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Are the 'cave' minerals archerite $(K,NH_4)H_2PO_4$ and biphosphammite $(K,NH_4)H_2PO_4$ Identical? – A molecular structural study

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Abstract

The molecular structure of the mineral archerite $((K,NH_4)H_2PO_4)$ has been determined and compared with that of biphosphammite $((NH_4,K)H_2PO_4)$. Raman spectroscopy and infrared spectroscopy has been used to characterise these 'cave' minerals. Both minerals originated from the Murra-el-elevyn Cave, Eucla, Western Australia. The mineral is formed by the reaction of the chemicals in bat guano with calcite substrates. Raman and infrared bands are assigned to $H_2PO_4^-$, OH and NH stretching vibrations. The Raman band at 981 cm^{-1} is assigned to the HOP stretching vibration. Bands in the 1200 to 1800 cm^{-1} region are associated with NH_4^+ bending modes. The molecular structure of the two minerals appear to be very similar, and it is therefore concluded that the two minerals are identical.

Keywords: archerite, biphosphammite, 'cave' minerals, brushite, mundrabillaite, dihydrogen phosphate, Raman spectroscopy.

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INTRODUCTION

The minerals archerite and biphosphammite originated from the Murra-el-elevyn Cave, Eucla, Western Australia. Archerite $(K,NH_4)(H_2PO_4)$ [1] is commonly found in these cave systems. Another mineral commonly found in these caves is mundrabillaite $(NH_4)_2Ca(HPO_4)2·H_2O$ [2]. Other minerals found in the Murra-el-elevyn Cave and the Petrogale cave include aphthitalite $((K,Na)_3Na(SO_4)_2)$, halite $(NaCl)$, syngenite $((K,Na)_3Na(SO_4)_2)$, stercorite $(H(NH_4)Na(PO_4)·4H_2O)$, oxammite $((NH_4)_2(C_2O_4)·H_2O)$, weddellite $(Ca(C_2O_4)·2H_2O)$, whitlockite $(Ca_9Mg(PO_4)_6(HPO_4))$, guanine $(C_5H_5N_5O)$, newberyite $(Mg(HPO_4)·3H_2O)$ and calcite $(CaCO_3)$. These minerals occur as stalactites and form on wall and floor crusts. 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. The mineral archerite is soluble in cold water and may translocate through the Murra-el-elevyn cave network [3].

Some studies on the growth kinetics of archerite have been undertaken [4]; however these authors state that they are using potassium hydrogen phosphate, but this is not the formula of the mineral archerite. Archerite has the ammonium cation in the structure. An alternative name for the mineral may be biphosphammite [5], a name which is derived from the combination of phosphate and ammonium. Whether archerite and biphosphammite are the same mineral or not is open to question. The crystal structure is close to that of synthetic potassium dihydrogen phosphate [6]. This is not surprising since the size of the potassium and ammonium cations are very close. Some studies of the ferroelectric properties of KH_2PO_4 have been undertaken, which involved structural studies of KH_2PO_4 [7, 8]. Because of the ferroelectric properties of this chemical there have been some detailed Raman spectroscopic studies of KH_2PO_4 [9-15]. Kim and Choi [11] found broad bands for KH_2PO_4 at 1800, 2400 and around 2700 cm^{-1}. These bands were attributed to O…H stretching and bending bands [11]. A detailed study of calcium phosphates including calcium dihydrogen phosphate has been reported [16].

The amount of published data on the vibrational spectroscopy of 'cave' minerals including phosphates is quite limited. Further there is almost no data on the Raman spectroscopy of the phosphate 'cave' minerals. The Raman spectra of the phosphate mineral archerite and

biphosphammite have never been reported. Raman spectroscopy has proven most useful for the study of mineral structures [17-22]. The objective of this research is to report the Raman and infrared spectra of archerite and biphosphammite and to relate the spectra to the molecular structure of the minerals.

EXPERIMENTAL

Mineral

The mineral archerite was supplied by Museum Australia and originated from Murra-el-elevyn Cave, about 200 km east of Balladonia, Western Australia and also from the Petrogale Cave, Madura, Western Australia. Details of the mineral have been published (page 21) [23]. The mineral biphosphammite was obtained privately by one of the authors.

