# Raman spectroscopy of the multianion mineral gartrellite -$PbCu(Fe^{3+},Cu)(AsO_4)_2(OH,H_2O)_2$

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## Abstract

The multianion mineral gartrellite $PbCu(Fe^{3+},Cu)(AsO_4)_2(OH,H_2O)_2$ has been studied by a combination of Raman and infrared spectroscopy. The vibrational spectra of two gartrellite samples from Durango and Ashburton Downs were compared. Gartrellite is one of the tsumcorite mineral group based upon arsenate and sulphate anions. 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. Characteristic Raman spectra of the minerals enable the assignment of the bands to specific vibrational modes. These spectra are related to the structure of gartrellite. 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.

**Keywords:** Raman spectroscopy, gartrellite, tsumcorite, thometzekite, arsenate, sulphate

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## Introduction

The mineral gartrellite $PbCu(Fe^{3+},Cu)(AsO_4)_2(OH,H_2O)_2$ is triclinic with space group: *P*1, *a* = 5.431–5.460, *b* = 5.628–5.653, *c* = 7.565–7.589, α = 67.52−67.77, β = 69.27−69.57, γ = 70.04−70.31 and Z = 1 [1]. Gartrellite [2] is a rare mineral found in the oxidised mineralised shear zone cutting graywackes and shales as in the Anticline prospect, Australia and on fine-grained quartz-spessartine rocks at Broken Hill, Australia. The mineral is associated with hidalgoite–beudantite, quartz, spessartine (Broken Hill, Australia); mimetite, duftite, beudantite, bayldonite and quartz (Tsumeb, Namibia) [3].

Gartrellite is a member of the tsumcorite mineral group. The tsumcorite group of minerals are a mineral group based upon monoclinic and triclinic arsenates, phosphates, vanadates and sulphates of the general formulae $(M1)(M2)_2(XO_4)_2(OH,H_2O)_2$ where M1 is Pb,Ca or Na, M2 is Cu, Zn, $Fe^{3+}$, Co or Mn and X is As, P, V or S. The minerals gartrellite $Pb[(Cu,Zn)(Fe^{3+}, Zn, Cu)](AsO_4)(OH,H_2O)_2$, helmutwinklerite $Pb(Zn,Cu)_2(AsO_4)_2.2H_2O$ and thometzekite [4] are triclinic. The minerals ferrilotharmeyerite [5] $Ca(Fe^{3+},Zn)_2(AsO_4)_2(OH,H_2O)_2$ , lotharmeyerite $Ca(Mn^{3+},Zn)_2(AsO_4)_2(OH,H_2O)_2$, mawbyite [6] $Pb(Fe^{3+},Zn)_2(AsO_4)_2(OH,H_2O)_2$, mounanaite $Pb(Fe^{3+})_2(VO_4)_2(OH)_2$, natrochalcite [7] $NaCu_2(SO_4)_2(OH,H_2O)_2$ and tsumcorite [8] $Pb(Zn,Fe^{3+})_2(AsO_4)_2(OH,H_2O)$ are monoclinic. [8].

There are some problems associated with writing the mineral formula, in that the formula may change as a function of the degree of solid solution formation and the amount of isomorphic substitution. Both anion and cation substitution may occur. Sulphate, phosphate and carbonate may replace arsenate. For example, it is quite comprehensible that a formula such as $PbCu(Fe^{3+}, Cu)(AsO_4)_2(OH,H_2O)_2$ is possible Variation in mineral composition is expected for gartrellites from different origins. The formula may be written as $Pb[(Cu,Fe^{2+})(Fe^{3+}, Zn, Cu)] (AsO_4)(CO_3,H_2O)_2$. For example, the gartrellite found at Ashburton Downs, Western Australia has a calculated formula of $PbCu_{1.5}Fe^{2+}_{0.5}As_{1.5}(SO_4)_{0.5}(CO_3)_{0.5}(H_2O)_{0.2}$. 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 as to whether the mineral is triclinic or not.

