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The molecular structure of the mineral sarmientite $Fe_2(AsO_4,SO_4)_2(OH)_6{\cdot}5H_2O$ – Implications for arsenic accumulation and removal

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ABSTRACT

Sarmientite is an environmental mineral; its formation in soils enables the entrapment and immobilisation of arsenic. The mineral sarmientite is often amorphous making the application of X-ray diffraction difficult. Vibrational spectroscopy has been applied to the study of sarmientite. Bands are attributed to the vibrational units of arsenate, sulphate, hydroxyl and water.

Raman bands at 794, 814 and 831 cm^{-1} are assigned to the ν_3 $(AsO_4)^{3-}$ antisymmetric stretching modes and the ν_1 symmetric stretching mode is observed at 891 cm^{-1}. Raman bands at 1003 and 1106 cm^{-1} are attributed to SO_4^{2-} vibrations. The Raman band at 484 cm^{-1} is assigned to the triply degenerate $(AsO_4)^{3-}$ bending vibration. The high intensity Raman band observed at 355 cm^{-1} (both lower and upper) is considered to be due to the $(AsO_4)^{3-}$ ν_2 bending vibration. Bands attributed to water and OH stretching vibrations are observed.

1. Introduction

The mineral sarmientite $Fe_2(AsO_4,SO_4)_2(OH)_6{\cdot}5H_2O$ [1] is a mineral containing three anions namely sulphate, arsenate and hydroxyl. The mineral is monoclinic of point group 2/*m*. The crystals are prismatic and are aggregated into nodules [2]. The mineral was discovered in 1941 [3] and the single crystal X-ray study [1] yields the unit cell data: *a* 6.55, *b* 18.55, *c* 9.70 Å, *β* 97°39′, *P*21/*c*, *Z* = 4, *d* = 2.58. The mineral is analogous to the mineral destinezite. The mineral destinezite is a hydrated hydroxy phosphate of ferric iron with some sulphate substitution of formula $Fe_2(PO_4,SO_4)_2(OH){\cdot}6H_2O$ with the iron in the ferric state [4–7]. According to Peacor et al. [6] the crystal structure consists of infinite chains of $Fe(O,OH,H_2O)_6$ octahedra, sulphate tetrahedra and phosphate tetrahedra linked by a unique system of vertex sharing. The chains are weakly bonded into layers by hydrogen bonding between OH and H_2O of the Fe(III) octahedra and oxygen ions of the sulphate tetrahedra [6]. Layers of tetrahedral/octahedral chains alternate with sheets of H_2O molecules. Peacor et al. [6] stated that the structure resembles hydrated clay minerals, with H_2O molecules that act as hydrogen bond donors and acceptors to oxygen atoms of adjacent slabs. The mineral has a clay-like appearance under the SEM. The amorphous form of the sarmientite mineral is an example of a colloidal mineral [5,8–10]. These minerals are X-ray non-diffracting and so vibrational spectroscopy is very important for the characterisation of this mineral and forms the objective of this research.

Sarmientite can be described as an environmental mineral in that its formation, for example in soils, enables the entrapment and immobilisation of arsenic [11,12]. This mineral is essential for the formation of compounds containing arsenic [13–15]. It is formed in old mine sites and slag piles [14–16]. Complex equilibria exist with the formation of the mineral which may redissolve in heavy rainfall events [14]. Such mineral formation can be made to control the concentrations of lead and arsenic in mine tailings [17]. Arsenate is accumulated in the formation of secondary minerals in the beudantite–jarosite mineral groups [13]. The formation of secondary arsenate containing minerals is extremely important in the accumulation and immobilization of arsenic and heavy metals [18]. Of course other minerals such as segnitite, jarosite, bukovskýite may also function as metal collectors. Such mineral formation will depend upon the conditions of formation and the associated equilibria. The reason for this research is that minerals such as sarmientite are found in soils and in old mine sites. Further, the formation of such a mineral can be used as the basis for arsenic accumulation. Therefore, this research focuses on the molecular structure of sarmientite.

