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An experimental alteration of montmorillonite to a di + trioctahedral smectite assemblage at 100 and 200°C

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ABSTRACT: Hydrothermal experiments were performed at 100 and 200°C and at different clay:water ratios in order to investigate the transformation of smectitic layers during the alteration of a montmorillonitic starting material. This study focused on three phenomena: (1) the amount and localization of charge within the layer of the newly-formed dioctahedral smectite; (2) the stacking of low- and high-charge layers in the dioctahedral smectitic material; and (3) the neoformation of trioctahedral smectites.

In all of the runs, the formation of beidellite from montmorillonite induced morphological changes in clay particles which suggests a reaction proceeding by a dissolution-crystallization mechanism. Illite layers were detected in K-saturated montmorillonite runs after the transformation of ~50% of the starting montmorillonite into beidellite (i.e. after 5 months of reaction with distilled water at 200°C). These illite layers were interstratified with both high-charge and low-charge dioctahedral smectites in a hypothetical three-component mixed-layer mineral.

KEYWORDS: montmorillonite, beidellite, illite-smectite, experimental illitization.

The smectite-to-illite reaction, which proceeds via an intermediate mixed-layer series (illitization), has been well documented by clay mineralogists through studies of natural samples and hydrothermal experiments. From the literature it appears that illitization is a complex phenomenon considered as an overall reaction controlled by several poorly understood processes: solid state transformation, dissolution-crystallization, Ostwald ripening, or crystal growth and coalescence (Whitney & Velde, 1993; Altaner & Ylagan, 1997; Meunier *et al.*, 2000). Hydrothermal experiments give an insight into the chemical and physical variables which affect the rate of the overall

reaction (Eberl *et al.*, 1978; Howard & Roy, 1985; Whitney & Northrop, 1988; Guven & Huang, 1991). Several kinetic models have been proposed (Pytte & Reynolds, 1989; Huang *et al.*, 1993, among others). However, such models (which aimed to fit the multiple-step reaction of illitization with a kinetic expression using a single rate law) remain questionable (Meunier *et al.*, 1998). Indeed, numerous studies which proved changes in the layer charge of smectites subjected to hydrothermal treatments (Howard & Roy, 1985; Whitney & Northrop, 1988) or diagenetic conditions (Sato *et al.*, 1996) were based on the assumption that the smectitic layers remain unchanged (i.e. montmorillonite) while the illite layers were formed in the I-S series. Little attention has been paid to the transformation processes which affect the smectitic material prior

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to the occurrence of illite layers (i.e. prior to the identification of true I-S mixed layers by X-ray diffraction (XRD)).

The purpose of the present study is to provide insights into the transformations which affect a montmorillonite starting material at the beginning of montmorillonite-to-illite reaction under hydrothermal conditions. Several hydrothermal experiments were performed at 100 and 200°C and at different clay:water ratios and our crystal-chemical investigations of the products were based on XRD and transmission electron microscopy (TEM) analyses.

EXPERIMENTAL PROTOCOL AND ANALYTICAL TECHNIQUES

Two series of experiments were conducted in batch reactors. The first series investigated at 100 and 200°C the reaction of a mixture of quartz (Montredon-Labessonnié, France), sanidine (Rhineland, Germany) and Na-montmorillonite (Crook County, USA) with an aqueous solution at neutral pH. The experiments were conducted under saturated water vapour pressure in Savilex® teflon vials. At each temperature, several hermetically closed vials corresponding to different water:rock ratios were introduced with water in a Parr® hydrothermal vessel and held at constant temperature for 39 to 330 days. After completion of the run, the vials were opened and the progress of reaction was monitored by analysing both the solution and the

clay fraction. The starting solids were prepared as follows. The quartz and sanidine samples were crushed, sieved for grain size (0.2–1 mm and 0.25–0.5 mm respectively) and cleaned ultrasonically to remove fine particles. The bulk smectitic material was used without treatment. Its chemical composition, determined by ICP-AES, indicated that it was a mixture of Na-montmorillonite with minor amounts of quartz, K-feldspar, calcite and mica, also detected by XRD analysis. The starting solution contained 23 ppm Si for the 100°C runs and 103 ppm Si for the 200°C runs in order to be saturated with respect to quartz from the beginning of the runs. These starting concentrations were obtained by dissolving appropriate amounts of Backer® silicic acid in deionized water under hydrothermal conditions. We assumed that such concentrations, below or close to the amorphous silica solubility at 25°C, did not allow the polymerization of aqueous silica during stocking at room temperature before the runs. Several experiments were conducted at various solution:solid mass ratios ranging from 0.7 to 2. The relative proportion of the constituents in the starting assemblages was 47 to 50% for quartz and feldspar and 0.5 to 5% for the bentonite. These conditions are assumed to broadly model arkosic sediments.

The second series of experiments investigated the water-smectite reaction. The starting material was the <0.1 µm fraction of the Crook County bentonite, extracted from bulk material by centrifugation. The XRD patterns (Fig. 1) indicated that

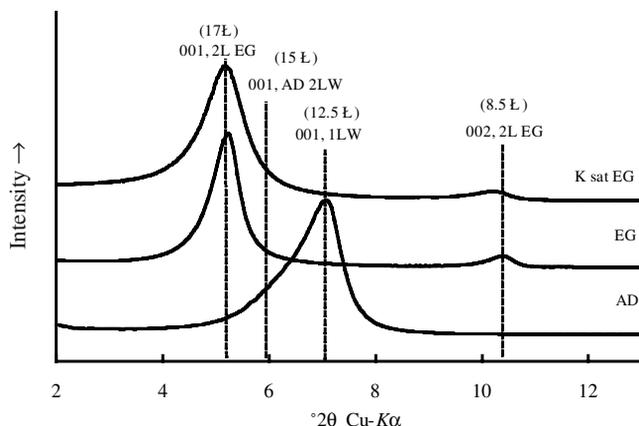
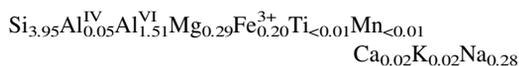


FIG. 1. XRD patterns of the starting material (Crook County bentonite). AD = air dried, EG = after ethylene-glycol solvation, K sat EG = after K saturation and ethylene-glycol solvation, 2L W = interlayer cation hydrated by two sheets of water, 1L W = interlayer cation hydrated by one sheet of water, 2L EG = interlayer cation hydrated by two sheets of ethylene glycol.

this fraction was composed of a nearly pure smectite. It was a naturally Na-saturated montmorillonite in which <10% of the layers are high-charged ones (reversibly collapsed to 10 Å in the K-saturated state). The structural composition calculated from the microprobe analyses of the <0.1 µm fraction of the Crook County bentonite was consistent with a low-charge montmorillonite (i.e. very low tetrahedral charge <0.05, interlayer charge of 0.34 for 11 oxygens):



The K- and Ca-saturated samples were obtained by dispersion of the smectite in 1 N KCl or CaCl₂ solutions followed by repeated washings with distilled water. 50 mg of each smectite were reacted at 100 and 200°C for 90 to 150 days with 5 ml of the same starting solution as that in the previous series of experiments.