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 and space group C2/m. The triclinic members of the tsumcorite group are gartrellite, zincian gartrellite, phosphogartrellite, helmutwinklerite, and probably (sulphate-free) thometzekite; the space group is P1 with a pronounced monoclinic C-centered pseudocell. The triclinic distortion is caused by an ordered arrangement of $Fe[6]O_6$ octahedra and tetragonal bi-pyramidal $Cu[4+2]O_6$ polyhedra [5].

Raman spectroscopy has proven very useful for the study of minerals [9-15]. Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with minerals containing sulphate, arsenate and/or phosphate groups. Raman spectroscopy is especially useful when the minerals are X-ray non-diffracting or poorly diffracting and very useful for the study of amorphous and colloidal minerals. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. In this work we attribute bands at various wavenumbers to vibrational modes of gartrellite using Raman spectroscopy and relate the spectra to the structure of the mineral.

## Experimental

### Minerals

Gartrellite was obtained from Museum Victoria with sample number m39987 and originated from the Anticline Deposit, Ashburton Downs, WA. A second sample of the mineral gartrellite was supplied by The Mineralogical Research Company. The sample originated from the Ojuela Mine, Mapini, Durango. Mexico. Details of the gartrellite mineral have been published (page 207) [3].

### Raman spectroscopy

Crystals of gartrellite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 $cm^{-1}$ and a precision of ± 1 $cm^{-1}$ in the range between

100 and 4000 $cm^{-1}$. Repeated acquisition on the crystals using the highest magnification (50x) was accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 $cm^{-1}$ line of a silicon wafer.

**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 $cm^{-1}$ range were obtained by the co-addition of 128 scans with a resolution of 4 $cm^{-1}$ and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Band component analysis was undertaken using the Jandel 'Peakfit' (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations ( $r^2$) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

**Results and discussion**

**Arsenate vibrations**

According to Myneni *et al.* [16, 17] and Nakamoto [18], $(AsO_4)^{3-}$ is a tetrahedral unit, which exhibits four fundamental vibrations: the Raman active $\nu_1$ symmetric stretching vibration ($A_1$) 818 $cm^{-1}$; the Raman active doubly degenerate $\nu_2$ symmetric bending vibration ($E$) 350 $cm^{-1}$, the infrared and Raman active triply degenerate $\nu_3$ antisymmetric stretching vibration ($F_2$) 786 $cm^{-1}$, and the infrared and Raman active triply degenerate $\nu_4$ bending vibration ($F_2$) 405 $cm^{-1}$. Protonation, metal complexation, and/or adsorption on a mineral surface will cause the change in $(AsO_4)^{3-}$ symmetry from $T_d$ to lower symmetries, such as $C_{3v}$, $C_{2v}$ or even $C_1$. This loss of degeneracy causes splitting of degenerate vibrations of $(AsO_4)^{3-}$ and the shifting of the As-OH stretching vibrations to different wavenumbers. Sulphates as with other oxyanions lend themselves to analysis by Raman spectroscopy [19]. In aqueous systems, the sulphate anion is of $T_d$ symmetry and is characterised by Raman bands at 981 $cm^{-1}$ ($\nu_1$), 451 $cm^{-1}$ ($\nu_2$), 1104 $cm^{-1}$ ($\nu_3$) and 613 $cm^{-1}$ ($\nu_4$). Reduction in

symmetry in the crystal structure of sulphates, such as in a number of minerals, will cause the splitting of these vibrational modes.

