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Distinguishing Features and Identification Criteria for K-Dioctahedral 1M Micas (Illite-Aluminoceladonite and Illite-Glaucanite-Celadonite Series) from Middle-Infrared Spectroscopy Data

Bella B. Zviagina ¹, Victor A. Drits ¹ and Olga V. Dorzhieva ^{2,*}

¹ Geological Institute, Russian Academy of Science (GIN RAS), 7 Pyzhevsky per., 119017 Moscow, Russia; zbella2001@yahoo.com (B.B.Z.); victor.drits@mail.ru (V.A.D.)

² Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Science (IGEM RAS), 119017 Moscow, Russia

* Correspondence: dorzhievaov@gmail.com

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Abstract: A representative collection of K-dioctahedral 1M micas ranging in composition from (Mg, Fe)-poor illites to aluminoceladonites through Mg-rich illites (Fe-poor varieties) and from Fe-bearing, Mg-rich illites to celadonites through Fe-illites, Al-glaucanites and glaucanites (Fe-bearing varieties) was studied by Fourier-transform infrared (FTIR) spectroscopy in the middle-infrared region. Analysis and comparison of the relationships between the band positions and cation compositions of Fe-poor and Fe-bearing K-dioctahedral micas provided a generalized set of FTIR identification criteria that include the band positions and profiles in the regions of Si–O bending, Si–O stretching, and OH-stretching vibrations. FTIR data allow unambiguous identification of illites, aluminoceladonites, and celadonites, as well as distinction between Fe-illites and illites proper, as well as between Al-glaucanites and glaucanites. Specifically, a sharp maximum from the AlOHMg stretching vibration at $\sim 3600\text{ cm}^{-1}$, the presence of a MgOHMg stretching vibration at $3583\text{--}3585\text{ cm}^{-1}$, as well as characteristic band positions in the Si–O bending ($435\text{--}439$, $468\text{--}472$ and $509\text{--}520\text{ cm}^{-1}$) and stretching regions ($985\text{--}1012$ and $1090\text{--}1112\text{ cm}^{-1}$) are clearly indicative of aluminoceladonite. The distinction between Fe-illites and Al-glaucanites, which have similar FTIR features, requires data on cation composition and unit-cell parameters.

Keywords: IR spectroscopy; illite; aluminoceladonite; glaucanite; celadonite

1. Introduction

Low-temperature K-dioctahedral micas, which are abundant in various geological settings, normally occur as fine-dispersed, interlayer-deficient varieties and 1M and 1Md polytypes. These micas display a wide diversity of isomorphous cation substitutions in the tetrahedral and octahedral sheets and form two intersecting isomorphous series. The first series includes varieties with iron contents of ≤ 0.3 cations per half-formula unit (*p.h.f.u.*), which range in composition from (Mg, Fe)-poor illites to aluminoceladonites through Mg-rich illites. The second series comprises Fe-bearing micas, from Fe-bearing, Mg-rich illites to celadonites through Fe-illites, Al-glaucanites and glaucanites [1–8]. Fe-bearing, Mg-rich illites with a total Fe content of ~ 0.3 cations *p.h.f.u.* are a common joint between the two mica series [8].

The complexity and heterogeneity of chemical composition and structural features, as well as the ambiguity in conventional nomenclature, complicate the identification of these mica varieties. Zviagina et al. [7,8] formulated a set of diagnostic criteria based on combinations of unit-cell parameters

and cation composition variation ranges that are specific for each mica group in the two series. In particular, the distinctive features of aluminoceladonite, which has been often confused with illite, are reduced values of $c\sin\beta$ and $|ccos\beta/a|$ parameters in combination with b parameters that are smaller than those for Mg-rich illites, and slightly greater than those of (Mg, Fe)-poor illites. The compositional boundary between (Mg, Fe)-poor illite and Mg-rich illite occurs at Si ~ 3.4 and Mg + Fe²⁺ ~ 0.2 cations *p.h.f.u.*, and that between Mg-rich illite and aluminoceladonite occurs at Si ~ 3.7 and Mg + Fe²⁺ ~ 0.6 cations *p.h.f.u.* [7].

The basic compositional parameters characterizing the Fe-bearing mica varieties are the total contents of Fe and Al cations and the ratio of octahedral Al cation contents to the total amount of octahedral Al and Fe³⁺ cations *p.h.f.u.*, K_{Al} . In particular, the K_{Al} values are ~ 0.9 in Fe-bearing, Mg-rich illites, 0.65–0.75 in Fe-illites, 0.5–0.6 in Al-glaucanites, <0.5 in glaucanites and (in most cases) <0.2 in celadonites [8].

In certain instances, however, the composition and unit-cell parameters variation ranges for different mica groups may overlap (e.g., Al-glaucanites and glaucanites) leading to complications in the identification. Moreover, simulation of powder X-ray diffraction (XRD) patterns of finely dispersed dioctahedral Fe-bearing dioctahedral micas shows that they may display phase microheterogeneity [9]. This, in turn, may lead to the presence of atypical bands in the IR spectra of micas of highly heterogeneous compositions.

Important additional diagnostic information for K-dioctahedral 1M mica varieties may be obtained from Fourier-transform infrared (FTIR) spectroscopy data and, in particular, from the spectra in the middle-infrared (MIR) region. The MIR spectroscopy of K-dioctahedral micas is addressed in numerous studies (e.g., [7,8,10–30] and references therein). For the most part, however, these works either deal with high-temperature 2M₁ varieties (muscovite and/or phengite) or cover a limited range of 1M mica compositions (e.g., illite or celadonite). Beran [20] deliberately chose not to include illite and glaucanite in his survey of the IR spectroscopic data on micas, as these minerals were “vaguely defined” and occurred “in clay-size fractions”. Slonimskaya et al. [13] and Besson and Drits [17,18], who analyzed the 1M K-dioctahedral micas within a wide compositional range (illites, glaucanites, aluminoceladonites and celadonites), only focused on the OH-stretching vibrations. The most recent IR studies deal with geological applications of spectroscopy data on white mica (e.g., [29,31] or with other groups of silicate minerals [32,33]).

Recently, a number of diagnostic features that include the band positions and profile in the regions of Si–O bending, Si–O stretching, and OH-stretching vibrations were suggested for the illite-aluminoceladonite series [7] and the Fe-bearing K-dioctahedral micas [8]. The objectives of the present work were to (a) compare the relationships between the band positions in all the diagnostic MIR spectral regions and cation compositions of Fe-poor K-dioctahedral micas with those observed in the Fe-bearing varieties; (b) to provide, on this basis, a generalized set of reliable FTIR identification criteria to supplement the diagnostic features obtained from X-ray diffraction and chemical data. For this purpose, MIR spectroscopy data were analyzed for a representative collection of samples of diverse compositions, from (Mg, Fe)-poor illites to aluminoceladonites through Mg-rich illites and from Fe-bearing, Mg-rich illites to celadonites through Fe-illites, Al-glaucanites and glaucanites.

2. Materials and Methods

2.1. Samples

The 43 samples studied range in composition from (Mg, Fe)-free illite to aluminoceladonite through Mg-rich illite, and from (Mg, Fe)-rich illite to celadonite through Fe-illite, Al-glaucanite and glaucanite (see Table 1 for the mineral identity, location, and the references to publications containing mineralogical characterizations). The chemical compositions and the corresponding crystal-chemical formulae (Table 2) for samples RM30, M422, Zempleni, KJMC3, 60/3, 602-1, 136, 68-69, PILT, BAB, TAIH, 69 and Z1 were taken from [5]; for aluminoceladonites Mal-4 and Mal-6, from [7]; for samples 37/71, 37/71a, 103 and 821-057, from [8]; and for the other samples, from the respective publications (see Table 1).

Table 1. Sample description.

#	Sample Name	Mineral Variety	Origin, Location, and Reference
1	RM30	illite, (Mg, Fe)-poor	Miocene hydrothermal, Silverton Caldera, San Juan Mountains., Colorado [34]
2	SG4	illite, (Mg, Fe)-poor	Miocene hydrothermally altered volcanics, Silverton Caldera, San Juan Mountains., Colorado [34]
3	RM35C	illite, (Mg, Fe)-poor	Miocene hydrothermally altered volcanics, Silverton Caldera, San Juan Mountains., Colorado [34]
4	Fuzz-5	illite-smectite, (Ws ¹ = 16%)	Miocene hydrothermally altered volcanics, Fuzzeradvany, Hungary [35,36]
5	Fuzz-6	illite-smectite, (Ws ¹ = 16%)	Miocene hydrothermally altered volcanics, Fuzzeradvany, Hungary [35,36]
6	Zempleni	illite-smectite, (Ws ¹ = 13%)	Miocene hydrothermally altered volcanics, Fuzzeradvany, Hungary [35,36]
7	L-2A-1	illite, Mg-rich	Triassic sandstone, Poland [1]
8	Swe-151	illite-smectite, (Ws ¹ = 15%)	Ordovician K-bentonite, Röstånga, Sweden [37]
9	IWi-1	illite, Mg-rich	Waukesha illite, Silurian, Wisconsin, USA [38]
10	60	illite, Mg-rich, Fe-bearing	Silty shales, Upper Riphean, South Urals, Russia [9,39]
11	60/3	illite, Mg-rich, Fe-bearing	Clayey siltstones, Upper Riphean, South Urals, Russia [5,39]
12	602-1	aluminoceladonite	Altered tuff in the Leeds Creek member of Twin Creek formation, Wyoming [5]
13	Z2	aluminoceladonite	Devonian bentonite, Barcza, Poland [40,41]
14	99-3/5	aluminoceladonite	Vitric tuff in saliferous strata, Inder, Russia [42]
15	Mal-4	aluminoceladonite	Silurian K-bentonite, Podolia, Ukraine [43]
16	Mal-6	aluminoceladonite	Silurian K-bentonite, Podolia, Ukraine [43]
17	136	aluminoceladonite	Upper-Jurassic conglomerates, Tushleg, Mongolia [44]
18	560/3	Fe-illite	Sandstones, Lower Riphean, Olenek Uplift, northern Siberia, Russia [45]
19	553/1	Fe-illite	Siltstones, Middle Riphean, Olenek Uplift, northern Siberia, Russia [46]
20	2076A	Fe-illite	Sandstones, Lower Riphean, Olenek Uplift, northern Siberia, Russia [45]
21	BSH11	Fe-illite	Siltstones, Upper Riphean, South Urals, Russia [47,48]
22	BSH12	Fe-illite	Siltstones, Upper Riphean, South Urals, Russia [47,48]
23	KUL1	Fe-illite	Siltstones, Upper Riphean, South Urals, Russia [47,48]
24	400/3	Al-glaucanite	Gravelly sandstones, Lower Riphean, Anabar Uplift, northern Siberia, Russia [9,49]
25	KUL2	Al-glaucanite	Siltstones, Upper Riphean, South Urals, Russia [47,48]
26	551	Al-glaucanite	Gravelly sandstones, Middle Riphean, Olenek Uplift, northern Siberia, Russia [9,46]
27	555A	Al-glaucanite	Gravelly sandstones, Middle Riphean, Olenek Uplift, northern Siberia, Russia [46]

Table 1. Cont.

