Vibrational spectroscopy of synthetic archerite $(K,NH_4)H_2PO_4$ – and in comparison with the natural cave mineral

Ray L. Frost, • Yunfei Xi, Sara J. Couperthwaite, Keqin Tan and Graeme Millar

Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Abstract

In order to mimic the formation of archerite in cave minerals, the mineral analogue has been synthesised. The cave mineral is formed by the reaction of the chemicals in bat guano with calcite substrates. X-ray diffraction proves that the synthesised archerite analogue was pure. The vibrational spectra of the synthesised mineral are compared with that of the natural cave mineral. Raman and infrared bands are assigned to $H_2PO_4^-$, OH and NH stretching and bending vibrations. The Raman band at 917 cm^{-1} is assigned to the HOP stretching vibration of the $H_2PO_4^-$ units. Bands in the 1200 to 1800 cm^{-1} region are associated with NH_4^+ bending modes. Vibrational spectroscopy enables the molecular structure of archerite to be analysed.

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

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)
T: +61 7 3138 2407 F: +61 7 3138 1804
Queensland University of Technology, Faculty of Science and Technology, 2 George St., Brisbane, Queensland Australia 4001

INTRODUCTION

The minerals archerite 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 $(NH_4)_2Ca(HPO_4)_2{\cdot}H_2O$ [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 $(H(NH_4)Na(PO_4){\cdot}4H_2O)$, oxammite $((NH_4)_2(C_2O_4){\cdot}H_2O)$, weddellite $(Ca(C_2O_4){\cdot}2H_2O)$, whitlockite $(Ca_9Mg(PO_4)_6(HPO_4))$, guanine $(C_5H_5N_5O)$, newberyite $(Mg(HPO_4){\cdot}3H_2O)$ 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 is the same mineral or not is open to question [6]. The crystal structure is close to that of synthetic potassium dihydrogen phosphate [7]. 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 [8, 9]. Because of the ferroelectric properties of this chemical, there have been some detailed Raman spectroscopic studies of KH_2PO_4 [10-16]. Kim and Choi [12] 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 [12]. A detailed study of calcium phosphates including calcium dihydrogen phosphate has been reported [17].

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. Some studies of phosphate minerals in caves have been undertaken by the authors [6, 18-20]. Raman spectroscopy has proven most useful for the study of mineral structures [21-27]. The objective of this research is to report the Raman and

infrared spectra of the synthetic archerite analogue, to compare the spectra of the synthesised archerite and the natural cave mineral and to relate the spectra to the molecular structure of the mineral archerite.

EXPERIMENTAL

Synthesis of archerite

All starting chemicals: mono-potassium phosphate (KH_2PO_4), mono-ammonium phosphate ($NH_4H_2PO_4$) and phosphoric acid (H_3PO_4, 85%wt) were from Sigma-Aldrich. A solution of KH_2PO_4 was prepared by adding 27.0967g of KH_2PO_4 to 150ml of water, along with 22.9033g of $NH_4H_2PO_4$. This was followed by the addition of 10ml of H_3PO_4 to decrease the pH to about 7. The mixture was stirred continuously for 10 days under ambient conditions until most of the gel like material was crystallised. The whole mixture was transferred to an oven to dry at 105°C overnight.

Mineral

The mineral archerite was supplied by the Australian Museum 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) [28].

Raman spectroscopy

Crystals of the archerite analogue 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

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} [29-31]. S.D. Ross in Farmer (page 404) listed some well-known minerals containing phosphate, which were either hydrated or hydroxylated or both [32]. 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 position of the PO stretching vibration for calcium dihydrogen phosphate is found at 915 cm^{-1}. The POH antisymmetric stretching mode is at 947 cm^{-1} and the $P(OH)_2$ bending mode at 380 cm^{-1}. The band at 1150 cm^{-1} is assigned to the PO_2 antisymmetric stretching mode. The position of these bands will shift according to the crystal structure of archerite.

X-ray diffraction

The X-ray diffraction patterns of the synthesised archerite analogue and the standard reference pattern are provided in Figure 1. Obviously the two patterns are identical, thus proving purer archerite was synthesised. Further the synthesised archerite analogue does not contain any impurity.

