

The phosphate mineral sigloite $\text{Fe}^{3+}\text{Al}_2(\text{PO}_4)_2(\text{OH})_3 \cdot 7\text{H}_2\text{O}$, an exception to the paragenesis rule – A vibrational spectroscopic study

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HIGHLIGHTS

- ▶ We have studied the molecular structure of the phosphate mineral sigloite $\text{Fe}^{3+}\text{Al}_2(\text{PO}_4)_2(\text{OH})_3 \cdot 7\text{H}_2\text{O}$.
- ▶ Vibrational spectroscopy identifies both phosphate and hydrogen phosphate units in the sigloite structure.
- ▶ Sigloite is the exception to the rule that phosphate mineral paragenesis is related to the final phase of hydrothermal mineralization.
- ▶ The observation of multiple OH bands gives credence to the non-equivalence of the OH units in the sigloite structure.

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ABSTRACT

The secondary phosphate mineral sigloite $\text{Fe}^{3+}\text{Al}_2(\text{PO}_4)_2(\text{OH})_3 \cdot 7\text{H}_2\text{O}$ is the exception to the rule that phosphate mineral paragenesis is related to the final phase of hydrothermal mineralization at low temperatures. Sigloite was formed as an oxidation pseudomorph after paravauxite, during the last supergene paragenetic stage.

We have studied the secondary phosphate mineral sigloite $\text{Fe}^{3+}\text{Al}_2(\text{PO}_4)_2(\text{OH})_3 \cdot 7\text{H}_2\text{O}$ using vibrational spectroscopic techniques. Because the mineral is a phosphate mineral, it is readily studied by spectroscopic techniques as the phosphate and hydrogen phosphate units are readily measured. Indeed, sigloite shows the presence of both phosphate and hydrogen phosphate units in its structure. Raman bands at 1009 cm^{-1} with shoulders at 993 and 1039 cm^{-1} are assigned to stretching vibrations of PO_4^{3-} and HPO_4^{2-} units. The Raman band at 993 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the POH units, whereas the Raman band at 1009 cm^{-1} is assigned to the ν_1 PO_4^{3-} symmetric stretching mode. Raman bands observed at 506 , 528 , 571 , 596 , 619 and 659 cm^{-1} are attributed to the ν_4 out of plane bending modes of the PO_4 and H_2PO_4 units. The Raman bands at 2988 , 3118 and 3357 cm^{-1} are assigned to water stretching vibration. The series of bands at 3422 , 3449 , 3493 , 3552 and 3615 cm^{-1} are assigned to the OH stretching vibrations of the hydroxyl units. The observation of multiple bands gives credence to the non-equivalence of the OH units in the sigloite structure.

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1. Introduction

Sigloite is a rare ferric aluminum hydrous phosphate with general chemical formula given as $\text{Fe}^{3+}\text{Al}_2(\text{PO}_4)_2(\text{OH})_3 \cdot 7\text{H}_2\text{O}$. It crystallizes in the triclinic system, $P-1$ space group, with unit cell parameters $a = 5.26$, $b = 10.52$, $c = 7.06\text{ Å}$ and $\alpha = 106^\circ 58'$, $\beta = 111^\circ 30'$, $\gamma = 69^\circ 30'$. Sigloite belongs to the stewartite group [1]. By analogy with the mineral stewartite as described by Moore and Araki [2], the structure of sigloite consists of three non-equiv-

alent $\text{Al}^{3+}\text{-O}$ octahedra – Al(1), Al(2) and Al(3) linked at opposing vertices by hydroxyl groups OH(1) and OH(2) to form corner-sharing chains of octahedral, parallel to [102]. PO_4 tetrahedra bridge these chains to form sheets of $[\text{Al}^{3+}(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)]^{1-}$ composition oriented parallel to {010}. These sheets are bridged along [010] by *trans*- $\text{Fe}^{2+}(\text{H}_2\text{O})_4(\text{O}_p)_2$ octahedra, where O_p is the oxygen associated with the PO_4 tetrahedron. Sigloite was first described by Hurlbut and Honea [3], in the Siglo XX mine, also known as Lallagua mine, Potosi department, Bolivia. The mineral occurs in open fractures cutting major cassiterite veins. It was found in a complex paragenesis that includes wavellite, paravauxite, metavauxite, crandallite, childrenite and other secondary phosphate. Despite the type locality, sigloite was also described in the Coon Creek

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Mine (Arkansas) and in the LCA Mine (North Caroline), both in USA [4].

