Infrared and Raman spectroscopic characterization of the silicate–carbonate mineral carletonite – $\text{KNa}_4\text{Ca}_4\text{Si}_8\text{O}_{18}(\text{CO}_3)_4(\text{OH},\text{F})\cdot\text{H}_2\text{O}$

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ABSTRACT

An assessment of the molecular structure of carletonite a rare phyllosilicate mineral with general chemical formula given as $\text{KNa}_4\text{Ca}_4\text{Si}_8\text{O}_{18}(\text{CO}_3)_4(\text{OH},\text{F})\cdot\text{H}_2\text{O}$ has been undertaken using vibrational spectroscopy. Carletonite has a complex layered structure. Within one period of *c*, it contains a silicate layer of composition $\text{NaKSi}_8\text{O}_{18}\cdot\text{H}_2\text{O}$, a carbonate layer of composition $\text{NaCO}_3\cdot 0.5\text{H}_2\text{O}$ and two carbonate layers of composition $\text{NaCa}_2\text{CO}_3(\text{F},\text{OH})_{0.5}$.

Raman bands are observed at 1066, 1075 and 1086 cm^{-1} . Whether these bands are due to the CO_3^{2-} ν_1 symmetric stretching mode or to an SiO stretching vibration is open to question.

Multiple bands are observed in the $300\text{--}800\text{ cm}^{-1}$ spectral region, making the attribution of these bands difficult. Multiple water stretching and bending modes are observed showing that there is much variation in hydrogen bonding between water and the silicate and carbonate surfaces.

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1. Introduction

Carletonite is a rare phyllosilicate mineral with general chemical formula given as $\text{KNa}_4\text{Ca}_4\text{Si}_8\text{O}_{18}(\text{CO}_3)_4(\text{OH},\text{F})\cdot\text{H}_2\text{O}$. The mineral is a member of the apophyllite mineral group [1]. The only known world occurrence of carletonite is its type locality, the Poudrette Quarry, Mont Saint-Hilaire, Canada [2]. The crystal structure of carletonite has been solved by Chao [3]. The mineral crystallizes in the tetragonal crystal system and the cell dimensions are Space Group: *P4/mbm*, *a* = 13.178(3) Å, *c* = 16.695(4) Å, *Z* = 4. Carletonite crystals shows tetragonal prismatic habitus. The mineral is shows variable colors including light blue, deep blue, pink, purple and colorless. Due to its intense color, carletonite can be a valuable gemstone [4].

Carletonite has a complex layered structure. Within one period of *c*, it contains a silicate layer of composition $\text{NaKSi}_8\text{O}_{18}\cdot\text{H}_2\text{O}$, a carbonate layer of composition $\text{NaCO}_3\cdot 0.5\text{H}_2\text{O}$ and two carbonate layers of composition $\text{NaCa}_2\text{CO}_3(\text{F},\text{OH})_{0.5}$. In the silicate layer two apophyllite-like Si_4O_{10} single-sheets on four- and eight-membered rings share half their non-bridging oxygen atoms to form a Si_8O_{18} double-sheet [3].

The objective of this paper is to report the vibrational spectroscopic study of a carletonite mineral and relate the spectra to the molecular chemistry and the crystal chemistry of this complex silicate mineral. We have characterized carletonite using Raman and

infrared spectroscopy, with support of scanning electron microscopy in the mineral characterization.

2. Experimental

2.1. Samples description and preparation

The carletonite sample studied in this work was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAA-137. The samples are from the Poudrette Quarry, Mount Saint Hilaire, Quebec, Canada, the only locality for the mineral. Carletonite was found in the cores of wall-rock inclusions in the nepheline syenite. The mineral is related to the contact metamorphism [2]. Other common minerals in association are calcite, quartz and fluorite.

The carletonite sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) in the EDS mode 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>).

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Carletonite cleavage fragment up to 2 mm was coated with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. A qualitative and semi-quantitative chemical analysis in the EDS mode was performed with a ThermoNORAN spectrometer model Quest and was applied to support the mineral characterization.

3. Raman spectroscopy

Crystals of carletonite 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 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} . Some of these mineral fluoresced badly at 633 nm; as a consequence other laser excitation wavelengths were used especially the 785 nm laser. Repeated acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique. Alignment of all crystals in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation.

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 [supplementary 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' 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.

