

# A Raman spectroscopic study of selected minerals of the rosasite group

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Minerals in the rosasite mineral group, namely, rosasite, glaukosphaerite, kolwezite, mcguinnessite, nullaginite and pokrovskite have been studied by Raman spectroscopy at 298 and 77 K, complemented with infrared spectroscopy. The spectral patterns for the minerals rosasite, glaukosphaerite, kolwezite and mcguinnessite are similar to those of malachite, implying that the structure is the same as that of malachite, i.e. monoclinic. A comparison is made with the spectra of malachite. The symmetry of the carbonate anion in the rosasite mineral group is  $C_{2v}$  or  $C_s$  and is composition dependent. Two  $(CO_3)^{2-}$  symmetric stretching modes are observed for the rosasite minerals at 1060 and 1090  $cm^{-1}$ . Two hydroxyl stretching modes are observed for the rosasite mineral group. The position of these bands is determined to be a function of the hydrogen bond lengths. Hydrogen bond distances for rosasite are calculated as 2.867, 2.799 and 2.780 Å, whereas for pokrovskite the distances are 3.280 and 2.999 Å. The effect of lowering the temperature from ambient to 77 K results in a decrease of the hydrogen bond distances by 5%. Multiple Raman bands are observed in the 800 to 850  $cm^{-1}$  and the 720 to 750  $cm^{-1}$  regions and are attributed to  $\nu_2$  and  $\nu_4$  bending modes confirming the reduction of the carbonate anion in the rosasite structure. Copyright © 2006 John Wiley & Sons, Ltd.

**KEYWORDS:** glaukosphaerite; kolwezite; mcguinnessite; nullaginite; rosasite; hydroxycarbonate

## INTRODUCTION

The carbonates are a group of over 60 naturally occurring minerals containing the essential structural building block  $(CO_3)^{2-}$ . Most of these minerals are relatively rare and are often in association with other building blocks such as hydroxyls, halogens, sulphate, silicate, phosphate, etc. The common simple rock-forming carbonates can be divided into three main groups: (1) the calcite group, (2) the dolomite group and (3) the aragonite group. Peter Williams reports that while metal substitution in azurite is extremely uncommon, such is not the case for malachite.<sup>1</sup> In minerals related to malachite, ions identified together with Cu(II) are Zn(II), Co(II), Ni(II) and Mg(II). The most common congener of malachite is rosasite. No single crystal study of rosasite has been forthcoming. Powder diffraction studies of rosasite suggest that the mineral is triclinic.<sup>2</sup>

The rosasite mineral group comprises monoclinic or triclinic hydroxy carbonates with the general formula

$A_2(CO_3)(OH)_2$  or  $AB(CO_3)(OH)_2$  where A and B are cobalt, copper, magnesium, nickel and zinc.<sup>3</sup> The chemical composition of these minerals means that the minerals are highly colourful, often green to blue. Minerals in the rosasite group are related to the mineral malachite.<sup>4,5</sup> Minerals in this group include rosasite  $[(Cu,Zn)_2(CO_3)(OH)_2]$ ,<sup>6–8</sup> glaukosphaerite  $[(Cu,Ni)_2(CO_3)(OH)_2]$ ,<sup>9–11</sup> kolwezite  $[(Cu,Co)_2(CO_3)(OH)_2]$ ,<sup>12</sup> mcguinnessite  $[(Mg,Cu)_2(CO_3)(OH)_2]$ <sup>13–16</sup> and nullaginite  $[(Ni)_2(CO_3)(OH)_2]$ .<sup>17–19</sup> Apart from rosasite the other minerals are rare secondary minerals. Besides the chemical composition, the structural relationships between these minerals are demonstrated by the similarity of their powder diffraction patterns.<sup>20</sup> A significant feature of these minerals is their microcrystalline fibrous habit. This characteristic precludes in most cases single crystal studies. The space group symmetry and cell parameters are mainly derived from powder pattern indexing. Apart from that of malachite, no other structural determinations are available for the rosasite minerals. Rosasite forms spheroidal aggregates in extremely thin fibrous crystals, as do the other minerals of this group. Rosasite forms in the oxidation zones of zinc-copper deposits. It is found typically as crusts and botryoidal masses or nodules. Crystals are fibrous and are

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found in tufted aggregates. Rosasite may be associated with aurichalcite, smithsonite and hemimorphite.

Raman and infrared spectroscopy have been used to investigate carbonates including azurite and malachite.<sup>21,22</sup> A detailed single crystal Raman study has been undertaken.<sup>5,21</sup> Goldsmith and Ross reported the infrared spectra of azurite and malachite.<sup>21</sup> However, vibrational spectroscopy of minerals of the rosasite group has not been undertaken. No infrared spectra of the minerals of the rosasite group have been forthcoming.<sup>22–25</sup> An infrared stretching vibration of the hydroxyl unit of azurite was observed at  $3425\text{ cm}^{-1}$ , whereas two bands were reported for malachite at  $3400$  and  $3320\text{ cm}^{-1}$ . The observation of two bands for malachite suggests coupling of the hydroxyl stretching vibrations.<sup>5</sup> This coupling was not observed for azurite.<sup>5</sup> Azurite and malachite form the basis of pigments in samples of an archaeological or medieval nature.<sup>26–29</sup> It is not known whether minerals of the rosasite group have been used in pigments for paintings and other artworks of archeological significance. The colour of the minerals suggests that this is a real possibility, especially for rosasite. However, a complete Raman spectroscopic analysis is not required as individual Raman bands are simply used to identify the mineral pigments in the samples. Malachite has a characteristic intense band at  $\sim 430\text{ cm}^{-1}$  and azurite has an intense band at  $\sim 400\text{ cm}^{-1}$ . The deformation modes of azurite were reported at  $1035$  and  $952\text{ cm}^{-1}$  and at  $1045$  and  $875\text{ cm}^{-1}$  for malachite.<sup>22,30</sup> Thus even though the two carbonate minerals have the same space group, the molecular structure of the minerals is sufficiently different to show infrared bands at slightly different wavenumbers. Differences between the spectra of malachite and azurite may be explained by the molecular structure of azurite being based upon a distorted square planar arrangement compared to a distorted octahedral arrangement about the copper in malachite.

The symmetric stretching bands of carbonate for azurite and malachite were observed at  $1090$  and  $1095\text{ cm}^{-1}$ . Goldsmith and Ross<sup>21</sup> report the infrared bending modes of carbonate at  $837$  and  $817\text{ cm}^{-1}$  for azurite and at  $820$  and  $803\text{ cm}^{-1}$  for malachite. Two  $\nu_3$  modes were observed at  $1490$  and  $1415\text{ cm}^{-1}$  for azurite and at  $1500$  and  $1400\text{ cm}^{-1}$  for malachite. The observation of these two bands shows a loss of degeneracy. Such a conclusion is also supported by the observation of two  $\nu_4$  modes at  $769$  and  $747\text{ cm}^{-1}$  for azurite and  $710$  and  $748\text{ cm}^{-1}$  for malachite. The vibrational spectroscopy of these two minerals is complicated by this loss of degeneracy. Schmidt and Lutz<sup>31</sup> report some vibrational spectroscopic data. Two infrared bands at  $3415$  and  $3327\text{ cm}^{-1}$  were observed for malachite. Although the Raman spectra of the mineral brochantite  $[\text{Cu}_4(\text{OH})_6\text{SO}_4]$  have been reported, the Raman spectra of malachite and azurite were not.<sup>31</sup>

In this work the vibrational spectroscopy of minerals of the rosasite group is reported and the same is related to the mineral structure.

## EXPERIMENTAL

### Minerals

The minerals used in this study and their formula and origin are listed in Table 1. Selected minerals were obtained from the Mineral Research Company and other sources including Museum Victoria. The samples were phase analysed by X-ray diffraction (XRD) and their chemical composition was determined by EDX measurements.

### X-ray diffraction

XRD patterns were recorded using  $\text{Cu K}\alpha$  radiation ( $n = 1.5418\text{ \AA}$ ) on a Philips PANalytical X' Pert PRO diffractometer operating at  $40\text{ kV}$  and  $40\text{ mA}$  with  $0.125^\circ$  divergence slit,  $0.25^\circ$  anti-scatter slit, between  $3$  and  $15^\circ$  ( $2\theta$ ) at a step size of  $0.0167^\circ$ . For low angle XRD, patterns were recorded between  $1$  and  $5^\circ$  ( $2\theta$ ) at a step size of  $0.0167^\circ$  with variable divergence slit and  $0.5^\circ$  anti-scatter slit.

### SEM analysis

Mineral samples of the rosasite were coated with a thin layer of evaporated carbon, and secondary electron images were obtained using an FEI Quanta 200 scanning electron microscope (SEM). For X-ray microanalysis (EDX), three samples were embedded in Araldite resin and polished with diamond paste on Lamplan 450 polishing cloth using water as a lubricant. The samples were coated with a thin layer of evaporated carbon for conduction and examined in a JEOL 840A analytical SEM at  $25\text{ kV}$  accelerating voltage. Preliminary analyses of the rosasite mineral samples were carried out on the FEI Quanta SEM using an EDAX microanalyser, and microanalysis of the clusters of fine crystals was carried out using a full standards quantitative procedure on the JEOL 840 SEM using a Moran Scientific microanalysis system. Oxygen was not measured directly but was calculated using assumed stoichiometries to the other elements analysed.

