COVER SHEET

Raman spectroscopy of dawsonite $NaAl(CO_3)(OH)_2$

Ray L. Frost[•] and Jocelyn M. Bouzaid

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Abstract

Raman spectroscopy at both 298 and 77 K complimented with infrared spectroscopy has been used to study the structure of dawsonite. Previous crystallographic studies concluded that the structure of dawsonite was a simple one, however both Raman and infrared spectroscopy show that this conclusion is incorrect. Multiple bands are observed in both the Raman and infrared spectra in the antisymmetric stretching and bending regions showing that the symmetry of the carbonate anion is reduced and in all probablity the carbonate anions are not equivalent in the dawsonite structure. Multiple OH deformation vibrations centred upon 950 cm^{-1} in both the Raman and infrared spectra show that the OH units in the dawsonite structure are non-equivalent. Calculations using the position of the Raman and infrared OH stretching vibrations enabled estimates of the hydrogen bond distances of 0.2735, 0.27219 pm at 298 K and 0.27315, 0.2713 pm at 77 K to be made. This indicates strong hydrogen bonding of the OH units in the dawsonite structure.

Key words: barentsite, dawsonite, tunisite, smithsonite, carbonate, hydroxyl, Infrared and Raman spectroscopy

Introduction

Dawsonite, a sodium aluminium hydroxy carbonate $NaAl(CO_3)(OH)_2$, is orthrhombic with point group 2/m [1] and is acicular to bladed crystals and often occurs in rosettes and radial fibrous to tufted aggregates [2]. The mineral is formed through low temperature hydrothermal decomposition of aluminous silicates [3,4]. Varities other than sodium dawsonite are known [5-7]. Indeed dawsonites with yttrium and cerium are also known [8,9]. Many of these types of synthetic compounds are used as catalyst precursors [10-13]. Dawsonite formation is used in water purification for the removal of alumina species [14]. It is possible that this type of mineral can be used to trap carbon dioxide and remove green house gases. A model of the mineral is given in Figure 1. Rotaion of the figure shows that the mineral contains a hole in the structure which makes the mineral take on a zeolite type structure. It is possible that this space might be used to trap heavy metals.

The infrared spectra of dawsonite has been published [15-21]. Alumina surfaces have been analysed by FTIR spectroscopy [18]. Some reports of the Raman spectra have been published [16,19]. The free ion, CO_3^{2-} with D_{3h} symmetry exhibits four normal vibrational modes; a symmetric stretching vibration (ν_1), an out-of-plane bend (ν_2), a

[•] Author to whom correspondence should be addressed (r.frost@qut.edu.au)

doubly degenerate asymmetric stretch (ν_3) and another doubly degenerate bending mode (ν_4) [22-25]. 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. Generally, strong Raman modes appear around 1100 cm^{-1} due to the symmetric stretching vibration (ν_1), of the carbonate groups, while intense IR and weak Raman peaks near 1400 cm^{-1} are due to the antisymmetric stretch (ν_3). Infrared modes near 800 cm^{-1} are derived from the out-of-plane bend (ν_2). Infrared and Raman modes around 700 cm^{-1} region are due to the in-plane bending mode (ν_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-}.

To date little Raman spectra of dawsonite has been published, even though a significant number of infrared analyses have been undertaken [15,17-21]. X-ray crysatllography suggests the mineral has a regular structure. However the infrared data suggests otherwise.

Experimental

Minerals

Selected dawsonite minerals were obtained from the Mineral Research Company (http://www.minresco.com/default.htm) and other sources including Museum Victoria (Museum Victoria, Melbourne, Victoria, Australia). The samples were phase analysed by powder X-ray diffraction and for chemical composition by EDX measurements.

Raman microprobe spectroscopy

The crystals of dawsonite 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 3.5 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio.

Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the technique have been published by the authors [26-29].

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 4000–525 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.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc 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 Lorentz -Gauss 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 0.9995.

Results and discussion

The Raman spectra of dawsonite at 298 and 77 K are shown in Figures 2a and 2b. The infrared spectrum of the two selected dawsonites are shown in Figure 3. The spectral region centred upon 1090 cm^{-1} is complex with a number of overlapping bands. Two distincit bands are observed in the 298 K spectra at 1090 and 1065 cm^{-1} for the dawsonite from Italy and 1090 and 1066 cm^{-1} for the dawsonite from Canada. These bands are attributed to the ν_1 symmetric stretching modes. According to Farmer [30] the structure of dawsonite is stated to be quite regular. The structural analysis of dawsonite suggests that the $(CO_3)^{2-}$ ion is regular and is not involved with bonding [3,4,31]. This suggestion is not consistent with the Raman spectrum as multiple bands are observed in the $(CO_3)^{2-}$ stretching region. This observation is even more pronounced upon obtaining the Raman spectra at 77 K. Three resolvable bands are observed at 1103, 1091 and 1070 cm^{-1} for the dawsonite from Italy and at 1103, 1091 and 1070 cm^{-1} for the dawsonite from Canada. Farmer also reported the ν_1 band to be two quite distinct bands unusual for a single $(CO_3)^{2-}$ ion [30]. Fundamentally there is no difference between the spectra of the two mineral samples. Any differences are very small.