Solution analysis

At the end of the experiments, 200 µl of the reacted solution were sampled, diluted in 2 ml deionized water and immediately ultrafiltered through Centricon[®]-10 filters (10,000 da). The aqueous silica concentration was measured using the molybdate colorimetric method (Strickland & Parsons, 1972). The dissolved Al and K concentrations were measured by atomic adsorption/emission spectroscopy (Perkin-Elmer Zeemann 5000), in flame for K or in graphite furnace for Al, after addition of 2% HNO₃. The pH was measured in the Savilex[®] vials, immediately after the sampling of the solution, using an Ingold[®] micro-electrode. However, in the runs conducted with more than 0.05 g of smectite per g of solution, the final solution could not be retrieved (because of the formation of 'gel') and there are no solution data for these experiments.

Solid analysis

XRD patterns for the solids were obtained at ambient conditions using oriented powder preparations on a Siemens D501 diffractometer equipped with a stepping motor drive on the goniometer and a KEVEX PSI counting system. Motor and intensity acquisition were monitored using a Socabim DACO system. Diffracted-beam-monochromated Cu-Kα was used (30 kV, 50 mA). The divergence slit, receiving

slit and scatter slit were 1°, 0.1 mm and 1°, respectively. The experimental conditions used for XRD were the following: angular range 2–30°2θ Cu-Kα; (44.00–2.98 Å); step size 0.02°2θ Cu-Kα; counting time 5 s/step. No smoothing procedure was applied to the XRD patterns.

Clay mounts from run products were X-rayed in the air-dried (AD) state at ambient relative humidity conditions and after solvation with ethylene glycol (EG) under low-vacuum conditions for 12 h. The glycolated samples were then dried to drive off the ethylene-glycol complex and saturated with Ca (run products having incorporated K during the experiments) or K and then Ca (other runs) before being glycolated and X-rayed again (the K-samples were heated to 110°C overnight prior to EG solvation according to the procedure published by Bouchet *et al.*, 1988).

On the basis of the XRD procedure above, three types of layers were distinguished: (1) low-charged layers which always remain fully expandable; (2) high-charge layers which collapse to 10 Å after K saturation but re-expand to 17 Å after Ca saturation; and (3) illite layers which remain irreversibly collapsed to 10 Å in all cases. The relative proportions of the different layers in the run products were estimated by comparison of experimental XRD patterns with simulated ones (NEWMOD program; Reynolds, 1985). According to Schultz (1969), the formation of a double-layer EG complex (17 Å) occurs if the layer charge per half unit is 0.43 or less. The Greene-Kelly test was used to evaluate the relative proportions of tetrahedral and octahedral charges (Greene-Kelly, 1953).

The TEM examination of very small particles was performed using a JEOL 100C device. Carbon-coated Cu grids were prepared with the <1 µm clay fraction dispersed ultrasonically in deionized water. Semi-quantitative chemical analyses of individual particles were performed using a Philips CM120 transmission electron microscope by means of X-ray analysis (EDS) using a scanning transmission electron microscope (STEM) mode and a standard-less procedure (EDAX).

RESULTS

Fluid chemistry

The pH and the concentration of silica, Al and K of the reacted solutions (when extraction was possible) are reported in Table 3 as a function of

the experimental conditions. Except in one run, the pH values increased slightly during the runs, from 5.7 (equilibration with atmospheric CO₂) to 7–8 at 100°C and to 6–7 at 200°C. Aqueous silica exhibits more significant variations. In the bulk system, Si concentration remained close to the quartz solubility at 200°C. At 100°C, by contrast, it increased strongly at the beginning of the run and then decreased with time towards the quartz solubility. In the purified clay system, the concentration of aqueous silica increased strongly to 55 ppm Si at 100°C and 275 ppm Si at 200°C, which corresponds to the solubilities of β -cristobalite at 100°C and 200°C, respectively. A possible explanation is that the purified clay fraction concentrated the finest

particles and therefore the less crystallized but more reactive phases. The Al and K show steady state values in the bulk system, one order of magnitude greater than in the purified system. This probably reflects a chemical control of these elements by the detrital K-feldspar and mica.

X-ray diffraction

Reaction of bulk bentonite with sanidine, quartz and water. The XRD patterns of the starting material (Fig. 1) and the reacted samples from runs at 100 and 200°C are different (XRD patterns of the reacted products obtained after experiments at 200°C are presented in Fig. 2).

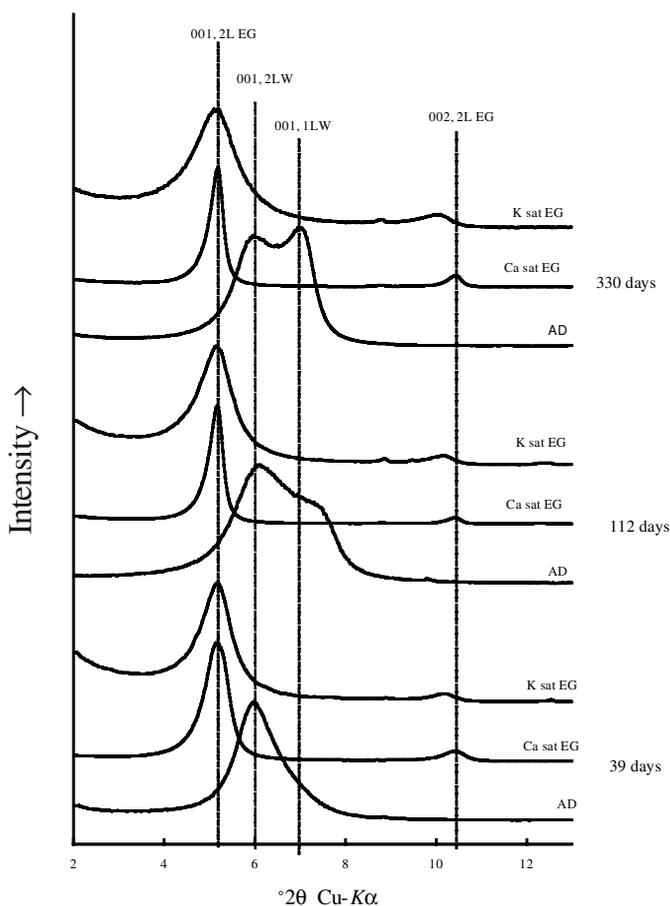


FIG. 2. XRD patterns of the reacted products obtained after three different runs (at 39, 112 and 330 days) of hydrothermal treatment of the Crook County bentonite at 200°C in presence of sanidine and quartz. Ca EG = after Ca saturation and ethylene-glycol solvation.