Such chemical interactions reduce $(AsO_4)^{3-}$ tetrahedral symmetry, as mentioned above, to either $C_{3v}/C_3$ (corner-sharing), $C_{2v}/C_2$ (edge-sharing, bidentate binuclear), or $C_1/C_s$ (corner-sharing, edge-sharing, bidentate binuclear, multidentate) [16, 17]. In association with $(AsO_4)^{3-}$ symmetry and coordination changes, the $A_1$ band may shift to different wavenumbers and the doubly degenerate *E* and triply degenerate *F* modes may give rise to several new $A_1$, $B_1$, and/or *E* vibrations [16, 17]. In the absence of symmetry deviations, $(AsO_3OH)^{2-}$ in $C_{3v}$ symmetry exhibit the $\nu_s$ As-OH and $\nu_{as}$ and $\nu_s$ $(AsO_3OH)^{2-}$ vibrations together with corresponding the δ As-OH in-plane bending vibration, δ As-OH out-of-plane bending vibration, $\nu_s$ $(AsO_3OH)^{2-}$ stretching vibration and $\delta_{as}$ $(AsO_3OH)^{2-}$ bending vibration [20-22]. Keller [20] observed the following infrared bands in $Na_2(AsO_3OH)\cdot 7H_2O$ 450 and assigned bands at 360 $cm^{-1}$ to $\delta_{as}$ ($\nu_4$) $(AsO_3OH)^{2-}$ bend (*E*), 580 $cm^{-1}$ to the δ As-OH out-of-plane bend, 715 $cm^{-1}$ to the ν As-OH stretch ($A_1$), 830 $cm^{-1}$ to the $\nu_{as}$ $(AsO_3OH)^{2-}$ stretch (*E*), and 1165 $cm^{-1}$ to the δ As-OH in plane bend. In the Raman spectrum of $Na_2(AsO_3OH)\cdot 7H_2O$, Vansant *et al.* [21] attributed Raman bands to the following vibrations 55, 94, 116 and 155 $cm^{-1}$ to lattice modes, 210 $cm^{-1}$ to ν (OH…O) stretch, 315 $cm^{-1}$ to $(AsO_3OH)^{2-}$ rocking, 338 $cm^{-1}$ to the $\delta_s$ $(AsO_3)^{2-}$ bend, 381 $cm^{-1}$ to the $\delta_{as}$ $(AsO_3OH)^{2-}$ bend, 737 $cm^{-1}$ to the $\nu_s$ As-OH stretch ($A_1$), 866 $cm^{-1}$ to the $\nu_{as}$ $(AsO_3OH)^{2-}$ stretch (*E*).

## Raman and Infrared Spectroscopy

The Raman spectrum of the Durango gartrellite in the 700 to 1000 $cm^{-1}$ region is displayed in Figure 1a. Five Raman bands are observed at 799, 811, 830, 866 and 891 $cm^{-1}$. The last two bands are assigned to the Raman active $\nu_1$ symmetric stretching vibration ($A_1$). The first three bands are assigned to the infrared and Raman active triply degenerate $\nu_3$ antisymmetric stretching vibration ($F_2$). The Raman spectrum of the Ashburton Downs gartrellite is reported in Figure 1b. Raman bands are observed at 754, 810, 842 and 868 $cm^{-1}$. The gartrellite sample from Ashburton Downs displays additional bands at 995, 1096 and 1158 $cm^{-1}$. These bands were not observed in the spectrum of the Durango gartrellite. The band at 995 $cm^{-1}$ is assigned to the $SO_4^{2-}$ symmetric stretching mode and the two bands at 1096 and 1158 $cm^{-1}$ to the $SO_4^{2-}$ antisymmetric stretching mode.

The infrared spectrum of Durango gartrellite is shown in Figure 2. The infrared spectrum consists of a broad profile which may be resolved into component bands at 723, 782, 804, 826, 842 and 897 $cm^{-1}$. Other low intensity bands are found on the low wavenumber side at 579, 587 and 629 $cm^{-1}$; and on the high wavenumber side at 1002, 1023, 1076 and 1105 $cm^{-1}$. One probable assignment, in harmony with the Raman data is that the bands at 723, 782 and 804 $cm^{-1}$ are due to the $\nu_3$ antisymmetric stretching vibrations and the bands at 842 and 897 $cm^{-1}$ are due to the $\nu_1$ symmetric stretching vibration. The low intensity bands between 1000 and 1200 $cm^{-1}$ are attributed to the sulphate stretching vibrations.

