View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by Queensland University of Technology ePrints Archive

QUT Digital Repository:
http://eprints.qut.edu.au/

This is the author's version published as:

Frost, Ray L. & Palmer, Sara J. (2011) ***Infrared and infrared emission spectroscopy of nesquehonite Mg(OH)(HCO3)•2H2O : implications for the formula of nesquehonite.*** Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy, 78(4), pp. 1255-1260.

Copyright 2011 Elsevier

# Infrared and infrared emission spectroscopy of nesquehonite $Mg(OH)(HCO_3)\cdot 2H_2O$ – implications for the formula of nesquehonite

**Ray L. Frost• and Sara J Palmer**

Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

## Abstract

The mineral nesquehonite $Mg(OH)(HCO_3)\cdot 2H_2O$ has been analysed by a combination of infrared (IR) and infrared emission spectroscopy (IES). Both techniques show OH vibrations, both stretching and deformation modes. IES proves the OH units are stable up to 450°C. The strong IR band at 934 $cm^{-1}$ is evidence for MgOH deformation modes supporting the concept of $HCO_3^-$ units in the molecular structure.

Infrared bands at 1027, 1052 and 1098 $cm^{-1}$ are attributed to the symmetric stretching modes of $HCO_3^-$ and $CO_3^{2-}$ units. Infrared bands at 1419, 1439, 1511, and 1528 $cm^{-1}$ are assigned to the antisymmetric stretching modes of $CO_3^{2-}$ and $HCO_3^-$ units. IES supported by thermoanalytical results defines the thermal stability of nesquehonite

IES defines the changes in the molecular structure of nesquehonite with temperature. The results of IR and IES supports the concept that the formula of nesquehonite is better defined as $Mg(OH)(HCO_3)\cdot 2H_2O$.

**Keywords:** Nesquehonite, chemical formula, infrared spectroscopy, infrared emission spectroscopy

• Author for correspondence (r.frost@qut.edu.au)

## Introduction

The mineral nesquehonite is one of several magnesium carbonate minerals, which may result as a product of geosequestration. Other hydrous carbonates including hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$, or $Mg_4(CO_3)_3(OH)_2{\cdot}3H_2O$), artinite ($Mg_2CO_3(OH)_2{\cdot}3H_2O$), nesquehonite ($MgCO_3{\cdot}3H_2O$), and lansfordite ($MgCO_3{\cdot}5H_2O$) are extremely important to the sequestration process for the removal of atmospheric $CO_2$. Geo-sequestration is a method where by various greenhouse gases such as carbon dioxide ($CO_2$) can be trapped either physically or chemically in systems other than that of the atmosphere in order to prevent the detrimental effects on global warming due to greenhouse gases. The feasibility for various carbonate and other minerals to provide long term stable $CO_2$ storage options has been explored by various authors [1-6]. The formation of carbonate minerals is important for the removal of greenhouse gases from the atmosphere.

The name nesquehonite comes from the location of a coal mine at Nesquehoning, Pennsylvania, USA, where the mineral was first located. Nesquehonite exhibits the crystal structure of monoclinic-prismatic and has the symmetry point group of P21/n [7, 8]. There is some argument in the literature as to the true empirical formula of nesquehonite [9-14]. Nesquehonite belongs to a group of secondary carbonate minerals known as hydroxy-carbonates to which other mineral variations belong such as hydromagnesite. The chemical formula is commonly written as ($MgCO_3{\cdot}3H_2O$) or $Mg(HCO_3)(OH){\cdot}2H_2O$. At a unit cell level, the mineral appears to be a layer structure as may be observed with other hydroxy-carbonate minerals. Magnesium ions are contained in an octahedrally coordinated site which exhibits distortion. The water of hydration is understood to be located within the layers of the greater structure, although the exact nature is not clearly understood [15, 16].

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

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

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

## Experimental

### *Nesquehonite mineral*

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

### *Infrared emission spectroscopy*

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

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

*Mid-IR spectroscopy*

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. The powdered mineral was placed upon the plates of the ATR cell. Spectra over the 4000–525 $cm^{-1}$ range were obtained by the co-addition of 64 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.

## Band component analysis

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

## Results and Discussion

## Background

Carbonates in a range of minerals have been studied by vibrational spectroscopy. It is important to understand the spectroscopy of the carbonate ion, is a function of its symmetry. The free ion, $CO_3^{2-}$ with $D_{3h}$ symmetry exhibits four normal vibrational modes; a symmetric stretching vibration ($\nu_1$), an out-of-plane bend ($\nu_2$), a doubly degenerate antisymmetric stretch ($\nu_3$) and another doubly degenerate bending mode ($\nu_4$). The symmetries of these modes are $A_1'$ (R) + $A_2''$ (IR) + $E'$ (R, IR) + $E''$ (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 ($\nu_1$), of the carbonate

groups, while intense IR and weak Raman peaks near 1400 $cm^{-1}$ are due to the antisymmetric stretch ($\nu_3$). Infrared modes near 800 $cm^{-1}$ are derived from the out-of-plane bend ($\nu_2$). Infrared and Raman modes around 700 $cm^{-1}$ region are due to the in-plane bending mode ($\nu_4$). 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 [7]. However, even though the effects of hydrogen bonding are apparent in vibrational spectroscopy of hydrated magnesium carbonates, it is not expected to greatly affect the internal modes of the $CO_3^{2-}$ in nesquehonite, so sharp bands are still expected.

