

REFINED RELATIONSHIPS BETWEEN CHEMICAL COMPOSITION OF DIOCTAHEDRAL FINE-GRAINED MICA MINERALS AND THEIR INFRARED SPECTRA WITHIN THE OH STRETCHING REGION. PART I: IDENTIFICATION OF THE OH STRETCHING BANDS

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Abstract—A large and representative collection of clay-size dioctahedral mica minerals differing in their chemical compositions has been studied by infrared (IR) spectroscopy in the OH stretching vibration region. Decomposition of the IR spectra in the individual OH bands has provided unambiguous identification of the band positions for each defined pair of octahedral cations bonded to OH groups. The presence of pyrophyllite-like local structural environments in samples having a deficiency of K in interlayers has been established. A set of the relationships between the OH frequencies corresponding to pairs of cations having different valency and mass has been found.

Key Words—Celadonite, Glauconite, Illite, IR Spectra, Leucophyllite, OH Stretching Frequency.

INTRODUCTION

One of the characteristic features of dioctahedral micas, and especially their microdivided species, is a wide spectrum of chemical compositions. Micas having different compositions differ in their fine structural features, and in particular, isomorphous cations in octahedra and tetrahedra of 2:1 layers, distribute with different degrees of order-disorder. Reconstruction of the cation distribution patterns in terms of short- and long-range ordering is one of the main problems in determination of actual mica crystal structures.

Infrared spectroscopy is an effective tool for the determination of local cationic environments as well as fine structural features. The utility of IR spectroscopy in this respect is unique because this method can be used to study samples of any chemical composition, unlike other techniques. For example, nuclear magnetic resonance (NMR) spectroscopy can be used to study Fe-free samples, whereas the Mössbauer method provides information on local environments only around Fe.

To solve questions concerning cation distributions in mica structures by IR spectroscopy, researchers concentrate their attention on identification of the individual absorption bands revealed in mica IR spectra. As a result, the main relationships between structure, composition and IR spectra of various dioctahedral micas have been established (Saksena 1964; Vedder 1964; Farmer 1974; Velde 1978, 1983; Langer et al. 1981; Slonimskaya et al. 1986; Besson et al. 1987; Russell 1987; Robert and Kodama 1988). However, the potential of this method with respect to these minerals has not been exhausted; up until now, identifi-

cation of some absorption bands has not been established unambiguously, and there are few published reports of quantitative analysis of mica IR spectra.

This is particularly true for the OH stretching region, although important progress has recently been achieved in interpretation of this part of the mica IR spectra (Slonimskaya et al. 1986; Robert and Kodama 1988).

As a rule, the relationships between wave numbers of the OH stretching bands and the local cationic configurations around the OH groups have been established for dioctahedral mica samples having limited variations in their chemical compositions (Slonimskaya et al. 1986; Robert and Kodama 1988). For example, Velde (1978) and Robert and Kodama (1988) studied Al-Mg-containing micas, while Slonimskaya et al. (1986) analyzed Fe-rich micaceous minerals. As a result, there are uncertainties in identification of the OH stretching frequencies.

Some problems exist in establishing the factors responsible for the regularities observed in dioctahedral mica IR spectra (Farmer 1974; Vedder 1964; Velde 1983; Brindley and Kao 1984; Robert and Kodama 1988). For example, even if attribution of the band to the specific atomic configuration around the OH groups is known, it is not always clear why the given frequency and intensity of the vibration correspond to the given local cation environment.

The aim of this work is to clarify the relationships between structure, composition and IR spectra of dioctahedral micas based upon the IR study of a representative collection of samples. The IR spectrum of each sample in the OH stretching region (3400 to 3700

cm^{-1}) was decomposed into individual bands to determine their number, position and intensity more precisely. This approach was developed by Slonimskaya et al. (1986), who first tried to quantify the OH stretching vibrations of the glauconite IR spectra. In the present work, this approach was improved by using a more modern spectrometer, changing some details in the decomposition procedure and getting higher quality fitting between experimental IR spectra and those synthesized by summation of all individual bands.

This paper considers the results of the decomposition of the IR spectra of illites, leucophyllites, celadonites and glauconites in the region of the OH-stretching frequencies. We have determined the position and intensity of each individual band in the spectra under study in order to solve the following problems:

- 1) To refine relationships between the nearest OH group cationic environments and the corresponding OH-stretching frequencies;
- 2) To reveal the main factors responsible for the observed dependence between the sequence of the bands corresponding to different cation configurations and their wave numbers;
- 3) To refine the technique of quantitative analysis of the OH-stretching vibrations.

In Part I of this paper, we will describe the results of the study of the first of these problems.

SAMPLES AND EXPERIMENTS

Chemical compositions of the samples under study include the wide compositional range from Al-Mg-rich end members (leucophyllites) to Fe^{3+} -Mg-rich end members (celadonites) with minimal Al for Si substitution, as well as from illites to glauconites containing a high amount of Al^{IV} cations in tetrahedral sheets. Some of these samples have compositions intermediate between illite, celadonite and leucophyllite with different contents of Fe^{3+} , Al, Fe^{2+} and Mg in octahedra, and different degrees of Al for Si substitution.

The structural formulae of the samples, as well as the references describing their mineralogical and structural characteristics, are given in Table 1. All samples have been studied by X-ray and oblique texture electron diffraction methods. It was found that the samples are monomineralic, belong to $1M$ or $1M_d$ polytypes, and have vacant *trans*-sites in their 2:1 layers.

The IR spectra in the OH-stretching region were obtained with a Bruker 113 spectrometer. The alkali halide pressed-disk technique was used: 3 mg of $< 2 \mu\text{m}$ equivalent spherical diameter sample was added to ≈ 200 mg of KBr in a steel capsule. Steel balls were added, and the mixture was ground and mixed for 2 min in a vibratory grinder. The disk obtained after pressing was heated at $\approx 120^\circ\text{C}$ for 12 h to remove most of the absorbed water. Absorption intensities were recorded from 2200 to 4000 cm^{-1} at 1-cm^{-1} in-

tervals. The transmission intensity, I_t , for each frequency, ν , was transformed to optical density, $I\nu$, according to the equation:

$$I\nu = \text{Log} (I_0/I_t) \quad [1]$$

where I_0 is the intensity of the incident beam.

Positions of individual bands were revealed from the analysis of the modulations of the curves obtained as a result of the first and second derivations of the functions $I\nu = f(\nu)$ describing the profiles of the experimental IR spectra. The extracted individual band positions were used for decomposition of the OH-stretching spectra for the individual bands. As proposed by Slonimskaya et al. (1986), the wide band of molecular water with its absorption maximum at 3400 cm^{-1} , which usually overlaps on its high-frequency side the spectrum of the structural OH stretching vibrations, was included on the spectrum being decomposed as one of the components. In fact, we have found that the IR spectra under study contain 2 absorption bands at 3420 cm^{-1} and 3260 cm^{-1} corresponding to 2 types of structurally connected water molecules.