The Raman spectra of the Durango and Ashburton Downs gartrellite in the 100 to 600 $cm^{-1}$ region are shown in Figures 3a and 3b respectively. This spectral region is where the arsenate and sulphate bands overlap. This makes the exact assignment of bands difficult. Raman bands for the Durango gartrellite are observed at 421, 454, 487 and 507 $cm^{-1}$ and for the Ashburton Downs gartrellite at 435, 473 and 498 $cm^{-1}$. These may be ascribed to the $AsO_4^{3-}$ $\nu_4$ bending modes. It is probable that the Raman bands at 554 $cm^{-1}$ (Durango) and 558 $cm^{-1}$ (Ashburton) are associated with $SO_4^{3-}$ bending modes. The Raman bands at 313, 338 and 382 $cm^{-1}$ (Durango) and 302, 328 and 355 $cm^{-1}$ (Ashburton) are assigned to the $AsO_4^{3-}$ $\nu_2$ bending modes. The Raman spectra in the 100 to 300 $cm^{-1}$ region of the two gartrellite samples are different. Intense Raman bands are observed at 180 $cm^{-1}$ (Durango) and 200 $cm^{-1}$ (Ashburton) are thought to be associated with hydrogen bonding of OH units and water units to the arsenate and sulphate anions. It is also expected that some bands are associated with Pb or Cu oxygen stretching bands.

The Raman spectrum of the Durango and Ashburton Downs gartrellites in the hydroxyl stretching region are displayed in Figures 4a and 4b, respectively. The spectrum consists of a broad spectral profile centred upon 3090 $cm^{-1}$ and a sharp band at 3514 $cm^{-1}$. This broad spectral profile may be resolved into component bands at 2975, 3090 and 3240 $cm^{-1}$. These latter three bands are assigned to water stretching bands, whilst the band at 3514 $cm^{-1}$ is assigned to the OH stretching vibration. Raman bands of the Ashburton Downs gartrellite are observed at 2989 and 3217 $cm^{-1}$ are assigned to the water stretching vibrations and the band at 3396 $cm^{-1}$ assigned to the OH stretching band. What is immediately obvious is that the spectra in this spectral region are different. The position of the band assigned to the OH stretching vibration is very different. This difference is attributed to the strength of the

hydrogen bond between the OH units and the arsenate anions. The hydrogen bonding in the Ashburton Downs gartrellite is significantly stronger.

The infrared spectrum of the Durango gartrellite is reported in Figure 5. The infrared spectrum strongly resembles the Raman spectrum. The spectrum consists of a broad spectral profile and a sharp intense band at 3515 $cm^{-1}$. This sharp band is assigned to the OH stretching vibration of the OH units. The broad spectral profile may be resolved into component bands at 2525, 2762, 2956 and 3088 $cm^{-1}$. The position of these bands provides evidence for strong hydrogen bonding between the water and the arsenate anions in the mineral structure.

The Raman spectrum in the 1350 to 1850 $cm^{-1}$ is displayed in Figure 6a. The concept of strong hydrogen bonding in gartrellites is supported by the infrared spectrum in the 1250 to 1750 $cm^{-1}$ region (Figure 6b) where an infrared band at 1677 $cm^{-1}$ is found. This band is attributed to water HOH bending modes. The bands at 1445, 1523 and 1586 $cm^{-1}$ are attributed to OH deformation modes. The Raman equivalent water bending mode is not observed in the Raman spectrum. This is not unexpected as water is a notoriously bad Raman scatterer. The Raman spectrum suffers from a lack of signal to noise. The bands observed are attributed to OH deformation modes.