#	Sample Name	Mineral Variety	Origin, Location, and Reference
28	402/1	glauconite	Silty shale, Lower Riphean, Anabar Uplift, Russia [9,49]
29	103	glauconite	Glauconitites, Lower Ordovician, Parila, Estonia [8]
30	37/71	glauconite	Glauconitites, Lower Ordovician, Vergale, Latvia [8]
31	37/71A	glauconite	Siltstones, Middle Cambrian, Vergale, Latvia [8]
32	PILT	glauconite	Ordovician sandstone, Latvia [5,50,51]
33	68-69	glauconite	Leningrad region, Russia [5,50,51]
34	G294	glauconite	Ordovician, Sweden [52]
35	GT6-69	glauconite	Cretaceous, Bornholm Island [52]
36	GT8-66	glauconite	Cambrian, Wyoming [52]
37	821-057	glauconite	Greensand, Birmingham, New Jersey, Ward's Natural Science Establishment Inc., Rochester, NY [8]
38	541	glauconite	Lower Cambrian, East Siberia, Russia [48]
39	79/73	glauconite	Zeolite-free sandstones, the Dnieper river, Ukraine [53]
40	372/70	glauconite	Zeolite-free sands, the Tyk-Butak river, Kazakhstan [53]
41	TAIH	celadonite	Taiheizan, Akita Prefecture, Japan [5,54]
42	69	celadonite	Krivoi Rog mining district, Russia [5,55]
43	Z1	celadonite	Russia [5,56]

¹ Ws (%) is the proportion of smectite interlayers.

Table 2. Sample description.

#	Sample	Cation Composition											K_{Al}^2
		Tetrahedra		Octahedra					Interlayer				
		Si	^{IV} Al	^{VI} Al	Fe ³⁺	Fe ²⁺	Mg	Σ_{oct}^1	K	Ca	Na	NH ₄	
1	RM30	3.27	0.73	1.86	0	0	0.14	2.00	0.80	0.0	0.01	n.d.	1.00
2	SG4	3.24	0.76	1.88	0.02	n.d.	0.1	2.00	0.79	0.01	0.05	n.d.	0.99
3	RM35C	3.30	0.70	1.82	0.05	n.d.	0.13	2.00	0.73	0.04	0.02	n.d.	0.97
4	Fuzz-5	3.38	0.62	1.83	0.01	n.d.	0.14	1.98	0.68	0.06	0	0.01	0.99
5	Fuzz-6	3.42	0.58	1.75	0.02	n.d.	0.23	2.00	0.70	0.05	0	0.01	0.99
6	Zempleni	3.43	0.57	1.78	0.01	n.d.	0.22	2.01	0.66	0.03	0.03	n.d.	0.99
7	L-2A-1	3.45	0.55	1.57	0.13	n.d.	0.28	1.98	0.78	0.02	0.06	n.d.	0.92
8	Swe-151	3.49	0.51	1.68	0.04	n.d.	0.27	1.99	0.58	0.06	0.01	0.06	0.99
9	IWi-1	3.56	0.44	1.44	0.14	n.d.	0.39	1.97	0.72	0	0.16	n.d.	0.91
10	60	3.63	0.37	1.32	0.13	0.16	0.46	2.07	0.77	0	0.01	n.d.	0.91
11	60/3	3.65	0.35	1.38	0.13	0.15	0.40	2.06	0.75	0.02	0.01	n.d.	0.91
12	602-1	3.71	0.29	1.39	0.04	0.09	0.51	2.03	0.75	0.01	0.03	n.d.	0.97
13	Z2	3.81	0.19	1.19	0.06	0.17	0.57	1.99	0.86	0.04	0	n.d.	0.95
14	99-3/5	3.78	0.22	1.28	0.11	0.06	0.59	2.04	0.65	0.05	0.01	n.d.	0.92
15	Mal-4	3.84	0.16	1.33	0.09	n.d.	0.55	1.97	0.65	0.05	0.01	0.05	0.93
16	Mal-6	3.86	0.14	1.29	0.09	n.d.	0.60	1.98	0.67	0.04	0.01	0.05	0.93
17	136	4.00	0	1.08	0.13	0.19	0.60	2.00	0.78	0	0.01	n.d.	0.89
18	560/3	3.62	0.38	1.12	0.37	0.20	0.32	2.01	0.80	0	0.05	n.d.	0.75
19	553/1	3.57	0.43	1.13	0.50	0.19	0.19	2.01	0.69	0.04	0.02	n.d.	0.69
20	2076A	3.68	0.32	1.03	0.55	0.09	0.34	2.01	0.69	0.01	0.01	n.d.	0.65
21	BSH11	3.71	0.29	1.06	0.36	0.23	0.39	2.04	0.74	0.02	0	n.d.	0.75
22	BSH12	3.73	0.27	0.88	0.37	0.37	0.47	2.09	0.78	0.02	0	n.d.	0.70
23	KUL1	3.71	0.29	0.99	0.43	0.27	0.37	2.06	0.78	0.01	0	n.d.	0.70
24	400/3	3.63	0.37	0.91	0.60	0.20	0.34	2.05	0.76	0.01	0.02	n.a	0.60
25	KUL2	3.72	0.28	0.86	0.54	0.25	0.39	2.04	0.76	0.02	0	n.d.	0.61
26	551	3.67	0.33	0.85	0.77	0.15	0.22	1.99	0.77	0.01	0.02	n.d.	0.52
27	555A	3.63	0.37	0.77	0.76	0.16	0.34	2.03	0.73	0.01	0.02	n.d.	0.50
28	402/1	3.80	0.20	0.52	0.78	0.28	0.47	2.05	0.74	0	0.04	n.d.	0.40
29	103	3.67	0.33	0.37	1.15	0.11	0.40	2.03	0.74	0	0	n.d.	0.24
30	37/71	3.57	0.43	0.38	1.15	0.10	0.45	2.08	0.72	0.01	0.02	n.d.	0.25

Table 2. Cont.

#	Sample	Cation Composition											K_{Al}^2	
		Tetrahedra			Octahedra					Interlayer				
		Si	^{IV} Al	^{VI} Al	Fe ³⁺	Fe ²⁺	Mg	Σ_{oct}^1	K	Ca	Na	NH ₄		
31	37/71A	3.56	0.44	0.64	0.96	0.19	0.28	2.07	0.68	0	0.01	n.d.	0.40	
32	PILT	3.73	0.27	0.44	0.92	0.22	0.47	2.05	0.77	0	0.03	n.d.	0.32	
33	68-69	3.73	0.27	0.43	0.92	0.30	0.39	2.04	0.80	0.01	0.03	n.d.	0.32	
34	G294	3.72	0.28	0.74	0.82	n.d.	0.40	1.96	0.67	0.06	0.02	n.d.	0.47	
35	GT6-69	3.78	0.22	0.57	0.95	n.d.	0.47	1.99	0.69	0.01	0	n.d.	0.38	
36	GT8-66	3.60	0.40	0.37	1.26	n.d.	0.32	1.95	0.72	0	0.12	n.d.	0.23	
37	821-057	3.74	0.26	0.33	1.23	n.d.	0.41	1.97	0.68	0.03	0.01	n.d.	0.22	
38	541	3.53	0.47	0.68	0.72	0.29	0.40	2.09	0.78	0.06	0.01	n.d.	0.49	
39	79/73	3.65	0.35	0.37	1.16	0.05	0.44	2.02	0.67	0.06	0.01	n.d.	0.27	
49	372/70	3.68	0.32	0.51	1.01	0.08	0.40	2.00	0.65	0.06	0.02	n.d.	0.27	
41	TAIH	3.72	0.28	0.16	1.07	0.10	0.71	2.04	0.82	0	0.18	n.d.	0.13	
42	69	3.94	0.06	0.06	1.15	0.36	0.41	1.98	0.83	0.03	0.01	n.d.	0.05	
43	Z1	3.96	0.04	0.05	0.96	0.26	0.73	2.00	0.89	0	0.07	n.d.	0.05	

The contents of TiO₂ were excluded from the calculation of the crystal-chemical formulae. Samples 2–9, 15–16, and 34–37 were not analyzed for Fe oxidation state, and the formulae were calculated assuming all Fe as Fe³⁺; “n.d.” = not determined. ¹ Σ_{oct} = Al + Mg + Fe²⁺ + Fe³⁺; ² K_{Al} = ^{VI}Al (^{VI}Al + Fe³⁺).

2.2. FTIR Spectroscopy

2.2.1. Experiment

The absorption spectra of samples RM30, RM35C, SG4, Zempleni, L-2A-1, 60/3, 602-1, Seifert, 99-3/5, 136, BSH11, KUL1, 68/69, PILT, 821-057, K294, GT 7-66, GT 8-69, 79/73, 372/70, TAIH, 69 and Z1 (Supplementary materials Figure S1) were recorded with a Nicolet ESP-260 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), and for samples Fuzz-5, Fuzz-6, Mal-4, Mal-6, 60, 560/3, 553/1, 2076, BSH12, KUL2, 400/3, 402/1, 551, 555A, 103, 37/71, 37/71A and 541 (Supplementary materials Figure S1), the IR spectra were obtained using a Bruker VERTEX 80v FTIR spectrometer (Bruker Optics, Ettlingen, Germany). Both spectrometers were equipped with an IR source, a KBr beam splitter and a DTGS KBr detector. For each sample, 128 (Nicolet) and 256 (Bruker) scans were recorded (on the Bruker spectrometer, in vacuum) in the MIR region ($400\text{--}4000\text{ cm}^{-1}$) with a resolution of 4 cm^{-1} .

All the samples were prepared using the KBr pressed-disc technique. To obtain a KBr pellet, 0.5 mg of sample was dispersed in 200 mg of KBr, the resulting mixture was placed in a 13 mm pellet die and pressed under vacuum for 15 min. The pellet was then placed into a glass desiccant box with CaCl_2 and heated in a furnace at $105\text{--}150\text{ }^\circ\text{C}$ for at least 20 h.

The IR absorbance conversion was made automatically with the Nicolet®Omnic Software Version 5.0 and the OPUS 7.0 software package (Bruker Ltd.).

