



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

A vibrational spectroscopic study of the silicate mineral pectolite – $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$



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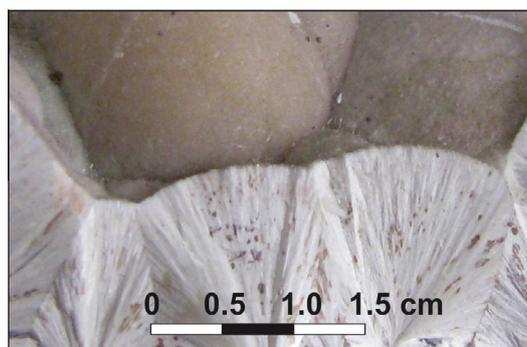
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HIGHLIGHTS

- We have studied mineral pectolite $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$.
- Potential to be used in plaster boards and other industrial applications.
- Raman bands are assigned to the SiO stretching vibrations of linked units of Si_3O_8 units.
- Raman spectroscopy with complimentary infrared spectroscopy enables the characterisation of the silicate mineral pectolite.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 March 2014

Received in revised form 2 June 2014

Accepted 16 June 2014

Available online 24 June 2014

Keywords:

Silicate

Raman spectroscopy

Pectolite

Infrared spectroscopy

Molecular structure

ABSTRACT

The mineral pectolite $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$ is a crystalline sodium calcium silicate which has the potential to be used in plaster boards and in other industrial applications.

Raman bands at 974 and 1026 cm^{-1} are assigned to the SiO stretching vibrations of linked units of Si_3O_8 units. Raman bands at 974 and 998 cm^{-1} serve to identify Si_3O_8 units. The broad Raman band at around 936 cm^{-1} is attributed to hydroxyl deformation modes. Intense Raman band at 653 cm^{-1} is assigned to OSiO bending vibration. Intense Raman bands in the $2700\text{--}3000\text{ cm}^{-1}$ spectral range are assigned to OH stretching vibrations of the OH units in pectolite. Infrared spectra are in harmony with the Raman spectra. Raman spectroscopy with complimentary infrared spectroscopy enables the characterisation of the silicate mineral pectolite.

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Introduction

Pectolite is a white to gray mineral, of formula $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$ and may be described as a sodium calcium inosilicate hydroxide and is the calcium analogue of serandite. It crystallizes in the triclinic system typically occurring in radiated or fibrous crystalline masses

and is primary mineral in nepheline syenites. A hydrothermal mineral in cavities in basalts and diabases; in serpentinites and peridotites; from metamorphosed high-calcium rocks. Pectolite is triclinic, space group $\bar{P}1$, with 15 nonhydrogen atoms in the asymmetric unit [1]. A review of the structure of pectolite and related minerals has been published [2]. The structure of pectolite is related to that of wollastonite [3]. A number of Ca and Mn pyroxenes and pyroxenoids are known and such minerals forms paragenesis in contact metamorphic rocks, including pectolite, rhodonite, pyroxmangite,

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nambulite among others. The development and application of spectroscopy technics can be an important tool in the non-destructive study of minerals mineral deposits.

No Raman spectroscopic analyses of pectolite and related minerals have been forthcoming. There are spectra in the RRUFF data base but no band assignments are given. Some infrared studies have been undertaken [4]. Studies of hydrogen bonding in silicates relates the position of the hydroxyl stretching vibration to the hydrogen bond distances [5]. Raman studies of cement phases have been forthcoming [6–9]. In this way, identification of mineral phases using Raman spectroscopy has been made. Some infrared studies of calcium silicates have been undertaken, the purpose of which is for mineral identification and mineral content [10–12]. Some Raman spectra of calcium silicates have been collected and a number of the spectra were shown to be dependent upon the number of condensed silica tetrahedra [8]. Such detailed assignment of infrared and Raman bands for a wide range of silicate structures was made by Dowty [13–16]. The thermal decomposition of calcium silicates has also been measured [17–19]. Pectolite is readily synthesised and is often found as components in cements [20,21]. Pectolite may be used to make reinforced organic polymers. It can be used for the removal of organic polyelectrolytes and their metal complexes by adsorption onto pectolite. Pectolite and related minerals can be used for heavy metal uptake for example Nd(II) [20]. Because of the number and wide variation of the applications of the mineral pectolite, it is important to be readily able to identify the mineral pectolite using vibrational spectroscopic techniques.

