

POTASSIUM- AND AMMONIUM-TREATED MONTMORILLONITES. I. INTERSTRATIFIED STRUCTURES WITH ETHYLENE GLYCOL AND WATER

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Abstract—Monoionic K- and NH₄-smectites saturated with ethylene glycol form mixed-layer structures which usually consist of three kinds of layers: a 10-Å, non-expanded layer; a 14-Å, partly expanded layer; and a 16.8-Å, completely expanded layer. In some samples, the 14-Å layers formed 60–70% of all layers present. When saturated with water vapor the smectites commonly consisted of three kinds of layers (10-, 12.6-, and 15.5-Å). Generally these samples contained fewer expanded layers than those saturated with ethylene glycol. This result is attributed to the smaller dipole moment of water compared with that of ethylene glycol. The greater solvation energy of NH₄⁺ in comparison with that of K⁺ causes the expansion of a part of layers which did not expand in the K forms. This result indicates that there is an inhomogeneous distribution of layer charge in the smectite structure. The prevalent type of mixed layering in the studied samples is that of random distribution of layers.

Key Words—Ethylene glycol complex, Interstratification, Layer charge, Mixed layer, Montmorillonite.

INTRODUCTION

By saturation of montmorillonites with monovalent ions with low solvation energy, minerals with mixed-layer structure are formed. Layers in these structures differ in thickness, with the thickness of the layers depending on the kind of cations and molecules sorbed in the interlayer space and on the local charge on the layers. If water molecules are sorbed in the interlayer space, the interstratified structure consists of 2–4 kinds of layers which differ from each other in the number of interlayer water molecules. Their mutual ratio depends on the relative humidity of the environment. The interstratified structures are usually analyzed after glycerol or ethylene glycol (EG) treatment because of the greater stability of the interlayer complexes that are formed.

Analyses of mixed-layer minerals are usually made with the aid of curves which show how diffraction peaks migrate as the relative proportions of different layers change (MacEwan *et al.*, 1961). This method is viable only if the number and kind of layers present in the analyzed sample are known. Comparison of calculated and experimental diffraction patterns has similar limitations. The application of these methods led to the assumption that the montmorillonite structures with monovalent cations and with interlayer glycerol or ethylene glycol molecules consist of non-expanded (10-Å) layers and expanded (17.6- and/or 16.8-Å) layers (Dyal and Hendricks, 1952; Sawhney, 1969; Reynolds and Hower, 1970).

Papers reporting the application of Fourier transform analysis show that the structures may be more complicated. Three kinds of layers were identified in mont-

morillonites saturated with potassium and solvated with glycerol (Tettenhorst and Johns, 1966; Shutov *et al.*, 1969; Muravyov and Sakharov, 1970). Also, in EG-saturated montmorillonites three kinds of layers were detected (Tettenhorst and Johns, 1966; Machajdík and Číčel, 1973).

Since the existence of three kinds of layers in K- and NH₄-treated smectites was confirmed by previous studies, the present work attempted: (1) to characterize the individual kinds of layers found in smectites; (2) to estimate the frequency of occurrence of smectites which, after treatment with K⁺ and/or NH₄⁺ and after subsequent saturation with water vapor or EG vapor, give rise to mixed-layer mineral with three kinds of layers; and (3) to determine which type of mixed layering prevails in twelve smectites from Czechoslovakia, the Soviet Union, the United States, and Bulgaria.

MATERIALS AND METHODS

Twelve samples of smectites in which the average negative charge on the layer varied between 0.63 and 1.27 esu per unit cell were studied. Their localities and unit-cell formulae are listed in Table 1. Heretofore unpublished chemical analyses of three samples follow: Borša: SiO₂ = 53.59, Al₂O₃ = 18.09, Fe₂O₃ = 5.41, MgO = 2.10, CaO = 2.37, total H₂O = 16.93; Chambers: SiO₂ = 51.52, Al₂O₃ = 16.85, Fe₂O₃ = 3.92, TiO₂ = 0.79, MgO = 4.02, CaO = 3.64, total H₂O = 19.37; Zajsanskij: SiO₂ = 53.32, Al₂O₃ = 20.80, Fe₂O₃ = 1.36, TiO₂ = 1.53, MgO = 1.65, CaO = 0.82, total H₂O = 19.21.

