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CHANGES IN LAYER ORGANIZATION OF Na- AND Ca-EXCHANGED SMECTITE MATERIALS DURING SOLVENT EXCHANGES FOR EMBEDMENT IN RESIN

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ABSTRACT

The embedding process designed for impregnation in resin of hydrated clays for TEM observation comprises four steps of exchange by solvents and resin. Clay pastes of Na- and Ca-exchanged Wyoming smectite were prepared at low suction pressures (3.2 and 100 kPa, respectively), and their layer organization was examined at different steps of the embedding process. X-ray diffraction was used in order to follow the evolution of layer distances and particle orientation during solvent exchanges. At 3.2 kPa as well as at 100 kPa, the water-saturated clay exhibits interlayer distances of 1.9 nm. After methanol exchange, interlayer distances collapsed to 1.6–1.7 nm. With 1,2-epoxypropane and resin saturation, clays behave in a similar way as with methanol. Examination of layer-stacking coherency by measurement of peak widths indicates that the first exchange by methanol is the most critical step in the embedding process because it induces reduction of the layer distances and aggregation, especially in the case of dilute Na-exchanged clay. The final polymerization of resin introduces further slight changes in organization of the clay.

Keywords: smectite, organization, embedment, solvent, resin, X-ray diffraction.

SOMMAIRE

Le procédé d'inclusion établi pour l'imprégnation dans une résine d'échantillons d'argile hydratée pour les observations en microscopie électronique par transmission comporte quatre étapes d'échanges par des solvants et de la résine. Des pâtes de smectite du Wyoming saturée en Na ou en Ca ont été préparées à de faibles pressions de succion (3.2 kPa et 100 kPa, respectivement), et l'organisation des feuillets a été examinée aux différentes étapes du procédé d'inclusion. La diffraction des rayons X a été utilisée pour suivre l'évolution des distances interfoliaires et l'orientation des particules pendant les échanges par les solvants. A 3.2 kPa aussi bien qu'à 100 kPa, l'argile saturée en eau a présenté des distances interfoliaires de 1.9 nm. Après les échanges par le méthanol, les distances sont tombées à 1.6–1.7 nm. Avec l'epoxy-1,2 propane et la résine, les argiles ont conservé le même type de comportement qu'avec le méthanol. L'examen de la cohérence de l'empilement des feuillets par la mesure de la largeur des pics a indiqué que le premier échange est l'étape la plus critique dans le processus de fixation parce qu'il a provoqué un effondrement des distances interfeuillets et une agrégation des feuillets, particulièrement dans le cas de l'argile diluée saturée en Na. La polymérisation finale de la résine a introduit à nouveau des changements légers dans l'organisation de l'argile.

Mots-clés: smectite, organisation, imprégnation, solvant, résine, diffraction X.

INTRODUCTION

Literature on sample preparation of swelling materials for transmission electron microscopy is abundant and diversified. All steps of the preparation process, as well as the sequence of these steps, are usually justified by specific constraints. Embedding in resin was favorably tested decades ago as a method that preserves the original fabric of clays. Foster & De (1971) were the first to investigate in detail the impregnation techniques of hydrated samples, using a series of diffusing liquids to replace the original water. The hardened block of resin is then sliced up at the appropriate thickness (McKee & Brown 1977).

The aim of the present paper is not to discuss the pros and cons of all of the preparation processes, but to analyze the evolution of clay microstructure in contact with solvents and resin. This analysis will allow us to derive simple rules to follow when embedding samples containing highly hydrated clays in order to study the morphology of the clays, the fabric of the material, as well as the chemical composition and the crystal structure. The embedding process described below has been followed step by step, and the variations in the

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properties of the smectitic clay, such as macroscopic swelling and interlayer spacing, have been monitored in the course of the exchanges in different liquid media.

Important variables in the impregnation technique

Originally developed for curing biological specimens (Spurr 1969), the embedding technique, which is used for hydrated samples, has been refined by soil scientists and clay mineralogists at "Soil Science – INRA". The process can be applied either to clay fractions, rock chips or lumps of soil, including organo-mineral complexes, as commonly found in soils (Tessier 1987).

There are various adaptations and options to be chosen according to the type of material studied and the objectives of the study. The duration of the exchanges should take into account the size of the aliquot and its pore-size distribution. The latter parameter is related to the type of clay (interlayer swelling or not), to particle morphology (size, shape and plastic properties), and to the state of compaction (soils, sediments, materials, rocks).

