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1 **A vibrational spectroscopic study of the silicate mineral pectolite - NaCa₂Si₃O₈(OH)**

2
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15
16 **Abstract:**

17 The mineral pectolite NaCa₂Si₃O₈(OH) is a crystalline sodium calcium silicate which has the
18 potential to be used in plaster boards and in other industrial applications.

19 Raman bands at 974 and 1026 cm⁻¹ are assigned to the SiO stretching vibrations of linked
20 units of Si₃O₈ units. Raman bands at 974 and 998 cm⁻¹ serve to identify Si₃O₈ units. The
21 broad Raman band at around 936 cm⁻¹ is attributed to hydroxyl deformation modes. Intense
22 Raman band at 653 cm⁻¹ is assigned to OSiO bending vibration. Intense Raman bands in the
23 2700 to 3000 cm⁻¹ spectral range are assigned to OH stretching vibrations of the OH units in
24 pectolite. Infrared spectra are in harmony with the Raman spectra. Raman spectroscopy with
25 complimentary infrared spectroscopy enables the characterisation of the silicate mineral
26 pectolite.

27
28 **Keywords:** silicate, Raman spectroscopy, pectolite, infrared spectroscopy, molecular
29 structure

30
31

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32 **Introduction**

33 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
34 sodium calcium inosilicate hydroxide and is the calcium analogue of serandite. It crystallizes
35 in the triclinic system typically occurring in radiated or fibrous crystalline masses and is
36 primary mineral in nepheline syenites. A hydrothermal mineral in cavities in basalts and
37 diabases; in serpentinites and peridotites; from metamorphosed high-calcium rocks. Pectolite
38 is triclinic, space group $\bar{P}1$, with 15 nonhydrogen atoms in the asymmetric unit [1]. A review
39 of the structure of pectolite and related minerals has been published [2]. The structure of
40 pectolite is related to that of wollastonite [3]. A number of Ca and Mn pyroxenes and
41 pyroxenoids are known and such minerals forms paragenesis in contact metamorphic rocks,
42 including pectolite, rhodonite, pyroxmangite, nambulite among others. The development and
43 application of spectroscopy technics can be an important tool in the non-destructive study of
44 minerals mineral deposits.

45

46 No Raman spectroscopic analyses of pectolite and related minerals have been forthcoming.
47 There are spectra in the RRUFF data base but no band assignments are given. Some infrared
48 studies have been undertaken [4]. Studies of hydrogen bonding in silicates relates the
49 position of the hydroxyl stretching vibration to the hydrogen bond distances [5]. Raman
50 studies of cement phases have been forthcoming [6-9]. In this way, identification of mineral
51 phases using Raman spectroscopy has been made. Some infrared studies of calcium silicates
52 have been undertaken, the purpose of which is for mineral identification and mineral content
53 [10-12]. Some Raman spectra of calcium silicates have been collected and a number of the
54 spectra were shown to be dependent upon the number of condensed silica tetrahedra [8].
55 Such detailed assignment of infrared and Raman bands for a wide range of silicate structures
56 was made by Dowty [13-16]. The thermal decomposition of calcium silicates has also been
57 measured [17-19]. Pectolite is readily synthesised and is often found as components in
58 cements [20, 21]. Pectolite may be used to make reinforced organic polymers. It can be used
59 for the removal of organic polyelectrolytes and their metal complexes by adsorption onto
60 pectolite. Pectolite and related minerals can be used for heavy metal uptake for example
61 Nd(II) [20]. Because of the number and wide variation of the applications of the mineral
62 pectolite, it is important to be readily able to identify the mineral pectolite using vibrational
63 spectroscopic techniques.

64

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

71

72 **Experimental**

73 *Samples description and preparation*

74 The pectolite sample studied in this work occurs as single crystals with fibrous to acicular
75 habitus up to 3 cm (please see Figure 1). The mineral forms radial aggregates. The sample is
76 part of the collection of the Geology Department of the Federal University of Ouro Preto,
77 Minas Gerais, Brazil, with sample code SAC-100. The sample was gently crushed and single
78 crystals were selected under a stereomicroscope Leica MZ4. The pectolite sample studied in
79 this work was analyzed by scanning electron microscopy (SEM) in the EDS mode to support
80 the mineral characterization.

