Frost, Ray L., Palmer, Sara J., Henry, Dermot A., & Pogson, Ross (2011) A Raman spectroscopic study of the 'cave' mineral ardealite Ca2(HPO4)(SO4)•4H2O. *Journal of Raman Spectroscopy*, *42*(6), pp. 1447-1454.

http://dx.doi.org/10.1002/jrs.2855

A Raman spectroscopic study of the 'cave' mineral ardealite $Ca_2(HPO_4)(SO_4)\cdot 4H_2O$

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Abstract

The mineral ardealite $Ca_2(HPO_4)(SO_4)\cdot 4H_2O$ is a 'cave' mineral and is formed through the reaction of calcite with bat guano. The mineral shows disorder and the composition varies depending on the origin of the mineral. Raman spectroscopy complimented with infrared spectroscopy has been used to characterise the mineral ardealite. The Raman spectrum is very different from that of gypsum. Bands are assigned to SO_4^{2-} and HPO_4^{2-} stretching and bending modes.

Keywords: Raman spectroscopy, phosphate, sulphate, ardealite

Introduction

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The mineral ardealite is known as a cave mineral and has been found in many caves worldwide [1-6]. Phosphates have been known to exist in the Jenolan caves for a very long time [7-9]. Dating of clays in these caves suggest the caves are very old around 350 million years [10]. The mineral is a mixed anion sulphate phosphate of calcium and is formed by the reaction of bat guano with calcite. The mineral is monoclinic of point group *m* and forms very thin platy crystals or powdery crusts. The mineral is intimately associated with brushite and gypsum. The formula of the mineral is given as $Ca_2(HPO_4)(SO_4)\cdot 4H_2O$ but the composition of the mineral can vary according to the cave of origin. The mineral is often yellowish probably due to the presence of iron in the mineral composition.

Raman spectroscopy has proven very useful for the study of minerals [11-24]. Indeed Raman spectroscopy has proven most useful for the study of diagentically related minerals as often occurs with minerals containing sulphate and phosphate groups. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. In this work we attribute bands at various wavenumbers to vibrational modes of ardealite using Raman spectroscopy and relate the spectra to the structure of the mineral.

Experimental

Minerals

The mineral ardealite was sourced from two sources namely (a) The Australian Museum and originated from the Jenolan caves, New South Wales, Australia and (b) from Museum Victoria where the ardealite mineral originated from Moorba Cave, Jurien Bay, Western Australia, Australia. The mineral has been analysed and the data published [25].

Raman spectroscopy

Crystals of ardealite 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 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.

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

The Raman spectroscopy of the aqueous sulphate tetrahedral oxyanion yields the symmetric stretching (ν_1) vibration at 981 cm^{-1}, the in-plane bending (ν_2) mode at 451 cm^{-1}, the antisymmetric stretching (ν_3) mode at 1104 cm^{-1} and the out-of-plane bending (ν_4) mode at 613 cm^{-1} [26]. Ross reports the interpretation of the infrared spectra for potassium alum as ν_1, 981 cm^{-1}; ν_2, 465 cm^{-1}; ν_3, 1200, 1105 cm^{-1}; ν_4, 618 and 600 cm^{-1} [27]. Water stretching modes were reported at 3400 and 3000 cm^{-1}, bending modes at 1645 cm^{-1}, and librational modes at 930 and 700 cm^{-1} [28]. The Raman spectrum of the mineral chalcanthite shows a single symmetric stretching mode at 984.7 cm^{-1}. Two ν_2 modes are observed at 463 and 445 cm^{-1} and three ν_3 modes at 1173, 1146 and 1100 cm^{-1}. The ν_4 mode is observed as a single band at 610 cm^{-1}. A complex set of overlapping bands is observed in the low wavenumber region at 257, 244, 210 136 and 126 cm^{-1}. Recently, Raman spectra of four basic copper sulphate minerals, namely antlerite, brochiantite, posnjakite and langite, were published [29]. The SO symmetric stretching modes for the four basic copper sulphate minerals are observed at 985, 990, 972 and 974 cm^{-1}. Only the mineral brochantite showed a single band in this region. Multiple bands were observed for these minerals in the antisymmetric stretching region. Some sulphates have their symmetry reduced through acting as monodentate and bidentate ligands [30]. In the case of bidentate behaviour both bridging and chelating ligands are known. This reduction in symmetry is observed by the splitting of the ν_3 and ν_4 into two components under C_{3v} symmetry and 3 components under C_{2v} symmetry. Raman spectra of hydrogen phosphate oxyanions show a symmetric stretching mode (ν_1) at ~860 cm^{-1}, the antisymmetric stretching mode (ν_3) at ~1150 cm^{-1}, the symmetric bending mode (ν_2) at ~460 cm^{-1} and the ν_4 mode at ~590 cm^{-1}.