There is an apparent lack of information on the vibrational spectra of pectolite, even though some spectra are provided in the RRUFF data base. The reason for such a lack of information is not known; yet the mineral contains OH units and siloxane units; Raman spectroscopy has proven most useful for the study of mineral structure. The objective of this research is to report the Raman and infrared spectra of pectolite and to relate the spectra to the mineral structure.

Experimental

Samples description and preparation

The pectolite sample studied in this work occurs as single crystals with fibrous to acicular habitus up to 3 cm (please see Fig. 1). The mineral forms radial aggregates. The sample is part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-100. The

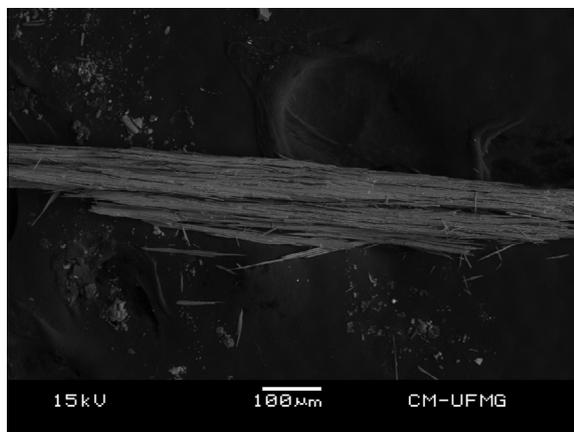


Fig. 1. Backscattered electron image (BSI) of a pectolite group of acicular crystals up to 1.0 mm in length.

sample was gently crushed and single crystals were selected under a stereomicroscope Leica MZ4. The pectolite sample studied in this work was analyzed by scanning electron microscopy (SEM) in the EDS mode to support the mineral characterization.

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>). Pectolite 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.

Raman microprobe spectroscopy

Crystals of pectolite 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 ±1 cm⁻¹ in the range between 200 and 4000 cm⁻¹. Repeated acquisitions on the crystals using the highest magnification (50×) 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.

It is noted that there are four spectra of pectolite provided in the RRUFF data base. However, no attribution of the bands is given. One spectrum has been downloaded for comparative purposes and is given in the [supplementary information](#).

Infrared spectroscopy

Infrared spectra of pectolite 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.

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.

Results and discussion

Mineral characterization

The SEM image of pectolite sample studied in this work is shown in Fig. 1. The image shows a group of acicular crystals up to 1 mm. Qualitative chemical analysis shows a homogeneous phase, composed by Ca, Na and Si. No other contaminant elements

were observed and the sample can be considered as a single phase (Fig. 2). Zonation was also not observed.

Vibrational spectroscopy

The Raman spectrum of pectolite over the 100–4000 cm^{-1} spectral range is shown in Fig. 3a. This figure shows the position and relative intensity of the Raman bands. It is noted there are large parts of the spectrum where little or no intensity is observed. The Raman spectrum is therefore subdivided into sections based upon the types of vibration being studied. The infrared spectrum of pectolite over the 500–4000 cm^{-1} spectral range is displayed in Fig. 3b. This figure shows the position and relative intensities of the infrared bands. The infrared spectrum is subdivided into sections based upon the type of vibration being studied.

The Raman spectrum of pectolite over the 800–1200 cm^{-1} spectral range is reported in Fig. 4a. The structure of pectolite $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$ consists of a single chain with linked silica tetrahedra [22]. Dowty calculated the band positions for the different ideal silicate units and showed that the $-\text{SiO}_3$ units had a unique band position of 1025 cm^{-1} [16] (see Figs. 2 and 4 of this reference). Pectolite has chains of linked units of Si_3O_8 . Dowty calculated the Raman spectrum for these type of silicate networks and predicted two bands at around 1040 and 1070 cm^{-1} with an additional band at around 600 cm^{-1} . In Fig. 3a, we observe two bands at 1026 and 1047 cm^{-1} in harmony with Dowty's predictions. Two other Raman bands are observed at 974 and 998 cm^{-1} . These Raman bands identify Si_3O_8 units. A significantly broader band is observed at 911 cm^{-1} . This band is not associated with siloxane units but is attributed to hydroxyl deformation modes.

