VERMICULITE GELATION: STRUCTURAL AND TEXTURAL EVOLUTION

J. A. RAUSELL-COLOM, J. SAEZ-AUÑÓN* AND C. H. PONS†

Instituto de Ciencia de Materiales, CSIC, Serrano, 115 bis, 28006 Madrid, Spain
*Laboratorio de Geotecnia, Cedex, Alfonso XII, 3, 28014 Madrid, Spain
†Laboratoire de Cristallographie (ERA 841), UER de Sciences Fondamentales et Appliquées, R. Chartres, Orléans, France

(Received 25 November 1988)

ABSTRACT: Millimetre-sized flakes of a homogeneous, high layer charge vermiculite from S. Olalla (Spain) saturated with l'ornithine cations were made to swell in l'ornithine hydrochloride solutions of various concentrations, and the gel-like structures formed were subjected to uniaxial loads up to 150 g/cm². Small-angle X-ray diffraction measurements from the swollen flakes show well-modulated intensity patterns from which the equilibrium interlayer distances were obtained for the various swelling conditions. The interlayer spacings can be adequately expressed as normal-logarithmic distribution functions of probability density. The gel texture is described in terms of the average number of elementary layers, all in parallel orientation, constituting independent coherent domains within the swollen flake. Changes in structure and in texture taking place as the gel volume increases, or as water is expelled from the interlayer volume under mechanical compression, are followed by the variation of the corresponding parameters of order.

In contact with water or with dilute electrolyte solutions, expanding-lattice clay minerals, particularly Na-montmorillonite, take up large amounts of the liquid phase (20 g H₂O/g clay, or more), forming gel structures in which the elementary silicate layers are separated by water films several hundred Å thick (Norrish, 1973). The swelling properties of clays are important in controlling soil structure, drainage, mechanical stability of slopes etc. (Murray & Quirk, 1980). Clay-water pastes or suspensions have been thoroughly investigated for their electrokinetic, rheological or mechanical behaviour using Na-montmorillonite as a reference material (Swartzen-Allen & Matijevic, 1974; Van Olphen, 1977; Low, 1980).

Small angle X-ray diffraction (SAXRD) techniques have provided a useful means for measuring preferred equilibrium distances between parallel clay platelets as constrictions of various kinds are imposed on the gel. These measurements have lead to the understanding of the major factors affecting the forces originating at the clay-water interfaces (Norrish, 1954; Norrish & Rausell-Colom, 1963; Andrews et al., 1967). Recently developed methods of interpretations of SAXRD diagrams from disordered layer structures together with experimental improvements involving the use of very strong X-ray sources (synchrotron radiation) have made possible significant advancements in the study of the microstructure of montmorillonite clay gels, enabling quantitative determinations of interlayer distance distributions, order-disorder relationships, pore size distribution and particle geometry analysis under controlled swelling conditions (Pons, 1980; Pons et al., 1981; Ben Rhaiem et al., 1987).
Vermiculite is very similar to montmorillonite in many respects, the most significant differences being a higher and more homogeneous surface charge density, and a considerably larger particle size. It has been known for some time that millimetre-sized crystals of this mineral, when saturated with Li⁺ or with certain organic cations, swell in water to form very highly ordered gel structures. Swelling takes place exclusively in the direction normal to the crystal plane and the parallel orientation of the silicate layers is well preserved (Garrett & Walker, 1962; Walker, 1975). As a reference system for the study of clay-water interactions, vermiculite gels have the advantage over polycrystalline smectite gels of giving stronger diffraction intensities, with fewer ambiguities in interpretation (Norrish & Rausell-Colom, 1963; Rausell-Colom & Salvador, 1971; Viani et al., 1985).

In a previous publication (Saez-Auñón et al., 1983) a method was presented for the interpretation of small-angle diffraction patterns from vermiculite gels in which experimental modulation functions obtained from the diffraction intensities were compared with modulation functions calculated for stacking models. In the present communication, this method has been used to study the gel-forming properties of a high structural charge vermiculite from S. Olalla (Spain) in solutions of l-ornithine hydrochloride of various concentrations. Gelation of vermiculite depends largely on the surface charge density of the mineral layers as well as on the kind and valence of the interlayer cations. Because of the high layer charge of the vermiculite used, saturation with Li⁺ failed to yield gels in which all elementary layers are separated from their neighbours, but full dissociation occurs spontaneously with samples saturated with l-ornithine⁺. The changes in structure and in texture that take place as the gel volume increases, or as water is expelled from the interlayer volume under mechanical compression, are followed by the variation of the parameters of order from the corresponding SAXRD diagrams.

EXPERIMENTAL

Materials and sample preparation

Vermiculite from S. Olalla (Spain), the structural formula of which is

(Si₅.₃₉Al₂.₆₂)(Mg₅.₁₇Al₀.₂₉Fe⁵⁺₀.₀₄Fe³⁺₀.₄₄Ti₀.₃₀Mn₀.₀₂)O₂₀(OH)₄g₀.₉₂nH₂O

has a high, homogeneous, structural layer charge of 1.84 per formula unit, i.e., a charge approaching that of phlogopite.

