

Comparison of the structures of natural and synthetic Pb-Cu-jarosite-type compounds

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Abstract: Jarosite minerals are effective scavengers of potentially toxic elements such as Pb and Cu, and are abundant in acid rock drainage systems, acid sulfate soils and metallurgical wastes. We used XRD, SEM, and infrared, Raman and X-ray absorption (EXAFS and XANES) spectroscopy to determine the structural differences between natural and synthetic Pb-Cu-jarosites. Differences in the a_0 unit cell dimensions for the natural and synthetic samples (7.2288(27) Å and 7.32088(26) Å, respectively), and c_0 unit cell values (34.407(14) Å and 17.0336(7) Å, respectively) are attributed to different proportions of H₂O, Fe and Pb in the jarosite structures. The synthetic Pb-Cu-jarosite has sharper Raman and IR spectra, with narrower and more intense bands, suggesting that it is more crystalline than the natural sample. EXAFS fitting of the Fe and Pb data for the natural and synthetic Pb-Cu-jarosite samples are similar to each other, and are also similar to previously reported EXAFS data for jarosites, suggesting that Fe occupies the B sites, and Pb the A sites. The natural sample's Pb EXAFS data are only fitted over a short k -range, however, and the comparison is based on only the first two shells around Pb. Our Cu fits for the natural Pb-Cu-jarosite are similar to the first and third shell fittings for Fe, except that the Cu occupies a tetrahedral rather than an octahedral site (4 O in first shell at $r = 1.94$ – 1.95 Å; 4 Fe in third shell at $r = 3.59$ – 3.60 Å). In the synthetic Pb-Cu-jarosite, Cu also shares the B site with Fe, but fits of 4 Cu around the Cu atom at a bond distance of 2.60 Å and XANES evidence also suggest the presence of metallic Cu within the structure. Variations in the structures of the natural and synthetic samples are likely due to their differing chemistries and conditions of formation.

Key-words: beaverite, jarosite, EXAFS, XANES, Raman, natural, synthetic, copper, lead, metallic coppers.

Introduction

Jarosite minerals are effective scavengers of potentially toxic elements such as Pb and Cu, and are abundant in acid rock drainage systems, acid sulfate soils, metallurgical wastes and archaeological sites (Arregui *et al.*, 1979; Rewitzer & Hochleitner, 1989; Hyashi, 1994; Hudson-Edwards *et al.*, 1999; Dutrizac & Jambor, 2000). Jarosite minerals are members of the isostructural jarosite-alunite group of minerals that has a general formula of $AB_3(TO_4)_2(OH)_6$, where A represents cations with a coordination number greater than or equal to 9, and B and T represent cation sites with octahedral (O) and

tetrahedral (T) coordination, respectively (Jambor, 1999). One important toxic element-bearing jarosite is beaverite $[Pb(Fe,Cu)_3(SO_4)_2(OH)_6]$, in which the A-site is filled with divalent Pb^{2+} , and this is charge-balanced by substitution of divalent Cu or Zn in the normally trivalent B site. The T site is filled by a sulfate unit (SO_4^{2-}), as with other jarosites (Kubisz, 1964; Brophy & Sheridan, 1965). Beaverite was first described at the Horn Silver mine, Utah, in 1911 (Butler & Schaller, 1911), and has subsequently been observed in mines in Cornwall (Kingsbury, 1952), the Lake District in the UK (Kingsbury & Hartley, 1957) and many other localities (*e.g.*, Taguchi *et al.*, 1972; Dutrizac & Jambor, 2000).

Studies on jarosite structure and dissolution mechanisms normally use synthetic jarosites precipitated in the laboratory, but it is unclear how similar the structures of these synthetic jarosites are to those of natural jarosites. Using Raman spectroscopy, Frost *et al.* (2005a) demonstrated that although the crystal structures of the synthetic and natural K- and Na-jarosites may be identical, their molecular structures may differ. Raman analysis on a synthetic Pb-Cu-jarosite Frost *et al.* (2005b) as well as some XAS work on synthetic and natural As-bearing jarosite have been undertaken (*e.g.*, Paktunc & Dutrizac, 2003; Gault *et al.*, 2005; Savage *et al.*, 2005), but no spectroscopic analysis has been carried out to compare the molecular-level architecture of synthetic and natural Pb-Cu-jarosites. Knowledge of the structural differences between these jarosites will enable more realistic synthetic analogues to be prepared, and will further our understanding of the incorporation of potentially toxic Pb and Cu in the jarosite structure. If molecular-level differences, not detectable by XRD, do exist, then further work will be required to understand the underlying reasons behind them.

The aims of this paper, following on from our previous work on jarosites (Smith *et al.*, 2006a, b, c), are therefore to (i) determine if there are structural differences between natural beaverite and synthetic Pb-Cu-jarosite and (ii) investigate how Pb and Cu are held in the jarosite structure, and how this may affect the stability and symmetry of the structure.

Experimental methods

Jarosite samples

A sample previously identified as beaverite was obtained from the mineral collection of the Natural History Museum, London. The sample [BM1913, 202] is from the type locality for beaverite at the Horn Silver Mine, Beaver County, Utah. Synthetic Pb-Cu-jarosite was prepared according to the methods of Dutrizac & Dinardo (1983) and Jambor & Dutrizac (1983, 1985), using a 1 L aqueous solution containing 0.054 M $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and 0.02 M H_2SO_4 , with the addition of 0.315 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The solution was subsequently placed in a 2 L reaction vessel fitted with spiral condensers, then heated by means of a sand bath to 95 °C (1 atm) with constant stirring (400 rpm). When the solution temperature reached 95 °C, 200 mL of 0.03 M $\text{Pb}(\text{NO}_3)_2$ (Aldrich) was added, with stirring, to the solution at a rate of 6 mL h⁻¹. Once all the $\text{Pb}(\text{NO}_3)_2$ had been added, the precipitates were stirred (400 rpm) for a further 5 h, after which they were allowed to settle and the residual supernatant solutions decanted. The precipitates were then washed several times with ultrapure water (18 M Ω cm⁻¹) and dried at 110 °C for 24 h.

Chemical analysis

The natural beaverite sample was analysed by electron microprobe spectroscopy (Jeol JXA-8100) in wavelength-dispersive mode for Cu, Fe, Pb, O and S. For quantitative

total elemental analysis of the synthetic jarosite, approximately 60 mg of each material was dissolved in polypropylene beakers by adding concentrated HCl dropwise, with stirring, until no solid remained. The acidified solutions were then diluted to 50 mL with 2 % HNO_3 , and analysed for Pb, Fe, Cu and S by inductively coupled plasma optical emission spectrometry (ICP-OES) using a simultaneous solid-state detector (CCD) (Varian Vista-Pro, axial configuration).