81

82 *Scanning electron microscopy (SEM)*

83 Experiments and analyses involving electron microscopy were performed in the Center of
84 Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais,
85 Brazil (<http://www.microscopia.ufmg.br>). Pectolite crystals were coated with a 5nm layer of
86 evaporated carbon. Secondary Electron and Backscattering Electron images were obtained
87 using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses
88 in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and was
89 applied to support the mineral characterization.

90

91 *Raman microprobe spectroscopy*

92 Crystals of pectolite were placed on a polished metal surface on the stage of an Olympus
93 BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is
94 part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a
95 filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a
96 Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and
97 collected at a nominal resolution of 2 cm^{-1} and a precision of $\pm 1\text{ cm}^{-1}$ in the range between

98 200 and 4000 cm^{-1} . Repeated acquisitions on the crystals using the highest magnification
99 (50x) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra
100 were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

101

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

105

106 *Infrared spectroscopy*

107 Infrared spectra of pectolite were obtained using a Nicolet Nexus 870 FTIR spectrometer
108 with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1}
109 range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror
110 velocity of 0.6329 cm/s . Spectra were co-added to improve the signal to noise ratio.

111

112 Spectral manipulation such as baseline correction/adjustment and smoothing were performed
113 using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH,
114 USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package
115 that enabled the type of fitting function to be selected and allows specific parameters to be
116 fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product
117 function with the minimum number of component bands used for the fitting process. The
118 Gaussian-Lorentzian ratio was maintained at values greater than 0.7 and fitting was
119 undertaken until reproducible results were obtained with squared correlations of r^2 greater
120 than 0.995.

121

122 **Results and discussion**

123 *Mineral characterization*

124 The SEM image of pectolite sample studied in this work is shown in Figure 1. The image
125 shows a group of acicular crystals up to 1 mm. Qualitative chemical analysis shows a
126 homogeneous phase, composed by Ca, Na and Si. No other contaminant elements were
127 observed and the sample can be considered as a single phase (Figure 2). Zonation was also
128 not observed.

129

130 **Vibrational Spectroscopy**

131 The Raman spectrum of pectolite over the 100 to 4000 cm^{-1} spectral range is shown in Figure
132 3a. This figure shows the position and relative intensity of the Raman bands. It is noted there
133 are large parts of the spectrum where little or no intensity is observed. The Raman spectrum
134 is therefore subdivided into sections based upon the types of vibration being studied. The
135 infrared spectrum of pectolite over the 500 to 4000 cm^{-1} spectral range is displayed in Figure
136 3b. This figure shows the position and relative intensities of the infrared bands. The infrared
137 spectrum is subdivided into sections based upon the type of vibration being studied.

138

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

150

151 The 1042 cm^{-1} Raman band is not observed in the infrared spectrum (Figure 4b). This
152 indicates that the vibration contains a centre of symmetry. Infrared bands are observed at
153 1028 and 1065 cm^{-1} . This latter band is not observed in the Raman spectrum. Strong infrared
154 bands are observed at 901, 925, 966 and 991 cm^{-1} . Dowty calculated the position of infrared
155 bands for silicate structures and also showed measured spectra of the equivalent theoretical
156 system. The infrared bands shown in Dowty's work were broad. In this work the infrared
157 bands of pectolite are reasonably sharp and readily resolved. Black *et al.* [23] reported the
158 Raman spectra of a series of hydrated calcium silicate compounds with varying Ca/Si ratios.
159 There is some resemblance between the spectra of this reference (see Figure 3 of this
160 reference) and these spectra. However, it must be pointed out that the compounds
161 synthesised by Black *et al.* were hydrated calcium silicates. In comparison, pectolite is a
162 hydroxy sodium calcium silicate. Richardson *et al.* [9] published a review of cement phases
163 and their characterisation of calcium silicate phases by a number of techniques including
164 Raman spectroscopy.