The (001) reflection of the starting Na-montmorillonite is centred near 12.5 Å in AD conditions (one water layer). However, it is weakly asymmetrical toward the lower angular range. This suggests the presence of minor amounts of smectitic component with two water layers (15 Å). The (001) reflections of the reacted samples are typical of an interstratification between the two hydration states. The relative proportion of each hydration state changes with the duration of the reaction: at 200°C for example, the two-layer hydration state predominates largely up to 39 days of reaction whereas the one-layer hydration state increases significantly after 112 days and predominates after 330 days of reaction.

After glycolation, the XRD patterns of the starting material and all the Ca-saturated reacted samples are similar. They are typical of a 100% expandable smectite with rational (001) and (002) reflections at 17.02 Å and 8.50 Å, respectively.

After glycolation, the XRD patterns of all the K-saturated samples (starting and reacted material) are characterized by a broad (001) reflection and a deviation from the rationality of the basal reflections. This indicates a random mixed layering of variable amounts of high-charge smectite layers (reversibly collapsed to 10 Å in the K-saturated state) with low-charge layers (always fully expandable). As summarized in Fig. 3, the proportion of high-charge layers increases with run duration and/

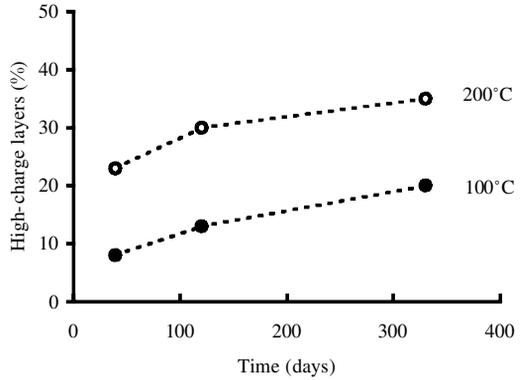


FIG. 3. Variation of the proportion of high-charge layers (H.C.) in the reacted products obtained after hydrothermal treatment of the Crook County bentonite in the presence of sanidine and quartz as a function of temperature and run duration.

or temperature. It increases progressively, from <10% in the starting material up to 20% and 35% after 330 days of reaction at 100 and 200°C respectively. The Greene-Kelly test indicates that, in the reacted samples, the amount of tetrahedrally-charged layers (beidellite) increases with increasing reaction time. Nevertheless, they are always associated with octahedrally-charged layers (unreacted starting montmorillonite, Fig. 4a).

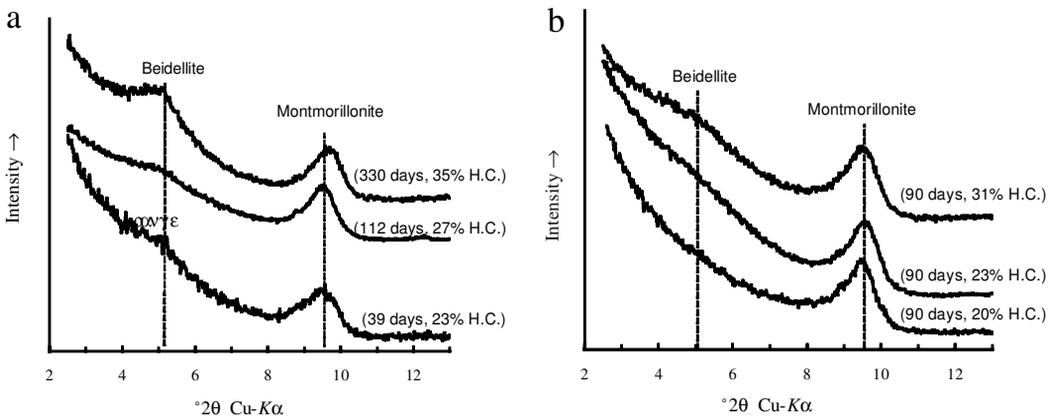


FIG. 4. XRD patterns of the reacted products after the Greene-Kelly test. (a) After hydrothermal treatment of the Crook County bentonite at 200°C in the presence of sanidine and quartz. (b) After hydrothermal treatment of the K-saturated <0.1 μm fraction of the Crook County bentonite at 100°C in the presence of water saturated in Si vs. quartz. The run duration and percentage of high-charge (H.C.) layers are given in parentheses and the index reflections of montmorillonite (solid line) and beidellite (dashed line) are shown.

The 90 day runs at 100°C using <0.1 μm samples. The XRD patterns of the reacted samples from hydrothermal experiments (3 months at 100°C) are quite similar in the Ca-saturated state (Fig. 5): they are typical of a 100% expandable smectite with rational (001) and (002) reflections. The proportion of high-charge layers (Table 1) is the highest (31%) for K-saturated starting montmorillonite and the lowest for Ca- and Na-saturated ones (23 and 20% respectively). The Greene-Kelly test indicates that larger amounts of tetrahedrally-substituted smectites were formed from the K-saturated starting material (Fig. 4b).

The 150 day runs at 200°C using <0.1 μm samples. The reaction of the K-saturated starting material produces illite layers which are interstratified with the smectitic ones. The broad and weak superstructure which appears near 24 Å on the AD diffraction pattern, shifts toward 27 Å after ethylene-glycol solvation (Fig. 6). This is typical of regularly-ordered I-S mixed layers ($R = 1$). However, the rational reflections of this I-S ($R = 1$) mixed layer are partly hindered by the basal reflections of smectites and/or randomly mixed-layer I-S which are also present in the reacted material. Such a mixture of clay minerals gives complex and

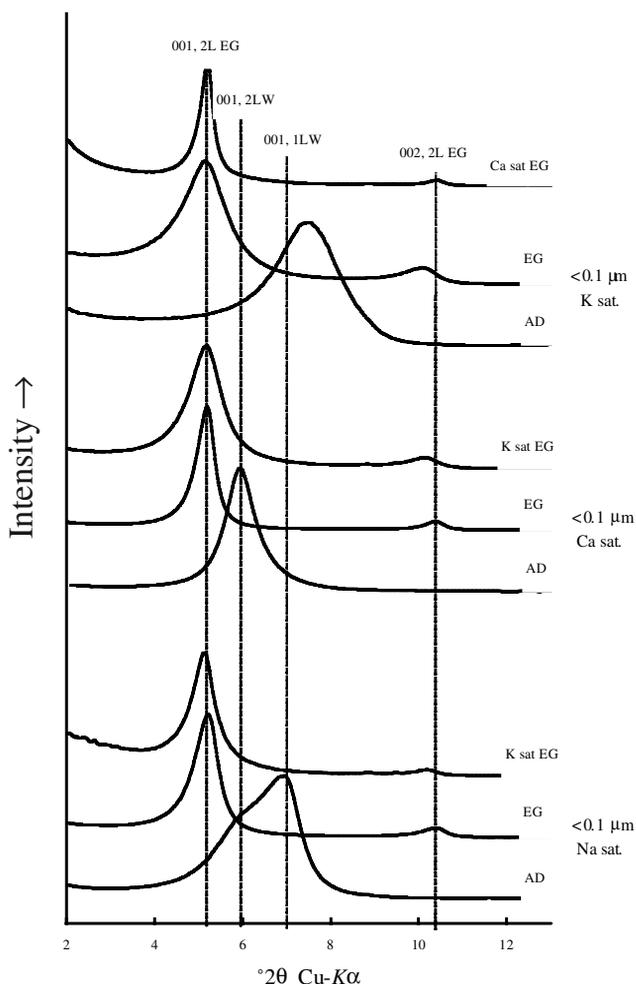


FIG. 5. XRD patterns of the reacted products obtained after hydrothermal treatment of the <0.1 μm fraction of the Crook County bentonite for 90 days at 100°C in the presence of water saturated in Si vs. quartz. Na sat = Na-saturated starting material, Ca sat EG = after Ca saturation and ethylene-glycol solvation, K sat EG = after K saturation and ethylene-glycol solvation.

