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1 **Infrared and infrared emission spectroscopy of nesquehonite $\text{Mg}(\text{OH})(\text{HCO}_3)\cdot 2\text{H}_2\text{O}$ –**
2 **implications for the formula of nesquehonite**

3
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5
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8
9 **Abstract**

10
11 The mineral nesquehonite $\text{Mg}(\text{OH})(\text{HCO}_3)\cdot 2\text{H}_2\text{O}$ has been analysed by a combination of
12 infrared (IR) and infrared emission spectroscopy (IES). Both techniques show OH
13 vibrations, both stretching and deformation modes. IES proves the OH units are stable up to
14 450°C. The strong IR band at 934 cm^{-1} is evidence for MgOH deformation modes supporting
15 the concept of HCO_3^- units in the molecular structure.

16 Infrared bands at 1027, 1052 and 1098 cm^{-1} are attributed to the symmetric stretching modes
17 of HCO_3^- and CO_3^{2-} units. Infrared bands at 1419, 1439, 1511, and 1528 cm^{-1} are assigned to
18 the antisymmetric stretching modes of CO_3^{2-} and HCO_3^- units. IES supported by
19 thermoanalytical results defines the thermal stability of nesquehonite
20 IES defines the changes in the molecular structure of nesquehonite with temperature. The
21 results of IR and IES supports the concept that the formula of nesquehonite is better defined
22 as $\text{Mg}(\text{OH})(\text{HCO}_3)\cdot 2\text{H}_2\text{O}$.

23
24 **Keywords:** Nesquehonite, chemical formula, infrared spectroscopy, infrared emission
25 spectroscopy

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29 **Introduction**

30

31 The mineral nesquehonite is one of several magnesium carbonate minerals,
32 which may result as a product of geosequestration. Other hydrous carbonates including
33 hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, or $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), artinite
34 ($\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), and lansfordite ($\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$) are
35 extremely important to the sequestration process for the removal of atmospheric CO_2 .
36 Geo-sequestration is a method where by various greenhouse gases such as carbon dioxide
37 (CO_2) can be trapped either physically or chemically in systems other than that of the
38 atmosphere in order to prevent the detrimental effects on global warming due to greenhouse
39 gases. The feasibility for various carbonate and other minerals to provide long term stable
40 CO_2 storage options has been explored by various authors [1-6]. The formation of carbonate
41 minerals is important for the removal of greenhouse gases from the atmosphere.

42

43 The name nesquehonite comes from the location of a coal mine at Nesquehoning,
44 Pennsylvania, USA, where the mineral was first located. Nesquehonite exhibits the crystal
45 structure of monoclinic-prismatic and has the symmetry point group of $\text{P}2_1/\text{n}$ [7, 8]. There is
46 some argument in the literature as to the true empirical formula of nesquehonite [9-14].
47 Nesquehonite belongs to a group of secondary carbonate minerals known as hydroxy-
48 carbonates to which other mineral variations belong such as hydromagnesite. The chemical
49 formula is commonly written as ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) or $\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2\text{H}_2\text{O}$. At a unit cell
50 level, the mineral appears to be a layer structure as may be observed with other hydroxy-
51 carbonate minerals. Magnesium ions are contained in an octahedrally coordinated site which
52 exhibits distortion. The water of hydration is understood to be located within the layers of
53 the greater structure, although the exact nature is not clearly understood [15, 16].

54

55 Nesquehonite is found in nature as either prismatic crystals with a slender prism shape
56 or radial crystals which radiate from a nucleation centre without producing stellar forms.
57 Large single crystals of nesquehonite are found in the natural mineral. It is probable that the
58 deposits found in caves known as 'moon milk' contain significant amounts of nesquehonite
59 [17]. The nesquehonite and related minerals are formed through crystallisation from solutions
60 percolating through the caves. The mineral has been successfully synthesised and
61 characterised [18, 19]. The physical properties of the crystal structure and twinning seen in
62 nesquehonite have been discussed in depth by various authors [20-23]. This is not the focus

63 in this study and will not be discussed further at this point even though the empirical
64 chemical formula is under constant investigation. The mineral nesquehonite has been studied
65 by infrared spectroscopy for an extended period of time [24-26]. Some infrared studies have
66 been undertaken and the conclusion was made that no bicarbonate groups existed in the
67 structure [14]. It is probable that nesquehonite exists as an equilibrium product between
68 other magnesium hydroxy carbonates such as hydromagnesite and dypingite. These equilibria
69 depend upon the temperature and the partial pressure of carbon dioxide.

70

71 Infrared and infrared emission spectroscopy have proven very useful for the study of
72 minerals. Indeed IR and IES spectroscopy have proven most useful for the study of
73 diagenetically related minerals as often occurs with these hydrated hydroxyl carbonate
74 minerals. Some previous studies have been undertaken by the authors using infrared
75 emission spectroscopy to study complex secondary minerals formed by crystallisation from
76 concentrated carbonate solutions [27-32]. The aim of this paper is to present the infrared and
77 infrared emission spectra of nesquehonite and to discuss the spectra from a structural point of
78 view. The paper is a part of systematic studies of vibrational spectra of minerals of secondary
79 origin in the oxide supergene zone and their synthetic analogs.

