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Raman spectroscopy of newberyite $Mg(PO_3OH)\cdot 3H_2O$ – a cave mineral

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Abstract

Newberyite $Mg(PO_3OH)\cdot 3H_2O$ is a mineral found in caves such as from Moorba cave, Jurien Bay, Western Australia, the Skipton Lava tubes (SW of Ballarat, Victoria, Australia) and in the Petrogale Cave (Madura , Eucla, Western Australia). Because these minerals contain oxyanions, hydroxyl units and water, the minerals lend themselves to spectroscopic analysis. Raman spectroscopy can investigate the complex paragenetic relationships existing between a number of 'cave' minerals.

The intense sharp band at 982 cm^{-1} is assigned to the PO_4^{3-} ν_1 symmetric stretching mode. Low intensity Raman bands at 1152, 1263 and 1277 cm^{-1} are assigned to the PO_4^{3-} ν_3 antisymmetric stretching vibrations. Raman bands at 497 and 552 cm^{-1} are attributed to the PO_4^{3-} ν_4 bending modes. An intense Raman band for newberyite at 398 cm^{-1} with a shoulder band at 413 cm^{-1} is assigned to the PO_4^{3-} ν_2 bending modes. The values for the OH stretching vibrations provide hydrogen bond distances of 2.728Å (3267 cm^{-1}), 2.781Å (3374cm^{-1}), 2.868Å (3479 cm^{-1}), and 2.918Å (3515 cm^{-1}). Such hydrogen bond distances are typical of secondary minerals. Estimates of the hydrogen-bond distances have been made from the position of the OH stretching vibrations and show a wide range in both strong and weak bonds.

Keywords: newberyite, Raman spectroscopy, cave mineral, struvite, hannayite, stercorite, mundrabillaite

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Introduction

Newberyite $Mg(PO_3OH)\cdot 3H_2O$ is a mineral found in Australian caves such as the Skipton Lava tubes and in the Petrogale Cave. A comprehensive study of cave minerals has been published [1]. Many minerals are found in caves world-wide [2-4]. Newberyite has been found in many sites [5-9]. Newberyite is a hydrated magnesium hydrogen phosphate and is related to many cave minerals such as dittmarite $(NH_4,Mg)PO_4\cdot H_2O$, niahite $(NH_4)(Mn^{2+},Mg,Ca)PO_4\cdot H_2O$, hannayite $(NH_4)_2Mg_3(PO_3OH)_4\cdot 8H_2O$, schertelite $(NH_4)_2Mg(HPO_4)_2\cdot 4H_2O$, stercorite $(NH_4)Na(HPO_4)\cdot 4H_2O$, swaknoite $(NH_4)_2Ca(HPO_4)_2\cdot H_2O$, and mundrabillaite $(NH_4)_2Ca(HPO_4)\cdot 2H_2O$. Many of these minerals are in diagenetic relationships. Newberyite can be formed from struvite $NH_4Mg(PO_4)\cdot 3H_2O$. Many of these cave minerals are the result of formation from bat guano [5, 10-13]. Interest in newberyite formation has also arisen due to its in urinary tracts and kidneys [14-19]. Indeed the discovery of newberyite has been found in very old and large calculi [20]. The authors' interest in this cave mineral and other cave minerals rests with the diagenetic relationships between this mineral and other cave minerals.

The amount of published data on the Raman spectra of 'cave' mineral phosphates is limited [21-25]. A comparison of the molecular structure of newberyite, hannayite and struvite has been published [26]. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1}, the antisymmetric stretching mode (ν_3) at 1017 cm^{-1}, the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} [23, 24, 27]. S.D. Ross in Farmer (1974) (page 404) listed some well-known minerals containing phosphate, which were either hydrated or hydroxylated or both [28]. The value for the ν_1 symmetric stretching vibration of PO_4 units as determined by infrared spectroscopy was given as 930 cm^{-1} (augelite), 940 cm^{-1} (wavellite), 970 cm^{-1} (rockbridgeite), 995 cm^{-1} (dufrenite) and 965 cm^{-1} (beraunite). The position of the symmetric stretching vibration is mineral dependent and a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the PO_4 units. Some studies have been undertaken on $MgHPO_4.3H_2O$ [29, 30]. It is not known whether a mineral was studied or whether a synthetic chemical was used. Infrared bands were found at 1162, 1057 and 1017 cm^{-1} and were assigned to the ν_3

antisymmetric stretching modes. Some more recent studies of newberyite have been undertaken [31, 32].