***Infrared spectroscopy***

The infrared spectrum of nesquehonite in the 2900 to 3700 $cm^{-1}$ is displayed in Figure 1. Clearly there are eight bands observed at 3012, 3125, 3261, 3346, 3441, 3483, 3560 and 3605 $cm^{-1}$. The first four bands are assigned to water stretching vibrations. The authors assign the latter four bands to the OH stretching vibrations of OH units. The observation of OH stretching bands supports the concept that the formula is $Mg(HCO_3)(OH).2H_2O$. W.B. White, [14] reported five infrared bands for nesquehonite at 2930, 3140, 3270, 3430 and 3568 $cm^{-1}$. There is good general agreement between the band positions of this work and that reported by White. The authors assign the band at 3012 $cm^{-1}$ to water strongly hydrogen bonded to carbonate or bicarbonate units. The position of the band suggests that water is strongly hydrogen bonded in the nesquehonite structure. In the Raman spectrum of a synthetic nesquehonite [18] at 25°C, four bands are resolved at 3124, 3295, 3423 and 3550 $cm^{-1}$. The first three bands are attributed to water stretching vibrations. The last Raman band is assigned to the symmetric stretching mode of the OH units. The authors assign the higher infrared wavenumber bands at 3560 and 3605 $cm^{-1}$ to non-hydrogen bonded OH stretching vibrations. The two infrared bands at 3441 and 3483 $cm^{-1}$ are attributed to hydrogen bonded OH units. These observations support the concept of firstly the non-equivalence of the OH units in the molecular structure of nesquehonite and also that some OH units are hydrogen-bonded and some are not hydrogen bonded. The reason why different bands are observed depends upon whether the OH units are involved in hydrogen bonding [14]. According to

our calculations from thermogravimetric (TG) measurements [34], two moles of water are lost in two steps. Thus the dehydration steps may be written as

$Mg(HCO_3)(OH)\cdot 2(H_2O) \rightarrow Mg(HCO_3)(OH)\cdot(H_2O) + H_20$ at 157°C

and $Mg(HCO_3)(OH)\cdot(H_2O) \rightarrow Mg(HCO_3)(OH) + H_20$ at 180°C. According to the differential thermal analysis (DTA) patterns of Beck [35] (page 995 of this reference), water of crystallisation is lost in two steps. The reaction begins at 140°C and is complete by 300°C. The dehydration steps as reported is in general agreement with the values of Beck [35]. White [14] presented infrared data and made the conclusion that no bicarbonate existed in the nesquehonite structure. Gasiunas et al.[15] presented pmr data (proton magnetic resonance) that supported the concept of $(HCO_3)$ units in the nesquehonite structure. These authors reported an infrared band at 2380 $cm^{-1}$ supporting this concept. Hopkinson et al. [36] researched the low temperature equilibrium between hydromagnesite and nesquehonite and presented data based on the FT-Raman and FT-IR that supported the bicarbonate formulation of nesquehonite as $Mg(HCO_3)(OH)\cdot 2(H_2O)$.

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

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

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

An intense band at 934 $cm^{-1}$ (Fig. 3) is assigned to the MgOH deformation mode. The observation of this band proves that OH units exist in the nesquehonite molecular structure and supports the concept that bicarbonate units are also involved in the nesquehonite structure. Infrared bands are observed at 836 and 855 $cm^{-1}$ (Fig. 4). These bands are assigned to the out-of-plane $\nu_2$ $CO_3^{2-}$ and $\nu_2$ $HCO_3^-$ bending modes. Farmer reported a single band at 852 $cm^{-1}$ [7]. Infrared bands are observed at 710, 748 and 792 $cm^{-1}$ and are assigned to the in-plane bending mode ($\nu_4$). 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 $CO_3^{2-}$. Farmer 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 [7]. However, even though the effects of hydrogen bonding are apparent in vibrational spectroscopy of hydrated magnesium carbonates, it is not expected to greatly affect the internal modes of the $CO_3^{2-}$ in nesquehonite, so sharp bands are still expected. Data for the $\nu_4$ mode of nesquehonite was not forthcoming in the work of White [7]. A series of infrared bands are observed at 624, 653, 660 and 680 $cm^{-1}$. These bands are attributed to the $\nu_4$ in-plane bending mode of the $HCO_3^-$ units. White tabulated the band positions of acid carbonates (page 261) and the band positions of for example $KHCO_3$ correspond well with these band positions.