## Conclusions

A combination of Raman spectroscopy and infrared spectroscopy has been used to characterise the arsenates and sulphates in the mineral gartrellite. Two gartrellite minerals from different origins were studied. The spectra of the two mineral samples were different. Extensive isomorphic substitution of sulphate for arsenate is observed. The fundamental internal modes in the spectra are related to the structure of the minerals. Gartrellite shows a much greater sulphate isomorphic substitution. The range of OH stretching wavenumbers shows a range of hydrogen bond strengths based upon the range of calculated hydrogen bond distances. High wavenumber bands around 3400-3500 $cm^{-1}$ indicate the presence of OH units in the gartrellite structure. Gartrellite minerals are characterised by typical spectra of

the $AsO_4^{3-}$ units. The symmetric stretching modes are observed in the 840 to 880 $cm^{-1}$ region; while the antisymmetric stretching modes are observed in the 812 to 840 $cm^{-1}$ region. Some bands are observed around 765 $cm^{-1}$ and are attributed to water librational modes. The $\nu_4$ bending modes are observed around 499 $cm^{-1}$ and the $\nu_2$ bending modes in the 300 to 360 $cm^{-1}$ region. Multiple bands are observed in these regions indicating a loss of symmetry of the $AsO_4$ unit.

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# List of Figures

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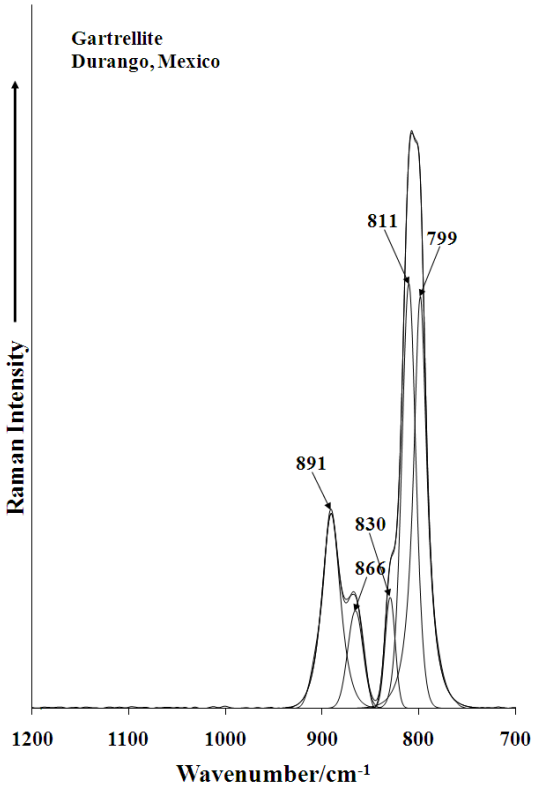


