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**Hydrated double carbonates – a Raman and infrared spectroscopic study**

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**Abstract**

The Raman spectra of selected double carbonates including pirssonite, gaylussite, shortite and quintinite complemented with infrared spectra have been used to characterise the structure of these carbonate minerals. By using a Libowitzky type function hydrogen bond distances for these minerals of 2.669 to 2.766 Å are estimated. The variation in the hydrogen bond distances contributed to the stability of the mineral. The Raman spectrum of pirssonite shows a single band at 1080 cm<sup>-1</sup> attributed to the (CO<sub>3</sub>)<sup>2-</sup> symmetric stretching mode, in contrast to shortite and quintinite where two bands are observed. Multiple bands are observed for the antisymmetric stretching and bending region for these minerals proving that the carbonate unit is distorted in the structure of pirssonite and gaylussite.

*Key words:* hydrated carbonates, smithsonite, pirssonite, gaylussite, tunisite, shortite, infrared and Raman spectroscopy

**Introduction**

In nature there exists a number of hydrated double carbonates including pirssonite Na<sub>2</sub>CO<sub>3</sub>.CaCO<sub>3</sub>.2H<sub>2</sub>O of space group *Fdd2* and symmetry *C2v*, gaylussite Na<sub>2</sub>CO<sub>3</sub>.CaCO<sub>3</sub>.5H<sub>2</sub>O of space group *C2/c* and symmetry *C2h*, dawsonite NaAl(CO<sub>3</sub>)(OH)<sub>2</sub> of space group *Ima2* and symmetry *C2v* and tunisite NaHCa<sub>2</sub>Al<sub>4</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>10</sub> of space group *P4/nmm* and symmetry *D4h* [1]. Pirssonite is one of several carbonate minerals that form in non-marine evaporite deposits. Other evaporite carbonates include trona, gaylussite, northupite, nahcolite and thermonatrite. Evaporite minerals are geologically important since these minerals clearly relate to the environmental conditions that existed at the time of their deposition, usually arid. Pirssonite and gaylussite differ only in the number of water molecules, yet their symmetries are quite different [2-6]. This is an indication of a change in their respective crystal structures. The two are best distinguished by their crystal habits in which pirssonite has a distinctive tabular diamond-shaped crystal form.

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The infrared spectra of these double carbonates have been published [7-9]. Adler and Kerr predicted, based upon the infrared spectra, that all of the carbonate units in the crystal structure of pirssonite and gaylussite were equivalent [8]. Farmer states that the carbonate ion in gaylussite is on a site with  $C_1$  point symmetry. The carbonate ion is regular with bond lengths between 1.280 and 1.290Å which implies very little distortion of the carbonate ion. Adler and Kerr reported infrared bands of pirssonite at 1068  $\text{cm}^{-1}$  ( $\nu_1$ ), 870  $\text{cm}^{-1}$  ( $\nu_2$ ), 1414 and 1488  $\text{cm}^{-1}$  ( $\nu_3$ ), 699 and 712  $\text{cm}^{-1}$  ( $\nu_4$ ) [8]. In contrast, the carbonate ion in pirssonite is highly distorted and CO bond lengths vary from 1.281 to 1.300Å. This distortion manifests itself in the infrared spectra where splitting of the  $\nu_2$  and  $\nu_4$  modes occurs [1]. Adler and Kerr reported infrared bands of gaylussite at 875  $\text{cm}^{-1}$  ( $\nu_2$ ), 1414  $\text{cm}^{-1}$  ( $\nu_3$ ), 692 and 720  $\text{cm}^{-1}$  ( $\nu_4$ ) [8]. The position of the symmetric stretching mode of gaylussite was not published. In contrast the infrared spectrum of gaylussite shows no intensity in the  $\nu_1$  position and no splitting of the  $\nu_3$  mode. Johan et al. published the position of the infrared bands of tunisite at 1155  $\text{cm}^{-1}$  ( $\nu_1$ ), 850  $\text{cm}^{-1}$  ( $\nu_2$ ), 1530  $\text{cm}^{-1}$  ( $\nu_3$ ) [7]. No band position was given for the ( $\nu_4$ ) mode. For these minerals the position as determined by infrared spectroscopy of the water bands was not forthcoming.