80

81

82 **Experimental**

83

84 *Nesquehonite mineral*

85

86 The mineral nesquehonite (museum reference number M35945) was supplied by
87 Museum Victoria and is a type mineral [33]. The mineral originated from Lansford,
88 Pennsylvania, USA.

89 *Infrared emission spectroscopy*

90 FTIR emission spectroscopy was carried out on a Nicolet spectrophotometer equipped
91 with a TGS detector, which was modified by replacing the IR source with an emission cell. A
92 description of the cell and principles of the emission experiment have been published
93 elsewhere [27-32]. Spectral resolution is nominally 4 cm^{-1} . Approximately 0.2 mg of
94 carbonate mineral was ground to a fine powder and spread as a thin layer (approximately 0.2

95 microns) on a 6 mm diameter platinum surface and held in an inert atmosphere within a
96 nitrogen-purged cell during heating.

97

98 *Mid-IR spectroscopy*

99 Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a
100 smart endurance single bounce diamond ATR cell. The powdered mineral was placed upon
101 the plates of the ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-
102 addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra
103 were co-added to improve the signal to noise ratio.

104

105 **Band component analysis**

106

107 Band component analysis was undertaken using the Jandel ‘Peakfit’ (Erkrath,
108 Germany) software package which enabled the type of fitting function to be selected and
109 allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a
110 Lorentz-Gauss cross-product function with the minimum number of component bands used
111 for the fitting process. The Lorentz-Gauss ratio was maintained at values greater than 0.7 and
112 fitting was undertaken until reproducible results were obtained with squared correlations (r^2)
113 greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band
114 separation or changes in the spectral profile.

115

116 **Results and Discussion**

117

118 **Background**

119

120 Carbonates in a range of minerals have been studied by vibrational spectroscopy. It is
121 important to understand the spectroscopy of the carbonate ion, is a function of its symmetry.
122 The free ion, CO_3^{2-} with D_{3h} symmetry exhibits four normal vibrational modes; a symmetric
123 stretching vibration (ν_1), an out-of-plane bend (ν_2), a doubly degenerate antisymmetric stretch
124 (ν_3) and another doubly degenerate bending mode (ν_4). The symmetries of these modes are
125 A_1' (R) + A_2'' (IR) + E' (R, IR) + E'' (R, IR) and occur at 1063, 879, 1415 and 680 cm^{-1}
126 respectively (R=Raman active; IR=infrared red active). Generally, strong Raman modes
127 appear around 1100 cm^{-1} due to the symmetric stretching vibration (ν_1), of the carbonate

128 groups, while intense IR and weak Raman peaks near 1400 cm^{-1} are due to the antisymmetric
129 stretch (ν_3). Infrared modes near 800 cm^{-1} are derived from the out-of-plane bend (ν_2).
130 Infrared and Raman modes around 700 cm^{-1} region are due to the in-plane bending mode (ν_4).
131 This mode is doubly degenerate for undistorted CO_3^{2-} groups. As the carbonate groups
132 become distorted from regular planar symmetry, this mode splits into two components.
133 Infrared and Raman spectroscopy provide sensitive test for structural distortion of CO_3^{2-} .
134 White in Farmer's treatise (Chapter 12) stated that the overall results expected from this
135 phenomenon is a progression from normally sharp bands, distinctive to carbonate proceed
136 into more broad and shifted bands resulting in diffuse spectra [7]. However, even though the
137 effects of hydrogen bonding are apparent in vibrational spectroscopy of hydrated magnesium
138 carbonates, it is not expected to greatly affect the internal modes of the CO_3^{2-} in
139 nesquehonite, so sharp bands are still expected.

140

141 *Infrared spectroscopy*

142

143 The infrared spectrum of nesquehonite in the 2900 to 3700 cm^{-1} is displayed in Figure
144 1. Clearly there are eight bands observed at 3012 , 3125 , 3261 , 3346 , 3441 , 3483 , 3560 and
145 3605 cm^{-1} . The first four bands are assigned to water stretching vibrations. The authors
146 assign the latter four bands to the OH stretching vibrations of OH units. The observation of
147 OH stretching bands supports the concept that the formula is $\text{Mg}(\text{HCO}_3)(\text{OH})\cdot 2\text{H}_2\text{O}$. W.B.
148 White, [14] reported five infrared bands for nesquehonite at 2930 , 3140 , 3270 , 3430 and 3568
149 cm^{-1} . There is good general agreement between the band positions of this work and that
150 reported by White. The authors assign the band at 3012 cm^{-1} to water strongly hydrogen
151 bonded to carbonate or bicarbonate units. The position of the band suggests that water is
152 strongly hydrogen bonded in the nesquehonite structure. In the Raman spectrum of a
153 synthetic nesquehonite [18] at 25°C , four bands are resolved at 3124 , 3295 , 3423 and 3550
154 cm^{-1} . The first three bands are attributed to water stretching vibrations. The last Raman band
155 is assigned to the symmetric stretching mode of the OH units. The authors assign the higher
156 infrared wavenumber bands at 3560 and 3605 cm^{-1} to non-hydrogen bonded OH stretching
157 vibrations. The two infrared bands at 3441 and 3483 cm^{-1} are attributed to hydrogen bonded
158 OH units. These observations support the concept of firstly the non-equivalence of the OH
159 units in the molecular structure of nesquehonite and also that some OH units are hydrogen-
160 bonded and some are not hydrogen bonded. The reason why different bands are observed
161 depends upon whether the OH units are involved in hydrogen bonding [14]. According to