110 ***Vibrational Spectroscopy***

111 The Raman spectrum of synthetic archerite is displayed in Figure 2. The position of this band
112 is in harmony with that reported by Ross in Farmer [32] (Table 17.IX page 396). In aqueous
113 systems, the band is found at 878 cm^{-1}. The infrared spectrum of the archerite analogue is
114 given in Figure 3, with infrared bands observed at around 890 and 1080 cm^{-1}. The infrared
115 bands at 1080 and 1115 cm^{-1} are attributed to the ν_3 symmetric PO_2 vibrations, while bands at
116 837, 894 and 930 cm^{-1} are assigned to the ν_4 $P(OH)_2$ symmetric stretching vibrations. The
117 spectra of the archerite analogue may be compared with that of the natural mineral. Raman
118 bands of the cave mineral archerite are observed at 981, 1005, 1139 and 1165 cm^{-1}. The
119 Raman band at 981 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the POH units,
120 whereas the Raman band at 1005 cm^{-1} is assigned to the ν_1 symmetric stretching mode of the
121 PO_4^{3-} units. Galy [33] first studied the polarized Raman spectra of the $H_2PO_4^-$ anion, while
122 Choi *et al.* reported the polarization spectra of NaH_2PO_4 crystals. Casciani and Condrate
123 [17] published spectra on brushite and monetite together with synthetic anhydrous
124 monocalcium phosphate ($Ca(H_2PO_4)_2$), monocalcium dihydrogen phosphate hydrate
125 ($Ca(H_2PO_4)_2 \cdot H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$). These authors
126 determined band assignments for $Ca(H_2PO_4)$ and reported bands at 1002 and 1011 cm^{-1} as
127 POH and PO stretching vibrations, respectively. The two Raman bands at 1139 and 1165cm^{-1}
128 are attributed to both the HOP and PO antisymmetric stretching vibrations. Casciani and
129 Condrate [17] tabulated Raman bands at 1132 and 1155 cm^{-1} and assigned these bands to P-
130 O symmetric and the P-O antisymmetric stretching vibrations. The first assignment, however,
131 differs from what is stated in this work.

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133 Infrared bands for the cave mineral archerite are found at 980 and 1000 cm^{-1} and at 983 and
134 1002 cm^{-1} for biphosphammite. These bands are attributed to the HOP and PO symmetric
135 stretching vibrations and are the equivalent of the Raman bands at ~981 and 1005 cm^{-1}
136 (Casciani and Condrate [17]). Infrared bands are observed at 1021, 1060, 1094, 1139 and
137 1192 cm^{-1} for archerite and at 1025, 1063, 1100, 1140 and 1192 cm^{-1} for biphosphammite.
138 These bands may be attributed to the HOP and PO antisymmetric stretching vibrations.
139 Infrared bands for the mineral dittmarite $(NH_4)MgPO_4 \cdot H_2O$ are found at 978, 1063 and 1105
140 cm^{-1} (this work). The infrared bands at 830 and 982 cm^{-1} for archerite and at 843, 883 and
141 909 cm^{-1} are thought to be associated with the POH deformation modes. Choi *et al.* [34]

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 [17] reported bands assigned to these vibrational modes for $Ca(H_2PO_4)_2$ at 876 and 901 cm^{-1}.

The Raman spectrum of archerite analogue in the 100 to 700 cm^{-1} region is displayed in Figure 4. Raman bands are observed at 533 and 562 cm^{-1}. These bands are attributed to the ν_4 out of plane bending modes of the H_2PO_4 units. The Raman spectrum of NaH_2PO_4 shows Raman bands at 526, 546 and 618 cm^{-1}. Raman bands are found at 620, 637, 643 and 660 cm^{-1} for the cave mineral archerite. Raman bands are determined at 461 and 477 cm^{-1}. These bands are attributed to the ν_2 H_2PO_4 bending modes. Raman bands are observed at 429, 441 and 492 cm^{-1} for the cave mineral archerite. The Raman spectrum of NaH_2PO_4 shows Raman bands at 460 and 482 cm^{-1}. Intense Raman bands are observed at 347 and 593 cm^{-1} assigned to metal-oxygen vibrations. Other Raman bands are observed at 144, 180 and 270 cm^{-1}, and are simply described as external vibrations or lattice modes.

