LAYER-CHARGE HETEROGENEITY IN SMECTITES OF I–S PHASES IN PELITIC SEDIMENTS FROM THE MOLASSE BASIN, AUSTRIA

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Abstract—The purpose of this study was to characterize more fully the surface charge characteristics of the end-member smectite in illite–smectite (I–S) mixed-layer phases found previously in pelitic sediments of the Molasse Basin in Austria. The smectite end member was shown to have an unusually high interlayer charge (0.58). Based on earlier work on pure smectites, it was hypothesized that this high charge represents the mean of a mixture of a higher- and lower-charged smectite component intermixed with illite. To test this hypothesis, the magnitude of the interlayer charge of the smectites was evaluated using 2 different methods: alkylammonium ion orientation and K-fixation by wetting and drying.

Using 2 I–S samples of different I–S ratios, saturated with alkyammonium ions of chain lengths $n_c = 5$–18, X-ray diffraction patterns (XRD) could be interpreted as representing a 3-component system, consisting of randomly interlayered high- and low-charged smectite and illite.

K-fixation, carried out by K-treatment and followed by 100 wetting and drying (WD) cycles, confirmed the presence of a high-charged smectite component admixed with low-charged smectite, both interlayered with illite. The wetting and drying of the K-treated samples led to interlayer collapse of the high-charged smectite component and to the production of illite layers stable against exchange with 0.1 N $SrCl_2$. The 2 smectites occur in the ratio of about 1:1 and consist of 1 phase with an interlayer charge of about 0.76 and another phase with a normal charge of about 0.40. During diagenesis, the 2 kinds of smectite are altering simultaneously to the same end-member illite along 2 different reaction paths.

Key Words—Alkylammonium Method, Austria, Charge Heterogeneity, Illite–Smectite, K-Fixation, Molasse Basin.

INTRODUCTION

The ubiquity of I–S mixed-layer minerals in pelitic sediments has been established over the last decades (Eslinger and Pevear 1988). The increase in I–S ratio during burial diagenesis is observed as a primary mineral transformation during diagenesis and low-grade metamorphism (Środoń and Eberl 1984). As a result of the development of increasingly precise XRD techniques for I–S characterization (Moore and Reynolds 1997), when used in conjunction with chemical analysis of pure phases, it has been possible to establish end-member compositions with some precision. The strategy in determining end-member I–S compositions was first applied to Vienna Basin (Austria) diagenetic sequences (Horton et al. 1985). Based on chemical analysis, structural formulas were calculated for a depth sequence of I–S phases. Chemical variations varied linearly with increasing smectite or illite content, indicating that chemical variations depend only on relative proportions of illite and smectite. Therefore, extrapolation to 100% smectite (or illite) gave the end-member compositions.

In a recent study of burial diagenesis in the western part of the Molasse Zone in Austria (Gier 1998), the ubiquitous transformation of smectite to illite, through I–S mixed intermediates, was noted. The I–S characterization was carried out using the <0.2 μm fractions

of shales from 2 drillings (Puchkirchen 1 and Geretsberg 1) from the Molasse Zone. Based on the $\Delta 2\theta$ method described by Moore and Reynolds (1997), X-ray study of samples, collected from depths of 590 to 2475 m, showed an increase with depth from 25% to 70% illite in the I–S phases (Figure 1).

Since the <0.2 μm fractions of each sample consisted of essentially pure I–S phases, chemical analyses could be used to calculate structural formulas for I–S phases of differing I–S ratio, and by linear extrapolation the end-member compositions. These were then plotted in a Yoder-type (Yoder and Eugster 1955) muscovite-pyrophyllite-celadonite diagram (Figure 2), which emphasizes silicate layer-charge, dependent upon either tetrahedral or octahedral substitutions and composition. Shown also in Figure 2 are the illite and smectite fields established by Köster (1981). Particularly noteworthy is the smectite high layer-charge (0.58 per $O_{10}(OH)_2$) for the Molasse Basin end-member smectite, reflecting its more celadonitic composition.

