

The structure of the kaolinite minerals — a FT-Raman study

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ABSTRACT: The Fourier transform Raman spectra of the kaolinite minerals have been measured in the 50–3800 cm^{-1} region using near infrared spectroscopy. Kaolinites are characterized by remarkably intense bands in the 120–145 cm^{-1} region. These bands, attributed to the O–Si–O and O–Al–O symmetric bending modes, are both polymorph and orientation dependent. The 200–1200 cm^{-1} spectral range is a finger-print region for clay minerals and each kaolinite clay has its own characteristic spectrum. The structure of clays is fundamentally determined by the position of hydroxyl groups. Fourier-transform Raman spectroscopy readily enables the hydroxyl stretching region to be examined allowing identification of the component bands. The advantages of FT-Raman spectroscopy are shown to enhance the study of the kaolinite structure.

The kaolinite clay minerals have been extensively studied using infrared (IR) spectroscopy (Lazarev, 1972; Farmer, 1974). However, there have been only a few Raman studies of these clay minerals (Wiewiora *et al.*, 1979; Johnston *et al.*, 1985; Michaelian, 1986; Frost *et al.*, 1993). Further, such papers concentrated on the study of kaolinites and, to date, no detailed Raman studies of dickites and halloysites have been forthcoming. Detailed IR studies of the hydroxyl stretching region of kaolinites and dickites have been undertaken (Brindley *et al.*, 1986; Prost *et al.*, 1989; Johnston *et al.*, 1990). Few detailed analyses of halloysites have been forthcoming, and these studies did not refer to the lattice vibrations of these clay minerals. Often the assumption is made that because of the similarity between the IR spectra of kaolinites and halloysites that the lattice structures are also similar. This is not necessarily so, because of the folding of the halloysite layers. Studies of the hydroxyl stretching region and the lattice vibrations of the clay minerals are important for the analysis of clay adsorbent interactions.

The information obtained from Raman spectral studies may not be the same as that from IR spectroscopy as the Raman technique measures the symmetric vibrations and the physics of the Raman emission is very different from the physics of IR absorption where the spectral results depend on changes in dipole moments. Raman spectral studies would complement these IR studies and provide additional information on other kaolinite polymorphs. Further Raman spectroscopy can provide information on the lattice region of the clay minerals (Frost, 1995). Such information can be difficult to obtain using FTIR spectroscopy. The introduction of Fourier transform Raman spectroscopy (FTRS), often called FT-Raman, has brought a new impetus to Raman spectroscopy. It has allowed the study of clay minerals that were previously difficult to measure because of laser induced fluorescence and provides ready access to the extensive data handling facilities that are available with a commercial FT-IR spectrometer (Frost *et al.*, 1993). The purpose of this paper is to report the detailed study of FT-Raman spectroscopy

of the kaolinite minerals with particular emphasis on the lattice and hydroxyl stretching regions.

EXPERIMENTAL

Clay mineral samples

Clay minerals were obtained from Wards natural science establishment, Rochester, New York, from The Clay Minerals Society repository and from the Commonwealth Scientific and Industrial Research Organisation, Glen Osmond, South Australia. Minerals were also collected from a number of Australian mineral deposits. The analysis of the minerals reported in this paper are chiefly the Clay Mineral Society standards. The minerals were dried in a desiccator to remove adsorbed water and were used without further purification. Samples were analysed for phase purity using X-ray diffraction techniques before Raman spectroscopic analysis. X-ray diffraction was also used to check the layer spacings and the crystal domain size of the minerals.

Raman spectroscopy

Raman spectra were obtained using two instruments; firstly the Perkin-Elmer 2000 series Fourier Transform spectrometer fitted with a Raman accessory and a Biorad series 2 FTIR spectrometer. The Perkin-Elmer 2000 series FTIR spectrometer equipped with a Raman accessory comprised a Spectron Laser Systems SL301 Nd-YAG laser operating at a wavelength of 1064 nm, and a Raman sampling compartment incorporating 180° optics. The FT-IR spectrometer contained a quartz beam splitter capable of covering the spectral range 15000–4000 cm⁻¹. The Raman detector was a highly sensitive indium-gallium-arsenide detector and was operated at room temperatures. Under these conditions Raman shifts would be observed in the spectral range 3000–150 cm⁻¹. Spectra were corrected for instrumental function and detector response. Raman spectra below 150 cm⁻¹ and in the 3500–3800 cm⁻¹ range were obtained using a Biorad series 2 FTIR spectrometer equipped with a Raman accessory comprising a spectraphysics T10-1064C Nd-YAG diode laser operating at 1064 nm. Measurement times between 0.5 and 2 h were used to collect the Raman spectra with a signal to noise ratio better than 100/1 at a resolution of 2 cm⁻¹. Raman spectra were collected as single beam

spectra and were corrected for instrumental effects. A laser power of 100 mW was used, being low enough to prevent damage to the minerals, but was found to be sufficient to produce quality spectra in a reasonable time. No heating, as may be evidenced by the lack of thermoluminescent background, was observed. Raman spectra were obtained directly by using a sample of the unpurified mineral directly in the incident beam. It was found that the best spectra were obtained by simply placing a piece of the non-powdered kaolinite clay sample in the beam, whereas the powdered clay gave inferior spectra. Spectral manipulation such as baseline adjustment, smoothing and normalization were performed using the Spectrocalc software package (Galactic Industries Corporation, NH, USA). Band component analysis was carried out using the peakfit software package by Jandel Scientific.

Spectroscopy and spectral manipulation

Spectral bands were 'ratioed' to the instrument profile function determined by recording the spectrum of a calibrated grey body, calibrated at the National Standards Laboratory at CSIRO, Linfield, Sydney, Australia. Such a method ensures the correct instrumental function is taken into account and that the true spectrum is measured. Spectra such as illustrated for example in Figs. 1 a,c,d and e, were smoothed using a nine point Savitsky-Golay method and were then interpolated at 0.2 cm⁻¹ intervals for band component analysis. This 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 Lorentz-Gauss ratio was maintained at values >0.7 and fitting was undertaken until reproducible results were obtained giving fits with correlations >0.995.

