

Determination of the content and distribution of fixed ammonium in illite-smectite by X-ray diffraction: Application to North Sea illite-smectite

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ABSTRACT

A new X-ray diffraction method for the determination of the amount and distribution of fixed NH_4^+ in illite-smectite has been developed. Illite-smectite was saturated with K^+ and heated at 150 °C. The 002 and 005 reflections were recorded with steps of $0.01^\circ 2\theta$, and the experimental d values and the values for full-width at half-height (FWHH) were determined using a peak-profile-fitting procedure. Peak profiles were calculated with the NEWMOD program for illite structures having different amounts of NH_4^+ and different patterns for the distribution of NH_4^+ in interlayers. For Upper Jurassic illite-smectite from North Sea oil source rocks, the amount and the distribution of NH_4^+ in illite interlayers were determined by comparing the experimental values for d_{005} and FWHH with the values calculated for the selected illite structures. The amounts of NH_4^+ determined in this manner correlate well with the amounts determined by an isotopic dilution method. The results demonstrate that these illite-smectite samples have K end-member illite and NH_4 end-member illite (tobelite) layers and that the illite layers formed during diagenesis and oil generation actually are tobelite layers.

INTRODUCTION

Smectite illitization is accompanied by formation of mixed-layer illite-smectite (I-S) or illite-smectite-vermiculite (I-S-V) having different interstratified interlayer types. In oil source rocks, diagenetic alterations of I-S and I-S-V often take place simultaneously with oil generation. For example, in the Upper Jurassic oil source rocks in the North Sea, the increase in the number of illite layers and the ordering of I-S take place simultaneously with oil generation (Hansen and Lindgreen 1989). In this Upper Jurassic shale, illitization is the transformation of single smectite interlayers to illite interlayers in I-S-V (Drits et al. 1997) through tetrahedral substitution of Al for Si and subsequent fixation of K^+ and NH_4^+ (Lindgreen et al. 1991; Lindgreen 1991).

Generally, the fixed cation in illite interlayers in I-S is assumed to be K^+ . However, Stevenson (1960) found a significant amount of fixed NH_4^+ (0.2–0.5% N) in clay minerals from Paleozoic shale and suggested that during smectite illitization NH_3 , released from the decomposition of organic matter can be fixed in illite interlayers as NH_4^+ . According to Stevenson (1960), the presence of fixed NH_4^+ in clay-mineral structures may be considered as evidence of oil generation. Cooper and Abedin (1981) found that the amount of fixed NH_4^+ in Tertiary Gulf Coast shales increased with depth and eventually constituted 7% of the fixed interlayer cations in clay fractions. Williams et al. (1989, 1992) investigated NH_4^+ -bearing sandstones and mudstones from Gulf Coast Tertiary sediments and concluded that NH_4^+ , released during oil gen-

eration from organic matter, migrated with oil through sandstones to become incorporated into clay-mineral structures.

Recently, Lindgreen (1994), using an isotopic dilution method, studied NH_4^+ -bearing I-S formed during diagenesis in Upper Jurassic shales that are the main source rocks for oil in the North Sea. Lindgreen (1994) found that with increasing depth of sample, the ratio NH_4^+/K^+ for soluble cations in the pore fluids of core samples increased as did the same ratio for fixed cations in interlayers of the I-S structures. Lindgreen concluded that NH_4^+ fixation may be a general process during burial diagenesis in oil source rocks.

The presence of NH_4^+ in mineral structures cannot be detected by most microprobes, which usually determine elements atomic number 11 and higher. Nor can NH_4^+ be detected by atomic absorption spectrometry, another method commonly applied in elemental analysis of rocks. IR spectroscopy is a very useful technique for detection of NH_4^+ (Vedder 1965) but is difficult to use for quantitative determination of NH_4^+ (Sterne et al. 1982). The isotopic dilution method requires a very small amount (~5 mg) of sample and is highly accurate (Middelboe 1977; Middelboe and Johansen 1991), but the procedure requires special equipment. Because of these analytical difficulties, fixed NH_4^+ in I-S is often not detected.

Fixed NH_4^+ in illite interlayers of I-S should modify the structure and the diffraction patterns of these minerals. Thus, natural and synthetic NH_4^+ -bearing dioctahedral micas are different from pure K end-member illite and mus-

covite, especially with respect to the unit-cell parameters and the distribution of basal reflection intensities (Vedder 1965; Sterne et al. 1982; Juster et al. 1987; Daniels and Altaner 1990, 1993). However, until now X-ray diffraction (XRD) has not been used for the determination of fixed NH_4^+ in NH_4^+ -bearing I-S.

In this work we describe an XRD technique for the determination of the amount of fixed NH_4^+ in I-S samples and for the determination of the distribution of K^+ and NH_4^+ among the illite layers. Furthermore, the distribution of fixed NH_4^+ in the structure of I-S-V from North Sea oil source rocks is discussed.

DIFFRACTION CRITERIA

A main problem in the determination of fixed NH_4^+ in I-S samples by XRD is that these minerals have no strict period along the c^* direction. Accordingly, the positions, widths, and profiles of the basal reflections are influenced by the nature, number, proportion, and distribution of layer types in the mixed-layer structures. However, K^+ saturation of the I-S and subsequent heating at 150 °C for 1 h result in identical or at least very similar layer periods along c^* . After this treatment, K^+ -saturated smectite layers collapse to 9.98 Å in comparison with 9.60 Å for Na^+ - or Ca^{2+} -saturated smectite layers. Accordingly, if the illite interlayers contain only K^+ , then the basal reflections of K^+ -saturated and heated I-S samples should form a rational series with $d_{001} = 9.98$ Å. The rationality of this series may be destroyed if the I-S samples consist of very thin coherent scattering domains (CSDs), which, however, mainly influences the 001 and 002 peak positions. After correction for the angular reflection broadening that results from crystal-size effects, all 00 l reflections of the K^+ -saturated and heated I-S should have practically the same full-width at half-height (FWHH) values because the profile of the 00 l interference function does not depend on l . Corrected FWHH(00 l) values were obtained by multiplication of the experimentally measured FWHH(00 l) by $\cos \theta$, where θ is the Bragg angle of the corresponding 00 l reflection. The efficiency of this procedure for increasing structural ordering of I-S was demonstrated by Drits et al. (1995, 1996).