Raman spectroscopy has proven very useful for the study of minerals [10-12]. Indeed Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with carbonate minerals [13-17]. Some previous studies have been undertaken by the authors using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated sulphate solutions [18]. Very few spectroscopic studies of the hydrated double carbonates have been forthcoming and what studies that are available are not new. Few Raman studies of any note are available [19, 20]. The aim of this paper is to present Raman and infrared spectra of natural hydrated double carbonates including pirssonite, gaylussite and tunisite. 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**

### **Minerals**

Selected minerals were obtained from the Mineralogical Research Company and other sources including Museum Victoria. The samples were phase analysed by X-ray diffraction for phase analysis and for chemical composition by EDX measurements.

The origin of the minerals are as follows:

Pirssonite - Green River, Sweetwater Co., Wyoming labelled as pirssonite 1

Pirssonite - Searles Lake, San Bernardino Co., California labelled as pirssonite 3

The mineral pirssonite 3 is a type mineral [21] and is used as a standard or reference mineral (please go to page 552 of reference [21])

Gaylussite - Teels Marsh, Esmeralda County, Nevada. Gaylussite is listed on page 241 of reference [21].

Tunisite - near Condorcet, Drome, France (page 716 of reference [21])

### **Raman microprobe spectroscopy**

The crystals of halogenated carbonates were placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of  $2\text{ cm}^{-1}$  in the range between 100 and  $4000\text{ cm}^{-1}$ . Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the  $520.5\text{ cm}^{-1}$  line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique. Details of the technique have been published by the authors [22-25].

### Mid-IR spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the  $4000\text{--}525\text{ cm}^{-1}$  range were obtained by the co-addition of 64 scans with a resolution of  $4\text{ cm}^{-1}$  and a mirror velocity of  $0.6329\text{ cm/s}$ . Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which 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 Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz 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

The Raman spectra of two pirssonite minerals and gaylussite, shortite and quintinite in the  $950\text{ to }1450\text{ cm}^{-1}$  region are shown in Figure 1. Adler and Kerr predicted from their infrared data that the carbonate units were crystallographically single units in the structure of pirssonite [8]. This was later confirmed by crystallographic studies of synthetic pirssonite and gaylussite [26]. The Raman spectra of pirssonite as shown in Figures 1a and 1b show a single intense band at around  $1080\text{ cm}^{-1}$ . The position of this band is sample dependent. The band is observed at  $1074\text{ cm}^{-1}$  for the second pirssonite mineral sample. A low intensity band at  $1050\text{ cm}^{-1}$  is observed in the Raman spectrum and it is considered this band is a hot band. Adler and Kerr reported based on infrared spectra the position of the  $\nu_1$  band as  $1068\text{ cm}^{-1}$  [8]. The carbonate unit in gaylussite is on a  $C_1$  site and is crystallographically distinct. Thus no splitting of the carbonate bands should be observed. This is confirmed by a single Raman band for gaylussite at  $1078\text{ cm}^{-1}$ . Adler and Kerr did not report an infrared band for gaylussite in the  $\nu_1$  position. In contrast the Raman spectrum of shortite (Figure 1d) shows two Raman bands at  $1070$  and  $1090\text{ cm}^{-1}$ . Adler and Kerr reported two infrared bands at  $1069$  and  $1089\text{ cm}^{-1}$  in excellent agreement with the Raman data reported in this work [8]. The Raman

spectra of quintinite (a hydrotalcite) shows two bands at 1062 and 1050  $\text{cm}^{-1}$  which may be attributed to  $(\text{CO}_3)^{2-}$  symmetric stretching modes. Often the Raman spectra of carbonate in the interlayer of hydrotalcites show two or more bands for the symmetric stretching mode.

The infrared spectra of the minerals pirssonite, gaylussite, tunisite and quintite are reported in Figure 2. The infrared spectra of pirssonite shows a low intensity band at 1067-8  $\text{cm}^{-1}$  in close agreement with the results published by Adler and Kerr [8]. The observation of the Raman band supports the concept of distortion of the carbonate unit in pirssonite. No infrared band was observed in this position for gaylussite. In tunisite two bands are observed at 1065 and 1118  $\text{cm}^{-1}$ . An infrared band was reported by Johan et al. for tunisite at 1155  $\text{cm}^{-1}$  [7]. No infrared bands were observed for quintinite in this spectral region confirming the lack of distortion of the carbonate units in quintinite. This is expected since the carbonate units are held in the interlayer of the quintinite structure.