Raman spectroscopy has proven very useful for the study of minerals. Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with minerals containing sulphate and arsenate groups, including sarmientite, beudantite and bukovskyite. Raman spectroscopy is especially useful when the minerals are X-ray non-diffracting or poorly diffracting and very useful for the study of amorphous

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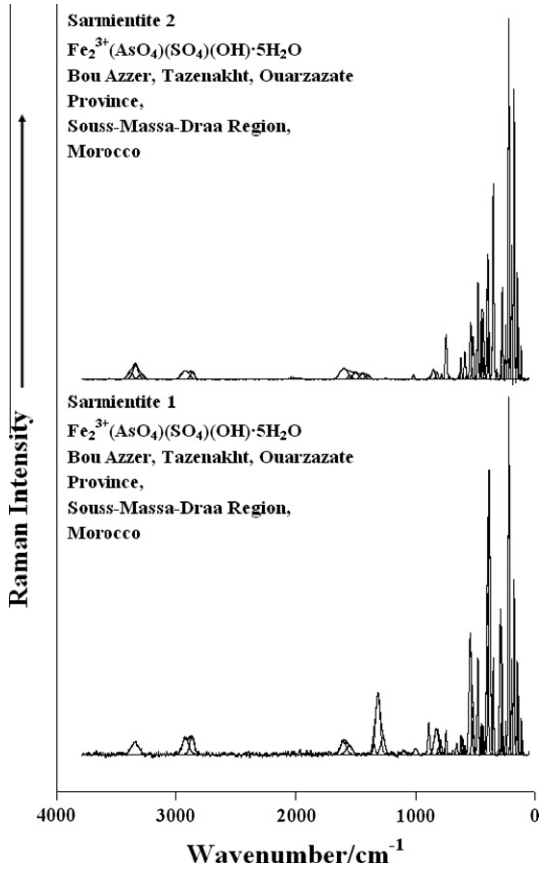

Fig. 1. Raman spectra of sarmientite in the 100–4000 cm^{-1} region.

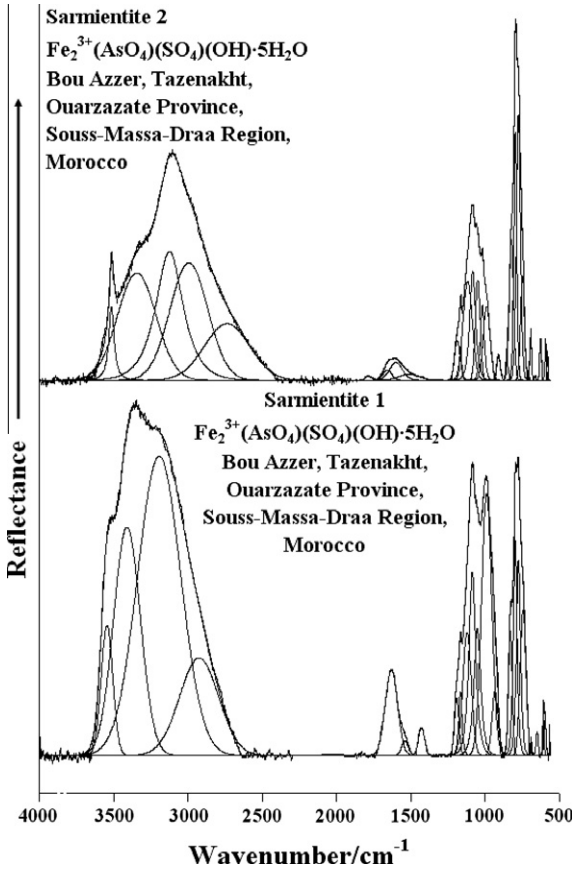

Fig. 2. Infrared spectra of sarmientite in the 500–4000 cm^{-1} region.

and colloidal minerals as is the case for sarmientite. 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 sarmientite using Raman spectroscopy and relate the spectra to the structure of the mineral.

2. Experimental

2.1. Mineral

The mineral sarmientite samples were supplied by The Mineralogical Research Company. The minerals originated from Bou Azzer, Tazenakht, Ouarzazate Province, Souss-Massa-Draa Region, Morocco. The mineral data has been published (page 522) [2].

2.2. Raman spectroscopy

Crystals of sarmientite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, 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. Further details of the technique have been published [19–25].

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.

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

S.D. Ross in Farmer's treatise [26] reported the infrared spectrum of beudantite (Table 18.IX page 433). The spectroscopy of beudantite should be close to that of sarmientite. This table compares the infrared spectra of minerals from the alunite–jarosite supergroups. Ross reported infrared bands at 985, 1006 cm^{-1} (ν_1), 430, 466 cm^{-1} (ν_2), 1078, 1160 cm^{-1} (ν_3), 600, 625 and 670 cm^{-1} (ν_4). OH vibrations were reported at 3420 and