L-ornithine hydrochloride C₅H₁₂N₂O₂·HCl was obtained from Sigma Chem. Co. The acid dissociation constants are pK₁ = 1.96, pK₂ = 8.65 and pK₃ = 10.76 (Dawson et al., 1969). Solutions in water at pH = 5.3 were used for all treatments. At pH = 5.3, solutions are at the point of maximum charge, where monovalent cations of the organic salt are the predominating species (ratio [A⁺]/[A⁻] of cations to dipolar ions of about 2000/1).

Flakes of uniform thickness (0.2 mm) were cleaved from large pieces of the natural Mg-vermiculite specimen, cut to an approximate size of 10 mm × 1 mm, saturated with Na⁺ by repeated leaching with 1 N NaCl at 60°C for several days, washed free of salt, dried on filter paper, and stored dry.

For saturation with l-ornithine⁺, each Na-saturated flake was immersed in 2 cm³ of 1 M solution of l-ornithine hydrochloride. Exchange was complete in 30 min for crystals of the above dimensions (Mifsud et al., 1971). The treatment was repeated three more times with fresh solution in order to eliminate traces of the interlayer Na⁺ ions released. Octahedral
Mg$^{2+}$ ions were also released by acid dissolution, and at equilibrium, the Mg$^{2+}$ concentration in solution, determined by atomic absorption spectrometry, was found to be $<1$ mg/dm$^3$.

Finally, to allow swelling, crystals were placed in ornithine hydrochloride solutions at the concentrations chosen and the solutions renewed twice during the following 24 h to permit equilibration.

**Small-angle X-ray diffraction measurements**

The SAXRD arrangement consisted of a 12 kW rotary anode Rotaflex RU-200 generator as X-ray source, operating at 40 kV, 200 mA with Ni-filtered, Cu radiation. A goniometer of the horizontal axis type was modified to contain a slit-collimating system consisting of a set of Soller vertical slits, a divergence slit of $1/30^\circ$ aperture placed next to the X-ray window, and a second slit of adjustable aperture incorporated just before the goniometer axis, 240 mm from the target. The detection system was by means of a LETI linear-position proportional counter placed at $2\theta = 0^\circ$, perpendicular to the X-ray beam direction, 420 mm from the goniometer axis. The linear resolution was better than 120 $\mu$m. Background intensities near the direct beam are sufficiently low to allow recordings down to $s = 2.5 \times 10^{-3}$ Å$^{-1}$, at point intervals of $s = 2.13 \times 10^{-4}$ Å$^{-1}$.

The specimen holder consisted of a perspex rectangular enclosure limited by X-ray transparent mylar windows. The swollen crystal lay flat on the holder base, 10 mm long $\times$ 2 mm wide, which was filled with ornithine hydrochloride solution up to a height of 1.5 cm. A fine mechanical displacement allows positioning of the specimen at the goniometer axis. Independent $\theta$-2$\theta$ movements allow rotation of the holder to enable the crystal to be oriented with its basal plane parallel to the X-ray beam. Swelling takes place at right angles to the layer planes, and diffraction is recorded in the transmission mode. Pressure can be applied to the crystal externally, via a flat plate (Fig. 1).

![Fig. 1. Schematic representation of sample holder. 1. Goniometer axis. 2. Swollen vermiculite flake. 3. Perspex cell with X-ray transparent windows. 4. Setting for application of uniaxial loads.](image-url)
Fig. 2 shows some selected small-angle X-ray intensity profiles from vermiculite gels in equilibrium with ornithine hydrochloride solutions of the concentrations indicated, and at various confining loads. X-ray intensities form well defined modulations extending to several (00l) reflections, these becoming sharper as the applied pressure increases. At maximum swelling (distilled water) the X-ray intensity decays continuously with s, without any apparent inflection or modulation.

INTERPRETATION OF X-RAY INTENSITY PROFILES

Several authors (Guinier, 1964; Mering & Tchoubar, 1968) have derived methods for direct analysis and interpretation of small-angle X-ray scattered intensities which are applicable
when central scattering extends over a narrow zone of the reciprocal space around the 000 reciprocal lattice node. Such a condition normally imposes restrictions relating to the extent of structural disorder present within the scattering particles themselves. Thus, it has been shown (Pons, 1980) that, for particles with high structural disorder, central scattering often decays slowly enough to overlap with the diffraction within the Bragg's domain corresponding to the first (001) reflection. Then, the application of the laws governing intensity distribution along each one of the two separate domains (000 and 001) is meaningless, and any quantitative interpretation based on these methods may be misleading. It is best, in these cases, to use indirect methods of interpretation which consist, essentially, in arriving at the best possible match between the interference function, extracted from the experimental intensity data, and theoretical modulation functions calculated for stacking models (Pons et al., 1981; Saez-Auñón et al., 1983; Ben Rhai'em et al., 1987).