A very low intensity band is observed in both spectra at 1367 cm^{-1}. In the infrared spectra of dawsonite (this work) an intense asymmetric band is observed at 1390 cm^{-1} (Figure 3). Component bands may be resolved as is shown in this figure. This value is in excellent agreemnet with previously published data [30,32]. Two Raman bands are also observed in the 298 K spectra at 1505 and 1483 cm^{-1}. In the infrared spectra an asymmetric band at 1542 cm^{-1} is observed with band components resolved at 1588, 1542, 1489 cm^{-1}. These spectra confirm the assertion that the spectra of dawsonite is not simple but shows complexity in each spectral region. The observation of multiple bands in the antisymmetric stretching region is an indication of the reduction in symmetry of the carbonate ion in the dawsonite structure. An alternaitive explanation is that in the structure not all the carbonates are identical as is observed in Figure 1. These bands at 1505 and 1483 are attributed to the ν_3 antisymmetric stretching mode. Estep and Karr assigned an infrared band at 1550 cm^{-1} to the OH bending mode and the band at 1390 cm^{-1} to the antisymmetric stretching mode [15]. The fact that multiple bands may be resolved in the infrared spectra suggest that the infrared bands as described by Frueh and Golightly is an over

simplification. They assigned both the high wavenumber bands to the ν_3 antisymmetric stretching mode [32]. The normal average band position of the ν_3 antisymmetric stretrching mode is around 1470 cm^{-1}. Farmer, based upon infrared spectroscopy of Frueh and Golightly, reported two antisymmetric stretching modes at 1550 and 1390 cm^{-1} [30]. Upon the collection of Raman spectral data at 77 K, bands are observed at 1505, 1484 and 1367 cm^{-1}. The last band is of very low intensity in the Raman spectra and is only observed through scale expansion.

In the infrared spectrum of dawsonite as reported by Frueh and Golightly, bands were observed at 858 and 842 cm^{-1} and were attributed to the ν_2 bending mode of the carbonate anion [32]. In the Raman spectrum of dawsonite from Italy a band is observed at 822 cm^{-1} assigned to the ν_2 bending mode (Figure 4a). The infrared spectra of the two dawsonites are shown in Figure 5. A quite low intensity band is observed for dawsonite from Canada at 826 cm^{-1}. Multiple bands are observed in the infred spectra around 845 cm^{-1}. bands are observed at 883, 863, 845 and 841 cm^{-1} for the dawsonite from Italy. Bands in an almost identical position are observed for the dawsonite from Canada.

Two bands are observed in the Raman spectra for both dawsonite samples at 934 and 897 cm^{-1}. In the infrared spectrum (Figure 5) multiple bands are observed at around 950 cm^{-1} with component bands at 953, 934 and 920 cm^{-1}. For the dawsonite from Italy the latter band is higher in intensity and for the dawsonite from Canada the former band is of higher intensity. This indicates an orientation effect on the Raman spectra of dawsonite. Frueh and Golightly reported two infrared bands at 950 and 930 cm^{-1} and Farmer assigned these bands to OH deformation modes. Thus the two Raman bands at 934 and 897 cm^{-1} are attributed to the OH deformation bands of dawsonite. These bands show significant shifts to higher wavenumbers upon cooling to 77 K (Figure 4b). The bands are observed at 948 and 902 cm^{-1}. This is a 14 and 7 cm^{-1} shift. Such a shift is not observed for the other low wavenumber bands and supports the concept that these bands are assignable to OH deformation modes. The observation of multiple bands proves that all the OH units are not equivalent. In the Xray crystallographic structure of dawsonite all OH units are defined as equivalent. Both Raman and infrared spectroscopy suggests this is not correct.

At 77 K only one band is observed at 826 cm^{-1} assigned to the ν_2 bending mode of carbonate anion. In the Raman spectra of the low wavenumber region two bands are observed for both the dawsonite mineral samples at 746 and 729 cm^{-1}. Frueh and Golightly reported only one band at 727 cm^{-1} in the infrared spectrum of dawsonite. The band is attributed to the ν_4 bending mode. In the infrared spectrum of dawsonite from Italy bands are observed at 730, 696 and 670 cm^{-1} and are assigned to the ν_4 bending mode. The infrared spectrum of the dawsonite from Canada is identical with bands in the same positions. The observation of multiple bands in the ν_4 region provides further evidence for the nonequivalence of the carbonate units in the dawsonite structure.

In the region below 700 cm^{-1} a significant number of Raman bands are observed. An intense band at 587 cm^{-1} observed in the 298 K spectrum (Figure 4a) and at 592 cm^{-1} in the 77 K spectrum (Figure 4b) is assigned to an AlO stretching vibration. Frueh and Golightly reported a band at 685 cm^{-1} and assigned the band to

this vibrational mode [32]. Serna et al. attributed most of the vibrational bands below 700 cm^{-1} to AlO modes [19]. It is probable that the band at 519 cm^{-1} is also attributable to an AlO symmetric stretching vibration. Two bands are observed at ~386 and 360 cm^{-1} and may be assigned to OAlO bending modes. A number of Raman bands are observed at 260, 218, 189 and 150 cm^{-1}. Significant band narrowing is observed for these bands upon obtaining the Raman spectra at 77 K.