The ability of FT-Raman spectroscopy to measure adequately the Raman spectra of the kaolinite and other clay minerals is apparently very much dependent on the crystallinity of the clay. The more crystalline the kaolinite clay mineral, the more easily can the FT-Raman spectrum of the clay be determined. The spectra of powdered or ground samples are more difficult to obtain. This does not mean that disordered or

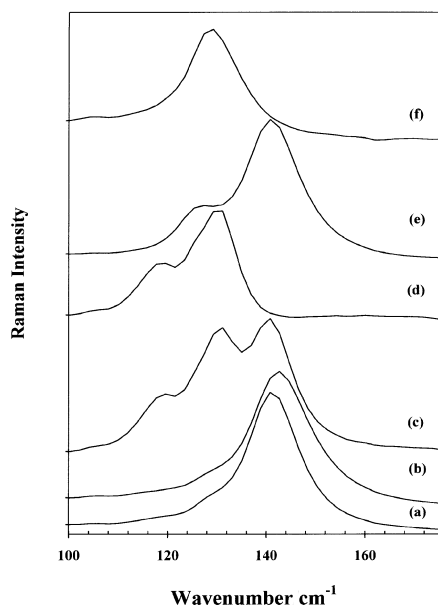


FIG. 1. The FT-Raman spectra in the 100–150 cm^{-1} region, of (a) kaolinite (KGa-1); (b) kaolinite (KGa-2); (c) dickite (San Juanito); (d) dickite (Sainte Claire); (e) halloysite (Eureka); and (f) halloysite (New Zealand).

powdered samples cannot be measured, it simply means that data collection times are longer. The intensity of the FT-Raman scattering depends on the Raman cross-section which it is considered depends on the long-range order of the kaolinite crystals. Consequently, the FT-Raman spectra of disordered clays are more difficult to obtain.

RESULTS AND DISCUSSION

Low wavenumber region

The FT-Raman spectra in the 100–200 cm^{-1} region for a series of selected kaolinites, dickites and halloysites are shown in Fig. 1. In general, the kaolinite minerals are characterized by very intense bands centred at $\sim 143 \text{ cm}^{-1}$ for kaolinite, $\sim 141 \text{ cm}^{-1}$ for halloysite and $\sim 130 \text{ cm}^{-1}$ for dickites and are at least an order of magnitude more intense than the other bands in the 200–1200 cm^{-1} region. By using band component analysis of the FT-Raman band profiles between 100 and 200 cm^{-1} , bands were also found at 131, 121, and 119 cm^{-1} for the respective clays (Fig. 2, A–F).

Similar bands have been identified using conventional dispersive Raman spectroscopy (Wiewiora *et al.*, 1979; Johnston *et al.*, 1985; Michaelian, 1986). The bands were not well defined and their existence was tentative (Wiewiora *et al.*, 1979). The bands were superimposed on a strongly fluorescent background making interpretation difficult (Michaelian, 1986). The major advantage of FT-Raman spectroscopy is the ability to measure bands in the low-frequency region with no fluorescent background. This enables the accurate determination of spectra in the low frequency range. Such bands are difficult to determine by conventional far IR techniques.

The detailed results of the band component analyses are reported in Table 1 and the band component analyses of the 100–200 cm^{-1} spectral region are shown in Fig. 2, A–F. The bands in this region are attributed to the symmetric bending modes of the O–Si–O and O–Al–O groups. The results of the band component analyses show that for halloysites and kaolinites the predominant band is centred at 141 cm^{-1} with >85% of the total area. The band centre for the New Zealand halloysite is the same as that of the ordered kaolinite with that

TABLE 1. Band component analyses of the symmetric bending region of a series of kaolinites, dickites and halloysites.

Clay mineral	Band centres	Half-width	% area
Kaolinite KGa-1	120 cm^{-1}	19 cm^{-1}	6
	131	15	7
	141	14	88.5
Kaolinite KGa-2	121	19	2
	132	15	5
	143	15	93.6
	141	15	93.6
Dickite, San Juanito	119	11	17
	131	10	33
	141	9	32
Dickite, Sainte Claire	118	9	31
	125	8	11.6
	131	8	57.3
Halloysite (Eureka)	105	29	12
	118	19	7
Halloysite (NZ)	129	12	80
	118	19	2
	126	9	13
	141	13	85

