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SOME EVIDENCE SUPPORTING THE EXISTENCE OF POLAR LAYERS IN MIXED-LAYER ILLITE/SMECTITE

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Abstract—The fraction <20 μm of a bentonitic material was selected to study the transformation of smectite into illite under hydrothermal conditions. Powder XRD showed that the studied material was composed of 97% dioctahedral smectite and 3% of quartz, cristobalite and plagioclase. The XRD analysis of the oriented, glycolated sample showed that the smectitic phase was actually a randomly interstratified illite/smectite with 11% illite. The chemical analysis of the sample yielded the structural formula: $K_{0.25}Na_{0.25}Ca_{0.12}Mg_{0.13}(Al_{2.76}Fe_{0.33}Mg_{1.03})(Si_{7.66}Al_{0.34})O_{20}(OH)_4$. The reaction conditions of the hydrothermal experiments were: KCl concentrations 0.025, 0.05, 0.1, 0.3, 0.5, 1 M; temperature 60, 120, 175, 200°C; run time 1, 5, 15, 30, 90, 180 days; solid : solution ratio 1:5. XRD of run products showed an important transformation of smectite into illite, in contrast with all other techniques (DTA, IR, NMR), which did not detect any transformation of the original material. This suggests that illite quantification in I/S by means of XRD patterns after hydrothermal experiences can be much affected by other variables. The original material and the run products were analysed by means of DTA. The starting material displayed two dehydroxylation peaks, one at 560°C corresponding to illite, and the other at 650°C corresponding to smectite. Quantification of the two dehydroxylation peaks also yielded a content of 11% illite. The run products displayed DTA diagrams in which the smectitic peak remained unaltered, but the illitic one was reduced or eliminated by the presence of exchangeable K in the interlayer. When exchangeable K was removed the illitic dehydroxylation peak appeared again. The coherence of XRD and DTA in quantifying the proportion of illite layers and the effect of exchangeable K on dehydroxylation of illite layers in mixed-layer illite/smectite seem to be positive proofs of the existence of polar layers.

Key Words—Differential Thermal Analysis, Mixed-layer illite/smectite, Polar layer.

INTRODUCTION

Mixed-layer illite/smectite (hereafter I/S) can be structurally interpreted in two different ways. The first possibility is to suppose that the two tetrahedral sheets of a TOT unit have the same charge. The second interpretation is that each one of the tetrahedral sheets in the TOT unit has a different charge, one of them being smectitic and the other illitic. The two interpretations are valid in principle and no definitive evidence supporting one model or the other has been found up to date.

The concept of polar layers, i.e., of TOT units in which each tetrathedral sheet has a different charge, was first proposed by Sudo *et al* (1962). Some authors have discussed the two models. Newman and Brown (1987) and Jiang *et al* (1990) stated the difficulties that the concept of symmetric TOT units has to explain why some layers expand and others do not, or to explain the existence of perfectly ordered interstratifications. Brown (1984) and Velde (1985) went further and asserted that I/S can be only explained by the polar layer concept. Güven (1991a) newly emphasized the advantages of the polar layer model and encouraged researchers to test it.

Obviously, the problem has important implications. The most direct one is the determination of the actual structure and crystal-chemistry of mixed-layer I/S. Another relevant topic related with this question is the understanding of the transformation reaction of smectite into illite, as well as the reverse reaction. Both processes yield I/S as intermediate products, so, the knowledge of the true structure of the insterstratified minerals will project light on the reaction mechanism.

This paper presents some results of XRD and DTA analyses carried out on a mixed-layer I/S that support the polar layer model.

MATERIALS AND METHODS

The sample studied is the fraction <20 μm of a bentonite from Cabo de Gata (SE Spain). This bentonite is the product of hydrothermal alteration of volcanic tuffs (Caballero *et al* 1983). The mineralogical composition of the fraction <20 μm was determined by XRD to be: 97% dioctahedral smectite, 3% quartz, plagioclase and cristobalite. XRD of the oriented, glycolated specimen was carried out by dispersing 0.5 g of sample in 10 ml of water; placing some drops of this dispersion on a glass slide and leaving it dry; placing the oriented aggregate in ethylene-glycol atmo-

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Table 1. Chemical analysis of the smectitic sample (<20 μm). Weight percentages are referred to as oxides and exchange cations as meq/100 g.

