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Frost, Ray L. and Martens, Wayde N. and Williams, Peter A. (2003) The basic copper phosphate minerals pseudomalachite, ludjibaite and reichenbachite: an infrared emission and Raman spectroscopic study. *Neues Jahrbuch fur Mineralogie - Monatshefte* 8(1):pp. 337-362.

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The basic copper phosphate minerals pseudomalachite, ludjibaite and reichenbachite: an infrared emission and Raman spectroscopic study

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Abstract:

The molecular structures of the trimorphous basic copper phosphate minerals pseudomalachite, ludjibaite and reichenbachite have been studied using a combination of infrared emission spectroscopy and Raman spectroscopy. Infrared emission spectra have been obtained over the temperature range 100 to 1000°C. Infrared emission spectra of the three minerals are different, in line with differences in crystal structure and composition. IR emission spectra show that the minerals are completely dehydroxylated by 550°C. The thermal decomposition patterns for the three minerals are different and reflect their stability. Raman spectra are similar, particularly in the stretching region, but characteristic differences in the deformation regions are observed. Differences are also observed in the phosphate stretching and bending regions.

Key words: copper, phosphate, pseudomalachite, ludjibaite, reichenbachite, infrared emission, Raman

Introduction

Many examples of molecular assembly occur in Nature and when minerals crystallize (particularly those containing phosphate and arsenate), they may display end-member composition or solid solution behaviour. Phosphates and arsenates are

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ubiquitous in the mineral kingdom and are found in all kinds of mineralogical settings.(ANTHONY JW 2000) Phosphate formation is controlled by factors such as pH and concentration(WILLIAMS 1990) and these variables can lead to very complex stoichiometries. Elaboration of these stoichiometries is at its greatest in the oxidized zones of base metal ore bodies. Our attention has been drawn to certain classes of secondary phosphates, particularly those of copper(II), because of their widespread nature and importance with respect to geochemical exploration and aspects of mineral processing. More particularly their presence is often the only surface indicator of underlying base and/or noble metal ore bodies.

Normal copper(II) phosphate is not known as a naturally occurring mineral. However a number of basic double salts of copper and phosphate are well known; these include pseudomalachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$,(ANTHONY JW 2000) and its polymorphs reichenbachite and ludjibaite. Pseudomalachite is comparatively common, being frequently accompanied by libethenite, $\text{Cu}_2\text{PO}_4(\text{OH})$; a rather rarer congener is cornetite, $\text{Cu}_3\text{PO}_4(\text{OH})_3$.(BRAITHWAITE 1983; BRAITHWAITE & RYBACK 1994; HYRSL 1991; LHOEST 1995) These minerals have been structurally characterised and their relative stabilities determined.(WILLIAMS 1990) Pseudomalachite and reichenbachite are both monoclinic, space group $P2_1/a$, but with significantly different cells, whereas ludjibaite is triclinic, space group $P\bar{1}$. **Table 1** summarises crystallographic information¹ for the three polymorphs. The crystal structures of the polymorphs are very similar, consisting of layers of edge-sharing, copper-containing polyhedra linked in the third dimension by PO_4 tetrahedra and hydrogen bonds. The copper layers contain frameworks which may be derived from a layer of close-packed, edge-sharing octahedra from which 1/3 of the octahedra have been removed as edge-sharing pairs. Studies of the bond distances, coordination and bond valence sums and probable locations of H bonds prove that the formation of hydrogen bonds is important in stabilizing the pseudomalachite structure.

Pseudomalachite is aptly named and is frequently overlooked or confused with other green secondary copper minerals, especially malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$.(WILLIAMS 1990) The vibrational spectroscopy of many of these minerals has received little detailed attention although Farmer reported the spectra of

libethenite, cornetite and pseudomalachite.(FARMER 1974) Raman spectra of aqueous phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1} , an antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , a symmetric bending mode (ν_2) at 420 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) Infrared spectra of reichenbachite and ludjibaite have been briefly reported.(BRAITHWAITE & RYBACK 1994) As part of a comprehensive study of the IR and Raman properties of minerals containing oxyanions, we report here the vibrational spectroscopy of the pseudomalachite polymorphs pseudomalachite, ludjibaite and reichenbachite using a combination of infrared emission and Raman spectroscopy.