***Infrared emission spectroscopy***

The infrared emission spectra of nesquehonite over the temperature range 150 to 900°C over the full spectral range are shown in Figure 5. The formula of nesquehonite shows the presence of both water and OH units. At temperatures above 150°C, no water stretching vibrations which would be expected in the 3400 to 3500 $cm^{-1}$ region are observed. The expanded spectra are displayed in Figures 6 and 7. The infrared band observed at 3636 $cm^{-1}$ is assigned to the OH stretching band of the hydroxyl units. The intensity of this band approaches zero by 500°C. A new broad asymmetric band at around 3720 $cm^{-1}$ is found above this temperature. Intensity in this band is lost by ~650°C. This band may be attributed to OH units which are not hydrogen bonded. The presence of the distinct OH vibrations at elevated temperatures is significant and it suggests that the formula of the mineral sample used in this study has the structural formula of $Mg(HCO_3)(OH).2H_2O$, the magnesium hydrogen-carbonate hydroxy, dihydrate. If the formula of nesquehonite which is commonly quoted in the literature as $MgCO_3.3H_2O$, then one would not expect the distinct OH band to be found. This is not the case. The study by White did not show evidence of bicarbonate ions in nesquehonite [39]. This evidence suggests the possibility of there being a structural isomer of the mineral either $MgCO_3.3H_2O$ or in this case $Mg(HCO_3)(OH).2H_2O$.

The infrared emission spectra of nesquehonite in the 600 to 2000 $cm^{-1}$ region are shown in Figure 7. Four bands are observed at 1417, 1460, 1545 and 1605 $cm^{-1}$. The first three bands are attributed to the $\nu_3$ $HCO_3^{2-}$ antisymmetric stretching modes. The reason for the multiple bands is related to the structure of the bicarbonate anion in the unit cell. Two independent bicarbonate anions are suggested. The band separation of these bands is lost by 450°. This temperature corresponds to the loss of the OH units. Intensity in the very broad bands is lost by 600°C. Two low intensity bands are observed at 1022 and 1054 $cm^{-1}$. These bands are assigned to the infrared forbidden symmetric stretching mode of the $HCO_3^-$ units. The observation of two bands supports the concept that two independent bicarbonate units are found in the nesquehonite structure. Only a single band at 1098 $cm^{-1}$ is observed in the Raman spectrum [40]. According to our calculations from the TG patterns of nesquehonite [34], three moles of water are lost in two steps. The chemical reactions have been provided above. According to the DTA patterns of Beck [35] (page 995 of this reference), water of crystallisation is lost in two steps. The reaction begins at 140°C and is complete by 300°C. The dehydration steps as reported is in close agreement with the values of Beck [35]. Thus, after 175°C in the Raman spectra, the compound being studied is $Mg(HCO_3)(OH)$. Thus the appearance of new peaks at 1385 and 1405 $cm^{-1}$ in the Raman spectrum, are attributed to the

antisymmetric stretching modes of the $(HCO_3)^-$ units. The intensity of these bands approaches zero by 425°C.

The IES band at 856 $cm^{-1}$ is attributed to the $\nu_2$ in-plane bending mode. The band shifts to 860 $cm^{-1}$ at 550°C. The Raman band which might be expected to be observed at around 870 $cm^{-1}$ is not found. The two bands at 677 and 796 $cm^{-1}$ are assigned to the $\nu_4$ out of plane bending mode. Two Raman bands at 765 and 699 $cm^{-1}$ assigned to the $\nu_4$ out of plane bending mode are readily observed in the thermo-Raman spectra even though the spectra are of a low intensity. The intensity of these bands approaches zero by 400°C.

**Explanation of the formula of the mineral**

The mineral nesquehonite has two possible formulations namely $Mg(OH)(HCO_3)\cdot 2H_2O$ or $MgCO_3)\cdot 3H_2O$. Controversy over the formula of the mineral exists. A possible explanation of the formulae rests with rapid proton transfer. The following possible reactions occur:

$$H_2O \rightarrow H^+ + OH^-$$

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

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

**Conclusions**

A combination of infrared and infrared emission spectroscopy has proved the existence of OH units and $HCO_3^-$ units in the nesquehonite structure. Indeed infrared emission spectroscopy enables the formula of nesquehonite to be better defined as $Mg(OH)(HCO_3)\cdot 2H_2O$. This research has defined the thermal stability of nesquehonite. The stability is limited to a maximum temperature of around 400 to 450°C. The mineral decomposes in steps at ~50, 175 and 400°C. Infrared emission spectroscopy enables the thermal stability of the mineral nesquehonite to be defined and further the changes in the formula of nesquehonite with temperature change can be defined.

296 The hydration-carbonation or hydration-and-carbonation reaction path in the MgO-
297 $CO_2$-$H_2O$ system at ambient temperature and atmospheric $CO_2$ 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 ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, or $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$), artinite ($Mg_2CO_3(OH)_2 \cdot 3H_2O$),
302 nesquehonite ($MgCO_3 \cdot 3H_2O$), and lansfordite ($MgCO_3 \cdot 5H_2O$) is extremely important to the
303 sequestration process for the removal of atmospheric $CO_2$.
304
305 **Acknowledgments**
306
307 The financial and infra-structure support of the Queensland University of Technology,
308 Chemistry Discipline is gratefully acknowledged. The Australian Research Council (ARC) is
309 thanked for funding the instrumentation. Dermot Henry of Museum Victoria is thanked for
310 the loan of the nesquehonite and related minerals.
311
312
313
314
315
316
317
318

## References


[1] J. Harborne, Mat. Aus., 39 (2006) 38.