### Raman microprobe spectroscopy

The crystals of hydroxycarbonates were placed and orientated on the stage of an Olympus BHSM microscope, equipped with  $10\times$  and  $50\times$  objectives and 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 He–Ne laser ( $633\text{ nm}$ ) at a resolution of  $2\text{ cm}^{-1}$  in the range between  $100$  and  $4000\text{ cm}^{-1}$ . Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the  $520.5\text{ cm}^{-1}$  line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal

**Table 1.** Table of the hydroxycarbonate minerals, their chemical formulae and their origin

Mineral	Locality of origin	Formulae	Analysis (% by mass)
Rosasite	Mapimi, Durango, Mexico	$(\text{Cu,Zn})_2(\text{CO}_3)(\text{OH})_2$	CuO 35.7 ZnO 36.5
Glaukosphaerite	Carr Boyd Nickel Mine, Carr Boyd Rocks, W.A. <sup>17,19</sup>	$(\text{Cu,Ni})_2(\text{CO}_3)(\text{OH})_2$	CuO 41.6 NiO 25.2
Kolwezite	Mupine, Shaba Province, Zaire <sup>32</sup>	$(\text{Cu,Co})_2(\text{CO}_3)(\text{OH})_2$	CuO 48.4 CoO 23.0
Mcguinnessite	Red Mountain, Mendocino County, California <sup>16</sup>	$(\text{Mg,Cu})_2(\text{CO}_3)(\text{OH})_2$	CuO 39.6 MgO 23.7
Mcguinnessite	Rockville Crushed Stone Quarry, 6.4 km W. of Rockville, Maryland	$(\text{Mg,Cu})_2(\text{CO}_3)(\text{OH})_2$	CuO 43.7 MgO 22.2
Nullaginite	Otway Prospect, W.A. <sup>17,19</sup>	$\text{Ni}_2(\text{CO}_3)(\text{OH})_2$	NiO 68.7 Cr <sub>2</sub> O <sub>3</sub> 0.4 MgO 1.0
Pokrovskite	Lytton, Sonoma County, California <sup>33</sup>	$\text{Mg}_2(\text{CO}_3)(\text{OH})_2 \cdot \frac{1}{2} \text{H}_2\text{O}$	MgO 50.8 Fe <sub>2</sub> O <sub>3</sub> 1.9 MnO 1.2

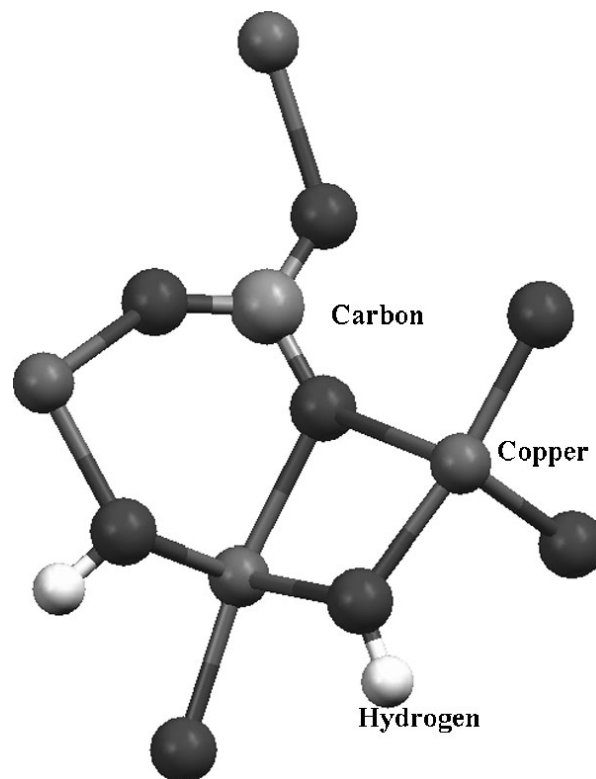
stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the technique have been published by the authors.<sup>34–37</sup>

### 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 4000–525  $\text{cm}^{-1}$  range were obtained by the co-addition of 64 scans with a resolution of 4  $\text{cm}^{-1}$  and a mirror velocity of 0.6329  $\text{cm/s}$ . Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS<sup>®</sup> software package (Galactic Industries Corporation, Salem, NH, USA).

## RESULTS AND DISCUSSION

The minerals of the rosasite group have not been studied by single crystal XRD, invariably because most of the crystals are composed of thin fibres. Extensive powder XRD suggests that the minerals are triclinic, although Anthony *et al.* state that the mineral is monoclinic.<sup>32</sup> This statement is apparently based upon the assumption that the structures are similar to that of malachite as shown in Fig. 1. The structure shows that two of the three oxygens bond to separate copper atoms but one carbonate oxygen bonds to two copper atoms (Fig. 1). The OH unit serves to bridge two copper atoms. The model of the structure of malachite shows that the carbonate anion is of  $C_{2v}$  symmetry if the two cations (e.g. Cu) bonding to the carbonate anion are identical. If, however, the two cations are different (e.g. Cu

**Figure 1.** Model of the structure of malachite.

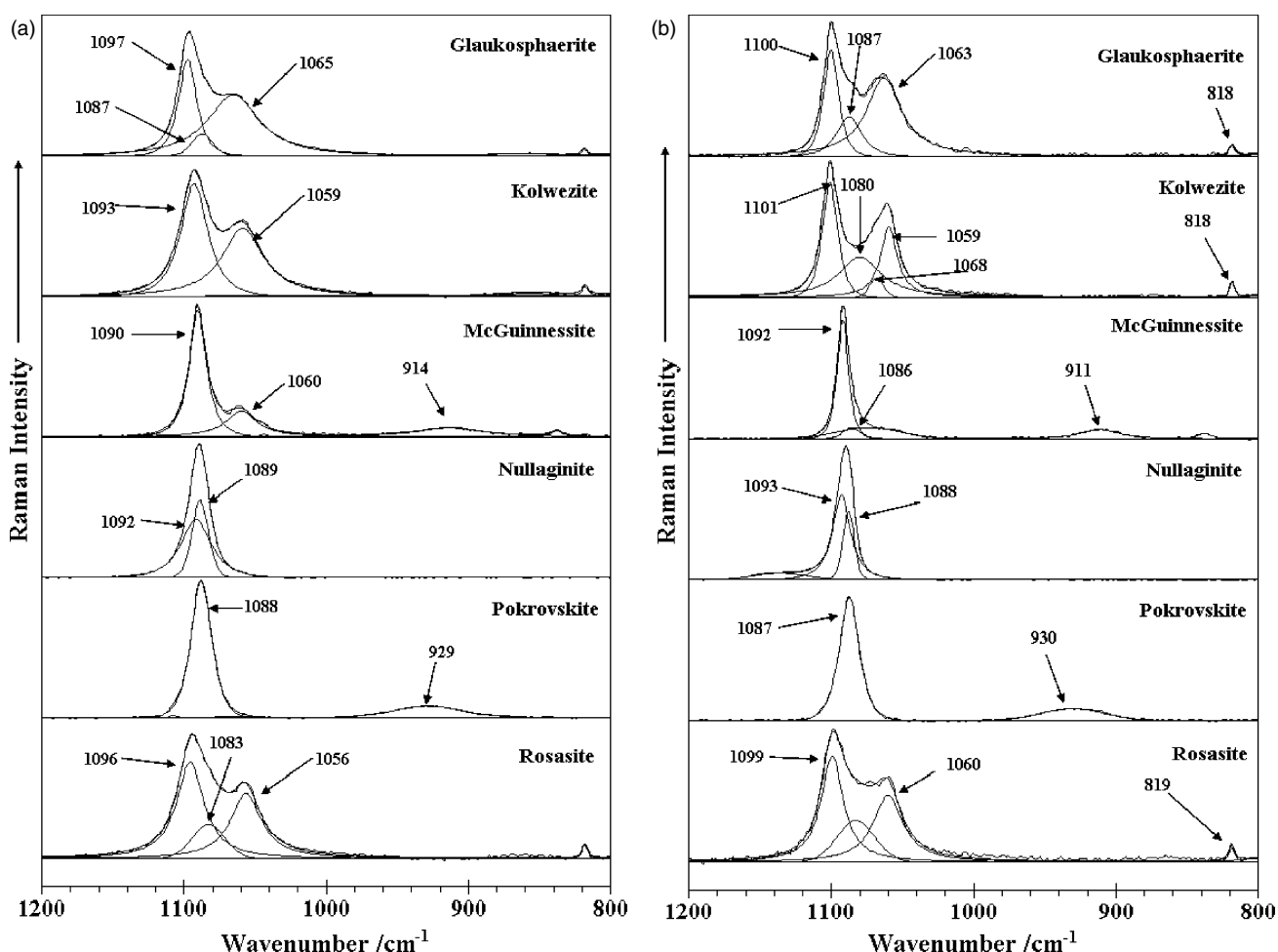
and Ni or Cu and Zn) then the symmetry of the carbonate anion would be  $C_s$ . The mineral glaukosphaerite is equally enigmatic and may be monoclinic. Williams<sup>1</sup> reported the structure of the rosasite group of minerals to be triclinic. It

is not necessarily true that rosasite has the same structure as malachite.<sup>1</sup> In the structure of rosasite some of the copper atoms in the model of malachite will be replaced by zinc atoms.

