

REACTIONS INVOLVING CALCIUM AND MAGNESIUM SULFATES AS POTENTIAL SOURCES OF SULFUR DIOXIDE DURING MSL SAM EVOLVED GAS ANALYSES. A.C. McAdam¹, C.A. Knudson^{1,2}, B. Sutter^{3,4}, H.B. Franz^{1,5}, P.D. Archer, Jr.^{3,4}, J.L. Eigenbrode¹, D.W. Ming³, R.V. Morris³, J.A. Hurowitz⁶, P.R. Mahaffy¹, R. Navarro-Gonzalez⁷, ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771, Amy.McAdam@nasa.gov, ²CRESST, Univ. of Maryland, College Park, MD 20742, ³NASA Johnson Space Center, Houston, TX, 77058, ⁴Jacobs, Houston, TX 77258, ⁵Univ. of Maryland, Baltimore, MD 21228, ⁶Stony Brook University, Stony Brook, NY 11794, ⁷Universidad Nacional Autónoma de México, México, D.F. 04510.

Introduction: The Sample Analysis at Mars (SAM) and Chemistry and Mineralogy (CheMin) instruments on the Mars Science Laboratory (MSL) have analysed several subsamples of <150 μm fines from ten sites at Gale Crater. Three were in Yellowknife Bay: the Rocknest aeolian bedform (RN) and drilled Sheepbed mudstone from sites John Klein (JK) and Cumberland (CB). One was drilled from the Windjana (WJ) site on a sandstone of the Kimberly formation. Four were drilled from sites Confidence Hills (CH), Mojave (MJ), Telegraph Peak (TP) and Buckskin (BK) of the Murray Formation at the base of Mt. Sharp. Two were drilled from sandstones of the Stimson formation targeting relatively unaltered (Big Sky, BY) and then altered (Greenhorn, GH) material associated with a light colored fracture zone [1]. CheMin analyses provided quantitative sample mineralogy. SAM's evolved gas analysis mass spectrometry (EGA-MS) detected H_2O , CO_2 , O_2 , H_2 , SO_2 , H_2S , HCl , NO , and other trace gases. This contribution will focus on evolved SO_2 .

All samples evolved SO_2 above 500°C. The shapes of the SO_2 evolution traces with temperature vary between samples but most have at least two "peaks" within the wide high temperature evolution, from ~500-700 and ~700-860°C (Fig. 1). In many cases, the only sulfur minerals detected with CheMin were Ca sulfates (e.g., RN and GH), which should thermally decompose at temperatures above those obtainable by SAM (>860°C). Sulfides or Fe sulfates were detected by CheMin (e.g., CB, MJ, BK) and could contribute to the high temperature SO_2 evolution, but in most cases they are not present in enough abundance to account for all of the SO_2 . This additional SO_2 could be largely associated with x-ray amorphous material, which comprises a significant portion of all samples. It can also be attributed to trace S phases present below the CheMin detection limit, or to reactions which lower the temperatures of SO_2 evolution from sulfates that are typically expected to thermally decompose at temperatures outside the SAM temperature range (e.g., Ca and Mg sulfates). Here we discuss the results of SAM-like laboratory analyses targeted at understanding this last possibility, focused on understanding if reactions of HCl or an HCl evolving phase (oxychlorine phases,

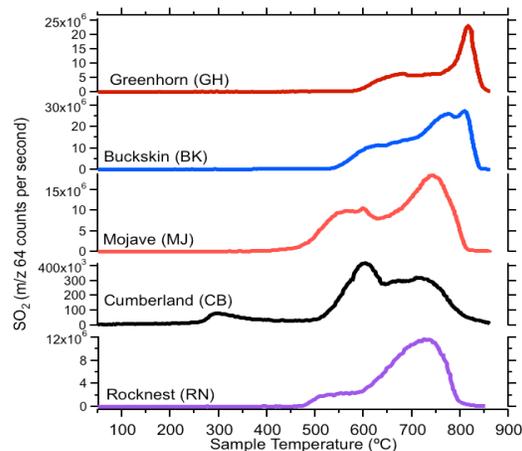


Figure 1. SO_2 EGA traces from several SAM analyses.

chlorides, etc.) and Ca and Mg sulfates can result in SO_2 evolution in the SAM temperature range.

Methods: For SAM EGA-MS analyses, sample fines were heated to ~860°C at 35°C/min. Evolved gases were carried by an He carrier gas to the SAM MS where they are detected by their mass-to-charge (m/z) ratio (e.g., SO_2 is m/z 64). The pressure of He in the oven was ~25 mb and the flow rate was ~0.8 standard cubic centimeters per minute. For SAM-like laboratory analyses, an Agilent EGA-MS system consisting of a Frontier PY-3030 pyrolyzer attached to a 5975C inert XL MS was used. The pyrolyzer was ramped at 35°C/min to 1050°C, under 30 mbar of He. Analogs made for this ongoing work include several mixtures of 1 wt% perchlorate or chloride and 1 wt% either Ca sulfate (gypsum) or Mg sulfate (kieserite) in a balance of silica glass powder. Ca, Mg and Fe^{3+} perchlorates and Ca, Mg, Fe^{3+} , and Na chlorides were used. Two blanks were run between each sample.