For gels of 2:1 phyllosilicates, the basic unit for defining the model is the elementary 9.2 Å thick silicate layer, having lateral dimensions considerably larger than its thickness.

The swollen flake is assumed to contain a large number of scattering particles, commonly referred to as tactoids in Na-montmorillonite gels (Aylmore & Quirk, 1971). An average particle consists of a stack of M elementary layers, all structurally identical. Particles within the flake may be slightly misaligned, whereas all layers within a particle are assumed to be strictly parallel. The average particle has a thickness which is determined by M and by a, the mean interlayer spacing. For studying the gel-forming properties of layered materials, precise determination of M is desirable as it allows a quantitative evaluation, by means of a single parameter, of the particle-building process by face-to-face association of individual layers.

Particles are assumed to have a structure relating to the order existing in the sequence of spacings separating the M layers. Such a sequence is defined as a series of r different translations, d_i, affected by probabilities of occurrence p_i. The interlayer distance distribution function p(d_i) characterizes the order within the particles.

Calculation of the theoretical modulation function for a stacking model

The general expression for the X-ray intensity scattered by a disordered stack of parallel layers, all structurally identical and large enough in lateral dimensions, is (Mering, 1949):

\[ I_{00}(s) = \frac{1}{2\pi s^2} \left| F_{00}(s) \right|^2 \sum M \alpha(M) G_{00}(s, M) \]

where \( s = 2 \sin \theta / \lambda, \ F_{00}(s) = \) structure factor along the (00l) reciprocal lattice rod, \( \Omega = \) surface area of the layer unit-cell, \( \alpha(M) = \) weight fraction of particles of M layers within the flake, and \( G_{00}(s, M) = \) modulation function corresponding to the stacking sequence.

If it is assumed that there is no correlation in the sequence of translations between first neighbour layers, then the modulation function is

\[ G_{00}(s, M) = 1 + 2 \text{Re} \left[ \sum_{n=1}^{M-1} \frac{M - |n|}{M} \cdot Q(s) \right] \]

where \( \text{Re} \) indicates the real component of the complex summation within brackets, and \( Q(s) \) is a function accounting for the interference between each pair of adjacent layers (Plançon, 1976; Pons, 1980; Saez-Auñón et al., 1983). If the model consists of layers separated at
discrete distances with probabilities $p_i(d_i)$, then $Q(s)$ in equation (1) may be computed by

$$Q(s) = \sum_{i=1}^{r} p_i \exp(-i\pi s d_i)$$  \hspace{1cm} (2)

with $i = (-1)^i$ and the normalizing condition $\sum_{i=1}^{r} p_i(d_i) = 1$.

If the interlayer distance can vary continuously within a certain range, then the model may also be specified by probabilities generated from analytical functions of probability density, taking the distances $d_i$ at small regular intervals (e.g. $\Delta d = 1 \text{ Å}$). In such a case, the probability of occurrence is $p_i(d_i) = p'(d) \Delta d$, $p'(d)$ being density of probability, and the normalizing condition for equation (2) is

$$\sum_{i=1}^{r} p'(d_i) \Delta d = 1$$

The interpretation of the scattered intensity profile from a particular vermiculite gel is thus reduced to finding a distribution of spacings $p_i(d_i)$ and a number $M$ of layers for which the corresponding modulation function ($G(s,M,p_i,d_i)$) would account as closely as possible for the experimental data. The matching procedure is by trial and error refinement of, simultaneously, the values of $M$ and the set of distances and their probabilities (Pons et al., 1981; Saez-Auñón et al., 1983).

It will be seen in the following sections that models generated from the normal-logarithmic distribution of probability density suitably account for the experimental data in all cases studied. The usual expression for the normal-logarithmic distribution is:

$$p'(d) = \frac{(\sigma \sqrt{2\pi})^{-1}}{(d-d_0)^{-1}} \exp \{ -[\ln (d-d_0) - d_m]^2/2\sigma^2 \}$$  \hspace{1cm} (3)

This is clearly derived from the Gaussian distribution simply by substituting the random variable $(d-d_0)$ for its natural logarithm (Cramer, 1960). The parameters $d_m$ and $\sigma$ are, respectively, the mean and the standard deviation of the ‘original’ Gaussian distribution, and $d_0$ is the value of the minimum distance present in the system.

For the purpose of comparing experimental and calculated modulation functions, log-normal probability densities are more conveniently generated by using as parameters $d_{\text{max}}$ and $\sigma_D$, i.e. the modal distance and the ‘true’ standard deviation, respectively. In fact, $d_{\text{max}}$ is directly accessible from the diffraction data, while $\sigma_D$ is left free for adjustment. The value of $d_0$ is initially taken as 40 Å, i.e., the interlayer spacing measured in the vermiculite flake at high electrolyte concentrations ($c \geq 0.5$ mole/dm$^3$) before swelling to the gel state has taken place. Its final value is the last to be refined. The relationship between $d_{\text{max}}$ and $\sigma_D$, on one side, and $d_m$ and $\sigma$ on the log-normal distribution function (eq. 3), is given by the equations

$$d_m = \ln(d_{\text{max}} - d_0) + \sigma^2$$

$$\sigma = (\ln y)^{\frac{1}{2}}$$

$$y^4 - y^3 = \sigma_D^2/(d_{\text{max}} - d_0)^2$$

The experimental interference function

Interpretation of scattered intensity patterns by comparison with modulation functions calculated from models normally implies a knowledge of all terms relating to diffraction
geometry (adsorption, Lorentz-polarization, particle orientation) as well as to the absolute intensity scattered by the unit-cell of the diffracting element, so that the experimental intensity data can be converted to the absolute scale (Pons et al., 1980).