Raman Spectroscopy

Raman spectroscopy is a very powerful tool for the analysis of the molecular structure of minerals especially minerals containing oxyanions. The Raman spectrum of ardealite from the two sources in the 800 to 1200 cm^{-1} is shown in Fig. 1. There appears to be two overlapping bands at around 998 and 1002 cm^{-1}. These bands are assigned to the ν_1 SO_4^{2-} stretching mode. In the white material from the Jenolan caves, attributed to gypsum an intense Raman band is observed at 1008 cm^{-1} (Fig. S1). The band is perfectly symmetric and not asymmetric as occurs in the Raman spectrum of ardealite. It is suggested that there are two non-equivalent sulphate units in the ardealite structure. Alternatively a band from the sulphate and hydrogen phosphate anions overlaps. The low intensity Raman band at 1140 cm^{-1} is assigned to the ν_3 SO_4^{2-} antisymmetric stretching modes. A band occurs for gypsum at 1139 cm^{-1}. A second Raman band is observed for the ardealite for the sample D49535 at 1102 cm^{-1}. One possibility is that this band is assignable to the ν_3 HPO_4^{2-} antisymmetric stretching mode. The band is not observed in the Raman spectrum of gypsum. The Raman spectrum of the phosphate mineral newberyite has been reported [31]. Raman bands were observed at 1154 and 1195 cm^{-1}.

A Raman band is found at 862 cm^{-1} for ardealite. This band is assigned to the ν_1 HPO_4^{2-} symmetric stretching mode. The band is due to the presence of hydrogen phosphate units in the ardealite structure. The band is not observed in the Raman spectrum of gypsum. A Raman band was observed in the spectrum of newberyite $Mg(PO_3OH)\cdot 3H_2O$ at 887 cm^{-1} and was attributed to HPO_4^{2-} symmetric stretching mode [31]. Such bands are normally intense in the infrared spectrum but of low intensity in the Raman spectrum. Rajendran and Keefe [32] studied the growth and characterisation of calcium hydrogen phosphate dihydrate and reported the FTIR and Raman spectra. These researchers observed a band at 875 cm^{-1} and assigned this band to the HPO_4^{2-} POP antisymmetric stretching mode. However this assignment differs from our interpretation. Soptrajanov *et al.* [33] reported the FT-IR and Raman spectra of a manganese hydrogen phosphate trihydrate and assigned an observed band at 889 cm^{-1} to a P-O(H) stretching vibration. These workers showed that the band was deuterium sensitive.

The Raman spectra of ardealite in the 350 to 700 cm^{-1} region are shown in Fig. 2. For the ardealite from WA, a Raman band is found at 610 cm^{-1}. This band is assigned to the ν_4 $(SO_4)^{2-}$ bending modes. In the Raman spectrum of the NSW sample, Raman bands are found at 598, 613 and 670 cm^{-1} and are assigned to this vibrational mode. The intense Raman band at 502 cm^{-1} for the WA sample and at 505 and 528 cm^{-1} for the NSW sample are assigned to the ν_4 $(HPO_4)^{2-}$ bending modes. The mineral newberyite $Mg(PO_3OH)\cdot 3H_2O$ also contains a hydrogen phosphate anion. The Raman spectrum of this mineral has been reported [31]. An intense band was observed for this mineral at 498 cm^{-1}. Rajendran and Keefe [32] reported Raman bands at 521 and 586 cm^{-1} and assigned these bands to (H-O)P=O absorption bands. This assignment is in contrast to the assignment of bands by Farmer [34]. The Raman bands at 421 and 448 cm^{-1} (NSW) and 418 and 453 cm^{-1} (WA) are assigned to the ν_2 $(SO_4)^{2-}$ bending modes. The Raman band at 363 cm^{-1} (both NSW and WA) is assigned to the ν_2 $(HPO_4)^{2-}$ bending mode. In the Raman spectrum of gypsum (Fig. S2), no bands are found at 502 and 363 cm^{-1}. Raman bands for gypsum are observed at 415, 494, 620 and 671 cm^{-1}. Raman spectra in the low wavenumber region are shown in Fig. 3. It is considered that these bands in this spectral region are associated with water hydrogen bonded to the sulphate and phosphate anions. There is a resemblance to the Raman spectrum of gypsum in this spectral region (Fig. S3). A Raman spectrum of gypsum in the OH stretching region is given in Fig. S4. However it was not possible to obtain a Raman spectrum of ardealite in this spectral region. This is attributed to the poor crystallinity of the mineral sample and the fact that water has a very poor Raman scattering cross section.