Ahlfeld [5,6] and Gordon [7] considered the origin of the Siglo XX mine as due to a supergene process. Later, Bandy [8] and Ahlfeld and Rayes [5] have described the phosphate mineral paragenesis is related to the final phase of hydrothermal mineralization at low temperatures however, sigloite appears to be an exception. This mineral was formed as an oxidation pseudomorph after paravauxite, during the last supergene stage.

In recent years, the application of spectroscopic techniques for the understanding the structure of phosphate minerals is increasing, with special attention to Al phosphates [9–12].

Farmer [13] divided the vibrational spectra of phosphates according to the presence, or absence of water and hydroxyl units. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1} , the antisymmetric stretching mode (ν_3) at 1017 cm^{-1} , the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} [14–17]. The value for the ν_1 symmetric stretching vibration of PO_4 units as determined by infrared spectroscopy was given as 930 cm^{-1} (augelite), 940 cm^{-1} (wavelite), 970 cm^{-1} (rockbridgeite), 995 cm^{-1} (dufrénite) and 965 cm^{-1} (beraunite). The position of the symmetric stretching vibration is mineral dependent and a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the PO_4 units.

The value for the ν_2 symmetric bending vibration of PO_4 units as determined by infrared spectroscopy was given as 438 cm^{-1} (augelite), 452 cm^{-1} (wavelite), 440 and 415 cm^{-1} (rockbridgeite), 455 , 435 and 415 cm^{-1} (dufrénite) and 470 and 450 cm^{-1} (beraunite). The observation of multiple bending modes provides an indication of symmetry reduction of the PO_4 units. This symmetry reduction is also observed through the ν_3 antisymmetric stretching vibrations. Augelite shows infrared bands at 1205 , 1155 , 1079 and 1015 cm^{-1} (Frost and Weier, 2004); wavelite at 1145 , 1102 , 1062 and 1025 cm^{-1} ; rockbridgeite at 1145 , 1060 and 1030 cm^{-1} ; dufrénite at 1135 , 1070 and 1032 cm^{-1} ; and beraunite at 1150 , 1100 , 1076 and 1035 cm^{-1} .

In this work, spectroscopic investigation of a pure, monomineral sigloite sample from the Siglo XX mine, Potosi department, Bolivia has been carried out. The analysis includes spectroscopic characterization of the structure with infrared and Raman spectroscopy. Chemical analysis was applied to support the mineral characterization.

2. Experimental

2.1. Samples description and preparation

The sigloite sample studied in this work was collected from the Siglo XX mine (also named Llallagua), a tin deposit located in the Andes Mountain, Bustillo Province, northern of Potosi department, Bolivia. In the middle of the 20th century Siglo XX was the most productive tin mine in the world. The mine is also an important source for rare and unusual secondary phosphate minerals and is the type locality for a number of rare phosphates such as vauxite, paravauxite, metavauxite and jeanbandyite. The host rock is a conical subvolcanic stock of Tertiary age and the ore deposit is made up of porphyry and porphyry breccias. Hydrothermal alteration was responsible for the replacement of the primary mineralogy and the development of cericitization and tourmalinization [18].

In the Siglo XX mine, light brown to whitish sigloite aggregates of crystals up to 8.0 mm in length mainly occur in association or as pseudomorph of paravauxite. Other secondary phosphates such as wavelite, metavauxite, crandallite and childrenite also can be found in association. The sigloite sample forms part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-127. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The sigloite sample was phase analyzed by X-ray diffraction.

2.2. 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 (<http://www.microscopia.ufmg.br>).

Sigloite crystals were coated with a 5 nm layer of evaporated carbon. 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.