Another technique for determining the layer charge of smectites is the alkylammonium method. Even charge heterogeneities in smectites can be analyzed by this method (Lagaly and Weiss 1969; Stul and Mortier 1974; Lagaly et al. 1976; Lagaly and Weiss 1976; Lagaly 1981; Laird et al. 1989; Lagaly 1994; Laird 1994).
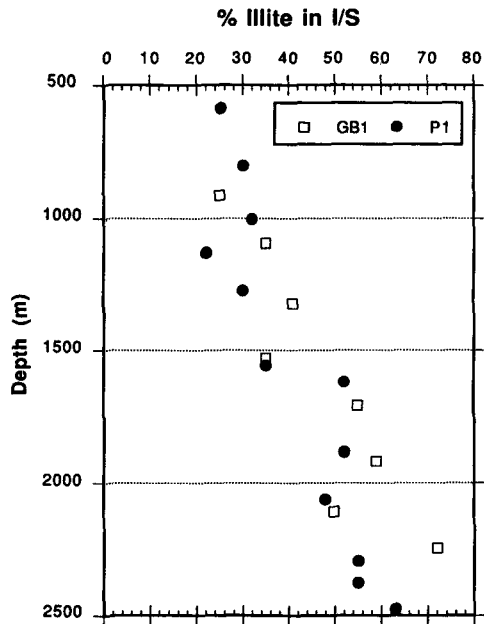
Figure 1.   % Illite in I–S with depth in the drillings Puchkirchen 1 (P1) and Geretsberg 1 (GB1).
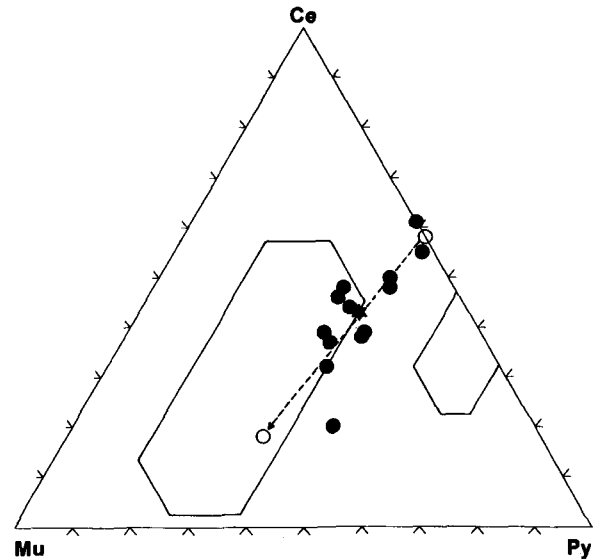

Figure 2.   Charge-variations of the I–S, plotted in the Muscovite (Mu)–Celadonite (Ce)–Pyrophyllite (Py) diagram. O = end members smectite and illite, * = mean composition, arrow indicates diagenetic trend, illite and smectite fields (Köster 1981).

Studies of K-fixation (Eberl et al. 1986) and NH$_4$-fixation (Sucha and Siranova 1991), had indicated that, in the case of pure smectites, high-charged varieties (>0.40 per O$_{10}$(OH)$_2$) are usually a mixture of high- and low-charged components. Thus it was proposed that the Molasse I–S phases might occur as 3-component interlayered mixtures of illite and high- and low-charged smectites, rather than simpler 2-component I–S mixtures, as generally presumed in diagenetic studies.

The purpose of this present study is to test this hypothesis by developing chemical strategies to detect variations in layer charge in the smectite from the Molasse diagenetic sequence.

MATERIALS AND METHODS

To test this hypothesis, 2 different methods of investigation were used. The first was the alkylammonium method as developed by Lagaly and Weiss (1969), where alkylammonium ion surface orientation can presumably be related to smectite layer charge. The second method involved K-fixation, following repeated WD cycles, as used by Eberl et al. (1986).

These further investigations were carried out on the <0.2 μm fractions from 12 Puchkirchen 1 (P1) core samples previously studied and chemically characterized from the Molasse Zone. The well cores had been made available by the Rohöl Aufsuchungs AG (RAG).

Alkylammonium-Ion Orientation

Alkylammonium ion exchange provides a method for analysis of layer charge magnitude in smectites.

Charge heterogeneity in conventional smectites is recognized by a continuously increasing d(001) spacing between the monolayer (13.6 Å) and the bilayer plateau (17.7 Å) with increasing alkyl chain length, as shown by Lagaly and Weiss (1976) and Lagaly (1994). When random interstratification of smectites with cation densities varying between 2 limits and with mica-like interlayers also present occurs, the interpretation of the X-ray patterns, based on a single low-angle reflection of the alkylammonium derivatives, is difficult (Lagaly 1979). It requires interpretation of the entire diffraction pattern, that is, of as many higher orders as possible.

The <0.2 μm fractions of 2 Puchkirchen samples 6P1 (I/S = 35/65) and 12P1 (I/S = 63/37), were treated for 24 h with aqueous solutions of alkylammonium chloride ions of chain lengths n$_c$ = 5–18. The solutions after the first centrifugation were saved and analyzed for K by atomic adsorption spectrometry (AAS) to detect possible replacement of K-ions by alkylammonium ions in admixed discrete illite during the saturation, as discussed by Laird et al. 1987 and Laird 1994. Each sample was washed 4 times with ethanol and the last time with half ethanol, half water. Oriented films were deposited on ceramic tiles for XRD analysis (Philips diffractometer, PW1710, CuKα radiation, 40 KV, 45 mA).

Potassium Fixation by Wetting and Drying

To quantify the percentage of high-charged smectite layers in each of the 12 Puchkirchen samples and to estimate the interlayer charges, the method of K-fixa-

tion by wetting and drying, as used by Eberl et al. (1986) for pure smectites, was applied to these I–S mixed phases. These authors had shown that irreversible K-fixation occurs between highly charged 2:1 layers only after repeated wetting and drying, and that the quantity of illite (collapsed) layers formed after 100 WD cycles and one Sr^{2+} exchange is proportional to the number of high-charged layers. The fixation of K-ions occurred only when they were firmly enclosed in the 2 hexagonal (trigonal) vacancies formed when contiguous 2:1 layers were superimposed, so as to trap the K-ions in the large vacancies formed on the surface of silicate sheets. Repeated wetting and drying at modest temperatures promoted K-ion migration and/or layer translation and led to final K-fixation (Eberl et al. 1986).

