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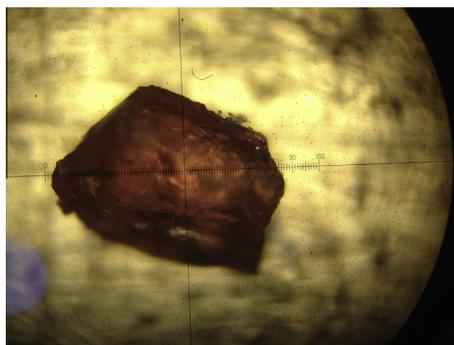
## Structural characterization and vibrational spectroscopy of the arsenate mineral wendwilsonite

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### HIGHLIGHTS

- We have studied the arsenate mineral wendwilsonite.
- A comparison is made with the roselite mineral group.
- The Raman arsenate stretching region shows strong differences between that of wendwilsonite and roselite.
- By using a Libowitzky empirical equation, hydrogen bond distances of 2.65 and 2.75 Å are estimated.
- Vibrational spectra enable the molecular structure of the wendwilsonite mineral to be determined.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In this paper, we have investigated on the natural wendwilsonite mineral with the formulae  $\text{Ca}_2(\text{Mg,Co})(\text{AsO}_4)_2 \cdot 2(\text{H}_2\text{O})$ . Raman spectroscopy complimented with infrared spectroscopy has been used to determine the molecular structure of the wendwilsonite arsenate mineral. A comparison is made with the roselite mineral group with formula  $\text{Ca}_2\text{B}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$  (where B may be Co,  $\text{Fe}^{2+}$ , Mg, Mn, Ni, Zn).

The Raman spectra of the arsenate related to tetrahedral arsenate clusters with stretching region shows strong differences between that of wendwilsonite and the roselite arsenate minerals which is attributed to the cation substitution for calcium in the structure.

The Raman arsenate  $(\text{AsO}_4)^{3-}$  stretching region shows strong differences between that of wendwilsonite and the roselite arsenate minerals which is attributed to the cation substitution for calcium in the structure. In the infrared spectra complexity exists of multiple to tetrahedral  $(\text{AsO}_4)^{3-}$  clusters with anti-symmetric stretching vibrations observed indicating a reduction of the tetrahedral symmetry. This loss of degeneracy is also reflected in the bending modes. Strong Raman bands around  $450 \text{ cm}^{-1}$  are assigned to  $\nu_4$  bending modes. Multiple bands in the  $350\text{--}300 \text{ cm}^{-1}$  region assigned to  $\nu_2$  bending modes provide evidence of symmetry reduction of the arsenate anion. Three broad bands for wendwilsonite found at 3332, 3119 and  $3001 \text{ cm}^{-1}$  are assigned to OH stretching bands. By using a Libowitzky empirical equation, hydrogen bond distances of 2.65 and 2.75 Å are estimated. Vibrational spectra enable the molecular structure of the wendwilsonite mineral to be determined and whilst similarities exist in the spectral patterns with the roselite mineral group, sufficient differences exist to be able to determine the identification of the minerals.

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## Introduction

Wendwilsonite is an arsenate of calcium and magnesium and is ideally of formula  $\text{Ca}_2\text{Mg}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$  [1]. The mineral is the magnesium analogue of roselite [2] and forms a continuous series with this mineral. The mineral is pale pink to red and may be color zoned. The mineral has a triclinic structure with point group  $(2/m)$ . The space group is  $(P21/c)$  and unit cell data are  $a = 5.806(1) \text{ \AA}$ ,  $b = 12.912(2) \text{ \AA}$ ,  $c = 5.623(1) \text{ \AA}$ ,  $\beta = 107^\circ 24'$ ,  $V = 402.2(1) \text{ \AA}^3$ , and two molecular formula per unit cell ( $Z = 2$ ).

The vibrational modes of oxyanions in aqueous systems are well known. The symmetric stretching vibration of the arsenate anion ( $\nu_1$ ) is observed at  $810 \text{ cm}^{-1}$  and coincides with the position of the antisymmetric stretching mode ( $\nu_3$ ). The symmetric bending mode ( $\nu_2$ ) is observed at  $342 \text{ cm}^{-1}$  and the antisymmetric bending mode ( $\nu_4$ ) at  $398 \text{ cm}^{-1}$ . The positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring oxyanions. Farmer [3] lists a number of infrared spectra of arsenates including roselite, annabergite, erythrite, sympleosite and köttigite. The effect of reduced site symmetry in the crystal (compared with the free arsenate ion) will remove the degeneracy and allow splitting of the bands according to factor group analysis. Farmer based upon the work of Moenke reported the infrared spectra of roselite [3]. Farmer listed two bands at  $985$  and  $920 \text{ cm}^{-1}$  and assigned these bands to the  $\nu_1$  ( $\text{AsO}_4$ )<sup>2-</sup> symmetric stretching vibrations [3]. The  $\nu_3$  ( $\text{AsO}_4$ )<sup>2-</sup> symmetric stretching vibrations were listed as  $870$ ,  $850$  and  $805 \text{ cm}^{-1}$ . The assignment of these bands does not appear to be correct. The  $\nu_4$  bending modes were found at  $453$  and  $435 \text{ cm}^{-1}$ . No  $\nu_2$  bands were provided. A band at  $535 \text{ cm}^{-1}$  was not assigned but may well be attributed to a water libration mode. No OH stretching vibrations were tabled. For comparison Farmer listed the  $\nu_1$  and  $\nu_3$  bands of annabergite at  $832 \text{ cm}^{-1}$  and  $795 \text{ cm}^{-1}$ . The  $\nu_4$  bending modes were found at  $510$ ,  $460$  and  $427 \text{ cm}^{-1}$  for annabergite. Two OH stretching vibrations were observed at  $3430$  and  $3160 \text{ cm}^{-1}$  for annabergite. A number of bands were listed which were unassigned. To the best of our knowledge, few Raman spectra of the fairfieldite or roselite mineral subgroups have been undertaken [4].

