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An infrared spectroscopic study of the basic copper phosphate minerals: cornetite, libethenite, and pseudomalachite

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ABSTRACT

The molecular structures of the three-phase related basic copper phosphate minerals pseudomalachite, libethenite, cornetite have been studied using a combination of infrared emission spectroscopy, infrared absorption and Raman spectroscopy. Infrared emission spectra of these minerals have been obtained over the temperature range 100 to 1000°C.

Infrared spectra of the three minerals are different, in line with differences in crystal structure and composition. The absorption spectra are similar, particularly in the OH stretching region, but characteristic differences in the bending regions are observed. Differences are also observed in the phosphate stretching and bending regions. The IR emission of the basic copper phosphates studied shows that the minerals are completely dehydroxylated by 550°C.

Key Words- copper, phosphate, libethenite, cornetite, pseudomalachite, infrared emission, Raman spectroscopy

INTRODUCTION

There exist a number of dark green copper phosphate minerals, including pseudomalachite [Cu₅(PO₄)₂(OH)₄], (Anthony et al. 2000) and its polymorphs reichenbachite and ludjibaite (Braithwaite and Ryback 1994; Hyrsl 1991; Lhoest 1995; Sieber et al. 1987). The relative stabilities of the basic copper phosphates have been determined using estimated chemical parameters (Moore 1984) and experimentally determined solubility products are available (Williams 1990). Normal copper(II) phosphate is not known as a naturally occurring mineral. The more basic stoichiometries occupy fields at higher pH as expected. Pseudomalachite is the stable phase under chemical conditions intermediate to those that serve to stabilize libethenite and cornetite. Paragenetic relationships have been explored (Williams 1990). Such relationships are important as the formation of these minerals can occur in the corrosion of copper piping carrying potable water.

Pseudomalachite is monoclinic, space group $P2_1/a$ (Piret and Deliens 1988). Pseudomalachite is isomorphous with cornwallite (refined in different setting with a and c interchanged, space group $P2_1/c$). The pseudomalachite crystal structure contains one P atom in the asymmetric unit (total of 2 in the cell). The phosphorus is bonded to 4 crystallographically independent oxygen atoms. There are two crystallographically independent OH ions. These minerals occur in the oxidized zones

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of copper deposits and pseudomalachite is by far the most common (Anthony et al. 2000). It is frequently accompanied by libethenite [$\text{Cu}_2\text{PO}_4(\text{OH})$], which is monoclinic, space group $P2_1/n$ (Anthony et al. 2000). The multiplicity of atoms associated with the phosphate group is the same as with the other minerals above, with four formula units in the unit cell. There is one crystallographically independent OH group in the unit cell (total of four). A rarer congener is cornetite [$\text{Cu}_3\text{PO}_4(\text{OH})_3$] (orthorhombic, space group $Pbca$). There is one unique P atom in the asymmetric unit (eight in the unit cell) bonded to four independent O atoms. There are three crystallographically independent OH ions in the unit cell.

The structure of the above mentioned minerals may be explored at the molecular level using vibrational spectroscopy. Farmer (1974) reported the infrared absorption spectra of libethenite, cornetite and pseudomalachite. Raman spectra can provide information as to the symmetry of the molecular species and to position, or energy of the bands. The Raman spectra of aqueous phosphate oxyanions show the symmetric stretching mode (ν_1) at 938 cm^{-1} , the symmetric bending mode (ν_2) at 420 cm^{-1} , the antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , and the ν_4 mode at 567 cm^{-1} . The pseudomalachite vibrational spectrum consists of ν_1 at 953, ν_2 at 422 and 450 cm^{-1} , ν_3 at 1025 and 1096 and ν_4 at 482, 530, 555 and 615 cm^{-1} (Farmer 1974). Libethenite vibrational modes occur at 960 (ν_1), 445 (ν_2), 1050 (ν_3) and 480, 522, 555, 618 and 637 cm^{-1} (ν_4) (Farmer 1974). Cornetite vibrational modes occur at 960 (ν_1), 415 and 464 (ν_2), 1000, 1015 and 1070 (ν_3) and 510, 527, 558, 582, 623 and 647 cm^{-1} (ν_4). Vibrational spectra of reichenbachite and ludjibaite have not as yet been reported.