Infrared Spectroscopy

The infrared spectra of the two ardealite minerals in the 900 to 1300 cm^{-1} region are displayed in Fig. 4. The infrared band at 998 cm^{-1} (NSW) and 995 cm^{-1} (WA) are assigned to the infrared forbidden $(SO_4)^{2-}$ stretching vibration. The band has become activated because of the reduction in symmetry of the sulphate/phosphate anion. It is thought that coupling occurs between the sulphate and phosphate vibrations resulting in the observation of a single asymmetric band. The infrared band at ~1093 cm^{-1} is assigned to the $(HPO_4)^{2-}$ ν_3 antisymmetric stretching vibration. The series of bands at 1131, 1147, 1171 cm^{-1} (NSW) and 1130, 1148 and 1179 cm^{-1} are attributed to the $(SO_4)^{2-}$ ν_3 antisymmetric stretching vibrations. The observation of multiple ν_3 bands supports the concept of a reduction in symmetry of the sulphate anion. The Raman spectrum of gypsum is very different in this spectral region (Fig. S5). Farmer [34] reported infrared bands at 948, 1068 and 1150 cm^{-1} for Na_2HPO_4 and assigned these bands to the $(HPO_4)^{2-}$ ν_3 antisymmetric stretching vibrations. Soptrajanov et al. [33] for manganese hydrogen phosphate trihydrate reported infrared bands at 971, 1035, 1135 and 1154 cm^{-1} and assigned these bands to PO_3 stretching vibrations.

The infrared spectra of ardealite in the 550 to 900 cm^{-1} region are reported in Fig. 5. Intense infrared bands are observed at ~862 cm^{-1}. The band is asymmetric in the infrared spectrum of the NSW sample. This band is assigned to the $(HPO_4)^{2-}$ ν_1 symmetric stretching mode. Farmer [34] tabulated the band positions of minerals containing the hydrogen phosphate anion (Table 17 III page 386). In this work, the infrared band at 860 cm^{-1} was described as the $(HPO_4)^{2-}$ ν_1 symmetric stretching mode.

The band at ~670 cm^{-1} is assigned to the infrared ν_4 $(SO_4)^{2-}$ bending modes. The strong infrared band at ~590 cm^{-1} is assigned to the ν_4 $(HPO_4)^{2-}$ bending modes. Farmer [34] reported the position of bands attributed to $(HPO_4)^{2-}$ bending vibrations. These bands are observed in the 520 to 590 cm^{-1} spectral region. The ν_2 $(HPO_4)^{2-}$ bending modes are found below 500 cm^{-1} which is below the limits of the infrared spectrometer. These infrared bands are found at ~430 to 460 cm^{-1} range.

The infrared spectra of ardealite in the 1400 to 1800 cm^{-1} region are reported in Fig. 6. This spectral region is where the water bending vibration is found. The spectrum for the NSW sample shows complexity with infrared bands observed at 1619, 1653 and 1683 cm^{-1}. The position of these bands supports the concept that water is in different environments in the structure of ardealite. The band at 1619 cm^{-1} is due to weakly hydrogen bonded water. The bands at 1653 and 1683 cm^{-1} are attributed to strongly hydrogen bonded water molecules. In the infrared spectrum of the WA mineral, infrared bands are observed at 1604, 1651, 1684 cm^{-1}. In the infrared spectrum of gypsum, two distinct and clearly resolved bands are observed at 1619 and 1682 cm^{-1} (Fig. S7). Infrared bands observed at 1346 and 1439 cm^{-1} (WA) and 1440 cm^{-1} (NSW) are assigned to POH in-phase deformation modes. The band positions are in agreement with the position of POH bands reported by Farmer [34]. The infrared spectrum of ardealite in the 2600 to 3800 cm^{-1} region is shown in Fig. 7. The spectral profile is complex with a series of overlapping bands. Infrared bands are resolved at 3026, 3160, 3257, 3333, 3405 and 3521 cm^{-1} for the NSW sample. The complexity of the water stretching bands is in harmony with the water bending modes centred upon ~1650 cm^{-1}. The infrared spectrum of gypsum is very different (Fig. S8).

