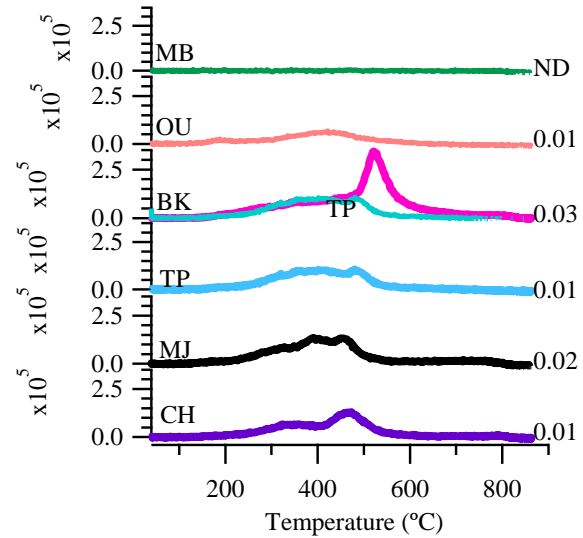


Fig. 3. Evolved NO detected by SAM-EGA. wt. % NO₃ indicated along right side.

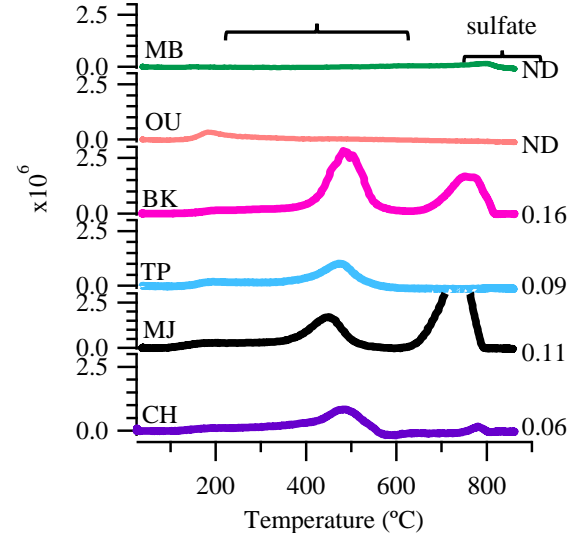


Fig. 4. Evolved O₂ detected by SAM-EGA. wt. % ClO₄ indicated along right side

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] Sutter et al. (2016) *JGR*, submitted. [7] Rampe, E.B. et al. (2016), *EPSL* submitted. [8] Vaniman, D.T. et al., 48th LPSC (this meeting).