Phosphate mineral formation is important in corrosion and leaching studies. Minerals can form in the zones of secondary oxidation. As part of a comprehensive study of the IR and Raman properties of minerals containing oxyanions, we report changes in the molecular structure as a function of temperature of the three basic copper phosphate minerals-: pseudomalachite, libethenite and cornetite as determined using infrared emission spectroscopy.

EXPERIMENTAL

Minerals

The minerals were obtained from Australian sources and were checked for purity by X-ray diffraction. Pseudomalachite originated from the West Bogan Mine, Tottenham, New South Wales and also from the Burra Burra Mine, Mt Lofty Ranges, South Australia. The libethenite also originated from the Burra Burra Mine. The cornetite was obtained from the Blockade Mine, near Mount Isa, Queensland, Australia.

Infrared spectroscopy

Infrared Absorption Spectroscopy.

Absorption spectra using KBr pellets were obtained using a Perkin-Elmer Fourier transform infrared spectrometer (2000) equipped with a TGS detector.

Spectra were recorded by accumulating 1024 scans at 4-cm⁻¹ resolution in the mid-IR over the 400 to 4000 cm⁻¹ range.

Infrared Emission Spectroscopy.

FTIR emission spectroscopy was carried out on a Nicolet spectrometer equipped with a TGS detector, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission experiment have been published elsewhere (Frost et al. 1995; Frost et al. 1999a; Frost et al. 1999b; Frost and Vassallo 1996; Frost and Vassallo 1997;) Klopogge and Frost 1999; Klopogge and Frost 2000a; Klopogge and Frost 2000b). Approximately 0.2 mg of finely ground basic copper phosphate mineral was spread as a thin layer (approximately 0.2 microns) on a 6 mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating. Apart from milling the mineral no other sample preparation was involved. The sample simply rests on the Pt holder.

Three sets of spectra are obtained: firstly the black body radiation at selected temperatures; secondly the platinum plate radiation at the same temperatures and thirdly; the spectra from the platinum plate covered with the sample. Only one set of black body and platinum radiation is required for each temperature. These sets of data were then used for each mineral. One set of blackbody and Pt data were collected per analytical session. The emittance spectrum (E) at a particular temperature was calculated by subtraction of the single beam spectrum of the platinum backplate (Pt) from that of the platinum + sample (S), and the result ratioed to the single beam spectrum of an approximate blackbody (C-graphite). The following equation was used to calculate the emission spectra. The equation provides comparative sets of data on an absorption-like scale.

$$E = -0.5 * \log \frac{Pt - S}{Pt - C}$$

The 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. It was considered that this was sufficient time for the heating block and the powdered sample to reach thermal equilibrium. The spectra were acquired by coaddition of 64 scans at each temperature (approximate scanning time 45 seconds), with a nominal resolution of 4 cm⁻¹. Good quality spectra can be obtained providing the sample thickness is not too large. If too large a sample is used then the spectra become difficult to interpret because of the presence of combination and overtone bands. Spectral manipulation that is baseline adjustment, smoothing and normalisation, was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting, function to be selected and allows 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 of r^2 greater than 0.995. The basis of selecting peaks for the curve fitting procedure is based upon (a) fitting the least number of peaks (b) when the r^2 value does not exceed 0.995, an additional peak is added (c) all parameters of peak fitting are allowed to vary.