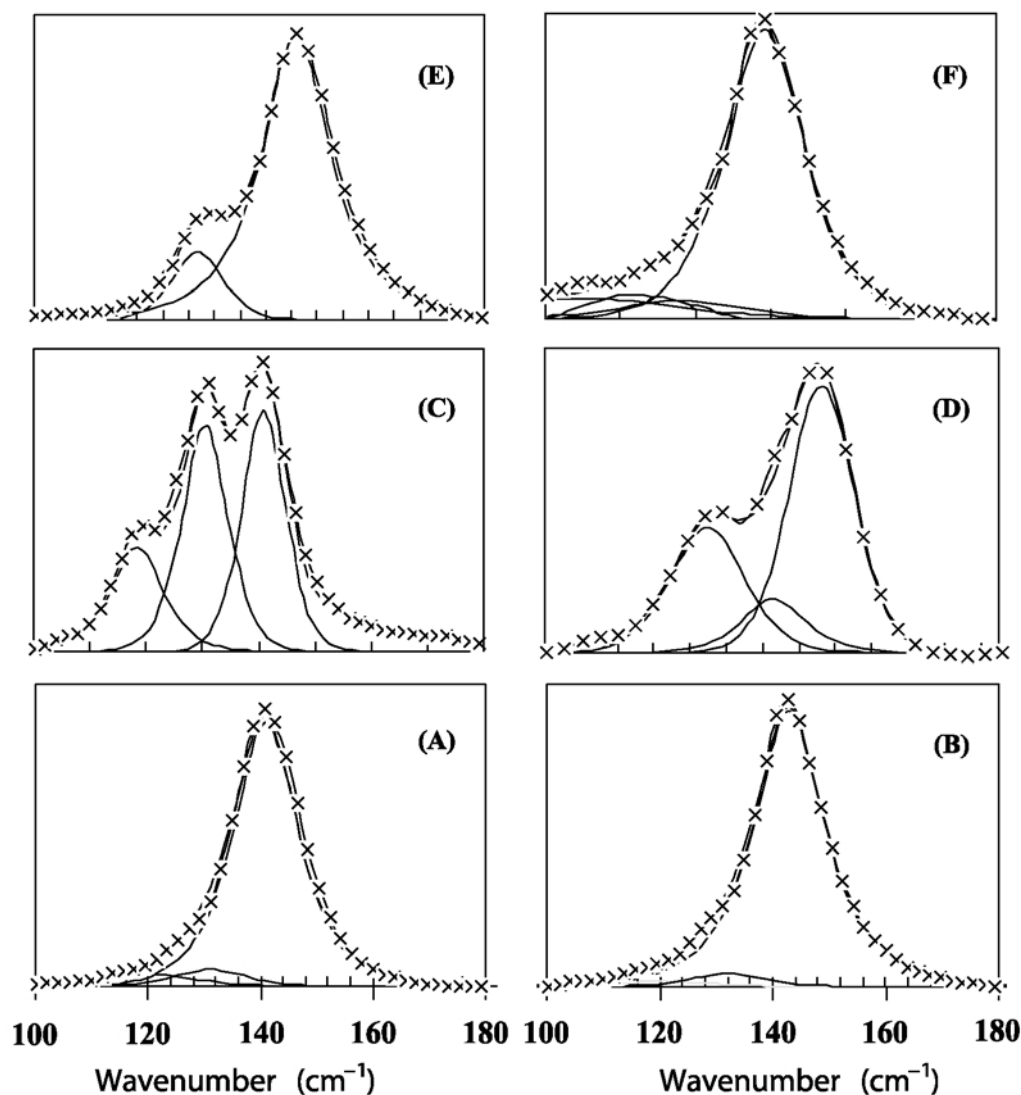


FIG. 2. The band component analysis of the FT-Raman spectrum of (A) kaolinite (KGa-1); (B) kaolinite (KGa-2); (C) dickite, San Juanito; (D) dickite, Sainte Claire; (E) halloysite, New Zealand; and (F) halloysite, Eureka, in the $100\text{--}150\text{ cm}^{-1}$ spectral region.

band centre for the disordered kaolinite (KGa-2) frequency occurring at a higher frequency than that of the ordered kaolinite (KGa-1). The Raman spectrum of the dickite mineral from San Juanito is complex with bands at 119 , 131 and 141 cm^{-1} , the distribution of band areas between these bands being in the ratio of $1/2/2$. The dickite mineral from Sainte Claire shows three peaks at 118 , 125 and 131

cm^{-1} . The ratio of the areas of the bands for this dickite is $3/1/6$. The halloysite from New Zealand shows peaks at 127 and 143 cm^{-1} . These frequencies are similar to those of kaolinite whereas the spectrum of Eureka halloysite with peaks at 120 and 129 cm^{-1} resembles that of dickite more closely. The half-width at half-height is 12.7 cm^{-1} for the Eureka halloysite, 12.0 cm^{-1}

for the New Zealand halloysite, 13.6 cm^{-1} for the ordered kaolinite and 14.8 cm^{-1} for the disordered kaolinite. Half-widths are an indication of the crystallinity of the kaolinite mineral with the more highly crystalline kaolinite having the smallest half-width and the more disordered kaolinite the greatest half-width. This observation is very true for the dickites with the half-widths of these bands being $\sim 10\text{ cm}^{-1}$. The half-widths are significantly less for all dickite bands compared with those for the kaolinites and halloysites. These results and the results obtained from the analysis of a large number of Australian kaolinite minerals indicate that this part of the kaolinite spectral region is very much sample orientation dependent. Similar bands and positions were observed by Johnston *et al.* (1985) for Georgia Kaolinite (KGa-1) and the Mesa Alta kaolinite at 141 and 131 cm^{-1} , but the bands for Keokuk kaolinite were observed at 132 and 120 cm^{-1} . The band at 141 cm^{-1} is Raman active only whereas the 130 cm^{-1} band is both Raman and IR active. It is considered that the band at $\sim 143\text{ cm}^{-1}$ in kaolinite and halloysites consists of two overlapping bands of similar widths to the dickite bands and this results in a much broader band with a width of 15 cm^{-1} .

The question arises as to the assignment of these band components in this spectral region. It is interesting that in the titania mineral anatase, a very intense band occurs in the $143\text{--}154\text{ cm}^{-1}$ range and this band has been shown to be pressure dependent (Balachandran & Eror, 1982, and Ohsaka *et al.*, 1978). The band has been attributed to the symmetric bend of O–Ti–O. The Georgia kaolinite was analysed using ICP-AES methods and the concentration of TiO_2 was found to be 2.63%. The band profile in the 141 cm^{-1} region of the kaolinites KGa-1 and KGa-2 may have some spectral component of the titania impurity in the overall band profile. However, the orientation dependence of these bands would support the hypothesis that the presence of titania is not contributing intensity to the band profile. Preliminary temperature-dependence studies show that increased temperature moves these bands to higher wavenumbers.

Farmer (1974) reported the predicted vibrations of an ideal hexagonal (Si_2O_5) layer. Ishii *et al.* (1967) predicted the frequencies of these vibrations one of which is the Raman active symmetric bend with a predicted frequency of 127 cm^{-1} . One possible assignment of the bands in this region is

that the higher frequency (143 cm^{-1}) is the O–Al–O symmetric bend and the lower frequency band (127 cm^{-1}) is that of the O–Si–O symmetric bend. This conclusion is supported by the dispersive Raman microprobe analysis of tremolite and talc with the strongest bands occurring at 125 cm^{-1} and the weaker band at 147 cm^{-1} (Blaha & Rosaco, 1978; Rosaco & Blaha, 1980). In the study of sheet silicates by Loh (1973), which included Raman and far IR spectra of a series of minerals including lepidolite, muscovite, phlogopite and chlorites, it was found that Raman bands occurred at ~ 105 , 135 , and 157 cm^{-1} . In this study, these bands were attributed to the vibrational modes of the AlO_6 octahedron. These bands were assigned to the A_{1g} (ν_1), E_g (ν_2) and F_{2g} (ν_3) vibrational modes of the point group O_h . This analysis supports the conclusion that the 141 cm^{-1} band is the vibrational mode of the symmetric bend of the AlO_6 group of kaolinite. In any event, the very large intensity of these bands can only occur as a result of a vibrational mode which induces a very large change in polarizability. It is likely that the variation in the peak position is related to the stress on the kaolinite crystal structure and as a consequence is sample dependent. The high frequency of KGa-2 at 143 cm^{-1} is indicative of this tension compared with that of the other kaolinites and this in all probability is related to layer stacking.