The Raman spectra of the OH stretching region at 298 and 77 K are shown in Figures 6a and 6b. The infrared spectra of the two dawsonites in the OH stretching region are shown in Figure 7. A complex set of bands with an overlapping profile is observed. Two bands are found at 298 K for the dawsonites at 3282 and 3250 cm^{-1}. There is a distinct shift to lower wavenumbers upon cooling to 77 K where bands at 3274 and 3227 cm^{-1} are observed. In the infrared spectrum two component bands at 3275 and 3244 cm^{-1} are observed with additional low intensity bands at 3461 and 3364 cm^{-1}. The infrared spectrum of dawsonite is strongly asymmetric on the low wavenumber side and component bands are resolved as shown in Figure 7. These bands may be attributed to adsorbed water. Studies have shown a strong correlation between OH stretching frequencies and both O···O bond distances and H···O hydrogen bond distances [33-36]. 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 [37]. The function is described as: $\nu_1 = (3592 - 304) \times 109^{\frac{-d(O-O)}{0.1321}}$ cm^{-1}. Thus OH---O hydrogen bond distances may be calculated using the Libowitzky empirical function. The values for the OH stretching vibrations listed above provide hydrogen bond distances of 0.2735 pm (3282 cm^{-1}), 0.27219 pm (3250 cm^{-1}) for the 298 K spectra and 0.27315 pm (3274 cm^{-1}), 0.2713 pm (3227 cm^{-1}) for the 77 K spectra. Frueh and Golightly suggested some hydrogen bonding exists for dawsonite [32]. The values calculated here support the concept of strong hydrogen bonding between the OH units and the carbonate anions in the dawsonite structure.

Conclusions

This study has shown the structure of dawsonite is not a simple structure as is evidenced from X-ray crystallography. Multiple bands are observed in both the Raman and infrared spectra in the carbonate sttretching and bending modes indicating a symmetry reduction of the carboante anion. An alternative explanation for the observation of mutiple bands is the nonequivalence of the carbonate anions in the dawsonite structure. Multiple bands attributed to the OH deformation modes support the concept of nonequiavelnt OH units in the dawsonite structure. Calculations based on a Libowitzky type expression enabled estimates of the hydrogen bond distances between the OH units in dawsonite and the carbonate anions to be made. Hydrogen bond distances of 0.2735 and 0.27219 pm show strong hydrogen bonding.

Acknowledgments

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References

1. Corazza, E, Sabelli, C, Vannucci, S. *Neues Jahr. Mineral.* 1977: 381.
2. Anthony, JW, Bideaux, RA, Bladh, KW, Nichols, MC *Handbook of Mineralogy*; Mineral Data Publishing: Tiscon, Arizona, USA, 2003; Vol. 5.
3. Smirnov, MN, Bitner, AA, Tsekhovol'skaya, DI, Nikolaeva, LY. *Nov. Nebok.* 1982: 228.
4. Kwon, SW. *Taehan Hwahakhoe Chi* 1969**; 13**: 157.
5. Dunning, GE, Henderson, WA, Jr. *Riv. Mineral. Ital.* 2003: 102.
6. Iga, T, Kato, S. *Yogyo Kyokaishi* 1978**; 86**: 509.
7. Zhang, X, Wen, Z, Gu, Z, Xu, X, Lin, Z. *J. Solid State Chem.* 2004**; 177**: 849.
8. Grice, JD, Gault, RA. *Can. Min.* 2006**; 44**: 105.
9. Grice, JD, Gault, RA, Roberts, AC, Cooper, MA. *Can. Min.t* 2000**; 38**: 1457.
10. Kwon, SW, Kim, BH, Ishikawa, H. *Kogyo Kagaku Zasshi* 1971**; 74**: 1992.
11. Kwon, SW, Kim, BH, Ishikawa, H. *Kogyo Kagaku Zasshi* 1971**; 74**: 1987.
12. Li, J-G, Ikegami, T, Lee, J-H, Mori, T, Yajima, Y. *J. Euro. Ceram. Soc.* 2001**; 21**: 139.
13. Ali, AA, Hasan, MA, Zaki, MI. *Chem. Mater.* 2005**; 17**: 6797.
14. Alvarez-Ayuso, E, Nugteren, HW. *Water Res.* 2005**; 39**: 2096.
15. Estep, PA, Karr, C, Jr. *Am. Miner.* 1968**; 53**: 305.
16. Garcia-Ramos, JV, Serna, CJ. *Rev. Acad. de Cien.* 1987**; 81**: 397.
17. Karr, C, Jr., Kovach, JJ. *App. Spec.* 1969**; 23**: 219.
18. Lee, DH, Condrate Sr, RA. *Mat. Let.* 1995**; 23**: 241.
19. Serna, CJ, Garcia-Ramos, JV, Pena, MJ. *Spect. Acta,* 1985**; 41A**: 697.
20. Su, C, Suarez, DL. *Clays Clay Miner.*1997**; 45**: 814.
21. Tsekhovol'skaya, DI, Nikolaeva, LY. *Nov. Neboksit. Vidy Glinozem. Syr'ya, M.* 1982: 231.
22. Frost, RL, Weier, ML, Cejka, J, Ayoko, GA. *Spectrochim. Acta,* 2006**; 65**: 529.
23. Frost, RL, Erickson, KL, Weier, ML, Carmody, O, Cejka, J. *J. Mol. Struc.*2005**; 737**: 173.
24. Frost, RL, Williams, PA, Martens, W. *Min. Mag.*2003**; 67**: 103.
25. Frost, RL, Martens, WN, Rintoul, L, Mahmutagic, E, Kloprogge, JT. *J.of Ram. Spec* .2002**; 33**: 252.
26. Frost, RL, Henry, DA, Erickson, K. *J.of Ram. Spec.* 2004**; 35**: 255.
27. Frost, RL. *Spectrochim. Act., y* 2004**; 60A**: 1469.
28. Frost, RL, Carmody, O, Erickson, KL, Weier, ML, Cejka, J. *J. Mol. Struct.* 2004**; 703**: 47.
29. Frost, RL, Carmody, O, Erickson, KL, Weier, ML, Henry, DO, Cejka, *J.Mol. Struct* 2004**; 733**: 203.
30. Farmer, VC *Mineralogical Society Monograph 4: The Infrared Spectra of Minerals*, 1974.
31. Mandarino, JA, Harris, DC. *Can. Min.* 1965**; 8**: 377.
32. Frueh, AJ, Jr., Golightly, JP. *Can. Min.* 1967**; 9**: 51.
33. Emsley, J. *Chem. Soc. Rev.* 1980**; 9**: 91.
34. Lutz, H. *Structure and Bonding (Berlin, Germany)* 1995**; 82**: 85.
35. Mikenda, W. *J. Mol. Struct.* 1986**; 147**: 1.
36. Novak, A. *Struct. Bond.* 1974**; 18**: 177.
37. Libowitsky, E. *Monat.e fÜr chem.* 1999**; 130**: 1047.