For vermiculite gels, Saez-Auñón et al. (1983) have shown that for recordings in the transmission mode, and because of the fact that the orientation between layers varies little as the gel volume increases (Rausell-Colom & Norrish, 1962), the experimental interference function may be obtained simply as the quotient

\[ G_{p,c}(s) = k \frac{I_{p,c}(s)}{I_{0,0}(s)} \]  

where \( I_{p,c}(s) \) is the experimental intensity obtained from a vermiculite flake swollen in a solution of concentration \( c \) and under a constraining load \( P \), \( I_{0,0}(s) \) is the intensity recorded for unconstrained swelling in distilled water (\( c = 0, P = 0 \)) for the same specimen, and \( k \) is a normalizing constant, taken as the inverse of the value of \( G_{p,c}(s) \) at large values of \( s \) where all modulations have decayed to a flat, horizontal line.

**Corrections to the theoretical modulation function**

The use of an X-ray beam with the shape of a line of finite width instead of an ideally narrow point-collimated beam causes a deformation on the intensity profile whose extent and significance should be properly recognized. For the specimens studied, there is no deformation from beam height, as the layer stacks are oriented parallel to the beam. But the deformation due to finite beam width, combined with finite resolution of the detection system, can be considerable and should not be neglected if the scattering curves have sharp modulations. In such cases, experimental \( G_{p,c}(s) \) functions and theoretical modulation functions \( G(s, M) \) are not comparable unless the instrumental deformation is accounted for in the following way.

Let \( I_{\text{line}}(s) \) be the scattered intensity that should be obtained from a narrow line-collimated beam, and \( T(s) \) the intensity profile of the direct beam as affected by the deformation caused by the detection system. According to Guinier & Fournet (1955) the observed intensity profile is obtained by the convolution product of the two functions

\[ I_{p,c}(s) = T(s) \ast I_{\text{line}}(s) \]

It has been shown (Saez-Auñón et al., 1983; Ben-Rhaïem et al., 1987) that for swollen vermiculite crystals the ‘ideal’ undeformed intensity \( I_{\text{line}}(s) \) may be expressed as

\[ I_{\text{line}}(s) = I_{0,0}(s). G(s, M, p, d) \]

where the \( G \) function is the theoretical modulation function corresponding to the model, as defined in the preceding section. As \( I_{0,0}(s) \) is a continuously decaying function free from any modulations (Fig. 2), its deconvolution for \( T(s) \) should leave a practically unaltered profile, therefore

\[ G_{\text{conv}}(s, M, p, d) = \frac{1}{I_{0,0}(s)} \cdot \{ [G(s, M, p, d) \cdot I_{0,0}(s)] \ast T(s) \} \]

Thus, for the purpose of comparing experimental interference functions \( G_{p,c}(s) \) with the corresponding theoretical modulation function for the model, it is sufficient in practice to substitute the latter for a modulation function \( G_{\text{conv}}(s, M) \) incorporating a convolution
product with the intensity profile of the direct beam (recorded for the same experimental conditions) as for the expression above.

Fig. 3 illustrates the extent to which a calculated modulation function may be affected by a convolution product with \( T(s) \). Fig. 3a shows \( G(s, M) \) functions calculated for stacking models with \( M = \infty \) and with \( M = 12 \) layers, at distances and probabilities as in the log-normal density distribution in the upper right corner. Fig. 3b shows the corresponding \( G_{\text{conv}}(s, M) \) profiles, the trace of the X-ray beam being that in the upper right corner. In the convoluted profile, peaks are broader than in \( G(s, M) \), and their height is considerably reduced (66\% reduction for \( M = \infty \), and 50\% reduction for \( M = 12 \) on the first peak at \( s = 7.14 \times 10^{-3} \text{Å}^{-1} \)). Notice that in Fig. 3a both peak-broadening and intensity reduction will also result in \( G(s, M) \) from the assumption of less layers in the stacking model. This implies that neglecting the correction on \( G(s, M) \) will normally lead to a misinterpretation of the experimental \( G_{\text{exp}}(s) \) profile, as an acceptable fitting with a calculated \( G(s, M) \) function would result in the acceptance of a stacking model which sensibly underestimates \( M \).

Fig. 4 shows the reduction of the intensity of the first peak in \( G(s, M) \) that might be expected after correcting for beam width for the present experimental conditions. The effect is larger for profiles with sharp, intense modulations, rapidly decaying to <10\% for profiles with broad modulations.