	SiO_2	Al_2O_3	MgO	Fe_2O_3	CaO	Na_2O	K_2O	H_2O^+	Total
Total (%)	58.21	19.88	5.72	3.62	1.38	1.59	1.42	8.02	99.84
Crystalline phases (%)	2.29	0.45			0.17	0.09			
Non-crystalline phases (%)	0.66	0.54		0.42					
Exchange cations (meq/100 g)			37.7		26.2	24.3	3.3		91.5
CEC (meq/100 g)									91.9

sphere at 60°C for 24 hours; and X-raying it. The sample was analysed in its natural state, without previous cation exchange. XRD analyses were run in a Philips PW 1710/00 diffractometer, with Cu-Kα radiation, graphite monochromator and automatic theta-compensating slit.

The sample was chemically analysed, including analysis of non-crystalline phases and determination of exchange cations and CEC (Table 1). The bulk sample and non-crystalline phases were analysed by the wet method. CEC and exchangeable cations were analysed by displacement of the latter by ammonium acetate at pH 7 and subsequent determination of CEC by the Kjeldahl's method, and of the exchangeable cations by chemical analysis of the exchange solutions (Soil Conservation Service 1972). After correction for the non-crystalline and other crystalline phases present, the structural formula was calculated by Marshall's (1949) method to be: $K_{0.25}Na_{0.25}Ca_{0.12}Mg_{0.13}(Al_{2.76}Fe_{0.33}Mg_{1.03})$-$(Si_{7.66}Al_{0.34})O_{20}(OH)_4$. The value of the layer charge and its location, mainly octahedral, situates the sample in the compositional field of montmorillonite (Güven 1991b).

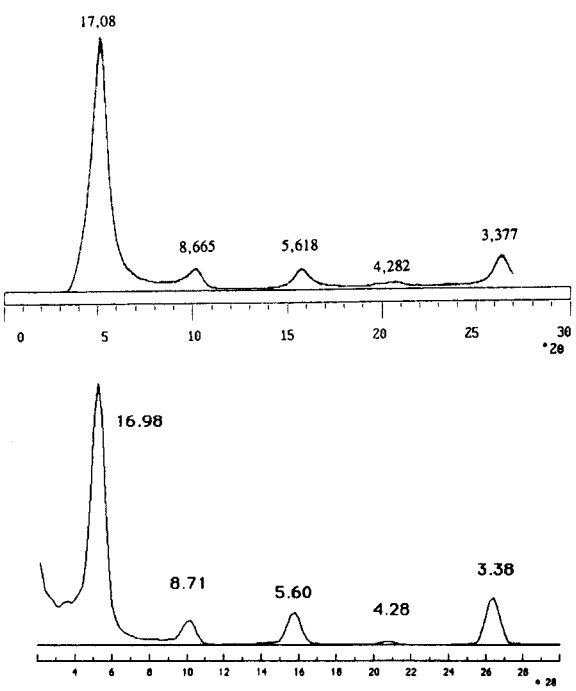


Figure 1. XRD patterns of the glycolated smectitic material (above) and the NEWMOD simulation of random I/S with 11% illite. Peak labels are in Å.

The sample was subjected to hydrothermal treatment to carry out an experimental study on the smectite to illite transformation kinetics. The run conditions were combinations of the following variables: KCl concentration 0.025, 0.05, 0.1, 0.3, 0.5, 1 M; temperature 60, 120, 175, 200°C; run time 1, 5, 15, 30, 90, 180 days. The solid : solution ratio was 5 g:25 ml.

The starting material and the solid products were studied by means of DTA in a NETZSCH STA 409 EP, in air, with alumina holders, alumina as reference, and a heating rate of 10°C/min. The sample mass was around 50 mg in all cases. Analysis of the DTA results, peak position and peak area, was carried out by means of the software facilities of the Netzsch apparatus. The peak position corresponds to the minimum value of the DTA curve in a selected range. The calculation of peak area is explained below.

Reaction products were also studied by means of XRD as oriented aggregates, prepared as it was already quoted for the original material.

RESULTS

The XRD analysis of the glycolated starting material (Figure 1) revealed that d-values were irrational. For this reason, the presence of interstratified minerals was investigated. XRD patterns were simulated using the NEWMOD program (Robert. C. Reynolds, 8 Brook Rd., Hanover N.H. 03755, USA). The fitting simulation was a random I/S with 11% illite (Figure 1). A tiny peak is observed in the experimental diffractrogram just before the one at 4.282 Å. It corresponds to the 02*l*, 11*l* bands, due to the lack of perfect orientation of the specimen on the glass slide.

