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Raman spectroscopic study of the magnesium carbonate minerals– artinite and dypingite

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Magnesium minerals are important in the understanding of the concept of geosequestration. The two hydrated hydroxy magnesium carbonate minerals artinite and dypingite have been studied by Raman spectroscopy. Intense bands are observed at 1092 cm⁻¹ for artinite and at 1120 cm⁻¹ for dypingite attributed CO₃²⁻ v₁ symmetric stretching mode. The CO₃²⁻ v₃ antisymmetric stretching vibrations are extremely weak and are observed at 1412 and 1465 cm⁻¹ for artinite and at 1366, 1447 and 1524 cm⁻¹ for dypingite. Very weak Raman bands at 790 cm⁻¹ for artinite and 800 cm⁻¹ for dypingite are assigned to the CO₃²⁻ v₂ out-of-plane bend. The Raman band at 700 cm⁻¹ of artinite and at 725 and 760 cm⁻¹ of dypingite are ascribed to CO₃²⁻ v₂ in-plane bending mode. The Raman spectrum of artinite in the OH stretching region is characterised by two sets of bands: (a) an intense band at 3593 cm⁻¹ assigned to the MgOH stretching vibrations and (b) the broad profile of overlapping bands at 3030 and 3229 cm⁻¹ attributed to water stretching vibrations. X-ray diffraction studies show the minerals are disordered. This is reflected in the difficulty of obtaining Raman spectra of reasonable quality and explains why the Raman spectra of these minerals have not been previously or sufficiently described.

KEYWORDS: Sequestration of greenhouse gases; Magnesium Carbonate; (CO₃)²⁻; artinite; dypingite; Raman spectroscopy

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INTRODUCTION

The ability to be able to easily and readily detect minerals is of importance,^{1,2} especially so where carbonate minerals are concerned. The technique of infrared spectroscopy does meet these requirements. What is not known is that many carbonate-containing minerals especially the secondary minerals are soluble and can translocate. The proposal to remove greenhouse gases by pumping CO₂ several kilometres below the ground implies that many carbonate containing minerals will be formed. Two magnesium carbonate minerals which may form under such conditions of high CO₂ partial pressure are dypingite Mg₅(CO₃)₄(OH)₂·5H₂O³⁻⁷ and artinite Mg₂(CO₃)(OH)₂·3H₂O⁸⁻¹⁷.

Vibrational spectroscopy has proven very useful for the study of minerals¹⁸⁻²³. Indeed, Raman spectroscopy has also proven to be very useful for the study of diagenetically related minerals as often occurs with many carbonate minerals²⁴⁻³³. Some previous studies have been undertaken by the authors, using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated sulphate solutions. This paper reports the detection and structural analysis of two magnesium carbonate minerals namely artinite and dypingite using Raman spectroscopy complimented with infrared spectroscopy. The application of this work is important for the understanding of the geosequestration of greenhouses gases and the consequential detection of carbonate bearing minerals.

EXPERIMENTAL

Minerals

The following minerals were used in this research (a) Dypingite - Yoshikawaite, Shinshiro Shi, Aichi Prefecture, Japan (b) Sample 4 Dypingite - Clear Creek District, Southern San Benito County, California (c) Sample 3 Artinite - Clear Creek District, Southern San Benito County, California (d) Sample 7 Artinite - Higasi-Kuroda-Guchi, Inasa-Cho, Inasa-Gun, Aichi Prefecture, Japan. Where possible the phase purity of

the minerals was checked by X-ray diffraction and the chemical composition by EDX measurements.

Raman microprobe spectroscopy

The crystals of halogenated carbonates were placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a nominal resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Details of the technique have been published by the authors^{18-23,34-36}.

