CHARACTERIZATION OF OCTAHEDRAL SUBSTITUTIONS IN KAOLINITES USING NEAR INFRARED SPECTROSCOPY

S. PETIT,[1] J. MADEJOVÁ,[2] A. DECARREAU[1] AND F. MARTIN[3]

[1] Université de Poitiers, UMR CNRS 6532 "Hydr.A.S.A", 40, avenue du recteur Pineau, F-86022 Poitiers CEDEX, France
[2] Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-842 36 Bratislava, Slovakia
[3] Université Paul Sabatier, Laboratoire de Minéralogie-Cristallographie, UMR 5563 CNRS, 39 Allées Jules Guesde, F-31000 Toulouse, France

Abstract—Fourier transform infrared (FTIR) spectroscopy investigations in the near infrared (NIR) region of synthetic and natural kaolinites with various octahedral substitutions have been carried out in order to elucidate the relationships between the substituted cations and specific features of the NIR spectra. The combination modes of the OH stretching and bending vibrations characterizing Fe(III), Ga(III) and Cr(III) octahedral substitutions are identified in the NIR region at 4466, 4498 and 4474 cm^{-1}, respectively, and the first overtones of the OH stretching vibrations at 7018, 7018 and 6986 cm^{-1}, respectively. As far as we know, the bands of kaolinites containing Ga(III) or Cr(III) have not been reported yet. For both Ga(III) and Cr(III), the NIR observations explain why the bending vibration bands of AlGaOH and AlCrOH groups are not observed in the middle infrared (MIR) region.

Key Words—Kaolinites, Near Infrared Spectroscopy, Octahedral Substitution.

INTRODUCTION

For a long time, kaolinite was considered to have no substitution. In fact, the crystallochemical studies of natural, as well as of synthetic, kaolinites showed that they can act as effective potential traps of elements. Ferric iron can substitute for Al in octahedral sites of kaolinite even to a relatively high level in synthetic samples (Petit and Decarreau 1990). The presence of Ga (Martin et al. 1998) and Cu (Petit, Decarreau et al. 1995) in the octahedra of synthetic kaolinites has been confirmed recently. Chromium substitutions were proved in natural samples (Brookins 1973; Maksimovic and Brindley 1980; Macksimovic et al. 1981; Singh and Gilkes 1991; Mosser et al. 1993; Gaite and Mosser 1993). Titanium is also considered as a potential candidate for substitution in kaolinites (Jepson and Rowse 1975; Rengasamy 1976; Weaver 1976). However, the presence of ancillary minerals has to be expected, and bulk chemical analysis is of little use because it is not possible to distinguish whether the "unusual" (for kaolinite) elements are really present in their structure or in an admixture. FTIR spectroscopy is a powerful tool to characterize various substitutions due to the possibility of recognizing the cationic environment of the OH groups via hydroxyl bond vibrations. However, it has been mainly used in the MIR region (4000–400 cm^{-1}) so far. In addition to the region where fundamental vibrational modes appear, the NIR region (11,000–4000 cm^{-1}) is useful for determining the composition of the octahedral sheets of kaolinites. This is because the latter region contains various overtone modes which are often sensitively affected by changes in the crystallochemical status of kaolinites.

The main NIR spectral features of kaolinite (and other clay minerals) are located in the 7500–6500-cm^{-1} and 5000–4000-cm^{-1} regions. The observed signals correspond either to the first overtone ($2\nu_{OH}$) of OH stretching fundamental vibration modes, to combinations ($\nu_{OH} + \delta_{Al-OH}$) of OH stretching and bending fundamental modes or to combinations of OH stretching fundamental modes with lattice vibrations (Hunt and Salisbury 1970). In practice, the band wavenumbers that are measured in the NIR region are close to the sum of the wavenumbers of bands observed in the MIR. Post and Noble (1993) pointed out that the small changes in the OH stretching and bending band positions are additive in the combination bands, making them more readily differentiated in the NIR region. This merit has been applied to the identification of clay mineral composition, particularly in the smectite group (Pontual and Cocks 1994; Post and Noble 1993). Delineau et al. (1994) used NIR spectra to detect Al/Fe(III) substitutions in natural kaolinites. They observed 2 absorption bands at 4465 and 7025 cm^{-1}, due to Fe for Al substitution, and they attributed them to the combination of the 3598-cm^{-1} ($\nu AlOHFe^{3+}$) and 875-cm^{-1} ($\delta AlOHFe^{3+}$) bands, and to the $2\nu_{OH}$ overtone of the band at 3598 cm^{-1}, respectively.