The value for the ν_2 symmetric bending vibration of PO_4 units as determined by infrared spectroscopy was given as 438 cm^{-1} (augelite), 452 cm^{-1} (wavellite), 440 and 415 cm^{-1} (rockbridgeite), 455, 435 and 415 cm^{-1} (dufrenite) and 470 and 450 cm^{-1} (beraunite). The observation of multiple bending modes provides an indication of symmetry reduction of the PO_4 units. This symmetry reduction is also observed through the ν_3 antisymmetric stretching vibrations. Augelite shows infrared bands at 1205, 1155, 1079 and 1015 cm^{-1}; wavellite at 1145, 1102, 1062 and 1025 cm^{-1}; rockbridgeite at 1145, 1060 and 1030 cm^{-1}; dufrenite at 1135, 1070 and 1032 cm^{-1}; beraunite at 1150, 1100, 1076 and 1035 cm^{-1}. Some Raman spectra of these minerals have been published [31, 33]. Studies of synthetic newberyite showed bands at 398 cm^{-1} assigned to the ν_2 bending mode and at 554 and 509 cm^{-1} corresponding to the ν_4 bending modes [30, 34].

Raman spectroscopy has proven most useful for the study of mineral structures. The detailed comparative Raman spectra of the cave mineral newberyite have not been published. The objective of this research is to report the Raman and infrared spectra of newberyite and to relate the spectra to the mineral structure.

Experimental

Minerals

The mineral newberyite was supplied by The Australian Museum and originated from Moorba cave, Jurien Bay, Western Australia. A sample of newberyite was also obtained from Skipton Lava Tubes, Victoria, Australia (D41293). Details of the mineral have been published (page 408) [35].

Raman spectroscopy

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

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

Infrared 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 128 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 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

Sutor [36] studied the crystal structure of newberyite and determined the bond distances. The PO bond distances are 1.545, 1.542, 1.500 Å with most OPO angles showing considerable deviation from the tetrahedral value. In the phosphate group the P-OH bond distance is 1.588 Å. This distortion probably results from the participation of 3 phosphate O atoms in the octahedral coordination of Mg atoms. The Mg-O distances fall into 2 groups depending on whether the O belongs to a H_2O molecule or a phosphate group.

The Raman spectrum and infrared spectrum over the full wavenumber range is given in supplementary information as Figure S1. The Raman spectrum of newberyite over the 850 to 1350 cm^{-1} range and the infrared spectrum over the 900 to 1300 cm^{-1} range are reported in Figures 1a and 1b respectively. Raman bands are observed at 893, 982, 1152, 1263 and 1277 cm^{-1}. The intense sharp band at 982 cm^{-1} is assigned to the PO_4^{3-} ν_1 symmetric stretching mode. The position of the band compares well with many phosphate minerals. This band is

observed in the infrared spectrum at 1018 cm^{-1}. The band at 893 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the HPO_4^{2-} units. The position of this band is lower than that of the PO_4^{3-} stretching band and based upon the results of Sutor [36] is expected. The O-P bond distance is longer and therefore the band position is at lower wavenumbers. Low intensity Raman bands are found at 1152, 1263 and 1277 cm^{-1} and are assigned to the PO_4^{3-} ν_3 antisymmetric stretching vibrations. These vibrational modes are of low intensity in the Raman spectrum but show intensity in the infrared spectrum. Infrared bands assigned to these vibrational modes are recorded at 1055, 1163 and 1235 cm^{-1}. In the Raman spectrum of newberyite downloaded from the RRUFF database (Figure S2) Raman bands are observed at 893, 983, 1053, 1152 and 1171 cm^{-1}. The position of these bands fits well with the position of the Raman bands reported in this work. The Raman data is in agreement with published infrared data for synthetic $MgHPO_4 \cdot 3H_2O$ where IR bands were found at 1162, 1057 and 1017 cm^{-1}.

