

Raman and infrared spectroscopic study of the vivianite-group phosphates vivianite, baricite and bobierrite

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ABSTRACT

The molecular structure of the three vivianite-structure compositionally related phosphate minerals vivianite, baricite and bobierrite of formula $M_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ where M is Fe or Mg, has been assessed using a combination of Raman and infrared (IR) spectroscopy. The Raman spectra of the hydroxyl-stretching region are complex with overlapping broad bands. Hydroxyl stretching vibrations are identified at 3460, 3281, 3104 and 3012 cm^{-1} for vivianite. The high wavenumber band is attributed to the presence of FeOH groups. This complexity is reflected in the water HOH-bending modes where a strong IR band centred around 1660 cm^{-1} is found. Such a band reflects the strong hydrogen bonding of the water molecules to the phosphate anions in adjacent layers. Spectra show three distinct OH-bending bands from strongly hydrogen-bonded, weakly hydrogen bonded water and non-hydrogen bonded water. The Raman phosphate PO-stretching region shows strong similarity between the three minerals. In the IR spectra, complexity exists with multiple antisymmetric stretching vibrations observed, due to the reduced tetrahedral symmetry. This loss of degeneracy is also reflected in the bending modes. Strong IR bands around 800 cm^{-1} are attributed to water librational modes. The spectra of the three minerals display similarities due to their compositions and crystal structures, but sufficient subtle differences exist for the spectra to be useful in distinguishing the species.

KEYWORDS: baricite, bobierrite, vivianite, iron, phosphate, Raman spectroscopy, infrared spectroscopy.

Introduction

THE vivianite group of minerals are of the general formula $A_3^{2+}(\text{XO}_4)_2 \cdot 8\text{H}_2\text{O}$ where A^{2+} may be Co, Fe, Mg, Ni, Zn and X is As or P. Vivianite and baricite are the Fe- and Mg-dominant phosphates in the group, respectively. Baricite possesses a more common diamorph, bobierrite, with a doubled unit-cell volume. Extensive solid solution formation occurs between baricite and vivianite. Isomorphous substitution in this group occurs readily and intermediate compositions are often observed. The minerals are of interest because of their occurrence in environments such as the coatings of water pipes and soils from peat bogs,

morasses and sediments (Henderson *et al.*, 1984). If groundwaters are high in both Mg^{2+} and Fe^{2+} then it is possible that both the minerals of the vivianite group such as baricite and bobierrite may form, particularly when phosphate fertilizers have been used in the surrounding farmlands. In fact, these minerals have been found in sediments in New Zealand (Anthony *et al.*, 2000). The vivianite minerals are all monoclinic and belong to point group $2/m$ (Anthony *et al.*, 2000). The minerals may be divided into two groups according to the oxyanion being either arsenate or phosphate (Wolfe 1940). The phosphates in this mineral group are arupite ($\text{Ni}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), vivianite ($\text{Fe}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), baricite ($(\text{Mg}, \text{Fe}^{2+})_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and bobierrite ($\text{Mg}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$).

Some IR data exist for the vivianite-group phosphate and arsenate minerals (Farmer, 1974).

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However, most IR data predate the advent of Fourier transform IR spectroscopy (Gevork'yan and Povarennykh, 1973, 1980; Hunt 1977; Hunt *et al.*, 1972; Omori and Seki, 1960; Sitzia, 1966). Although some Raman studies of the vivianite phosphate minerals have been undertaken (Melendres *et al.*, 1989; Piriou and Poullen, 1984), no Raman spectroscopic investigation of these phosphate phase-related minerals has been forthcoming. The Raman spectra of the tetrahedral anions in aqueous systems are well known. The symmetric stretching vibration of the phosphate anion in aqueous systems (ν_1) is observed at 938 cm^{-1} , the asymmetric stretching mode (ν_3) at 1018 cm^{-1} . The ν_2 mode is observed at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} . In solids, the position of the bands will be dependent on the chemical environment. Farmer (1974) lists a number of IR spectra of phosphates including vivianite. The symmetric

stretching mode was not listed but the antisymmetric mode was found at 990 and 1040 cm^{-1} . Bands at 890 and 872 cm^{-1} were not assigned. It is probable that these are the symmetric stretching modes of the hydrogen-bonded phosphate. Bands for the ν_4 mode were observed at 475 , 560 and 590 cm^{-1} . The formula is close to that of bobierrite. Griffith (1970) reported the Raman spectra of vivianite.

