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The basic copper arsenate minerals olivenite, cornubite, cornwallite, and clinoclase: An infrared emission and Raman spectroscopic study

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ABSTRACT

Molecular structures of the basic copper arsenate minerals olivenite, cornubite, cornwallite, and clinoclase were studied using a combination of infrared emission spectroscopy and Raman spectroscopy. Infrared emission spectra of the basic copper arsenates were obtained over the temperature range 100 to 1000 °C. The IR emission spectra of the four minerals are different, in line with differences in crystal structure and composition. The Raman spectra are similar, particularly in the OH-stretching region, but characteristic differences in the deformation regions are observed. Differences are also observed in the arsenate stretching and bending regions. Infrared emission studies show that the minerals are completely dehydroxylated by 550 °C.

INTRODUCTION

Several dark emerald-green copper arsenate minerals containing no water of crystallization are known from the oxidized zones of base metal deposits (Anthony et al. 2000). These include olivenite (Cu_2AsO_4OH), the most common member of the group. Related species are the dimorphous pairs cornwallite and cornubite [$Cu_5(AsO_4)_2(OH)_4$] and clinoclase and gilmarite [$Cu_3AsO_4(OH)_3$]. Gilmarite is extremely rare, having been reported from a single locality in France (Sarp and Černý 1999). Olivenite is monoclinic (pseudo-orthorhombic), space group $P2_1/n$ (Berry 1951; Burns and Hawthorne 1995; Toman 1977). Cornwallite (monoclinic, space group $P2_1/c$; Arit and Armbruster 1999) is isomorphous with pseudomalachite [$Cu_5(PO_4)_2(OH)_4$] and is more common than its triclinic (space group $P\bar{1}$) dimorph cornubite (Tillmanns et al. 1985). The rare species clinoclase has also been structurally characterized; it is monoclinic, space group $P2_1/a$ (Eby and Hawthorne 1990; Ghose et al. 1965). A summary of crystallographic properties of the basic copper arsenates relevant to this study is given in Table 1.

The relative stabilities of some of the anhydrous basic copper arsenate minerals are shown in Figure 1, based on the experimentally derived data of Magalhães et al. (1988). As expected, the more basic stoichiometries occupy fields at higher pH. Cornwallite (or cornubite) is the stable phase under chemical conditions intermediate to those that serve to stabilize olivenite and clinoclase, and the paragenetic relationships between the phases were explored by Williams (1990). Normal anhydrous Cu^{2+} arsenate is known as the naturally occurring species lammerite [$Cu_3(AsO_4)_2$], but it is very rare (Anthony et al. 2000). Similarly, yvonite [$CuHAsO_4 \cdot 2H_2O$] is known from only one locality (Sarp and Černý 1998). Thus this study has concentrated on the more common anhydrous minerals of the group. Their chemical similarities suggest that they would have similar vibrational spectra, but structural differences indicate that these should be readily distinguishable.

Whilst the infrared spectra of many minerals have been forthcoming, few comprehensive studies of related minerals such as the basic copper arsenates have been undertaken (Braithwaite 1983; Gevork'yan and Povarennykh 1975; Paques-Ledent and Tarte 1974). Structural investigations of some arsenates and the nature of the hydrogen bonds present have been done, but the minerals selected in this study were fundamentally unrelated. Sumin De Portilla (1974) found that the hydroxyl unit was coordinated directly to the metal ion and formed hydrogen bonds to the arsenate anion. Cation substitution and ordering in the olivenite-adamite (Zn_2AsO_4OH) series was investigated by IR methods (Chisholm 1985), but similar studies for related species are lacking. In addition, very few Raman studies of these species have been undertaken (Griffith 1969a, 1969b, 1970). As part of a comprehensive study of the molecular structure of secondary minerals containing oxyanions using IR and Raman spectroscopy, we report the vibrational properties of olivenite, cornubite, cornwallite, and clinoclase, together with an infrared emission study of their dehydration.

EXPERIMENTAL METHODS

Minerals

The sample of cornubite from the Daly mine, Flinders Ranges, South Australia was obtained from the collections of the Mineralogy Section, Victoria Museum, Melbourne, Victoria, Australia (specimen M37793). Cornwallite and olivenite from the Penberthy Croft mine, St. Hilary, Cornwall, U.K., were supplied by J. Betterton. Samples of olivenite and clinoclase from the Tin Stope, Majuba Hill mine, Utah, were purchased from the Mineralogical Research Company. All were checked for purity by powder X-ray diffraction and by SEM and micro-

