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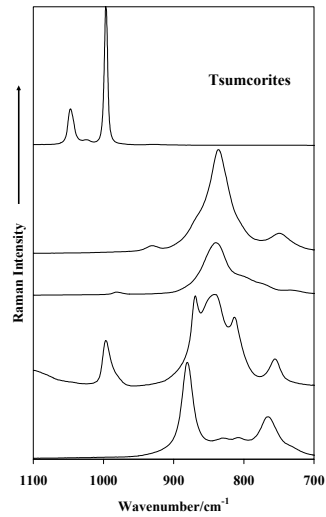


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The structures of the sulphates and arsenates of the tsumcorites mineral group have been determined using Raman microscopy. Extensive isomorphic substitution is observed.



**Ray L. Frost, J. Theo Kloprogge and Wayde N. Martens**

*Raman spectroscopy of the sulphates and arsenates of the tsumcorite mineral group*

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## Raman spectroscopy of the arsenates and sulphates of the tsumcorite mineral group

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### Abstract

The structure of a selection of arsenate and sulphate based minerals of the tsumcorite group has been studied by the combination of Raman and infrared spectroscopy. A comparison is made with the sulphate bearing mineral natrochalcite. Isomorphic substitution of sulphate for arsenate is observed for gartrellite and thometzekite. The position of the hydroxyl and water stretching vibrations are related to the strength of the hydrogen bond formed between the OH unit and the  $\text{AsO}_4$  anion. Estimates of the hydrogen bond distances are calculated using a Libowitzky type function. Characteristic Raman spectra of the minerals enable the assignment of the bands to specific vibrational modes.

**Key Words-** Raman spectroscopy, tsumcorite, natrochalcite, gartrellite

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## INTRODUCTION

The tsumcorite group of minerals are a mineral group based upon monoclinic and triclinic arsenates, phosphates, vanadates and sulphates of the general formulae  $(\text{M1})(\text{M2})_2(\text{XO}_4)_2(\text{OH},\text{H}_2\text{O})_2$  where M1 is Pb,Ca or Na, M2 is Cu, Zn,  $\text{Fe}^{3+}$ , Co, Mn and X is As, P, V, S. The minerals gartrellite  $\text{Pb}[(\text{Cu},\text{Zn})(\text{Fe}^{3+}, \text{Zn}, \text{Cu})](\text{AsO}_4)(\text{OH},\text{H}_2\text{O})_2$ , helmutwinklerite  $\text{Pb}(\text{Zn},\text{Cu})_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$  and thometzekite<sup>1</sup> are triclinic. The minerals ferrilotharmeyerite<sup>2</sup>  $\text{Ca}(\text{Fe}^{3+},\text{Zn})_2(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$ , lotharmeyerite  $\text{Ca}(\text{Mn}^{3+},\text{Zn})_2(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$ , mawbyite<sup>3</sup>  $\text{Pb}(\text{Fe}^{3+},\text{Zn})_2(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_2$ , mounanaite  $\text{Pb}(\text{Fe}^{3+})_2(\text{VO}_4)_2(\text{OH})_2$ , natrochalcite<sup>4</sup>  $\text{NaCu}_2(\text{SO}_4)_2(\text{OH},\text{H}_2\text{O})_2$  and tsumcorite<sup>5</sup>  $\text{Pb}(\text{Zn},\text{Fe}^{3+})_2(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})$  are monoclinic.<sup>5</sup> There is some problem associated with writing mineral formula as above in that the formula may change as a function of the degree of solid solution formation and the amount of isomorphic substitution. For example it is quite comprehensible that a formula such as The minerals gartrellite  $\text{Pb}[(\text{Cu},\text{Fe}^{2+})(\text{Fe}^{3+}, \text{Zn},$

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Cu)] (AsO<sub>4</sub>)(CO<sub>3</sub>,H<sub>2</sub>O)<sub>2</sub>, can be written for gartrellite. For example the gartrellite found at Ashburton Downs, Western Australia has a calculated formula of PbCu<sub>1.5</sub>Fe<sup>2+</sup><sub>0.5</sub>As<sub>1.5</sub>(SO<sub>4</sub>)<sub>0.5</sub>(CO<sub>3</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>0.2</sub>. Of course Raman spectroscopy will readily determine the presence of carbonate in the mineral. The presence or absence of two moles of water is the determining factor in whether the mineral is triclinic or not. It has been shown that crystals of ferrilotharmeyerite, tsumcorite, thometzekite (sulfatian), and mounanaite have monoclinic symmetry, space group C2/m.<sup>2</sup> The triclinic members of the tsumcorite group have the space group is P1, with a pronounced monoclinic C-centred pseudocell.<sup>2</sup> The tsumcorite minerals are often formed in the oxidised zones of arsenic bearing Pb-Zn deposits. The particular mineral formed depends upon the composition of the polymetallic ore deposit. The minerals are of a rare nature.

The Raman spectra of the tetrahedral anions in aqueous systems are well known. The symmetric stretching vibration of the arsenate anion ( $\nu_1$ ) is observed at 810 cm<sup>-1</sup> and coincides with the position of the asymmetric stretching mode ( $\nu_3$ ).<sup>6-8</sup> The symmetric bending mode ( $\nu_2$ ) is observed at 342 cm<sup>-1</sup> and the out-of-plane bending modes ( $\nu_4$ ) is observed at 398 cm<sup>-1</sup>. Of all the tetrahedral oxyanions spectra, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions spectra. Farmer lists a number of spectra of arsenates including the basic copper arsenates olivenite and euchroite.<sup>9</sup> The effect of the arsenate ion in a crystal will be to remove the degeneracy and allow splitting of the bands according to factor group analysis. The  $\nu_1$  and  $\nu_3$  bands of olivenite and euchroite were observed at 860, 828, 790 cm<sup>-1</sup> and 830 and 770 cm<sup>-1</sup> respectively. The bending modes were found at 493 and 452 cm<sup>-1</sup> for olivenite and at 475 and 410 cm<sup>-1</sup> for euchroite.