Our interest in these minerals arose because of the observation of some blue materials found in some acid drainage soils in both the Shoalhaven Plateau in NSW, Australia and in some soil drainage materials in South Australia. There is currently a lack of comprehensive spectral knowledge of the vivianite phosphate minerals and as part of a wider comprehensive study of the vibrational spectroscopy of secondary minerals, we report the molecular structure of the phosphate minerals of the vivianite group.

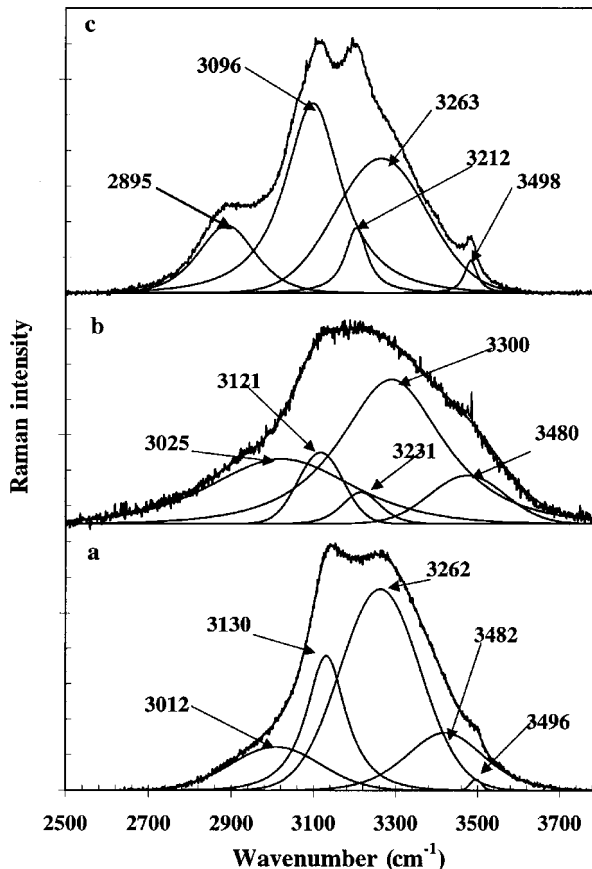


Fig. 1. Raman spectra of the hydroxyl-stretching region of (a) vivianite, (b) baricite and (c) bobierrite.

Experimental

Minerals

The vivianite was obtained from BK minerals (Brisbane, Queensland, Australia) and was in the form of large, deep blue, prismatic crystals. The mineral originated from the Ukraine. The baricite was lent to us by the South Australian museum, registered sample number SAM 15065, and originated from Big Fish River/Rapid creek, Richardson Mountains, Yukon, Canada. A sample of baricite was also obtained from sediment in a raised beach, Marlborough Province, New Zealand. The bobierrite came from the Zheleznyi Mine, Kovdor deposit, Kovdor Massif, Kola peninsula, Russia. Bobierrites were also obtained from Wodinga, Pilbara, Western Australia and from Marlborough, New Zealand.

Raman microprobe spectroscopy

The crystals of the vivianite minerals were placed and oriented 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 in the spectra. 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).

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000 to 525 cm⁻¹ range were obtained by the co-addition of 64 scans with a resolution of 4 cm⁻¹ and a mirror velocity of 0.6329 cm/s.

Spectroscopic manipulation such as baseline adjustment, smoothing and normalization were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, 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 to achieve a satisfactory fit. 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 $r^2 > 0.995$.