[2] A.-h. Park, L.-s. Fan, Carbon dioxide sequestration using magnesium-containing minerals, in, (USA). Application: US, 2005, pp. 13 pp.

[3] E.H. Oelkers, J. Schott, Chem. Geol., 217 (2005) 183-186.

[4] P.J. Cook, B. Hooper, Pub. Aust. In. of Min.Met., 2/2004 (2004) 15-19.

[5] K. Kyaw, T. Shibata, F. Watanabe, H. Matsuda, M. Hasatani, En. Conv.Man., 38 (1997) 1025-1033.

[6] K.S. Lackner, C.H. Wendt, D.P. Butt, E.L. Joyce, D.H. Sharp, Energy, 20 (1995) 1153-1170.

[7] V.C. Farmer, White, W.B., Carbonate Minerals in: V.C. Farmer (Ed.) The Infrared spectra of minerals, Mineralogical Society, London, 1974, pp. 227-279.

[8] G. Giester, C.L. Lengauer, B. Rieck, Min. Petrol., 70 (2000) 153-163.

[9] A. Botha, C.A. Strydom, J.Therm. Anal. Cal., 71 (2003) 987-995.

[10] W. Cheng, Z. Li, Crys.Res.Tech., 44 (2009) 937-947.

[11] M. Dong, W. Cheng, Z. Li, G.P. Demopoulos, J. Chem. Eng. Data, 53 (2008) 2586-2593.

[12] F. Halla, Zeit.Phys. Chem.73 (1970) 268-276.

[13] L. Tucek, K. Cechovska, J. Derco, Z. Nemeth, M. Radvanec, L. Kucharic, Slovak Geol. Mag., (2009) 67-72.

[14] W.B. White, Amer. Min., 56 (1971) 46-53.

[15] K. Gasiunas, A. Kaminskas, I. Kapacauskas, B. Valuziene, P. Kicas, Z. Neorgan. Khim., 18 (1973) 2332-2335.

[16] S.J. Gaffey, J. Sed. Petr., 58 (1988) 397-414.

344 [17] I. Martinez-Arkarazo, M. Angulo, O. Zuloaga, A. Usobiaga, J.M. Madariaga,
345 Spectrochim. Acta, 68A (2007) 1058-1064.
346 [18] M.C. Hales, R.L. Frost, W.N. Martens, J. Raman Spectros., 39 (2008) 1141-1149.
347 [19] J.T. Kloprogge, W.N. Martens, L. Nothdurft, L.V. Duong, G.E. Webb, J. Mat. Sc. Let.,
348 22 (2003) 825-829.
349 [20] G. Giester, C.L. Lengauer, B. Rieck, Min. Petr., 70 (2000) 153-163.
350 [21] G.W. Stephan, C.H. MacGillavry, Structural Crys.Crys.Chem., B28 (1972) 1031-1033.
351 [22] R. Pepinsky, Phys. Rev., 59 (1941) 925-926.
352 [23] G. Cesaro, Bull. Sci. Acad. Roy. Belg., (1910) 749-768.
353 [24] T. Pobeguin, Compt. Rend., 248 (1959) 3585-3587.
354 [25] T. Pobeguin, Compt. Rend., 248 (1959) 2220-2222.
355 [26] T. PobeguinCompt. Rend. Congr. Soc., (1960) 405-416.
356 [27] H. Cheng, R.L. Frost, J. Yang, Q. Liu, J. He, Spectrochim. Acta, 77 (2010) 1014-1020.
357 [28] R.L. Frost, S. Bahfenne, J. Graham, Spectrochim. Acta, 71A (2009) 1610-1616.
358 [29] J. Yang, Y. Zhao, R.L. Frost, Spectrochim. Acta, 74A (2009) 398-403.
359 [30] R.L. Frost, S. Bahfenne, J. Graham, Spectrochim. Acta, 71 (2008) 1610-1616.
360 [31] R.L. Frost, W.N. Martens, D.L. Wain, M.C. Hales, Spectrochim. Acta, 70 (2008) 1120-
361 1126.
362 [32] R.L. Frost, D. Wain, J. Therm. Anal.Cal., 91 (2008) 267-274.
363 [33] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, Handbook of Mineralogy,
364 Mineral Data Publishing, Tuscon, Arizona, USA, 2003.
365 [34] V. Vagvoelgyi, M. Hales, R.L. Frost, A. Locke, J. Kristof, E. Horvath, J. Therm.
366 Anal.Cal., 94 (2008) 523-528.
367 [35] C.W. Beck, Amer. Min., 35 (1950) 985-1013.
368 [36] L. Hopkinson, K. Rutt, G. Cressey, J. Geol., 116 (2008) 387-400.