If illite interlayers contain some NH_4^+ in addition to K^+ , then the basal reflections of K^+ -saturated and heated I-S samples should shift to smaller θ angles, and the corresponding d_{001} values should increase because of the different ionic radii of K^+ and NH_4^+ . According to Eugster and Munoz (1966), the thickness of NH_4^+ end-member muscovite layers determined from d_{005} is 10.33 Å. A successive increase in the amount of NH_4^+ in illite interlayers should be accompanied by an increase in the period along c^* . Moreover, Shigorova et al. (1981) and Juster et al. (1987) have found that for NH_4^+ -bearing synthetic muscovite there is a linear relationship between d_{001} and the content of NH_4^+ in muscovite interlayers.

NH_4^+ can be fixed in illite layers of I-S according to one of two patterns or a combination of the two patterns. In the first pattern, K^+ and NH_4^+ are distributed homo-

geneously, i.e., each illite interlayer contains equal amounts of K^+ and NH_4^+ . By analogy with the results of Shigorova et al. (1981), the d_{001} value for K^+ -saturated and heated I-S samples should then increase proportionally to the average content of NH_4^+ in illite interlayers. However, after correction for angular reflection broadening, the FWHH(00 l) value should be the same for different l .

The second pattern of NH_4^+ and K^+ distribution is represented by I-S structures in which each illite interlayer contains either K^+ or NH_4^+ . Accordingly, in these I-S structures smectite layers alternate with two illite-layer types, which differ in thickness and scattering power. The d_{001} value for K^+ -saturated and heated I-S should then increase with the proportion of tobelite interlayers, w_{NH_4} . For such interstratified structures it is characteristic that an increase in w_{NH_4} from 0 to 0.5 results in an increase in the ratios FWHH(005)/FWHH(002) and FWHH(005)/FWHH(003) because the angular interval of the basal reflection broadening depends on both w_{NH_4} and l . For example, for pure K end-member illite the angular positions of the 002 and 005 reflections are equal to $2\theta_{002\text{K}} = 20.66^\circ$ and $2\theta_{005\text{K}} = 53.29^\circ$, respectively, and for pure tobelite, to $2\theta_{002\text{NH}_4} = 19.96^\circ$ and $2\theta_{005\text{NH}_4} = 51.35^\circ$, respectively (CoK α radiation, $\lambda = 1.7903$ Å). Accordingly, the maximum angular intervals at which 9.98 and 10.33 Å layers may contribute to the intensities of 002 and 005 are confined by $\Delta 2\theta_{002} = 2\theta_{002\text{K}} - 2\theta_{002\text{NH}_4} = 0.70^\circ$ and $\Delta 2\theta_{005} = 2\theta_{005\text{K}} - 2\theta_{005\text{NH}_4} = 1.94^\circ$, respectively. Thus, for a given w_{NH_4} , 005 should be wider than 002. The maximum reflection width and the maximum value for FWHH(005)/FWHH(002) will be obtained for $w_{\text{NH}_4} = 0.50$, where 9.98 and 10.33 Å layers equally contribute to the total reflection intensity. A decrease in the amount of one layer type increases the contribution to the reflection intensity from layers of the other type. Therefore, an increase in w_{NH_4} from 0.5 to 1.0 results in a decrease in the 00 l reflection widths and in FWHH(005)/FWHH(002). When $w_{\text{NH}_4} = 0$ or 1.0, the basal reflection widths corrected by the $\cos \theta$ factor should be the same for the two patterns of NH_4^+ distribution.

The aim of this paper is to apply the structural and diffraction criteria mentioned above to the determination of the amount and distribution of NH_4^+ in NH_4^+ -bearing I-S-V samples.

MATERIALS AND METHODS

Samples

The Upper Jurassic shale samples investigated from Danish and Norwegian wells are core and cutting materials from the Mandal, Farsund, and Haugesund Formations in the Central Trough and from the Børglum, Sauda, and Tau Formations in the Norwegian-Danish Basin (Hansen and Lindgreen 1989). The proportion of illite interlayers and the amounts of fixed K^+ and NH_4^+ in the samples, as given by Lindgreen (1994) and Drits et al. (1997), are shown in Table 1. The samples were pretreat-

TABLE 1. Amount of nonexpandable layers and fixed interlayer NH₄⁺ in Upper Jurassic I-S-V

Sample	Well, depth (m)	w _f *	NH ₄ **	NH ₄ †
North Sea Central Trough shales				
x1	E. Rosa, 1520	0.85	0.03	0.02
112	E1, 2984	0.69	0.06	n.d.
82	U1, 2899	0.73	0.08	0.01
x3	S.E. Igor, 2502	0.80	0.06	0.09
x17	Jeppe 1, 4418	0.87	0.10	0.09
87	2/11-1, 4548	0.80	n.d.	0.14
89	2/7-3, 3789	0.84	0.22	0.17
86	2/11-1, 3877	0.85	0.20	0.19
x18	Elin 1, 4418	0.90	0.19	0.19
x12	Iris 1, 3966	0.85	0.20	0.20
x13	Iris 1, 4168	0.85	0.21	0.21
Danish Sub-basin shales				
99	Frederikshavn, 649	0.70	n.d.	0.05
95	Haldager, 1049	0.70	n.d.	0.05

Note: n.d. = not determined.

* Fraction of nonexpandable layers (Lindgreen et al. 1991; Drits et al. 1997).

** Moles of NH₄⁺ per O₁₀(OH)₂ determined by the isotopic dilution method (Lindgreen 1994).

† Moles of NH₄⁺ per O₁₀(OH)₂ determined by XRD.

ed with NaOCl for removal of organic matter (Anderson 1963). This treatment may, however, remove up to 15% of the NH₄⁺ (Daniels 1989). Furthermore, iron and aluminum oxides have been removed (Mehra and Jackson 1958) and a fine clay fraction isolated by centrifugation (Hansen and Lindgreen 1989). The particles of this fraction are, according to atomic force microscopy, predominantly <500 Å in diameter and <100 Å thick. This fraction is dominated by mixed-layer I-S-V and also contains kaolinite.