Results and discussion

Hydroxyl-stretching region

The Raman and IR spectra of vivianite, baricite and bobierrite are shown in Figs 1 and 2 respectively. The analysis of the Raman and IR spectra are reported in Table 1. Vivianite shows well-resolved bands in the hydroxyl-stretching region at 3496, 3482, 3262, 3130 and 3012 cm⁻¹. The bands are broad with bandwidths >200 cm⁻¹. Previous studies have not reported the Raman spectra of the hydroxyl-stretching region (Griffith, 1970; Piriou and Poullen, 1984). In the IR spectra of vivianite, three distinct hydroxyl-stretching bands are observed at 3460, 3281 and 3104 cm⁻¹. Previous study gave bands at 3475, 3260 and 3125 cm⁻¹, which are in reasonable agreement with this work, considering the breadth of the bands in the hydroxyl-stretching region (Piriou and Poullen, 1987). The band at 3262 cm⁻¹ is most intense in the Raman spectrum and is assigned to the water OH symmetric stretching mode whilst the bands at 3460 and 3104 cm⁻¹ are more intense in the IR spectra and are attributed to the water OH-antisymmetric stretching modes.

The Raman spectra of both baricite and bobierrite are less well resolved than that of vivianite, although the spectral profiles are similar (Fig. 1). In the Raman spectrum of baricite, bands were fitted at 3480, 3300, 3231, 3121 and 3025 cm⁻¹. Correspondingly, bands were found in the IR spectrum at 3498, 3373, 3168 and 2927 cm⁻¹. The Raman spectrum of the hydroxyl-stretching region of baricite shows somewhat more definition than the equivalent IR spectrum. The spectral profile in both the Raman and IR spectra extends to quite low wavenumbers for the hydroxyl-stretching region (Figs 1 and 2). Both the Raman and IR spectra of bobierrite show more definition than for either vivianite or baricite. The Raman spectrum has bands at

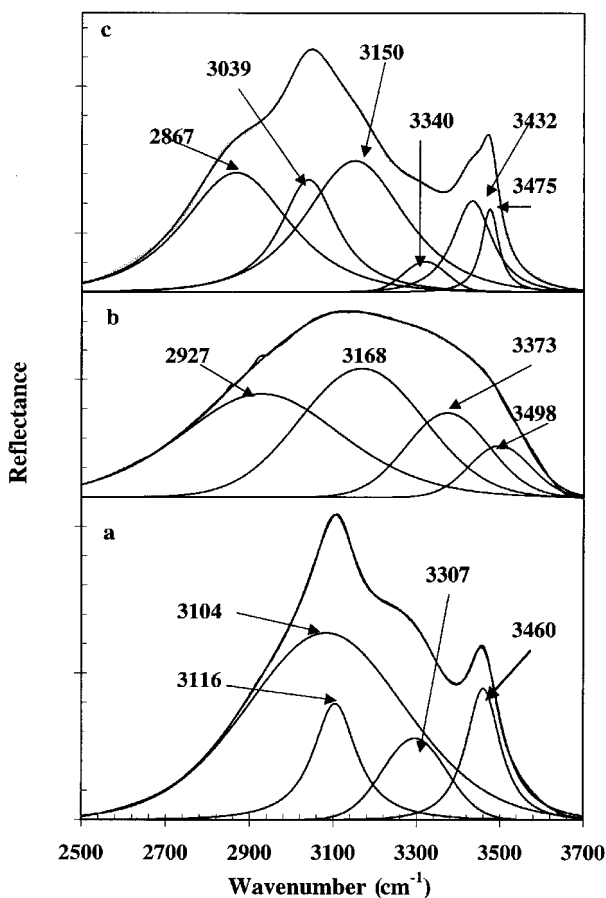


FIG. 2. IR spectra of the hydroxyl-stretching region of (a) vivianite, (b) baricite and (c) bobierrite.