The K- and NH₄-forms of each smectite were pre-

Table 1. Unit-cell formulae and layer charges of studied smectites.

Sample number	Location	Q _t	Q ^{VI}	Q ^{IV}	Crystallochemical composition	Impurity ⁵
1	Askangel, U.S.S.R. ¹	1.06	0.98	0.08	(Si _{7.92} Al _{0.08})(Al _{2.78} Fe _{0.36} Mg _{0.80})O ₂₀ (OH) ₄ Ca _{0.52}	
2	Borša, Czechoslovakia	0.74	0.56	0.18	(Si _{7.82} Al _{0.18})(Al _{2.93} Fe _{0.59} Mg _{0.44})O ₂₀ (OH) ₄ Ca _{0.37}	SiO ₂ 5%
3	Braňany, Czechoslovakia ¹	0.96	0.19	0.77	(Si _{7.23} Al _{0.77})(Al _{2.24} Fe _{1.57} Mg _{0.19})O ₂₀ (OH) ₄ Ca _{0.48}	K 5%
4	Chambers, Arizona, U.S.A. ¹	1.17	0.87	0.30	(Si _{7.70} Al _{0.30})(Al _{2.67} Fe _{0.44} Mg _{0.90})O ₂₀ (OH) ₄ Ca _{0.58}	
5	Belle Fourche, South Dakota, U.S.A. ^{2,4}	0.86	0.72	0.14	(Si _{7.86} Al _{0.14})(Al _{3.03} Fe _{0.43} Mg _{0.45})O ₂₀ (OH) ₄ Ca _{0.43}	I 5%
6	Jelšový Potok, Czechoslovakia ²	0.95	0.54	0.41	(Si _{7.59} Al _{0.41})(Al _{3.06} Fe _{0.34} Mg _{0.63})O ₂₀ (OH) ₄ Ca _{0.48}	K 5%
7	Manito, Washington, U.S.A. ^{2,4}	1.27	0.25	1.02	(Si _{6.98} Al _{1.02})(Al _{0.30} Fe _{3.59} Mg _{0.04})O ₂₀ (OH) ₄ Ca _{0.64}	
8	Michajlov, Bulgaria ³	1.16	0.86	0.30	(Si _{7.70} Al _{0.30})(Al _{3.20} Fe _{0.04} Mg _{0.71})O ₂₀ (OH) ₄ Ca _{0.58}	
9	Polkville, Mississippi, U.S.A. ^{2,4}	1.13	0.69	0.43	(Si _{7.57} Al _{0.43})(Al _{2.74} Fe _{0.65} Mg _{0.57})O ₂₀ (OH) ₄ Ca _{0.56}	
10	Pyževskij, U.S.S.R. ³	0.97	0.82	0.15	(Si _{7.85} Al _{0.15})(Al _{3.05} Fe _{0.19} Mg _{0.73})O ₂₀ (OH) ₄ Ca _{0.48}	C 5%
11	Sampor, Czechoslovakia ¹	1.12	0.41	0.71	(Si _{7.29} Al _{0.71})(Al _{0.00} Fe _{3.85} Mg _{0.02})O ₂₀ (OH) ₄ Ca _{0.57}	
12	Zajsanskij, U.S.S.R.	0.63	0.47	0.16	(Si _{7.84} Al _{0.16})(Al _{3.44} Fe _{0.15} Mg _{0.38})O ₂₀ (OH) ₄ (Ca _{0.13} Mg _{0.20})	K 5%

Q_t = total charge calculated for O₂₀(OH)₄ (esu/unit cell); Q^{VI} = octahedral charge (esu/unit cell); Q^{IV} = tetrahedral charge (esu/unit cell).

¹ Novák and Čičel (1978).

² Machajdik and Čičel (1977).

³ Horváth and Novák (1976).

