FOURIER TRANSFORM RAMAN SPECTROSCOPY OF KAOLINITE, DICKITE AND HALLOYSITE

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Abstract—The vibrational modes of clay minerals are uniquely accessible to FT Raman spectroscopy, but this potentially powerful technique has found limited application to the study of clay mineral structure. Raman spectra in the 50 to 3800 cm^{-1} region were obtained for a number of kandite clays. The kandite clay minerals are characterised by relatively intense bands centred at 142.7 cm^{-1} for kaolinite, 143 cm^{-1} for halloysite and 131.2 cm^{-1} for dickite with prominent shoulders at 129, 127, and 120 cm^{-1} respectively. These vibrational modes are attributed to the O-Al-O and O-Si-O symmetric bends. Differences in the lattice modes for the kandite clay minerals in the 200 to 1200 cm^{-1} were obtained. Four OH bands were obtained for kaolinite 3621, 3652, 3668, and 3695 cm^{-1}; three OH bands were found for a selection of dickites and halloysites. The San Juan Dickite and the Eureka Halloysite show further resolution of the low frequency 3620 cm^{-1} hydroxyl band. This splitting is attributed to variation in the position of the inner hydroxyls. Variation in band intensity and position was found to be sample dependent.

Key Words—Dickite, FT Raman spectroscopy, Halloysite, Infrared spectroscopy, Kandite clay, Kaolinite.

INTRODUCTION

Vibrational spectroscopy in particular has been widely used for the study of clay mineral structure for a very long period of time (Lazarev 1972, Farmer 1974). Definitive analysis of the IR spectra has enabled structural analysis to take place. Recently infrared emission spectroscopy has enabled the clay mineral structure at elevated temperatures to be measured *in situ* (Vassallo 1992, Frost 1994, 1995). The Raman spectroscopy of clay minerals has received less attention (Wiewiora 1979, Johnston 1985, Pajcini 1994). The reason why Raman spectroscopy has received less attention is the weakness of the Raman scattered signal, the photo-degradation of the sample and the occurrence of fluoresence which swamps the signal. More recently the advent of FT Raman spectroscopy (Chase 1986, Cutler 1990) which uses near infrared radiation as the excitation source and a Fourier Transform spectrometer enables the study of clay mineral structure to be further investigated. The use of FT Raman spectroscopy offers the advantages of reduced fluoresence, improved signal to noise by coadding of scans and the longer wavelength of light reduces sample degradation.

EXPERIMENTAL

Mineral samples

Clay minerals were obtained from a number of sources: Wards natural science establishment, Rochester, New York, The Clay Mineral Society repository and from the Australian Commonwealth Scientific and Industrial Organisation, Glen Osmond South Australia. Minerals were also collected from a number of Australian mineral deposits. Whilst a considerable number of kandite clays from these sources have been studied, the content of the paper is based where possible on CMS standards. The minerals were dried in a desiccator to remove adsorbed water and were used without further purification. Samples were analysed using Xray diffraction techniques before Raman and infrared spectroscopic analysis.

Infrared and Raman spectroscopy

The Raman and infrared spectra were obtained using a Perkin-Elmer 2000 series FTIR spectrometer equipped with a Raman accessory. This comprised a Spectron Laser Systems SL301 Nd-YAG laser operating at a wavelength of 1064 nm, and a Raman sampling compartment incorporating 180 degree optics. The FT-IR spectrometer contained a quartz beam splitter capable of covering the spectral range 15,000–4000 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}. Raman spectra below 150 cm^{-1} and in the 3500–3800 cm^{-1} 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. Raman spectra were obtained directly by using a sample of the raw mineral directly in the incident beam. If the raw mineral was not available then a powdered sample was used. No observable differences were found between the two methods. Measurement times of between 0.5 and 2 h were used to collect the Raman spectra with a signal to noise ratio of better than 100/1 at a resolution of 4 cm^{-1}. Raman spectra were collected as a single beam spectra and were not corrected for instrumental effects.
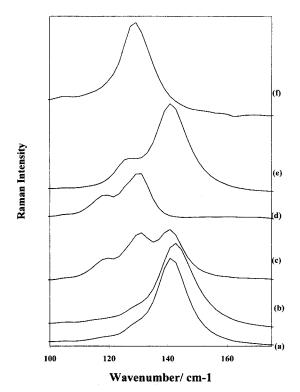
Figure 1. FT-Raman spectra of kandite clays: (a) Kaolinite KGa-1 (b) Kaolinite KGa-2 (c) Dickite (San Juan) (d) Dickite (Saint Claire) (e) Halloysite (Eureka) (f) Halloysite (New Zealand).