**Parameters of order and their significance**

A precise analysis of the X-ray intensity data will result in full characterization of the swelling status of a particular specimen by means of a set of interlayer distances and probabilities and of an average size for its particles. To correlate swelling to the variables involved, \( P \) and \( c \), the following parameters relating to the texture and structure of the gel may be conveniently used.

The structure of the particles can be adequately expressed in terms of:

(i) \( \bar{d} \), mean value of the interlayer distance distribution, to which physical swelling is proportional.

(ii) \( d_{\text{max}} \), the mode of the distribution, which would correspond to the minimum in a potential energy curve if the separation of neighbouring layers is regarded as a stable position resulting from opposing forces (Norrish & Rausell-Colom, 1963).

(iii) \( \delta^2/\bar{d}^2 \), a parameter which characterizes the disorder existing within the particles (Schiller & Mering, 1967; Saez-Auñón et al., 1983). The term \( \delta^2 \) is the weighted mean of the squares of the fluctuations \( d_i - \bar{d} \). The higher the regularity of the interlayer distance distribution, the lower the value of this parameter.

(iv) \( \bar{d}/d_{\text{max}} \), which characterizes the dissymmetry of the distribution.

When \( p(d_i) \) is expressed as an analytical function of probability density, then the parameter of skewness \( \mu_3/\sigma_{\text{B}} \) is more adequate (\( \mu_3 = \text{third central moment}, \sigma_{\text{B}} = \text{standard deviation} \)). For the log-normal density function

\[
\mu_3/\sigma_{\text{P}} = [2 + \exp (3\sigma^2) - 3 \exp (\sigma^2)]/[\exp (\sigma^2) - 1]^{3/2}
\]

The texture of the flake is related to:

(i) \( M \): average number of layers stacked together in parallel orientation forming a single particle. The average particle thickness in the direction perpendicular to the layer plane is then equal of \( M \bar{d} \).
Fig. 3. Modulation function calculated for a log-normal distribution of interlayer spacings as in upper right corner. Parameters $d_0 = 40\ \text{Å}, d_m = 4.62\ \text{Å}, \sigma = 0.1172$. a: $G(s,M)$ for $M = \infty$ (broken line) and for $M = 12$ (continuous line). b: Same functions after deformation from beam width. Direct-beam intensity profile in lower right corner.
FIG. 4. Intensity reduction of first peak in $G(s, M)$ after deformation for beam width, for stacking models with increasing disorder. $M$ = average number layers in the stacking model.

(ii) $m$: average number of layers in the coherent domain over the (001) reflection. The value of $m$ is that of $G(s, M)$ at $s = 1/d_{\text{max}}$ prior to convolution with $T(s)$. This parameter would indicate the presence of small, well-ordered stacks of $m$ layers, all nearly equally spaced at the distance $d_{\text{max}}$, within the larger, less-ordered domains of $M$ layers which constitute the particles. Thus $m$ is related both to order and to texture so that for very highly ordered gel structures, the value of $m$ closely approaches that of $M$ (Pons, 1980; Ben Rhaïem et al., 1987).

RESULTS AND DISCUSSION

In the following paragraphs, the gel-forming properties of S. Olalla vermiculite saturated with l-ornithine cations are studied by referring to the textural and structural status of swollen flakes. The changes concerning interlayer separation and particle rearrangement are followed as the gel volume increases (reducing electrolyte concentration) or as water is expelled from the interlayer volume by the effect of the loads applied.

X-ray measurements have been taken from flakes immersed in l-ornithine hydrochloride solutions of four different concentrations (between 0.12 mole/dm$^3$ and 0.0035 mole/dm$^3$), varying the load applied at constant electrolyte concentration (between 10 g/cm$^2$ and 150 g/cm$^2$).
Structural and textural evolution of vermiculite gels

In Fig. 5, the three representative patterns shown in Fig. 2 are analysed for illustration. In each case an interlayer distance distribution as shown in the upper right corner of the Figs. in the central row is assumed. Point patterns show the experimental modulation functions obtained from the intensity profiles as per equation (4). Broken line patterns (central row) are theoretical modulation functions calculated for the proposed distributions assuming particles constituted by a very large number of elementary layers, $M = \infty$, whereas patterns in continuous trace have been calculated for models with the same distribution of spacings, but for particles that have, on the average, a number of layers as indicated by $M$. The latter afford the best possible fitting with the experimental modulation functions, and therefore the models assumed, i.e. interlayer separations and $M$ values are retained as representative of the gel status. Patterns in the first and in the third rows of Fig. 5 correspond to models with a higher and with a lower number of layers per particle, respectively. They show theoretical modulation functions that suitably account for the position of the experimental modulations but not for their intensity.