Complex solution chemistry involving mixtures of the cations of lead, zinc, and ferric iron may result in the formation of the tsumcorite group of minerals. The type of mineral formed is a function of concentration, pH, temperature and the available anion present in the mother solution. The complex set of variable requires a multidimensional phase diagram.<sup>10</sup> Raman spectroscopy has proven an excellent technique for the study of oxyanions in both solution and in secondary mineral formation. In this work we extend our studies to the arsenates of the tsumcorite mineral group.

## EXPERIMENTAL

### The mineral samples

Mineral samples were obtained from Museum Victoria. The following table shows the type number of the tsumcorite mineral and its origin.

Mineral	Type number	Origin
gartrellite	M39987	Anticline deposit, Ashburton Downs, Western Australia
ferrilotharmeyerite	M36822	Tsumeb, Namibia

natrochalcite	M32894	Chuquicamata, Chile
tsumcorite	M37949	Tsumeb, Namibia
thometzekite	M43672	Tsumeb, Namibia

### Raman microprobe spectroscopy

Crystals of the minerals were orientated on a polished metal surface on the stage of an Olympus BHSM microscope 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). Details have been published.<sup>11-13</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 to 525 cm<sup>-1</sup> range were obtained by the co-addition of 64 scans with a resolution of 4 cm<sup>-1</sup> and a mirror velocity of 0.6329 cm/s.

Spectroscopic manipulations such as baseline adjustment 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 specific parameters to be fixed or varied accordingly.<sup>11-13</sup> 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 regression coefficient of R<sup>2</sup> greater than 0.995.

## RESULTS and DISCUSSION

The tsumcorite minerals are based upon the formula M<sub>(I)</sub>M<sub>(II)</sub>(XO<sub>4</sub>)<sub>2</sub>·(OH,H<sub>2</sub>O)<sub>2</sub>. There is apparent some uncertainty of the crystal structure of some of these minerals. The majority are monoclinic and some namely gartrellite, helmutwinklerite, phosphogartrellite and thometzekite are triclinic. The factor group analysis (FGA) for the monoclinic variety is given in Table 1 and the triclinic in Table 2. The factor group analysis for the monoclinic crystal structure shows two modes A<sub>g</sub> and B<sub>g</sub>. Thus for the monoclinic structure two AsO<sub>4</sub> Raman bands should be observed. Also for the OH stretching vibrations only one OH stretching mode should be observed. For the triclinic tsumcorites only one mode is predicted namely the A<sub>g</sub> mode.

The Raman spectra of the hydroxyl stretching region of the tsumcorite arsenate minerals: ferrilotharmeyerite, gartrellite, thometzekite and tsumcorite together with that of the sulphate mineral natrolite are shown in Figure 1. The results of the band component analysis of the hydroxyl stretching region are reported in Table 3. It should be noted that in the formulation of the tsumcorite minerals the

minerals may contain either/or water and OH units or both. The Raman spectrum of ferrilotharmeyerite shows a low intensity band at 3440  $\text{cm}^{-1}$  and two more intense bands at 2973 and 2636  $\text{cm}^{-1}$ . The first band is assigned to the hydroxyl stretching vibration of the OH unit and the latter two bands to the OH stretching of the water units. The FGA suggests that there should be two Raman active modes; one for the water and one for the OH unit. The position of the bands suggests that the OH units are strongly hydrogen bonded and the OH—OAs distances are short.

For gartrellite three Raman bands are observed in a similar position to that of ferrilotharmeyerite with bands observed in the hydroxyl stretching region at 3404, 3229 and 2999  $\text{cm}^{-1}$ . The band assignments are as for ferrilotharmeyerite. Here we are comparing the position of the band at 3440 with a band at 3404  $\text{cm}^{-1}$ . The intensity of the band at 3404  $\text{cm}^{-1}$  is much stronger than the band at 3440  $\text{cm}^{-1}$  for ferrilotharmeyerite. The band at 3440 is broad and of low intensity as a consequence the defining of its position is more difficult. This implies that the degree of substitution of hydroxyls is much greater in gartrellite as compared with ferrilotharmeyerite. Such observations by the authors have been made for the vivianite phosphates. The implication is that the amount of ferric iron in the gartrellite mineral ( $\text{Pb}[(\text{Cu},\text{Zn})(\text{Fe}^{3+}, \text{Zn}, \text{Cu})](\text{AsO}_4)(\text{OH},\text{H}_2\text{O})_2$ ) is much greater than for ferrilotharmeyerite. The band at 3229  $\text{cm}^{-1}$  in the Raman spectrum of gartrellite is not observed in the spectrum of ferrilotharmeyerite. This band is attributed to the hydroxyl stretching modes of weakly hydrogen bonded water. A reasonable comparison can be made between the bands at 2973 and 2999  $\text{cm}^{-1}$ . These bands are ascribed to more strongly hydrogen bonded OH groups of water. In the spectrum of ferrilotharmeyerite, a band is observed at 2636  $\text{cm}^{-1}$  assigned to strongly hydrogen bonded water. This band is not observed in the Raman spectrum of gartrellite. It is proposed based upon these Raman spectra that as the intensity of the band assigned to the stretching of OH units increases, the intensity of bands assigned to strongly hydrogen bonded water decreases.