TABLE 1. Percentage of high-charge layers (collapsed to 10 Å after K-saturation, heating to 110°C, and EG solvation) produced in the purified Crook County montmorillonite (<0.1 µm fraction, 10 mg/ml) as a function of time/temperature and the nature of the compensating cation.

Experimental conditions	Ca-saturated	Na-saturated	K-saturated
90 days at 100°C	20	23	31
150 days at 200°C	35	38	50

asymmetric XRD reflections with maximum intensities near 16 and 9.06 Å. The position of the maximum intensity of the (002) and (003) XRD

reflections (9.06 Å and 5.40 Å, respectively) indicates that ~50% of the layers were collapsed to 10 Å. However, the XRD pattern of same sample after Ca

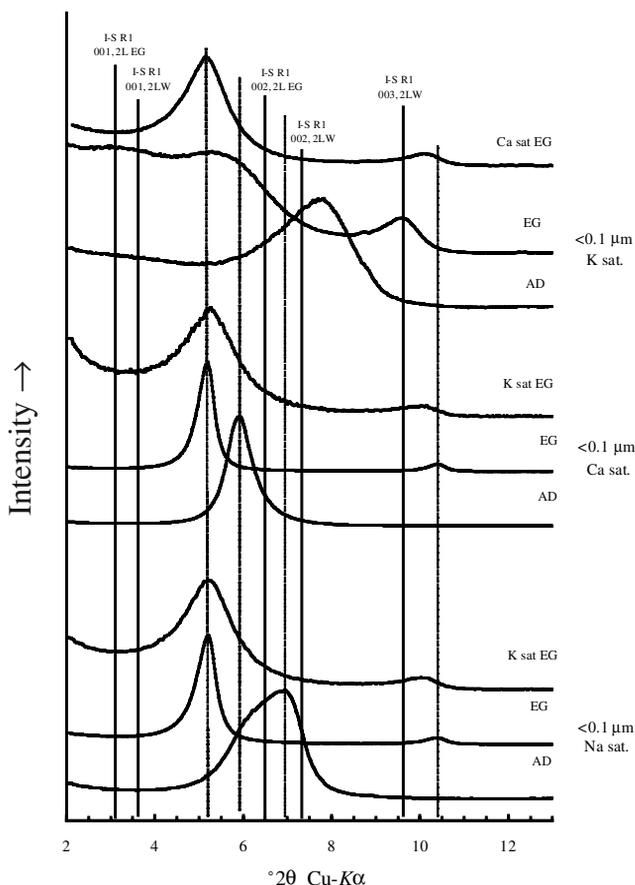


FIG. 6. XRD patterns of the reacted products obtained after hydrothermal treatment of the <0.1 µm fraction of the Crook County bentonite for 150 days at 200°C in the presence of water saturated in Si vs. quartz. The index positions of the XRD reflections of I-S (R = 1) with 50% of fully expandable layers are illustrated by the solid lines and those of 100% expandable smectite are illustrated by dashed lines.

saturation and then after glycolation, is significantly different: the position of the maximum intensities of the (001), (002) and (003) reflections have shifted toward 17, 8.70 and 5.55 Å respectively. This is typical of randomly oriented I-S ($R = 0$) mixed-layers with 25% of illite (i.e. 25% of the layers remained irreversibly collapsed to 10 Å).

The XRD patterns of the Na- and Ca-saturated starting materials, reacted for 150 days at 200°C, are quite similar and characteristic of a 100% expandable smectite with 35 and 38% of high-charge layers, respectively.

Textural and compositional variations of the clay particles. The TEM micrographs of particles (<0.1 µm fraction) are presented in Fig. 7. Both morphology and size change with the nature of the interlayer cation. The Na-saturated smectite particles are frequently elongated and sometimes lath shaped. The Ca-saturated smectite particles are thicker (more opaque to the electrons) and consist of packets of subhexagonal plates. The K-saturated smectite particles present a ragged and frayed aspect which reveals a random spatial arrangement due to a high degree of deformation.

The TEM observations indicate that the morphological characters of the clay particles obtained from both types of experiments change with increasing temperature and/or reaction time. The particles of the reacted products tend to become euhedral, i.e. hexagonal in shape (Fig. 8). Such a morphological change is accompanied by aggregation and stacking of individual subhexagonal plates forming coarse multiparticle structures. These structures are similar to the island-and-step patterns indicative of a dissolution-precipitation process.

The particle semi-quantitative chemical analyses of the starting product are constant whereas they are highly variable for the reacted products of all our experiments. Three compositional poles have been found on the basis of EDS spectra (Fig. 9) and calculated Si:Al and Si:Mg ratios (Table 2): (1) the chemical composition of the starting montmorillonite; (2) the chemical composition of beidellite which differs from the starting montmorillonite in having a lower Si:Al ratio and Mg content; and (3) the chemical composition of trioctahedral smectites (saponite or stevensite) characterized by high Mg and very low Al contents. The intermediate chemical compositions between montmorillonite and beidellite have frequently been measured in euhedral particles. Type 1 and 2 particles are the most numerous. Type 3 particles are scarce.

DISCUSSION

Formation of high-charge beidellitic layers

The present study indicates that illitic layers were formed in restricted conditions: i.e. from K-montmorillonite after 5 months of reaction at 200°C. In all the other runs, significant structural transformations and compositional change occurred but no illitic layers were formed. In the absence of (or prior to) the formation of illite layers, the most obvious transformation is the development of high-charge expandable layers replacing the low-charge layers of the starting montmorillonite.

The amount of high-charge layers increased with increasing temperature and run duration (Fig. 3) and was enhanced when clays previously saturated with K were used (Table 1). These results are consistent with previous studies: (1) Howard & Roy (1985) indicated that high-charge layers were formed when montmorillonite reacted at 150 and 250°C, even in K-deficient systems; and (2) Eberl (1978) and Whitney (1992) stated that the formation rate of high-charge layers is promoted by an increase of K-content in the system. However, it should be noted that this transformation progressed at a slower rate in the bulk bentonite systems (cf. Fig. 3 and Table 1). This rate difference can be explained by differences in the solution chemistry between the two experimental series. The greater Al concentration in the bulk systems, when compared to the purified systems, probably decreased the reaction rates since Al is well known to be an inhibitor of dissolution of aluminosilicates. (Oelkers *et al.*, 1994). The formation of high-charge layers is obviously linked to an increase in the tetrahedral charge (Fig. 4). Nevertheless, at present, a question remains: is the tetrahedral charge added to the octahedral charge of the starting montmorillonite by

TABLE 2. Average values of Si:Al and Si:Mg ratios measured in the different clay particles of the reacted products from hydrothermally-altered Crook County montmorillonite (TEM analyses).