⁴ Obtained from Ward's Natural Science Establishment, Rochester, New York. Sample 4 = A.P.I. Reference Clay 23; Sample 5 = A.P.I. Reference Clay 27; Sample 7 = Nontronite, A.P.I. Reference Clay 33b; Sample 9 = A.P.I. Reference Clay 19.

⁵ K = kaolinite; I = illite; C = calcite.

pared by the method described by Horváth and Novák (1975). The Ca-form, saturated with EG, was checked for the absence of mixed layering. The K- and NH₄-forms were analyzed after saturation by water vapor or EG vapor (the latter at 60°C for up to 15 hr until equilibrium between the sample and the vapor had been reached). X-ray powder diffraction (XRD) patterns were taken with Ni-filtered CuK α radiation. For samples with high iron content, CoK α radiation was used. The XRD data are listed in Table 2.

The XRD patterns were analyzed by the method of Fourier transforms according to MacEwan (1956). For calculation of structure factors of samples saturated with water vapor, the montmorillonite coordinates of Cole and Lancucky (1966) were used. For calculation of structure factors of EG-saturated samples the coordinates of Reynolds (1965) were used. An angular factor (Θ), which represents the combined Lorentz-polarization and geometrical factors, was calculated from the equation, $\Theta_{\text{CuK}\alpha} = (1 + \cos^2 2\theta)/\sin 2\theta$, where θ is the Bragg angle, assuming an ideally oriented sample.

The trial and error method was used to evaluate the probability coefficients from the calculated distribution function W(R). To estimate the degree of reliability of calculated probability coefficients, the measure:

$$r = (h_0 - h_c)^2/h_0^2$$

was used, where r is the reliability factor, h₀ is the peak heights found on W(R) calculated from the XRD patterns, h_c is the peak heights calculated with the aid of suggested probability coefficients. The best fit between

the calculated and proposed probability coefficients is thus indicated by the lowest value of r.

RESULTS AND DISCUSSION

Identified layers

The following layers were found in the structures studied: layer A (d_A = 10 Å), layer B (d_B = 12.6 Å), layer C (d_C = 14 Å), layer D (d_D = 15.5 Å), layer E (d_E = 16.8 Å), and layer AA (d_{AA} = 20 Å). Layers A, B, and D occurred in water-saturated structures and layers A, C, and E in EG-saturated structures. On the basis of literature data (Kinter and Diamond, 1958; MacEwan, 1961; Reynolds, 1965; Tettenhorst and Johns, 1966; Cole, 1966; Brindley, 1966) the above layers can be described in the following way:

A = a non-expanded montmorillonite layer with the interlayer K⁺ or NH₄⁺ localized much like the K⁺ in muscovite.

B = a montmorillonite layer with one interlayer of H₂O molecules.

C = a montmorillonite layer with one interlayer of EG molecules.

D = a montmorillonite layer with two interlayers of H₂O molecules.

E = a montmorillonite layer with two interlayers of EG molecules.

AA = two adjacent layers of type A, which represent one unit in the structure.

The occurrence of layer A in interstratified structures is well known. Layers B and D exist also in Na-montmorillonites, and layer E is typical for Ca-montmoril-

Table 2. X-ray powder diffraction data of monoionic smectites saturated with ethylene glycol (EG) or water.