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TABLE 1. Summary of the crystallographic properties of the basic copper arsenates

olivenite	cornubite	cornwallite	clinoclase	gilmarite
(Burns and Hawthorne 1995; Toman 1977) Monoclinic, $P2_1/n$	(Tillmanns et al. 1985) Triclinic, $P\bar{1}$	(Arit and Armbruster 1999) Monoclinic, $P2_1/c$	(Eby and Hawthorne 1990) Monoclinic, $P2_1/a$	(Sarp and Černý 1999) Triclinic, $P1$
Forms a series with adamite,Zn_2AsO_4OH	Dimorphous with cornwallite	Dimorphous with cornubite	Dimorphous with gilmarite	Dimorphous with clinoclase
Forms a series libethenite, $Cu_2PO_4(OH)$.	Comparable with the corresponding phosphate trimorphs pseudomalachite, ludjibaite and reichenbachite	Isomorphous with pseudomalachite	Comparable with cornetite, $Cu_3PO_4(OH)_3$ is orthorhombic. orthorhombic, *Pbca*	Comparable with cornetite, $Cu_3PO_4(OH)_3$,
Pseudo-orthorhombic with one crystallographically independent arsenate ion containing four independent O atoms	The cornubite crystal structure contains one As atom in the asymmetric unit (total of 2 in the cell) The arsenic is bonded to 4 crystallographically independent O atoms	Cornwallite, although crystallizing in a different space group, has the same number of independent As and arsenate O atoms and OH ions asdoes cornubite	There are three crystallographically independent OH ions in the unit cell, with a total of twelve	With the space group constraints, all atoms in the unit cell (one formula unit) are crystallographically independent
One independent OH group in the unit cell	There are two crystallographically independent OH ions	There are two crystallographically independent OH ions	There is one As atom (total 4) bonded to four independent O atoms	

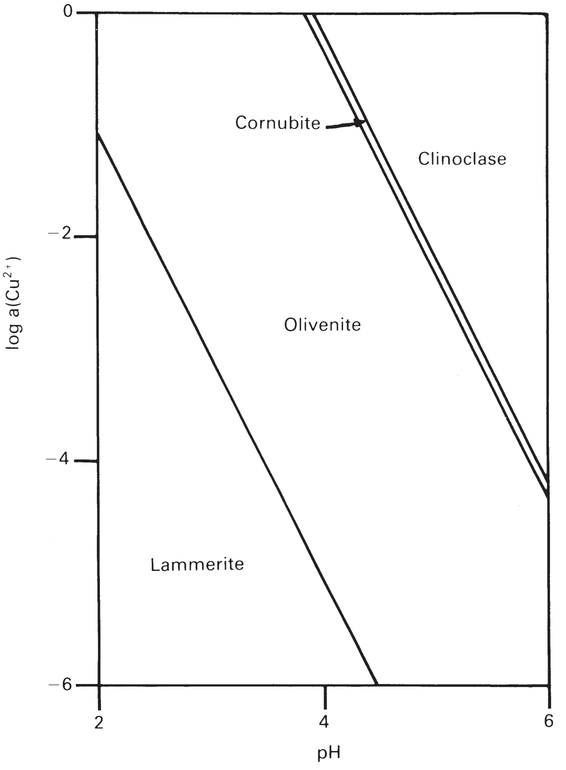

FIGURE 1. Phase relationship of some of the basic copper arsenate minerals (after Williams 1990).

probe methods. Negligible amounts of phosphorus or transition metals other than copper were found in the samples used for the spectroscopic study.

Infrared emission spectroscopy

FTIR emission spectroscopy was carried out with a Nicolet spectrometer equipped with a TGS detector, modified by replacing the IR source with an emission cell. A description of the cell and the principles of the emission experiment was published elsewhere (Frost et al. 1999; Frost and Vassallo 1996; Kloprogge and Frost 2000). Approximately 0.2 mg of each basic copper arsenate was spread as a thin layer (approximately 0.2 micrometers thick) on a 6 mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating.

In the normal course of events, three sets of spectra are obtained. First, black-body radiation over the temperature range selected at the various temperatures was obtained. Secondly, the platinum plate radiation was obtained at the same temperatures, and then spectra were obtained from the sample covering the platinum plate. Normally only one set of black body and platinum radiation is required. The emittance spectrum (E) at a particular temperature was calculated by subtracting the single beam spectrum of the platinum backplate from that of the platinum (Pt) + sample (S), and the result was ratioed to the single beam spectrum of an approximate black body (graphite, C). The following equation was used to calculate the emission spectra:

$$E = -0.5\log\{(Pt - S)/(Pt - C)\}$$

This manipulation was carried out after all the spectroscopic data had been collected. Emission spectra were collected at intervals of 50 °C over the range 200–750 °C. The time between scans (while the temperature was raised to the next hold point) was approximately 100 seconds. We considered that this was sufficient time for the heating block and the powdered sample to reach temperature equilibrium. Spectra were acquired by co-addition of 64 scans for the entire temperature range (approximate scan time 45 seconds), with a nominal resolution of 4 cm^{-1}. Good quality spectra can be obtained providing the sample thickness is not too great. If too thick a sample is used, the spectra become difficult to interpret because of the presence of combination and overtone bands. Spectroscopic manipulation such as baseline adjustment, smoothing, and normalization was performed using the GRAMS software package (Galactic Industries Corporation, Salem, New Hampshire, U.S.A.).