165

166 The Raman spectra of pectolite in the 300 to 800 cm^{-1} region and in the 100 to 300 cm^{-1}
167 region are displayed in Figure 5. A single intense sharp Raman band is observed at 653 cm^{-1} .
168 The Raman band at 653 cm^{-1} is assigned to the OSiO bending vibrations of the Si_3O_8 units.
169 The equivalent bands in the infrared spectrum are observed at 667, 674, 689 and 693 cm^{-1}
170 (Figure 4b). These bands are assigned to OSiO bending modes. Black *et al.* [23] reported the
171 spectra of hydrated calcium silicates and reported a strong Raman band at 670 cm^{-1} and
172 attributed this band to a Si-O-Si symmetric bending mode. The band is in a higher
173 wavenumber position than for a single silicate chain [9]. This difference is related to the
174 differences in the structures between pectolite and the hydrated calcium silicates. The series
175 of Raman band at 500, 508, 518 and 532 cm^{-1} are assigned to the OSiO out-of-plane bending
176 vibrations of the Si_3O_8 units. A series of low intensity Raman bands are observed at 317,
177 325, 358, 370, 378, 415 and 463 cm^{-1} . These bands are considered to be associated with Ca-
178 O bonds. Two Raman bands are observed at 505 and 524 cm^{-1} . Bands in these positions are
179 assigned to the OSiO bending modes of SiO_2 units [16]. Some intense Raman bands are
180 observed in the far low wavenumber region. Strong Raman bands are observed at 111, 143,
181 152, 186, 203, 225 and 276 cm^{-1} with bands of lower intensity at 134 and 259 cm^{-1} . These
182 bands are simply described as lattice vibrations. It is suggested that these bands are related to
183 the OH units and the hydrogen bonding to the silicate units.

184

185 The Raman spectrum of pectolite in the 2600 and 3100 cm^{-1} is reported in Figure 6. No
186 intensity was found in this spectral region in the infrared spectrum. Intense bands are
187 observed in the Raman spectrum. Intense Raman bands are observed at 2809, 2851, 2879
188 and 2896 cm^{-1} . These bands are assigned to the OH stretching bands of the OH units in
189 pectolite. The range of peak positions provides evidence for a range of hydrogen bond
190 strengths in the structure of pectolite. Both Raman and infrared bands at around 2900 cm^{-1}
191 are attributed to strong hydrogen bonding. The hydrogen bond distance is very short. The
192 infrared band at 3529 cm^{-1} is attributed to water stretching vibration with intermediate
193 hydrogen bond strength. Such a range of hydrogen bond strengths is also reflected in the
194 water bending modes (Figure 7) where the band at 1615 cm^{-1} . This latter band is attributed to
195 the water bending modes of water involved in hydrogen bonding.

196

197 **Conclusions**

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

205

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

213

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220 equipment and technical support for experiments involving electron microscopy.