162 our calculations from thermogravimetric (TG) measurements [34], two moles of water are
163 lost in two steps. Thus the dehydration steps may be written as
164 $\text{Mg}(\text{HCO}_3)(\text{OH})\cdot 2(\text{H}_2\text{O}) \rightarrow \text{Mg}(\text{HCO}_3)(\text{OH})\cdot (\text{H}_2\text{O}) + \text{H}_2\text{O}$ at 157°C
165 and $\text{Mg}(\text{HCO}_3)(\text{OH})\cdot (\text{H}_2\text{O}) \rightarrow \text{Mg}(\text{HCO}_3)(\text{OH}) + \text{H}_2\text{O}$ at 180°C. According to the
166 differential thermal analysis (DTA) patterns of Beck [35] (page 995 of this reference), water
167 of crystallisation is lost in two steps. The reaction begins at 140°C and is complete by 300°C.
168 The dehydration steps as reported is in general agreement with the values of Beck [35].
169 White [14] presented infrared data and made the conclusion that no bicarbonate existed in
170 the nesquehonite structure. Gasiunas et al.[15] presented pmr data (proton magnetic
171 resonance) that supported the concept of (HCO_3) units in the nesquehonite structure. These
172 authors reported an infrared band at 2380 cm^{-1} supporting this concept. Hopkinson et al. [36]
173 researched the low temperature equilibrium between hydromagnesite and nesquehonite and
174 presented data based on the FT-Raman and FT-IR that supported the bicarbonate formulation
175 of nesquehonite as $\text{Mg}(\text{HCO}_3)(\text{OH})\cdot 2(\text{H}_2\text{O})$.

176

177 The infrared spectrum of nesquehonite in the 1200 to 1800 cm^{-1} region is shown in
178 Fig. 2. The higher wavenumber bands in this spectrum at 1636 and 1683 cm^{-1} are attributed to
179 water bending vibration. Based upon the band position of water stretching vibrations, the
180 authors propose that water is strongly hydrogen bonded in the structure of nesquehonite. The
181 water bending mode at 1683 cm^{-1} reaffirms this concept. The water bending mode is
182 normally observed for liquid water at 1625 cm^{-1} and for water in the vapour phase at 1595
183 cm^{-1} . The fact that the water bending mode is found at 1683 cm^{-1} implies that the water is
184 very strongly hydrogen bonded. The observation of multiple water bending modes supports
185 the concept of water existing in different bonding environments in the structure of
186 nesquehonite.

187

188 A series of bands at 1382, 1419, 1439 and 1462 cm^{-1} is assigned by the authors to HCO_3^- and
189 CO_3^{2-} antisymmetric stretching modes. The most intense band at 1419
190 cm^{-1} is attributed to the CO_3^{2-} antisymmetric stretching band. The authors assign the
191 additional bands at 1511, 1528, 1584 cm^{-1} to the HCO_3^- antisymmetric stretching vibrations.
192 White (Chapter 12 in Farmer's treatise) reported infrared bands at 1415, 1469 and 1518 cm^{-1} .
193 The splitting of these bands is related to the formation of HCO_3^- units [37]. Ponizovskii et al.
194 stated that the splitting of the bands at 1430 and 1540 cm^{-1} resulted from bicarbonate
195 formation. Smolin and Ziborova [38] studied natural and synthetic hydromagnesite and

196 nesquehonite and identified a band at 595 cm^{-1} and proposed that this band proved the
197 presence of OH units in the nesquehonite structure [38]. In this analysis bicarbonate anions
198 result from the presence of the OH units. Two quite intense bands are found at 1027 and 1052
199 cm^{-1} (Fig. 3). The authors assign these bands to the Raman forbidden HCO_3^- bicarbonate
200 symmetric stretching mode. The band at 1098 cm^{-1} is attributed to the CO_3^{2-} carbonate
201 symmetric stretching mode. The bands are very intense in the Raman spectrum. White in
202 Farmer's treatise (Chapter 12) reported an infrared band at 1097 cm^{-1} , although other low
203 intensity bands may be observed in the spectrum of White [14]. The observation of two
204 bands supports the concept of two non-equivalent carbonate units in the nesquehonite
205 structure.