Raman spectroscopy

Crystals of the minerals were placed and orientated on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10× and 50× objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system, and a Charge Coupled Device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisitions using the highest magnification were accumulated to improve the signal-to-noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd., Waterfield, Surrey, England).

Spectroscopic manipulation such as baseline adjustment, smoothing, and normalization were performed as described above. Band-component analysis was undertaken using the Jandel "Peakfit" software package, which enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995.

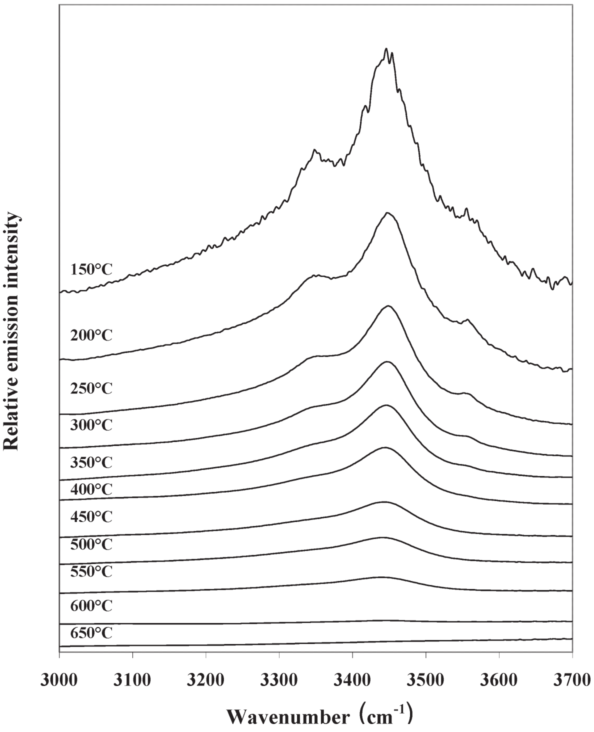

FIGURE 2. Infrared emission spectra of the hydroxyl-stretching region of olivenite from 150 to 600 °C at 50 °C intervals.

RESULTS AND DISCUSSION

Assignment of spectra of the tetrahedral anions in aqueous solutions is comparatively simple. The symmetric stretching vibration of the arsenate anion (ν_1) is observed at 810 cm^{-1} and coincides with the position of the asymmetric stretching mode (ν_3). The symmetric bending mode (ν_2) is observed at 342 cm^{-1} and the out-of-plane bending mode (ν_4) is observed at 398 cm^{-1}. Of all tetrahedral oxyanion spectra, the positions of the arsenate vibrations occur at lower wavenumbers than is the case for most other naturally occurring oxyanions. Farmer (1974) lists a number of spectra of arsenates including those of the basic copper arsenates olivenite and the related hydrated phase euchroite ($\text{Cu}_2\text{AsO}_4\text{OH}\cdot3\text{H}_2\text{O}$). In the crystalline state, degeneracy is lifted and this allows splitting of the bands according to factor group analysis. Thus the ν_1 and ν_3 bands of olivenite and euchroite were observed at 860, 828, 790 cm^{-1} and 830 and 770 cm^{-1}, respectively. Bending modes were found at 493 and 452 cm^{-1} for olivenite and at 475 and 410 cm^{-1} for euchroite. No ν_2 bands were shown. This is no doubt related to the fact the bands are found below 400 cm^{-1}, which makes their measurement by infrared spectroscopy less appealing. Two OH-stretching vibrations were observed at 3580 and 3440 cm^{-1} for olivenite. A number of bands were unassigned.

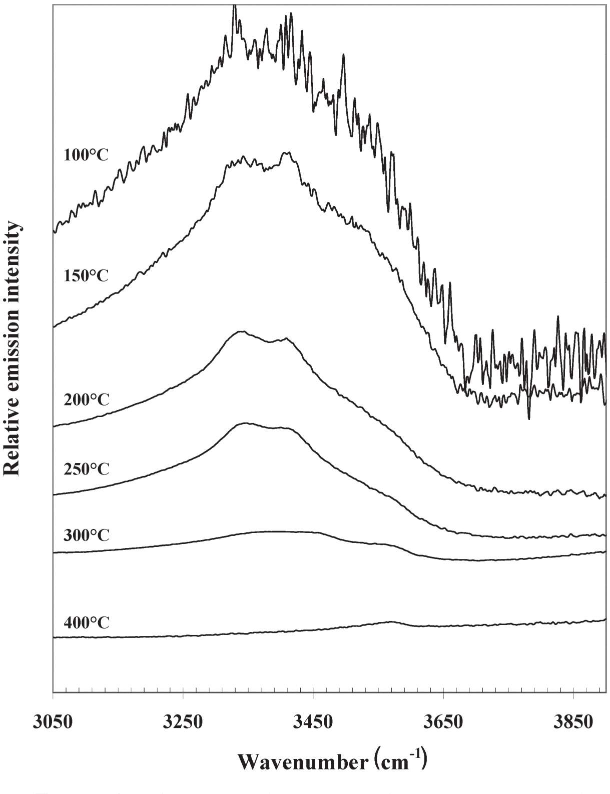

FIGURE 3. Infrared emission spectra of the hydroxyl-stretching region of cornubite from 150 to 600 °C at 50 °C intervals.

