

TRANSMISSION X-RAY DIFFRACTION (XRD) PATTERNS RELEVANT TO THE MSL CHEMIN AMORPHOUS COMPONENT: SULFATES AND SILICATES. R.V. Morris¹, E.B. Rampe², T.G. Graff³, P.D. Archer, Jr.³, L. Le³, D.W. Ming¹, and B. Sutter³. ¹NASA-JSC, Houston, TX 77058, richard.v.morris@nasa.gov.
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Introduction and Background: The Mars Science Laboratory (MSL) CheMin instrument on the Curiosity rover is a transmission X-ray diffractometer (Co-K α radiation source and a ~5° to ~52° 2 θ range) where the analyzed powder samples are constrained to have discrete particle diameters <150 μ m by a sieve [1]. To date, diffraction patterns have been obtained for one basaltic soil (Rocknest (RN)) and four drill fines of coherent rock (John Klein (JK), Cumberland (CB), Windjana (WJ), and Confidence Hills (CH)) [2-4]. The CheMin instrument has detected and quantified the abundance of both primary igneous (e.g., feldspar, olivine, and pyroxene) and secondary (e.g., Ca-sulfates, hematite, akaganeite, and Fe-saponite) minerals [2-5]. The diffraction patterns of all CheMin samples are also characterized by a broad diffraction band centered near 30° 2 θ and by increasing diffraction intensity (scattering continuum) from ~15° to ~5°, the 2 θ minimum.

Both the broad band and the scattering continuum are attributed to the presence of an XRD amorphous component. Estimates of amorphous component abundance, based on the XRD data itself [2,4] and on mass-balance calculations using APXS data, crystalline component chemistry derived from XRD data, martian meteorites, and/or stoichiometry [e.g., 6-9], range from ~20 wt.% to ~50 wt.% of bulk sample. The APXS-based calculations show that the amorphous component is rich in volatile elements (esp. SO₃) and is not simply primary basaltic glass, which was used as a surrogate to model the broad band in the RN CheMin pattern [2]. For RN, the entire volatile inventory (except minor anhydrite) is assigned to the amorphous component because no volatile-bearing crystalline phases were reported within detection limits [2]. For JK and CB, Fe-saponite, basanite, and akaganeite are volatile-bearing crystalline components.

Here we report transmission XRD patterns for sulfate and silicate phases relevant to interpretation of MSL-CheMin XRD amorphous components.

Samples and Methods: For sulfate experiments, 10 acid-sulfate solutions were prepared from standard reagents (Table 1). Cryoprecipitation (precipitation by removing water as ice) was induced by freezing solutions using liquid N₂. After freeze drying, the precipitates were stored in closed containers in a glove box purged with dry-N₂ gas. For silicate experiments, silicate liquids having compositions equivalent to representative MER rocks and soils (SO₃- and Cl-free) [e.g., 10, 11] were equilibrated at 1350-1450°C in a 1-atm gas mixing furnace at IW+1 oxygen fugacity and

quenched in water to room temperature. Transmission XRD diffraction patterns were obtained on a CheMin-4 diffractometer which is a laboratory version of the MSL CheMin instrument. Dry N₂ purge gas was used for the sulfate measurements.

Table 1. Compositions of Starting Acid-Sulfate Solutions for Cryoprecipitation of Sulfates

Cation(s)	Concentration (M)	Volume (mL)	Cation Ratio
Fe ³⁺	1.00	20	---
Fe ²⁺	1.00	15	---
Mg ²⁺	1.00	20	---
Ca ²⁺	0.015	500	---
K ⁺	0.50	40	---
Na ⁺	0.25	100	---
Fe ²⁺ , Mg ²⁺	0.5, 0.5	20	1:1
Fe ³⁺ , Mg ²⁺	0.5, 0.5	40	1:1
Fe ²⁺ , Ca ²⁺	0.015, 0.015	500	1:1
Fe ³⁺ , Mg ²⁺ , K ⁺ , Na ⁺	0.2, 0.2, 0.02, 0.02	100	10:10:1:1