3482, 3263, 3096 and 2888 cm^{-1} . The IR spectrum shows bands at 3475, 3432, 3150, 3039 and 2895 cm^{-1} . In the crystal structure of bobierrite, the distance between the oxygen and the hydrogen in the OH units varies from 0.79 to 0.89 Å with an average value of 0.84 Å (Takagi *et al.*, 1986). All the hydrogens are involved with hydrogen bonding and it is this hydrogen bonding which holds adjacent sheets together.

Water HOH bending

The IR spectra of the water HOH-bending mode is shown in Fig. 3 and the data reported in Table 1. For vivianite three bands are observed at 1666, 1615 and 1586 cm^{-1} . A previous study has suggested a single band at 1620 cm^{-1} (Piriou and Poullen, 1987). Farmer (1974) reported the band at 1635 cm^{-1} . Importantly the observation of the

band at 1666 cm^{-1} suggests that water is strongly hydrogen bonded to the phosphate oxygen. The band at 1615 cm^{-1} is assigned to the bending mode of water hydrogen bonded to water, whilst the band at $\sim 1586\text{ cm}^{-1}$ may be attributed to non-hydrogen bonded water, equivalent to that found for water as water vapour.

It is apparent that in the molecular structure of vivianite, three different types of water are observed. For baricite the IR spectrum shows a broad profile similar to that observed for the hydroxyl-stretching region of baricite. Three bands may be fitted at 1669, 1631 and 1589 cm^{-1} . The description of these bands is as for vivianite. The IR spectrum of bobierrite in this region shows two bands resolved at 1655 and 1587 cm^{-1} . The 1655 cm^{-1} band is assigned to the water strongly hydrogen bonded to the adjacent layers. For this mineral no band for

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TABLE 1. Raman and IR spectral analysis of the phosphates of the vivianite group.

Vivianite		IR *		Baricite		Bobierrite		Suggested assignment
Raman				Raman	IR	Raman	IR	
3496		3460	3400	3480	3498	3482	3475	Hydroxyl stretching
3262		3281		3300	3373	3263	3432	
3130		3104		3121	3168	3096	3150	
3012				3025	2927	2895	3039 2867	
		1666	1635		1669		1655	Water HOH bending
		1615			1631		1587	
		1586			1589			
1081	1053	1079	1040	1057	1100	1072	1089	PO stretching
1050	1018	1027	990	953	1039	998	1034	
1015	990	950		859	998	951	998	
949	951	923			970	909	969	
					942		943	
		813	890		802	842	832	Water librational modes
		783	872			787		
584		634	600	632		717	703	Out-of-plane bends
569			575	576		693	677	
545		561	560	545		668		
530			492	527		631		
						583		
						557 542		
456				461		468		In-plane bends
423				428		435		
				390		420		
344				340		364		
307				314		318		
281				281		290		
						282 262		
236				243		233		
186				212		215		
				201		182		
				170		170		
				140		149		
						136		

* Published by Piriou and Poullen (1984)

adsorbed water at ~ 1620 to 1630 cm^{-1} was observed. The band at $\sim 1587\text{ cm}^{-1}$ ascribed to non-hydrogen bonded water is attributed to included water. In the unit cell of vivianite there are two formula units ($\text{Fe}_3^{2+}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) per unit cell since $Z = 2$. This means that there are 16 water molecules in the unit cell. Thus the two

types of water can explain the number of bands in the IR and Raman spectra. This explanation is also useful to explain the bands at ~ 1630 and $\sim 1660\text{ cm}^{-1}$. However in the hydroxyl deformation region, bands are observed around 1590 cm^{-1} , which is the band position of non-hydrogen bonded water. One possible explanation

