

Raman and infrared spectroscopy of tsumcorite mineral group

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With 3 figures and 2 tables

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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. Isomorphous substitution of sulphate for arsenate is observed for gartrellite and thometzekite. A comparison is made with the sulphate bearing mineral natrochalcite. 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 AsO_4 anion. Characteristic Raman spectra of the minerals enable the assignment of the bands to specific vibrational modes.

Key words: Raman spectroscopy, tsumcorite, thometzekite, natrochalcite, gartrellite.

Introduction

The tsumcorite mineral group has been studied for some considerable time (CESBRON & FRITSCH 1969, COCCO 1952, PALACHE 1939, PALACHE & WARREN 1908, SKRAMOVSKY & STEPAN 1939). Many of the minerals were found in the oxidised zones of the famous Tsumeb ore deposit (GEIER et al. 1971). Many new minerals have been discovered from the oxidised zones (KELLER et al. 1979, 1981, 1986, KHARISUN et al. 1997, KRAUSE et al. 1998 b). Many of the minerals are based upon arsenates of lead and zinc in combination with other cations. 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, 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

(SCHMETZER et al. 1985) are triclinic. The minerals ferrilotharmeyerite (KRAUSE et al. 1998 a) $\text{Ca}(\text{Fe}^{3+}, \text{Zn})_2(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$, lotharmeyerite $\text{Ca}(\text{Mn}^{3+}, \text{Zn})_2(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$, mawbyite (KHARISUN et al. 1997) $\text{Pb}(\text{Fe}^{3+}, \text{Zn})_2(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$, mounanaite $\text{Pb}(\text{Fe}^{3+})_2(\text{VO}_4)_2(\text{OH})_2$, nat-rochalcite (RUMANOVA & VOLODINA 1958) $\text{NaCu}_2(\text{SO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$ and tsumcorite (TILLMANN & GEBERT 1973) $\text{Pb}(\text{Zn}, \text{Fe}^{3+})_2(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})$ are monoclinic (TILLMANN & GEBERT 1973). Tsumcorite crystallizes in the monoclinic space group $C2/m$ with a 9.124 (4), b 6.329 (2), c 7.577 (2) $\beta = 115$. degree. 17 (2)', $Z = 2$ (TILLMANN & GEBERT 1973). Crystal symmetry is either triclinic in the case of an ordered occupation of two cationic sites, triclinic due to ordering of the H bonds in the case of species with 2 water molecules per formula unit, or monoclinic in the other cases. Crystals of ferrilotharmeyerite, tsumcorite, thometzekite (sulfatian), and mounanaite have monoclinic symmetry, space group $C2/m$. The triclinic members of the tsumcorite group are gartrellite, zincian gartrellite, phosphogartrellite, helmutwinklerite, and probably (sulfate-free) thometzekite; the space group is $P\bar{1}$, with a pronounced monoclinic C-centered pseudocell. The triclinic distortion is caused by an ordered arrangement of $\text{Fe}[6]\text{O}_6$ octahedra and tetragonal bi-pyramidal $\text{Cu}[4+2]\text{O}_6$ polyhedra (KRAUSE et al. 1998 a).

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 $\text{Pb}[(\text{Cu}, \text{Fe}^{2+})(\text{Fe}^{3+}, \text{Zn}, \text{Cu})] (\text{AsO}_4)(\text{CO}_3, \text{H}_2\text{O})_2$, can be written for gartrellite. For example the gartrellite found at Ashburton Downs, Western Australia has a calculated formula of $\text{PbCu}_{1.5}\text{Fe}^{2+}_{0.5}\text{As}_{1.5}(\text{SO}_4)_{0.5}(\text{CO}_3)_{0.5}(\text{H}_2\text{O})_{0.2}$. 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 $C2/m$ (KRAUSE et al. 1998 a). The triclinic members of the tsumcorite group have the space group $P\bar{1}$, with a pronounced monoclinic C-centred pseudocell (KRAUSE et al. 1998 a). 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. 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 (WILLIAMS 1990). 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.

Table 1. Table of the tsumcorite minerals studied.

Mineral	Type number	Formulae	Origin
gartrellite	M39987	$\text{Pb}[(\text{Cu}, \text{Zn})(\text{Fe}^{3+}, \text{Zn}, \text{Cu})](\text{AsO}_4)_2(\text{OH} \cdot \text{H}_2\text{O})$	Anticline deposit, Ashburton Downs, Western Australia
ferrilotharmeyerite	M36822	$\text{Ca}(\text{Fe}^{3+}, \text{Zn})_2(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$	Tsumeb, Namibia
natrochalcite	M32894	$\text{NaCu}_2(\text{SO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$	Chuquicamata, Chile
tsumcorite	M37949	$\text{Pb}(\text{Zn}, \text{Fe}^{3+})_2(\text{AsO}_4)_2(\text{OH} \cdot \text{H}_2\text{O})$	Tsumeb, Namibia
thometzekite	M43672	$\text{Pb}(\text{Cu}, \text{Zn})_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$	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 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). Details have been published (FROST et al. 2001 a, 2001 b, 2002).