RESULTS AND DISCUSSION

Infrared absorption of the hydroxyl-stretching vibrations

The infrared absorption spectra of the hydroxyl-stretching region of the three phase related basic copper phosphate minerals pseudomalachite, libethenite and cornetite are shown in Figure 1. Table 1 reports the results of the spectral analysis of these three minerals and compares the results with the Raman data and with infrared data previously published (Farmer 1974; Frost et al. 2002). All three minerals show complex hydroxyl-stretching vibrations. Pseudomalachite infrared spectra display two bands at 3442 and 3388 cm^{-1} of approximate equal intensity with additional broad bands at 3357 and 3199 cm^{-1} . One means of describing these bands is that the bands represent energy levels of the hydroxyl stretching modes and the intensity of the bands is a population measurement of the hydroxyl units in any of these energy levels. These results are in good agreement with our Raman spectra (Frost et al. 2002) in which two bands are observed at 3442 and 3402 cm^{-1} . The results are in excellent agreement with the infrared absorption spectra reported by Farmer (1974). This means that there are two distinct OH units in pseudomalachite.

Curve fitting of the libethenite spectrum shows a single band at 3471 cm^{-1} with a shoulder at 3454 cm^{-1} . The Raman spectrum of the hydroxyl-stretching region of libethenite shows a single band at 3467 cm^{-1} . A shoulder is observed at 3454 cm^{-1} . This is in close agreement with the published IR band observed at 3465 cm^{-1} . This observation implies there are two hydroxyl sites with an unequal distribution of hydroxyl units in libethenite. The infrared absorption spectrum of cornetite contains three bands observed at 3405, 3313 and 3205 cm^{-1} analogous to bands in the Raman spectrum at 3400, 3300 and 3205 cm^{-1} . The infrared absorption spectrum of cornetite is, however, more complex with multiple hydroxyl-stretching vibrations observed. A broad band at around 3360 cm^{-1} is observed and may be attributed to adsorbed water.

Infrared absorption of the hydroxyl-bending vibrations

Associated with the hydroxyl stretching vibrations are the hydroxyl-bending absorption bands (Figure 2). Two infrared absorption bands for pseudomalachite are observed at 810 and 756 cm^{-1} . These bands do not fit into the pattern of the infrared absorption spectra of phosphates and these may be assigned to the hydroxyl-bending modes of the OH unit. Bands are observed in similar positions in the Raman spectra. Two bands were reported by Farmer at 810 and 762 cm^{-1} but were unassigned (Farmer 1974). The observation of two hydroxyl-bending modes is in agreement with the observation of two hydroxyl-stretching vibrations.

The infrared spectrum of libethenite shows two bands at 810 and 793 cm^{-1} . This result fits well with the suggestion that the hydroxyl stretching vibration consists of two overlapping hydroxyl-stretching bands. Farmer based upon the data base

established by Moenke reported a band at 815 cm^{-1} which was unassigned. This band fits well with the 810 cm^{-1} band observed in this work. The infrared spectrum of cornetite contains four bands at $817, 773, 750$ and 710 cm^{-1} . Farmer reported a band at 850 cm^{-1} , which was also unassigned. This value is at variance with the results reported in this work. The infrared spectrum of the hydroxyl-stretching region of cornetite displays three partially resolved bands and its probable that only the first three bands are ascribed to the hydroxyl bending modes. In the Raman spectrum three bands are observed at $817, 772$ and 748 cm^{-1} .

The application of infrared emission spectroscopy to these minerals should allow the correlation of the hydroxyl stretching and bending vibrations and the intensity of these bands as a function of temperature and will assist in the assignment of these bands.