In the Raman spectrum of pirssonite three bands are observed at 1406, 1468 and 1511  $\text{cm}^{-1}$ . These bands are assigned to the  $\nu_3$  antisymmetric stretching modes. In the infrared spectra of pirssonite three bands are observed at 1402, 1465 and 1480  $\text{cm}^{-1}$ . Adler and Kerr reported two infrared bands at 1414 and 1488  $\text{cm}^{-1}$  [8]. Although the crystallographic data show there is only one crystallographically distinct carbonate unit in the structure of pirssonite, the observation of three antisymmetric stretching modes supports the concept that some carbonate units are distorted in the pirssonite structure. In contrast two Raman bands for gaylussite are observed for gaylussite at 1398 and 1429  $\text{cm}^{-1}$ . In the infrared spectrum of gaylussite only a single broad band is observed at 1398  $\text{cm}^{-1}$ . These results differ from that found by Adler and Kerr who found only a single infrared band at 1414  $\text{cm}^{-1}$  for gaylussite. The low site symmetry of the carbonate unit in shortite results in the splitting of the  $\nu_3$  antisymmetric stretching modes. Four Raman bands are observed at 1410, 1445, 1476 and 1511  $\text{cm}^{-1}$ . Adler and Kerr found four infrared bands at 1410, 1453, 1481 and 1522  $\text{cm}^{-1}$  [8]. For the mineral quintinite a very low intensity broad band at 1414  $\text{cm}^{-1}$  is observed. In the infrared spectrum of quintinite three bands are observed at 1346, 1406 and 1586  $\text{cm}^{-1}$ . The first two bands are assigned to the  $\nu_3$  antisymmetric stretching modes whilst the intense band at 1346  $\text{cm}^{-1}$  is ascribed to an OH deformation mode.

The Raman spectra of two pirssonite minerals and gaylussite, shortite and quintinite in the 100 to 950  $\text{cm}^{-1}$  region are shown in Figure 3. Further confirmation of the distortion of carbonate units in the pirssonite structure is obtained through the observation of the  $\nu_2$  bending mode at around 879  $\text{cm}^{-1}$ . Adler and Kerr reported an infrared band in this position in the infrared spectra [7]. For gaylussite a Raman band is observed at 898  $\text{cm}^{-1}$  and is attributed to this assignment. This band for shortite is of very low intensity and is only observed through scale expansion. For quintinite low intensity bands are observed at 801 and 852  $\text{cm}^{-1}$ . In contrast in the infrared spectra the band should show considerable intensity as may be observed in the infrared spectra of the double carbonates. The infrared spectra of pirssonite displays two bands at 832 and 868  $\text{cm}^{-1}$ . Three bands for gaylussite are observed at 802, 857 and 874  $\text{cm}^{-1}$ . The infrared spectrum of quintinite shows a broad band at 859  $\text{cm}^{-1}$ .

The Raman spectrum of pirssonite shows two bands at 644 and 719  $\text{cm}^{-1}$ . These bands are assigned to the  $\nu_4 (\text{CO}_3)^{2-}$  bending modes. Adler and Kerr reported two infrared bands at 699 and 712  $\text{cm}^{-1}$ . In the infrared spectra of pirssonite (Figure 2) two bands are observed at 650 and 704  $\text{cm}^{-1}$  in harmony with the position of the Raman results. For gaylussite three Raman bands are observed in this  $\nu_4$  spectral region at 664, 699 and 719  $\text{cm}^{-1}$ . Adler and Kerr reported only two bands in the infrared spectrum at 692 and 720  $\text{cm}^{-1}$  [8]. Four Raman bands are observed for shortite at 695, 715, 719 and 730  $\text{cm}^{-1}$ . Adler and Kerr reported four infrared bands at 693, 709, 719 and 730  $\text{cm}^{-1}$  [8]. The observation of two symmetric stretching modes with different wavenumbers for shortite offers the distinction between two crystallographic different carbonate units. The low site symmetry of the carbonate unit in shortite results in the splitting of the  $\nu_4$  bending modes. According to Farmer [1], the shortite structure is complex with the  $\text{Ca}^{2+}$  is 9 coordinated, one  $\text{Na}^+$  8 coordinated and one  $\text{Na}^+$  6 coordinated. In the structure of shortite there are two distinct  $(\text{CO}_3)^{2-}$  units one on site symmetry  $C_{2v}$  and a second on a site  $C_s$  symmetry. This complexity is reflected in the Raman spectrum of shortite as shown in Figure 1d. For the carbonate quintinite only a single low intensity band at 700  $\text{cm}^{-1}$  is observed.