The Raman spectrum of newberyite over the 50 to 650 cm^{-1} range and the infrared spectrum over the 550 to 950 cm^{-1} range are reported in Figures 2a and 2b respectively. Raman bands are found at 497 and 552 cm^{-1}. These bands are attributed to the PO_4^{3-} ν_4 bending modes. Published Raman spectra of newberyite gave the two bands at 554 and 509 cm^{-1} as the ν_4 bending modes [30, 34]. Therefore, the observed bands in this investigation are in good agreement with those of Miller and Lehr. The Raman spectrum of newberyite (Figure S3) from the RRUFF data base shows a complex set of overlapping bands at 501, 519 and 534cm^{-1}. In the infrared spectrum bands are observed at 592, 604, 680, 728, and 882 cm^{-1}. In the infrared spectrum, a broad band is observed at 531cm^{-1}, which may be the corresponding infrared band. The observation of multiple ν_4 bending modes is a strong indication of the reduction of symmetry of the HPO_4 anion. An intense Raman band for newberyite is observed at 398 cm^{-1} with a shoulder band at 413 cm^{-1} and is assigned to the PO_4^{3-} ν_2 bending modes. In the RRUFF Raman spectrum bands were observed at 398 and 419 cm^{-1}.

In the infrared spectrum a series of overlapping broad bands are observed at 648, 680, 728 and 760 cm^{-1}. These bands are attributed to water librational modes. The Raman spectrum in the 1500 to 1800 cm^{-1} region (Figure 3a) shows low intensity bands at 1645 and 1660 cm^{-1}. These bands are assigned to water bending modes. The position of the band provides evidence for the water to be strongly hydrogen bonded to the phosphate anions in the newberyite structure. The observation of multiple bands shows that the water molecules are not equivalent in the newberyite structure. Such a concept was inferred from the X-ray

crystallographic study by Sutor [36]. This non-equivalence of the water molecules in the newberyite structure is supported by the infrared spectrum (Figure 3b) where intense infrared bands are observed at 1648 and 1699 cm^{-1}.

The Raman spectrum of newberyite and the infrared spectrum in the 3000 to 3700 cm^{-1} region are displayed in Figures 4a and 4b. Raman bands are observed at 3267, 3374, 3479 and 3515 cm^{-1}. The reason for the multiple bands depends upon the different hydrogen bond distances between the water molecules and the adjacent O of the phosphate or hydrogen phosphate units. The infrared spectrum of newberyite displays bands at 3264, 3373, 3477 and 3513 cm^{-1}. The position of the infrared bands is almost identical with the position of the Raman bands.

Studies have shown a strong correlation between OH stretching wavenumbers and both O···O bond distances and H···O hydrogen bond distances [37-40]. 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 [41]. 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 2.728Å (3267 cm^{-1}), 2.781Å (3374cm^{-1}), 2.868Å (3479 cm^{-1}), and 2.918Å (3515 cm^{-1}). Such hydrogen bond distances are typical of secondary minerals. 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 mineral newberyite may be termed a 'cave' mineral as it is found in many caves. These minerals are formed as deposits on cave walls by the reaction of simple carbonates with bat guano. Newberyite is formed through the chemical reaction of phosphoric acid from bat guano and magnesium ions. It is likely the magnesium comes from the corrosion of basalt.

Newberyite has been analysed by Raman spectroscopy and band assignments and hydrogen bond distances have been determined. The mineral newberyite contains hydrogen phosphate units (HPO_4^{2-}) as opposed to phosphate (PO_4^{3-}) anions as is found in the 'cave' mineral struvite. The HPO_4 and PO_4 units are characterised by intense sharp bands at 980 cm^{-1} and 942 cm^{-1}. Characteristic POH stretching bands are observed at 3382 and 3350 cm^{-1}. Such

bands are absent in the Raman spectrum of struvite. Estimates of the hydrogen-bond distances have been made from the position of the OH stretching vibrations and show a wide range in both strong and weak bonds. Raman bands at 497 and 552 cm^{-1} are attributed to the PO_4^{3-} ν_4 bending modes. Intense Raman band for newberyite at 398 cm^{-1} with a shoulder band at 413 cm^{-1} is assigned to the PO_4^{3-} ν_2 bending modes.

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Figure 4b Infrared spectrum of newberyite in the 3000 to 3700 cm^{-1} region.