Results: When analysed in SAM-like lab systems by itself, the Ca sulfate will not produce any SO_2 in the SAM temperature range. However, SO_2 evolves from the mixtures with perchlorates (Fig. 2). In all three mixtures shown, though the specific shape of the SO_2 traces vary, the major SO_2 evolution starts near 600°C and then increases until the end of the temperature range indicating that the sulfate has not fully decomposed by 860°C (Fig. 2). HCl evolution starts at a lower temperature, around 350-400°C (Fig. 3). The SO_2 evolution may result from reaction between the

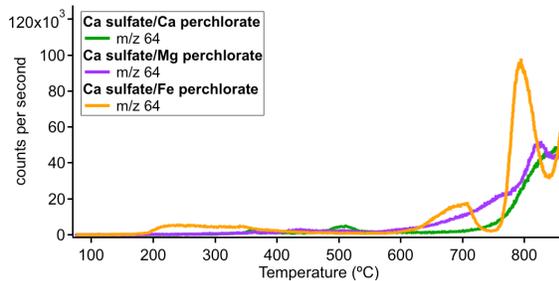
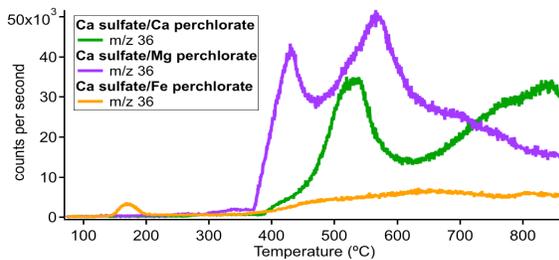
Figure 2. SO₂ traces from Ca sulfate/perchlorate mixtures.

Figure 3. HCl traces from Ca sulfate/perchlorate mixtures.

HCl and Ca sulfate, or could result from reaction between chloride products of perchlorate decomposition and sulfate to produce new phases that then decompose at lower temperatures (for example the small 650-700°C SO₂ peak from the Ca sulfate/Fe perchlorate mixture could result from formation of an Fe sulfate that then decomposes to give SO₂ at this temperature).

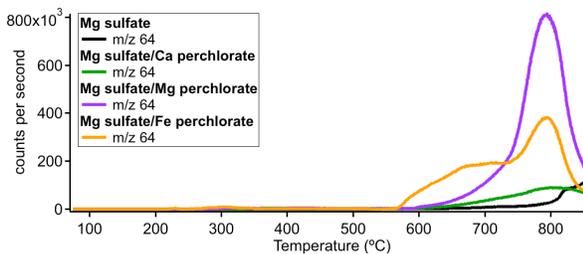
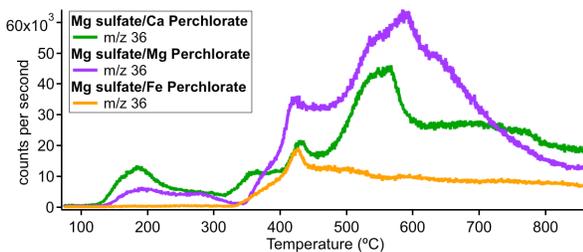
Figure 4. SO₂ traces from Mg sulfate/perchlorate mixtures.

Figure 5. HCl traces from Mg sulfate/perchlorate mixtures.

The SO₂ and HCl traces for the Mg sulfate/perchlorate mixtures are shown in Figures 4 and 5, respectively. When analyzed in SAM-like systems by itself, the Mg sulfate will start to evolve small amounts of SO₂ near the high end of the SAM temperature range and does not have a peak (black line on Figure 4). In the mixtures, SO₂ evolution starts near 600°C, as

for the Ca sulfate mixtures, but the shapes of the SO₂ traces are different and show peaks that complete or mostly complete within the SAM temperature range. The HCl evolution starts around 350-400°C. The SO₂ may result from HCl and the Mg sulfate reactions, or from reaction between chloride products of perchlorate decomposition and the sulfate to produce new phases that decompose at lower temperatures (for example the small 600-700°C SO₂ peak from the Mg sulfate/Fe perchlorate mixtures could result from formation of Fe sulfate that then produces SO₂ at this temperature).

Work with mixtures of Ca and Mg sulfates with chlorides is ongoing, but early results indicate that the temperatures of SO₂ evolution are also lowered compared to runs of the sulfates individually.

Discussion: The 1:1 Ca sulfate/perchlorate mixtures show SO₂ evolving until the end of the temperature range. This is different than SAM SO₂ traces observed so far, which all show SO₂ evolution peaks that complete or mostly complete within the SAM temperature range. It is possible that other ratios between Ca sulfate and the Cl phase, and/or addition of other components relevant to the Mars samples (e.g., Fe minerals) will further decrease in SO₂ evolution temperatures. GH, for example, has the most Ca sulfate observed in any sample analyzed by SAM and CheMin (8 wt%) and has a large amount of Fe minerals (magnetite and hematite) [1]. It also exhibits a prominent very high temperature SO₂ peak. It is possible that mixtures with different Ca sulfate/Cl phase ratios or which include Fe oxides will result in SO₂ evolution which more closely resembles part of the GH SO₂ evolution.

The 1:1 Mg sulfate/perchlorate mixtures show SO₂ peaks in the SAM range and the interactions responsible for the SO₂ evolution could contribute some of the SO₂ in several of the SAM samples analyzed to date. Different ratios of sulfate to Cl-bearing mineral, different Cl minerals or addition of other sample components could further lower SO₂ evolution temperatures. For example, 1:1 mixtures with Mg chloride resulted in a ~50°C reduction in SO₂ evolution temperature compared to the mixture with Mg perchlorate. If these interactions occurred in SAM samples, the Mg sulfates were present below the CheMin detection limit or were amorphous, but these types of sulfate materials have been proposed components of samples such as Murray formation samples [e.g., 2]. Data from MSL's chemical instruments indicate both features dominated by Ca or Mg sulfates (Ca sulfate veins or Mg sulfate nodules), as well as trends indicating that Ca and Mg sulfates are likely present together throughout the Murray formation, perhaps as part of a cement.

References: [1] Yen, A.S. et al., (2016) this meeting. [2] Blaney, D.L. et al., (2015) AGU Fall Mtg., abstr# P53F-03.