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Identification of montgomeryite mineral [$Ca_4MgAl_4(PO_4)_6.(OH)_4{\cdot}12H_2O$] found in the Jenolan Caves - Australia

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Abstract

In this paper, we report on many phosphate containing natural minerals found in the Jenolan Caves - Australia. Such minerals are formed by the reaction of bat guano and clays from the caves. Among these cave minerals is the montgomeryite mineral [$Ca_4MgAl_4(PO_4)_6.(OH)_4.12H_2O$]. The presence of montgomeryite in deposits of the Jenolan Caves - Australia has been identified by X-ray diffraction (XRD). Raman spectroscopy complimented with infrared spectroscopy has been used to characterize the crystal structure of montgomeryite. The Raman spectrum of a standard montgomeryite mineral is identical to that of the Jenolan Caves sample. Bands are assigned to $H_2PO_4^-$, OH and NH stretching vibrations. By using a combination of XRD and Raman spectroscopy, the existence of montgomeryite in the Jenolan Caves - Australia has been proven. A mechanism for the formation of montgomeryite is proposed.

Keywords: Montgomeryite, XRD, Raman spectroscopy, cave minerals, phosphates, Jenolan Cave.

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1. Introduction

Many minerals may be formed in caves [1]. The reaction of the chemical reagents contained in bat guano (or even bird guano) with calcite and clays results in the formation of many phosphate containing minerals and diagenetic relationships are formed between these minerals. Among the many phosphate minerals formed are montgomeryite and taranakite. Other phosphate minerals found in cave systems include archerite [$K,NH_4)(H_2PO_4$], mundrabillaite [$NH_4)_2Ca(HPO_4)_2\cdot H_2O$], stercorite [$H(NH_4)Na(PO_4)\cdot 4H_2O$], whitlockite [$Ca_9Mg(PO_4)_6(HPO_4)$], newberyite [$Mg(HPO_4)\cdot 3H_2O$]. These minerals occur on stalactites and form on wall and floor crusts. Moreover, these minerals are formed through the chemical reactions of calcite with bat guano, or with chemicals from bat guano that are water soluble and crystallise out on the calcite surfaces. It is obvious that the formation of these minerals will be very much a function of pH, temperature and concentration of the ions [2, 3]. Montgomeryite is known from many caves worldwide [4-8]. It is known in other caves in Australia for example in the Parwan Lava Cave, 5 km south-east of Bacchus Marsh, Victoria, Australia.

Moore and Araki [9] reported the crystal structure of montgomeryite. It is monoclinic with space group (C2/c), (a = 10.023(1), b = 24.121(3), c = 6.243(1) Å), β 91.55(1)°, clusters per unit cell Z = 2). The structure consists of chains of corner-linked octahedral (AlO_6) clusters which are topological and geometrically equivalent to the chains in vauxite, $Fe^{2+}{}_2(H_2O)_4[Al_4(OH)_4(H_2O)_4(PO_4)_4]\cdot 4H_2O$. According to Moore and Araki [9] the (AlO_6) octahedra are linked by the (OH)-ligands and are alternatively in cis- and trans- configurations. The octahedral (AlO_6) clusters octahedral chain and associated tetrahedral (PO_4) clusters can be written as $[Al_4(OH)_4(PO_4)_6]^{10-}$; for vauxite, it is $[Al_4(OH)_4(H_2O)_4(PO_4)_4]^{4-}$. These units are proposed to be underlying features of the 2 structures with the more weakly bonded cations intercalated in the remaining spaces. In montgomeryite, the (PO_4) tetrahedra bridge to equivalent chains along the *c*-axis, forming slabs parallel to {010}, which is the direction of perfect cleavage. The Mg atoms are disordered and occupy only half of its available sites.

Indeed, Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with minerals containing phosphate groups as may be found in cave systems. The Raman spectroscopy is considered a powerful tool in order to estimate the degree of structural order–disorder at short-range of the materials [10]. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. Therefore, in this work we attribute bands at various wavenumbers to vibrational modes of montgomeryite using Raman spectroscopy and relate the spectra to the structure of the mineral.