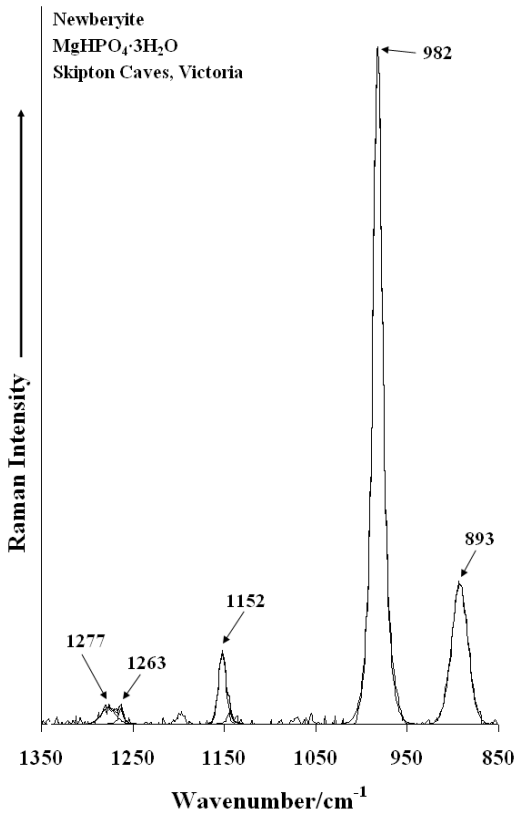
Supplementary Information Figure legends

Figure S1a Raman spectrum of newberyite over the 100 to 4000 cm^{-1} range

Figure S1b Infrared spectrum of newberyite over the 500 to 4000 cm^{-1} range

Figure S2 Raman spectrum of newberyite in the 850 to 1250 cm^{-1} range. The data was extracted from the RRUFF data base

Figure S3 Raman spectrum of newberyite in the 350 to 600 cm^{-1} range. The data was extracted from the RRUFF data base



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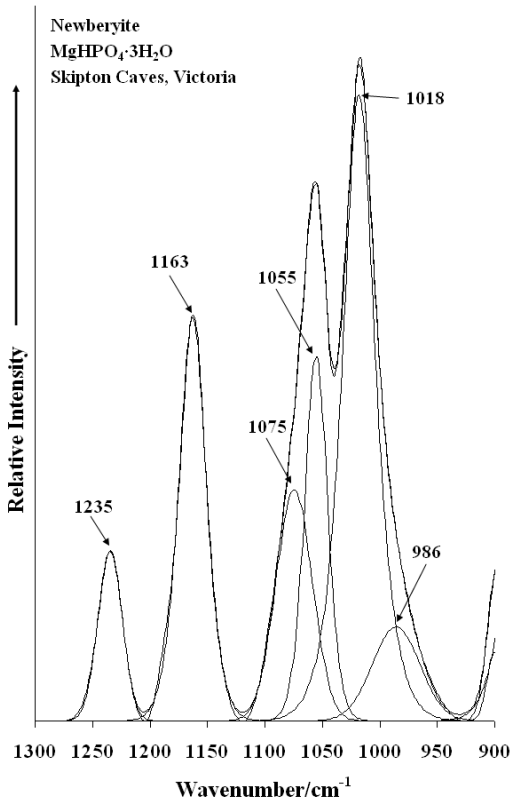

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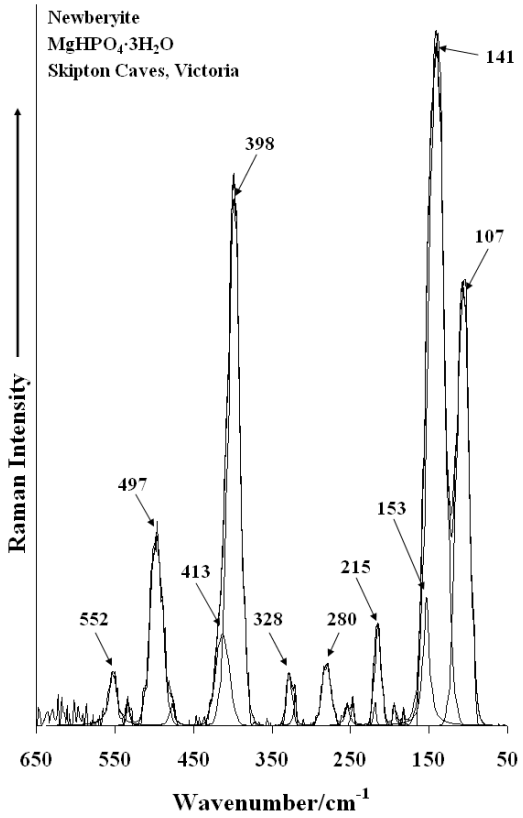