Askangel												Borša											
Ca-form, EG		K-form		K-form, EG		NH ₄ -form		NH ₄ -form, EG		Ca-form, EG		K-form		K-form, EG		NH ₄ -form		NH ₄ -form, EG					
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I				
17.14	100.0	12.52	100.0	16.02	100.0	12.41	100.0	17.08	100.0	17.41	100.0	12.08	100.0	17.48	100.0	12.49	100.0	17.84	100.0				
8.48	2.5	6.09	3.4	8.82	1.0	6.13	5.5	8.65	1.0	8.48	2.6	5.89	4.8	9.00	3.1	6.05	13.5	8.82	2.6				
3.61	3.3	4.78	2.5	5.52	2.7	3.09	9.0	5.70	2.0	5.61	2.7	5.05	4.8	5.66	3.6	3.09	10.5	5.66	2.4				
4.24	1.1	3.24	12.0	4.49	2.3	2.05	1.0	4.41	1.5	4.24	0.6	3.22	18.0	4.41	2.2	2.03	1.0	4.31	1.4				
3.37	4.8			3.42	8.6			3.42	4.5	3.35	4.4	2.03	2.4	3.42	8.5			3.43	4.1				
2.81	1.5			2.83	2.5			2.84	1.3	2.82	0.9			2.86	3.0			2.86	1.3				
2.10	0.7			1.95	0.6			2.13	0.4	2.12	0.5			2.13	0.8			2.13	0.3				
1.87	0.3							1.92	0.3	1.87	0.1			1.93	0.9			1.91	0.3				
1.68	0.3																						

Brašany												Chambers											
Ca-form, EG		K-form		K-form, EG		NH ₄ -form		NH ₄ -form, EG		Ca-form, EG		K-form		K-form, EG		NH ₄ -form		NH ₄ -form, EG					
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I				
16.95	100.0	11.51	100.0	16.63	100.0	11.91	100.0	17.14	100.0	17.48	100.0	12.31	100.0	14.84	100.0	12.49	100.0	16.14	100.0				
8.82	4.9	5.03	5.7	9.19	6.9	5.74	3.2	8.53	3.9	8.48	1.9	6.09	5.3	4.63	9.6	6.09	5.8	5.46	3.2				
5.66	4.4	3.26	31.4	5.49	7.7	3.20	18.1	5.59	1.9	5.59	2.4	5.05	2.9	3.42	15.1	3.09	6.7	4.54	1.9				
4.38	4.7	2.59	1.1	4.43	8.8	2.63	1.3	4.22	2.8	4.22	2.4	3.20	15.9	2.79	3.5	2.05	0.6	3.43	6.4				
3.42	14.9	2.01	2.0	3.39	40.4	8.06	1.3	3.37	8.4	3.35	4.2	2.07	2.1	1.98	2.4			2.82	1.9				
2.85	4.5			2.88	8.5	1.90	0.3	2.84	1.9	2.79	1.1							2.06	0.4				
2.12	0.4									2.54	0.8												
1.89	0.2									2.09	0.3												
										1.86	0.1												

Belle Fourche												Jeřšovský Potok											
Ca-form, EG		K-form		K-form, EG		NH ₄ -form		NH ₄ -form, EG		Ca-form, EG		K-form		K-form, EG		NH ₄ -form		NH ₄ -form, EG					
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I				
16.63	100.0	11.51	100.0	16.75	100.0	11.72	100.0	16.95	100.0	16.82	100.0	11.66	100.0	16.69	100.0	11.69	100.0	16.32	100.0				
8.40	2.8	4.97	11.0	8.77	5.4	5.59	10.0	8.65	3.2	8.45	2.7	4.98	7.6	9.09	3.6	5.66	7.1	8.65	1.0				
5.59	2.4	3.23	21.7	5.64	4.4	3.20	12.5	5.70	2.7	5.61	2.6	3.23	16.9	5.52	6.0	3.19	9.8	5.64	3.1				
4.24	0.8	2.00	2.2	4.36	2.1	2.63	0.8	4.30	1.9	4.20	1.3	2.63	0.8	4.61	4.8	2.03	0.9	4.47	2.4				
3.37	3.5			3.41	7.7	2.04	1.2	3.43	6.2	3.36	4.6	2.01	1.6	3.39	16.3			3.42	7.0				
2.81	1.0			2.86	2.5			2.86	2.3	2.80	1.0			2.84	4.0			2.83	2.0				
2.11	0.3			2.12	0.7			2.14	0.3	2.10	0.02			2.38	0.1			2.11	0.4				
1.87	0.1			1.92	0.8			1.91	0.1	1.87	0.01			1.95	1.8			1.98	0.3				

Table 2. Continued.