Decomposition of the spectra was carried out using a computer program written for the purpose by B. Lanson. Our experience has shown that a maximum number of different octahedral cation pairs bonded to OH groups is equal to 14, and that 2 types of structurally connected water require 2 additional bands. Therefore, the program can extract up to 16 individual bands within an experimental spectrum within the interval of wave numbers from 3400 to 3800 cm^{-1} . It was assumed that all OH bands have a Lorentzian form and that the variable parameters describing individual bands were its position, width at half height and intensity. The quality of the decomposition was estimated by the χ^2 values as well as by common agreement of all parts of the experimental IR spectrum profile with those of the IR spectrum synthesized by summation of all extracted individual bands. It was assumed that the integrated optical densities were proportional to the areas of the corresponding bands transformed to optical density. The main difference between the procedures used by Slonimskaya et al. (1986) and in the present work is the level of accuracy. In their work, each spectrum was digitized at 2.5-cm^{-1} intervals, and as a result, it contained only 150–200 points. In this paper, the contributions of molecular water were also measured with the precision higher than that achieved by those authors.

As mentioned, the first stage of the IR spectra treatment includes determination of the number and position of the bands based upon analysis of the derivations of the experimental spectrum profile. This formal method was applied at first to spectra with rather well-modulated intensity distribution (samples: MOL, 31, 69, Z1, TAH). The individual band positions that were

Table 1. Cation composition of the study samples calculated for O₁₀(OH)₂.

	1	2	3	4	5	6	7	8	9	10	11
Sample	933	132	1040	Z1	69	5/1	655	TAH	PIL	68/69	E8/2
Cation											
Si	3.88	3.96	3.79	3.96	3.94	3.69	3.71	3.72	3.73	3.78	3.65
Al	0.02	0.04	0.21	0.04	0.06	0.31	0.29	0.28	0.27	0.22	0.35
Fe	0.10										
Tet Ch	0.12	0.04	0.21	0.04	0.06	0.31	0.29	0.28	0.27	0.22	0.35
Al	0.00	0.00	0.01	0.05	0.05	0.13	0.16	0.16	0.44	0.55	0.68
Fe ³⁺	1.47	1.32	1.33	0.96	1.15	1.30	1.10	1.07	0.93	0.89	0.79
Fe ²⁺	0.00	0.07	0.27	0.26	0.36	0.07	0.12	0.14	0.21	0.18	0.10
Mg	0.53	0.57	0.39	0.73	0.41	0.50	0.63	0.64	0.42	0.39	0.43
Oct Cat	2	1.96	2	2	1.97	2	2.01	2.01	2	2.01	2
Oct Ch	0.53	0.76	0.66	0.99	0.86	0.57	0.72	0.75	0.63	0.54	0.53
K	0.43	0.67	0.70	0.89	0.83	0.78	0.92	0.82	0.75	0.80	0.78
Na	0.08	0.02	0.07		0.01			0.18	0.06		0.01
Ca	0.02	0.04		0.08	0.03	0.02					0.03
Mg	0.05		0.05			0.02	0.05		0.05		
Int Cat	0.58	0.73	0.82	0.97	0.87	0.82	0.97	1	0.86	0.8	0.82
Tot Ch	0.65	0.8	0.87	1.03	0.92	0.88	1.01	1.03	0.9	0.76	0.88

Key: 1, 2, 3—celadonites (Lipkina et al. 1987; Drits et al. 1993); 4—celadonite (Malkova 1956; Dainyak et al. 1984; Drits et al. 1993); 5—celadonite (Pavlishin et al. 1978; Drits et al. 1993); 6, 12—glaucanites (Ivanovskaya 1986, 1989); 7, 9, 11—glaucanites (Nicolaeva 1977; Drits et al. 1993); 8—glaucanite (Kimbara and Shimoda 1973); 10—glaucanite (Shutov et al. 1975; Drits and Kossovskaya 1991); 13—Fe-illite from illite stratum, Syria, given by V.I. Muraviev (GIN RAN, Moscow); 14, 15—leucophyllites (Raskazov 1984); 16—Fe-illite (Nikolaeva 1977; Drits et al. 1993); 17, 18—leucophyllites (Sokolova et al. 1976); 19—illite (Ivanovskaya et al. 1989); 20, 21—illites (Eberl et al. 1987); 22—Synthetic muscovite (Besson collection); 23—Synthetic pyrophyllite (Besson collection).

established unambiguously for these samples were used for the spectra decomposition of the other samples.

RESULTS AND DISCUSSION

Refinement of the Correlations between the Cation Environment of the OH Groups and Wave Numbers

The results of the decomposition of all studied IR spectra are given in Table 2, and selected spectra are shown in Figures 1 through 8.

The data in Table 2 show a very small variation interval of the wave numbers corresponding to each given cationic pair. For example, wave numbers of each specific band corresponding to different samples usually vary ± 2 cm⁻¹ around a mean value and more rarely ± 3 cm⁻¹ (Figures 9 and 10). Thus the band positions have relatively low sensitivity to the variation of the sample chemical compositions. We have found only a few deviations from the regularities mentioned above. For example, wave numbers for the

Table 2. Decomposition of the IR spectra of the studied samples in individual OH bands corresponding to different pairs of cations bonded to OH groups. The OH frequencies corresponding to mica-like and pyrophyllite-like local environments are separated.

Sample pair	933	132	1040	Z1	69	5/1	655	TAH	PIL	68/69
Mica like										
Fe ²⁺ Fe ²⁺	3504	3506	3504	3507	3503	3505	3503	3504		
Fe ²⁺ Fe ³⁺	3521	3520	3521	3526	3526	3522	3519	3520	3523	3521
Fe ³⁺ Fe ³⁺	3536	3534	3537	3533	3533	3533	3535	3533	3538	3537
Mg Fe ²⁺				3545	3542	3543	3545		3544	
Mg Fe ³⁺										
Al Fe ²⁺	3560	3558	3558	3556	3556	3559	3562	3558	3559	3558
Al Fe ³⁺	3575		3572	3573	3571	3573		3571	3572	3573
Mg Mg	3585	3580	3583	3581	3581	3585	3583	3580	3584	3584
Al Mg		3601	3604	3601	3601	3604	3605	3603	3605	3604
Al Al				3621		3617	3618	3621	3623	3622
Al Al								3641	3640	3640
Al Al								3658		
Pyr. like										
Fe ³⁺ Fe ³⁺	3629	3630	3630		3629	3629	3637			
Al Fe ³⁺										
Al Al										

Table 1. Extended.