206
207 An intense band at 934 cm^{-1} (Fig. 3) is assigned to the MgOH deformation mode. The
208 observation of this band proves that OH units exist in the nesquehonite molecular structure
209 and supports the concept that bicarbonate units are also involved in the nesquehonite
210 structure. Infrared bands are observed at 836 and 855 cm^{-1} (Fig. 4). These bands are assigned
211 to the out-of-plane $\nu_2\text{ CO}_3^{2-}$ and $\nu_2\text{ HCO}_3^-$ bending modes. Farmer reported a single band at
212 852 cm^{-1} [7]. Infrared bands are observed at 710, 748 and 792 cm^{-1} and are assigned to the in-
213 plane bending mode (ν_4). This mode is doubly degenerate for undistorted CO_3^{2-} groups. As
214 the carbonate groups become distorted from regular planar symmetry, this mode splits into
215 two components. Infrared and Raman spectroscopy provide sensitive test for structural
216 distortion of CO_3^{2-} . Farmer stated that the overall results expected from this phenomenon is a
217 progression from normally sharp bands, distinctive to carbonate proceed into more broad and
218 shifted bands resulting in diffuse spectra [7]. However, even though the effects of hydrogen
219 bonding are apparent in vibrational spectroscopy of hydrated magnesium carbonates, it is not
220 expected to greatly affect the internal modes of the CO_3^{2-} in nesquehonite, so sharp bands are
221 still expected. Data for the ν_4 mode of nesquehonite was not forthcoming in the work of
222 White [7]. A series of infrared bands are observed at 624, 653, 660 and 680 cm^{-1} . These
223 bands are attributed to the ν_4 in-plane bending mode of the HCO_3^- units. White tabulated the
224 band positions of acid carbonates (page 261) and the band positions of for example KHCO_3
225 correspond well with these band positions.

226 227 *Infrared emission spectroscopy*

228

229 The infrared emission spectra of nesquehonite over the temperature range 150
230 to 900°C over the full spectral range are shown in Figure 5. The formula of nesquehonite
231 shows the presence of both water and OH units. At temperatures above 150°C, no water
232 stretching vibrations which would be expected in the 3400 to 3500 cm⁻¹ region are observed.
233 The expanded spectra are displayed in Figures 6 and 7. The infrared band observed at 3636
234 cm⁻¹ is assigned to the OH stretching band of the hydroxyl units. The intensity of this band
235 approaches zero by 500°C. A new broad asymmetric band at around 3720 cm⁻¹ is found
236 above this temperature. Intensity in this band is lost by ~650°C. This band may be attributed
237 to OH units which are not hydrogen bonded. The presence of the distinct OH vibrations at
238 elevated temperatures is significant and it suggests that the formula of the mineral sample
239 used in this study has the structural formula of Mg(HCO₃)(OH).2H₂O, the magnesium
240 hydrogen-carbonate hydroxy, dihydrate. If the formula of nesquehonite which is commonly
241 quoted in the literature as MgCO₃.3H₂O, then one would not expect the distinct OH band to
242 be found. This is not the case. The study by White did not show evidence of bicarbonate ions
243 in nesquehonite [39]. This evidence suggests the possibility of there being a structural isomer
244 of the mineral either MgCO₃.3H₂O or in this case Mg(HCO₃)(OH).2H₂O.

245
246 The infrared emission spectra of nesquehonite in the 600 to 2000 cm⁻¹ region are
247 shown in Figure 7. Four bands are observed at 1417, 1460, 1545 and 1605 cm⁻¹. The first
248 three bands are attributed to the ν₃ HCO₃²⁻ antisymmetric stretching modes. The reason for
249 the multiple bands is related to the structure of the bicarbonate anion in the unit cell. Two
250 independent bicarbonate anions are suggested. The band separation of these bands is lost by
251 450°. This temperature corresponds to the loss of the OH units. Intensity in the very broad
252 bands is lost by 600°C. Two low intensity bands are observed at 1022 and 1054 cm⁻¹. These
253 bands are assigned to the infrared forbidden symmetric stretching mode of the HCO₃⁻ units.
254 The observation of two bands supports the concept that two independent bicarbonate units are
255 found in the nesquehonite structure. Only a single band at 1098 cm⁻¹ is observed in the
256 Raman spectrum [40]. According to our calculations from the TG patterns of nesquehonite
257 [34], three moles of water are lost in two steps. The chemical reactions have been provided
258 above. According to the DTA patterns of Beck [35] (page 995 of this reference), water of
259 crystallisation is lost in two steps. The reaction begins at 140°C and is complete by 300°C.
260 The dehydration steps as reported is in close agreement with the values of Beck [35]. Thus,
261 after 175°C in the Raman spectra, the compound being studied is Mg(HCO₃)(OH). Thus the
262 appearance of new peaks at 1385 and 1405 cm⁻¹ in the Raman spectrum, are attributed to the

263 antisymmetric stretching modes of the $(\text{HCO}_3)^-$ units. The intensity of these bands
264 approaches zero by 425°C .

265

266 The IES band at 856 cm^{-1} is attributed to the ν_2 in-plane bending mode. The band
267 shifts to 860 cm^{-1} at 550°C . The Raman band which might be expected to be observed at
268 around 870 cm^{-1} is not found. The two bands at 677 and 796 cm^{-1} are assigned to the ν_4 out
269 of plane bending mode. Two Raman bands at 765 and 699 cm^{-1} assigned to the ν_4 out of
270 plane bending mode are readily observed in the thermo-Raman spectra even though the
271 spectra are of a low intensity. The intensity of these bands approaches zero by 400°C .

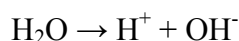
272

273 **Explanation of the formula of the mineral**

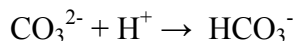
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275 The mineral nesquehonite has two possible formulations namely $\text{Mg}(\text{OH})(\text{HCO}_3)\cdot 2\text{H}_2\text{O}$ or
276 $\text{MgCO}_3\cdot 3\text{H}_2\text{O}$. Controversy over the formula of the mineral exists. A possible explanation
277 of the formulae rests with rapid proton transfer. The following possible reactions occur:

278



279



280 The proton may oscillate between the carbonate and water units. If this oscillation is very
281 rapid and faster than the picoseconds time scale then vibrational spectroscopy will observe
282 two species, both the carbonate and bicarbonate units and as a consequence the infrared (and
283 Raman) spectrum of both anions will be observed.