	Si:Al	Si:Mg
Montmorillonite	≈ 1.9	≈ 10
Beidellite	≈ 1.25	>100
Stevensite/saponite	≈ 40	<1.6

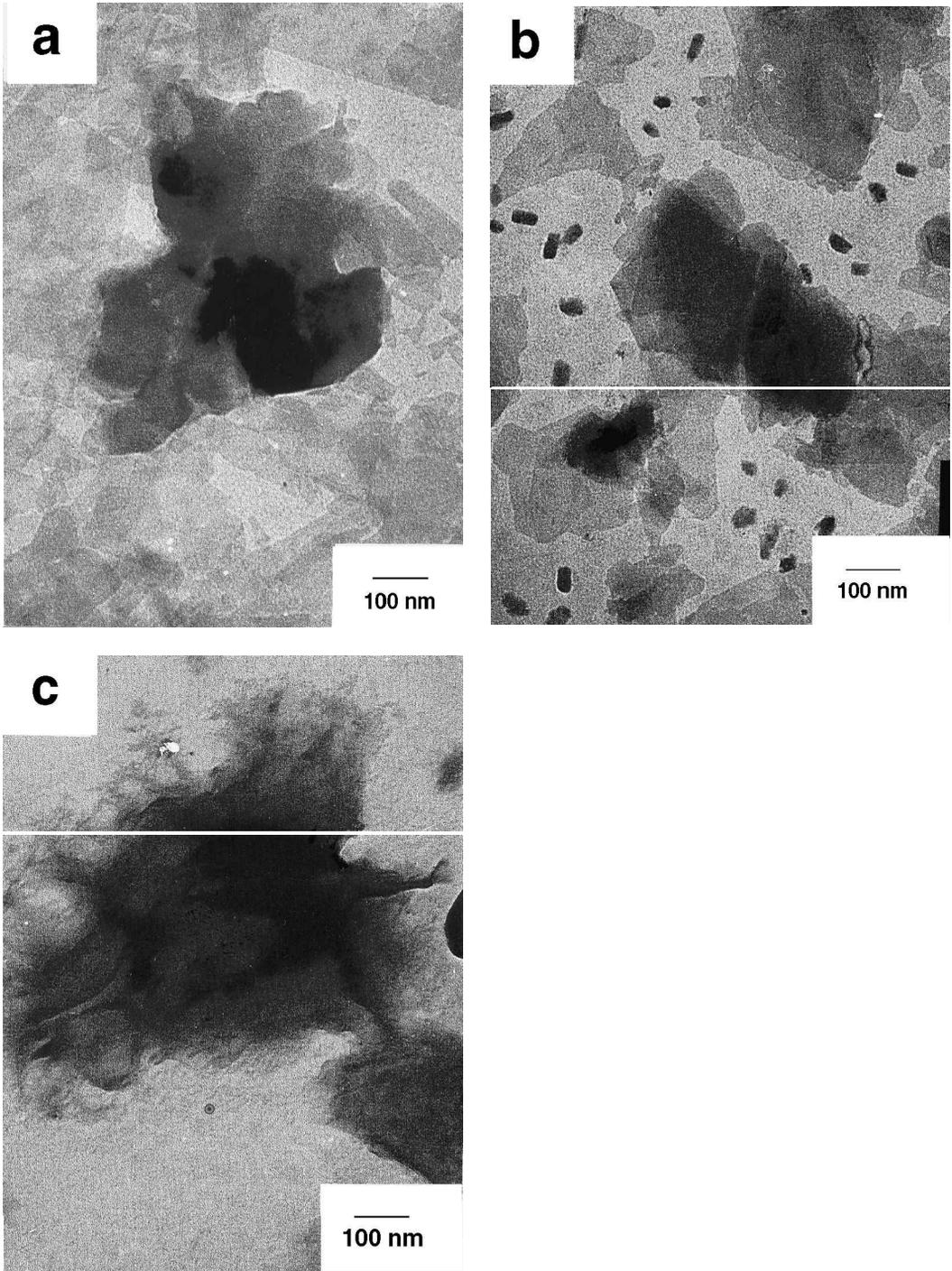


FIG. 7. TEM photomicrographs of the $<0.1 \mu\text{m}$ fraction of montmorillonite particles from the Crook County starting material. (a) Particles of Na-saturated starting material. (b) Particles of Ca-saturated starting material. (c) Particles of K-saturated starting material.