The Raman spectrum of the archerite analogue in the 2800 to 3600 cm^{-1} region is shown in Figure 5. A broad spectral envelope is observed, which may be resolved into component bands at 3018, 3089, 3151, 3191, 3235 cm^{-1}. These bands are attributed to water stretching vibrations. These band assignments are supported by the 1660 cm^{-1} band in the water bending region (Figure 6). Additional bands at 1421 and 1704 cm^{-1} are attributed to the NH_4^+ bending modes. The Raman bands at 1283, 1409, 1443 and 1546 cm^{-1} for the natural cave mineral archerite are assigned to these bending modes. The bands at around 1406 and 1444 cm^{-1} are assigned to the doubly degenerate ν_2 modes, whereas the band at around 1283 cm^{-1} is 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 structure and probably has C_s symmetry.

The infrared spectrum of the archerite synthetic analogue is shown in Figure 7. A broad infrared band centred upon 1620 cm^{-1} may be deconvoluted into component bands at 1545, 1606 and 1712 cm^{-1}. These bands are assigned to the deformation modes of the ammonium

ion and a water bending vibration. Infrared bands are observed in two sets: the first set is comprised of bands at 1388, 1407, 1426 and 1445 cm^{-1}, and a second set at 1240, 1278 and 1303 cm^{-1}. The first set is assigned to NH_4^+ ν_2 bending modes and the second set to NH_4^+ ν_4 bending modes. 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}. Infrared bands are observed at 2099, 2272 and 2387 cm^{-1} for the cave mineral archerite. 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 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 [17] 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. Infrared bands are observed at 2674, 2852, 2921, 3070, 3153, 3252, 3308 and 3374 cm^{-1} for the cave mineral archerite. 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, while the infrared bands at 3070 and 3153 cm^{-1} are attributed to NH stretching vibrations.

CONCLUSIONS

The mineral archerite is an ammoniated hydrogen potassium phosphate commonly found in caves in Western Australia, such as the Petrogale Cave and in the Murra-el-elevyn Cave. However, archerite has been found in many caves worldwide. The synthetic analogue of archerite has been synthesised and the spectra of the natural cave mineral has been compared with the synthetic analogue. X-ray diffraction patterns prove the synthesised compound was indeed archerite. 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.

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 mineral archerite. Raman spectroscopy proves the anion in the synthetic archerite analogue is the dihydrogen phosphate anion. No observation of phosphate or hydrogen phosphate units was found in the archerite analogue. The Raman spectra of the

natural cave mineral archerite shows the presence of both the dihydrogen and mono hydrogen phosphate units.

Acknowledgments

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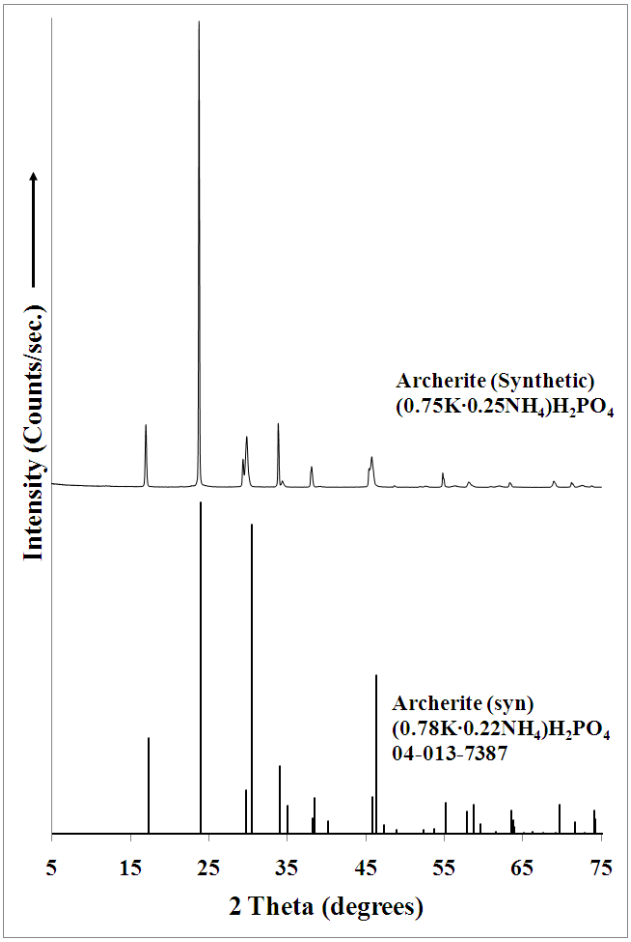