2.2.2. Spectra Decomposition and Curve-Fitting

The OH-stretching regions of selected spectra were decomposed and fitted using the Galactic PeakSolve™ program. The baseline correction for the $3000\text{--}4000\text{ cm}^{-1}$ region was made using the linear function, as it provided better fitting results than the Concave Rubberband method. The second derivative method was used for initial estimation of the band positions. Although theoretically the vibrational bands should be Lorentzian, various instrumental and/or compositional factors may affect their shape leading to a Gaussian or mixed Gaussian–Lorentzian distribution [57,58]. Indeed, a variety of band shapes has been used previously for the decomposition of the OH-bending and OH-stretching regions of dioctahedral 2:1 phyllosilicates: Lorentzian [17,18,59], Gaussian [60,61] and mixed Gaussian–Lorentzian [62,63]. For the FTIR spectra under study, the best fitting results were obtained assuming a Lorentzian peak shape for each OH band in celadonites, a mixed Gaussian–Lorentzian shape for aluminoceladonites and Al-glaucónites, and a Gaussian peak shape for illites, Fe-illites, and glaucónites (Supplementary materials Table S1). The variable parameters were position, width at half-height and the intensity of each component. The complex wide absorption band of the residual water was included in the fitted spectrum as two broad maxima around 3200 and 3420 cm^{-1} . The quality of spectra decomposition was estimated by the minimization function, χ^2 , the correlation coefficient, R^2 , and the agreement between cation compositions obtained from FTIR data and the crystal-chemical formulae.

3. Results and Discussion

The positions of the absorption bands in the FTIR spectra of the samples in the MIR region were assigned to specific vibration modes (Tables 3 and 4) following the interpretations of [12,14–18,22,26,64]. The FTIR spectra of all the samples are typical for dioctahedral micas. The following FTIR regions were analyzed: the Si–O bending ($600\text{--}400\text{ cm}^{-1}$), Si–O stretching ($\sim 1200\text{--}700\text{ cm}^{-1}$) and OH-stretching ($3700\text{--}3500\text{ cm}^{-1}$) regions, as well as the $950\text{--}600\text{ cm}^{-1}$ region, which contains, along with the OH-bending bands, other types of vibrations and bands corresponding to admixtures (see below). Most of the diagnostic information for all the groups of mica varieties is provided by the three characteristic Si–O bending bands, the most intense absorption band(s) due to the Si–O stretching vibrations, and the positions and profile of the OH-stretching bands (Figure 1, Table 3).

Table 3. Characteristic band positions (cm^{−1}) in the Si–O bending, Si–O stretching, and OH-stretching regions in the FTIR spectra of K-dioctahedral 1M micas.

#	Sample	Si–O Bend	Si–O–Si Bend	Si–O–Si Bend (Additional)	Si–O–Fe Bend	Si–O–Al Bend	Si–O Stretch	Si–Oap Stretch	OH-Stretch, Visually Discernable Absorption Maxima			
1	RM30	414	477	-	-	534	1023	1066sh	-	-	-	3629
2	SG4	414	477	-	-	535	1024	1067sh	-	-	-	3627
3	RM35C	415	476	-	-	533	1023	1068sh	-	-	-	3629
4	Fuzz-5	418	474	-	-	534	1024	1090	-	-	-	3630
5	Fuzz-6	425	471	-	-	525	1027	1082sh	-	-	-	3625
6	Zempleni	423	474	-	-	529	1027	1070sh	-	-	-	3624
7	L-2A-1	419	472	-	-	523	1021	1075	-	-	-	3618
8	Swe-151	422	472	-	-	524	1019	1088sh	-	-	-	3626
9	IWi-1	424	472	-	-	520	1015	1090	-	-	-	3617
10	60	434	471	-	-	519	1008	1089	-	-	-	3606
11	60/3	435	470	-	-	519	1010	1084	-	-	-	3607
12	602-1	436	470	-	-	518	1007	1091	-	-	-	3601
13	Z2	437	472	-	-	512	989	1090	3538	3559	3583	3603
14	99-3/5	435	470	-	-	520	1012	1098	-	-	-	3605
15	Mal-4	435	470	-	-	518	1010	1090	-	-	-	3606
16	Mal-6	435	470	-	-	518	1006	1091	-	-	-	3603
17	136	439	468	-	-	509	985	1112	3541	3562	3583	3603
18	560/3	436	471	-	-	518	1008	1084	3528	-	-	3612
19	553/1	434	471	451sh	-	526	1017	1083sh	3534	-	-	3624
20	2076	437	469	453	486sh	517	1000	1085	3530	3554	-	3607
21	BSh11	437	467	450sh	496*	517	1004	1084	3536	3558	-	3605
22	BSh12	437	467	-	-	515	1007	1084	3534	3555sh	3582sh	3602
23	KUL1	438	467	454sh	490	514	998	1087	3533	3554	3584	3602
24	400/3	438	468	455sh	484sh	515sh	994	1079	3532	3555sh	-	3603
25	KUL2	438	469	454sh	484sh	518	1012	1081sh	3533	3555sh	-	3602, 3618sh
26	551	434	465	454	486sh	514sh	1006	1084sh	3533	3560sh	-	3610
27	555A	437	469	455	486sh	518sh	1002	1080sh	3532	3560sh	-	3609
28	402/1	438	453	467	483sh	-	990	1082	3533	3555sh	-	3603*
29	103	434	455	-	491	-	991	1074	3537	3559	-	3602sh
30	37/71	434	456	-	491	-	995	1072	3535	3561	-	3603sh
31	37/71A	435	457	-	487	-	1001	1079sh	3538	-	3581sh	3603sh
32	PILT	439	459	-	494	-	1010	1081sh	-	3550	-	-
33	68/69	437	457	-	494	-	1013	1082sh	(3530 + 3542 + 3567) (2nd drv)			-
34	G294	435	463	-	499sh	-	995	1082	3534	3558	-	3604
35	GT6-69	437	458	-	492	-	987	1084	3536	3559	3583sh	3603
36	GT8-66	434	454	-	489	-	992	1075	3536	3564sh	-	3604sh
37	821-057	438	456	-	492	-	992	1078	3538	3568	-	3602
38	541	438	458	-	483	526sh	1000	1072	3533	3558	-	3621
39	79/73	439	461	-	496	-	1016	1099sh	(3537 + 3558) (2nd drv)			3601sh
40	372/70	440	460	-	496	-	1014	1101	(3538 + 3563) (2nd drv)			3614sh
41	TAIH	439	459	-	493	-	978	1090	3532	3556	-	3601
42	69	440	457	-	491	-	975, 995sh	1072, 1100sh	3533	3555sh	-	3603 (2nd drv)
43	Z1	n.d.	n.d.	-	n.d.	-	957, 978	1074, 1113	3533	3556	-	3602

*—weak, 2nd drv—determined from the second derivative, sh—shoulder, n.d.—not determined.

Table 4. Positions (cm^{-1}) of absorption bands of the mica structure and common admixtures in the 950–600 cm^{-1} region.

#	Sample	Coupled Al–O and Si–O out-of-Plane of Smectite	Si–O; Fe–O out-of-Plane; Quartz; Carbonates	Al–O–Si in-Plane; $\delta(\text{Fe}^{2+}\text{OHFe}^{3+})?$	Al–O–Al; $\delta(\text{Fe}^{3+}\text{OHMg})$; $\delta(\text{Fe}^{2+}\text{OHFe}^{3+})$; Silica/Quartz; Goethite	$\delta(\text{Fe}^{3+}\text{OHFe}^{3+})$	$\delta(\text{AlOHMg})$ / Al–O out of Plane/ Second $\delta(\text{Fe}^{3+}\text{OHFe}^{3+})$	Al–O–Al; $\delta(\text{AlOHFe}^{3+})$; Goethite	$\delta(\text{AlOHAl})$
1	RM30	623sh	697	756	806	-	830	876sh	(912, 932) ***
2	SG4	626sh	695	756	804	-	831	876sh	(917, 933) ***
3	RM35C	624sh	695	756	803	-	826	876 sh	(918, 934) ***
4	Fuzz-5	626sh	694	755	803sh	-	826	876sh	(913, 932) ***
5	Fuzz-6	618	699	754	799 *	-	823, 848	882sh	913
6	Zempleni	618	695	755	804	-	826	882 *	917
7	L-2A-1	615sh	687	752	801sh	-	827	871 **	913
8	Swe-151	620sh	693	753	782, 799 *	-	832	876	912
9	IWi-1	628	690sh	753	795 *	-	834	870	911
10	60	627 **	682	748	803	-	834	864	912
11	60/3	635	681	750	790	-	831	868	909
12	602-1	-	686	753	794 *	-	835	877	912
13	Z2	-	686	750	780, 800 *	-	835	874	912sh
14	99-3/5	623	688	752 **	780, 800 **	-	838	873 *	914
15	Mal-4	625	685	752	802sh	-	839	875sh	912
16	Mal-6	626 **	686	752	787 *	-	836	876 *	913
17	136	-	687	749	780, 799	-	835	875sh	911sh
18	560/3	-	683	753	~799sh	829	829	862, 878	915
19	553/1	620	683	753	~800sh	824	824	870sh	913sh
20	2076A	-	682	754	795sh	-	830	864, 878	915sh
21	BSH11	-	680	754sh	798sh	-	831	860, 874	910
22	BSH12	-	691	751sh	780, 799	-	833	877sh	914sh
23	KUL1	625	681	752sh	~797sh	-	830	(860, 876)	910sh
24	400/3	-	682	754sh	797sh	823	838	863sh	911sh
25	KUL2	625	683	752sh	801	824	824	870sh	912sh
26	551	625	681	760sh	796sh	819	839	865sh *	910sh *
27	555A	-	682	759sh	798sh	822	841	865sh *	911sh *
28	402/1	-	683	753	797sh	821sh	838	(861, 878)	907
29	103	622	676	760sh	798	815	835sh	864sh	907
30	37/71	620 **	678	764sh	800	812	837sh	865sh	905sh
31	37/71A	624	681	753sh	780, 797 **	820	834 *	871sh	911sh
32	PILT	620 **	670, 698sh	760	798	815	836	872sh	907
33	68-69	-	677, 696srp	762sh	778 **, 796	815	834	863sh	907
34	G294	-	683	760sh	804sh	817*	836	861sh	911sh
35	GT6-69	620 **	681	762sh	776sh, 801	811	835	861sh	907sh *
36	GT8-66	620	680	760sh	776	814	836	864sh	907sh
37	821-057	-	676	755	779, 800	815sh	835sh	866sh	908
38	541	625	684	755	780, 800	812	834	870sh	913sh
39	79/73	-	678, 698srp	760	797	817 *	838 *	870sh	907sh
40	372/70	623 **	677, 698srp	760	-	816	834 *	867sh *	910sh
41	TAIH	618	681, 695srp	760 *	799	821	840	(873, 888) *	908sh
42	69	-	678, 697srp	757sh	779sh, 797	818sh	843	872sh	-
43	Z1	-	684	746*	800	822	843 **	-	-

*—weak; **—very weak; ***—poorly resolved; sh—shoulder; srp—sharp. Band positions revealed from the second derivative are shown in italics and are only given where there is no visually distinct band.