2. Experimental

2.1 Minerals

The sample of montgomeryite (D58073) was sourced from The Australian Museum and originated from the Katies Bower, Chifley Cave, Jenolan Caves, New South Wales, Australia. The mineral has been analysed and the data published [11]. A standard reference sample of montgomeryite was supplied by The Australian Museum. The type mineral originated from Middleback Range, Iron Knob, Iron Monarch mine, South Australia

2.2 X-ray diffraction

The cave mineral montgomeryite was powdered and X-ray diffraction patterns were collected using a Philips X'pert wide angle X-Ray diffractometer, with Cu Kα radiation (1.54052 Å).

2.3 Raman spectroscopy

Crystals of montgomeryite 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.

2.4 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.

3. Results and discussion

3.1 X-ray diffraction

The X-ray diffraction patterns of the Jenolan Caves montgomeryite sample together with the standard reference patterns of montgomeryite and variscite are illustrated in Figure 1. Clearly the sample contains montgomeryite as the principal phase and with a minor phase of variscite. The formula of montgomeryite is given as Ca4MgAl4$(PO_4)_6(OH)_4 \cdot 12(H_2O)$. The structure as reported by clearly indicates that the mineral contains hydrogen phosphate units. The mineral also may contain Na as a substitution for the Ca^{2+} anion. Some substitution of Al^{3+} by Fe^{3+} may also occur [12].

3.2 Background to the spectroscopy

In aqueous systems, the Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1}, an antisymmetric stretching mode (ν_3) at 1017 cm^{-1}, a symmetric bending mode (ν_2) at 420 cm^{-1} and a ν_4 bending mode at 567 cm^{-1} [13-15]. S.D. Ross in Farmer listed some well-known minerals containing phosphate which were either hydrated or hydroxylated or both [16]. The vibrational spectrum of the dihydrogen phosphate anion has been reported by Farmer [16]. The PO_2 symmetric stretching mode occurs at 1072 cm^{-1} and the POH symmetric stretching mode at ~878 cm^{-1}. The POH antisymmetric stretching mode was found at 947 cm^{-1} and the $P(OH)_2$ bending mode at 380 cm^{-1}. The band at 1150 cm^{-1} was assigned to the PO_2 antisymmetric stretching mode. The position of these bands will shift according to the crystal structure of the mineral.

The vibrational spectra of phosphate minerals have been published by Farmer's treatise Chapter 17 [16]. The Table 17.III in ref. [11] reports the band positions of a wide range of phosphates and arsenates. The band positions for the monohydrogen phosphate anion of disodium hydrogen phosphate dihydrate is given as ν_1 at 820 and 866 cm^{-1}, ν_2 at around 460 cm^{-1}, ν_3 as 953, 993, 1055, 1070, 1120 and 1135 cm^{-1}, ν_4 at 520, 539, 558, 575 cm^{-1}. The POH unit has vibrations associated with the OH specie. The stretching vibration of the POH units was tabulated as 2430 and 2870 cm^{-1}, and bending modes at 766 and 1256 cm^{-1}. Water stretching vibrations were found at 3050 and 3350 cm^{-1}. The position of the bands for the disodium hydrogen phosphate is very dependent on the waters of hydration. There have been several Raman spectroscopic studies of the monosodium dihydrogen phosphate chemicals [17-21].