EXPERIMENTAL

Minerals

Specimens of ludjibaite from Ludjiba, Zaire, in association with pseudomalachite and libethenite, and together with reichenbachite from Shituru, Shaba, Zaire, plus pseudomalachite and reichenbachite from Kipushi, Shaba, Zaire, were purchased from Summit Minerals, Albuquerque, NM, USA. Minerals were analyzed by electron probe and X-ray diffraction to check for phase purity and composition and were found to be contain negligible other substituting species, other than traces of As in the African material. Pure pseudomalachite from the West Bogan mine, Collerina Hall, NSW, Australia, was obtained from the collection of one of the authors (PAW).

Infrared emission spectroscopy

FTIR emission spectroscopy was carried out on a Nicolet spectrophotometer 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 & VASSALLO 1996; FROST & VASSALLO 1997)¹⁵ Approximately 0.2 mg of 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.

In the normal course of events, three sets of spectra are obtained: first the black body radiation over the temperature range selected at the various temperatures, secondly the platinum plate radiation at the same temperatures and thirdly spectra from the platinum plate covered with the sample. Normally only one set of black body and platinum radiation data is required. The emittance spectrum (E) at a particular temperature was calculated by subtraction of the single beam spectrum of the platinum backplate from that of the platinum + sample, and the result ratioed to the single beam spectrum of an approximate blackbody (graphite). The following equation was used to calculate the emission spectra.

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

This manipulation is carried out after all the data is 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. It was considered that this was sufficient time for the heating block and the powdered sample to reach thermal equilibrium. Spectra were acquired by co-addition of 64 scans for the whole 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 large. If too large a sample is used then spectra become difficult to interpret because of the presence of combination and overtone bands. Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

Raman Spectroscopy

Crystals of the basic copper phosphate minerals were placed and orientated on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x and 50x 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 signal-to-noise ratios. 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 was carried out 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 of r^2 greater than 0.995.

Results and discussion

Theory

Factor Group analysis of pseudomalachite and reichenbachite

Table 2 Factor group analysis of the phosphate ion in pseudomalachite and reichenbachite

Point group	Site group	Crystal
T_d	C_1	C_{2h}^5
A_1 E $2T_2$	$9A$	$9A_g$ $9A_u$ $9B_g$ $9B_u$

Table 3 Factor group analysis of the Cu(I) lattice modes in pseudomalachite and reichenbachite

Site group	Crystal
Cu(I)	
C_i	C_{2h}^5
$3A_u$	$3A_u$
	$3B_u$

Table 4 Factor group analysis of the Cu(II), Cu(III), PO₄, OH(I), and OH(II) lattice modes in pseudomalachite and reichenbachite.

Site group	Crystal
Cu(II), Cu(III), PO ₄ , OH(I), and OH(II)	
C_1	C_{2h}^5
$24A$	$24A_g$
	$24A_u$
	$24B_g$
	$24B_u$

$$\Gamma = 23A_g + 22B_g + 26A_u + 25B_u$$

The factor group analysis predicts 36 vibrations for the phosphate ion in pseudomalachite represented by $\Gamma = 23A_g + 22B_g + 26A_u + 25B_u$. For the factor group analysis for the prediction of the Raman spectra, we must use a value of $Z = 2$. The reason for this is that there are two phosphate ions in the unit cell. The PO₄ splitting should be the same for reichenbachite but will have different lattice vibrations due to different splitting patterns and different bond lengths. Thus the vibrational modes for

the phosphate ion in pseudomalachite is given by: factor group analysis predicts 36 vibrations for the phosphate ion represented by $\Gamma = 9A_g + 9A_u + 9B_g + 9B_u$. Thus there should be 18 Raman active modes and 18 infrared active modes for the phosphate ion for pseudomalachite.

