



The structure of the mineral arthurite $\text{CuFe}_2^{3+}(\text{AsO}_4, \text{PO}_4, \text{SO}_4)_2(\text{O}, \text{OH})_2 \cdot 4\text{H}_2\text{O}$ – A Raman spectroscopic study

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ABSTRACT

Arthurite minerals $[\text{A}(\text{Fe}^{3+})_2(\text{XO}_4)_2(\text{O}, \text{OH})_2 \cdot 4(\text{H}_2\text{O})]$ where A = Cu(II), Zn(II), Pb(II) or Fe(II) and X = As, P, S] from different origins (Nevada and Cornwall) have been studied using Raman spectroscopy and complemented with infrared spectroscopy. These two arthurite minerals have the following formula $\text{Cu}(\text{Fe}^{3+})_2(\text{AsO}_4, \text{PO}_4, \text{SO}_4)_2(\text{O}, \text{OH})_2 \cdot 4(\text{H}_2\text{O})$. The presence of arsenate, phosphate, sulphate, and hydroxyl anions are readily characterised by Raman spectroscopy. The two arthurite samples observed significant differences in the position of Raman and infrared bands. The differences in band positions have been attributed to the different hydrogen bond strength of water in the two samples. Arthurite (a) has strongly hydrogen bonded water, whilst arthurite (b) has weakly hydrogen bonded water. The strength of the hydrogen bonded water influenced the position of the counter anions arsenate, phosphate and sulphate. For example, bands for (b) generally appeared at lower wavenumbers. A comparison with the Raman spectrum of cobaltarthurite has also been reported.

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1. Introduction

Arthurite is a rare copper iron arsenate mineral, which typically appears as green acicular crystals and belongs to the Arthurite Group [1]. The Arthurite Group is a group of monoclinic, hydrated iron arsenates and phosphates with a general formula of $\text{XFe}_2(\text{AO}_4)_2(\text{O}, \text{OH})_2 \cdot 2\text{H}_2\text{O}$. The X in the formula can be either copper, iron, manganese and/or zinc. The A in the formula can be either arsenic, phosphorus, or sulphate. The general formula for arthurite is $\text{CuFe}_2^{3+}(\text{AsO}_4, \text{PO}_4, \text{SO}_4)_2(\text{O}, \text{OH})_2 \cdot 4\text{H}_2\text{O}$, which is a mixed anionic mineral of copper and ferric iron [2]. In natural specimens of arthurite, the arsenate anion is the dominant counter anion, however all anions are usually present. The mineral is formed as a secondary mineral in the oxidation zone of some copper deposits by the alteration of arsenopyrite or enargite. Related species are earlshannonite, $(\text{Mn}, \text{Fe})\text{Fe}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, ojuelaite $\text{ZnFe}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, and whitmoreite $\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ [3]. The minerals are all monoclinic with space group: $P2_1/c$ with $a = 10.189(2)$, $b = 9.649(2)$, $c = 5.598(1)$ and $\beta = 92.16(2)$. The coordination polyhedron of Cu^{2+} is distinctly tetragonally elongated [4].

Raman spectroscopy has proven very useful for the study of minerals [1]. Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with minerals containing sulphate and phosphate groups. 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 arthurite using Raman spectroscopy and relate the spectra to the molecular structure of the mineral.

2. Experimental

2.1. Mineral

The mineral arthurite was purchased from The Mineralogical Research Company and originated from The Majuba Hill mine, Pershing County, Nevada, USA (referred to as arthurite a). A sample of arthurite was also purchased from the Mineralogical Research Company and originated from Hingston Down, Consols Mine, Calstock, Cornwall, England (referred to as arthurite b).

The minerals were confirmed by X-ray powder diffraction and the chemical analyses determined using an electron probe.

Raman spectra were also downloaded from the RRUFF database (<http://rruff.info/arthurite/display=default/>). An arthurite spectrum from Copper Stope, Majuba Hill mine, Pershing County, Nevada, USA was downloaded, along with a spectrum of cobaltarthurite from Dolores prospect, Pastrana, Mazarrón-Aguilas, Murcia, Spain. These arthurite spectra are given in the [Supplementary Information](#). The Raman spectra of RRUFF arthurite are shown in [Figs. S1a and S2a](#), while the Raman spectra of RRUFF cobaltarthurite are displayed in [Figs. S1b and 2b](#).