The ability of clay minerals to swell is mainly linked to the organization of the clay layer and clay particle, and to its environment (Tessier 1991). The parameters to take into account are: the nature of the saturating cation, the osmotic potential in relation to the presence of salts in solution, and the suction pressure of water or the external mechanical pressure applied to the material. In nature, the saturating cation differs according to clay genesis and environmental conditions, whereas in the laboratory, one assumes that the environmental parameters are well controlled. The osmotic potential (ionic strength) can be briefly described as the salt content of the solution. The suction pressure is the water pressure filling the clay matrix by capillary action while a mechanical pressure is simultaneously applied at the periphery of the sample. All these factors together modify the geometry of the clay matrix as well as the crystal structure of the clay. Any change in one of these parameters is expected to change some aspect of the organization of the clay.

In this paper, the specific effect of suction pressure and of the nature of the exchangeable cation will be described. The clays were prepared at two suction pressures, 3.2 and 100 kPa, which are rather representative of realistic conditions, *i.e.*, Ca-exchanged clays in soils as well as clay gels for industrial purposes. To control suction pressure, we used a filtration cell to set the hydration state of the material (Tessier 1984).

CHARACTERISTICS OF THE STARTING MATERIAL

The clay chosen for the study is a Wyoming montmorillonite, provided by the Comptoir des Minéraux et Matières Premières, France. The structural formula of this smectite, as received in our laboratory, was first established by Gaultier & Mamy (1988), on the basis of bulk chemical analyses, with results normalized to 22 negative charges:

$$(Si_{3.96}Al_{0.04})\ (Al_{1.53}Fe^{3+}_{0.18}Mg^{2+}_{0.26}Ti^{4+}_{0.01})\ (Ca^{2+}_{0.07}Na^{+}_{0.20}K^{+}_{0.01})$$

The compensation of charges is naturally bi-ionic, *i.e.*, partitioned between Ca and Na. Compositions reported for the Wyoming smectite in the literature are commonly different, depending on the degree of purity of the clay and its origin. The samples used for our study are <2 μm clay fractions, separated by sedimentation and of mono-ionic compensation (Ca- or Na-saturated). The clay fraction was analyzed by two different methods: i) conventional total wet-chemical analysis (INRA, Laboratoire d'analyse des sols, Arras, France, as described in AFNOR 1994); ii) mean composition of 20 aggregates of micrometric size, with analyses performed with an analytical transmission electron microscope, coupled with an energy-dispersion system (EDS). The resulting compositions are, respectively: 1) $(Si_{3.84}Al_{0.16})$ $(Al_{1.48}Fe^{3+}_{0.19}Mg^{2+}_{0.30}Ti^{4+}_{0.01})$ $(Ca^{2+}_{0.24}\ Na^{+}_{0.01}K^{+}_{0.01})$, and 2) $(Si_{3.85}Al_{0.15})$ $(Al_{1.59}Fe^{3+}_{0.15}\ Mg^{2+}_{0.31})$ $(Ca^{2+}_{0.09}Na^{+}_{0.06}K^{+}_{0.03})$.

Observations by TEM with EDS reveal small grains of quartz present in the clay, even after sedimentation of the clay fraction. Iron is also present in the form of an oxyhydroxide phase, detectable as individual granules in addition to clay particles. The two compositions are quite similar, showing that minor impurities can be neglected. These results show a good agreement concerning the chemical composition of the tetrahedral and octahedral sheets. On the other hand, data on exchangeable cations measured by EDS must be interpreted with caution. As a matter of fact, damage in the interlayer spaces of clays due to radiation is well known to mineralogists (Peacor 1992). Such damage affects the detection of the saturating cations, in the present case, Na and Ca. Furthermore, as the limits of detection are relatively high for light elements, low concentrations are affected by a large relative error, especially for Na, the characteristic X-rays of which overlap with the Cu*Lα* radiation emitted by the copper grid.

The total surface-area (S EGME) was determined by adsorption of ethylene glycol monoethylether (Carter *et al.* 1965). The cation-exchange capacity (CEC) and concentration of exchangeable cations, after Ca-saturation, were determined by extraction by cobalt-hexamine (Norm X 31–130, AFNOR 1994; Ciesielski & Sterckeman 1997a, b). The values are reported in Table 1.