XRD measurements

Diffraction patterns of K⁺-saturated I-S samples heated at 150 and 300 °C were recorded on a Philips PW 1050 diffractometer using CoKα radiation and a thin iron filter. For whole XRD patterns, 0.25° fixed divergence and antiscatter slits were used, and intensities were measured for 100 s with 0.1° 2θ steps and two iron filters. For individual basal reflections, intensities were measured for 10 s per 0.01° 2θ with a thin iron filter for the 005 reflection and for 4 s per 0.01° 2θ with two iron filters for the 003 and 002 reflections. A linear background was subtracted and FWHH(00l) determined using a digital step-scanning procedure. Corrected values for FWHH were obtained by multiplication with cos θ. Graphite and quartz were used as standards. The *d* values for basal reflections were determined by fitting the reflection profile with the use of the technique described by Salyn (1988) and Drits et al. (1993). Errors in the *d* values do not exceed 0.005 and 0.001 Å for the 002 and the 005 reflections, respectively.

Structural models for XRD simulations

The NEWMOD program of Reynolds (Reynolds 1985; Bethke and Reynolds 1986) was used to calculate the

profiles of the individual basal reflections of two groups of structural models, the two patterns described above. The first group of models represents illite structures that are strictly periodic along the *c** direction. These models vary in layer thickness, *d*₀₀₁, and interlayer composition. It was assumed that

$$d_{001} = 10.33 C_{\text{NH}_4} + 9.98 (1 - C_{\text{NH}_4}) \\ = 9.98 + 0.35 C_{\text{NH}_4}$$

or

$$C_{\text{NH}_4} = 2.857 d_{001} - 28.51 \quad (1)$$

where *C*_{NH₄} is the amount of NH₄⁺ cations in the interlayer per O₁₀(OH)₂. The thicknesses of the NH₄⁺ and K⁺ end-member illite layers are 10.33 and 9.98 Å, respectively. For these calculations, *C*_{NH₄} was varied from 0 to 1.0 with increments of 0.1.

The second group of models represents interstratified structures in which 9.98 Å K end-member illite and 10.33 Å tobelite layers alternate at random. The profiles were calculated for fractions of the tobelite layers from 0.0 to 1.0 with intervals of 0.1. It was assumed that the 2:1 layers of both layer types are Fe free and of the same composition. It was also assumed that the interlayers of 9.98 and 10.33 Å layers have 0.75 K⁺ and 0.75 NH₄⁺ per O₁₀(OH)₂, respectively. In addition, XRD patterns were calculated for models having different amounts of the interlayer cations in the interstratified layer types and, in particular, for amounts of K⁺ and NH₄⁺ in the range of 0.5–1.0 atoms per O₁₀(OH)₂.

It was assumed that the maxima of the scattering amplitudes for K⁺ and NH₄⁺ are 18 and 10 electron units, respectively, and that the mean thickness of CSDs is six layers, a value previously determined for the North Sea I-S-V samples. For the second group of models, each XRD pattern was calculated as the sum of two patterns: one pattern for CoKα₁ and the second for CoKα₂, in the proportion 0.67:0.33. The intensities of the basal reflections for each model were calculated for steps of 0.010 2θ, and the peak positions were determined as the positions at maximum intensity. Errors in the determination of *d*₀₀₁ values do not exceed 0.002 and 0.0005 Å for the 002 and 005 reflections, respectively. The FWHH(00l) values were corrected for angular reflection broadening by multiplication with the corresponding cos θ.

RESULTS

Analysis of the simulated XRD patterns

For NH₄⁺-bearing illite models with identical contents of NH₄⁺ and K⁺ in each interlayer, the periodic structures, the calculated values for *d*₀₀₁, and the FWHH(00l) values for the 002, 003, and 005 basal reflections are given in Table 2. This table does not contain data for the 001 and 004 reflections because 001 is very sensitive to the thickness of CSDs and 004 has a very low intensity. As expected, *d*₀₀₁ values increase with increasing amounts of NH₄⁺. Note that only the *d*₀₀₁ value calculated from *d*₀₀₅ is equal to the actual layer periodicity along the *c** axis

TABLE 2. Calculated values for d_{00l} and FWHH(00 l) for illite structures periodic along c^* and having the same K⁺/NH₄⁺ ratio in each interlayer

Actual period d_{001} (Å)	$C_{\text{NH}_4^+}$ *	d_{002} (Å)	$d_{001} = 2d_{002}$ (Å)	d_{003} (Å)	$d_{001} = 3d_{003}$ (Å)	d_{005} (Å)	$d_{001} = 5d_{005}$ (Å)	FWHH(005) (°θ)	FWHH(003) FWHH(002)	FWHH(005) FWHH(002)
9.98	0.00	5.009	10.017	3.327	9.981	1.9967	9.983	0.819	0.962	1.006
10.02	0.10	5.026	10.051	3.340	10.020	2.0047	10.024	0.805	0.958	0.987
10.05	0.20	5.040	10.080	3.350	10.049	2.0107	10.054	0.807	0.971	1.004
10.09	0.30	5.057	10.115	3.362	10.087	2.0185	10.093	0.801	0.969	0.990
10.12	0.40	5.072	10.114	3.372	10.115	2.0246	10.123	0.801	0.970	0.994
10.16	0.50	5.089	10.179	3.385	10.154	2.0321	10.161	0.798	0.955	0.990
10.19	0.60	5.107	10.213	3.396	10.187	2.0383	10.192	0.794	0.955	0.985
10.23	0.70	5.130	10.259	3.409	10.226	2.0460	10.230	0.793	0.950	0.990
10.26	0.80	5.145	10.289	3.420	10.259	2.0522	10.261	0.789	0.954	0.989
10.30	0.90	5.160	10.320	3.432	10.295	2.0600	10.300	0.782	0.950	0.986
10.33	1.00	5.175	10.351	3.442	10.325	2.0664	10.332	0.778	0.939	0.989

* Proportion of NH₄⁺ in each interlayer.