Infrared emission spectroscopy of the hydroxyl-stretching vibrations

The infrared emission spectra of the hydroxyl-stretching region of olivenite, cornubite, cornwallite and clinoclase are

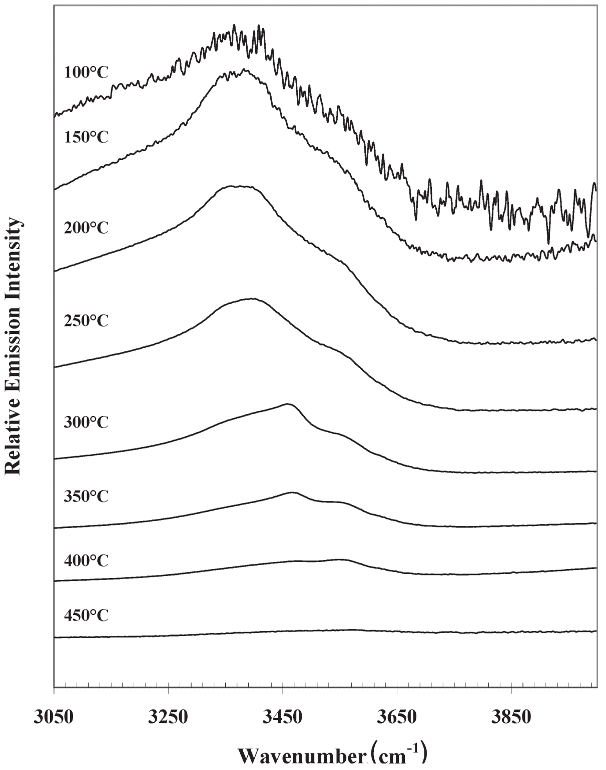

FIGURE 4. Infrared emission spectra of the hydroxyl-stretching region of cornwallite from 150 to 600 °C at 50 °C intervals.

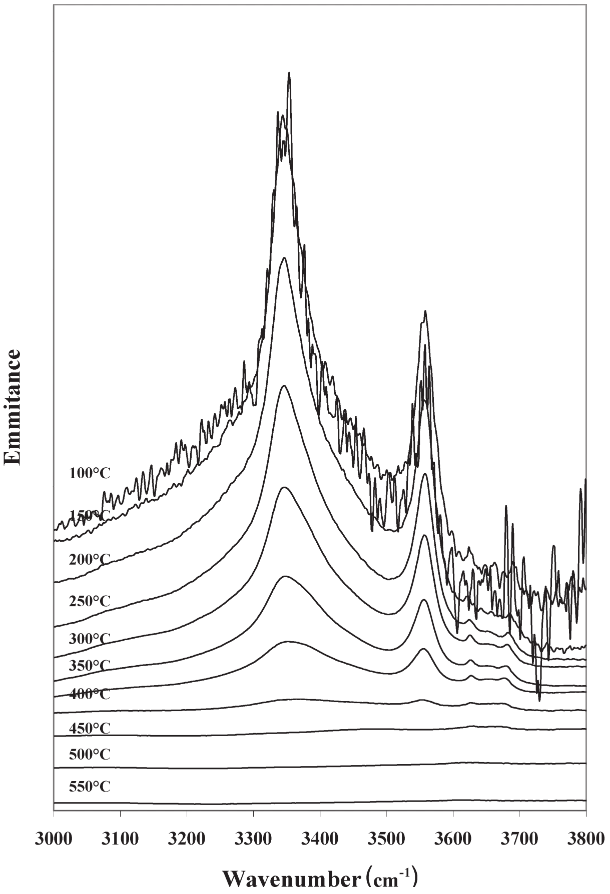

FIGURE 5. Infrared emission spectra of the hydroxyl-stretching region of clinoclase from 150 to 600 °C at 50 °C intervals.