The 1042 cm^{-1} Raman band is not observed in the infrared spectrum (Fig. 4b). This indicates that the vibration contains a centre of symmetry. Infrared bands are observed at 1028 and 1065 cm^{-1} . This latter band is not observed in the Raman spectrum. Strong infrared bands are observed at 901, 925, 966 and 991 cm^{-1} . Dowty calculated the position of infrared bands for silicate structures and also showed measured spectra of the equivalent theoretical system. The infrared bands shown in Dowty's work were broad. In this work the infrared bands of pectolite are reasonably sharp and readily resolved. Black et al. [23] reported the Raman spectra of a series of hydrated calcium silicate compounds with varying Ca/Si ratios. There is some resemblance between the spectra of this reference (see Fig. 3 of this reference) and these spectra. However, it must be pointed out that the compounds synthesised by Black et al. were hydrated calcium silicates. In comparison, pectolite is a hydroxy sodium calcium silicate. Richardson et al. [9] published a review of cement phases and their

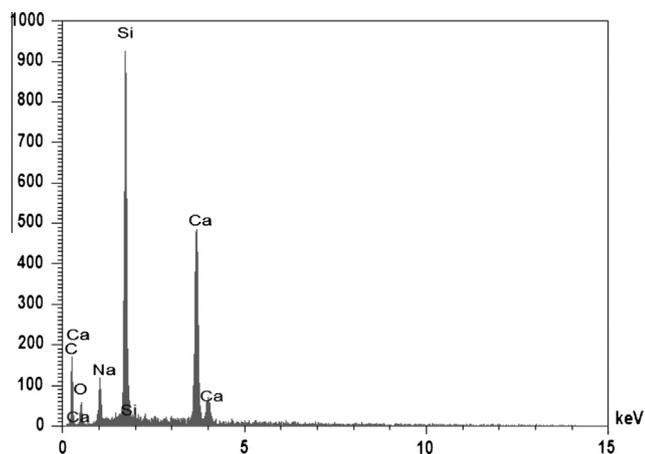


Fig. 2. EDS analysis of pectolite.

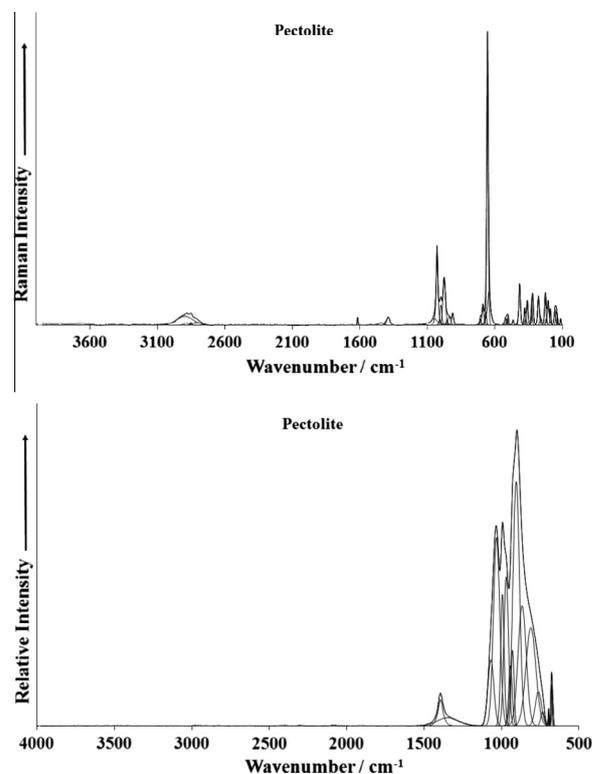


Fig. 3. (a) Raman spectrum of pectolite (upper spectrum) over the 100–4000 cm^{-1} spectral range and (b) infrared spectrum of pectolite (lower spectrum) over the 500–4000 cm^{-1} spectral range.