Mid-IR spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the $4000\text{--}525\text{ cm}^{-1}$ 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.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be selected and allows 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 Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

RESULTS AND DISCUSSION

Spectroscopy of the carbonate anion

Nakamoto *et al.* first published and tabulated the selection rules for unidentate and bidentate anions including the carbonate anion³⁷. The free ion, CO_3^{2-} with D_{3h} symmetry exhibits four normal vibrational modes; a symmetric stretching vibration (ν_1), an out-of-plane bend (ν_2), a doubly degenerate asymmetric stretch (ν_3) and another doubly degenerate bending mode (ν_4). The symmetries of these modes are A_1' (R) + A_2'' (IR) + E' (R, IR) + E'' (R, IR) and occur at 1063, 879, 1415 and 680 cm^{-1} respectively. Generally, strong Raman modes appear around 1100 cm^{-1} due to the symmetric stretching vibration (ν_1), of the carbonate groups, while intense IR and weak Raman peaks near 1400 cm^{-1} are due to the asymmetric stretch (ν_3). Infrared modes near 800 cm^{-1} are derived from the out-of-plane bend (ν_2). Infrared and Raman modes around 700 cm^{-1} region are due to the in-plane bending mode (ν_4). This mode is doubly degenerate for undistorted CO_3^{2-} groups³⁷. As the carbonate groups become distorted from regular planar symmetry, this mode splits into two components³⁷. Infrared and Raman spectroscopy provide sensitive test for structural distortion of CO_3^{2-} .

Raman Spectroscopy

The Raman spectra of two artinite mineral samples from Aichi Prefecture and Clear Creek in the 170 to 1170 cm^{-1} are shown in Fig. 1. The Raman spectra of dypingite from Clear Creek and Yoshikawaite in this spectral region are shown in Fig. 2. A very sharp band is observed at 1092 cm^{-1} for artinite and is assigned to the CO_3^{2-} ν_1 symmetric stretching mode. For the mineral dypingite the band is observed at 1120 cm^{-1} . Farmer³⁸ reported the ν_1 mode for artinite as 1087 cm^{-1} but the band for dypingite was not stated. Farmer also shows the Raman spectrum of artinite (page 266) and states that the Raman spectra of several hydrated magnesium carbonates could not be obtained and concluded that this was a result of disorder in the structure of the minerals. In both sets of Raman spectra an additional low intensity band is observed at 1060 cm^{-1} (artinite) and ~1092 cm^{-1} (dypingite). Coleyshaw *et al.*³⁹ reported the Raman and infrared spectra of selected synthetic and natural hydrated magnesium carbonate minerals. These authors³⁹ gave the position of the ν_1 band for synthetic lansfordite as 1098 cm^{-1} and for natural nesquehonite as 1100 cm^{-1} . Sharp infrared bands at 1071 (Yoshikawaite) with a shoulder at 1078 cm^{-1} (Clear Creek) are attributed to the $(\text{CO}_3)^{2-}$ carbonate symmetric stretching mode. The

observation of this mode in the infrared spectrum provides evidence for the distortion of the carbonate anion and consequential loss of symmetry. Such a band should be not observed in the infrared spectrum but is very intense in the Raman spectrum, as is observed. The infrared band is observed at 1076 cm^{-1} for artinite (Clear Creek) and 1083 cm^{-1} for the Aichi artinite.

A low intensity band around 920 cm^{-1} is ascribed to MgOH deformation vibration. Such a vibration is likely to be of very low intensity in the Raman spectrum and of high intensity in the infrared spectrum. The band is very weak in the Raman spectrum of dypingite but may be observed at around 934 cm^{-1} . In the infrared spectrum two intense infrared bands are observed at 948 and 1008 cm^{-1} (Yoshikawaite dypingite) and 947 and 1012 cm^{-1} (Clear Creek). These bands are observed at 947 and 1017 cm^{-1} for the artinite Clear Creek sample and at 952 and 995 cm^{-1} for the Aichi artinite.