2.3. Raman microprobe spectroscopy

Crystals of sigloite 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 Reni-

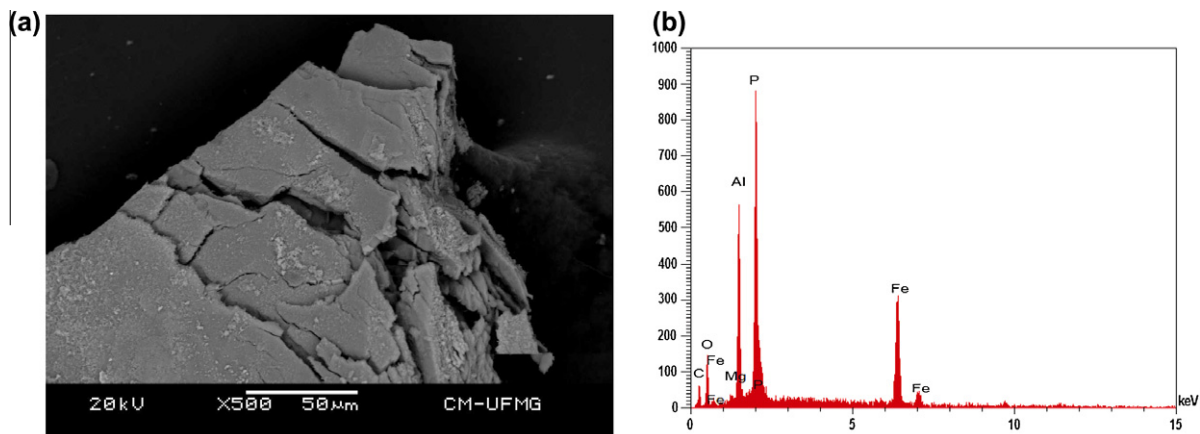


Fig. 1. (a) A backscattered electron image (BSI) of a sigloite single crystal up to 0.5 mm in length. (b) EDS analysis of sigloite.

shaw 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 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of $\pm 1\text{ cm}^{-1}$ in the range between 200 and 4000 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 cm^{-1} line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

An image of the sigloite crystals measured is shown in the supplementary information as Figure S1. Clearly the crystals of sigloite are readily observed, making the Raman spectroscopic measurements readily obtainable.

2.4. 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 $4000\text{--}525\text{ cm}^{-1}$ 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 given in the supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc 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.

3. Results and discussion

3.1. Chemical characterization

The SEM image of sigloite sample studied in this work is shown in Fig. 1. Sigloite crystal shows pinacoid form with perfect cleavage parallel to $\{100\}$. Qualitative chemical composition shows a pure and homogeneous Al and Fe phosphate as expected for sigloite. Traces of Mg were also observed.

3.2. Spectroscopy

One most beneficial way of studying phosphate minerals is to undertake vibrational spectroscopy. In this was the symmetry and distortion of the phosphate units in the mineral structure can be ascertained. Further if there are different sometimes called non-equivalent phosphate units, then vibrational spectroscopy can determine if the phosphate units are identical or different. The Raman spectrum of sigloite over the $100\text{--}4000\text{ cm}^{-1}$ spectral region is displayed in Fig. 2a. This figure shows the position and relative intensity of the Raman bands. It is obvious that the most intense spectral region is over the $2600\text{--}4000\text{ cm}^{-1}$ region. This region is where the water and OH stretching vibrations are likely to be observed. The overall spectrum may be subdivided into sections depending upon the type of vibration being studied. The infrared