(Table 2). According to Equation 2, which was obtained by regression analysis, the amount of NH₄⁺, $C_{\text{NH}_4^+}$, increases linearly with the d_{001} values calculated from the 005 reflection positions:

$$C_{\text{NH}_4^+} = 2.884 d_{001} - 28.80. \quad (2)$$

This equation is almost identical to Equation 1. Note that after correction for the angular reflection broadening the ratio FWHH(005)/FWHH(002) is equal to 0.992 ± 0.014 , independent of $C_{\text{NH}_4^+}$ (Table 2).

The values for d_{00l} and FWHH(00 l) ($l = 2, 3$, and 5) calculated for the interstratified structure models are shown in Table 3. As in the case of the periodic structures, for each given l the value for d_{00l} increases as the amount of NH₄⁺-bearing interlayers increases (Fig. 1). Three features are noteworthy. First, $w_{\text{NH}_4^+}$ depends almost linearly on d_{001} in spite of the different thicknesses and scattering powers of the interstratified layer types. A regression describing this relationship for the 005 reflection is as follows:

$$\begin{aligned} w_{\text{NH}_4^+} &= 13.93 d_{005} - 27.79 \\ &= 2.786 d_{001} - 27.79. \end{aligned} \quad (3)$$

This equation is similar to Equation 2 for NH₄⁺-bearing illite models with identical contents of NH₄⁺ and K⁺ in

each interlayer. Second, the calculations have shown that the values for d_{001} and FWHH(00 l) depend only on the proportion of layer types, not on the cation occupancy of interlayers. Thus, for a fixed proportion of layer types the values for d_{001} and FWHH(00 l) do not change significantly for different amounts of K⁺ and NH₄⁺ in interlayers of 9.98 and 10.33 Å layers, respectively. Moreover, the basal reflection intensities change little with the content of NH₄⁺ in 10.33 Å layers because of the low scattering power of this cation. Third, for all models the basal reflections do not form a strict rational series because $5d_{005} \approx 3d_{003} < 2d_{002} < d_{001}$. This is mainly due to the small CSD thickness and to the different intensities of the 00 l reflections of pure K end-member illite and tobelite. For example, the intensity of the 002 reflection of pure K end-member illite is smaller than that of tobelite. Therefore, the contribution from the 10.33 Å layers to the 002 reflection should be larger than that from the 9.98 Å layers, and this effect results in an additional shift of this reflection to a smaller θ angle. This effect is absent for the 005 reflection because the intensity of this reflection is quite similar for pure K end-member illite and tobelite. For the models of the interstratified structures, the correlation between $w_{\text{NH}_4^+}$ and FWHH(005)/FWHH(002) is remarkable.

TABLE 3. Calculated values for d_{00l} and FWHH(00 l) for mixed-layer structures

$w_{\text{NH}_4^+}$ *	d_{002} (Å)	$d_{001} = 2d_{002}$ (Å)	d_{003} (Å)	$d_{001} = 3d_{003}$ (Å)	d_{005} (Å)	$d_{001} = 5d_{005}$ (Å)	FWHH(002) (Å)	FWHH(005) (°θ)	FWHH(003) FWHH(002)	FWHH(005) FWHH(002)
0.00	5.009	10.017	3.327	9.980	1.9967	9.983	0.826	0.840	0.962	1.017
0.10	5.026	10.051	3.337	10.011	2.0026	10.013	0.846	0.975	0.999	1.153
0.20	5.040	10.080	3.350	10.049	2.0089	10.045	0.866	1.110	1.021	1.282
0.30	5.060	10.119	3.360	10.080	2.0160	10.080	0.885	1.206	1.027	1.363
0.40	5.077	10.154	3.373	10.119	2.0242	10.121	0.887	1.255	1.041	1.415
0.50	5.097	10.194	3.385	10.154	2.0318	10.159	0.885	1.266	1.042	1.430
0.60	5.112	10.224	3.397	10.190	2.0394	10.197	0.876	1.221	1.037	1.394
0.70	5.132	10.264	3.409	10.226	2.0471	10.236	0.863	1.159	1.023	1.343
0.80	5.145	10.289	3.420	10.259	2.0537	10.269	0.843	1.057	1.002	1.254
0.90	5.160	10.320	3.433	10.298	2.0600	10.300	0.820	0.935	0.976	1.140
1.00	5.175	10.351	3.442	10.325	2.0664	10.332	0.791	0.794	0.941	1.004

Note: Mixed-layer structures consist of 9.98 and 10.33 Å layers with K⁺ and NH₄⁺ interlayer cations, respectively.* Fraction of NH₄⁺ interlayers with $d_{001} = 10.33$ Å.

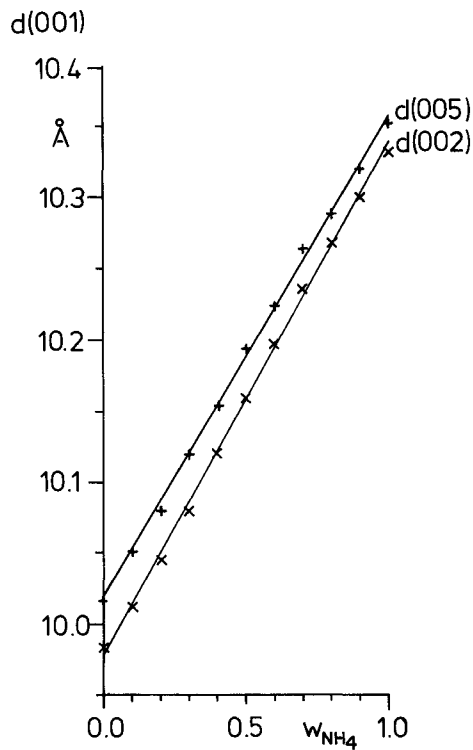


FIGURE 1. Values for d_{001} calculated from the d_{002} and d_{005} values determined for illite samples with different amounts of K (illite) $(1 - w_{\text{NH}_4})$ and NH_4 (tobelite) (w_{NH_4}) interlayers.