The simulation conditions were the following. The amount of Fe in both smectite and illite is 0.33 atoms per formula unit, according to the calculated structural formula. The amount of K in the illite layers is 1.5 atoms per formula unit. The interlayer cation in smectite is Ca, but the results proved to be exactly the same using Mg or Na. The high and low values of N (number of layers per crystallite) are 7 and 4, respectively, and were chosen according to two facts: (1) the mean experimental value of N measured by means of the Scher-

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rer equation is 6, and (2) the best agreement with the experimental XRD pattern.

The presence of illite was also suggested by the occurrence of non-exchangeable K. The exchangeable K determined (Table 1) corresponds only to 0.02 atoms in the structural formula. The rest of the K is fixed in the interlayer. It could correspond to the interstratified illite. This possibility was tested as follows. Chemical analyses of mineralogically pure illites from Newman and Brown (1987) having less than 10% expandable layers were selected and their average weight percentage of K_2O was calculated. The average value was 8.24%. If this value is assumed to be the K composition of the interlayered illite in our sample, the total amount of illite present is 15%, in good agreement with XRD data.

DTA diagrams are shown in Figure 2. The first one (Figure 2a) corresponds to the original sample. It presents two dehydroxylation peaks. According to Mackenzie (1970) and SCIFAX DTA Data Index (1962) the peak occurring at lower temperature (560°C) corresponds to illite, and the one occurring at higher temperature (650°C) to montmorillonite. This assignment is confirmed for montmorillonite by other studies, which find it at temperatures above 600°C (Schultz 1969; Koster van Groos and Guggenheim 1987, 1989; Kloprogge *et al* 1990). The number of illite DTA analyses available in the literature is much lower. So, although the margin of illite dehydroxylation is less definitively established, the cited references reasonably agree in placing it in a lower range with respect to montmorillonite.

The DTA peaks were quantified as follows. The onset and end of the peaks were united by a straight line and the area under it was measured. As montmorillonite and illite have the same amount of hydroxyls, a measurement of the relative areas of their dehydroxylation peaks is a direct measurement of their relative amounts in the sample. The area of the peak at lower temperature was 11% of the total dehydroxylation peak area, i.e., of the summation of the two peak areas. This result completely agrees with the proportion of illite detected by means of XRD.

The accuracy of DTA peak area and peak position measurements is highly depending on peak shape. Sharp peaks can be placed and quantified with higher accuracy. Smectite dehydroxylation peaks, as those presented here, are generally broad. Nevertheless, repeated analysis of our samples showed no appreciable variation in the peak position. Differences in peak area were within 2%.

The effect of the different variables of the hydrothermal treatment on the DTA diagrams can be observed in Figure 2. Attention is focused only on the dehydroxylation peaks. The dehydration peak (around 200°C) decreases as K content in the reaction solution increases, as expected, because K enters the interlayer and causes its dehydration. The two dehydroxylation peaks are marked on the DTA diagram of the original material. The position of these peaks *in the original sample* is also marked on the DTA diagrams of the treated samples to make easier to follow the evolution of these peaks after treatment.

The montmorillonitic peak, at 650°C remained unaltered, but the illitic one, at 560°C was affected by the hydrothermal treatment. The main variable affecting it was K concentration in solution. A very high temperature and a long run time did not affect the dehydroxylation peak if K concentration was low (Figure 2b). A high K concentration made the illite dehydroxylation peak disappear independently of the other reaction conditions (compare Figure 2c–2f). The K adsorbed in the interlayer during the hydrothermal treatment could be removed in its totallity in all cases. No detectable K fixation occurred. When the run products were exchanged with Ca, the illitic dehydroxylation peak recovered again (Figure 2g and 2h).

These results show that *exchangeable K,* situated in the adjacent smectitic interlayers, interacts in some way with hydroxyls in the illitic layers displacing their evolution temperature to higher ranges, which coincide with montmorillonite hydroxyl loss.