Factor Group analysis of Ludjibaite

Table 5 Factor group analysis of the phosphate ion in ludjibaite

Point group	Site group	Crystal
T_d	C_1	C_i
A_1 E $2T_2$	$9A$	$9A_g$ $9A_u$

Table 6 Factor group analysis of the Cu(I), Cu(II) and Cu(III) lattice modes in ludjibaite

Site group	Crystal
Cu(I), Cu(II), and Cu(III)	
C_i	C_i
$9A_u$	$9A_u$

Table 7 Factor group analysis of the Cu(IV), PO₄, OH(I), and OH(II) lattice modes in ludjibaite

Site group	Crystal
Cu(IV), PO ₄ , OH(I), and OH(II)	
C_1	C_i
	$21A_g$
$21A$	$21A_u$

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$$\Gamma = 27A_g + 18A_u$$

The irreducible representation is given by: $\Gamma = 27A_g + 18A_u$. Predictably the vibrational spectra of ludjibaite will be different because in the unit cell $Z=1$. For the phosphate ion there should be 9 Raman and 9 infrared active modes for ludjibaite.

Infrared emission spectroscopy of the hydroxyl stretching vibrations

Infrared emission spectra of the hydroxyl-stretching region of pseudomalachite, ludjibaite and reichenbachite are shown in **Figures 1-3**. Results of band component analysis are reported in **Table 8**. The table reports band centres and relative normalised band intensities. In the spectroscopic profile of pseudomalachite hydroxyl-stretching bands are observed at 3440, 3430, 3382, 3352 and 3021 cm^{-1} . **Figure 4** displays the Raman spectra of the hydroxyl-stretching region of pseudomalachite, ludjibaite and reichenbachite. Raman bands for the hydroxyl-stretching vibrations of pseudomalachite are observed at 3434 and 3385 cm^{-1} . The positions of these two bands are in excellent agreement with the two IES bands at 3430 and 3382 cm^{-1} . In the infrared absorption spectrum of pseudomalachite bands are observed at 3442, 3388 and 3357 cm^{-1} . It is probable that the band at 3440 cm^{-1} is infrared active-Raman inactive, and may be attributed to antisymmetric stretching. Factor group analysis predicts two Raman active and two infrared active modes for the hydroxyl-stretching region. Two Raman modes and four infrared modes are observed. **Figure 5** displays the variation in intensity of the hydroxyl stretching vibrations of pseudomalachite as a function of temperature. In accordance with **Figure 1**, there is a steady decrease in intensity of the hydroxyl-stretching bands as the temperature is increased until at around 450°C no intensity remains. Significant changes in intensity are observed as dehydroxylation of the pseudomalachite takes place between 400 and 450°C. Such changes are indicative of significant changes in the structure of the material such as occurs with a phase change.

Infrared emission spectra of ludjibaite show a strong band at 3422 cm^{-1} and minor component bands at 3213 and 3151 cm^{-1} . These low intensity bands may be due to the presence of adsorbed water. Infrared absorption spectra of ludjibaite show bands at 3470, 3446 and 3401 cm^{-1} and the Raman spectra show a single band at 3473 cm^{-1} . Factor group analysis predicts one Raman active and one infrared active mode. Here, as predicted, we observe one Raman active (3473 cm^{-1}) and one infrared active mode (3422 cm^{-1}). Intensities of the bands are constant up to 250°C, and then decreases until no intensity remains at 400°C (**Figure 5b**). The dehydroxylation