A laser power of 200 mw was used. This power is 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. Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectrocalc software package (Galactic Industries Corporation, NH, USA).

RESULTS AND DISCUSSION

Low wavenumber region

The FT-Raman kandite spectra in the < 200 cm^{-1} region are shown in Figure 1. The kandite clay minerals are characterised by very intense bands centred at 142.7 cm^{-1} for kaolinite, 143 cm^{-1} for halloysite and 131.2 cm^{-1} for dickite and are an order of magnitude more intense than the other bands in the 200 to 1200 cm^{-1} region. FT Raman bands were also found at 129, 127, and 120 cm^{-1} for the respective clays. Similar bands have been identified using conventional dispersive Raman spectroscopy (Wiewiora 1979, Johnston 1985). The spectra indicate that the disordered kaolinite (KGa-2) frequency occurs at a higher frequency than that of the ordered kaolinite (KGa-1). The dickite min-

eral from San Juan shows complexity with bands at 143, 130 and 120 cm^{-1}. The dickite mineral from Saint Claire shows only two peaks at 131 and 120 cm^{-1}. The halloysite from New Zealand shows peaks at 143 and 127 cm^{-1}. These frequencies are similar to those of kaolinite. The spectrum of Eureka halloysite with peaks at 129 and 120 cm^{-1} is similar to that of dickite. This part of the kandite spectral region is very much sample dependent.

Farmer (1974) predicts the vibrations of an ideal hexagonal (Si$_2$O$_5$) layer and Ishii (1967) predicts 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. 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 polarisability. It is interesting that in the titania mineral anatase that a very intense band occurs in the 143–154 cm^{-1} range and has been shown to be pressure dependent (Balanchandran 1982, Ohsaka 1978). The band has been attributed to the symmetric bend of O-Ti-O. It is likely that the variation in the peak position of the particular clay is related to the stress on the kandite 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 kandites and this may be related to layer stacking. The FT-Raman spectroscopy is excellent for the study of low frequency lattice vibrations of clay minerals and is providing new information in the < 200 cm^{-1} region of kandites. Such a spectral region can be determined using Far infrared techniques but this normally requires the use of vacuum which would dehydrate the clay minerals.

Frequency region 200–1000 cm^{-1}

The spectra of the range of kandites studies are shown in Figure 2. The corresponding infrared spectra are illustrated in Figure 3. Although the number and peak positions of the bands in the spectra of Figure 2 are similar, there is no correspondence among the relative intensities between the kandite clay minerals. In fact this spectral region can be used to finger print clay minerals (Frost 1993). The spectral region from 200–400 cm^{-1} of kandites contains several peaks. Halloysite (Eureka) has an intense band at 205 cm^{-1} which is present in the other kandites but is of relatively weak intensity in the other kandites. It is suspected that this part of the spectral region is sample orientation dependent and this requires further investigation. Dickites have intense bands at 235 and 275 cm^{-1} which are again present in the other kandites, including nacrites but are considerably weaker in halloysites and kaolinites. There is some variation in peak position for
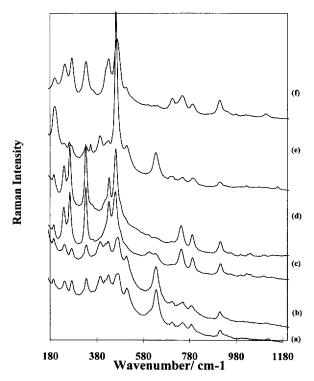
Figure 2. FT-Raman spectra of kandite clays 200–1200 cm⁻¹: (a) Kaolinite Kga-1 (b) Kaolinite Kga-2 (c) Dickite (San Juan) (d) Dickite (Saint Claire) (e) Halloysite (Eureka) (f) Halloysite (New Zealand).
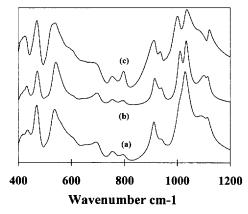

Figure 3. Infrared spectra of kandite clays: New Zealand Halloysite, San Juan Dickite and kaolinite Kga-1.