3.3 Raman Spectroscopic analyses

The Raman spectrum of montgomeryite from the Jenolan Caves in the 100 to 1200 cm^{-1} region is shown in Figure 2a and its infrared spectrum in the 500 to 1300 cm^{-1} range is shown in Figure 2b. The Raman spectrum of a sample of montgomeryite is illustrated in Figure 3. The Raman spectrum of montgomeryite is dominated by two intense sharp bands at 981 and 1012 cm^{-1}. The positions of these bands in the reference spectrum are 979 and 1011 cm^{-1}. The higher wavenumber band at 1012 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the PO_4^{3-} anions. The band at 981 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the $HOPO_3^{2-}$ units. According to the XRD patterns, units of $[Al_4(OH)_4(PO_4)_6]^{10-}$ form the basis of the structure of montgomeryite. According to Moore and Araki [9], there are no hydrogen phosphate units. However, Raman spectroscopy clearly shows a band attribute to hydrogen phosphate units. The two Raman peaks of the Jenolan caves sample at 1091 and 1151 cm^{-1} are attributed to ν_3 antisymmetric stretching mode of the PO_4^{3-} anions. The Raman bands in the reference sample are observed at 1088 and 1143 cm^{-1}. The infrared spectral profile of the Jenolan Caves sample shows complexity with a series of overlapping bands. The two infrared bands at 974 and 1000 cm^{-1} in harmony with the Raman spectrum, are assigned to the ν_1 symmetric stretching modes of the $HOPO_3^{2-}$ and PO_4^{3-} anions. The infrared bands at 1024, 1057, 1112 and 1186 cm^{-1} are attributed to the ν_3 antisymmetric stretching modes of the $HOPO_3^{2-}$ and PO_4^{3-} units. The Raman spectrum of the Jenolan Caves sample is identical to the standard montgomeryite reference sample. This is conclusive evidence for the existence of montgomeryite in the Jenolan caves.

The Raman spectrum of montgomeryite in the 300 to 700 cm^{-1} is reported in Figure 2a. This spectral region is where the PO_4^{3-} and $HOPO_3^{2-}$ bending vibrations are found. A series of bands are observed at 590, 608 and 636 cm^{-1}. These bands are attributed to the ν_4 out of plane bending modes of the PO_4 and H_2PO_4 units. The Raman spectrum of crystalline NaH_2PO_4 shows Raman bands at 526, 546 and 618 cm^{-1} (this work). The montgomeryite reference sample shows bands at 591, 609 and 655 cm^{-1}. A series of Raman bands for the Jenolan Caves sample are observed at 391, 459, 477 and 513 cm^{-1}. These bands are attributed to the ν_2 PO_4 and H_2PO_4 bending modes. The Raman spectrum of NaH_2PO_4 shows Raman bands at 460 and 482 cm^{-1}. The montgomeryite reference sample shows bands at 391, 457, 475 and 511 cm^{-1}. The Raman spectrum of the Jenolan Caves sample is identical to the standard montgomeryite reference sample, thus proving that montgomeryite exists in the Jenolan Caves. Low intensity Raman bands are found at 160, 200, 239, 269, 297 and 315 cm^{-1}. These bands are simply described as lattice modes.

The infrared spectrum of montgomeryite in the OH stretching region is illustrated in Figure 4. A complex set of overlapping bands are observed. Bands are resolved at 2739, 2884, 3049, 3245, 3369 and 3494 cm^{-1}. These bands are assigned to water stretching vibrations. The infrared spectrum of the Jenolan caves sample shows an intense water bending vibration at 1641 cm^{-1} (Figure 4b). The Raman spectrum displays the water bending mode at 1606 cm^{-1} (Figure 4a). Other Raman bands are observed at 1214, 1260, 1286 and 1339 cm^{-1} and also at 1667 and 1709 cm^{-1}. The strong Raman band at 1260 cm^{-1} is attributed to POH bending modes. The shoulder bands at 1286 and 1339 cm^{-1} may be also assigned to this vibrational mode. The vibrational spectra of phosphate minerals has been published by Farmer's treatise Chapter 17 [16]. The stretching vibration of the POH units was tabulated as 2430 and 2870 cm^{-1}, and bending modes at 766 and 1256 cm^{-1}. A series of bands of low intensity are shown in Figure 5. Some bands are observed at 2330, 2365 cm^{-1} with shoulder bands at 2341 and 2357 cm^{-1}. It is possible that these bands are due to the POH stretching vibration.