Raman spectroscopy

Crystals of archerite or biphosphammite 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 $\pm$ 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

Background

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} [24-26]. S.D. Ross in Farmer (page 404) listed some well-known minerals containing phosphate which were either hydrated or hydroxylated or both [27]. The vibrational spectrum of the dihydrogen phosphate anion has been reported in Farmer. 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 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 archerite.

Spectroscopy

The spectra may be conveniently divided into subsections as a function of the particular set of vibrations. The Raman spectrum of (a) archerite and (b) biphosphammite in the 900 to 1300 cm^{-1} region are displayed in Figure 1. The spectra of the two minerals in this spectral region are almost identical. In both spectra, Raman bands are observed at 981, 1005, 1139 and 1165 cm^{-1}. The Raman band at 981 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the POH units, whereas the Raman band at 1005 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the PO_4^{3-} units. Galy [28] first studied the polarized Raman spectra of the $H_2PO_4^-$ anion. Choi *et al.* reported the polarization spectra of NaH_2PO_4 crystals. Casciani and Condrate [16] published spectra on brushite and monetite together with synthetic anhydrous monocalcium phosphate ($Ca(H_2PO_4)_2$), monocalcium dihydrogen phosphate hydrate ($Ca(H_2PO_4)_2 \cdot H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$). These authors

determined band assignments for $Ca(H_2PO_4)$ and reported bands at 1002 and 1011 cm^{-1} as POH and PO stretching vibrations, respectively. The two Raman bands at 1139 and 1165 cm^{-1} are attributed to both the HOP and PO antisymmetric stretching vibrations. Casciani and Condrate [16] tabulated Raman bands at 1132 and 1155 cm^{-1} and assigned these bands to P-O symmetric and the P-O antisymmetric stretching vibrations. The first assignment, however, differs from what is stated in this work.

The infrared spectrum of (a) archerite and (b) biphosphammite in the 800 to 1200 cm^{-1} region are displayed in Figure 2. The infrared spectra of the two minerals are very similar. Infrared bands are found at 980 and 1000 cm^{-1} for archerite and at 983 and 1002 cm^{-1} for biphosphammite. These bands are attributed to the HOP and PO symmetric stretching vibrations and are the equivalent of the Raman bands at ~981 and 1005 cm^{-1} (Casciani and Condrate [16]). Infrared bands are observed at 1021, 1060, 1094, 1139 and 1192 cm^{-1} for archerite and at 1025, 1063, 1100, 1140 and 1192 cm^{-1} for biphosphammite. These bands may be attributed to the HOP and PO antisymmetric stretching vibrations. Infrared bands for the mineral dittmarite $(NH_4)MgPO_4 \cdot H_2O$ are found at 978, 1063 and 1105 cm^{-1} (this work). The infrared bands at 830 and 982 cm^{-1} for archerite and at 843, 883 and 909 cm^{-1} are thought to be associated with the POH deformation modes. Choi *et al.* [29] published spectra of NaH_2PO_4; however these authors did not tabulate or mark the position of the peaks. Therefore, it is very difficult to make any comparison of the peak positions of archerite and that of published data by Choi *et al.* Casciani and Condrate [16] reported bands assigned to these vibrational modes for $Ca(H_2PO_4)_2$ at 876 and 901 cm^{-1}.

The Raman spectra of archerite and biphosphammite in the 400 to 700 cm^{-1} region are displayed in Figures 3a and 3b, respectively. A set of Raman bands are found at 620, 637, 643 and 660 cm^{-1} for archerite and at 609, 620, 633, 643 and 662 cm^{-1} for biphosphammite. 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 NaH_2PO_4 shows Raman bands at 526, 546 and 618 cm^{-1}. Raman bands are observed at 429, 441 and 492 cm^{-1} for archerite and at 442, 472 and 493 cm^{-1} for biphosphammite. 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}. In the infrared spectrum of dittmarite $((NH_4)MgPO_4 \cdot H_2O)$ bands are observed at 635 and 656 cm^{-1} and are assigned to the PO_4^{3-} ν_4 bending mode.

