

INVESTIGATING THE POTENTIAL OF X-RAY DIFFRACTION COUPLED WITH EVOLVED GAS ANALYSIS IN OUR SEARCH FOR ORGANIC SALTS ON MARS. M. L. Craddock¹, J. M. T. Lewis^{2,3,4}, A. C. McAdam³, J. L. Eigenbrode³, C. N. Achilles^{3,5}, ¹Virginia Polytechnic Institute and State Univ. (cmax@vt.edu), ²Howard University, ³NASA/GSFC, ⁴CRESST, ⁵USRA

Introduction: Indigenous and exogenous organic compounds on the surface of Mars are likely susceptible to destruction and transformation by ionizing radiation and oxidation [1-3]. Several Martian samples acquired by the Mars Science Laboratory (MSL) Curiosity rover were observed to evolve aliphatic and aromatic products during thermal analyses by the Sample Analysis at Mars (SAM) instrument suite, which indicated that organic matter does persist on Mars; however, determining its composition has remained elusive [4]. Laboratory experiments have shown that organic salts, such as oxalates, may be metastable under Martian surface conditions [2,5]. Oxalates are known to be oxidative breakdown products of fatty acids and aromatic carboxylic acids, and they constitute the largest class of organic minerals in the terrestrial geologic record [2,6-8]. It is possible a portion of the Martian organic record may persist as oxalate salts [5,9,10].

In addition to SAM, Curiosity is equipped with the Chemistry and Mineralogy (CheMin) X-ray Diffraction (XRD) instrument [11], which could potentially detect a crystalline oxalate if it was present at sufficient abundance. In this work, we examined oxalate salts with Fe, Ca, and Mg cations in a basalt matrix with CheMin-like XRD methods and investigated how the mixtures decomposed during SAM-like pyrolysis.

CheMin has a minimum mineral detection limit of ~1 wt. % [12]. Meanwhile, SAM has a carbon detection threshold of less than a few ppb [13]. Though organic salts are potential contributors to CO₂ and CO measured by SAM, the instrument cannot conclusively identify their presence [9,10,14,15]. However, the sensitivity of SAM could instruct further analysis of CheMin data and potentially subsequent confirmation of organic salts if present in sufficient abundances. Thus, we aim to further assess the tandem use of XRD and SAM-like pyrolysis in the pursuit of organic salt detection.

Methods: A number of oxalate standards were physically mixed in powdered Columbia River Basalt (CRB) in order to represent a Mars-like mineral matrix. CRB, and tholeiitic basalts in general, are mineralogically similar to the soils analyzed by CheMin in Gale

crater [12]. Previous SAM analyses from the Windjana drill sample infer maximum concentrations of oxalate in the form of ferrous oxalate to be 1.84 ± 0.46 wt. % under the assumption that oxalate produced all of the evolved CO₂ observed [10]. CO₂ evolved during EGA of the Rocknest aeolian drift sample suggests a maximum oxalate mineral concentration of 0.26-0.70 wt. % [16]. These values were used as context for the work described here.

Ferrous (FeC₂O₄), ferric (Fe₂(C₂O₄)₃), calcium (CaC₂O₄), and magnesium (MgC₂O₄) oxalates were mixed with the CRB by mortar and pestle in 0.1, 1.0, and 5.0 wt. % abundances. Aliquots of these mixtures were analyzed using a TERRA portable XRD instrument set to 550 exposures coupled with a mylar screen. Signatures of oxalate material were evaluated between 19-24 2 θ as strong peaks for the selected oxalates occur in this region and interferences from the CRB are minimal. For the SAM-like analyses, 5.0 mg samples of the CRB-oxalate mixtures were weighed out in Frontier Laboratory stainless steel sample cups for Evolved Gas Analysis Mass Spectrometry (EGA-MS). Samples were then loaded on Frontier Lab AS-1020E Auto-Shot Loader for analysis through an Agilent Technologies 5975T LTM-GC/MSD system. Samples were heated at a rate of 35°C min⁻¹ up to 1050°C. Mass-to-charge ratios (*m/z*) 18, 28, and 44 were monitored and interpreted as H₂O, CO, and CO₂ respectively in each sample. The *m/z* 28 plots were corrected for the CO fragment from CO₂ in the mass spectrometer.

