Chapter B: Understanding Jarosite—From Mine Waste to Mars

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Overview

The presence of jarosite, an iron-sulfate mineral, in soil or in mining waste is an indicator of acidic, sulfate-rich conditions. Physical and chemical properties of synthetically prepared jarosites are commonly used as analogs in laboratory studies to determine solubility and acid-generation potential of naturally occurring jarosites. In our work we have mineralogically and chemically characterized both natural and synthetic jarosites. Analyses of natural potassium (K)- and sodium (Na)-jarosites from hydrothermal and weathering environments indicate that there is little solid solution (chemical mixing); instead, they revealed that samples consist of discrete mixtures of potassium- and sodium-endmembers. Hydronium (H_3O^+)-bearing jarosite was detected in only one relatively young natural sample, suggesting that terrestrial H_3O-bearing jarosites are unstable over geologic timescales. Although the presence of H_3O^+ in jarosite is very difficult to measure directly with traditional analytical methods, we found that heating H_3O-bearing samples at high temperatures (greater than 200 to 300 degrees Celsius) produces an $Fe(OH)SO_4$ compound. $Fe(OH)SO_4$ is easily detected by X-ray diffraction and reflectance spectroscopy; hence, it can be used as a "post-mortem" indicator of the presence of H_3O^+ in jarosite. Results from our synthetic jarosite studies indicate that natural H_3O-bearing jarosite, alkali-site deficient, and iron-deficient forms of natural jarosite are metastable and likely are significant factors in acid generation of some mining wastes, but that these natural phases are not accurately represented by synthetic jarosite prepared by commonly used methods. The widespread practice of heating synthetic jarosites to at least 110 degrees Celsius (°C) after synthesis appears to drive off structural water, resulting in samples with crystal structures similar to those of the hydrothermal jarosites, which are a much more stable form of jarosite. Therefore, synthetic jarosite should not be heated above 60°C if it is to be used as an analog for low-temperature natural jarosite found in mine waste. An extension of our work on jarosite reveals that reflectance spectroscopy can be used in remote sensing studies to identify H_3O-bearing and iron-deficient jarosites on the surface of the Earth and Mars.

Introduction

In 1852, a German mineralogist named August Breithaupt discovered a yellowish-brown mineral in Barranco del Jaroso (Jaroso Ravine) in the Sierra Almagrera along the southeastern coast of Spain. He named this potassium-iron-sulfate-hydro xide mineral "jarosite" (Anthony and others, 1990). Jarosite has the chemical formula $KFe_3(SO_4)_2(OH)_6$ but its "garbage can"-like structure can accommodate many other elements to produce chemically diverse varieties like natrojarosite [$NaFe_3(SO_4)_2(OH)_6$], hydronium jarosite [$H_3OFe_3(SO_4)_2(OH)_6$], ammoniojarosite [$NH_4Fe_3(SO_4)_2(OH)_6$], and plumbojarosite [$PbFe_6(SO_4)_4(OH)_{12}$], among others. These are examples of endmember jarosites; intermediate jarosites consist of mixtures of alkali-site cations (for example, K^+ and Na^+, or H_3O^+ and K^+).

Jarosite has been in the headlines as one of the hydrated minerals discovered using the Mossbauer spectrometer on the Opportunity Rover at Eagle Crater on Mars (Klingelhöfer and others, 2004). Here on Earth jarosite is common in acidic soils, in mine waste formed by oxidation of sulfide minerals, or as a product of iron precipitation prior to electrolytic refining of zinc. Because of its association with sulfide minerals, acidic conditions, and heavy metals in mine waste, jarosite can be used as a proxy in remote-sensing studies to locate areas of high acidity and metal leachability (Swayze and others, 2000), thereby providing a rapid way to screen mined areas for potential sources of acidic drainage (fig. 1).