X-ray diffraction

The natural beaverite sample was characterised by powder X-ray diffraction (XRD) analysis at 25 °C with a Enraf-Nonius PDS 120 configured in vertical geometry with a 2-theta detection range of 120° and utilizing $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at 45 kV and 45 mA. The precipitation products were identified by crystallography using powder XRD analysis at 25 °C with a Philips PW1050 vertical powder diffractometer utilizing $\text{Co K}\alpha_1\text{K}\alpha_2$ ($\lambda\alpha_1 = 1.788965 \text{ \AA}$ or $\lambda\alpha_2 = 1.792850 \text{ \AA}$) radiation at 35 kV and 30 mA. For both the natural and synthetic samples, unit cell parameters were calculated through Rietveld refinement using GSAS (Larson & Von Dreele, 1998) and the 'model free' Le Bail Method (Le Bail *et al.*, 1988), where individual ' $|F_{\text{obs}}|$ ' are obtained by Rietveld decomposition from arbitrarily identical values. In addition to the structure factors, free refinement was made of the lattice parameters constrained according to the rhombohedral symmetry of the space group in the centred hexagonal setting, background, profile parameters and the instrumental zero-point. In all cases, a pseudo-voigt profile was used (Larson & Von Dreele, 1998).

Infrared and Raman spectroscopy

Infrared spectroscopy (IR) was used to characterize the vibrational modes present within the natural and synthetic jarosites. The IR spectra were collected with a PerkinElmer Spectrum One FTIR spectrometer using the KBr pellet ($\varnothing 13 \text{ mm}$) technique. Spectra were recorded in transmission mode immediately after pellet preparation; the scanning range was 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹, and five scans were accumulated.

Laser Raman microspectroscopic analyses were carried out using a Renishaw RM1000 Raman Spectrometer, equipped with a thermoelectrically cooled CCD detector and a 514.5 nm Ar ion laser. The instrument was calibrated daily on a silicon standard at 520.5 cm⁻¹. The system was operated in confocal mode with the laser focussed on the sample through the objective lens ($\times 50$ – $\times 100$) of an Olympus petrological microscope. Under these conditions the Raman analysis was restricted to an area of less than 2 μm diameter. The laser power was reduced using neutral density filters and was typically between 1 mW and *ca.* 220 μW at the sample. The sample was inspected optically for any laser damage, and no damage was observed. Spectra were recorded over the frequency range

100 to 4000 cm^{-1} , using an integration time of 10–45 s (total analysis time = 100–450 s). Errors on the spectra were $< 0.1 \text{ cm}^{-1}$. Peak fitting was performed using Galactic GRAMS/32 software, which uses a mixed Gaussian-Lorentzian curve. In order to test the variability of the spectra, at least 10 spectra were obtained in the low frequency region for each sample. The variation between individual spectra was small and therefore the samples were assumed to be homogeneous.

X-ray absorption spectroscopy

X-ray absorption spectroscopies (XAS) were used to investigate how Cu, Fe and Pb coordination environments within the natural and synthetic Pb-Cu-jarosites. For this study, X-ray absorption spectra at the Cu and Fe K-edges and Pb LIII-edge were collected at the minifocus XAS Station 9.2 at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory, UK. The storage ring operated at 2 GeV with a current of between 125 and 250 mA. Spectra were collected using a water-cooled, double crystal Si111 monochromator detuned 70 % to remove high energy harmonics. Two Kirkpatrick-Baez mirrors (substrate ULE glass coated with 15 nm Rh on 20 nm Pt) were used to focus the beam horizontally and vertically to a spot size of $\sim 50 \mu\text{m}$. Stability of the focussed beam was less than the spot size. For fluorescence measurements a Canberra 13-element solid state Ge detector with full electronics including semi-automatic windowing was used. For both the natural and synthetic samples (encased in polished epoxy blocks) an XRF map of the elements of interest (Cu, Fe, Pb) was collected using GDA Acquisition Version 5.6.0 software. To test for homogeneity of the samples, three ‘hotspots’, where concentrations of the respective element were high, were selected from the XRF map for further analysis by XAS. Between 6 and 16 XAS scans were collected for each element at each of the ‘hotspots’. The edge positions and traces for each point were identical for the three points for each individual elements in each sample (Fe 7124; Cu 8987; Pb 13036 eV), allowing all of the spectra to be summed for each element prior to conducting the EXAFS and XANES fitting. One scan each was also collected in transmission mode for each of the standards: Cu(II) oxide, Cu(II) nitrate, Cu(II) sulfate, Pb(II) oxide, Pb(II) nitrate, Pb(II) sulfate, Fe(III) oxide, Fe(III) nitrate and a synthetic sample of goethite (FeOOH). Incident and transmitted intensities were measured using ionisation chambers filled with a He/Ar mix appropriate for the X-ray energy of interest.

The X-ray absorption spectra of the Cu and Fe K-edges (8987 and 7124 eV, respectively) and the Pb LIII-edge ($\sim 13036 \text{ eV}$) were measured. Data were collected from $\sim 200 \text{ eV}$ before to $\sim 600 \text{ eV}$ above the standard edge position. In the pre-edge region the X-ray energy step size was large ($\sim 9 \text{ eV}$), across the edge the step size was $0.6\text{--}1 \text{ eV}$ and in the post edge region the step size was $1.5\text{--}2 \text{ eV}$. The spectra were processed using the computer programs EXCALIB, EXBROOK, EXSPLINE and EXCURV98 compiled at the SRS (Ellis, 1995; Binstead, 1998). The spectra

were summed using the EXCALIB program. This process also converted the monochromator angle into X-ray energy.

For XANES analysis of each of the three elements analysed, the edge position was determined and the data normalised such that the edge step was equal to one using the EXBROOK program. For analysis of the EXAFS oscillations, the background was subtracted from the raw XAS spectra and the data normalised using the EXSPLINE program (Ellis, 1995). A spline curve, which estimates the smooth background absorbance, was used to remove the smooth background absorbance. No more than three spline points were used. The data were then normalised so that the edge step equalled one. The energy range of the spectrum was reduced if there was significant noise present in the higher energy region of the spectra. The spectrum was then converted to k space using E_0 values for Cu, Fe and Pb of 8987, 7124 and 13036 eV. The EXAFS spectrum was then weighted by k^3 to amplify the upper k range. The final step was the Fourier Transform (FT) of the data in order to convert energy into a radial distribution function over a k range of 2 to $13 \text{ \AA}^{-1}$.

Once the EXAFS and the FT had been calculated the data were fitted to gain structural information. EXCURV98 (Rehr & Albers, 1990; Binstead, 1998) used exact curved wave theory (Lee & Pendry, 1975; Gurman *et al.*, 1984) to simulate EXAFS. The element, coordination number (CN), distance and Debye-Waller factor were determined using the phase and amplitude functions from this program. Standard compound EXAFS traces were compared with experimental samples in order to determine similarities in the spectra. Single and multiple scattering were considered, but multiple scattering did not improve the fit for any sample. During fitting the E_0 value, distance, Debye-Waller factor and CN were varied. Identification of possible elements was determined by differences in the amplitude and phase and possible structural configurations taken from databases, *e.g.* Inorganic Chemical Structural Database (www.cds.dl.ac.uk/icsd). The accuracy of the fit was determined using the R factor statistical parameter for which a lower value indicates a better fit. The fitting procedure accurately determines distances to within $0.02 \text{ \AA}$, but coordination number is highly correlated to the Debye-Waller factor and hence larger errors (± 1) exist.