XRD Results: XRD analyses of the 5 wt. % mixtures indicated readily discernible peaks of oxalates (Fig. 1A). Mixtures containing 1.0 wt. % oxalates demonstrated peaks nearly indistinguishable from pure CRB (Fig. 1B). The 0.1 wt. % mixtures were entirely indistinguishable from CRB. These trends held for all oxalates investigated and did not change with cation composition. In future work, we aim to further investigate samples containing 1-2 wt. % oxalates and other borderline detectable concentrations, as well as an additional matrix material simulating smectite-bearing mudstones that have been observed by Curiosity [e.g., 17, 18].

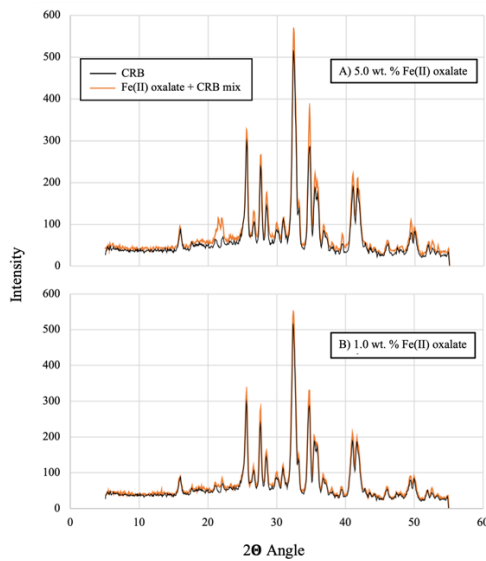


Figure 1. XRD patterns for Fe(II) oxalate in A) 5.0 wt. % and B) 1.0 wt. % mixtures to Columbia River Basalt (CRB).

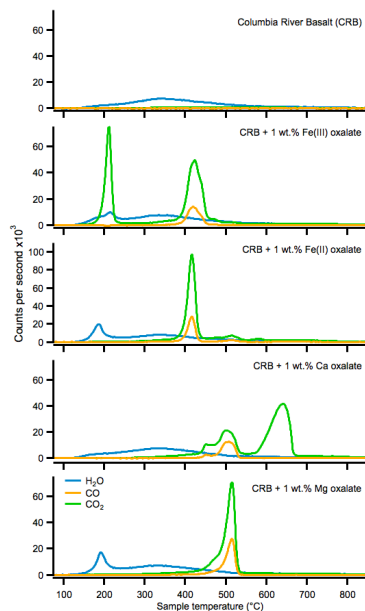


Figure 2. Evolved H₂O, CO, and CO₂ during SAM-like EGA of the Columbia River Basalt (CRB) and CRB subsamples with 1 wt.% oxalates.

Pyrolysis Results: CRB produced a broad H₂O release that peaked at 340°C as the sample dehydrated (Fig. 2). No significant CO or CO₂ evolutions were observed. All samples containing ferric oxalate evolved sharp CO₂ peaks at 210°C and 420°C and a CO release was detected with the 420°C peak. Associated CO₂ and

CO evolutions were a recurring feature in our analyzed mixtures. Small H₂O peaks were observed from ~100 to 250°C in most mixtures and resulted from dehydration of the hydrated oxalate salts. Samples containing ferrous oxalate evolved CO and CO₂ at 415°C and a release of H₂O occurred at ~190°C. Calcium oxalate evolved CO₂ and CO at ~420 and 500°C and at 640°C a large CO₂ peak was detected. Magnesium oxalate samples evolved CO₂ and CO at 515°C and evolved H₂O at 190°C.

Conclusions and Future Work: We have demonstrated that oxalates are detectable by XRD analysis in tholeiitic basalt mixtures when present at elevated abundances. However, while mixtures containing ≤ 1.0 wt. % oxalate salts evolved prominent CO₂ and CO peaks during SAM-like EGA, XRD could not readily distinguish the oxalate patterns from the CRB background at such mixing ratios. EGA can highlight potential oxalate-hosting samples and compel detailed scrutiny of XRD patterns for possible oxalate peaks. In future work, we will explore the limits of oxalate detectability in more complex Mars-like materials and mixing ratios. This work will provide us with a better understanding of our capabilities in detecting and confirming materials in our continuous search for extraterrestrial organic matter.

Acknowledgments: This project was supported by the Undergraduate Research Associates in Astrobiology Program at NASA Goddard Spaceflight Center.

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