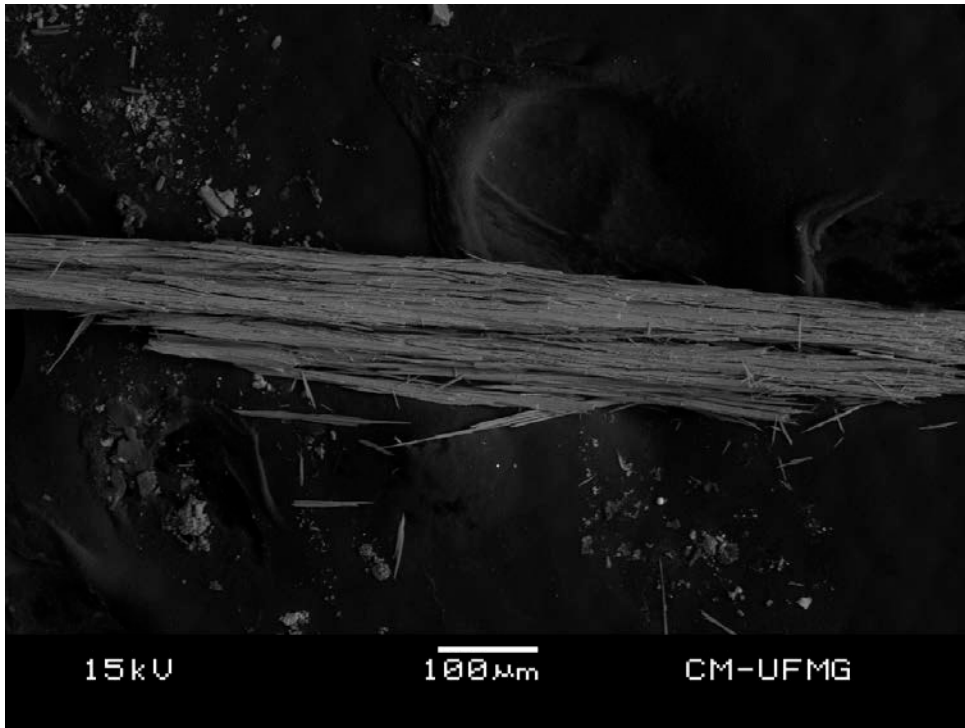
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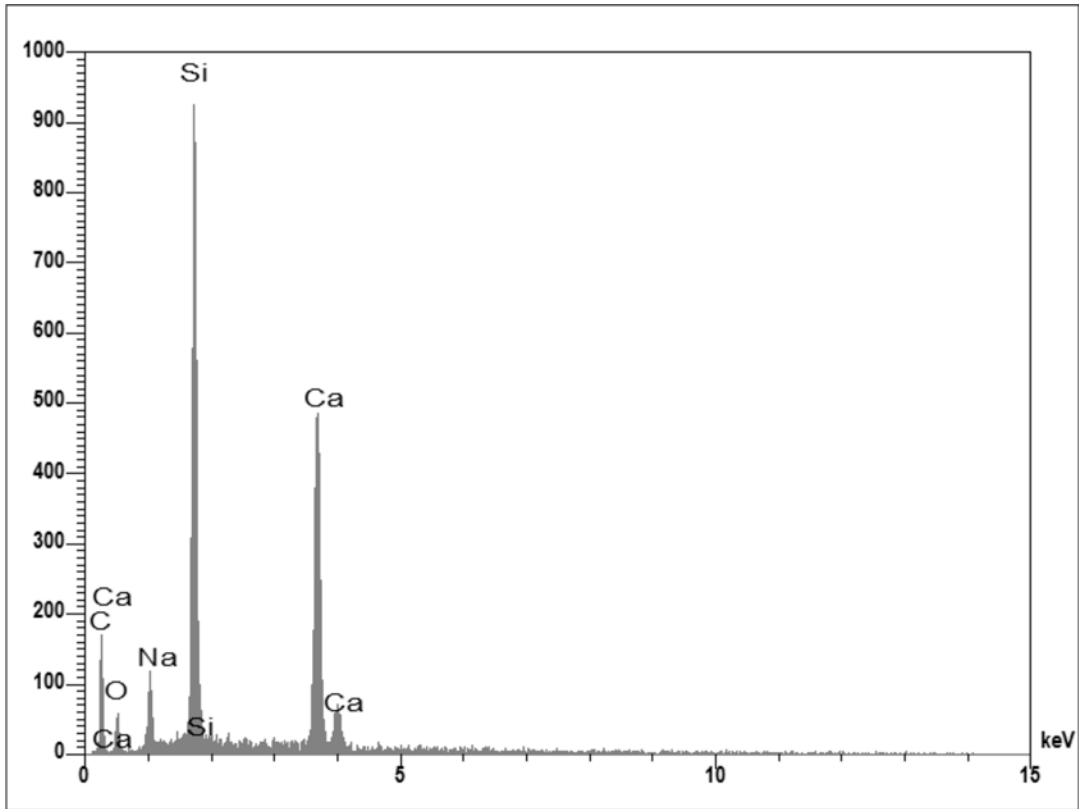
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284 **Figure 1 - Backscattered electron image (BSI) of a pectolite**

285 **group of acicular crystals up to 1.0 mm in length.**

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290 **Figure 2 - EDS spectra of pectolite**