Few comprehensive studies of the fairfieldite and roselite mineral subgroups and related minerals such as divalent cationic arsenates have been undertaken [3]. Most of the infrared data predates the advent of Fourier transform infrared spectroscopy [5–10]. Although some Raman studies of some arsenate minerals have been undertaken [11,12] no Raman spectroscopic investigation of roselite arsenate minerals has been forthcoming. Griffith [13] did report the results of the Raman spectrum of a synthetic annabergite. The symmetric stretching mode of the tetrahedral ( $\text{AsO}_4$ )<sup>2-</sup> clusters was observed at  $859 \text{ cm}^{-1}$ ; the antisymmetric stretching mode at  $880 \text{ cm}^{-1}$ , the symmetric bending mode at  $438 \text{ cm}^{-1}$  and antisymmetric bending mode at  $452 \text{ cm}^{-1}$ ; other bands were located at  $797$  and  $820 \text{ cm}^{-1}$  [13]. The structural investigation of some arsenates and the nature of the hydrogen bond in these structures have been undertaken [14]. It was found that the hydroxyl unit was coordinated directly to the metal ion and formed hydrogen bonds to the arsenate anion [14].

As part of a comprehensive study of the molecular structure of minerals containing oxyanions using of the IR and Raman spectroscopy, we report the vibrational spectroscopic properties of the above named wendwilsonite.

## Experimental

### Samples description and preparation

The wendwilsonite sample studied in this work was collected from the Bou Azzer district, Morocco. The mineral occurs in

association with dolomite and shows prismatic habitus. The sample was incorporated into the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-112. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) was applied to support the chemical characterization.

The Bou Azzer district is well known as an important source of arsenates. The region is the type locality of a number of minerals, including wendwilsonite.

### Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil.

Wendwilsonite crystal aggregate was coated with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and was applied to support the mineral characterization.

### Raman microprobe spectroscopy

Crystals of wendwilsonite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with  $10\times$ ,  $20\times$ , and  $50\times$  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 polarized light at  $633 \text{ nm}$  and collected at a nominal resolution of  $2 \text{ cm}^{-1}$  and a precision of  $\pm 1 \text{ cm}^{-1}$  in the range between  $200$  and  $4000 \text{ cm}^{-1}$ . Repeated acquisitions on the crystals using the highest magnification ( $50\times$ ) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the  $520.5 \text{ cm}^{-1}$  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  $4000$ – $525 \text{ cm}^{-1}$  range were obtained by the co-addition of 128 scans with a resolution of  $4 \text{ cm}^{-1}$  and a mirror velocity of  $0.6329 \text{ cm/s}$ . Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of  $r^2$  greater than 0.995.

## Results and discussion

### Chemical characterization

The SEM image of wendwilsonite sample studied in this work is shown in Fig. 1. The image shows a wendwilsonite crystal with prismatic habitus. The mineral occurs in association with small amounts of dolomite. Qualitative chemical analysis shows Ca and As as the dominant elements (Fig. 2). Minor amounts of Co, Mg, P and S were found (Fig. 2).

### Vibrational spectroscopy background

According to Myneni et al. [15,16] and Nakamoto [17],  $(\text{AsO}_4)^{3-}$  is a tetrahedral unit, which exhibits four fundamental vibrations: the Raman active  $\nu_1$  symmetric stretching vibration ( $A_1$ ) at  $818\text{ cm}^{-1}$ ; the Raman active doubly degenerate  $\nu_2$  symmetric bending vibration ( $E$ ) observed at  $350\text{ cm}^{-1}$ , the infrared and Raman active triply degenerate  $\nu_3$  antisymmetric stretching vibration ( $F_2$ ) found around  $786\text{ cm}^{-1}$ , and the infrared and Raman active triply degenerate  $\nu_4$  bending vibration ( $F_2$ ) observed at  $405\text{ cm}^{-1}$ . Protonation, metal complexation, and/or adsorption on a mineral surface will cause the change in  $(\text{AsO}_4)^{3-}$  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  $\text{AsO}_4^{3-}$  and the shifting of the As-OH stretching vibrations to different wavenumbers.