3.4 Mechanism for the formation of montgomeryite $Ca_4MgAl_4(PO_4)_6(OH)_4\cdot 12(H_2O)$

The occurrence of montgomeryite in caves in other caves is well known [6, 22, 23]. Bat guano provides a source of phosphate anions, both phosphate and hydrogen phosphate anions. Palaeolithic bones also provide the base materials for the formation of phosphate minerals [24]. Montgomeryite is formed on the calcite surfaces and the calcite provides a source of Ca^{2+} ions. The Al^{3+} ions come from clays in the floors of the caves. Research has shown using dating of the clays in the caves that the caves are very old probably more than 450 million years old. These cave clays are used for the dating of the cave system. The Al^{3+} ions are released through the action of the phosphoric acids on the clays. The montgomeryite is formed from the reaction of the ions in solution. The following reaction is proposed for the formation of montgomeryite:

$$4Ca^{2+} + Mg^{2+} + 4Al^{3+}(OH)_3 + 6H_3PO_4 + + 4H_2O \rightarrow [Ca_4MgAl_4(PO_4)_6.(OH)_4.12H_2O] + 10H^+$$

An important concept is pH compatibility as well as the being stoichiometrically correct. One of the important considerations for the nucleation and crystallisation of montgomeryite is the temperature and humidity within the Jenolan Caves. The temperatures within the caves are quite low and vary only by a small amount throughout the year. Temperature sensing determines the temperature to vary from 12.8 to 15.6°C. The higher temperatures are only achieved near the cave entrances. The humidity within the caves is high and never goes below 75% relative humidity and the air is often saturated.

4. CONCLUSIONS

In summary, we have found that the chemicals found in bat guano, a range of phosphate bearing minerals including montgomeryite, brushite, archerite, and taranakite may be formed. The presence of montgomeryite in the Jenolan Caves – Australia has been identified through the use of XRD patterns and vibrational Raman/infrared spectroscopic techniques. Bands attributed to PO_4 and HPO_4 groups were identified.

Acknowledgements

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Figure 2a Raman spectra of the Jenolan Caves montgomeryite over the 100 to 1200 cm^{-1} range and (b) the infrared spectrum over the 500 to 1300 cm^{-1} range.

Figure 3 Raman spectra of a standard montgomeryite over the 100 to 1200 cm^{-1} range

Figure 4 Infrared spectra of the Jenolan Caves montgomeryite over the 2500 to 3700 cm^{-1} range

Figure 5 Raman spectra of (a) the Jenolan Caves montgomeryite over the 1190 to 1790 cm-1 range and (b) infrared spectrum of the Jenolan Caves montgomeryite over the 1350 to 2000 cm^{-1} range

Figure 6 Infrared spectra of the Jenolan Caves montgomeryite over the 2000 to 2500 cm^{-1} range