The absence of detectable K fixation after the hydrothermal runs indicates that no observable transformation of the smectite layers happened. This is supported by the fact that the changes produced on the DTA diagrams after treatment were reversible by Ca exchange. Those changes were not due to structural transformation, but simply to K exchange. Additional evidence for the lack of observable transformation was obtained by means of FTIR and NMR (experimental study still in progress). Nevertheless, XRD analysis of the products (Figure 3) showed a gradual increment of the presence of illite with temperature, K concentration and run time, up to a value of 30% of illite layers for the extreme conditions. These results are in contrast with those given by all other techniques. For that reason we considered that the apparent transformation detected by XRD is due to other effects produced during the hydrothermal treatment. The mean crystallite thickness of run products, measured by means of the Scherrer equation, diminished with hydrotheral treatment. Also, it is possible that the crystallite area in the *ab* plane diminished in the same way, as it is suggested by the increase of the intensity of the non-basal reflection at 4.5 Å (Figure 3) with reaction conditions. Smaller crystallites in the *ab* plane would likely have a worse orientation on the glass slide, and non-basal reflections would be enhanced. Some authors have already reported that XRD patterns are effectively affected by variables as mean crystallite thickness and crystallite size in the *ab* plane, and by crystallite size distribution (Ross 1968, Lanson and Velde 1992, Eberl *et al* 1993).

It seems that hydrothermal treatments, as those typ-

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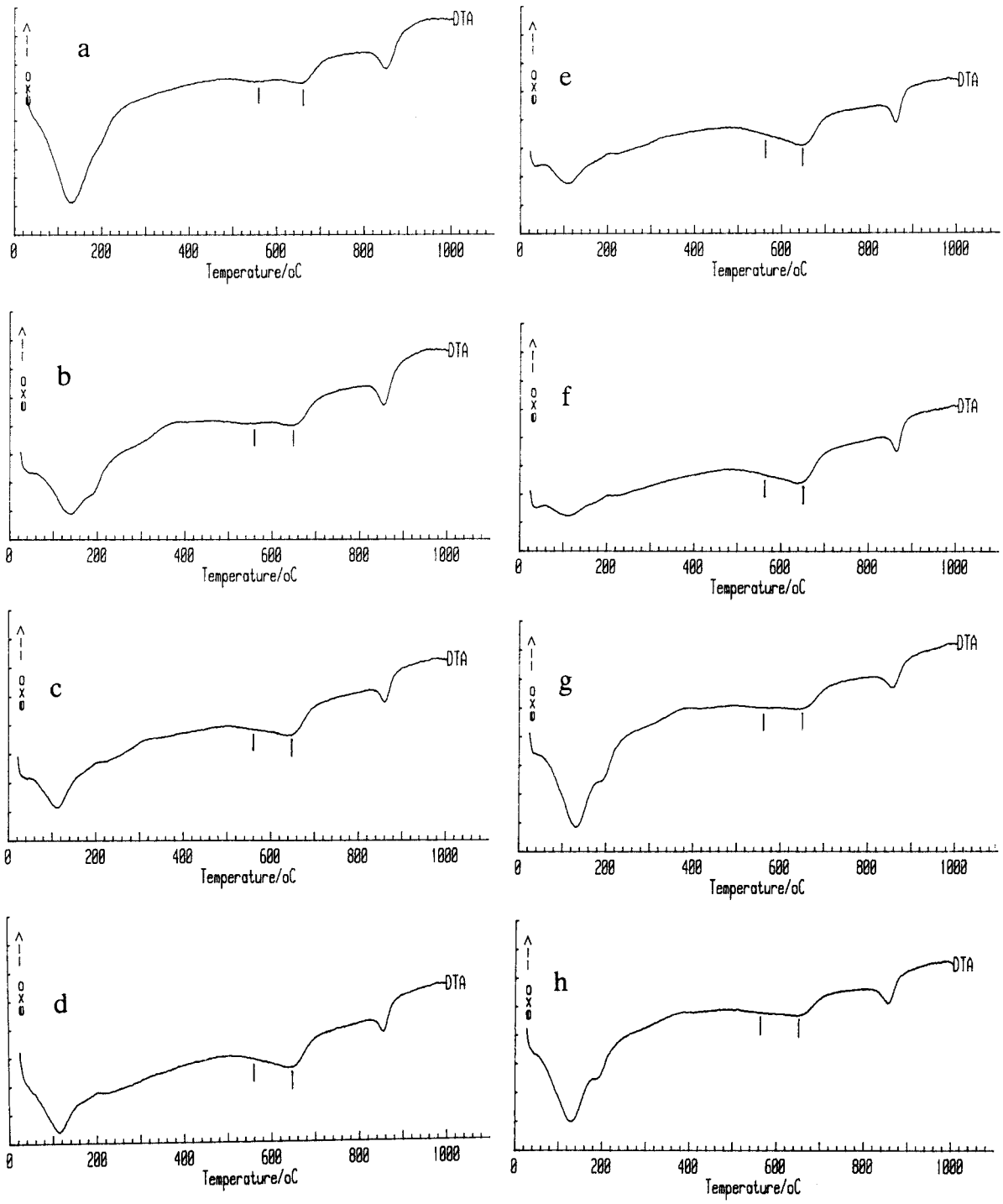