The purpose of this paper is to investigate the NIR spectra of natural and synthetic kaolinites with various octahedral substitutions (Fe(III), Ga(III), Cr(III) and Cu(II)).

MATERIALS AND METHODS

Eleven well-characterized synthetic and natural kaolinites were investigated (Table 1). The descriptions, origins, conditions of synthesis and MIR spectra of these kaolinites have been published elsewhere (see

Table 1. Description of kaolinite samples used in the study.

Sample	Substitution	Substituent element content[†]	Origin[‡]	References	Sample designation in the respective papers
Al	—	—	S	Martin et al. (1998)	No. 1
	Al(III)/Fe(III)			Petit and Decarreau (1990)	
Fe1		0.6	S		$a = 0.02$
Fe2		2.0	S		$a = 0.1$
Fe3		4.1	S		$a = 0.2$
Fe4		4.6	S		$a = 0.3$
	Al(III)/Cr(III)			Mosser et al. (1993)	
Cr1		0.5	N		Milo
Cr2		1.8	N		Gey
	Al(III)/Ga(III)			Martin et al. (1998)	
Ga		3.6	S		No. 2
	Al(III)/Cu(II)			Petit, Decarreau et al. (1995)	
Cu1		0.1	S		S1
Cu2		2.8	S		S2
Cu3		4.0	S		S3

† In wt% oxide assuming 14% structural water.
‡ S = synthesized samples, N = natural samples.

references in Table 1), and only the main features will be summarized here.

One synthetic kaolinite containing only Al in the octahedra is used as the reference (Sample Al, Table 1). The Fe-bearing kaolinites are synthetic, and the Fe content ranges from 0.6 to 5% Fe_2O_3 from sample Fe1 to sample Fe4. The Ga-bearing kaolinite (Sample Ga, Table 1) is synthetic and the Ga_2O_3 content is 3.6%. The Cr1 and Cr2 samples are Cr-bearing kaolinites, also named "miloschites" (Brookins 1973), and they are natural. The Cr contents are 0.5 and 1.8%, respectively. The Cu-bearing kaolinites (Cu1, Cu2, Cu3) are synthetic and the Cu amount ranges from 0.1 to 4% as CuO.

NIR spectra were obtained using a Nicolet Magna 750 FTIR spectrometer with the diffuse reflectance (DRIFT) accessory "Collector" from Spectra-Tech. The spectrometer was equipped with a CaF_2 beam splitter and a PbSe detector. Samples were analyzed at room temperature without any dilution in KBr. They were poured loosely into a sample cup of about 1 mm depth and 3 mm diameter and should have had a random orientation. It would have been better to fill the cup, but the lack of some samples prevented this. In those cases, the spectra obtained from a few grains only were noisy but readable. Such spectra are given without correction. Freshly prepared MgO was used for background measurement. Averages were made of 128 scans at a resolution of 4 cm^{-1}.

The use of spectral reflectance measurements in either NIR (11000–4000-cm^{-1} or 0.9–2.5-μm) or the MIR (4000–400-cm^{-1} or 2.5–25-μm) regions avoids significant problems associated with transmission measurements of clay minerals. The first problem is that grinding and pressing kaolinites to prepare pellets can cause structural damage (Hlavay et al. 1977; Bell et al. 1991). On the other hand, since clay samples consist of aggregates of small particles whose dimensions are about the same as the wavelength of the NIR light, most radiation incident on a sample is scattered. For this reason, direct transmission measurement using alkali halide pressed disks does not give satisfactory results in the NIR region (Lindberg and Snyder 1972).

RESULTS

Reference Al-kaolinite

Major NIR spectral features of kaolinites are located in the 5000–4000-cm^{-1} and 7000-cm^{-1} regions (Figure 1).

