

DISTINCT PARTITIONING BEHAVIOR OF BROMIDE AND CHLORIDE DURING JAROSITE PRECIPITATION – IMPLICATIONS FOR CL/BR FRACTIONATION AND JAROSITE CRYSTAL CHEMISTRY ON MARS. Yu-Yan Sara ZHAO and Rui CHANG, 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 Gale Crater [2] and other locations across the Martian surface [e.g., 3-4]. 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 water history of early Mars [e.g., 5]. Previous study shows that 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 room temperature can preferentially incorporate Br^- over Cl^- , which may result in Br enrichment and Cl/Br fractionation in the solids [6]. However, previous work was unable to systematically evaluate the partitioning behavior of Br^- and Cl^- during jarosite precipitation, and how the incorporation of large amount of halide anions would affect crystal chemistry of jarosite.

In this study, we synthesized series of halogen-bearing K- and Na-jarosite with gradient halogen concentrations. Both 25 °C and 140 °C synthesis methods were used to evaluate the partitioning behavior of Br^- and Cl^- under room temperature and hydrothermal conditions. Structure characteristics of halogen-bearing jarosite were conducted to obtain the influence of halide anions on jarosite crystal chemistry.

Experimental Methods:

Synthesis of jarosite at 25 °C. For K-jarosite, 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. Source of initial Cl^- and Br^- were added as KCl or KBr. For 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.%, respectively. For the Br,Cl-bearing jarosite, 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.%). For natrojarosite, initial $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were increased to 258 g in order to prevent goethite from forming. 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, and stirred for 15 days. At the end of experiments, the suspensions were 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.

Synthesis of jarosite by forced hydrolysis. Halogen-free and Br,Cl-jarosite were synthesized at 140 °C (K- and Na- endmembers) using chloride brine described in [7,8]. For Br,Cl-jarosite synthesis, initial Cl/ Br^- molar ratios were set as 4, 10, 25, 50, and 100, so that Cl^- was constant in each brine of 5.6 wt.%, and the Br^- was gradually decreasing from 2.8 wt.% to 0.33 wt.%.

For K-jarosite, 5 mL of 1.23 M FeCl_3 , 0.5 g KCl and certain amount of KBr based on the Cl/Br ratio settings were dissolved in 12 mL saturated LiCl solution; 6g of $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in 25 mL deionized water and slowly mix into the chloride solution. For Na-jarosite, 5 mL of 1.23 M FeCl_3 , 0.5 g NaCl and certain amount of KBr based on the Cl/Br ratios were dissolved in 12 mL saturated LiCl solution; 6g of $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and 0.85 g Na_2SO_4 were dissolved in 25 mL deionized water and slowly mix into the chloride solution. The final solutions were sealed in autoclaves and heated in oven at 140 °C for 48 h [7, 8]. After returning to room temperature, the suspensions were centrifuged and solids were washed by ultrapure water for three times and heated to dry at 75 °C.

Characteristics of solid and solution samples. Synthesized jarosite samples were characterized by X-ray Diffraction (XRD), infrared and Raman spectrometry. Powder XRD data were collected between 10° and 60° 2 θ for characterizing and an upgraded XRD Rietveld analysis were performed on selected samples of interest. Raman spectrometry were collected by a laser Raman spectrometer, with 532 nm wavelength laser and scanned from 100 cm^{-1} to 4000 cm^{-1} . Scanning Electron Microscope (SEM) with EDS obtained particle composition, size and morphology information. Halogen contents in jarosite were determined by X-ray Fluorescence (XRF) with calibration standards parenthesized the target concentration as close as possible. Detection limit of Br is 0.29 wt.% and of Cl is 0.67 wt.%. Major cations Na, K, Fe, Mg concentration of jarosite were determined by Atomic Absorption Spectrophotometer (AAS) after digestion. Total sulfur of jarosite were analyzed by an infrared carbon and sulfur analyzer. Anions (Cl^- , Br^- , and SO_4^{2-}) of solution samples were measured by Ion Chromatography (IC) and cations were measured by the AAS.

Results of K-jarosite series:

1. *Effect of Br⁻ on jarosite morphology.* At both room temperature (RT) and hydrothermal (HT) conditions, halogen free samples show good crystallinity and crystal shapes (Fig. 1.A, C, E, G). In comparison, with Br⁻ present in initial brines, the Br-only and Br,Cl-bearing jarosite prefer to gathering into clusters (Fig. 1. B, D, F, H).

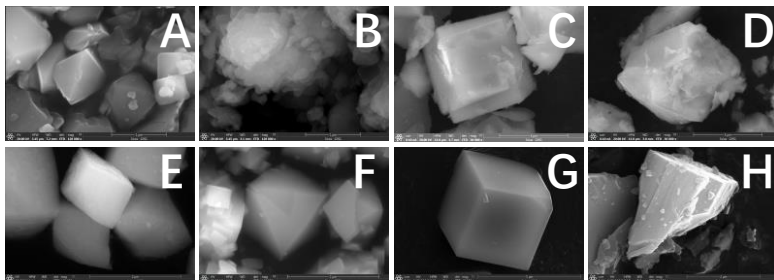


Fig. 1. Synthesized K-jarosite and natrojarosite under RT and HT conditions. (A) to (D) are of jarosite and (E) to (H) are of natrojarosite. Each row from left to right are: RT-halogen free, RT-Br only, HT-halogen free, HT-Br,Cl.

