THE USE OF SYNTHETIC JAROSITE AS AN ANALOG FOR NATURAL JAROSITE

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Abstract. The presence of jarosite in soil or mining waste is an indicator of acidic sulfate-rich conditions. Physical and chemical properties of synthetic jarosites are commonly used as analogs in laboratory studies to determine solubility and acid-generation of naturally occurring jarosites. In our work we have mineralogically and chemically characterized both natural and synthetic jarosites. Analysis of 32 natural hydrothermal and supergene K- and Na-jarosites indicates no (< 5 mole %) solid solution between K and Na end members. Instead, our detailed study of cell dimensions and composition reveals discrete mixtures of K and Na end members. Hydronium-bearing jarosite was detected in only one natural sample, and it appears that hydronium-bearing jarosites are metastable. Although the presence of hydronium in jarosite cannot be directly measured, we found that when synthetic hydronium-bearing jarosites are heated at 120°C for 78 days or 240°C for 24 hours, Fe(OH)SO₄ is formed. The Fe(OH)SO₄ is easily detected by X-ray diffraction and, hence, can be used as a post-mortem indicator of the presence of hydronium jarosite. Results from our synthetic jarosite studies indicate that natural metastable hydronium-bearing jarosite or iron-deficient forms of natural jarosite likely play an important role in acid generation in some mining wastes, but are not accurately represented by synthetic jarosite prepared by commonly used methods. The widespread practice of heating to at least 110°C after jarosite synthesis appears to drive off structural waters from protonated hydroxyl sites, which changes the properties of the jarosite. Therefore, synthetic jarosite should not be heated above 95°C if it is to be used as an analog for low-temperature natural jarosite in mining wastes.

Additional Key Words: mining waste, acid generation, hydronium jarosite, natrojarosite

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**Introduction**

Jarosites are minerals of the alunite group. The term “jarosite” generally refers to the potassium end member, KFe$_3$(SO$_4$)$_2$(OH)$_6$; natrojarosite is the sodium analog of jarosite. Jarosites form as a byproduct of the oxidation of sulfide minerals. They form naturally in many mining wastes and soils, and are an indicator of acidic conditions (pH <3; Swayze et al., 2000). An overview of jarosite minerals is given by Stoffregen et al., (2000).

It is important to be able to predict the quality of drainage from mining wastes prior to mining. Based on pre-mining predictions, waste-management plans are developed and potential environmental costs are assessed. Studies of mining wastes, that have acid-generating potential due to pyrite oxidation, have led to the examination of jarosites as potential acid generators. Dissolution of the K-jarosite end member can be written as:

$$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6(s) + 3\text{H}_2\text{O} = \text{K}^+_{(aq)} + 2\text{SO}_4^{2-}_{(aq)} + 3\text{H}^+_{(aq)} + 3\text{Fe(OH)}_3(s)$$

The role of jarosites in acid generation has been a controversial subject. Acid can be generated by mining wastes due to the oxidation of sulfide minerals, the dissolution of soluble sulfate salts (e.g., Cravotta, 1994; Jambor et al., 2000), and the dissolution of less soluble sulfate minerals, such as jarosite minerals (Alpers et al., 1994). Even minor amounts of soluble sulfate salts can contribute to acidic conditions upon wetting (Nordstrom and Alpers, 1999). In systems where all these materials are mixed together, it is difficult to apportion the various contributions to acid generation. As a further complication, jarosite minerals can accommodate numerous substitutions in their structure, resulting in a wide variety of jarosite minerals with variable compositions and reactivities. For example, hydronium (H$_3$O$^+$) can substitute for K$^+$ in the jarosite structure, but the H$_3$O$^+$ component cannot be directly measured. Preferential dissolution of H$_3$O$^+$-bearing jarosite is thought to contribute to acid generation in mining wastes (e.g., Lapakko and Berndt, 2003).

