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Molecular assembly in secondary minerals-
Raman spectroscopy of the arthurite group species arthurite and
whitmoreite

Ray L. Frost*, L Duong and W. Martens
Centre for Instrumental and Developmental Chemistry, Queensland University of
Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Abstract:

Two members of the arthurite mineral group, arthurite and whitmoreite
A(Fe$^{3+}$)$_2$(XO$_4$)$_2$(O,OH)$_2$$\cdot$4(H$_2$O) where A = Cu(II), Zn(II), Pb(II) or Fe(II) and X =
As, P, S have been studied using Raman spectroscopy. The minerals are based upon
the combination of a divalent cation such as Cu(II), Zn(II), Pb(II) or Fe(II) and the
trivalent cation, Fe(III), with counterbalancing of hydroxyl, arsenate, phosphate and
sulphate anions. Such minerals lend themselves to analysis by Raman spectroscopy.

For arthurite Cu(Fe$^{3+}$)$_2$(AsO$_4$,PO$_4$,SO$_4$)$_2$(O,OH)$_2$$\cdot$4(H$_2$O), arsenate and hydroxyl
anions are observed as well as minor phosphate and significant carbonate anions. For
whitmoreite Fe$^{2+}$Fe$^{3+}$$_2$(PO$_4$)$_2$(OH)$_2$$\cdot$4(H$_2$O), hydroxyls and phosphate are the major
anions with significant sulphate and some carbonate. Raman spectroscopic analysis
of two whitmoreite samples from the same mineral field suggests that differentiation
by concentration of the anions occurs in the molecular assembly of the anions as
crystallisation occurs as a function of the equilibrium conditions. Changing solution
conditions are reflected in the varying compositions in the lattice

Introduction

The mineral arthurite CuFe$^{3+}$$_2$(AsO$_4$,PO$_4$,SO$_4$)$_2$(O,OH)$_2$$\cdot$4H$_2$O is a mixed
anionic mineral of copper and ferric iron. (DAVIS & HEY 1964; DAVIS & HEY
1969) The mineral is formed as a secondary mineral in the oxidation zone of some
copper deposits, by the alteration of arsenopyrite or enargite. Related species are
earlshannonite, (Mn,Fe)Fe$^2$(PO$_4$)$_2$(OH)$_2$$\cdot$4H$_2$O, Ojuelaite ZnFe$_2$(AsO$_4$)$_2$(OH)$_2$$\cdot$4H$_2$O,
and whitmoreite Fe$^{2+}$Fe$^{3+}$$_2$(PO$_4$)$_2$(OH)$_2$$\cdot$4H$_2$O (MOORE & KAMPF 1977; MOORE
et al. 1974; PEACOR et al. 1984) The minerals are all monoclinic space group: P$2_1/c$
with a = 10.189(2), b = 9.649(2), c = 5.598(1) and $\beta$ = 92.16(2)$^\circ$. Arthurite is isotypic
with whitmoreite, Fe$^{2+}$ being replaced by Cu$^{2+}$ and P by As. The coordination
polyhedron of Cu$^{2+}$ is distinctly tetragonally elongated. (KELLER & BARTELKE
1982)

Recently the authors have applied Raman spectroscopy to the study of
minerals containing oxyanions including the elucidation of the structure of the basic
copper phosphate and arsenate minerals. (FROST et al. 2002b). Single crystal
Raman spectra of azurite and malachite have been obtained. (FROST et al. 2002a)
Raman spectra of the isomorphous series descloizite [PbZn(VO4)(OH)] and
mottramite [PbCu(VO4) (OH)] were obtained at 298 and 77 K. (FROST et al.

* Author to whom correspondence should be addressed (r.frost@qut.edu.au)
Raman spectroscopy has also been used to study the mixed anionic mineral chillagite. Further the molecular structure of some naturally occurring alums has been determined. The method has proven extremely powerful for studying hydrated (such as the vivianite minerals), hydroxylated (basic copper arsenates and phosphates) sulphated (natural alums) minerals. In this work we report the study of the mineral arthurite, an example of a multi-anionic mineral and an example of self assembled anions in Nature.