The 5000–4000-cm^{-1} region: the major band at 4526 cm^{-1} and the associated one at 4620 cm^{-1} correspond to the combination of OH stretching and deformation vibrations of Al_2OH groups. The weaker band at 4730 cm^{-1} is likely due to a combination of
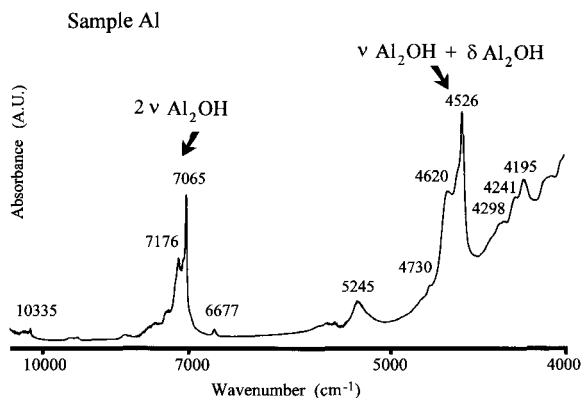

Figure 1. Diffuse reflectance spectrum in the 11,000–4000-cm^{-1} region of the pure Al-kaolinite, described in Table 1. The wavenumber scale is nonlinear in order to display clear features throughout the broad range of the NIR spectrum.

Table 2. Observed and calculated wavenumbers of the vibrations of the OH groups linked to various octahedral cations.

| Cationic pairs | Observed wavenumbers (cm⁻¹) | | | | Calculated δ_{OH} wavenumbers (cm⁻¹) | | | |
| | NIR | | MIR | | from (2) and (3) cor. | | from (1) and (2) cor. | |
	$2\nu_{OH}$ (1)	$\nu_{OH} + \delta_{OH}$ (2)	ν_{OH} (3)	δ_{OH} (4)				
Al-Al*	7065	4526	3620	914	906	914	994	914
Al-Fe³⁺	7018	4466	3598	875	868	876	957	877
Al-Cr³⁺	6986	4474	3586	/	888	*896*	981	*901*
Al-Ga³⁺	7018	4498	3599	/	899	*907*	989	*909*

Key: * = bonded to internal OH; / = not observed; cor. = corrected after comparison with the known δ_{OH} values (4).

the internal OH stretching vibrations (3620 cm⁻¹) with lattice vibration (Si-O stretching near 1100 cm⁻¹). Three little bands between 4100 and 4300 cm⁻¹ are combinations of OH stretching bands of kaolinite with lattice deformation vibrations (Hunt and Salisbury 1970; Hunt et al. 1973; Delineau et al. 1994).

The 7000-cm⁻¹ region: Two bands are clearly observed at 7176 and 7065 cm⁻¹. Between these 2 bands, 1 doublet is more or less resolved. These bands correspond to the $2\nu_{OH}$ overtones of OH stretching fundamental modes of Al₂OH groups (Hunt and Salisbury 1970).

By comparison with the MIR, Crowley and Vergo (1988) assigned the sharp intense band at 7065 cm⁻¹ to the inner hydroxyl groups and the others to hydroxyl groups located on the exterior surface of the octahedral sheet of kaolinites. The appearance of the overtones at wavenumbers lower than twice the fundamentals (Table 2) is due to the anharmonic character of vibrations (Alpert et al. 1964).

The band at 5245 cm⁻¹ is a diagnostic band of adsorbed water ($\nu_w + \delta_w$) (Hunt and Salisbury 1970). It is only observed in spectra recorded at ambient atmosphere, and it disappears under vacuum (Delineau et al. 1994).

The other small bands are not clearly assigned. Two of them can be here tentatively attributed. The relatively sharp 6677-cm⁻¹ band may be due to the first

overtone of the 3434-cm⁻¹ vibration band, present in the MIR spectrum (Martin et al. 1998). It is commonly observed in MIR spectra of synthetic kaolinites (De Kimpe et al. 1981; Tomura et al. 1985; Petit and Decarreau 1990) as well as in the natural ones (Kato et al. 1977; Delineau et al. 1994), but it was not assigned. The 10335-cm⁻¹ band may be attributed to the second overtone of OH stretching fundamental modes of Al₂OH groups by analogy with the observations of Vedder (1964) in muscovite, although Hunt and Salisbury (1970) attributed it to the presence of Fe(II) in kaolinite.