Gartrellite is said to have a triclinic structure which means the FGA would predict two Raman bands in the OH stretching region. The infrared spectra of selected tsumcorites are shown in Figure 2. The infrared spectra of gartrellite show component bands at 3394, 3158, 2875 and 2601  $\text{cm}^{-1}$ . The IR band at 3394  $\text{cm}^{-1}$  may be compared with the Raman band at 3404  $\text{cm}^{-1}$ . Similarly the IR band at 3158  $\text{cm}^{-1}$  may be compared with the Raman band at 3229  $\text{cm}^{-1}$ . However in the infrared spectral profile intensity is strong in the 2600 to 2900  $\text{cm}^{-1}$  region. This observation is interpreted as the infrared spectrum of strongly coordinated water. Raman spectroscopy of water is often of low intensity as water is a very poor Raman scatterer. Hence it is not unexpected that bands are observed in the infrared spectrum but not the Raman spectrum.

The observation of multiple hydroxyl stretching frequencies reflects the hydrogen bond distances between the OH units and the adjacent  $\text{AsO}_4$  units.<sup>14</sup> Studies have shown a strong correlation between OH stretching frequencies and both the O···O bond distances and the H···O hydrogen bond distances. The work of Libowitzky (1999) showed that a regression function can be employed relating the above correlations with regression coefficients better than 0.96.<sup>14</sup> The function is  $\nu_1 = 3592 - 304 \times 10^9 \exp(-d(\text{O}-\text{O})/0.1321) \text{ cm}^{-1}$ . Two types of OH units are identified in the

structure and the known hydrogen bond distances used to predict the hydroxyl stretching frequencies and vice versa. For instance bands observed at  $3404\text{ cm}^{-1}$  reflect weak hydrogen bonds and the distance between the OH---O<sub>4</sub>As is long. In comparison the bands observed at  $2636\text{ cm}^{-1}$  for ferrilotharmeyerite and  $2999\text{ cm}^{-1}$  for gartrellite are indicative of strong hydrogen bonds and the distances between the OH and AsO<sub>4</sub> units considerably shorter.

The band component analysis of the Raman spectrum of the hydroxyl stretching region of thometzekite shows bands at  $3519$ ,  $3282$ ,  $2821$  and  $2345\text{ cm}^{-1}$ . The bands are broad. It is certainly problematic that a band observed at  $2345\text{ cm}^{-1}$  can be attributed to the OH stretching vibrations of water. Although such cases are not unknown. Libowitzky in determining a relationship between infrared OH stretching wavenumbers and O...O and O...H bond distances, used OH stretching vibrations well below this number.<sup>15</sup> The spectral profile in the Raman spectrum of thometzekite clearly shows a band centred around  $2345\text{ cm}^{-1}$ . Deuteration would prove whether or not the band may be attributed to an hydroxyl stretching vibration. Such studies are rare and beyond the scope of this work. Collection of spectral data at  $77\text{ K}$  would also assist in the attribution of this band. Careful studies of the Raman spectra of the hydroxyl stretching region of ferrilotharmeyerite and tsumcorites show low intensity bands around  $2345\text{ cm}^{-1}$ , even though the bands are of very low intensity.

The band at the high wavenumber position ( $3519\text{ cm}^{-1}$ ) may be assigned to the symmetric stretching mode of hydroxyl units. The remaining three bands may be assigned to the hydroxyl stretching vibrations of water. The infrared spectrum of this region also shows complexity with a number of overlapping bands observed at  $3538$ ,  $3469$ ,  $3286$ ,  $2929$ ,  $2549$  and  $2329\text{ cm}^{-1}$ . The two bands in the IR spectrum at  $3538$  and  $3469\text{ cm}^{-1}$  may be compared with the Raman band at  $3519\text{ cm}^{-1}$ . The Raman spectrum of thometzekite suffers from a lack of signal to noise; it should be kept in mind that the collection of spectral data for the hydroxyl stretching region of these selected tsumcorites is not easy. The signal is quite weak. Thus it is possible that two bands may be curve resolved in the Raman spectrum at around  $3519\text{ cm}^{-1}$ . The infrared band at  $3286\text{ cm}^{-1}$  may be compared with the Raman band at  $3282\text{ cm}^{-1}$ ; both bands are assigned to the stretching modes of OH units of water. Similarly the broad spectral profile in the infrared spectrum at  $2929\text{ cm}^{-1}$  may be compared with the broad spectral profile in the Raman spectrum at  $2821\text{ cm}^{-1}$ . Such broad profiles indicate a continuum of states of hydrogen bonding of water molecules. The broad peaks in the spectra indicate variation in the hydrogen bond distances. Bands in the infrared spectrum of thometzekite at  $2329\text{ cm}^{-1}$  may be compared with the band at  $2345\text{ cm}^{-1}$  in the Raman spectrum. Such band positions indicate strong hydrogen bonding. The series of sharp peaks at around  $2850\text{ cm}^{-1}$  in the IR spectra of gartrellite and thometzekite are attributed to the presence of organic impurities. By use of the Libowitzky equation above, calculations of the hydrogen bond distances can be estimated. For thometzekite, the infrared bands at  $3538$ ,  $3469$  and  $3286\text{ cm}^{-1}$  leads to estimated hydrogen bond distances of  $2.96_5$ ,  $2.85_9$ , and  $2.73_6\text{ \AA}$  respectively. These hydrogen bond distances may be considered as relatively long. The bands at  $2929$ ,  $2549$  and  $2329\text{ cm}^{-1}$  provide estimates of hydrogen bond distances of  $2.63_4$ ,  $2.57_4$  and  $2.54_9\text{ \AA}$ . These shorter hydrogen bond distances provide an indication of stronger hydrogen bonds.