Another example of acid generation by jarosite minerals is the large quantities of K-rich or Na-rich synthetic jarosites formed as a by-product of hydrometallurgical recovery of Zn from ores. These by-products have been generated worldwide and have become recognized as acid-producing wastes (Dutrizac and Kaiman, 1976; Dutrizac and Jambor, 2000). Because these synthetic by-product jarosites are unstable, they require additives to stabilize the waste to prevent acid generation (Seyer et al., 2001).

Because natural end-member jarosites are difficult to physically segregate, synthetic jarosites have been used as analogs for natural jarosites to determine solubility and dissolution properties of jarosites. Solubility data from synthetic jarosites are used to interpret various predictive tests conducted on mining wastes and to predict future acid generation of mine-waste materials. Synthesis of various kinds of jarosites and jarosite mixtures has been conducted by several researchers during the past 70 years (e.g., Kubisz, 1970; Dutrizac and Kaiman, 1976).

Field and laboratory studies of 130 metal mine-waste piles in the Rocky Mountain region by the U.S. Geological Survey (USGS) showed that the presence of jarosite in mining wastes was the best indicator of acid-generation potential (Desborough et al., 1999). As an extension of this work, we wanted to know if it was possible to identify jarosites with significant H$_3$O$^+$ substituted for K$^+$ in the monovalent cation site. Scanning electron microscope (SEM) studies by the USGS showed that many of the jarosites in mining wastes are smaller than 0.5 μm. Because of this small grain size, separations of jarosite for analysis could not be achieved and most of the grains
were also too small (<2 μm) for elemental microbeam analysis (Fig. 1). We found that jarosites in mining wastes are concentrated in the <325 mesh (<45 μm) screen fraction, but are intimately admixed with associated minerals, such as quartz and iron oxides.

![Scanning electron micrograph of potassium jarosite](image)

Figure 1. Scanning electron micrograph of potassium jarosite (identified by X-ray diffraction) from a mine-waste pile showing the typical small grain size of supergene jarosite minerals observed in mining wastes. The circle represents the diameter of the electron beam defocused to 10-μm for electron microprobe analysis of jarosite, and illustrates the difficulty of obtaining an elemental analysis of individual grains.

In this study, we have conducted a detailed mineralogical and chemical comparison of natural and synthetic jarosite minerals. We emphasize the mineralogical and compositional differences between (1) naturally occurring K jarosites and natrojarosites, (2) synthetic K jarosites, and (3) H₃O⁺-bearing jarosites. In addition to chemical composition, we examine the influence of grain size on K-jarosite solubility.
**Methods**

X-Ray Diffraction

X-ray powder diffraction (XRD) patterns were obtained with a Shimadzu XRD-6000 diffractometer operated at 40 kV and 30 mA at a scan speed of 2° 20/min. using Cu Kα radiation (λ = 1.54056 Å). Diffractometer patterns of all synthetic and natural samples were first obtained to determine the number of phases present (i.e., purity). Calibration was obtained using Linde C, 1.0 micron alumina powder (Union Carbide Corp.) as an internal standard at a concentration of 10 weight % in each sample; PDF No. 46-1212 of the International Center for Diffraction Data (ICDD) Powder Diffraction Files (Release 2002) was used for the lines and cell parameters of the alumina internal standard. Cell parameters for the natural and synthetic samples were calculated by least squares refinement method with JADE (v.7.0) software of Materials Data Inc.

**Electron Microprobe Analysis**

Electron probe microanalysis (EPMA) was performed on polished thin sections of eight solid samples and one polished thin section grain mount with 100-200 μm grains (sample PBII). Chemical compositions were obtained for the nine polished thin sections of natural samples using a JEOL JXA-8900L electron microprobe. Well-characterized silicate and oxide standards were used for calibration. Operating conditions were 15 kV, 10 nA (cup), and an electron beam defocused to 5 μm diameter in order to reduce Na and K migration. The excitation volume was approximately 8 μm³ under the analytical conditions used. Analytical uncertainty for major and minor elements is ±2% (1σ) and ±3% for trace elements, based on counting statistics. For the electron microprobe data, we assumed that there was one mole of combined K⁺ + Na⁺ + H₃O⁺ for each two sulfur atoms. Wavelength dispersive EPMA operating at 10 KeV, 30 nA, and 5 μm beam diameter was used for maps and chemical analysis (Lowers et al., 2005).