Jarosite's function as a potential source of acid in mine waste is not completely understood. The traditional view is that acid can be generated in mine waste due to the oxidation of sulfide minerals, the dissolution of highly soluble sulfate salts, and the dissolution of less-soluble sulfate minerals, such as jarosite. In waste where all of these materials are mixed together, it is difficult to decipher which ones contribute the most to acid generation. As a further complication, jarosite's compositional variability allows multiple levels of chemical reactivity. Because natural endmember jarosites are very difficult to physically segregate, synthetic jarosites have been used as analogs to determine solubility and dissolution properties of the natural jarosites. Solubility data from synthetic jarosites are used to predict the acid-generation potential of mine-waste materials. Hydronium-bearing jarosite, in particular, is thought to contribute to acid generation in mine wastes because the hydronium ion (H_3O^+) accelerates jarosite dissolution (Gasharova and others, 2005, and references therein).

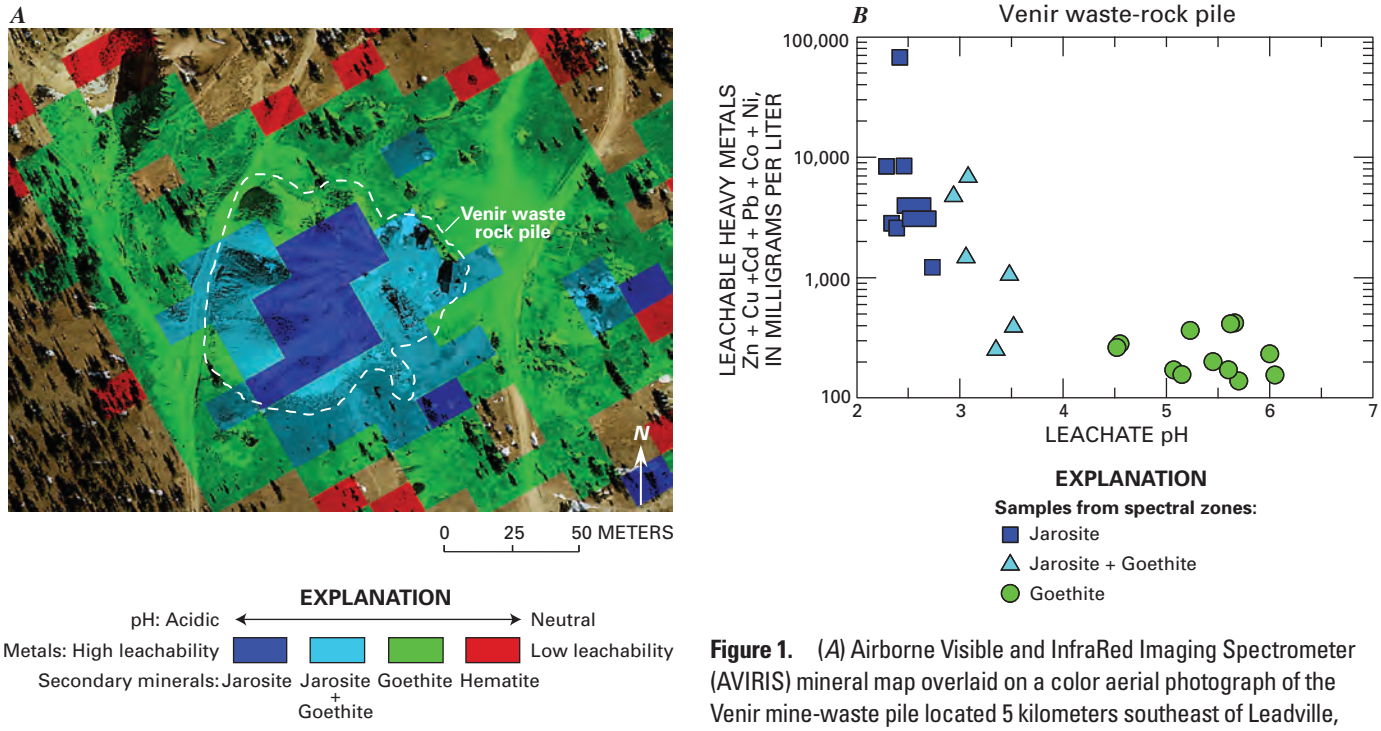

Figure 1. (*A*) Airborne Visible and InfraRed Imaging Spectrometer (AVIRIS) mineral map overlaid on a color aerial photograph of the Venir mine-waste pile located 5 kilometers southeast of Leadville, Colorado. In the aerial photograph white areas are snow, rectangular objects are abandoned mine structures, and dark green objects are lodgepole pines casting shadows. The mineral map overlay shows the spectrally dominant iron-bearing secondary minerals, jarosite, goethite, hematite, and mixtures, for each 20-by-15-meter pixel on the ground. (*B*) Comparison of field and laboratory measurements with AVIRIS mapping demonstrates that jarosite-bearing areas have low pH and higher metal leachability and goethite-bearing areas have more neutral pH and lower metal leachability. Because imaging spectroscopy measures reflected sunlight, it cannot be used to detect minerals deeper than can typically be seen with the human eye; hence, the data can only provide information on minerals exposed in the top few millimeters of the surface.