Infrared emission spectroscopy of the hydroxyl stretching vibrations

The infrared emission spectra (IES) of the hydroxyl-stretching region of pseudomalachite, libethenite and cornetite are shown in Figure 3. Each of IES is similar to the correlated room temperature infrared absorption spectrum in accordance with Kirchoff's law. The results of the band component analysis of these spectra are reported in Table 2. For pseudomalachite and libethenite the intensity of the hydroxyl stretching region approaches zero intensity by 550°C . The intensity of the hydroxyl-stretching region of cornetite approaches zero by 450°C . These results are in harmony with thermal analysis results, which show that the hydroxyls of pseudomalachite are lost by 510°C . The loss of intensity of the hydroxyl-stretching bands is shown in Figure 4. In general, the loss of intensity of the hydroxyl-stretching bands is a linear function of temperature. As the phosphates approach dehydroxylation, peak intensity decreases more rapidly with increasing temperature. Such observations are attributed to the minerals undergoing phase changes.

The infrared absorption bands for pseudomalachite are observed at 3442 and 3388 cm^{-1} . In the IES measured at 100°C bands are found at $3440, 3431$ and 3382 cm^{-1} in good agreement with the position of the absorption bands. Additional bands are observed at 3352 and 3021 cm^{-1} .

The IES of libethenite show strong emission at 3468 cm^{-1} with a shoulder at 3398 cm^{-1} . The first value agrees well with the infrared absorption band at 3454 cm^{-1} .

Cornetite IES shows three bands at $3411, 3323$ and 3245 cm^{-1} in good agreement with the absorption bands observed at $3405, 3313$ and 3205 cm^{-1} . Figure 5 shows the variation in the IES OH-stretching band centres of the three basic copper phosphates as a function of temperature. Not all bands as listed in table 2 are shown for the reason of simplicity. The bands of pseudomalachite at 3431 and 3382 cm^{-1} display a shift to lower wavenumbers upon temperature increase. Such a shift indicates a lessening of the bond strength of the hydroxyl units upon thermal treatment. The pseudomalachite bands at 3440 and 3352 cm^{-1} show a slight increase in band position with increasing temperature. The peak position/temperature plots are linear over the temperature range 100 to 400°C and show discontinuity beyond this temperature, indicating significant changes in the molecular structure at this temperature. For both libethenite and cornetite, the band centres of the principal band shifts to lower wavenumbers upon thermal treatment. Graphs such as those shown in Figure 5 are useful in that (a) the variation in peak position with temperature is

observed and in this case the bands moved to lower wavenumbers and (b) discontinuities in the graphs are indicative of phase changes of the phosphates.

Changes in the structure of the phosphates through thermal decomposition may also be explored through changes in the bandwidths of the component peaks in the spectral profile of the hydroxyl-stretching region of the basic copper phosphates. Figure 6 illustrates the variation in peak width as a function of the temperature. In general the peak widths increase with temperature. This means that the structure is becoming more disordered. An abrupt change is observed in the pseudomalachite peak widths at 450°C, indicating a change in the molecular structure. The variation of peak width with temperature of libethenite shows similar features except the break in the data is at 300 to 350°C. This may indicate some thermal decomposition at this point although no variation in band centres was observed (Figure 5b). Two additional bands are observed only at temperatures above 300°C at 3459 and 3625 cm^{-1} . These may be the bands of an additional phase observed after 300°C.

Phosphate modes

The infrared absorption peaks observed for the various phosphate vibrations are shown in Table 1. Figure 2 shows the infrared absorption spectra of the three stoichiometrically related minerals. In this work we find the ν_1 modes of pseudomalachite at 996 and 978 cm^{-1} , the ν_2 modes at 448 and 416 cm^{-1} , the ν_3 modes at 1095 and 1037 cm^{-1} . Bands observed for pseudomalachite at 612, 549, 525 and 478 cm^{-1} , are attributed to the ν_4 vibrational modes. These values correspond well with the results of the Raman spectra of these minerals (Frost et al. 2002). However some disparity between these results and the published infrared absorption data is observed. Farmer observed the ν_1 mode at 953 cm^{-1} . There is better agreement between the published infrared absorption data and the results reported here for the ν_2 , ν_3 and ν_4 data. The observation of two sets of phosphate modes implies two different phosphate units in the molecular structure of pseudomalachite. Such a concept fits well with the X-ray crystallographic data where two phosphate units are observed in the unit cell with different geometries.