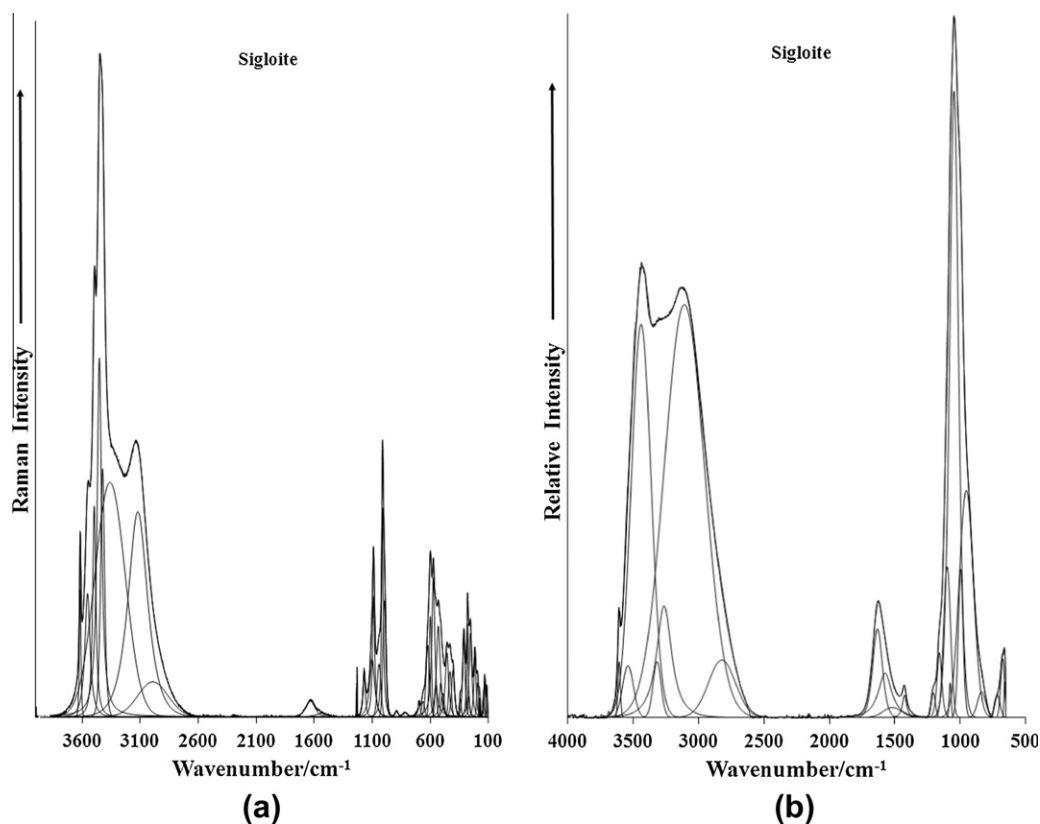


Fig. 2. (a) Raman spectrum of sigloite over the $100\text{--}4000\text{ cm}^{-1}$ spectral range. (b) Infrared spectrum of sigloite over the $500\text{--}4000\text{ cm}^{-1}$ spectral range.