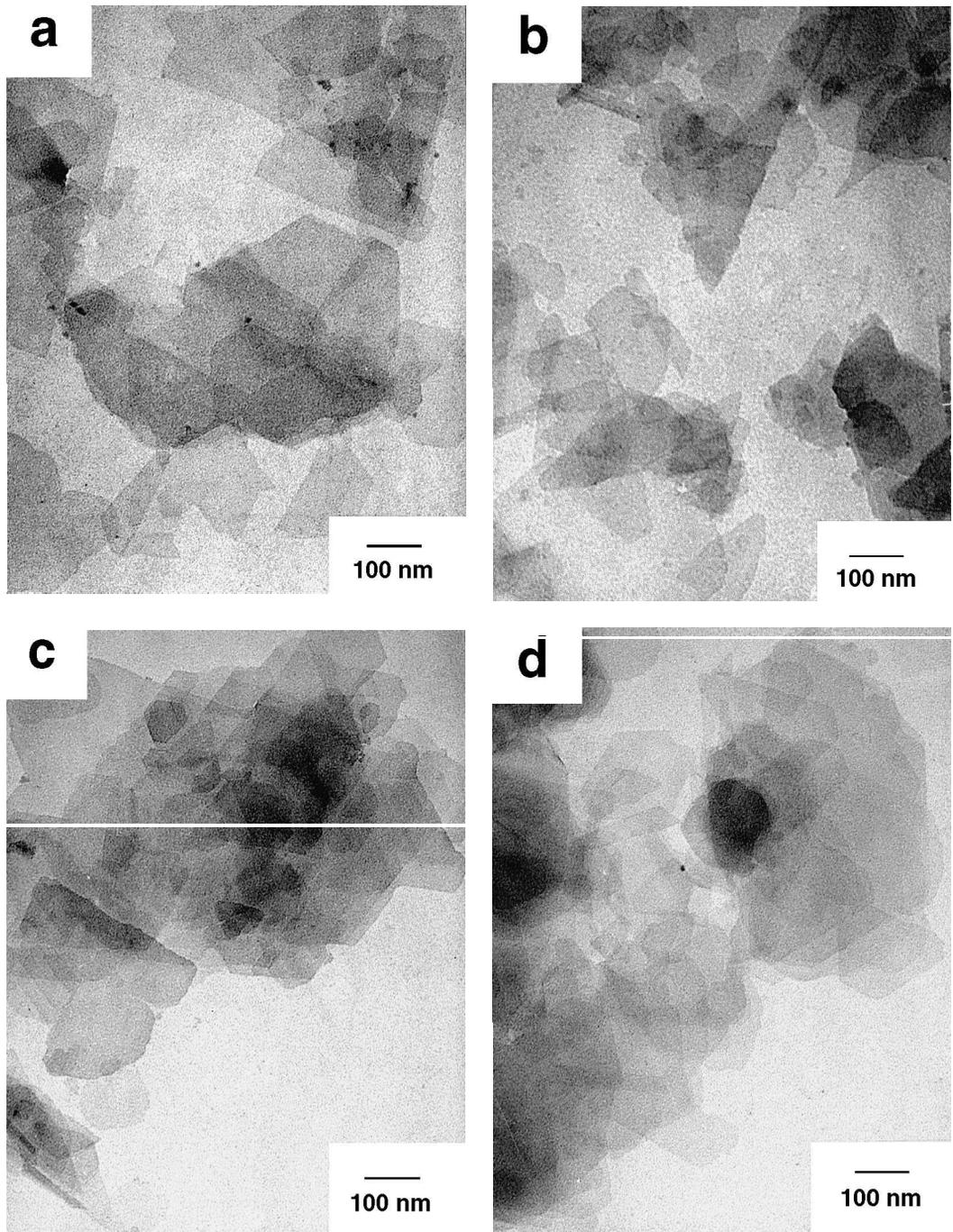


FIG. 8. TEM photomicrographs of clay particles after hydrothermal reaction of the $<0.1 \mu\text{m}$ fraction of the Crook County starting material. (a) Reacted product of hydrothermal treatment of bulk bentonite with sanidine, quartz and water for 330 days at 200°C . (b) Reacted product of hydrothermal treatment of K-saturated starting material for 90 days at 100°C . (c) Reacted product of hydrothermal treatment of K-saturated starting material for 150 days at 200°C . (d) Reacted product of hydrothermal treatment of Ca-saturated starting material for 150 days at 200°C .

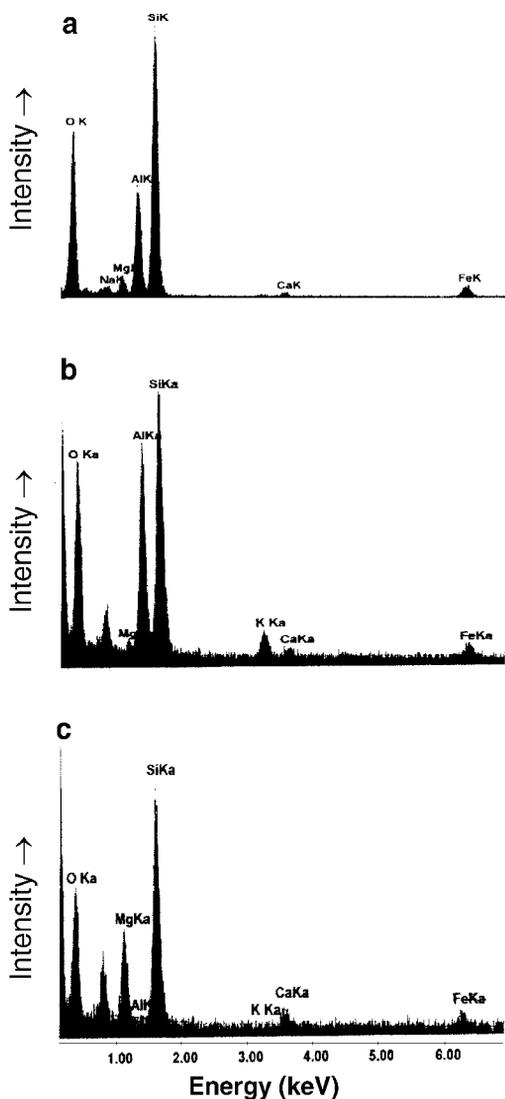


FIG. 9. EDS spectra of different types of clay particles analysed in this study. (a) Montmorillonite particle in Na-saturated $<0.1 \mu\text{m}$ fraction of the Crook County bentonite. (b) Beidellite particle in reacted product of hydrothermal treatment of the bulk bentonite with sanidine, quartz and water for 330 days at 200°C . (c) Saponite/stevensite particle in reacted product of hydrothermal treatment of the Ca-saturated $<0.1 \mu\text{m}$ fraction of the Crook County starting material for 157 days at 200°C .

a solid state transformation process or does it result from the growth of a dioctahedral smectite controlled by a dissolution-crystallization process?

The STEM analyses (Fig. 9, Table 2) give evidence of particles having beidellitic composition or mixed montmorillonite-beidellite composition in most of the reacted smectitic materials.

The formation of an additional layer charge in the tetrahedral sheet of smectite by the substitution of Al for Si is considered to be a step in the illitization process (Eberl & Hower, 1976). High-charge expandable layers resulting from the formation of tetrahedral charges from a low-charge montmorillonitic reacted material was experimentally investigated by Howard & Roy (1985). Sato *et al.* (1996) described the formation of tetrahedral charges causing the conversion of montmorillonite to beidellite in the early diagenetic stages of shale and sandstone from the Eocene sedimentary formations in Japan.

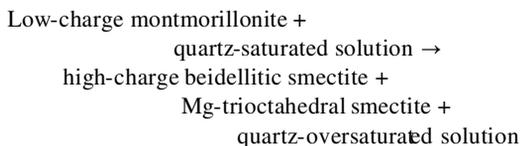
The TEM observations show that the formation of beidellite from montmorillonite is concomitant with morphological changes of clay particles: flakes are replaced by hexagonal particles. This suggests a dissolution-crystallization mechanism (Altaner & Ylagan, 1997).

The montmorillonite to high-charge beidellitic + Mg-smectite reaction

The montmorillonite-beidellite transformation corresponds to an increase in the Al content of the particles. With montmorillonite being the sole source of Al in our experiments on the water-smectite reaction, the excess Mg and Si released by this reaction is either incorporated in secondary Al-poor phases or remains in the aqueous phase. Previous experimental alteration of montmorillonite indicated that these components concentrated in by-products of the reaction as quartz (Howard & Roy, 1985; Whitney & Northrop, 1988), unidentified non-crystalline (Al, Mg) (OH) phases (Howard & Roy, 1985) and chlorite (Whitney & Northrop, 1988; Whitney, 1992). In the present study, we did not observe the crystallization of quartz or chlorite but the formation of Mg-smectite. Using the composition of the starting montmorillonite, we deduce that the formation of one unit of a 3Mg-trioctahedral smectite results from the dissolution of 10 montmorillonite units. This explains the scarcity of Mg-rich particles which cannot be identified by XRD (their reflections are hindered by the intense reflections of the dioctahedral smectitic phases). We did not observe the precipitation of quartz either (at least in the runs conducted

with purified samples), but Table 3 indicates aqueous silica concentrations twice as high as that required for quartz saturation.