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 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. (FROST et al. 2001 a, b, 2002) 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^2 greater than 0.995.

Results and discussion

The Raman spectra of gartrellite at 298 and 77 K in the 700 to 1100 cm^{-1} region are shown in Fig. 1a. The results of the analysis of the spectra are reported in Table 2. Included in this table are the results of the infrared spectra. The mineral gartrellite $\text{Pb}[(\text{Cu}, \text{Zn})(\text{Fe}^{3+}, \text{Zn}, \text{Cu})] (\text{AsO}_4)(\text{OH}, \text{H}_2\text{O})_2$, is an arsenate based mineral. The mineral may have arsenate isomorphically substituted by sulphate or carbonate as is indicated by the formula for the gartrellite from Ashburton Downs, Western Australia. The Raman spectrum of gartrellite shows bands in the AsO_4 stretching region in the spectrum obtained at 298 K region at 869, 842, 812 and 785 cm^{-1} . The bands are observed in the 77 K spectrum at 871, 843, 814 and 763 cm^{-1} . The first band is assigned to the AsO_4 symmetric stretching vibration and the next three to the antisymmetric stretching modes. A band is also observed at 785 cm^{-1} and is attributed to a water librational mode. The band shifts to 763 cm^{-1} in the 77 K spectrum.

In the Raman spectrum of gartrellite, a band is observed at 995 cm^{-1} in the 298 K spectrum and at 982 cm^{-1} in the 77 K spectrum. This band is assigned to the SO_4 symmetric stretching vibration with the additional bands observed at 1099 and 1161 cm^{-1} attributed to the SO_4 antisymmetric stretching modes. These last two bands show almost no intensity in the 77 K spectrum. There is a significant shift of 13 cm^{-1} in the position of the SO_4 symmetric stretching vibration upon cooling to liquid nitrogen temperature. This shift may be attributed to an increase in hydrogen bonding between the

sulphate anion and water molecules upon cooling to liquid nitrogen temperature. The observation of these sulphate modes is an indication of isomorphic substitution of arsenate by sulphate. Both anions have characteristic spectra in this spectral region. There was no Raman spectroscopic evidence of carbonate anions.

The infrared spectra of gartrellite show two bands at 892 and 860 cm^{-1} . The bands are assigned to the antisymmetric and symmetric stretching modes of the AsO_4 anion. The symmetric stretching mode was not observed in the infrared spectrum; however the antisymmetric SO_4 modes were observed at 1165, 1087 and 1006 cm^{-1} . Two intense bands are observed at 794 and 713 cm^{-1} and are attributed to the infrared bands of the water librational modes.

The most intense Raman bands for ferrilotharmeyerite are observed at 880, 830, 814 and 765 cm^{-1} (Fig. 1 b). One possible assignment is that the band at 880 cm^{-1} is attributable to the AsO_4 antisymmetric stretching vibration and the two bands at 830 and 814 cm^{-1} to the AsO_4 symmetric stretching vibrations. Previous studies by the authors have suggested that the band at 765 cm^{-1} may be attributed to a water librational mode. This mineral is monoclinic and two 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 spectrum of ferrilotharmeyerite at 77 K is quite different from the spectrum at 298 K. Two intense bands are observed at 845 and 1000 cm^{-1} . The bands are attributed to the symmetric stretching modes of AsO_4 and SO_4 respectively. Three additional bands are observed 1134, 1110 and 1086 cm^{-1} . These bands are attributed to the SO_4 antisymmetric stretching vibrations.

The fact that Raman spectroscopy determines the presence of sulphate in the mineral ferrilotharmeyerite means that the formula is more likely to be written as $\text{Ca}(\text{Fe}^{3+}, \text{Zn})_2(\text{AsO}_4, \text{SO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$.