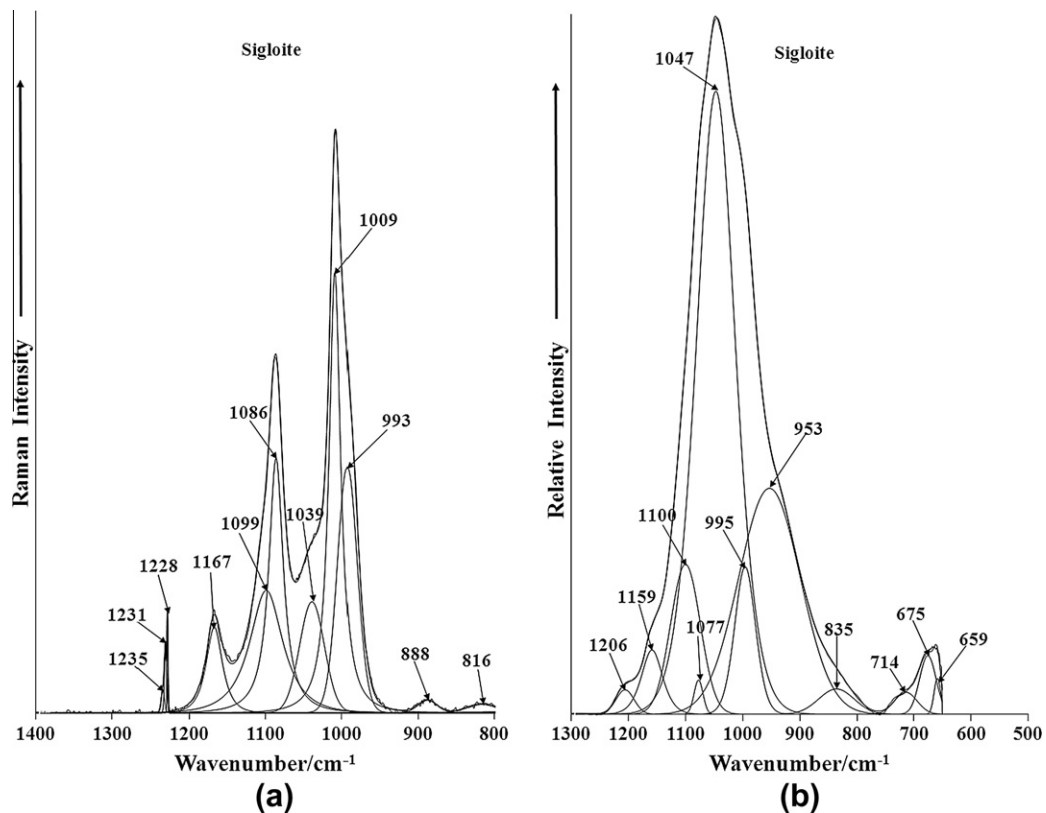


Fig. 3. (a) Raman spectrum of sigloite over the 800–1400 cm⁻¹ spectral range. (b) Infrared spectrum of sigloite over the 500–1300 cm⁻¹ spectral range.

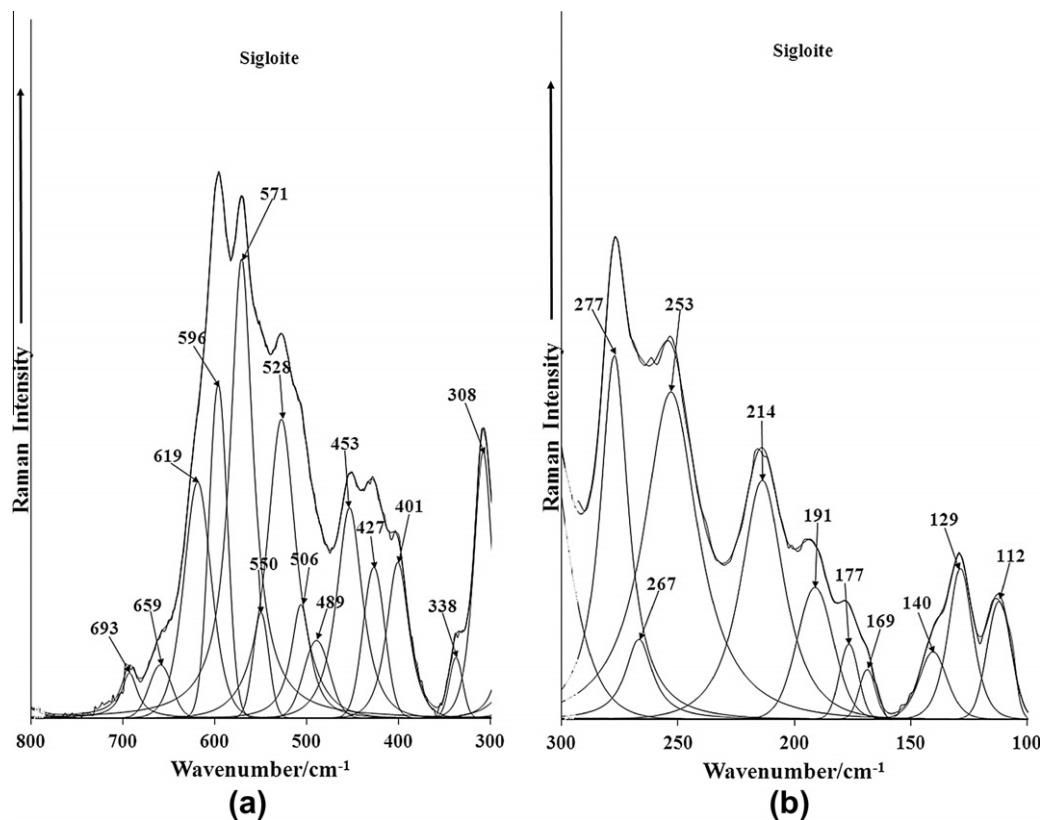


Fig. 4. (a) Raman spectrum of sigloite over the 300–800 cm⁻¹ spectral range. (b) Raman spectrum of sigloite over the 100–300 cm⁻¹ spectral range.