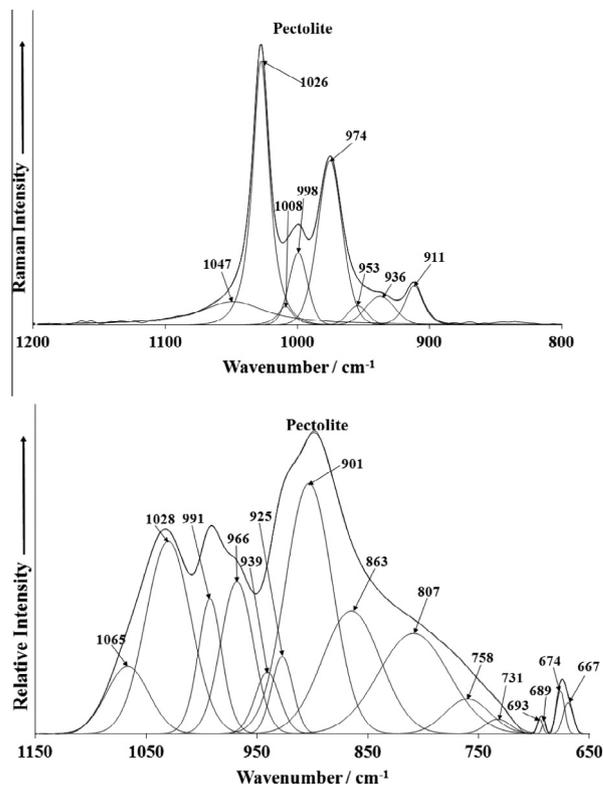


Fig. 4. (a) Raman spectrum of pectolite over the 800–1200 cm^{-1} spectral range and (b) infrared spectrum of pectolite over the 650–1150 cm^{-1} spectral range.

characterisation of calcium silicate phases by a number of techniques including Raman spectroscopy.

The Raman spectra of pectolite in the 300–800 cm^{-1} region and in the 100–300 cm^{-1} region are displayed in Fig. 5. A single intense sharp Raman band is observed at 653 cm^{-1} . The Raman band at 653 cm^{-1} is assigned to the OSiO bending vibrations of the Si_3O_8 units. The equivalent bands in the infrared spectrum are observed at 667, 674, 689 and 693 cm^{-1} (Fig. 4b). These bands are assigned to OSiO bending modes. Black et al. [23] reported the spectra of hydrated calcium silicates and reported a strong Raman band at 670 cm^{-1} and attributed this band to a Si–O–Si symmetric bending mode. The band is in a higher wavenumber position than for a single silicate chain [9]. This difference is related to the differences in the structures between pectolite and the hydrated calcium silicates. The series of Raman band at 500, 508, 518 and 532 cm^{-1} are assigned to the OSiO out-of-plane bending vibrations of the Si_3O_8 units. A series of low intensity Raman bands are observed at 317, 325, 358, 370, 378, 415 and 463 cm^{-1} . These bands are considered to be associated with Ca–O bonds. Two Raman bands are observed at 505 and 524 cm^{-1} . Bands in these positions are assigned to the OSiO bending modes of SiO_2 units [16]. Some intense Raman bands are observed in the far low wavenumber region. Strong Raman bands are observed at 111, 143, 152, 186, 203, 225 and 276 cm^{-1} with bands of lower intensity at 134 and 259 cm^{-1} . These bands are simply described as lattice vibrations. It is suggested that these bands are related to the OH units and the hydrogen bonding to the silicate units.

The Raman spectrum of pectolite in the 2600 and 3100 cm^{-1} is reported in Fig. 6. No intensity was found in this spectral region in the infrared spectrum. Intense bands are observed in the Raman spectrum. Intense Raman bands are observed at 2809, 2851, 2879 and 2896 cm^{-1} . These bands are assigned to the OH stretching bands of the OH units in pectolite. The range of peak positions provides evidence for a range of hydrogen bond strengths in the structure of pectolite. Both Raman and infrared bands at around

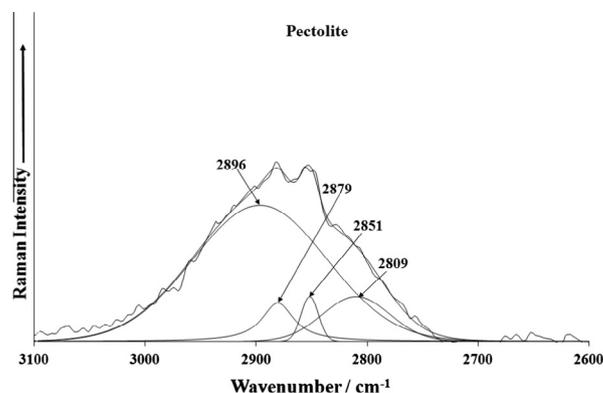


Fig. 6. Raman spectrum of pectolite over the 2600–3100 cm^{-1} spectral range.