The advantage of using FT-Raman spectroscopy is that bands in the $100\text{--}400\text{ cm}^{-1}$ region are easily measured and such bands are not easily obtained using FT-IR techniques. Dispersive conventional Raman spectroscopy inherently has the clay spectrum superimposed on the intense Rayleigh line, particularly if an excitation at 532 nm is used. Such spectroscopy was performed using triple monochromators with cooled photomultipliers and although such monochromators have excellent stray light rejection capabilities, the clay spectrum must still be removed from the background. The use of Raman microscopy employing CCD detectors is currently being explored and a useful comparison of FT-Raman and RMS spectroscopy cannot be made at this stage. The disadvantage of using FT-Raman spectroscopy is the loss of efficiency on using near-IR excitation at 1064 nm . The Raman scattering decreases as the fourth power of the excitation radiation, so the efficiency of the FT-Raman scattering at 1064 nm compared with 532 nm is 16 times less. Nevertheless, this loss of efficiency can be

minimized by the use of more laser power. Use of 100 mW is often ample power for FT-Raman but for weak scatterers 200 mW of power can be used. It is advantageous to use the minimum power required to obtain quality spectra. Care must be exercised when using higher powers because of local heating effects which may dehydrate the sample. This is particularly true when measuring the spectrum of halloysites. The use of FT-Raman has enabled detailed studies of the bands in the 100–200 cm^{-1} region to be obtained. This is important as the symmetric bending vibrations of the lattice occur in this region. Such bands would not normally be IR active, although because of a lack of symmetry, may appear as weak bands in the IR.

The hydroxyl stretching region

Table 2 reports the band centres, full widths at half heights and the normalized band areas for the series of kaolinites studied. The FT-Raman spectra of the hydroxyl stretching region is shown in Fig. 3. The band component analyses of the hydroxyl stretching region for the series of kaolinite minerals studied are shown in Fig. 4 (A–F). Five FT-Raman bands were found for the ordered kaolinite (KGa-1) and the disordered kaolinite (KGa-2) with peak centres at 3619, 3650, 3667, 3686 and 3695 cm^{-1} . These values are in excellent agreement with those values reported for the dispersive Raman spectroscopy of the ordered kaolinites (Johnston *et al.*, 1985). Spectra obtained using conventional Raman techniques are often limited by the signal to noise levels. Indeed, such effects are even more pronounced when using micro Raman spectroscopy, as may be observed in the work of Pajcini & Dhalemcourt (1994). The advantage of using FTRS is the improved signal to noise ratio allowing high quality spectra of all types of the kaolinite minerals to be measured. This then enables band fitting of the experimental profile to be determined.

The FT-Raman peak positions for the disordered kaolinite are in similar peak positions to those of the ordered kaolinite. The effect of disordering apparently moves the band centre for the outer hydroxyl to lower energy, corresponding to increased or more readily available hydrogen bonding, and moves the inner hydroxyl to higher energies. The half-widths of the bands for the disordered kaolinite are similar to those of the ordered kaolinite but the inner hydroxyl shows an increased half-width for the disordered kaolinite.

TABLE 2. Band component analyses of the hydroxyl symmetric stretching region of a series kaolinites, dickites and halloysites.

Clay mineral	Band centre (cm^{-1})	Half-width (cm^{-1})	% area
Kaolinite (KGa-1)	3619	8	31.6
	3650	20	15.3
	3667	21	8.8
	3686	13.5	13.8
	3695	11.5	30.5
Kaolinite (KGa-2)	3621	9	39.5
	3648	20	10.8
	3664	21	10.8
	3685	13	15.8
	3693	11	21.2
Dickite, San Juanito	3620.8	8	40.1
	3639	13	30
	3652	13	6
	3703	15	22.7
Dickite, Sainte Claire	3620	8	23.5
	3627	8	22
	3638	17	36.8
	3652	13	5.4
	3700	19	22.8
Halloysite, (NZ)	3622	15	32.2
	3630	17	22
	3660	28	8.2
	3680	22	9.2
	3698	19	28.4
Halloysite, Eureka	3620.5	15	32.2
	3630.5	17	11.3
	3655	28	9.5
	3679	28	16.2
	3698	17	28
	3712	29	3.6

Kaolinite contains two types of hydroxyl group, as do the other polymorphs: the first are the outer hydroxyl groups designated OuOH; and secondly the inner hydroxyl groups designated InOH. The OuOH hydroxyl groups are situated in the outer upper, unshared plane whereas the InOH groups are located in the lower shared plane of the octahedral sheet. In a highly ordered kaolinite such as the Georgia kaolinite (KGa-1), the four distinct bands are assigned as follows: the three higher frequency vibrations (ν_1, ν_2, ν_3) are due to the three outer or so-called inner surface hydroxyls (OuOH) and that the ν_4 band at about 3620 cm^{-1} is due to the inner hydroxyl (InOH) (Johnston *et al.*, 1990). The 3620 cm^{-1} IR band for kaolinite has been assigned