As expected, $\text{FWHH}(005)/\text{FWHH}(002)$ increases with increasing w_{NH_4} up to $w_{\text{NH}_4} = 0.5$ and decreases with $w_{\text{NH}_4} > 0.5$ (Fig. 2).

Analysis of the experimental XRD data

The results obtained from the XRD calculations were used to analyze the content and distribution of NH_4^+ in illite interlayers of NH_4^+ -bearing samples. XRD patterns obtained for samples 95, 82, 87, and 89, which were saturated with K^+ and heated at 150°C , are shown in Figure 3. Qualitatively, apart from different amounts of kaolinite, the XRD patterns are quite similar. They resemble the XRD pattern of illite and do not indicate the presence of structural NH_4^+ . However, a precise analysis of individual basal reflections recorded with steps of $0.01^\circ 2\theta$ provides essential data for investigating the amount and distribution of NH_4^+ . The values for d_{002} , d_{005} , $\text{FWHH}(002)$, and $\text{FWHH}(005)$ determined from the individual reflection profiles of samples saturated with K^+ and heated at 150°C are shown in Table 4, the value for $\text{FWHH}(00l)$ having been multiplied by the corresponding $\cos \theta$ value. Initially, the presence of NH_4^+ in illite interlayers expands the structure to a larger d_{001} , and the increase of d_{005} for the sequence of samples x1, 82, 99, 95, x3, x17, 87, 89, 86, x18, x12, x13 (Table 4) thus probably reflects an increase in the amount of NH_4^+ in illite interlayers. The amount of NH_4^+ was calculated from the values for d_{005}

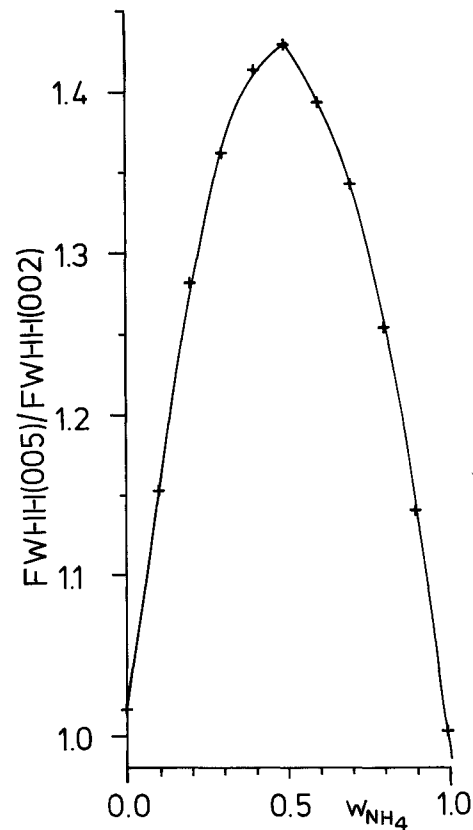


FIGURE 2. The ratio between peak widths, full-width at half-height (FWHH), for 005 and 002 reflections calculated for illite samples with different amounts of K (illite) $(1 - w_{\text{NH}_4})$ and NH_4 (tobelite) (w_{NH_4}) interlayers.

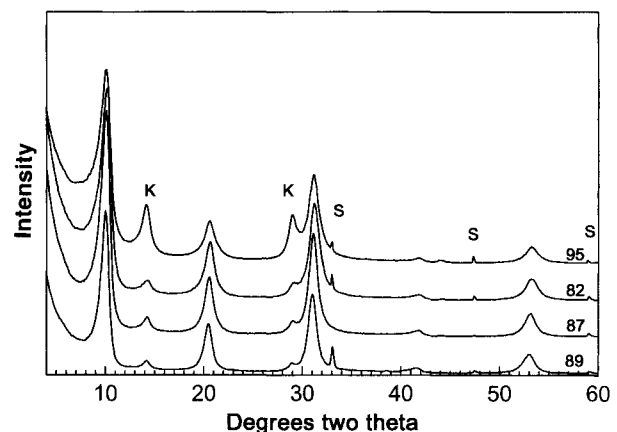


FIGURE 3. XRD patterns for samples 95, 82, 87, and 89. Specimens were oriented, K^+ -saturated, and heated at 150°C for 1 h. $\text{CoK}\alpha$ radiation. Values for d_{002} and d_{005} are given in Table 4. K = peak from kaolinite, S = peak from KCl.

TABLE 4. NH_4 content determined by XRD for the K^+ -saturated and heated (150 °C) I-S-V samples

Sample	d_{002} (Å)	$d_{001} = 2d_{002}$ (Å)	d_{005} (Å)	$d_{001} = 5d_{005}$ (Å)	$C_{\text{NH}_4}^*$	$w_{\text{NH}_4}^{**}$	FWHH(002) (°)	FWHH(005) (°)	$\frac{\text{FWHH}(005)}{\text{FWHH}(002)}$	$w_{\text{NH}_4}^\dagger$
x1	4.988	9.976	1.997	9.985	0.00	0.03	0.56	0.56	1.00	0.00
82	5.007	10.014	1.998	9.990	0.01	0.01	0.57	0.57	1.00	0.00
99	5.011	10.022	1.999	9.995	0.03	0.06	0.66	0.72	1.09	0.06
95	5.007	10.014	1.999	9.995	0.03	0.06	0.58	0.65	1.12	0.08
x3	5.003	10.006	2.002	10.010	0.07	0.10	0.55	0.61	1.11	0.08
x17	5.029	10.058	2.002	10.010	0.07	0.10	0.53	0.59	1.11	0.08
87	5.041	10.082	2.006	10.030	0.13	0.15	0.49	0.60	1.20	0.15
89	5.046	10.092	2.008	10.040	0.16	0.18	0.51	0.62	1.22	0.17
86	5.034	10.068	2.009	10.045	0.17	0.20	0.60	0.75	1.25	0.19
x18	5.039	10.078	2.009	10.045	0.17	0.20	0.48	0.54	1.125	0.09
x12	5.044	10.088	2.010	10.050	0.18	0.21	0.56	0.70	1.25	0.19
x13	5.061	10.122	2.011	10.055	0.20	0.22	0.57	0.71	1.25	0.19

* Amount of NH_4^+ [moles per $\text{O}_{10}(\text{OH})_2$] calculated from d_{005} using Eq. 2.** Amount of NH_4^+ calculated from d_{005} using Eq. 3.† Amount of NH_4^+ calculated from $\text{FWHH}(005)/\text{FWHH}(002)$ using Figure 2.