In this study, a detailed laboratory examination of the mineralogical, microscopic, thermal, and spectral characteristics of jarosite was conducted in order to find clues to its place in the acid-mine drainage story. We studied both natural and synthetic jarosites to see if lessons learned from past research on synthetic jarosites can be used to accurately predict the geochemical behavior of natural ones and to define the environmental conditions under which their comparison to natural samples is valid. While conducting this research we were mindful of how these findings might be used to better understand jarosite formation on Mars and how its presence there constrains Martian surface chemistry.

Jarosite Geochemistry

Jarosites found in mining wastes generally are very fine grained (<5 micrometers), making it very difficult to determine the composition of individual grains. The unit cell of a mineral is the smallest group of atoms that possess the crystallographic symmetry and chemical properties of the mineral. Changes in unit cell parameters can be diagnostic of element substitutions or vacancies within the unit cell, which can lead to decreased stability of a mineral phase. The a- and c-cell dimensions of natural jarosites were examined using X-ray diffraction (XRD) analysis, and it was found that both hydrothermal and low-temperature samples consisted of single K- or Na-jarosite endmembers or pairs of endmembers. This is in contrast to the existence of complete solid solution (chemical mixing) across the sodium-potassium compositional series in jarosites synthesized at hydrothermal temperatures (>100°C). We concluded from these observations that natural jarosites rarely, if at all, form crystals with intermediate composition.