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2.2. Raman spectroscopy

Crystals of arthurite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is 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 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 (50×) were 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.

2.3. 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.

The infrared spectra are provided in the [Supplementary Information](#). The infrared spectra of arthurite (this work) from the Majuba Hill Mine and from Cornwall England is shown in Supplementary Fig. S3a and S3b (650–1100 cm⁻¹), Fig. S4a and S4b (875 to 1275 cm⁻¹) and Fig. S5a and S5b (2400–3800 cm⁻¹). These spectra are the result of the authors' research.

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.

3. Results and discussion

3.1. Background

The free arsenate ion ((AsO₄)³⁻) has tetrahedral symmetry and thus has four fundamental vibrations: the *v*₁ symmetric stretching vibration (*A*₁) at 820 cm⁻¹ (Raman active); the doubly degenerate *v*₂ symmetric bending vibration (*E*) at 350 cm⁻¹ (Raman active); the triply degenerate *v*₃ antisymmetric stretching vibration (*F*₂) at 785 cm⁻¹ (Raman and infrared active); and the triply degenerate *v*₄ bending vibration (*F*₂) at 405 cm⁻¹ (Raman and infrared active). In aqueous systems, the sulphate anion is of *T*_d symmetry and has a symmetric stretching mode (*v*₁) at 981 cm⁻¹, an antisymmetric stretching mode (*v*₃) at 1104 cm⁻¹, a symmetric bending mode (*v*₂) at 451 cm⁻¹ and a *v*₄ mode at 613 cm⁻¹. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (*v*₁) at 938 cm⁻¹, an antisymmetric stretching mode (*v*₃) at 1017 cm⁻¹, a symmetric bending mode (*v*₂) at 420 cm⁻¹ and a *v*₄ mode at 567 cm⁻¹.

Protonation, metal complexation and/or adsorption on a mineral surface should cause a change in the anions symmetry from *T*_d to lower symmetries, such as *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). Upon coordination

of the arsenate, phosphate, and sulphate anions to the copper atom in the arthurite mineral samples, the symmetry of the anions will reduce to *C*_{3v} and may further reduce to *C*_{2v}. The implication of this is that all bands will be both infrared and Raman active. In association with the anions 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.

3.2. Raman and infrared spectroscopy

The Raman spectrum of the anion-oxygen stretching region of arthurite from two different origins is shown in Fig. 1. For arthurite (a), Raman bands are observed at 779, 811, 845, 902, 976, 1044, 1057 and 1104 cm⁻¹. For arthurite (b), Raman bands are observed at 791, 866, 883, 991 and 1036 cm⁻¹. In the Raman spectra of these arthurite samples a very intense band is observed at 845 (a) and 883 (b) cm⁻¹. This band is assigned to the (AsO₄)³⁻ *v*₁(*A*₁) symmetric stretching mode. Significant differences are observed in the band position between the two samples. The authors have proposed an explanation of this observation in a latter section of the discussion. The Raman spectra of arthurite from the RRUFF database are displayed in the supplementary information in Fig. S1 (600 to 1200 cm⁻¹ region) and S2 (100–600 cm⁻¹ region). A very intense band is observed at 845 cm⁻¹ for the RRUFF arthurite and at 837 cm⁻¹ for cobaltarthurite. The positions of these bands correspond well with those observed for arthurite (a). These bands are also assigned to the (AsO₄)³⁻ *v*₁(*A*₁) symmetric stretching vibration.

Two Raman bands are observed at 779 and 811 cm⁻¹ (a) and at 791 cm⁻¹ (b) (Fig. 1). The intensity and broadness of the band at 791 cm⁻¹ for arthurite (b) may be the cause for the absence of the other band at around 810 cm⁻¹. The RRUFF spectra showed peaks at 780 and 813 cm⁻¹ for arthurite and 771 and 802 cm⁻¹ for cobaltarthurite. These bands are the second most intense band and are assigned to the (*B*_{2u}) mode. Griffith reported the Raman spectrum of the arsenate mineral olivenite [5] with bands at 880 (*A*¹), 856 (*B*_{2u}), 810 (*A*¹) and 790 (*B*_{2u}) cm⁻¹. The observation of the bands at 779 and 811 cm⁻¹ for the (AsO₄)³⁻ units of arthurite is in good agreement with the data published by Griffith [5].