A very weak Raman band is observed at 790 cm^{-1} for artinite and 800 cm^{-1} for dypingite and is assigned to the CO_3^{2-} out-of-plane bend (ν_2). In the Raman spectrum of artinite as shown by Farmer a low intensity band at 810 cm^{-1} for artinite may be assigned to this vibration. For the Yoshikawaite dypingite, two infrared bands are observed at 852 and 882 cm^{-1} . These bands are assigned to the $(\text{CO}_3)^{2-}$ ν_2 bending modes. A very low intensity band is observed for the Clear Creek artinite at 844 cm^{-1} which may correspond with this assignment. Farmer also commented on the difficulty of obtaining spectra for hydrated and hydrated hydroxy carbonate magnesium minerals and commented that the internal modes of the internal CO_3^{2-} vibrations are either broadened or not observed. The observations reported here are in harmony with Farmer's commentary. Coleyshaw *et al.*³⁹ also did not find any intensity of bands in this position for the Raman spectra of lansfordite and nesquehonite. These authors reported the infrared spectra of CO_3^{2-} out-of-plane bend (ν_2) as 854 cm^{-1} . In the Raman spectra of artinite a reasonably intense band at around 700 cm^{-1} is assigned to the CO_3^{2-} ν_2 in-plane bend. Only a single band is observed for artinite whereas two bands are found for dypingite at 725 and 760 cm^{-1} . Farmer³⁸ in the Raman spectrum of artinite reported two bands for this vibrational mode at 693 and 704 cm^{-1} . Coleyshaw *et al.*³⁹ reported bands at 698 and 774 cm^{-1} for synthetic lansfordite, 705 and 771 cm^{-1} for natural nesquehonite and 713 and 781 cm^{-1} for

synthetic nesquehonite. For the Yoshikawaite dypingite infrared spectrum low intensity bands are observed at 755 and 799 cm^{-1} . For the Aichi artinite these bands are found at 722 and 762 cm^{-1} . These bands are assigned to the $(\text{CO}_3)^{2-}$ ν_4 bending modes. The observation of more than one band supports the concept that there are multiple $(\text{CO}_3)^{2-}$ bending modes as a result of the distortion of the $(\text{CO}_3)^{2-}$ units in the dypingite and artinite structures.

The Raman spectra of artinite and dypingite in the 1250 to 2300 cm^{-1} region are displayed in Figs. 3 and 4. A very low intensity band at 1453 cm^{-1} is observed for the Aichi artinite and two very low intensity bands at 1412 and 1465 cm^{-1} for the Clear Creek artinite. Very weak bands are also observed for dypingite in this spectral region. For the Yoshikawaite dypingite Raman bands are observed at 1366, 1447 and 1524 cm^{-1} and at 1365 and 1527 cm^{-1} for Clear creek dypingite. These bands are assigned to CO_3^{2-} ν_3 antisymmetric stretching vibrations. These bands were not observed in the Raman spectrum of artinite as reported by Farmer³⁸. Based upon infrared spectra, Farmer³⁸ reported ν_3 bands for artinite at 1320, 1355 and 1440 cm^{-1} . No infrared bands were provided for dypingite. Coleyshaw *et al.*³⁹ published results for the ν_3 bands for lansfordite and nesquehonite. Raman bands for synthetic lansfordite were found at 1424 and 1514 cm^{-1} and for synthetic nesquehonite at 1423 and 1516 cm^{-1} ³⁹. Even though these bands are of very low intensity in the Raman spectrum, the bands are of high intensity in the infrared spectrum. The $(\text{CO}_3)^{2-}$ symmetric stretching mode is complimented with the antisymmetric stretching modes found in the 1300 to 1450 cm^{-1} region where a series of overlapping infrared bands are observed providing a complex spectral infrared profile. For artinite the $(\text{CO}_3)^{2-}$ antisymmetric stretching modes are observed at 1325, 1381, 1439 cm^{-1} (Aichi) and 1376, 1441, 1535 cm^{-1} (Clear Creek). For the dypingite from Clear Creek, these $(\text{CO}_3)^{2-}$ anti symmetric stretching bands are observed at 1312, 1438, 1534 and 1585 cm^{-1} . These bands appear better defined for the Yoshikawaite dypingite with clearly resolved bands at 1380, 1405, 1479 1509 cm^{-1} .