Such chemical interactions reduce  $\text{AsO}_4^{3-}$  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) [15,16]. In association with  $\text{AsO}_4^{3-}$  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 [15,16]. In the absence of symmetry deviations,  $\text{AsO}_3\text{OH}^{2-}$  in  $C_{3v}$  symmetry exhibit the  $\nu_s$  As-OH and  $\nu_{as}$  and  $\nu_s$   $\text{AsO}_3\text{OH}^{2-}$  vibrations together with corresponding the  $\delta$  As-OH in-plane bending vibration,  $\delta$  As-OH out-of-plane bending vibration,  $\nu_s$   $\text{AsO}_3\text{OH}^{2-}$  stretching vibration and  $\delta_{as}$  ( $\text{AsO}_3\text{OH}^{2-}$ ) bending vibration [18–20]. Keller [18] assigned observed the following infrared bands in  $\text{Na}_2(\text{AsO}_3\text{OH})\cdot 7\text{H}_2\text{O}$   $450$  and  $360\text{ cm}^{-1}$  to the  $\delta_{as}$  ( $\nu_4$ ) ( $\text{AsO}_3\text{OH}^{2-}$ ) bend ( $E$ ),  $580\text{ cm}^{-1}$  to the  $\delta$  As-OH out-of-plane bend,  $715\text{ cm}^{-1}$  to the  $\nu$  As-OH stretch ( $A_1$ ),  $830\text{ cm}^{-1}$  to the  $\nu_{as}$   $\text{AsO}_3\text{OH}^{2-}$  stretch ( $E$ ), and  $1165\text{ cm}^{-1}$  to the  $\delta$  As-OH in plane bend. In the Raman spectrum of  $\text{Na}_2(\text{AsO}_3\text{OH})\cdot 7\text{H}_2\text{O}$ , Vansant and Veken [19] attributed observed Raman bands to the following vibrations  $55$ ,  $94$ ,  $116$  and  $155\text{ cm}^{-1}$  to lattice modes,  $210\text{ cm}^{-1}$  to  $\nu(\text{OH}\cdots\text{O})$  stretch,  $315\text{ cm}^{-1}$  to ( $\text{AsO}_3\text{OH}^{2-}$ ) rocking,  $338\text{ cm}^{-1}$  to the  $\delta_s$

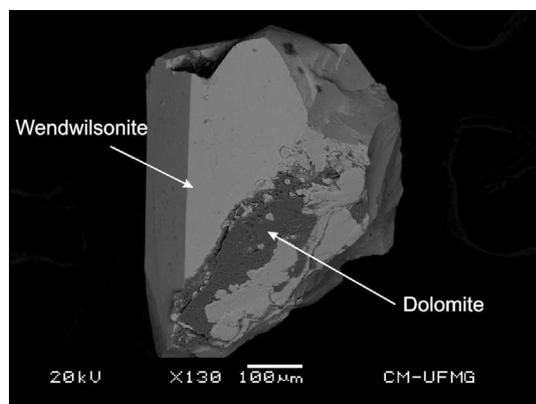


Fig. 1. Backscattered electron image (BSI) of a wendwilsonite single crystal up to 1.0 mm in length.

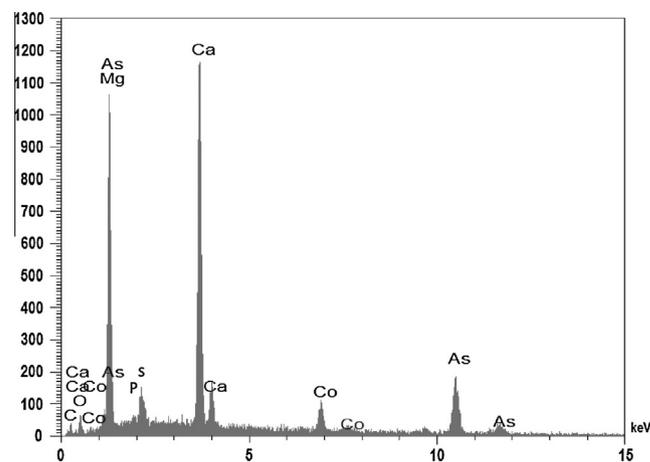


Fig. 2. EDS analysis of wendwilsonite.

( $\text{AsO}_3$ ) $^{2-}$  bend,  $381\text{ cm}^{-1}$  to the  $\delta_{as}$  ( $\text{AsO}_3\text{OH}^{2-}$ ) bend,  $737\text{ cm}^{-1}$  to the  $\nu_s$  As-OH stretch ( $A_1$ ),  $866\text{ cm}^{-1}$  to the  $\nu_{as}$  ( $\text{AsO}_3\text{OH}^{2-}$ ) stretch ( $E$ ).

### Vibrational spectroscopy

Spectroscopic methods are the most direct and powerful means of obtaining experimental information on the electronic structure of materials. Moreover, Raman spectroscopy is considered a powerful tool in order to estimate the degree of structural order–disorder at short-range in different types of the materials. The Raman spectrum of wendwilsonite over the  $100$ – $4000\text{ cm}^{-1}$  spectral range