12	13	14	15	16	17	18	19	20	21	22	23
40/7	CH	136	31	BP	Z2	MOL	60	RM4	RM30	38/60	BIN
3.7	3.42	4	3.94	3.46	3.80	3.75	3.63	3.34	3.27	3.18	3.93
0.3	0.58	0	0.06	0.54	0.20	0.25	0.37	0.66	0.73	0.82	0.07
0.3	0.58	0	0.06	0.54	0.2	0.25	0.37	0.66	0.73	0.82	0.07
0.87	0.92	1.05	1.10	1.11	1.18	1.27	1.41	1.75	1.86	2.00	1.96
0.64	0.74	0.17	0.17	0.41	0.17	0.05	0.10	0.09			0.04
0.20	0.07	0.21	0.07	0.13	0.06	0.00	0.07				
0.29	0.27	0.59	0.64	0.35	0.57	0.68	0.42	0.15	0.14		
2	2	2.02	1.98	2	1.98	2	2	1.99	2	2	2
0.49	0.34	0.74	0.77	0.48	0.69	0.68	0.49	0.18	0.14	0	0.00
0.62	0.79	0.72	0.81	0.74	0.86	0.78	0.77	0.79	0.89	0.79	0.07
0.03	0.02	0.01	0.03	0.01	0.02	0.05	0.07	0.01	0.01	0.01	
0.02	0.05			0.06			0.01				
0.03				0.07		0.04					
0.7	0.86	0.73	0.84	0.88	0.88	0.87	0.85	0.8	0.9	0.8	0.07
0.79	0.92	0.74	0.83	1.02	0.89	0.93	0.86	0.84	0.87	0.82	0.07

Al-Al and Al-Mg bands in the IR spectra of Fe-free samples (RM4, RM30 and 38/60) have higher values in comparison with wave numbers of these bands for the other samples (Table 2). However, even in these cases, the differences between specific and mean values of wave numbers for these bands do not exceed 6 cm^{-1} .

The identification of the majority of individual bands given in Table 2 supports that proposed by Slonimskaya et al. (1986), but there are some differences. They assumed that the band at 3505 cm^{-1} corresponds to the Mg-Mg cationic environment of the OH groups. The value of this frequency differs substantially from the peak at 3595 cm^{-1} found for the Mg-Mg band in the IR spectrum of tetrasilicic magnesium mica (TMM), having the composition

$[\text{K}_1\text{Mg}_{2.5}\text{Si}_4\text{O}_{10}(\text{OH})_2]$. Slonimskaya et al. (1986) interpreted this difference as a result of different distribution of vacancies over *cis*- and *trans*-octahedral sites. However, they had no mica sample whose IR spectrum contained a sufficiently strong absorption maximum belonging to the Mg-Mg band. The IR spectrum (Figure 1) obtained from the leucophyllite sample (MOL), whose octahedra contain only 0.05 Fe atoms per unit formula, shows the band at 3583 cm^{-1} (Table 2). Relation of this band to the Mg-Mg cation environment is evident because the Al-Al and Al-Mg bands in this spectrum locate at frequencies higher than 3595 cm^{-1} (Farmer 1974). Velde (1978), studying the IR spectra of synthetic micas in the muscovite-leucophyllite series, observed the weak band at 3580 cm^{-1} for the samples

Table 2. Extended.

E8/2	40/7	CH	136	31	BP	Z2	MOL	60	RM4	RM30	38/60	BIN	Aver. Freq.
					3505								3505
3518	3519		3521		3520								3521
3534	3532	3537	3535		3532	3535	3535	3537					3535
3546	3544		3542	3540	3543	3542	3543						3543
3560	3558	3557	3561	3562	3558	3560	3562	3560					3559
3575	3573	3576	3576		3574	3573		3572					3573
3586	3584	3586	3583	3583	3585	3584	3583	3584					3583
3604	3603	3605	3603	3605	3604	3603	3605	3601	3607	3610			3604
3619	3622	3621	3616	3619	3623	3620	3622	3620	3624	3625	3626		3621
	3644	3640	3639	3640	3641	3641	3636	3640	3642	3640	3645		3641
3657				3654		3658	3655	3659	3658	3658	3661		3658
3633	3633	3631	3629	3631		3631	3633						3631
	3652	3652	3651		3653				3652			3654	3652
	3672		3683						3675	3671	3674	3675	3675

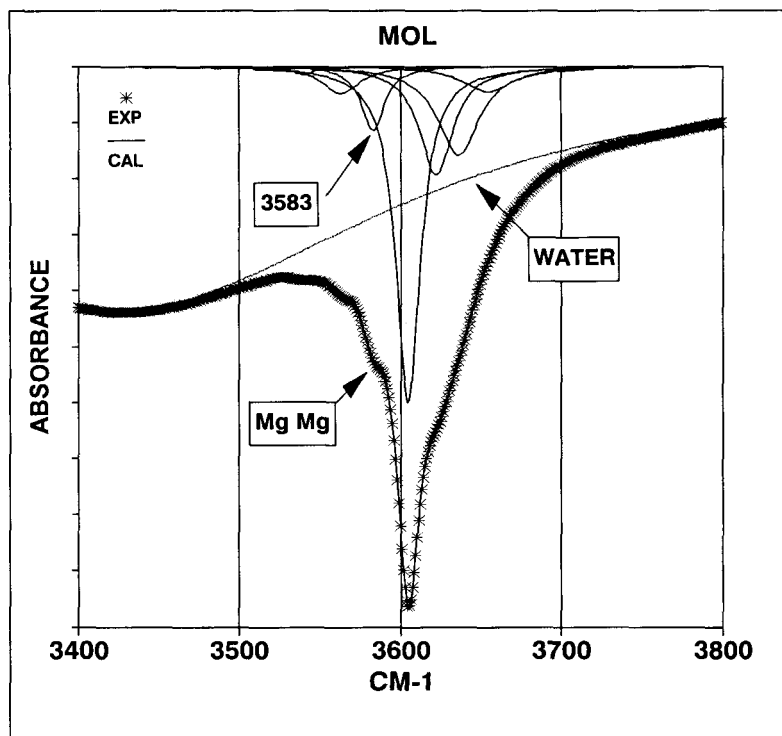


Figure 1. Decomposition of the IR spectrum of sample MOL having leucophyllite chemical composition.

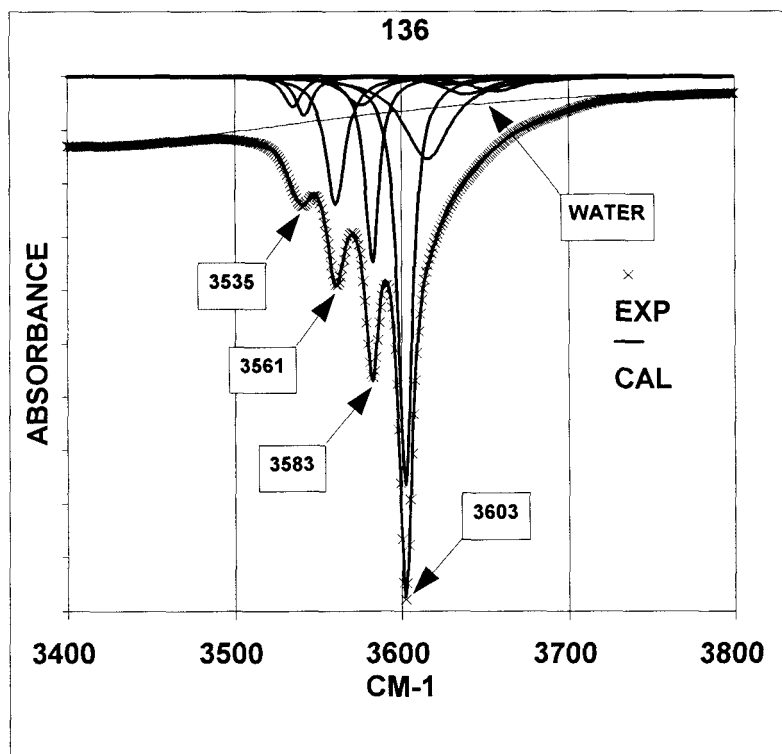


Figure 2. Decomposition of the IR spectrum of sample 136 having leucophyllite chemical composition.