By shaking overnight, 200 mg of the <0.2 μm fraction of each of the 12 Puchkirchen samples were saturated 3 times with 1 N KCl solution (50 mL). The samples were repeatedly washed in distilled water until no chloride ion was detected by the $AgNO_3$ test. For the WD experiments, 200 mg of each sample were placed in polyethylene weighing boats and wetted with 20 mL of distilled water. One hundred WD cycles were carried out, completing 2 cycles daily at 60 °C in a drying oven (Eberl et al. 1986; Sucha and Siranova 1991).

At intervals of 10, 20, 40, 60 and 100 cycles, samples of each clay were removed, X-rayed, then treated with 0.1 N $SrCl_2$ solution overnight to replace any non-fixed and exchangeable K-ions. After several washings, oriented specimens were prepared on glass substrates (4 mg/mL) (Eberl et al. 1986; Sucha and Siranova 1991). Before X-ray analysis (PAD V Scintag diffractometer, Cu$K\alpha$ radiation, 40 kV, 30 mA), the specimens were treated with ethylene glycol vapor (8 h at 60 °C), to reexpand residual (low-charge) smectite layers.

The illite content (representing now the original plus nonexpandable, newly formed illite layers), was determined by measuring the 2θ difference values of the diffraction peak positions 001/002 and 002/003 (Moore and Reynolds 1997). Precise peak positions were found with the support of the fit profile option of the Philips APD-software 3.5B (1992).

In addition, pairs of the oriented specimens, representing 0 and 100 WD cycles, were analyzed for K, Sr and Al by wavelength-dispersive spectrometry (WDS) housed on a scanning electron microscope (Amray 1600T; analytical conditions 10 kV, 70 nA beam current) to confirm and correlate K-fixation with layer collapse. Because of the slightly different thicknesses of the 0 and 100 cycle samples, K- and Sr-intensities were normalized to Al-intensities.

RESULTS AND DISCUSSION

Alkylammonium Ion Exchange

The X-ray patterns of alkylammonium complexes of these samples (Figures 3 and 4), are typical of multi-component I–S mixed-layer phases, but the broadness in particular of 00l reflections in the 17–20 2θ and 25–30 2θ ranges, as well as the low-angle 5–10 2θ range, is suggestive of a randomly interlayered low- and high-charged smectite-system combined with illite (Frey and Lagaly 1979). We reach this conclusion because, if we plot only the series of apparent $d(001)$ low-angle spacings for each of the alkylammonium clays as a function of chain length, as first proposed by Jordan (1949), then by Lagaly and Weiss (1969) and later by Lagaly (1994), for normal pure smectites, we do not observe the normal $d(001)$ values expected for monolayers of flat-lying alkyl chains to chain lengths up to n_c 12 (13.6 Å) and the increase due to bilayer configuration forming at longer chain lengths (17.7 Å). Instead, as Figures 3 and 4 show, $d(001)$ spacings are intermediate between those expected for high- and low-charged smectite, suggesting qualitatively that the alkylammonium interlayers are randomly disposed between more than 1 type of smectite layer and that 1 type of layer exhibits an inclination of alkyl-chains, compatible with high charge (Lagaly and Weiss 1969).

In addition, in the case of complexes with alkyl chain length greater than n_c 12, a series of very low-angle spacings (22–30 Å) and higher orders are superimposed on the I–S patterns and are indicative of alkylammonium ion replacement of K from the expanded discrete illite phase not involved in the interlayered I–S (Laird 1994). Also, the K analyses of the alkylammonium solutions after treatment showed only trace amounts of K with short alkyl chain lengths, but significant K-release into solution above n_c 12, commensurate with the expansion of the discrete illite present. From these data, where the focus is on a single low-angle spacing only, it is not possible to estimate the proportions of what may be a random mixing of illite and high- and low-charged smectite components (Lagaly and Weiss 1976). These data do, however, strongly suggest the presence of high-charged expandable layers as a component of the I–S clays.