284

285 **Conclusions**

286

287 A combination of infrared and infrared emission spectroscopy has proved the
288 existence of OH units and HCO_3^- units in the nesquehonite structure. Indeed infrared
289 emission spectroscopy enables the formula of nesquehonite to be better defined as
290 $\text{Mg}(\text{OH})(\text{HCO}_3)\cdot 2\text{H}_2\text{O}$. This research has defined the thermal stability of nesquehonite. The
291 stability is limited to a maximum temperature of around 400 to 450°C . The mineral
292 decomposes in steps at ~ 50 , 175 and 400°C . Infrared emission spectroscopy enables the
293 thermal stability of the mineral nesquehonite to be defined and further the changes in the
294 formula of nesquehonite with temperature change can be defined.

295

296 The hydration-carbonation or hydration-and-carbonation reaction path in the MgO-
297 CO₂-H₂O system at ambient temperature and atmospheric CO₂ is of environmental
298 significance from the standpoint of carbon balance and the removal of greenhouse gases from
299 the atmosphere. The understanding of the thermal stability of the carbonates of magnesium
300 and the relative metastability of hydrous carbonates including hydromagnesite
301 (Mg₅(CO₃)₄(OH)₂·4H₂O, or Mg₄(CO₃)₃(OH)₂·3H₂O), artinite (Mg₂CO₃(OH)₂·3H₂O),
302 nesquehonite (MgCO₃·3H₂O), and lansfordite (MgCO₃·5H₂O) is extremely important to the
303 sequestration process for the removal of atmospheric CO₂.

304

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306

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311

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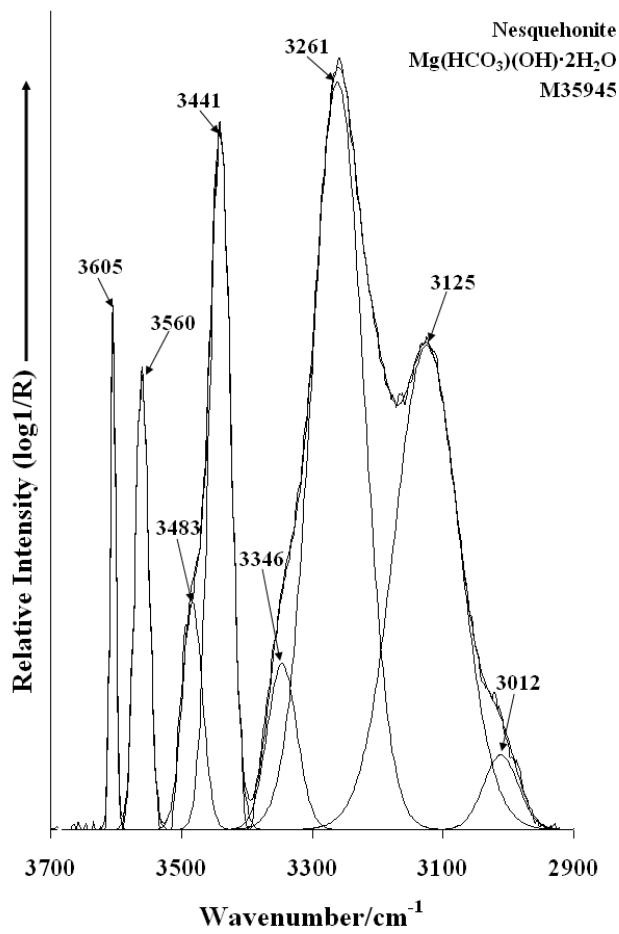
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390 **Figure 6 Infrared emission spectra of nesquehonite in the 3400 to 4000 cm⁻¹ over the 150**
391 **to 900°C temperature range**

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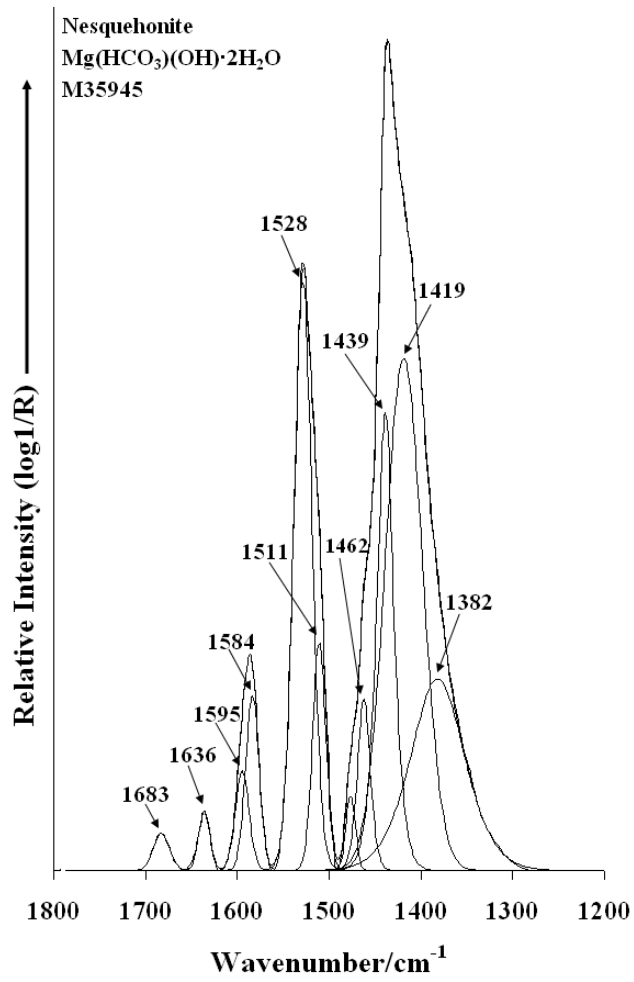
393 **Figure 7 Infrared emission spectra of nesquehonite in the 600 to 1800 cm⁻¹ over the 150**
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Figure 1