Manitow											
Ca-form, EG			K-form, EG			NH ₄ -form, EG			Ca-form, EG		
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
16.66	100.0	13.10	100.0	11.80	100.0	15.79	100.0	17.76	100.0	11.98	100.0
8.32	3.7	3.37	22.4	4.61	2.7	5.16	1.2	8.56	18.7	6.09	6.3
5.52	0.8	2.71	3.4	3.45	23.0	3.25	15.0	5.69	36.2	4.97	10.2
3.34	4.3	2.01	1.4	2.80	4.8	2.62	0.5	4.25	47.6	3.22	27.8
2.79	0.9			2.01	1.4	2.06	1.2	3.38	4.6	2.03	5.0
2.17	0.2							2.82	14.9		
								2.41	0.3		
								2.11	4.3		
								1.88	2.4		
								1.69	0.3		
								1.53	0.6		
								1.40	0.6		

Pyževskij											
Ca-form, EG			K-form, EG			NH ₄ -form, EG			Ca-form, EG		
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
16.69	100.0	11.60	100.0	11.82	100.0	16.75	100.0	17.48	100.0	12.35	100.0
8.45	4.4	5.03	9.2	9.09	10.9	5.75	7.5	8.48	2.3	6.09	6.5
5.55	3.6	3.24	25.3	5.26	8.9	3.19	17.4	5.64	3.7	5.11	2.0
4.22	5.4	2.01	2.4	4.71	15.3	2.63	0.9	4.43	3.4	3.18	17.0
3.35	10.0			3.38	46.0	2.05	1.1	3.42	10.8	2.07	2.0
2.80	2.1			2.88	13.0	1.89	0.1	2.85	2.4	2.81	1.3
2.51	0.3			2.10	2.8			2.10	0.5	2.42	0.3
2.1	0.4			1.98	4.0			2.10	0.6	2.09	0.3
1.87	0.2							1.87	0.3		

Zajčanskij											
Ca-form, EG			K-form, EG			NH ₄ -form, EG			Ca-form, EG		
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
15.79	100.0	12.37	100.0	14.18	100.0	12.22	100.0	16.56	100.0	12.18	100.0
8.22	0.9	5.89	1.3	4.57	1.6	5.99	1.8	9.17	3.8	6.05	2.1
5.33	0.7	3.22	13.0	3.46	15.3	3.20	12.5	5.51	0.8	5.08	2.6
4.08	0.3	2.61	1.0	2.79	3.1	2.61	0.5	3.44	6.6	3.19	14.5
3.25	4.8	2.08	1.2	2.00	1.0	2.07	0.9	2.84	1.2	2.04	2.0
								2.81	1.1		
								2.39	0.1		
								2.11	0.4		
								1.87	0.2		
								1.69	0.1		
								1.53	0.1		

Table 3. Probability coefficients of mixed-layer structures of K- and NH₄-smectites calculated from X-ray powder diffraction data listed in Table 2.