Table 1 reports the chemical composition of the cations in the mineral samples used in this work. If the atom ratio of Cu/Zn is 1:1, then every second position in the model will be taken up by a Zn atom. The rosasite sample used in this work analysed to a Cu/Zn ratio of close to 1:1. Rosasite does not necessarily maintain a ratio of 1:1. For example, the rosasite from Rosas mine, Narcao, Cagliari, Sardegna (Sardinia), Italy analyses as CuO 53.7 and ZnO 18.3%. This gives a formula of the Narcao rosasite as  $(\text{Cu}_{1.5}\text{Zn}_{0.5})_2(\text{CO})_3(\text{OH})_2$ . The mineral glaukosphaerite from the Carr Boyd Nickel Mine analyses as CuO 41.6 and NiO 25.2%. This gives the formula of glaukosphaerite as  $(\text{Cu}_{1.1}\text{Ni}_{0.7}\text{Mg}_{0.06})_2(\text{CO})_3(\text{OH})_2$ . According to Anthony *et al.*<sup>32</sup> a glaukosphaerite sample from Kasompi, Congo gave a formula of  $(\text{Cu}_{1.23}\text{Zn}_{0.71})_2(\text{CO})_3(\text{OH})_2$ . It is noted

that the Cu/Zn ratio is not 1:1 and the total cations is not 2.0, but 1.94. A similar formula exists for the mineral kolwezite from Zaire, namely,  $(\text{Cu}_{1.33}\text{Co}_{0.67})_2(\text{CO})_3(\text{OH})_2$ . The fact that the ratio of the two cations is not 1:1 may have implications for the structure of the mineral and therefore for the vibrational spectroscopy of the mineral. The mcguinnessite from California gives a cation ratio of Cu/Mg as 1:1. Other measurements record a ratio of Mg/Cu as 1.5/0.5. The formula for nullaginite based upon the chemical analysis is  $(\text{Ni}_{1.93}\text{Mg}_{0.05}\text{Cr}_{0.01})_2(\text{CO})_3(\text{OH})_2$ . This mineral is totally composed of Ni, and may be regarded as a single cation hydroxy carbonate. The mineral pokrovskite could be expected to be clear or white/opaque. However, the presence of traces of Fe and Mn gives the mineral a brownish colour. The formula may be regarded as a pure hydroxy magnesium carbonate.

Vibrational spectroscopy can be used to characterise these minerals even though no definitive crystallographic studies have been undertaken. Since the definitive crystallographic



**Figure 2.** (a) Raman spectra of rosasite, pokrovskite, nullaginite, mcguinnessite, kolwezite and glaukosphaerite at 298 K in the 1200 to 800 cm<sup>-1</sup> region. (b) Raman spectra of rosasite, pokrovskite, nullaginite, mcguinnessite, kolwezite and glaukosphaerite at 77 K in the 1200 to 800 cm<sup>-1</sup> region. (c) Infrared spectra of rosasite, pokrovskite, nullaginite, mcguinnessite, kolwezite and glaukosphaerite in the 1750 to 550 cm<sup>-1</sup> region. (d) Raman spectra of azurite and malachite in the 1200 to 1000 cm<sup>-1</sup> region.

studies have not been forthcoming, it is not possible to undertake a factor group analysis. If the structure of rosasite is monoclinic with  $P2_1/a$ , two symmetric carbonate stretching vibrations would be expected.

## RAMAN SPECTROSCOPY

### Raman spectroscopy of the 1200 to 800 $\text{cm}^{-1}$ region

The Raman spectra of rosasite, pokrovskite, nullagite, mcguinnessite, kolwezite and glaukosphaerite in the 800 to 1200  $\text{cm}^{-1}$  region at 298 and 77 K are shown in Fig. 2(a) and (b). The infrared spectra of these minerals in the 550 to 1750  $\text{cm}^{-1}$  region are shown in Fig. 2(c). For comparison, the Raman spectra of azurite and malachite in the 1000 to 1200  $\text{cm}^{-1}$  region are shown in Fig. 2(d).

The Raman spectra of rosasite displays three bands at 1096, 1083 and 1056  $\text{cm}^{-1}$  with bandwidths of 23, 27 and 26  $\text{cm}^{-1}$ , respectively. In the 77 K spectrum the bands shift to slightly higher wavenumbers with reduced bandwidths. These bands are assigned to the  $\nu_1(\text{CO}_3)^{2-}$  symmetric stretching vibration. In the infrared spectrum bands of low intensity are observed at 1096, 1044 and 1021  $\text{cm}^{-1}$ . These infrared

bands correspond to the Raman bands. These values may be compared with those of malachite at 1097 and 1055  $\text{cm}^{-1}$  (298 K) and 1099 and 1058  $\text{cm}^{-1}$  (77 K). The values for rosasite and malachite are almost identical; the observation of three symmetric stretching bands indicates the presence of three different carbonate anions in the rosasite structure. The analysis of the rosasite mineral shows that the percentage of CuO is 19.5 and that of ZnO is 24.6 weight percent. Thus the carbonate anion may be associated with two different cations, thus giving rise to two carbonate vibrations. It is noted that azurite, which is monoclinic with point group  $2/m$ , shows only a single Raman band at 1095  $\text{cm}^{-1}$  at 298 and 77 K.<sup>4,5,38</sup> Malachite is also monoclinic with the same point group.

The Raman spectrum of the mineral pokrovskite  $[\text{Mg}_2(\text{CO}_3)(\text{OH})_2 \cdot \frac{1}{2}\text{H}_2\text{O}]$  shows a single intense band at 1088  $\text{cm}^{-1}$  at 298 K with a bandwidth of 17.0  $\text{cm}^{-1}$  and at 1087  $\text{cm}^{-1}$  at 77 K with a bandwidth of 16.0  $\text{cm}^{-1}$ . In the infrared spectrum only a single low intensity band at 1080  $\text{cm}^{-1}$  is found. Although chemical analysis does show traces of other cations in the mineral,  $\text{Mg}^{2+}$  is the major cation and the carbonate anion is associated with only one cation,

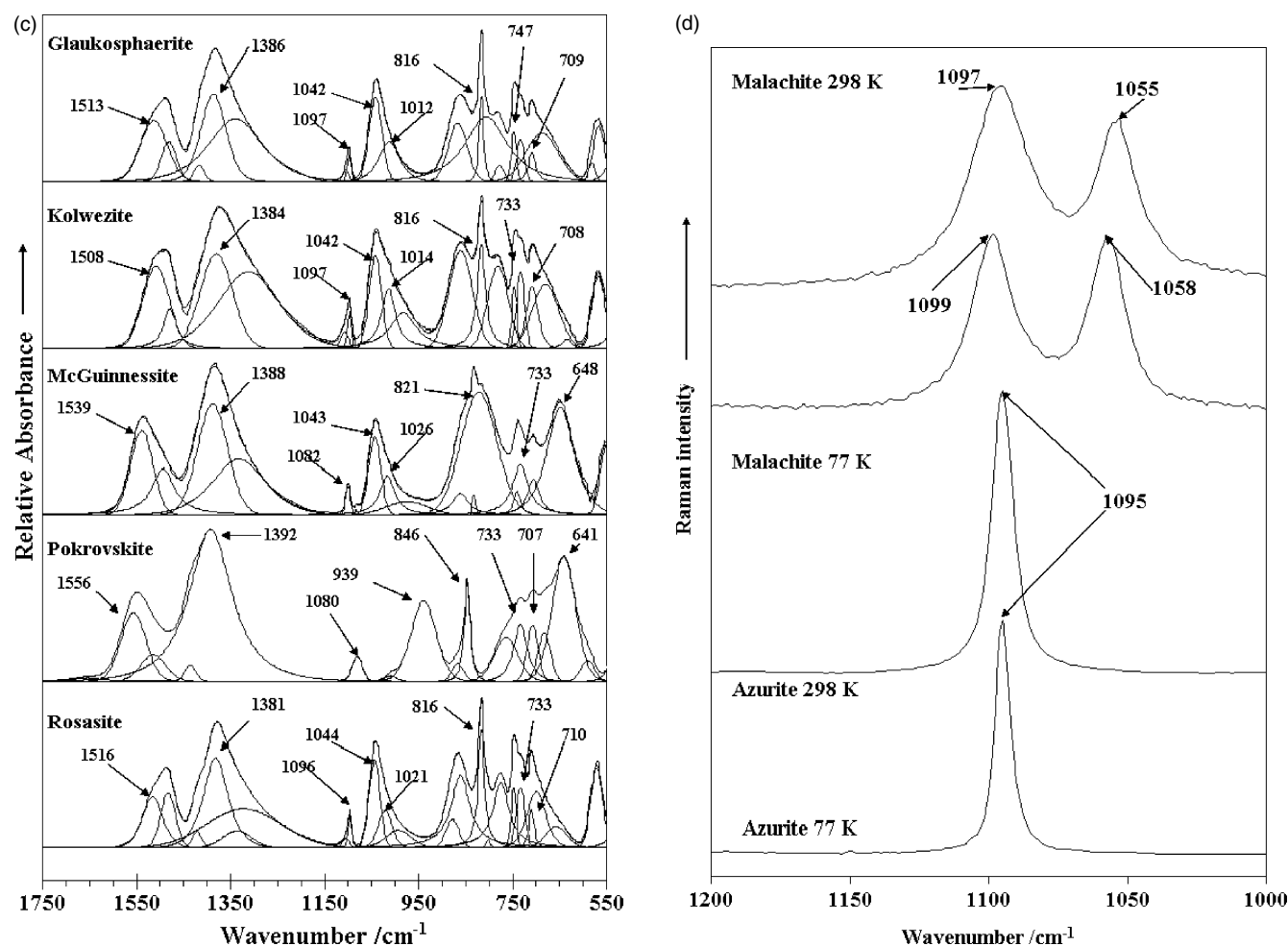


Figure 2. (Continued).