Two facts emerge from the results of the above analysis. First, they show the precision with which interlayer spacings based on the log-normal distribution function account for all the features of the experimental modulation function. This holds true for the X-ray patterns of all the samples studied, clearly indicating the existence of a formal relationship between this particular type of probability distribution and the potential energy variation governing vermiculite swelling. Second, because the gel structures are sufficiently ordered (several well-resolved (00l) modulations present in the X-ray patterns), the interpretation procedure is capable of yielding information relating to particle thickness from X-ray data beyond the angular domain of the (000) reflection, which is hardly accessible to experimental recording with conventional goniometers. It should be pointed out, however, that for more disordered structures (X-ray patterns with broad peaks) the intensity distribution along (00l) reflections other than (000) becomes progressively insensitive to particle thickness (Pons, 1980; Saez-Auñón et al., 1983).

The picture obtained for the structure of a gel-like crystal is rather more complex than that of a single homogeneous batch of irregularly spaced parallel layers. Taking for instance the example of the flake swollen in l-ornithine hydrochloride solution of concentration $c = 2.10^{-2}$ mole/dm$^3$ and a confining load of $P = 99.4$ g/cm$^2$, it can be seen that it consists of independently diffracting particles having, on average, 19 elementary layers spaced as per the probabilities in the distribution of Fig. 5b, at a mean distance $d = 135$ Å. These particles have an average thickness $M_{av} \approx 2600$ Å, and they are separated by large spaces, or macropores, of dimensions comparable to their thickness. Both interlayer and interparticle spaces are filled with the solution phase. Within the stack of layers forming the average particle there exist ordered coherent domains of $m = 6$ layers all nearly equally spaced at $d_{max} = 131$ Å, which are themselves separated by regions containing layers also in parallel orientation, but less regularly spaced. Such a picture is consistent with the description given by Tessier (1984) from SEM photographs of polycrystalline aggregates of specimens of analogous nature. The need to introduce a texture parameter among the variables relating swelling to the overall behaviour of microcrystalline clay-water systems was first recognized by Pedro (1976) and has recently been developed by Ben-Rhaïem et al. (1987) in their study of montmorillonite-water pastes. Our results broaden the applicability of that concept as they reveal the existence of an interparticle swelling associated to intraparticle, or interlayer, swelling even when the mineral specimen is prepared in the form of a single macrocrystalline flake.
Fig. 5. Interpretation of experimental interference functions by comparison with calculated modulation functions from stacking models. Point patterns: experimental. Line patterns: calculated. Broken line, $M = \infty$. Continuous line, $M$ as indicated. Probability density of interlayer spacings for stacking models are shown in upper right corners of Figs. in central row. Parameters for the log-normal distribution functions are:

\[
\begin{align*}
&d_0 = 40 \text{ Å} \quad d_m = 49 \text{ Å} \quad \sigma = 0.2114 \quad \text{for } c = 0.02, P = 20.9 \\
&d_0 = 40 \text{ Å} \quad d_m = 454 \text{ Å} \quad \sigma = 0.1674 \quad \text{for } c = 0.02, P = 99.4 \\
&d_0 = 40 \text{ Å} \quad d_m = 51 \text{ Å} \quad \sigma = 0.084 \quad \text{for } c = 0.0035, P = 100.6
\end{align*}
\]
Structural and textural evolution of vermiculite gels

Plotted in Fig. 6 is the variation of the mean spacing \( \bar{d} \) as a function of the load supported by the flake. The resulting trend is similar to that reported by Norrish & Rausell-Colom (1963) for the swelling of Li-vermiculite, and by Rausell-Colom & Salvador (1971) for vermiculite swollen in solutions of \( \gamma \)-aminobutyric acid. It shows that the effect of pressure is small when the electrolyte concentration is high, so that the volume increase upon gelation is essentially controlled by concentration and very little by pressure, whereas at low electrolyte concentrations the application of small loads (> 50 g/cm\(^2\)) results in a significant contraction of the interlayer volume by exclusion of the liquid phase.

It is generally accepted that at the clay-water interface, there is a tendency for the clay-compensating cations to diffuse away from the mineral surface as their concentration is lower in the bulk solution. On the other hand, compensating cations are also attracted to the negatively charged layers; the result is the creation of a diffuse electrical 'double layer' next to the layer surfaces, the compensating cations between the layers of the stack being confined to the narrow space between opposing layer surfaces.

Unless the interlayer separation is very large, diffuse 'double layers' overlap, and a net electrostatic repulsion results from their interaction. To a first approximation the energy per unit area for that repulsion decays exponentially with layer separation according to the expression (Van Olphen, 1977):

\[
V_R(d) = \frac{64kTN}{1000x} y^2 c \exp \left[ -\kappa(d - d_0) \right]
\]

where \( c \) is the electrolyte concentration (mole/dm), and \( d_0 = 2 \times 10^{-7} \) cm is the effective thickness of the mineral layer, i.e., assuming two monolayers of water molecules strongly adsorbed on either side of each layer (Norrish, 1954; Norrish & Rausell-Colom, 1963). Other variables are: \( \kappa = \frac{8\pi N\epsilon^2}{ekT} \) is the inverse of the Deby-Hückel characteristic length, \( y = \left[ \exp \left( \frac{z}{2} \right) - 1 \right] / \left[ \exp \left( \frac{z}{2} \right) + 1 \right] \) is related to \( \psi_0 \), the electrical potential at the surface of the mineral layer by \( z = e \psi_0/kT \), and \( k, T, N, \epsilon, e \) have their usual electrochemical meaning (Verwey & Overbeek, 1948).