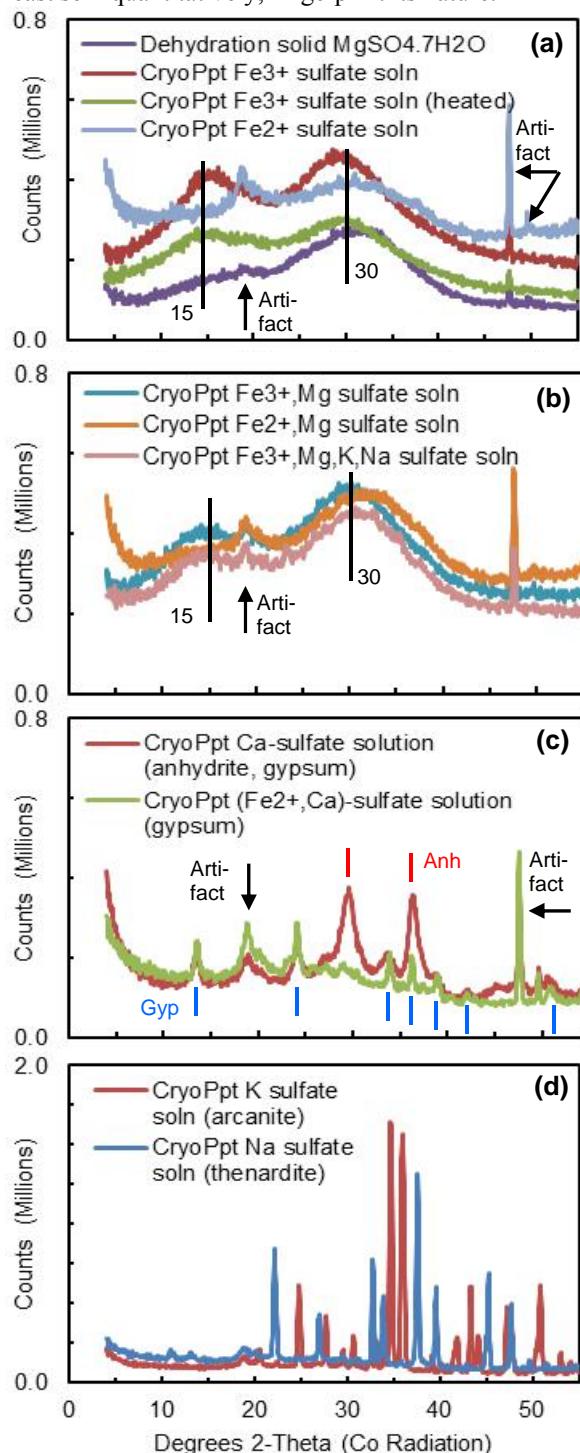
Results: Single and mixed cation sulfate solutions of Mg²⁺, Fe²⁺, and Fe³⁺ in any proportion are likely capable of forming amorphous products by cryoprecipitation (Fig. 1a,b). Single cation Ca²⁺, K⁺, and Na⁺ sulfate solutions did not form amorphous precipitates (anhydrite plus gypsum, arcanite, and thenardite, respectively, with gypsum the only hydrated sulfate), and neither did a solution with Fe²⁺:Ca²⁺=1:1 (Fig. 1c,d), although only gypsum was detected. However, a solution with Fe³⁺:Mg²⁺:Na⁺:K⁺ = 10:10:1:1 formed an XRD amorphous precipitate (Fig 1b.). Additional experiments will define the compositions over which mixed cation sulfate solutions produce amorphous and mixed amorphous-crystalline precipitates. Especially relevant are sulfate solutions involving Ca²⁺, because crystalline Ca-sulfates are detected by CheMin [2,4].

In general, amorphous sulfates have a broad intensity maximum near ~30° 2 θ and another one with less intensity at lower 2 θ (Fig. 1a,b). Their overall shapes and 2 θ locations (esp. Mg²⁺ and/or Fe²⁺ compositions) are not inconsistent with CheMin results, e.g., compare with basaltic soil glass (Fig. 2a) which was used by [2] for RN amorphous calculations. However, a quantitative analysis has not been done.

With one exception, the silicate glasses were predominantly amorphous with a single broad diffraction feature whose peak position increased from ~25° to ~31° 2 θ with increasing SiO₂ (Fig 2a). The Mg-rich composition (Algonquin) produced forsterite plus the most SiO₂-poor glass as indicated by the maximum

diffraction intensity at $\sim 34^\circ$ 2 θ (Fig. 2b). The diffraction pattern of the high-SiO₂ residue of acid-sulfate leached terrestrial basaltic tephra (HWK051) has a diffraction maximum ($\sim 26^\circ$ 2 θ) just longward of that for commercial SiO₂ glass ($\sim 25^\circ$ 2 θ) (Fig. 2c).

Our results show that the shape and position of the amorphous component of MSL CheMin data may, at least semiquantitatively, fingerprint its nature.



References: [1] Blake et al. (2012) *SSR*, DOI 10.1007/s11214-11012-19905-11211. [2] Bish et al. (2013) *Science*, 341, DOI:10.1126/science.1238932. [3] Blake et al. (2013) *Science*, 341, DOI:10.1126/science.1239505. [4] Vaniman et al., (2013) *Science*, 343 DOI:10.1126/science.1243480. [5] Treiman et al. (2014) *Am. Min.*, 99, 2234. [6] Morris et al. (2013) *LPSC44*, abs. #1653. [7] Morris et al. (2014) *LPSC45*, abs.#1319. [8] Dehouck et al. (2014) *JGR*, 10.1002/2014JE004716. [9] Morris et al. (2015) *LPSC46*, this volume. [10] Ming et al. (2008) *JGR*, 113, E12S39, doi:10.1029/2008JE003195. [11] Morris et al. (2008) *JGR*, 113, E12S42, doi:10.1029/2008JE003201.

Fig. 1 (left). XRD patterns of cryoprecipitated single and mixed cation acid sulfate solutions and rapid dehydration of solid MgSO₄·7H₂O (same as cryoprecipitation).

Fig. 2 (below). XRD patterns of **(a)** commercial SiO₂ glass and MER-composition (SO₃- and Cl-free) silicate liquids quenched from 1350-1450°C and IW+1 oxygen fugacity, **(b)** similarly quenched Algonquin liquid with olivine and glass, and **(c)** high-SiO₂ residue of basalt leached under natural acid sulfate conditions (HWK051) compared to SiO₂ and Adirondack glasses.