Conclusions

Raman complimented with infrared spectroscopy has been used to characterise the ‘cave’ mineral ardealite $Ca_2(HPO_4)(SO_4)\cdot 4H_2O$. The mineral is an unusual mineral from a chemistry point of view as the mineral contains hydrogen phosphate and sulphate anions. The mineral is formed by the reaction of phosphates from bat guano and calcite. The Raman and infrared spectra reflect the composition of the mineral with bands attributed to H_2O, HPO_4 and SO_4 stretching and bending modes.

Acknowledgements

The financial and infra-structure support of the Queensland University of Technology Chemistry Discipline of the Faculty of Science and Technology, is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation.

References

[1] D.-G. Dumitras, S. Marincea, E. Bilal, F. Hatert, *Can. Min.* **2008,** *46,* 431-445.

[2] C. A. Hill, Cave Minerals, 1976.

[3] D. Moravansky, M. Orvosova, *Miner. Slov.* **2007,** *39,* 203-216.

[4] D. Moravansky, P. Zenis, *Miner. Slov.* **1997,** *29,* 61-72.

[5] B. P. Onac, J. E. Mylroie, W. B. White, *Carb.Evap.* **2001,** *16,* 8-16.

[6] W. B. White, *Sci. Speleol.* **1976,** 267-327.

[7] J. C. H. Mingaye, *Rept. Australian Assoc.* **1898,** *7,* 111-116.

[8] J. C. H. Mingaye, *Records Geol. Survey N.S.W.* **1899,** *6,* 111-116.

[9] C. A. Suessmilch, W. G. Stone, *J. Royal Soc. N.S.W.* **1916,** *49,* 332-384.

[10] R. A. L. Osborne, H. Zwingmann, R. E. Pogson, D. M. Colchester, *Aust. J. Earth Sc.***2006,** *53,* 377-405.

[11] S. Bahfenne, R. L. Frost, *J. Raman Spectrosc.* **2010,** *41,* 329-333.

[12] S. Bahfenne, R. L. Frost, *J. Raman Spectrosc.* **2010,** *41,* 465-468.

[13] J. Cejka, S. Bahfenne, R. L. Frost, J. Sejkora, *J. Raman Spectrosc.* **2010,** *41,* 74-77.

[14] J. Cejka, J. Sejkora, J. Plasil, S. Bahfenne, S. J. Palmer, R. L. Frost, *J. Raman Spectrosc.* **2010,** *41,* 459-464.

[15] R. L. Frost, S. Bahfenne, *J. Raman Spectrosc.* **2010,** *41,* 207-211.

[16] R. L. Frost, S. Bahfenne, *J. Raman Spectrosc.* **2010,** *41,* 325-328.

[17] R. L. Frost, S. Bahfenne, J. Cejka, J. Sejkora, S. J. Palmer, R. Skoda, *J. Raman Spectrosc.* **2010,** *41,* 690-693.

[18] R. L. Frost, S. Bahfenne, J. Cejka, J. Sejkora, J. Plasil, S. J. Palmer, *J. Raman Spectrosc.* **2010,** *41,* 814-819.

[19] R. L. Frost, K. H. Bakon, S. J. Palmer, *J. Raman Spectrosc.* **2010,** *41,* 78-83.

[20] R. L. Frost, J. Cejka, J. Sejkora, J. Plasil, S. Bahfenne, S. J. Palmer, *J. Raman Spectrosc.* **2010,** *41,* 571-575.

[21] R. L. Frost, J. Cejka, J. Sejkora, J. Plasil, S. Bahfenne, S. J. Palmer, *J. Raman Spectrosc.* **2010,** *41,* 566-570.

[22] R. L. Frost, S. J. Palmer, L.-M. Grand, *J. Raman Spectrosc.* **2010,** *41,* 791-796.

[23] R. L. Frost, J. Sejkora, E. C. Keeffe, J. Plasil, J. Cejka, S. Bahfenne, *J. Raman Spectrosc.* **2010,** *41,* 202-206.

[24] J. Sejkora, J. Cejka, R. L. Frost, S. Bahfenne, J. Plasil, E. C. Keeffe, *J. Raman Spectrosc.* **2010,** *41,* 1038-1043.

[25] J. W. Anthony, R. A. Bideaux, K. W. Bladh, M. C. Nichols, Handbook of Mineralogy, Mineral Data Publishing, Tuscon, Arizona, USA, 2000.