shown in Figures 2 to 5, respectively. The IE spectrum of olivenite shows three curve-resolved hydroxyl stretches at 3553, 3447, and 3346 cm^{-1} (at 150 °C). Farmer (1974) reported two bands at 3580 and 3440 cm^{-1}. The additional band reported here is a curve resolved component. These bands are in reasonable agreement with the IES data reported here. Raman spectra of the hydroxyl-stretching region of the four basic copper arsenate minerals are shown in Figure 6 and reveal the presence of two hydroxyl-stretching vibrations at 3464 and 3437 cm^{-1}. In the structure of olivenite there is one crystallographically independent hydroxyl group (Burns and Hawthorne 1995; Toman 1977) and this suggests that one infrared emission band should be observed. However, there are three emission and two Raman stretching modes. If the proton on the hydroxyl unit was delocalized such that it could attach to the arsenate ion then AsOH moieties could provide the additional hydroxyl vibrations. The unit cell contains one crystallographically independent arsenic atom bonded to four independent O atoms. Hence the four AsOH units would not be identical and the spectrum of the hydroxyl vibrations would not be degenerate. The intensity of the higher wavenumber band observed at 3553 cm^{-1} is lost before the other two hydroxyl-stretching bands and that at 3346 cm^{-1} by 450 °C. Variation of intensity-temperature plots in the 450 to 600 °C region shows the temperature range over which dehydroxylation takes place. The positions of the hydroxyl-stretching bands shift to higher wavenumbers with increasing temperature. This reflects a weakening of the bonding of the OH unit.

Three curve-resolved hydroxyl-stretching IES bands are observed for cornubite at 3535, 3416, and 3349 cm^{-1} (100 °C spectrum). Two additional low intensity bands are observed at 3329 and 3152 cm^{-1}. Three bands are observed even in the 300 °C spectrum. The two hydroxyl-stretching bands at 3416 and 3349 cm^{-1} are not observed at 400 °C. The infrared spectrum of cornubite has not been previously published. Raman spectra show two bands at 3324 and 3042 cm^{-1} (Frost et al. 2002). Cornubite contains two crystallographically independent OH units. Thus two hydroxyl-stretching vibrations should be observed. However, we observe three bands in the IES spectra. The two lower wavenumber vibrations observed at 3416 and 3349 cm^{-1} could be attributed to these independent OH units. The higher wavenumber band at 3535 cm^{-1} may be assigned to an AsOH unit if the protons are delocalized.

The data show that the intensities of the hydroxyl bands diminish at different rates. Importantly, the IES data provide information on the temperature of dehydroxylation of cornubite, such information being complementary to thermoanalytical techniques. However, where rare minerals are involved less than 0.2 mg of sample is required for the IES technique as op-

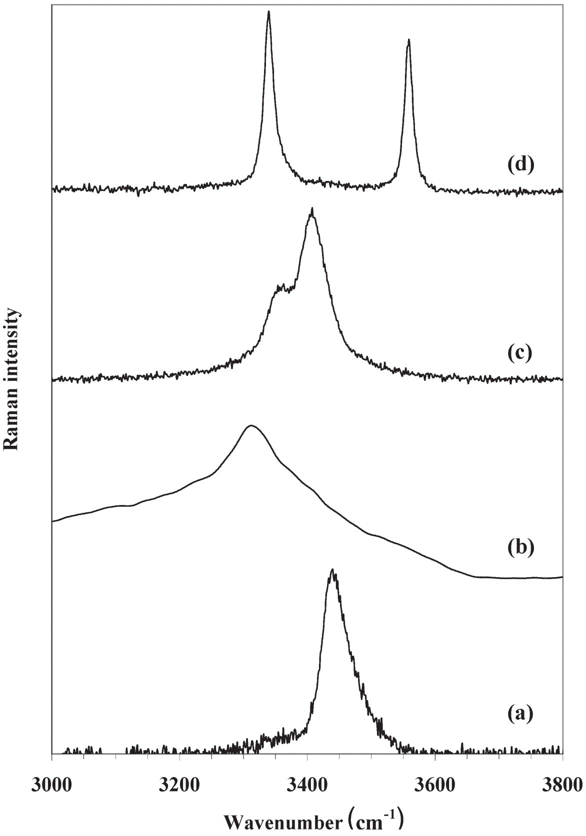

FIGURE 6. Raman spectra of the hydroxyl-stretching region of (**a**) olivenite (**b**) cornubite (**c**) cornwallite (**d**) clinoclase

posed to the thermoanalytical techniques where significantly more sample is required. The data for cornubite suggest that some intensity remains in the 3565 cm^{-1} band up to 700 °C. One possible explanation of the differences in the band positions between the Raman and infrared data rests with the symmetry of the molecule. The Raman technique measures the symmetric stretching modes whereas the infrared technique determines the antisymmetric stretching vibrations.

The IES spectra of cornwallite show bands at 3526, 3417, and 3352 cm^{-1}, with two additional low intensity bands at 3291 and 3132 cm^{-1}. Cornubite and cornwallite are dimorphs and hence might be expected to have similar spectra in the hydroxyl-stretching region. The spectra in Figures 3 and 4 show similar profiles, but the bands for cornwallite are observed at lower wavenumbers. The Raman spectra for cornwallite show two bands at 3411 and 3350 cm^{-1} (Frost et al. 2002), in excellent agreement with the latter two IES bands. Cornwallite contains two crystallographically independent OH units, while three bands are observed in the IES spectra. The two lower wavenumber vibrations at 3417 and 3352 cm^{-1} could be attributed to the independent OH units and the higher wavenumber band at 3526 cm^{-1} to an AsOH moiety. As for cornubite the intensity approaches zero by 400 °C and cornwallite is completely dehydroxylated by 400 °C.