The Raman spectra of natrochalcite at 298 and 77 K in the 700 to 1100 cm^{-1} region are shown in Fig. 1 c. The spectra are less complex than that of gartrellite and ferrilotharmeyerite as natrochalcite ($\text{NaCu}_2(\text{SO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$) is a mineral based upon sulphate. The band at 997 cm^{-1} in both the 298 and 77 K spectra is assigned to the SO_4 symmetric stretching vibration. The two bands in the 298 K spectrum at 1046 and 1023 cm^{-1} are attributed to the SO_4 antisymmetric stretching modes. The bands are resolved into components at 1051, 1049 and 1035 cm^{-1} in the 77 K spectrum. The infrared spectrum

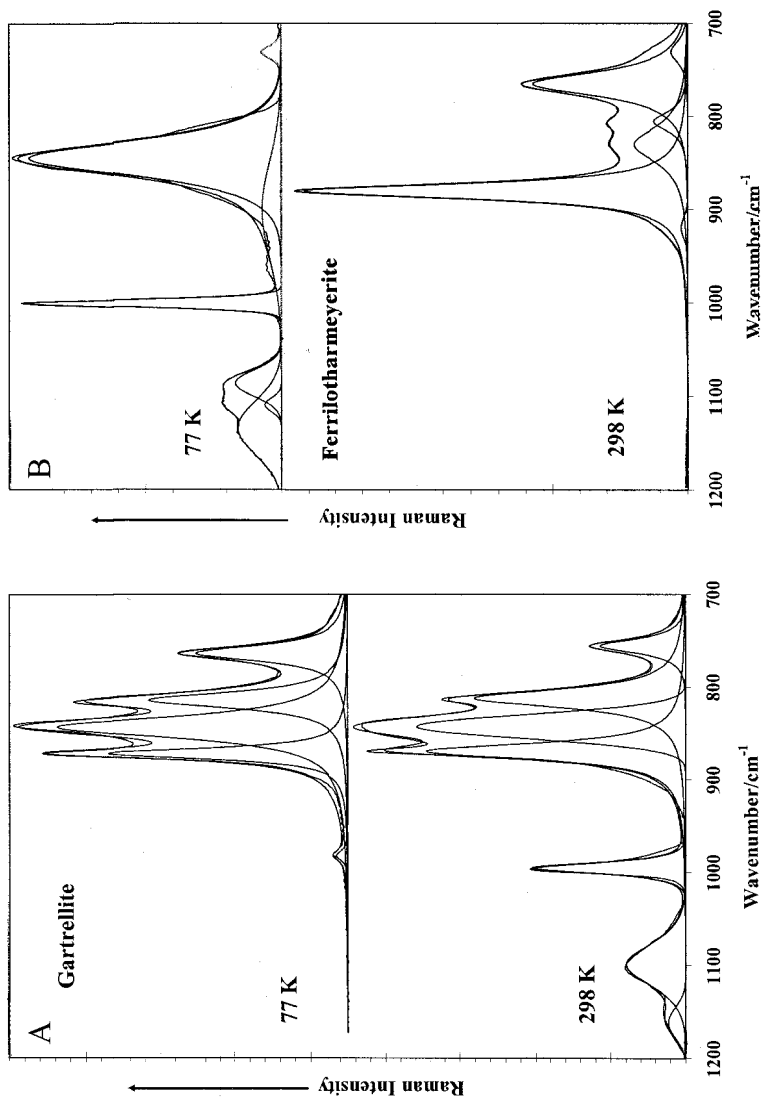


Fig. 1. A. Raman spectrum of gartrellite in the 700 to 1200 cm⁻¹ region at 298 and 77 K. B. Raman spectrum of ferrillotharmeyerite in the 700 to 1200 cm⁻¹ region at 298 and 77 K.