For tsumcorite, Raman bands are observed at 3510, 3329 and 2938  $\text{cm}^{-1}$ . Infrared bands are observed at 3533, 3403, 3234, 2929, 2601 and 2462  $\text{cm}^{-1}$ . The Raman band at 3510  $\text{cm}^{-1}$  is assigned to the stretching mode of hydroxyl units. This band may be compared with the infrared band at 3533  $\text{cm}^{-1}$ . The two Raman bands at 3329 and 2938  $\text{cm}^{-1}$  may be compared with the two infrared bands at 3234 and 2929  $\text{cm}^{-1}$ . These bands are assigned to the stretching modes of water. Low intensity bands are observed at around 2850  $\text{cm}^{-1}$  and are assigned to organic impurities. Bands are observed in the infrared spectra at 2601 and 2462  $\text{cm}^{-1}$ . The assignment of these bands is open to question. If the bands are due to water OH stretching vibrations, then the hydrogen bond distances must be very short. Deuteration studies would be required to prove whether or not these bands are due to water OH stretching vibrations.

In contrast the Raman spectrum of the hydroxyl stretching region for natrochalcite is much simpler with Raman bands observed at 3196 and 3156  $\text{cm}^{-1}$ . Infrared bands for natrochalcite are observed at 3394, 3164, 3158 and 2906  $\text{cm}^{-1}$ . The two Raman bands at 3196 and 3156  $\text{cm}^{-1}$  may be compared with the two infrared bands at 3164 and 3158  $\text{cm}^{-1}$ . These bands are assigned to the hydroxyl stretching vibrations of water. It is suggested that the degree of OH substitution at least for this sample of tsumcorite is small. The spectra of natrolite in both the Raman and infrared appear different from the spectra of the other minerals. It is suggested that the water molecules are in a more rigid structure with little variation in hydrogen bond lengths.

The Raman and infrared spectra of the selected arsenates of the tsumcorite mineral group are shown in Figures 3 and 4 respectively. The most intense Raman bands for ferrilotharmeyerite are observed at 880, 830, 814 and 765  $\text{cm}^{-1}$ . One possible assignment is that the band at 880  $\text{cm}^{-1}$  is attributable to the  $\text{AsO}_4$  symmetric stretching vibration and the two bands at 830 and 814  $\text{cm}^{-1}$  to the  $\text{AsO}_4$  antisymmetric stretching vibrations. Previous studies by the authors have suggested that the band at 765  $\text{cm}^{-1}$  may be attributed to a water librational mode. This mineral is monoclinic and two  $\text{AsO}_4$  stretching vibrations are predicted. It was not possible to obtain the infrared spectrum of ferrilotharmeyerite as the mineral was on the surface of a rock matrix and as the sample was on loan, the mineral had to be kept intact. The Raman spectrum of gartrellite shows bands in the  $\text{AsO}_4$  stretching region at 869, 842, 812 and 785  $\text{cm}^{-1}$ . The first band is assigned to the  $\text{AsO}_4$  symmetric stretching vibration and the next three to the antisymmetric stretching modes. A band is also observed at 765  $\text{cm}^{-1}$  and is attributed to a water librational mode. In the Raman spectrum of gartrellite, a band is observed at 995  $\text{cm}^{-1}$ . This band is assigned to the  $\text{SO}_4$  symmetric stretching vibration with the additional bands observed at 1099 and 1161  $\text{cm}^{-1}$  attributed to the  $\text{SO}_4$  antisymmetric stretching modes. The observation of these sulphate modes is an indication of isomorphic substitution of arsenate by sulphate. Both anions have characteristic spectra in this region.

A comparison may be made with the spectrum of natrochalcite which is the sulphate based tsumcorite mineral. The identification of sulphate in the mineral shows the isomorphic substitution of sulphate for arsenate in the gartrellite mineral from Ashburton Downs, Western Australia. Confirmation of the presence of sulphate is confirmed by the infrared spectrum where intense bands are observed at 1087 and 1006  $\text{cm}^{-1}$  attributed to the antisymmetric  $\text{SO}_4$  stretching modes (Figure 4). Other infrared reflectance bands are observed at 892, 794 and 713  $\text{cm}^{-1}$ . A probable

assignment is that the first band is the symmetric stretching mode of the  $\text{AsO}_4$  unit and corresponds to the Raman band observed at  $869\text{ cm}^{-1}$ . The second band is attributed to the  $\text{AsO}_4$  antisymmetric stretching mode. The  $713\text{ cm}^{-1}$  band may be assigned to the water librational mode which would be expected in or about this position and is predicted to be a broad band.