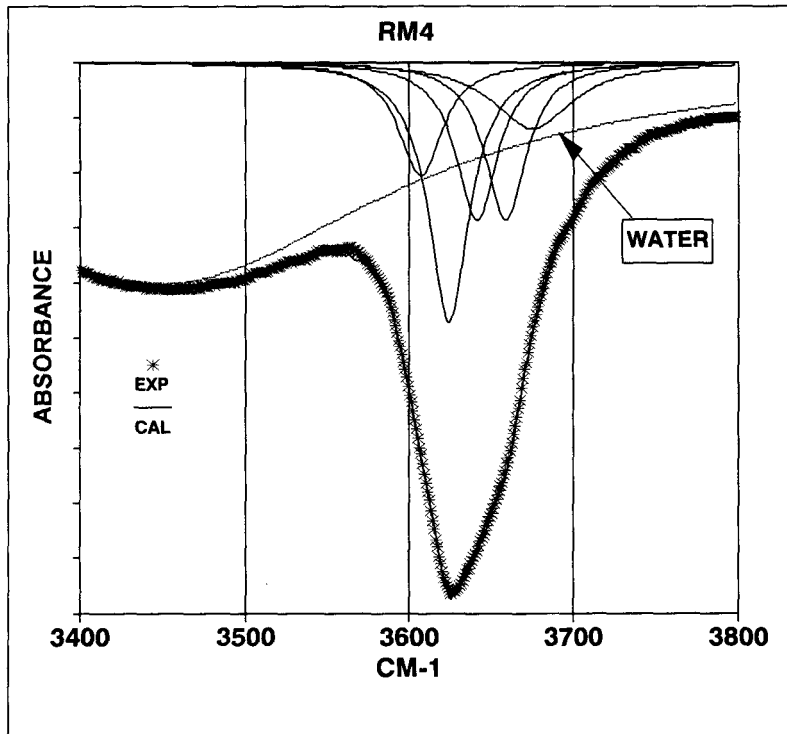


Figure 3. Decomposition of the IR spectrum of sample RM4 having illite chemical composition.

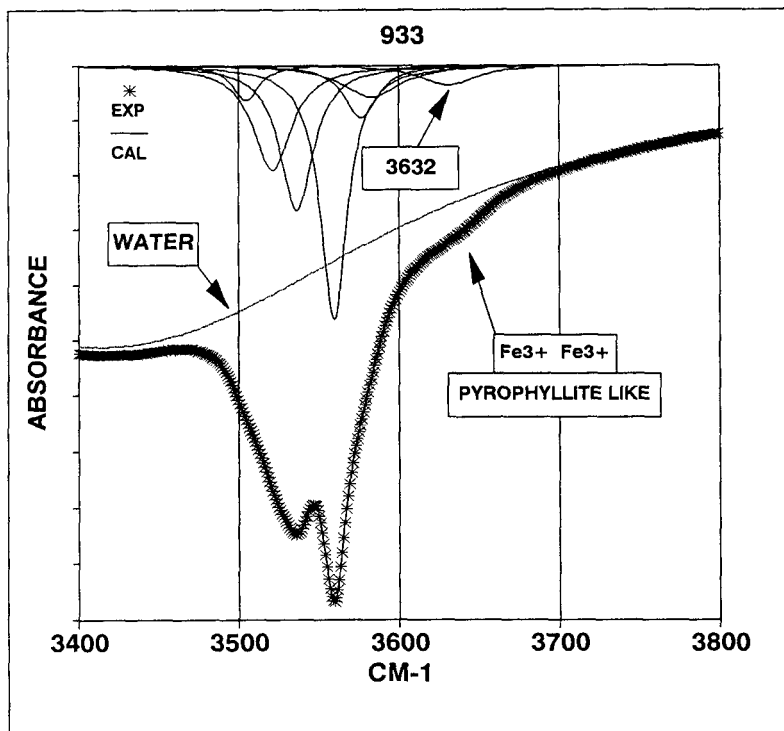


Figure 4. Decomposition of the IR spectrum of sample 933 having glauconite-like chemical composition and a deficiency of K cations.

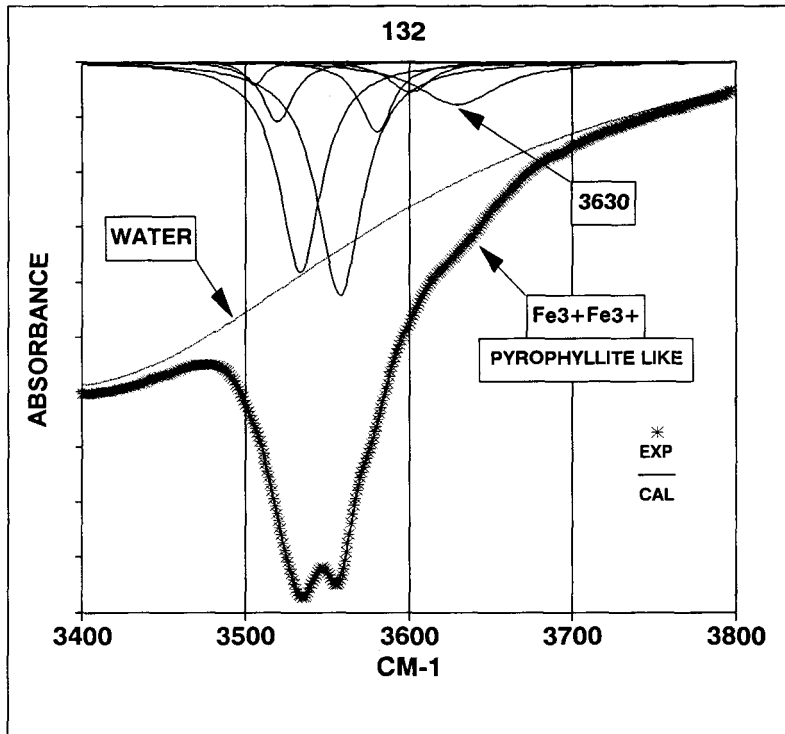


Figure 5. Decomposition of the IR spectrum of sample 132 having celadonite chemical composition and a deficiency of K cations.