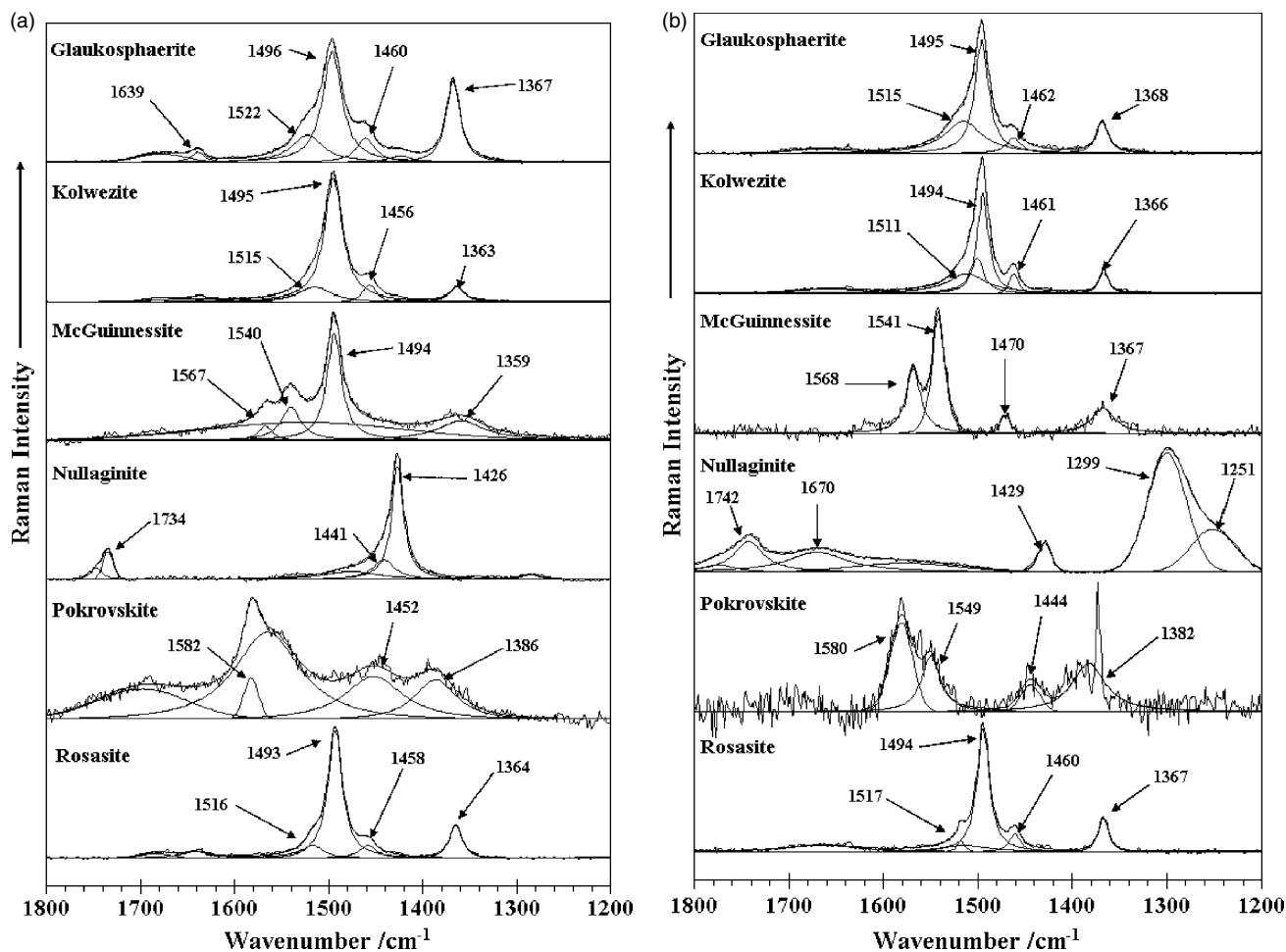
thus giving rise to only one band. A similar spectral analysis exists for the mineral nullaginite  $[\text{Ni}_2(\text{CO}_3)(\text{OH})_2]$ , which has only a single cation in the structure. The chemical analysis of nullaginite shows traces of Fe, Cr, Cu and Mg. The Raman spectrum at 298 K of nullaginite shows an intense band at  $1089\text{ cm}^{-1}$  with a bandwidth of  $13.0\text{ cm}^{-1}$ . In the 77 K spectrum the bandwidth reduces to  $9.0\text{ cm}^{-1}$ . The Raman spectrum at 298 K of mcguinnessite  $[(\text{Mg,Cu})_2(\text{CO}_3)(\text{OH})_2]$  shows two bands at  $1090$  and  $1060\text{ cm}^{-1}$  with bandwidths of  $14$  and  $26\text{ cm}^{-1}$  respectively. The bandwidths are significantly reduced in the 77 K spectrum. Again as for rosasite, two carbonate symmetric stretching vibrations are observed for mcguinnessite. The infrared spectrum of mcguinnessite resembles that of rosasite. Three infrared bands are observed at  $1082$ ,  $1042$  and  $1026\text{ cm}^{-1}$ . The band at  $1043\text{ cm}^{-1}$  is the most intense.

The Raman spectrum of kolwezite  $[(\text{Cu,Co})_2(\text{CO}_3)(\text{OH})_2]$  displays two intense bands at  $1093$  and  $1059\text{ cm}^{-1}$  with bandwidths of  $22.0$  and  $35.0\text{ cm}^{-1}$ . The bands shift to higher wavenumbers upon cooling to 77 K with the spectral profile

showing increased complexity. Raman bands are observed at  $1101$ ,  $1080$ ,  $1068$  and  $1059\text{ cm}^{-1}$ . The bandwidths are  $13.0$ ,  $36.0$ ,  $12.0$  and  $14.0\text{ cm}^{-1}$ . The infrared spectrum of kolwezite is similar to that of mcguinnessite and rosasite in this spectral region. Three infrared bands are observed at  $1097$ ,  $1042$  and  $1014\text{ cm}^{-1}$ . According to Anthony *et al.* The mineral kolwezite is triclinic. However, the spectrum is close to that of rosasite and it seems that this attribution of structure may not be correct.

The Raman spectrum of the mineral glaukosphaerite  $[(\text{Cu,Ni})_2(\text{CO}_3)(\text{OH})_2]$  strongly resembles that of rosasite and kolwezite. Three bands are observed in the 298 K spectrum at  $1097$ ,  $1087$  and  $1065\text{ cm}^{-1}$  with bandwidths of  $15.0$ ,  $17.0$  and  $44.0\text{ cm}^{-1}$ . In the 77 K spectrum the bands are observed at  $1100$ ,  $1087$  and  $1063\text{ cm}^{-1}$  with significantly reduced bandwidths. In the infrared spectrum bands are observed at  $1097$ ,  $1042$  and  $1012\text{ cm}^{-1}$ .

It is concluded that if the mineral contains cations of different sizes multiple carbonate stretching modes are observed in both Raman and infrared spectra. For the



**Figure 3.** (a) Raman spectra of rosasite, pokrovskite, nullaginite, mcguinnessite, kolwezite and glaukosphaerite at 298 K in the 1800 to 1200  $\text{cm}^{-1}$  region. (b) Raman spectra of rosasite, pokrovskite, nullaginite, mcguinnessite, kolwezite and glaukosphaerite at 77 K in the 1800 to 1200  $\text{cm}^{-1}$  region. (c) Raman spectra of azurite and malachite in the 1600 to 1300  $\text{cm}^{-1}$  region.

minerals pokrovskite and nullaginite only a single  $(\text{CO}_3)^{2-}$  symmetric stretching mode is observed in the Raman spectrum at around  $1088\text{ cm}^{-1}$ . For the minerals kolwezite and mcguinnessite two  $(\text{CO}_3)^{2-}$  symmetric stretching modes is observed at around  $1090$  and  $1059\text{ cm}^{-1}$ . Replacement of the Cu by Ni, Zn or Co causes a significant shift and splitting of the  $(\text{CO}_3)^{2-}$  symmetric stretching vibration.