Experimental

Minerals:

The mineral arthurite was obtained from the Australian Museum, registered number D46007 and originated from The Majuba Hill mine, Pershing County, Nevada, USA. A sample of arthurite was purchased from the mineralogical research Co. and originated from Hingston Down, Consols Mine. Calstock, Cornwall, England.

Whitmoreite was obtained from the South Australian museum registered number G11383 and originated from Hargendorf-Sud, Bavaria, Germany. Other minerals in the arthurite series were not able to be sourced. The minerals were confirmed by X-ray powder diffraction and the chemical analyses determined using an electron probe.

Electron Probe microanalysis

The electron probe uses the characteristics X-ray generated from the interaction between the electron beam and the sample to identify elemental composition of the sample. Selected arthurite samples for electron probe were coated with carbon to provide a good conducting surface. The EPMA analyses were done on the Jeol 840 A Electron probe microanalyser at 20KV, 39mm working distance. Three samples were embedded in Araldite, polished with diamond paste on Lamplan 450 polishing cloth with water as lubricant. The Moran EDS software was used to analyse the samples in the fully standard mode. The secondary electron images were taken from the Jeol 35CF Scanning Electron Microscope, at 15 KV using Image Slave software to capture the image.

Raman microprobe spectroscopy

Crystals of the arthurite minerals were placed and orientated on a polished metal surface on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm\(^{-1}\) in the range between 100 and 4000 cm\(^{-1}\). Repeated acquisition using the highest magnification 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. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).
Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc 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 allows specific parameters to be fixed or varied accordingly. 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 correlations of $r^2$ greater than 0.995.

Results and discussion

Molecular assembly of cations and anions in secondary minerals is extremely elaborate. Arthurite is a classic example of such an assembly and it crystallises from an aqueous solution with whichever relevant anions are available in the solution. Anions may be phosphate, arsenate, sulphate and carbonate. The arthurite structure depends upon the combination of Cu(II) and Fe(III) ions (the presence of the ferric ion usually means that hydroxyl groups will be involved in the structure). The spectroscopy of arthurite may be conveniently divided into several regions depending on the type of coordinating anion. Such a description is applicable to many oxy-anion-containing minerals. The spectrum may be divided into (a) the OH stretching region (b) the anion XO stretching region where X may be As, P, S or some other non-metal (c) the OXO bending region and (d) the low wavenumber region.

Electron probe analysis

The electron probe analyses of the arthurite samples from USA and UK are shown in Figures 1 and 2. The analysis of the whitmoreite is shown in Figure 3. The analysis of the arthurite sample shows that the mineral is composed of CuO, FeO and As$_2$O$_5$ in the weight % ratio of 23.25, 50.76 and 26.01%. The mineral is true to the formula of arthurite as Cu(Fe$^{3+}$)$_2$(AsO$_4$)$_2$(OH)$_2$·4(H$_2$O). No phosphate or sulphate was detected. In comparison the oxide composition of the arthurite from the UK was determined as CuO, FeO, As$_2$O$_5$, P$_2$O$_5$ as 16.3, 41.77, 16.01 and 25.91%. This arthurite is a mixed anionic species of formula Cu(Fe$^{3+}$)$_2$(AsO$_4$,PO$_4$)$_2$(OH)$_2$·4(H$_2$O). The analysis of whitmoreite shows that the sample contains some Mn and the analysis is MnO, FeO, P$_2$O$_5$, As$_2$O$_5$ in the weight % ratio of 10.43, 41.19, 34.92 and 13.49%. The whitmoreite is of a formula (Mn$^{2+}$,Fe$^{2+}$)Fe$^{3+}$$_2$(PO$_4$,AsO$_4$)$_2$(OH)$_2$·4H$_2$O. Figures 4,5 and 6 shows the SEM images of arthurite from USA, arthurite from UK and whitmoreite from Germany.