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282 **Figure 1**

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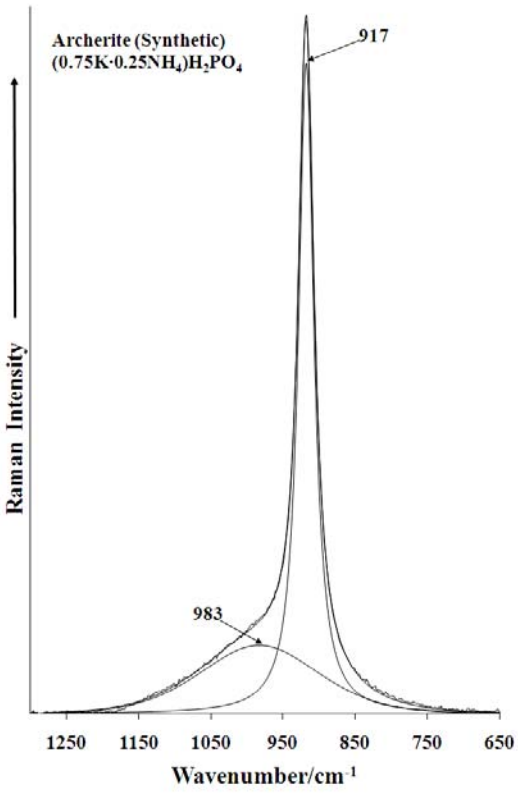

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286 **Figure 2**

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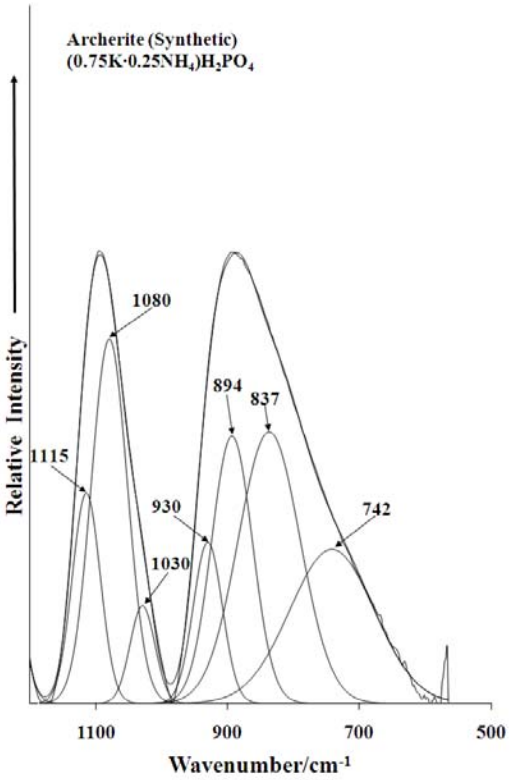

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292 **Figure 3**

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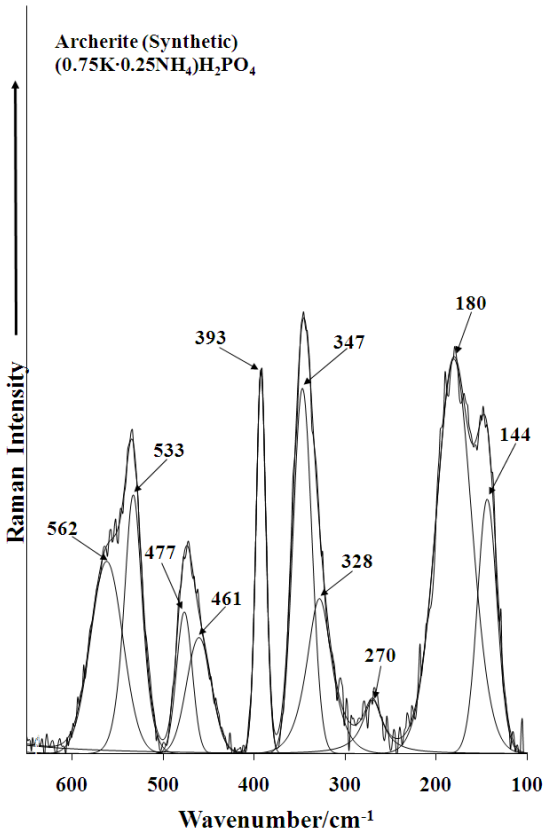