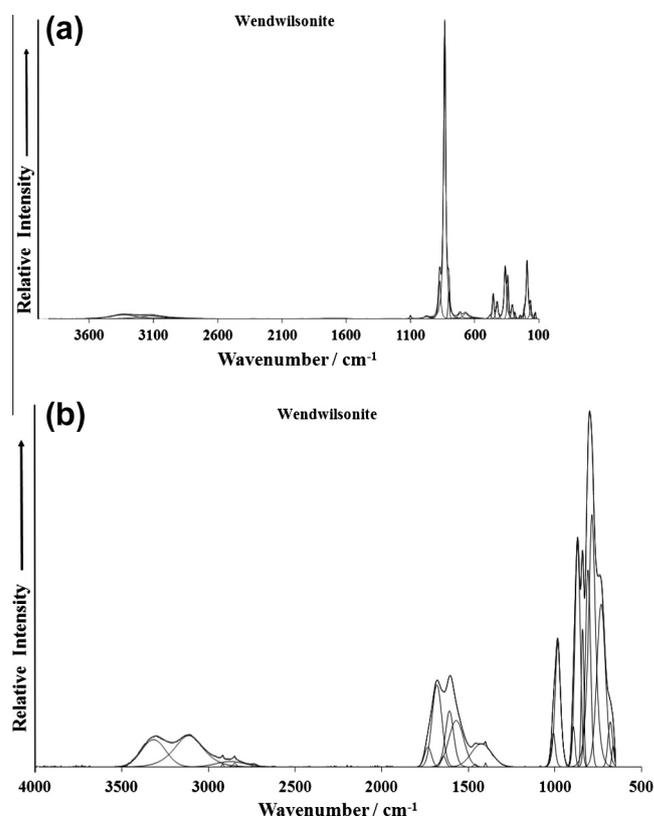


Fig. 3. (a) Raman spectrum of wendwilsonite over the  $4000$ – $100\text{ cm}^{-1}$  spectral range. (b) Infrared spectrum of wendwilsonite over the  $4000$ – $500\text{ cm}^{-1}$  spectral range.

is illustrated in Fig. 3a. This spectrum displays the position of the Raman bands and their relative intensities. Importantly, the intensity in the 3300–3100  $\text{cm}^{-1}$  region is low. There are large parts of the spectrum where no intensity or little intensity is observed, and therefore the spectrum is subdivided into sections depending upon the type of vibration being studied. It is noted that the intensity in the OH stretching region (3000–3600  $\text{cm}^{-1}$ ) is low. The infrared spectrum of wendwilsonite over the 500–4000  $\text{cm}^{-1}$  spectral range is shown in Fig. 3b. Significantly, more intensity is now observed in the infrared spectrum of the OH stretching region. This spectrum may be subdivided into subsections depending upon the type of vibration being studied.

The Raman spectrum of wendwilsonite in the 800–1300  $\text{cm}^{-1}$  spectral range is shown in Fig. 4a. The spectrum is dominated by a sharp band at 832  $\text{cm}^{-1}$  assigned to the  $\nu_1$  symmetric  $\text{AsO}_4^{3-}$  clusters symmetric stretching mode. A low intensity band is observed at 800  $\text{cm}^{-1}$  which may be assigned to the  $\nu_3$  antisymmetric tetrahedral  $\text{AsO}_4^{3-}$  clusters stretching vibration. A very low intensity band is found at 970  $\text{cm}^{-1}$ . This band is due to a  $\nu_1$  symmetric  $\text{PO}_4^{3-}$  stretching vibration [21,22]. The presence of this band indicates some phosphorus substitution for As in the wendwilsonite structure. Another very low intensity band is observed at 1098  $\text{cm}^{-1}$  and is indicative of the presence of carbonate.

The position of tetrahedral  $\text{AsO}_4$  clusters stretching bands appears to vary depending on the cation in the formula of the roselite subgroup mineral. Bands are observed for talmessite ( $\text{Ca}_2\text{Mg}$ ) at 828, 814 and 781  $\text{cm}^{-1}$ . For the talmessite ( $\text{Ca}_2\text{Co}$ ) Raman bands are observed at 868, 841 and 824  $\text{cm}^{-1}$ . For the mineral roselite two bands are observed at 864 and 798  $\text{cm}^{-1}$ . Raman bands have been observed at 854 and 800  $\text{cm}^{-1}$  for annabergites. In the roselite subgroup, Raman spectra, there does not appear to be

any phosphate isomorphic substitution. In the infrared spectra of roselite as reported by Farmer [3], two infrared bands were reported at 985 and 920  $\text{cm}^{-1}$ . These bands were assigned by Farmer [3] to the  $\nu_1$  symmetric stretching mode of the tetrahedral  $(\text{AsO}_4)^{3-}$  anions. Such an assignment in the light of these Raman results for roselite seems unlikely. A more likely assignment is to the  $\nu_1$  symmetric stretching mode of the tetrahedral  $(\text{PO}_4)^{3-}$  anion. This isomorphic substitution of phosphate for arsenate may in itself be unusual as whilst cationic isomorphic substitution is common, it is not known whether the anionic substitution is common. Current literature does not report any anionic isomorphic substitution. Raman spectral studies of the vivianite phosphates show that there is a band at 951  $\text{cm}^{-1}$  for vivianite and bobierite [21]. The bands are observed at 852 and 792  $\text{cm}^{-1}$  for erythrite and at 875 and 807  $\text{cm}^{-1}$  for hörnesite. No bands are observed in these positions for the roselite minerals. Bands at 841 (talnessite-Co), 828  $\text{cm}^{-1}$  (talnessite) 798  $\text{cm}^{-1}$  (roselite) are assigned to the  $\nu_1$  symmetric stretching modes of  $A_1$  symmetry. Griffith [13] reported Raman bands for a synthetic annabergite at 880, 859, 820 and 797  $\text{cm}^{-1}$ . The low intensity band observed around 864  $\text{cm}^{-1}$  for roselite is assigned to the  $E_{1g}$  mode.