METHODS

Conditioning of the samples

Ca- and Na-exchanged fractions were concentrated according to the well-known procedure of extraction by sedimentation after Na dispersion. The clay fraction was

TABLE 1. CHEMICAL CHARACTERISTICS OF WYOMING CLAY

S EGME	CEC	Ca^{2+}	Mg^{2+}	Na^+	K^+
719	87.1	83.8	2.4	0.3	0.5

Surface (S EGME) and cation-exchange capacity (CEC) were measured after purification of the clay and Ca saturation. The surface is expressed in m^2/g, and the cation-exchange capacity, in meq/100 g.

then saturated with either $CaCl_2$ or NaCl 1M solutions, and further washed three times with diluted solutions (10^{-3} M) of $CaCl_2$ or NaCl, respectively (Robert & Tessier 1974). The suspensions were centrifuged at 2000 G, and the clay pastes were homogenized by mechanical stirring and stocked in a refrigerator. The hydrated form of the samples was then placed in a filtration cell that used a gas pressure to equilibrate the water potential (Tessier 1984). Figure 1 shows the water content *versus* the water potential. The water content decreases rapidly as gas pressure is applied to the material. Our aim was to obtain pastes with a consistency of a soft gel and a plastic solid. The clay pastes were prepared at a constant suction pressure of 3.2 kPa or 100 kPa, these conditions corresponding to the limiting values for transitions from suspension to gel and from gel to plastic solid. These suction pressures correspond to equilibrium with very high relative humidity, *i.e.*, 99.99776% and 99.9275%, respectively. The equilibrium was established after about 72 hours, and the water content was measured by weighing the sample when wet and after heating at 105°C during 24 hours. The difference in weight of the sample before and after drying was attributed to the liquid fraction of the material that consists of the ionic solution.

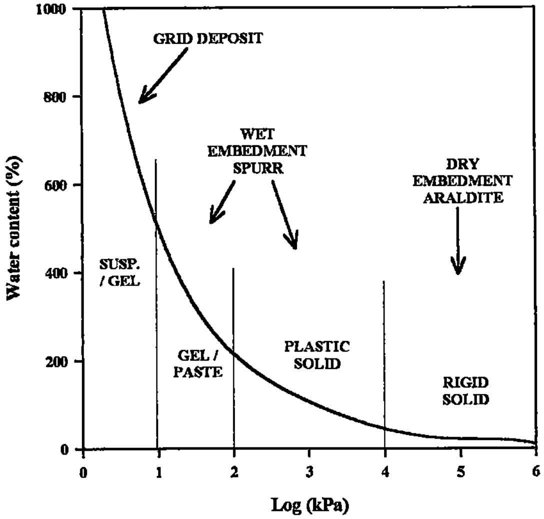

FIG. 1. Schematic curve of hydration for smectites. Different domains have been distinguished, corresponding to the main rheological characteristics.

Embedding process

The embedding process consisted of ten successive exchanges, as described in Table 2. The process started with a sample saturated with a solution, in which the initial H_2O pressure is controlled. The first step consisted in replacing the solution by immersing the samples in methanol (four exchanges). Then the methanol was progressively replaced by 1,2-epoxypropane (four baths of four different proportions of methanol and 1,2-epoxypropane: 1/4, 1/2, 3/4 and 4/4). Finally, the 1,2-epoxypropane was replaced by Spurr resin. The resin was first diluted with 1,2-epoxypropane to lower its viscosity. Then the 1,2-epoxypropane was left to evaporate overnight. The last bath was made of pure resin. All exchanges with solvents were made at air pressure and room temperature.

The size of the samples was about 16 mm^3 (0.4 × 0.4 × 0.1 cm). The dilution of the liquid phase was taken to be the ratio of the exchanging liquid poured into the container to the liquid content retained by the clay matrix, the volume of solvent being approximately 10 mL of saturating liquid in each exchange. As the volume of the samples was about 16 mm^3 (50% of solid + 50% of liquid in the Ca-gel and 15% of solid + 85% of liquid in the Na-gel), the dilution factor of the saturating liquid was about 10^3. With the clay fraction showing the most swelling (Na-exchanged montmorillonite), three exchanges with methanol led to a dilution on the order of 10^9 of the water originally saturating the sample. With the clay fraction showing the lesser swelling, the dilution of the water was still larger. When applying this procedure as a routine preparation, we usually carry out four exchanges to ensure complete dehydration. The same protocol can be used with other resins such as LRWhite and Epon.