The Raman spectra of two pirssonite minerals and gaylussite, shortite and quintinite in the 3100 to 3800  $\text{cm}^{-1}$  region are shown in Figure 4. No Raman spectrum was observed for shortite in this spectral region as is expected. This confirms the shortite mineral is anhydrous. The Raman spectrum of pirssonite (sample 1) in the 2500 to 3700  $\text{cm}^{-1}$  region show three bands at 3085, 3202, 3307  $\text{cm}^{-1}$ . For the second pirssonite mineral three bands are observed at 3065, 3302 and 3284  $\text{cm}^{-1}$ . In the infrared spectrum of pirssonite a complex system of overlapping bands is observed. This spectral region may be resolved into band components at 2954, 3058, 3188 and 3326  $\text{cm}^{-1}$ . Adler and Kerr did not provide any information on the IR bands for pirssonite or gaylussite in the OH stretching region. The Raman spectrum of gaylussite in the OH stretching region shows three bands at 2950, 3250 and 3347  $\text{cm}^{-1}$ . In the infrared spectrum three bands at 2944, 3268 and 3334  $\text{cm}^{-1}$  are observed (Figure 5). For quintinite the Raman spectrum shows two bands at 3464 and 3546  $\text{cm}^{-1}$ . In the infrared spectrum two bands at 3167 and 3373  $\text{cm}^{-1}$  are observed.

Studies have shown a strong correlation between OH stretching frequencies and both O...O bond distances and H...O hydrogen bond distances [27-30]. Libowitzky (1999) showed that a regression function can be employed relating the hydroxyl stretching frequencies with regression coefficients better than 0.96 using infrared spectroscopy [31]. The function is described as:  $\nu_1 = (3592 - 304) \times 109^{\frac{-d(O-O)}{0.1321}} \text{ cm}^{-1}$ . Thus OH...O hydrogen bond distances may be calculated using the Libowitzky empirical function. Thus for pirssonite hydrogen bond distances from the infrared data of 2.639 Å (2954  $\text{cm}^{-1}$ ), 2.663 Å (3058  $\text{cm}^{-1}$ ), 2.699 Å (3188  $\text{cm}^{-1}$ ) and 2.755 Å (3326  $\text{cm}^{-1}$ ) are calculated. The Raman bands at 3085, 3202 and 3307  $\text{cm}^{-1}$  provide values of 2.669, 2.75 and 2.746 Å. From the infrared bands of gaylussite at 2950, 3250 and 3347  $\text{cm}^{-1}$  hydrogen bond distances of 2.639, 2.721 and 2.766  $\text{cm}^{-1}$  are estimated. For the mineral quintinite, the IR bands at 3167 and 3373  $\text{cm}^{-1}$  provide hydrogen bond distances of 2.693 and 2.780 Å. The Raman OH stretching band give slightly longer distances of 2.851 and 2.986 Å. The large variation hydrogen bond distances which are present in pirssonite and gaylussite can also be seen in other mixed anion

minerals such as peisleyite where the distances ranging between 3.052 and 2.683 Å. Such hydrogen bond distances are typical of secondary minerals. For pirssonite and gaylussite hydrogen bond distances from 2.669 to 2.766 Å are observed. A range of hydrogen bond distances are observed from reasonably strong to weak hydrogen bonding. This range of hydrogen bonding contributes to the stability of the mineral.

## **Conclusions**

The double carbonates pirssonite, gaylussite, tunisite and shortite were characterised by both Raman and infrared spectroscopy. These double carbonates are characterised by  $\nu_1$  stretching bands around 1060 to 1080  $\text{cm}^{-1}$ . The position of the band appears to be dependent on the symmetry of the carbonate units in the structure. For pirssonite and gaylussite only a single band is observed whilst for shortite and for comparison quintinite two bands are observed in the symmetric stretching region. This confirms the concept of more than one crystallographically distinct carbonate unit in the crystal. Multiple antisymmetric stretching modes are, however, observed for pirssonite indicating distortion of the carbonate unit in the crystal. This distortion is also observed by the number of bands in the  $\nu_4$  in phase bending region where multiple bands are observed for pirssonite, gaylussite and shortite.