**Figure 1a**

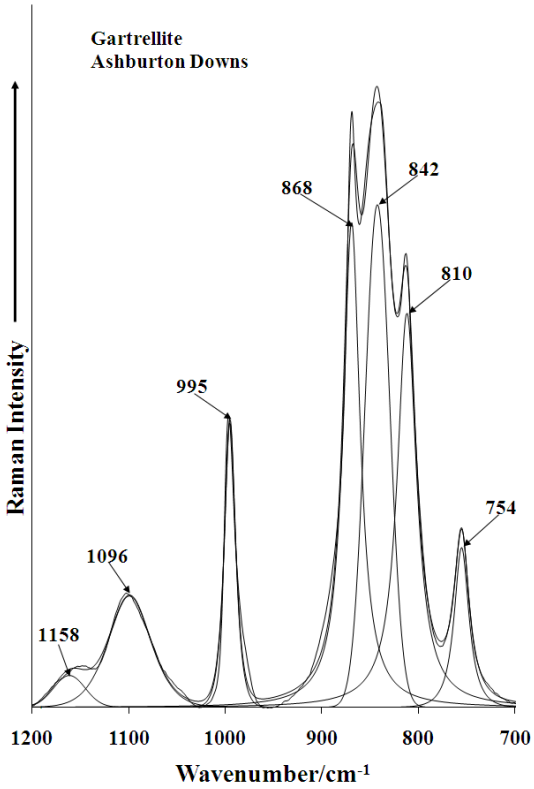


**Figure 1b**

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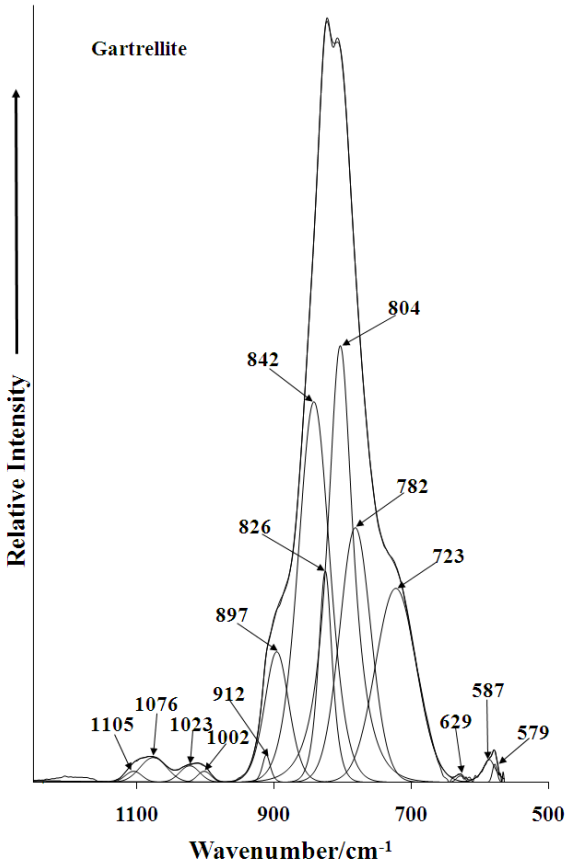


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284 **Figure 2**

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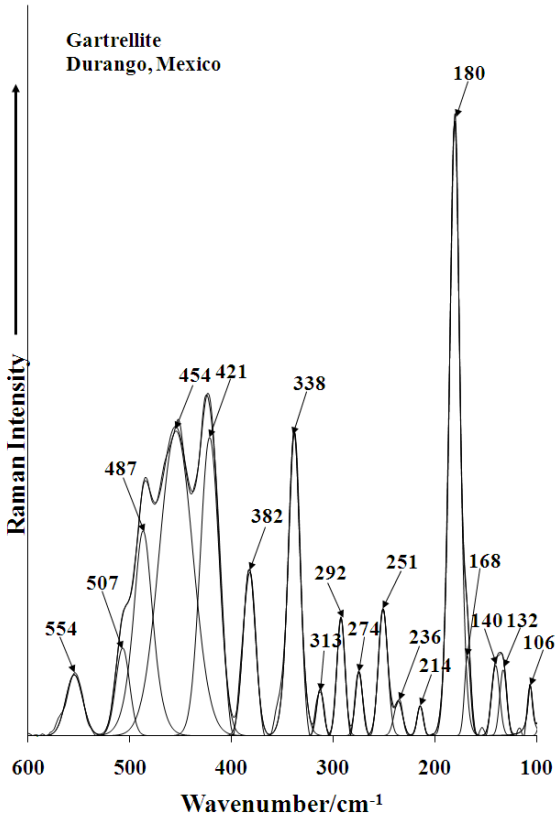


