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

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ABSTRACT

The secondary phosphate mineral sigloite Fe$^{3+}$Al$_2$(PO$_4$)$_2$(OH)$_3$·7H$_2$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 Fe$^{3+}$Al$_2$(PO$_4$)$_2$(OH)$_3$·7H$_2$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 v$_1$ symmetric stretching mode of the POH units, whereas the Raman band at 1009 cm$^{-1}$ is assigned to the v$_4$ PO$_4^3-$ symmetric stretching mode. Raman bands observed at 506, 528, 571, 596, 619 and 659 cm$^{-1}$ are attributed to the out of plane bending modes of the PO$_4$ and H$_2$PO$_4$ units. The Raman bands at 2988, 3118 and 3577 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 OH 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 Fe$^{3+}$Al$_2$(PO$_4$)$_2$(OH)$_3$·7H$_2$O. It crystallizes in the triclinic system, P-1 space group, with unit cell parameters $a = 5.26$, $b = 10.52$, $c = 7.06$ Å and $\alpha = 106.58^\circ$, $\beta = 111.30^\circ$, $\gamma = 69.30^\circ$. 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-
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 stage 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.

Ahlfeld and Rayes [5] have described the phosphate mineral pseudomorph after paravauxite, during the last supergene stage. 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 jeandibanye. The host rock is a conical subvolcanic stock of Tertiary age and the ore deposit is made up of porphyry and porphyry brecias. 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 childhoodite 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. Experimental

2.1. Samples description and preparation

The sigloite sample studied in this work was collected from the Siglo XX mine, Potosi Department, Bolivia. 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.

2.2. 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 placed on a polished metal surface on a stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, and 50× 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.](image-url)
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 col-
clected at a nominal resolution of 2 cm\(^{-1}\) and a precision of
±1 cm\(^{-1}\) in the range between 200 and 4000 cm\(^{-1}\). Repeated acqui-
sitions on the crystals using the highest magnification (50×) were
accumulated to improve the signal to noise ratio of the spectra. Ra-
man 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 sup-
plementary information as Figure S1. Clearly the crystals of sigloite
are readily observed, making the Raman spectroscopic measure-
ments 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 4000–525 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 given in the sup-
plementary information.

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' soft-
ware package that enabled the type of fitting function to be se-
lected 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 under-
taken until reproducible results were obtained with squared corre-
lations 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 Ra-
man spectrum of sigloite over the 100–4000 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 2600–4000 cm\(^{-1}\) region. This region is
where the water and OH stretching vibrations are likely to be ob-
served. 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 100–4000 cm\(^{-1}\) spectral range. (b) Infrared spectrum of sigloite over the 500–4000 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.
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 cm\(^{-1}\) spectral region.

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.
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 v\(_1\) symmetric stretching mode of the POH units, whereas the Raman band at 1009 cm\(^{-1}\) is assigned to the v\(_1\) symmetric stretching mode of the PO\(_4^{3-}\) units. Caly [19] first studied the polarized Raman spectra of the H\(_2\)PO\(_4\) anion. Choi et al. reported the polarization spectra of NaH\(_2\)PO\(_4\) crystals. Casciani and Condrate [20] published spectra on brushite and monetite together with synthetic anhydrous monocalcium phosphate (Ca(H\(_2\)PO\(_4\))\(_2\)), monocalcium dihydrogen phosphate hydrate (Ca(H\(_2\)PO\(_4\))\(_2\):H\(_2\)O) and octacalcium phosphate (Ca\(_9\)(H\(_2\)PO\(_4\))\(_6\):5H\(_2\)O). These authors determined band assignments for Ca(H\(_2\)PO\(_4\)) 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 HPO\(_4^{2-}\)-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 v\(_4\) out of plane bending modes of the PO\(_4\) and H\(_2\)PO\(_4\) units. The Raman spectrum of crystalline NaH\(_2\)PO\(_4\) 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 v\(_2\) PO\(_4\) and H\(_2\)PO\(_4\) bending modes. The Raman spectrum of NaH\(_2\)PO\(_4\) 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 Fe\(^3+\)Al\(_2\)(PO\(_4\))\(_2\)(OH)\(_3\)H\(_2\)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, Potosí 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 bands at 993 cm\(^{-1}\) is assigned to the v\(_1\) symmetric stretching mode of the POH units, whereas the Raman band at 1009 cm\(^{-1}\) is assigned to the v\(_1\) PO\(_4^{3-}\) symmetric stretching mode. Raman bands observed at 506, 528, 571, 596, 619 and 659 cm\(^{-1}\) are attributed to the v\(_4\) out of plane bending modes of the PO\(_4\) and H\(_2\)PO\(_4\) 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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