

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF OH-BEARING FERRIC SULFATES. Yanli Lu and Alian Wang, Dept. of Earth & Planetary Sciences, McDonnell Center for Space Sciences, Washington University in St. Louis (ylu@levee.wustl.edu, alianw@levee.wustl.edu)

Ferric sulfates on Mars: Among the Martian sulfates, Ca- and Mg-sulfates were observed with wide spatial distributions and large quantities [1], while Fe-sulfates were found only in localized areas [2], by orbital remote sensing (OMEGA and CRISM observations). In contrast, Mg-, Ca-, and Fe-sulfates were identified with more mineralogical detail during the MER missions [3-6]. Especially, the dehydration of ferric sulfates excavated from subsurface was implied on the basis of a set of seven consecutive Pancam observations at Gusev [7].

Laboratory investigation of the fundamental properties of ferric sulfates: Knowledge on the fundamental properties of sulfates, such as stability field, phase transition pathways, reaction rates, can greatly enhance the understanding of mission observations and Mars hydrologic evolution. For ferric sulfates, a few early studies [8, 9] investigated the solubility relationships of minerals in the $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ system, but only in 200 °C-50 °C temperature range. Recently, Xu et al. [10] studied the rehydration of two anhydrous ferric sulfates at 21 °C; Wang et al [11] studies the stability fields and phase transition pathways of five hydrous ferric sulfates at 50 °C, 21 °C, and 5 °C. Kong et al. [12] defined the first phase boundary below 50 °C between two normal ferric sulfates. The ferric sulfates studied in these recent works belong to *normal* $[\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}]$, *acidic* $[\text{FeH}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}]$, and *slightly basic* $[\text{Fe}_{4.67}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}]$ types. We report here our attempt to start the study of two major types of basic ferric sulfates: jarosite group and fibroferrite-butlerite group.

Synthesis of basic ferric sulfates: We have successfully synthesized three jarosites $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, and $\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6$, a dehydrated form of butlerite, $\text{Fe}(\text{OH})\text{SO}_4$, and a normal paracoquimbite $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

The synthesis of jarosites followed the procedure presented by Dutrizac and Kaiman [13]. K-jarosite was precipitated from a solution of 30g/l KNO_3 , 35g/l $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and 0.01 M H_2SO_4 . That solution was heated to 88-92 °C in air for 1.5-2.5 hours with constant agitation. The precipitated yellowish powder was washed with DI water, then dried in air first then in a 110 °C oven for < 5 min. XRD measurement confirmed its identity as K-jarosite (Fig. 1).

The Na-jarosite (Fig.1) was prepared in the same way, but using 64g/l NaSO_4 and 43.57g/l $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ instead. We found that once the yellowish powder exposed to air after washing with DI water, a color

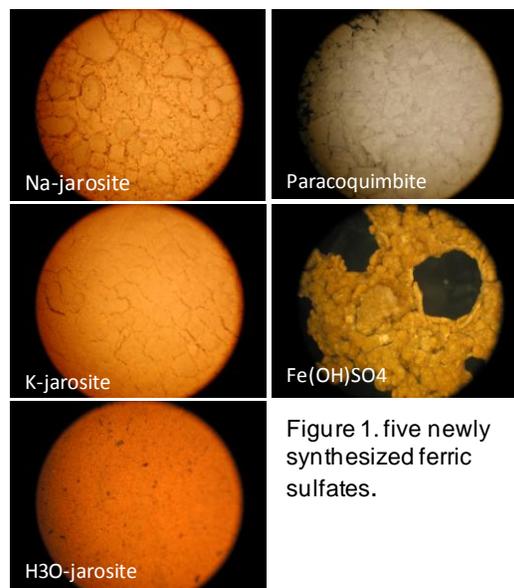


Figure 1. five newly synthesized ferric sulfates.

change (to orange) is very easy to happen. The dry process at 110 °C in an oven can also cause a similar color change. The spectra of synthesized Na-jarosite was compared with those of a commercial product whose ID (Na-jarosite) was confirmed by XRD.

The hydronium jarosite (Fig. 1) was synthesized in a very different way. An aqueous solution $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ (~ 3.9375 g in 60ml solution) was put into a Teflon cup, which was then placed into a Parr bump with spring-loaded pressure cap (thus air-tight). This Parr bump was stored in an oven at 140 °C. After 2-2.5 days, a dark yellowish powdery precipitate formed. In several batches of products, black or red colored grains were seen at the edge of precipitated yellowish powder, stick to the wall of Teflon cup. To separate them, the yellowish powdery precipitate was washed out using DI water, then dried in an oven at 110 °C. XRD measurement confirmed its ID as hydronium jarosite.

A dehydrated form (Fig. 1) of butlerite $\text{Fe}(\text{OH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$ was formed from a saturated aqueous solution of $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$. The mixture of solution & solid was put into an ultrasonic bath for 40-60 minutes until the disappearance of all solid $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$. The solution was then placed into a Teflon cup that was sealed with spring loaded pressure cap of a Parr bump. The bump was placed in an oven at 120 °C. The synthesis goes very slow. An orange colored solid precipitate only formed after 1-2 months. The solid was washed with DI water and dried at room T. XRD measurement confirmed its ID as $\text{Fe}(\text{OH})\text{SO}_4$.