Fe(III)-kaolinites

In comparison with the pure Al-kaolinite, 2 supplementary features are observed at 4466 and 7018 cm⁻¹ in the spectra of Fe-rich synthetic kaolinites (Figure 2). These bands were attributed by Delineau et al. (1994) to the combination of the bands at 3598 and 875 cm⁻¹, and to the $2\nu_{OH}$ overtone of the band at 3598 cm⁻¹, respectively. Mendelovici et al. (1979) and Petit and Decarreau (1990) assigned the 3598- and 875-cm⁻¹ bands to νAlFeOH and δAlFeOH vibrations, respectively. The 7018-cm⁻¹ absorption occurs only as a shoulder of various intensity in all the spectra of this series (Figure 2). The very weak inflexion near 4466 cm⁻¹ in the spectrum of the Fe-poorest synthetic kaolinite of the series (Fe1) increases in intensity for the intermediary samples (Fe2 and Fe3), and broadens for the Fe-richest sample Fe4 (Figure 2).

Delineau et al. (1994) correlated the area of the 4468-cm⁻¹ band with the area of the electron paramagnetic resonance (EPR) signals due to Fe(III) present inside the X-ray diffraction (XRD)-coherent domains of kaolinite. The 4526-cm⁻¹ major band overlaps the 4466-cm⁻¹ band on its high-wavenumber side (Figure 2). This overlapping increases with the increase of the structural Fe content, and with structural disorder (Delineau et al. 1994). Any quantification of the Fe substitution in synthetic kaolinites based on this band would be highly imprecise.

Cr(III)-kaolinites

Two additional bands at 4474 and 6986 cm⁻¹ are observed for the 2 chromian kaolinites Cr1 and Cr2, in comparison with the pure kaolinite (Figure 3).
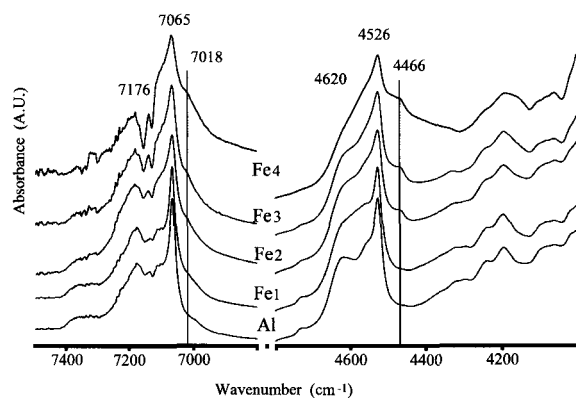

Figure 2. Diffuse reflectance NIR spectra in the 4800–4000-cm⁻¹ and 7500–6800-cm⁻¹ regions of the Fe-bearing kaolinites described in Table 1.
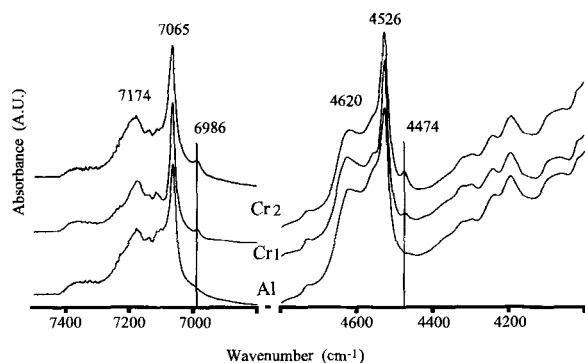
Figure 3.   Diffuse reflectance NIR spectra in the 4800–4000-cm^{-1} and 7500–6800-cm^{-1} regions of the Cr-bearing kaolinites described in Table 1.

Figure 4.   Diffuse reflectance NIR spectra in the 4800–4000-cm^{-1} and 7500–6800-cm^{-1} regions of the Ga-bearing kaolinites described in Table 1.

These bands had never been mentioned in the literature and can be assigned to the combination of OH stretching and deformation modes ($\nu_{OH} + \delta_{OH}$) of AlCrOH groups, and to the $2\nu_{OH}$ overtone of the ν-AlCrOH vibration, respectively. This assignment is supported by the fact that both bands are more intense for Cr2 than for Cr1 (Figure 3), in accordance with the higher Cr contents in Cr2 (Table 1).