In the infrared spectrum of the two arthurite minerals are displayed in Fig. S3. Arthurite (a) has intense infrared bands observed at 729, 757, 807, 837 and 868 cm⁻¹, while arthurite (b) has intense infrared bands found at 693, 755, 779, 798 and 825 cm⁻¹. Just as for the Raman data, significant differences are observed in the infrared spectra of the two arthurite minerals. The bands at 720 and 757 cm⁻¹ for arthurite (a) and at 779 and 798 cm⁻¹ for arthurite (b) are attributed to the (AsO₄)³⁻ *v*₃(*B*_{2u}) mode. The infrared bands for (a) at 807, 837 and 868 cm⁻¹, and 825 cm⁻¹ for (b) may be attributed to the (AsO₄)³⁻ *v*₁(*A*₁) symmetric stretching vibration.

The question arises as to the assignment of bands in the 900–1150 cm⁻¹ region. The mineral is renowned for isomorphic substitution, where the arsenate anion is replaced with either phosphate or sulphate or both anions. In the case of replacement by the sulphate anion, to maintain neutrality an additional negative charge must be introduced. This is done through the addition of a hydroxyl anion. In the spectrum of sample (a), the Raman band at 902 cm⁻¹ may be attributed to the (PO₄)³⁻ *v*₁(*A*₁) symmetric stretching vibration. A Raman band is observed for RRUFF arthurite (Fig. S1a) at 902 cm⁻¹. For cobaltarthurite (Fig. S1b) a strong band is observed at 897 cm⁻¹.

The peak at 976 cm⁻¹ for sample (a), may be attributed to the (SO₄)²⁻ *v*₁(*A*₁) symmetric stretching vibration. For sample (b), a bands may be curve resolved at 991 and 1036 cm⁻¹. The first band may be attributed to the sulphate stretching mode. The second