The infrared spectra of archerite and biphosphammite in the 500 to 800 cm^{-1} region are displayed in Figures 4a and 4b, respectively. Intense broad infrared bands are observed at 712 and 747 cm^{-1} for archerite and 700, 732 and 751 cm^{-1} for biphosphammite. These bands may be assigned to ammonium librational modes. Two infrared bands are found for NaH_2PO_4 at 700 and 740 cm^{-1}. Infrared bands for archerite are observed at 598, 642 and 657 cm^{-1}, while the infrared spectrum of biphosphammite in this part of the spectrum shows some differences from that of archerite. Biphosphammite infrared bands are observed at 583, 601, 642 and 658 cm^{-1}. These bands are the infrared equivalent of the Raman bands above and are attributed to the ν_4 out of plane bending modes of the PO_4 and H_2PO_4 units. In the infrared spectrum of NaH_2PO_4 a broad band is found at 622 cm^{-1}.

The infrared spectra of archerite and biphosphammite in the 1200 to 1800 cm^{-1} region are reported in Figures 5a and 5b, respectively. The infrared spectra of the two cave minerals are almost identical in this spectral region. Infrared bands are found at 1652 and 1676 cm^{-1} for archerite and at 1644, 1670 and 1698 cm^{-1} for biphosphammite. These bands may be attributed to water bending modes. The position of the bands gives support for the concept of strong hydrogen bonding of the water in the structure of these minerals. Another possibility is that the bands are due to combination bands resulting from the ammonium ion. The ammonium ion is of T_d symmetry and thus displays the non-degenerate ν_1 symmetric stretching mode of A_1 symmetry; the doubly degenerate ν_2 vibration of E symmetry and the triply degenerate ν_3 and ν_4 modes of symmetry species F_2. All modes are both infrared and Raman active.

The bands at 1283, 1409, 1443 and 1546 cm^{-1} for archerite and at 1263, 1293, 1406, 1444 and 1552 cm^{-1} for biphosphammite are assigned to bending modes of the NH_4^+ ion. The bands at around 1406 and 1444 cm^{-1} are assigned to the doubly degenerate ν_2 modes, whereas the bands at around 1283 cm^{-1} are assigned to the ν_4 modes. The observation of so many bands in the ammonium ion bending region indicates that the ammonium ion is strongly distorted in the archerite and biphosphammite structure and probably has a C_s symmetry. In the infrared spectrum of protiated dittmarite $((NH_4)MgPO_4{\cdot}H_2O)$ bands are observed at 1663, 1536, 1482 and 1432 cm^{-1} with a shoulder at 1472 cm^{-1}.

The infrared spectra of archerite and biphosphammite in the 2000 to 2500 cm^{-1} region are shown in Figures 6a and 6b, respectively. Infrared bands are observed at 2099, 2272 and

2387 cm^{-1} for archerite and at 2100, 2276 and 2399 cm^{-1} for biphosphammite. These bands are attributed to the symmetric stretching vibrations of the hydroxyl units of $H_2PO_4^-$ ions. The observation of multiple bands supports the concept of the non-equivalence of ~~the~~ dihydrogen units in the archerite structure. In the infrared spectrum of NaH_2PO_4, bands are found at 2290, 2379, 2682 and 2777 cm^{-1}. Casciani and Condrate [16] reported the infrared bands of $Ca(H_2PO_4) \cdot H_2O$ at 2310, 2400 and 2900 cm^{-1} and assigned these bands to the hydroxyl stretching vibrations of the hydroxyls of the $H_2PO_4^-$ units.

The infrared spectra of archerite and biphosphammite in the 2500 to 3700 cm^{-1} region are shown in Figures 7a and 7b, respectively. Infrared bands are observed at 2674, 2852, 2921, 3070, 3153, 3252, 3308 and 3374 cm^{-1} for archerite, and at 2668, 2851, 2894, 3040, 3095, 3240, 3314 and 3377 cm^{-1} for biphosphammite. The latter three bands are attributed to the OH stretching vibrations of water. The first two bands are associated with the stretching vibrations of POH units of the dihydrogen phosphate anion. The infrared bands at 3070 and 3153 cm^{-1} for archerite and at 3040 and 3095 cm^{-1} for biphosphammite are attributed to NH stretching vibrations.