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## References

- [1] V.C. Farmer, Mineralogical Society Monograph 4: The Infrared Spectra of Minerals, 1974.
- [2] T.-J. Chi, Y.-H. Kwan, Changchun Dizhi Xueyuan Xuebao (1978) 39-42.
- [3] E. Corazza, C. Sabelli, Acta Crystallographica 23 (1967) 763-770.
- [4] S. Menchetti, Atti della Accademia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti 44 (1968) 680-694.
- [5] E.A. Monroe, Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie 124 (1967) 459.
- [6] E.A. Pobedinskaya, T. Chinh Le, Vestnik Moskovskogo Universiteta, Seriya 4: Geologiya (1985) 91-100.
- [7] Z. Johan, P. Povondra, E. Slansky, American Mineralogist 54 (1969) 1-13.
- [8] H.H. Adler, P.F. Kerr, American Mineralogist 48 (1963) 839-853.
- [9] A.J. Frueh, Jr., J.P. Golightly, Canadian Mineralogist 9 (1967) 51-56.
- [10] R.L. Frost, S.J. Palmer, J.M. Bouzaid, B.J. Reddy, J. Raman Spectrosc. 38 (2007) 68-77.
- [11] R.L. Frost, D.A. Henry, M.L. Weier, W. Martens, J. Raman Spectrosc. 37 (2006) 722-732.
- [12] R.L. Frost, A.W. Musumeci, J.T. Klopogge, M.O. Adebajo, W.N. Martens, J. Raman Spectrosc. 37 (2006) 733-741.
- [13] R.L. Frost, J. Cejka, M. Weier, W.N. Martens, J. Raman Spectrosc. 37 (2006) 879-891.
- [14] R.L. Frost, M.L. Weier, J. Cejka, J.T. Klopogge, J. Raman Spectrosc. 37 (2006) 585-590.
- [15] R.L. Frost, J. Cejka, M.L. Weier, W. Martens, J. Raman Spectrosc. 37 (2006) 538-551.
- [16] R.L. Frost, M.L. Weier, B.J. Reddy, J. Cejka, J. Raman Spectrosc. 37 (2006) 816-821.
- [17] R.L. Frost, M.L. Weier, W.N. Martens, J.T. Klopogge, J. Kristof, J. Raman Spectrosc. 36 (2005) 797-805.
- [18] R.L. Frost, R.-A. Wills, M.L. Weier, W. Martens, J. Raman Spectrosc. 36 (2005) 435-444.
- [19] H. Fan, K. Tao, Y. Xie, K. Wang, Yanshi Xuebao 19 (2003) 169-172.
- [20] W. Hong, S. He, S. Huang, Y. Wang, H. Hou, X. Zhu, Guangpuxue Yu Guangpu Fenxi 19 (1999) 546-549.
- [21] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, Handbook of Mineralogy, Mineral Data Publishing, Tucson, Arizona, USA, 2003.
- [22] R.L. Frost, D.A. Henry, K. Erickson, J. Raman Spectrosc. 35 (2004) 255-260.
- [23] R.L. Frost, Spectrochim. Acta, Part A 60A (2004) 1469-1480.
- [24] R.L. Frost, O. Carmody, K.L. Erickson, M.L. Weier, J. Cejka, J. Mol. Struct. 703 (2004) 47-54.
- [25] R.L. Frost, O. Carmody, K.L. Erickson, M.L. Weier, D.O. Henry, J. Cejka, J. Mol. Struct. 733 (2004) 203-210.
- [26] B. Dickens, W.E. Brown, Inorganic Chemistry 8 (1969) 2093-2103.
- [27] J. Emsley, Chemical Society Reviews 9 (1980) 91-124.
- [28] H. Lutz, Structure and Bonding (Berlin, Germany) 82 (1995) 85-103.
- [29] W. Mikenda, Journal of Molecular Structure 147 (1986) 1-15.
- [30] A. Novak, Structure and Bonding (Berlin) 18 (1974) 177-216.
- [31] E. Libowitsky, Monatshefte für chemie 130 (1999) 1047-1049.

### *List of Figures*

**Figure 1 Raman spectra of pirssonite (sample 1), pirssonite (sample 2), gaylussite, shortite, quintinite in the 950 to 1450  $\text{cm}^{-1}$  region.**

