

Vermiculitization of smectite interfaces and illite layer growth as a possible dual model for illite-smectite illitization in diagenetic environments: a synthesis

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ABSTRACT: A structural model is proposed for illite-smectite (I-S) from diagenetic environments which accounts for the presence of three different layer types which are defined as follows: montmorillonite (low-charge, octahedrally substituted, fully expandable), vermiculite (high-charge, octa- and tetrahedrally substituted, only partly expandable) and illite ($K_{0.9}Si_{3.3}Al_{0.7}R_{1.8}^{3+}R_{0.2}^{2+}O_{10}(OH)_2$). All three layers may be found within the MacEwan crystallites, whereas external edges of the crystallites are only vermiculitic during the illitization process. In the proposed model, a layer is defined symmetrically on each side of the interlayer space, leading to the existence of polar 2:1 units. It is proposed that the I-S growth is a three step mechanism: (1) formation, from sediments of variable composition, of montmorillonite crystallites; (2) vermiculitization of the montmorillonite crystallite interfaces and of inner montmorillonite layers; and (3) precipitation of illite of fixed chemical composition. The I-S crystal grows by addition of illite layers linked by K^+ or NH_4^+ ions saturating the vermiculitic interfaces.

KEYWORDS: montmorillonite, vermiculite, illite-smectite, illitization, crystal growth.

The illitization of smectite and illite-smectite (I-S) mixed-layer minerals in sediments is probably the most documented process of clay diagenesis but, in spite of the huge amount of available data, the illitization mechanism remains controversial. In most studies, information obtained from X-ray diffraction (XRD), chemical, or transmission electron microscope (TEM) studies has been devoted mainly to the determination of chemical composition and crystal structures of I-S series. Recently, the two concepts used to describe these structures, i.e. MacEwan crystallites (MacEwan, 1958) and fundamental particles (Nadeau *et al.*, 1984a), have been reconciled since fundamental particles are fragments of larger

MacEwan crystallites (Veblen *et al.*, 1990; Reynolds, 1992; Dong & Peacor, 1996). However, no general agreement has been reached on important issues such as the number of elementary layer types (2 or 3) involved in these mixed-layered structures, or as the actual composition of the expandable component. In particular the location (tetrahedral beidellite-like or octahedral montmorillonite-like) and the amount (low-charge smectite-like or high-charge vermiculite-like) of charges in expandable layers remain poorly constrained.

The determination of the crystal-chemical structure of I-S minerals and of their modifications is a preliminary step, essential to the understanding of the reaction mechanisms leading to the formation of illite. However, the models based on the MacEwan crystallite or fundamental particle concepts are restricted to the one-dimensional description of I-S

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structures parallel to the *c*-axis and ignore how these crystals grow. In a comprehensive literature review, Altaner & Ylagan (1997) reported the main mechanisms proposed for this transformation; (1) solid-state transformation (SST); (2) dissolution and crystallization (DC); and (3) Ostwald ripening (OR). Despite the statistical analysis of I-S particle dimensions that commonly leads to steady-state distributions, as expected with OR (Inoue *et al.*, 1988; Eberl & Środoń, 1988; Eberl *et al.*, 1990), this mechanism describes poorly the illitization process because the necessary conditions for its application are much more restrictive than that found in natural systems (Baronnet, 1991; Varajao & Meunier, 1995). In particular, this mechanism is restricted to isothermal and monomineralic systems and cannot account for the smectite-to-illite transition. According to Altaner & Ylagan (1997), the other two mechanisms may occur as a function of the rock permeability, both being active in shales.

The present work explores further these reaction mechanisms in the case of burial diagenesis and proposes a structural model for I-S based on polar 2:1 layers. This structural model is based on the huge amount of published data, reconsidered from the I-S growth point of view. Special attention is paid to the nature of the outer edges of I-S crystals, which should be compatible with the crystal growth observed during the illitization process, and to the nature and composition of expandable interlayers.

The goals of this paper were to extract the key factors underlying the apparent disagreement in the literature, and to propose a model for illitization in diagenetic environments consistent with the observed growth of I-S particles. The first part of the paper is devoted to the analysis of the current knowledge concerning I-S crystalline and chemical properties. It is based on a review of some of the most significant articles that have explored the crystal structure, the evolution of chemical composition, and of I-S particle morphology (shape and size) during illitization. In the second part, an improved model for I-S illitization accounting for the observed I-S crystal growth, and I-S ordering sequences, is proposed.

DATA FROM THE LITERATURE

In the authors' opinion, most of the disagreement on this subject in the literature results from incomplete definitions of the measured objects,

and, as a consequence, it seemed necessary to define as precisely as possible the various terms used hereafter (see Glossary). As an example, the most universal parameter used in I-S studies is the percentage of illite layers (% illite), generally measured by methods using XRD of air-dried and/or glycol-saturated oriented preparations (Środoń, 1980; Watanabe, 1988; Inoue *et al.*, 1989; Moore & Reynolds, 1989). These methods give the proportions of expandable vs. non-expandable layers in clay samples. Large uncertainties are expected because the % illite is determined only from peak positions and not from complete profile fitting, which is the only accurate way to characterize mixed-layer minerals (MLM, Drits & Tchoubar, 1990). However, despite these uncertainties, these methods are self-consistent and yield a reasonable estimate of the actual illite content. The most important problem, in our opinion, arises from the heterogeneity of expandable interlayers and, in particular, from the presence of high-charge vermiculitic layers with swelling properties different from that of low-charge smectitic ones (Shutov *et al.*, 1969; Reynolds, 1980; Drits *et al.*, 1997a). The coexistence of both types of expandable layers adds even more complexity to the interpretation of smectite-to-illite evolution.