The bands observed at 1660 cm^{-1} for Clear Creek artinite and at 1673 cm^{-1} for Aichi artinite are assigned to the water bending mode. This band is normally strongly infrared active and very weakly Raman active if observed at all. The position of this

band provides evidence of strongly hydrogen bonded water in the artinite mineral structure. Weakly or non-hydrogen bonded water is normally observed at around 1595 cm^{-1} as may be found in the infrared spectrum of water vapour. For liquid water the water bending vibration is found at 1630 cm^{-1} . A second band for artinite is found at around 1750 cm^{-1} . This band provides evidence for some water molecules being very strongly hydrogen bonded in the artinite structure. In the single crystal X-ray study of artinite, Akao and Iwai indicated the hydrogen bonding in artinite was very strong¹⁰. This work proved the water is hydrogen bonded to the carbonate anion in the artinite structure. Other studies by Smolin³ support the concept of very strong hydrogen bonding in hydrated magnesium carbonate minerals. Some authors comment on the disorder in artinite and suggest that water is strongly hydrogen bonded water is necessary for the stability of the mineral^{11,13,14}. The structure of dypingite has not been as well researched⁷. However it is thought that a similar hydrogen bonding network of water and carbonate units exist for dypingite. In the Raman spectra of the two dypingites, a band is observed at around 1603 cm^{-1} which is assigned to weakly hydrogen bonded water. For the Yoshikawaite dypingite Raman bands are observed at 1713 , 1751 and 1767 cm^{-1} . The first band is likely to be due to strongly hydrogen bonded water in the dypingite structure.

The Raman spectra of artinite and dypingite in the 2525 to 3800 cm^{-1} region are shown in Figs. 5 and 6. The Raman spectrum of artinite in this spectral region is characterised by two sets of bands: (a) an intense band at 3593 cm^{-1} assigned to the MgOH stretching vibrations and (b) the broad profile of overlapping bands at 3030 and 3229 cm^{-1} attributed to water stretching vibrations. For the Clear Creek artinite three water bands are observed at 2922 , 3015 and 3209 cm^{-1} . For dypingite an intense band at 3648 cm^{-1} is assigned to the MgOH stretching bands. For the Clear Creek dypingite two bands are found at 3421 and 3515 cm^{-1} and are assigned to water OH stretching vibrations. For the Yoshikawaite dypingite the water bands are observed at 3427 and 3519 cm^{-1} . For the Clear Creek dypingite other low intensity bands are shown at 2859 , 2930 and 3139 cm^{-1} . The position of these bands fits well with the concept of some water units being strongly hydrogen bonded in the dypingite structure.

The infrared spectra of dypingite in the OH stretching region also displays these two features: (a) two sharp bands at around 3647 and 3686 cm^{-1} and (b) a number of broad overlapping bands centred upon 3289, 3380, 3447 cm^{-1} (Yoshikawaite). The first two bands are assigned to the hydroxyl stretching vibrations of OH units whereas the broad bands are assigned to water stretching bands. The variation in intensity of the water OH stretching bands shows that some variation in the formula of dypingite may occur and is a function of the water partial pressure. Such variation in intensity of the bands assigned to water stretching vibrations may be complicated by the adsorption of water on the mineral surface. The same explanation is suitable for the mineral artinite. Two sharp bands at 3649 and 3685 cm^{-1} are observed for the Clear creek artinite and three bands at 3651, 3685 and 3696 cm^{-1} for the Aichi artinite. These bands are attributed to the stretching vibrations of the OH units. The other bands in the spectra are assigned to water stretching bands.

CONCLUSIONS

The concept of geosequestration involves the pumping of green house gases to significant depths below the surface of the earth. The high partial pressure of CO_2 is significant in that many different types of carbonates will be formed. Of significance are the magnesium carbonate minerals which will be formed by reaction of the liquefied CO_2 with magnesium minerals such as brucite and periclase. Among these minerals there is the possibility of the formation of dypingite and artinite which are formed at reasonably low temperatures.

Raman spectroscopy has been used to characterise the two minerals artinite and dypingite and the bands related to the mineral structure. X-ray diffraction studies show the minerals are disordered. This is reflected in the difficulty of obtaining spectra of reasonable quality and explains why the Raman spectra of these minerals have not been previously or sufficiently described. The minerals are characterised by CO_3^{2-} ν_1 symmetric stretching modes but very weak antisymmetric stretching and bending modes. These bands are difficult to detect.