(Table 4) by two methods. First, Equation 2, corresponding to the linear Relationship 1 between $d_{001} = 5d_{005}$ and C_{NH_4} , was used to calculate the amounts of NH_4^+ (C_{NH_4}). Second, Equation 3 was used to determine the proportion of NH_4^+ -bearing illite interlayers (w_{NH_4}). The values obtained for C_{NH_4} and w_{NH_4} (Table 4) are practically identical for each sample. The mean values for C_{NH_4} and w_{NH_4} and the content of NH_4^+ determined by the isotopic dilution method are shown for each sample in Table 1. For each sample, the difference between the amounts of NH_4^+ determined by use of the two methods is equal on average to 0.02 NH_4^+ per $\text{O}_{10}(\text{OH})_2$, and the maximum deviation is 0.07 NH_4^+ for sample 82 (Table 1). The experimental values for $\text{FWHH}(005)/\text{FWHH}(002)$ are shown in Table 4. An increase in $\text{FWHH}(005)/\text{FWHH}(002)$ is accompanied by an increase in d_{005} and vice versa. The amount of NH_4^+ -bearing interlayers, w_{NH_4} , was determined (Table 4) using the relationship between $\text{FWHH}(005)/\text{FWHH}(002)$ and w_{NH_4} calculated for the mixed-layer structures consisting of 9.98 and 10.33 Å layers (Fig. 2).

It should be noted that the values for d_{005} determined for the samples saturated with K^+ and heated at 300 °C differ substantially from those obtained for the same samples heated at 150 °C (Table 5). IR spectroscopy on KBr pellets heated at various temperatures has demonstrated that the thermal release of NH_4 takes place only above 400 °C, so the different d_{005} values for the samples heated

at 300 °C must therefore be due to structural changes in the interlayers.

DISCUSSION

Interstratification of ammonium interlayers

For the dioctahedral mixed-layer 2:1 minerals having nonexpandable (mica-like) and expandable (smectite- and vermiculite-like) interlayers and containing a significant amount of NH_4^+ , the following three terms are used for the interstratified structures. I-S corresponds to interstratification of K-rich illite and smectite (or vermiculite) interlayers, respectively. NH_4^+ -bearing I-S corresponds to structures having a homogeneous cation composition in all mica interlayers, or to structures for which the distribution of K^+ and NH_4^+ has not been determined. Illite-tobelite-smectite, or I-T-S, corresponds to NH_4^+ -bearing structures in which three types of interlayers, K-rich illite, tobelite, and smectite (or vermiculite), alternate with some order-disorder.

The data obtained show that the K^+ -saturated and heated samples have a mixed-layer structure with 9.98 and 10.33 Å layers containing K^+ and NH_4^+ interlayer cations, respectively, interstratified in different proportions. It is remarkable that the C_{NH_4} and w_{NH_4} values determined using Equations 2 and 3, as well as the relationship between w_{NH_4} and $\text{FWHH}(005)/\text{FWHH}(002)$ (Fig. 2), are practically the same for each sample (Table 4). In fact, the functional relationships between C_{NH_4} and d_{001} and between w_{NH_4} and $\text{FWHH}(005)/\text{FWHH}(002)$ are independent. The d_{001} value depends on the average amount of fixed NH_4^+ in a structure but not on the distribution of K^+ and NH_4^+ . On the contrary, the value for $\text{FWHH}(00l)$ depends on the distribution of these cations among the available mica interlayers. Therefore, samples having equal amounts of K^+ and NH_4^+ and the same d_{001} values may have different 00l basal reflection widths. Coincidence within errors of the values for w_{NH_4} determined by Equation 3 and from Figure 2 is evidence of the interstratified nature of the NH_4^+ -bearing samples. Moreover, this coincidence shows that all the studied I-S samples,

TABLE 5. Values for d_{005} and $\text{FWHH}(005)$ determined for the K^+ -saturated I-S-V samples heated at 300 °C for 1 h

Sample	d_{005} (Å)	$d_{001} = 5d_{005}$ (Å)	FWHH(005) (°)
x1	1.992	9.960	0.57
82	1.997	9.985	0.56
x3	1.992	9.960	0.56
x17	2.000	10.00	0.59
89	2.004	10.02	0.63
x18	1.999	9.995	0.53
x12	1.998	9.990	0.68
x13	2.004	10.020	0.69

except for x18, consists of 9.98 and 10.33 Å layers because only this structure provides agreement between the values for w_{NH_4} determined from the values for d_{001} and FWHH(005)/FWHH(002), respectively. Lastly, all NH₄⁺ must be located only in 10.33 Å layers because only in this case is the C_{NH_4} value obtained from Equation 2 equal to the w_{NH_4} value determined from the reflection-width ratios.

Sample x18 has a very different pattern of distribution of NH₄⁺. For this sample, the amount of NH₄⁺ determined by Equations 2 (C_{NH_4}) and 3 (w_{NH_4}) is almost twice the value of w_{NH_4} determined from the basal reflection-width ratio (Table 4). The nonexpanding interlayers in this sample must have a mixed-layer structure, but K⁺-bearing layers are interstratified with layers having a mixed cation composition. Calculations of basal reflection profiles for the structural model with $d_{001} = 10.045$ Å and $C_{\text{NH}_4} = 0.19$ NH₄⁺ per O₁₀(OH)₂ (Table 4) show that the experimental value FWHH(005)/FWHH(002) = 1.125 corresponds to a mixed-layer structure in which 70% of 9.98 Å layers are interstratified with 30% of 10.19 Å layers. According to Equation 1, the cation composition of the 10.19 Å layers is 60% NH₄⁺ and 40% K⁺. The product of the amount of NH₄⁺ in the interlayers (0.60) and the proportion of 10.19 Å layers (0.30) is equal to 0.18 ions per O₁₀(OH)₂.