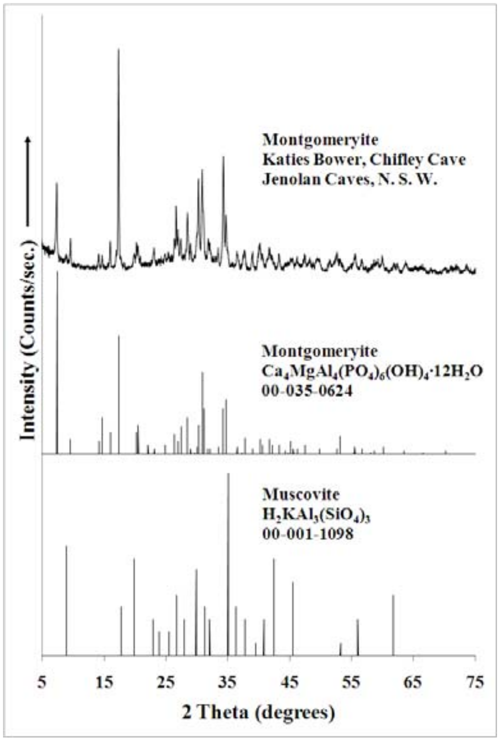
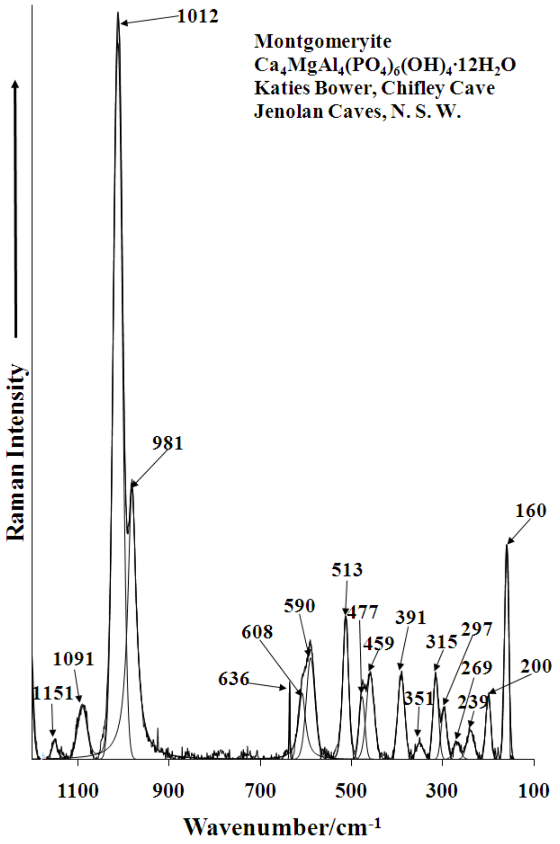

Montgomeryite
Katies Bower, Chifley Cave
Jenolan Caves, N. S. W.
Montgomeryite
$Ca_4MgAl_4(PO_4)_6(OH)_4 \cdot 12H_2O$
00-035-0624
Muscovite
$H_2KAl_3(SiO_4)_3$
00-001-1098
Intensity (Counts/sec.)
5
15
25
35
45
55
65
75
2 Theta (degrees)

Figure 1



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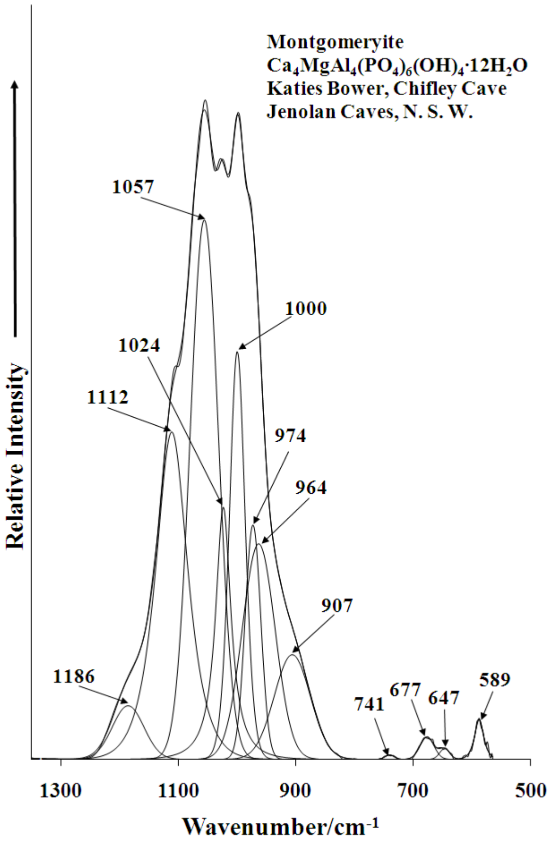