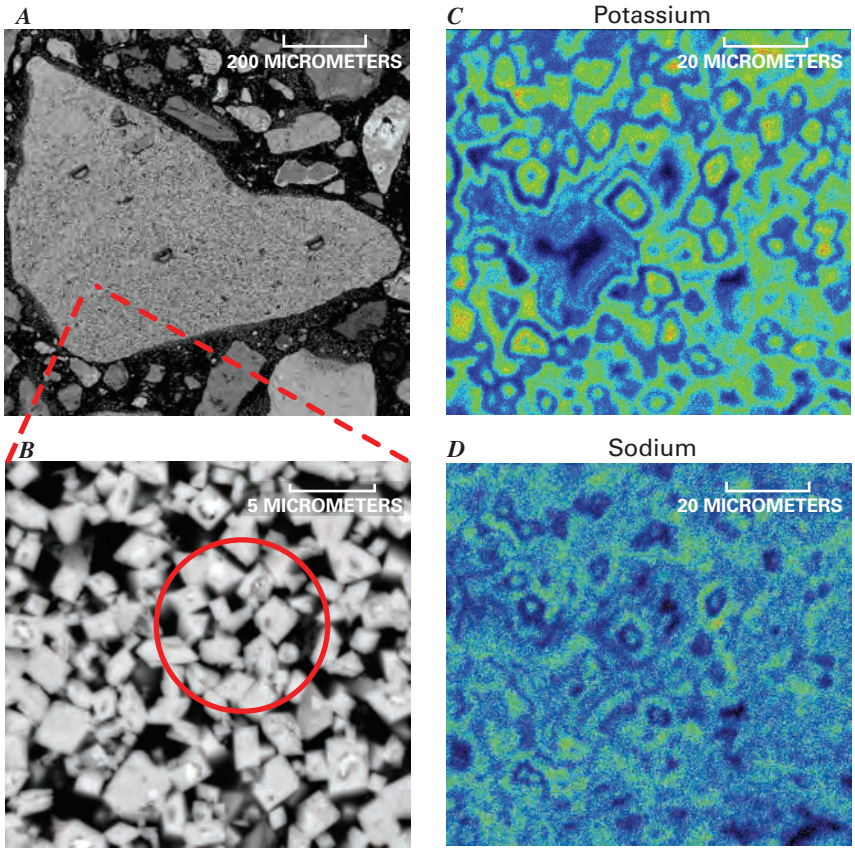

Figure 2. (*A*) Backscattered electron image of a potassium-jarosite sample, originally identified by X-ray diffraction, from a waste-rock pile showing the typical small grain size of low-temperature jarosite minerals observed in mine waste. (*B*) Blowup of (*A*) where the circle represents the diameter of the electron beam defocused to 10 micrometers (µm) for electron microprobe analysis of jarosite, which illustrates the difficulty of obtaining an elemental analysis of compositional zoning within individual grains. (*C*) and (*D*) Electron microprobe X-ray intensity maps of potassium (K) (top) and sodium (Na) (bottom) of about 5- to 10-micrometer jarosite crystals from the Richmond Mine at Iron Mountain in California. Green and orange areas depict regions with greater elemental intensity than blue regions. Note the K- and Na-zoning is less than 2 micrometers across, which suggests that potassium- and sodium-jarosites grew at different times and have limited solid solution (chemical mixing).

Quantitative electron probe microanalysis data of several natural hydrothermal jarosite samples show only endmember compositions for individual grains or zones, and no detectable alkali-site deficiencies, which indicates that there is no H_3O^+ substitution within the analytical uncertainty of the method (fig. 2). In addition, there is no evidence of deficiencies in the natural hydrothermal jarosite samples. X-ray diffraction data for the natural low-temperature (<100°C) K- and Na-jarosites we studied have cell dimensions similar to the "mature" high-temperature hydrothermal jarosites. Hence, it is inferred that these samples also lack alkali- or iron-site vacancies, lack an H_3O^+ component, and instead consist of a mixture of potassium- and sodium-jarosite endmembers. In other words, they chemically resemble the more stable hydrothermal jarosites and do not resemble low-temperature synthetic jarosites.

There is an explanation for the apparent discrepancy between low-temperature synthetic jarosites and natural low-temperature jarosites. A series of five synthetic jarosites were prepared in pressure vessels at 95°C and dried at 60°C for one hour. These samples vary from H_3O-poor and iron-deficient to H_3O-rich (fig. 3). After heating these samples at 110°C for 20 and 40 hours, respectively, structural water losses ranged from 3.5 to 9 weight percent and cell dimensions were reduced significantly. Post-synthesis heating is a common practice used to remove "excess" water from nonstoichiomeric (non-ideal chemical formula) jarosite samples. Heating these samples causes some H_3O^+ in alkali sites near iron vacancies to permanently transfer protons to hydroxyls surrounding these iron vacancies, thereby converting this H_3O^+ to H_2O and the hydroxyls to protonated hydroxyls (OH_2), which are then both lost as water vapor at temperatures near 200°C. Samples with little to no H_3O^+ tend to gradually lose their protonated hydroxyl component as H_2O vapor at temperatures lower than 200°C. Both water-loss processes produce relatively stable stoichiometric (ideal chemical formula) jarosite that may no longer be representative of the chemically reactive type of nonstoichiometric jarosite, which can potentially contribute to acid-mine drainage.