**Jarosite Synthesis**

The K-H₂O jarosites, Na-H₂O jarosites, and pure hydronium end-member jarosites were synthesized using reagent-grade hydrated iron (III) sulfate (Fe₂(SO₄)₃•5H₂O), potassium hydroxide (KOH), and sodium hydroxide (NaOH) at 95°C in an open beaker or at 140°C in a Teflon-lined bomb (Driscoll and Leinz, 2005). Preparation methods of Baron and Palmer (1996) and Brophy et al., (1962) were incorporated into the synthesis procedures. No attempt was made to synthesize K-Na combinations.

**K-H₂O jarosite series.** Following the methods of Baron and Palmer (1996), end-member K jarosite was prepared by dissolving 5.6 g of reagent grade KOH and 17.2 g of reagent grade Fe₂(SO₄)₃•5H₂O in 100 ml of deionized water (18 MΩ), sealed in a Teflon-lined bomb, and heated at 95°C. After 4 hours, the precipitate was allowed to settle and the solution decanted; the precipitate was then washed twice with deionized water and dried at 60°C for 1 hour. X-ray diffraction analysis verified that this synthetic sample is end-member K jarosite. A series of seven hydronium-bearing jarosites was prepared using the same method, but decreasing amounts of KOH (2.8, 1.4, 0.7, 0.4, 0.3, 0.2, and 0.1g), in order to see if a continuous set of K-H₂O solid solutions could be synthesized. Additionally, two near end-member H₃O⁺ jarosites were prepared in Teflon-lined bombs using the same amounts of iron sulfate and water, but with no KOH, and heating at 140°C for either 24 hours or one week. X-ray diffraction analysis showed that these are single-phase products. All synthetics were dried at 60°C for 1 hour.
Static Heating

Heating studies were done in a thermocouple-controlled Thermolyne furnace using about 0.2-0.35 grams of jarosite mixed with 10 weight % Linde alumina (Al₂O₃; for use as an internal standard) in 10-mL mullite crucibles. Sixteen synthetic jarosites were exposed to a temperature of 240°C in 10-mL ceramic crucibles for periods ranging from 24 to 96 hours. Cell-dimension measurements were made after heating.

Leaching Studies

For the leaching studies, 0.2 g of jarosite was combined with 20 mL of deionized water in 50 mL sealed polypropylene containers. The mixtures remained in the containers for eight days and 27.5 months, and the pH was measured after each time period. After the longer time period, some of the samples had lost volume due to evaporation and are not shown in this report. Sized fractions of leached jarosite samples were obtained by wet-sieving ground material in stainless steel sieves using ethanol.

Results and Discussion

In our work we studied both hydrothermal and supergene natural jarosites. Hydrothermal jarosites are formed at high temperature (typically 100-300°C) whereas supergene jarosites are formed at near-surface temperature and are secondary products from the weathering of primary minerals (i.e., they formed from low-temperature oxidation of iron-bearing sulfide minerals). Hydrothermal jarosites are well crystallized and larger in size whereas supergene jarosites are generally very fine grained (< 5 µm). As mentioned earlier, the small grain size of supergene jarosites, such as those found in mining wastes (Fig. 1), make it very difficult to determine the composition of individual grains.