Figure 1. Selected FTIR spectra of K-dioctahedral 1M micas: RM30-(Mg, Fe)-poor illite; Iwi-1-Mg-rich illite; 136—aliminoceladonite; 602-1—aluminoceladonite; 60—Mg-rich, Fe-bearing illite; BSH11—Fe-illite; 551—Al-glaucanite; GT6-69 and 103—glaucanites; 69—celadonite; Z1—celadonite.

3.1. Si–O Bending Vibration Modes

Three sharp bands in the region of 600–400 cm^{-1} are typical for all dioctahedral micas and are conventionally assigned to the Si–O (δ_1), Si–O–Si (δ_2) and Si–O–M (δ_3) bending vibrations, where δ_1 and δ_3 are the lower- and the higher-wavenumber bands, respectively, and M = octahedral Al or Fe cation [19,26]. According to [12], the Si–O bending vibrations are strongly coupled with the vibrations of the octahedral cations and with translator vibrations of hydroxyl groups.

In Fe-poor K-dioctahedral 1M micas (the illite-aluminoceladonite series), strong correlations are observed between the spectroscopic characteristics of the Si–O bending region and both tetrahedral and octahedral cation composition. With increasing Si and Mg contents from (Mg, Fe)-poor illite to aluminoceladonite through Mg-rich illite, the two “outer” bands in the Si–O bending vibrations triplet (δ_1 and δ_3) move toward the “middle” one, so that δ_1 and δ_3 are shifted from 414 to 439 cm^{-1} and from 535 to 509 cm^{-1} , respectively; the wavenumber of the “middle” Si–O–Si bending vibration, δ_2 , decreases slightly from 477 to 468 cm^{-1} (Figure 1; Table 3). These regularities are similar to those reported by [14] for the transition from synthetic muscovite to synthetic aluminoceladonite, although in the Si–O bending region, Velde [14] only discussed the shifts δ_3 to lower wavenumbers.

Beran et al. [65] assigned the band at 437 cm^{-1} in silicate structures to Mg–O stretch + O–Si–O bend. The shift of the Si–O bending mode δ_1 to greater wavenumbers in the series illite-aluminoceladonite may be therefore associated with the growing influence of the Mg–O stretching vibration, taking into account that the relative intensity of δ_1 with respect to δ_2 increases with increasing Mg contents (Figure 1). The correlations between the position of this band and $^{\text{IV}}\text{Al}$ and Mg contents are equally strong and described by a quadratic (Figure 2a) and linear (Figure 2b) regressions, respectively.

Figure 2. Band positions (cm^{-1}) of δ_1 in Fe-poor K-dioctahedral 1M micas plotted vs. (a) $^{\text{IV}}\text{Al}$ and (b) Mg contents (cations *p.h.f.u.*). Symbols: triangle = (Mg,Fe)-poor illites, square = Mg-rich illites, circle = aluminoceladonites.

The absorption band δ_2 is interpreted as the Si–O–Si bending vibration [20,22,64] coupled with Al–O–Al bend [65]. The decrease in δ_2 with decreasing tetrahedral and octahedral Al and increasing octahedral Mg contents is described by quadratic regression equations with $R^2 = 0.77$, 0.77 and 0.81, respectively, with considerable scatter (Figure 3a–c).

Figure 3. Band positions (cm⁻¹) of δ_2 and δ_3 in Fe-poor K-dioctahedral 1M micas plotted vs. octahedral cation contents: (a) δ_2 vs. ^{IV}Al; (b) δ_2 vs. ^{VI}Al; (c) δ_2 vs. Mg; (d) δ_3 vs. ^{VI}Al (cations p.h.f.u.). Symbols as in Figure 2.

The δ_3 mode is assigned to Si–O–Al bending vibration (octahedral Al) [22]. The shift of δ_3 to lower wavenumbers in the transition from muscovite-like illite to phengite-like illite to aluminoceladonite may be associated with the increasing Si–O–Al angle as a result of increasing tetrahedral elongation in combination with increasing octahedral sheet thickness. Experimental structural data show that the tetrahedral elongation angle $\text{O}_{\text{bas}}\text{--T--O}_{\text{ap}}$ is $\sim 110\text{--}111^\circ$ in muscovite [66], $\sim 112^\circ$ in phengite [67] and $\sim 113^\circ$ in aluminoceladonite [68], while the octahedral sheet thickness simultaneously increases from ~ 2.090 to 2.164 Å [69,70]. The increase in the Si–O–Al angle should lower the vibration energy [14], so that the δ_3 mode shifts to lower wavenumbers. The position of δ_3 in the series illite–aluminoceladonite is strongly correlated with ^{VI}Al ($R^2 = 0.93$, Figure 3d).

The equations given in Figures 2 and 3d can be used to evaluate the amounts of tetrahedral Al, octahedral Mg, and octahedral Al cation contents with an *esd* of 0.06, 0.05, and 0.075 cations p.h.f.u., respectively [7].

A possible explanation for the band shifts in the Si–O bending region in the series (Mg, Fe)-poor illite–Mg-rich illite–aluminoceladonite is provided by a comparison of the spectra of samples RM30 and 136 (Mg, Fe-poor illite and aluminoceladonite, respectively) with that of pyrophyllite $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ (Figure 4) in the region $550\text{--}400$ cm⁻¹. Owing to the identical tetrahedral cation composition, the spectrum of aluminoceladonite in the region of Si–O bending vibrations might be expected to be

similar to that of pyrophyllite. In reality, however, the band positions in spectra of aluminoceladonite 136 and pyrophyllite differ dramatically: 439 vs. 419, 468 vs. 482 and 509 vs. 541 cm^{-1} (Figure 4). At the same time, the maximum absorption in the pyrophyllite spectrum is observed at positions close to those of the illites of muscovite-like composition having 0.70–0.85 IV Al (e.g., 414, 477 and 534 cm^{-1} , sample RM30) (Figure 4). These results may imply that the influence of octahedral cation composition on the band positions in the Si–O bending region is stronger than that of the composition of the tetrahedral sheet and the presence or absence of the interlayer cations. In other words, the presence of the interlayer K and tetrahedral Al in the muscovite structure (as opposed to pyrophyllite) are mutually compensated, so that the similarity in the octahedral composition becomes a major factor responsible for the similarity of the muscovite and pyrophyllite spectra. In particular, the similar albeit slightly higher δ_3 in pyrophyllite as compared to that of muscovite is associated with somewhat smaller tetrahedral elongation angle (109.4°) and octahedral sheet thickness (2.079 Å) in the pyrophyllite structure, as compared to $110\text{--}111^\circ$ and 2.090–2.095 Å, respectively, in muscovite [69,70] leading to an even smaller Si–O–Al angle.

Figure 4. FTIR spectra of (a) aluminoceladonite 136, (b) illite RM30 and (c) pyrophyllite (North Carolina) in the Si–O bending region ($600\text{--}400\text{ cm}^{-1}$).

In the Si–O bending region of Fe-bearing, K-dioctahedral micas, the positions of the lower wavenumber band, δ_1 , varies within a narrow range ($440\text{--}434\text{ cm}^{-1}$) for all the samples with a very loose trend to decreasing with increasing Fe contents. The position of the δ_2 band, which corresponds to the Si–O–Si bending vibration, tends to decrease with decreasing Al and increasing Fe cation contents from $\sim 470\text{ cm}^{-1}$ in illites and Fe-illites to $453\text{--}463\text{ cm}^{-1}$ in glauconites and celadonites. Simultaneously, the δ_3 band shifts from $514\text{--}526\text{ cm}^{-1}$ corresponding to the Si–O–Al vibration, to $483\text{--}499\text{ cm}^{-1}$ (Si–O–Fe) (Table 3). The shift of the δ_3 mode to lower wavenumbers with increasing Fe for Al substitution may be associated with an increase in the Si–O– VI M angle due to an increase in the octahedral sheet thickness, which, in turn, reduces the vibration energy [14]. Another reason is that an increase in the total mass of cations in the vibrating system for cations of the same valence (Si–O–Al vs. Si–O– Fe^{3+}) decreases the wavenumber [18].

The samples in the Fe-bearing mica series therefore fall into two distinct groups: for $K_{Al} \geq 0.6$, δ_2 is at $469 \pm 2 \text{ cm}^{-1}$ and δ_3 is at $520 \pm 6 \text{ cm}^{-1}$; for $K_{Al} < 0.5$, δ_2 is at $458 \pm 5 \text{ cm}^{-1}$ and δ_3 is at $491 \pm 8 \text{ cm}^{-1}$ (Figure 5a,b). Samples of highly heterogeneous cation composition, such as Fe-illites and Al-glaucanites, display, in addition, vibration modes typical for δ_2 and δ_3 of glaucanites and celadonites, either as distinct maxima of minor intensity or as shoulders. Specifically, in samples 551 and 555A ($K_{Al} \sim 0.5$), the Si–O bending region contains, in addition to the δ_1 mode, two well-resolved bands at $465\text{--}469 \text{ cm}^{-1}$ and $454\text{--}455 \text{ cm}^{-1}$ and shoulders at $514\text{--}518 \text{ cm}^{-1}$ and 486 cm^{-1} (Table 3, Figure 1 (sample 551), Figure 5). Similarly, the glaucanite sample 402/1 ($K_{Al} = 0.40$), in addition to δ_2 at 453 cm^{-1} , shows a second Si–O–Si bending band at 467 cm^{-1} (Table 3). These peculiarities reflect the phase microheterogeneity, which was revealed by XRD powder diffraction for samples 551 and 402/1 [9] and is likely to be present in sample 555A, as its cation composition is very close to that of sample 551. On the whole, the plots of δ_2 and δ_3 vs. $\text{Fe}_{\text{total}} = \text{Fe}^{2+} + \text{Fe}^{3+}$ (Figure 5) show a wider scatter of points than similar dependencies of bending and stretching Si–O vibration band positions on cation composition in Fe-poor dioctahedral micas 1M. This may be associated with a much higher degree of crystal-chemical heterogeneity of Fe-bearing varieties and especially glaucanites and Al-glaucanites [9].