Identification of Hydronium-Bearing Jarosite

Heating synthetic H_3O-bearing jarosite samples up to 240°C results in the production of an XRD-detectable compound with the chemical formula $Fe(OH)SO_4$. The loss of H_3O^+ from the jarosite crystal structure is accompanied by a small but significant change in cell dimensions, which coincides with the development of endmember K-jarosite (Desborough and others, 2006). Formation of crystalline $Fe(OH)SO_4$ from H_3O-bearing jarosite requires the loss of water and formation of amorphous iron hydroxide, as shown in the reaction equation:

$$\underset{\text{hydronium-jarosite}}{(H_3O)Fe_3(SO_4)_2(OH)_6} \rightarrow 2Fe(OH)SO_4 + 2H_2O + \underset{\text{amorphous Fe-hydroxide}}{Fe(OH)_3},$$

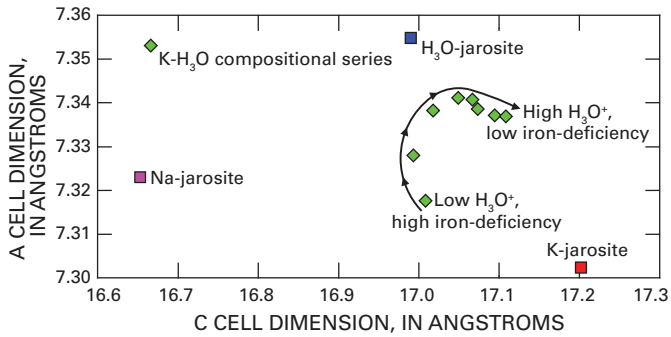

Figure 3. Crystallographic unit-cell dimensions for eight synthetic jarosites with variable hydronium (H_3O^+) content prepared in a pressure vessel at 95 degrees Celsius and then dried in air at 60 degrees Celsius for one hour. Unit-cell dimensions refer to the lengths, usually given in Angstroms (one ten-millionth of a millimeter), of the sides of a unit cell, the smallest group of atoms whose arrangement produces a crystal's symmetry and whose repetition in three dimensions produces a crystal's lattice. Unit-cell values for endmember H_3O-jarosite, sodium (Na)-jarosite, and potassium (K)-jarosite are also shown for reference. Arrow shows trend of unit-cell dimension changes as samples become H_3O-rich. Unit-cell dimensions calculated from X-ray diffraction analysis can be used to measure the H_3O^+ content of natural jarosites, thus helping scientists predict how much acidity and leachable metals they can potentially contribute to acidic mine drainage.

with the remaining jarosite recrystallizing to endmember K-jarosite. Thermogravimetric analysis of synthetic H_3O-bearing jarosite shows evidence of rapid H_2O loss near 200°C (fig. 4), although there is no evidence of rapid H_2O loss at this temperature when H_3O^+ is absent. There is also no XRD-detectable $Fe(OH)SO_4$ produced by heating when H_3O^+ is absent from jarosite samples. Therefore, we conclude that H_3O^+ loss from jarosite is the cause of $Fe(OH)SO_4$ production. Consequently, the easily XRD-detectable $Fe(OH)SO_4$ phase can be used as a "post-mortem" indicator of the presence of H_3O^+ in jarosite.

In the natural jarosites studied, no $Fe(OH)SO_4$ was detected after heating, in agreement with the quantitative electron probe microanalysis results that show no detectable alkali-site deficiencies or H_3O^+ substitution. The sole exception is a sample from the Richmond mine in California, where jarosite-rich stalactites are actively forming from dripping acidic water (Jamieson and others, 2005). These samples yield $Fe(OH)SO_4$ after thermal treatment at 240°C, which indicates that their jarosite contains H_3O^+.