[26] R. L. Frost, P. A. Williams, W. Martens, J. T. Kloprogge, P. Leverett, *Journal of Raman Spectroscopy* **2002,** *33,* 260-263.

[27] S. D. Ross, *in The infrared spectra of minerals,* **1974,** *Chapter 18 pp 423,* The Mineralogical Society London.

[28] S. D. Ross, Inorganic Infrared and Raman Spectra (European Chemistry Series), 1972.

[29] W. Martens, R. L. Frost, J. T. Kloprogge, P. A. Williams, *Journal of Raman Spectroscopy* **2003,** *34,* 145-151.

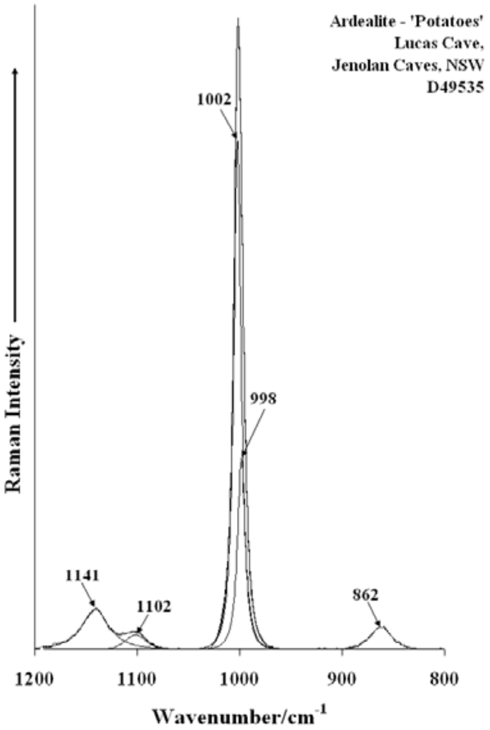
[30] R. L. Frost, J. T. Kloprogge, P. A. Williams, P. Leverett, *Journal of Raman Spectroscopy* **2000,** *31,* 1083-1087.

[31] R. L. Frost, M. L. Weier, W. N. Martens, D. A. Henry, S. J. Mills, *Spectrochimic. Acta,* **2005,** *62A,* 181-188.

[32] K. Rajendran, C. D. Keefe, *Cryst. Res. technol.* **2010,** *45,* 939-945.

[33] B. Soptrajanov, V. Stefov, I. Kuzmanovski, G. Jovanovski, *J. Molec. Struc.***1999,** *482-483,* 103-107.

[34] V. C. Farmer, Mineralogical Society Monograph 4: The Infrared Spectra of Minerals, 1974.



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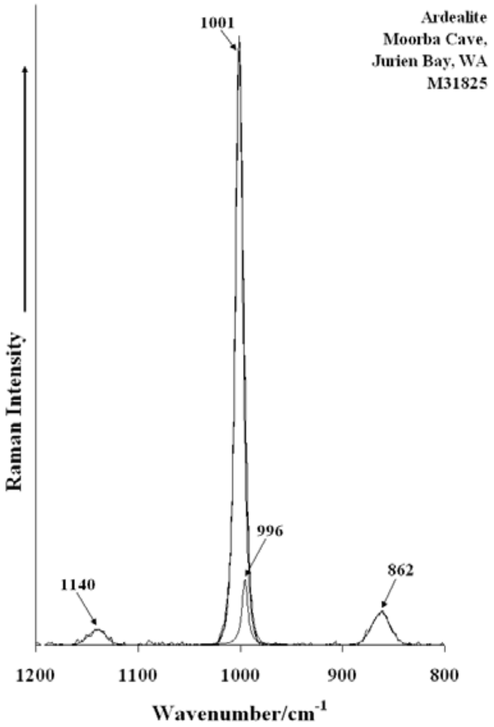

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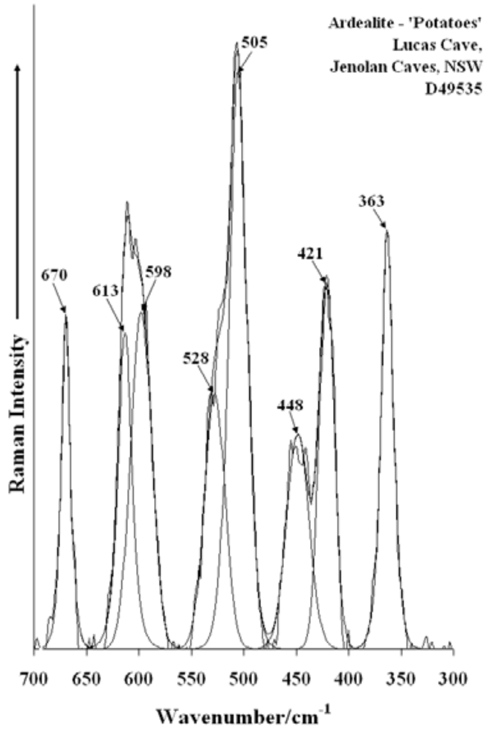