2. *Preferred incorporation of Br⁻ over Cl⁻ during jarosite precipitation.* Under room temperature, we find that Br content in jarosite positively correlated to its concentration in initial brine for both Br-only and Br,Cl-bearing settings (Fig. 2A). The highest Br content of 11.2 wt.% was yielded in Br-only experiment with an initial Br⁻ of ~3.5 wt.%. The Cl content in jarosite also increased with increasing initial Cl⁻ in the Cl-only experiment, but to a level about two orders of magnitude lower than that of Br⁻ (Fig. 2B). Interestingly, in the Br,Cl-experiment, significant decrease of Cl content in jarosite was observed due to increasing initial Br/Cl⁻ ratios, suggesting that presence of Br⁻ can substantially interfere the partition of Cl⁻ into jarosite when they are coexisting in brines (Fig. 2B).

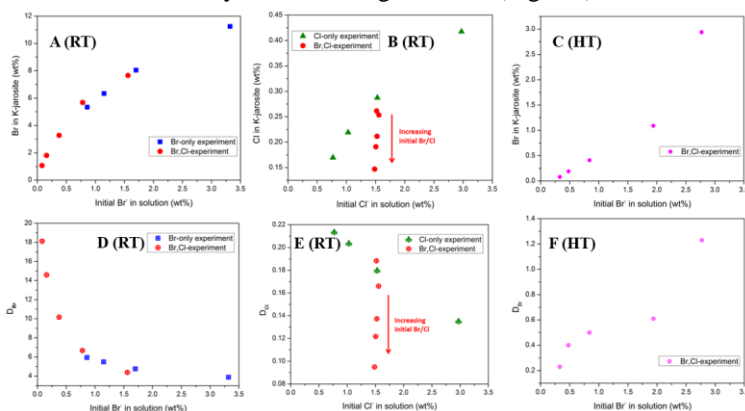


Fig. 2. Halogen contents in synthesized K-jarosite (A, B, C) and Distribution Coefficients (D, E, F) versus halide concentrations in initial brine. (A), (B), (D), (E) are of RT conditions and (C), (F) are of HT conditions.

Under hydrothermal conditions, Cl was undetectable in any jarosite sample (Cl detection limit = 0.67 wt.%). This is consistent with many works using chloride brines to synthesize jarosite, that no Cl content greater than 1 wt.% was reported [e.g., 7, 9]. Bromine contents in synthesized jarosite correlate positively with initial Br⁻ in brine (Fig. 2C), but to a much lower level compared to that been produced under RT conditions. Two data points with lowest Br contents in Fig. 2C were actually below detection limit of Br (0.29 wt.%), but were still shown in the plot due to consistent linear change with other valid points.

The distribution coefficient of D_{Br} and D_{Cl} were shown in Figs. 2D to 2F. Bromide tends to partition into the solid while Cl⁻ tends to remain in the solution during K-jarosite precipitation under both RT and HT conditions, may efficiently fractionate Cl/Br ratios and result in elevated Br abundances in K-jarosite solids.

3. *Crystal alteration due to Br incorporation.* Raman spectrometry and IR spectroscopy analyzed samples with high Br level and show no significant changes in general structure and sulfate position, but peaks corresponding to OH demonstrate gradual weakening as the Br contents increase. Bromine partitioning into jarosite is likely by substituting for OH position. Rietveld analysis was performed on samples with high Br content samples. Preliminary results show that the cell volume of Br-bearing jarosite substantially decreases as the Br content increases, suggesting an increase degree of crystal defects in the jarosite due to Br⁻ incorporation.

Natrojarosite samples demonstrate similar features, however, with poor degree of crystallinity compared to K-jarosite, the Br contents in synthesized natrojarosite where at a much lower level compared to that of K-jarosite starting with similar initial brines for both RT and HT conditions. Chloride shows same tendency to remain in solution as it does during K-jarosite experiments at both RT and HT conditions.

References: [1] Klingelhöfer, G. et al. (2004) Science, 306, 1740-1745. [2] Rampe, E. B. et al. (2017) EPSL, 471, 172-185. [3] Milliken, R.E. et al. (2008) Geology, 36, 847-850. [4] Farrand, W.H. et al. (2009) Icarus, 204, 478-488. [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] Basciano, L. C. and Peterson, R. C. (2008) American Mineralogist, 93: 853-862. [8] Ling Z. C. et al. (2016) Icarus, 271: 19-29. [9] Driscoll, R. L. and Leinz, R. W. (2005) Techniques and Methods 5-D1.