Results

Composition of natural and synthetic Pb-Cu jarosites

The natural sample [BM1913, 202] was identified as beaverite by comparing its XRD pattern to that of beaverite in the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF 17-0476). This comparison suggested that all peaks arise from the structure of the beaverite, and the absence of additional peaks indicated that no other compounds were present at detectable levels (Fig. 1a). The calculated lattice parameters of the natural beaverite are $a_0 = 7.2288(27) \text{ \AA}$ and $c_0 = 34.407(14) \text{ \AA}$, in contrast to the standard ICDD PDF file values ($a_0 = 7.20 \text{ \AA}$; $c_0 = 16.94 \text{ \AA}$).

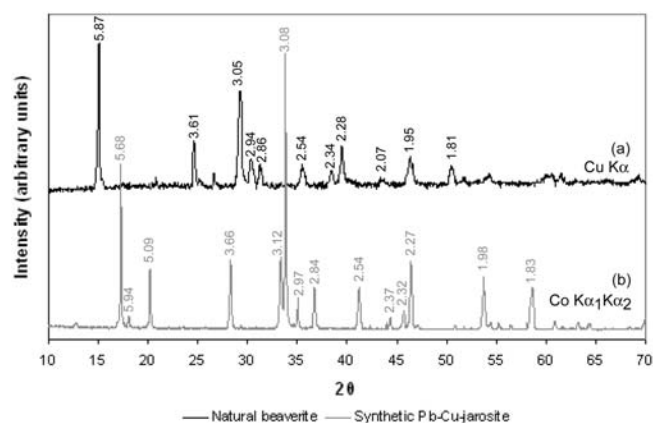


Fig. 1. Powder X-ray diffraction patterns for (a) natural beaverite [BM1913,202] and (b) synthetic Pb-Cu-jarosite. d-spacings have been indicated for the strongest peaks.

The jarosite synthesis produced yellow precipitates with Munsell colour 10YR 7/5. Comparison of the powder X-ray diffraction pattern for the synthetic Pb-Cu-jarosite with that for beaverite in the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF 17-0476) suggested that all peaks arise from the structure of the beaverite, and the absence of additional peaks indicated that no other compounds were present (Fig. 1b). For the synthetic Pb-Cu-jarosite, the calculated lattice parameters are $a_0 = 7.32088(26)$ Å and $c_0 = 17.0336(7)$ Å. Doubling the unit cell for the synthetic Cu-Pb-jarosite did not improve the refinement of the lattice parameters, in contrast to the work done by Jambor & Dutrizac (1983, 1985). χ^2 values for single and doubled unit cells were 2.57 and 2.45, respectively.

The natural beaverite sample is grossly euhedral (Fig. 2a). The synthetic Pb-Cu-jarosite precipitates occur as spherical or cauliflower-like aggregates of individual crystals with diameters $< 2 \mu\text{m}$ (Fig. 2b).

Mole percentages of the A-, B- and T-site elements in the synthetic Pb-Cu-jarosite were determined using the total elemental analysis data. Iron deficiencies in the B site in synthetic jarosites are represented through the Fe:SO₄ molar ratio, which typically is significantly lower than the ideal of 3:2 (Kubisz, 1970), with ratios as low as 2.20:2 to 2.57:2 (Härtig *et al.*, 1984). These deficiencies are charge balanced by the incorporation of water (as hydronium) into the jarosite structure (Kubisz, 1970; Härtig *et al.*, 1984; Ripmeester *et al.*, 1986). In end-member beaverite, the theoretical Pb(II) occupancy in the A-site is set at 1.0 (thus, the A-site is charge-ordered). On this basis, the formula of the synthetic Pb-Cu-jarosite is calculated as $(\text{H}_3\text{O})_{0.67}\text{Pb}_{0.33}\text{Fe}_{2.71}\text{Cu}_{0.25}(\text{SO}_4)_2(\text{OH})_{5.96}(\text{H}_2\text{O})_{0.04}$ (assuming that all of the Cu enters the B-site, which will be explored further below). This formula suggests that our synthetic jarosite is not true beaverite, despite the fact that its crystal structure, as revealed by XRD, matches that of this mineral. For this reason, the synthetic jarosite will continue to be referred to as 'Pb-Cu-jarosite'. The calculated formula is similar, however,

to those reported by Dutrizac & Dinardo (1983) and Jambor & Dutrizac (1983, 1985). The stoichiometry of the natural beaverite [BM1913, 202], calculated using the electron microprobe data, is $\text{PbFe}_{1.69}\text{Cu}_{0.98}(\text{SO}_4)_2(\text{OH})_6$, and is thus very close to the previously published formula for beaverite from the Horn Silver mine locality $(\text{Pb}_{0.99}\text{Fe}_{1.62}\text{Cu}_{0.92}\text{Al}_{0.54}(\text{SO}_4)_2(\text{OH})_6$; Palache *et al.*, 1951). We did not, however, detect any Al in our natural beaverite [BM1913, 202].

Raman spectra

Raman spectroscopy can give information on the stretching and bending vibrations associated with the interactions of atoms in minerals, and has been used for synthetic and natural jarosites to give information on site symmetry (Serna *et al.*, 1986; Sasaki, 1997; Sasaki *et al.*, 1998; Frost *et al.*, 2005a, b; Savage *et al.*, 2005). Raman spectra for the natural beaverite and synthetic Pb-Cu-jarosite are shown in Fig. 3 and their wavenumbers are listed in Table 1, where they are compared with data for synthetic beaverite published by Frost *et al.* (2005b). Peaks were assigned on the basis of data from Sasaki *et al.* (1998) and Frost *et al.* (2005b). The Raman spectra show four main groups of bands: those due to O-H stretching or bending vibrations ($3300\text{--}ca. 3700 \text{ cm}^{-1}$), internal modes of the SO₄ group occurring over two regions ($430\text{--}650$ and $980\text{--}1200 \text{ cm}^{-1}$) and Fe-O (and/or possibly Cu-O or Cu-Cu) stretches (less than 440 cm^{-1}). These are discussed in more detail below.

The OH stretching region shows a single broad Raman band for the synthetic sample, but two bands for the natural sample. The two OH stretching bands for the natural sample suggest the OH groups in the structure are not equivalent, while they appear to be so in the synthetic sample. Such non-equivalence is often due to Cu substitution for Pb (Frost *et al.*, 2005b), and this appears to be much more important in our natural sample than in the synthetic one.