The possible existence of NH₄⁺-bearing illite having a mixed-layer structure containing K-rich illite layers and NH₄⁺-bearing illite layers was noted for the first time by Higashi (1982). For this structure, Juster et al. (1987) analyzed the XRD pattern of the 0–0.5 μm fraction of an NH₄⁺-bearing illite and found that the 00*l* reflections did not form a rational series. In particular, the observed d_{001} value of 10.179 Å was identical to that of the NH₄⁺-bearing illite in coarser fractions of the same sample, whereas the positions of the 002 and 003 reflections were those of a normal K end-member illite. This shift of d_{001} to small angles was probably due to the effect of thin CSDs. Unfortunately, basal reflection widths were not investigated. The results of the present investigation demonstrate that the absence of a rational series of basal reflections is not proof of a mixed-layer structure. Thus, the nature of the structure described by Juster et al. (1987) remains unclear.

Mechanism of I-T-S formation

Stevenson (1960) suggested that during diagenesis of oil source rocks, the new illite interlayers might trap some NH₃ formed during oil generation as NH₄⁺. Preferential absorption of NH₄⁺ in neofomed illite interlayers may be due to the different reactions of different cations to increasing layer charge. For example, Eberl (1986) studied the Na⁺-K⁺ exchange during smectite illitization and concluded that for a given layer charge the larger cation in the dehydrated state is more easily dehydrated, e.g., K⁺ is preferred to Na⁺, when the layer charge required for K⁺ dehydration has been exceeded. A similar mechanism may be responsible for the preferential fixation of NH₄⁺

relative to K⁺ (Lindgreen 1994) because the ionic radii of dehydrated NH₄⁺ and K⁺ are 1.43 and 1.33 Å, respectively (Sterne et al. 1982; Eberl 1986). At low layer charge all cations are hydrated. With increasing interlayer charge in smectite, NH₄⁺ is dehydrated and fixed first because of its larger size and the possible formation of hydrogen bonds with the O atoms at the interlayer surfaces.

During diagenesis in the Central Trough, soluble and exchangeable K⁺ and NH₄⁺ decrease and increase, respectively, with depth, probably contributing to the preferential fixation of NH₄⁺ during smectite illitization (Lindgreen 1994). Cation demixing (Gaultier and Mamy 1979, 1982) and selective adsorption (Drits and Kossowskaya 1980) may have caused the segregation of K⁺ and NH₄⁺. Gaultier and Mamy (1979, 1982) studied montmorillonite saturated with K⁺ + Na⁺ and K⁺ + Ca²⁺ and showed that cation segregation takes place in the interlayers, leading, in particular, to K fixation. Drits and Kossowskaya (1980) described selective absorption of interlayer cations in montmorillonite. They showed that one of the characteristic features of some oceanic montmorillonite specimens is that K⁺ dominates over the other exchangeable cations despite the fact that Na⁺ is the dominant cation in seawater. During the I-S transformation resulting in maximum degree of ordering for R = 1, different smectite interlayers may be occupied preferentially either by K⁺ or NH₄⁺ as a result of cation demixing. Then, increasing interlayer charge can fix NH₄⁺, while K⁺ remains exchangeable. This process of cation exchange and cation demixing can continue to form new NH₄⁺ interlayers.

The hypothesis for preferential fixation of NH₄⁺ between the neofomed illite layers during diagenesis in oil source rocks can be experimentally confirmed from the data obtained for samples 95, 87, and 89. These samples were selected because, first, the error in the determination of the content of nonexpandable interlayers in these samples is <2%, whereas the error for the other samples is ±5%; and second, these samples differ in degree of illitization. The difference between the proportion of nonexpandable interlayers, w_i , and the proportion of NH₄⁺ interlayers, w_{NH_4} , is equal to the amount of K⁺ interlayers. As shown previously, for all studied samples (except sample x18) the proportion of NH₄⁺ interlayers is equal to the w_{NH_4} value determined by Equation 3. The difference between w_i and w_{NH_4} is 0.64, 0.65, and 0.66 for samples 95, 87, and 89, respectively (Tables 1 and 4). Because these values correspond to the amount of K⁺ interlayers in these samples having very different degrees of diagenesis, it can be concluded that all the mica-like interlayers formed during diagenesis are pure tobelite interlayers.

However, during the deeper diagenetic alteration of I-S in oil source rocks, a distinct increase in interlayer charge may occur and result in increasing fixation of K⁺ together with NH₄⁺ in mica-like interlayers. This would decrease the proportion of initial K⁺ interlayers and increase the proportion of mica-like interlayers with mixed cation

composition. This process can explain the interlayer composition of sample $\times 18$.

Comparison of data obtained by different methods

The most remarkable result of this investigation is that for each sample the amount of NH_4^+ per $\text{O}_{10}(\text{OH})_2$ found by the isotopic dilution method is identical or very similar to the amount determined by the XRD technique (Table 1). For the mixed-layer models consisting of 9.98 and 10.33 Å layers, d_{001} and FWHH(00 l) depend strongly on the layer types but very little on the proportion of NH_4^+ in interlayers. Accordingly, identical values for d_{001} and identical values for FWHH(00 l) can be obtained for mixed-layer structures having quite different amounts of NH_4^+ per $\text{O}_{10}(\text{OH})_2$. In the I-S-V investigated, the approximately equal amounts of NH_4^+ determined by the two independent methods can be explained only if all available interlayer sites within each 10.33 Å layer are occupied by NH_4^+ , i.e., the amount of NH_4^+ per $\text{O}_{10}(\text{OH})_2$ in these interlayers is 1.0. Theoretically, even in this case the amount of NH_4^+ determined by the XRD technique should be greater than the amount determined by the isotopic dilution method. This is because, first, the studied samples have rather thin CSDs (six to seven layers) and, second, the amounts of NH_4^+ determined by the latter method were not corrected for the small amount of kaolinite (~5%) in the I-S samples (Lindgreen 1994). However, for a CSD of seven layers, in which five interlayers have 1.0 K^+ and one has 1.0 NH_4^+ per $\text{O}_{10}(\text{OH})_2$, $w_{\text{NH}_4} = \frac{1}{6}$ (a value that can be determined by XRD) and $C_{\text{NH}_4} = \frac{1}{7} \text{NH}_4^+$ per $\text{O}_{10}(\text{OH})_2$ (a value that can be determined by chemical analysis). The difference of 0.02 NH_4^+ per $\text{O}_{10}(\text{OH})_2$ corresponds to the errors in the determination of NH_4^+ by both methods.