5. Results and discussion

5.1. Chemical characterization

The SEM/BSE image of carletonite sample studied in this work is shown in [Fig. 1](#). The sample is a cleavage fragment and no zonation is observed. The mineral was analyzed in the EDS mode and the qualitative chemical composition shows a homogeneous phase, composed by Na, K, Ca, Si and C ([Fig. 2](#)). Fluorine and other cations were not detected. The formula of the mineral was determined as $\text{K}(\text{Na}_{3.6}, \text{K}_{0.4})\text{Ca}_{4.1}\text{Si}_8\text{O}_{18}(\text{CO}_3)_4(\text{OH}, \text{F})\cdot\text{H}_2\text{O}$. The X-ray diffraction pattern was obtained and is included in [supplementary information](#).

Fig. 1. Shows a backscattered electron image (BSI) of a carletonite cleavage fragment up to 2.0 mm in length.

5.2. Vibrational spectroscopy

5.2.1. Background

Carbonates in a range of minerals have been studied by vibrational spectroscopy. It is important to understand the spectroscopy of the carbonate ion, as a function of its symmetry. The free ion, CO_3^{2-} with D_{3h} symmetry, exhibits four normal vibrational modes; a symmetric stretching vibration (ν_1), an out-of-plane bend (ν_2), a doubly degenerate antisymmetric stretch (ν_3) and another doubly degenerate bending mode (ν_4). The symmetries of these modes are $A'_1(\text{R}) + A'_2(\text{IR}) + E'(\text{R, IR}) + E''(\text{R, IR})$ and occur at 1063 , 879 , 1415 and 680 cm^{-1} respectively (R = Raman active; IR = infrared red active). Generally, strong Raman modes appear around 1100 cm^{-1} due to the symmetric stretching vibration (ν_1), of the carbonate groups, while intense IR and weak Raman peaks near 1400 cm^{-1} are due to the antisymmetric stretch (ν_3). Infrared modes near 800 cm^{-1} are derived from the out-of-plane bend (ν_2). Infrared and Raman modes around 700 cm^{-1} region are due to the in-plane bending mode (ν_4). This mode is doubly degenerate for undistorted CO_3^{2-} groups. As the carbonate groups become distorted from regular planar symmetry, this mode splits into two components. Infrared and Raman spectroscopy provide sensitive test for structural distortion of CO_3^{2-} . White in Farmer's treatise (Chapter 12) stated that the overall results expected from this phenomenon is a progression from normally sharp bands, distinctive to carbonate, proceed into more broad and shifted bands resulting in diffuse spectra [5]. However, even though the effects of hydrogen bonding are apparent in vibrational spectroscopy of mixed anionic minerals, it is not expected to affect greatly the internal modes of the CO_3^{2-} in carletonite, so sharp bands are still expected.

5.3. Vibrational spectroscopy of carletonite

The Raman spectrum of carletonite $\text{KNa}_4\text{Ca}_4\text{Si}_8\text{O}_{18}(\text{CO}_3)_4(\text{OH}, \text{F})\cdot\text{H}_2\text{O}$ in the $100\text{--}4000\text{ cm}^{-1}$ spectral range is displayed in [Fig. 3a](#). This spectrum shows the position and relative intensities of the bands. It is noted that there are large parts of the spectrum where no intensity or minimal intensity is observed. Thus, the spectrum is subdivided into subsections depending upon the type of vibration being studied. The infrared spectrum of carletonite in the $500\text{--}4000\text{ cm}^{-1}$ spectral region is shown in [Fig. 3b](#). This figure shows the position of the infrared bands and their relative intensities. This spectrum displays the position and relative intensities of the infrared bands. As for the Raman spectrum, there are parts of the spectrum where little or no intensity is observed.

Fig. 2. EDS spectra of carletonite.

Fig. 3. (a) Raman spectrum of carletonite over the 100–4000 cm⁻¹ spectral range and (b) infrared spectrum of carletonite over the 500–4000 cm⁻¹ spectral range.

Fig. 4. (a) Raman spectrum of carletonite over the 800–1400 cm^{-1} spectral range and (b) infrared spectrum of carletonite over the 500–1300 cm^{-1} spectral range.