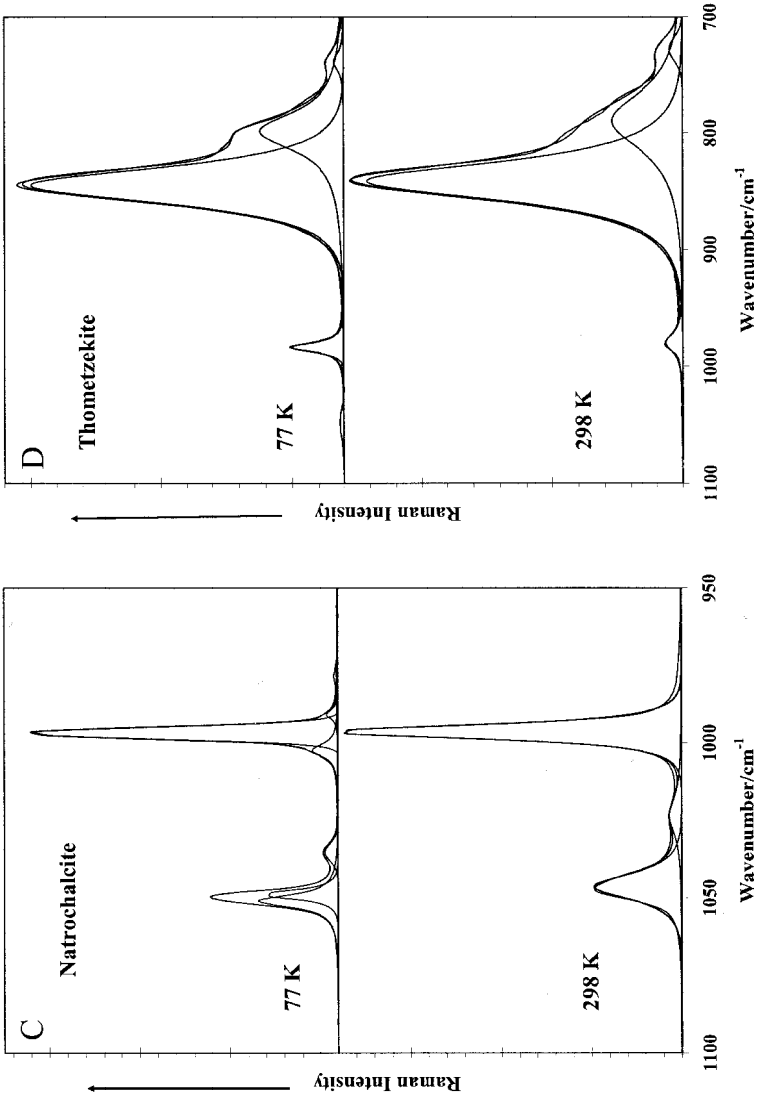


Fig. 1. (Continuation). C. Raman spectrum of natrochalcite in the 700 to 1200 cm^{-1} region at 298 and 77 K. D. Raman spectrum of thometzekite in the 700 to 1200 cm^{-1} region at 298 and 77 K.

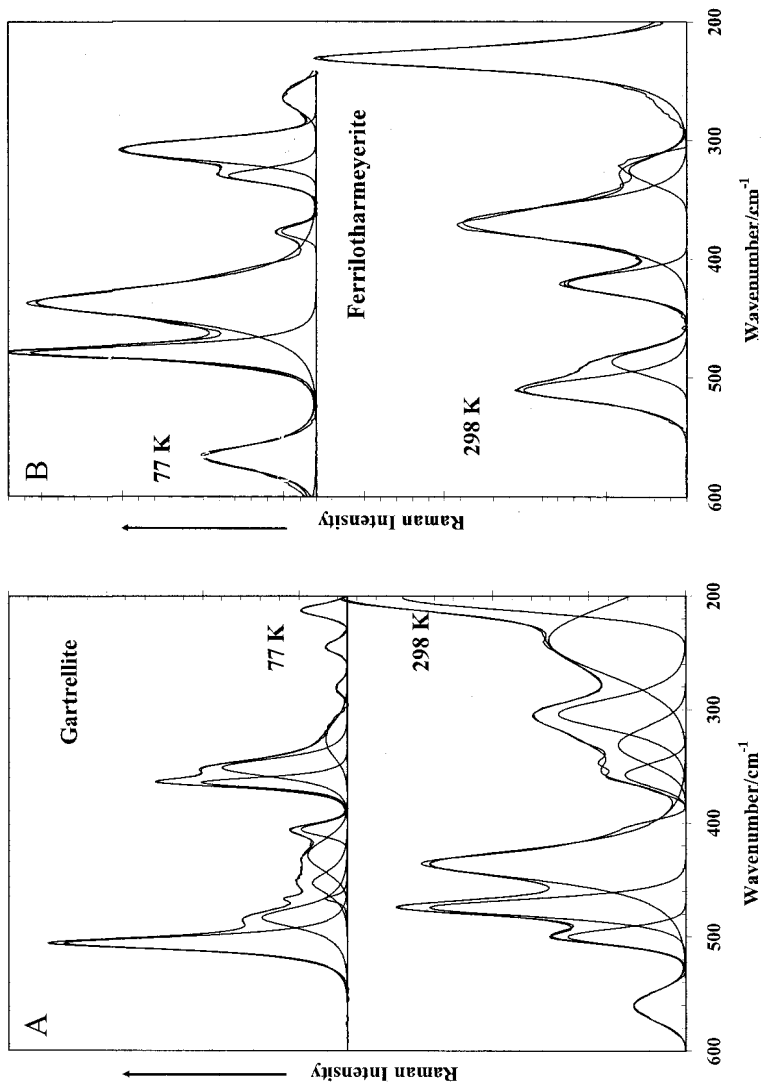


Fig. 2. A. Raman spectrum of gartrellite in the 200 to 600 cm⁻¹ region at 298 and 77 K. B. Raman spectrum of ferrillotharmeyerite in the 200 to 600 cm⁻¹ region at 298 and 77 K.