When a load is applied to the flake, it leads to a potential

\[
V_P(d) = P(d - d_0) \quad (P \text{ in dyne/cm}^2)
\]

so that, if the distance is large enough for Van der Vaals interaction to be neglected, the total energy of interaction is:

\[
V_T(d) = \frac{64kTN}{1000x} y^2 c \exp \left[ -\kappa(d - d_0) \right] + P(d - d_0) \quad (5)
\]

For the various values of \( c \) and \( P \), the potential \( V_T(d) \) may be computed from the expression above if \( \psi_0 \) is known. Alternatively, \( \psi_0 \) may be determined as the value for which the minimum in the potential curve appears at a distance \( d \) that coincides with the value \( d_{\max} \) found experimentally. Fig. 7 gives, for each of the electrolyte concentrations used here, the values of \( \psi_0 \) that best reproduce the experimental \( d_{\max} \). The values change with concentration but, for a given concentration, they remain nearly constant, irrespectively of \( P \). Besides, these values would correspond to a variable surface-charge density, ranging from 12 to 20% of the total mineral charge, indicating that a large proportion of the counterions remain adsorbed to the mineral surfaces as a Stern layer.

Once the potential energy variation is known, the corresponding distribution of distances within the layer stack may also be obtained if an equipartition function of the Boltzman type is admitted. Thus the expression

\[
p(d) = \exp \left\{ - \frac{|V_T(d) - V_T(\min)|.S}{kT} \right\} \int_0^\infty p(d)dd \quad (6)
\]
yields in terms of a single parameter ($S$, the surface extension of the layer stacks in cm$^2$) the probability density of interlayer distances that should be expected from a potential energy variation (equation 5) based on a mechanism of interaction of diffuse ionic 'double layers'. Fig. 7 shows, for comparison, the probability functions $p(d)$ resulting from diffuse 'double layer' interaction and from the analysis of the interference functions from the X-ray data. The electrolyte concentration and load applied are indicated in each case. Despite the approximations implied in the expression for the energy of 'double layer' repulsion, the coincidence between the two sets of curves is quite satisfactory, in support of the osmotic nature of intraparticle swelling.

The evolution of internal disorder has been followed in terms of the variation of the parameters $\delta^2/\bar{d}^2$ and $\mu_3/\sigma^3_0$ with pressure at constant electrolyte concentration (Fig. 8). In addition to causing a reduction of interlayer separation (Fig. 6), the application of pressure is accompanied by intraparticle ordering, i.e., the probability distributions become more symmetrical and the fluctuations of interlayer distances with respect to the mean distance are also reduced. Such effect is consistent with interlayer repulsion originating from diffuse
Structural and textural evolution of vermiculite gels

0.04
0.03
0.02
0.01
0.00

c = 0.12 M. 
P = 55 grs/cm²

0.02
0.01
0.00

FIG. 7. Interlayer distance distributions resulting from diffuse 'double layer' interaction (broken line) and from interpretation of X-ray data (continuous line). Parameters for the Boltzman distribution and for the log-normal distribution are:

\[ \psi_0 = 40 \text{ mV} \quad S = 5 \times 10^4 \text{ Å}^2 \quad d_0 = 40 \text{ Å} \quad d_m = 5.42 \text{ Å} \quad \sigma = 0.1561 \]
for \( c = 0.0035 \text{ M}, P = 37.2 \text{ g/cm}^2 \)

\[ \psi_0 = 78 \text{ mV} \quad S = 6.5 \times 10^4 \text{ Å}^2 \quad d_0 = 40 \text{ Å} \quad d_m = 4.9 \text{ Å} \quad \sigma = 0.2114 \]
for \( c = 0.02 \text{ M}, P = 20.9 \text{ g/cm}^2 \)

\[ \psi_0 = 100 \text{ mV} \quad S = 1.3 \times 10^5 \text{ Å}^2 \quad d_0 = 80 \text{ Å} \quad d_m = 3.9 \text{ Å} \quad \sigma = 0.2683 \]
for \( c = 0.037 \text{ M}, P = 33.76 \text{ g/cm}^2 \)

\[ \psi_0 = 115 \text{ mV} \quad S = 8 \times 10^4 \text{ Å}^2 \quad d_0 = 45 \text{ Å} \quad d_m = 3.53 \text{ Å} \quad \sigma = 0.3023 \]
for \( c = 0.12 \text{ M}, P = 55 \text{ g/cm}^2 \)

'double layer' interaction, as sharper and more symmetrical interlayer distance distributions would result from deeper potential energy wells as the pressure term of equation (5) increases. Except for the lowest electrolyte concentration, the two sets of curves in Fig. 8 have minima at about 80-100 g/cm², showing that for that pressure the system reaches a maximum of regularity. For higher pressures, the gel structure becomes progressively disordered, independently of the actual extent of physical swelling that the flake has undergone which, of course, varies considerably with \( c \) at constant \( P \) (Fig. 6).