behaviour of ludjibaite appears to be somewhat different to that of pseudomalachite in that decomposition starts at a lower temperature. High-resolution differential thermogravimetric analysis confirms this result. Infrared emission spectra of reichenbachite show a strong band at 3407 cm^{-1} with a component band at 3397 cm^{-1} . Infrared absorption spectra display bands at 3441 and 3397 cm^{-1} and the Raman spectra of reichenbachite displays two bands at 3438 and 3389 cm^{-1} . The positions of the bands in the infrared absorption and Raman spectra are in good agreement. Factor group analysis predicted 2 Raman active and two infrared active modes. The observations in both the IES and Raman spectra of two bands are thus in excellent agreement. Dehydroxylation occurs over the 400 to 450°C range and at 550°C no intensity remains in the hydroxyl stretching bands. Thermal decomposition behaviour of reichenbachite is different again from that of either pseudomalachite or ludjibaite. Decomposition starts at quite low temperatures (200°C) and is complete at 400°C . The decomposition patterns as indicated by the loss of intensity of the hydroxyl stretching bands as a function of temperature are an indication of the relative stabilities of the phases. It is apparent that the most stable phase is pseudomalachite followed by ludjibaite. The behaviour of reichenbachite gives every indication of an unstable phase. Such behaviour is reflected in the occurrence of these polymorphs in nature in that pseudomalachite is by far the most commonly found species of the three.

Infrared emission spectroscopy of the hydroxyl-deformation vibrations

Infrared emission spectra of the 650 to 1450 cm^{-1} region of pseudomalachite, ludjibaite and reichenbachite are shown in **Figures 6-8**. Raman spectra of the hydroxyl-deformation region are displayed in **Figure 9**. Data for band component analysis of the IES spectra of the 650 to 1450 cm^{-1} region are reported in **Table 9**. In IES spectra of pseudomalachite bands are identified at 756 , 816 and 885 cm^{-1} . The intensities of these bands decrease as temperature is increased such that no intensity remains at 450°C . The behaviour of these bands thus parallels that of the hydroxyl-stretching vibrations. Consequently it is proposed that these bands are attributable to hydroxyl deformation modes. In the Raman spectrum of pseudomalachite three bands are observed at 752 , 805 and 875 cm^{-1} . These correspond well with the three IES

bands. The fact that three bands are observed for pseudomalachite in the hydroxyl-stretching region harmonises well with the three bands in the hydroxyl deformation region.

In the IES spectrum of ludjibaite, two bands are observed at 766 and 832 cm^{-1} . The intensities of these bands decrease and they are thus assigned to hydroxyl deformation modes as above. Two bands are observed in the Raman spectrum at 760 and 820 cm^{-1} . Hence the observation of the two Raman bands harmonises well with the observation of the two infrared bands. In the IES spectrum of reichenbachite, bands are observed at 749, 770, 800 and 834 cm^{-1} . The Raman spectrum of the mineral shows three bands at 749, 804 and 866 cm^{-1} . In IES spectra only the band at 834 cm^{-1} appears to decrease in intensity approaching the dehydroxylation temperature. The other bands may be due to the presence of very low levels of arsenate. Such isomorphous substitution is very likely and not unexpected. The identification of the arsenate bands amply demonstrates the power of Raman spectroscopy in determining the presence of oxyanions. **Figure 10** displays the variation of intensity of these hydroxyl deformation modes as a function of temperature. Fundamentally, there is a steady decrease in intensity of the bands for pseudomalachite and reichenbachite such that at 400°C, little intensity remains. The dehydroxylation behaviour of ludjibaite using the hydroxyl deformation mode appears somewhat different. Intensity is constant up to 300°C and then decreases up to the dehydroxylation temperature.

Phosphate vibrational modes

The spectra illustrated in **Figures 6, 7 and 8** show the phosphate stretching vibrations, found between 900 and 1100 cm^{-1} . For pseudomalachite IES bands are observed at 949, 990, 1039 and 1107 cm^{-1} . **Figure 11** displays Raman spectra of the phosphate stretching vibrations of the three polymorphs. In the Raman spectrum bands are observed at 970, 995, 1053 and 1085 cm^{-1} . The 970 cm^{-1} Raman band is the most intense and is assigned to the phosphate symmetric stretching vibration. The other low intensity bands are assigned to antisymmetric stretching modes. Thus in the IES data the two bands at 949 and 990 cm^{-1} may be ascribed to symmetric stretching

modes and the bands at 1053 and 1085 cm^{-1} to antisymmetric stretching modes. These observations are in harmony with the predictions of factor group analysis where two infrared-active and two Raman-active modes are predicted.