The infrared spectrum of wendwilsonite over the 500–1300  $\text{cm}^{-1}$  spectral range is shown in Fig. 4b. A series of overlapping infrared bands are observed which may be resolved into component bands. The broad infrared band at around 800  $\text{cm}^{-1}$  resolved into component bands at 809 and 786  $\text{cm}^{-1}$  is assigned to the  $\nu_3$  antisymmetric tetrahedral  $\text{AsO}_4^{3-}$  clusters stretching modes. The infrared bands at 869 and 840  $\text{cm}^{-1}$  with a low intensity shoulder at 894  $\text{cm}^{-1}$  are attributed to the  $\nu_1$  symmetric tetrahedral  $\text{AsO}_4^{3-}$  clusters symmetric stretching mode. The infrared bands at 733, 680 and 663  $\text{cm}^{-1}$  are likely to be a water librational modes.

The spectra are a complex set of overlapping bands which may be curve-resolved into component bands as is shown. The pattern is similar for talnessite, roselite and messelite. However the pattern for the talnessite appears better resolved. The most intense infrared band for the roselite arsenates is observed at 785  $\text{cm}^{-1}$  and is assigned to the tetrahedral  $(\text{AsO}_4)^{3-}$  clusters antisymmetric stretching vibration. This band corresponds to the second intense band in the Raman spectra. The most intense band for vivianite arsenates was found to be at around 768–795  $\text{cm}^{-1}$  which corresponds well to the bands for the roselite mineral subgroup. Griffith [13] reported infrared bands at 795 and 832  $\text{cm}^{-1}$  for a synthetic annabergite. A band at around 825  $\text{cm}^{-1}$  is observed in all of the infrared spectra. The infrared spectrum of erythrite showed bands at 825 and 768  $\text{cm}^{-1}$ . Based upon the infrared spectra Farmer [3] reported bands at 825 and 783  $\text{cm}^{-1}$  for erythrite. Farmer found that the  $\nu_1$  and  $\nu_3$  modes using infrared spectroscopy were at 832 and 795  $\text{cm}^{-1}$  for annabergite, 825 and 783  $\text{cm}^{-1}$  for erythrite. Infrared bands were observed at 890, 868, 845, 828 and 790  $\text{cm}^{-1}$ . The complexity of the infrared spectra of this region is in agreement with Raman data. This complexity simply reflects the mixed cationic species in this hydrated roselite arsenates. The number of peaks reflects the bonding of the arsenate to different cations with consequent reduction in symmetry of the arsenate anion. This is in agreement with our Raman data, it is suggested that the two vibrations at 854 and around 790  $\text{cm}^{-1}$  are the tetrahedral  $\text{AsO}_4$  clusters symmetric and antisymmetric stretching vibrations respectively. Two additional bands are observed in the infrared spectra at around 560 and 690  $\text{cm}^{-1}$ . These two bands are not attributed to arsenate vibrations and since water is the only other molecule present in the structure then, these two bands are assigned to water librational modes. It is interesting that based upon the work of Moenke, Farmer [3] reported bands at 605  $\text{cm}^{-1}$  for the arsenate minerals annabergite and at 555  $\text{cm}^{-1}$  for erythrite, which were unassigned.

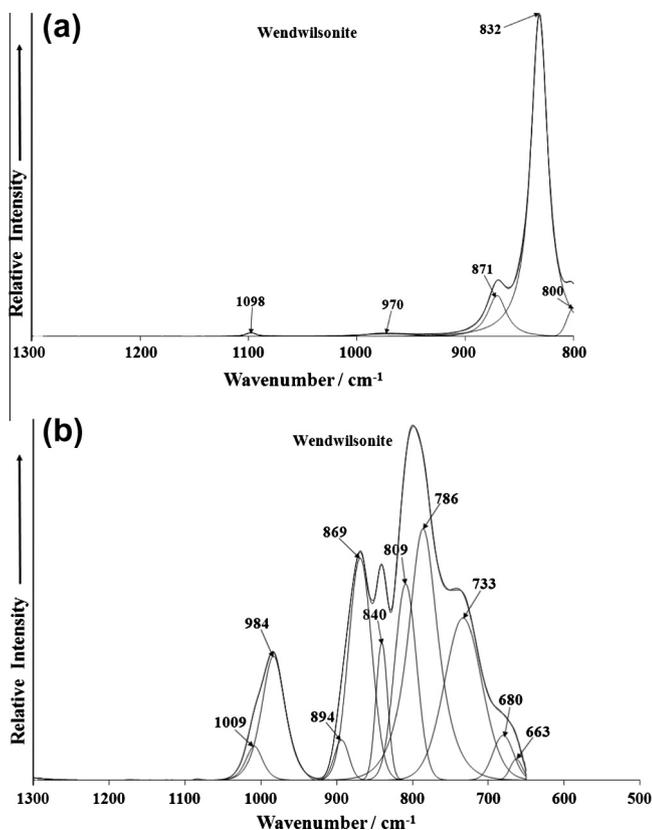


Fig. 4. (a) Raman spectrum of wendwilsonite over the 1400–800  $\text{cm}^{-1}$  spectral range. (b) Infrared spectrum of wendwilsonite over the 1300–500  $\text{cm}^{-1}$  spectral range.