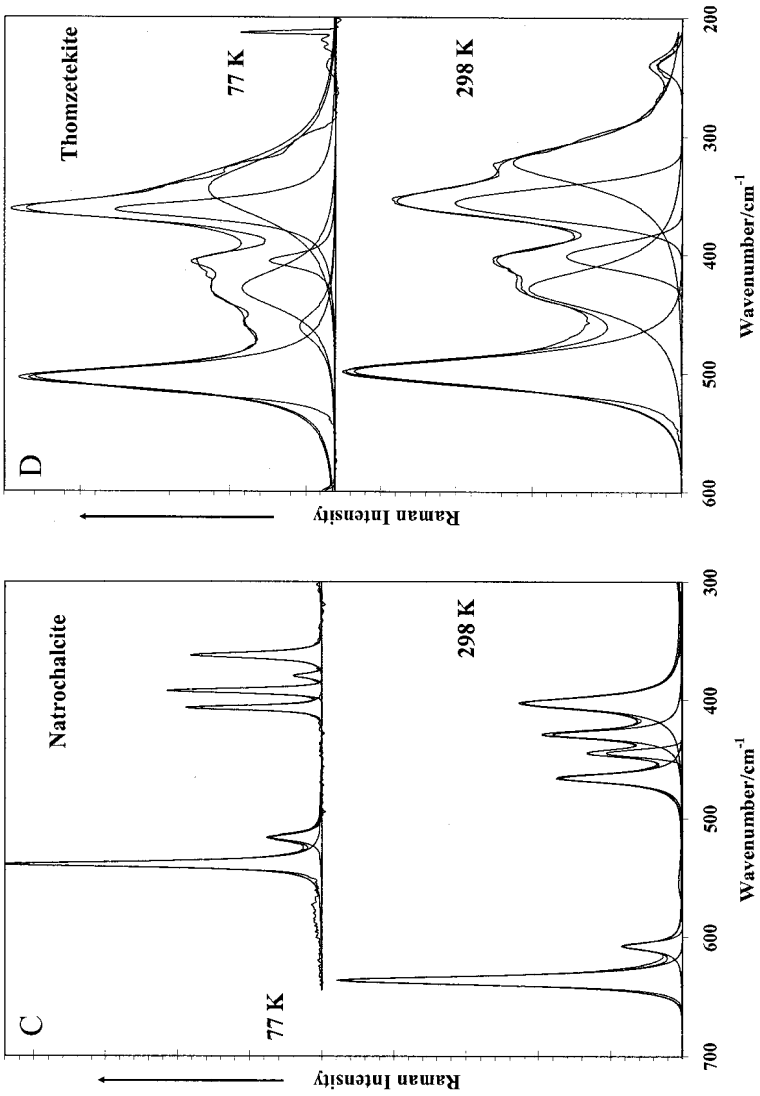


Fig. 2. (Continuation). C. Raman spectrum of natrochalcite in the 200 to 600 cm⁻¹ region at 298 and 77 K. D. Raman spectrum of thomzetekite in the 200 to 600 cm⁻¹ region at 298 and 77 K.

shows two bands at 1041 and 993 cm^{-1} which are attributed to the SO_4 anti-symmetric and symmetric stretching vibrations.

The Raman spectrum of thomtezekite at 298 and 77 K in the 700 to 1100 cm^{-1} region are shown in Fig. 1d. The Raman spectrum at the two different temperatures is very similar. An intense band is observed at 841 cm^{-1} in the 298 K spectrum and at 844 cm^{-1} in the 77 K spectrum and is assigned to the AsO_4 symmetric stretching vibration. Additional bands are observed at 790 and 728 cm^{-1} (298 K) and 798 and 738 cm^{-1} (77 K). In addition a band is observed at 984 cm^{-1} (298 K) and 983 cm^{-1} (77 K). This band is ascribed to the SO_4 symmetric stretching vibration. Infrared bands are observed at 1174, 1085, 1049 cm^{-1} attributed to the SO_4 antisymmetric stretching vibrations; 987 cm^{-1} attributed to the SO_4 symmetric stretching vibration; and 863 cm^{-1} the AsO_4 antisymmetric stretching vibration. The Raman spectrum of tsumcorite shows a pattern similar to that observed for thomtezekite with bands observed at 869 and 836 cm^{-1} . A low intensity band is observed at 929 cm^{-1} . The infrared spectrum shows bands at 892, 800 and 784 cm^{-1} .

The Raman spectra of the low wavenumber region of gartrellite at 298 and 77 K are shown in Fig. 2a. 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 cm^{-1} . These may be ascribed to the ν_4 bending modes of SO_4 units. A set of bands are observed at 357, 331 and 304 cm^{-1} and are attributed to the ν_2 bending modes of the AsO_4 unit. A set of bands which may be attributed to the ν_4 bending modes are observed at 506, 483, 456 and 452 cm^{-1} in the 77 K spectrum. The ν_2 bending modes are more clearly resolved in the 77 K spectrum. Two intense bands are observed at 364 and 351 cm^{-1} and are attributed to the ν_2 bending modes of AsO_4 units.