The internal modes of the free SO₄²⁻ ion give four fundamental vibrations, which occur at intermediate and low frequencies (in the free ion these are: ν_1 983, ν_2 450, ν_3 1105 and ν_4 611 cm^{-1} ; Ross, 1974). Within the jarosite crystal lattice the T_d symmetry of the tetrahedron will be reduced, removing the degeneracy of some of the vibrations, and splitting the bands (*e.g.* Frost *et al.*, 2005a, b). The bands for the natural and synthetic samples in this study also show splitting of the sulfate vibrational modes (Fig. 3, Table 1). Frost *et al.* (2005b) attributed such splitting to the non-equivalence of the sulfate units in the beaverite structure as a result of the substitution of Cu²⁺ for Fe³⁺, but the splitting could also be due to the incomplete filling of the A site by Pb²⁺, which affects the force constants of the S-O bonds (*cf.* Sasaki *et al.*, 1998). These workers proposed that the ν_1 SO₄²⁻ and ν_3 SO₄²⁻ values assigned to S-O bonds in sulfate adjacent to Pb²⁺ are smaller than those in SO₄²⁻ not adjacent to Pb²⁺. Relative differences in the peak intensities for the split sulfate bands may be due to such a factor (Fig. 3). The bands for the natural and synthetic samples in this study are broadly similar, and also broadly similar to those of

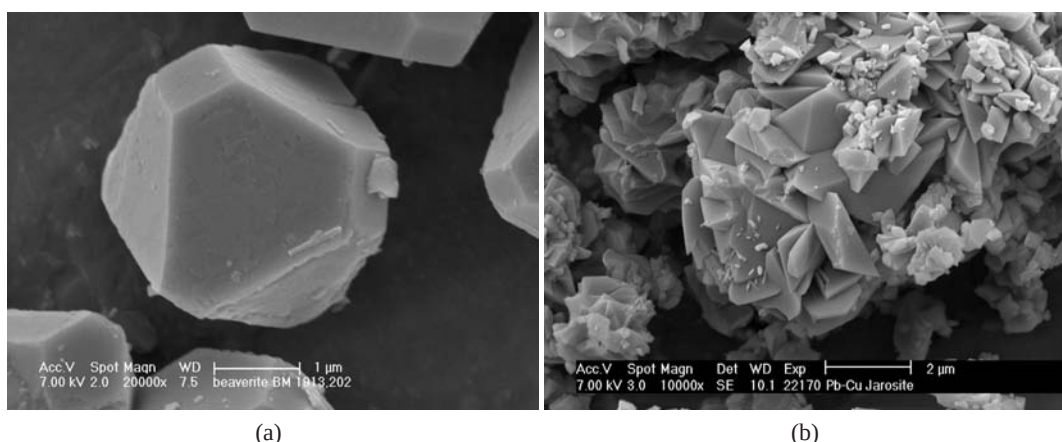


Fig. 2. Scanning electron microscope (SEM) images of (a) natural beaverite and (b) synthetic Pb-Cu-jarosite.

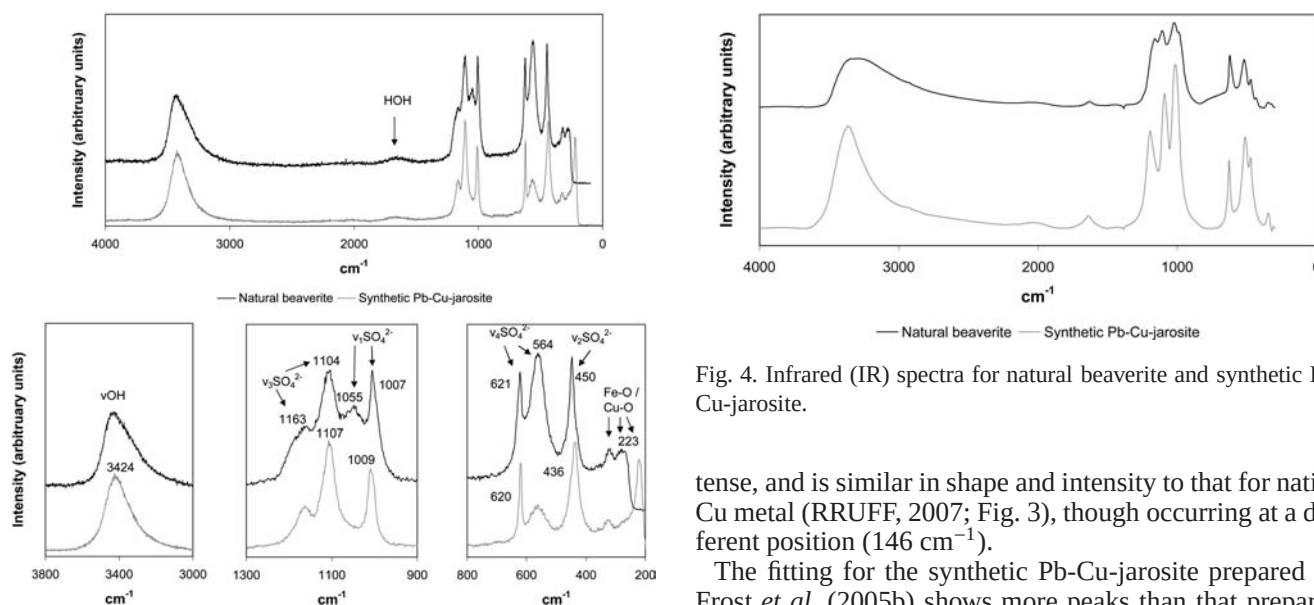


Fig. 3. Raman spectra for natural beaverite and synthetic Pb-Cu-jarosite. Peak assignments based on Sasaki *et al.* (1998) and Frost *et al.* (2005a).

Frost *et al.* (2005b; Table 1), although there are some differences. Our natural sample shows an additional band at 1046 cm^{-1} , which is not reported by Frost *et al.* (2005b) and may reflect the presence of a contaminant (*i.e.*, another mineral). The bands also have different relative intensities [compare 1104 cm^{-1} (natural) with 1107 cm^{-1} (synthetic); and 561 cm^{-1} in both the natural and synthetic (Table 1, Fig. 3)].

In Pb-Cu-jarosites, the replacement of some of the Fe by Cu in the B-site should result in weaker Fe-O modes, and likely new Cu-O bands. The bands assigned to Fe-O (or Cu-O) vibrations are 328.9 cm^{-1} for the natural sample, and 319.8 and 222.6 cm^{-1} for the synthetic sample. The first two are broadly similar to each other and to the 327.6 cm^{-1} band of Frost *et al.* (2005b) (Table 1, Fig. 3). The 222.6 cm^{-1} band in the synthetic sample is very in-

Fig. 4. Infrared (IR) spectra for natural beaverite and synthetic Pb-Cu-jarosite.

tense, and is similar in shape and intensity to that for native Cu metal (RRUFF, 2007; Fig. 3), though occurring at a different position (146 cm^{-1}).

The fitting for the synthetic Pb-Cu-jarosite prepared by Frost *et al.* (2005b) shows more peaks than that prepared by us for this study (Table 1). We do not have a definitive explanation for this difference, but suggest that it may be due to differences in preparation of the synthetic Pb-Cu-jarosite, and spectral peak fitting procedures.