For libethenite, two ν_1 absorption bands are observed at 955 and 917 cm^{-1} , the first value compares well with published result of 960 cm^{-1} . The Raman band is found at 975 cm^{-1} . The ν_3 band is found at 1031 cm^{-1} , a value that is less than the Raman result of 1050 cm^{-1} . Two ν_2 vibrations are observed at 448 and 420 cm^{-1} . The 448 cm^{-1} band corresponds well with the Raman results and with published data. Absorption bands at 648, 631, 610 and 548 cm^{-1} are attributed to the ν_4 modes with the degeneracy arising from loss of symmetry. A number of bands were also observed in similar positions in the Raman spectra. For cornetite two IR absorption symmetric stretching modes were observed at 989 and 955 cm^{-1} . These values correspond well with the results of our Raman studies. The published value is at 960 cm^{-1} . The value for ν_3 seems to vary considerably depending on the technique used for measurement. Two bands were observed at 1093 and 1041 cm^{-1} to be compared with the Raman result of 1054 cm^{-1} . Three absorption peaks were observed by Farmer (1974) at 1070, 1015 and 1000 cm^{-1} . Only a single absorption band for ν_2 for cornetite was observed at 452 cm^{-1} . This value compares with 462 cm^{-1} observed in the Raman spectrum and

464 cm^{-1} as the published result. Infrared absorption bands found at 618, 573 and 560 cm^{-1} are assigned to the ν_4 vibrational mode.

Infrared emission of the phosphate

The IES between 700 and 1800 cm^{-1} of the three basic copper phosphates are shown in Figure 7. The infrared emission spectroscopy configuration only enables bands above 650 cm^{-1} to be detected. In general the results of the infrared emission spectra agree with the absorption data. The spectral definition, which is observed in the low wavenumber spectra taken over the 100 to 400°C range, is lost above this temperature. In the 450 to 750°C temperature range the spectra show no definition; however at the higher temperatures increased definition is observed. The appearance of new bands at temperatures above 750 °C suggests that new phosphate phases are being generated.

Figure 8 displays the variation in peak intensity of the hydroxyl bending bands as a function of temperature. The intensity of these bands parallels the loss of intensity of the hydroxyl stretching bands and approaches zero by 450°C. Other bands retain intensity up to quite high temperatures (Figure 7).

For pseudomalachite three bands are observed at 885, 813 and 755 cm^{-1} ie at energies associated with the OH bending vibrations based upon the position of these bands and a similar number of hydroxyl stretching modes observed. These bands are assigned to the hydroxyl-bending vibrations.

For libethenite, the assignment is simpler. In parallel to the observation of one band of significant intensity in the hydroxyl stretching region only one band is observed in the hydroxyl bending region (at 814 cm^{-1}). The intensity of this band reaches zero by 450°C. For cornetite four bands are observed in the 750 to 880 cm^{-1} region. The intensity of each of these bands approaches zero by 350 or 400°C. These four modes correlate with the four hydroxyl stretching modes supporting there assignment to the hydroxyl bending vibrations. The variation in peak width shows the increase in bandwidth with increasing temperature. When the basic copper phosphate undergoes a phase change such as dehydroxylation, discontinuities in peak width are observed. Such variation is illustrated over the 350 to 450°C temperature range for both pseudomalachite and cornetite.