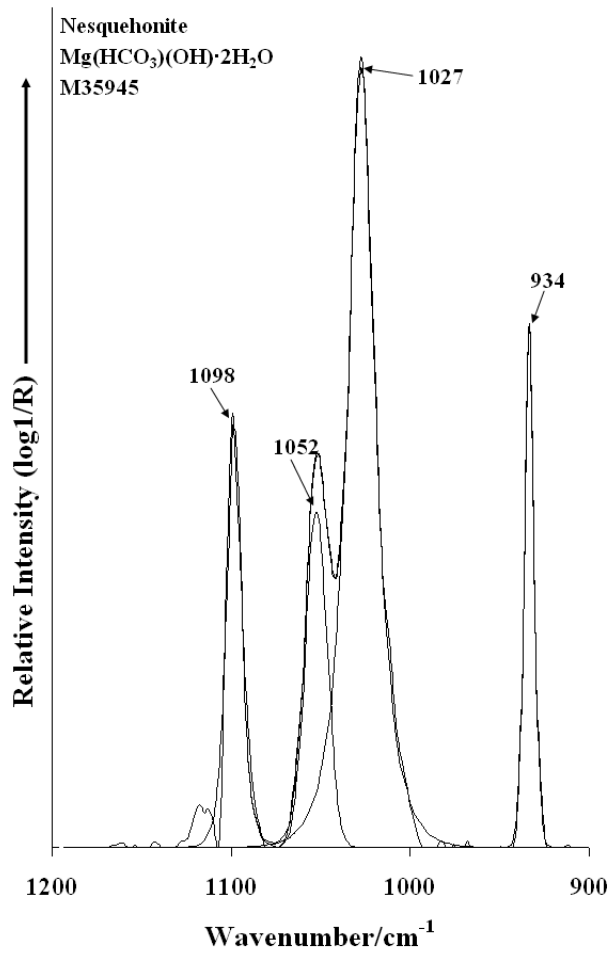


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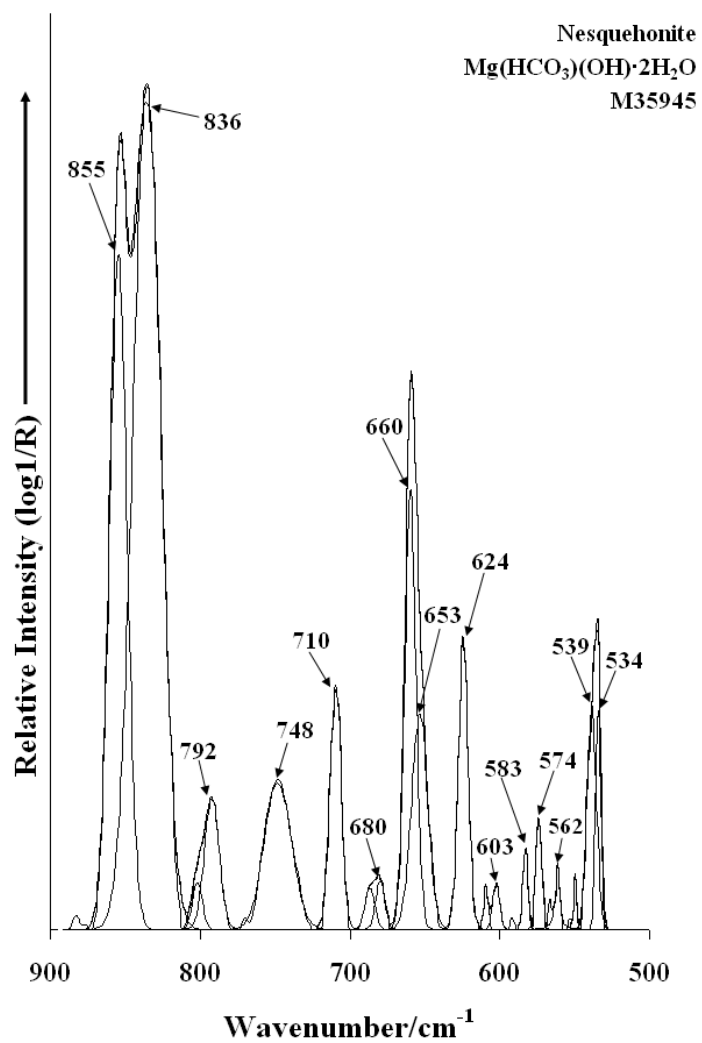
403 **Figure 2**