Clinoclase is dimorphous with gilmarite and contains three crystallographically independent OH units. The IES spectrum of gilmarite was not obtained, as no specimen was available. For clinoclase, two prominent IES bands are observed at 3354 and 3346 cm^{-1} with component bands also observed at 3558 and 3349 cm^{-1}. Another band is observed at 3115 cm^{-1} but it has very low intensity. We propose that the bands at 3354, 3346, and 3349 cm^{-1} are due to the three independent OH units. The higher-wavenumber band at 3558 cm^{-1} is ascribed to an AsOH unit. The Raman spectra of clinoclase display two bands at 3559 and 3339 cm^{-1}. A possible interpretation of the vibrational data of clinoclase for the hydroxyl-stretching region is that the two Raman bands are attributable to the symmetric stretching vibrations, which are observed in the IES spectra but are weak. The intense bands in the IES spectra are attributable to antisymmetric stretching vibrations. As for the other basic copper arsenates, intensity approaches zero by 400 °C and the intensity of each band appears to decrease at the same rate.

Infrared emission spectroscopy of the hydroxyl-deformation vibrations

Infrared spectra in the 650 to 1850 cm^{-1} region for the four basic copper arsenates are shown in Figures 7 to 10 respectively. This region shows several features: bands in the region between 1200 and 1850 (overtone bands), features between 950 to 990 cm^{-1} corresponding to hydroxyl-deformation modes, and absorption in the 650 to 900 cm^{-1} region where the AsO symmetric and antisymmetric stretching modes are located. For olivenite, two low intensity bands are observed at 987 and 943 cm^{-1}. The intensity of these bands approaches zero by 350 °C. These bands are assigned to hydroxyl-deformation modes. The observation of two hydroxyl-deformation modes is in harmony with the observation of two major hydroxyl-stretching vibrations. In Raman spectra of olivenite a single band at 957 cm^{-1} was observed (Fig. 11); a second band at 1033 cm^{-1} may also be a hydroxyl-deformation mode although the position is high for this type of vibration.

In the IES spectra of cornubite, two low intensity bands are observed at 983 and 970 cm^{-1}; these disappear by 300 °C. Two Raman bands were observed for cornubite at 962 and 1051 cm^{-1}, in line with its crystal structure, and these are assigned to hydroxyl-deformation modes of the OH units. For cornwallite two bands are found at 989 and 958 cm^{-1}, but low intensity Raman bands were observed at 962, 997, 1035, and 1093 cm^{-1}. The first two are in harmony with the two IES bands and diminish in intensity with increasing temperature and disappear at 400 °C. The bands are attributed to hydroxyl-deformation modes of OH units bonded to Cu atoms. For clinoclase, more intense bands are observed at 985, 1078, and 1114 cm^{-1}, and these decrease in intensity with increasing temperature. In the Raman spectrum, a single band at 985 cm^{-1} is observed (identical to the IES band). These three bands are attributed to hydroxyl-deformation modes of clinoclase and fit well with the observation of three independent OH units in the unit cell.

Arsenate vibrational modes

IES spectra of the low wavenumber region of the AsO_4 units of the four basic copper arsenates are shown in Figures 7 to 10. Whilst infrared emission spectroscopy is excellent for the de-

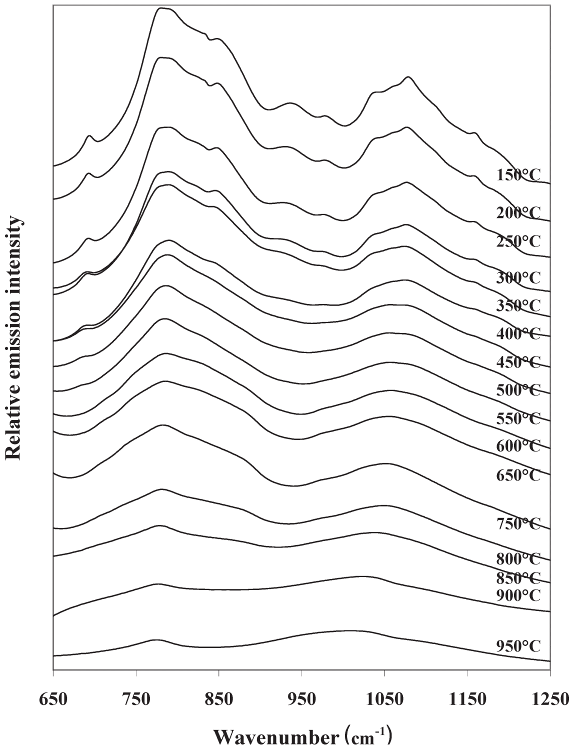

FIGURE 7. Infrared emission spectra of the low wavenumber region of olivenite from 150 to 600 °C at 50 °C intervals.