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Figure 3 Infrared spectra of dawsonite in the 1200 to 1800 cm^{-1} range

Figure 4a and 4b Raman spectra of dawsonite in the 100 to 1000 cm^{-1} range at 298 and 77 K.

Figure 5 Infrared spectra of dawsonite in the 500 to 1200 cm^{-1} range

Figure 6a and 6b Raman spectra of dawsonite in the 3100 to 3500 cm^{-1} range at 298 and 77 K.

Figure 7 Infrared spectra of dawsonite in the 2700 to 3700 cm^{-1} range

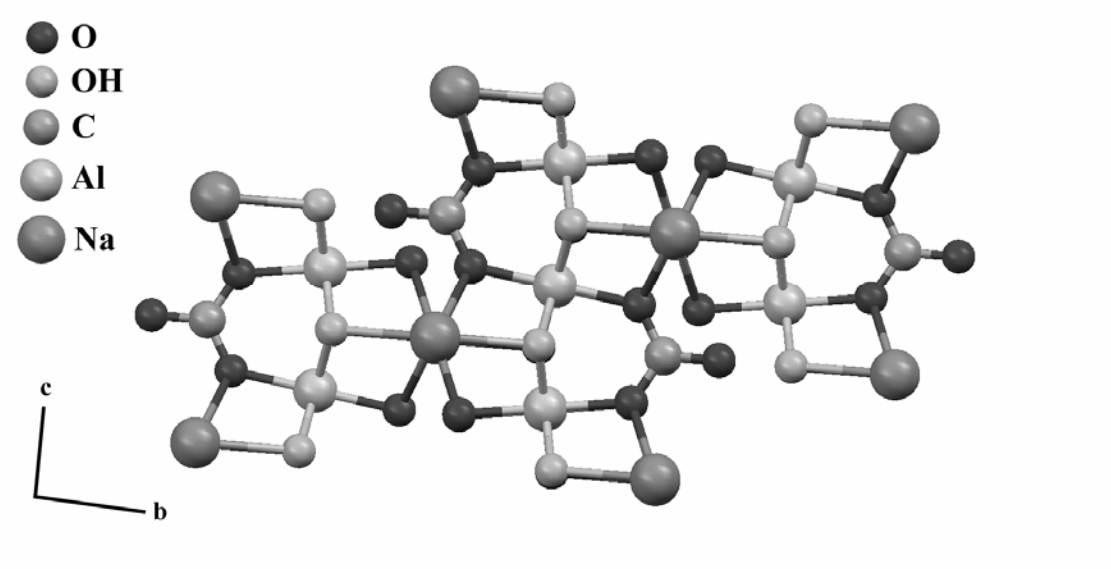


Figure 1

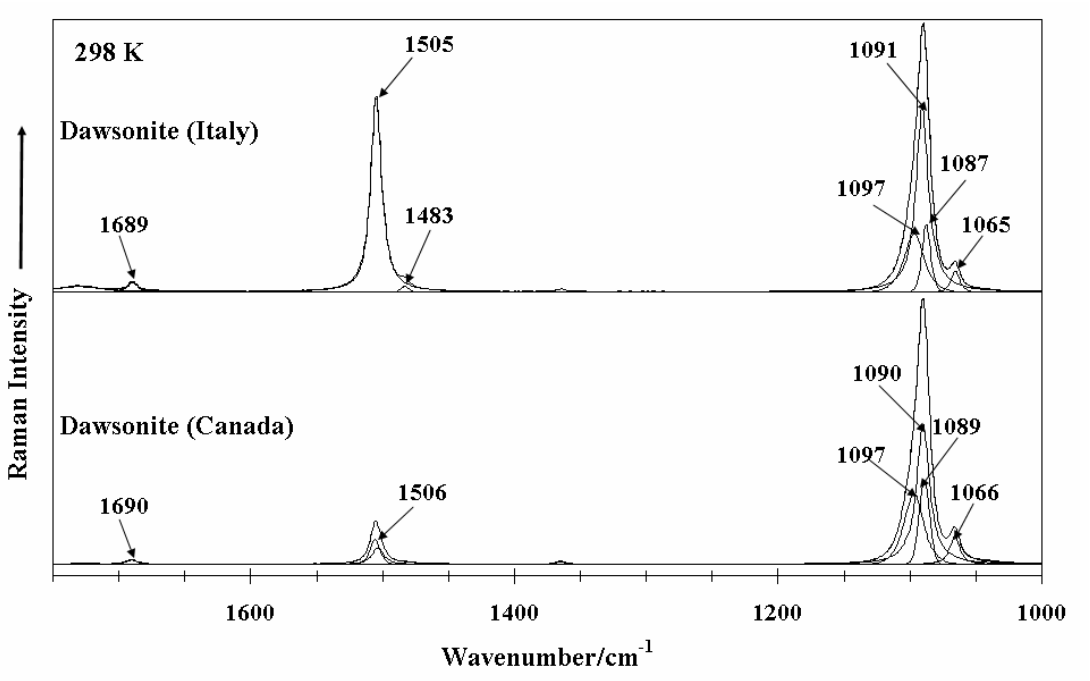


Figure 2a

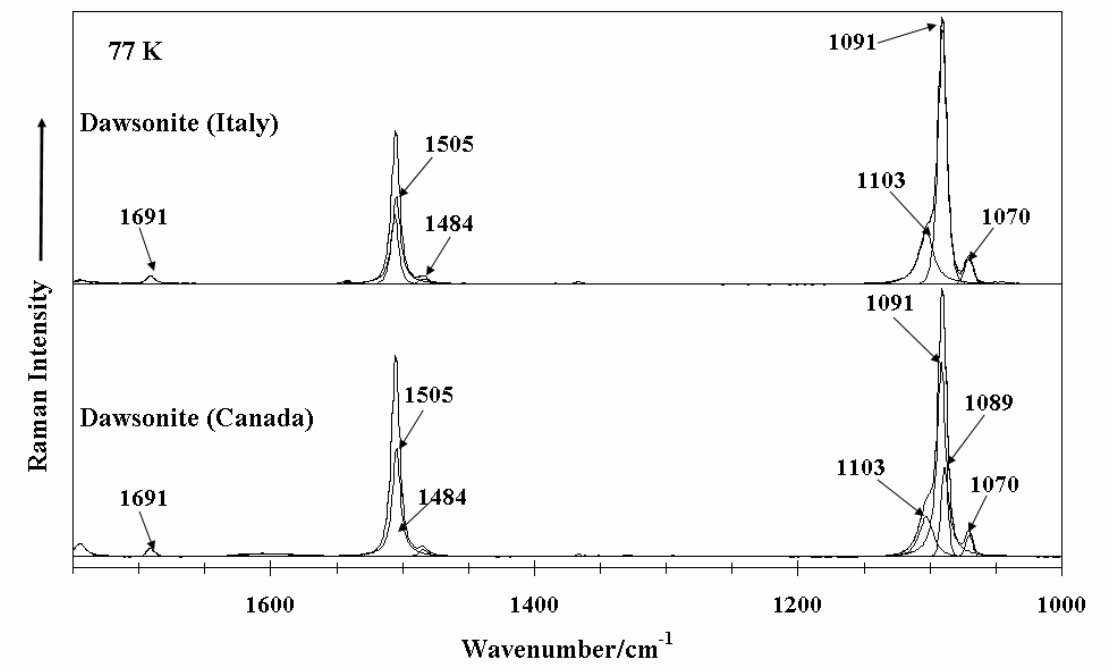


Figure 2b

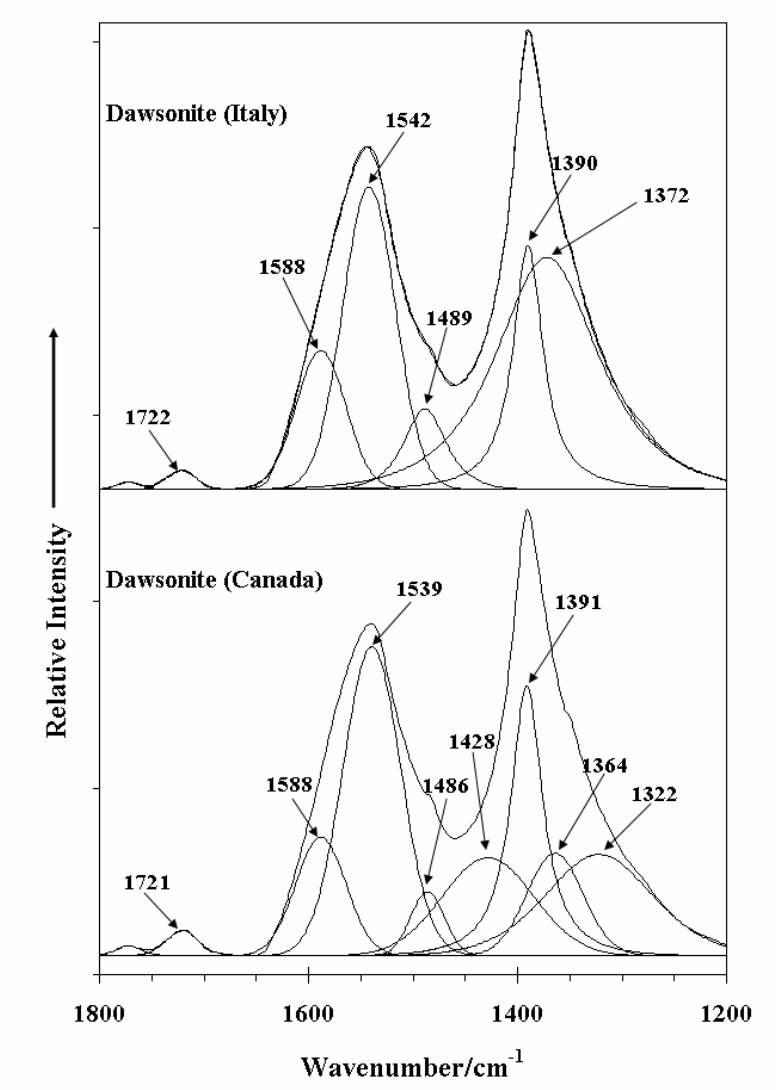

Dawsonite (Italy)
1542
1390
1372
1588
1489
1722
Dawsonite (Canada)
1539
1391
1428
1364
1588
1486
1322
1721
Relative Intensity
1800
1600
1400
1200
Wavenumber/cm-1