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406 **Figure 3**

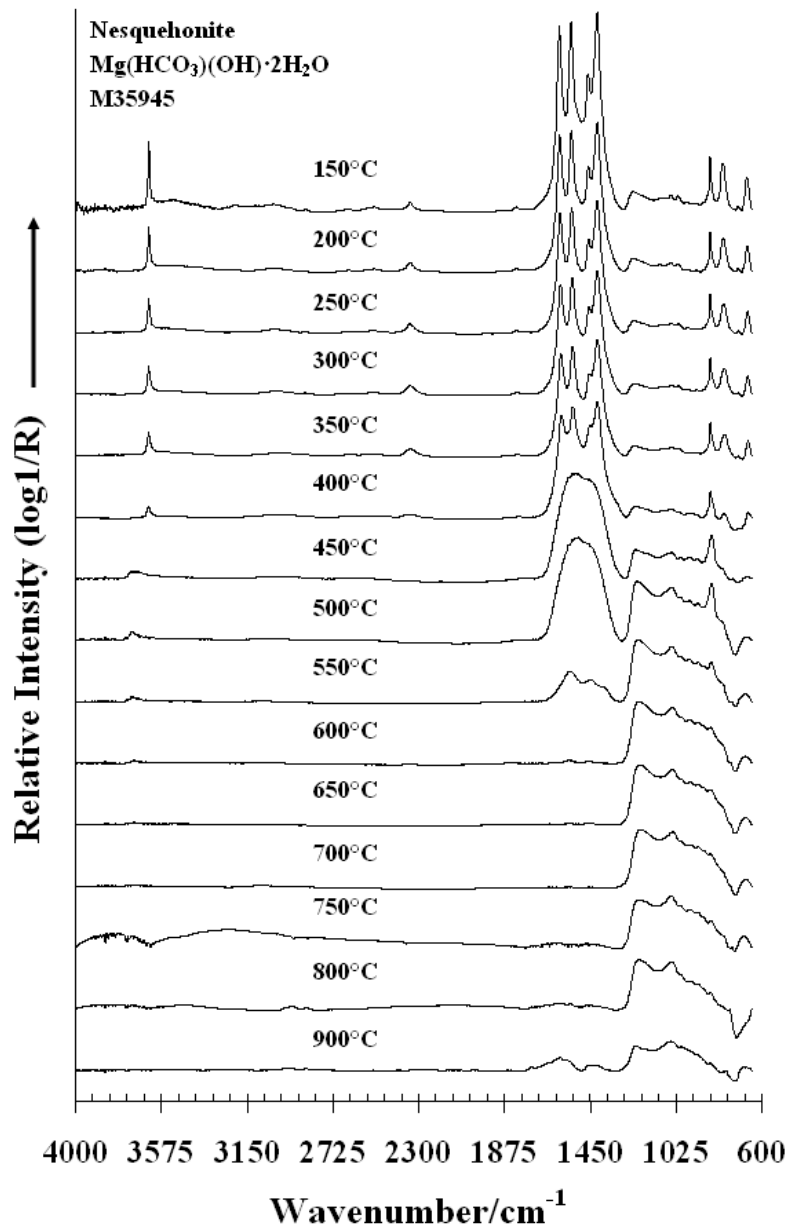


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410 **Figure 4**



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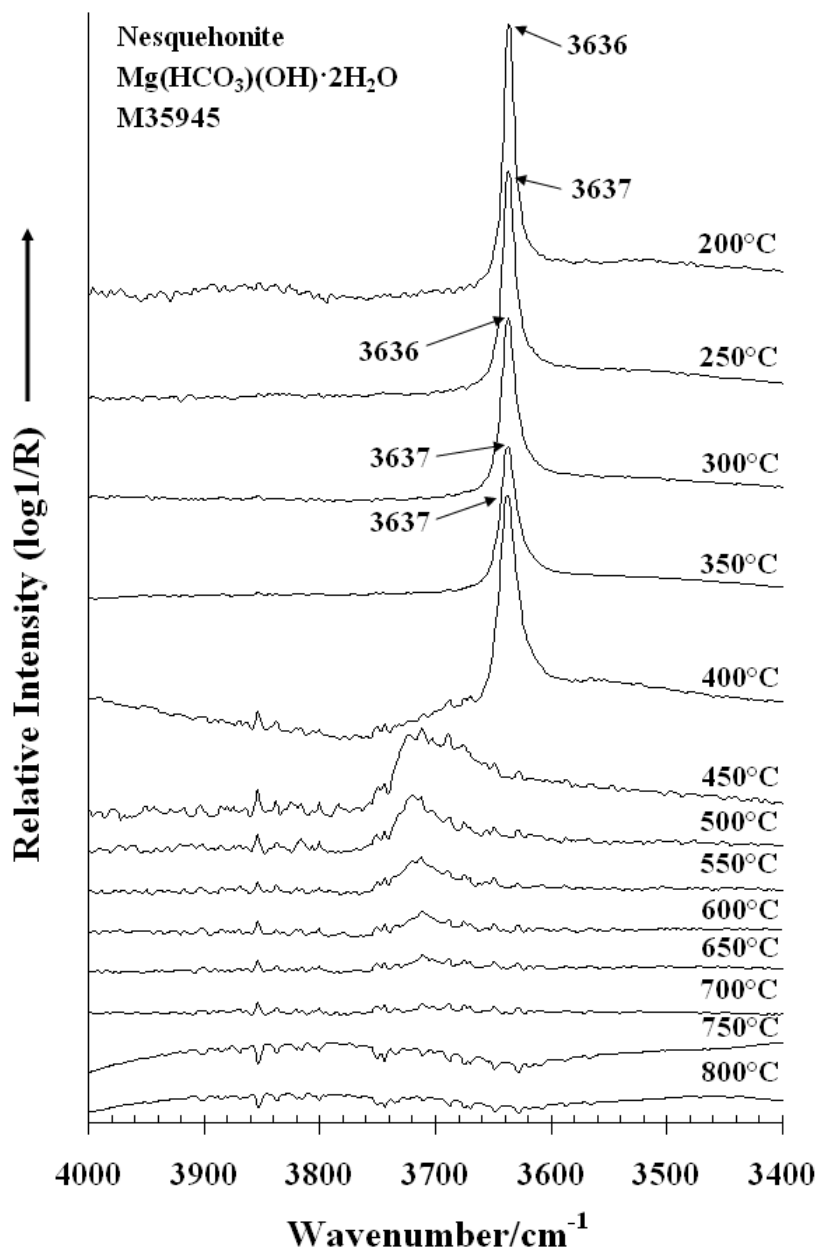