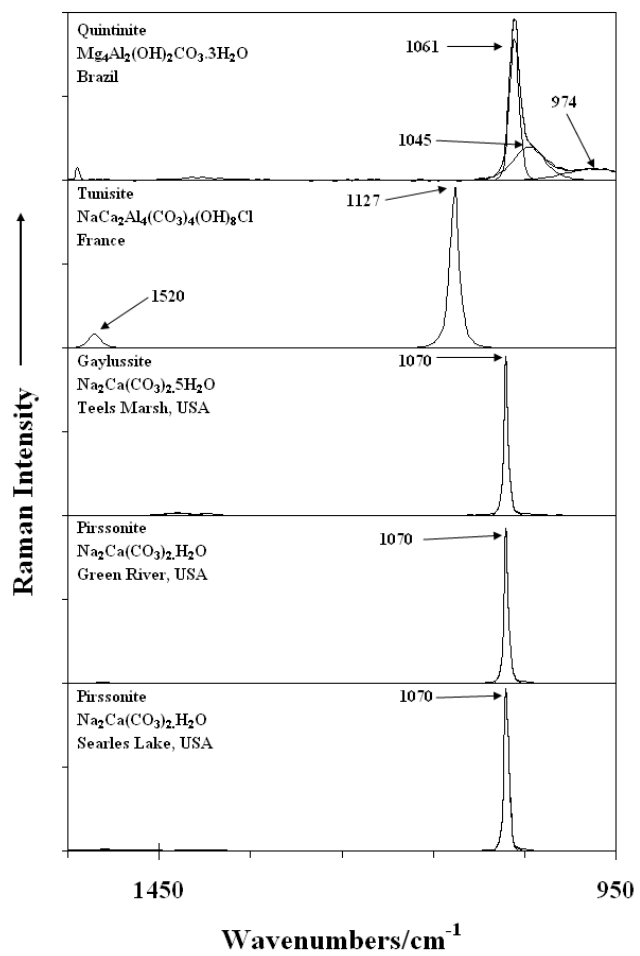
**Figure 2 Infrared spectra of pirssonite, gaylussite, tunisite, shortite and quintinite in the 550 to 1600  $\text{cm}^{-1}$  region.**

**Figure 3 Raman spectra of pirssonite (sample 1), pirssonite (sample 2), gaylussite, shortite, quintinite in the 100 to 950  $\text{cm}^{-1}$  region.**

**Figure 4 Raman spectra of pirssonite (sample 1), pirssonite (sample 2), gaylussite, shortite, quintinite in the 3100 to 3800  $\text{cm}^{-1}$  region.**

**Figure 5 Infrared spectra of pirssonite, gaylussite, tunisite and quintinite in the 2550 to 4000  $\text{cm}^{-1}$  region.**