The Raman spectra of the low wavenumber region of ferrillotharmeyerite are shown in Fig. 2b. The Raman spectrum of ferrillotharmeyerite shows two bands at 510 and 487 cm^{-1} . These bands are assigned to the out-of-plane bending modes of the AsO_4 unit. Three bands are observed at 421, 370 and 325 cm^{-1} and are attributed to the AsO_4 in-plane bending modes. These bands are observed at 377, 330 and 308 cm^{-1} in the 77 K spectrum. An intense band is observed at 230 cm^{-1} . It is not known what this band may be assigned to but one possibility is the MO stretching vibration. Another possibility is that the band is an instrument artefact and is due to a laser line caused by the breakdown of the HeNe laser.

The Raman spectra of the low wavenumber region of natrochalcite are shown in Fig. 2 c. Two sets of bands are observed. Firstly bands at 636 and 607 cm^{-1} and secondly bands at 466, 445, 429 and 402 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. The ν_4 bending modes are observed at 639 and 610 cm^{-1} in the 77 K spectrum and the ν_2 bands are observed at 468, 449, 433 and 410 cm^{-1} in the 77 K spectrum. The Raman spectrum of thometzekite and tsumcorite are similar. Bands for thometzekite are observed at 499, 428 and 401 cm^{-1} (Fig. 2 d). These bands are attributed to the ν_4 AsO_4 bending modes. These bands are observed at 504, 461, 429 and 405 cm^{-1} in the 77 K spectrum. A second set is observed at 356 and 322 cm^{-1} . The bands are observed at 362 and 344 cm^{-1} at 77 K are assigned to the ν_2 bending modes. For tsumcorite the first set of bands are observed at 523, 494, 428 and 401 cm^{-1} . The second set consists of bands at 362, 341 and 294 cm^{-1} .

Much information can be obtained from the study of the hydroxyl stretching region of the tsumcorites. The minerals may contain hydroxyl units or water molecules in the structure or both. A comparison of the Raman spectrum and the infrared spectrum of the hydroxyl stretching region of gartrellite is shown in Fig. 3 a. The Raman spectrum of gartrellite shows three bands at 3404, 3229 and 2999 cm^{-1} . 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 gartrellite show component bands at 3394, 3158, 2875 and 2601 cm^{-1} . The IR band at 3394 cm^{-1} may be compared with the Raman band at 3404 cm^{-1} . Similarly the IR band at 3158 cm^{-1} may be compared with the Raman band at 3229 cm^{-1} . However in the infrared spectral profile intensity is strong in the 2600 to 2900 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 mineral gartrellite $\text{Pb}[(\text{Cu}, \text{Zn})(\text{Fe}^{3+}, \text{Zn}, \text{Cu}) (\text{AsO}_4)(\text{OH}, \text{H}_2\text{O})_2]$ has both OH and H_2O units. It is probable that the high wavenumber band which is comparatively sharp may be assigned to the symmetric stretching vibration of the OH unit.

The Raman spectrum at 298 and 77 K of the hydroxyl stretching region of ferrilotharmeyerite are shown in Fig. 3 b. The results of the band component analyses are shown in Table 2. The Raman spectrum of ferrilothar-