Taking the analysis further than is usually done, the full range of d-values for each diffraction pattern was examined, using the Méring method (Méring 1949) of mixed-phase analysis, where X-ray reflections occur at intermediate positions between the defining 00l peaks for members of the mixture. In this case the illite member is defined by a 10-Å reflection and its integrally related higher orders, the low-charged smectite by a rational series related to a 13.6-Å monolayer phase at low values of alkyl-chain length, and 17.7 Å at chain lengths above n_c 12 (Lagaly and Weiss 1969). Based on earlier studies (Johns and Sen Gupta 1967), the high-charged alkylammonium smectites were assigned the likely $d(001)$ values as follows: n_c 6 = 14.5 Å, n_c 10 = 18.5 Å, n_c 14 = 22.5 Å, n_c 18 = 26.5 Å. These values would be related to chain orientations
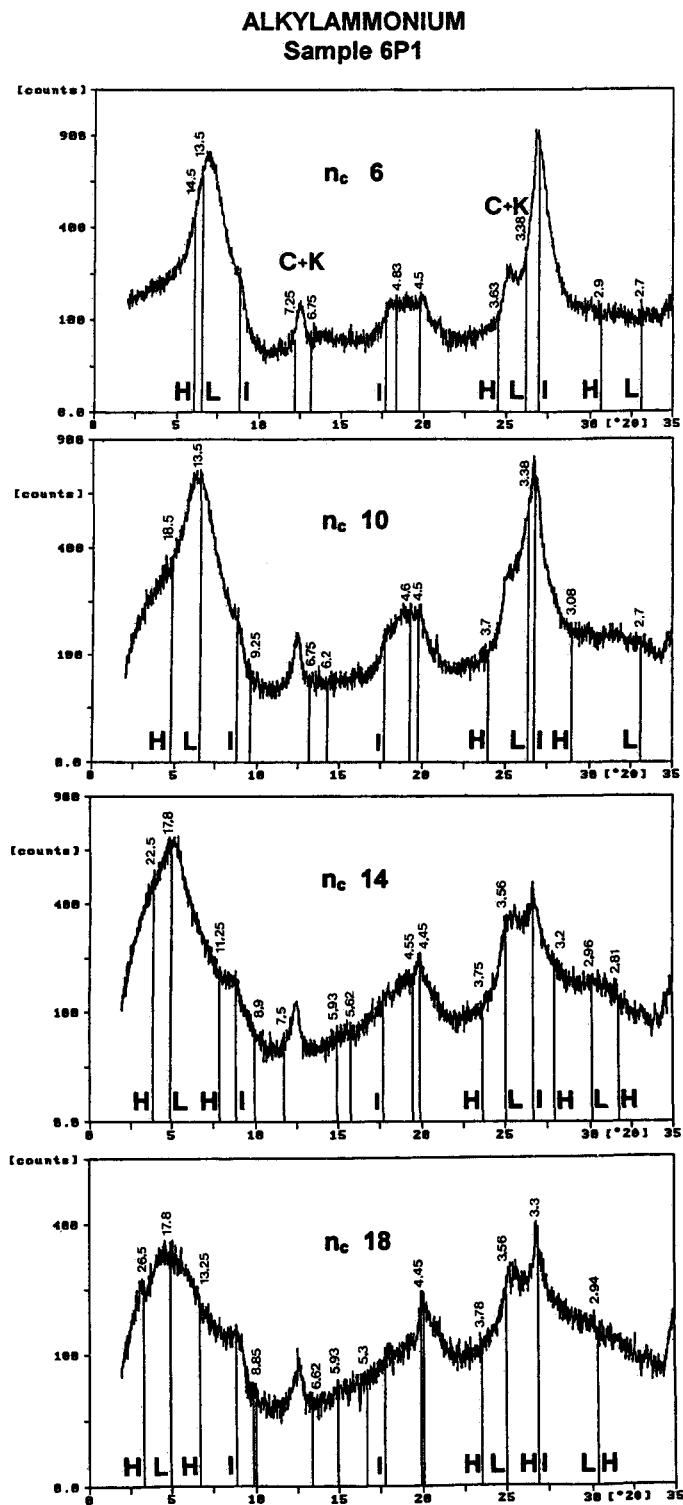
ALKYLAMMONIUM
Sample 6P1