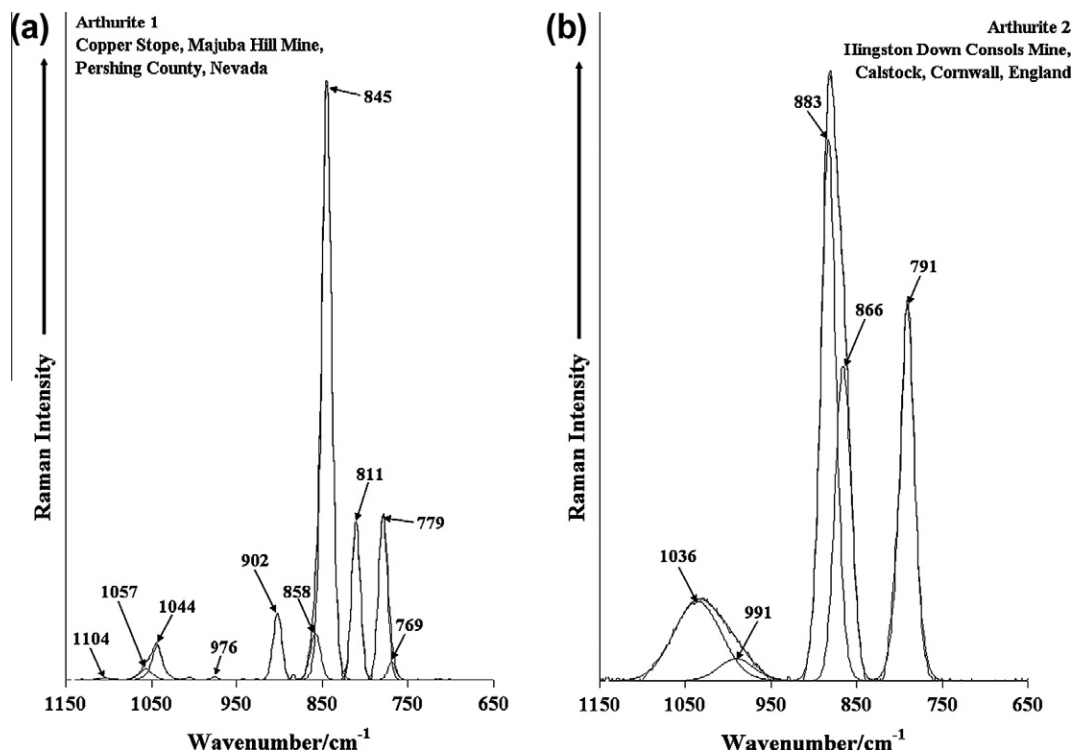


Fig. 1. Raman spectra of arthurite from (a) Nevada (b) Cornwall in the 650–1150 cm^{-1} range.

band at 1036 cm^{-1} may be composed of several overlapping components, which are attributable to the $(\text{PO}_4)^{3-}$ and $(\text{SO}_4)^{2-} \nu_3(E)$ antisymmetric stretching modes. The Raman bands for sample (a) at 1044, 1057 and 1104 cm^{-1} are also assigned to these antisymmetric vibrations. In the Raman spectrum of RRUFF arthurite, Raman bands were observed at 1045, 1060 and 1105 cm^{-1} . For cobaltarthurite a broad band at 1034 cm^{-1} was observed. A band in this position might also be assigned to a hydroxyl deformation mode.

The infrared bands of arthurite in the $875\text{--}1225\text{ cm}^{-1}$ region are given in Fig. S4. In this spectral region, the vibrations of the sulphate and phosphate oxyanions are expected. In the infrared spectrum of arthurite (a), the bands at 975 and 1005 cm^{-1} are assigned to the $(\text{PO}_4)^{3-}$ and $(\text{SO}_4)^{2-} \nu_1(A_1)$ symmetric stretching vibrations. The positions of these bands correspond well with the Raman bands observed, however, these bands are not so obvious in the infrared spectrum of (b). The resolved component bands at 963 and 995 cm^{-1} for (b) may be ascribed to these vibrational modes. The infrared bands for (a) at 1040, 1061, 1087 and 1094 cm^{-1} , and for (b) at 1037, 1084, 1119, 1167 cm^{-1} are attributed to $(\text{PO}_4)^{3-}$ and $(\text{SO}_4)^{2-} \nu_3(E)$ antisymmetric stretching vibrational modes. The assignment of each of these bands is difficult and questionable, however, the lower wavenumber bands are more likely to be due to the $(\text{PO}_4)^{3-}$ anion and the higher wavenumber bands to the $(\text{SO}_4)^{2-}$ anion.

In the Raman spectrum of arthurite (a), an intense band is observed at 504 cm^{-1} and for (b) at 478 cm^{-1} (Fig. 2). The band is found at 504 cm^{-1} for the RRUFF arthurite and at 500 cm^{-1} for cobaltarthurite. These bands are assigned to the $(\text{AsO}_4)^{3-} \nu_4(F_2)$ bending mode. Raman bands are observed for arthurite (a) at 421, 435 and 449 cm^{-1} and are assigned to the $(\text{AsO}_4)^{3-} \nu_2(E)$ bending mode. For arthurite (b), the $\nu_2(E)$ bending mode Raman bands are observed at 397 and 478 cm^{-1} . The far wavenumber region ($75\text{--}375\text{ cm}^{-1}$) is shown in Fig. 3. The Raman spectrum is significantly different between the two arthurite mineral samples in this spectral region.

Low intensity Raman bands are observed in the $1200\text{--}1800\text{ cm}^{-1}$ region (Fig. 4). For arthurite (a), Raman bands are observed at 1391, 1662 and 1735 cm^{-1} , and at 1385 and 1619 cm^{-1} for (b). The band at 1662 cm^{-1} is attributed to a very strongly hydrogen bonded water bending mode. The band position indicates that the water is strongly hydrogen bonded in the arthurite (a) structure. A low intensity band is also observed at 1735 cm^{-1} . The band remains unassigned [4]. In contrast, the spectrum of arthurite (b) has a band at 1619 cm^{-1} and is ascribed to weakly hydrogen bonded water. This difference in hydrogen bond strength of water is understood to have influenced the position of arsenate, phosphate, and sulphate bands. Thus, making the spectra of arthurite (a) and (b) appear different. It is not known what the band at 1391 cm^{-1} is due to, but perhaps it is an overtone such as the doubling of the symmetric stretching vibration. Just as for the water HOH bending region, the Raman spectra of the OH stretching region is different for the two arthurite samples (Fig. 5).