In the MIR, the νAlCrOH vibration band was observed at 3586 cm^{-1}, but no δAlCrOH vibration band was detected (Mosser et al. 1993; Maksimovic et al. 1981). However, the wavenumber of the δAlCrOH vibration band can be calculated from the NIR data, following this simple equation (Cariati et al. 1981, 1983a, 1983b; Post and Noble 1993; Bishop et al. 1994):

$$(\nu_{OH} + \delta_{OH})_{NIR} - (\nu_{OH})_{MIR} = (\delta_{OH}) \qquad [1]$$

Due to anharmonicity, the calculated wavenumber of the δ_{OH} vibration is lower compared to actual value. The comparison of the observed and calculated wavenumbers of the Al$_2$OH$_{(inner)}$ and AlFeOH groups obtained for Al and Fe kaolinites shows that approximately 10 cm^{-1} should be added (Table 2) to the calculated δ_{OH} value to obtain the experimental value. The δAlCrOH vibration band would be located at about 900 cm^{-1} and thus overlapped by the main δAl$_2$OH band at 915 cm^{-1}. Such location is in accordance with the broadening towards the low-wavenumbers side of the δAl$_2$OH band observed in the MIR spectra of halloysites relatively very rich in Cr (up to 12% Cr$_2$O$_3$) given by Maksimovic and White (1973).

Ga(III)-kaolinite

The NIR spectrum of the Ga-rich synthetic kaolinite shows, in comparison with the pure kaolinite spectrum, 2 additional bands at 4498 and 7018 cm^{-1} (Figure 4). As far as we know, these bands had never been mentioned in the literature. They can be assigned to the combination of OH stretching and deformation
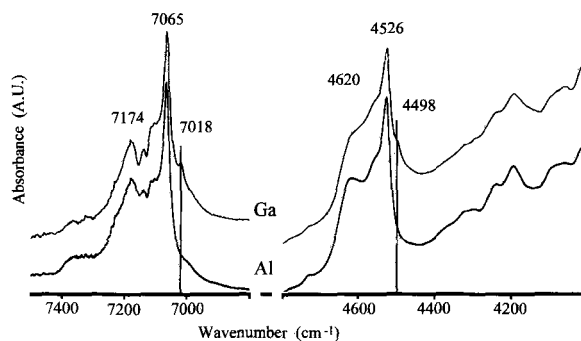
modes of AlGaOH groups, and to the first overtone of the νAlGaOH vibration band, respectively.

The νAlGaOH vibration band was observed in MIR at 3600 cm^{-1}, but no δAlGaOH vibration band was detected in the MIR spectrum of this Ga-kaolinite (Martin et al. 1998, sample 2). Based on Equation [1], the position of the δAlGaOH vibration band would be at about 910 cm^{-1} (Table 2). A shift of the δOH band from 914 cm^{-1} for the Al end member (a kaolinite), to 903 cm^{-1} for the Ga end member (a smectite), was observed in the MIR spectra of synthetic kaolinites and smectites with various Ga-contents (Martin et al. 1998).

The 914-cm^{-1} band was attributed to δAl$_2$OH either in kaolinites or in smectites, while the band at 903 cm^{-1} was attributed to δGa$_2$OH in smectites by Stubican and Roy (1961) and Martin et al. (1998). After a simple calculation, assuming that in the same environment the wavenumber of the band of the OH group bonded to a cationic pair involving 2 different homovalent cations can be deduced from the mean of the vibration wavenumbers of the OH groups bonded to the 2 cationic pairs involving the same cations (Decarreau et al. 1992; Petit, Robert et al. 1995), the obtained value is 909 cm^{-1} [914 (δAl$_2$OH) + 903 (δGa$_2$OH)]/2. Such a wavenumber for the δAlGaOH vibration is in accordance with the results obtained from the NIR spectra. The coincidence of wavenumber of the δAlGaOH vibrational band with the main δAl$_2$OH band at 915 cm^{-1} can explain the impossibility of observing the δAlGaOH absorption in the MIR region.