Spectroscopic Studies of Jarosite

Reflectance spectroscopy can be a useful tool for jarosite identification in remote-sensing studies and for detecting the presence of H_3O^+ and iron-deficiencies in jarosite with portable field spectrometers. In the spectral region spanning the ultraviolet to the near-infrared wavelengths (about 0.35 to 2.5 micrometers [µm]), jarosite has many diagnostic absorptions (fig. 5). Most notable is the wide absorption band near 0.9 µm caused by an Fe^{3+}-electronic transition. This spectral feature was used to map for the presence of jarosite in mine waste near Leadville, Colorado (fig. 1*A*). Variations in the wavelength position and shape of vibrational absorptions near 1.4, 1.85, and 2.26 µm can be used to differentiate potassium- from sodium-jarosite and assess the temperature of jarosite formation (Swayze and others, 2006). Hydronium-bearing and iron-deficient jarosites have relatively weak spectral features compared to those of the potassium- and sodium-endmembers, thus allowing them to be recognized using airborne and orbital imaging spectrometers. The relative proportion of protonated hydroxyl (OH_2) to H_3O^+ can be directly measured based on the depth of absorption bands at 1.93 and 1.96 µm, respectively (see vertical arrows in fig. 5). Using this information, it may now be possible to spectrally identify which areas of mine waste have the highest concentrations of H_3O-bearing jarosite and are thus more likely contribute to acidic drainage.

Is synthetic jarosite a suitable analog for natural jarosite in mine waste?

The chemical composition, cell dimensions, and other properties of synthetic jarosites formed at low temperature (<100°C) may simulate relatively young jarosites in mining wastes. Most of the low-temperature synthetic jarosites seem to be metastable (easily changed and more chemically reactive) due to either substitution of H_3O^+ in the mineral's structure or to iron- and

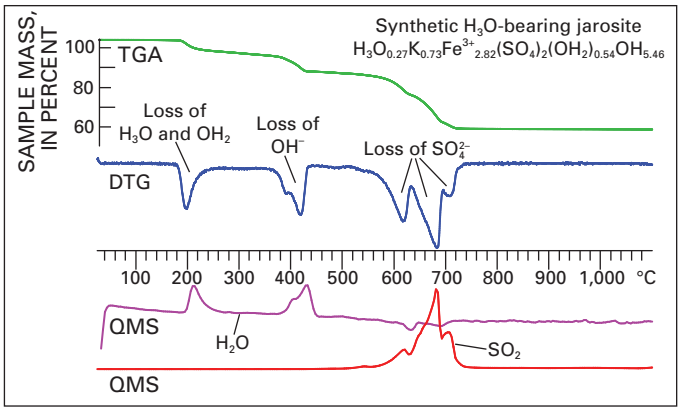

Figure 4. Top: Thermogravimetric Analysis (TGA) curve shows the mass loss as a function of heating a synthetic H_3O-bearing jarosite at a rate of 10 degrees Celsius per minute up to 1,100 degrees Celsius in an inert gas. Middle: Derivative thermogravimetry (DTG) curve shows the first derivative of the TGA curve highlighting changes in the rate-of-mass-loss during heating. Bottom: Quadrupole Mass Spectrometer (QMS) curves record the ion current associated with masses 18 (H_2O) and 64 (SO_2) released during heating. In this jarosite sample, progressive heating drives off H_3O^+ and OH_2 at about 200 degrees Celsius. Near 400 degrees Celsius hydroxyl (OH) is converted to H_2O, and near 680 degrees Celsius SO_4 is converted to SO_2. These kinds of measurements help scientists understand the composition of jarosite.