Acknowledgments

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List of Figs

Fig. 1 Raman spectra of artinite from Clear Creek and Aichi Prefecture in the 170 to 1170 cm^{-1} region.

Fig. 2 Raman spectra of dypingite from Clear Creek and Yoshikawaite in the 170 to 1170 cm^{-1} region.

Fig. 3 Raman spectra of artinite from Clear Creek and Aichi Prefecture in the 1250 to 2500 cm^{-1} region.

Fig. 4 Raman spectra of dypingite from Clear Creek and Yoshikawaite in the 1250 to 1800 cm^{-1} region.

Fig. 5 Raman spectra of artinite from Clear Creek and Aichi Prefecture in the 2525 to 3600 cm^{-1} region.

Fig. 6 Infrared spectra of dypingite from Clear Creek and Yoshikawaite in the 2525 to 3600 cm^{-1} region.

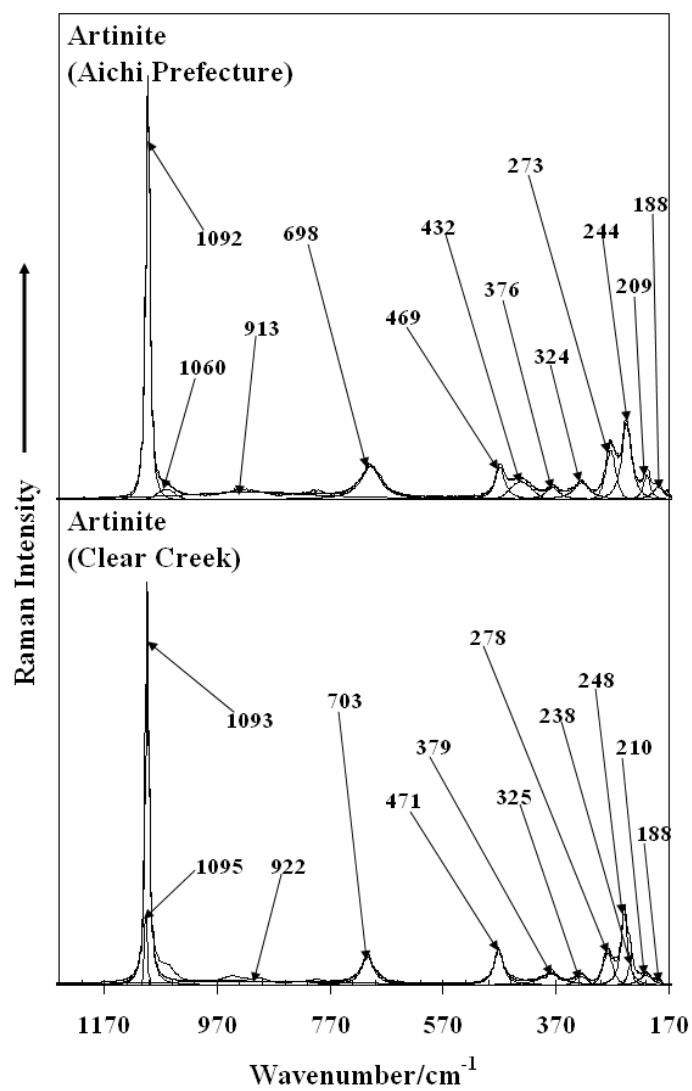


