

ESTIMATING THE CHEMICAL COMPOSITION OF ALUNITE-JAROSITE GROUP MINERALS AT MSL DRILL SITES USING XRD PATTERNS FROM SYNTHETIC ANALOGS. C. Donaldson and T. M. McCollom, Laboratory for Atmospheric and Space Physics, 1234 Innovation Dr., Boulder, CO 80303 (mccollom@lasp.colorado.edu).

Introduction: The Chemical and Mineralogy (CheMin) instrument onboard the Mars Science Laboratory's (MSL) Curiosity rover has detected the presence of jarosite at several locations along its traverse up Mount Sharp [1]. Since jarosite is typically deposited from acidic aqueous solutions, its occurrence provides an opportunity to place constraints on the chemical environment at the time the jarosite precipitated, which, in turn, can provide insights into fluid-rock interactions during diagenesis of the sediments that compose the lower slopes of Mount Sharp. Jarosite and other members of the alunite group can have considerable compositional variability, including Al-for-Fe and Na- or H₃O-for-K substitutions, and more clearly defining the chemical composition of the jarosite at Mt. Sharp can potentially provide additional insight into the processes involved in its formation. Accordingly, our study investigated how X-ray diffraction (XRD) patterns and spectral features change in response to compositional variability for minerals in the alunite-jarosite group. The results allow preliminary constraints to be placed on the chemical composition of the jarosite at Mt. Sharp.

Methods: Solid solutions of minerals in the alunite-jarosite group were synthesized and analyzed using XRD, visible-near infrared (VNIR) spectroscopy, and Raman spectroscopy. Common minerals in this group have the basic formula [(K,Na,H₃O)(Al,Fe)₃(SO₄)₂(OH)₆]. Previous work had investigated the effect of Al-Fe mixing on XRD and spectral properties of the Na-bearing endmembers [2], so our current study expanded coverage to include K and hydronium (H₃O) substitution for Na in addition to Fe-for-Al substitution. Minerals were synthesized in Teflon vessels at 155 ± 5 °C and ambient pressure, using mixtures of Al₂(SO₄)₃, Fe₂(SO₄)₃, FeCl₃, Na₂SO₄, and/or KCl salts in H₂O or 0.1M H₂SO₄ media. XRD analyses were performed on an inXitu Terra XRD instrument with a Cu-Kα radiation source. To allow for comparison of our results to CheMin, we used the PowDLL Converter v2.69 to convert our spectra to the equivalent for Co-Kα radiation.

Results: Our results indicate that minerals in the alunite-jarosite group display systematic shifts in XRD peaks with both Fe-Al and Na-K-H₃O substitutions that can be diagnostic for chemical composition. For example, the alunite-jarosite series (K) exhibits a gradual shift in the position of its primary peak to lower dif-

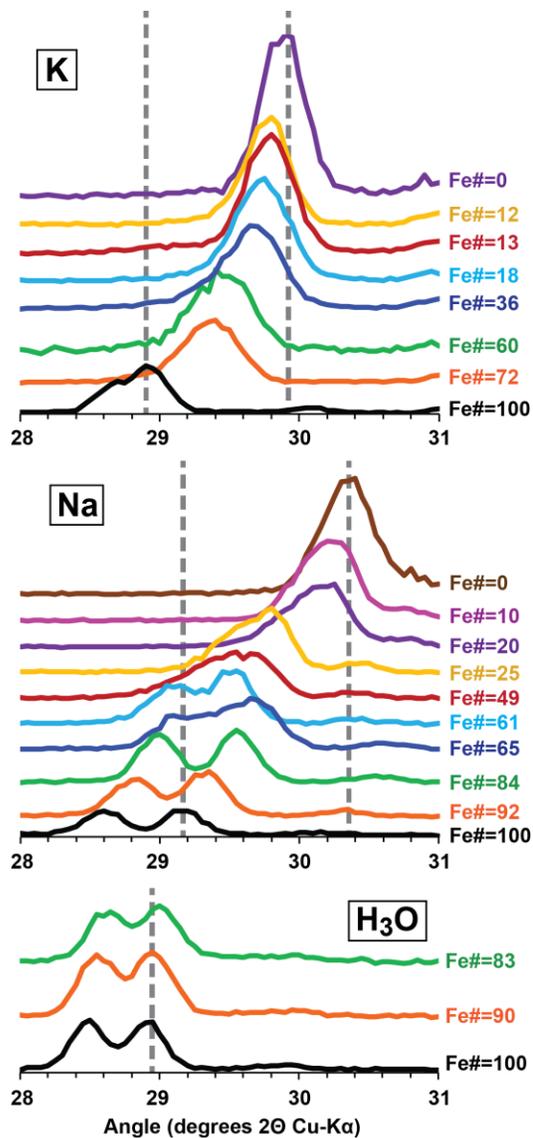


Figure 1. Partial X-ray diffractograms for synthetic members of the alunite-jarosite group for K (top), Na (middle), and H₃O (bottom) endmembers with variable amounts of Al-for-Fe substitution.