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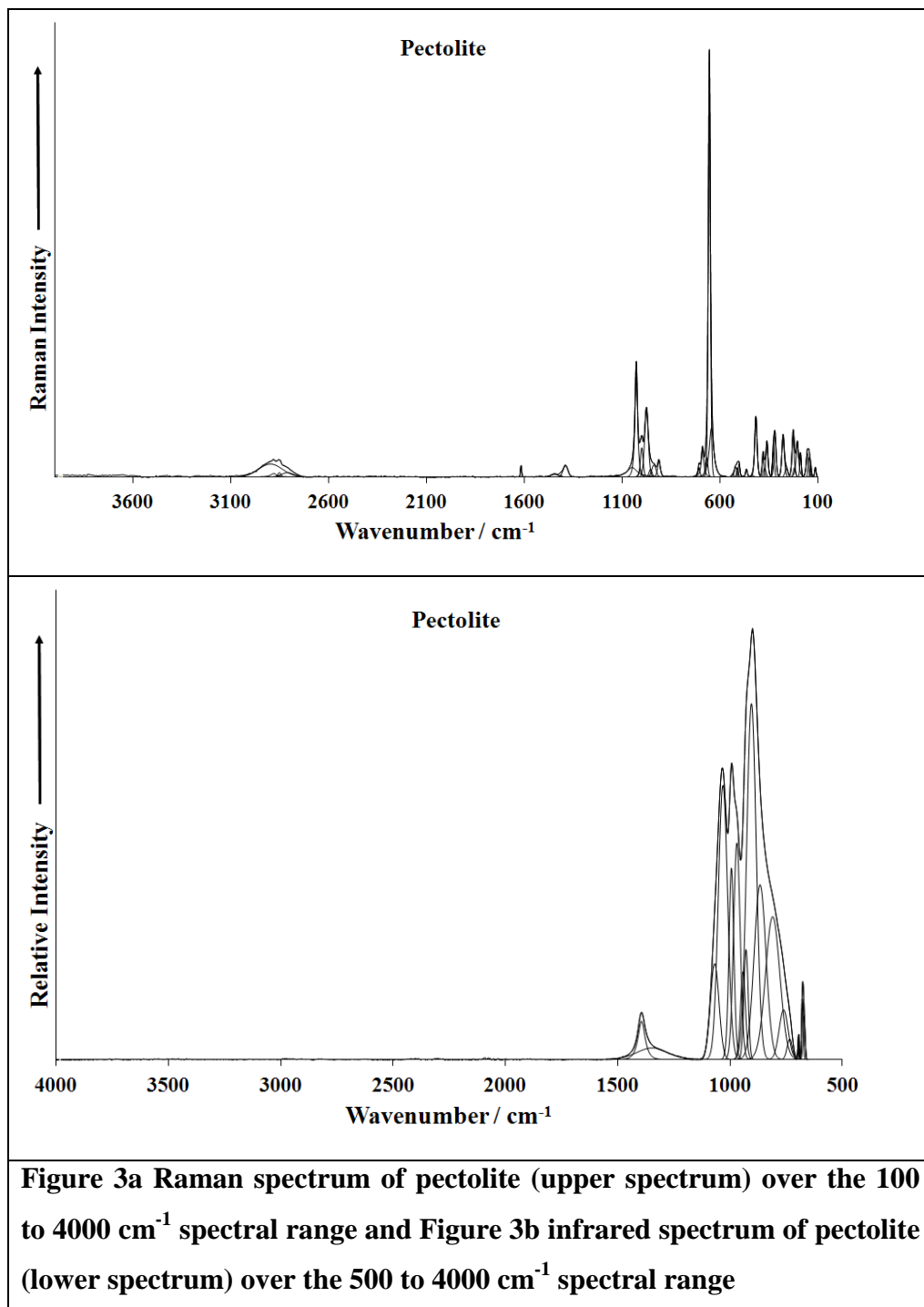
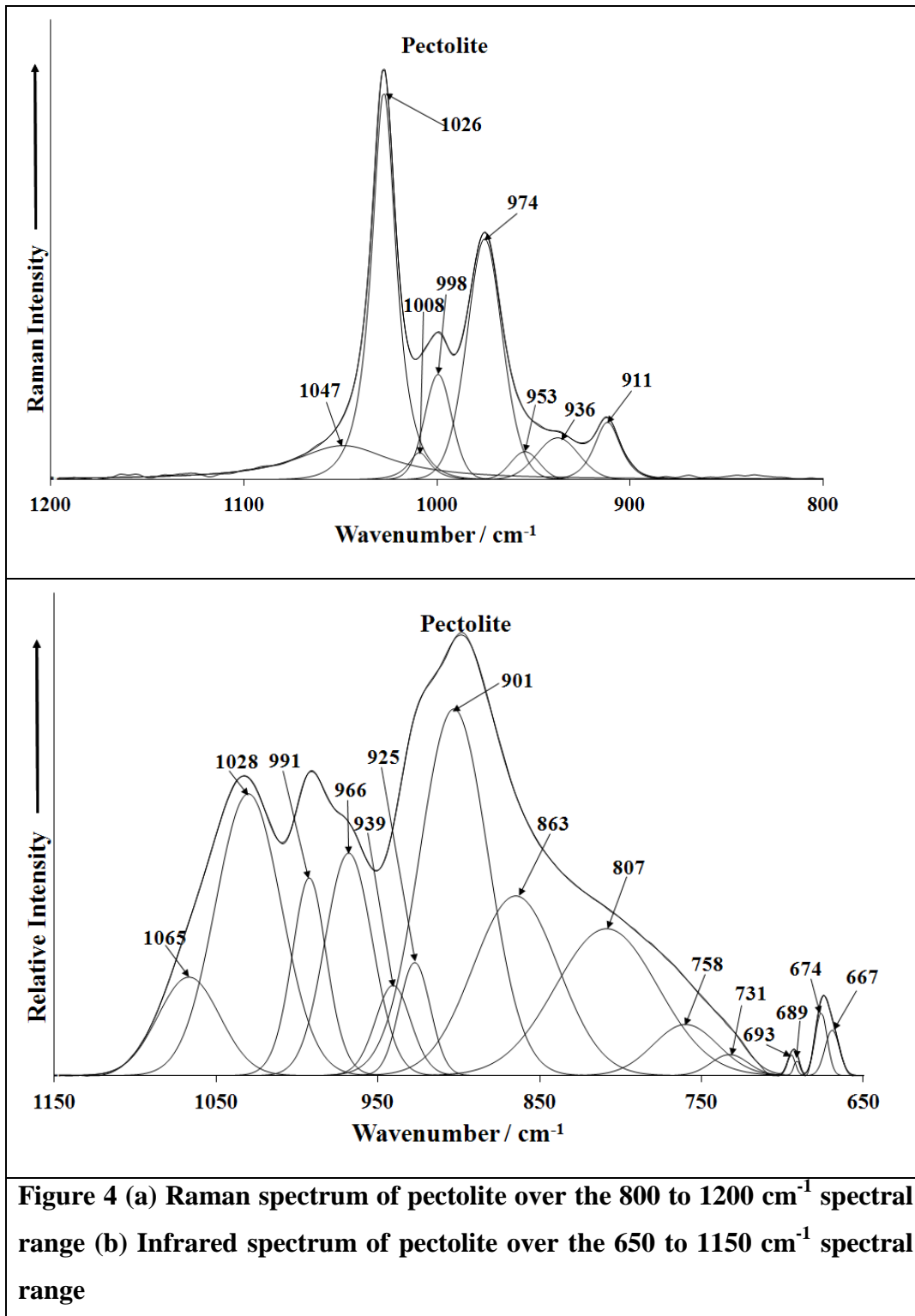