IR spectra

The IR spectra for the natural beaverite and synthetic Pb-Cu-jarosite (Fig. 4, Table 1) are similar to those previously reported (Powers *et al.*, 1975; Serna *et al.*, 1986; Baron & Palmer, 1996; Drouet & Navrotsky, 2003; Frost *et al.*, 2005a, b; Smith *et al.*, 2006b, c). The intense absorption observed in the region 2900 to 3700 cm^{-1} is attributed to O-H stretching (ν_{OH}). The band shift toward lower frequencies for the natural beaverite (3347 cm^{-1}) and synthetic Pb-Cu-jarosite (3362 cm^{-1}), compared with end-member K-jarosite (3385 cm^{-1}) (Smith *et al.*, 2006c), is probably due to an increase in hydrogen bonding within the structure (Powers *et al.*, 1975; Drouet & Navrotsky, 2003). Sulfate oxygen atoms are located on trigonal axes, parallel to the *c*-axis of the unit cell, and are surrounded by three hydroxyl

Table 1. Raman and infrared (IR) wavenumbers (cm^{-1}) of natural beaverite, synthetic Pb-Cu-jarosite, and synthetic beaverite (from Frost *et al.*, 2005a).

Assignment	Beaverite BM1913, 202	Raman spectra Synthetic Pb- Cu-jarosite	Synthetic beaverite (Frost <i>et al.</i> , 2005)	Beaverite BM1913, 202	IR spectra Synthetic Pb- Cu-jarosite	Synthetic beaverite (Frost <i>et al.</i> , 2005)
	Centre (cm^{-1})	Centre (cm^{-1})	Centre (cm^{-1})	Centre (cm^{-1})	Centre (cm^{-1})	Centre (cm^{-1})
ν_{OH}		3424.5		3704.1	3362.2	3446.0
ν_{OH}	3416.1		3420.9	3620.9		
ν_{OH}	3272.3		3380.1			
ν_{OH}	3146.5		3354.4			3346.1
ν_{OH}				3347.7		3342.6
ν_{OH}						3178.1
HOH	1631.0	1650.0		1633.1	1641.8	
Not given						1239.4
$\nu_3(\text{SO}_4^{2-})$					1194.9	1191.7
$\nu_3(\text{SO}_4^{2-})$			1175.7			
$\nu_3(\text{SO}_4^{2-})$	1162.6	1162.6	1163.9	1160.8		
$\nu_3(\text{SO}_4^{2-})$	1104.4		1156.3			1144.9
$\nu_3(\text{SO}_4^{2-})$	1055.4		1116.5			
$\nu_3(\text{SO}_4^{2-})$			1102.7	1107.5		1106.1
$\nu_3(\text{SO}_4^{2-})$			1080.8		1091.7	
$\nu_3(\text{SO}_4^{2-})$			1076.3			1077.3
$\nu_1(\text{SO}_4^{2-})$			1018.4	1022.5	1015.6	
$\nu_1(\text{SO}_4^{2-})$		1107.1	1009.9			1104.3
$\nu_1(\text{SO}_4^{2-})$	1006.7	1008.5				
$\nu_1(\text{SO}_4^{2-})$						
γ_{OH}			999.1	990.2		993.5
Not given						900.0
Not given						790.3
Not given						689.2
Not given						671.4
Not given			645.2			
$\nu_4(\text{SO}_4^{2-})$	621.1		624.3	622.3	627.8	625.5
$\nu_4(\text{SO}_4^{2-})$		619.7	619.4			
$\nu_4(\text{SO}_4^{2-})$						586.1
$\nu_4(\text{SO}_4^{2-})$	563.5	561.4	576.5			
$\nu_4(\text{SO}_4^{2-})$			560.4			
Either $\nu_4(\text{SO}_4^{2-})$ or $\nu_2(\text{SO}_4^{2-})$			520.3	512.5	511.9	
Either $\nu_4(\text{SO}_4^{2-})$ or $\nu_2(\text{SO}_4^{2-})$		480.5	474.0	474.6		
$\nu_2(\text{SO}_4^{2-})$			455.8			
$\nu_2(\text{SO}_4^{2-})$	449.9	436.4	441.0	434.8		
$\nu_2(\text{SO}_4^{2-})$	431.2		432.9			
Not given			391.5			
Not given			356.3			
Not given			335.4			
Fe-O or Cu-O	328.9	319.8	327.6			
Not given			298.4			
Fe-O or Cu-O			278.0			
Not given	260.1		258.5			
Not given	221.7		242.0			
Fe-O or Cu-O or Cu metal		222.6	216.4			
Not given			201.8			
Not given			172.5			

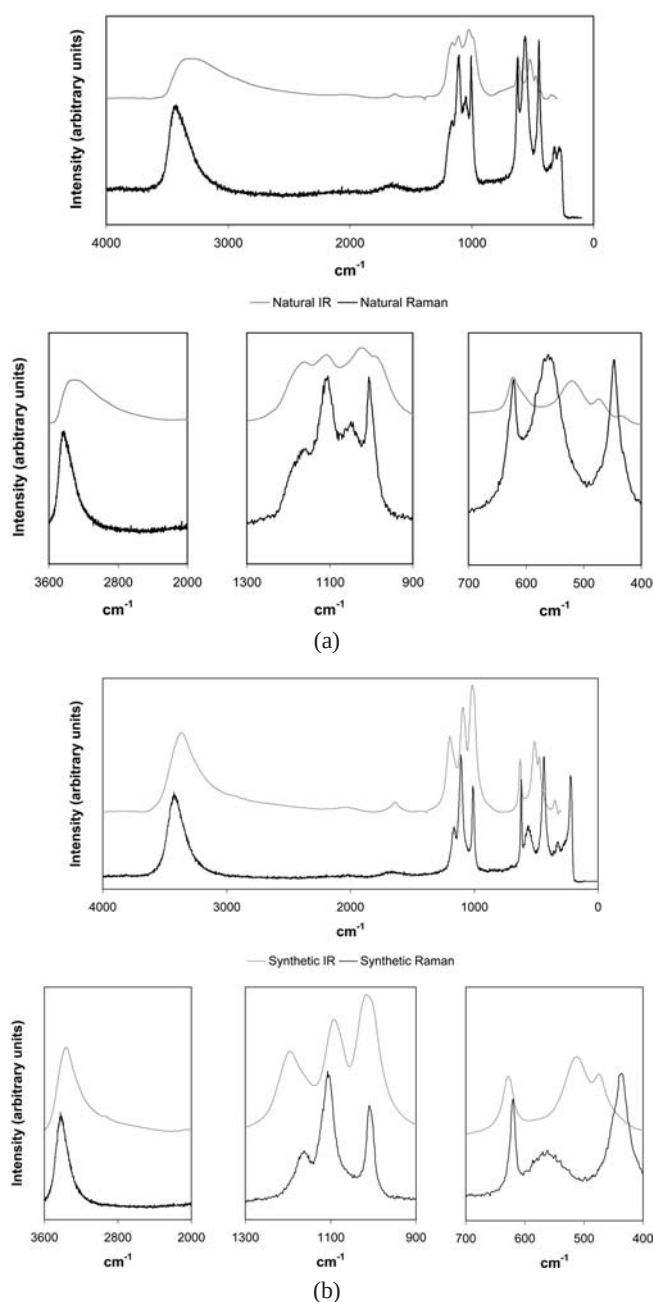


Fig. 5. Comparison of IR and Raman spectra for (a) natural beaverite and (b) synthetic Pb-Cu-jarosite.

groups (Hendricks, 1937). It is therefore possible to distinguish two vibrational modes, O-H and H-OSO₃, around the hydrogen. The bands observed at 1634 and 1641 cm⁻¹ (Fig. 4) are attributed to HOH deformation, in agreement with the results of others (Powers *et al.*, 1975; Baron & Palmer, 1996; Drouet & Navrotsky, 2003). The HOH deformation mode is directly related to the 'additional' water groups formed from the protonation of the hydroxyl groups. The bands below 1500 cm⁻¹ are assigned to sulfate vibrational modes (*cf.* Sasaki *et al.*, 1998).