It has been presumed in the literature that there is solid solution between jarosite (K end member) and natrojarosite (Na end member). Based on our work with natural hydrothermal jarosites and natrojarosites, most of which are older than 1 million years, we find no evidence of solid solution between K and Na jarosite end members. X-ray diffraction data show the presence of only Na- or K-jarosite end members or physical mixtures of the end members (i.e., no solid solution between Na and K; see data below). Quantitative X-ray EPMA data of several natural hydrothermal jarosite samples show only end-member compositions for individual grains or zones, and no detectable alkali-site deficiency, which indicates that there is no H₃O⁺ substitution within the analytical uncertainty of the method. In addition, we find no evidence of Fe³⁺-site deficiencies in the natural hydrothermal jarosite samples (Desborough et al., 2004).

X-ray diffraction data for the natural supergene jarosites and natrojarosites we studied have cell dimensions similar to the “mature” hydrothermal jarosites and natrojarosites (see data below). Hence, we infer that these samples also lack the alkali-site and Fe³⁺-site vacancies and hydronium substitution, and consist of a mixture of Na- and K-jarosite end members. It is important to understand the differences between natural and synthetic jarosites, because synthetic jarosites typically are used as analogs for natural jarosites to determine their thermodynamic and geochemical properties and behavior.
Cell Dimensions of Natural and Synthetic Jarosites

The unit cell of a mineral is the smallest unit that possesses the symmetry and properties of the mineral. Differences in the dimensions of the three-dimensional unit cell can be diagnostic of element substitutions or vacancies within the unit cell. Element substitutions or vacancies can lead to decreased stability of the mineral phase. Figure 2 shows the a- and c-cell dimensions for 19 natural jarosites and 12 natural natrojarosites from our study. Nine samples, including both hydrothermal and supergene samples, consisted of both jarosite (K end member) and natrojarosite (Na end member), that is, they consisted of a physical mixture of the K and Na end members. The jarosites and natrojarosites form two distinct groups that do not overlap in their c-cell dimensions. We conclude from this observation that natural jarosites do not have significant solid solution between the K and Na end members under supergene or hydrothermal conditions. Instead, they appear to exist as physical mixtures of end members.

The a- and c-cell dimensions for our synthetic jarosites are shown in Fig. 3, along with the cell dimensions of the 21 synthetic jarosites and natrojarosites of Brophy and Sheridan (1965) and of the ICDD Powder Diffraction File. Note that there are small but significant differences between the cell dimensions of mature natural samples (Fig. 2) and synthetic samples (Fig. 3). For example, synthetic samples tend to have larger a-cell dimensions than their natural counterparts, and synthetic K jarosites tend to have smaller c-cell dimensions. The reasons that synthetic jarosites might have larger a-cell and smaller c-cell dimensions include (1) hydronium substitution in the alkali site, (2) vacancies in the alkali site, or (3) vacancies in the Fe$^{3+}$ site and associated protonated hydroxyl sites.

Cell dimensions of jarosite concentrates from five historical mine-waste piles in Colorado reveal mixtures of two or more jarosites. These include two samples with natrojarosite and three samples with end-member K jarosite. Cell dimensions for these concentrates are plotted in Fig. 4. Note that the cell dimensions for some of these concentrates resemble those for synthetic samples, and others resemble cell dimensions for mature samples. Samples from abandoned underground mine workings at the Richmond Mine, California, are the only natural samples we have studied that show intermediate cell dimensions (Fig. 5). Note that the cell dimensions for these samples most closely resemble those of synthetic jarosites. Figure 6 shows an EPMA X-ray intensity map of one of these samples that illustrates the small particle size and segregation of K- and Na-jarosite end members. The Na and K zoning indicates that K- and Na-jarosite grew at different times and thus have limited solid solution. This is further evidence that significant solid solution between K- and Na-jarosite end members does not occur under supergene conditions.
Figure 2. Cell dimensions of 19 natural jarosites (K end member) and 12 natrojarosites (Na end member) measured for the present study. Ten weight % alumina (Al₂O₃) was used as an internal standard for each sample. [“+/-” values are the mean least-square errors for a and c, respectively.]