Figure 3.   XRD-patterns of sample 6P1, treated with alkylammonium ions of chain lengths n_c 6, 10, 14 and 18. H = high-charged smectite, L = low-charged smectite, I = illite, d-values in Å. C + K = chlorite + kaolinite.
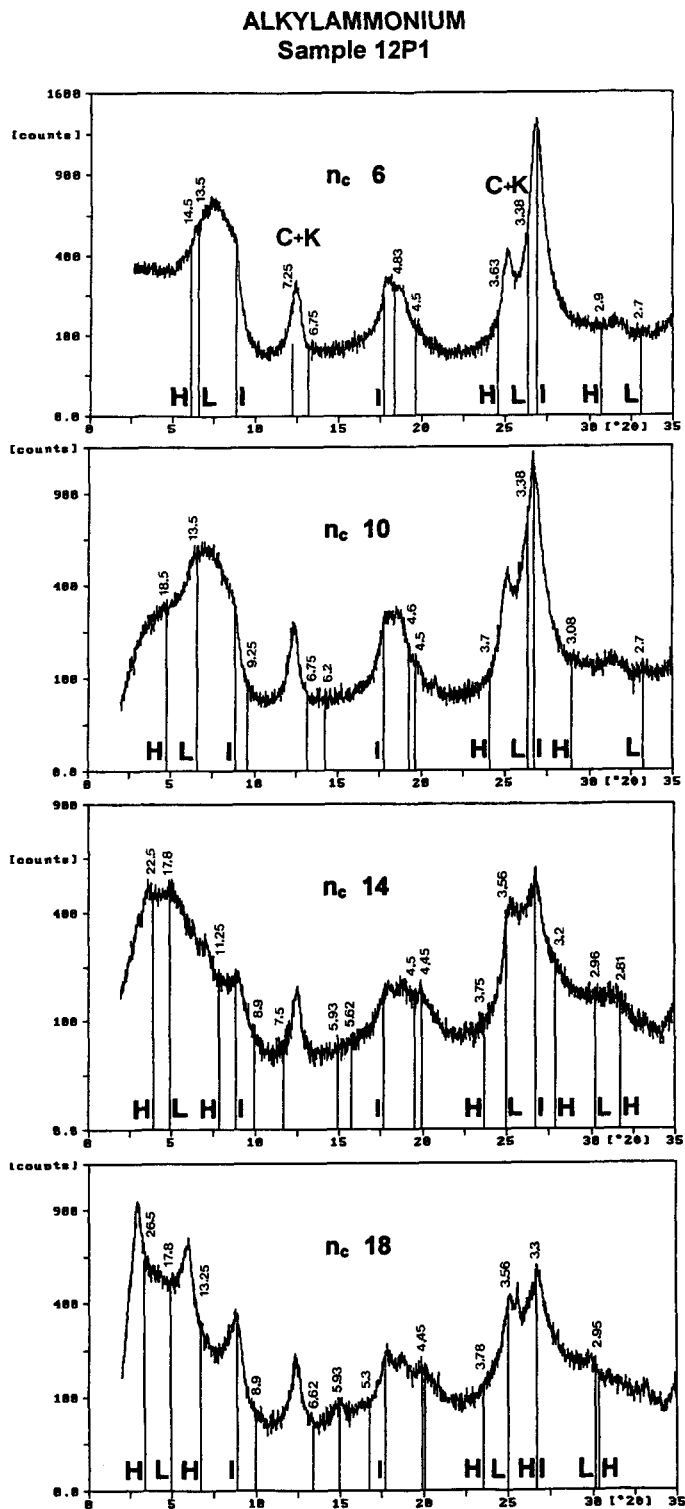
Figure 4. XRD patterns of sample 12P1, treated with alkylammonium ions of chain lengths n_c 6, 10, 14 and 18. H = high-charged smectite, L = low-charged smectite, I = illite, *d*-values in Å. C + K = chlorite + kaolinite.
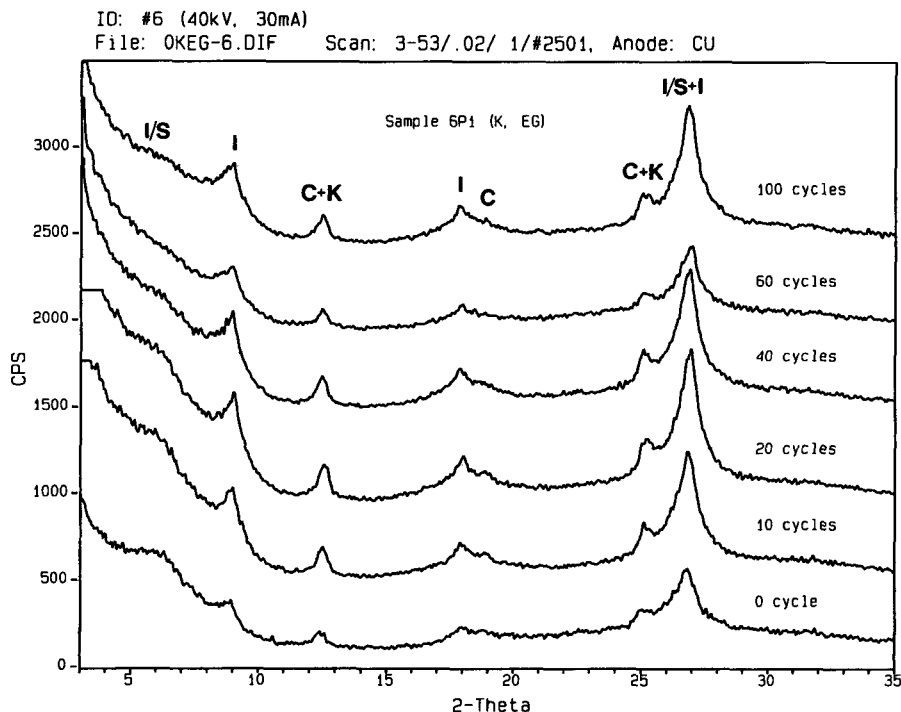
Figure 5. XRD patterns for sample 6P1 after K-saturation and EG-treatment for 0 to 100 WD cycles. I–S = illite–smectite, I = illite, C + K = chlorite + kaolinite.

intermediate between vertical paraffin and pseudotri-layer orientations (Lagaly and Weiss 1969). It is clear from Figures 3 and 4 that combinations of 3 primary spacings in each diffracting region would give rise to the peak broadening observed. This effect is particularly apparent and diagnostic in the high-angle diffraction regions. In Figures 3 and 4 these spacings for each of the 3 mixed phases are superimposed on the actual X-ray patterns and indicated by H (high charged smectite), L (low charged smectite) and I (illite). Relative intensities are taken from the intensity distribution curve of Bradley (1945), which is especially appropriate, since it was derived experimentally from measurements of many high-spacing organic complexes such as those studied here.