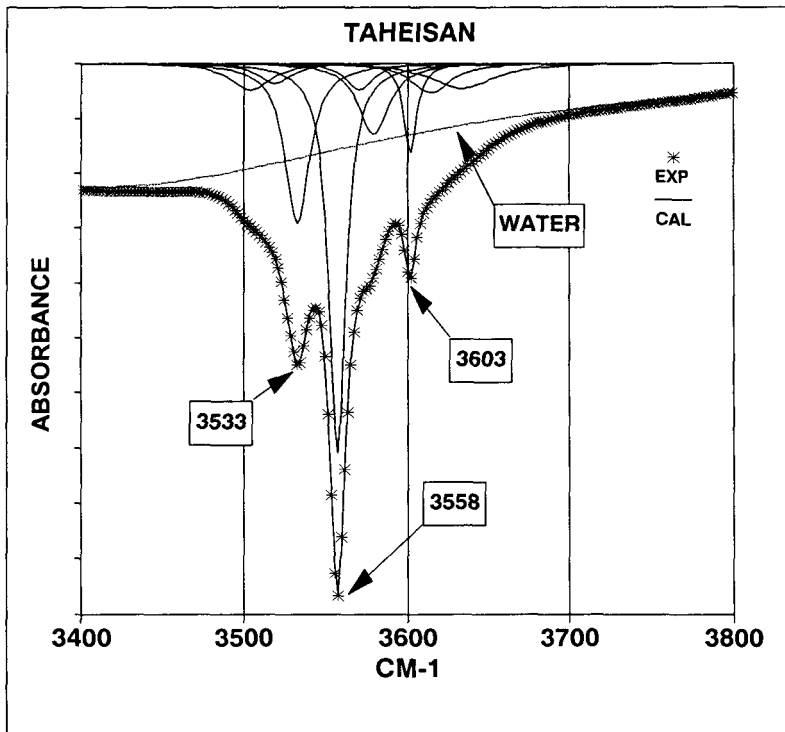


Figure 6. Decomposition of the IR spectrum of sample TAH having glauconite chemical composition.

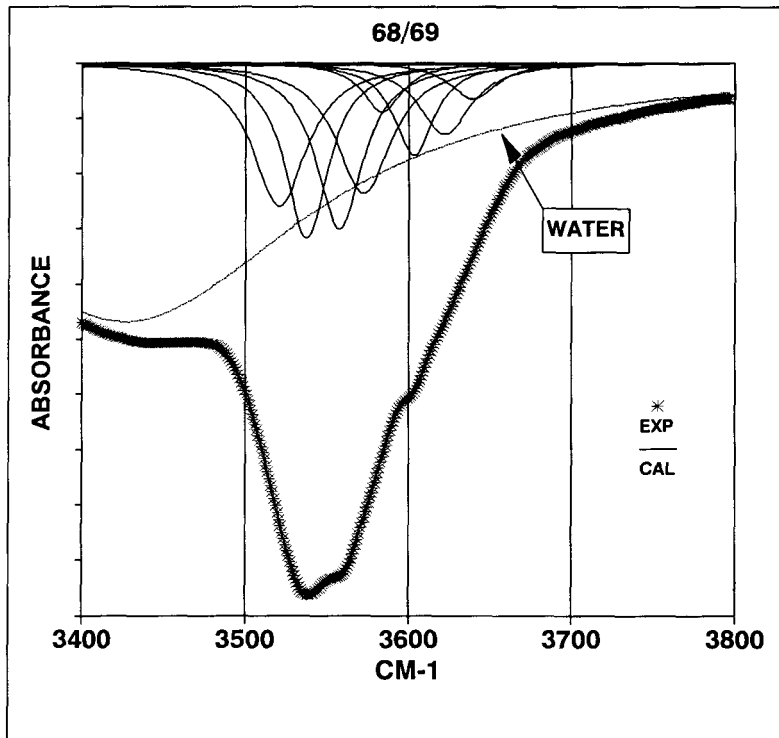


Figure 7. Decomposition of the IR spectrum of sample 68/69 having glauconite chemical composition.

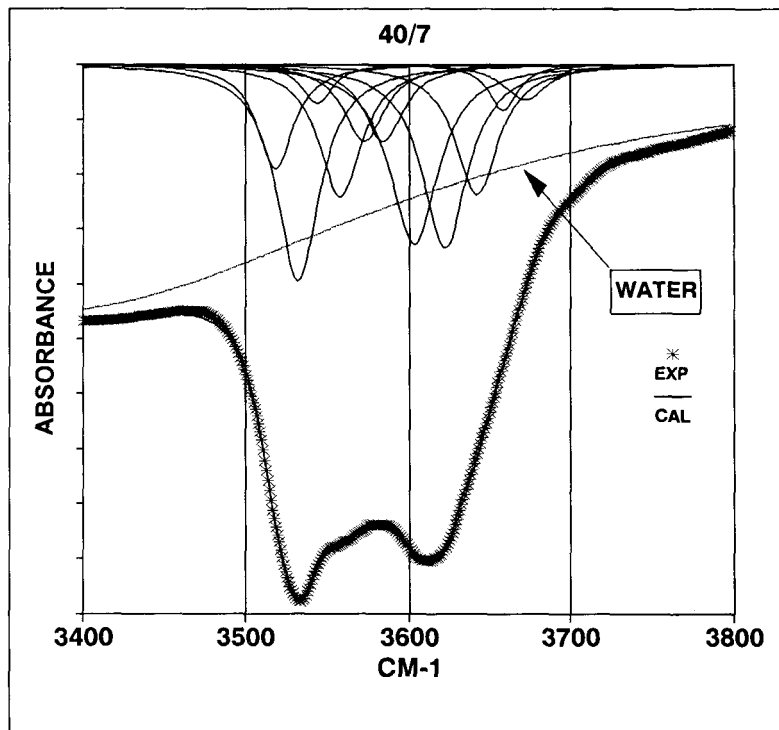


Figure 8. Decomposition of the IR spectrum of sample 40/7 having Fe³⁺-illite chemical composition.

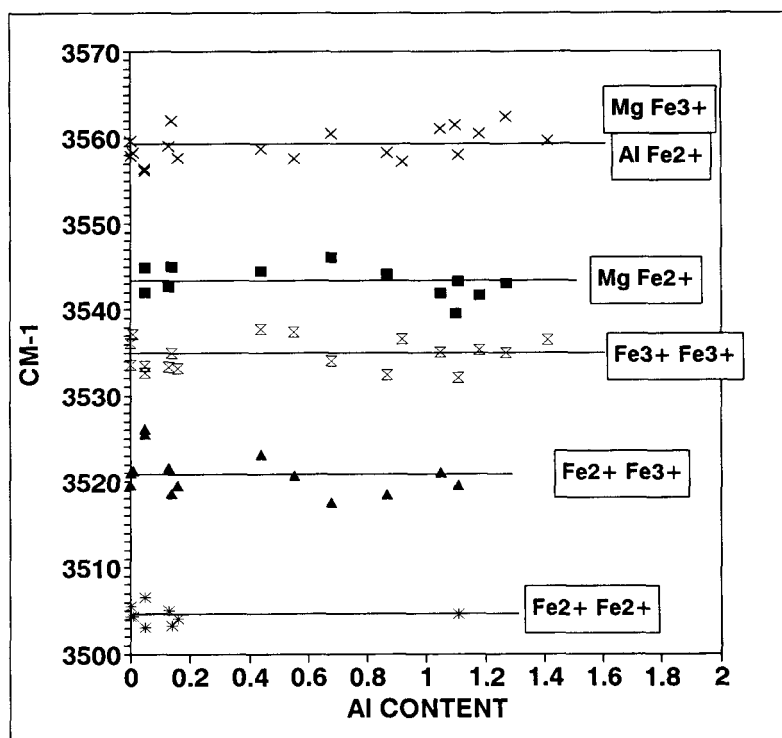


Figure 9. Variation of the observed OH stretching frequencies around mean value (solid line) for the defined cations bonded to OH groups. The values of octahedral Al content along the horizontal axis correspond to those in the samples under study.

containing 70–80 percent of leucophyllite component. These data support identification of the Mg-Mg band at 3580–3583 cm^{-1} . Thus, the transition from di-trioctahedral TMM to dioctahedral mica decreases the wave number of the Mg-Mg band by 10–15 cm^{-1} .