Complexes with water												
1. Askangel		2. Borša		3. Braňany		4. Chambers		5. Belle Fourche		6. Jeřšový Potok		
K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	
pA	0.39	0.02	0.41	0.06	0.50	0.34	0.33	0.03	0.64	0.41	0.54	0.40
pB	0.56	0.98	0.35	0.94	0.27	0.49	0.52	0.94	0.20	0.44	0.26	0.60
pD	0.05		0.24		0.23	0.17	0.15	0.03	0.16	0.15	0.20	
pAA	0.40	1.00	0.10	0.06	0.45		0.10	0.20	0.60		0.46	0.10
pAB	0.50		0.35	0.94	0.25	0.70	0.50	0.80	0.20	0.70	0.30	0.90
pAD	0.10		0.55		0.30	0.30	0.40		0.20	0.30	0.24	
pBA	0.40		0.50	0.06	0.40	0.56	0.40		0.50	0.70	0.60	0.60
pBB	0.58	1.00	0.46	0.94	0.44	0.30	0.57	0.97	0.38	0.21	0.36	0.40
pBD	0.02		0.04		0.16	0.14	0.03	0.03	0.12	0.09	0.04	
pDA	0.20		0.81		0.69	0.41	0.59	0.80	0.92	0.63	0.68	
pDB	0.80		0.19		0.11	0.59	0.41	0.20	0.03	0.37	0.02	
pDD					0.20				0.05		0.30	
7. Manito		8. Michajlov		9. Polkville		10. Pyževskij		11. Sampor		12. Zajsanskij		
K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	
pA	0.33	0.42	0.46	0.02	0.56	0.35	0.27	0.16	0.32	0.25	0.35	
pB	0.41	0.38	0.30	0.98	0.23	0.51	0.59	0.68	0.50	0.75	0.48	0.90
pD	0.26	0.20	0.24		0.21	0.14	0.14	0.16	0.18		0.17	0.10
pAA	0.10	0.20	0.20	0.02	0.45			0.20	0.30			
pAB	0.65	0.65	0.40	0.98	0.30	0.90	0.50	0.80	0.50	1.00	0.65	
pAD	0.25	0.15	0.40		0.25	0.10	0.50		0.20		0.35	
pBA	0.40	0.60	0.50	0.02	0.60	0.55	0.40		0.40	0.33	0.40	
pBB	0.17	0.25	0.31	0.98	0.28	0.27	0.59	0.79	0.37	0.67	0.50	1.00
pBD	0.43	0.15	0.19		0.12	0.18	0.01	0.21	0.23		0.10	
pDA	0.51	0.54	0.91		0.80	0.50	0.24	0.80	0.13		0.93	
pDB	0.49	0.06	0.09		0.40	0.40	0.76	0.10	0.87		0.07	
pDD		0.40			0.20	0.10		0.10				1.00
Complexes with ethylene glycol												
1. Askangel		2. Borša		3. Braňany		4. Chambers		5. Belle Fourche		6. Jeřšový Potok		
K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	
pA		0.07	0.20	0.12	0.30	0.16		0.06	0.14		0.26	0.09
pC	0.36				0.10		0.75	0.33			0.12	0.16
pE	0.64	0.93	0.80	0.88	0.60	0.84	0.25	0.61	0.86	1.00	0.62	0.75
pAA		0.20	0.10	0.20	0.30			0.20			0.30	
pAC								0.20			0.10	0.05
pAE		0.80	0.90	0.80	0.70	1.00		0.60	1.00		0.60	0.95
pCA					0.10						0.30	
pCC	0.40				0.10		0.70	0.37			0.45	0.60
pCE	0.60				0.80		0.30	0.63			0.25	0.40
pEA		0.06	0.23	0.11	0.39	0.19		0.08	0.16		0.23	0.12
pEC	0.34				0.01		0.90	0.32			0.07	0.08
pEE	0.66	0.94	0.77	0.89	0.60	0.81	0.10	0.60	0.84	1.00	0.70	0.80
pAA												
7. Manito		8. Michajlov		9. Polkville		10. Pyževskij		11. Sampor		12. Zajsanskij		
K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	K	NH ₄	
pA	0.21	0.14	0.35	0.02	0.39	0.09	0.05		0.15	0.30		
pC	0.16	0.69			0.18	0.11	0.17	0.25	0.70		0.60	0.05
pE	0.10	0.31	0.65	0.98	0.43	0.80	0.78	0.75	0.15	0.70	0.40	0.83
pAA			0.30	0.02	0.50				0.10	0.40		
pAC	0.60					0.05			0.60			
pAE	0.40		0.70	0.98	0.50	0.95	1.00		0.30	0.60		
pCA	0.20				0.20							
pCC	0.78				0.45	0.32	0.15	0.40	0.85		0.50	
pCE	0.02				0.35	0.68	0.85	0.60	0.15		0.50	
pEA	0.72		0.38	0.02	0.37	0.11	0.06		0.90	0.26		
pEC	0.28				0.23	0.09	0.19	0.20	0.10		0.75	
pEE			0.62	0.98	0.40	0.80	0.75	0.80		0.74	0.25	
pAA		0.25										0.12

pA, pB, etc. = probability coefficient of frequency of occurrence of layer A, B, etc. in sample.

pAA, pBB, etc. = coefficient of probability that layer A succeeds to layer A, layer B succeeds to layer B, etc.

lonites saturated with EG. Layer AA was found only in two samples of NH₄-montmorillonites (specimens 7 and 12). When saturated with potassium, layer AA was absent.