Although somewhat complicated by some interference from discrete illite, chlorite and kaolinite peaks, these alkylammonium complexes can be interpreted as 3-component mixtures of randomly interlayer illite, high-charged and low-charged smectite. The effect on the diffraction patterns (Figures 3 and 4) of the high-charged component is best noted in the three 2θ regions referred to earlier. As noted previously, when the alkyl-chain length exceeds n_c 12, the discrete illite impurity forms a discrete (not interlayered) phase with alkyl chains assuming the paraffin-like high-angle orientation (Laird 1994). This is best seen in Figure 4 for n_c 18. Collectively the XRD data confirm the notion that these I–S clays are very likely 3-component in-

terlayered systems, consisting of illite and 2 smectites of different interlayer charge.

K-Fixation by Wetting and Drying (WD)

K-fixation and layer collapse of the Molasse I–S clays, as monitored by XRD, is shown in Figures 5 and 6. Figure 5 shows the diffraction patterns for sample 6P1, following K-saturation, WD cycles as shown and finally ethylene glycol saturation (without previous Sr^{2+} exchange). It is clear that substantial layer collapse results from simple K-saturation and dehydration at 60 °C. However, Figure 6 shows that the same K-saturated samples, followed by wetting and drying, and then finally exchanged with Sr-ions, reexpand appreciably, indicating that some of the previously collapsed K-saturated layers were not fixed irreversibly, and that Sr-ions could still replace some K-ions associated with lower-charged smectite layers, presumably because of the greater hydration energy of Sr^{2+} (Eberl et al. 1986). Progressive WD cycles (Figure 6) stabilized more and more 10-Å layers against Sr^{2+} exchange.

Figure 7 shows the increase in illite content following K-fixation for 3 different samples with different initial I–S ratios (6P1, 7P1, 12P1), as related to increasing number of WD cycles. Most of the high-charged layer-collapse and accompanying K-fixation occurs after 20 WD cycles and is completed after 100 WD cycles. When analyzed by XRD studies, these
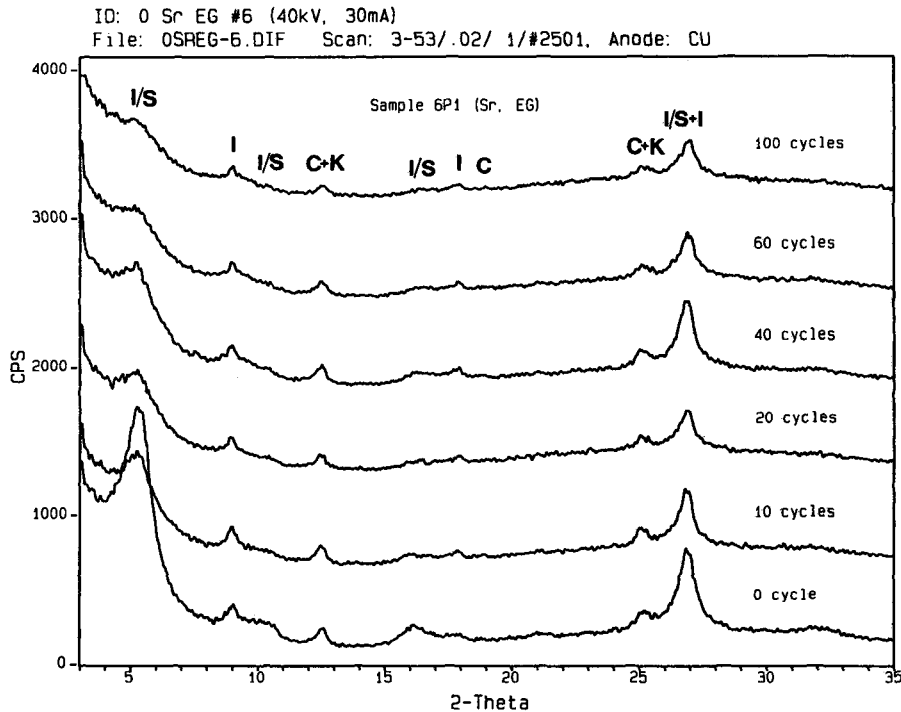
Figure 6.   XRD patterns for sample 6P1 after K-saturation and after Sr- and EG-treatment for 0 to 100 WD cycles. I–S = illite–smectite, I = illite, C + K = chlorite + kaolinite.