Figure 3a Raman spectrum of pectolite (upper spectrum) over the 100 to 4000 cm⁻¹ spectral range and Figure 3b infrared spectrum of pectolite (lower spectrum) over the 500 to 4000 cm⁻¹ spectral range

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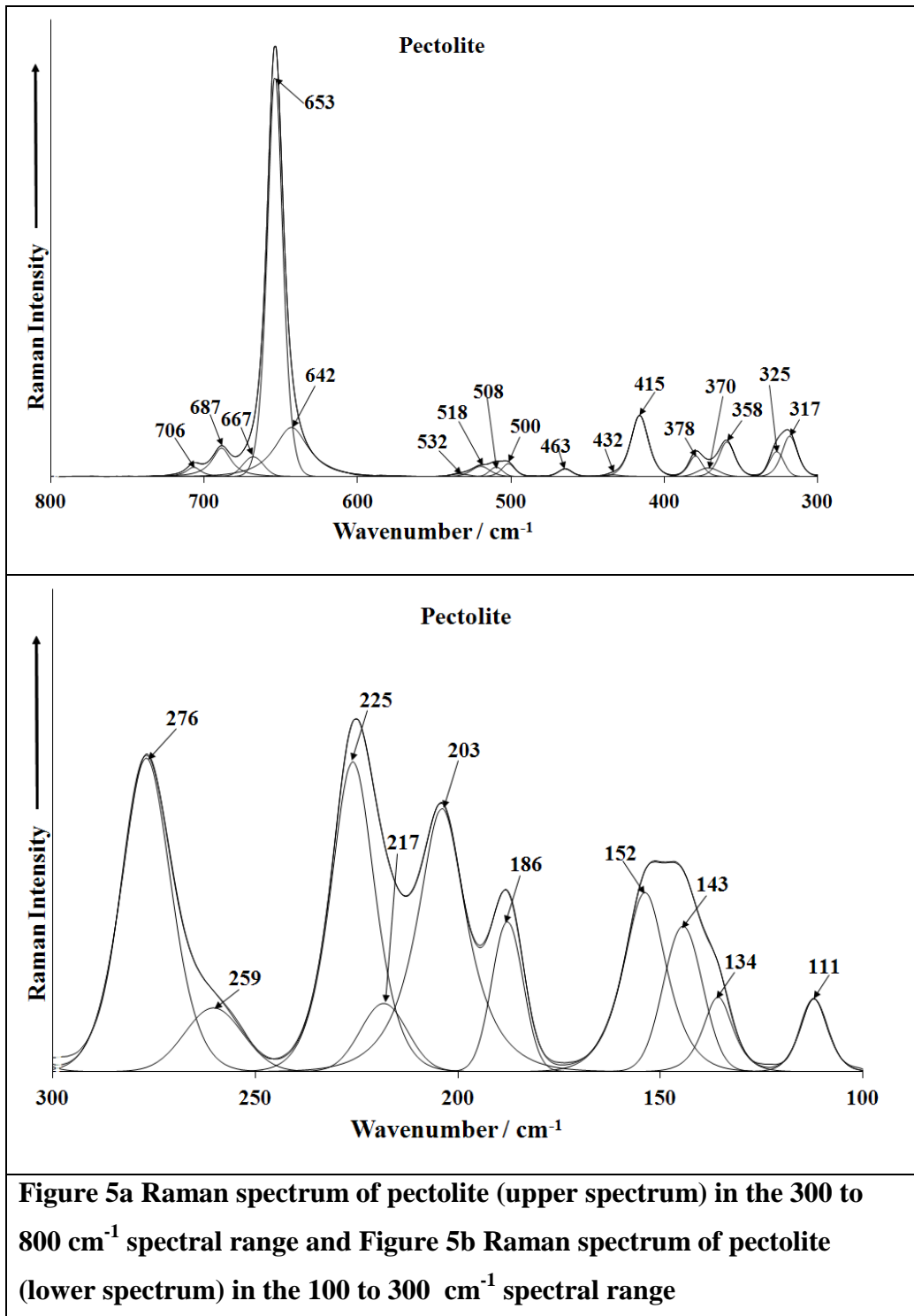
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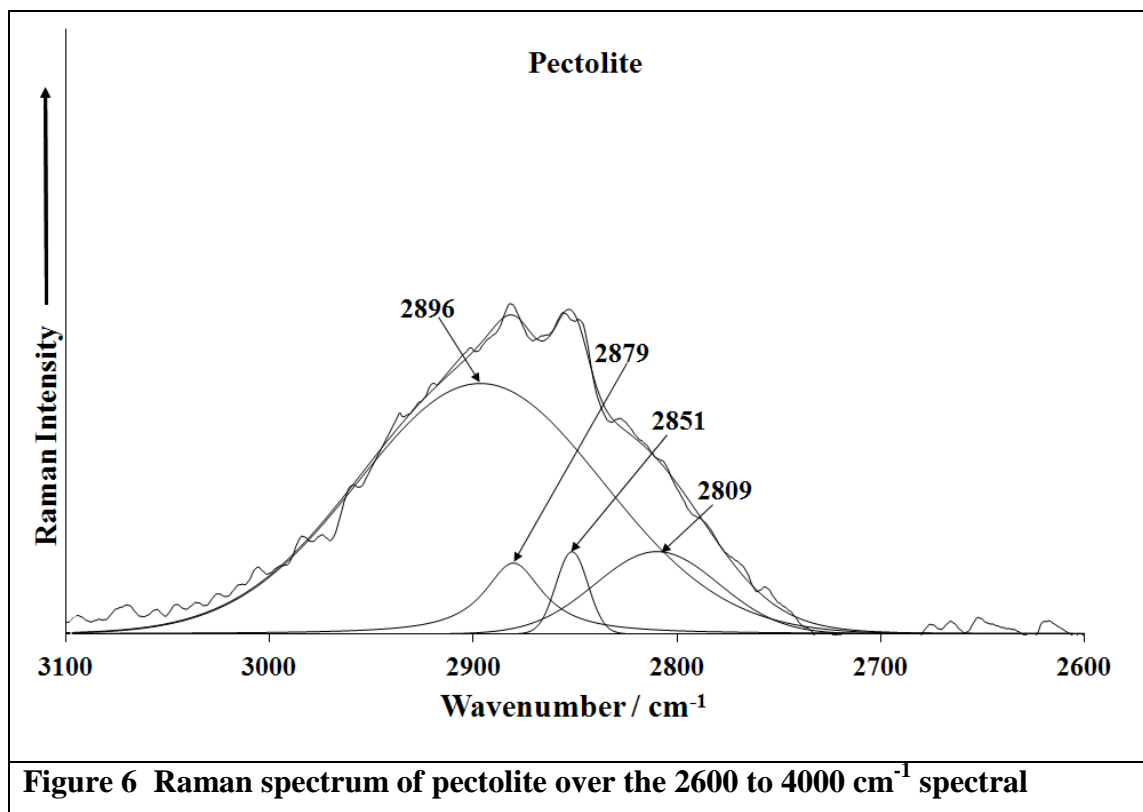