### Raman spectroscopy of the $1800$ to $1200\text{ cm}^{-1}$ region

The  $298\text{ K}$  Raman spectra of the  $1200$  to  $1800\text{ cm}^{-1}$  region of the rosasite group of minerals are shown in Fig. 3(a). The spectra at  $77\text{ K}$  are shown in Fig. 3(b). For comparison the Raman spectra of azurite and malachite are shown in Fig. 3(c).

Four minerals, namely, rosasite, mcguinnessite, kolwezite and glaukosphaerite show similar spectra in this region. The spectra of nullaginite and pokrovskite are different. For rosasite Raman bands for the  $298\text{ K}$  spectrum are observed at  $1516$ ,  $1493$ ,  $1458$  and  $1364\text{ cm}^{-1}$ . The widths of these bands are  $26.0$ ,  $19.0$ ,  $21.0$  and  $16.0\text{ cm}^{-1}$ . The bands are observed in similar positions in the  $77\text{ K}$  spectra but with significantly reduced bandwidths. The Raman spectrum of

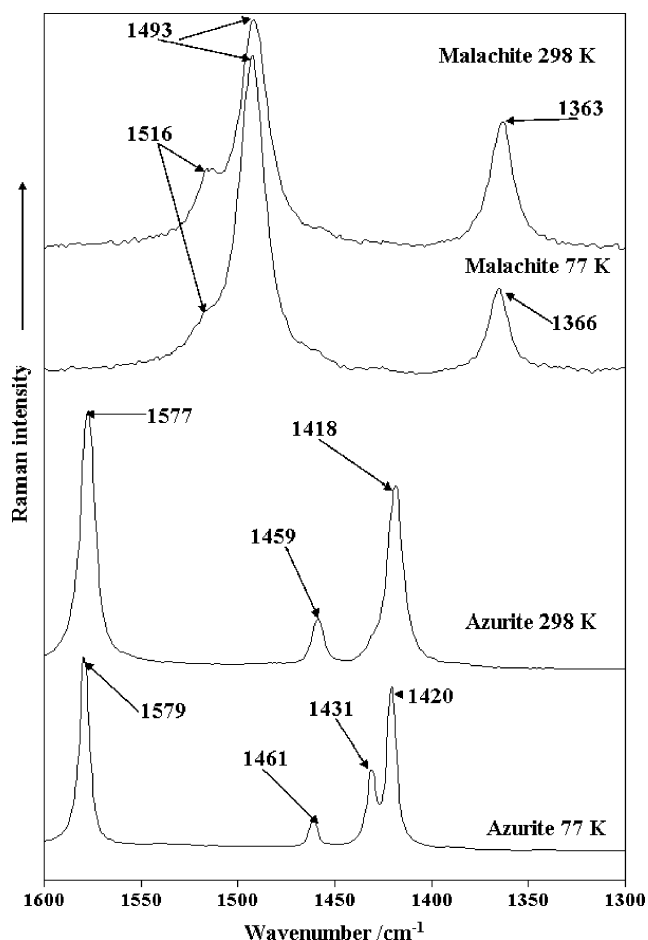


Figure 3. (Continued).

malachite in this spectral region displays bands at  $1516$ ,  $1493$  and  $1363\text{ cm}^{-1}$ . Thus the band positions for rosasite and related minerals strongly resembles those of malachite. These bands may be ascribed to the  $\nu_3$   $(\text{CO}_3)^{2-}$  antisymmetric stretching modes. In the infrared spectrum of rosasite in this spectral region infrared bands are observed at  $1516$ ,  $1483$ ,  $1421$  and  $1381\text{ cm}^{-1}$ . These infrared bands are in almost identical positions to the Raman bands. Ross reports the  $\nu_3$  bands for carbonates to vary between  $1379$  for sodium carbonate decahydrate to  $1495\text{ cm}^{-1}$  for lithium carbonate.<sup>39</sup> For cerium carbonate multiple bands were found in the infrared spectra with bands observed<sup>39</sup> at  $1550$ ,  $1460$  and  $1370\text{ cm}^{-1}$ . The position of the  $\nu_3$   $(\text{CO}_3)^{2-}$  antisymmetric stretching bands seems to be affected by the hydration of the compound.

The  $298\text{ K}$  Raman spectrum of mcguinnessite displays four bands at  $1567$ ,  $1540$ ,  $1494$  and  $1359\text{ cm}^{-1}$ . In the  $77\text{ K}$  spectrum the bands are found at  $1568$ ,  $1541$ ,  $1470$  and  $1367\text{ cm}^{-1}$ . In the infrared spectrum bands are found at  $1539$ ,  $1493$  and  $1388\text{ cm}^{-1}$ . These results indicate two concepts: (1) the identification of more than one carbonate anion in the structure as implied from the symmetric stretching vibrations and (2) the reduction of symmetry of the carbonate anion. These two factors combine to give multiple bands in this spectral region. The Raman spectrum of kolwezite in  $\nu_3$   $(\text{CO}_3)^{2-}$  antisymmetric stretching region shows bands at  $1515$ ,  $1495$ ,  $1456$ ,  $1426$  and  $1363\text{ cm}^{-1}$ . The bandwidths are quite sharp with widths of  $40.0$ ,  $23.0$ ,  $17.0$ ,  $13.0$  and  $19.0\text{ cm}^{-1}$ . The bands in the  $77\text{ K}$  spectrum are observed at  $1511$ ,  $1494$ ,  $1461$ , and  $1366\text{ cm}^{-1}$  with significantly reduced bandwidths. In the infrared spectrum bands of much greater bandwidth are observed at  $1508$ ,  $1479$  and  $1384\text{ cm}^{-1}$ . The Raman spectrum of glaukosphaerite shows four bands at  $1522$ ,  $1496$ ,  $1460$  and  $1367\text{ cm}^{-1}$ . The bandwidths are  $48.0$ ,  $24.0$ ,  $24.0$ ,  $30.0$  and  $18.0\text{ cm}^{-1}$  respectively. The bands are found at  $1515$ ,  $1495$ ,  $1462$  and  $1368\text{ cm}^{-1}$  in the  $77\text{ K}$  spectrum. In the infrared spectrum of glaukosphaerite bands are observed at  $1513$ ,  $1481$ ,  $1417$  and  $1386\text{ cm}^{-1}$ .

The Raman spectra of the four minerals rosasite, mcguinnessite, kolwezite and glaukosphaerite are very similar, suggesting that these four minerals have the same structure. Anthony *et al.*<sup>32</sup> state that the structure of glaukosphaerite is monoclinic or pseudo-orthorhombic, that of kolwezite is triclinic, that of mcguinnessite is triclinic or possibly monoclinic and that of rosasite is monoclinic. For the mineral nullaginite the Raman spectrum of the  $1300$  to  $1500\text{ cm}^{-1}$  region shows an intense sharp band at  $1426\text{ cm}^{-1}$  (with bandwidth  $15.0\text{ cm}^{-1}$ ) with an additional higher wavenumber component at  $1441\text{ cm}^{-1}$ . The  $1426\text{ cm}^{-1}$  band shifts to  $1429\text{ cm}^{-1}$  at  $77\text{ K}$ . Although these bands are in different positions to those of rosasite the bands are attributed to the  $\nu_3(\text{CO}_3)^{2-}$  antisymmetric stretching vibrations.