Farmer (1974) supposed that in celadonites and leucophyllites there are only $\text{R}^{3+}\text{R}^{2+}$ groups bonded to OH groups. For this reason, he identified the band at 3577 cm^{-1} in the IR spectra of these minerals as corresponding to Al- Fe^{2+} . Slonimskaya et al. (1986) and Russell (1987) also observed a band at 3578–3580 cm^{-1} in the IR spectra of samples containing relatively high contents of Al and Fe^{2+} . However, according to our interpretation, the Al- Fe^{2+} and Mg- Fe^{3+} bands locate at the same positions ($3559 \pm 3 \text{ cm}^{-1}$), whereas the band at 3573 $\pm 3 \text{ cm}^{-1}$ corresponds to Al- Fe^{3+} . Discussion of these new correlations will be given in the section on factors responsible for the regularities observed in the OH-stretching region (Besson and Drits 1997).

As noted in many papers (Saksena 1964; Vedder 1964; Farmer 1974; Slonimskaya et al. 1978, 1986; Langer et al. 1981), within the frequency interval 3615–3670 cm^{-1} , there are several bands corresponding to the Al-Al configuration. For example, Saksena (1964) observed 4 peaks in a broad Al-Al band of the muscovite IR spectrum which occurred at 3618, 3634,

3650 and 3660 cm^{-1} . For the studied IR spectra, the number of the Al-Al bands depends upon the sample chemical composition. We have found 2 or 3 Al-Al bands for illites and leucophyllites (Figures 1–3), 2 Al-Al bands for Fe-illites and glauconites (Figures 6–8) containing relatively high content of Al^{VI} and Al^{IV} (samples E8/2, BP, 40/7, 68/69, PIL, CH, Table 2) and only 1 Al-Al band for samples having a very low content of Al (Z1, 5/1, 655, Table 2). The Al-Al band between 3617 and 3624 cm^{-1} is common for the spectra of all Al-containing samples. Thus, the contribution of the Al-OH-Al configurations to the absorption bands at the higher frequencies increases with increasing Al cations.

Slonimskaya et al. (1986) noted that, for some glauconite samples, a distinct discrepancy was observed between the distribution of the optical density at the low and high frequencies and the contents of Fe^{3+} and Al in the structural formula. In fact, the IR spectra of these samples have shown relatively strong absorption at the high frequencies (3630–3680 cm^{-1}) despite the low Al content in the chemical analysis. The same regularity was observed for some IR spectra of the studied samples. The IR spectra of samples 933 and 132 (Figures 4 and 5) are remarkable in this respect. According to the structural formulae (Table 1), octahedra and tetrahedra of these samples contain little or no Al^{IV} cations. However, even visual observation of

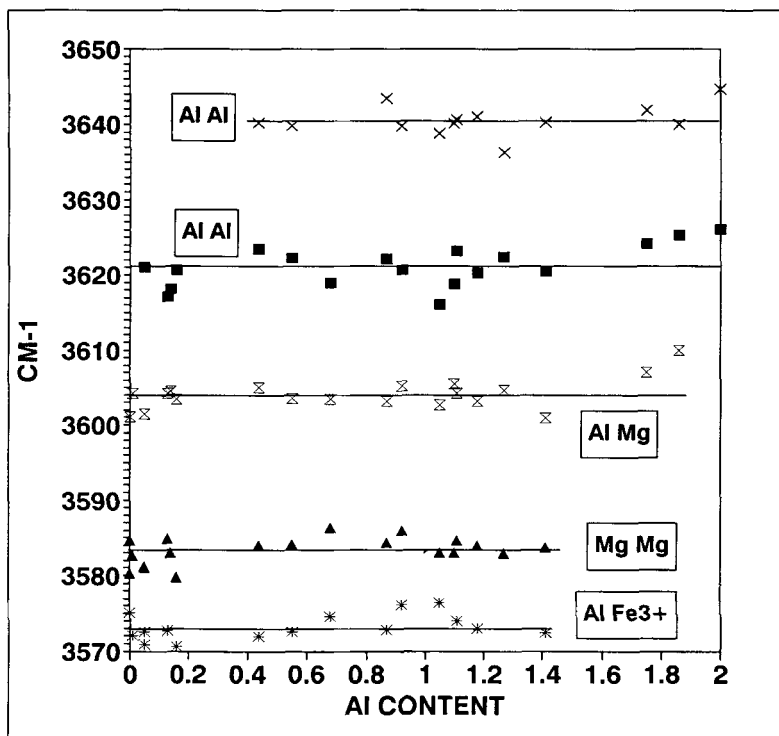


Figure 10. Variation of the observed OH stretching frequencies around mean value (solid line) for the defined pair of cations bonded to OH groups. The values of octahedral Al content along the horizontal axis correspond to those in the samples under study.

these sample spectra shows that they contain a distinct absorption band at 3632 cm^{-1} (Figures 4 and 5, Table 2). We suppose that this band relates to the $\text{Fe}^{3+}\text{-Fe}^{3+}$ cation pair that has the local environment corresponding to that in ferripyrophyllite (Chukhrov et al. 1978). The probability of such local environments follows from the sample chemical composition in which content of Fe^{3+} cations considerably exceeds that of Mg cations in the octahedral sheets (see Table 1, samples 933 and 132). This suggests that, among all possible cationic pairs coordinating OH groups, the $\text{Fe}^{3+}\text{-Fe}^{3+}$ pairs have to prevail. Taking into account the very low degree of Si for R^{3+} substitution in tetrahedra, as well as the presence of vacancies in the interlayers due to a deficiency of K, the existence of the ferripyrophyllite-like local structural environments in these samples is very probable.