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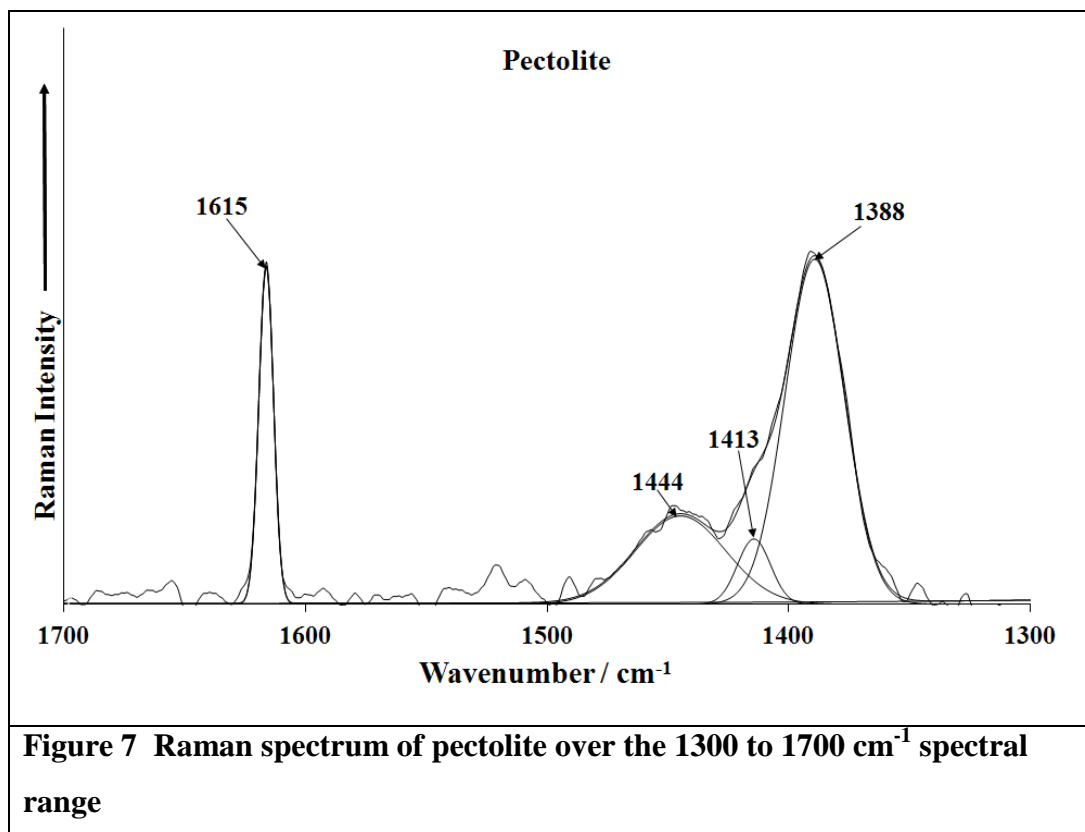


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