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REFERENCES CITED

- Anthony JW, Bideaux B.R., Bladh KW and Nichols MC. (2000) Handbook of Mineralogy Volume IV arsenates, phosphates and vanadates. Mineral Data Publishing, Tuscon, Arizona, USA, 2000.
- Braithwaite, R.S.W. and Ryback, G. (1994) Reichenbachite from Cornwall and Portugal. *Mineral. Mag.*, 58, 449-51.
- Farmer, V.C. (1974) Mineralogical Society Monograph 4: The Infrared Spectra of Minerals.
- Frost, R.L., Collins, B.M., Finnie, K. and Vassallo, A.J. (1995) Infrared emission spectroscopy of clay minerals and their thermal transformations. *Clays Controlling Environ., Proc. Int. Clay Conf.*, 10th, 219-24.
- Frost, R.L., Kloprogge, J.T., Russell, S.C. and Szetu, J. (1999a) Dehydroxylation and the vibrational spectroscopy of aluminium (oxo)hydroxides using infrared emission spectroscopy. Part III: diaspore. *Appl. Spectrosc.*, 53, 829-835.
- Frost, R.L., Kloprogge, J.T., Russell, S.C. and Szetu, J. (1999b) Dehydroxylation of aluminium (oxo)hydroxides using infrared emission spectroscopy. Part II: Boehmite. *Appl. Spectrosc.*, 53, 572-582.
- Frost, R.L. and Vassallo, A.M. (1996) The dehydroxylation of the kaolinite clay minerals using infrared emission spectroscopy. *Clays Clay Miner.*, 44, 635-651.
- Frost, R.L. and Vassallo, A.M. (1997) Fourier-transform infrared emission spectroscopy of kaolinite dehydroxylation. *Mikrochim. Acta, Suppl.*, 14, 789-791.
- Hyrsl, J. (1991) Three polymorphs of $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$ from Lubietova, Czechoslovakia. *Neues Jahrb. Mineral., Monatsh.*, 281-7.
- Kloprogge, J.T. and Frost, R.L. (1999) Infrared emission spectroscopy of Al-pillared beidellite. *Appl. Clay Sci.*, 15, 431-445.
- Kloprogge, J.T. and Frost, R.L. (2000a) Infrared emission spectroscopy study of the dehydroxylation of 10 .ANG. halloysite from a Neogene cryptokarst of southern Belgium. *Geol. Belg.*, 2, 213-220.
- Kloprogge, J.T. and Frost, R.L. (2000b) Study of the thermal behaviour of rectorite by in-situ infrared emission spectroscopy. *Neues Jahrb. Mineral., Monatsh.*, 145-157.
- Lhoest, J.J. (1995) Famous mineral localities: the Kipushi Mine, Zaire. *Mineral. Rec.*, 26, 163-92.
- Magalhaes MCF, Pederosa de Jesus J D., Williams PA. (1986) *Mineral Mag.*, 50, 33.
- Magalhaes MCF, Pederosa de Jesus J D., Williams PA. (1988) *J. Russell Soc.*, 2, 13.
- Moore PB, N.J.e. (1984) *Phosphate Minerals*. Springer-Verlag, Berlin.
- Piret, P. and Deliens, M. (1988) Description of ludjibaite, a polymorph of pseudomalachite $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$. *Bull. Mineral.*, 111, 167-71.
- Sieber, N.H.W., Tillmanns, E. and Medenbach, O. (1987) Hentschelite, $\text{CuFe}_2(\text{PO}_4)_2(\text{OH})_2$, a new member of the lazulite group, and reichenbachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$, a polymorph of pseudomalachite, two new copper phosphate minerals from Reichenbach, Germany. *Am. Mineral.*, 72, 404-8.
- Williams, P.A. (1990) *Oxide Zone Geochemistry*. Ellis Horwood Ltd, Chichester, West Sussex, England.