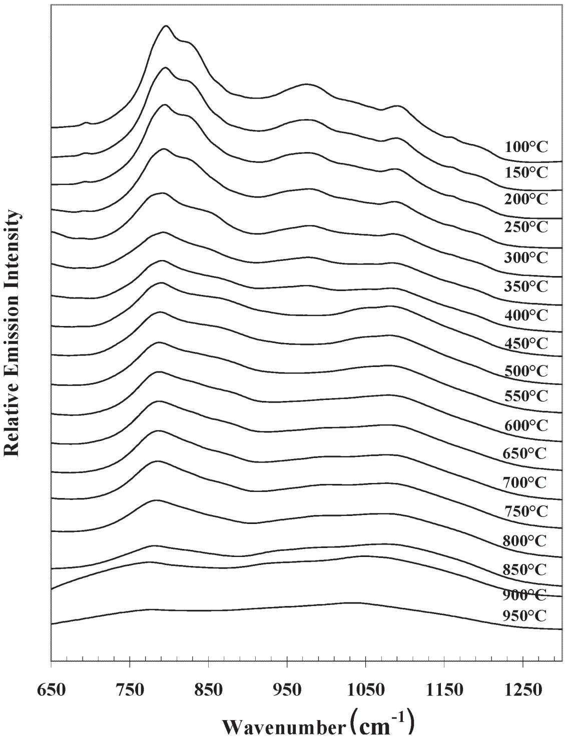

FIGURE 9. Infrared emission spectra of the low wavenumber region of cornwallite from 150 to 600 °C at 50 °C intervals.

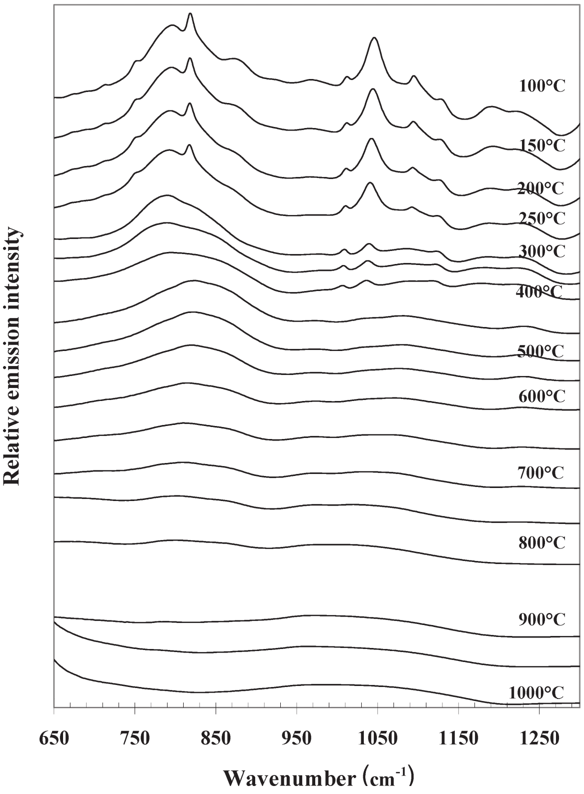

FIGURE 8. Infrared emission spectra of the low wavenumber region of cornubite from 150 to 600 °C at 50 °C intervals.

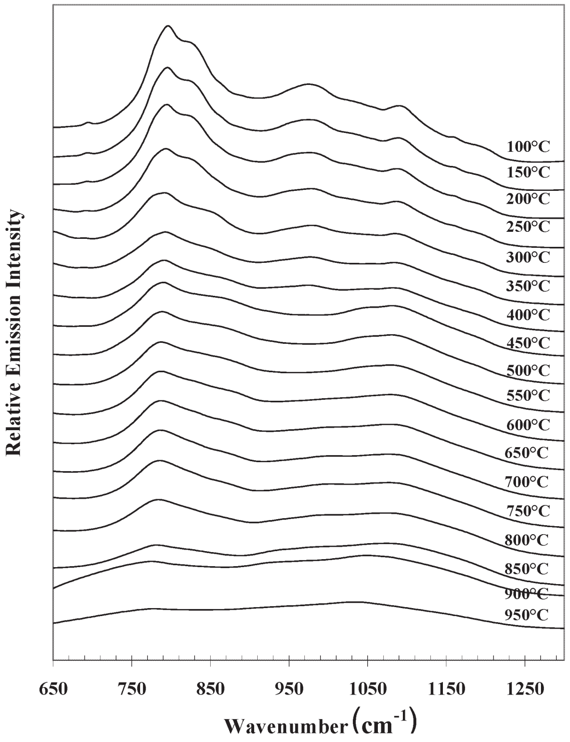

FIGURE 10. Infrared emission spectra of the low wavenumber region of clinoclase from 150 to 600 °C at 50 °C intervals.