### Raman spectroscopy of the $850$ to $250\text{ cm}^{-1}$ region

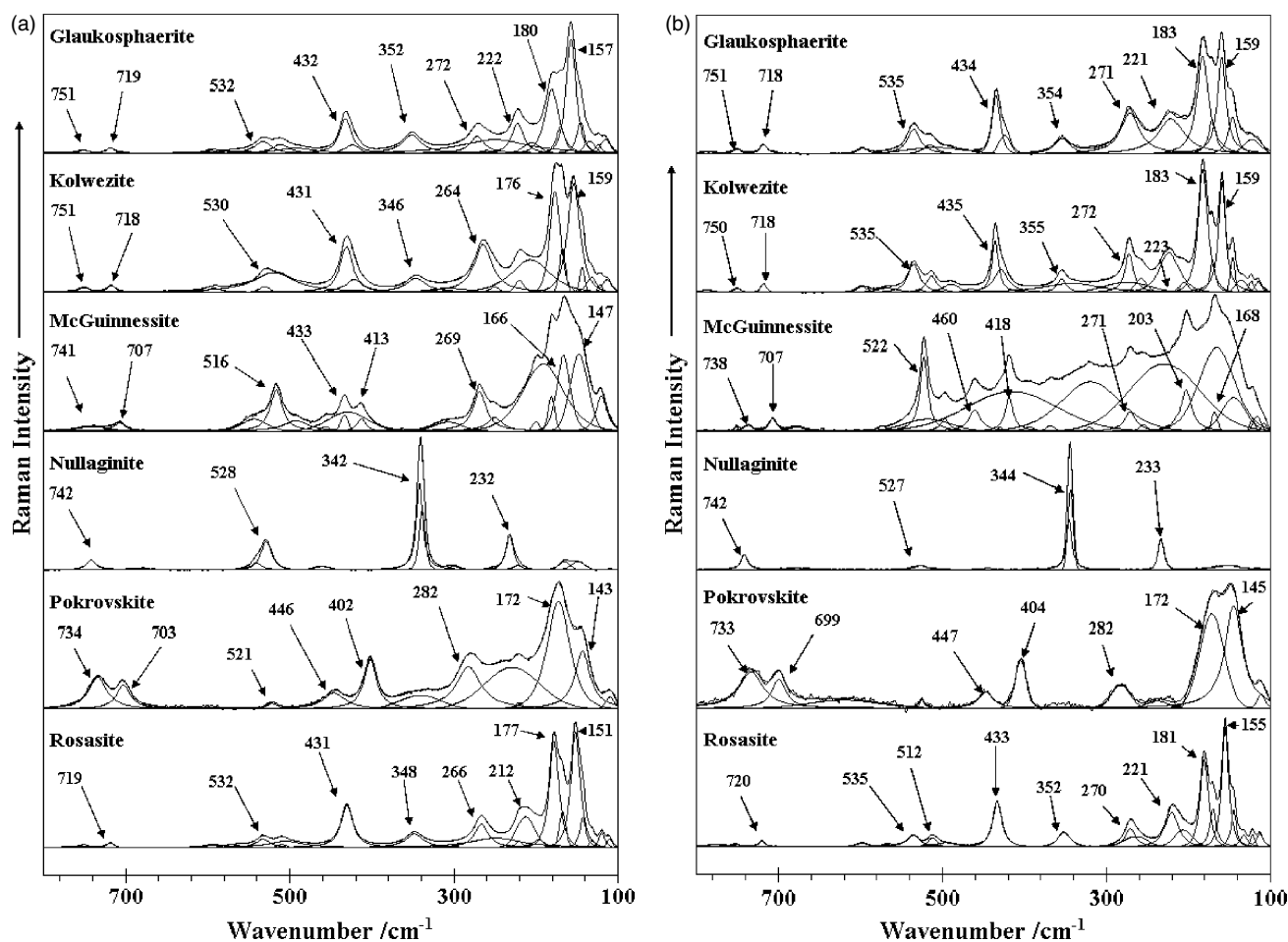
The Raman spectra of the rosasite mineral group including pokrovskite in the  $100$  to  $750\text{ cm}^{-1}$  region are shown in

Fig. 4(a) (298 K) and Fig. 4(b) (77 K). The low intensity bands at around  $800\text{ cm}^{-1}$  may be observed in Fig. 2(a). The Raman spectra in the  $900\text{ to }600\text{ cm}^{-1}$  region of azurite and malachite are shown in Fig. 4(c). The  $\nu_2$  bending modes for carbonates vary from around  $890\text{ to }850\text{ cm}^{-1}$ . For azurite two bands are observed at  $834\text{ and }765\text{ cm}^{-1}$  and are attributed to the out of phase and in phase bending modes of carbonate in azurite, respectively. A component band is observed at  $739\text{ cm}^{-1}$  and is also assigned to the  $\nu_4$  mode. Only a single band at  $817\text{ cm}^{-1}$  is observed in this region for malachite. The FTIR spectrum of malachite shows two bands at  $879\text{ and }821\text{ cm}^{-1}$ . This FTIR spectral region is more complex for azurite with bands observed at  $872, 837, 815\text{ and }796\text{ cm}^{-1}$ . This complexity is again ascribed to the loss of degeneracy. The equivalent Raman bands for malachite are observed at  $752\text{ and }717\text{ cm}^{-1}$ . In the infrared spectra bands are observed at  $779, 754\text{ and }701\text{ cm}^{-1}$  for azurite and at  $780, 750\text{ and }715\text{ cm}^{-1}$  for malachite.

In the Raman spectra of the rosasite group of minerals in the  $850\text{ to }800\text{ cm}^{-1}$  only very low intensity bands are

observed. For rosasite a single band is observed at  $817\text{ cm}^{-1}$ . This band is in exactly the same position as for malachite. An infrared band of much greater intensity is observed at  $816\text{ cm}^{-1}$ . Other bands are found at  $878\text{ and }861\text{ cm}^{-1}$ . For kolwezite the Raman band is at  $818\text{ cm}^{-1}$  and the infrared bands are at  $860\text{ and }816\text{ cm}^{-1}$ . The observation of more than one  $\nu_2$  mode suggests symmetry reduction of the carbonate anion in the structure. For glaukosphaerite the Raman band is at  $819\text{ cm}^{-1}$  and the infrared bands are found at  $867\text{ and }816\text{ cm}^{-1}$ . For the mineral mcguinnessite two Raman bands are observed at  $838\text{ and }818\text{ cm}^{-1}$ . Additional bands are also found for mcguinnessite in the infrared spectrum at  $861, 832\text{ and }821\text{ cm}^{-1}$ . For pokrovskite a very low intensity Raman band is observed at  $845\text{ cm}^{-1}$  and two infrared bands are found at  $867\text{ and }846\text{ cm}^{-1}$ . These bands are assigned to the  $\nu_2$  bending modes. No Raman band was observed in this position for nullaginite.

In the Raman spectrum at  $298\text{ K}$  of rosasite, two bands are observed at  $750\text{ and }719\text{ cm}^{-1}$  (Fig. 4(a)). The bands shift to  $752\text{ and }720\text{ cm}^{-1}$  at  $77\text{ K}$ . In the infrared spectra great



**Figure 4.** (a) Raman spectra of rosasite, pokrovskite, nullaginite, mcguinnessite, kolwezite and glaukosphaerite at  $298\text{ K}$  in the  $800\text{ to }100\text{ cm}^{-1}$  region. (b) Raman spectra of rosasite, pokrovskite, nullaginite, mcguinnessite, kolwezite and glaukosphaerite at  $77\text{ K}$  in the  $800\text{ to }100\text{ cm}^{-1}$  region. (c) Raman spectra of azurite and malachite in the  $900\text{ to }600\text{ cm}^{-1}$  region.



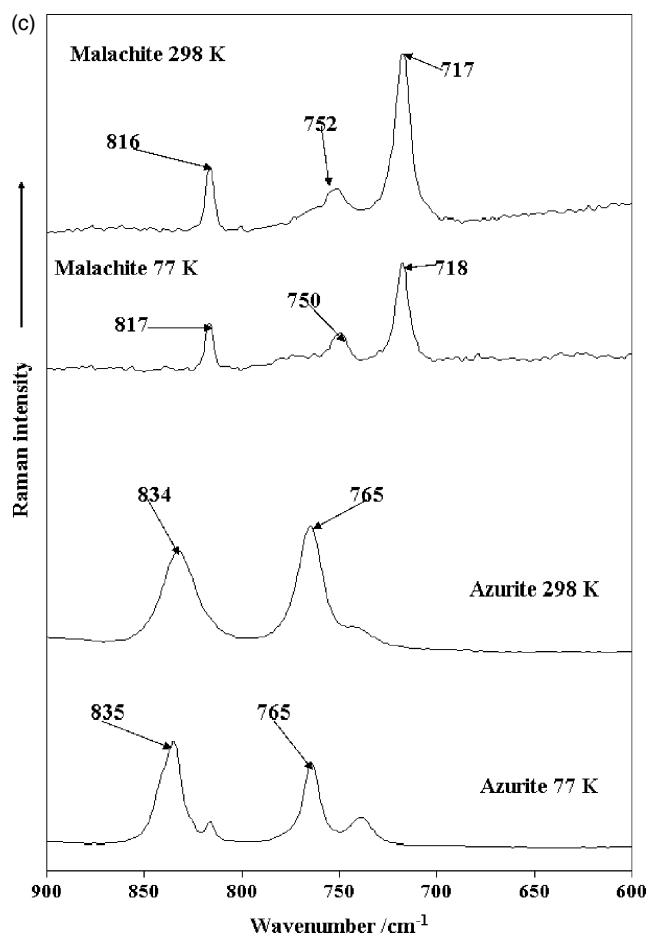


Figure 4. (Continued).

complexity is observed in this spectral region with multiple overlapping bands. Infrared bands are observed at 775, 747, 733 and 710  $\text{cm}^{-1}$  (Fig. 2(c)). These bands are assigned to the  $\nu_4$  bending modes. For the pokrovskite mineral, two Raman bands are found at 734 and 703  $\text{cm}^{-1}$  in the 298 K spectrum and at 733 and 699  $\text{cm}^{-1}$  in the 77 K spectrum. The infrared spectrum in this spectral region is complex and bands may be resolved at 763, 733, 707, 683 and 641  $\text{cm}^{-1}$ . Whether all of these bands are due to bending vibrations is not known. For nullaginite two Raman bands are observed at 742 and 683  $\text{cm}^{-1}$  at 298 K and are found at 742 and 678  $\text{cm}^{-1}$  in the 77 K spectrum. For mcguinnessite, two  $\nu_4$  bending modes are observed at 741 and 707  $\text{cm}^{-1}$  in the 298 K spectrum, which is resolved into four bands at 751, 738, 707 and 677  $\text{cm}^{-1}$  in the 77 K spectrum. The infrared spectrum of kolwezite displays a series of overlapping bands that may be resolved at 781, 746, 733 and 708  $\text{cm}^{-1}$ . A similar pattern exists for glaukosphaerite; Raman bands are observed at 777, 751, 719 and 706  $\text{cm}^{-1}$  in the 298 K spectrum and at 786, 751 and 718  $\text{cm}^{-1}$  in the 77 K spectrum. Infrared bands for this mineral are observed at 777, 747, 733 and 709  $\text{cm}^{-1}$ . What is clear from the spectra is that (a) a reduction in symmetry of the carbonate anion occurs and (b) at least two types of carbonate anions exist in the structure.