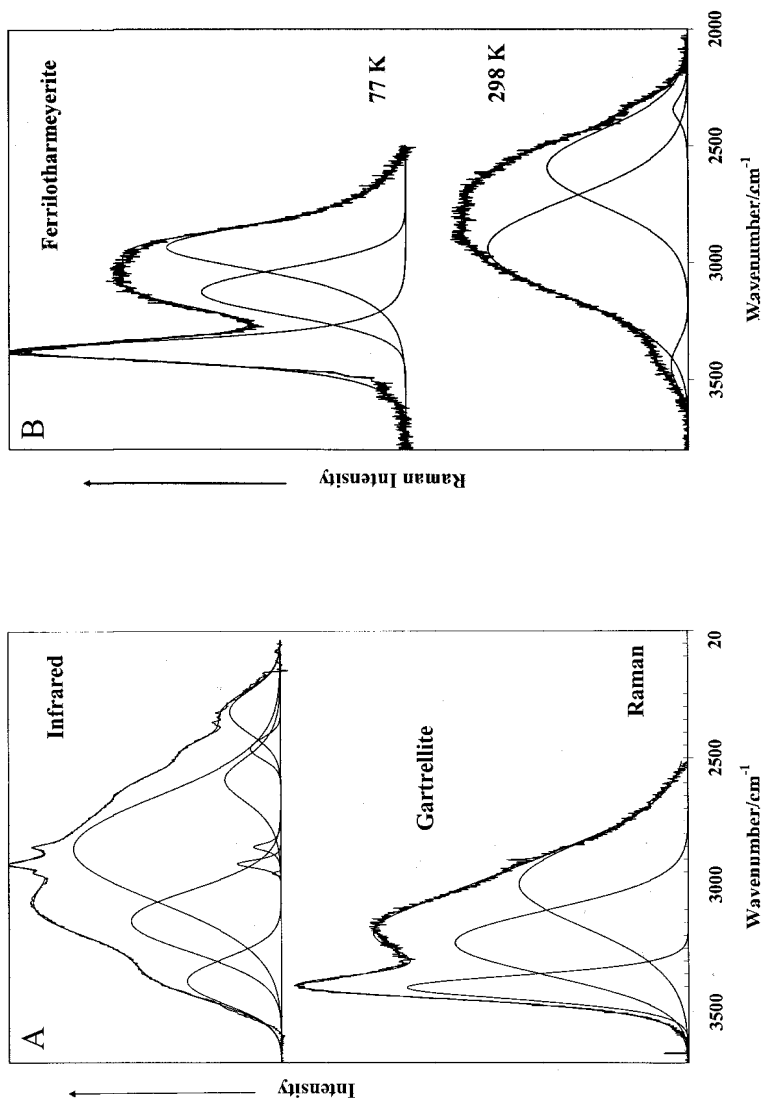


Fig. 3. A. Raman and infrared spectra of the hydroxyl stretching region of gartrellite. B. Raman and infrared spectra of the hydroxyl stretching region of ferrillotharmeyerite.

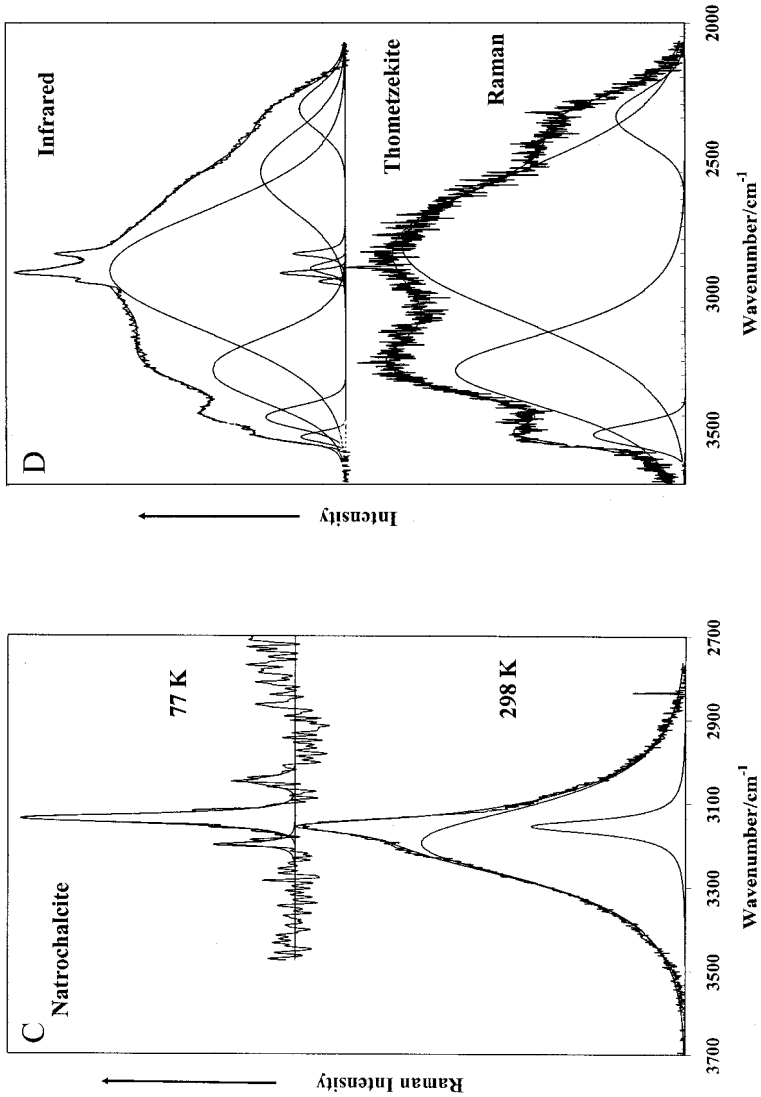


Fig. 3. (Continuation). C. Raman and infrared spectra of the hydroxyl stretching region of natrochalcite. D. Raman and infrared spectra of the hydroxyl stretching region of thometzekite.