For ludjibaite IES bands are observed at 936, 981 and 1044 cm^{-1} . The Raman spectrum of ludjibaite displays bands at 974, 1006 and 1020 cm^{-1} . Low intensity bands are also observed in the Raman spectrum at 1052 and 1067 cm^{-1} . The IES spectrum of reichenbachite bands are observed at 956, 963, 988, 1035, 1045 and 1096 cm^{-1} . In the Raman spectrum, bands are observed at 972, 1000, 1061 and 1083 cm^{-1} . The most intense band is at 972 cm^{-1} and is assigned to the symmetric stretching vibration. **Figure 12** displays variations in band positions of the phosphate as a function of temperature. The clearly shows (compared with the variation of the hydroxyl stretching and deformation modes) that the positions of the bands are constant up 650°C. Changes in the positions of the bands alter after this temperature suggesting some further phase change.

CONCLUSIONS

Application of infrared emission and Raman spectroscopy has enabled the molecular structure of the three polymorphous basic copper phosphates of pseudomalachite composition to be probed. A comparison is made between the molecular structures of these three related phases. Infrared emission spectroscopy was used to explore the dehydroxylation of the minerals and confirm the band position of the hydroxyl deformation modes. The loss of intensity of the hydroxyl deformation modes paralleled that of the hydroxyl stretching vibrations and approached zero at the dehydroxylation temperature. Phase changes were also observed through variation in the band centres and the peak width of selected bands. Such spectroscopic studies are significant as not only are the basic copper phosphates indicators of precious metal ore bodies but also basic copper phosphates are found in environmental situations such as in the drinking water pipes. These vibrational spectroscopic techniques enable offer a method of analysis of these complex basic copper phosphate phase systems.

ACKNOWLEDGMENTS

The financial and infrastructure support of the Queensland University of Technology Centre for Instrumental and Developmental Chemistry is gratefully acknowledged. The Australian research Council (ARC) is thanked for funding.

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Mineral	Crystal structure	Space group	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$	Z
Pseudomalachite	Triclinic	$P2_1/a$	17.02-17.08	5.75-5.77	4.47-4.50		90.95-91.52		2
Ludjibaite	Triclinic	$P\bar{1}$	4.446(3)	5.871(4)	8.680(7)	103.9(2)	90.3(2)	93.2(2)	1
Reichenbachite	Monoclinic	$P2_1/a$	9.186(2)	10.684(2)	4.461(2)		92.31(1)		2

Table 1 Comparison of crystallographic data for pseudomalachite, ludjibaite and reichenbachite

Table 8 Band component analysis of the hydroxyl-stretching region of the infrared emission spectra of pseudomalachite, ludjibaite and reichenbachite.