Figure 2b

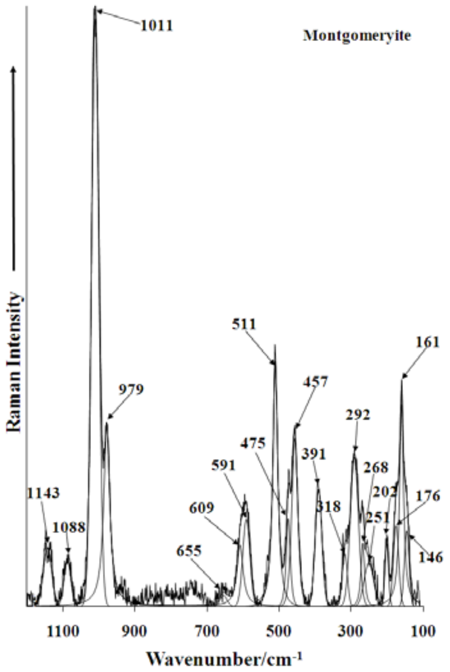
Montgomeryite
Raman Intensity
1011
979
1143
1088
655
609
591
511
475
457
391
318
292
268
251
202
176
161
146
1100
900
700
500
300
100
Wavenumber/cm⁻¹

Figure 3

331

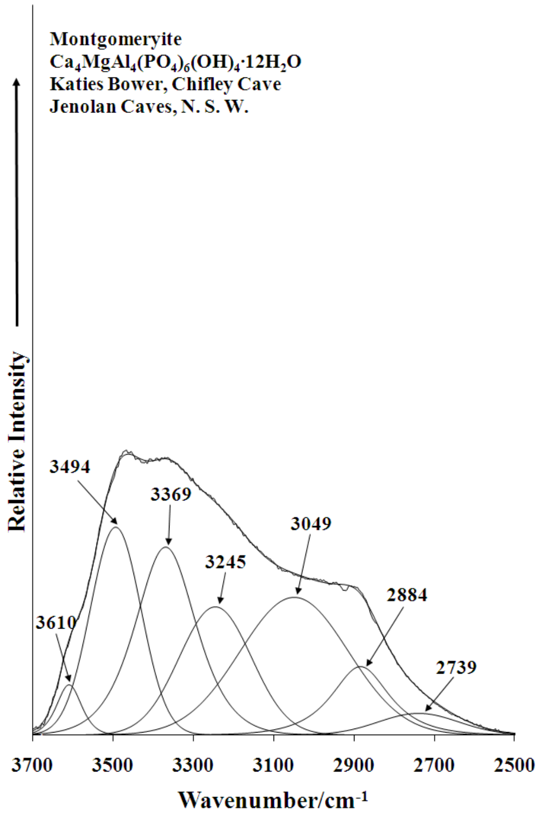

Figure 4

332

333

334