The characteristics of the organic solvents are summarized in Table 3. The first three compounds are the

TABLE 2. STEPS OF THE EMBEDMENT PROCEDURE USED IN THE PRESENT STUDY

Liquid	Exchanges	Time	Temperature
Water	initial state		25°C
Methanol	4 exchanges	1 hour	25°C
1,2-epoxypropane	4 exchanges	1 hour	25°C
Resin/1,2-epoxypropane	1 exchange	12 hours	25°C
Resin	1 exchange	4 hours	25°C
Polymerization of resin		24 hours	60°C

The duration of the exchanges must be adapted to the type of sample.

TABLE 3. CHARACTERISTICS OF SOME POLAR ORGANIC COMPOUNDS USED IN TREATMENTS OF CLAY SAMPLES

Organic compound		Formulae	Density
Methanol	$C H_4 O$		0.79
1,2-epoxypropane	C_3H_6O	CH_3 O CH CH_2	0.83
Spurr resin	$C_8H_{12}O_2$	CH O CH 3CH_2 CH CH O CH_2	1.22
LR White resin	$C_{15}H_{16}O_2$	HO C_6H_4 (CH_3 C CH_3)C_6H_4 OH	
Ethylene glycol	$C_2H_6O_2$	HO CH_2 CH_2 OH	1.11
Polyethylene glycol		CH_2 OH (CH_2 O CH_2)$_n$ CH_2 OH	1.13
Alkyl-ammonium		C_nH_{2n+1} CH_{3+}	

The number of C atoms determines the length of the organic chain and the degree of filling of the interlayer spaces.

ones used in this study. Characteristics of other compounds are given for comparison, because of the availability of data in the literature relative to their effect on the swelling of clays (Brindley *et al.* 1969, Lagaly & Weiss 1969, Lagaly 1982, Vali & Köster 1986).

X-ray diffraction

In order to study the structure and to characterize the clay material at the different steps of the embedment procedure, the extent of the interlayer swelling or shrinkage was measured by X-ray diffraction (XRD). Measurements were performed on gels or pastes saturated with all the different liquids and the polymerized resin. Slices of the sample cakes, about 1 mm thick, were cut normal to the plane of the support of the filtration cells.

The apparatus used was a Siemens D5000 θ–2θ X-ray diffractometer, mounted in transmission mode and fitted with a copper tube ($K\alpha_1$ = 1.54056 Å), a primary monochromator (germanium), Soller slits, divergence slits, a ϕ circle and a linear location detector (Elphyse). Diffraction patterns were evaluated using the Socabim DIFFRAC AT software.

A brass cell was used during data acquisition. It was mounted with two mica windows and closed by a screw cap with a doughnut ring to avoid the evaporation of solvents. The samples were directly transferred from the filtration cell into the air-tight cell. A slice of the clay paste was set between the two mica windows, and the cell was closed immediately.

TABLE 4. WATER AND METHANOL CONTENTS (cm³/g) REFLECTING THE MACROSCOPIC SWELLING OF THE WYOMING CLAY

Wyoming Smectite	Relative Humidity	Water Content	Methanol Content	Ratio %
Ca, 3.2 kPa	99.99776	333	416	+25
Na, 3.2 kPa	99.99776	755	830	+10
Ca, 100 kPa	99.9275	113	172	+52
Na, 100 kPa	99.9275	260	338	+30

Na and Ca saturation, 3.2 and 100 kPa.

The setting in transmission mode was described by Tessier *et al.* (1997). The θ ring remains stationary. The sample rotates in a plane normal to the X-ray beam. The detector is positioned to record the transmitted X-rays in the angular range chosen, in our case 1.5°–13.5°2θ (Cu*K*α radiation).

RESULTS

Macroscopic swelling

The water and methanol contents of the Ca- and Na-exchanged montmorillonite at two different suction pressures are reported in Table 4. The proportion of liquid was determined by weighing the samples before and after drying at 105°C. This value represents the quantity of liquid retained in the sample; the ratio of the mass of the liquid phase *versus* the mass of the solid phase is expressed in percent. This ratio corresponds to mass intake or loss (*i.e.*, the macroscopic swelling or shrinking of the clay) upon exchange of the water for methanol.