Figure 2. DTA diagrams of the (a) starting material and run products (b) 0.025 M KCl, 200°C, 180 days; (c) 1 M KCl, 60°C, 5 days; (d) 1 M KCl, 60°C, 180 days; (e) 1 M KCl, 200°C, 30 days; (f) 1 M KCl, 200°C, 180 days; (g) 1 M KCl, 60°C, 5 days, exchanged with Ca after reaction; (h) 1 M KCl, 200°C, 180 days, exchanged with Ca after reaction. The lines mark the dehydroxylation peak temperatures of the starting material to show the evolution of dehydroxylaion behaviour after treatment.

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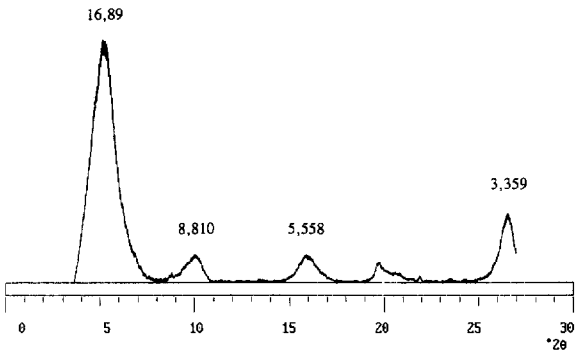


Figure 3. XRD patterns of the glycolated hytdrothermal run product corresponding to 1 M KCl, 200°C, 180 days.

ically carried out in the laboratory, can modify the particle size distribution in such a way that XRD patterns can be seriously affected. We will focus on XRD results of the original material and on the DTA analysis.

DISCUSSION

The results of XRD of the oriented aggregate and DTA are now discussed in relation with the structure of I/S. Consider the non-polar layer concept. Each TOT unit is symmetric regarding the tetrahedral sheet charge. As it was stated before, this concept raises the problem of whether a specific interlayer will swell or not. Now, we assume that the interlayer collapses if one of the tetrahedral sheets around it is illitic. This is shown in Figure 4a. In this case, each illitic TOT unit originates two illitic interlayers, so the number of illitic interlayers is twice the number of illitic octahedral sheets. In our study, XRD and DTA "saw" the same number of illite layers (11%). As XRD "sees" the interlayer, and DTA "sees" the octahedral sheet, this model is not compatible with our results. Consider now that interlayers only collapse if the two tetrahedral sheets around them are illitic. This is shown in Figure 4b. In this case, two consecutive illite TOT units are necessary to originate one illitic interlayer. Again, the number of illitic interlayers cannot be the same as that of illitic octahedral sheets. In this case the number of illitic octahedral sheets is twice the number of illitic interlayers. This model is not compatible with our data, either.

The polar layer model is shown in Figure 4c. In this case some octahedral sheets are between tetrahedral sheets of different character, smectitic or illitic. It is likely that illitization of those octahedral sheets has begun, forced by the presence of the illitic tetrahedtral sheet, but not completed. In this case there would be domains of illitic character together with zones of smectitic character. If we assume that each of these domains comprises approximately 50% of the octahedral sheet, the number of illitic interlayers and illitic octahedral sheets coincides. Although in this case there