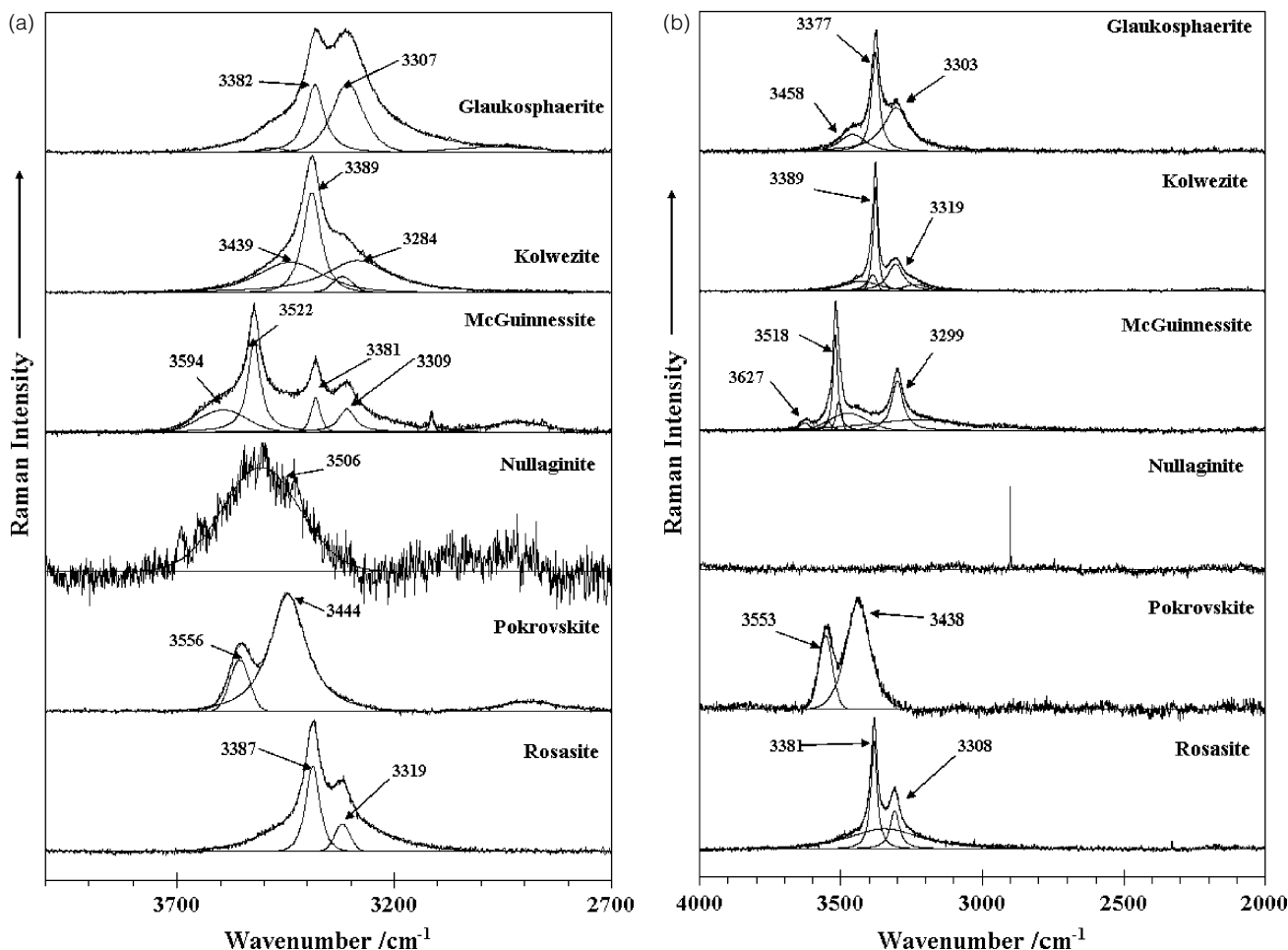
Table 2. Table of the hydroxyl stretching wavenumbers ( $\text{cm}^{-1}$ ) and the hydrogen bond distances

IR		Raman	
Wavenumber ( $\text{cm}^{-1}$ )	H-bond distance ( $\text{\AA}$ )	Wavenumber ( $\text{cm}^{-1}$ )	H-bond distance ( $\text{\AA}$ )
Rosasite			
3478	2.8670	–	–
3401	2.7989	3387	2.7895
3373	2.7800	3319	2.7517
Pokrovskite			
3587	3.2800	3556	3.0190
3550	2.9990	3444	2.8326
Mcguinnessite			
3539	2.9682	3522	2.9315
3501	2.8968	–	–
3425	2.8166	3381	2.7857
3304	2.7440	3309	2.7469
Kolwezite			
3454	2.8410	3439	2.8282
3396	2.7955	3389	2.7908
3299	2.7420	3319	2.7517
Glaukosphaerite			
3478	2.8670	3481	2.8457
3398	2.7968	3382	2.7864
3301	2.7430	3307	2.7406
Malachite			
3475	2.8636	–	–
3405	2.8017	–	–

The spectral patterns in the 600 to 100  $\text{cm}^{-1}$  region are similar for the rosasite minerals except for nullaginite. A common peak(s) occurs in all of the spectra around 530 to 520  $\text{cm}^{-1}$ . One possible assignment is that this band is due to hydroxyl deformation modes. In the structure of the rosasite minerals hydroxyl groups are bonded to the cations. Three bands are observed for rosasite at 595, 563 and 532  $\text{cm}^{-1}$ ; for pokrovskite at 521  $\text{cm}^{-1}$ ; for nullaginite at 528  $\text{cm}^{-1}$ ; for mcguinnessite at 543, 516  $\text{cm}^{-1}$ ; for kolwezite at 566, 530 and 519  $\text{cm}^{-1}$  and for glaukosphaerite at 566, 532 and 511  $\text{cm}^{-1}$ . For nullaginite intense sharp bands exist at 342 and 339  $\text{cm}^{-1}$  with bandwidths of 10.0 and 9.0  $\text{cm}^{-1}$ . The bands shift to 346 and 344  $\text{cm}^{-1}$  at 77 K with bandwidths of 8.0  $\text{cm}^{-1}$ . These bands are attributed to NiO stretching vibrations. A band is observed at around 431  $\text{cm}^{-1}$  for many of the rosasite group of minerals. This band is assigned to the MO stretching vibration. Other bands at lower wavenumbers may be described simply as lattice modes.

### Raman spectroscopy of the hydroxyl stretching region

The Raman spectra of the hydroxyl stretching region at 298 and 77 K are shown in Fig. 5(a) and (b). The infrared spectra are shown in Fig. 5(c). For comparison the Raman spectra of



**Figure 5.** (a) Raman spectra of rosasite, pokrovskite, nullaginite, mcguinnessite, kolwezite and glaukosphaerite at 298 K in the 3800 to 2700  $\text{cm}^{-1}$  region. (b) Raman spectra of rosasite, pokrovskite, nullaginite, mcguinnessite, kolwezite and glaukosphaerite at 77 K in the 4000 to 2000  $\text{cm}^{-1}$  region. (c) Infrared spectra of rosasite, pokrovskite, nullaginite, mcguinnessite, kolwezite and glaukosphaerite in the 3800 to 2600  $\text{cm}^{-1}$  region. (d) Raman spectra of azurite and malachite in the 3600 to 3300  $\text{cm}^{-1}$  region.

azurite and malachite are given<sup>5</sup> in Fig. 5(d). For rosasite two distinct bands are observed in the 298 K Raman spectrum at 3387 and 3319  $\text{cm}^{-1}$ . The bands are comparatively broad with bandwidths of 38.0 and 42.0  $\text{cm}^{-1}$ . In the 77 K spectrum the bands are observed at 3381 and 3308  $\text{cm}^{-1}$  with bandwidths of 26.0 and 38.0  $\text{cm}^{-1}$ . These bands are assigned to OH stretching vibrations. The observation of two bands is in harmony with the concept of two non-equivalent OH units, as shown in Fig. 1. In the infrared spectrum of rosasite four bands are observed at 3478, 3401, 3307 and 3196  $\text{cm}^{-1}$ . In comparison, only a single Raman band is observed at 3420  $\text{cm}^{-1}$  (298 K) and 3423  $\text{cm}^{-1}$  (77 K) for azurite. For malachite in the OH stretching region two Raman bands are observed at 3475 and 3405  $\text{cm}^{-1}$  (298 K) and 3468 and 3401  $\text{cm}^{-1}$  (77 K). These bands are at considerably higher wavenumbers than for rosasite. It is noted that infrared data for malachite have been reported<sup>31</sup> as 3400 and 3200 or 3415 and 3327  $\text{cm}^{-1}$ .<sup>31</sup> The Raman band positions of the OH stretching bands for malachite are at higher wavenumbers

than the published infrared data. In this work the Raman band positions for the malachite homologues are at lower wavenumbers or similar wavenumbers compared with the corresponding infrared bands.