At a suction pressure of 3.2 kPa, the clay–water system is about fully hydrated, very close to its maximum water content. At 100 kPa, about 70% of the water content at 3.2 kPa was lost both from the Ca- and Na-exchanged montmorillonite. On the other hand, the Na-exchanged clay is almost 2.5 times more hydrated than the Ca-exchanged clay, both at 3.2 and 100 kPa.

Starting from the hydrated state at 3.2 kPa or 100 kPa, there is a macroscopic swelling of the material after three exchanges in the methanol. This swelling is more important for the Ca-exchanged clay than for the Na-exchanged clay, and also more important at 100 kPa than at 3.2 kPa. The most contrasted behaviors are observed between the Na-exchanged clay at 3.2 kPa (+10%) and the Ca-exchanged clay at 100 kPa (+ 50%). In order to explain the corresponding differences occurring at the microscopic scale, the organization of the layers in these samples was studied by XRD.

Layer organization after exchanges

The position of the peaks corresponding to the first order of diffraction *d*(001) for smectite-group phases lies between 4 and 6°2θ (Cu*K*α). The peak positions and their full width at half maximum (FWHM) were measured after exchanges with the successive liquids and in the polymerized resin (Table 5). The measured values are characteristic of a strongly hydrated smectite (Figs. 2, 3). We observed that the peak profiles are almost symmetrical, like a Gaussian distribution, indicating that values of layer spacings are symmetrically grouped around a maximum. However, in dilute solution, the Na-exchanged clay at 3.2 kPa displays a weak maximum of diffraction at 1.9 nm, and an important scattering at low

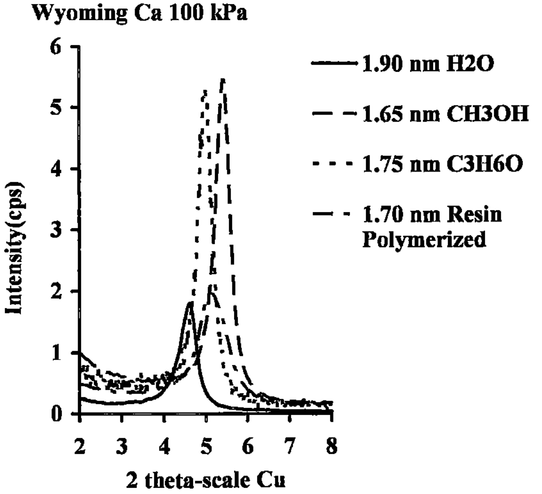

FIG. 2. X-ray-diffraction profiles of Ca-exchanged Wyoming smectite prepared in water at 100 kPa and exchanged by solvents and resin. First-order 001 in transmission mode. The intensity is recorded in counts per second.

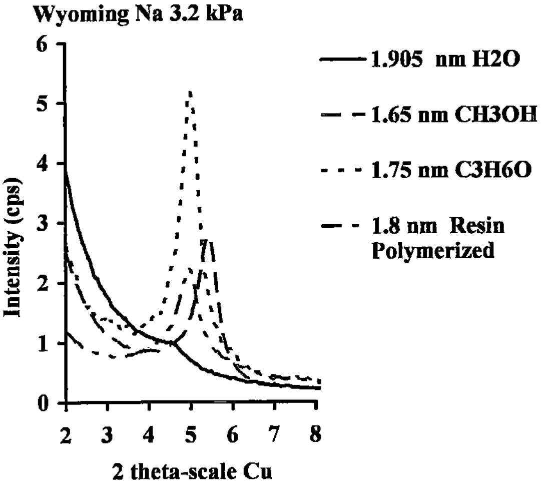

FIG. 3. X-ray-diffraction profiles of Na-exchanged Wyoming smectite prepared in water at 3.2 kPa and exchanged by solvents and resin. First-order 001 in transmission mode. The intensity is recorded in counts per second.

angles (Fig. 3). The broad band centered on 1.9 nm indicate the presence of layers separated by three molecules of H_2O. The low-angle scattering was interpreted as the presence of larger interlayer spacings (3–10 nm) due to the formation of diffuse double layers (Norrish 1954). Such patterns are usual with suspensions of Na-exchanged smectite prepared at low suction with dilute solutions, *i.e.*, after "infinite swelling". A large part of the clay thus is made of layers that are not aggregates, and that cannot produce interparticle diffraction in the sense of Nadeau *et al.* (1984). The difference in FWHM indicates that the particles are strongly disoriented with respect to the X-ray beam in the case of the Na-exchanged clay at 3.2 kPa, and more regularly oriented for the Ca-exchanged clay at 100 kPa.