Cu(II)-kaolinites

The NIR spectra of samples Cu1, Cu2 and Cu3 are shown in Figure 5. These 3 synthetic samples (Table 1) have been described in detail by Petit, Decarreau et al. (1995). No νOH vibration band involving Cu(II) was observed in the MIR spectra, and the νAl$_2$OH vibration bands appeared increasingly blurred when the Cu content of samples increased. Weak bands situated
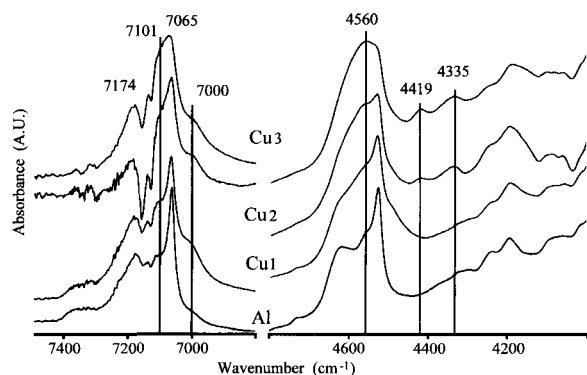
Figure 5.   Diffuse reflectance NIR spectra in the 4800–4000-cm^{-1} and 7500–6800-cm^{-1} regions of the Cu-bearing kaolinites described in Table 1.

at 868 and 840 cm^{-1} were tentatively attributed to $\delta AlCu^{2+}OH$.

In both the 7000-cm^{-1} and 4400-cm^{-1} regions (Figure 5), the characteristic bands of kaolinite involving structural OH are more blurred when the Cu content of samples increased, as was similarly observed in the MIR. This is partly due to the growth of new bands centered near 7100 and 4560 cm^{-1} in these regions. Another new band appears in the spectra of the 3 Cu-bearing samples at 7000 cm^{-1}, but its intensity does not change with the Cu content in the samples. Two other bands are observed at 4419 and 4335 cm^{-1} for the 2 Cu-richest samples, and can be clearly linked with the Cu amount in kaolinites. Due to the overlapping of the bands in both MIR and NIR spectra, it is not possible to attribute these bands with certainty.

DISCUSSION AND CONCLUSIONS

Even though the relationship between clay structure and IR spectrum is complex and has been only partially rationalized up till now, the IR spectrum reflects crystallochemical composition on which other techniques cannot easily give information (Petit, Robert et al. 1995). In the spectra of clay minerals other than kaolinite with various chemical compositions due to numerous cation substitutions, the vibrations of the OH groups are almost fully understood and have been found to be sensitive indicators of the hydroxyl environment (Robert and Kodama 1988; Madejová et al. 1994; Besson and Drits 1997). Each definite type of cation bonded to an OH group is determined by a definite position of the corresponding OH band.

In this way, from a series of diversely substituted synthetic and natural kaolinites, the OH absorption bands characterizing Fe(III), Cr(III) and Ga(III) octahedral substitutions were previously identified in the MIR. The corresponding bands are identified in the NIR region using the same series of kaolinites. The first overtones of the OH stretching vibrations ($2\nu AlR^{3+}OH$) are located at 7018, 6986 and 7018 cm^{-1}

for Fe(III)-, Cr(III)- and Ga(III)-bearing kaolinites, respectively. The combination of the OH stretching and bending vibrations are observed at 4466, 4474 and 4498 cm^{-1}, respectively. The $2\nu AlR^{3+}OH$ band, for R^{3+} being Fe(III) or Ga(III), has the same wavenumber, in accordance with the MIR data for the $\nu AlR^{3+}OH$ bands (Table 2).

The bands of Ga(III)- and Cr(III)-substituted kaolinites are reported for the first time. The NIR data can also be used to calculate "unknown" positions of some OH vibrations bands in the MIR. Thus, NIR spectra explain why the $\delta AlGaOH$ and $\delta AlCrOH$ vibration bands are not observed in the MIR. It is due to an overlapping of these bands by the δAl_2OH absorption.