Figure 5. Band positions (cm^{-1}) of (a) δ_2 and (b) δ_3 in Fe-bearing K-dioctahedral 1M micas plotted vs. Fe_{total} contents (cations *p.h.f.u.*). Symbols: open circles—Fe-bearing Mg-rich illites ($K_{Al} = 0.9$), open triangles—Fe-illites and Al-glaucanites ($K_{Al} = 0.6\text{--}0.75$), black triangles—Al-glaucanites ($K_{Al} = 0.5$), open squares—glaucanites ($K_{Al} < 0.5$), crosses—celadonites ($K_{Al} < 0.15$).

3.2. Si–O Stretching Vibration Modes

In Fe-poor K-dioctahedral 1M micas, the profiles and positions of the bands in this region are correlated with both tetrahedral and octahedral cation composition. With decreasing Al for Si substitution in the series (Mg, Fe)-poor illite–Mg-rich illite–aluminoceladonite, the Si–O stretching band, $\nu(\text{SiO})$ shifts from 1024 cm^{-1} ($^{\text{IV}}\text{Al} = 0.76$, sample SG-4) to 985 cm^{-1} ($^{\text{IV}}\text{Al} = 0$, sample 136), and the Si–O apical stretching mode, $\nu(\text{SiO}_{\text{apical}})$, transforms from a shoulder at 1067 cm^{-1} into a well-resolved band at 1112 cm^{-1} (Table 3, Figure 1). With increasing Si and decreasing octahedral Al contents, the non-bridging tetrahedral cation–anion ($\text{T–O}_{\text{apical}}$) distance is significantly shortened and strengthened with respect to the mean bridging ($\text{T–O}_{\text{basal}}$) distance due to increasing under-saturation of the apical oxygen anion with respect to negative charge. This effect is confirmed by numerous structure refinements of dioctahedral micas-2M₁ [66–68] and can be described quantitatively in terms of the bond strength sum variation [70]. Accordingly, the two Si–O stretching modes become resolved, as $\nu(\text{SiO})$ shifts to lower and $\nu(\text{SiO}_{\text{apical}})$ shifts to greater wavenumbers. Both trends can be described

by quadratic regressions relating $\nu(\text{SiO})$ and $\nu(\text{SiO}_{\text{apical}})$ to $^{\text{IV}}\text{Al}$ (Figure 6a,b), with the correlation coefficients $R^2 = 0.76$ and 0.77 , respectively. A much stronger correlation is observed between $\nu(\text{SiO})$ and octahedral Al contents, $^{\text{VI}}\text{Al}$ ($R^2 = 0.94$, Figure 6c).

Figure 6. Band positions (cm^{-1}) of (a) $\nu(\text{SiO})$ and (b) $\nu(\text{SiO}_{\text{apical}})$ plotted against $^{\text{IV}}\text{Al}$ contents (cations *p.h.f.u.*), and (c) $\nu(\text{SiO})$ plotted vs. $^{\text{IV}}\text{Al}$ contents for Fe-poor K-dioctahedral 1M micas (cations *p.h.f.u.*). Symbols as in Figure 2.

In Fe-bearing K-dioctahedral micas 1M, the Si–O stretching region is the least informative as to the distinguishing features [8], as the $\nu(\text{SiO})$ band is at $987\text{--}1017\text{ cm}^{-1}$ in Mg-rich, Fe-bearing illites, Fe-illites, Al-glaucanites and glaucanites show little or no correlation with either tetrahedral or octahedral cation composition. The $\nu(\text{SiO}_{\text{apical}})$ mode appears either as a distinct band or a shoulder within the $1070\text{--}1100\text{ cm}^{-1}$ range (Table 3). Celadonite is an exception showing either two sharp, well-resolved bands (978 and 1090 cm^{-1} , sample TAIH) or two sharp bands (975 and 1082 cm^{-1}) with shoulders at 995 and 1100 cm^{-1} (sample 69), or four sharp bands (957 , 978 , 1074 and 1113 cm^{-1} , sample Z1) (Table 3, Figure 1).

3.3. The $950\text{--}600\text{ cm}^{-1}$ Region

The region $950\text{--}600\text{ cm}^{-1}$ contains, along with the OH bending bands, which are located on the low-wavenumber side of the Si–O stretch, a number of absorption bands corresponding to other types of vibrations (Al–O and Fe–O out-of-plane, Al–O–Si in-plane modes, etc.), which is a series hindrance to unambiguous interpretation of this spectral region.

In most cases, the micas in the illite-aluminoceladonite series display the $\delta(\text{AlOHAl})$ vibration mode as a distinct band at $909\text{--}918\text{ cm}^{-1}$. Some muscovite-like illites (samples #1–4, Table 4; sample RM30, Figure 7) show a plateau resulting from a superposition of two bands at $912\text{--}918$ and $932\text{--}934\text{ cm}^{-1}$. Aluminoceladonites 136 and Z2 show the $\delta(\text{AlOHAl})$ mode as an inflection at $910\text{--}912\text{ cm}^{-1}$ on the low-wavenumber side of the $\nu(\text{SiO})$ band (Figure 7, Table 4). Depending on the octahedral Al cation content, the $\delta(\text{AlOHAl})$ band appears in the spectra of Fe-illites, Al-glaucanites and glaucanites, either as a distinct maximum (sample 560/3) or a shoulder, at $907\text{--}915\text{ cm}^{-1}$; in some glaucanites, it can only be identified in the second derivative (Table 4). Celadonite TAIH with $^{\text{VI}}\text{Al} = 0.16\text{ a.p.h.u.}$ shows a weak shoulder at 908 cm^{-1} , whereas in the other celadonite spectra, this band is absent.

Figure 7. FTIR spectra of selected samples in the region of $950\text{--}600\text{ cm}^{-1}$. RM30—(Mg, Fe)-poor illite; Iwi-1—Mg-rich illite; 136—aluminoceladonite; 602-1—aluminoceladonite; 60—Mg-rich, Fe-bearing illite; BSH11—Fe-illite; 551—Al-glaucanite; GT6-69 and 103—glaucanites; 69—celadonite; Z1—celadonite.

The band at $\sim 875\text{--}880\text{ cm}^{-1}$, which either appears as a shoulder or can be identified in the second derivative in the spectra of illites and aluminoceladonites, is attributed to the Al–O–Al vibration [20]. Most of the Fe-bearing mica varieties show a shoulder at $\sim 860\text{--}865$ or $\sim 870\text{--}880\text{ cm}^{-1}$ (Table 4), which, in most cases, is displayed as two components, $860\text{--}869$ and $873\text{--}888\text{ cm}^{-1}$ in the second derivative. These bands should refer to $\delta(\text{AlOHFe}^{3+})$, which Farmer [12] identified at 890 cm^{-1} , and Madejová et al. [26] at 865 cm^{-1} .

Independent of Mg content, all illites, Fe-illites, and aluminoceladonites show distinct bands at $824\text{--}838\text{ cm}^{-1}$, the $\delta(\text{AlOHMg})$ band coupled with the Al–O out-of-plane vibration [12,20] (Table 4). This band, therefore, cannot be considered as unambiguously indicative of Mg-rich illite or aluminoceladonite; and in Fe-illites, it may include a contribution from $\delta(\text{Fe}^{3+}\text{OH Fe}^{3+})$ at $\sim 820\text{ cm}^{-1}$. Al-glaucanites, glaucanites, and celadonites show a distinct band at $811\text{--}823\text{ cm}^{-1}$, $\delta(\text{Fe}^{3+}\text{OH Fe}^{3+})$ and a weak band, shoulder or second-derivative minimum at $835\text{--}843\text{ cm}^{-1}$, which may correspond, depending on the cation composition, to $\delta(\text{AlOHMg})$ and/or to a second $\delta(\text{Fe}^{3+}\text{OH Fe}^{3+})$ mode [71–73] (Al-glaucanite KUL2 is an exception, showing a broad band at 824 cm^{-1} poorly resolved from a band at 801 cm^{-1}). Gates [73] suggested that in natural nontronites, the band at $839\text{--}846\text{ cm}^{-1}$ is

related to tetrahedral Fe^{3+} . This might be true for celadonite TAIH, which may contain ~ 0.2 tetrahedral Fe^{3+} cations *p.h.u.*, but not for samples 69 and Z1, which have no tetrahedral Fe^{3+} [18].

Depending on the cation composition, the distinct band or shoulder or a minimum in the second derivative at $\sim 795\text{--}805\text{ cm}^{-1}$ present in all the spectra (Table 4) may refer to either the Al–O–Al vibration [20], to $\delta(\text{Fe}^{3+}\text{OHMg})$ and/or $\delta(\text{Fe}^{2+}\text{OH Fe}^{3+})$ [12,26], or to silica or quartz admixtures [26,74]. The conventional assignment of the band at $\sim 800\text{ cm}^{-1}$ to $\delta(\text{Fe}^{2+}\text{OH Fe}^{3+})$ is in fair agreement with *ab initio* calculations (808 cm^{-1} , [75]) but disagrees with the prediction of cation mass-valence sum (CM-VS) approach (766 cm^{-1} , [72,73]), making the interpretation still more complicated. Other types of OH-linked cation pairs, such as $\text{Fe}^{2+}\text{OHFe}^{2+}$, AlOHFe^{2+} and MgOHMg , which are revealed in the OH-stretching region (see below), are difficult to identify in the OH-bending region. The corresponding bending bands are predicted at 714 , 810 and 776 cm^{-1} , respectively, by the CM-VS approach [72,73] and at 691 , 820 and 765 cm^{-1} , respectively, by *ab initio* calculations [75] and would therefore overlap with other types of absorption bands.

Attempts have been made to decompose and curve-fit the OH-bending region, though not for micas but for smectites and mixed-layer illite-smectites [60,62,73]. The interpretation of the OH-bending vibrations, however, is complicated not only by bands overlapping but also by the ambiguity in band attributions [72,73,75], as well as by the uncertainty in the baseline correction in the OH-bending region.

The band at $\sim 750\text{ cm}^{-1}$ is conventionally attributed to the Al–O–Si in-plane vibration [12,16,26], although Beran [20] assigns it to the Al–O–Al in-plane vibration. In any event, the presence of this band indicates Al-for-Si substitution in the tetrahedral sheet. A well-defined band at $753 \pm 3\text{ cm}^{-1}$ is observed in the spectra of all illites irrespective of the amount of tetrahedral Al cations, whereas Fe-illites, Al-glaucanites and glaucanites display a band or shoulder at $753\text{--}763\text{ cm}^{-1}$ (Table 4). Despite the very low or zero tetrahedral Al contents, all aluminoceladonites and celadonites show a weak but distinct absorption band at $746\text{--}760\text{ cm}^{-1}$ (except for celadonite 69, which nevertheless shows a shoulder at 757 cm^{-1}). Further investigation is therefore needed to explain the presence of this band in celadonite and aluminoceladonite spectra.