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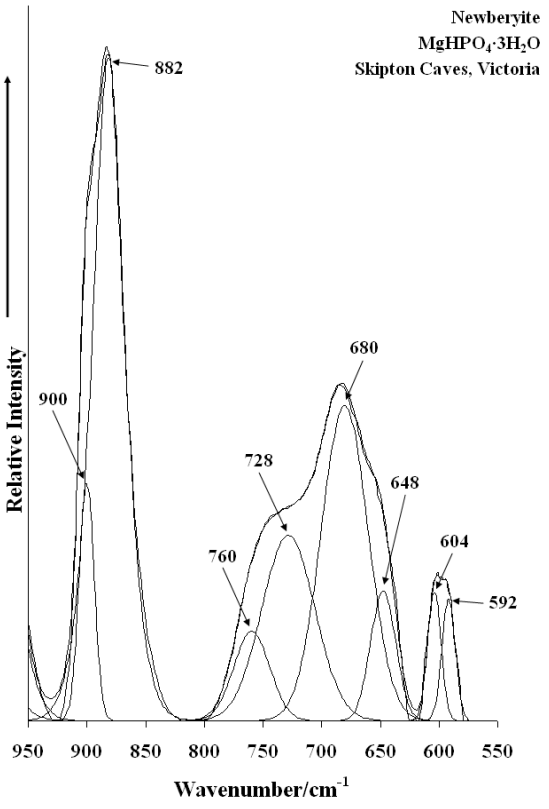

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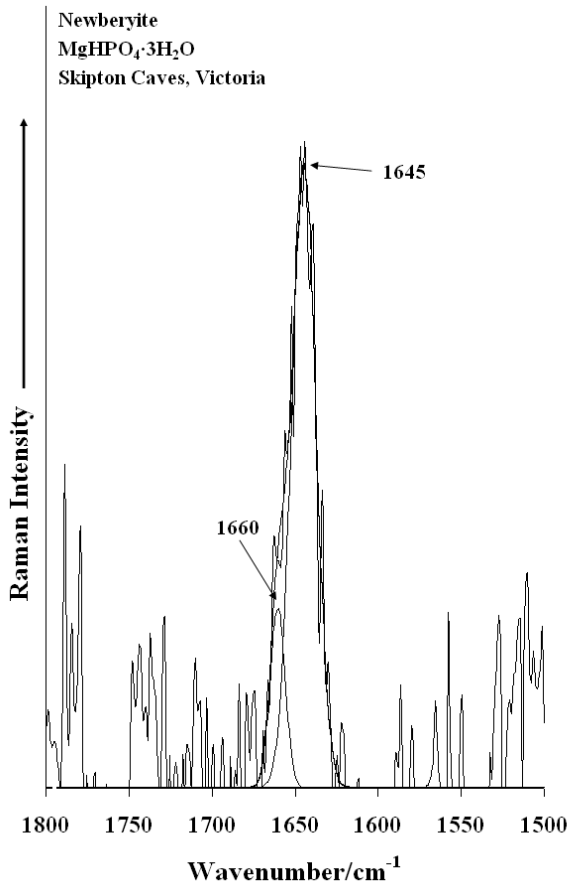