Even though amounts of the Cu(II) substitution in Cu(II)-bearing kaolinites are comparable with those of the Fe(III), Cr(III) and Ga(III) substitutions, more significant modifications occur in their NIR spectra: the νAl^{3+}_2OH bands become blurred and several new bands appear. However, unlike the case of Fe-, Cr- and Ga-bearing kaolinites, it is not possible to explicitly assign these additional bands of Cu-bearing kaolinite. Stubican and Roy (1961) showed that there are more radical changes in IR spectra of minerals when the substitution of ions with different charge takes place. Moreover, the Jahn-Teller effect, due to the electronic properties of Cu, induces important distortions in octahedral sites of clay minerals. The wide differences existing in the NIR and MIR spectra between pure and Cu-rich kaolinites may logically be reliable to the important perturbations of OH vibrations resulting from the Cu^{2+} cations in the octahedral sheets of kaolinite.

From these results, it appears clearly that NIR spectroscopy is a simple but very powerful tool to characterize octahedral substitutions in kaolinites. Because specific cationic substitutions reflect the crystallization conditions of kaolinite (Cases et al. 1986; Muller and Calas 1989), it can be used as a sensitive diagnostic tool, by itself or to complement MIR, in environmental geochemistry.

ACKNOWLEDGMENTS

REFERENCES

Alpert NL, Keiser WE, Szymanski HA. 1964. IR—Theory and practice of infrared spectroscopy. New York: Plenum Pr. 380 p.

Bell VBA, Citro VR, Hodge GD. 1991. Effect of pellet pressing on the infrared spectrum of kaolinite. Clays Clay Miner 39:290–292.

Besson G, Drits VA. 1997. Refined relationships between chemical composition of dioctahedral fine-grained mica-

ceous minerals and their infrared spectra within the OH stretching region. Part II: The main factors affecting OH vibrations and quantitative analysis. Clays Clay Miner 45: 170–183.

Bishop JL, Pieters CM, Edwards JO. 1994. Infrared spectroscopic analyses on the nature of water in montmorillonite. Clays Clay Miner 42:702–716.

Brookins DG. 1973. Chemical and X-ray investigation of chromiferous kaolinite ("miloschite") from The Geysers, Sonoma County, California. Clays Clay Miner 21:421–422.

Cariati F, Erre L, Micera G, Piu P, Gessa C. 1981. Water molecules and hydroxyl groups in montmorillonites as studied by near infrared spectroscopy. Clays Clay Miner 29:157–159.

Cariati F, Erre L, Micera G, Piu P, Gessa C. 1983a. Polarization of water molecules in phyllosilicates in relation to exchange cations as studied by near infrared spectroscopy. Clays Clay Miner 31:155–157.

Cariati F, Erre L, Micera G, Piu P, Gessa C. 1983b. Effects of layer charge on the near infrared spectra of water molecules in smectites and vermiculites. Clays Clay Miner 31: 447–449.

Cases JM, Cunin P, Grillet Y, Poinsignon C, Yvon J. 1986. Methods of analyzing morphology of kaolinite: Relations between crystallographic and morphological properties. Clay Miner 21:55–68.

Crowley JK, Vergo N. 1988. Near-infrared reflectance spectra of mixtures of kaolin-group minerals: Use in clay mineral studies. Clays Clay Miner 36:310–316.

Decarreau A, Grauby O, Petit S. 1992. The actual distribution of octahedral cations in 2:1 clay minerals: Results from clay synthesis. Appl Clay Sci 7:147–167.

Delineau T, Allard T, Muller JP, Barres O, Yvon J, Cases JM. 1994. FTIR reflectance vs. EPR studies of structural iron in kaolinites. Clays Clay Miner 42:308–320.

Gaite JM, Mosser C. 1993. Experimental and modelized electron paramagnetic resonance spectra of $Cr^{(III)}$ in kaolinites. J Phys Condens Matter 5:4929–4934.

Hlavay J, Jonas K, Elek S, Inczedy J. 1977. Characterization of the particle size and the crystallinity of certain minerals by infrared spectrophotometry and other instrumental methods—I. Investigations on clay minerals. Clays Clay Miner 25:451–456.

Hunt GR, Salisbury JW. 1970. Visible and infrared spectra of minerals and rocks: I. Silicate minerals. Modern Geol 1: 283–300.

Hunt GR, Salisbury JW, Lenhoff CJ. 1973. Visible and infrared spectra of minerals and rocks: VI. Additional silicate. Modern Geol 4:85–106.

Jepson WB, Rowse JB. 1975. The composition of kaolinite. An electron microscope microprobe study. Clays Clay Miner 23:310–317.