The Raman spectrum of carletonite in the 800–1400 cm^{-1} spectral range is reported in Fig. 4a. Intense Raman bands are observed at 1066, 1075 and 1086 cm^{-1} with bands of lesser intensity at 840 and 1217 cm^{-1} . The first three bands are assigned to the CO_3^{2-} ν_1 symmetric stretching mode. The observation of these three bands supports the concept that the carbonate units in the structure of carletonite are not equivalent. However, these bands may also be due to SiO stretching vibrations. The only means of determining whether this is true or not is to make a comparison with the spectra of apophyllite. The Raman spectrum of apophyllite-(KF) is dominated by a very intense sharp peak at 1059 cm^{-1} . Dowty showed that the $-\text{SiO}_3$ units had a unique band position of 980 cm^{-1} [6]. Dowty also showed that Si_2O_5 units had a Raman peak at around 1100 cm^{-1} . Apophyllite-(KF) consists of continuous sheets of Si_2O_6 parallel to the 001 plane. The band at 1059 cm^{-1} is assigned to the SiO stretching vibration of these Si_2O_6 units. Adams et al. [7] reported the single crystal Raman spectrum of apophyllite. Adams and co-workers reported the factor group analysis of apophyllite. Based upon Adams et al. [7] assignment this band is the A_{1g} mode. It is predicted that there should be three A_{1g} modes. However, only one is observed, perhaps because of accidental coincidence. Narayanan [8] collected the spectrum of an apophyllite mineral but did not assign any bands.

The Raman band at 1217 cm^{-1} is attributed to the SiO stretching vibration. The strong Raman band at 840 cm^{-1} is assigned to

the out-of-plane ν_2 CO_3^{2-} bending mode. In contrast to the sharp bands of carletonite observed in the Raman spectrum, the infrared spectrum in the 500–1300 cm^{-1} spectral range displays broad overlapping band which may be resolved into component bands (Fig. 4b). Two sets of bands in the higher wavenumber region are observed. Three bands are found at 1020, 1046 and 1071 cm^{-1} . These bands may be assigned to the CO_3^{2-} ν_1 symmetric stretching modes. The second set of bands is observed at 1146, 1166 and 1190 cm^{-1} . These bands may be assigned to the SiO vibrations.

A comparison may be made with the spectra of apophyllite [9]. The Raman spectrum of apophyllite-(KF) is dominated by a very intense sharp peak at 1059 cm^{-1} . Sengupta et al. reported the infrared spectra of some natural Indian zeolites including apophyllite [10]. Sidorov [11] reported the Raman spectrum of apophyllite and identified $\text{Si}_2\text{O}_5^{2-}$ ions in the structure and confirm the presence of these ions in silicates with double rings and double chains or layers. Adams et al. [7] determined the single crystal Raman spectrum of an apophyllite mineral. Duval and Lecomte [12] used vibrational spectroscopy to determine the role of water in the apophyllite structure. Vienne and Brunel [13] published the single crystal infrared spectrum of apophyllite and found the two A_2 modes, at 1048 and 1129 cm^{-1} . The significance of this observation is that it shows that both the Si–O bridge and terminal bonds yield stretching wavenumbers at comparable positions.

The Raman spectra of carletonite in the 300–800 cm^{-1} and 100–300 cm^{-1} spectral range are displayed in Fig. 5a and b. The spectrum in the 300–800 cm^{-1} spectral range may be divided into two sections: above 600 cm^{-1} and below 600 cm^{-1} . Raman bands are observed at 663, 685, 698, 706, 726, 756 and 782 cm^{-1} . These bands are due to the in-plane bending mode (ν_4). This mode is doubly degenerate for undistorted CO_3^{2-} groups. As the carbonate groups become distorted from regular planar symmetry, this mode splits into two components. Infrared and Raman spectroscopy provide sensitive test for structural distortion of CO_3^{2-} . The second set of bands is found at 465, 495 and 547 cm^{-1} with bands of lesser intensity at 316, 325, 342, 356, 401 and 430 cm^{-1} . As above, a comparison may be made with the spectrum of apophyllite. Three intense Raman bands for apophyllite are found at 431, 583 and 663 cm^{-1} . These bands are assigned to OSiO bending modes. There are many more bands observed in the spectra shown in Fig. 5a than is required from theory. Dowty calculated the band position of these bending modes for different siloxane units [6]. Dowty demonstrated the band position of the bending modes for SiO_3 units at around 650 cm^{-1} . This calculated value is in harmony with the higher wavenumber band observed at 663 cm^{-1} . According to Adams et al. [7] the band at 432 cm^{-1} is due to the coincidence of both the B_{2g} and E_g modes.

Raman bands are found at 142, 157, 174, 194, 217, 235 and 283 cm^{-1} and are simply described as lattice modes. For the apo-

phyllite mineral, quite intense Raman bands are observed at 106, 132, 161, 155, 209, 228 and 266 cm^{-1} . Strong Raman bands were also reported by Adams et al. [7] in the single crystal Raman spectrum of apophyllite in this spectral region. Adams et al. showed the orientation dependence of the spectra. Bands in these positions are due to framework vibrations and probably also involve water. The intense band at 209 cm^{-1} may involve hydrogen bonding of water. However until the Raman spectrum of deuterated apophyllite is measured, then no firm conclusion can be made. Raman bands are observed for the apophyllite-(KOH) at 106, 121, 134, 163, 185, 203, 236 and 254 cm^{-1} .