**Figure 1**

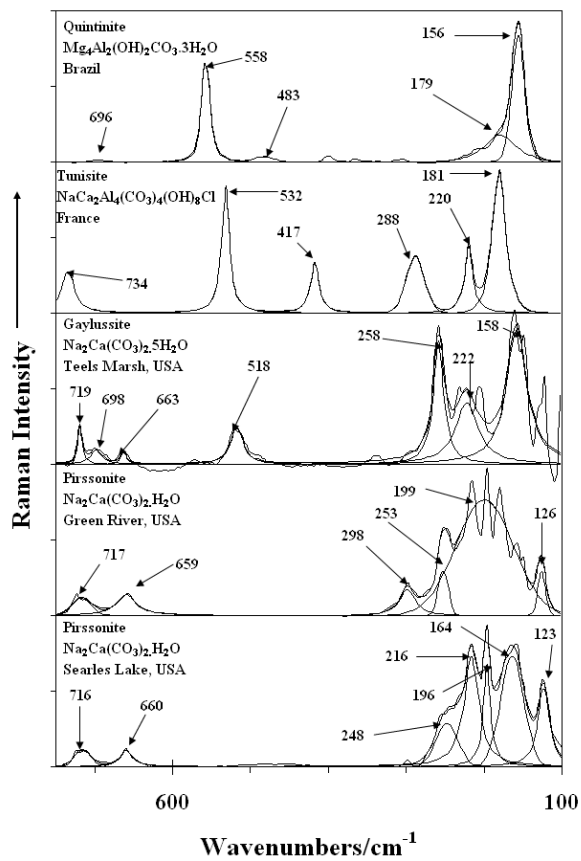


Figure 2

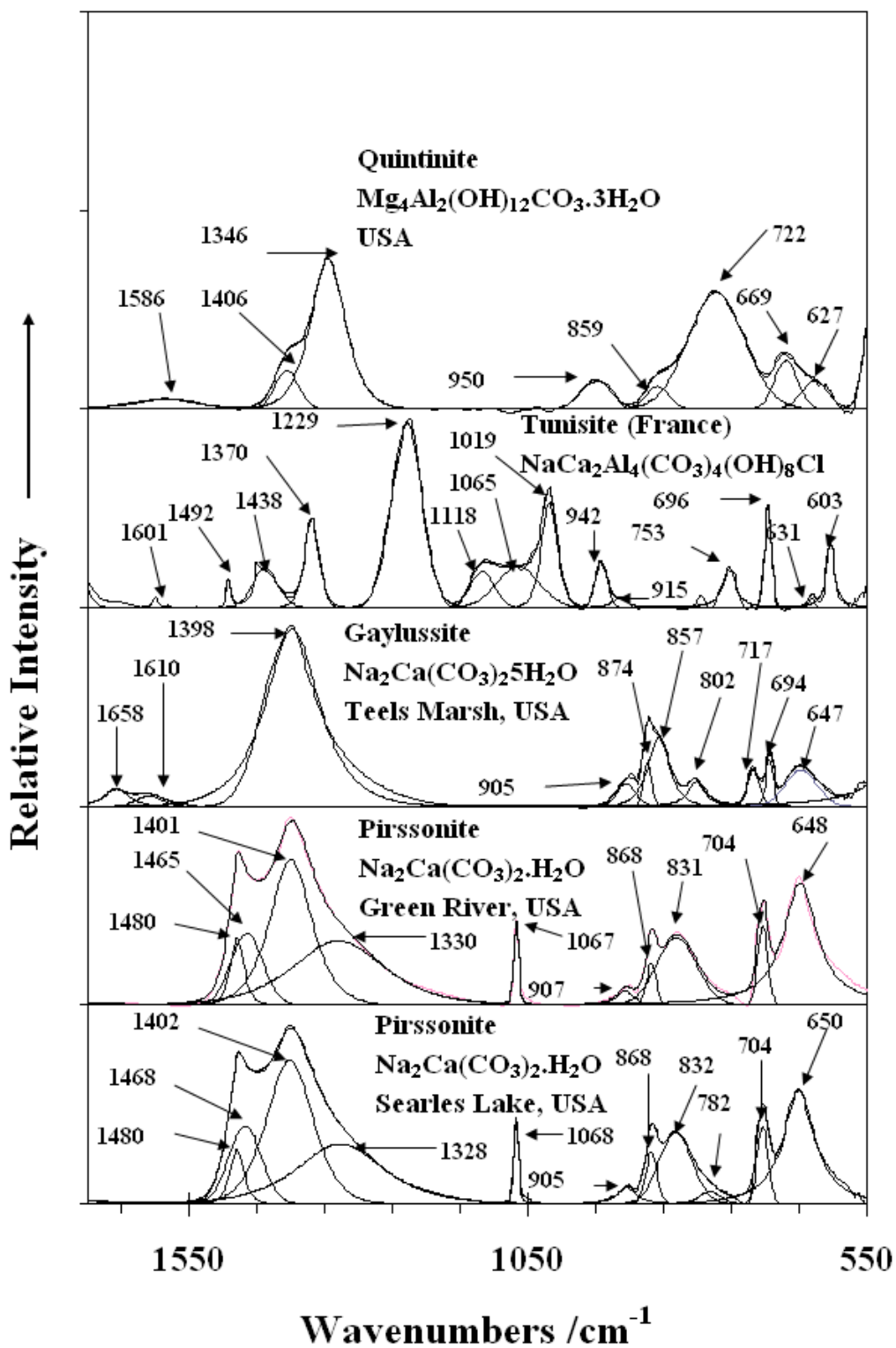