Mineral		Temp /°C	100	150	200	250	300	350	400	450	500	550
Pseudomalachi	Band Centre/cm ⁻¹	v ₁	3021	2965	2959	2957	2958	3013	3045	3146	2999	
	Relative Intensity/%		19.6	12.7	12.1	10.5	9.6	9.9	9.6	16.9	39.3	
	Band Centre/cm ⁻¹	v ₂	3352	3259	3266	3277	3272	3299	3307	3366	3272	
	Relative Intensity/%		37.4	26.7	24.3	24.0	24.0	26.4	27.5	7.5	18.8	
	Band Centre/cm ⁻¹	v ₃	3382	3419	3387	3376	3370	3362	3356	3397	3412	
Relative Intensity/%		12.6	37.6	25.4	22.5	20.7	15.1	12.5	50.5	28.3		
Pseudomalachi	Band Centre/cm ⁻¹	v ₄	3430	3441	3442	3440	3438	3435	3433	3430	3431	
	Relative Intensity/%		12.1	9.7	19.5	24.1	26.6	30.0	32.7	19.4	4.7	
	Band Centre/cm ⁻¹	v ₅	3440	3567	3545	3549	3554	3559	3564	3637	3595	
	Relative Intensity/%		18.4	13.4	18.7	19.0	19.2	18.6	17.7	5.6	8.9	
	Ludjibaite	Band Centre/cm ⁻¹	v ₁				3032	3076		3083	3097	3062
Relative Intensity/%					10.0	12.1		25.7	4.9	6.9		
Band Centre/cm ⁻¹		v ₂	3151	3130	3129			3115			3132	3127
Relative Intensity/%			31.1	17.5	17.9			14.8			7.8	18.6
Band Centre/cm ⁻¹		v ₃	3213	3312	3318	3266	3249	3248	3234	3237	3281	3290
Relative Intensity/%			6.6	27.4	27.8	22.0	21.1	21.9	17.0	24.0	26.9	22.4
Band Centre/cm ⁻¹		v ₄		3412	3419	3407	3408	3406	3418	3403	3402	3397
Relative Intensity/%			28.2	5.1	38.9	45.3	7.5	46.6	50.2	43.5	47.0	
Ludjibaite	Band Centre/cm ⁻¹	v ₅	3422	3424	3420	3410	3409	3408	3565	3405	3531	3519
	Relative Intensity/%		62.2	6.3	30.2	19.7	11.3	45.8	6.7	8.4	14.9	12.0
	Band Centre/cm ⁻¹	v ₆		3535	3548	3551	3560	3562	3786	3561		
	Relative Intensity/%			20.5	19.1	9.4	10.2	10.1	1.7	11.6		
	Band Centre/cm ⁻¹	v ₇						3876	3763			
	Relative Intensity/%							2.4	0.9			
	Reichenbachi	Band Centre/cm ⁻¹	v ₁		3045							
Relative Intensity/%				8.4								
Band Centre/cm ⁻¹		v ₂				3170	3158	3161	3134	3154		
Relative Intensity/%					5.4	9.0	10.2	12.9	10.7			
Band Centre/cm ⁻¹		v ₃	3277	3334	3215					3311		
Relative Intensity/%		30.0	22.0	16.0					15.2			
Reichenbachi	Band Centre/cm ⁻¹	v ₄	3407	3408	3406	3403	3398	3395	3388			
	Relative Intensity/%		70.0	47.9	43.3	50.2	44.5	49.5	41.7			
	Band Centre/cm ⁻¹	v ₅		3424	3412	3404	3403	3402	3401	3401		
Relative Intensity/%			21.7	40.6	44.4	46.6	40.3	45.4	74.1			

Table 9 Band component analysis of the phosphate-stretching region of the infrared emission spectra of pseudomalachite, ludjibaite and reichenbachite.