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297 **Figure 4**

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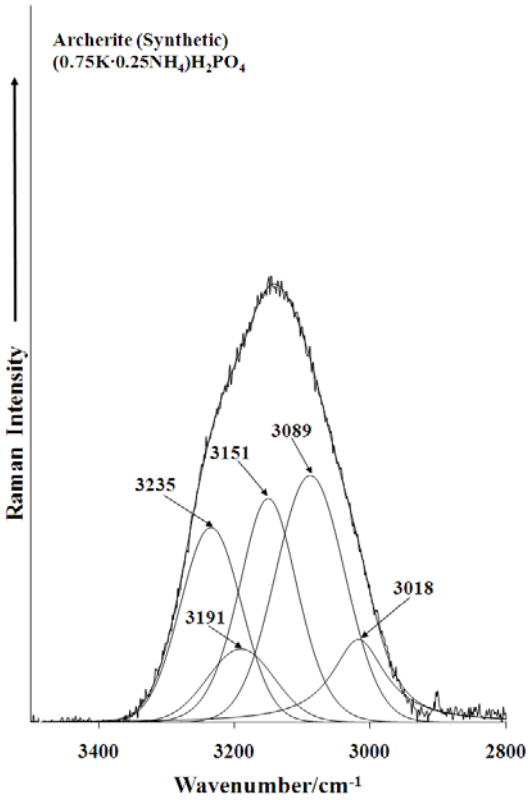

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304 **Figure 5**

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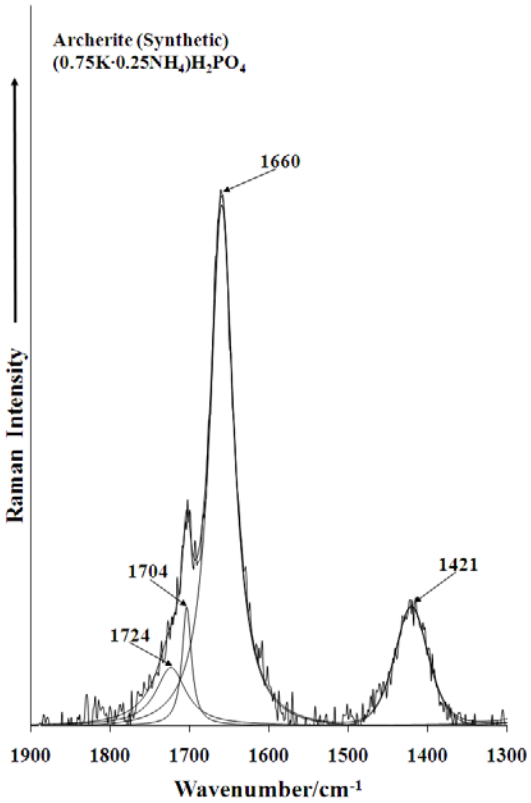

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309 **Figure 6**

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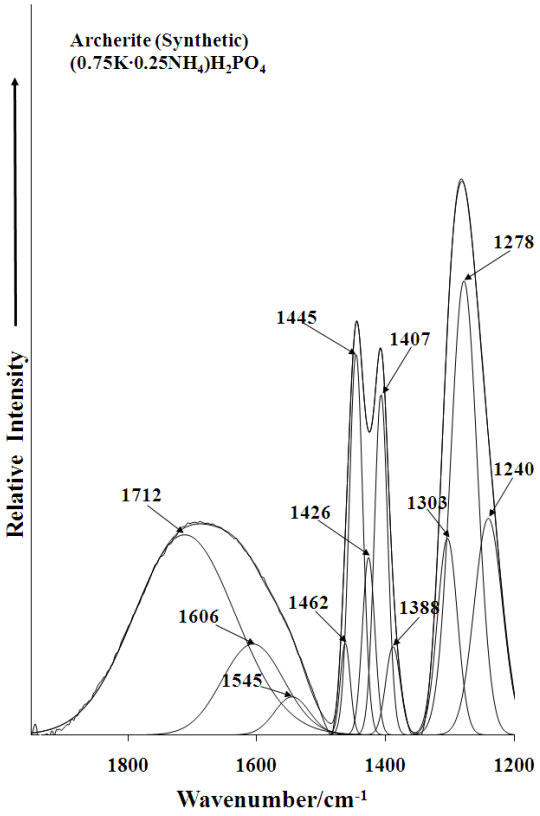

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313 **Figure 7**

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