The infrared spectrum of arthurite in the $1200\text{--}1800\text{ cm}^{-1}$ range is provided in Fig. S5 (supplementary information). The infrared spectrum of arthurite (a) shows strong asymmetric bands and are observed at 1301, 1593, 1638 and 1653 cm^{-1} . The latter two bands are assigned to water strongly hydrogen bonded. The observation of two bands provides evidence for two non-equivalent water molecules in the arthurite (a) structure. Additional bands in the infrared spectrum is not unexpected as the weak intensity of the Raman bands in this region may hinder multiple bands to be observed. The broad low intensity infrared band at 1301 cm^{-1} is thought to be an overtone, also observed in the Raman spectrum. For arthurite (b), a broad intense infrared band is observed at 1627 cm^{-1} and is attributed to weak hydrogen bonded water. Shoulder bands found at 1528 and 1572 cm^{-1} have been assigned to very weakly hydrogen bonded water. The infrared spectrum in the water deformation region clearly shows that multiple bands exist, which is indicative of non-equivalent water molecules. These observations have shown that arthurite (a) has more strongly hydrogen bonded water than arthurite (b). However,

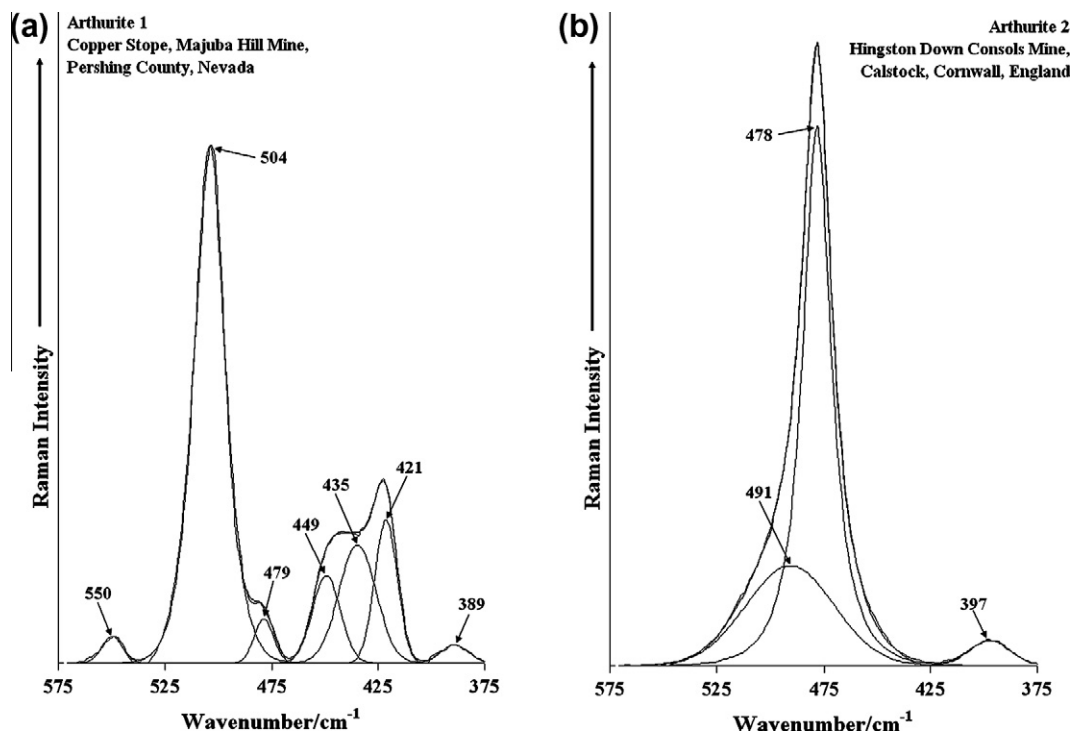


Fig. 2. Raman spectra of arthurite from (a) Nevada (b) Cornwall in the 375–575 cm^{-1} range.