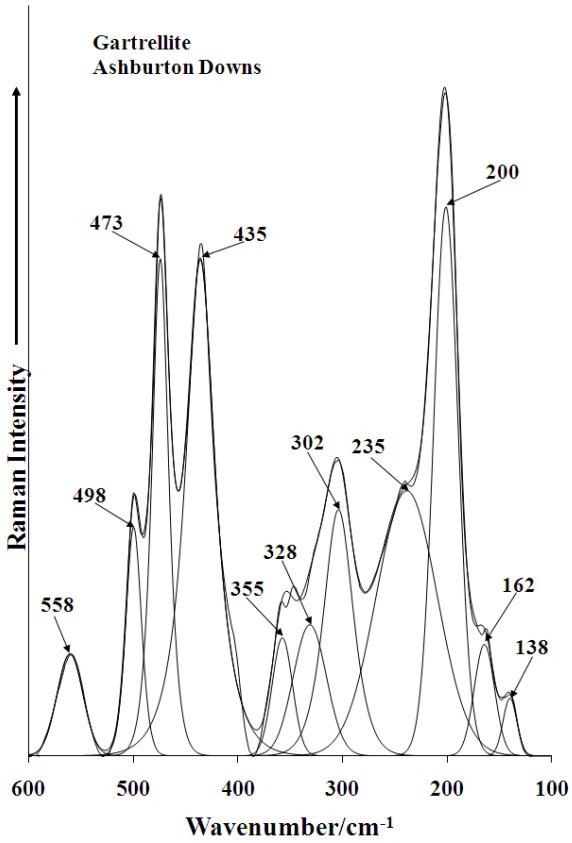


**Figure 3a**

**Figure 3b**

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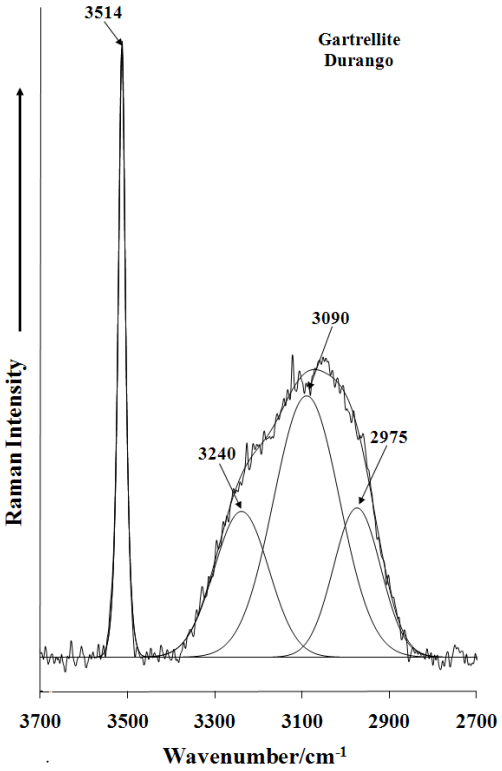