The band at $686\text{--}699\text{ cm}^{-1}$ in the spectra of Fe-poor mica varieties (Table 4) is assigned to Si–O [64] or Si–O–Al^{VI} [20] vibrations; the band at $\sim 680\text{--}685\text{ cm}^{-1}$ in Fe-bearing micas is attributed to the Fe–O out-of-plane vibration [26]. In varieties of mixed cation composition, such as Fe-illites and Al-glaucanites the band at $680\text{--}691\text{ cm}^{-1}$ may result from superposition of the above absorption bands. In celadonites, however, Weiszburg et al. [23] assigned this band to the second libration of $\text{Fe}^{3+}\text{--OH--Mg}$ and $\text{Fe}^{3+}\text{--OH--Fe}^{3+}$.

The band at $618\text{--}628\text{ cm}^{-1}$ in some of the illites and aluminoceladonites spectra (or spectra second derivatives) is most probably due to the presence of smectite interlayers ($5\text{--}16\%$, [7]) and corresponds to coupled Al–O and Si–O out-of-plane vibrations characteristic of Al-rich dioctahedral smectites [26]. The band at $620\text{--}625\text{ cm}^{-1}$ can be identified in the second derivatives of the spectra of several Fe-illites, Al-glaucanites and glaucanites, which contain $5\text{--}10\%$ of expandable layers.

The OH-bending bands may overlap not only with other types of vibrations of the mica structure but also with those of various common admixtures, such as quartz with characteristic absorption bands at $693\text{--}694\text{ cm}^{-1}$, $777\text{--}780\text{ cm}^{-1}$ and $797\text{--}801\text{ cm}^{-1}$, as well as amorphous silica ($\sim 800\text{ cm}^{-1}$) or cristobalite ($792\text{--}796\text{ cm}^{-1}$) [74,76]. The various carbonate minerals display absorption bands at $1420\text{--}1480\text{ cm}^{-1}$, $860\text{--}890\text{ cm}^{-1}$ and $700\text{--}740\text{ cm}^{-1}$ [77]; goethite, a common admixture in Fe-rich micas, shows absorption at 890 and 797 cm^{-1} [78]. The presence of these admixtures may complicate the interpretation of the spectra. For example, in glaucanites 79/73 and 372/70 and celadonites TAIH and 69, sharp absorption bands at $695\text{--}699\text{ cm}^{-1}$ in combination with bands at $1440\text{--}1450\text{ cm}^{-1}$ may indicate the presence of carbonate admixtures. At the same time, a weak shoulder at 779 cm^{-1} in combination with a band at 797 in sample 69 suggests that the sharp band at 698 may refer to quartz. In such cases the correct attribution of the absorption bands in the region of interest requires application of other methods, e.g., X-ray diffraction.

Partial overlap and coupling of the various bands, as well as the existing ambiguities in band assignments, complicate the interpretation of the 950–600 cm^{−1} region and make it less informative from the point of view of identification. On the other hand, in combination with the data on the Si–O bending and stretching modes, as well as the OH-stretching vibrations, the band positions in this region may provide helpful additional information.

3.4. The OH Stretching Vibration Modes

3.4.1. Methodology

The FTIR spectrum of a dioctahedral mica in the OH-stretching region results from a superposition of OH bands corresponding to specific types of OH-linked cation pairs. The relative integrated intensities of individual bands are proportional to the contents of the corresponding types of cations in the OH-sharing *cis*-octahedral sites with the absorption coefficients being the same for all cation-pair types [13,17,18].

The positions of the specific cation-OH-cation bands (Table 5), which were identified from spectra decomposition and curve-fitting of IR spectra of dioctahedral mica samples of diverse cation compositions [17,18], depend on the nature of cations in the two OH-sharing *cis*-octahedral sites and are determined by several competing factors. On the one hand, an increase in the total mass of cations bound to an OH group decreases the wavenumber. On the other hand, for cations having the same mass but different valences, two opposite trends interact. An increase in the total cation valence decreases the interaction within the OH group, but simultaneously increases the repulsion between the cations and the hydroxyl proton, thus weakening hydrogen bonds between OH and two apical oxygen anions in the octahedral sheet and strengthening the bond within the OH group. The latter effect dominates, and therefore an increase in the total cation valence increases the wavenumber. For the AlOHAl, AlOHMg and MgOHMg stretching vibrations, the valence effect prevails over the mass effect, and therefore $\nu(\text{AlOHAl}) > \nu(\text{AlOHMg}) > \nu(\text{MgOHMg})$. In addition to the OH-stretching vibrations of the mica structure proper, Besson and Drits [17,18] identified the AlOHAl, AlOHFe³⁺ and Fe³⁺OHFe³⁺ bands of pyrophyllite- and ferripyrophyllite-like structural fragments present in interlayer-deficient micas at positions close to those observed in pyrophyllite and ferripyrophyllite spectra [12,79,80] (Table 5).

The assumption of the absorption coefficients being the same for all individual OH-stretching bands [13,18] allows the evaluation of the octahedral cation contents from FTIR data and therefore provides a criterion for the validity of the interpretation of the spectrum. The content of a cation R_i *p.h.f.u.* is given by $R_i = 2A_{ii} + \sum_j A_{ijj}$ [18], so that, e.g.,

$$\text{Al} = 2A_{\text{AlAl}} + A_{\text{AlMg}} + A_{\text{AlFe}^{3+}} + A_{\text{AlFe}^{2+}},$$

where Al is the amount of Al cations *p.h.f.u.*, and A_{AlAl} , A_{AlMg} , $A_{\text{AlFe}^{3+}}$ and $A_{\text{AlFe}^{2+}}$ are the relative integrated intensities of the AlOHAl, AlOHMg, AlOHFe³⁺, and AlOHFe²⁺ bands, respectively. Correct band attributions and spectrum decomposition/curve-fitting should lead to agreement between the cation composition of the sample obtained from FTIR data and that provided by the crystal-chemical formula.

Table 5. Positions $\nu(\text{OH})$, cm^{-1} and relative integrated intensities I of OH stretching bands corresponding to specific OH-bonded cation pairs in the FTIR spectra of selected K-dioctahedral 1M micas; χ^2 is the minimization function. (Sample numbers as in Tables 1–4).

# Sample	1 RM30		9 IW1-1		12 602-1		17 136		26 551		27 555A		29 103		31 3771A		35 GT6-69		43 Z1		[17,18]	This work
Band	$\nu(\text{OH})$	A	$\nu(\text{OH})$	A	$\nu(\text{OH})$	A	$\nu(\text{OH})$	A	$\nu(\text{OH})$	A	$\nu(\text{OH})$	A	$\nu(\text{OH})$	A	$\nu(\text{OH})$	A	$\nu(\text{OH})$	A	$\nu(\text{OH})$	A	$\nu(\text{OH})$	$\nu(\text{OH})$
Fe ²⁺ OHFe ²⁺	-	-	-	-	-	-	-	-	3500	0.062	3505	0.087	3505	0.059	3505	0.051	3504	0.055	3505	0.091	3505±2	3503±3
Fe ²⁺ OHFe ³⁺	-	-	-	-	-	-	3523	0.032	3517	0.107	3517	0.022	3520	0.111	3516	0.048	3516	0.065	3527	0.151	3521±3	3521±6
Fe ³⁺ OHFe ³⁺	-	-	-	-	-	-	-	-	3535	0.16	3534	0.236	3533	0.138	3530	0.149	3531	0.134	3533	0.119	3535±2	3533±3
Fe ³⁺ OHFe ³⁺	-	-	-	-	-	-	3541	0.076	-	-	-	-	3547	0.127	3544	0.104	3545	0.105	-	-	-	3544±3
MgOHFe ²⁺	-	-	-	-	3542	0.020	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3543±3	3541
AlOHFe ²⁺	-	-	-	-	3567	0.052	3562	0.134	-	-	-	-	-	-	3560	0.071	-	-	-	-	3559±3	3563±3
MgOHFe ³⁺	-	-	3566	0.072	-	-	-	-	3558	0.114	3559	0.118	3562	0.148	3560	0.069	3560	0.154	3556	0.527	3559±3	3561±5
AlOHFe ³⁺	-	-	-	-	-	-	-	-	3578	0.14	3574	0.055	3575	0.095	3576	0.088	3574	0.098	-	-	3573±2	3576±2
MgOHMg	-	-	-	-	3586	0.099	3583	0.194	-	-	3587	0.073	3587	0.066	3587	0.051	3586	0.071	3579	0.073	3583±3	3583±4
AlOHMg	3610	0.166	3603	0.280	3604	0.247	3603	0.192	3602	0.135	3605	0.12	3601	0.088	3601	0.119	3602	0.116	3602	0.029	3604±3	3605±5
AlOHAl	3627	0.393	3620	0.366	3619	0.210	3615	0.276	3620	0.117	3623	0.101	3618	0.086	3616	0.076	3617	0.091	-	-	3621±4	3621±6
AlOHAl	3645	0.181	3640	0.109	3636	0.220	3640	0.027	3643	0.069	3638	0.074	-	-	-	-	3636	0.068	-	-	3641±3	3641±5
AlOHAl	3659	0.181	-	-	3661	0.042	3656	0.070	3666	0.041	3663	0.033	3663	0.034	3665	0.026	3656	0.026	-	-	3658±3	3661±5
Fe ³⁺ OHFe ³⁺ pyr	-	-	-	-	-	-	-	-	-	-	-	-	3638	0.049	3631	0.081	-	-	-	-	3631±3	3634±4
AlOHFe ³⁺ pyr	-	-	3656	0.079	3651	0.061	-	-	3654	0.035	3652	0.041	-	-	3649	0.05	-	-	-	-	3652±2	3652±4
AlOHAlpyr	3672	0.079	3672	0.094	3672	0.050	-	-	3690 *	0.020	3680	0.028	-	-	3679	0.017	3675	0.018	3677	0.009	3675±4	3675±5
χ^2	1.13		4.64		4.26		1.34		6.04		3.78		2.56		5.48		1.21		3.25			

* AlOHAl_{pyr} of the smectite component (?).