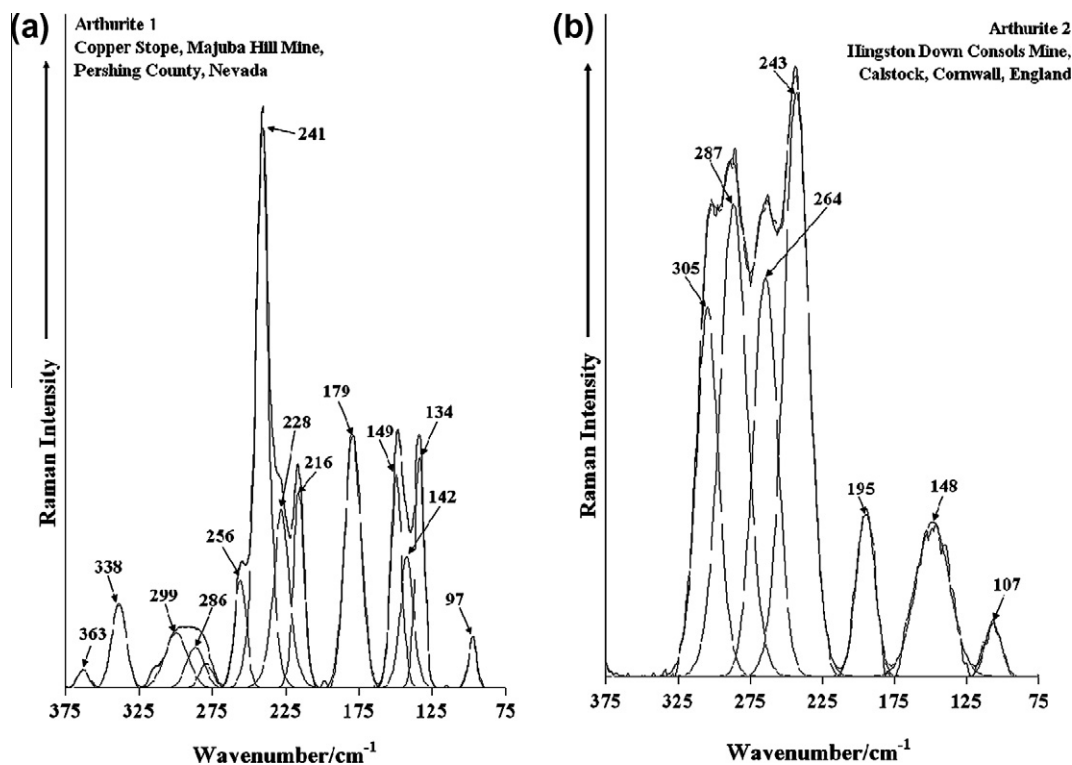


Fig. 3. Raman spectra of arthurite from (a) Nevada (b) Cornwall in the 75–375 cm^{-1} range.

arthurite (a) does also exhibit a small amount of weakly hydrogen bonded water.

The Raman spectra in the OH stretching region are displayed in Fig. 5. For arthurite (a), Raman bands are observed at 3161, 3240, 3324 and 3493 cm^{-1} . The latter band is sharp and is assigned to the stretching vibration of OH units. The first three bands are

ascribed to water stretching vibrations. For arthurite (b), Raman bands are observed at 3144, 3267, 3404, 3517 and 3609 cm^{-1} . The higher wavenumber bands between 3500 and 3650 cm^{-1} are assigned to the OH stretching vibrations, while the lower wavenumber bands are ascribed to water stretching vibrations. As in Fig. 4, the Raman spectra of the two arthurite samples are very