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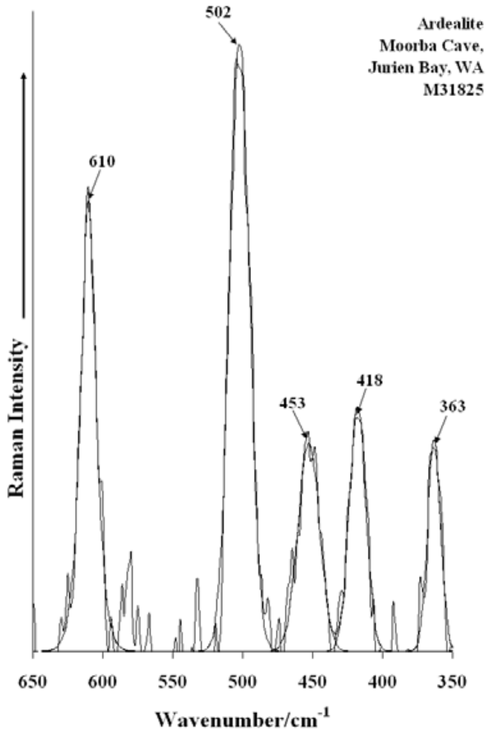

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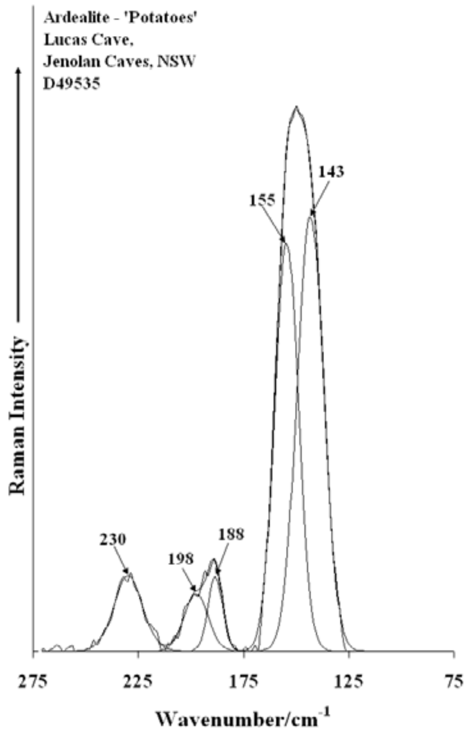

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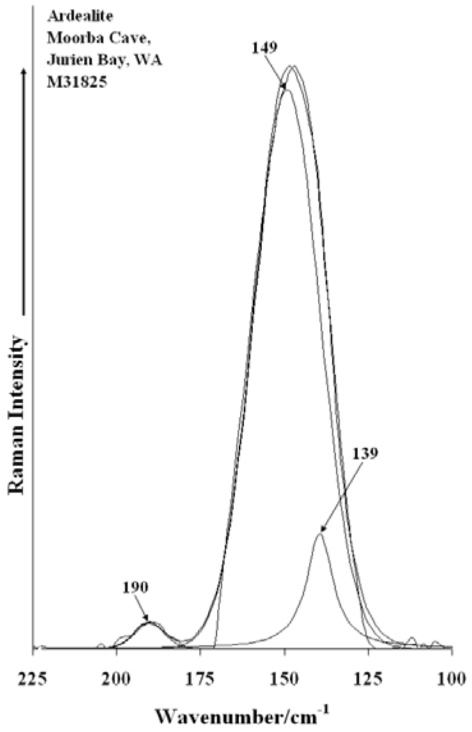