	Band Parameters	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950		
Pseudomalachite	Band Centre/cm ⁻¹																				
	Relative Intensity/%	608	606	607	606	606	605	604	599										663	859	
	Band Centre/cm ⁻¹																				
	Relative Intensity/%	8.4	8.1	8.0	8.9	7.2	6.4	3.6	2.7											716	
	Band Centre/cm ⁻¹																				
	Relative Intensity/%																				772
	Band Centre/cm ⁻¹																				
	Relative Intensity/%																				8.4
	Band Centre/cm ⁻¹	756	756	756	755	756	755	753	752		792					798	799	805	800		
	Relative Intensity/%	8.4	8.4	8.3	8.0	9.3	8.0	7.5	4.2		0.8					4.0	5.1	8.7	1.9		
	Band Centre/cm ⁻¹																				
	Relative Intensity/%																				807
	Band Centre/cm ⁻¹																				
	Relative Intensity/%																				3.9
Band Centre/cm ⁻¹	816	816	817	818	820	818	817	815	831	831	821	818	821								
Relative Intensity/%	7.9	8.3	8.2	8.1	7.2	8.8	8.9	6.0	4.1	2.9	2.9	3.1	5.0								
Band Centre/cm ⁻¹	885	883	881	881	879	881	881	886	893			901	894	886	881	874	863	915			
Relative Intensity/%	8.0	7.6	7.1	6.9	7.4	7.5	7.4	7.9	3.2			22.9	20.8	21.1	21.8	20.0	17.0	13.3			
Band Centre/cm ⁻¹	949	948	948	945	946	945	945	945	941	925	928		962	958	946	940	939	929			
Relative Intensity/%	9.9	10.3	10.9	10.3	11.3	11.6	12.6	16.2	23.4	24.0	25.6	0.0	6.2	4.5	6.0	10.1	9.4	22.1			
Band Centre/cm ⁻¹	990	989	987	991	985	985	984	989	987	982	979	964	1018	1021	1025						
Relative Intensity/%	11.6	11.8	9.9	13.7	9.7	9.9	10.0	10.5	2.4	5.4	5.6	6.5	33.2	32.9	29.6						
Band Centre/cm ⁻¹	1039	1038	1038	1038	1038	1035	1033	1034	1032	1033	1033	1022	1109	1106	1131	1041	1031	1032			
Relative Intensity/%	10.8	10.8	12.6	10.2	13.2	13.8	14.3	17.7	27.3	28.0	30.5	32.4	10.7	8.0	18.8	26.1	17.4	37.3			
Band Centre/cm ⁻¹	1089	1087	1087	1092	1084	1082	1079	1078	1081	1081	1089	1094	1148	1149	1162	1152	1148				
Relative Intensity/%	7.6	6.4	6.4	16.5	5.8	4.7	2.6	3.0	7.0	6.9	6.9	5.5	19.1	18.9	4.2	20.2	8.8	0.0			
Band Centre/cm ⁻¹	1107	1104	1107		1105	1102	1097	1100	1128	1130	1135	1140		1208	1203	1203	1197	1170			
Relative Intensity/%	10.7	11.8	11.4		11.6	13.0	15.8	17.3	22.1	21.4	23.1	23.3		7.3	11.6	8.4	3.9	21.7			
Band Centre/cm ⁻¹			1164	1158	1164	1166	1165	1165	1199	1193				1785							
Relative Intensity/%	0.0	0.0	1.4	2.4	3.0	3.5	4.8	7.9	5.0	5.6				0.7							
Ludjibaite	Band Centre/cm ⁻¹																				
	Relative Intensity/%	766	767	768	769	769	767	751	767	764	799								683	869	
	Band Centre/cm ⁻¹																				
	Relative Intensity/%	12.7	12.7	13.1	15.0	16.1	14.6	8.7	14.5	8.6	2.6									4.8	21.3
	Band Centre/cm ⁻¹	832	832	833	831	830	828	815	827	819			896	874						865	968
	Relative Intensity/%	9.6	9.6	9.4	11.7	12.6	12.1	13.5	10.7	7.5			12.6	10.4						26.2	24.9
Band Centre/cm ⁻¹	936	933	932	939	948	941	913	945	929	921	930	902	905	906	923	912	956				
Relative Intensity/%	14.6	13.2	13.8	17.0	18.9	19.9	13.0	23.1	24.6	23.8	28.9	13.6	17.9	21.2	32.5	38.3	8.8				
Band Centre/cm ⁻¹	981	981	979	981	976	978		975				970	973								
Relative Intensity/%	0.8	0.8	0.9	4.9	1.1	1.6		0.6				6.8	14.2								
Band Centre/cm ⁻¹	1044	1030	1028	1026	0	1022	1008	1020				1025	1028	1001	1027	1030					
Relative Intensity/%	13.9	0.7	0.6	1.8	0.0	1.3	11.9	1.4				8.6	12.5	10.6	21.9	18.1					
Band Centre/cm ⁻¹		1053	1056	1045	1046	1050		1072	1062	1048	1059	1062	1069	1062		1130	1101	1080			
Relative Intensity/%		16.2	17.4	14.0	14.2	14.7		20.7	39.0	46.7	45.1	32.9	23.2	17.3	0.0	30.8	28.3	21.2			