Kinter and Diamond (1958) thought that some montmorillonites formed the layer C complex, and in papers on mixed-layer structures of K-montmorillonites, such a layer was identified by Tettenhorst and Johns (1966). The orientation of the ethylene glycol molecules is not known, but it is probably identical with that of the vermiculite complex with one layer of EG. Here the symmetry plane of the molecule is perpendicular to the basal plane and parallel to the axis of the unit cell (Bradley *et al.*, 1963).

Layer C is common in the investigated samples. It was identified in nine samples of K-montmorillonites and in six samples of NH₄-montmorillonites solvated with EG. In some samples, layer C formed 60–70% of all layers present. This layer usually has not been identified in interstratified structures.

Relations between individual types of layers

The proportion of layers A, B, and D in the interstratified structures containing interlayer water molecules depends on the relative humidity of the environment. Unfortunately the XRD patterns were obtained at a relative humidity between 0.45 and 0.6; consequently only qualitative estimates can be made.

Apart from the sample 7, the proportion of 10-Å layers in K-montmorillonites is greater than in the NH₄-montmorillonites. The NH₄-smectites show a greater content of B layers which have one layer of interlayer water molecules. Samples 1, 2, 4, 8, and 12 contain as much as 90% B layers, and they nearly lose their character of interstratified structures.

A greater dehydration of the interlayer observed in K-smectites is caused by the lower hydration energy of K⁺ when compared with that of NH₄⁺. Naturally, with the same charge distribution on the structure of the smectite under consideration, K⁺ causes a greater dehydration of the interlayer (and consequently its collapse to 10 Å) than NH₄⁺.

Structures of monoionic K- and NH₄-smectites saturated with EG are more expanded than identical structures saturated with water. This is evidently caused by the fact that the dipole moment of EG ($\mu_{EG} = 2.28$ D) is greater than that of water ($\mu_W = 1.84$ D). Some of the 10-Å layers, which did not expand when the interlayer was saturated with water vapor, expanded after the interlayer was saturated with EG. This phenomenon indicates heterogeneity of the charge distribution on the layers of the structure.

Type of interstratification

Interpretation of interstratification in K- and NH₄-smectites is limited by the small number of basal re-

fections obtained with XRD analysis. Coefficients pA, pB, pC, pD, and pE, listed in Table 3, can be considered as good approximations of the actual proportions of individual kinds of layers in samples since the number of experimental data exceeds that of calculated parameters (twofold to fourfold in EG-saturated samples). This does not apply to parameters pAA, pBB, etc., which are also included in Table 3. Their values, especially for water-saturated samples, are informative only. Since both groups of coefficients (pA, pB, etc. and pAA, pAB, etc.) are needed for the determination of the type of interstratification, a certain caution is indicated in accepting such conclusions. Further it is necessary to remember that the deviations $\Delta p_{i,j}$ of the probability coefficients $p_{i,j}$ from the value which they would have at random mixing of layers indicate a tendency towards a regular arrangement or zonality of the structure only when the product $|p_i \cdot p_{i,j}| \geq 0.05$, which is probably the accuracy of the Fourier transform. Determination of the type of interstratification can be demonstrated on sample 6 (K-montmorillonite, EG-saturated). For random interstratification, $pA = pAA = pCA = pEA = 0.26$. In addition, $pC = pAC = pCC = pEC = 0.12$, and $pE = pAE = pCE = pEE = 0.62$. Comparing these values with those in Table 3 one finds that pCE values show the greatest discrepancy between the found and the expected value, 0.25 and 0.62, respectively. If the difference $\Delta pCE = 0.25 - 0.62 = -0.37$ is calculated and inserted into the relation $|p_i \cdot p_{i,j}| \geq 0.05$, the result $|-0.044| \geq 0.05$, which is not true. For this reason sample 6 is considered to be a randomly interstratified mineral. Hence, there appears to be a prevailing random distribution of layers in the structure, which, in some samples, shows a slight tendency to order. This tendency is especially prevalent in complexes with water. However, it is sometimes difficult to decide whether a sample formed by three kinds of layers represents a zonal or ordered mixed layering. Thus; for example, sample 2, a K-montmorillonite, favors the formation of the layers AD, which further leads to the zonality of layers B (Table 3). Thus, it is not possible to decide to which class this sample belongs.