Figure 3

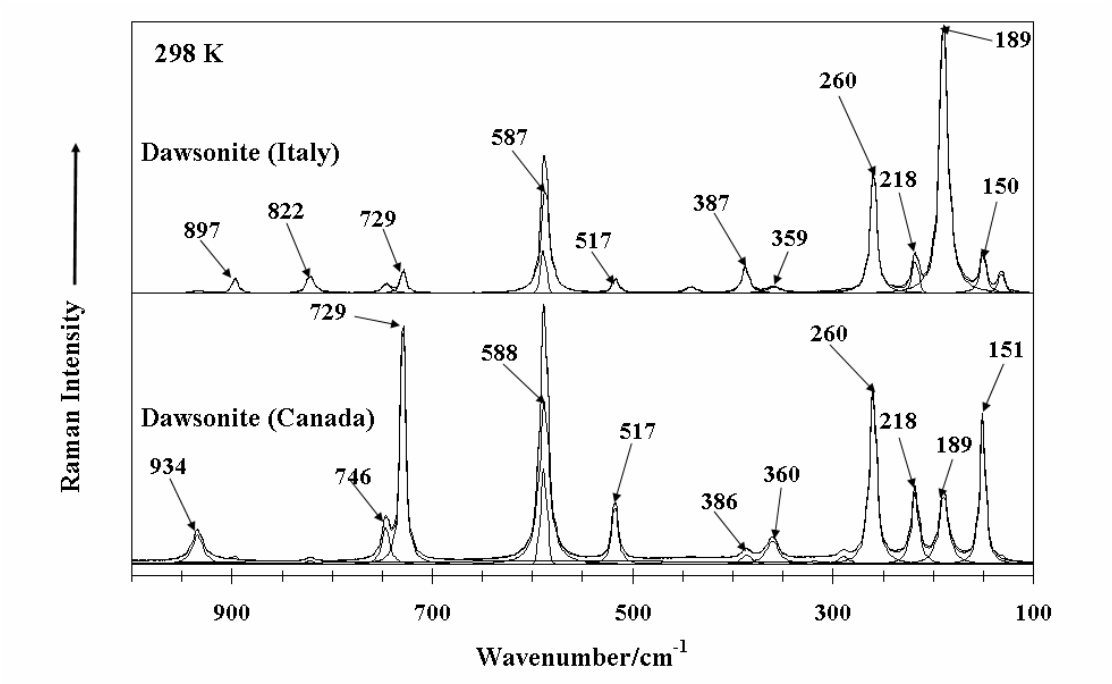


Figure 4a

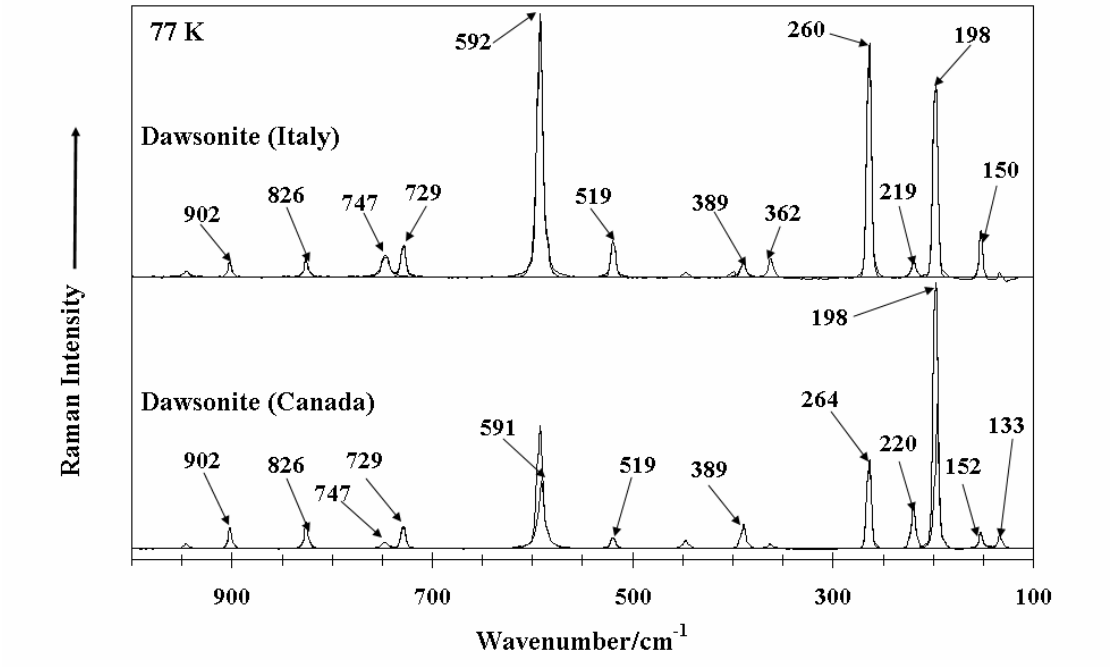
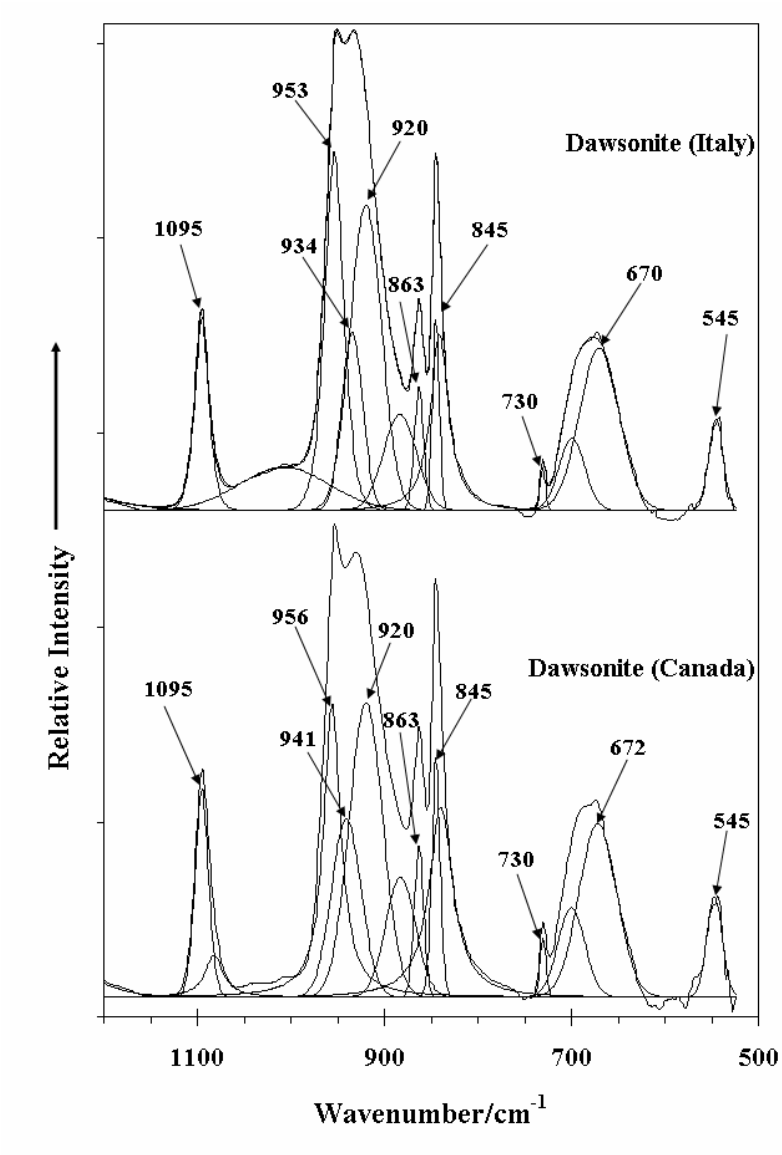


Figure 4b


953
920
Dawsonite (Italy)
1095
934
845
863
670
545
730
956
920
Dawsonite (Canada)
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845
863
941
672
545
730
Relative Intensity
1100
900
700
500
Wavenumber/cm-1