Figure 2

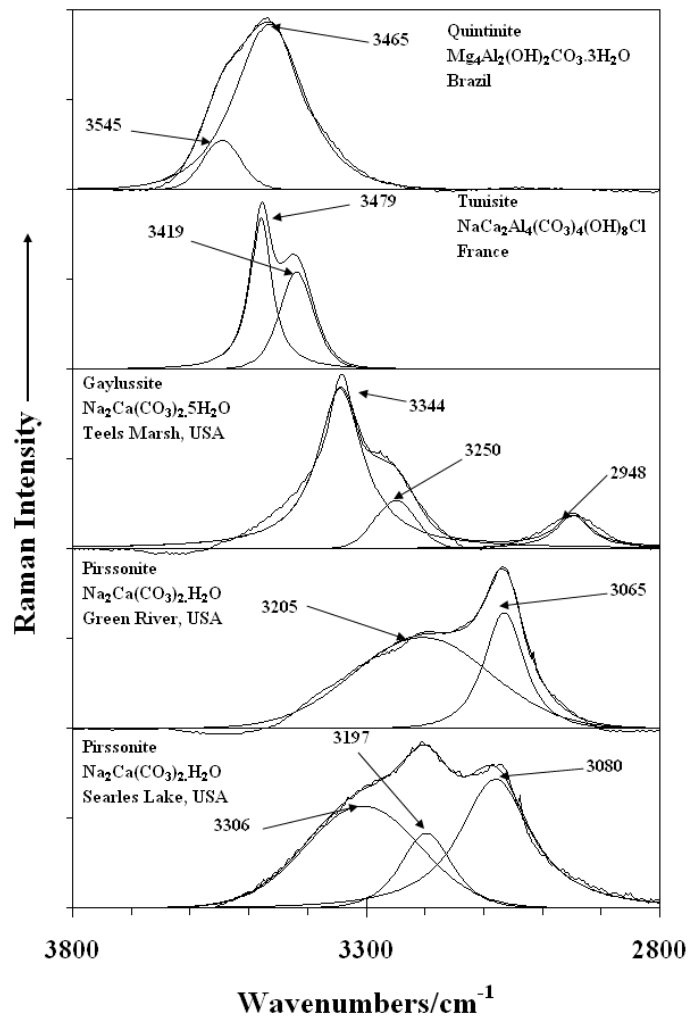


Figure 3

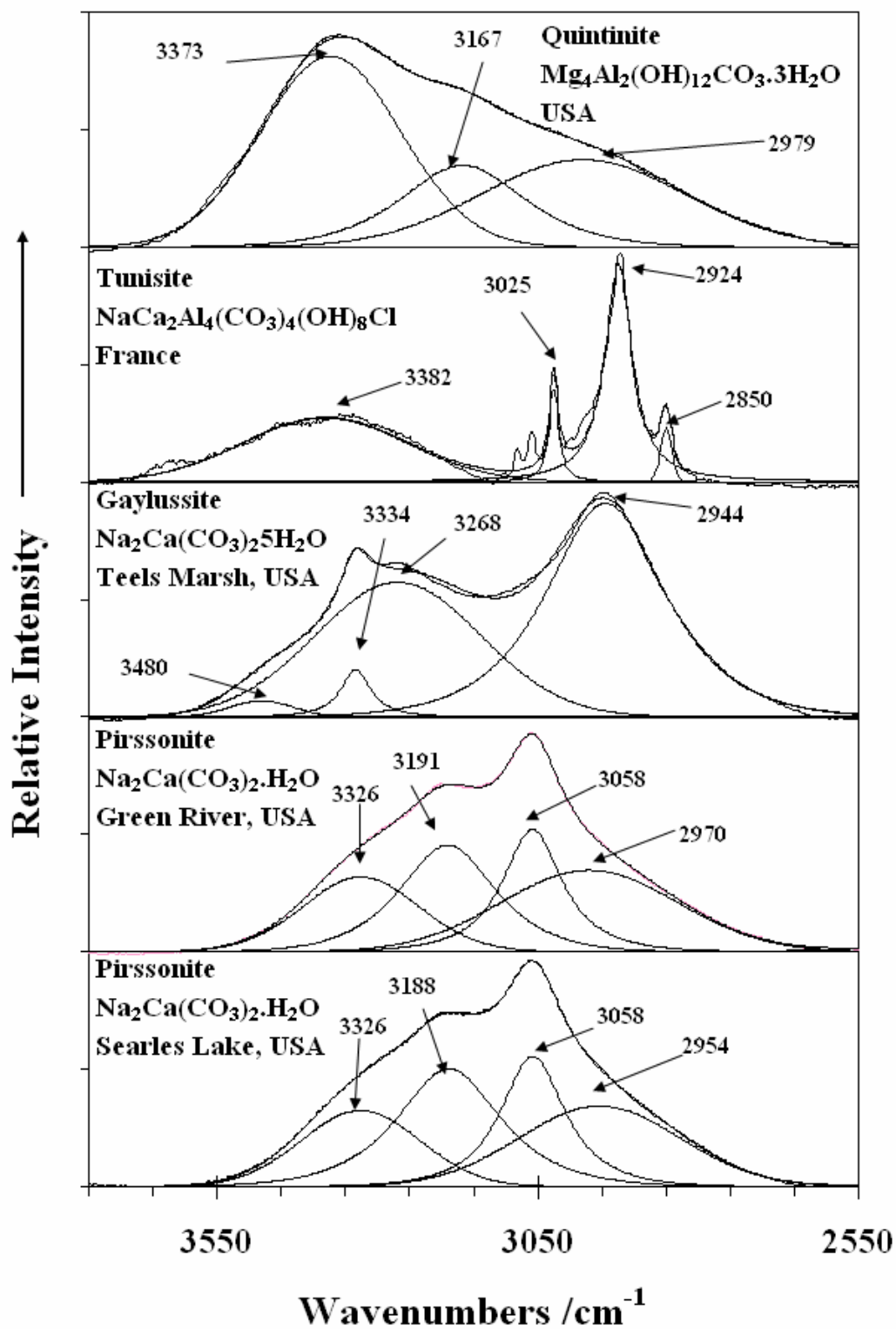


Figure 4