Kato E, Kanaoka S, Inagaki S. 1977. Infrared spectra of kaolin minerals in OH region (I); on the glass slide method for the measurement of the infrared spectra in OH region of clay minerals. Rept Govt Industr Agoya 26:203–210.

De Kimpe C, Kodama H, Rivard R. 1981. Hydrothermal formation of kaolinite material from aluminosilicate gels. Clays Clay Miner 29:446–450.

Lindberg JD, Snyder DG. 1972. Diffuse reflectance spectra of several clay minerals. Am Mineral 57:485–493.

Madejová J, Komadel P, Cícel B. 1994. Infrared study of octahedral site populations in smectites. Clay Miner 29: 319–326.

Maksimovic Z, Brindley GW. 1980. Hydrothermal alteration of a serpentinite near Takovo, Yugoslavia, to chromiumbearing illite/smectite, kaolinite, tosudite, and halloysite. Clays Clay Miner 28:295–302.

Maksimovic Z, White JL. 1973. Infrared study of chromiumbearing halloysites. In: Serratosa JM, editor. Proc Int Clay Conf; Madrid; 1972. Madrid: Div Ciencias, CSIC. p 61–73.

Maksimovic Z, White JL, Logar M. 1981. Chromium-bearing dickite and chromium-bearing kaolinite from Teslic, Yugoslavia. Clays Clay Miner 29:213–218.

Martin F, Petit S, Decarreau A, Ildefonse Ph, Grauby O, Béziat D, de Parseval Ph, Noack Y. 1998. Ga/Al substitutions in synthetic kaolinites and smectites. Clay Miner 33:231–241.

Mendelovici E, Yariv SH, Villalba R. 1979. Iron-bearing kaolinite in Venezuelan laterite. I. Infrared spectroscopy and chemical dissolution evidence. Clay Miner 14:323–331.

Mosser C, Petit S, Mestdagh M. 1993. ESR and IR evidences for chromium in kaolinites. Clay Miner 28:353–364.

Muller JP, Calas G. 1989. Tracing kaolinites through their defect centers; kaolinite paragenesis in a laterite (Cameroon). Econ Geol 84:694–707.

Petit S, Decarreau A. 1990. Hydrothermal (200 °C) synthesis and crystal chemistry of iron-rich kaolinites. Clay Miner 25:181–196.

Petit S, Decarreau A, Mosser C, Ehret G, Grauby O. 1995. Hydrothermal synthesis (250 °C) of copper-substituted kaolinites. Clays Clay Miner 43:482–494.

Petit S, Robert JL, Decarreau A, Besson G, Grauby O, Martin F. 1995. Apport des méthodes spectroscopiques à la caractérisation des phyllosilicates 2:1. Bull Elf Aquitaine Prod, 19.1:119–147.

Pontual S, Cocks T. 1994. The Pima II: A new technique for field-based alteration mapping. The AusIMM Annual Conference, Darwin. p 393–398.

Post JL, Noble PN. 1993. The near-infrared combination band frequencies of dioctahedral smectites, micas, and illites. Clays Clay Miner 41:639–644.

Rengasamy P. 1976. Substitution of iron and titanium in kaolinites. Clays Clay Miner 24:264–266.

Robert JL, Kodama H. 1988. Generalization of the correlations between hydroxyl-stretching wavenumbers and composition of micas in the system K_2O-MgO-Al_2O_3-SiO_2-H_2O: A single model for trioctahedral and dioctahedral micas. Am J Sci 288-A:199–212.

Singh B, Gilkes RJ. 1991. Weathering of a chromian muscovite to kaolinite. Clays Clay Miner 39:571–579.

Stubican V, Roy R. 1961. A new approach of assignment of infra-red absorption bands in layer-structure silicates. Z Kristall Bd 115, S:200–214.

Tomura S, Shibasaki Y, Mizuta H, Kitamura M. 1985. Growth conditions and genesis of spherical and platy kaolinite. Clays Clay Miner 33:200–206.

Vedder W. 1964. Correlations between infrared spectrum and chemical composition of mica. Am Mineral 49:736–768.

Weaver CE. 1976. The nature of TiO_2 in kaolinite. Clays Clay Miner 24:215–218.