Thus, agreement between the values for w_{NH_4} determined from Figure 2 and Equation 3 proves that a sample is a mixed-layer mineral and that the w_{NH_4} value corresponds to the proportion of 10.33 Å layers or, more correctly, NH_4^+ interlayers. If, in addition, all structural sites within each NH_4^+ interlayer are occupied solely by NH_4^+ and the correction for CSD mean thickness is taken into account, then the XRD technique can determine the number of NH_4^+ cations per $\text{O}_{10}(\text{OH})_2$. Without this correction for the thickness of CSDs, the error in the amount of NH_4^+ is 0.01–0.02, for a total amount of <0.25 NH_4^+ per $\text{O}_{10}(\text{OH})_2$ and a CSD thickness of six to seven layers. It should be noted that an error in d_{005} of 0.001 Å leads to an error in C_{NH_4} or w_{NH_4} of 0.015. Thus, under the conditions mentioned above, the correction for CSD mean thickness is not essential.

The results show that the C_{NH_4} and w_{NH_4} values determined by Equations 2 and 3 correspond within ± 0.02 – 0.03NH_4^+ to the actual content of NH_4^+ per $\text{O}_{10}(\text{OH})_2$, because the interlayers of 10.33 Å layers are occupied entirely by NH_4^+ .

For two NH_4^+ -bearing illite samples from Delong Mountains, Sterne et al. (1982) determined the d_{005} values

to be 2.020 and 2.033 Å and calculated that the sample with $d_{005} = 2.033 \text{Å}$ contained 0.507 sites occupied by NH_4^+ . For this d_{005} value, Equation 2 shows that $C_{\text{NH}_4} = 0.52$. The NH_4^+ content of the second sample was not determined by Sterne et al. (1982). According to Equation 3, the amount of NH_4^+ should be equal to 0.33 cations per $\text{O}_{10}(\text{OH})_2$ if all interlayer sites are filled with cations. Because basal reflection widths were not determined by Sterne et al. (1982), the NH_4 and K distribution in their samples cannot be determined.

Application of the XRD technique for determination of NH_4^+

The present method requires that the smectite interlayers, after saturation with K^+ and heating at 150 °C, contract to 9.98 Å. The validity of this assumption is supported by the agreement between the values for NH_4^+ obtained by the two independent XRD methods. However, application of XRD techniques is possible only for samples that are either monomineralic or do not contain phases having reflections located very close to the 002 and 005 reflections of illite, because then it would be impossible to determine precisely the d_{001} and the FWHH(00 l) values. Furthermore, the samples must not be heated at temperatures higher than 200 °C because d_{005} values are markedly different for the same sample heated at 150 and 300 °C (Tables 4 and 5, respectively). This difference may be due to a further decrease in the thickness of K^+ -saturated smectite layers or to a structural rearrangement of the NH_4^+ within the mica interlayers on heating to 350 °C. Juster et al. (1987) noted that the unusually large basal spacing and interlayer thickness of synthetic and natural NH_4^+ -bearing illite specimens cannot be easily explained by cation-radius arguments. NH_4^+ is not a spherical molecule, and its size is much too small to explain the observed d_{001} value for NH_4^+ -bearing illite and muscovite. Juster et al. (1987) assumed that interaction of protons of the tetrahedral NH_4^+ with their bonding environment, and perhaps especially with the OH groups, requires a loose, inefficient packing geometry that results in an anomalously large d_{001} . The heating at 300 °C may result in a reorientation of NH_4^+ and a more efficient packing geometry with a corresponding decrease in the d_{001} values. The smaller FWHH(005) values for the samples heated at 300 °C also support the hypothesis that heating at 300 °C decreases the thickness of NH_4^+ -bearing interlayers.

The reliability of the results strongly depends on the accuracy of the determination of the positions and profiles of basal reflections. The measurements require a precise adjustment of specimens in the diffractometer and good statistics for the recording of basal reflection profiles. Furthermore, the method may fail if the mica interlayers contain significant amounts of Na or Ca in addition to K.

In Upper Jurassic shales in Denmark and in the North Sea Central Trough, exchangeable NH_4^+ and soluble NH_4^+ are present in small amounts in the clays of the Danish Sub-basin and in the samples from shallow depth

(<2.5 km) in the Central Trough, but increases with depth in the Central Trough (Lindgreen 1994). NH₃ is generated from organic matter during diagenesis at 100–130 °C (Fig. 5.6 in Hunt 1979), and the presence of NH₄⁺ in groundwater indicates a past or present occurrence of oil (Bogomolov et al. 1970). Future investigations should show if the 100% occupancy of neoformed illite layers by NH₄⁺, as found in the North Sea oil source rocks, is common for I-S in such rocks and thus characteristic of oil generation.

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Note added in proof: We found that Šucha et al. [Šucha, V., Kraus, I., and Madejová, J. (1994) Ammonium illite from anchimetamorphic shales associated with anthracite in the Zemplinicum of the western Carpathians, *Clay Minerals*, 29, 369–378] calculated d_{001} positions and peak intensity ratios for 9.98 Å to 10.35 Å mixed-layer structures and used these data to determine the amount NH₄ in NH₄-bearing illites.