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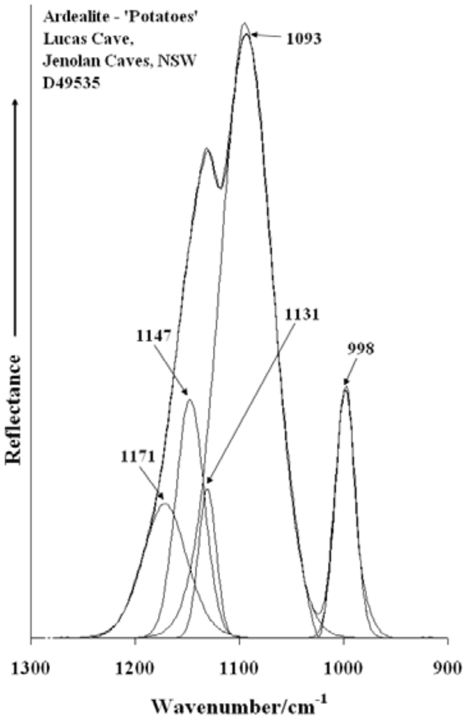

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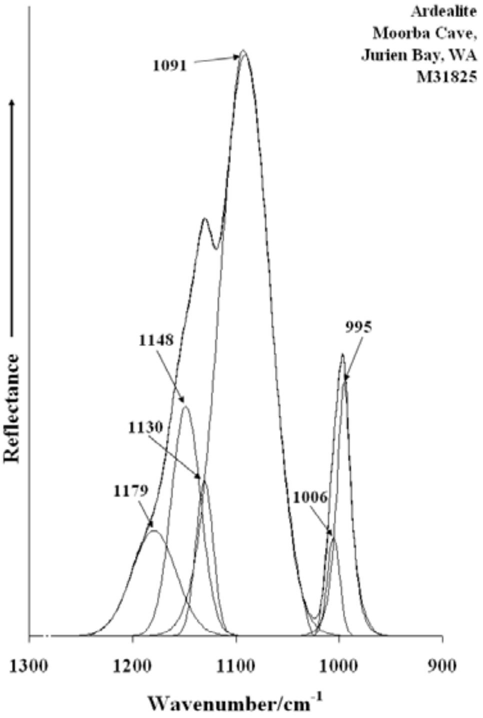

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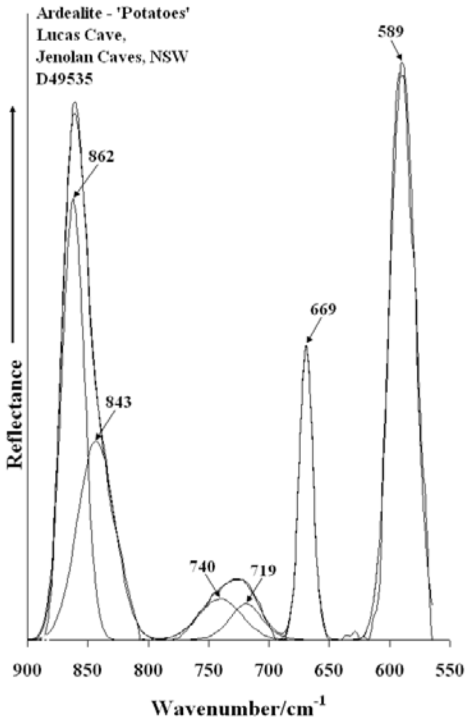

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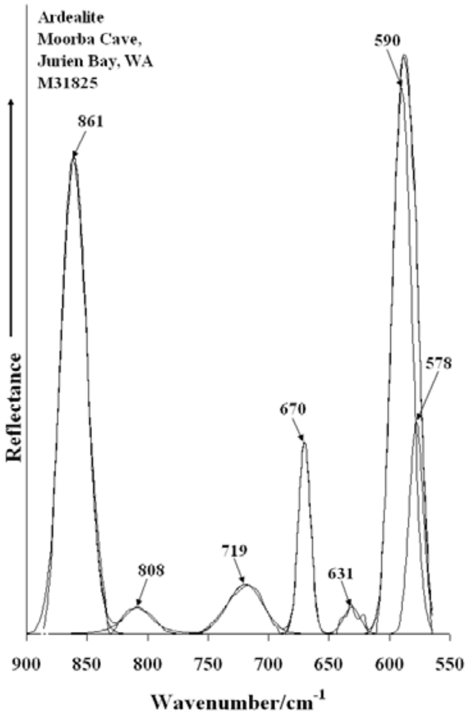