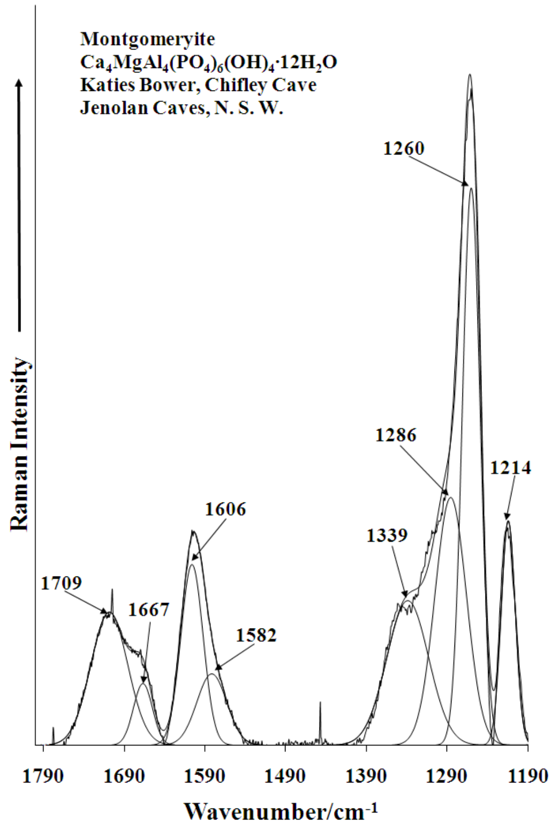

Figure 5a

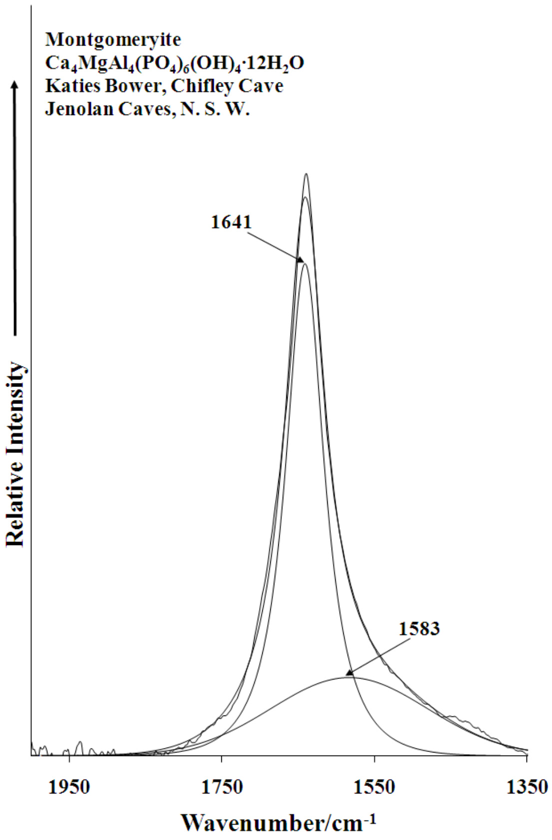

Figure 5b

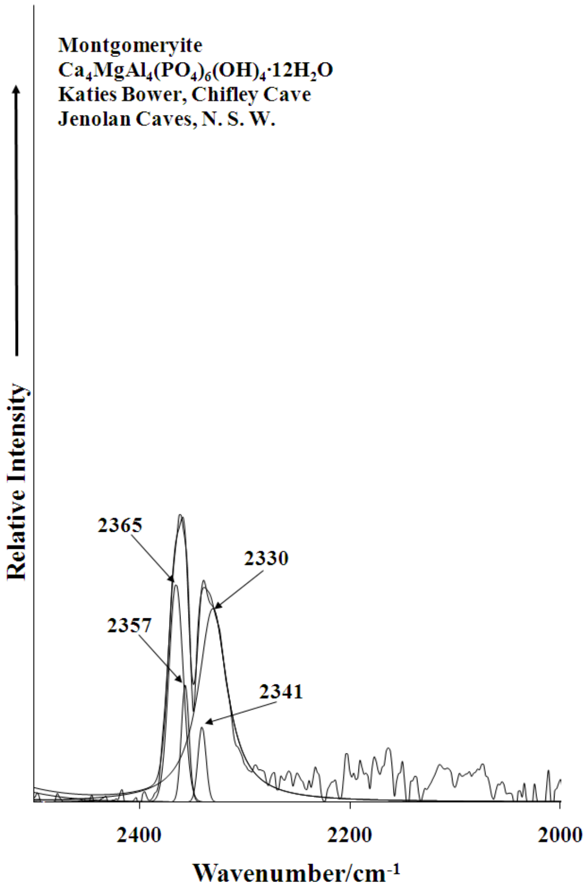
Montgomeryite
Ca4MgAl4(PO4)6(OH)4·12H2O
Katies Bower, Chifley Cave
Jenolan Caves, N. S. W.
Relative Intensity
2365
2330
2357
2341
2400
2200
2000
Wavenumber/cm-1

Figure 6