Mechanism of formation of archerite

In the laboratory, the mineral is readily synthesised by mixing aqueous solutions of potassium hydrogen phosphate K_2HPO_4 and ammonium hydrogen phosphate $(NH_4)_2HPO_4$ [3]. Platford [3] showed that the two chemicals were in congruency with their components. It is likely that low temperatures aid the formation of archerite, which may occur in caves on the Nullarbor Plains in Western Australia. Whether or not simply solubility effects from undersaturated solutions form the mineral archerite is open to question, but it does seem likely. The presence of the calcite surface serves as a surface for the crystallisation of archerite.

CONCLUSIONS

The mineral archerite is an ammoniated hydrogen potassium phosphate and is found in caves in Western Australia, and is especially known from the Petrogale Cave and in the Murra-el-elevyn Cave. A second mineral found in these cave systems is biphosphammite. The question arises as to whether these two minerals are identical or not. The minerals are formed by the reaction of chemicals from bat (or bird) guano on calcite surfaces. The mineral is associated with other phosphate minerals including struvite, stercorite and brushite. According to Platford [3], the mineral is formed from solution. Hence the basic components of the mineral can be translocated through a cave system. Archerite has been found in many caves worldwide.

The individual vibrating units of these minerals lends itself to vibrational spectroscopy. A combination of Raman and infrared spectroscopy has been used to identify vibrational modes associated with the minerals archerite and biphosphammite. Based upon the Raman spectroscopy, the two minerals display identical spectra and so the two minerals are identical. Raman spectroscopy proves the anions in the minerals are the dihydrogen phosphate anion. No observation of phosphate or hydrogen phosphate units were found. The detection of archerite by Raman spectroscopy shows that the mineral can be readily determined; as such the application of a portable Raman spectrometer in a 'cave' situation enables the detection of minerals in cave systems, some of which remain to be identified.