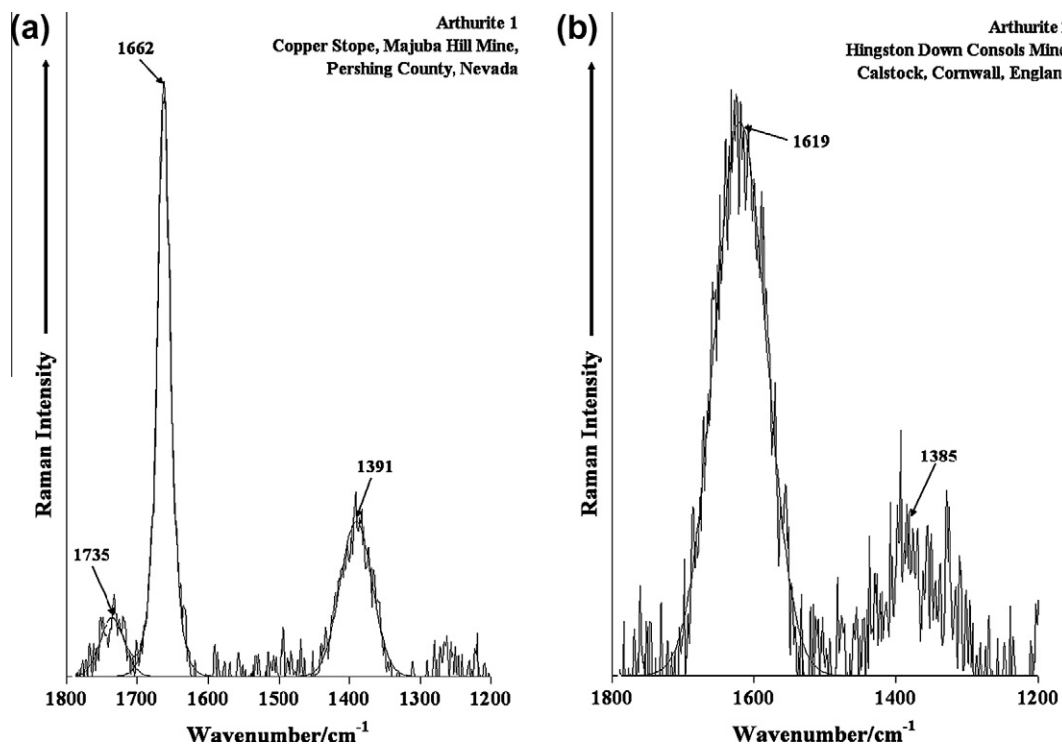


Fig. 4. Raman spectra of arthurite from (a) Nevada (b) Cornwall in the 1200–1800 cm⁻¹ range.

