

INFLUENCES OF HALOGENS ON JAROSITE CRYSTAL CHEMISTRY DURING LOW TEMPERATURE FE-OXIDATION PROCESSES ON MARS. Rui CHANG and Yu-Yan Sara ZHAO, Center for Lunar and Planetary Sciences, Institute of Geochemistry, Chinese Academy of Science, Guiyang, China. (zhaoyuyan@mail.gyig.ac.cn)

Introduction: Jarosite is an important component of Burns Formation outcrop at Meridiani Planum [1], and has been detected at various locations across the Martian surface [2-4]. Due to its strong indication of oxidizing aqueous condition and instability within fluids, presence of jarosite in the Martian sedimentary rocks is considered to be an important indicator of aqueous chemistry and history of early Mars [e.g., 5]. Previous study [6] shows that K-jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) precipitated by oxidation of ferrous sulfate (e.g., $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) at low temperature can preferentially incorporate Br^- rather than Cl^- , which may result in Br enrichment and Cl/Br fractionation in the solids. However, it remains unknown why jarosite structure preferred Br^- , and which substitution site did Br^- and/or Cl^- take.

In this study, we synthesize series of halogen bearing jarosite (K- and Na- endmember groups with gradient halogen concentrations), to evaluate the partitioning coefficients of Cl^- and Br^- into jarosite, and how the incorporation of halogens, if occur, would affect the crystal chemistry and dissolution rates of jarosite.

Experimental Methods:

Synthesis of jarosite: In each synthesis experiment, 100 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 454 mL of a 0.45 M MgSO_4 solution were added into a 1000 mL beaker to simulate diagenesis processes with a high ionic strength brine at Meridiani Planum. Source of initial Cl^- and Br^- were added as KCl/KBr or NaCl/NaBr respectively in synthesizing K- and Na-jarosite endmember groups. To synthesize Cl-only or Br-only samples, initial Cl^- was set at four levels from 0.77 wt% to ~3 wt%, and initial Br^- was set to four levels from 0.86 wt% to ~3 wt%. In experiments included both Cl^- and Br^- (Br, Cl experiments), the initial $\text{SO}_4^{2-}/\text{Cl}^-$ molar ratios were set to 2 (i.e., SO_4^{2-} of ~8 wt% and Cl^- of ~1.5 wt%), and Br^- concentrations were varied at five levels so that Cl/Br molar ratios were of 2, 4, 10, 25, and 50 (i.e., Br ranged from 0.08 wt% to 1.6 wt%).

Each beaker was then covered by a paraffin film with a 2 cm hole to allow the brine in contact with atmosphere and being oxidized, as well as serving as a monitoring port. The solution was stirred for 15 days at room temperature. At the end of experiments, the suspension was removed from beaker and centrifuged. The solids were washed with ultrapure water (18.2 M Ω) for three times, and air-dried in fume hood at room

temperature. The initial solution and final supernants were collected and diluted for further analyses.

For comparison, we also synthesized K- and Na-jarosite without halogens both at room temperature and elevated 98 °C. The room temperature synthesis followed the same procedure as synthesizing halogen bearing ones, with K- and Na- added as K_2SO_4 and Na_2SO_4 , respectively. The synthesis method at 98 °C was same as described by [7].

Characteristics of solid samples: Jarosite samples were characterized by X-ray Diffraction (XRD) and Raman spectrometry. Powder XRD data were collected between 10° and 60° 2 θ . Raman spectrometry data were collected using a laser Raman spectrometer, with 20 times magnification, 532 nm wavelength laser, and scanned from 100 cm^{-1} to 4000 cm^{-1} . Scanning Electron Microscope (SEM) was used to obtain morphology and particle size information.

Chemical Composition: In solid samples, halogen contents were determined by X-ray Fluorescence (XRF) with calibration standards parenthesized the target concentration as close as possible. Detection limits of Br^- is 0.35 wt% and of Cl^- is 0.13 wt% by the XRF. Although XRF can provide concentration of major elements of jarosite solids, more accurate concertation of cations Na, K, Fe, Mg and S were determined by Atomic Absorption Spectrophotometer (AAS) after digestion. Total sulfur abundances of solid jarosite were also analyzed by infrared carbon and sulfur analyzer. Concentrations of anions (Cl^- , Br^- , and SO_4^{2-}) in the solutions were measured by Ion Chromatography (IC) and of cations were measured by the AAS.

Preliminary Results:

Characteristics of precipitated jarosite: Synthetic K- and Na-jarosite under room temperature (both halogen bearing and halogen free samples) were pure but with different crystallinity. All K-jarosite samples were well crystalline (Fig. 1A), but the Na-jarosite samples were generally of less intensity or bearing more noise in the XRD patterns (Fig. 2A), suggesting a relatively poor crystallinity compared to K-jarosite. The crystallinity of jarosite is more relevant to the temperature rather than the presence of halogen in the system. Control samples produced at 98 °C (Halogen free-HT) were well crystallized for both K- and Na- jarosite, but the room temperature control samples (Halogen free-

RT) show similar crystallinity as the halogen bearing ones under room temperature.

Raman spectra are consistent with XRD results. For K-jarosite, Raman spectra match well to the standard spectra with clear and distinct peaks (Fig.1B). For Na-jarosite, two types of spectra are present, one is same as the standard spectra, the other one shows noise signals (Fig. 2, B and C).