Figure 3. Cell dimensions of synthetic jarosites from the present study, from Brophy and Sheridan (1965), and from the ICDD Powder Diffraction File. [“+/-” values are the mean least-square errors of all cell parameters of the synthetic samples of the present study.]
Figure 4. Range of cell dimensions for “mature” natural jarosites and natrojarosites versus metastable synthetic jarosites and natrojarosites formed at low temperature (90-100°C). Triangles are for jarosites from five Colorado mine-waste samples. The mean least-square error is shown for both the a-cell and c-cell dimension.

Figure 5. Range of cell dimensions for “mature” natural jarosites and natrojarosites versus metastable synthetic jarosites and natrojarosites formed at low temperature (90-100°C). Diamonds are for “modern” stalactite samples from the Richmond Mine, California.
Figure 6. EPMA X-ray intensity maps of ~5-10 μm jarosite crystals from the Richmond Mine, California. The top map shows the occurrence of K and the bottom map shows the occurrence of Na in brighter colors. Note the Na and K zoning, which is less than 2 μm. These images suggest K- and Na-jarosite grew at different times and have limited solid solutions.
Static Heating Studies at 240°C

Twelve synthetic jarosites and four synthetic natrojarosites were exposed to a temperature of 240°C in 10-mL mullite crucibles for periods ranging from 24 to 96 hours. Cell-dimension measurements of each sample were made after heating. All of the samples had a decrease in the a-cell dimension, and the jarosites had an increase in the c-cell dimension after heating; however, there was no significant change in cell volume. Figure 7 shows the cell dimensions before and after heating. It is noteworthy that the mean cell-dimension values of the 12 heated jarosites are identical (within 1 σ) to those of the mean of the 19 natural jarosites shown in Figure 2.

Figure 7. Changes in cell dimensions of 12 synthetic jarosites and 4 natrojarosites after heating at 240°C for 24 to 96 hours in atmosphere. The mean least-square error is shown for both the a-cell and c-cell dimension.

Indirect identification of H_3O^+-bearing jarosites. Heating of synthetic K-jarosites, including hydronium-bearing jarosites, at 240°C resulted in a measurable reduction in the a-cell dimension and an increase in the c-cell dimension. Of prime importance is the fact that the heated samples contain XRD-detectable Fe(OH)SO_4 for 10 samples, which ICP-MS chemical analysis has shown to contain 71-88 mole % of K. These results confirm that the loss of H_3O^+ from the jarosite crystal structure is accompanied by the small, but significant, change in cell dimensions, which may coincide with the development of end-member K-jarosite when H_3O^+ is lost. The formation of crystalline Fe(OH)SO_4 from (H_3O)Fe_3(SO_4)_2(OH)_6 may require the loss of water and formation of amorphous Fe_2(OH)_3, as shown in the equation:

\[(H_3O)Fe_3(SO_4)_2(OH)_{6(s)} \rightarrow 2Fe(OH)SO_4_{(s)} + 2H_2O + Fe(OH)_{3(s)}\]
with end-member K-jarosite also being produced. These results showing the temperature of hydronium loss from jarosite at 240°C are at odds with those of other researchers who have reported hydronium loss at higher temperatures (e.g., Kubisz, 1971; Drouet and Navrotsky, 2003). In support of our results, it is significant that the sample of “end member” synthetic K-jarosite has the smallest a-cell dimension of the samples synthesized, and did not produce the Fe(OH)SO₄ phase when heated at 240 or 280°C. Also, Alpers et al., (1989) observed that the presence of H₃O⁺ in jarosite may be recognized using thermogravimetric analysis (TGA) methods by the presence of a peak in the temperature range of about 175-300°C. This weight loss, which is in excess of about 3 weight %, is due to water generated by the above reaction. The fact that Fe(OH)SO₄ is not detected by XRD when H₃O⁺ is absent from jarosites, coupled with the fact that there is no TGA peak between 170-260°C when H₃O⁺ is absent (USGS, unpublished results), further supports our interpretation that H₃O⁺ loss from jarosite is the cause of Fe(OH)SO₄ production. Consequently, the easily XRD-detectable Fe(OH)SO₄ phase can be used as a post-mortem indicator of the presence of H₂O⁺-bearing jarosite.