From these observations, the reaction for the formation of beidellite from montmorillonite can be written as follows:



This reaction is consistent with a number of experimental and field observations. The formation of a beidellite + saponite assemblage was observed by Yamada & Nakasawa (1993) after experimental alteration of synthetic beidellite-montmorillonite mixed layers at high temperature. The beidellite + saponite assemblage was also identified between 100 and 320°C in active high-enthalpy geothermal fields where montmorillonite seems no longer stable at temperatures >100°C (Beaufort *et al.*, 1995a,b). This early beidellite + saponite assemblage is transformed to an Al-rich illite + Mg-rich chlorite assemblage via illite-beidellite mixed layers and corrensite, respectively, as the duration of the hydrothermal activity increases (Beaufort *et al.*,

1995a; Bril *et al.*, 1996). Further, data from hydrothermal experiments and from active geothermal fields indicate that Mg-smectites are the most likely Mg-phylosilicates to be formed in the 100–200°C thermal range considered here (Whitney, 1983) and may be considered as a precursor in the overall reaction of chloritization which occurs at higher temperature (Kristmannsdottir, 1979; Arnorsson *et al.*, 1983; Inoue & Utada, 1991; Buatier *et al.*, 1995).

The polarity of smectite layers

The ordered I-S (R = 1) obtained from the K-saturated starting material after 5 months of reaction at 200°C disappears after further Ca-saturation and glycolation. This demonstrates that high-charge layers alternate regularly with the low-charge ones (17 Å in the K- or Ca-saturated states) as represented schematically in Fig. 10. Such behaviour, previously reported by Whitney & Northrop (1988) in high-temperature experiments, may be explained by heterogeneities within the swelling layers. The results from our runs which did not produce illite indicate that the high-charge smectite component has a rather beidellitic nature and the low-charge component has a rather

TABLE 3. Solution data from the experimental runs.

Experimental conditions	pH (25°C)	Si (ppm)	Al (ppm)	K (ppm)
Bulk smectite+sanidine+quartz (5 to 10 mg clays/ml solution)				
100°C, 39 days	7.16	57	1.36	33.2
126 days	6.83	38	0.18	11.0
330 days	7.05	29	0.18	14.0
200°C, 39 days	6.01	120	1.09	13.3
112 days	6.42	129	1.07	17.5
330 days	4.51	124	0.77	23.6
330 days at 200°C (25 mg/ml)	6.50	170	0.18	10.8
Purified smectite (<0.1 µm fraction) 10 mg/ml solution				
Ca- saturated, 150 days at 200°C	5.90	275	0.20	3.74
90 days at 100°C	7.15	56	0.05	0.19
K- saturated, 150 days at 200°C	6.28	275	0.29	n.d.
90 days at 100°C	7.53	55	0.05	0.15
Na-saturated, 150 days at 200°C	7.05	275	0.34	3.65
90 days at 100°C	8.75	54	0.15	0.30

n.d. = not determined

montmorillonitic nature. This leads us to consider three components in the I-S mixed layers formed after 5 months of water-smectite reaction at 200°C, i.e. low- and high-charge expandable layers alternating with illite ones. The I-S minerals in which two types of expandable layers (differing by their layer charge) and illite are interstratified has been reported already in natural systems (Shutov *et al.*, 1969; Foscolos & Kodama, 1974; Drits *et al.*, 1997). These last authors have named them illite-smectite-vermiculite mixed layers (I-S-V). To our knowledge, this type of mixed layer has not been reported explicitly in experimental works before this study. The “non-expandable dehydrated smectite” component reported by Mosser-Ruck *et al.* (1999) within the reacted products of hydrothermal alteration of K-smectite at 300°C and 100 bar could probably be interpreted as a third interstratified component (high-charge smectite or vermiculite) of the I-S mineral. The heterogeneity within the swelling layers of these I-S minerals may be explained by polarized structures as proposed by Cuadros & Linares (1995). The polarization of the swelling structures is related to increase of the layer charge which itself is related to the formation of tetrahedrally-charged layers.

CONCLUSIONS

Low-charge montmorillonite is not a stable material in deep diagenetic conditions or in hydrothermal environments. This experimental study shows that thermal effects (100 to 200°C) drive important structural modifications. The reaction begins with the formation of high-charge beidellite (tetrahedral substitution) and minor amounts of a Mg-rich, Al-poor smectite (saponite or stevensite) which incorporates the excess of Si and Mg. This type of reaction, which is very similar to the reaction observed in some geothermal fields, may be considered as a first step in the overall illitization process of the montmorillonite. The amount of beidellitic layers increases with increasing temperature and/or run duration, but the reaction progresses more slowly at lower water:rock ratios. This latter observation is probably related to the higher aqueous Al concentrations measured in the ‘bulk’ experiments; hence the lower affinity of the dissolution reaction of the starting montmorillonite.

In our experiments, the low-charge montmorillonite to high-charge beidellite reaction is accompanied by morphological changes which suggest that it proceeded by a dissolution-crystallization

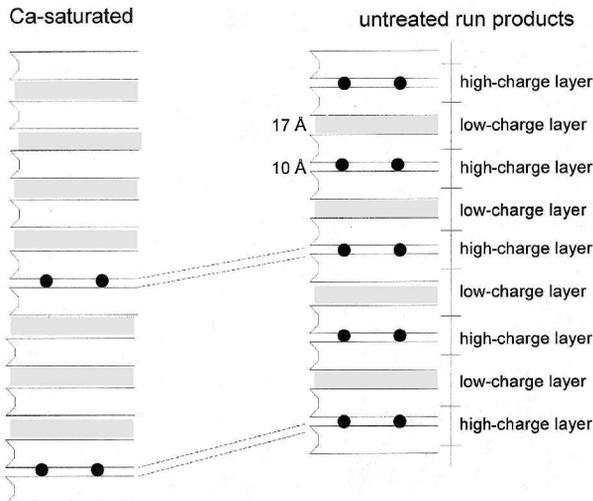


FIG. 10. Schematic representation of the layer stacking after ethylene-glycol solvation of the run products in the untreated and Ca-saturated states. In the untreated state, the interlayering between 10 Å layers (collapsed K-saturated high-charge layers) and 17 Å layers (expanded low-charge layers) is regular. In the Ca-saturated state, most of the high-charge layers re-expand giving a random stacking.

mechanism. The first illite layers occurred when ~50% of the starting montmorillonite had reacted (5 months of reaction of a K-saturated montmorillonite at 200°C). The illite layers were interstratified with both high-charge and low-charge dioctahedral smectites in a three component mixed layer similar to the I-S-V mixed layers already proposed as actual structure of some natural I-S mixed layers. The Al for Si tetrahedral substitution affecting only a half unit of the basic structure could explain the regular alternation of layers having the properties of illite, high charge beidellite (or vermiculite), and montmorillonite components.