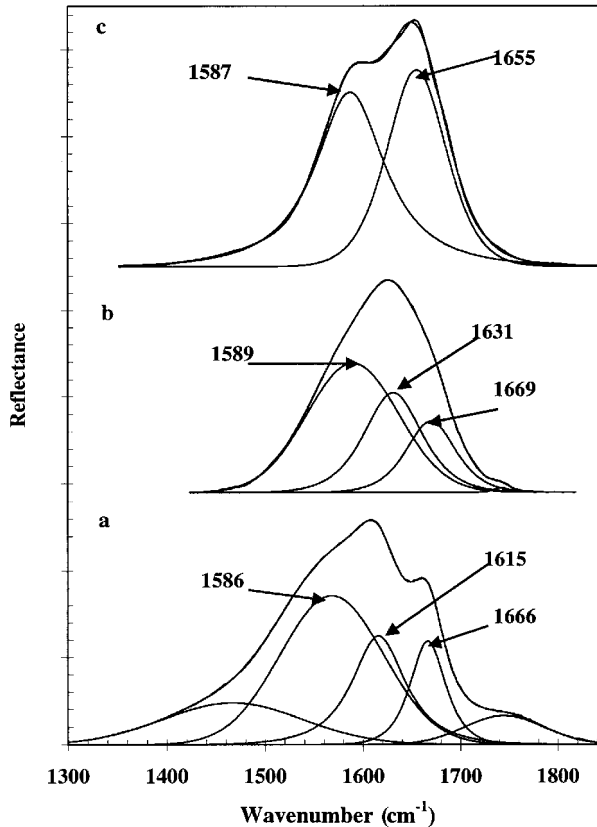
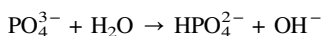


FIG. 3. IR spectra of the water HOH-bending region of (a) vivianite, (b) baricite and (c) bobierrite.

could be offered in terms of fluid inclusions, which could provide the explanation for this band.

In the hydroxyl-stretching region in both the IR and Raman spectrum of vivianite and bobierrite, a sharp band is observed at $\sim 3490\text{ cm}^{-1}$. The intensity of the band is greater in the IR spectrum. One possible explanation of this band is that it is due to hydroxyl groups associated with the presence of Fe^{3+} .

Bobierrite may contain some minor amounts of Fe, which could also be oxidized. If some oxidation of the ferrous ion to ferric occurs then this charge would need to be counterbalanced by the negative of the hydroxyl unit as no other negative charges could originate from the phosphate anion. (Wildner *et al.*, 1996) This then could mean that a free proton is available to form HPO_4 units. The following reaction is envisaged.



Any phenomenon such as the migration of a proton to a phosphate anion can be measured using vibrational spectroscopy. Likewise the bonding of a hydroxyl unit to the metal could be observed. Importantly $-\text{POH}$ units could be formed, the IR and Raman spectrum of which might show its presence. Significant intensity exists in the bands at 3012 cm^{-1} for vivianite, 3025 cm^{-1} for baricite and 2895 cm^{-1} for bobierrite. This latter band is quite distinct in the Raman spectrum of bobierrite. One explanation of this band is that it is due to the formation of the $-\text{POH}$ units and this band is the stretching vibration of this hydroxyl unit.

Phosphate PO-stretching region

The Raman and IR spectra of the phosphate symmetric stretching region of vivianite, baricite and bobierrite are shown in Figs 4 and 5. The analysis of the spectral data is reported in Table 1.