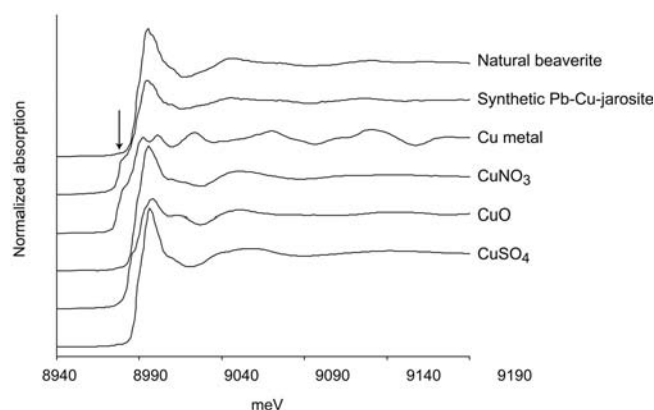


Fig. 6. XANES of Cu in natural beaverite, synthetic Pb-Cu-jarosite and model compounds. Arrow indicates pre-edge peak shown by the synthetic Pb-Cu-jarosite and the metallic Cu.

Comparison of IR with Raman spectra

The differences between the Raman and IR spectra are illustrated in Fig. 5. For the natural Pb-Cu-jarosite in the intermediate frequency range from 900 to 1300 cm⁻¹ (Fig. 5a), although the shapes of the spectra are broadly similar, they show marked differences in both frequencies and relative intensities. In the low frequency region below 700 cm⁻¹, the Raman and IR spectra show completely different patterns. The bands in this region represent BO₆ tetrahedra, ν_2 and ν_4 SO₄ bands and lattice vibrations. The overtone bands around 2036 cm⁻¹ and the OH-bending (ν -OH) region around 1631 cm⁻¹ are only observed (extremely weakly) in the Raman spectra.

For the synthetic Pb-Cu-jarosite the two spectra are similar in the intermediate range from 900 to 1300 cm⁻¹ (Fig. 5b). The IR spectra show three sharp and clearly defined bands (1016, 1092, and a weaker band at 1195 cm⁻¹). The Raman spectra also show three relatively sharp bands (1008, 1107 and a lesser band at 1163 cm⁻¹, which may in fact be a shoulder to the 1107 band). The relative intensities of the Raman and IR bands are dissimilar: in the IR spectra, the 1016 band is the most intense, and in the Raman, the 1107 band dominates. At frequencies below 700 cm⁻¹, the Raman and IR spectra for the synthetic Pb-Cu-jarosite are very different, as they were for the natural beaverite.

Bonding environments of Fe, Cu and Pb

XAS was used to determine the bonding environments of Fe, Cu and Pb in the natural beaverite and synthetic Pb-Cu-jarosite (Fig. 6, 7). Iron K-edge EXAFS spectra and the associated Fourier transform for the natural beaverite and synthetic Pb-Cu-jarosite are shown in Fig. 7, and the derived fit parameters in Table 2. The results from a first shell analysis suggest that Fe exists as Fe³⁺ in octahedral coordination. Crystallographic studies of beaverite suggest that the Fe site is distorted, with four equatorial O atoms at a distance of 1.94 Å and two axial O atoms at 2.10 Å

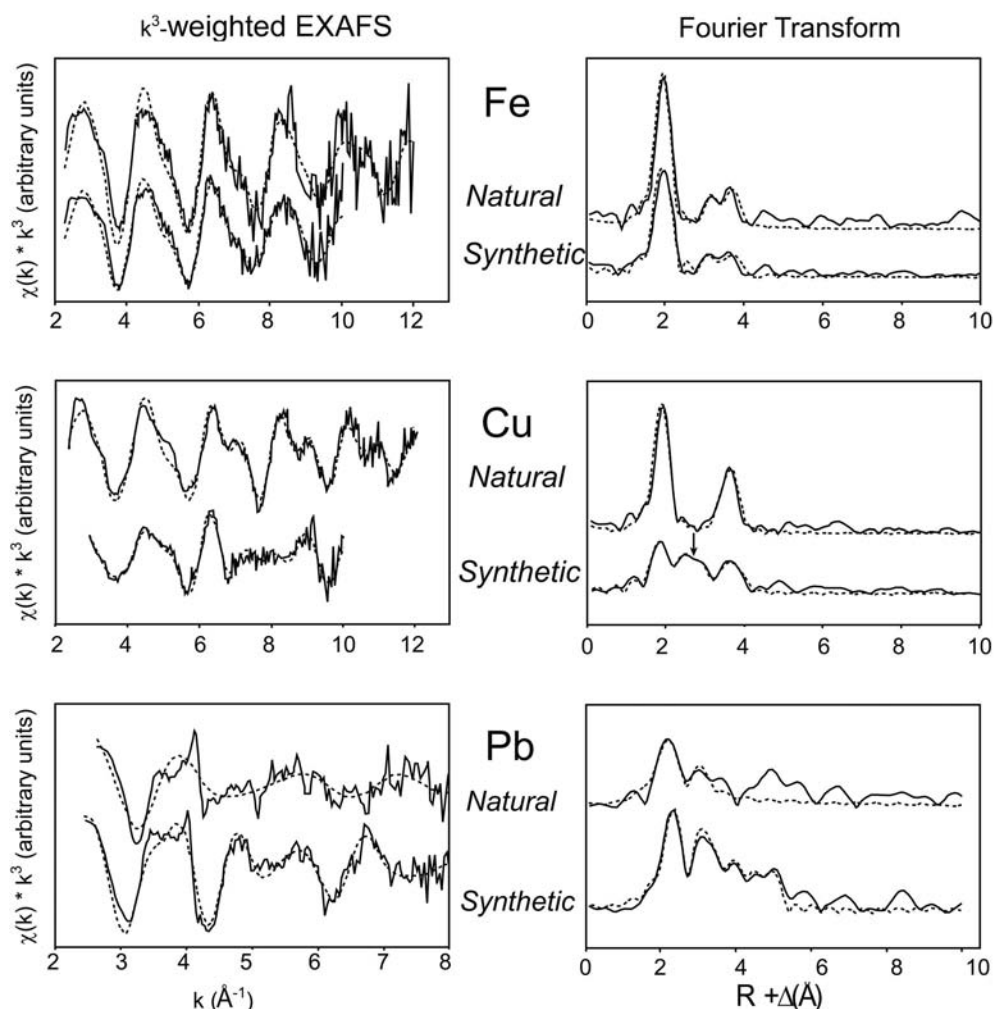


Fig. 7. Normalised Fe and Cu K-edge and Pb LIII-edge EXAFS spectra (left) and Phase Shifted Fourier Transform spectra (right) for natural beaverite and synthetic Pb-Cu-jarosite. Dashed lines are least-squares fits using parameters shown in Table 2. The peak positions in the Fourier Transform spectra are not corrected for backscatter phase-shift, but corrected distances are shown in Table 2. Arrow on the Fourier Transform for Cu for the synthetic Pb-Cu-jarosite indicates the peak fitted to 4 Cu atoms.