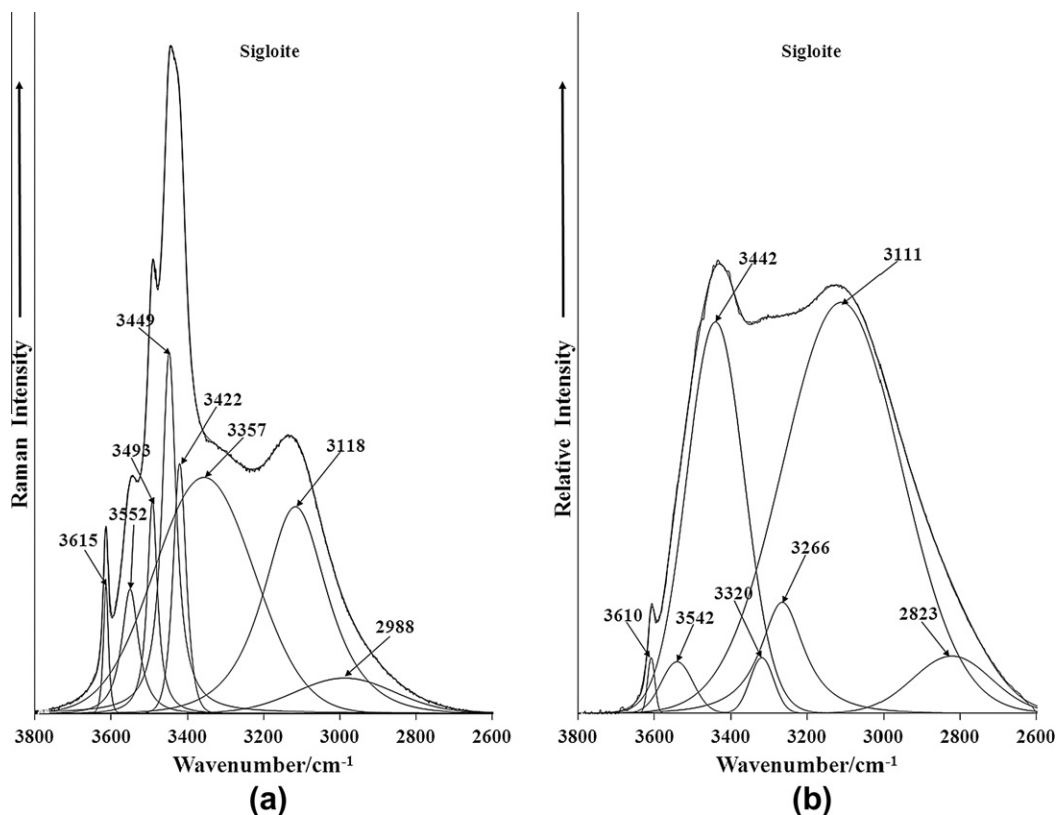


Fig. 5. (a) Raman spectrum of sigloite over the 2600–4000 cm⁻¹ spectral range. (b) Infrared spectrum of sigloite over the 2600–4000 cm⁻¹ spectral range.