TABLE 5. X-RAY-DIFFRACTION DATA FOR Ca-EXCHANGED WYOMING SMECTITE AT 100 kPa AND Na-EXCHANGED WYOMING SMECTITE AT 3.2 kPa

Wyoming Smectite	Water	Methanol	1,2-epoxy propane	Resin 1,2-epoxy propane	Resin	Polymerized Resin
	Ca-exchanged smectite, 100 kPa					
Peak (nm)	1.90	1.65	1.75	1.75	1.75	1.70
FWHM	0.45	0.41	0.39	0.45	0.44	0.76
	Na-exchanged smectite, 3.2 kPa					
Peak (nm)	1.90	1.65	1.75	1.75	1.75	1.80
FWHM	>1	0.53	0.48	0.45	0.44	0.59

Peak positions and full widths at half maximum (FWHM) measured using Socabim Diffrac AT software.

In the course of the exchange process, the *d* value of the peak maximum was found to vary between 1.9 nm and 1.65 nm in a similar way for Na- and Ca-exchanged clays. The smallest *d*-value (1.65 nm) was obtained in methanol, whereas it increased again slightly (~1.75 nm) after exchange with epoxy propane or the components of the resin. The fact that the first-order peak retains a similar shape with a single maximum after solvent exchanges (Figs. 2, 3) suggests a specific organization of the molecules intercalated between the clay layers (Lagaly 1981). The similarity of organization with the various organic compounds implies a regular saturation with solvents in the whole material.

The study of the peak shapes and their differentiation are of great importance in the interpretation of changes in the organization of the material during solvent exchange. Because both Ca- and Na-exchanged montmorillonite exhibit very similar spacings in water and solvents, it was possible to compare the peak shapes at the successive steps of the exchange process. It is known that the width of the diffraction peaks is broadly linked to the number of layers per coherent scattering domains (Moore & Reynolds 1989). Since the Ca-exchanged smectite forms thicker stacks of layers than the Na-exchanged smectite in water (Tessier & Pédro

1987), the diffraction peaks of the Ca-exchanged clay are more narrow than those of the Na-exchanged clay. This difference in aggregation was verified in our study, and it is present with all solvents (Table 5).

More specifically, the width of the peaks is linked to the lack of parallelism of the planar layers (Pons *et al.* 1981, 1982, 1987). The organization of the layers of the Na-exchanged clay changes drastically when exchanging water for methanol, the intense peak centered at 1.65 nm most likely reflecting the collapse of the diffuse double layers. The peak widths (FWHM) also decreased for Ca and reached the same value (0.45) for Ca- and Na-exchanged clays in epoxy propane and liquid unpolymerized resin. The discrepancy between Ca- and Na-exchanged clays was reversed in the polymerized resin, where the Ca-exchanged clay was less expanded (1.7 nm) and broader (FWHM = 0.76) than the Na-exchanged form (1.8 nm, FWHM = 0.59). The increase in FWHM after polymerization of the resin reflects a loss of parallelism of the layers, which was more dramatic for the Ca-exchanged clay than for the Na-exchanged clay.

DISCUSSION

During their preparation for study by transmission electron microscopy, the clay fractions were subjected to changes at two levels of organization, namely layer spacing and particle arrangement. These two aspects will be examined in turn.

Changes in interlayer spacing

It is important to recall that the clay fractions studied in this paper are prepared at very high water contents, *i.e.*, conditions commonly met in soils and gels at low suction pressures, or in sediments consolidated under low pressures. We observe that in contact with dilute solutions and with Ca and Na as exchangeable cations, the Wyoming montmorillonite exhibits a larger layer-spacing (1.9 nm) than under dry conditions, where it is approximately 1.5 and 1.26 nm for Ca and Na, respectively (Méring 1946, Tessier 1984). This finding means that oriented samples equilibrated at a certain relative humidity (air or vapor), as commonly run in clay mineralogy, do not exhibit layer-spacings similar to those prepared as pastes or gels and kept hydrated.