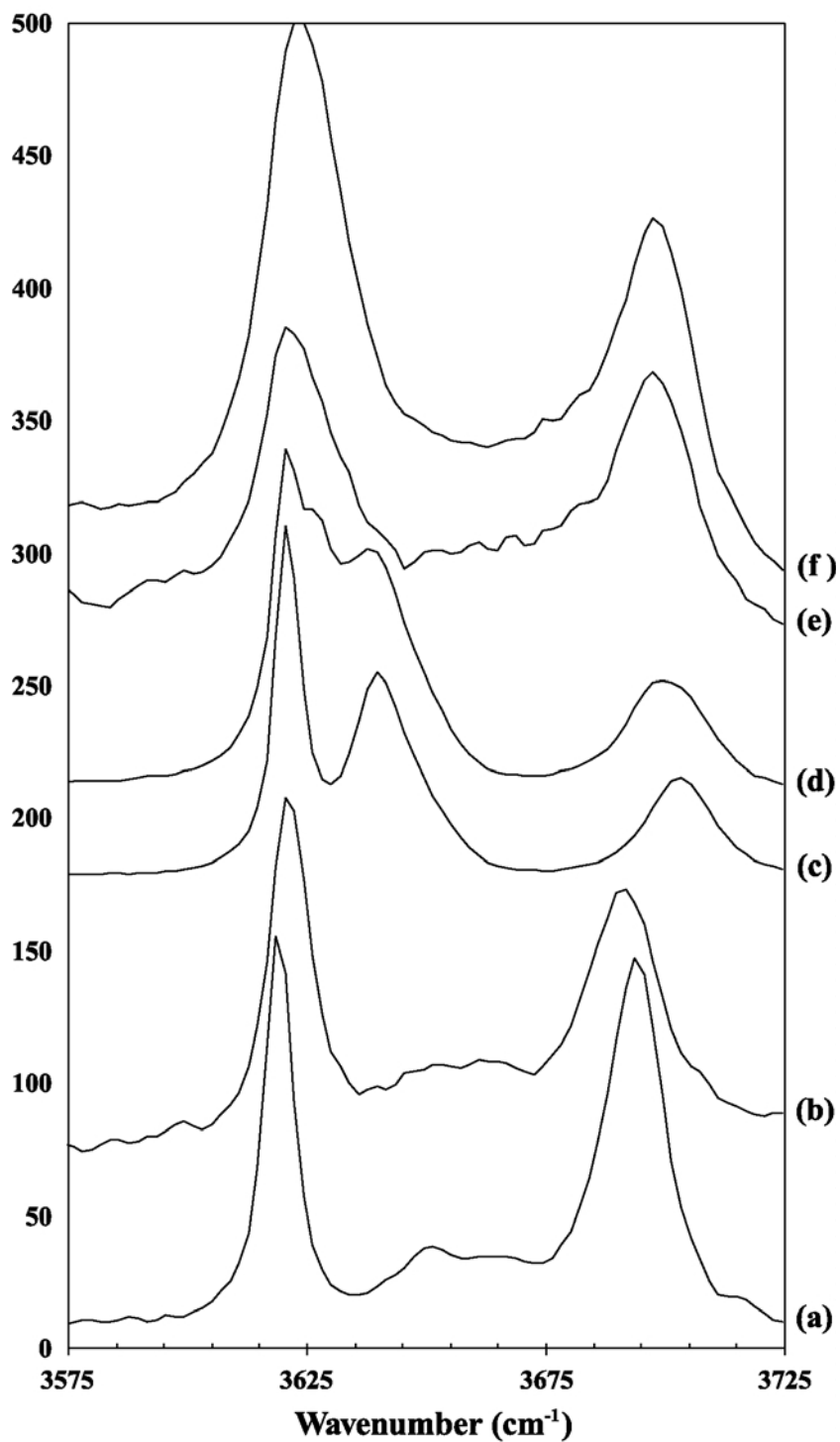


FIG. 3. The FT-Raman spectra in the 3550–3750 cm^{-1} region, of (a) kaolinite (KGa-1); (b) kaolinite (KGa-2); (c) dickite (San Juanito); (d) dickite (Sainte Claire); (e) halloysite (Eureka); and (f) halloysite (New Zealand).

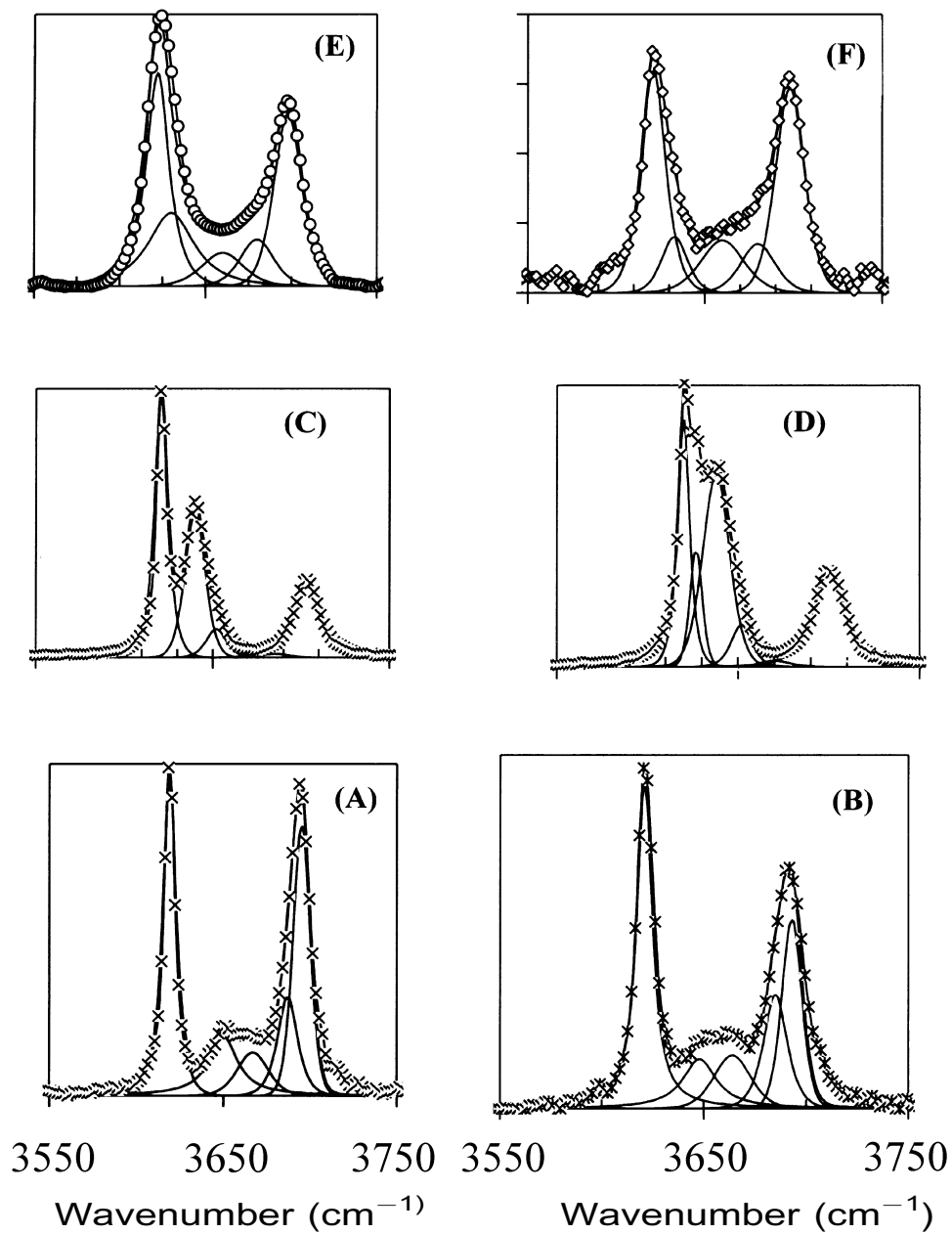


FIG. 4. The band component analysis of the FT-Raman spectrum of (A) kaolinite (KGa-1); (B) kaolinite (KGa-2); (C) dickite, San Juanito; (D) dickite, Sainte Claire; (E) halloysite, New Zealand; and (F) halloysite, Eureka, in the 3550–3750 cm^{-1} spectral region.