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Figure 1a

Figure 1b

Figure 2a
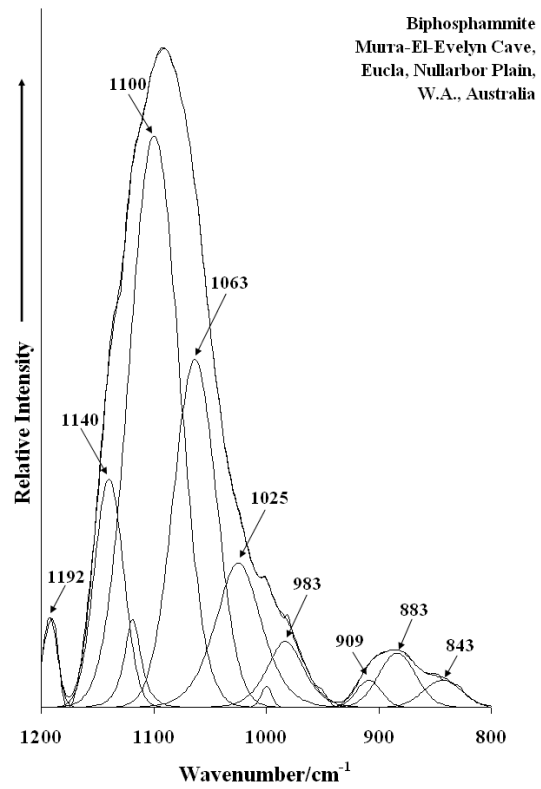
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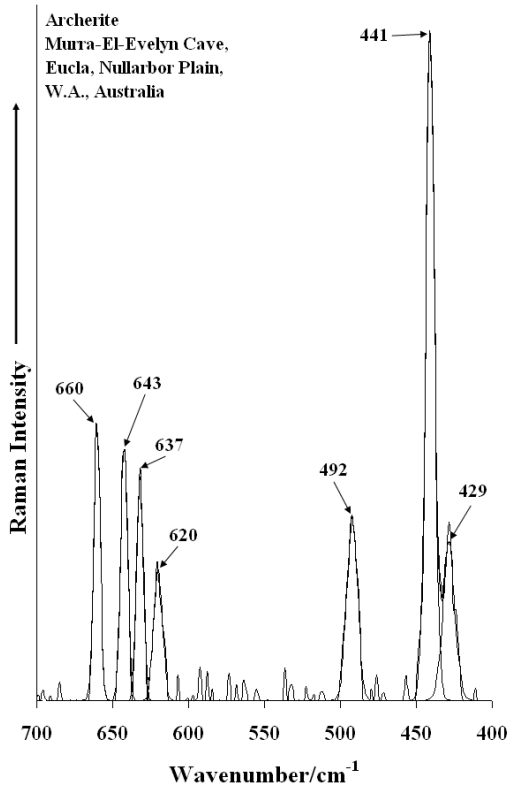
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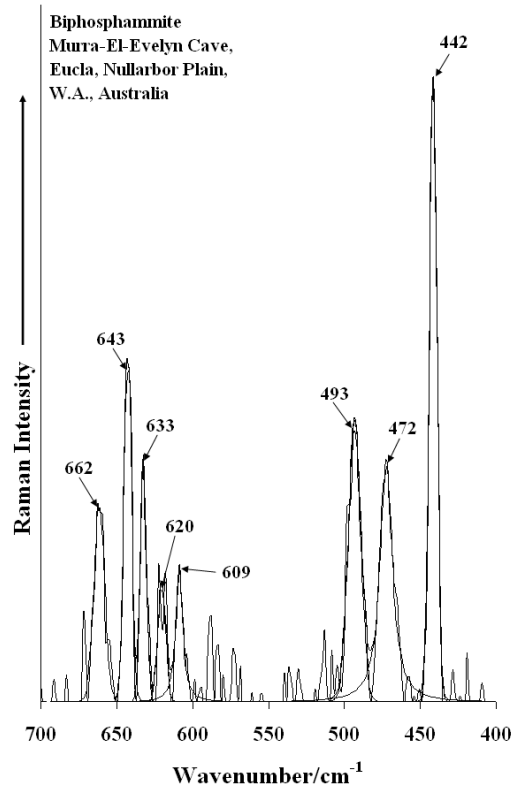