Figure 5

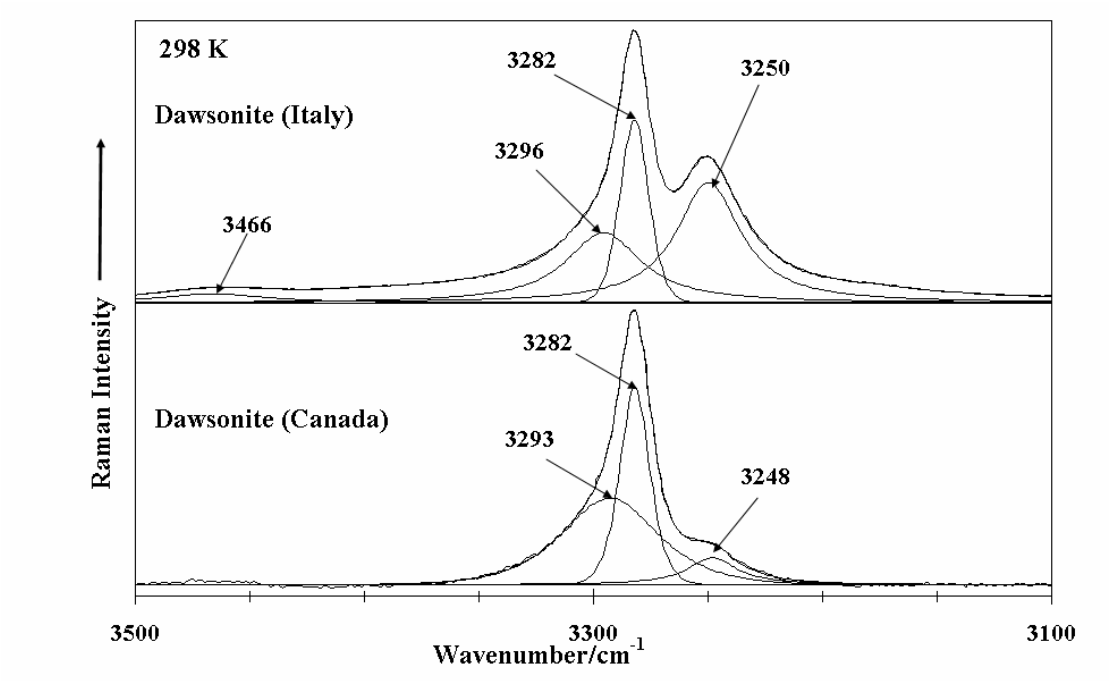


Figure 6a

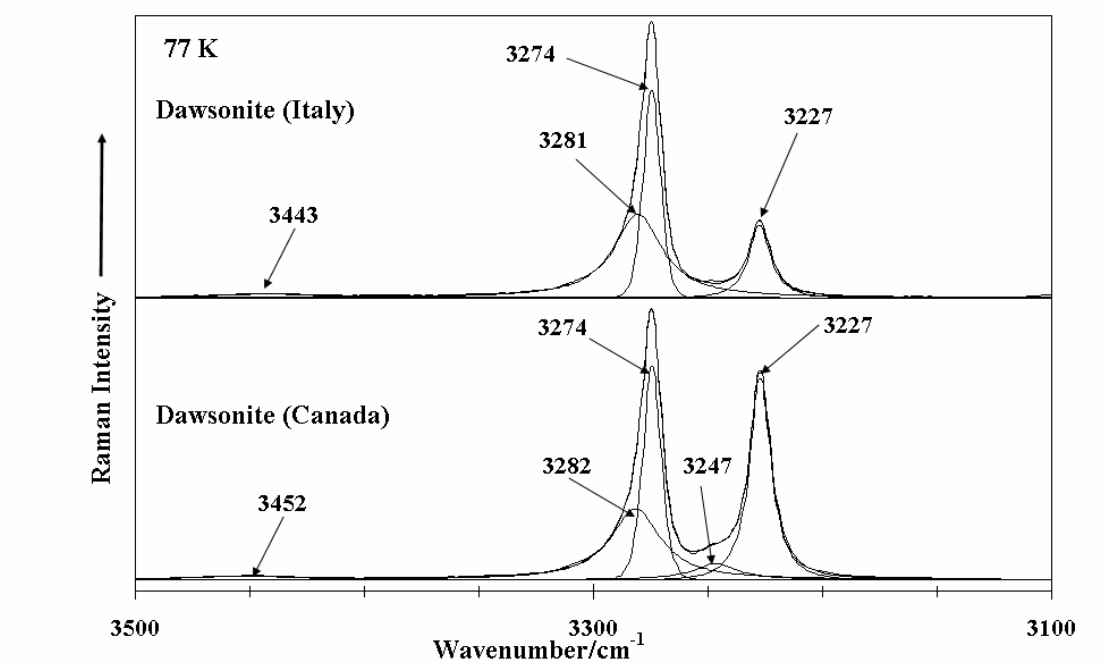
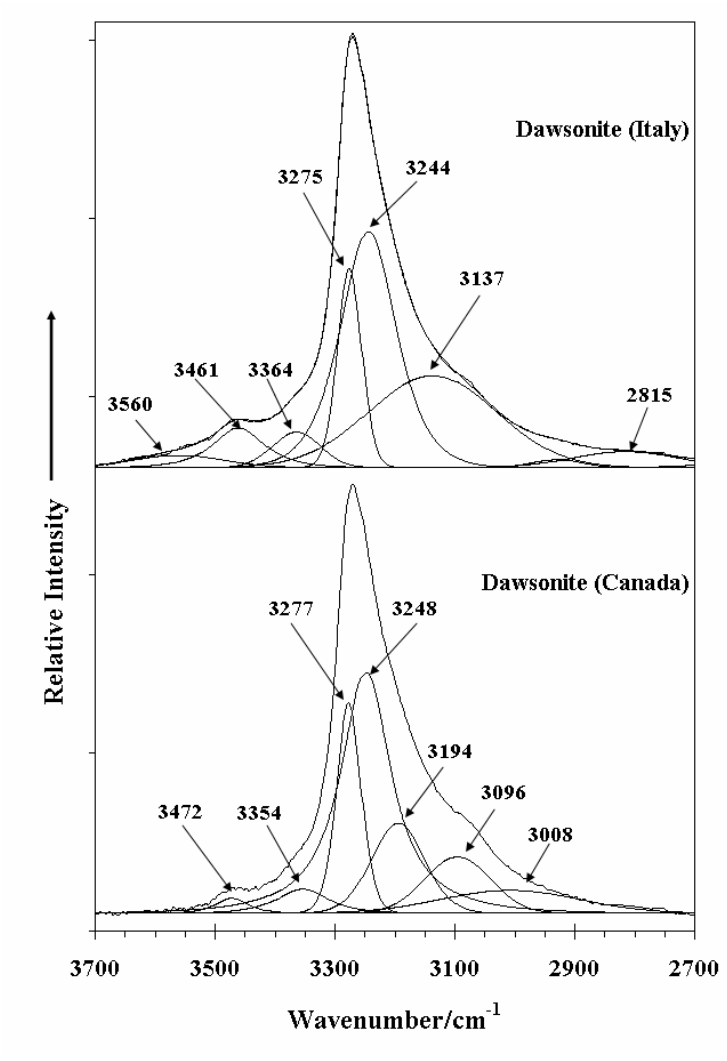


Figure 6b


Dawsonite (Italy)
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3244
3137
3461
3364
3560
2815
Dawsonite (Canada)
3277
3248
3194
3096
3472
3354
3008
Relative Intensity
3700
3500
3300
3100
2900
2700
Wavenumber/cm-1

Figure 7