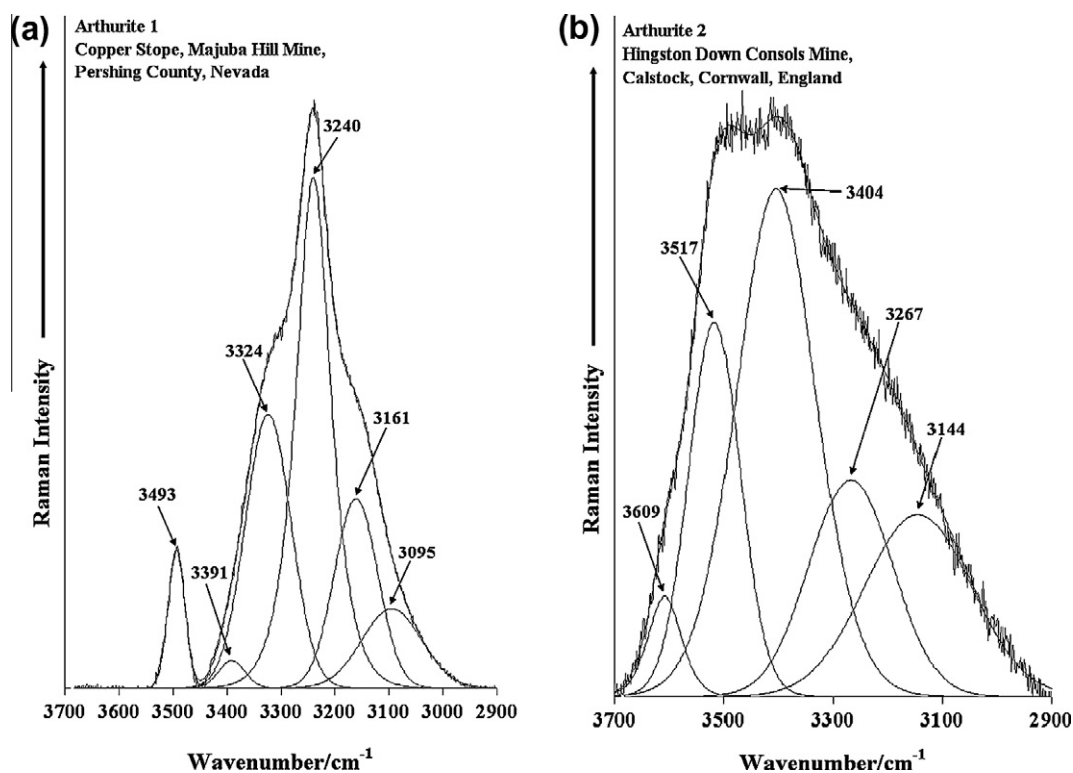


Fig. 5. Raman spectra of arthurite from (a) Nevada (b) Cornwall in the 2900–3700 cm⁻¹ range.

different. The infrared spectra of arthurite in this spectral region is displayed in Fig. S5. As seen for the Raman spectra, the spectral profile of the infrared spectrum is broad and a series of overlapping bands may be resolved. For arthurite (a), infrared bands are observed at 3026, 3156, 3232, 3317, 3409 and 3482 cm⁻¹. For

arthurite (b), infrared bands are observed at 3123, 3424, 3607 cm⁻¹. The distinct sharp bands at 3482 cm⁻¹ for arthurite (a) and at 3607 cm⁻¹ for (b) are assigned to the OH stretching vibration of OH units. The remaining bands are attributed to water stretching vibrations.

X-ray diffraction shows the two minerals have the same crystal structure, yet the molecular structure of the minerals are different. This difference is based upon the role of water in the arthurite structure (Fig. S6). Arthurite (a) exhibits water in two different hydrogen bonded states; (1) strongly hydrogen bonded water (1653 and 1638 cm^{-1} – IR) and (2) non-hydrogen bonded water (1593 cm^{-1} – IR). The structure of arthurite displays a layered type structure. Water can exist in the interlayer as non-hydrogen bonded water and simply functions as a space filler. Water in such a state has been observed for borates [6]. It is observed that only weakly or loosely hydrogen bonded water exists for arthurite (b), indicated by the significant shift of the water bending band to lower wavenumbers (1627 cm^{-1} – IR). Multiple bands in this region of the spectrum is evidence for non-equivalent water molecules in the arthurite mineral samples.

4. Conclusions

Raman complimented with infrared spectroscopy has been used to characterise the mineral arthurite. Arthurite is based upon a combination of hydroxyl, arsenate, phosphate and sulphate as counter ions in any variable ratio. The mineral is an unusual mineral from a chemistry point of view as the mineral contains both phosphate and sulphate anions. The assembly of anions in these minerals is important. Complex multi-anion minerals are formed rather than a mixture of separate minerals such as olivenite ($\text{Cu}_2\text{AsO}_4(\text{OH})$) and symplectite ($\text{Fe}^{3+}(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})$). It is assumed that such secondary mineral formation occurs under appropriate conditions of pH and temperature over long periods of time. The lattice content reflects changes in solution conditions when the free energy of formation of arthurite is less than the combination of the end members of simpler stoichiometry.

There were two types of water identified in the structure of the arthurite samples, namely weakly and strongly hydrogen bonded water molecules. The Raman and infrared spectra of arthurite (a) were different to arthurite (b), where the positions of bands for (b) generally appeared at lowered wavenumbers. An explanation of this observation is based on the strength of the hydrogen bonded water. Arthurite (a) had strongly hydrogen bonded water (Raman band at 1662 cm^{-1}), while arthurite (b) had weakly hydrogen bonded water (Raman band at 1619 cm^{-1}). The strength of the hydrogen bonded water then influenced the positions of arsenate, phosphate and sulphate band positions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.03.034.

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