treated samples now appear as 2-component systems, in each case with increased illite content, resulting from the collapsed, high-charged smectite layers. The illite layers of sample 6P1 increased from 32% to 63%, sample 7P1 from 58% to 78% and sample 12P1 from 70% to 84%. Table 1 gives the results for all samples. All of these increases are due to irreversible collapse of high-charged smectite layers (Schultz 1969; Eberl et al. 1986); they permit simple calculation of relative amounts of the initial illite, and the high- and low-charged smectites in the original 3-com-
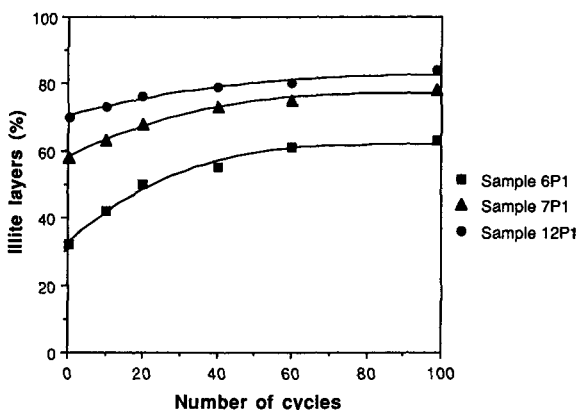
ponent systems. These percentages are summarized in Table 2.

Figures 8 and 9 show, respectively, the intensities (cps/nA) of K and Sr, measured with a wavelength dispersive spectrometer from oriented films after 0 and 100 WD cycles. As the illite content increases, so do K-spectral intensities, with commensurate decrease in exchanged-Sr intensities. Irreversible layer collapse is indeed accompanied by K-fixation, with the formation of illite-like layers.

As had been shown earlier by Schultz (1969), Eberl et al. (1986) and Sucha and Siranova (1991), irreversible K-fixation (or NH_4-fixation) and smectite layer collapse, as revealed by WD strategies, takes place in smectites in which the layer charge exceeds 0.40 (Wyoming type). The present study confirms that in the case of Molasse Basin sediments the I–S phase is an

Figure 7.   Increase of illite layers after 0 to 100 WD cycles for 3 Puchkirchen samples.

Table 1.   Percent illite in the Puchkirchen series from 0 to 100 WD cycles.

Sample cycle	2P1	6P1	7P1	9P1	10P1	12P1
0	30	32	58	54	58	70
10	43	42	63	62	65	73
20	49	50	68	66	71	76
40	55	55	73	69	71	79
60	55	61	75	73	76	80
100	63	63	78	75	76	84

Table 2. Percent smectite and illite layers after 0 WD cycles and 100 WD cycles, and % of high- and low-charged smectite.

Sample	S (0 WD)	I (0 WD)	S (100 WD)	I (100 WD)	S high	S low
2P1	70	30	37	63	33	37
6P1	68	32	37	63	31	37
7P1	42	58	22	78	20	22
9P1	46	54	25	75	21	25
10P1	46	54	24	76	22	24
12P1	30	70	16	84	14	16

Figure 9. Decrease in Sr after 100 WD cycles for the Puchkirchen series of decreasing initial smectite content.

admixture of high- and low-charged smectites interlayered with illite. The wetting and drying of K-treated samples did result in interlayer collapse of the high-charged smectite component and the production of new illite layers stable against exchange by Sr^{2+}. In Figure 10, the percentage of high-charged smectite (=% collapsed layers) and the percentage of low-charged smectite are plotted vs. % illite in the original samples. These linear plots, when extrapolated to 100% smectite, give values of 47% and 53%, respectively, for the proportions of high- and low-charged smectite in the original precursor smectite. As the smectite decreases during diagenesis, the relative proportion of high- to low-charged smectite remains fairly constant at about 50:50.

Results of the earlier chemical characterization of these clays (Gier 1998) are plotted (black dots, Figure 11) in the ternary diagram muscovite-pyrophyllite-celadonite, where variations in layer charge, as well as extent of tetrahedral and octahedral substitutions, can be readily observed. Extrapolation of the chemical data to 100% smectite (or illite) leads to the end-member phases indicated by the 2 open circles. The smectite end member has an interlayer charge of 0.58 and lies on the pyrophyllite–celadonite join, indicating the source of charge is the result of octahedral rather than tetrahedral substitution. Therefore, the end-member
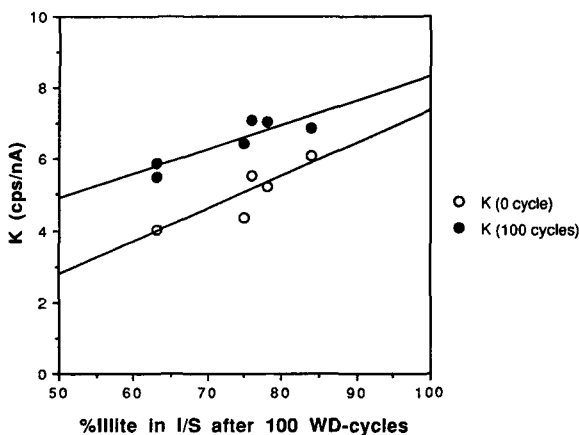
smectite has a significant celadonite component. The absence of significant tetrahedral substitution, characteristic of vermiculites, precludes using this name for this high-charged smectite.