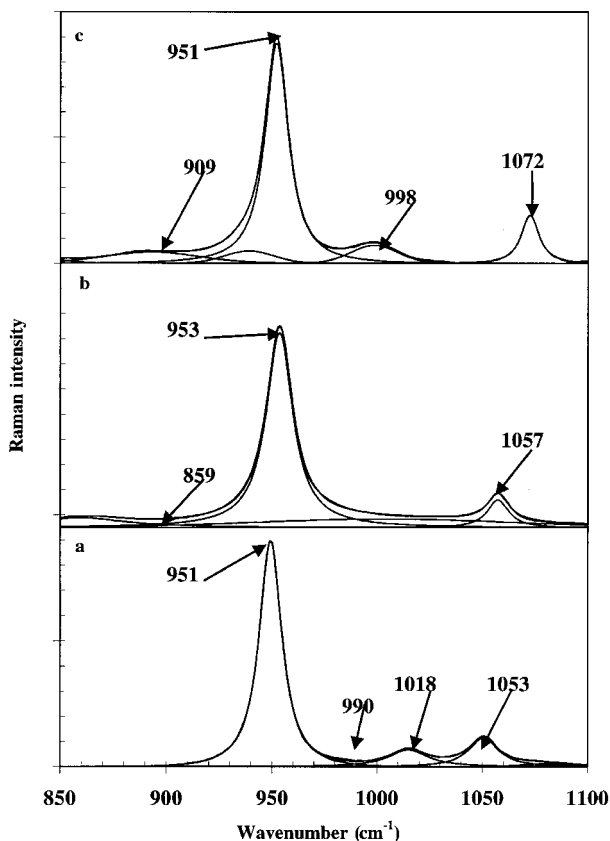


FIG. 4. Raman spectra of the phosphate-stretching region of (a) vivianite, (b) baricite and (c) bobierrite.

In the Raman spectrum of vivianite, a single intense band is observed at 949 cm^{-1} with low-intensity bands observed at 1081 , 1050 and 1015 cm^{-1} . The 949 cm^{-1} band is assigned to the Raman active PO-stretching vibration. The position of this band is in excellent agreement with the previously published result (Pirou and Poullen, 1987). The bands at 1081 , 1050 and 1015 cm^{-1} are assigned to the phosphate PO antisymmetric stretching vibrations. The 1081 cm^{-1} band is very low in intensity. Pirou and Poullen found bands at 1053 and 1018 cm^{-1} and are in agreement with our results. We did not observe the band at 990 cm^{-1} . The phosphate anion in an aqueous solution shows a single antisymmetric band at 1017 cm^{-1} . In this work three bands are observed, consistent with the reduction of the phosphate ion symmetry from T_d to C_{3v} or less to C_{2v} in accord with the crystal structure determination. This symmetry reduction

is borne out in the IR spectra. Infrared bands are observed at 1079 , 1027 , 950 and 923 cm^{-1} . The 950 cm^{-1} band is the symmetric stretching vibration also observed in the Raman spectrum. The two bands at 1079 and 1027 cm^{-1} correspond to the very low intensity Raman bands observed at 1081 and 1050 cm^{-1} . Previously published IR data reported by Farmer gave bands at 1040 and 990 cm^{-1} , which are different from the results reported here. One possibility is that the data are correct and the identification of the mineral used by Farmer incorrect.

In the spectra in Fig. 5 quite intense IR bands are observed at 813 and 783 cm^{-1} . There are two possibilities for the assignment of these bands: first the position of the band at $\sim 813\text{ cm}^{-1}$ could be assigned to the AsO-stretching vibration. However no band was observed at this position in the Raman spectrum and also the chemical analysis using the electron probe did not