to the inner hydroxyl InOH (Ledoux & White, 1964; Wada, 1967; White *et al.*, 1970; Rouxhet *et*

al., 1977). The commonly accepted view is that the ν_1 and ν_2 bands are the coupled antisymmetric and

symmetric vibrations (Brindley *et al.*, 1986; Michaelian, 1986). The assignment of the ν_3 band is open to question but the suggestion has been made that the band is due to symmetry reduction from an inner surface hydroxyl (Farmer & Russell, 1964). Furthermore, it has been shown using both Raman (Pajcini & Dhamelincourt, 1994; Johnston *et al.*, 1985) and FT-Raman spectroscopy (Frost, 1995) that a fifth band at 3684 cm^{-1} exists which is also photoacoustic IR active (Friesen & Michaelian, 1986). This band has been attributed to an uncoupled inner surface hydroxyl which is not IR active. Such bands are not observed in the IR spectra of the kaolinite clay minerals although a band at 3684 cm^{-1} was clearly identified in the low-temperature IR spectra of Prost *et al.*, (1989). The half-widths of the resolved component bands of the FT-Raman spectrum of kaolinite (KGa-1) are $5.7, 6.75, 10.5, 10, 4.4\text{ cm}^{-1}$ for the ν_1 to ν_5 bands respectively. These values agree well with the half-widths reported by Johnston *et al.* (1985). The band areas for the ν_1 and ν_5 bands are 30.5 and 31.6%. There is good agreement between the integrated intensities of the band areas for these bands and the predicted relative inner hydroxyl population. The inner sheet hydroxyl should always be 25% of the total hydroxyl population.

The band component analyses for the FT-Raman spectrum of the hydroxyl region of San Juanito dickite and St. Claire dickite are shown in Figs. 4, C and D. Four bands were identified for San Juanito dickite at $3620, 3639, 3652$ and 3703 cm^{-1} . Only three bands were observed in the room-temperature IR spectrum of dickite, i.e. $3621, 3654$ and 3704 cm^{-1} (Frost *et al.*, 1993). A similar result was obtained by Prost *et al.* (1989) using IR spectroscopy, where five bands in the 5 K low-temperature IR absorption spectrum of dickite at $3615, 3642, 3685, 3711$ and 3726 cm^{-1} were observed. Five bands were observed for St. Claire dickite at $3700, 3652, 3638, 3627$ and 3620 cm^{-1} . An additional band at 3627 cm^{-1} was observed in the FT-Raman spectra of St. Claire dickite. X-ray diffraction studies of the San Juanito dickite show that the clay is complex with a range of crystal sizes. This clay also contains some nacrite and it is probable that there are at least two dickites present in the San Juanito dickite. The dickite from St. Claire has traces of mica and chlorite but is a good quality dickite with thick layers in the crystal. The fact that two different InOH hydroxyl groups are observed in the FTR spectrum of the St. Claire

dickite may be attributed to the presence of more than one dickite in the bulk sample.

The 3686 cm^{-1} band observed in the FT-Raman spectra of kaolinites was not observed in the dickite spectra. The conclusion that this band is the result of uncoupled inner surface hydroxyls is supported by its absence in the dickite spectra. It is likely that all of the inner sheet hydroxyls will be hydrogen bonded to the next layer inner sheet hydroxyls and as a consequence all hydroxyls will be coupled. This inner sheet hydroxyl band shows considerable broadening compared to that of kaolinites. The band width is 15.7 cm^{-1} for San Juanito dickite and 19.6 cm^{-1} for the St. Claire dickite. This may be attributed to the range of hydrogen bonding between the inner sheet hydroxyls in dickites. The inner hydroxyl spectra of dickites showed the same half-widths as that of kaolinites, this is not unexpected since this part of the structure should be similar. Two inner hydroxyls were observed for the St. Claire dickite, one at 3620 cm^{-1} and a second at 3627 cm^{-1} . The reason for this result is not known at present. However, FTR spectroscopy determines the average spectra from all the crystals in the spot area of the laser beam. As a consequence, it is possible that subsets of spectra from the different orientations of the dickite crystal are being measured and that the resultant band is the addition of these spectra from all the different orientations.

The band component analysis of the FT-Raman spectrum of the two halloysites studied in this work are shown in Figs. 4C and 4D. Five bands were observed for the two halloysites at $3698, 3680, 3660, 3630,$ and 3622 cm^{-1} with an additional band observed for the Eureka halloysite at 3712 cm^{-1} . The band at 3680 cm^{-1} is the equivalent of the 3686 cm^{-1} band observed for kaolinite. Two inner hydroxyl bands were observed for the halloysites at 3620 and 3630 cm^{-1} . The fact that two inner surface hydroxyls are observed may result from the folding of the halloysite sheets and is attributed to the *b*-axis disordering of the halloysite layers. Not all of the halloysite InOH groups are identical. The halloysite hydroxyl bands are considerably broader than those of kaolinite, again, no doubt, resulting from the folding of the halloysite sheets. The width of the outer hydroxyl equivalent to the inner sheet hydroxyl of kaolinite is 19 cm^{-1} and the width of the inner hydroxyl is 15.6 cm^{-1} . The width of the inner sheet hydroxyl is more than twice that observed for kaolinite.

The advantage of FT-Raman spectroscopy in the determination of the kaolinite hydroxyl stretching bands rests with the resolution of the component bands. Indeed, in comparison with the IR profiles of the hydroxyl stretching region, the spectral profile does approach the base line. Further, the signal to noise ratio in FTRS provides quality spectra suitable for band component analysis. Also, the resolution of the instrument is such that component bands of the InOH groups of halloysite may be observed for the first time. Such observations cannot be concluded from FTIR spectroscopy, where a single broad band is observed.

Orientation dependence of the FT-Raman spectra of kaolinite

The FT-Raman spectra of a kaolinite from Williamstown, South Australia are shown in Fig. 5. In this case, the kaolinite deposit, in all probability, was formed hydrothermally and the clay particles are subsequently aligned. Thus, by taking the spectrum of the kaolinite from one face of the clay sample and then from the other two orthogonal faces of the clay sample using identical spectroscopic parameters, three different spectra are

obtained. By judicious selection of the face of the clay sample, it is possible to obtain the spectra along three directions which are at right angles and are likely to approach the kaolinite crystal axes. The question then arises as to whether the FT-Raman spectrum of the kaolinite clay is then being obtained along the three crystal axes. The figure clearly shows variation in band intensities and in band positions. The intensity of the band centred at 141 cm^{-1} in spectrum (a) has been reduced to very low intensities. Variation in the intensity of the 197 cm^{-1} band is considerable and the band is composed of at least two overlapping bands. The band at 238 cm^{-1} is maximized in spectrum (a) and minimized in spectrum (c). Similar variation is also noted for the peaks at ~ 265 and 340 cm^{-1} . Variation in the $400\text{--}500\text{ cm}^{-1}$ profile is complex and varies considerably with the clay sample orientation relative to the incident laser beam.