Since the end-member smectite has a mean layer charge of 0.58, and if it is assumed that the admixed low-charged smectite component has a normal layer charge of 0.40, simple calculation results in a charge of 0.76 for the high-charged smectite; it is more celadonitic in composition than conventional smectite. These values are plotted in Figure 11 (stars), which suggests that each of the differing smectites of the 3-component mixture is altering to a common illite along 2 different transformation paths. Using the muscovite–pyrophyllite–celadonite diagram as a guide to chemical trends, the low-charged smectite transforms to illite primarily as a result of Al^{3+} substitution for Si^{4+} in tetrahedral sites. The high-charged smectite alters to illite by simultaneous substitutions of Al^{3+} tetrahedrally and octahedrally, the coupled substitutions bal-

Figure 8. Increase in K after 100 WD cycles for the Puchkirchen series of increasing initial illite content.

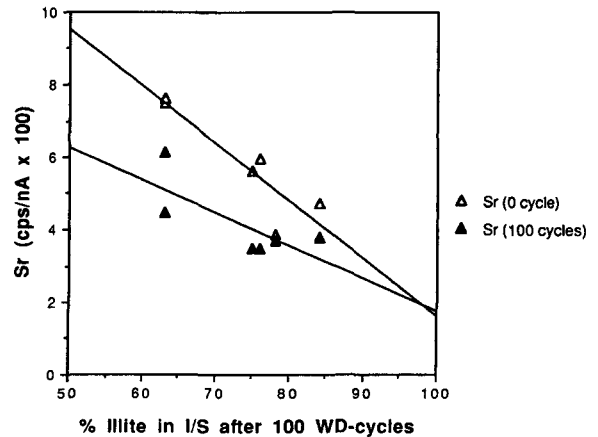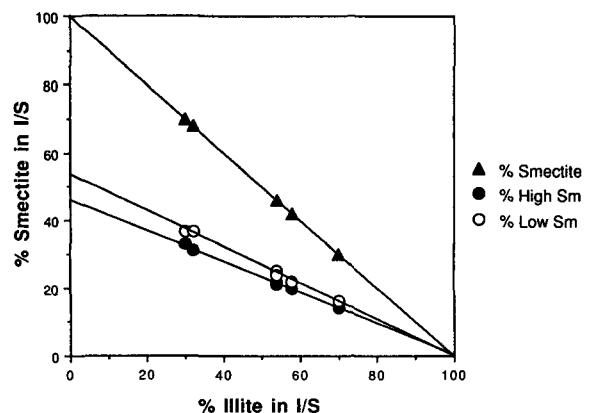Figure 10. Total smectite and percentage of high-charged smectite (=% collapsed layers) and of low-charged smectite plotted vs. % illite in the original sample.
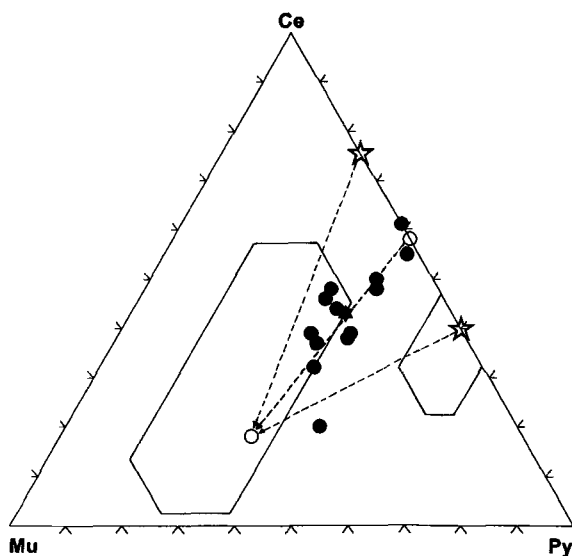
Figure 11. Composition of high- and low-charged smectite and their diagenetic trends as they transform to illite.

ancing each other, resulting in little change in layer charge during the illitization process.

The diagenetic trend shown for the low-charged smectite (Figure 11) is almost identical to compositional changes determined previously within the nearby Vienna Basin (Horton et al. 1985). The Vienna Basin end-member smectite has a layer charge of 0.38, typical of low-charged smectites (Köster 1981), and similar to that presumed for the low-charged Molasse Basin smectite (0.40).

CONCLUSIONS

From K-fixation and alkylammonium ion orientation studies, layer-charge heterogeneities in the smectite component of Molasse I–S phases could be confirmed. These I–S mixed-layer clays are 3-component mixtures of high- and low-charged smectite interlayered with illite. As the chemical compositional plots show (Figure 11), the high-charged smectite is more celadonitic than normal low-charged smectite, with an estimated layer charge of 0.76. The Yoder-type plot (Yoder and Eugster 1955) indicates that during diagenesis the 2 kinds of smectite are altering simultaneously to the same end-member illite along 2 different reaction paths. Whether this is an unique situation is yet to be determined, because there have been few previous attempts to characterize fully end-member smectite in diagenetic sequences.

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