	Band Centre/cm ⁻¹ Relative Intensity/%		1086 0.3	1088 1.0					1073 3.9	1132 7.9	1132 14.3	1139 18.8	1142 17.4	1138 16.3	1162 32.1	1135 34.7	1154 8.2	1176 29.1	1174 31.0	
	Band Centre/cm ⁻¹ Relative Intensity/%	1114 15.2	1114 11.5	1116 10.3	1106 16.6	1104 17.3	1107 17.1	1114 22.3	1116 8.0							1283 3.9				
Reichenbachite	Band Centre/cm ⁻¹ Relative Intensity/%		729 0.1	692 0.4	691 0.3					684 1.2								709 0.0	705 7.9	
	Band Centre/cm ⁻¹ Relative Intensity/%	770 7.6	771 8.1	772 8.2	774 8.8	775 8.7	774 8.2	780 11.7	783 10.1	784 11.3	785 9.7	783 8.8	782 10.1	778 10.4	778 13.5	774 11.5	773 11.2	773 6.6	767 9.5	
	Band Centre/cm ⁻¹ Relative Intensity/%	800 1.4	798 1.8	798 1.5	797 0.9	795 0.7	793 1.1	836 2.9	836 3.6											
	Band Centre/cm ⁻¹ Relative Intensity/%	834 5.5	835 4.6	835 4.4	835 4.4	835 4.4	834 3.7													
	Band Centre/cm ⁻¹ Relative Intensity/%	919 0.8	921 0.7	923 1.2	925 1.6	924 1.1							894 5.0	884 13.2	877 17.1	877 9.9	876 10.2	862 13.3	861 14.8	
	Band Centre/cm ⁻¹ Relative Intensity/%	956 2.3	954 2.5	952 3.1	951 3.4	950 14.4	942 16.6	950 17.6	935 20.5	931 8.8	946 19.0	1009 67.1	1009 58.9	1011 50.1	1013 39.7	1011 33.2	1005 32.2	1007 10.4	1013 28.8	
	Band Centre/cm ⁻¹ Relative Intensity/%	963 13.8	959 12.8	955 12.2	952 13.4	950 2.6	950 3.8													
	Band Centre/cm ⁻¹ Relative Intensity/%	988 6.9	988 9.9	987 11.3	985 11.7	984 11.7	983 9.0													
	Band Centre/cm ⁻¹ Relative Intensity/%	1035 2.4	1035 2.1	1034 1.8	1033 1.5	1031 1.1	1030 19.1	1033 4.5	1052 51.1	1038 71.9	1052 63.4									
	Band Centre/cm ⁻¹ Relative Intensity/%	1045 17.5	1043 14.3	1041 14.5	1039 15.8	1036 15.3		1035 31.4	1146 2.4											
	Band Centre/cm ⁻¹ Relative Intensity/%	1096 18.4	1096 19.2	1094 20.6	1092 22.2	1089 24.6	1086 24.3	1082 14.1				1130 16.5	1130 14.8	1131 13.3	1034 3.2	1042 13.1	1040 13.5	1039 35.0	1041 7.7	
	Band Centre/cm ⁻¹ Relative Intensity/%	1161 1.0	1161 1.6	1160 1.8	1160 2.2	1157 2.2	1174 7.3	1169 11.2	1208 5.8	1213 2.0	1227 1.9	1221 3.9	1204 5.9	1196 7.5	1156 20.3	1181 26.9	1178 28.2	1184 8.1	1165 20.4	
	Band Centre/cm ⁻¹ Relative Intensity/%	1193 2.9	1194 3.7	1194 3.5	1195 3.9	1193 4.3														

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