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REFERENCES

- Altaner S.P. & Ylagan R.F. (1997) Comparison of structural models of mixed-layer illite/smectite and reaction mechanisms of smectite illitization. *Clays Clay Miner.* **45**, 517–533.
- Amorsson S., Gunnlaugsson E. & Svavarsson H. (1983) The chemistry of geothermal waters in Iceland. II. Mineral equilibria and independent variables controlling water compositions. *Geochim. Cosmochim. Acta*, **47**, 547–566.
- Beaufort D., Papapanagiotou P., Patrier P. & Traineau H. (1995a) Les interstratifiés I-S et C-S dans les champs géothermiques actifs: sont-ils comparables ceux des séries diagénétiques? *Bull. Centr. Rech. Elf Aquitaine Prod.* **19**, 267–294.
- Beaufort D., Papapanagiotou P., Patrier P., Fujimoto K. & Kasai K. (1995b) High temperature smectites in active geothermal systems. Pp. 493–496 in: *Proc. 8th Int. Symp. Water-Rock Interaction* (Y.K. Kharaka & O.V. Chudayev, editors). Vladivostok.
- Bouchet A., Proust D., Meunier A. & Beaufort D. (1988) High-charge to low charge smectite reaction in hydrothermal alteration processes. *Clay Miner.* **23**, 133–146.
- Bril H., Papapanagiotou P., Patrier P., Lenain J. F. & Beaufort D. (1996) Fluid-rock interaction in the geothermal field of Chipilapa (El Salvador): Contribution of fluid inclusion data. *Eur. J. Mineral.* **8**, 515–531.
- Buatier M.D., Fruh-Green G.L. & Karpoff A.M. (1995) Mechanism of Mg-phylosilicate formation in a hydrothermal system at a sediment ridge (Middle Valley, Juan de Fuca). *Contrib. Mineral. Petrol.* **122**, 134–151.
- Cuadros J. & Linares J. (1995) Some evidence supporting the existence of polar layers in mixed-layer illite/smectite. *Clays Clay Miner.* **43**, 467–473.
- Drits V.A., Lindgreen H., Sakharov B.A. & Salyn A.S. (1997) Sequence structure transformation of illite-smectite-vermiculite during diagenesis of Upper Jurassic shales, North Sea. *Clay Miner.* **33**, 351–371.
- Eberl D.D. (1978) Reaction series for dioctahedral smectites. *Clays Clay Miner.* **26**, 327–340.
- Eberl D.D. & Hower J. (1976) Kinetics of illite formation. *Bull. Geol. Soc. Amer.* **87**, 1326–1330.
- Eberl D.D., Whitney G. & Khoury H. (1978) Hydrothermal reactivity of smectite. *Am. Miner.* **63**, 401–409.
- Foscolos A.E. & Kodama H. (1974) Diagenesis of clay minerals from lower cretaceous shales of North Eastern British Columbia. *Clays Clay Miner.* **22**, 319–335.
- Greene-Kelly R. (1953) The identification of montmorillonoids in clays. *J. Soils Sci.* **4**, 233–237.
- Guyen N. & Huang W.L. (1991) Effect of octahedral Mg²⁺ and Fe³⁺ substitutions on hydrothermal illitization reactions. *Clays Clay Miner.* **39**, 397–399.
- Howard J.J. & Roy D.M. (1985) Development of layer charge and kinetics of experimental smectite alteration. *Clays Clay Miner.* **33**, 81–88.
- Huang, W.H., Longo J.M. & Pevear D.R. (1993) An experimental derived kinetic model for the smectite-to-illite conversion and its use as a geothermometer. *Clays Clay Miner.* **41**, 162–177.
- Inoue A. & Utada M. (1991) Smectite to chlorite transformation in thermally altered volcanoclastic rocks in the Kamikita area, Northern Honshu, Japan. *Am. Miner.* **76**, 628–640.
- Kristmannsdottir H. (1979) Alteration of basaltic rocks by hydrothermal activity at 100–300°C. *Proc. Int. Clay Conf., Oxford*, 359–367.
- Meunier A., Velde B. & Griffault L. (1998) The reactivity of bentonites: a review. An application to clay barrier stability for nuclear waste storage. *Clay Miner.* **33**, 187–196.
- Meunier A., Lanson B. & Beaufort D. (2000) Vermiculitization of smectite interfaces and illite layer growth as a possible dual model for illite-smectite illitization in diagenetic environments: a synthesis. *Clay Miner.* **35**, 573–586.
- Mosser-Ruck R., Cathelineau M., Baronnet A. & Trouillet A. (1999) Hydrothermal reactivity of K-smectite at 300°C and 100 bar: dissolution-crystallization process and non-expandable dehydrated smectite formation. *Clay Miner.* **34**, 275–290.
- Oelkers E.H., Schott J. & Devidal J.L. (1994) The effect of aluminum, pH, and chemical affinity on the rates

- of aluminosilicate dissolution reactions. *Geochim. Cosmochim. Acta*, **58**, 2011–2024.
- Pytte A.M. & Reynolds R.C. (1989) The thermal transformation of smectite to illite. Pp. 133–140 in: *The Thermal History of Sedimentary Basins: Methods and Case History* (N.D. Naesser & T.H. McCulloh, editors). Springer-Verlag, New York.
- Reynolds R.C., Jr (1985) NEWMOD[©] a computer program for the calculation of one-dimensional diffraction patterns of mixed-layered clays. R.C. Reynolds, 8 Brook Rd., Hanover, NH, USA.
- Sato T., Murakami T. & Watanabe T. (1996) Change in layer charge of smectites and smectite layers in illite/smectite during diagenetic alteration. *Clays Clay Miner.* **44**, 460–469.
- Schultz L. G. (1969) Lithium and potassium absorption, dehydroxylation, temperature and structural water content in aluminous smectites. *Clays Clay Miner.* **17**, 115–149.
- Shutov V.D., Drits V.A. & Sakharov B.A. (1969) On the mechanism of a post-sedimentary transformation of montmorillonite to hydromica. *Proc. Int. Clay Conf., Jerusalem*, 523–531.
- Whitney G. (1983) Hydrothermal reactivity of saponite. *Clays Clay Miner.* **31**, 1–8.
- Whitney G. (1992) Dioctahedral smectite reaction at elevated temperatures: effect of K availability, Na:K ratio and ionic strength. *Appl. Clay Sci.* **7**, 97–112.
- Whitney G. & Northrop H.R. (1988) Experimental investigation of the smectite to illite reaction: dual reaction mechanisms and oxygen isotope systematics. *Am. Miner.* **73**, 77–90.
- Whitney G. & Velde B. (1993) Changes in particle morphology during illitization: an experimental study. *Clays Clay Miner.* **41**, 209–218.
- Yamada H. & Nakasawa H. (1993) Isothermal treatments of regularly interstratified montmorillonite-beidellite at hydrothermal conditions. *Clays Clay Miner.* **41**, 726–730.