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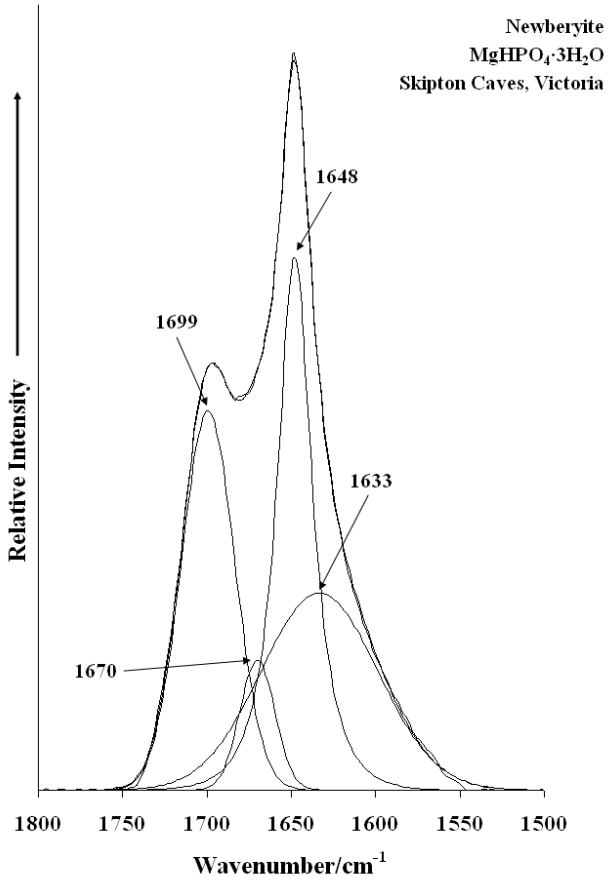

Figure 3b

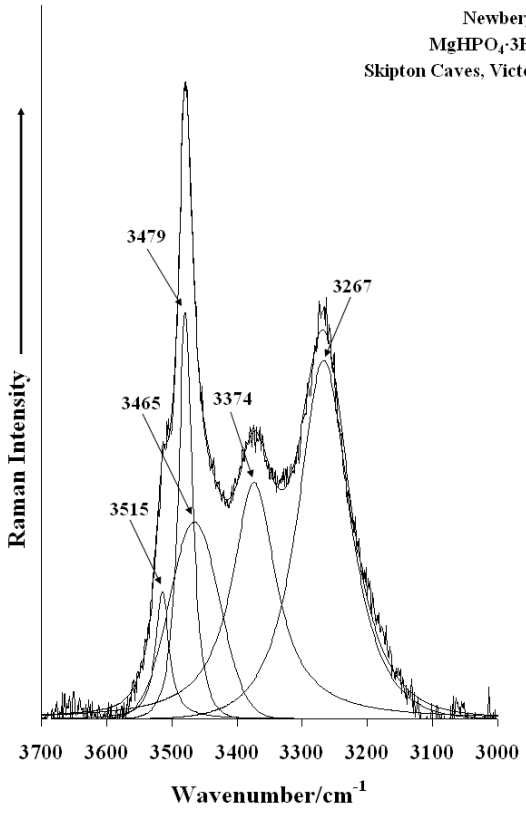

Figure 4a

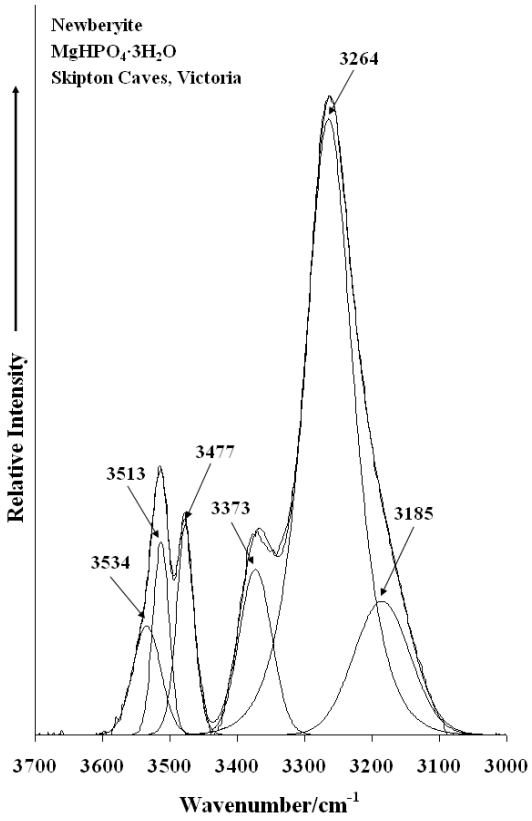

Figure 4b