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Резюме—Моноионные K- и NH_4^+ -сметиты, насыщенные этиленовым гликолем образуют структуры смешанных слоев, которые обычно состоят из трех типов: 10-Å, нерасширенный слой; 14-Å, частично расширенный слой; и 16,8-Å, полностью расширенный слой. В некоторых образцах 14-Å слой составляли 60–70% от всех слоев. Сметиты, насыщенные водяным паром обычно состояли из трех типов слоев (10-, 12,6-, и 15,5-Å). В основном эти образцы содержали меньше расширенных слоев, чем образцы, насыщенные этиленовым гликолем. Этот результат относится к меньшему дипольному моменту воды по сравнению с этиленовым гликолем. Большая энергия сольватации для NH_4^+ , чем для K^+ вызывает расширение части слоев, которые не расширяются в K-формах. Этот результат указывает, что имеется неомогенное распределение слойного заряда в структуре сметита. Преобладающим типом смешанных слоев в изученных образцах является беспорядочное распределение слоев. [E.C.]

Resümee—Mono-ionische, mit Ethylenglycol-gesättigte K- und NH_4^+ -Smektite bilden Wechsellagerungsstrukturen, die gewöhnlich aus drei Schichtarten bestehen: Eine nicht expandierte 10 Å-Schicht, eine teilweise expandierte 14 Å-Schicht und eine vollständig expandierte 16,8 Å-Schicht. In einigen Proben machten die 14 Å-Schichten 60–70% aller vorhandenen Schichten aus. Bei Wasserdampfsättigung bestanden die Smektite aus drei Schichtarten (10, 12,6, und 15,5 Å). Im allgemeinen enthielten diese Proben weniger expandierte Lagen als die Ethylenglycol-gesättigten Proben. Dieses Ergebnis wird auf das im Vergleich zu Ethylenglycol kleinere Dipolmoment des Wassers zurückgeführt. Die größere Solvationsenergie von NH_4^+ verglichen mit der von K^+ verursacht die Expansion eines Teils der Schichten, die in den K-Formen nicht expandierten. Dieses Ergebnis deutet darauf hin, daß in der Smektitstruktur eine inhomogene Verteilung der Schichtladung vorhanden ist. Der vorherrschende Typ von Wechsellagerung in den untersuchten Proben ist der mit einer statistischen Verteilung der Schichten. [U.W.]

Résumé—Des smectites monoioniques-K et $-NH_4^+$ saturées de glycol éthylène forment des structures à couches mélangées qui consistent généralement de trois sortes de couches: une couche 10-Å non-enflée, une couche 14-Å partiellement enflée, et une couche 16-Å entièrement enflée. Dans certains échantillons, les couches 14-Å formaient de 60 à 70% de toutes les couches présentes. Lorsqu'elles étaient saturées de vapeur d'eau, les smectites consistaient habituellement de trois sortes de couches (10-Å, 12,6-Å, et 15,5-Å). Ces échantillons contenaient généralement moins de couches enflées que ceux saturés de glycol éthylène. Ce résultat est attribué au plus petit moment dipôle de l'eau comparé à celui du glycol éthylène. L'énergie plus grande de solvation de NH_4^+ en comparaison avec celle de K^+ cause l'expansion d'une partie des couches qui ne s'était pas enflée dans les formes K. Ce résultat indique qu'il y a une distribution non-homogène de charge de couche dans la structure d'une smectite. Le type prévalent de mélange de couches dans les échantillons étudiés est celui de la distribution de couches au hasard. [D.J.]