3.4.2. Profiles and Positions of OH-Stretching Bands as a Function of Cation Composition

K-dioctahedral 1M micas display a variety of band positions and profiles in the OH-stretching region. In most cases (except aluminoceladonites and celadonites), they show a broad band, with or without modulations (Figures 1 and 8), resulting from the superposition of individual cation-OH-cation vibrations. For selected samples, these individual bands were identified from spectrum decomposition and curve-fitting (Table 5, Figure 8). The validity of the spectra interpretation was confirmed by good agreement between cation compositions obtained from FTIR data and those provided by the crystal-chemical formulae (Table 6). The χ^2 values varied from 1.13 to 6.04 (Table 5), and the R^2 values were ~1.00 for all the decompositions.

Table 6. Octahedral cation compositions of selected samples (cations *p.h.f.u.*): c.a.—obtained from chemical analysis data; FTIR—calculated from relative integrated intensities of OH-stretching bands.

Sample	Al		Mg		Fe ²⁺		Fe ³⁺		Fe _{tot} *		Σ _{oct} **	
	c.a.	FTIR	c.a.	FTIR	c.a.	FTIR	c.a.	FTIR	c.a.	FTIR	c.a.	FTIR
RM30	1.86	1.83	0.14	0.17	-	-	-	-	-	-	2.00	2.00
IWi-1	1.44	1.50	0.39	0.35	-	-	0.14	0.15	0.14	0.15	1.97	2.00
602-1	1.39	1.40	0.51	0.47	0.09	0.07	0.04	0.06	0.13	0.13	2.03	2.00
136	1.08	1.07	0.60	0.58	0.19	0.17	0.13	0.18	0.32	0.35	2.00	2.00
551	0.85	0.80	0.22	0.25	0.15	0.23	0.77	0.72	0.92	0.95	1.99	2.00
555A	0.76	0.70	0.34	0.39	0.16	0.20	0.76	0.72	0.92	0.92	2.03	2.00
103	0.37	0.42	0.40	0.37	0.11	0.23	1.15	0.98	1.26	1.21	2.03	2.00
3771A	0.64	0.56	0.28	0.29	0.19	0.22	0.96	0.92	1.15	1.14	2.07	2.00
GT6-69	0.57	0.62	0.47	0.41	n.d.	0.18	0.95	0.79	0.95	0.97	1.99	2.00
Z1	0.05	0.05	0.73	0.70	0.26	0.33	0.96	0.92	1.22	1.25	2.00	2.00

$$* \text{Fe}_{\text{tot}} = \text{Fe}^{2+} + \text{Fe}^{3+}; ** \Sigma_{\text{oct}} = \text{Al} + \text{Mg} + \text{Fe}^{2+} + \text{Fe}^{3+}.$$

In both (Mg,Fe)-poor and Mg-rich illites, the OH-stretching region shows a single wide absorption band; the position of maximum absorption depends on the octahedral cation composition. In samples having 0.1–0.27 Mg cations *p.h.f.u.*, the maximum absorption is determined by the AlOHAl vibration at $3627 \pm 3 \text{ cm}^{-1}$ (Table 3). For example, the OH-absorption band in sample RM30 results from the superposition of the AlOHMg band (3610 cm^{-1}), three AlOHAl bands (3627 , 3645 , and 3659 cm^{-1}) and the AlOHAl band of the pyrophyllite-like component (3672 cm^{-1}) (Table 5, Figure 8a). The presence of three AlOHAl stretching bands is explained by the various Si/Al configurations in the vicinity of the OH-sharing Al-octahedra [17,20]. The number and actual positions of these bands can be also affected by Mg for Al substitutions in the adjacent octahedra, as well as by the nearest interlayer site being occupied or vacant [61]. The positions of the three AlOHAl stretching bands of the mica structure of sample RM30 are similar to those reported for synthetic muscovite (3659 , 3644 and 3629 cm^{-1}) [81]. In illite samples with the Mg contents of ~0.4 cations *p.h.f.u.*, the maximum is either at 3606 cm^{-1} , determined by the AlOHMg vibration (samples 60 and 60/3, Table 3), or at 3617 cm^{-1} resulting from the superposition of AlOHMg (3603 cm^{-1}) and AlOHAl (3620 cm^{-1}) (sample IWi-1, Table 5, Figure 8b). The other vibrations contributing to the broad OH-stretching band of Mg-rich illite IWi-1 include MgOHFe³⁺ (3566 cm^{-1}), AlOHAl (3640 cm^{-1}) and the AlOHFe³⁺ (3656 cm^{-1}) and AlOHAl bands (3672 cm^{-1}) of the pyrophyllite-like component (Figure 8b, Table 5). The position of the pyrophyllite-like AlOHFe³⁺ band is somewhat higher than observed by Farmer [12] and Lantenois et al. [80] (3647 and 3645 cm^{-1} , respectively) but close to that reported by Besson and Drits [17,18] (3651 – 3654 cm^{-1}).

Figure 8. Decomposition and curve-fitting of the FTIR spectra of selected samples in the OH-stretching region: (a)—RM30; (b)—IWi-1; (c)—136; (d)—551; (e)—GT6-69; (f)—103; (g)—Z1.

The OH-stretching region of the aluminoceladonite spectra differs dramatically from that of illites. The spectra of samples 136 (Figures 1 and 8c) and Z2 (not shown) consist of several sharp and well-resolved peaks, the most intense at 3603 cm^{-1} (AlOHMg), and MgOHMg, AlOHFe $^{2+}$ and Fe $^{3+}$ OHFe $^{3+}$ at 3583, 3559–3562 and 3538–3540 cm^{-1} , respectively (Table 3). In addition, AlOHAl (3615, 3640 and 3656 cm^{-1}) and Fe $^{2+}$ OHFe $^{3+}$ (3523 cm^{-1}) bands are revealed by spectrum decomposition and curve-fitting (Figure 8c). In the other aluminoceladonites, the OH-stretching region contains a wide absorption band with one sharp maximum at 3601–3606 cm^{-1} and poorly resolved bands that can be identified from decomposition and curve-fitting (e.g., sample 602-1, Figure 1, Table 5). As shown by Besson et al. [82], the resolution of the OH-stretching spectral region of dioctahedral 2:1 phyllosilicates, and aluminoceladonite in particular, is associated with the degree of the order–disorder in the octahedral cation distribution. The typical feature of the aluminoceladonite spectra is therefore the sharp maximum at $\sim 3600\text{ cm}^{-1}$, which corresponds to the AlOHMg stretching vibration. Another

characteristic feature is the presence of the MgOHMg absorption band at $3583\text{--}3585\text{ cm}^{-1}$, which can be identified either by visual inspection or, in the poorly resolved spectra, in the second derivative.

The FTIR spectra of Fe-illites and Al-glaucanites in the OH-stretching region differ dramatically from those of illites and, in particular, Fe-bearing Mg-rich illites, as they contain two well-resolved broad bands (Figure 1): one, a superposition of individual vibrations that involve Fe and Mg, with the maximum corresponding to the $\text{Fe}^{3+}\text{OHFe}^{3+}$ band ($3532 \pm 4\text{ cm}^{-1}$), and another, resulting from vibrations involving Al and Mg, with the maximum corresponding to either AlOHMg at $3605 \pm 5\text{ cm}^{-1}$ (most samples) or AlOHAl (3624 cm^{-1} , sample 553/1), or a superposition of the AlOHMg and AlOHAl bands (3614 cm^{-1} , samples 560/3, 551) (Table 3). For $K_{Al} \geq 0.6$, the “Al, Mg” band is either stronger than or of similar intensity as the “Fe” band (e.g., sample BSH11, Figure 1); for $K_{Al} \sim 0.5$, the “Fe” band is stronger (sample 551, Figures 1 and 8d). The “Fe” band of Al-glaucanite 551 is a superposition of the following individual vibrations: $\text{Fe}^{2+}\text{OHFe}^{2+}$ (3500 cm^{-1}), $\text{Fe}^{2+}\text{OHFe}^{3+}$ (3517 cm^{-1}), $\text{Fe}^{3+}\text{OHFe}^{3+}$ (3535 cm^{-1}), MgOHFe^{3+} (3558 cm^{-1}) and AlOHFe^{3+} (3578 cm^{-1}), while the “Al, Mg” band involves AlOHMg (3602 cm^{-1}) and AlOHAl (3620 cm^{-1} , 3643 cm^{-1} and 3666 cm^{-1}) modes, as well as AlOHFe^{3+} band of the pyrophyllite-like component at 3654 cm^{-1} ; the band at 3690 cm^{-1} refers to the AlOHAl of either a pyrophyllite-like component or a minor kaolin admixture (Figure 8d, Table 5). The individual bands’ positions within the “Fe” band in the spectrum of sample 555A are close to those of sample 551 but the intensity distribution is different; the band positions and intensity distribution in the “Al, Mg” region are similar to those in sample 551 but for the presence of the MgOHMg band at 3587 cm^{-1} and lower intensity of the AlOHFe^{3+} band (Table 5).

The OH-stretching vibration regions of glauconites, with few exceptions, show worse resolution, as compared to Al-glaucanites. The distinguishing feature of glauconite spectra is the presence of maxima at $3533\text{--}3538\text{ cm}^{-1}$ and $\sim 3550\text{--}3560\text{ cm}^{-1}$ (corresponding to $\text{Fe}^{3+}\text{OHFe}^{3+}$ and $\text{Fe}^{3+}\text{OHMg}$, respectively), which can be either well- or poorly resolved (from sharp bands to shoulders) and have similar or different intensities (Figure 1, Table 3). For example, the OH-stretching region of sample 103 is a broad band with two poorly resolved maxima at ~ 3530 and $\sim 3560\text{ cm}^{-1}$, and a shoulder at $\sim 3600\text{ cm}^{-1}$ (corresponding to AlOHMg), whereas sample GT6-69 shows sharp bands at 3560 and 3602 cm^{-1} , and a broad but distinct shoulder at $\sim 3530\text{ cm}^{-1}$ (Figure 1). The spectrum decomposition and curve-fitting revealed similar types of individual cation-OH-cation bands at close positions with similar, albeit not identical, intensity distributions (Figure 8e,f, Table 5). There are, however, a few differences. The spectrum of sample GT6-69, which has more Al and less Fe ($K_{Al} = 0.38$), shows three AlOHAl bands (3617 , 3636 and 3656 cm^{-1}) and a pyrophyllite-like AlOHAl band at 3675 cm^{-1} , whereas in that of sample 103 ($K_{Al} = 0.24$) there are two AlOHAl bands (3618 and 3663 cm^{-1}). In sample 103, the band at 3638 cm^{-1} is identified as the $\text{Fe}^{3+}\text{OHFe}^{3+}$ band of the ferripyrophyllite-like structure fragments, as it is only this assignment that provides good agreement between the cation composition obtained from the FTIR data and that given by the crystal-chemical formula (Table 6). Although Besson and Drits [18] only found two AlOHAl bands in the OH-stretching regions of glauconites, the presence of three AlOHAl bands in the spectrum of sample GT6-69 may be associated with the highly heterogeneous cation composition, which, as shown by Drits et al. [9] can be realized as phase heterogeneity at micro- and nano-levels. The third AlOHAl band may therefore refer to Al-rich micro- or nanocrystals within the sample.