For pokrovskite two relatively broad bands are displayed at 3556 and 3444  $\text{cm}^{-1}$  (298 K) and at 3553 and 3438  $\text{cm}^{-1}$  at 77 K. The infrared spectrum of pokrovskite displays two bands at 3587 and 3446  $\text{cm}^{-1}$  with a broad feature at 3325  $\text{cm}^{-1}$ . This latter band may be assigned to adsorbed water. The Raman spectrum of nullaginite in this spectral region suffers from poor signal-to-noise ratio. This is, no doubt, a result of a lack of crystallinity. A Raman band was observed at 3506  $\text{cm}^{-1}$ . The spectrum at 77 K was not obtainable. Two infrared peaks are observed at 3520 and 3427  $\text{cm}^{-1}$ . The Raman spectrum of mcguinnessite shows three bands at 3522, 3381 and 3309  $\text{cm}^{-1}$  at 298 K and at 3518 and 3299  $\text{cm}^{-1}$  at 77 K. Infrared spectrum of mcguinnessite shows bands at 3539, 3501 and 3304  $\text{cm}^{-1}$ . The Raman spectrum of kolwezite shows a broad band at 3439  $\text{cm}^{-1}$

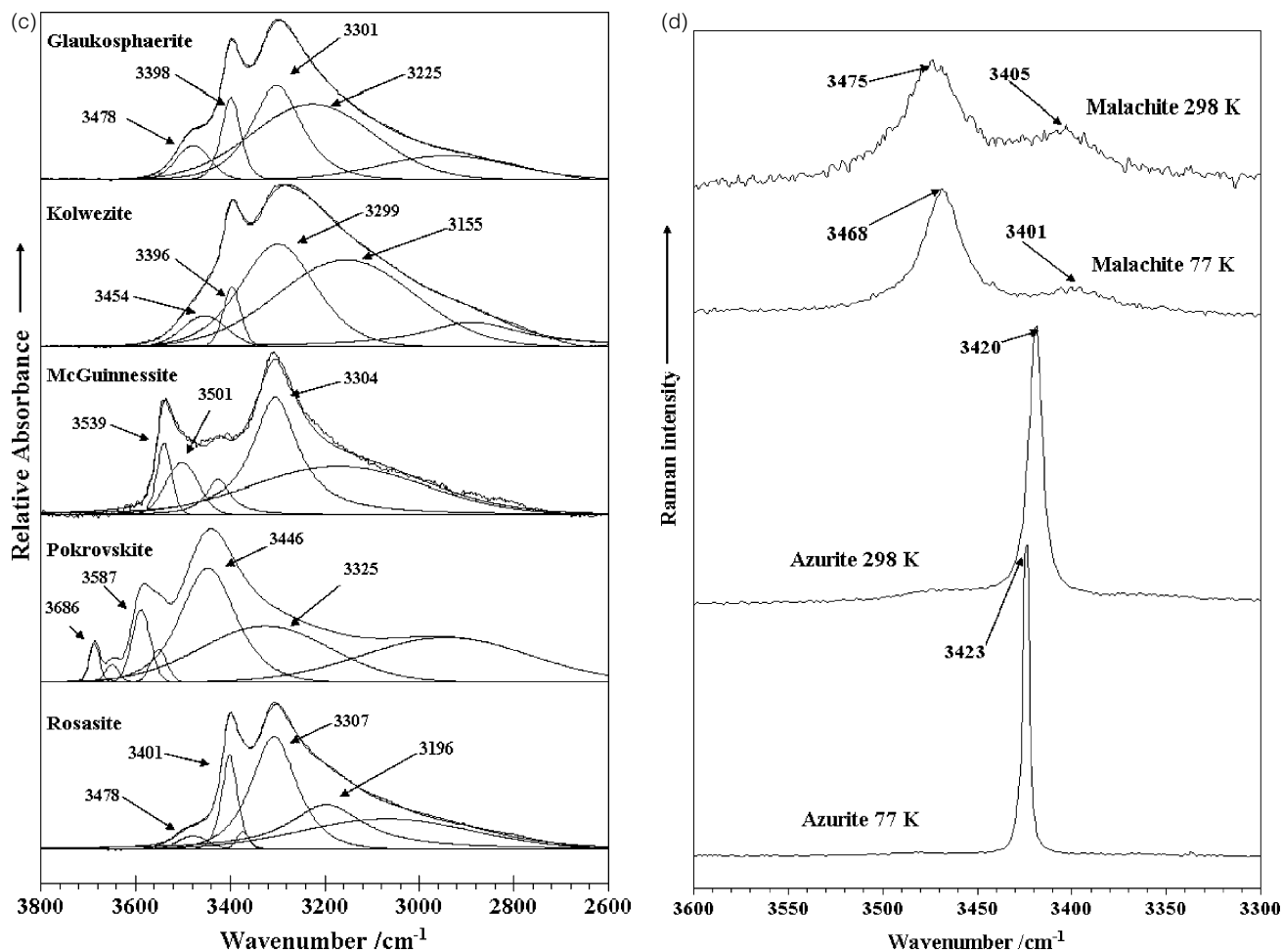


Figure 5. (Continued).

with two sharp features at 3389 and 3284 cm<sup>-1</sup>. Infrared bands are observed at 3454, 3396, 3299 and 3155 cm<sup>-1</sup>. The Raman spectrum of glaukosphaerite shows three bands: a low intensity band at 3481, and sharp bands at 3382 and 3307 cm<sup>-1</sup> at 298 K and at 3458, 3377 and 3303 cm<sup>-1</sup> at 77 K. Infrared bands are found at 3478, 3398, 3301 and 3325 cm<sup>-1</sup>. The values for the OH stretching vibrations of kolwezite and glaukosphaerite are similar to those of malachite.

The question can be asked as to why the bands in the hydroxyl stretching region occur in various positions for the different minerals. The reason is attributed to variations in hydrogen bond distances between the OH units and the oxygens of adjacent carbonate units. Table 2 lists the band positions of the hydroxyl stretching vibrations in the infrared and Raman spectra together with the hydrogen bond distance calculated according to a Libowitzky type function.<sup>40</sup> Hydrogen bond distances vary for rosasite from 2.78<sub>0</sub> to 2.86<sub>7</sub> Å. These values may be compared with the values for malachite, which are 2.86<sub>6</sub> and 2.801<sub>7</sub> Å. In comparison, the hydrogen bond distances for pokrovskite are significantly longer with values between 2.83 and 3.28<sub>0</sub> Å. The significance of this difference means that the

wavenumbers of the OH stretching vibrations occur at higher wavenumbers for pokrovskite than for rosasite. The mineral glaukosphaerite has hydrogen bond distances similar to those of rosasite. This means the hydroxyl stretching wavenumbers will be in similar positions. Hence the spectra of rosasite and glaukosphaerite should be similar, as may be observed in Fig. 5(c). Raman spectra measured at 77 K show a reduction in the hydrogen bond distance. For rosasite the values of the hydrogen bond distances are 2.7895 and 2.7517 Å at 298 and 2.7850 and 2.7465 Å at 77 K. For glaukosphaerite the hydrogen bond distance decreases from 2.806 to 2.8457, 2.7864 to 2.7831 and 2.7406 to 2.7442 Å.

## CONCLUSIONS

Raman spectroscopy at both 298 and 77 K has been used to characterise the structure of members of the rosasite mineral group. The spectra are related to the structure of the rosasite mineral group. The effect of cation substitution causes a splitting of the carbonate symmetric stretching vibration from ~1089 cm<sup>-1</sup> to ~1090 and 1060 cm<sup>-1</sup>. A similar cation substitution reliance is observed for the hydroxyl stretching

vibrational modes. This is related to the hydrogen bond distances of the OH units and the adjacent carbonate units in the rosasite structure.

The question arises as to why there are similar Raman spectral patterns for the rosasite minerals except for nulginitite and perhaps pokrovskite. It means the minerals must have the same structure or at least related structures. Malachite is monoclinic with point group  $2/m$ . The rosasite mineral group has spectra similar to that of malachite. Therefore it can be inferred that the structure of the rosasite group of minerals is monoclinic. This conclusion is in agreement with the assumptions of Anthony *et al.* who state that rosasite and related minerals have monoclinic structure by analogy with malachite.

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