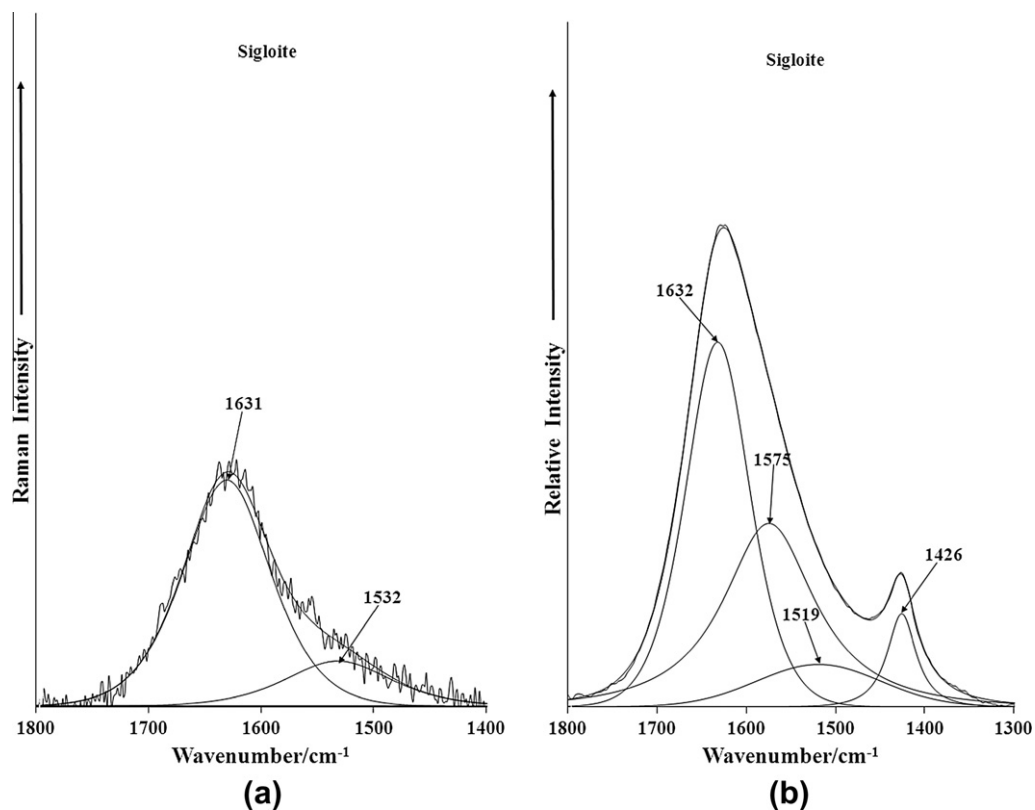


Fig. 6. (a) Raman spectrum of sigloite over the 1300–1800 cm⁻¹ spectral range. (b) Infrared spectrum of sigloite over the 1300–1800 cm⁻¹ spectral range.

spectrum over the 500–4000 cm⁻¹ spectral range is shown in Fig. 2b. As for the Raman spectrum there are spectral regions where no intensity is observed and therefore the spectrum may

be subdivided into sections depending upon the type of vibration. In the infrared spectrum strong absorption is observed in the 1000 spectral region.

The Raman spectrum in the 800–1400 cm^{-1} spectral range is reported in Fig. 3a. Intense Raman bands are observed at 1009 cm^{-1} with shoulders at 993 and 1039 cm^{-1} . These bands are assigned to PO_4^{3-} and HPO_4^{2-} stretching vibrations. The infrared spectrum of sigloite in the 500 to 1300 cm^{-1} spectral region is displayed in Fig. 3b. In this spectrum a very intense and somewhat broad band centered upon 1047 cm^{-1} is observed. Resolved component bands are found at 953, 1077, 1100, 1159 and 1206 cm^{-1} .

The Raman band at 993 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the POH units, whereas the Raman band at 1009 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the PO_4^{3-} units. Galy [19] first studied the polarized Raman spectra of the H_2PO_4^- anion. Choi et al. reported the polarization spectra of NaH_2PO_4 crystals. Casciani and Condrate [20] published spectra on brushite and monetite together with synthetic anhydrous monocalcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$), monocalcium dihydrogen phosphate hydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) and octacalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$). These authors determined band assignments for $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and reported bands at 1002 and 1011 cm^{-1} as POH and PO stretching vibrations, respectively. The two Raman bands at 1086 and 1167 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations. Casciani and Condrate [20] tabulated Raman bands at 1132 and 1155 cm^{-1} and assigned these bands to P–O symmetric and the P–O antisymmetric stretching vibrations.

The infrared spectrum displays greater complexity with multiple overlapping bands. The complexity of the spectrum makes it difficult to undertake band assignments. This complexity may be due to a mixture of taranakite and variscite. There is a difference between taking a Raman spectrum and an infrared spectrum. The sample spot size of the Raman spectrometer is around 1 micron. In infrared spectroscopy the measurement size is at best 30 μm . Thus in Raman spectroscopy it is possible to collect data for a pure mineral because that crystal was selected. It is more likely that the infrared spectrum is more likely to collect data for a mixture. This is why of course it is an advantage to run the Raman spectrum.