[37] A.M. Ponizovskii, A.I. Boldyrev, R.I. Arov, Z. Neorgan. Khim., 13 (1968) 2922-2924.

[38] P.P. Smolin, T.A. Ziborova, Dok. Akad.Nauk SSSR, 226 (1976) 923-926.

[39] W.B. White, Amer. Min., 56 (1971) 46-53.

[40] M.C. Hales, R.L. Frost, W.N. Martens, J. Raman Spectrosc., 39 (2008) 1141-1149.

## List of Figures

**Figure 1 Infrared spectrum of nesquehonite in the 2900 to 3700 $cm^{-1}$.**

**Figure 2 Infrared spectrum of nesquehonite in the 1200 to 1800 $cm^{-1}$.**

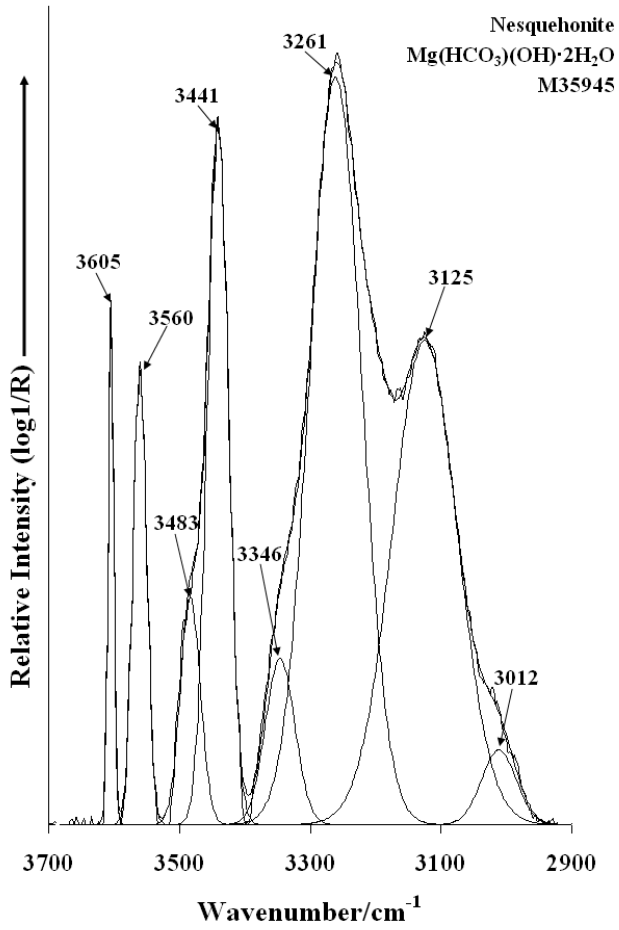
**Figure 3 Infrared spectrum of nesquehonite in the 900 to 1200 $cm^{-1}$.**

**Figure 4 Infrared spectrum of nesquehonite in the 500 to 900 $cm^{-1}$.**

**Figure 5 Infrared emission spectra of nesquehonite in the 600 to 4000 $cm^{-1}$ over the 150 to 900°C temperature range**

**Figure 6 Infrared emission spectra of nesquehonite in the 3400 to 4000 $cm^{-1}$ over the 150 to 900°C temperature range**

**Figure 7Infrared emission spectra of nesquehonite in the 600 to 1800 $cm^{-1}$ over the 150 to 900°C temperature range**