Starting from the fully hydrated state with maximum swelling in the interlayer spaces, there is no doubt that all the pore spaces are successively filled with methanol, 1,2-epoxypropane and, finally, resin. If collapse at *d*-values lower than 1.6 nm had occurred, it would have been detected by XRD. Absence of a collapse suggests that all interlayer spaces are intercalated by organic compounds of solvents and resin. With methanol, 1,2-epoxypropane or resin, the peaks are very similar, both in position and shape.

Measurements of *d*-values on HRTEM pictures of the embedded smectite give smaller values than by XRD. This discrepancy has been noted by several authors (Farmer *et al.* 1994, Kim *et al.* 1995, Righi & Elsass 1996), who invoked a possibility of charge heterogeneity due to incomplete intercalation by organic compounds of the resin. We admit that the present work failed to come up with a definitive answer. The question is still open and requires further investigations on other reference materials such as vermiculite and mixed-layer (illite–smectite) clays.

Another important aspect of the evolution of the interlayer spacings is related to the initial state of the sample. Annabi-Bergaya *et al.* (1979, 1980) reported layer spacings of 1.3 nm for the Camp Berteau Na-exchanged montmorillonite, in oriented deposits saturated with methanol vapor. However, the two clays (Wyoming and Camp Berteau) exhibit a very similar pattern of behavior with water and with different cations (Ben Rhaïem *et al.* 1987, Tessier 1991). Thus, if the layer spacings found with methanol in our work (1.65 nm) are considerably larger than those obtained from material in the dry state, it is certainly because they were prepared from a fully hydrated state. As a matter of fact, after a strong drying, crystal swelling is restored when the clay is immersed in the solvents (Brindley *et al.* 1969). We conclude that the layer spacing of clay immersed in solvent not only depends on the nature of the solvent itself, but also on the initial state of the sample. Crystal swelling with weak polar solvents therefore does not exhibit the reversibility typically observed with water (Tessier 1984).

Changes in clay microstructure

Except for Na-exchanged smectite, where water is mainly located in interlayers, water mainly fills the pores in the matrix in the case of other clays such as kaolinite and illite on one hand, and smectite prepared with divalent cations on the other hand, *i.e.*, in the arrangement of clay crystals or crystal aggregates (particles). The geometry of the clay matrix (Fig. 4) is of fundamental importance for an understanding of macroscopic properties such as water retention, hydraulic conductivity or rheological properties. The method used in this paper consists in replacing water with various solvents and, finally, an epoxy resin in order to preserve specific arrangements as far as possible.

In this method, the sample prepared at a given suction pressure is quickly dipped in methanol and in the successive solvents in order to avoid desiccation. It is important to avoid an irreversible shrinkage of the sample on contact with air due to capillary forces acting at the solid–liquid–gas interface. The sample is therefore permanently immersed in liquids during the whole embedding process.

By measuring the apparent volume and solution volume, we have verified that at 3.2 and 100 kPa, the pore spaces among the clay particles are saturated with water. This means that by measuring the solution content,