(Breidenstein *et al.*, 1992). The EXAFS analysis is unable to resolve these two discrete backscatter contributions in our jarosites, but a bond distance of 2.00 Å can be rationalised as being an average of 4×1.94 Å and 2×2.10 Å. In the jarosite structure, two of the equatorial O corner share with FeO_6 octahedra, while the remaining two bind to H. The axial ligands coordinate to the interconnecting S atoms, which we observe at a distance of 3.28 Å (natural) and 3.24 Å (synthetic). The identification of a shell of four Fe atoms at a distance of 3.66–3.67 Å is also typical of the jarosite structure (*e.g.*, Breidenstein *et al.*, 1992, Savage *et al.*, 2005).

Copper XANES spectra are shown in Fig. 6, K-edge spectra and Fourier transforms in Fig. 7 and the parameters of fit are summarized in Table 2. The first shell O distance for the natural and synthetic samples is similar, at 1.95 and 1.94 Å, respectively, but is slightly shorter than

the first shell oxygen distances for the Fe K-edge fits (Table 2). The shells of four Fe atoms at 3.59 Å (natural) and 3.60 Å (synthetic) in the second and third shell positions, respectively, have similar distances to those of the third Fe-Fe shells (*i.e.*, 3.67–3.68 Å) in the Fe K-edge fits (Table 2). There is no S in the second shell as there was for Fe in either the natural or synthetic samples. The most significant difference between the natural and synthetic Cu fitting is the second shell of Cu atoms in the synthetic sample (Table 2). The Cu-Cu bond distance, 2.60 Å, is close to that in Cu metal (2.5548 Å; Suh *et al.*, 1988). The presence of a second shell of Cu is further supported by the similarity of the Cu XANES for the Pb-Cu-jarosite and the Cu foil standard at 8979 eV (Fig. 6).

Lead LIII-edge spectra and Fourier transforms are shown in Fig. 7 and the parameters of fit are summarized in Table 2. EXAFS fits were attempted to be as close to

Table 2. Parameters used in fitting Fe and Cu K-edge, and Pb LIII-edge EXAFS data for natural beaverite and synthetic Pb-Cu-jarosite samples. $2\sigma^2$ is the Debye-Waller type factor, and the R factor indicates quality of fit (lower R factor indicates a better fit). Data for Pb fitting of plumbojarosite from Szymanski (1985) and non-Cu-bearing beaverite from Breidenstein *et al.* (1992) are shown for comparison purposes. The 'average Pb' shell data for the Szymanski (1985) plumbojarosite represent the averages of each shell of the Pb1 and Pb2 fits. Errors in this table are as follows: Number of atoms ± 1 ; $r \pm 0.02$ Å; DW ± 0.002 Å².

Element	Sample	Scatterer	No. of atoms	r (Å)	$2\sigma^2$ (Å ²)	R factor	No. of scans
Fe	Natural beaverite	O	6	2.00	0.010	38.2	29
		S	2	3.28	0.008		
		Fe	4	3.68	0.023		
Fe	Synthetic Pb-Cu-jarosite	O	6	2.00	0.018	43.2	18
		S	2	3.24	0.013		
		Fe	4	3.67	0.025		
Cu	Natural beaverite	O	4	1.95	0.011	34.5	28
		Fe	4	3.59	0.014		
Cu	Synthetic Pb-Cu-jarosite	O	2	1.94	0.014	36.7	20
		Cu	4	2.60	0.032		
		Fe	4	3.60	0.022		
Pb	Natural beaverite	O	3	2.48	0.037	68.2	18
		O	6	2.80	0.065		
Pb	Synthetic Pb-Cu-jarosite	O	3	2.59	0.022	42.9	26
		O	6	2.88	0.049		
		Fe	6	3.63	0.042		
		S	6	4.52	0.026		
		O	8	4.99	0.053		
Pb1	Plumbojarosite (Szymanski, 1985)	O	6	2.86	Average Pb		
		O	6	2.96			
		Fe	6	3.46			
		S	6	4.24			
		O	6	4.36			
Pb2		O	6	2.59		2.72	
		O	6	3.05		3.00	
		Fe	6	3.55		3.50	
		S	6	4.23		4.24	
		O	6	4.36		4.36	
Pb	Beaverite (non Cu-bearing) (Breidenstein <i>et al.</i> , 1992)	O	6	2.78			
		O	6	2.90			
		Fe	6	3.51			
		S	6	4.17			
Fe		O	6	4.31			
		O	4	1.94			
		O	2	2.10			
		Fe	2	3.28			
		S	4	3.60			

models presented previously for beaverite (Breidenstein *et al.*, 1992) and plumbojarosite (Szymanski, 1985). Better R -factors were achieved for the latter, so the modelling was carried out using the plumbojarosite structure as a basis. The model for plumbojarosite calculated by Szymanski (1985) defines two sites for Pb (Pb1 and Pb2, Table 2), but as the EXAFS fitting for the Pb-Cu-jarosites is an averaging technique, the fitted structure was assumed to be a

50:50 composite between the two sites. This results, for example, in the first shell for the Pb-Cu-jarosites comprising 3 O atoms rather than the 6 O atoms defined by Szymanski (1985). The results for the natural and synthetic samples are in broad agreement, with a first shell of three oxygens at 2.48 Å (natural) and 2.59 Å (synthetic), and a shell of six O atoms at 2.80 Å (natural; second shell) and 2.88 Å (synthetic; second shell). Extra shells were fit for

the synthetic sample, including a third shell of 6 Fe atoms at 3.63 Å, a fourth shell of 6 S atoms at 4.52 Å and a fifth shell of 6 O atoms at 4.99 Å. These results are also in broad agreement with Syzmanski's (1985) plumbojarosite model (Table 2), although the Pb-Fe and Pb-S distances in the synthetic Pb-Cu-jarosite are larger than in plumbojarosite.