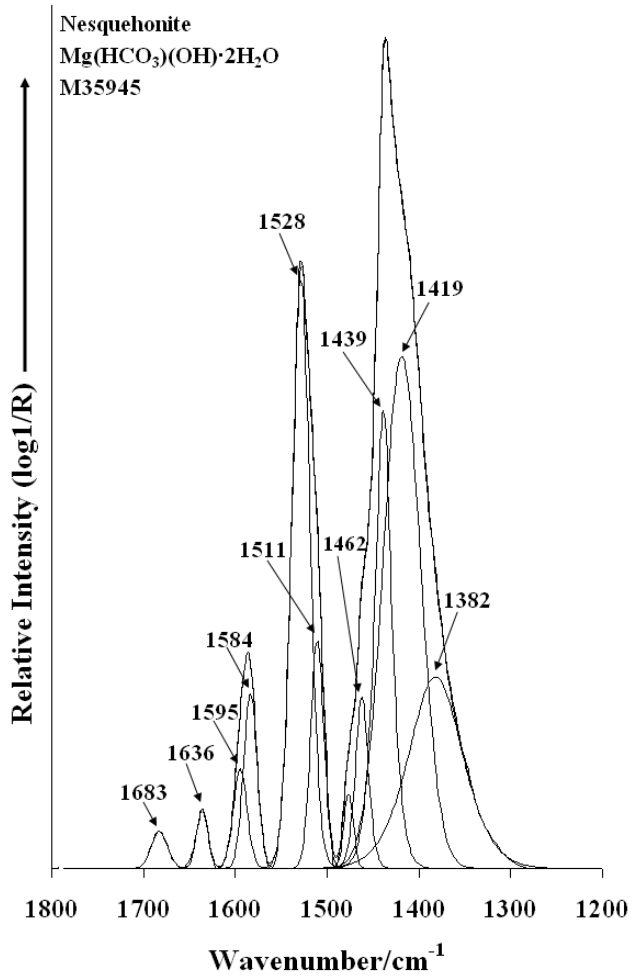



396

397

398 **Figure 1**

399

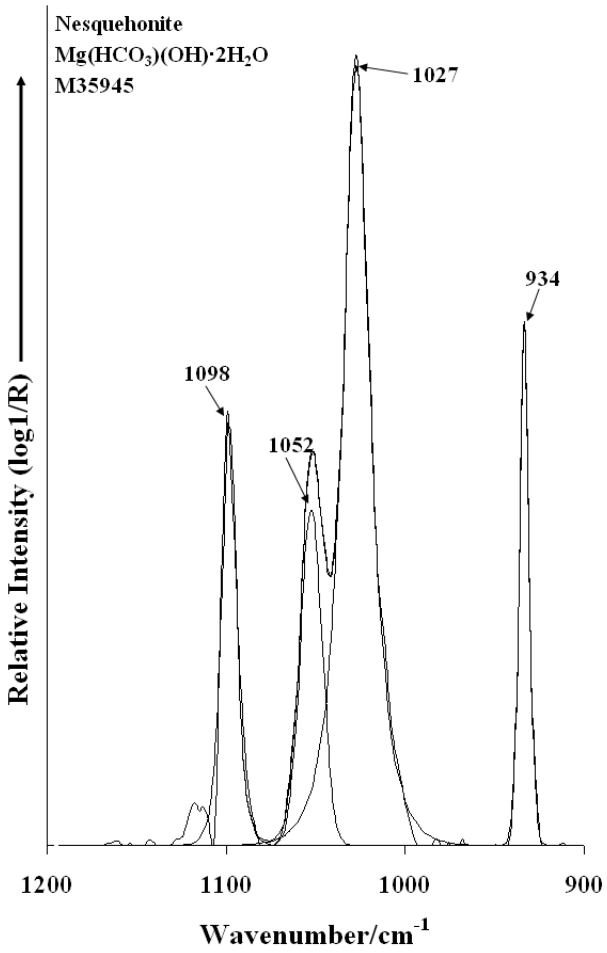



400

401

402

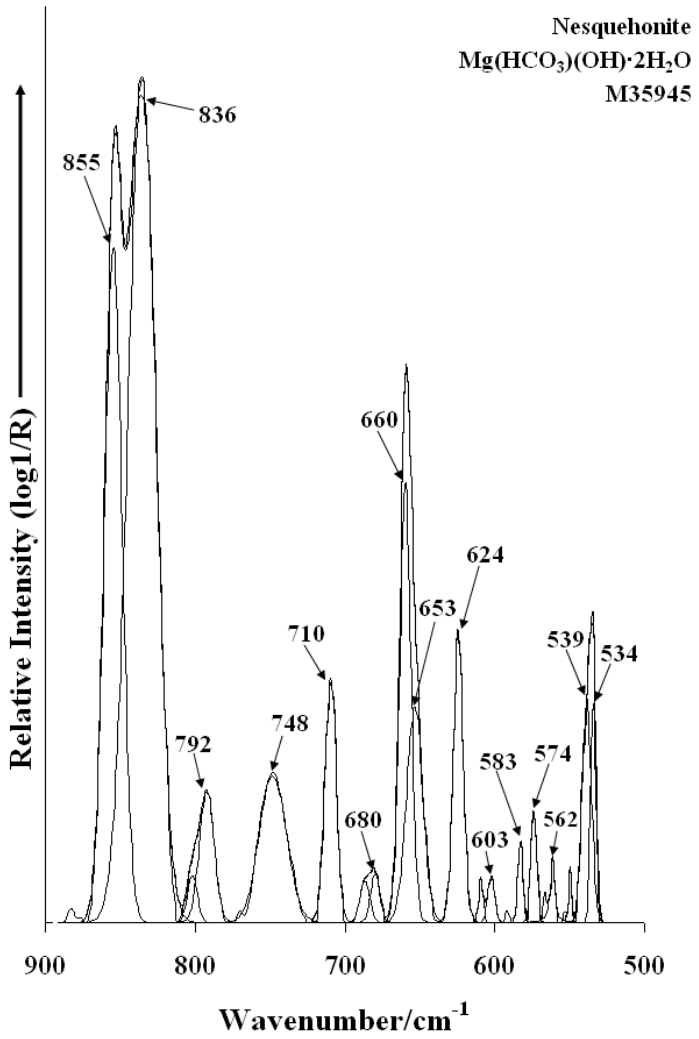
403 **Figure 2**




404

405

406 **Figure 3**