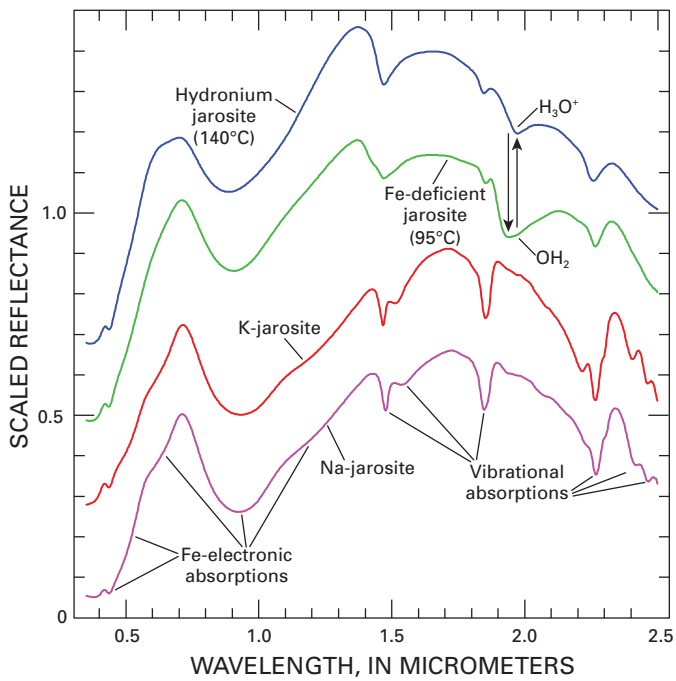

Figure 5. Reflectance spectra of synthetic jarosites (upper two curves) and natural jarosites (lower two curves). Hydronium (H_3O^+)-bearing jarosites have a diagnostic H_3O^+ spectral absorption at 1.96 micrometers. The iron (Fe)-deficient jarosite is potassium (K)-rich with about 10 percent vacancies in the iron site and a diagnostic H_2O spectral absorption at 1.93 micrometers. Synthesis temperatures are listed in parentheses for synthetic samples. Spectra of the natural samples have stronger vibrational absorptions than spectra of the synthetic samples because they do not contain H_3O^+ or protonated hydroxyl (OH_2). Spectra are offset vertically for clarity.

alkali-site deficiencies in the mineral structure. Heating synthetic jarosite samples drives off "excess" water (OH_2) and changes the properties of the jarosites. Over time, recrystallization and desiccation may do the same thing to natural jarosites (fig. 6). Metastable or "modern" low-temperature natural jarosites and synthetic jarosites have larger a- and smaller c-unit-cell dimensions than do "mature" natural jarosites. In addition, mature natural jarosites do not appear to have the site vacancies, iron-deficiencies, or significant H_3O^+ substitutions in the mineral structure that are observed in some synthetic and modern natural jarosites. Recognition of metastable jarosite phases is important because they 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 young jarosites from mining wastes, the synthetic jarosites should not be dried at temperatures above 60°C.

What can jarosite tell us about Mars?

As mentioned previously, one of the Mars exploration rovers found jarosite in what many interpret as sedimentary rocks on Mars (fig. 7). A remaining question about this jarosite occurrence is the type of geochemical environment in which it was deposited. One hypothesis suggests that this jarosite may have been deposited in shallow, acid-saline water, but another hypothesis suggests that hydrothermal fluids may have been instrumental in the formation of the jarosite (Golden and others, 2008). In 2007, jarosite was observed on Mars from orbit by the CRISM imaging spectrometer in layered materials south of the Valles Marineris Canyon System (Milliken and others, 2008). A spectrum of this jarosite shows H_3O^+ and protonated hydroxyl (OH_2) absorptions near 1.9 µm, which is consistent with formation of this mineral in an acidic, low-temperature environment. This observation supports an emerging picture of Mars as an initially wet planet that dried up over time. The ability to differentiate spectrally between low-temperature lake sediments and relict high-temperature hydrothermal deposits from Martian orbit can help focus future rover deployment and sample collection on areas with the highest potential of having preserved possible evidence of ancient life. In summary, our studies have led to the recognition that jarosite can, under the right conditions, preserve evidence of the geochemical and thermal conditions in which it formed.