Such isomorphous substitution by sulphate is also observed by the identification of the presence of sulphate in the Raman spectrum of thometzekite with the observation of a low intensity band at  $980\text{ cm}^{-1}$ . A comparison may be made with the spectrum of natrochalcite. Bands are also observed at  $841, 790$  and  $735\text{ cm}^{-1}$ . The attribution of these three bands is as for gartrellite. The infrared spectrum of thometzekite shows strong bands at  $863, 800$  and  $709\text{ cm}^{-1}$ . These bands correspond to the three Raman bands listed above. Other infrared bands are observed at  $1174, 1085, 1049$  and  $987\text{ cm}^{-1}$ . The first three bands are ascribed to the  $\text{SO}_4$  antisymmetric stretching modes and the last band to the  $\text{SO}_4$  symmetric stretching mode. Whilst the Raman spectrum shows a low intensity sulphate band; the infrared spectrum shows a much more intense sulphate spectrum. The Raman spectrum of tsumcorite shows a pattern similar to that observed for thometzekite with bands observed at  $869$  and  $836\text{ cm}^{-1}$ . A low intensity band is observed at  $929\text{ cm}^{-1}$ . The infrared spectrum shows bands at  $892, 800$  and  $784\text{ cm}^{-1}$ . The Raman spectrum of natrochalcite shows an intense band at  $997\text{ cm}^{-1}$  and a second band at  $1046\text{ cm}^{-1}$ . These bands are attributed to the  $\text{SO}_4$  symmetric and antisymmetric stretching modes of sulphate. No carbonate anion was observed in any of the minerals.

The Raman spectrum of the low wavenumber region of the tsumcorite mineral group is shown in Figure 5. One of the advantages of Raman spectroscopy of the arsenate mineral group is that bands below  $400\text{ cm}^{-1}$  are readily determined. What is readily determined is the sulphate spectrum of natrochalcite. Two sets of bands are observed. Firstly bands at  $636$  and  $607\text{ cm}^{-1}$  and secondly bands at  $466, 445, 429$  and  $402\text{ cm}^{-1}$ . The first set of bands is attributed to the out-of-plane bending modes whilst the second set to the in-plane bending modes. Some low intensity bands are observed in this region for gartrellite. This simply reflects the isomorphous substitution of sulphate for arsenate. The Raman spectrum of ferrilotharmeyerite shows two bands at  $510$  and  $487\text{ cm}^{-1}$ . These bands are assigned to the out-of-plane bending modes of the  $\text{AsO}_4$  unit. Three bands are observed at  $421, 370$  and  $325\text{ cm}^{-1}$  and are attributed to the  $\text{AsO}_4$  in-plane bending modes. An intense band is observed at  $230\text{ cm}^{-1}$ . It is not known what this band may be assigned to but one possibility is the MO stretching vibration. The difficulty with the low wavenumber region of the Raman spectrum of gartrellite is the overlap of the sulphate and arsenate bands attributable to the bending modes. Bands are observed at  $499, 474$  and  $438\text{ cm}^{-1}$ . These may be ascribed to the  $\nu_4$  bending modes. A set of bands are observed at  $357, 331$  and  $304\text{ cm}^{-1}$  and are attributed to the  $\nu_2$  bending modes of the  $\text{AsO}_4$  unit. The Raman spectrum of thometzekite and tsumcorite are similar. Bands for thometzekite are observed at  $499, 428$  and  $401\text{ cm}^{-1}$ . A second set is observed at  $356$  and  $322\text{ cm}^{-1}$ . For tsumcorite the first set of bands are observed at  $523, 494, 428$  and  $401\text{ cm}^{-1}$ . The second set consists of bands at  $362, 341$  and  $294\text{ cm}^{-1}$ .

## CONCLUSIONS

Raman spectroscopy has been used to characterise the arsenates of the tsumcorite mineral group. Structures of the minerals have been determined. A comparison is made with the Raman spectrum of the sulphate based mineral, natrochalcite. This comparison proves the presence of sulphate in the two minerals gartrellite and thometzekite. Gartrellite shows a much greater sulphate isomorphic substitution than thometzekite. Hydrogen bond distances were estimated for the OH—AsO<sub>4</sub> units using the Libowitzky type function. The range of OH stretching frequencies shows a range of hydrogen bond strengths based upon the range of calculated hydrogen bond distances. The tsumcorite arsenate minerals are characterised by typical spectra of the AsO<sub>4</sub> units. The symmetric stretching modes are observed in the 840 to 880 cm<sup>-1</sup> region; the antisymmetric stretching modes are observed in the 812 to 840 cm<sup>-1</sup> region. Some bands are observed around 765 cm<sup>-1</sup> region and are attributed to water librational modes. The  $\nu_4$  bending modes are observed around 499 cm<sup>-1</sup> and the  $\nu_2$  bending modes in the 300 to 360 cm<sup>-1</sup> region. Multiple bands are observed in these regions indicating a loss of symmetry of the AsO<sub>4</sub> unit.

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**Table 1 Factor group analysis of the monoclinic tsumcorites**

**Monoclinic C2/m Z=2**



Factor group analysis of the arsenate group

Point Group	Site Group	Factor Group	
$T_d$	$C_s$	$C_{2h}$	
$A_1$	$6A'$	$6A_g$	
$E$			$6B_u$
$2T_2$			$3A''$
		$3B_g$	
		$3A_u$	

Factor group analysis of the water molecule

Point Group	Site Group	Factor Group
$C_{2v}$	$C_s$	$C_{2h}$
$2A_1$	$3A'$	$3A_g$
$B_2$		

Lattice modes

$$\Gamma = 6A_g + 6B_g + 9A_u + 9B_u$$

**Monoclinic C2/m Z=2**



Factor group analysis of the arsenate group

Point Group	Site Group	Factor Group	
$T_d$	$C_s$	$C_{2h}$	
$A_1$	$6A'$	$6A_g$	
$E$			$6B_u$
$2T_2$			$3A''$
		$3B_g$	
		$3A_u$	

Lattice modes

$$\Gamma = 7A_g + 10B_g + 5A_u + 8B_u$$

Of this  $B_g + A_u$  are hydroxyl stretching vibrations

**Table 2 Factor group analysis of the triclinic tsumcorites**

**Triclinic P-1**



Factor group analysis of the arsenate group

Point Group	Site Group	Factor Group
$T_d$	$C_1$	$C_i$
$A_1$	$9A$	$9A_g$
$E$		
$2T_2$		$9A_u$