Raman Microscopy

The Raman spectrum of the hydroxyl-stretching region of arthurite is shown in Figure 7. The results of the spectroscopic analysis are reported in Table 1. In the curve resolved spectrum at 298 K as for the 77 K spectra, four bands may be resolved. In the 298 K spectrum these are observed at 3490, 3309, 3236 and 3166 cm$^{-1}$. Bandwidths are 45.8, 155.5, 52.7 and 156.9 cm$^{-1}$. Bands are identified in the 77K spectrum at 3487, 3357, 3224 and 3005 cm$^{-1}$. The band at 3490 cm$^{-1}$ (3487 cm$^{-1}$ at 77 K) is assigned to the symmetric OH stretching vibration. The other bands are
attributed to water OH stretching bands. For arthurite the Raman spectrum also shows a very weak band centre at 1660 cm$^{-1}$. This is assigned to the water HOH bending mode. This band is normally observed in the infrared spectrum with moderate intensity. The position of the band at 1660 cm$^{-1}$ is indicative of strongly coordinated water.

The free arsenate ion has tetrahedral symmetry and thus should have four bands of which two are infrared active with theoretical values of $v_3 (F_2) 887$ cm$^{-1}$ and $v_4 (F_2) 463$ cm$^{-1}$. (FROST RAY L. et al. 2002; SUMIN DE PORTILLA 1974) Raman active modes are observed at 837 ($A_1$) and 349 (E) cm$^{-1}$. Upon coordination of the arsenate ion to the copper atom, then the symmetry of the arsenate ion reduces to $C_{3v}$ and may further reduce to $C_{2v}$. The implication is that all bands will be both infrared and Raman active. For example Frost et al. reported the Raman spectra of a series of basic copper arsenate minerals. (FROST RAY L. et al. 2002). In this work, for each mineral two intense bands were observed in the 298 K spectra. The Raman spectrum of olivenite showed two bands at 853 and 820 cm$^{-1}$; cornwallite at 859 and 806 cm$^{-1}$, cornubite at 815 and 780 cm$^{-1}$ and clinoclase at 823 and 771 cm$^{-1}$. The most intense band was assigned to the arsenate AsO $v_1(A_1)$ symmetric stretching vibration.

The Raman spectrum of the anion-oxygen stretching region is shown in Figure 8. For arthurite, bands are observed at 1044, 901, 882, 861, 843, 809 and 778 cm$^{-1}$. Bandwidths of these peaks are 20.0, 19.6, 14.9, 32.4, 14.9, 17.0, 15.7 and 67.0 cm$^{-1}$, respectively. In the 298 K Raman spectrum of arthurite a very intense band is observed at 843 cm$^{-1}$. This band is assigned to the symmetric AsO stretching vibration. The second most intense band is observed at 778 cm$^{-1}$ and is attributed to the ($B_{2u}$) mode. Griffith reported the Raman spectrum of the arsenate mineral olivenite (GRIFFITH 1970) with bands at 880 ($A'_1$), 856 ($B_{2u}$), 810 ($A'_1$) and 790 ($B_{2u}$) cm$^{-1}$. The observation of the bands at 882, 861, 809 and 778 cm$^{-1}$ for arthurite is in good agreement with the data published by Griffith. At 77 K, Raman bands are observed at 1078, 1051, 901, 874, 844, 810 and 778 cm$^{-1}$ with bandwidths of 77.7, 10.5, 14.0, 46.4, 12.2, 21.0 and 12.3 cm$^{-1}$ respectively. Considerable band narrowing is observed.

The band observed at 1044 cm$^{-1}$ (1051 cm$^{-1}$ in the 77 K spectrum) is attributed to the CO symmetric stretching mode of carbonate. (FROST et al. 2002a). The observation of carbonate in the mineral is a classic example of isomorphous substitution. The arsenate anion of course carries three negative charges and the carbonate anion two negative charges. Thus to balance the replacement of arsenate anion by carbonate, an extra negative charge to balance the cationic charges must be observed. In this case the additional negative charge comes from the hydroxyl units. Figure 9 displays the Raman spectrum of arthurite from England. The presence of arsenate is observed and the spectrum of the arthurite from the UK is close to that from USA. The spectrum clearly shows that additional bands resulting from isomorphous substitution are observable. A band is observed at 978 cm$^{-1}$ and is assigned to the SO symmetric stretching mode of sulphate. The band at ~1050 cm$^{-1}$ is ascribed to the presence of carbonate.