One method of analysing the vibrations of sheet silicates (Loh, 1973) is to consider the molecular vibrations to be composed of four parts: (1) the vibrations of the distorted octahedron MO_6 with S_6 symmetry where M is the octahedral cation; (2) the H–O–H triangle of C_{2v} symmetry; (3) the distorted tetrahedron of SiO_4 of C_{3v} symmetry; and (4) the

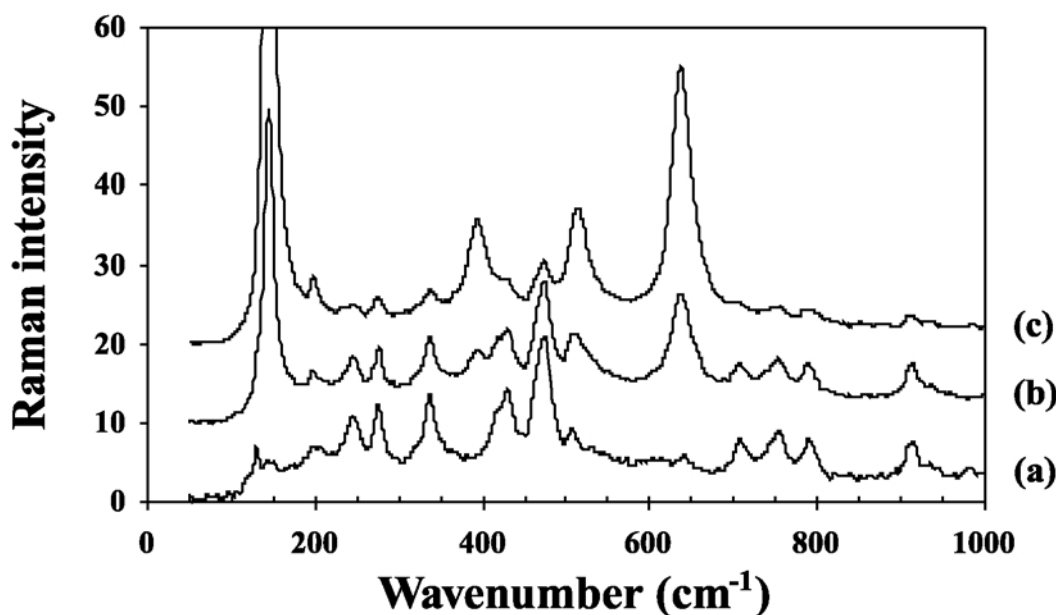


FIG. 5. FT-Raman spectra of the Williamstown kaolinite along three orthogonal directions in the $200\text{--}1200\text{ cm}^{-1}$ region.

librations of the OH group. The vibrations of the first group occur below 210 cm^{-1} , the second group between 200 and 300 cm^{-1} and the third group above 300 cm^{-1} (Griffiths, 1969; Herzberg, 1945). If the MO_6 moiety has octahedral symmetry, then the point group is O_h for a perfect octahedron or S_6 for the distorted octahedron, in which case Raman active bands would be predicted for the MO_6 octahedron at 196 cm^{-1} for the $A_{1g}(v_1)$ vibration, 162 cm^{-1} for the $E_g(v_2)$ vibration and 107 cm^{-1} for the $F_{2g}(v_5)$ mode. The other vibrations for this molecular unit are predicted at 162 and 92 cm^{-1} for the $2F_{1u}(v_3$ and $v_4)$ modes which are IR active but not Raman active. The mode predicted for the $F_{2u}(v_6)$ vibration at 89 cm^{-1} is neither Raman nor IR active (Herzberg, 1945). For the O–H–O isosceles triangle, the vibrational modes are $A_1(v_1) + A_1(v_2) + B_2(v_3)$ all of which are both Raman and IR active (Herzberg, 1945). The predicted values for these vibrations are calculated to be at 265 , 187 and 240 cm^{-1} , respectively. The predicted internal vibrations of the SiO_4 tetrahedral units are known and are the $v_1(a_1)$, $v_2(e)$, $v_3(f_2)$ and $v_4(f_2)$ modes. These vibrations are all Raman active and are predicted to occur at 678 , 363 , 1055 and 1020 and 455 and 470 cm^{-1} , respectively, for the point group T_d (Griffiths, 1969). The splitting of the F_2 modes, resulting in the doublets at 1055 and 1020 and 455 and 470 cm^{-1} , occurs when the symmetry is reduced from T_d to C_{3v} .

The band at 645 cm^{-1} is the $v_1(a_1)$ symmetric stretching mode of the SiO_4 tetrahedral unit. In spectrum (a), no intensity of this band is observed and consequently the direction of the incident laser beam is at right angles to the plane of these SiO_4 units. It is suggested then that this spectrum results from the incident beam being along the c axis of the kaolinite crystals. If the intensity of this band is maximized as is shown in spectrum (c), then this would require the laser beam to be parallel to the axis of the crystals and as such the spectrum along the a or b axes of the crystal is being determined.

The spectrum (b) shows the region in the 915 – 935 cm^{-1} region to be maximized. Such bands are attributed to the Al–OH librations. This would suggest that the (b) spectrum results from the laser beam being parallel to the b axis of the kaolinite crystals.

The FT-Raman spectra for the series of kaolinite clay minerals studied for the 800 – 1000 cm^{-1} region is shown in Fig. 6. These FT-Raman bands are of low intensity and as a consequence are noisy

but the bands are complex with several component bands in the overall profile. Thus this band profile which is attributed to the Al–OH libration suggests that a number of Al–OH librations exist corresponding to the range of hydroxyl-stretching vibrations.