Besides the 142 cm⁻¹ band the next most intense band for kaolinite is the 636.5 cm⁻¹ band. The band is very weak in halloysite and is almost nonexistent for dickite. The band is infrared active but is weak. The band has been attributed to an Si-O-Si stretch (Lazarev 1972). The bands at 704, 752, and 785 for kaolinite; 703, 744.5 and 792.7 for halloysite and 744.5 and 794.7 cm⁻¹ for dickite have been previously at-

the dickites studied in this region: The peak is at 275 cm⁻¹ for the San Juan Dickite and 280 cm⁻¹ for the Saint Claire Dickite. A similar observation is made for the 340 cm⁻¹ peak for the dickites. It is interesting that in this part of the spectral region that the FT-Raman spectra of the lattice modes of the New Zealand Halloysite resembles the spectra of dickites. The exact assignment of the vibrations in this part of the spectral region is not known at this stage of the research. Halloysite is characterised by the intense 459 cm⁻¹ band. This band is split into two bands for dickite (432 and 459 cm⁻¹) and consists of four bands for kaolinite (395.4, 426, 469 and 509 cm⁻¹) and has been attributed to the Si-O bending vibration and is both Raman and infrared active (Farmer 1974). The band positions are in good agreement with the spectra obtained by dispersive Raman spectroscopy (Johnston 1985, Wiewiora 1979). The multiplicity of peaks for kaolinite can be explained in terms of the reduction in symmetry from C_{6v} to C_s arising from the substantial deviations in the form of the layer from hexagonal symmetry. It is also noted that there is variation in the relative intensity of these peaks between the ordered (KGa-1) and disordered kaolinite (KGa-2). A similar variation was observed in this spectral region for wet and dry kaolinite (KGa-1) (Johnston 1985).
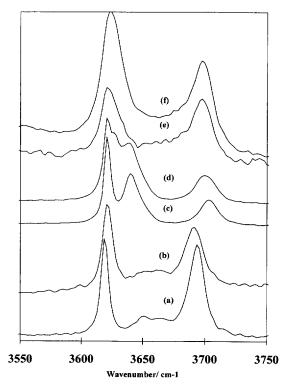

Figure 4. FT-Raman spectra of kandite clay hydroxyl region: (a) Kaolinite Kga-1 (b) Kaolinite Kga-2 (c) Dickite (San Juan) (d) Dickite (Saint Claire) (e) Halloysite (Eureka) (f) Halloysite (New Zealand).
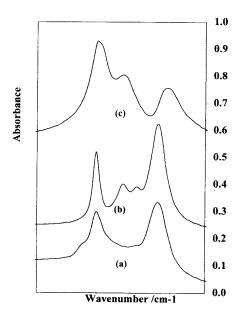
Figure 5. Infrared spectra of the hydroxyl region of kandite clays: New Zealand Halloysite, San Juan Dickite and kaolinite Kga-1.

tributed to the Al-OH vibrations of surface hydroxyls (Farmer 1974, Russell 1970). These bands are better resolved in the Raman spectra compared with the infrared. The reason why there are 3 peaks for kaolinite and 2 for halloysite is again related to symmetry reduction. The in plain bending vibrations of the surface hydroxyls in the kaolinite minerals lie at 936 cm^{-1} and the inner hydroxyl at 915 cm^{-1} (Farmer 1974). These bands are strongly infrared active but are weak in the Raman, with the inner hydroxyl showing sensitivity to structure. The peak positions are at 914, 910 and 912 cm^{-1} for dickite, halloysite and kaolinite. These bands have been shown to be distinguishable by selective deuteration (Wada 1967). Kaolinites being a dioctahedral layer silicate as opposed to trioctahedral possess lower effective symmetry thus imposing distortions on the tetrahedral sheet. Thus the intense infrared bands at 1014, 1036 and 1108 for kaolinite are attributed to the perpendicular Si-O vibrations. These bands are weak in the Raman but are observable at 1020, 1043 and 1110 cm^{-1}. The Raman spectra give less information in the 900 to 1200 cm^{-1} region of the spectrum. This is attributable to the differences in the two types of vibrational spectroscopy: Raman depends on the changes in the polarisability of the bonds and consequently is applicable to symmetric vibrations and vibrations that involve atoms of similar size; infrared on the other hand is a function of the change in bond dipole and thus is more useful for looking at asymmetric vibrations and vibrations that involve atoms of different sizes.