The Raman and infrared spectra of carletonite in the 2600–3800 cm^{-1} spectral range are displayed in Fig. 6a and b. The Raman spectrum is dominated by a set of bands at 3572, 3595 and 3584 cm^{-1} . These bands are attributed to the OH stretching vibration. The observation of three bands supports the concept that not all the OHs in the carletonite structure are equivalent. Other bands are observed at 3235 and 2905 cm^{-1} . The first band is attributed to water stretching vibration. In contrast the infrared spectrum suffers from a lack of signal. Infrared bands are found at 2998, 3126, 3398 and 3624 cm^{-1} . It is likely that these bands are attributable to water stretching vibrations. Overall two features are observed, namely bands due to water stretching vibrations and hydroxyl stretching bands. Again a comparison may be made with the spectra of apophyllite. It is noted that the hydroxyapophyllite Raman

Fig. 5. (a) Raman spectrum of carletonite over the 300–800 cm^{-1} spectral range and (b) Raman spectrum of carletonite over the 100–300 cm^{-1} spectral range.

Fig. 6. (a) Raman spectrum of carletonite over the 2600–4000 cm^{-1} spectral range and (b) infrared spectrum of carletonite over the 2600–4000 cm^{-1} spectral range.

spectrum has two OH stretching bands. The Raman spectrum of the apophyllite shows a complex set of bands which may be resolved into component bands at 2813, 2893, 3007, 3085 and 3365 cm^{-1} . These bands are attributed to water stretching vibrations. Neutron diffraction studies have shown that water is hydrogen bonded to the silicate framework structure [14]. In the model of Prince [14] approximately one-eighth of the water molecules are replaced by OH^- and the remaining protons bonded to fluoride to form HF molecules. Both OH^- and H_2O are hydrogen bonded to the silicate framework. Bartl and Pfeifer [15] presented a model of apophyllite in which some hydroxyl units are replaced by fluoride ions. This model seems more appropriate as the sizes of F^- and OH^- ions are very close. There are many examples in nature where in minerals the OH^- units are either completely or partially replaced by F^- ions.

The Raman spectrum of carletonite in the 1400–1800 cm^{-1} spectral range and the infrared spectrum in the 1300–1800 cm^{-1} spectral range are shown in Fig. 7a and b. The Raman spectrum in this spectral region shows considerable lack of intensity; nevertheless Raman bands are identified at 1426, 1481, 1548, 1617, 1662, 1732 and 1753 cm^{-1} . The two bands at 1617 and 1662 cm^{-1} are assigned to water stretching vibrations. These two bands are observed in the infrared spectrum at 1602 and 1623 cm^{-1} . The Raman bands at 1426, 1481 and 1548 cm^{-1} are assigned to the E' (R, IR) CO_3^{2-} antisymmetric stretching vibrations.

These vibrations are found in the infrared spectrum at 1395, 1449, 1479 and 1522 cm^{-1} .

The complexity of the water stretching region of apophyllite is reflected in the water bending region. Three water bending bands are observed at 1626, 1683 and 1705 cm^{-1} . There is a band at 1523 cm^{-1} which is thought to be a hydroxyl deformation mode.

6. Conclusions

The name apophyllite refers to a specific group of phyllosilicates, a class of minerals that also includes the micas [16,17]. Included in this group is the mineral carletonite. Carletonite has a complex layered structure. Within one period of c, it contains a silicate layer of composition $\text{NaSi}_8\text{O}_{18}\cdot\text{H}_2\text{O}$, a carbonate layer of composition $\text{NaCO}_3\cdot 0.5\text{H}_2\text{O}$ and two carbonate layers of composition $\text{NaCa}_2\text{CO}_3(\text{F},\text{OH})_{0.5}$. We have analyzed this mineral using EDS and SEM techniques. The formula of the mineral was determined.

We assessed the molecular structure of carletonite using vibrational spectroscopy. In order to ascertain which bands are due to carbonate or siloxane units, a comparison with the spectra of apophyllite-(KOH) has been made. Raman bands are observed at 1066, 1075 and 1086 cm^{-1} . Whether these bands are due to the CO_3^{2-} ν_1 symmetric stretching mode or to an SiO stretching vibration is open to question. For apophyllite-(KOH) and intense Raman band is found at 1059 cm^{-1} .

Fig. 7. (a) Raman spectrum of carletonite over the 1300–1800 cm^{-1} spectral range and (b) infrared spectrum of carletonite over the 1300–1800 cm^{-1} spectral range.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2013.03.036>.

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