Heating of natural jarosites and natrojarosites in atmosphere at 280°C for 24 hours did not result in any weight loss or change in cell dimensions. Also, no Fe(OH)SO₄ phase was detected upon heating the natural jarosites. This supports our earlier conclusions, based on quantitative EPMA, that there is no detectable alkali-site deficiency, and indicates that there is no H₂O⁺ substitution in the natural jarosites we studied. The exception to this is samples from the Richmond Mine in California. These samples yield Fe(OH)SO₄ after thermal treatment at 240°C, which indicates that they contain some H₂O⁺-bearing jarosite.

Heating Effects at 110°C

Water is produced by heating synthetic jarosites. The source of this water is either structural water related to protonated hydroxyl sites that result from Fe deficiencies, or water that develops when OH⁻ is removed from the alkali site. Most studies, including ours, that have synthesized jarosites at temperatures in the range of 90-100°C report cell dimensions that are different from those of “mature” natural jarosites (unless they “dried” them at temperatures above about 100°C to remove “excess” water). Studies of low-temperature (100 and 110°C) heating effects on the cell dimensions of synthetic jarosites and H₂O⁺-bearing jarosites show that “drying” at 110°C, as has been done in most studies, changes the cell dimensions and apparently drives off structural water from protonated OH⁻ sites. We synthesized a series of eight H₂O⁺-bearing jarosites, using from 0.1 g to 5.6 g of KOH, at 95°C and dried them at 60°C for 1 hour (Fig. 8). X-ray diffraction results showed that they had much larger cell dimensions than similar material that had been dried at 110°C. Heating of five of these synthetics at 110°C for 20 and 40 hours, respectively, produced structural water losses of 3.5 to 9 weight % and significant changes in the a- and c-cell dimensions. Additional heating at 240°C produced additional water losses of 2.5 to 5.5 weight % and generation of Fe(OH)SO₄ by the H₂O⁺-bearing jarosites.
Use of Synthetic Jarosite as an Analog for Natural Jarosite

The chemical composition, cell dimensions, and other properties of synthetic jarosites formed at low temperature (e.g., ≤ 95ºC) may simulate jarosites developed under natural conditions from low-temperature oxidation of iron sulfides, such as those found in mining wastes. Most of the low-temperature synthetic jarosites seem to be metastable due to substitution of H$_3$O$^+$ in the alkali site, deficiency of Fe$^{3+}$ and associated H$_2$O in the OH$^-$ site, or alkali-site deficiencies. Heating synthetic jarosite samples drives off structural waters and changes the properties of the jarosites. Consequently, the synthetic samples that result from heating may not be representative of the properties of the natural jarosites for which they are being used as an analog. Figure 9 is a schematic illustrating the effects that heating has on a synthetic jarosite sample.

Several natural supergene jarosites have chemical and mineralogical properties that differ significantly from those formed during the last century. Recently formed natural jarosites of supergene origin are similar to low-temperature (~100 ºC) synthetic jarosites with the important exception that there is no solid solution between jarosite and natrojarosite in the supergene jarosites. However, there may be solid solution between jarosite and H$_3$O$^+$ jarosite for both supergene and low-temperature synthetic jarosites. Both recently-formed supergene jarosites and low-temperature synthetic jarosites are considered metastable, and all of the supergene and low-temperature synthetic jarosites, including both mature and metastable varieties, seem to have crystal sizes smaller than about 5-10 µm.
Metastable or immature supergene jarosites and low-temperature synthetic jarosites have larger a- and smaller c-cell dimensions than mature natural jarosites. In addition, mature natural jarosites appear to have no alkali-site vacancies, no Fe deficiencies, and no significant H$_3$O$^+$ substitution in the alkali site. While Fe deficiencies can be estimated from EPMA, alkali-site vacancies cannot be recognized unless H$_3$O$^+$ can be determined to be absent. Hydronium presence or absence may be determined by heating at 240°C for 24 hours followed by X-ray diffraction analysis to determine if Fe(OH)SO$_4$ was formed. Hydronium presence in jarosite also may be recognized by TGA methods if a peak is present in the temperature range of about 175-300°C (Alpers et al., 1989), which generates weight losses in excess of about 3 weight % due to water generation. We have synthesized several jarosites and identified metastable natural jarosites in mining wastes and in an abandoned underground mine. Recognition of these metastable jarosites is important because their solubility and tendency to generate acid will be greater than natural mature jarosites.