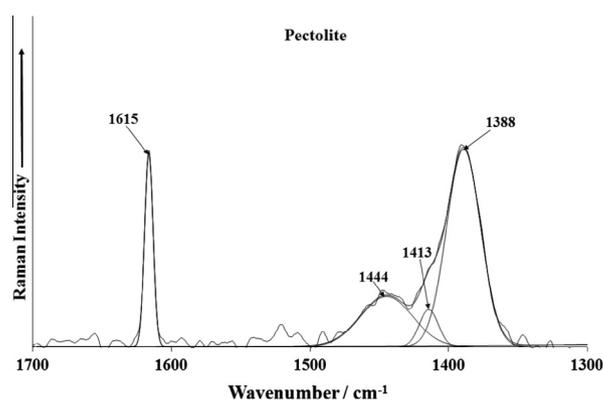


Fig. 7. Raman spectrum of pectolite over the 1300–1700 cm^{-1} spectral range.

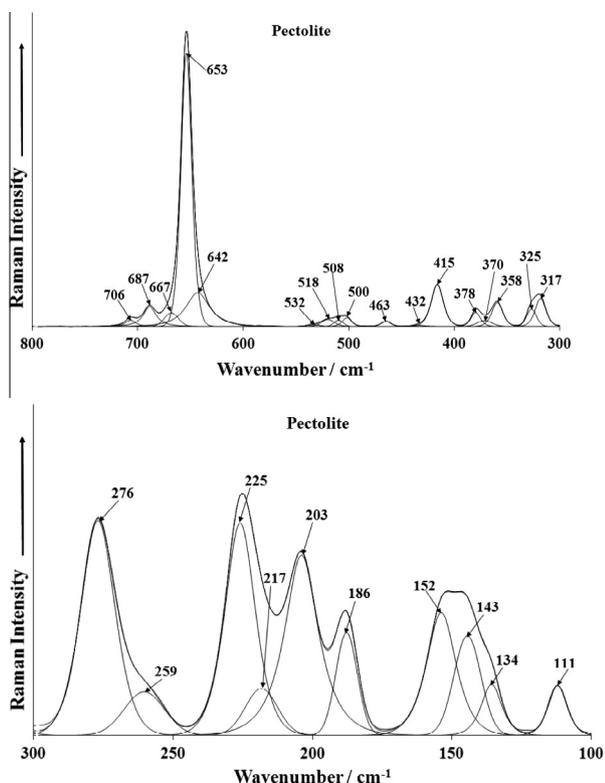


Fig. 5. Raman spectrum of pectolite (upper spectrum) in the 300–800 cm^{-1} spectral range and (b) Raman spectrum of pectolite (lower spectrum) in the 100–300 cm^{-1} spectral range.

2900 cm^{-1} are attributed to strong hydrogen bonding. The hydrogen bond distance is very short. The infrared band at 3529 cm^{-1} is attributed to water stretching vibration with intermediate hydrogen bond strength. Such a range of hydrogen bond strengths is also reflected in the water bending modes (Fig. 7) where the band at 1615 cm^{-1} . This latter band is attributed to the water bending modes of water involved in hydrogen bonding.

Conclusions

Pectolite as a building material has many and varied applications which are based upon the inherent properties of pectolite including porosity, thermal insulation and thermal decomposition temperature [24]. In order to raise the on-set combustion temperature of plaster boards, new types of plaster boards are made by combining gypsum with pectolite or some other suitable silicate mineral [24]. As part of this research, we have undertaken a vibrational spectroscopic study of pectolite to determine the characteristic bands of this mineral. In this way the ready identification of the mineral can be made.

The Raman spectrum of pectolite is characterised by intense sharp bands at 974, 998, 1026 and 1047 cm^{-1} . These bands are assigned to the SiO stretching vibrations of the Si_3O_8 units. Intense Raman bands at 642, 653, 667, 687 and 706 cm^{-1} are assigned to OSiO bending vibrations. The intense Raman band profile centred upon 2880 cm^{-1} is attributed to the OH stretching vibrations of the OH units in the pectolite structure. The mineral pectolite is well and truly characterised by its Raman spectrum. Further, Raman spectroscopy offers a technique for the study of pectolite and its admixtures including gypsum.

Acknowledgements

The financial and infra-structure support of the Discipline of Nanotechnology and Molecular Science, Science and Engineering Faculty of the Queensland University of Technology, is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation. The authors would like to acknowledge the Center of Microscopy at the Universidade Federal de Minas Gerais (<http://www.microscopia.ufmg.br>) for providing the equipment and technical support for experiments involving electron microscopy.

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.saa.2014.06.097>.

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