Discussion

Incorporation of Pb and Cu in natural and synthetic Pb-Cu-jarosites

EXAFS data suggest that Pb is incorporated in the A site of both the natural and synthetic Pb-Cu-jarosites. The higher degree of long-range order fitted around Pb in the synthetic sample (Table 2) is due to its higher concentration of Pb and to the larger number of scans collected compared to the natural sample. For Cu, the combined EXAFS, XANES, Raman and IR data suggest that Cu is incorporated differently in the two minerals. In the natural beaverite, the first and second shell fits around Cu are similar to the first and third shell fits around Fe, except that Cu is surrounded by 4 O, whereas Fe is surrounded by 6 O in the first shell for both. An attempt was made to fit 6 O around Cu in the first shell, but this gave much worse residuals than the 4 O fit. Four O atom fits around Cu have been observed for Cu in other compounds (*e.g.* Strawn *et al.*, 2004). These data suggest that Cu is incorporated into the B site that is normally filled by Fe, and thus agree with observations on beaverite made by others (Dutrizac, 1982, 1984; Dutrizac & Jambor, 2000; Dutrizac *et al.*, 1996; Frost *et al.*, 2005b). The lack of the shell of S atoms around Cu, observed for Fe, may be due to the inefficient scattering by S (a relatively light element), or to a lower degree of long-range ordering around Cu in our samples.

In the synthetic Pb-Cu-jarosite the first and third shell EXAFS fits around Cu are similar in distance and element to the first and second shell fits for the natural sample (Fig. 7; Table 2), and thus also suggest that Cu is sharing the B site with Fe. The EXAFS data, together with the XANES evidence (Fig. 6) and possibly to a lesser extent, the Raman spectra (Fig. 3, RRUFF 2007), suggest the presence of metallic Cu in the structure, which has not previously been reported. Previous work suggests that, following the B site, Cu is likely to occupy the A site (Smith *et al.*, 2006c). If this were true of our synthetic Pb-Cu-jarosite, then the Cu should show the same coordination and bond distances as Pb in beaverite (6 O at 2.78 Å and 6 O at 2.90 Å, Breidenstein *et al.*, 1992) or plumbojarosite (6 O at 2.86 Å and 6 O at 2.96 Å, Syzmanski, 1985), or K in jarosite (6 O at 2.98 Å and 6 O at 2.84 Å; Menchetti & Sabelli, 1976), which it does not. We also attempted to fit O around the Cu for this second shell (not shown), but this gave much worse residuals than the 4 Cu atoms shown in Table 2.

Cu-Cu bonds and metallic Cu nanoparticles have been reported in other mineral systems. Farquhar *et al.* (1996) and Strawn *et al.* (2004) identified Cu dimers sorbing onto

muscovite and smectite, respectively, with Cu-Cu bond distances of 2.65 Å and 2.64 Å, respectively. Figueiredo *et al.* (2006) and Roque *et al.* (2006) reported metallic Cu nanoparticles within glasses. It is thus conceivable that some type of Cu-Cu tetrahedral cluster has formed during the Pb-Cu-jarosite synthesis. This may be similar to that in BaCu₁₀P₄ (Young *et al.*, 1997), in which chains of edge-shared Cu₄ tetrahedra, linked by P atoms have Cu-Cu bond distances of 2.56 Å. The structural position of the Cu tetrahedra in the Pb-Cu-jarosite is unknown, but they may substitute for the sulfate tetrahedra. Similarly, the mechanism of formation of the Cu metal in the structure is presently unknown, but probably requires reduction of the Cu²⁺ in the CuSO₄·5H₂O used to synthesize the mineral.

Structural comparison of natural and synthetic Pb-Cu-jarosites

The a_0 values for the natural and standard ICDD PDF beaverites are similar (7.2288(27) Å and 7.20 Å, respectively), and can be explained by the fact that they are taken from the same locality. Both of these a_0 values, however, are less than that for the synthetic Pb-Cu-jarosite (7.32088(26) Å). Guiseppetti & Tadini (1980) carried out a structural study of osarizawaite, the isostructural alunite equivalent of beaverite. They found that Al, Fe and Cu had random occupancy in the B-sites and that a replacement of Fe³⁺ ($r = 0.67$ Å) and Al³⁺ ($r = 0.50$ Å) by Cu²⁺ ($r = 0.83$ Å) should expand the T-O-T jarosite structure mainly along a_0 . Jambor & Dutrizac (1983) also concluded that the length of a_0 seemed to be governed principally by the proportions of Fe and Cu and the total number of ions in the B-site in beaverite jarosites. According to our derived formula, the synthetic Pb-Cu-jarosite has less Cu in the B site than the natural sample, suggesting that variable Cu substitution is not the reason for the larger a_0 . Stoffregen *et al.* (2000) and Drouet *et al.* (2004) proposed that higher Fe contents increase the a_0 in Na- and K-jarosites and alunites, while Alpers *et al.* (1989) suggested that high contents of hydronium would elongate the a_0 . Both of these factors could explain the larger a_0 in the synthetic Pb-Cu-jarosite. It is also possible that the presence of the Cu metal in the synthetic structure may increase the a_0 dimension.

The c_0 values for the natural and synthetic samples are different (34.407(14) Å and 17.0336(7) Å, respectively) and even if the natural sample's c_0 value is halved to 17.2035 Å, it is still larger than the synthetic value. Jambor & Dutrizac (1985) compared plumbojarosite, beaverite and hydronium jarosite, and found that the Pb content did not affect the c_0 value. They suggested that this arises because additional Pb²⁺ can be accommodated in existing A-site vacancies without disturbing the structure. On this basis, it is unlikely that the differing Pb contents between our two samples are responsible for the different c_0 values.

The synthetic Pb-Cu-jarosite has a higher content of H₂O than the natural sample, which is typical of synthetic jarosites (*e.g.*, Smith *et al.*, 2006b, c), with multiple annealings required to get the A site fully occupied (Peterson,

pers. comm., 2007). Basciano & Peterson (2007) found that substitution of H_3O by K increased the c_0 value of synthetic jarosites. It is therefore possible that the lower c_0 value we observe for the synthetic sample may be due to its high H_3O content. The different H_3O contents do not explain the doubling of the natural sample's c_0 value, which requires some type of disorder on the A-site.

The synthetic Pb-Cu-jarosite has sharper IR and to a lesser extent, Raman spectra, with narrower (better resolved) and more intense bands, which would suggest that it is more crystalline than the natural sample (Fig. 3, 4). This finding contrasts with that of Frost *et al.* (2005a), who found that natural K- and Na-jarosites were more crystalline than synthetic analogues. Despite the differences in crystallinity, the main vibrational IR and Raman assignments are close (Table 1). The space group of sulfate in jarosites is C_{3v}^5 (Sasaki *et al.*, 1998; Frost *et al.* 2005b), but the splitting of the sulfate bands in the natural and synthetic Pb-Cu-jarosites, however, reduces the symmetry to C_s , in agreement with other studies (Frost *et al.*, 2005b). The natural sample has more ν_1 and ν_3 SO_4^{2-} bands than the synthetic, suggesting that its symmetry is lower.

Conclusions

XRD, SEM, and Raman, IR and X-ray absorption spectroscopic characterization of natural and synthetic Pb-Cu-jarosites show that these solids differ in both composition and structure. Synthesis of Pb-Cu-jarosite appears to have resulted in the formation of a Cu_4 tetrahedral complex that has not previously been described for jarosite-type minerals, but which may have important implications for the uptake of Cu in jarosites formed in metallurgical and contaminated natural environments. Our results agree with those of Sasaki & Konno (2000) and Frost *et al.* (2005a), who demonstrated differences in Raman and IR spectra for jarosite minerals formed under natural and synthetic conditions.

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