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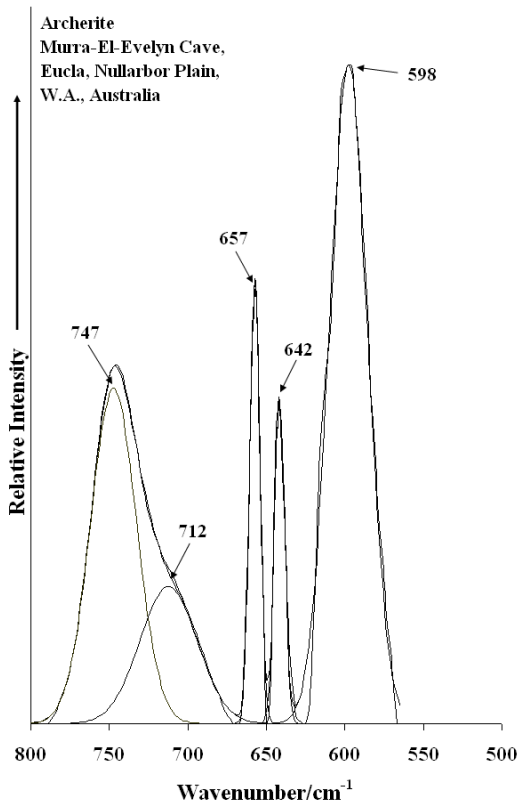
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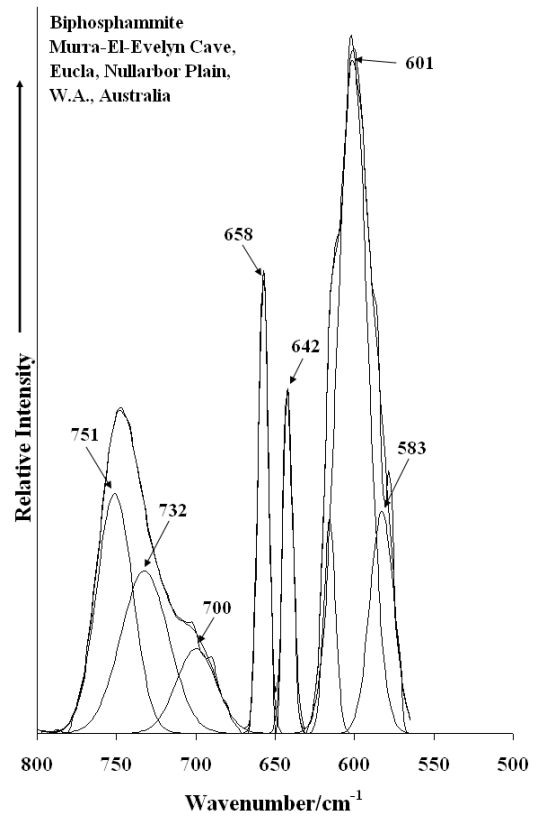
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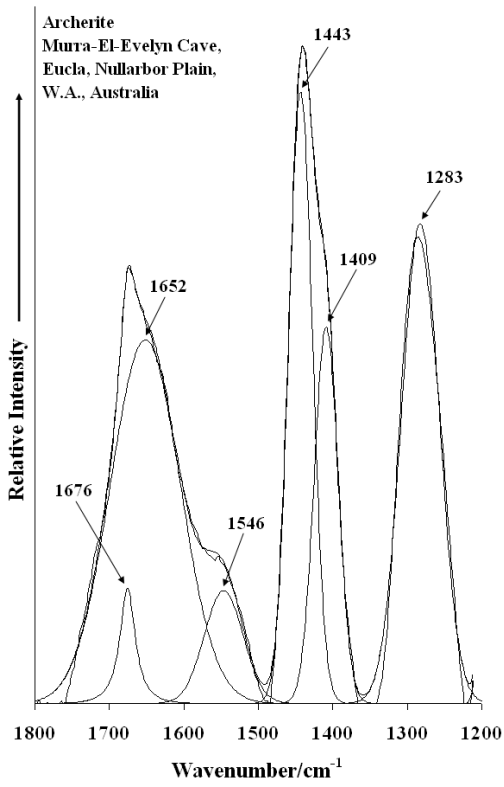