Factor group analysis of the water molecule

Point Group	Site Group	Factor Group
$C_{2v}$	$C_1$	$C_i$
$2A_1$	$3A$	$3A_g$
$B_2$		

Lattice modes

$\Gamma = 12A_g + 18A_u$

<b>ferrilotharmeyerite</b>	<b>gartrellite</b>	<b>thometzekite</b>	<b>tsumcorite</b>	<b>natrochalcite</b>	<b>Suggested assignment</b>
3440 2973 2636	3404 3229 2999	3519 3282 2821 2345	3510 3529 2938	3196 3156	OH stretching and water OH stretching
	1161 1099			1046 1023	SO <sub>4</sub> antisymmetric stretching
	995	984	929	997 930	SO <sub>4</sub> symmetric stretching
919 880	869 842	841	869 836		AsO <sub>4</sub> antisymmetric stretching
830 814	812				AsO <sub>4</sub> symmetric stretching
765 730	785	790 728	749		Water OH libration
510 487	618 560 499	499	523 494	636 607	SO <sub>4</sub> bending
421	474 438	428 401	441 402	466 445 429 402	AsO <sub>4</sub> bending
370	357	356	362		AsO <sub>4</sub>

325	331 304	322	341 294		bending
230	238 201 164 140	239	244 203 157	212	Lattice modes

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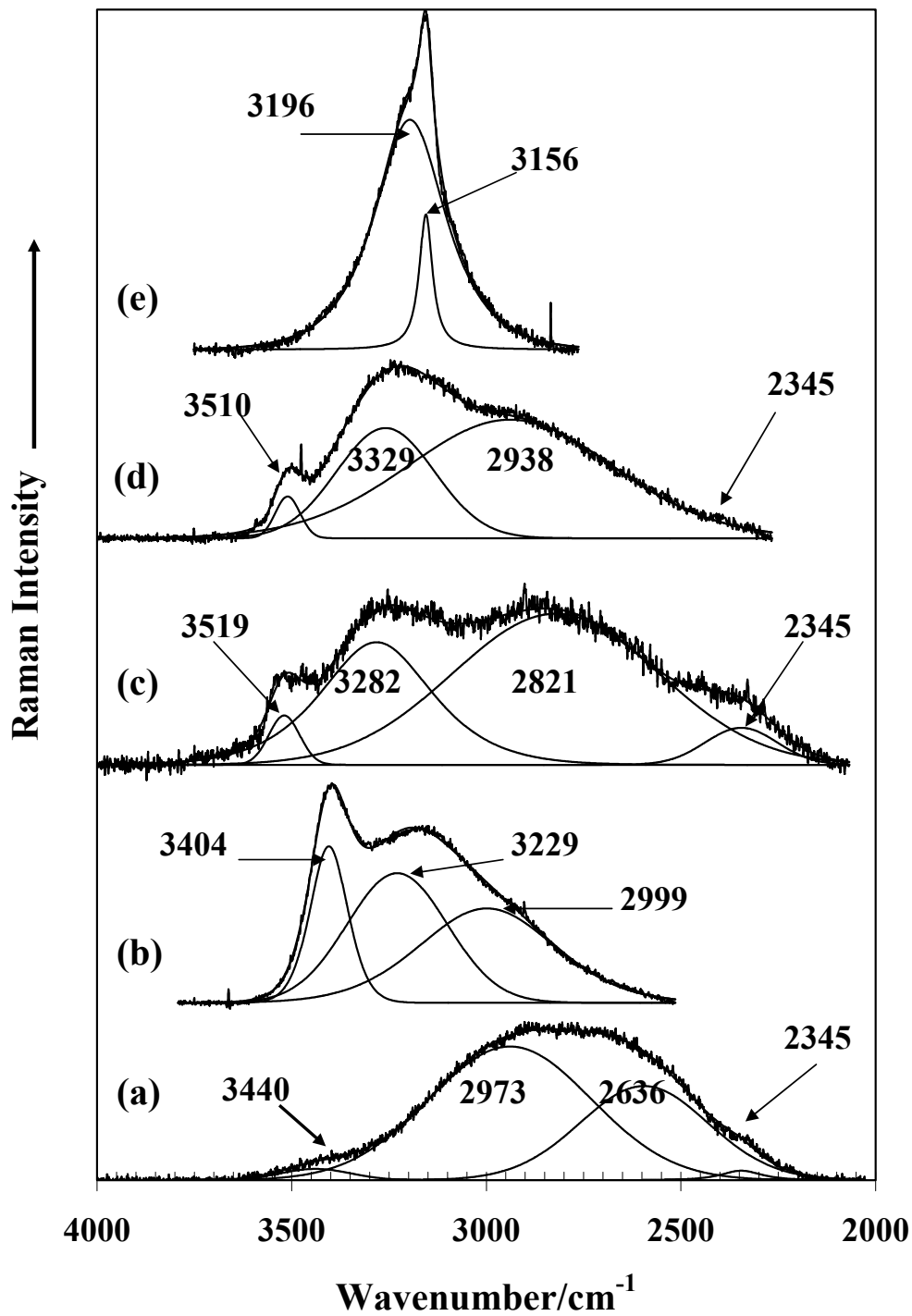
**Figure 5 Raman spectra of the AsO<sub>4</sub> and SO<sub>4</sub> low wavenumber region of (a) ferrilotharmeyerite (b) gartrellite (c) thometzekite (d) tsumcorite (e) natrochalcite**