The Raman spectra in the 300–800  $\text{cm}^{-1}$  and 100–300  $\text{cm}^{-1}$  spectral range are illustrated in Fig. 5a and b. Raman bands are observed at 425 and 454  $\text{cm}^{-1}$  and are assigned to the triply degenerate  $(\text{AsO}_4)^{3-}$  cluster bending vibration ( $F_2$ ,  $\nu_4$ ). Raman bands at 341 and 361  $\text{cm}^{-1}$  are due to the tetrahedral  $(\text{AsO}_4)^{3-}$  cluster  $\nu_2$  bending vibration. The band at 306  $\text{cm}^{-1}$  is ascribed to a metal oxygen stretching vibration. The band at 478  $\text{cm}^{-1}$  may be also assigned to the  $\nu_2$   $\text{PO}_4^{3-}$  bending mode. The Raman bands at 714, 669 and 626  $\text{cm}^{-1}$  may be due to water librational modes. An intense band is found at 191  $\text{cm}^{-1}$  with Raman bands of lower intensity observed at 127, 164, 212, 244 and 286  $\text{cm}^{-1}$ . These bands are simply described as external vibrations or lattice modes, although the last band at 286  $\text{cm}^{-1}$  may be due to a metal oxygen stretching band.

The low wavenumber region of roselite is complex and it is difficult to separate the Raman bands according to their symmetry. The spectrum of the low wavenumber region may be divided into three separate regions: (a) 450–400  $\text{cm}^{-1}$ , (b) 360–330  $\text{cm}^{-1}$  and (c) 250–100  $\text{cm}^{-1}$ . Three regions are assigned to (a)  $\nu_4$  modes, (b)  $\nu_2$  modes and (c) AsO stretching, bending and lattice modes. The  $\nu_4$  bending vibration should be common for all samples and should be intense. The most intense bands occur in two regions (a) around 450  $\text{cm}^{-1}$  and around 225  $\text{cm}^{-1}$ . The most intense band is observed at 452  $\text{cm}^{-1}$  for talmessite-Co, 466  $\text{cm}^{-1}$  for talmessite. Two bands are observed for roselite at 463 and 440  $\text{cm}^{-1}$ . The second most intense region in the Raman spectra is in the 360–300  $\text{cm}^{-1}$  region. For both the natural and synthetic annabergites, two bands are observed at 466 and 442  $\text{cm}^{-1}$  and for the arsenate mineral erythrite bands are observed at 457 and 439  $\text{cm}^{-1}$ . For the arsenate mineral köttigite bands are observed at 451 and 432  $\text{cm}^{-1}$ . These bands are

attributed to the  $\nu_4$  bending modes. The positions of these bands are observed at slightly lower wavenumbers for the arsenate mineral hörnesite and are found at 429 and 403  $\text{cm}^{-1}$ . Farmer [3] reported the infrared spectra of annabergite and erythrite and gave infrared band positions of 510, 460 and 427  $\text{cm}^{-1}$  for annabergite and at 490, 452 and 428  $\text{cm}^{-1}$  for erythrite. The latter two bands for these two minerals are in excellent agreement with the Raman bands reported in this work. Griffith [21] reported the  $\nu_4$  modes in the Raman spectra at 452 and 438  $\text{cm}^{-1}$ .

The Raman and infrared spectrum of wendwilsonite in the 2600–3800  $\text{cm}^{-1}$  spectral range are displayed in Fig. 6. Strong Raman bands are observed at 3332 and 3119  $\text{cm}^{-1}$  are attributed to water stretching vibrations. The infrared spectrum shows bands in similar positions at 3317 and 3113  $\text{cm}^{-1}$  ascribed to water stretching vibrations. Other low intensity infrared bands at 2918, 2848 and 2734  $\text{cm}^{-1}$  are described as CH stretching vibrations due to organic impurities.

Factor group analyses predict that there should be 12 active internal modes for each water site in these roselite hydrated arsenates including wendwilsonite. For talmessite-Co two Raman bands are observed at 3318 and 3167  $\text{cm}^{-1}$ , for talmessite three bands are observed at 3351, 3269 and 3180  $\text{cm}^{-1}$  and for roselite three broad bands are found at 3450, 3208 and 3042  $\text{cm}^{-1}$ . In general, four Raman bands should be observed in the hydroxyl-stretching region. Four bands have been found for annabergite, erythrite, köttigite and hörnesite. The lack of observation of four bands is not expected. This may be attributed to accidental degeneracy. There are two water molecules in the unit cell and consequently there are four OH units, which can vibrate both in-phase and out-of-phase, giving four bands. For annabergite four Raman