The low wavenumber region of the arthurites from Nevada (USA) and Cornwall UK is shown in Figure 10. The Raman spectra of the two arthurites are different in this region. The isomorphous substitution is even more evident in this
figure as additional bands are observed in the 500 cm$^{-1}$ region (Table 1). The intense sharp band at around 420 cm$^{-1}$ in the USA arthurite spectrum is assigned to the $v_4$ arsenate mode. The band is observed at 424 cm$^{-1}$ for the UK arthurite. Bands observed at 362 and 337 cm$^{-1}$ are assigned to $v_2$ bending modes.

The Raman spectra of two different whitmoreite samples from the same locality (Hargendorf-Sud, Bavaria, Germany) are shown in Figure 11. This particular arthurite group mineral is dominated by phosphate. The characteristic intense PO stretching band is observed at 973 cm$^{-1}$. The band appears to be split in spectrum (b). Two bands are observed at 986 and 968 cm$^{-1}$ and both bands are assigned to PO stretching vibrations. The antisymmetric ($v_3$) stretching modes are also evident in the spectra with bands observed at 1157 and 1144 cm$^{-1}$. Bands are also observed at around 1032 cm$^{-1}$ and may be attributed to the presence of carbonate. An intense band is also observed at around 935 cm$^{-1}$. It is probable that this band is also due to phosphate.

Figure 12 shows the Raman spectrum of the low wavenumber region of whitmoreite. The low wavenumber region is significant as the spectra in this region clearly show that the two samples are different. The band observed at 433 cm$^{-1}$ in spectrum (a) and assigned to the $v_2$ bending vibration is split into two components in spectrum (b) with bands observed at 411 and 439 cm$^{-1}$. The observation of two bands in this region is in agreement with two bands observed in the SO stretching region for the second sample of whitmoreite. The complex set of bands around 600 cm$^{-1}$ is ascribed to $v_4$ bending modes. For sample (a) bands are observed at 617, 593, 565 and 546 cm$^{-1}$ and for sample (b) bands are observed at 583, 561 and 541 cm$^{-1}$. In the Raman spectrum of sample (a) three intense bands are observed at 305 and 276 cm$^{-1}$ and also 243 cm$^{-1}$ but for sample (b) only a single band is observed at 305 cm$^{-1}$ with a second intense band at 243 cm$^{-1}$. It is considered that these are attributable to MO stretching vibrations.

The observation of the Raman spectra of two whitmoreite samples with different spectra has serious implications for the deposition of the secondary minerals and indicates the composition of the mineral changes over time of crystallization. This means that concentration zoning occurred. The kinetics of crystallization of the arthurite series must be such that thermodynamic equilibrium is not reached and pre-existing solution compositions are reflected in the zone structure. These results are also indicative of regular solid solution.

Conclusions

Raman spectroscopy has been used to study the molecular assembly of secondary minerals using the minerals arthurite and whitmoreite as examples. These contain hydroxyl, arsenate, phosphate, sulphate and carbonate as counter ions in any variable ratio. Arthurite is based upon a combination of arsenate and hydroxyl as counterions whilst whitmoreite is based upon the combination of phosphate, hydroxyl and some sulphate. Carbonate was also identified in both minerals. 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 and symplesite. It is assumed that such secondary mineral formation occurs under appropriate conditions of pH and temperature over long periods of time and lattice content reflect changes in
solution conditions when the free energy of formation of arthurite and whitmoreite is less than the combination of the end members of simpler stoichiometry.

The Raman technique is excellent for probing changes in chemistry associated with multiple substitution in complex lattices derived from multidimensional solid-solutions.

Acknowledgments

The financial and infra-structure support of the Queensland University of Technology Centre for Instrumental and Developmental Chemistry is gratefully acknowledged. The Australian research Council (ARC) is thanked for funding. Mr W.N. Martens is thanked for collecting some of the Raman data.

Mr Ross Pogson of the Australian Museum is thanked for the loan of a arthurite mineral. Prof Allan Pring, is thanked for the loan of arthurite and two whitmoreite minerals. The authors are indebted to the curators of the Museum mineral collections for their willingness to loan samples for spectroscopic analysis.

References


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