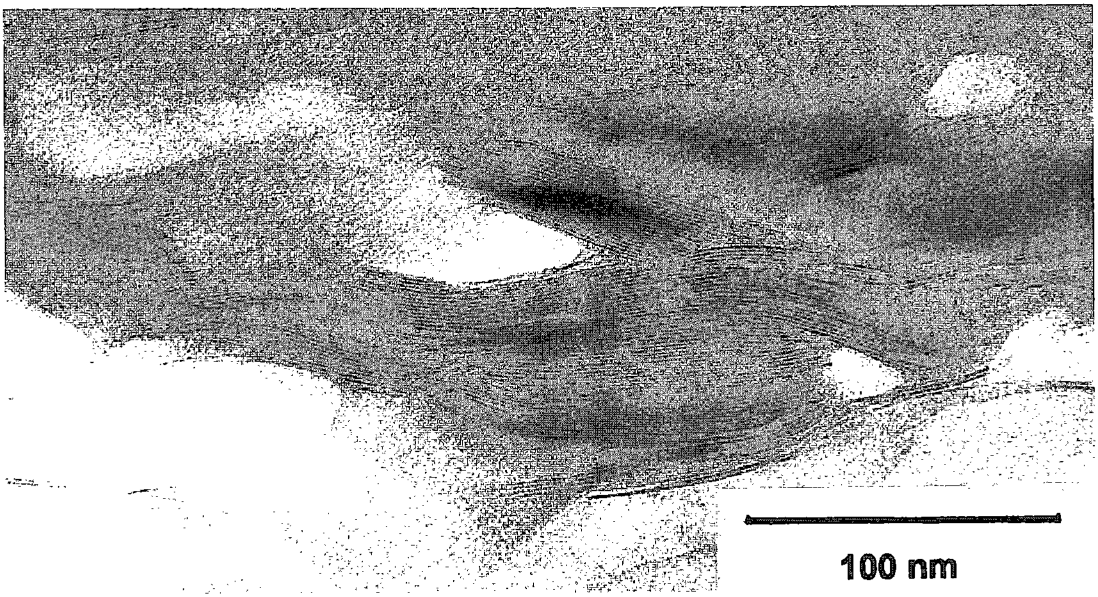

FIG. 4. Lattice-fringe image of Ca-exchanged Wyoming smectite, prepared at 100 kPa and embedded in Spurr resin, showing the curvature of layers and concomitant angular heterogeneity of orientation.

we can infer the extent of possible shrinking–swelling phenomena in the samples. At low suction (3.2 kPa), the volume change is small for the Na-exchanged clay, whereas for the Ca-exchanged clay, the swelling reaches 25%. We conclude that at low suction pressure, the rearrangement of the clay structure is mainly associated with contraction in the interlayer distance. The volume change also gives a good approximation of the contribution of interlayer spaces to the total pore-space. In the case of Ca-exchanged smectite, the contribution of layer spacing to volume change is small. In contrast, in Na-exchanged smectite, where there is a collapse of the 10 to 3.5 nm interlayer distances, the magnitude of the contraction is amplified.

A different pattern of pore distribution is obtained at higher suction pressure (100 kPa). The layer spacings are the same at 3.2 and 100 kPa, both for Ca- and Na-exchanged clays, whereas there is a notable swelling for the Ca-exchanged clay at 100 kPa, which is smaller for the Na-exchanged clay. However, this positive change in volume is associated with a decrease in layer distance. The Ca-exchanged clay is particularly well aggregated, with thick, weakly curved pore-walls (Fig. 4). This behavior is an expression of the nature of the clay matrix and of the cohesive forces acting among clay layers and particles. It was shown previously that Ca-exchanged smectite exhibits an oriented network structure, with strong cohesion forces acting between the clay layers (Chenu & Tessier 1995). Strong drying causes a preferential orientation of the particles, which was confirmed by low-angle X-ray scattering (Ben Rhaïem *et al.* 1986). These authors concluded that the behavior of Ca-exchanged smectites, as well as of other smectites equilibrated with divalent cations, is strongly influenced by the stresses to which the material was previously subjected. At 100 kPa, a certain relaxation of the material is observed in relation with the use of solvents less polar than water. This characteristic of the liquids explains the volume increase of the Ca-exchanged clay in methanol, at the first step of desiccation.

We can state that for pastes of Ca-exchanged smectites, there are limited changes in layer spacing during the embedding process. It is the clay matrix that is supposed to change the most after drying because of a certain relaxation of the clay. Similar conclusions can be drawn for samples of illite, kaolinite and interstratified clays (Chenu & Tessier 1995).

For Na-exchanged clays, to our knowledge, no method of preparation has yet allowed the preservation of fully expanded interlayers.

CONCLUSIONS

In the course of this study, devoted to an evaluation of the changes in microstructure of smectites during embedding exchanges in liquid media, we have been able to show that smectite-group phases exhibit a specific behavior in organic solvents, contrasting with their well-known behavior in water. This has been accomplished by using different techniques of analysis which, in combination, allow advances in the understanding of the laws controlling clay-surface reactivity.

1) The arrangement of the clay particles depends on the nature of the clay and, more specifically, on its atomic structure, which partly determines the spatial arrangement of elementary layers and their interaction.

2) Both clay fabric and crystal structure depend upon the initial state of the sample. The clay microstructure depends on the stresses under which the material is prepared. This is particularly true when studying the geometry of the clay matrix.

The clay microstructure observed in transmission electron microscopy is not the same as the original microstructure with water, but is a result of the history of the material, of its reaction with solvents and resin and, last but not least, of the changes in vacuum and under the electron beam in the microscope. Changes once in the microscope will be discussed elsewhere.

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