The Raman spectra of sigloite in the 300–800 cm^{-1} and in the 100–300 cm^{-1} are displayed in Fig. 4a and b. The first spectral region is the region of the phosphate bending modes. This spectral region is where the PO_4^{3-} and HOPO_3^{2-} -bending vibrations are found. A series of bands are observed at 506, 528, 571, 596, 619 and 659 cm^{-1} . These bands are attributed to the ν_4 out of plane bending modes of the PO_4 and H_2PO_4 units. The Raman spectrum of crystalline NaH_2PO_4 shows Raman bands at 526, 546 and 618 cm^{-1} (this work). A series of bands are observed at 401, 427, 453 and 489 cm^{-1} . These bands are attributed to the ν_2 PO_4 and H_2PO_4 bending modes. The Raman spectrum of NaH_2PO_4 shows Raman bands at 460 and 482 cm^{-1} . The Raman spectrum in the far wavenumber region is shown in Fig. 4b. Quite intense bands are found at 112, 129, 177, 191, 214, 253 and 277 cm^{-1} . These bands may be simply described as lattice vibrations.

The Raman spectrum of the OH stretching region is reported in Fig. 5a and in comparison the infrared spectrum of sigloite is shown in Fig. 5b. The Raman spectrum may be subdivided into two parts (a) bands below 3400 cm^{-1} and bands above 3400 cm^{-1} . The first set Raman bands are attributed to water stretching vibrations and the second set are attributed to OH stretching bands of the hydroxyl units. Thus, the Raman bands at 2988, 3118 and 3357 cm^{-1} are assigned to water stretching bands. These bands are very broad in comparison to the bands due to the hydroxyl units. The series of bands at 3422, 3449, 3493, 3552 and 3615 cm^{-1} are assigned to the OH stretching vibrations of the hydroxyl units. The observation of multiple bands gives credence to the non-equivalence of the OH units in the sigloite structure. A comparison may be made with the infrared spectrum where broad bands are observed at 3111, 3266, 3320 and 3442 cm^{-1} , assigned

to water stretching vibrational modes. It is noted that much greater intensity of the water bands is observed in the infrared spectrum as compared with the Raman spectrum. The reason for this is that water is a very poor Raman scatterer whereas water is a very strong infrared absorber. Again in comparison the hydroxyl units show greater intensity in the Raman spectrum, whereas the intensity of the OH absorption in the infrared spectrum is low. The low intensity infrared band at 3610 cm^{-1} is assigned to the stretching vibration of the OH units. The Raman spectrum of sigloite in the 1400–1800 cm^{-1} and the infrared spectrum in the 1300–1800 cm^{-1} are shown in Fig. 6a and b. This spectral region is where the water bending modes are observed. The Raman spectrum shows a reasonably strong band at 1631 cm^{-1} assigned to the water bending mode. A similar intense band at 1632 cm^{-1} is observed in the infrared spectrum. Other infrared bands are found at 1426 and 1575 cm^{-1} .

4. Conclusions

Sigloite is a rare ferric aluminum hydrated phosphate with formula $\text{Fe}^{3+}\text{Al}_2(\text{PO}_4)_2(\text{OH})_3 \cdot 7\text{H}_2\text{O}$ and belongs to the stewartite group. The crystals are prismatic to tabular with orange color and are transparent with a vitreous luster. The mineral was formed in a supergene stage. Sigloite was first described in the Siglo XX mine, Potosi department, Bolivia and occurs in association with other secondary phosphate minerals. The phosphate mineral paragenesis is related to the final phase of hydrothermal mineralization at low temperatures however, sigloite appears to be an exception. This mineral was formed as an oxidation pseudomorph after paravauxite, during the last supergene stage.

We have characterized the mineral sigloite using vibrational spectroscopic techniques. The mineral is characterized by an intense sharp Raman bands at 1009 cm^{-1} with shoulders at 993 and 1039 cm^{-1} are assigned to stretching vibrations of PO_4^{3-} and HPO_4^{2-} units. Raman band at 993 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the POH units, whereas the Raman band at 1009 cm^{-1} is assigned to the ν_1 PO_4^{3-} symmetric stretching mode. Raman bands observed at 506, 528, 571, 596, 619 and 659 cm^{-1} are attributed to the ν_4 out of plane bending modes of the PO_4 and H_2PO_4 units. The Raman bands at 2988, 3118 and 3357 cm^{-1} are assigned to water stretching vibration. The series of bands at 3422, 3449, 3493, 3552 and 3615 cm^{-1} are assigned to the OH stretching vibrations of the hydroxyl units. The observation of multiple bands gives credence to the non-equivalence of the OH units in the sigloite structure.

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