Fig. 1

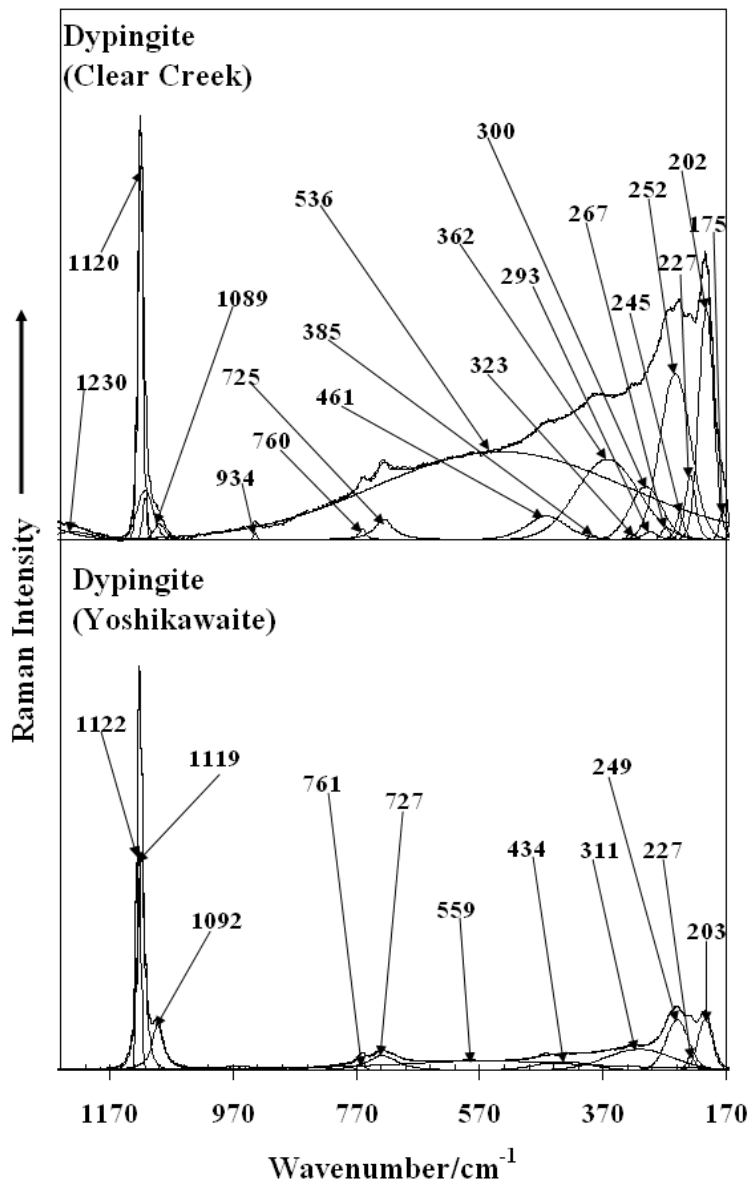


Fig. 2

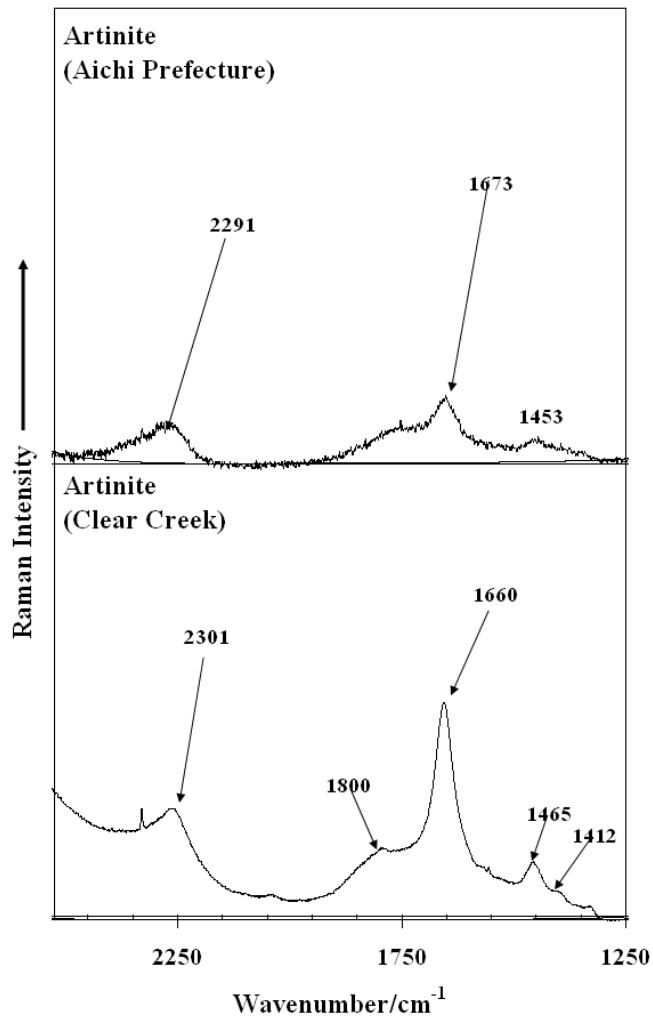


Fig. 3

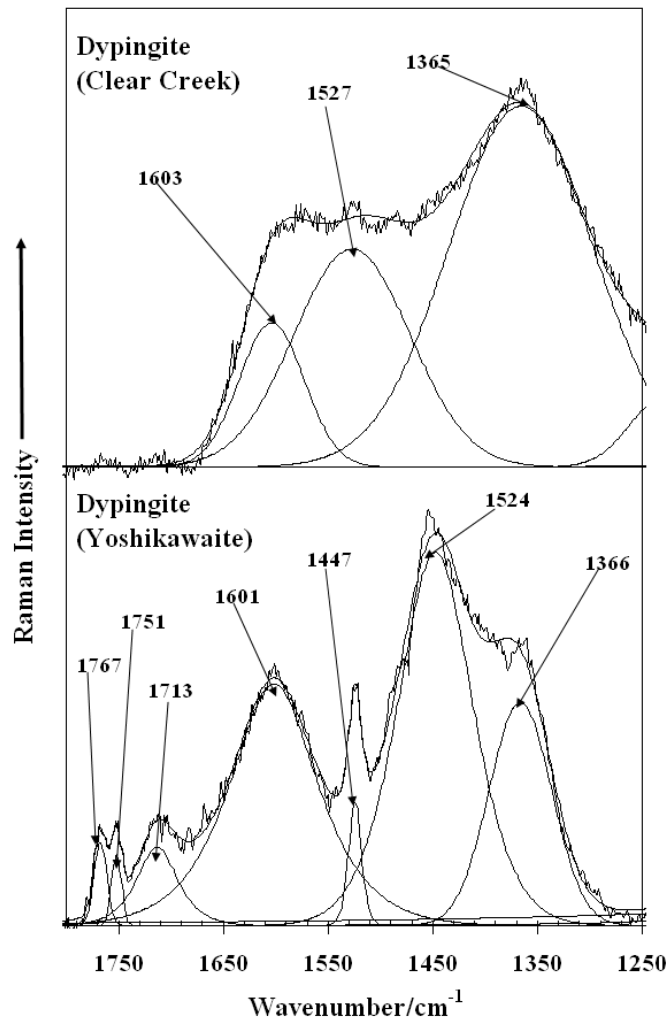


Fig. 4

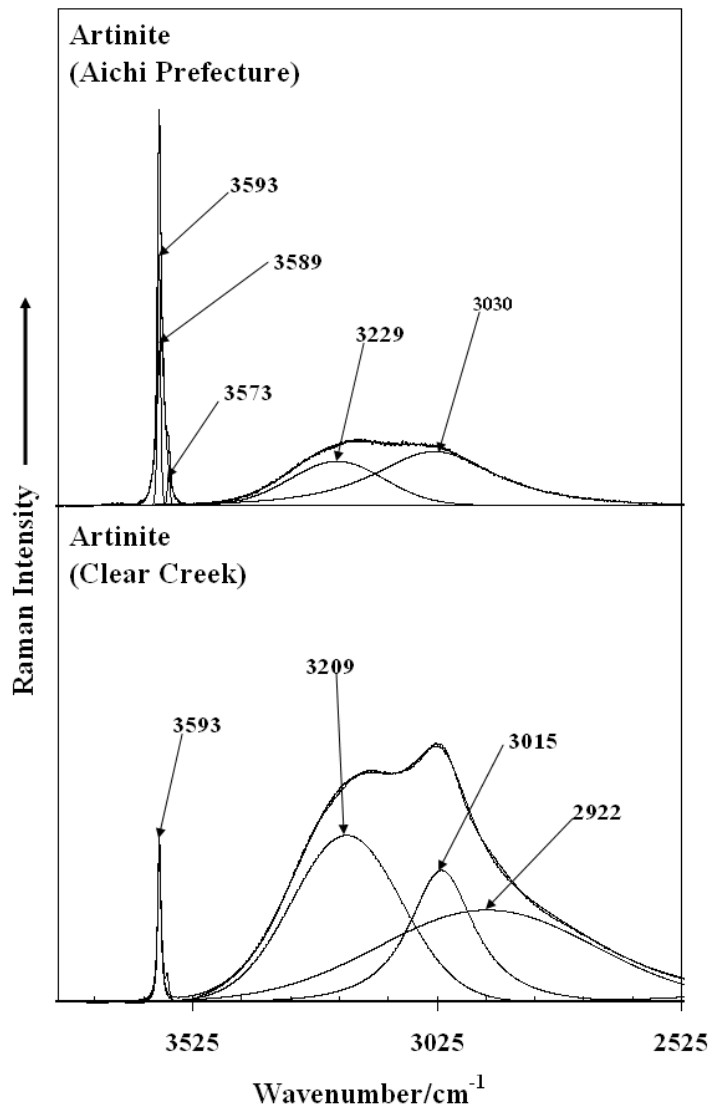


Fig. 5

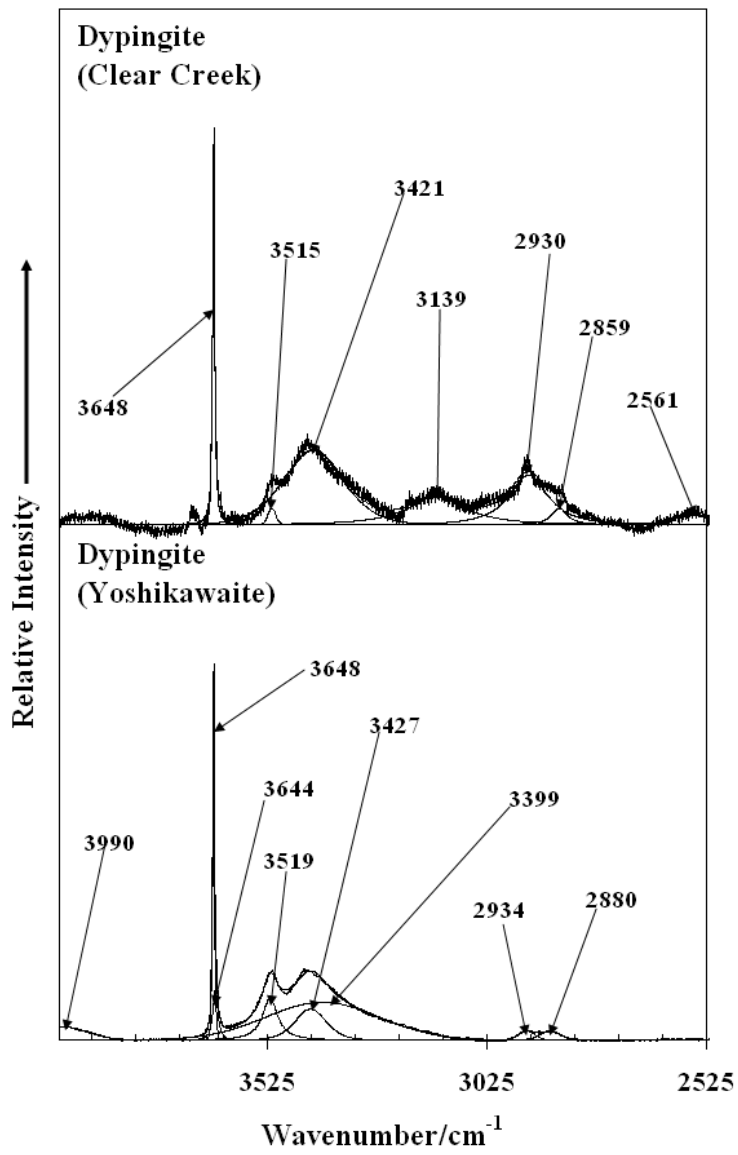


Fig. 6