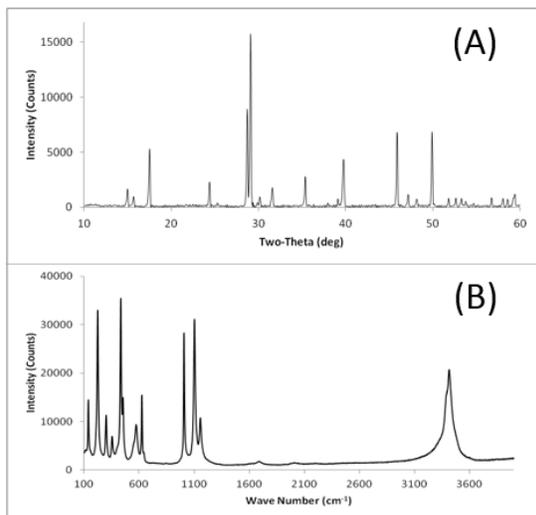


Fig. 1. XRD pattern (A) and Raman spectra (B) of synthesized K-jarosite in general. Both show clear and distinct peaks and in good match with standards.

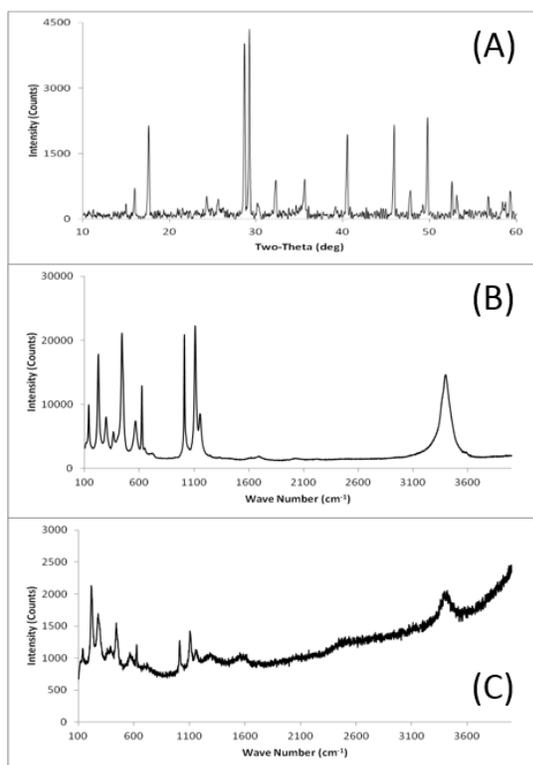


Fig. 2. XRD pattern and Raman spectra of synthesized Na-jarosite in general. XRD pattern (A) is of less intensity and bears more noise compared to K-jarosite. Raman spectra (B and C) suggest different degree of crystallinity in Na-jarosite.

Composition: In well-crystalline K-jarosite samples, we observe substantial incorporation of Br^- into jarosite, which is correlated with initial Br^- concentration (Fig. 3). Co-existing Cl^- in the initial solution would not interference much on the Br^- incorporation. In the Cl^- only experiment, gradual increase of Cl^- in K-jarosite is also observed in correlation to increasing initial Cl^- in brines, but is of one or two orders of magnitude less compared to the Br^- incorporation (data not shown).

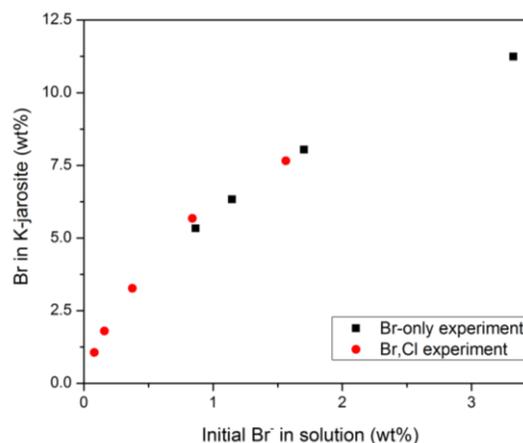


Fig. 3. Correlation between initial Br^- concentrations in the solution and final Br^- contents in K-jarosite produced by Br^- only and Br,Cl^- experiments.

Despite substantial Br^- incorporation in K-jarosite, we did not observe significant loss of Br^- from the solution (the difference was within the 5% analytical uncertainty). We interpret that is due to the large solution to jarosite ratio. Therefore, when K-jarosite precipitates from halide bearing solution, it would result in high Br^- signal in the solids, but would not affect much to the halide in the solution.

Currently, we have finished synthesis experiments and are working on analyses of solid and solution samples, as well as data interpretation. We will report more comprehensive results at the meeting.

References: [1] Klingelhöfer, G. et al. (2004) *Science*, 306, 1740-1745. [2] Milliken, R.E. et al. (2008) *Geology*, 36, 847-850. [3] Farrand, W.H. et al. (2009) *Icarus*, 204, 478-488. [4] Cavanagh, P.D. et al. (2015) *LPS XLVI*, Abstract #2735. [5] Madden, M. E. E. et al. (2004) *Nature*, 431(7010), 821-823. [6] Zhao, Y. Y. S. et al. (2014) *JGR-Planets*, 119(5), 998-1012. [7] Driscoll, R. L. and Leinz, R. W. (2005) *Techniques and Methods 5-D1*, p. 9.