The failure of the system to become ordered under the higher confining loads is not contradictory, as it would first appear, to a mechanism of diffuse 'double layer' interaction. The reason has to be found in other causes, operating concurrently, that affect the final shape and width of the interlayer distance distribution. When pressure is applied to the swollen flake, some of the solution phase is forced out from the interlayer volume. The parallel orientation of the silicate layers forming the particles, and the lateral extension of the particles themselves, will be preserved as long as the transfer of liquid to the bulk solution can take place under conditions of free homogeneous drainage. Because of the textural and structural complexity of the gel-like crystal it is conceivable that, for the higher loads, the liquid flux may cause some layers to bend, affecting either the parallelism or the lateral extension of the layer stacks, or both. Such changes do not affect the general trend of the
FIG. 8. Variation of structure parameters with pressure at constant electrolyte concentration

a: disorder $\sigma^2/\bar{a}^2$. b: skewness $\mu_3/\sigma_D^3$.

$\square$, $c = 0.0035$ Mole/dm$^3$  $\triangle$, $c = 0.02$ Mole/dm$^3$  $\bigcirc$, $c = 0.037$ Mole/dm$^3$

$\times$, $c = 0.12$ Mole/dm$^3$. 
Structural and textural evolution of vermiculite gels

Fig. 9. Variation of texture parameters with pressure at constant electrolyte concentration.
a: layers in ordered coherent domain. b: layers per particle.

\( \square, c = 0.0035 \text{ Mole/dm}^3 \)  \( \triangle, c = 0.02 \text{ Mole/dm}^3 \)  \( \circ, c = 0.037 \text{ Mole/dm}^3 \)

\( \times, c = 0.12 \text{ Mole/dm}^3 \).
potential energy variation for intraparticle swelling, i.e., a deeper energy well with a minimum at a shorter interlayer distance will still result from equation (5) for a higher pressure. However, the corresponding interlayer distance distribution from equation (6) may be broader if the surface extension $S$ of the layer stacks becomes smaller after compression.

Concerning the variation of $m$ and $P$ at constant $c$ (Fig. 9a), the following facts can be outlined. At small loads, $m$ is small at all concentrations (4 layers for $c = 0.12$ mole/dm$^3$, up to 5–6 layers for $c = 0.0035$ mole/cm$^3$). It seems as if the number of layers forming the coherent domain over the (001) reflection might be a property inherited from the textural characteristics of the mineral specimen that remains unaltered upon gelation and unaffected by any constrictions resulting from the concentration of the electrolyte used. Next, under increasing loads, two separate trends are inferred from Fig. 9a depending on concentration. First, for the lowest concentration, an important reorganization of the intraparticle structure is taking place as indicated by a steady increase of $m$ to about 15 layers at $P = 100$ g/cm$^2$. Second, for the higher concentrations, $m$ remains constant or increases little, and then drops to lower values at $P = 80–100$ g/cm$^2$ as for the minima observed in the curves of Fig. 8a and b. Therefore, the gain or the loss of order discussed above are accompanied by a simultaneous

![Graph showing the correlation between structural and textual parameters](image)

**Fig. 10.** Correlation between structural and textual parameters.

$\square$, $c = 0.0035$ Mole/dm$^3$  $\triangle$, $c = 0.02$ Mole/dm$^3$  $\bigcirc$, $c = 0.037$ Mole/dm$^3$

$x$, $c = 0.12$ Mole/dm$^3$. 
change in the size of the coherent domain in the (001) reflection. Fig. 10 shows a clear correlation between the two parameters.

In Fig. 9b the average number of layers per particle, $M$, is plotted against the load supported by the flake. When the concentration is high, $M$ is small and remains constant with $P$, showing that particle thickening by face-to-face association is not taking place under the loads applied. Again, it appears that the textural characteristics of the mineral specimen are still retained by the gel while the concentration of the swelling solution is high. At these concentrations, the applied loads may be effective in compressing the interlayer volume within the particles, but the exclusion of water from the pore space between particles would require higher loads, which would indicate that interparticle and intraparticle interactions are of a different nature. In contrast, when the electrolyte concentration is low, the number of layers per particle $M$ increases steadily, depending both on concentration and on pressure. As the textural constraints imposed by salt concentration are released, the loads applied become increasingly effective in particle thickening by forcing separate particles into parallel orientation. At the highest dilution ($c = 0.0035$ mole/dm$^3$), where intraparticle interactions are strong, both the texture and the structure of the swollen flake are affected by pressure in an almost identical manner, and any differentiation between interlayer and interparticle interactions, and between the structures of their respective volumes becomes impracticable. The gel system acquires a homogeneous configuration in which the structural disorder decreases as the applied load increases.

ACKNOWLEDGMENT

The financial support from CICYT (project no PB86-624) is gratefully acknowledged.

REFERENCES