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413 **Figure 5**

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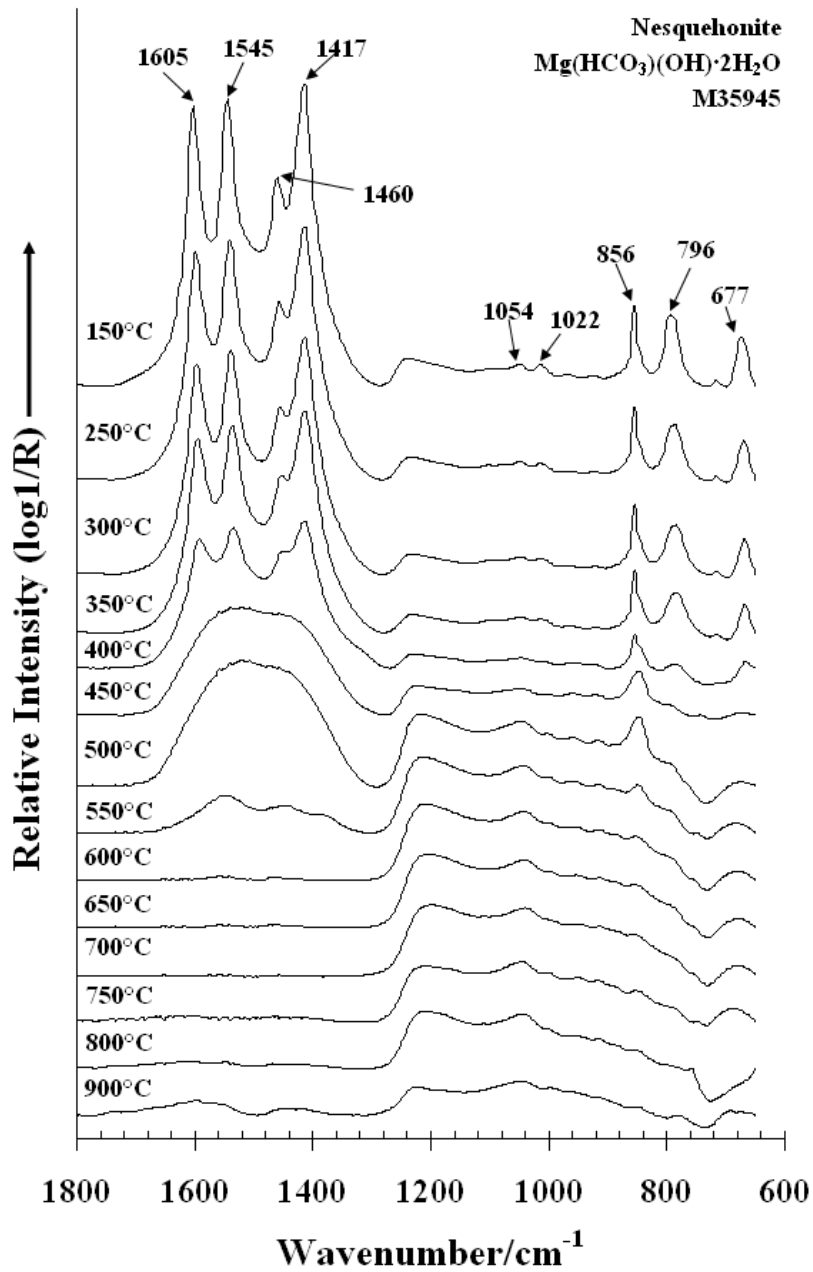
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Figure 6



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Figure 7