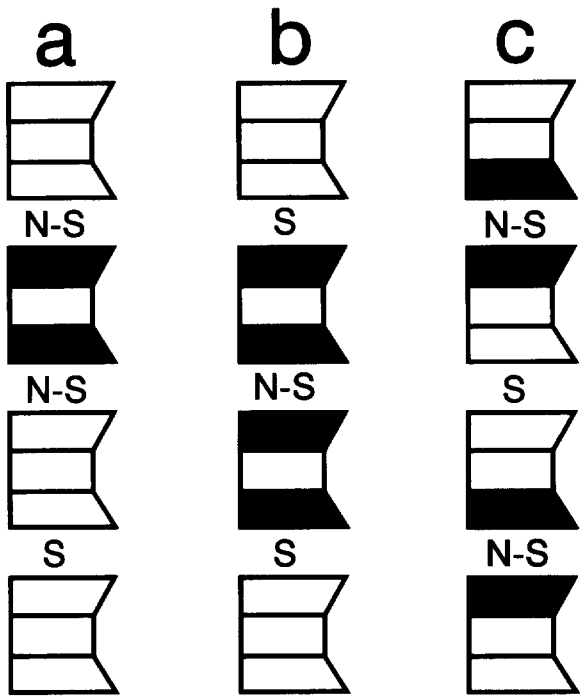


Figure 4. Sketch of models of I/S. Black tetrahedral sheets are illite-type and white ones are smectite-type. "S" stands for swelling interlayer and "N-S" for non-swelling interlayer.

are no complete illitic octahedral sheets, but octahedral units with domains of smectitic and illitic character. Hydroxyls in illitic or smectitic domains would behave in different ways during DTA analysis. This model is compatible with our results from XRD and DTA.

There is no problem in considering the presence of those domains in the octahedral sheet in a polar layer. The presence of domains in the octahedral sheet of 2:1 phyllosilicates has already been reported (Dainyak *et al* 1992; Grauby *et al* 1993, 1994). It is likely that the higher charge in an illitic tetrahedral sheet, or the charge distribution, forces the transformation of the octahedral sheet. This transformation could include composition, site occupancy (cis-trans) and charge distribution.

The other effect shown by DTA analysis is that exchangeable K interacts with hydroxyls in the illitic layers and alters their dehydroxylation behaviour. This interaction is only possible if exchangeable K can enter the interlayers adjacent to the illitic octahedral sheets or domains. The model of symmetric layers in Figure 4a in which interlayers collapse if one of the surrounding tetrahedral sheets is illite-type, prevents this interaction. The symmetric layer model in which collapse occurs only if the two adjacent tetrahedral sheets are illitic (Figure 4b) and the polar layer model (Figure 4c) permit the interaction K-hydroxyl through the interlayers labelled with S (swelling) in the figure.

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So far, we have implicitly considered the classic model of mixed-layer I/S, i.e. the MacEwan crystallite, in which smectitic and illitic layers, whatever their actual structure be, stack in variable proportions and ordering. The *fundamental particle* concept offers a different view. The interstratified I/S is regarded as a distribution of particles formed by coherently united layers. The interlayers within this particles behave as illitic ones. The contact surfaces between different particles behave as smectitic interlayers. To represent a random mixed-layer I/S with low illite content, like the sample in this study, through the fundamental particle model, it would be necessary a major population of single TOT units plus an appropriate number of other particles formed by two TOT units. The disordered stacking of both particles would generate the experimental XRD pattern.

The fundamental particle model views the particles as homogeneous in composition, and so each TOT unit as symmetrical. The scheme can be the one shown in Figure 4b. The two central TOT units form a 20 Å, illitic particle. The TOT units above and below are two single TOT units. The contact surface with both of them behaves as a smectitic interlayer. As it was shown before, this model is not compatible with our XRD and DTA results. So, they suggest that our randomly interstratified I/S is formed by MacEwan crystallites rather than by fundamental particles.

Now, a new question rises: why K exchange produces alterations in the dehydroxylation behaviour of illitic octahedral sheets? Precisely, K is the main interlayer cation in illite. This question cannot be answered now. Nevertheless, it can be speculated that exchangeable and fixed K are not located in equivalent positions with respect to hydroxyls in an illitic octahedral sheet. For example, the distances between K and OH groups may vary. Perhaps the configuration, total charge and charge distribution of an illitic tetrahedral sheet have a role in the K-OH interaction. New studies concerning K location and OH orientation in smectites and illites will be necessary to have a more accurate description of what we call mixed-layer I/S.

CONCLUSIONS

The comparison of the quantification of illite percentage in a random I/S by means of XRD and DTA, together with the effect of exchangeable K on illitic layer dehydroxylation, can only be interpreted after the polar layer concept of mixed-layer I/S. The symmetric layer concept is inconsistent with these experimental results. For the same reason, the *fundamental particle* model is not appropriate to describe an interstatified I/S like this.

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