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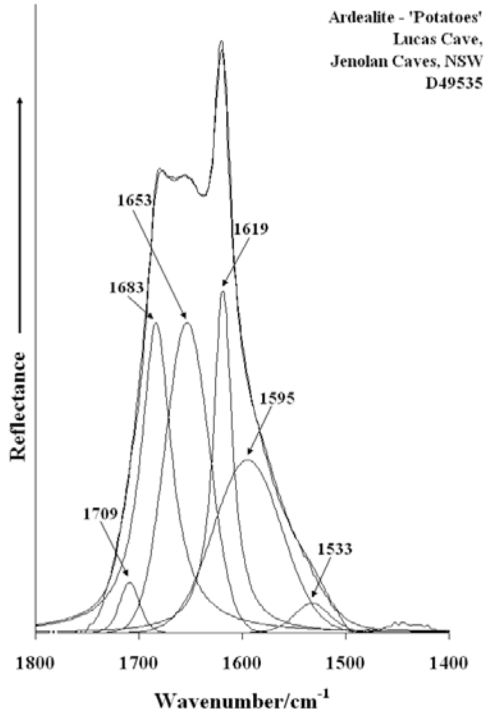

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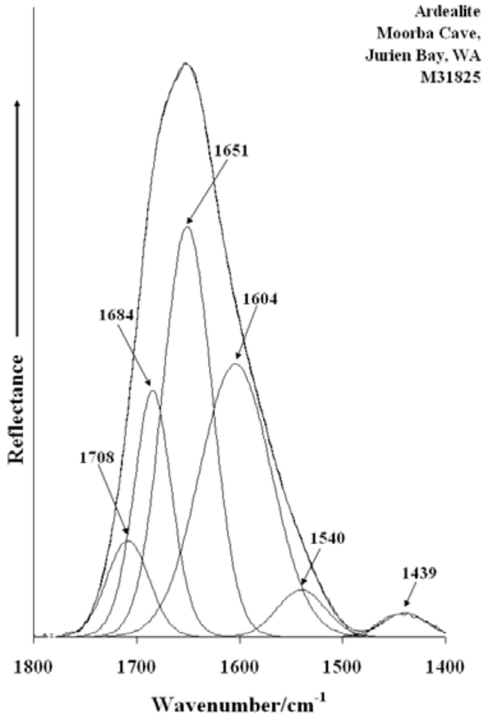

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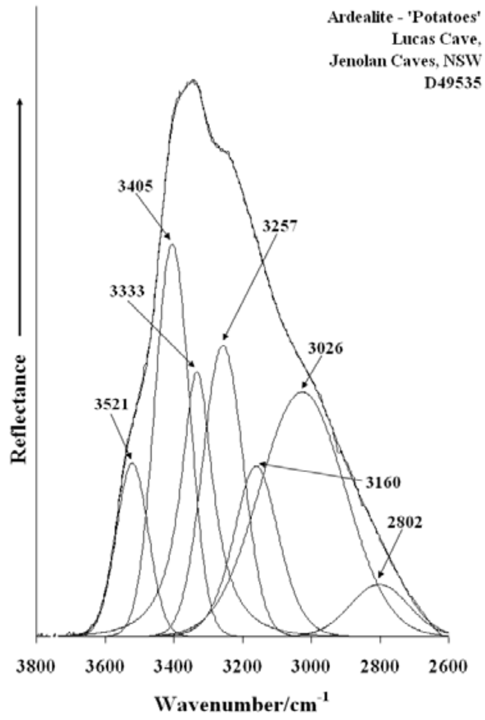

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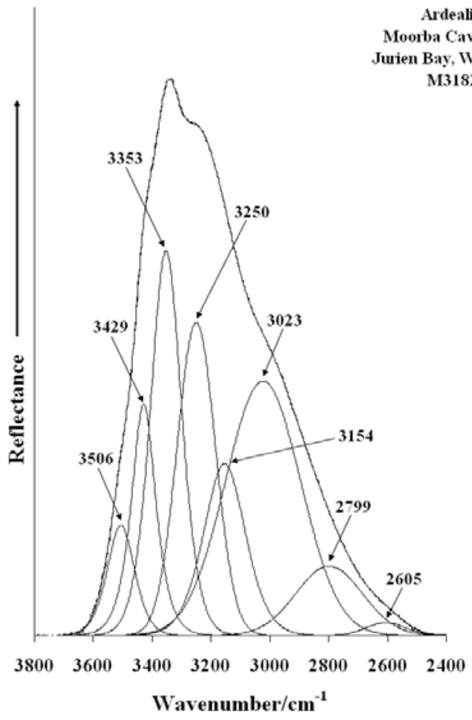

Figure 7b