Factors Affecting Jarosite Leachability

Leaching studies were performed to determine the effect of particle size and exposure time on jarosite solubility. Figure 10 shows the effect of leaching exposure time on leachate pH. The longer leaching time resulted in lower pH or greater acid generation. Figure 11 illustrates the effect of particle size on jarosite leachability and resulting pH. For the 27.5-month deionized water leaching time, the smaller particle-size samples appeared to equilibrate at a pH of about 3.5. It is apparent that both particle size and leaching exposure time have effects on jarosite solubility. However, for the 27.5-month time period, there appears to be a saturation control on jarosite solubility. Lapakko and Berndt (2003) reported that pH appeared to approach an equilibrium value near 3.8 for jarosite-bearing samples in humidity cells for nearly 200 weeks.
Figure 10. The a-cell dimension of synthetic K jarosites versus pH after eight-day (squares) and 27.5-month (triangles) exposures to deionized water. Jarosite-water ratio was 1-to-100 by weight.

Figure 11. Particle size versus pH for different size fractions of a hydrothermal end-member K-jarosite sample after eight-day (squares) and 27.5-month (triangles) exposures to deionized water. Jarosite-water ratio was 1-to-100 by weight. For the longer exposure time, only those samples that had not lost fluid due to evaporation are shown. Note that the three smallest size fractions appear to have equilibrated with a saturated solution.
Summary

Natural jarosites have a very narrow range of a- and c-cell dimensions, whether of hydrothermal or supergene origin. There is no evidence of solid solution between K-jarosite and Na-jarosite in the samples studied. Additionally, there is no evidence of significant H$_3$O$^+$ substitution ($\leq$5 mole %) in the monovalent site of natural hydrothermal or natural supergene jarosites, except for samples collected from the Richmond Mine in California.

Synthetic jarosites formed in the temperature range of 95-140ºC have larger a- and smaller c-cell dimensions than natural jarosites due to H$_3$O$^+$ substitution in the alkali site, vacancies in the alkali site, or vacancies in the Fe$^{3+}$ site and associated protonated OH$^-$ sites. Low-temperature heating (>95ºC) of synthetic jarosites for more than several hours removes water from the protonated OH$^-$ sites and causes a slight reduction in the a-cell dimensions and a slight increase in the c-cell dimension. Heating H$_3$O$^+$-bearing jarosite at 240ºC for about 24 hours removes H$_3$O$^+$ from the alkali site and produces Fe(OH)SO$_4$ and near-end member K jarosite. This Fe(OH)SO$_4$ product is a post-mortem indicator of H$_3$O$^+$ jarosite.

Metastable or immature supergene jarosites and low-temperature synthetic jarosites have larger a- and smaller c-cell dimensions than do mature natural jarosites. In addition, mature natural jarosites appear to have none of the alkali-site vacancies, Fe deficiencies, and significant H$_3$O$^+$ substitution that are observed in some synthetic and immature natural jarosites. Recognition of metastable jarosite phases is important because they will tend to have different solubility and acid-generation properties than mature or high-temperature synthetic jarosites. In order for synthetic jarosites to be representative of immature supergene jarosites in mining wastes, they should not be heated above 95ºC after preparation.

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