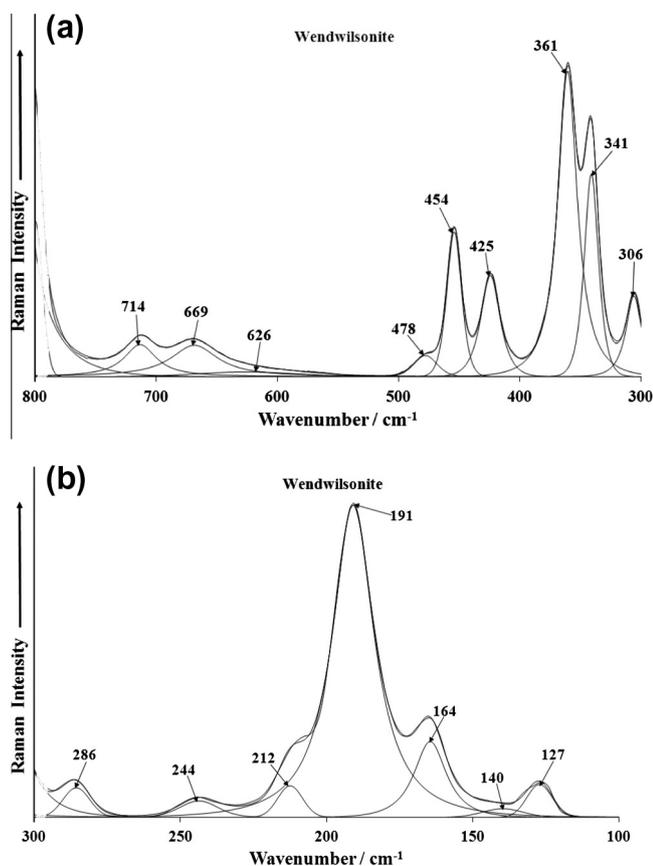


Fig. 5. (a) Raman spectrum of wendwilsonite over the 800–300  $\text{cm}^{-1}$  spectral range. (b) Raman spectrum of wendwilsonite over the 300–100  $\text{cm}^{-1}$  spectral range.

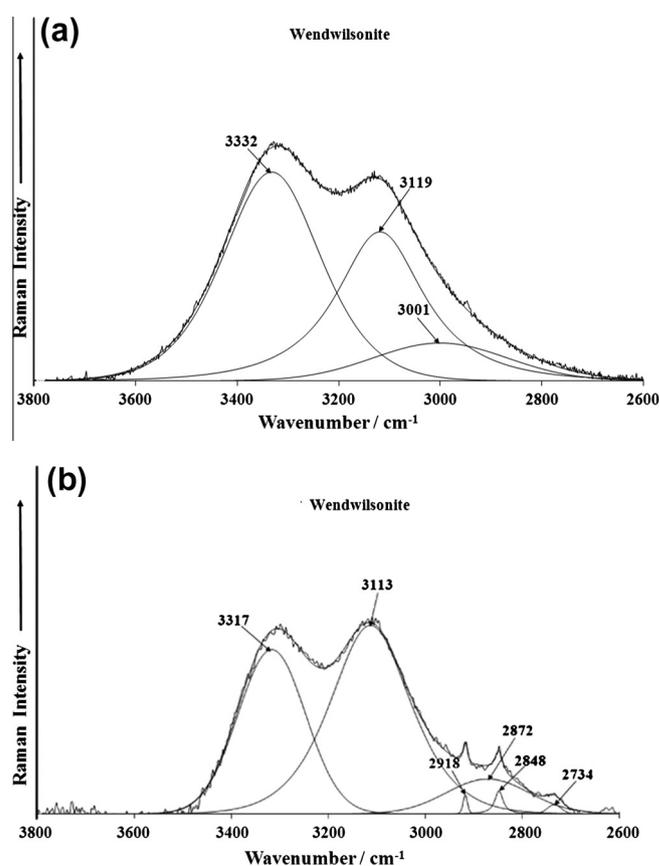


Fig. 6. (a) Raman spectrum of wendwilsonite over the 3800–2600  $\text{cm}^{-1}$  spectral range. (b) Infrared spectrum of wendwilsonite over the 3800–2600  $\text{cm}^{-1}$  spectral range.

bands are observed at 3419, 3209, 3185 and 3010  $\text{cm}^{-1}$ . The Raman spectrum of the natural köttigite like that of roselite is broad and two bands are observed at 3458 and 3215  $\text{cm}^{-1}$ . The Raman spectrum of hörnesite resembles that of annabergite and bands are observed at 3479, 3166 and 3030  $\text{cm}^{-1}$ . A comparison of the water OH stretching vibrations of these minerals enables the minerals to be classified.

The infrared spectra of the water OH stretching region of the roselite subgroup also show some similarity although some of the spectra are broad and suffer from a lack of signal to noise. Four infrared bands are found for talmessite at 3571, 3348, 3168 and 3027  $\text{cm}^{-1}$ . For talmessite infrared bands are resolved at 3339, 3265, 3239 and 3181  $\text{cm}^{-1}$ . An additional broad band is required at 3102  $\text{cm}^{-1}$  to fit the spectral profile. For roselite, infrared bands are found at 3320 and 3099  $\text{cm}^{-1}$ ; however the bands are broad and also suffer from a lack of signal. For comparison the infrared spectrum of annabergite showed OH stretching vibrations at 3412, 3155 and 2972  $\text{cm}^{-1}$ . These values may be compared with the published results of 3430 and 3160  $\text{cm}^{-1}$  [14]. The infrared spectra of erythrite appear to vary slightly depending on the origin of the natural sample. Without doubt this depends on the amount of cationic substitution. For the erythrite from Queensland, bands were observed at 3460, 3294 and 3099  $\text{cm}^{-1}$ . These values compare favourably with the published data [14]. For köttigite, IR bands were observed at 3440, 3185 and 3045  $\text{cm}^{-1}$ . These results may be compared with the published data of symplectite where only a single broad band at 3385  $\text{cm}^{-1}$  was observed. The infrared spectra of köttigite for a mixed cationic arsenate reported by Farmer [3] (page 399), showed three OH stretching bands at 3440, 3185 and 3045  $\text{cm}^{-1}$ . For hörnesite infrared bands were observed at 3478, 3273, 3142, 3038, and 3000  $\text{cm}^{-1}$ . The Raman spectrum