Table 1. Vibrational spectroscopic analysis of the infrared spectra of pseudo-malachite, libethenite and cornetite

Pseudomalachite				Libethenite				Cornetite				
IR Absorption	IES (100°C)	Raman (Frost et al. 2002)	Published IR data (Farmer 1974)	IR Absorb	IES (100°C)	Raman (Frost et al. 2002)	Published IR data (Farmer 1974)	Infrared	IES (100°C)	Raman (Frost et al. 2002)	Published IR data (Farmer 1974)	Suggested assignments
$\pm 1 \text{ cm}^{-1}$	$\pm 2 \text{ cm}^{-1}$	$\pm 1 \text{ cm}^{-1}$		$\pm 1 \text{ cm}^{-1}$	$\pm 2 \text{ cm}^{-1}$	$\pm 1 \text{ cm}^{-1}$		$\pm 1 \text{ cm}^{-1}$	$\pm 2 \text{ cm}^{-1}$	$\pm 1 \text{ cm}^{-1}$	Precision of data	
3442 3388	3440 3431 3382	3442 3402	3582 3435 3390	3454 3471	3464 3398	3467	3465	3405 3313 3205	3411 3323 3245	3400 3300 3205	3285 3200	
810 756	898 831 767	877 802 750	810 762	810 793	819	862 815	815?	817 773 750 710	887 823 761	817 772 748	850?	OH stretching vibration OH bending vibration
996 978	1002 971	998 971	953	955 917	960	975	960	989 955	1004	994 961 922	960	ν_1 Symmetric stretching vibration
448 416		481 451	450 422	448 420		450	445	452		462 433 411	464 415	ν_2 Symmetric bending vibration
1095 1037	1101 1047	1084 1053	1096 1025	1031	1056	1050 1019	1050	1093 1041	1053	1054	1070 1015 1000	ν_3 Anti-symmetric stretching vibration
612 549 525 478		609 537 517	615 555 530 482	648 631 610 548		645 626 582 556	637 618 555 522 480	618 573 560		570 541 518 487	647 623 582 558 527 510	ν_4 Out-of-plane bending vibration

Phase	Precision of data	Temp /°C ±1 °C	100.0	150.0	200.0	250.0	300.0	350.0	400.0	450.0	500.0
			±2 cm ⁻¹	±2 cm ⁻¹	±2 cm ⁻¹	±2 cm ⁻¹	±2 cm ⁻¹	±2 cm ⁻¹	±2 cm ⁻¹	±2 cm ⁻¹	±2 cm ⁻¹
Pseudomalachite	Band Centre/cm ⁻¹ Relative Intensity/%	P ₁	3021 19.6	2965 12.7	2959 12.1	2957 10.5	2958 9.6	3013 9.9	3045 9.6	3146 16.9	2999 39.3
		P ₂	3352 37.4	3259 26.7	3266 24.3	3277 24.0	3272 24.0	3299 26.4	3307 27.5	3366 7.5	3272 18.8
	Band Centre/cm ⁻¹ Relative Intensity/%	P ₃	3382 12.6	3420 37.6	3387 25.4	3376 22.5	3370 20.7	3362 15.1	3356 12.5	3397 50.5	3412 28.3
		P ₄	3431 12.1	3441 9.7	3443 19.5	3440 24.1	3439 26.6	3435 30.0	3433 32.7	3430 19.4	3431 4.7
	Band Centre/cm ⁻¹ Relative Intensity/%	P ₅	3440 18.4	3568 13.4	3545 18.7	3549 19.0	3554 19.2	3559 18.6	3564 17.7	3637 5.6	3595 8.9
		L ₁	3230 6.2	3249 7.8	3243 6.5	3271 7.2	3271 7.1	3284 8.0	3277 8.5	3203 5.6	
Libethenite	Band Centre/cm ⁻¹ Relative Intensity/%	L ₂	3411 19.9	3407 19.8	3397 19.3	3397 18.5	3394 19.3	3393 19.2	3390 21.7	3393 30.8	3366 28.9
		L ₃	3468 51.9	3466 37.6	3464 25.4	3462 22.5	3460 20.7	3458 15.1	3455 12.5	3454 50.5	3452 28.3
	Band Centre/cm ⁻¹ Relative Intensity/%	L ₄	3540 9.0	3560 6.1	3549 3.4	3540 3.3	3537 3.4	3537 3.5	3539 3.9		

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