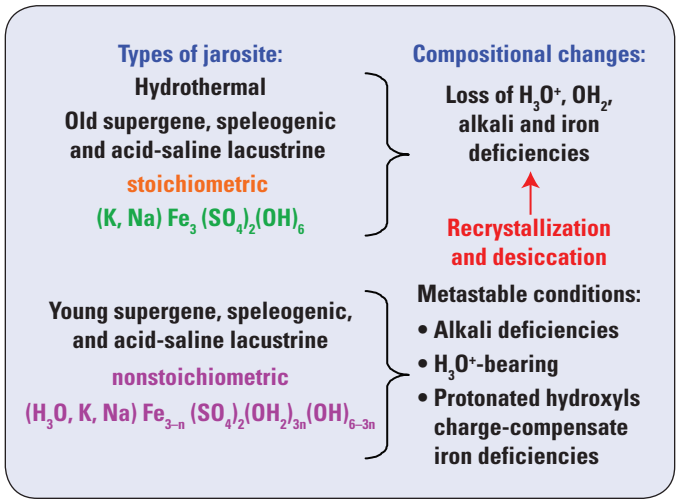

Figure 6. Terrestrial environments in which jarosites are known to form. Hydrothermal formation of jarosite usually involves precipitation from hot (greater than 100 degrees Celsius) fluids. Low-temperature (less than 100 degrees Celsius) sulfide oxidation is responsible for most supergene jarosite formation. Sulfuric acid associated with hydrocarbons may form speleogenic jarosite in caves, whereas highly acidic-saline fluids can cause precipitation of jarosite in lakes. Most hydrothermal jarosites are stoichiometric, having ideal jarosite chemical formulas. The other types of jarosite may be nonstoichiometric initially, but through long-term desiccation they usually recrystallize to stoichiometric forms. In the nonstoichiometric jarosite formula the letter "n" indicates the level of iron deficiency, and if this value is known it can be used to calculate the amount of protonated hydroxyl (OH_2) and normal hydroxyl (OH).

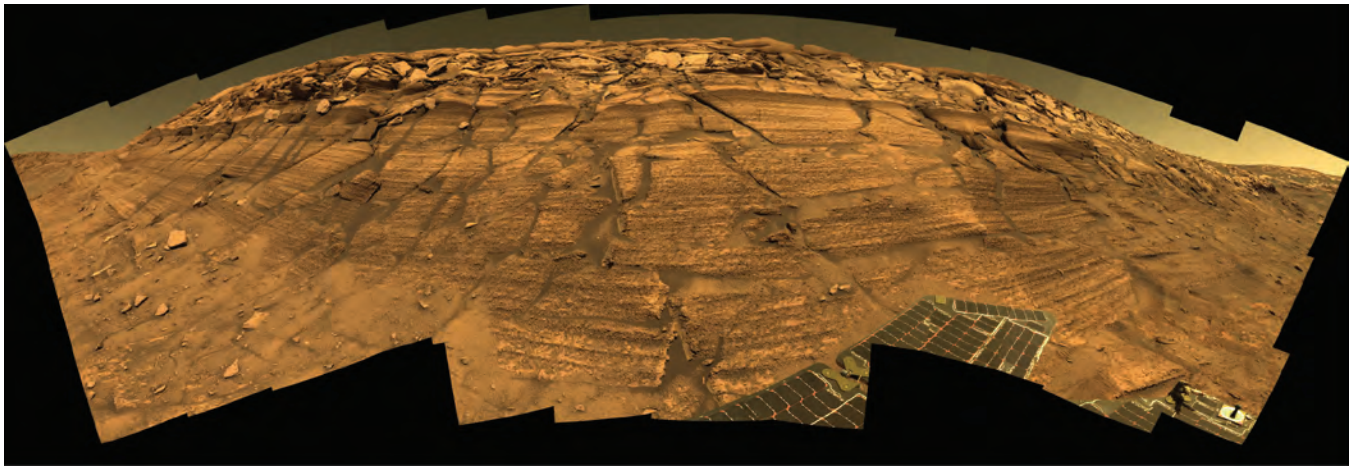

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Figure 7. Approximate true-color mosaic of "Burns Cliff" along the southeastern inner wall of Endurance Crater in Meridiani Planum on Mars. Images were collected by the panoramic camera on the Opportunity Rover. *In-situ* Mossbauer analyses of these crossbedded sediments indicate that they contain spherical hematite-rich concretions known as "blue berries," magnesium sulfates, and jarosite. The mosaic spans more than 180 degrees from side to side.

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Understanding Contaminants Associated with Mineral Deposits

Circular 1328

U.S. Department of the Interior
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Edited by Philip L. Verplanck

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Suggested citation:
Verplanck, P.L., ed., 2008, Understanding contaminants associated with mineral deposits: U.S. Geological Survey Circular 1328, 96 p.