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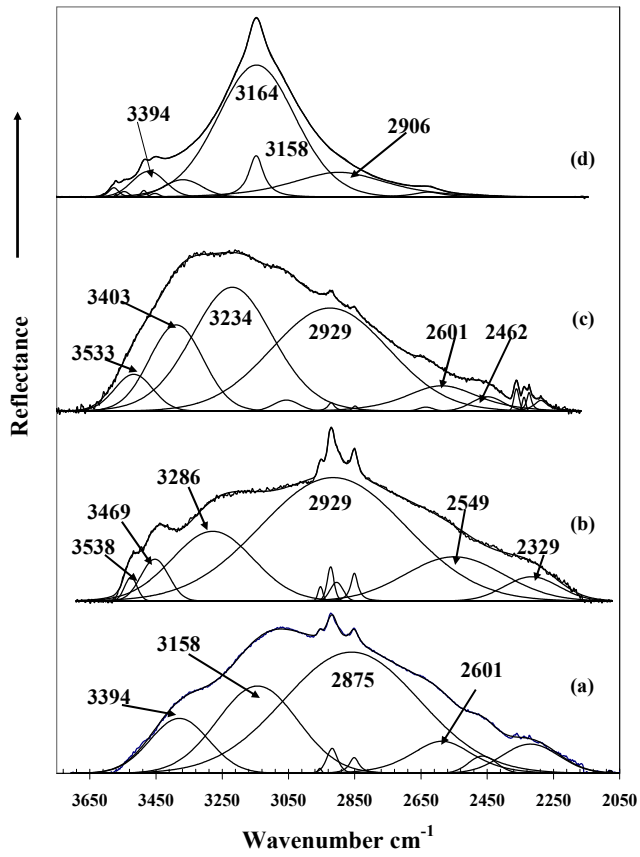
**Table 1 Factor group analysis of the triclinic tsumcorites**

**Table 2 Factor group analysis of the triclinic tsumcorites**

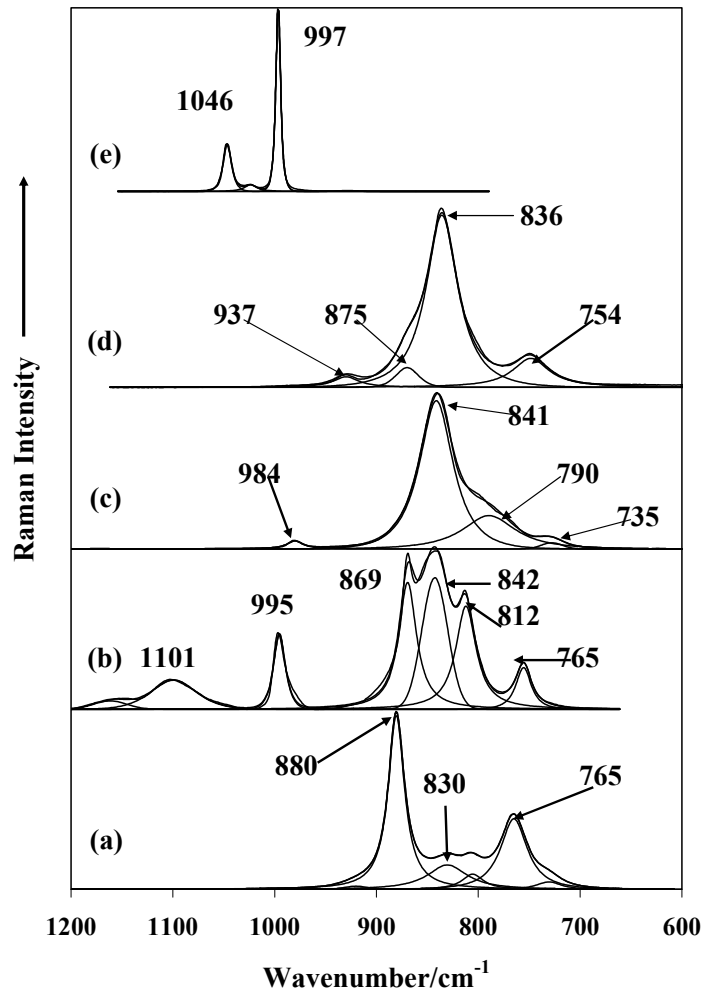
**Table 3 Raman spectroscopic analysis of selected tsumcorite minerals**