Chukhrov et al. (1978) observed 2 absorption bands at 3630 and 3590 cm^{-1} in the ferripyrophyllite IR spectra. X-ray diffraction study of ferripyrophyllite samples has shown that they consist of 2 compounds: 1) nonhydrated and nonswelled ferripyrophyllite and 2) hydroferripyrophyllite, containing water molecules in the interlayers and having swelling properties. It is possible to assume that the band at 3630 cm^{-1} corresponds to the $\text{Fe}^{3+}\text{-Fe}^{3+}$ cationic pairs in nonhydrated ferripyrophyllite. Coincidence of this wave number with

that found for the band in the IR spectra of $\text{Fe}^{3+}\text{-Mg}$ celadonite-like samples (132, 1040, 933) supports the possibility of the presence of ferripyrophyllite local environments in dioctahedral mica structures having a K deficiency in the interlayers. Two important conclusions follow from this interpretation. First, K cations in the mica interlayers change the wave number of the $\text{Fe}^{3+}\text{-Fe}^{3+}$ band from 3536 to 3635 cm^{-1} . Second, even for strictly dioctahedral potassic mica structures, the interval of wave numbers between 3630 and 3660 cm^{-1} is not only related to Al-Al bands. Moreover, pyrophyllite-like local environments in dioctahedral micaceous minerals may exist not only for $\text{Fe}^{3+}\text{-Fe}^{3+}$ cationic pairs, but also for $\text{Fe}^{3+}\text{-Al}$ and Al-Al ones. The corresponding bands should have higher frequencies than the $\text{Fe}^{3+}\text{-Fe}^{3+}$ band, as follows from the comparison of the IR spectra of ferripyrophyllite and pyrophyllite. Keeping in mind this new result, the interpretation given by Slonimskaya et al. (1986) for the IR spectra having the feature mentioned above needs to be reconsidered.

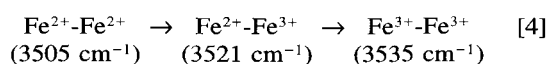
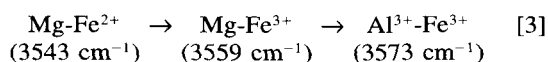
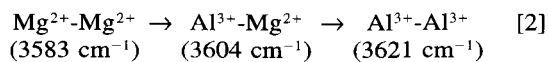
Decomposition of the IR spectrum of sample 38/60 indicates a relatively intensive band at 3674 cm^{-1} (Table 2). According to the structural formula (Table 1), the unit cell of this sample contains 4 Al^{VI} , $1.64\text{ Al}^{\text{IV}}$, 1.58 K and 0.42 vacancies in the interlayer. The presence of pyrophyllite-like local environ-

ments in the sample structure is very probable. This conclusion follows also from the coincidence of wave numbers for the Al-Al bands observed in the IR spectra of pyrophyllite (3675 cm⁻¹) and samples 38/60, RM4 and RM30 (Table 2). It is noteworthy that decomposition of some IR spectra, including the IR spectrum of pyrophyllite sample BIN containing a small amount of octahedral Fe³⁺ (Table 2), displayed a low intensive peak at about 3651–3653 cm⁻¹. Probably it corresponds to the Al-Fe³⁺ pairs, because the wave number of this OH band has a value intermediate between those of the wave numbers corresponding to the Al-Al and Fe³⁺-Fe³⁺ bands. Note that Farmer (1974) in the pyrophyllite IR spectrum observed a band at 3647 cm⁻¹, which was assigned to an Al-Fe³⁺ configuration.

Some Regularities in Distribution of the Positions of the Bands Corresponding to the Different Cationic Environments of the OH Groups

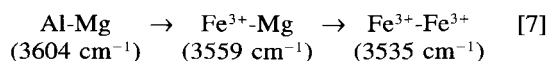
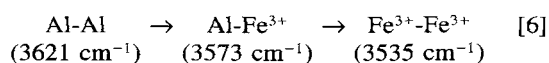
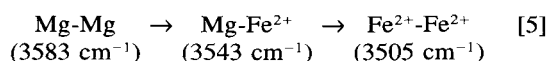
Analysis of the data given in Table 2 permits us to formulate some general relationships in the sequence of the bands corresponding to different types of cations bonded to OH groups:

1) For cations with similar or identical atomic mass coordinating OH groups, the increase of the sum of their valencies leads to an increase in wave number of the corresponding band. This regularity can be schematically illustrated by the following subsequences:



Here the upper line for each subsequence is the cation configuration around OH groups, and the lower one shows the corresponding wave numbers.

2) For the same sum of valencies of cations nearest to OH groups, increase of common mass of these cations leads to a decrease in wave number of the corresponding band. For example:



3) The positions of the bands corresponding to different cationic pairs are not independent, and some of them are related by the following equalities:

$$2\nu(\text{Mg-Fe}^{3+}) = \nu(\text{Mg-Mg}) + \nu(\text{Fe}^{3+}\text{-Fe}^{3+}),$$

$$2\nu(\text{Fe}^{2+}\text{-Mg}) = \nu(\text{Fe}^{2+}\text{-Fe}^{2+}) + \nu(\text{Mg-Mg}),$$

$$2\nu(\text{Fe}^{3+}\text{-Fe}^{2+}) = \nu(\text{Fe}^{3+}\text{-Fe}^{3+}) + \nu(\text{Fe}^{2+}\text{-Fe}^{2+}),$$

$$2\nu(\text{Al-Fe}^{3+}) = \nu(\text{Al-Al}) + \nu(\text{Fe}^{3+}\text{-Fe}^{3+}),$$

$$2\nu(\text{Al-Fe}^{2+}) = \nu(\text{Al-Al}) + \nu(\text{Fe}^{2+}\text{-Fe}^{2+}),$$

$$2\nu(\text{Al-Mg}) = \nu(\text{Al-Al}) + \nu(\text{Mg-Mg}) \quad [8]$$

These relations will be valid if:

$$\begin{aligned} \nu(\text{Al-Al}) &= 3621 \text{ cm}^{-1}, & \nu(\text{Mg-Mg}) &= 3583 \text{ cm}^{-1}, \\ \nu(\text{Fe}^{2+}\text{-Fe}^{2+}) &= 3505 \text{ cm}^{-1}, & \nu(\text{Fe}^{3+}\text{-Fe}^{3+}) &= 3535 \text{ cm}^{-1}, \\ \nu(\text{Fe}^{2+}\text{-Fe}^{3+}) &= 3520 \text{ cm}^{-1}, & \nu(\text{Al-Mg}) &= 3602 \text{ cm}^{-1}, \\ \nu(\text{Al-Fe}^{2+}) &= 3563 \text{ cm}^{-1}, & \nu(\text{Al-Fe}^{3+}) &= 3578 \text{ cm}^{-1}, \\ \nu(\text{Fe}^{3+}\text{-Mg}) &= 3559 \text{ cm}^{-1}, & \nu(\text{Fe}^{2+}\text{-Mg}) &= 3544 \text{ cm}^{-1} \end{aligned}$$

These values coincide with the mean wave numbers given for the corresponding bands in Table 2, except that the wave numbers for the Al-Fe³⁺ and Al-Fe²⁺ bands differ by 5 and 4 cm⁻¹, respectively. It is interesting to note that, for all samples, the Al-Mg band wave numbers within ±1 cm⁻¹ coincide with those calculated by adding 20 cm⁻¹ to the Mg-Mg band frequencies.