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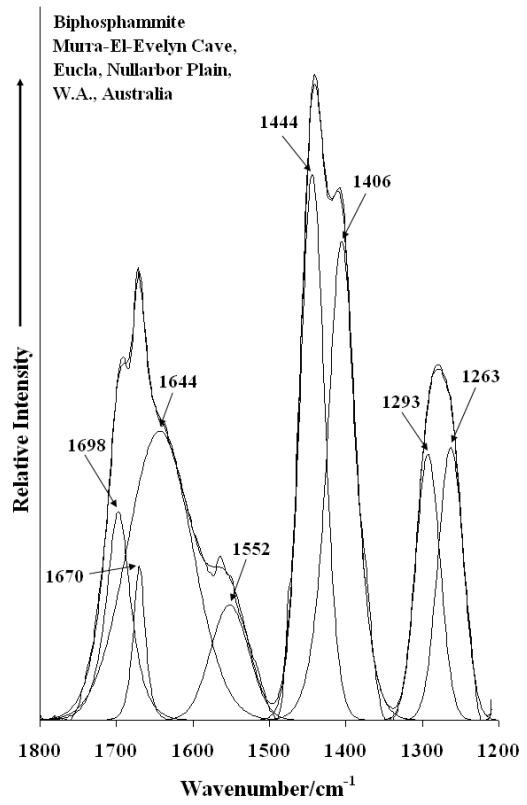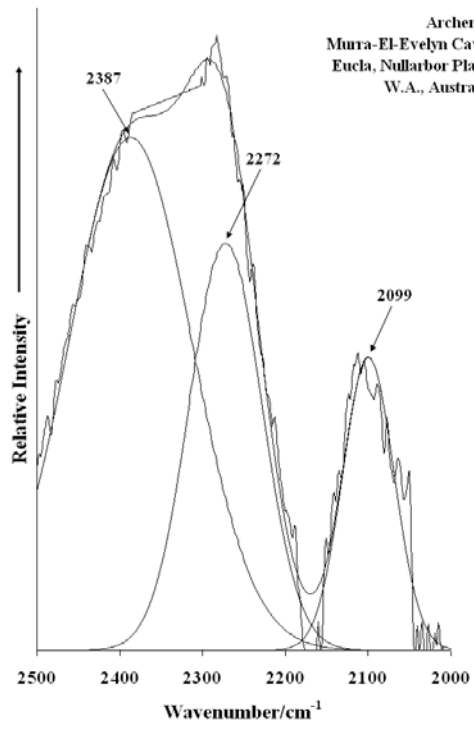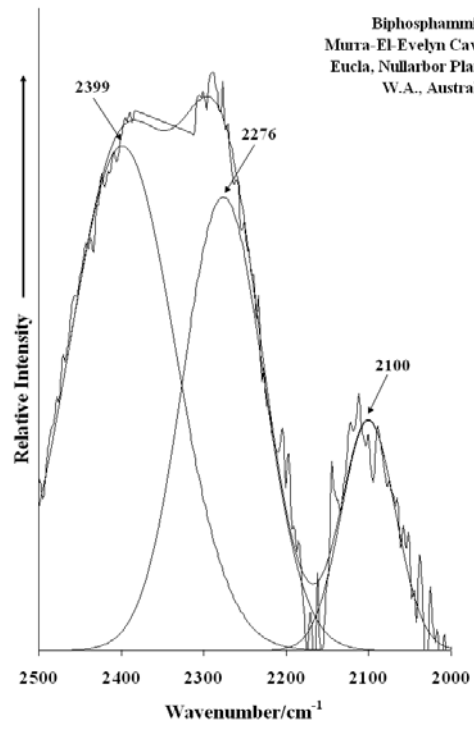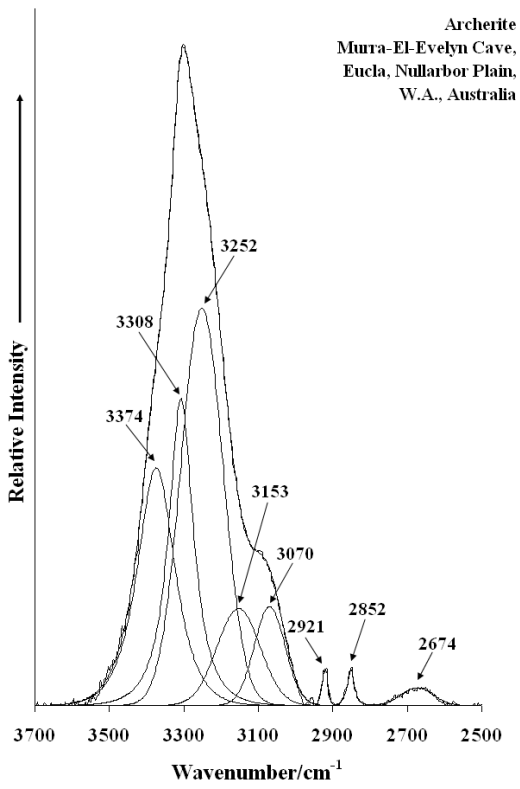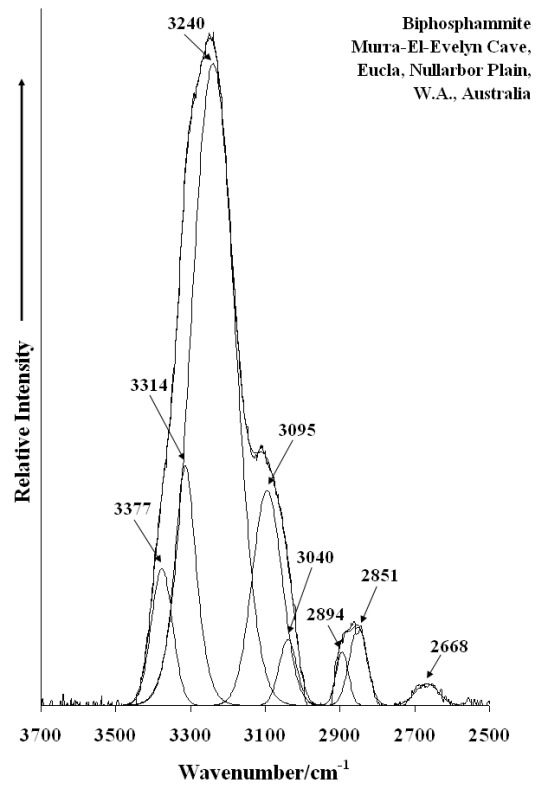

Figure 5b

Figure 6a

Figure 6b

Figure 7a

Figure 7b