**Figure 4a**

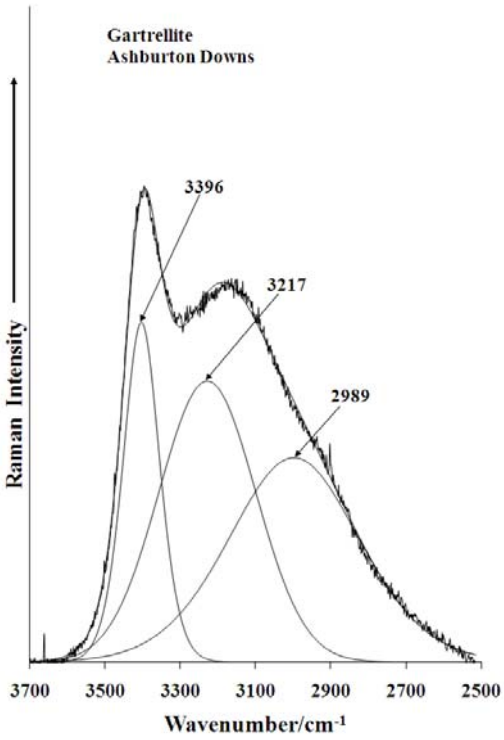


**Figure 4b**

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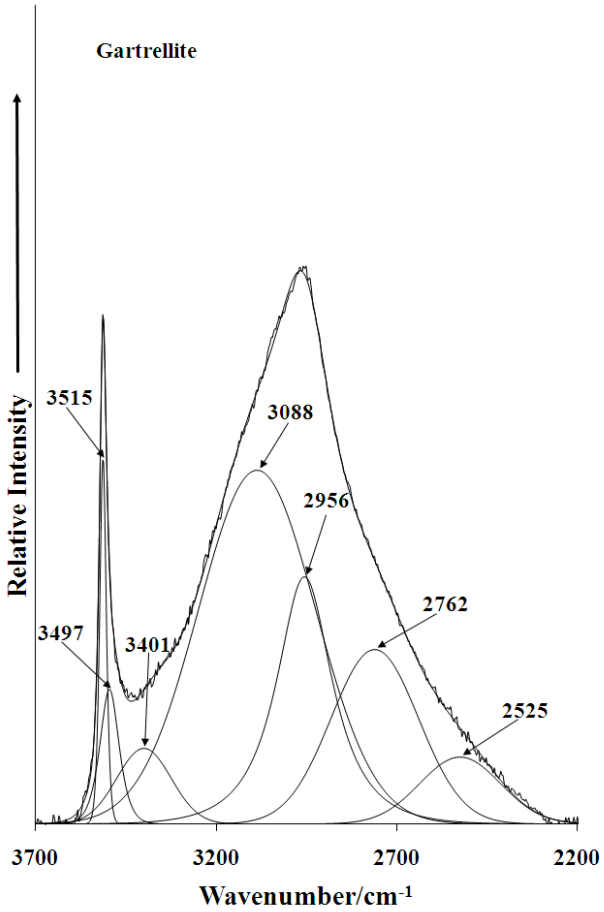


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297 **Figure 5**

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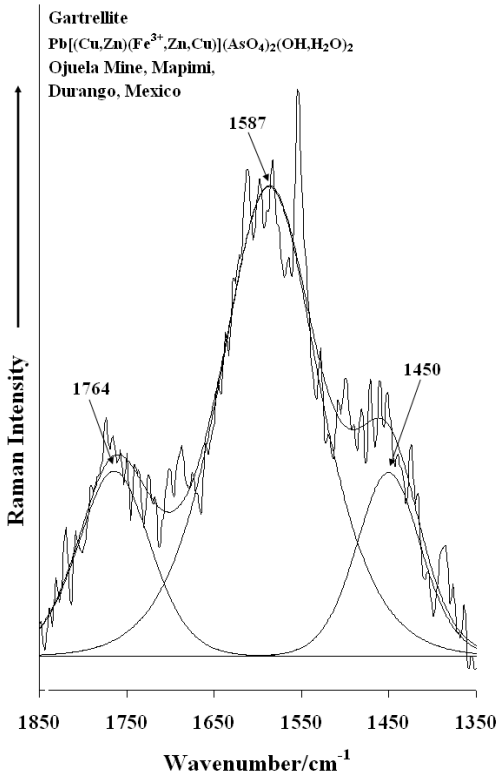


**Figure 6a**

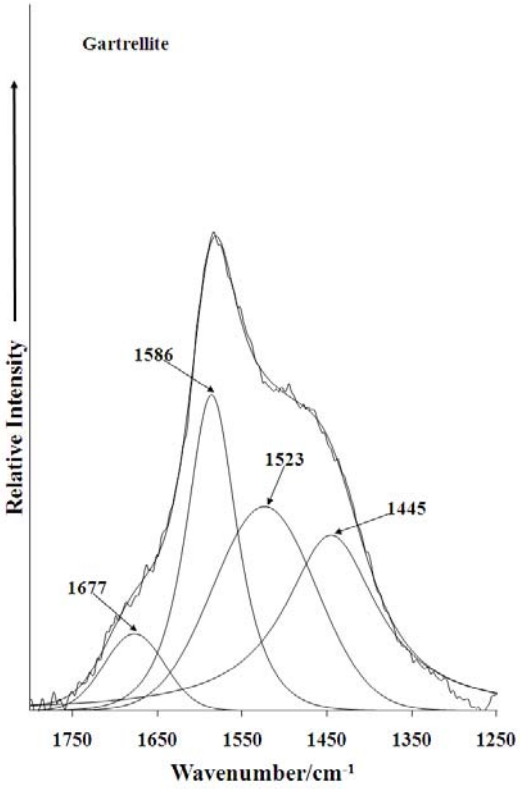


**Figure 6b**

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