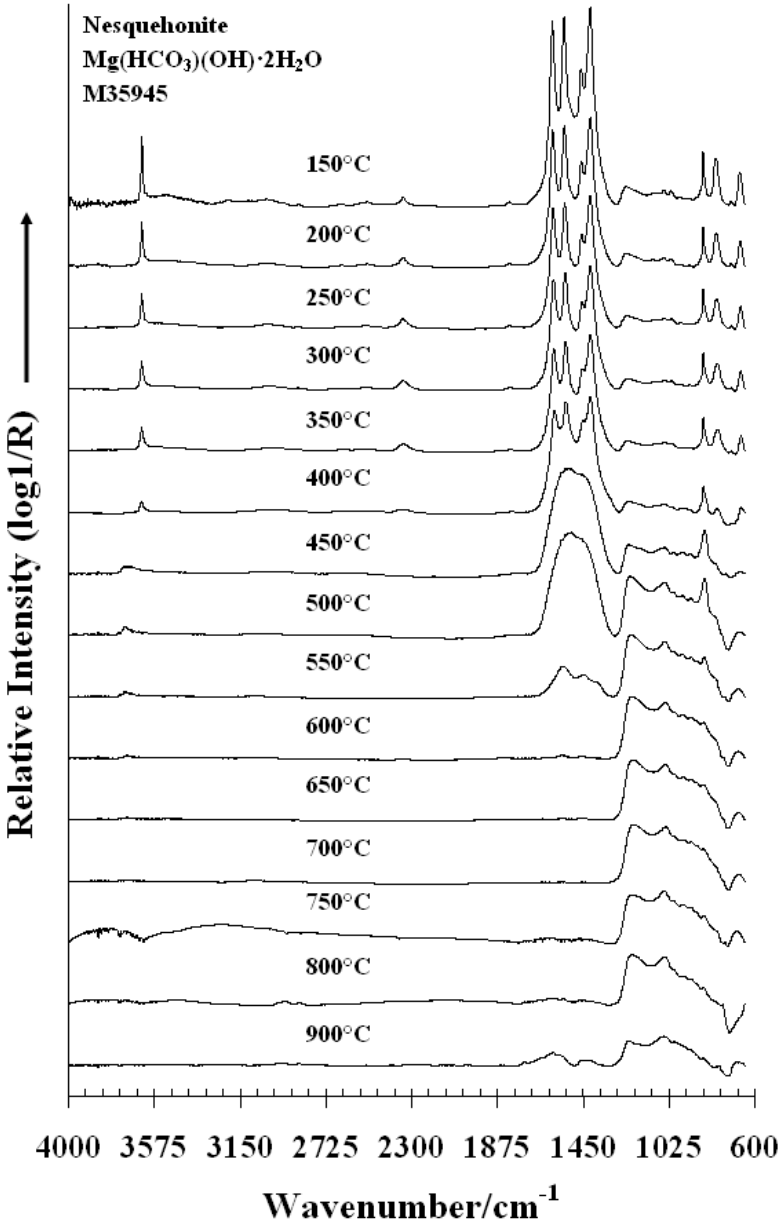



407

408

409

410 **Figure 4**




411

412

413 **Figure 5**

414

415

416

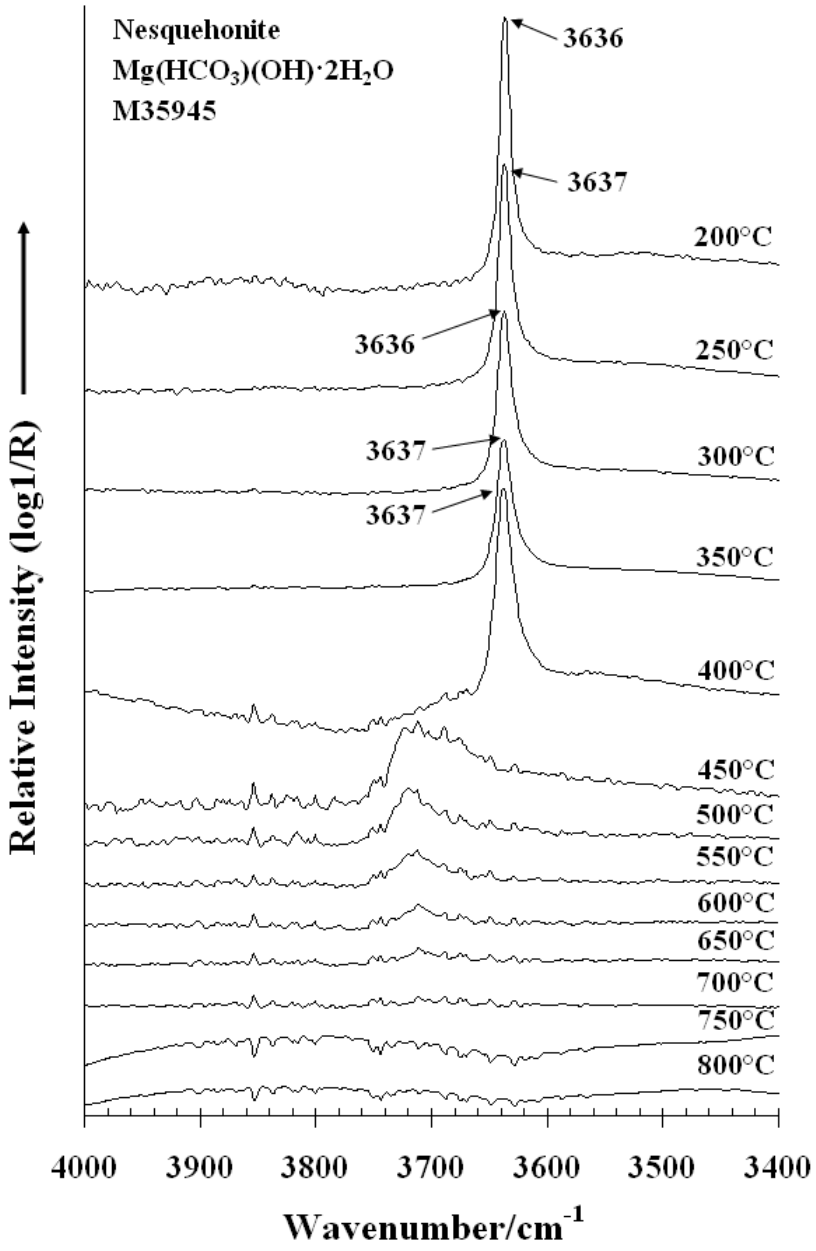
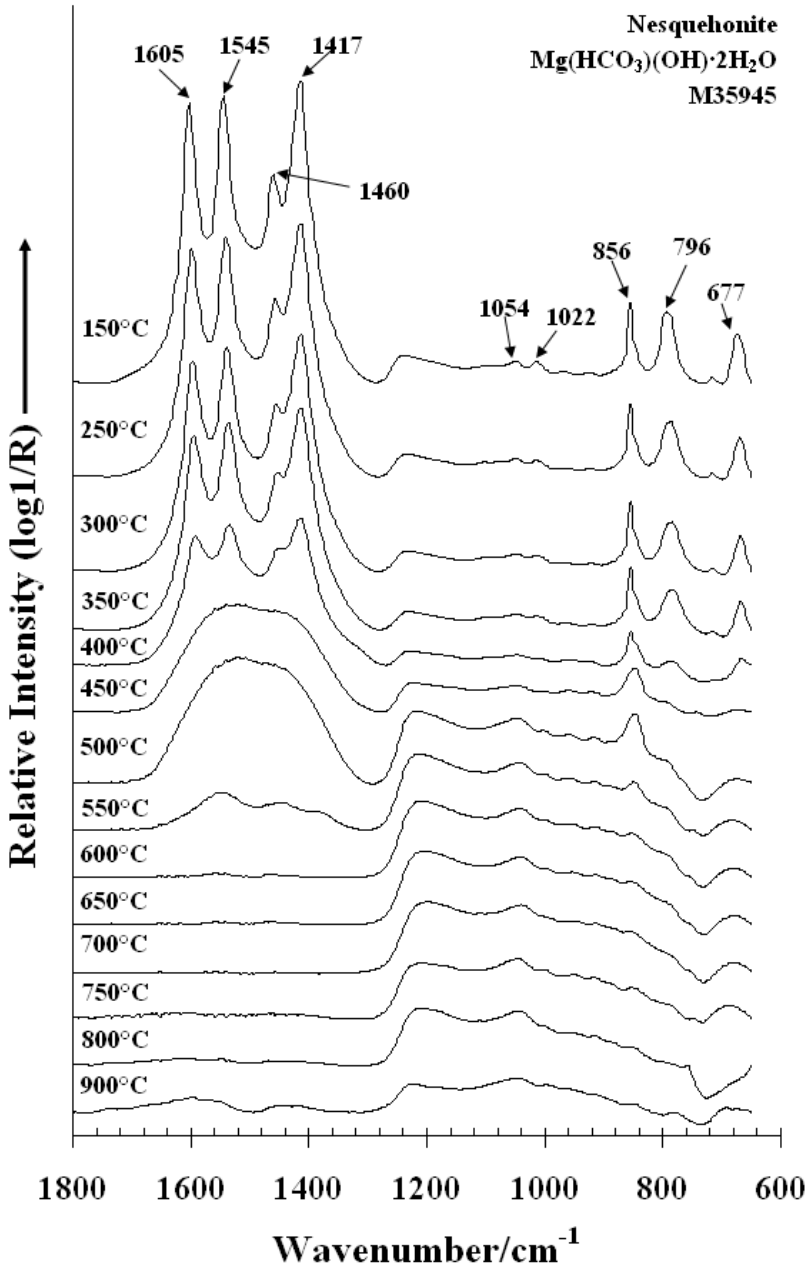

Nesquehonite
Mg(HCO3)(OH)·2H2O
M35945
3636
3637
200°C
3636
250°C
3637
300°C
3637
350°C
400°C
450°C
500°C
550°C
600°C
650°C
700°C
750°C
800°C
Relative Intensity (log1/R)
4000
3900
3800
3700
3600
3500
3400
Wavenumber/cm-1

**Figure 6**




423

424

425 **Figure 7**

426

427

428