Unlike the glauconites studied by Besson and Drits [17,18] both samples 103 and GT6-69, as well as sample 37/71A (Table 5), display two $\text{Fe}^{3+}\text{OHFe}^{3+}$ bands at $3531\text{--}3533\text{ cm}^{-1}$ and $3545\text{--}3547\text{ cm}^{-1}$ of similar intensity, and no spectra decomposition in terms of a single $\text{Fe}^{3+}\text{OHFe}^{3+}$ band would lead to a good cation composition fit. The presence of two $\text{Fe}^{3+}\text{OHFe}^{3+}$ bands in micas with high Fe content in combination with complex tetrahedral and octahedral cation compositions may be associated with the heterogeneity in the local environments around the vibrating OH group. The total amounts of Fe cations obtained from the FTIR data are nearly identical to those in the crystal-chemical formulae for both samples 103 and GT6-69 (Table 6). For sample GT6-69, the oxidation state of Fe was not determined and all Fe was assumed to be trivalent [52]; the FTIR data, however, indicate the presence

of 0.18 Fe^{2+} cations *p.h.f.u.* The ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ in sample 103 was assumed to be similar to that of sample 3771 based on a similar geological setting and overall cation composition [8]; according to the FTIR data, the actual content of Fe^{2+} should be higher than that in the crystal-chemical formula (0.23 vs. 0.11 cations *p.h.f.u.*) (Table 6).

The OH-stretching regions of celadonites differ dramatically from those of all the other Fe-bearing mica varieties (Figures 1 and 8g). They show two sharp, well-resolved maxima, the stronger at 3555–3556 cm^{-1} ($\text{Fe}^{3+}\text{OHMg}$) and a less intense one at 3532–3533 cm^{-1} ($\text{Fe}^{3+}\text{OHFe}^{3+}$). The AlOHMg stretching mode may appear as a minor sharp band (samples TAIH, not shown, and Z1, Figures 1 and 8g). As in the case of aluminoceladonites, the high resolution of the OH-stretching spectral region of celadonites is associated with the high degree of ordering in the octahedral cation distribution [82]. In addition to the sharp MgOHFe^{3+} and $\text{Fe}^{3+}\text{OHFe}^{3+}$ bands, the spectrum decomposition and curve-fitting of celadonite Z1 reveals the presence of the $\text{Fe}^{2+}\text{OHFe}^{2+}$ band (3505 cm^{-1}), the $\text{Fe}^{2+}\text{OHFe}^{3+}$ band (3527 cm^{-1}), and the MgOHMg band at 3579 cm^{-1} (Figure 8g, Table 5). The band positions and intensity distribution in this decomposition are in agreement with those of [17,18] for sample Z1, except that the weak MgOHFe^{2+} (3542 cm^{-1}), AlOH Fe^{3+} (3574 cm^{-1}) and AlOHAl (3621 cm^{-1}) bands reported by [17,18] were not found in this work. These minor discrepancies may be associated with the fact that different specimens of the same sample were used in the two studies in question.

On the whole, the results of the OH-stretching region decomposition and curve-fitting are in accordance with the interpretation and band assignments of [17,18]. The few differences include the presence of a second $\text{Fe}^{3+}\text{OHFe}^{3+}$ band and a third AlOHAl band in some glauconites with a high Fe content and highly heterogeneous cation composition, as well as slightly wider ranges of band position variations for specific cation-OH-cation vibration modes (Table 5).

4. Conclusions

The approach suggested for the interpretation of the FTIR spectroscopy data involves relationships between band positions and cation composition, and provides a set of distinguishing features and identification criteria for K-dioctahedral 1M micas that include the band positions and profile in the regions of Si–O bending, Si–O stretching and OH-stretching vibrations (Table 7). In particular, FTIR data allow unambiguous identification of illite and aluminoceladonite, which are often confused based on superficial interpretation of XRD data. Specifically, a sharp maximum from the AlOHMg stretching vibration at $\sim 3600 \text{ cm}^{-1}$, the presence of a MgOHMg stretching vibration at 3583–3585 cm^{-1} , as well as characteristic band positions in the Si–O bending (435–439, 468–472 and 509–520 cm^{-1}) and stretching regions (985–1012 and 1090–1112 cm^{-1}) are typical of aluminoceladonite. Distinguishing between Mg-poor and Mg-rich illites based solely on FTIR data appears problematic, but the position of the Si–O bending modes and the maximum absorption in the region of OH-stretching vibrations may serve as additional criteria. Regression equations relating the band positions in the Si–O bending region with the contents of tetrahedral Al, octahedral Al and octahedral Mg allow evaluation of the contents of corresponding cations in illites and aluminoceladonites. According to FTIR characteristics, the Fe-bearing K-dioctahedral 1M micas are divided into 4 groups differing in the value of $K_{Al} = \text{Al}/(\text{Al} + {}^{\text{VI}}\text{Fe}^{3+})$, where Al and ${}^{\text{VI}}\text{Fe}^{3+}$ are the amounts of Al and Fe^{3+} octahedral cations *p.h.f.u.*: Fe-bearing Mg-rich illites ($K_{Al} \sim 0.9$); Fe-illites ($0.65 \leq K_{Al} \leq 0.75$)/Al-glauconites ($0.5 \leq K_{Al} \leq 0.6$), with Al-glauconites having $K_{Al} \sim 0.5$ forming a special subgroup; glauconites ($K_{Al} < 0.5$); and celadonites ($K_{Al} < 0.2$) (Table 7).

Table 7. FTIR distinctive features for K-dioctahedral 1M micas (see text for details and explanation).

	Si–O Bend (δ_1 , cm^{-1})	Si–O–Si Bend (δ_2 , cm^{-1})	Si–O–Al Bend (δ_3 , cm^{-1})	Si–O–Fe Bend (δ_3 , cm^{-1})	Si–O Stretch (cm^{-1})	Si–O _{apical} Stretch (cm^{-1})	OH Stretch
Fe-poor, K-dioctahedral micas ($\text{Fe}_{\text{tot}} \leq 0.3$ cations <i>p.h.f.u</i>)							
(Mg, Fe)-poor illites	414–425	471–477	525–535	-	1023–1027	~1070–1080 (shoulder)	Broad band, maximum at ~3625–3630 cm^{-1}
Mg-rich illites	419–435	~470	519–525	-	1008–1021	1075–1090	Broad band, maximum at ~3605–3620 cm^{-1}
Aluminoceladonites	435–439	~470	509–520	-	985–1012	1090–1112	Sharp bands at ~3600 cm^{-1} (AlOHMg, strongest); 3583 cm^{-1} (MgOHMg); ~3560 cm^{-1} (AlOHFe ²⁺ or MgOHFe ³⁺); ~3540 cm^{-1} (FeOHFe); OR broad band with a sharp maximum at ~3600 cm^{-1}
Fe-bearing, K-dioctahedral micas ($\text{Fe}_{\text{tot}} \geq 0.3$ cations <i>p.h.f.u</i>)							
Fe-bearing Mg-rich illites ($K_{\text{Al}} \sim 0.9$)	434–440	~470	~520	-	~1010	1084–1089	Broad band, maximum at 3600–3610 cm^{-1}
Fe illites ($0.65 \leq K_{\text{Al}} \leq 0.75$) Al-glaucanites ($0.5 < K_{\text{Al}} \leq 0.6$)		467–471; 450–455 (* or sh)	514–526	484–496	987–1017	1072–1101 (band or shoulder)	Two bands, 3528–3534 (“Fe”) and 3600–3610 cm^{-1} (“Al, Mg”). Similar intensity or “Al, Mg” band stronger
Al-glaucanites ($K_{\text{Al}} \sim 0.5$)		465–469; 454–455	514–518 (sh)	486 (sh)			“Fe” band stronger
Glaucanites ($K_{\text{Al}} < 0.5$)			-				Bands at 3533–3538 cm^{-1} and ~3550–3560 cm^{-1} , variable resolution and relative intensity
Celadonites ($K_{\text{Al}} < 0.2$)		453–463		483–499	(957), 975–978 (sharp)	1090 or 1072–1074 (sharp), 1100–1113 (sharp band or shoulder)	Sharp, well-resolved bands at 3556 cm^{-1} (MgOHFe ³⁺) and 3532–3533 cm^{-1} (Fe ³⁺ OHFe ³⁺)

The band positions and profiles in the regions of Si–O bending, Si–O stretching and, most importantly, OH-stretching vibrations allow not only unambiguous identification of illites, aluminoceladonites and celadonites, but also distinction between Fe-illites and illites proper, as well as between Al-glaucanites and glaucanites. On the other hand, distinction between Fe-illites and Al-glaucanites, which have similar FTIR features, requires data on cation composition and unit-cell parameters.

The 950–600 cm^{−1} region is less informative from the point of view of identification because of partial overlap and coupling of the various bands, as well as ambiguities in band assignments. In combination with the data on the Si–O bending and stretching modes, as well as the OH-stretching vibrations, the band positions in this region may, however, provide helpful additional information.

The band positions and profiles in the OH-stretching regions, especially for Fe-bearing K-dioctahedral micas, can serve as additional diagnostic criteria for phase heterogeneity realized at the micro- and nano-levels. The validity of the decomposition and curve-fitting of OH-stretching regions was confirmed by the good agreement between cation compositions obtained from FTIR data and those provided by the crystal-chemical formulae for a representative collection of samples in terms of a unique set of individual OH band positions that vary within narrow wavenumber intervals. For monomineralic samples with known cation compositions, the proportions of various types of cation-OH-cation configurations obtained from the decomposition of the OH-stretching regions, in combination of the data of other methods, such as Mössbauer and NMR spectroscopies, can be used to reconstruct the two-dimensional octahedral cation distribution [82–84] and thus reveal the mechanisms for structural transformations (e.g., release of Mg and Fe during diagenetic transformations of illite-smectites into illite-tobelite smectites) [83]. Further research is needed to find out to what extent the Al and Mg cation contents obtained from the data on Si–O bending band positions may be used for the interpretation of OH-stretching vibration regions of Al-rich, (Mg, Fe)-poor micas in the absence of chemical analysis data.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/2/153/s1>, Figure S1: FTIR spectra of K-dioctahedral 1M micas, Table S1: Parameters of IR spectra decomposition.

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