fraction angles with increasing Fe content from the alunite to jarosite end-members (Fig. 1, top). The primary peak for natroalunite-natrojarosite solid solutions also shift gradually with increasing Fe content, but are shifted ~0.3° relative to the alunite-jarosite series (Figure 1, middle). Moreover, the single primary peak for natroalunite changes to a doublet for natro-

jarosite with $Fe\# > \sim 50$ [$Fe\# = 100 \times Fe/(Fe+Al)$, molal basis]. Only higher $Fe\#$ minerals could be synthesized for the hydronium (H_3O) series, and these exhibit the same doublet peaks as those observed for natrojarosite. However, for comparable Fe content ($Fe\#$), the hydronium doublets are shifted 0.2° to 0.5° lower angles than that of Na-rich samples (Fig. 1, bottom). Comparable shifts were observed for other diagnostic diffraction peaks in the 14 - 18° 2θ range. Successful syntheses of solid-solutions with K-Na- H_3O mixtures were more limited, but also exhibit systematic shifts in XRD peak positions with changing compositions.

The shifts in XRD patterns with varying composition that are illustrated in Fig. 1 suggests that using XRD patterns to infer chemical composition is feasible. Although ambiguities caused by multiple substitutions may increase the overall uncertainty of estimated compositions, use of multiple peaks and other features such as doublets should provide relatively narrow resolution in many cases. Comparable trends are also observed in VNIR and Raman spectra (to be presented at conference), indicating that these methods can also be useful for estimating compositions.

Comparison with MSL results: Based on X-ray diffraction measurements from CheMin, jarosite has been identified in several samples from the Murray formation at the base of Mount Sharp, including Confidence Hills (sol 759), Mojave2 (882) and Sebina (1496) [1]. The primary jarosite peak observed in these samples occurs at $\sim 34^\circ$ 2θ (Co-K α) with a secondary peak at $\sim 20.5^\circ$ (Fig. 2). The presence of a single diffraction peak at $\sim 34^\circ$ rather than a doublet indicates the minerals are dominated by K with little or no Na or H_3O substitution (Fig. 2). Furthermore, the position of this peak as well as additional peaks at 17 - 21° indicate the jarosite at these three locations most likely contains significant Al-for-Fe substitution with $Fe\#$ between 75 and 85, with a possible slight increase in Al contents from Confidence Hills to Sebina to Mojave2 (Fig. 2). For reference, the mineral from this group identified using Mössbauer spectroscopy at the Opportunity landing site in Meridiani Planum was inferred to have $Na > K > H_3O$ (which would make it natrojarosite rather than jarosite) with some possible Al-for-Fe substitution [3].

Jarosite is most abundant in the Mojave2 sample, which is estimated to contain 3.1 wt% of this mineral. Using the inferred chemical composition, the jarosite can account for ~ 0.30 wt% K_2O , approximately half of the total amount of K_2O in the sample (0.72 wt%).

In many terrestrial settings, jarosite forms by oxidative weathering of Fe-sulfide minerals, and sulfides have been identified in small amounts in other samples within Gale crater [4]. However, it is not clear that this

process could account for the inferred presence of substantial Al in the jarosite observed in the Murray formation samples, and may instead point to formation of the jarosite by interaction of acidic, sulfate-rich fluids with K-, Fe-, and Al-bearing silicate minerals.

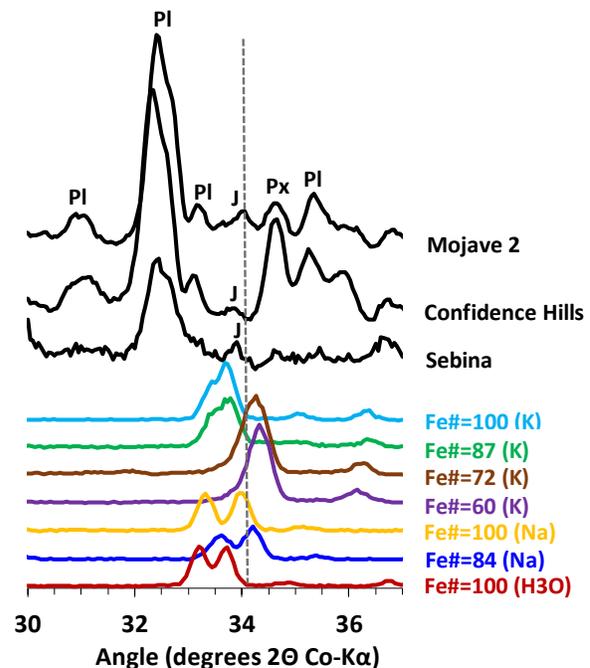


Figure 2. X-ray diffractograms for select synthetic K, Na, and H_3O samples compared to three jarosite-bearing samples from the Murray formation on Mt. Sharp, Gale crater [1,5]. Abbreviations: J = jarosite, PI = plagioclase, Px = pyroxene.

References: [1] Rampe E. B. et al. (2017) *EPSL*, 471, 172-185. [2] McCollom T. M. et al. (2014) *Am. Mineral.*, 99, 948-964. [3] Morris R. V. et al. (2006) *JGR*, 111, E12S15. [4] Vaniman D. T. et al. (2014) *Science*, 343, DOI: 10.1126/science.1243480. [5] Curiosity data downloaded from: odr.io/chemin.