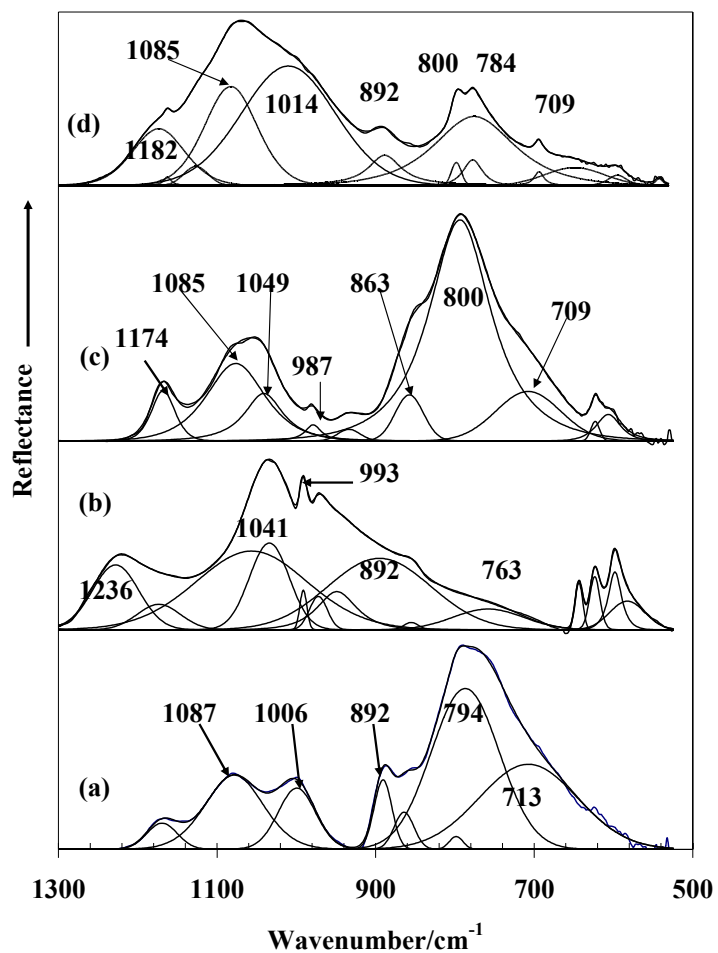
**Figure 1** Raman spectra of the hydroxyl stretching region of (a) ferrilotharmeyerite (b) gartrellite (c) thometzekite (d) tsumcorite (e) natrochalcite



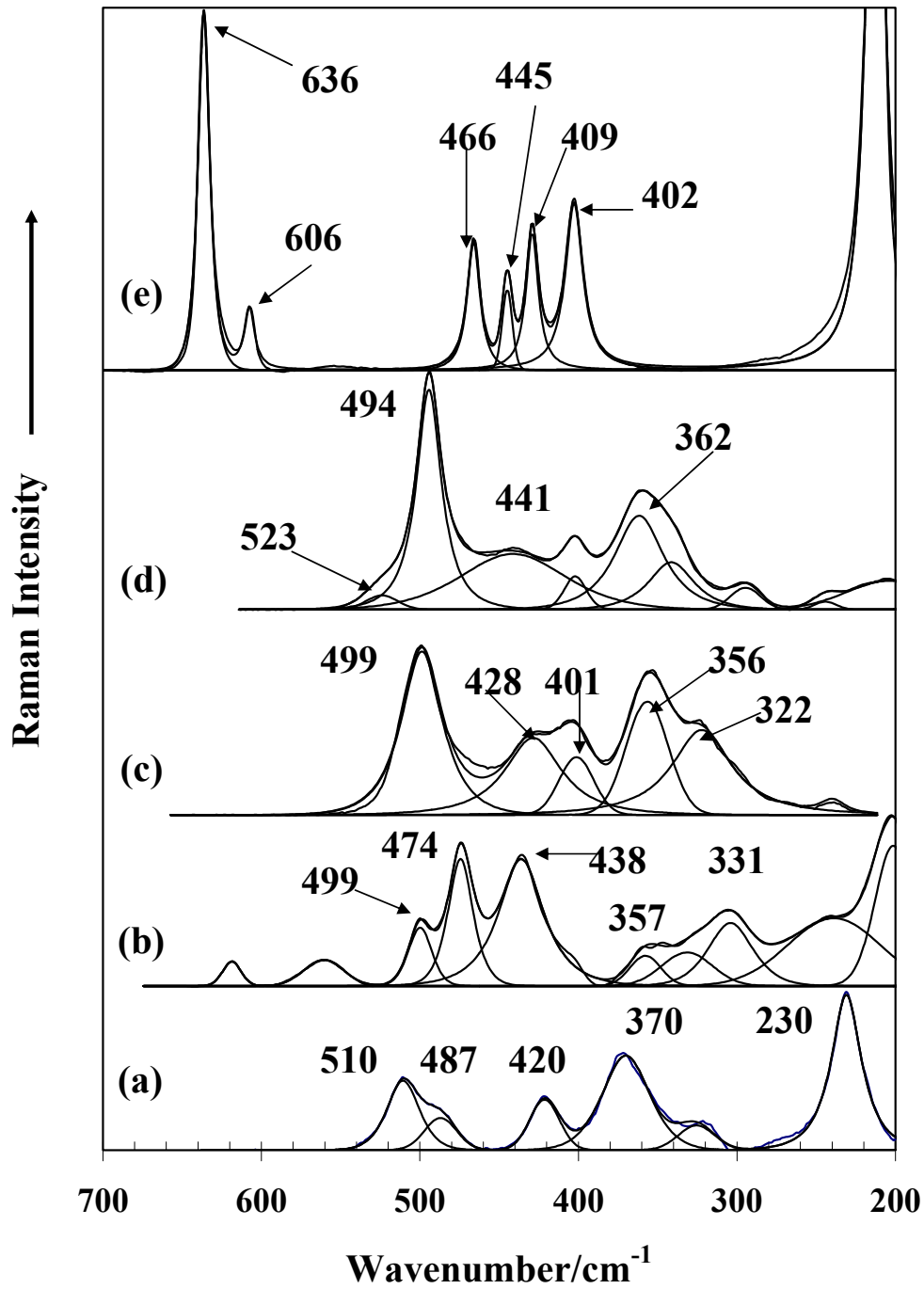
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**Figure 3** Raman spectra of the AsO<sub>4</sub> and SO<sub>4</sub> stretching region of (a) ferrilotharmeyerite (b) gartrellite (c) thometzekite (d) tsumcorite (e) natrochalcite



**Figure 4** Infrared spectra of the  $\text{AsO}_4$  and  $\text{SO}_4$  stretching region of (a) gartrellite (b) natrochalcite (c) thometzekite (d) tsumcorite



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