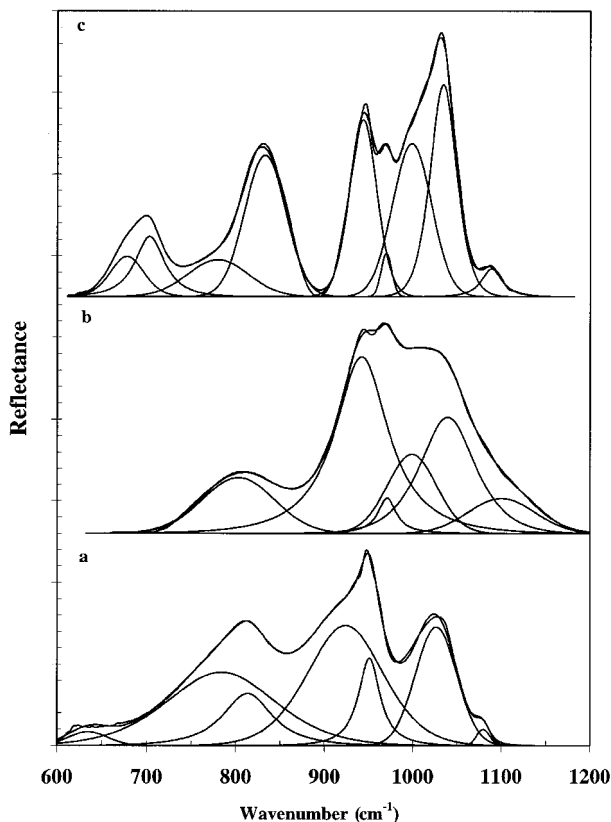


FIG. 5. IR spectra of the PO_4 -stretching region of (a) vivianite, (b) baricite and (c) bobierite.

determine an As value, which was below the detection limits. Bands in this position are common to all three minerals. The second possibility is the bands at 813 and 783 cm^{-1} are due to water librational modes. Such bands would be intense in the IR spectra but weak or of zero intensity in the Raman spectrum. The position of these bands is very sensitive to hydrogen bonding. The observation of more than one type of water molecule in the structure from the water bending modes implies that there should be more than one water librational mode.

The Raman spectrum of baricite (Fig. 4b) displays three bands in the PO-stretching region at 1057, 953 and 859 cm^{-1} . The simple description of these bands suggests that the 1057 cm^{-1} band is due to the PO antisymmetric stretching vibration and the 953 cm^{-1} to the PO symmetric stretching vibration. The IR spectrum of baricite (Fig. 5b) as for vivianite shows complexity. Infrared bands in this spectral region are observed

at 1039, 998, 970 and 942 cm^{-1} . A band is also observed at 802 cm^{-1} and is assigned to water librational modes of strongly hydrogen bonded water molecules. The observation of four anti-symmetric stretching vibrations is presumably a function of both low symmetry and substitution of Fe by Mg.

In the Raman spectrum of bobierite (Fig. 4c), an intense band is observed at 951 cm^{-1} . This band is assigned to the PO symmetric stretching vibration. Bands of low intensity are observed at 1072, 998 and 909 cm^{-1} . Low-intensity bands are also observed at 842 and 787 cm^{-1} . The IR spectrum of bobierite (Fig. 5c) is better defined than that of vivianite and baricite. Two distinct regions are observed centred upon bands in the 900 to 1100 cm^{-1} region and bands in the 850 cm^{-1} region and below. Five IR bands are observed at 1089, 1034, 998, 969 and 943 cm^{-1} . The 943 cm^{-1} band is assigned to the symmetric stretching mode and the other four bands to the

antisymmetric stretching modes. Strong IR bands are observed at 832, 703 and 677 cm^{-1} and are assigned to water librational modes.

Phosphate bending modes

The Raman spectrum of the low-wavenumber region for the three compositionally related vivianite minerals is shown in Fig. 6. The results of the spectral analysis are reported in Table 1. The use of the diamond ATR cell has a lower wavenumber limit of $\sim 600 \text{ cm}^{-1}$, and as a consequence no IR data for this region were obtained. One of the main advantages of Raman spectroscopy is the ability to obtain spectral data below 400 cm^{-1} . The difficulty in the study of this spectral region is a combination of the complexity of the overlap and the number of bands. The difficulty rests with the attribution of the multiple bands found in this region. In

aqueous solutions of the phosphate ion, the band observed at 420 cm^{-1} is assigned to the ν_2 bending mode. For vivianite, two bands are observed at 423 and 456 cm^{-1} , with the latter being the more intense. The observation of two bands for the OPO bending region suggests the loss of degeneracy of the bending mode. For baricite three bands are observed for the ν_2 bending mode at 461, 428 and 390 cm^{-1} . For bobierrite three bands are observed at 468, 435 and 420 cm^{-1} . The only Raman data for comparison is that reported by Griffith, who suggested the bending mode was at 316 cm^{-1} (Griffith, 1970). However this seems to be an error. Farmer (1974) also did not report the bending mode.