Frequency region 3500–3800 cm^{-1}

Raman and infrared spectra of the hydroxyl stretching region are shown in Figures 4 and 5. The FT Raman spectra are in good agreement with previously published work (Johnston 1984, Wiewiora 1979). In contrast to the low wavenumber region, there is good agreement between the infrared and Raman spectra of the hydroxyl stretching region. In the infrared spectra two bands are observable for halloysite, four for kaolinite and 3 for dickite, although the high frequency band at 3700 cm^{-1} is complex for all of the kandite clays and the asymmetry of the band indicates that more than one band may be present. Alternatively this band may be considered as a continuum of states which simply indicates this type of hydroxyl exists in a wide range of structural environments. Similar results were obtained by Prost (1987) using low temperature studies of kaolinite and Johnston (1990) using polarised single crystal FTIR microscopy. Similar observations have been made on the width of the 3700 cm^{-1} component with the conclusion that this band could not be adequately curve resolved (Pajcini 1994). The low frequency dickite hydroxyl shows splitting and is resolvable into two components at 3621 and 3654 cm^{-1} (Frost 1993). The FT Raman spectra of kandite hydroxyls show better resolution with the band profiles reaching baseline between the 3650 and 3700 cm^{-1} peaks. Low temperature studies of kaolinite show the presence of six bands with the 3652 cm^{-1} band being split into two components at 3650 and 3657 cm^{-1} and the 3621 cm^{-1} band exhibiting splitting at 3618 and 3628 cm^{-1} (Pajcini 1994). The FT-Raman spectra of kaolinites show four Raman peaks at room temperature and six at low temperature and this is difficult to reconcile when there are only four distinct crystallographic groups in kaolinite (Rouxhet 1977). The 3620 cm^{-1} IR band for kaolinite has been assigned to the inner sheet hydroxyl (Ledoux 1964, Wada 1967, White 1970, Rouxhet 1977). The FT Raman peak is at 3620 cm^{-1} for the well crystalline kaolinites but is found to be at 3624 cm^{-1} for the less crystalline kaolinites. There is a similar frequency for dickites and ordered halloysites. Less crystalline halloysites show this peak at 3627 cm^{-1}. The dickite (Saint Claire) shows a complex spectrum in the 3620 cm^{-1} region. Similarly halloysite (Eureka) shows a similar although less well resolved pattern for this hydroxyl. The two hydroxyl frequencies at 3652 and 3668 are in good agreement with published data (Johnston 1985). The second Raman peak for dickite was at 3642 cm^{-1} which corresponds well with the infrared data (Frost 1993, Prost 1989). The band profile centred at 3695 cm^{-1} is complex and is structure dependent. The Raman spectrum of kaolinite shows two bands at 3688 and 3695 cm^{-1} for KGa-^{1} and two bands at 3685 and 3692 cm^{-1} for KGa-2. This particular set of bands is at higher frequencies for dickite

and halloysite and is centred at 3705 cm^{-1} and 3702 cm^{-1}. The 3705 cm^{-1} band is in good agreement with the infrared spectra previously published (Prost 1989). The 3702 cm^{-1} band is at higher frequency in the Raman than in the infrared (3695 cm^{-1}) (Frost 1993).

CONCLUSION

FT Raman spectroscopy using near infrared excitation has been shown to be very useful for the study of the vibrational spectrum of kandite clays. The technique has several unique advantages (a) no sample treatment as the spectra can be obtained from the solid or powdered samples; (b) low wavenumber vibrational bands which are inaccessible to mid IR spectrometers are easily measured; and (c) vibrational bands which are not infrared active are observable.

The low frequency bands at 143 cm^{-1} was shown to be intense and kandite clay structure dependent. The low frequency region from 200 to 1200 cm^{-1} is useful for distinguishing between the kandite clay minerals. Again the band intensity and position is kandite clay structure dependent. The FT Raman spectra of kandite hydroxyl region is reported and is shown to be complex with FT Raman spectroscopy being sensitive to the variations in clay mineral structure.

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