of wendwilsonite in the 1300–2000  $\text{cm}^{-1}$  spectral range is displayed in Fig. 7a and the infrared spectrum in the 1300–1800  $\text{cm}^{-1}$  spectra region is shown in Fig. 7b. The Raman spectrum suffers from a lack of signal which is not unexpected as water is a very poor Raman scatterer. In contrast, the infrared spectrum in this spectral range shows intense bands at 1609, 1643 and 1682  $\text{cm}^{-1}$ , assigned to the water bending modes. Water is a very strong infrared absorber and so the bands are intense in this spectral region.

Studies have shown a strong correlation between OH stretching frequencies and both the O...O bond distances and with the H...O hydrogen bond distances [22–25]. The elegant work of Libowitzky showed that a regression function could be employed relating the above correlations with regression coefficients better than 0.96 [26]. The OH stretching vibrations in the infrared spectra of wendwilsonite, enable the calculation of predicted hydrogen bond distances of 2.623 Å (2872  $\text{cm}^{-1}$ ), 2.679 Å (3113  $\text{cm}^{-1}$ ) 2.6232 Å (3317  $\text{cm}^{-1}$ ). Four hydrogen bond distances for talmessite are 2.76 Å, 2.72 Å, 2.71 Å and 2.697 Å. For roselite, hydrogen bond distances of 2.75 and 2.67 Å are calculated. Two types of water molecules are identified in the structure and the known hydrogen bond distances used to predict the hydroxyl stretching frequencies. The data fundamentally distinguishes between two types of water according to the hydrogen bond distances, namely strongly hydrogen bonded water and weakly hydrogen bonded water. However the predicted values do not take into account factor group splitting, accidental degeneracy and in-phase and out-of-phase vibrations. The strong hydrogen bonding would suggest that the thermal decomposition of the minerals would take place at significantly high temperatures. Some thermal studies were performed on collinsite, fairfieldite, and talmessite, and show the dehydration temperature increased with the strength of H bonds [27,28].

## Conclusions

A combination of Raman spectroscopy at ambient temperatures complimented with infrared spectroscopy has been used to characterize the arsenate known as wendwilsonite and also arsenates of the roselite mineral subgroup. Extensive isomorphous substitution of calcium by Mg or Co has been found for the roselite minerals. The fundamental vibrations in the spectra are related to the structure of the minerals. The wendwilsonite arsenate mineral is characterized by typical spectra of the tetrahedral arsenate clusters. The symmetric stretching modes are observed in the 800–880  $\text{cm}^{-1}$  region; the antisymmetric stretching modes are observed in the 814–824  $\text{cm}^{-1}$  region. Some bands are observed around 780  $\text{cm}^{-1}$  region and are attributed to water librational modes. The  $\nu_4$  bending modes are observed around 454  $\text{cm}^{-1}$  and the  $\nu_2$  bending modes in the 340–365  $\text{cm}^{-1}$  region. Multiple bands are observed in these regions indicating a loss of symmetry of the arsenate unit.

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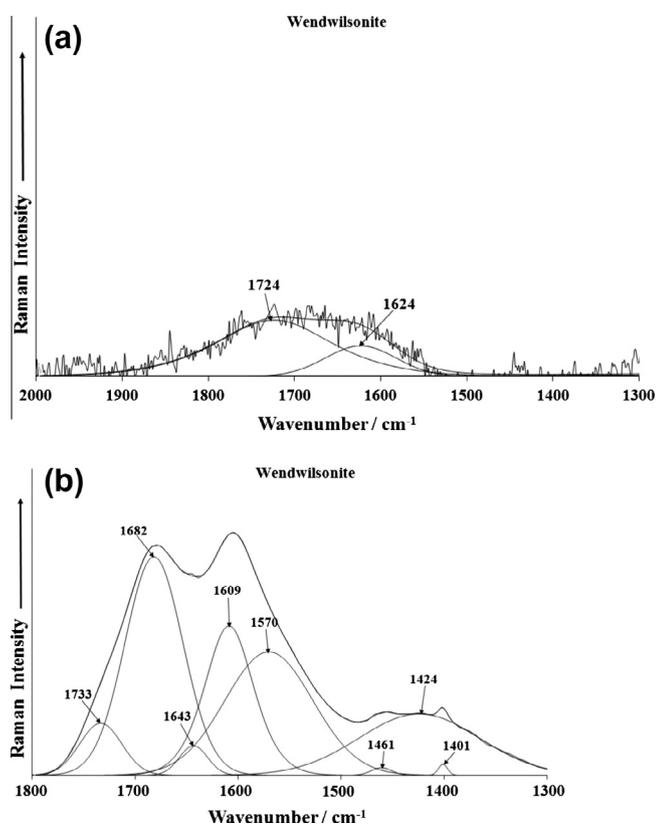


Fig. 7. (a) Raman spectrum of wendwilsonite over the 2000–1300  $\text{cm}^{-1}$  spectral range. (b) Infrared spectrum of wendwilsonite over the 1800–1300  $\text{cm}^{-1}$  spectral range.

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