For aqueous systems the ν_4 mode of phosphate is observed at 567 cm^{-1} . For vivianite, four bands are observed at 584, 569, 545 and 530 cm^{-1} . The 569 cm^{-1} band is intense and sharp. These bands

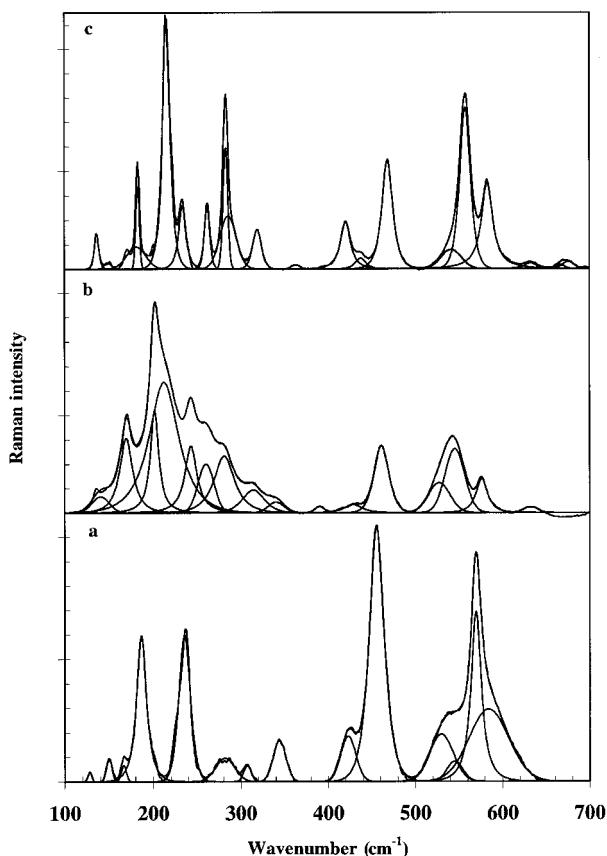


FIG. 6. Raman spectra of the low-wavenumber region of (a) vivianite, (b) baricite and (c) bobierrite.

are assigned to the ν_4 modes of vivianite. The spectral data reported by Griffith is at variance with these results (Griffith, 1970). Farmer reported IR bands at 590, 560 and 475 cm^{-1} (Farmer, 1974). For baricite, ν_4 bands are observed at 576, 545 and 527 cm^{-1} and for bobierrite, bands are found at 583, 557 and 542 cm^{-1} . In the Raman spectrum for vivianite, two intense bands are observed at 236 and 186 cm^{-1} . One possibility is that these bands are attributable to FeO-stretching vibrations. This spectral region for baricite is complex. Two intense bands are observed at 203 and 170 cm^{-1} . For bobierrite, an intense band is observed at 215 cm^{-1} and is assigned to the MgO-stretching vibration.

Conclusions

A combination of Raman and IR spectroscopy has been used to study a compositionally and structurally related set of vivianite phosphate minerals. Bands attributed to the water hydroxyl stretching, bending and librational modes are identified and show the existence of three types of water molecules in the structure, namely adsorbed, weakly and strongly hydrogen-bonded. A single phosphate symmetric stretching vibration is observed for each mineral but several antisymmetric stretching modes are observed consistent with a loss of symmetry of the phosphate anion in the mineral crystals. The loss of symmetry also results in several in-plane and out of plane bending modes. Vivianite is an intense blue colour whilst baricite and bobierrite vary from colourless to blue. The observation of blue materials in soils and sediments has suggested the use of Raman spectroscopy for the identification of vivianite in these soils. It is suspected that the other two minerals exist in groundwater drainage sites but this remains to be proved. Such minerals have been found in sediments from New Zealand. This study demonstrates that Raman and IR spectroscopy can be used to distinguish the vivianite Fe-Mg phosphate phases by their spectra.

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