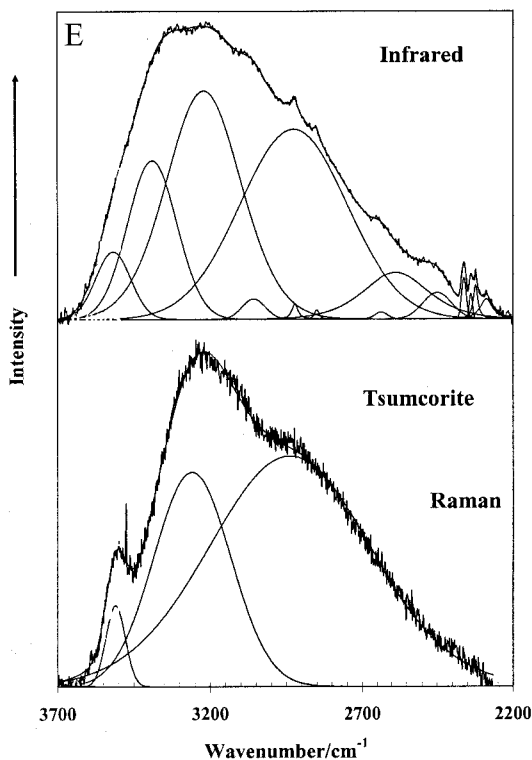


Fig. 3. E. Raman and infrared spectra of the hydroxyl stretching region of tsumcorite.

meyerite shows a low intensity band at 3440 cm^{-1} and two more intense bands at 2973 and 2636 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. The band assignments are as for gartrellite. Here we are comparing the position of the band at 3440 with a band at 3404 cm^{-1} . The intensity of the band at 3404 cm^{-1} is much stronger than the band at 3440 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. However in the Raman spectrum at 77 K, an intense band is observed at 3379 cm^{-1} . This band is attributed to the hydroxyl stretching of the OH units. The intensity is much greater in the 77 K spectrum compared with the 298 K spectrum. This difference may be attributed to the selection of a different crystal for Raman spectroscopy in obtaining the spectrum at 298 and 77 K. The difference may also be indicative of variable chemistry of the ferrilotharmeyerite. The observation of changes in intensity of bands assigned to OH stretching vibrations has 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 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 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 cm^{-1} assigned to strongly hydrogen bonded water. This band is not observed in the Raman spectrum of gartrellite.

The Raman spectrum of the hydroxyl stretching region of natrochalcite at 298 and 77 K are shown in Fig. 3 c. Two bands are observed in the 298 K spectrum at 3196 and 3156 cm^{-1} . The bands appear to be band separated in the 77 K spectrum and three bands are observed at 3199 , 3138 and 3049 cm^{-1} . Natrochalcite $(\text{NaCu}_2(\text{SO}_4)_2(\text{OH}, \text{H}_2\text{O})_2)$ contains both hydroxyl and water units. The positions of the hydroxyl stretching vibration of these two units appear to be similar. In the infrared spectrum bands are observed at 3349 , 3158 and 2906 cm^{-1} . The Raman and infrared spectrum of thometz-kite are shown in Fig. 3 d. The spectra in the hydroxyl stretching region of this mineral are more complex. Raman bands are observed at 3519 , 3282 , 2821 and 2345 cm^{-1} . Infrared bands are observed at 3538 , 3469 , 3286 , 2929 and 2549 cm^{-1} . The mineral thometzekite does not have any hydroxyl units in the formula. Thus all of the bands are due to OH stretching vibrations of water units. The Raman and infrared spectra of tsumcorite are shown in Fig. 3 e. Three bands are observed in the Raman spectrum at 3510 , 3272 and 2938 cm^{-1} . In the infrared spectrum bands are observed at 3533 , 3403 , 3234 , 2929 and 2601 cm^{-1} . The highest wavenumber band is probably due to the hydroxyl stretching vibration of the OH units. The other bands are attributed to water OH stretching bands.

Conclusions

A combination of Raman spectroscopy at both ambient and liquid nitrogen temperatures and infrared spectroscopy has been used to characterise the arsenates and sulphates of the tsumcorite mineral group. Extensive isomorphic substitution of sulphate for arsenate has been found. The fundamentals of the spectra are related to the structure of the minerals. 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. The range of OH stretching frequencies shows a range of hydrogen bond strengths based upon the range of calculated hydrogen bond distances. High wavenumber bands around $3400\text{--}3500\text{ cm}^{-1}$ indicate the presence of OH units in the tsumcorite minerals.

The tsumcorite arsenate minerals are characterised by typical spectra of the AsO_4 units. The symmetric stretching modes are observed in the $840\text{ to }880\text{ cm}^{-1}$ region; the antisymmetric stretching modes are observed in the $812\text{ to }840\text{ cm}^{-1}$ region. Some bands are observed around 765 cm^{-1} region and are attributed to water librational modes. The ν_4 bending modes are observed around 499 cm^{-1} and the ν_2 bending modes in the $300\text{ to }360\text{ cm}^{-1}$ region. Multiple bands are observed in these regions indicating a loss of symmetry of the AsO_4 unit.

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