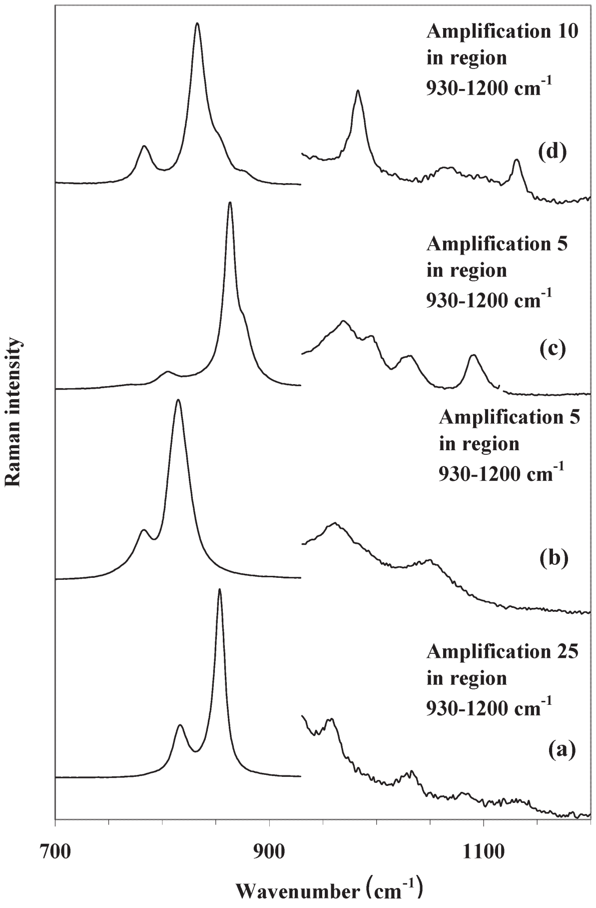

FIGURE 11. Raman spectra of the 700 to 1200 cm^{-1} region of (**a**) olivenite (**b**) cornubite (**c**) cornwallite (**d**) clinoclase.

termination of the hydroxyl-stretching region, measurement of the lower wavenumber region suffers from overlap of the bands and also from the observation of combination bands. The latter are observed in the region between 1300 and 2000 cm^{-1} and result from the combination of bands in the 650 to 1000 cm^{-1} region. Raman spectra from the 700 to 1200 cm^{-1} regions for the four basic copper arsenate minerals are shown in Figure 11. The advantage of Raman spectroscopy in the AsO stretching region is that the spectra are less complex and Raman spectra are therefore most useful for determining vibrational modes of the arsenate ion.

Raman spectra of olivenite show two bands at 853 and 819 cm^{-1}, and these are assigned to in-phase and out-of-phase AsO stretching. A band is observed in the IES spectrum at 853 cm^{-1} and a second intense band at 808 cm^{-1}. These values are in harmony with the Raman measurements. Crystallographically, olivenite contains one independent arsenate ion with four independent O atoms. Providing there is no loss of degeneracy one would expect only one symmetric and one antisymmetric stretching vibration. An IES band with significant intensity observed at 779 cm^{-1} with significant intensity is attributed to the antisymmetric stretching vibration. The spectra in Figure 6 show a low intensity band at 693 cm^{-1}, the intensity of which approaches zero during heating, and thus fits the pattern of a hydroxyl-deformation vibration. One possibility is that the band is due to the deformation of the AsOH unit formed from the delocalization of the hydroxyl proton. If the OH unit is weakly bonded, as could be expected for a delocalized proton, the hydroxyl-stretching band would occur at the upper end of the OH-stretching vibrations and the OH-deformation would occur at the lower wavenumbers.

For cornubite, two Raman bands are observed at 815 and 780 cm^{-1}, and these are assigned to the antisymmetric and symmetric stretching modes. Two bands are observed in the IES spectra at 819 and 788 cm^{-1}, in harmony with the Raman bands. These may correspond with the two independent OH units in the lattice. Two bands in the spectra are observed at 819 and 759 cm^{-1}, both of which appear to be hydroxyl-deformation modes since they are lost by 300 °C. Raman bands are observed for cornwallite at 877, 859, 806, and 763 cm^{-1} and IES bands at 829, 816, 796, and 779 cm^{-1}. It appears that two sets of symmetric and antisymmetric stretching modes are observed. Thus both the Raman and infrared spectra of cornwallite are quite different to those of cornubite, probably because of variable coupling phenomena in the different space groups. A low intensity band at 695 cm^{-1}, attributed to the AsOH unit, is lost by 300 °C. Raman spectra of clinoclase show bands at 850, 832, and 783 cm^{-1} and IES bands at 861, 831, 784 cm^{-1}, in harmony with the Raman data.

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