CONCLUSION

The high quality of the decomposition of the IR spectra of a representative collection of microdivided dioctahedral micaceous minerals has permitted us for the first time to establish unambiguously the positions of the OH stretching bands corresponding to each specific cationic pair bonded to OH groups. It pertains, in particular, to the wave numbers for the Mg-Mg, Al-Fe²⁺ and Al-Fe³⁺ bands. The analysis of data obtained has revealed several regularities. For example, wave numbers of the bands corresponding to different local cationic environments around the OH groups have a weak dependence from the sample chemical composition. A set of linear dependences between the wave numbers of bands corresponding to the defined cationic pairs was established. On the qualitative level, it was shown that the wave numbers of the bands depend first of all on the valency and mass of cations bonded to OH groups. Decomposition of the IR spectra permits us to establish a presence of pyrophyllite Al-Al, Fe³⁺-Fe³⁺ and probably Al-Fe³⁺ local structures within the mica matrix.

Nevertheless, the data obtained were limited only by empirical observations. The aim of Besson and Drits (1997) is to discuss the factors responsible for the appearance of these regularities. In addition, the procedure for the qualitative analysis of the OH stretching region for determination of the octahedral cation contents of the samples under study has to be refined.

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REFERENCES

- Besson G, Drits VA. 1997. Refined relationships between chemical composition of dioctahedral fine-grained micaeous 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.
- Besson G, Drits VA, Dainyak LG, Smoliar BB. 1987. Analysis of cation distribution in dioctahedral micaeous minerals on the basis of IR spectroscopy data. *Clay Miner* 22: 465–478.
- Brindley GW, Kao CC. 1984. Structural and IR relations among brucite-like divalent metal hydroxides. *Phys Chem Miner* 10:187–191.
- Chukhrov FV, Zvyagin BB, Drits VA, Gorshkov AI, Ermilova LP, Goilo EA, Rudnitskaya ES. 1978. The ferric analogue of pyrophyllite and related phases. In: Mortland M, Farmer VC, editors. *Proc Int Clay Conf Oxford 1978*. Amsterdam: Elsevier Science. p 55–64.
- Dainyak LG, Bookin AS, Drits VA. 1984. Interpretation of the Mössbauer spectra of dioctahedral Fe³⁺-layer silicates. 3 Celadonite. *Kristallografiya* 29:312–321 (in Russian).
- Drits VA, Kameneva MYu, Sakharov BA, Dainyak LG, Tsipursky SI, Smoliar BB, Bookin AS, Salyn AL. 1993. Determination of real crystal structure of glauconites and related phyllosilicates. Novosibirsk: Nauka. 200 p (in Russian).
- Drits VA, Kossovskaya AG. 1991. Clay minerals: Micas, chlorites. Moscow: Nauka. 175 p (in Russian).
- Eberl DD, Šrodoň J, Lee M, Nadeau PH, Northrop HR. 1987. Sericite from Silverston Caldera Colorado: Correlation among structure, composition, origin, and particle thickness. *Amer Mineral* 72:914–934.
- Farmer VC. 1974. The layer silicate. In: Farmer VC, editor. *The infrared spectra of minerals*. Monograph 4. London: Mineral Soc p 331–364.
- Ivanovskaya TA. 1986. Mineralogy of dioctahedral glauconites from sedimentary rocks of different ages [Ph.D. thesis.], Moscow: Moscow Univ. 25 p (in Russian).
- Ivanovskaya TA, Tsipursky SI, Yakovleva OV. 1989. Mineralogy of globular glauconites from Vendian and Rophean of the Ural and Siberia. *Litologiya and poleznye iskopaemye* 3:83–99 (in Russian).
- Kimbara K, Shimoda S. 1973. A ferric celadonite in amygdaloids of dolerite at Taiheizan, Akita Prefecture. *Japan Clay Sci* 4:143–150.
- Langer K, Chatterjee ND, Abraham K. 1981. Infrared studies of some synthetic and natural 2M₁ dioctahedral micas. *N Jb Miner Abh* 142:91–110.
- Lipkina MI, Drits VA, Tsipursky SI, Ustinov VI. 1987. Highly ferric dioctahedral layer silicates in hydrothermal rocks and sediments of volcanic formations of Japan sea. *Izvestiya Akad Nauk, Seriya Geol* 10:92–111 (in Russian).
- Malkova KM. 1956. On the celadonite of Pobuzhye. Collected papers on mineralogy. Lvov: Lvov Geol Soc 10: 305–318 (in Russian).
- Nikolaeva IV. 1977. Minerals of the Glauconite Group in Sedimentary Formation. Moscow: Nauka. 321 p (in Russian).
- Pavlishin VI, Platonov AN, Polshin EV, Semenova TF, Starova GK. 1978. Micas with iron in quadrupol coordination. *Trans All-Union Min Soc* 107:165–175 (in Russian).
- Raskazov AA. 1984. Clay Minerals in potassium deposit. Moscow: Nauka. 73 p (in Russian).
- Robert JL, Kodama H. 1988. Generalization of the correlations between hydroxyl-stretching wavenumbers and composition of micas in the system K₂O-Mg₂O-Al₂O₃-SiO₂-H₂O: A single model for trioctahedral and dioctahedral micas. *Amer J Sci* 228 A:196–212.
- Russell JD. 1987. Infrared methods. In: Wilson MJ, editor. *A handbook of determinative methods in clay mineralogy*. New York: Chapman and Hall. p 133–173.
- Saksena BD. 1964. Infrared hydroxyl frequencies of muscovite, phlogopite and biotite micas in relation to their structures. *Trans Farad Soc* 60:1715–1725.
- Shutov VD, Drits VA, Kats MYa. 1975. Crystal chemistry of glauconites as indicator of facial conditions of formation and postsedimental transformation of these minerals. In: Kossovskaya AG, editor. *Crystal chemistry of minerals and geological problems*. Moscow: Nauka. p 74–81 (in Russian).
- Slonimskaya MV, Besson G, Daynyak LG, Tchoubar C, Drits VA. 1986. Interpretation of the IR spectra of celadonites, glauconites in the region of OH-stretching frequencies. *Clay Miner* 21:377–388.
- Slonimskaya MV, Drits VA, Finko VI. 1978. Multistage dehydration of muscovites. *Izvestiya Akad Nauk SSSR, Seriya Geol* 11:98–105 (in Russian).
- Sokolova TN, Drits VA, Sokolova AL, Stepanova KA. 1976. Structural and mineralogical characterization and formation conditions of leucophyllite from saliferous deposits of Inder. *Litologiya and Poleznye Iskopaemye* 6:80–95 (in Russian).
- Vedder W. 1964. Correlations between infrared spectrum and chemical composition of mica. *Am Mineral* 49:736–768.
- Velde B. 1978. Infrared spectra of synthetic micas in the series muscovite-Mg-Al celadonite. *Am Mineral* 63:343–349.
- Velde B. 1983. Infrared OH-stretch bands in potassic micas, talc, and saponite; Influence of electronic configuration and site of charge compensation. *Am Mineral* 68:1169–1173.

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