The major advantage of FT-Raman spectroscopy for the determination of kaolinite structure rests with the ability of the technique in overcoming the problems of fluorescence which is normally associated with conventional dispersive Raman spectroscopy. Because FT-Raman spectroscopy operates at 1064 nm , electronic transitions which may cause the fluorescence are avoided. Thus, clay samples, particularly halloysites which may contain organic material, may be analysed using FT-Raman techniques. Further, the technique does have the capacity to measure disordered kaolinites which may be difficult with other Raman methods. Another major advantage of the technique is its ability to measure the spectrum without any sample preparation. No other vibrational spectroscopic technique possesses such an advantage.

CONCLUSIONS

Fourier-transform Raman spectroscopy has been shown to be a very useful technique for the study of the vibrational spectra of the kaolinite minerals, particularly for the observation of low-frequency modes not available to mid-IR spectroscopy. The FT-Raman spectra of a series of kaolinites of different orders, dickites of different complexity and halloysites have been measured in the hydroxyl-stretching region and in the lattice region. The spectra are strongly influenced by the sample orientation. Kaolinites were shown to possess five hydroxyl stretching frequencies at 3619 , 3650 , 3667 , 3686 and 3695 cm^{-1} . Dickites were characterized by bands at 3620 , 3627 , 3639 , 3652 , and 3700 cm^{-1} . Halloysites were characterized by hydroxyl stretching frequencies at 3622 , 3630 , 3660 , 3680 and 3698 cm^{-1} . Five hydroxyl bands have been identified for kaolinites, dickites and halloysites. The FTR spectroscopic technique determines an average spectrum of all the crystal orientations of the kaolinite polymorphs. The half-width of the InOH group of halloysites is 15 cm^{-1} and is considerably broader than that of the half-width of InOH groups of kaolinite or dickite. Two bands were identified for the InOH region of halloysites centred at 3620 and 3630 cm^{-1} . In particular, studies of the hydroxyl-stretching region

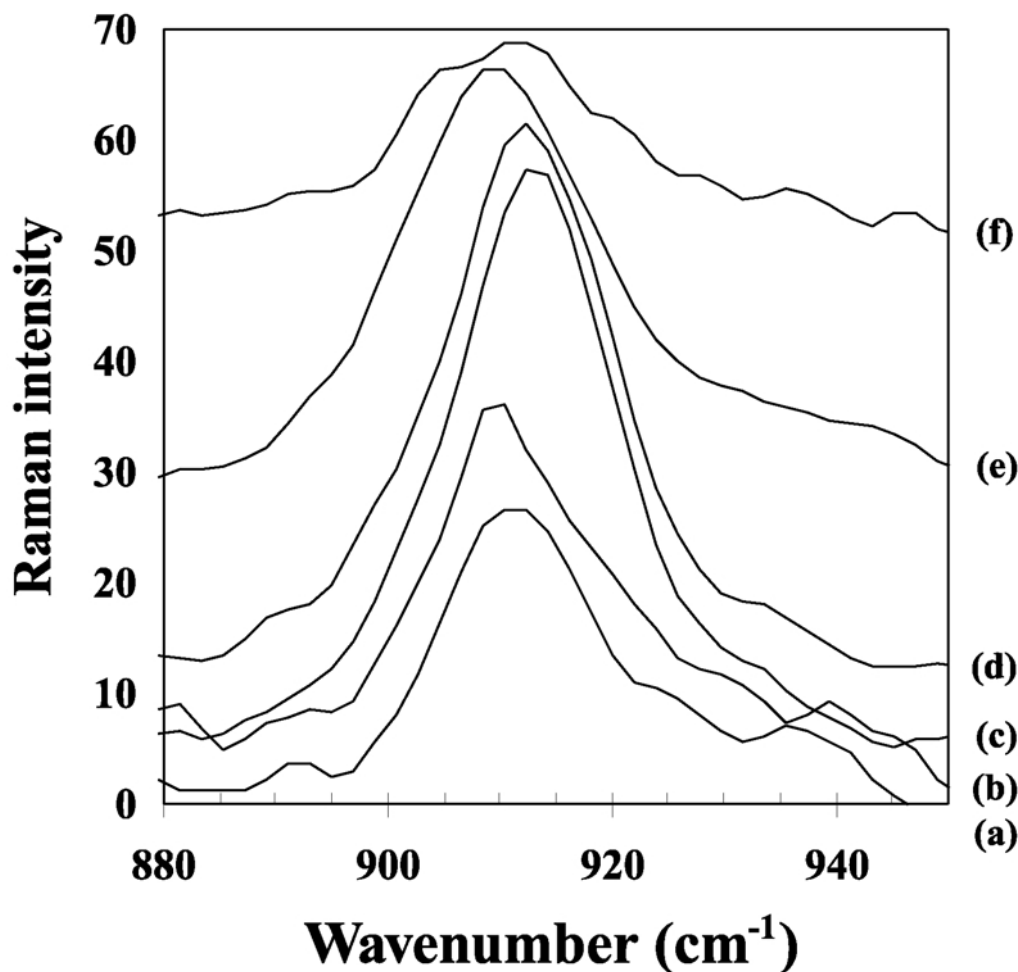


FIG. 6. FT-Raman spectra of (a) kaolinite (KGa-1); (b) kaolinite (KGa-2); (c) dickite (San Juanito); (d) dickite (Sainte Claire); (e) halloysite (New Zealand); and (f) halloysite (Eureka) in the 900 cm^{-1} region.

of halloysites and dickites, not previously documented, are reported. The band widths for these bands vary from 8.85 cm^{-1} for the inner hydroxyls of kaolinites to 15.0 for the outer hydroxyls of dickites.

Remarkably intense bands in the $100\text{--}200\text{ cm}^{-1}$ spectral region were found. Band widths of 9 cm^{-1} and 15 cm^{-1} were obtained for the bands centred at 141 cm^{-1} and 143 cm^{-1} for kaolinite and dickite. The predominant band for kaolinites was found to be the 141 cm^{-1} band which contained $\sim 90\%$ of the total area for this part of the Raman spectrum. This band has been attributed to the O–Al–O symmetric bending

mode in kaolinites. The other bands at ~ 120 and 131 cm^{-1} are attributed to the O–Si–O symmetric vibrations of the Si_2O_5 units of the kaolinite polymorph structure. The resolved component bands for halloysites were found to be considerably broader. The dependence of the FT-Raman spectral profiles of the Williamstown kaolinite from South Australia on the orientation of the clay sample was highlighted. It is proposed that the kaolinite crystals in this sample are uniformly aligned. This then allowed for the single crystal like spectra of the kaolinite along three orthogonal axes to be determined.

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