The purpose of synthesizing of paracoquimbite (p9w) is to start a new stability field experiment at $-10\text{ }^{\circ}\text{C}$. Because paracoquimbite appeared as a common phase at mid-T ($21\text{ }^{\circ}\text{C}$ & $5\text{ }^{\circ}\text{C}$) and mid-RH (64-54%) in a set of 150 stability field experiments [11], thus worth further study at a lower T ($-10\text{ }^{\circ}\text{C}$). Most of synthesis methods produced only mixtures of p9w with rhomboclase or kornelite. Pure p9w was produced using a modified procedure originally developed by A. S. Caramazana [14]. The precipitated solid has a light gray color (Fig. 1). XRD measurement confirmed its ID as $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

Spectroscopic characterization: Characteristic spectra of new OH-bearing ferric sulfates were obtained using laser Raman, MIR-Attenuated Total Reflectance (ATR), and NIR-Diffuse Reflectance (DR). Among them, the peaks in laser Raman and MIR-ATR spectra provide the information on the fundamental vibration modes thus can be directly linked to the crystal structural character of these sulfates. In addition, the standard Raman spectra will be used for the phase identification during the next step experiments, the study of stability field and phase transition pathway. Because the laser beam and the induced Raman photons of a Vis-LRS penetrate through optically the glass bottle that contains reaction product, thus these measurements can be made non-invasively. The peaks in NIR-DR are the overtones and combinational modes that can be used for interpreting the data from planetary orbital remote sensing.

Figure 2 compares the Raman spectra of jarosites [Na -, K -, H_3O - $\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$] and $\text{Fe}(\text{OH})\text{SO}_4$ with that of ferricopiapite ($\text{Fe}_{4.67}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$). The major difference in $\text{H}_2\text{O}/\text{OH}$ modes is the broad peak of ferricopiapite contributed by its 20 structural water per molecule. Sharp OH peak(s) exist in all five spectra. Na-jarosite has three pronounced sub-peaks, ferricopiapite has two, $\text{Fe}(\text{OH})\text{SO}_4$ has a single OH peak, while K - and H_3O -jarosite both have asymmetric wider OH peaks. These spectral differences are induced by

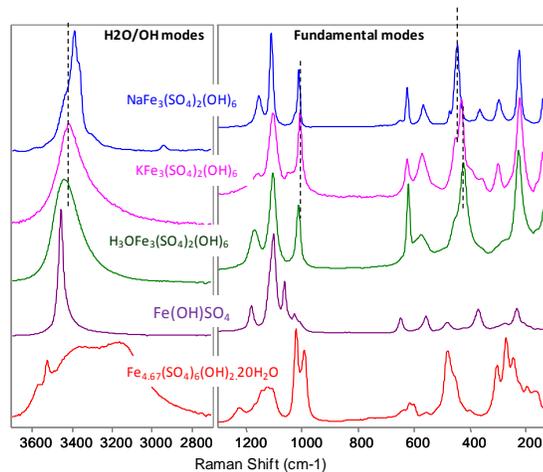


Figure 2. Raman spectra of three major groups of OH-bearing ferric sulfates, jarosite, fibroferrite-butlerite, and copiapite.

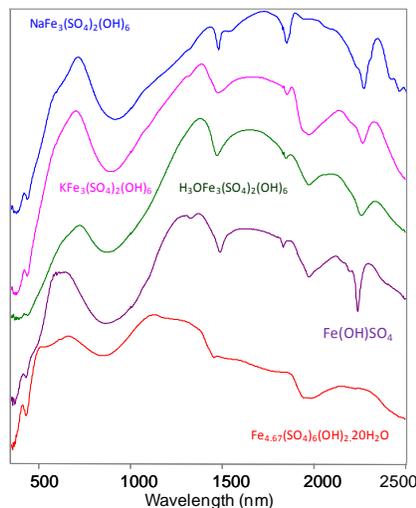


Figure 3. VIS-NIR reflectance spectra of three major groups of OH-bearing ferric sulfates: jarosite, fibroferrite-butlerite, and copiapite (spectra were shifted in y axis for viewing)

the different crystallographic sites occupied by OH (and H_2O) groups in these structures.

The fundamental modes of (SO_4) in three groups of OH-bearing ferric sulfates are obviously very different (Fig. 2). Among three jarosites, spectral peak shifts caused by the cation changes (K , Na , H_3O) in $3a$ sites are in the range of $2\text{-}14\text{ cm}^{-1}$ (dotted vertical lines in Fig. 2).

Figure 3 compares the VIS-NIR reflectance spectra of three jarosites and $\text{Fe}(\text{OH})\text{SO}_4$ with that of ferricopiapite. The site differences reflected in $\text{H}_2\text{O}/\text{OH}$ Raman peaks can all be seen in these overtones and combinational modes. Peaks near $1.9\text{ }\mu\text{m}$ of three synthesized samples are apparently contributed by H_2O . We are conducting a set of heating experiments to study their structural functions.

Next step study: We have started a set of 108 experiments on K -, Na -, H_3O -jarosite to study their stability field and phase transition pathways at $50\text{ }^{\circ}\text{C}$, $21\text{ }^{\circ}\text{C}$, $5\text{ }^{\circ}\text{C}$ with ten RH levels from 5% to 100%, and at $-10\text{ }^{\circ}\text{C}$ with six RH levels from 11% to 98%.

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