Crystalline and chemical structure of I-S

Presence of expandable high- and low-charge layers. To characterize the structure of I-S, the first requirement is, as for any other MLM, to determine the number of different layers that are interstratified. As shown by Reynolds & Hower (1970), Reynolds (1989), or Lanson & Velde (1992), major discrepancies exist between experimental XRD patterns of I-S and patterns calculated for a two-component illite-montmorillonite mixed-layer. In particular, the profile shape, and more especially the width of the diffraction lines, differ significantly between experimental and calculated XRD patterns in the 18.0–8.0 Å range. Recently, Drits *et al.* (1997a) showed that the XRD patterns of diagenetic I-S from North Sea shales are reproduced accurately using a mixed-layer structure in which three different components (smectite, vermiculite, illite) are interstratified. The existence of such a vermiculite component in the I-S structure had been shown previously from the Fourier analysis of XRD patterns (Shutov *et al.*, 1969; Foscolos & Kodama, 1974).

Furthermore, most natural smectites behave as MLM in which low- and high-charge expandable interlayers are stacked (Čičel & Machajdik, 1981; Machajdik & Čičel, 1981). In addition, the highly heterogeneous character of I-S interlayers has been established in samples from contrasting environments and having different compositions. High-charge expandable layers were identified by means of K-saturation tests in natural I-S samples (Howard, 1981) as well as in experimentally synthesized ones (Whitney & Northrop, 1988). Such high-charge expandable layers have also been identified in illitic minerals using XRD and HRTEM on alkylammonium-exchanged samples (Vali & Hesse, 1990; Vali *et al.*, 1991; Cetin & Huff, 1995a,b).

The chemical compositions of the diagenetically altered shales, sandstone or bentonite series studied by Środoń *et al.* (1986, 1992), Ramseyer & Boles (1986), Nadeau & Bain (1986), Awwiller (1993) or Cuadros & Altaner (1998) also plead for the formation of high-charge expandable layers together with the illitization process (Fig. 1). Indeed, even though the trend towards a vermiculite pole is not clearly defined, I-S compositions, and more especially their $K^+ + NH_4^+$ contents, scatter significantly (large double arrow, Fig. 1) for a

unique layer charge, e.g. 0.8 per Si_4O_{10} . The lower value clearly indicates the presence of high-charge layers not saturated with K^+ or NH_4^+ , and thus still expandable. Similarly, the experimental illitization of montmorillonite has shown that the proportion of high-charge layers increases during the first step of a dual reaction (Whitney & Northrop, 1988). These high-charge expandable layers are reminiscent of the vermiculitic component described by Shutov *et al.* (1969), Foscolos & Kodama (1974) and Drits *et al.* (1997a).

It may be concluded therefore, that a schematic description of I-S must include a minimum of three components: one non-expandable, one low-charge fully expandable, and one high-charge partly expandable layers (i.e. illite, montmorillonite, and vermiculite layers, respectively). Actually, these three layer types are only a simplified scheme of the heterogeneity observed in nature. As a first example, this description considers all non-expandable layers as illite, i.e. K-rich layers whereas several authors (Lindgreen, 1994; Drits *et al.*, 1997b, 1998b) have shown that NH_4 -rich non-expandable layers (tobelite layers) are generated preferentially during part of I-S illitization in Upper Jurassic oil source shales from the North Sea. The dichotomous description of expandable layers as

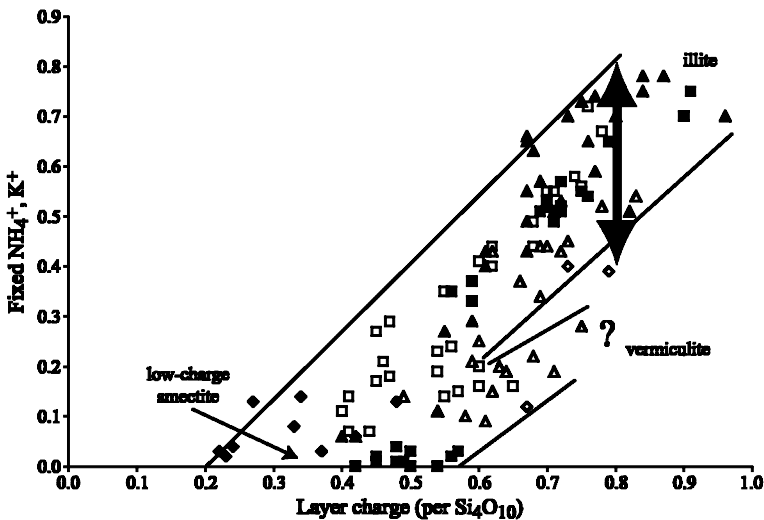


FIG. 1. Relationships between the total layer charge and the fixed K^+ and NH_4^+ cations in natural I-S series from shales, sandstones or bentonites. Solid diamonds: Ramseyer & Boles (1986); open diamonds: Środoń *et al.* (1992); solid squares: Nadeau & Bain (1986); open squares: Środoń *et al.* (1986); solid triangles: Cuadros & Altaner (1998); open triangles: Awwiller (1993). The large double arrow outlines the K content of the illite-vermiculite domain.

being either low-charge fully expandable or high-charge partly expandable is a second example of this simplified scheme. Indeed, Drits *et al.* (1997a) and Sakharov *et al.* (1999) have shown that the swelling behaviour of expandable layers in diagenetic I-S may be modified as a function of the exchangeable cation, indicating an intermediate composition between that of montmorillonite and that of vermiculite as described in the present article.

Chemical composition and structural order of montmorillonite, vermiculite and illite layers. The second requirement to characterize the structure of I-S is to determine the structural order and chemical composition of these three elementary layers. First, the amount and the location of the layer charge of these three layer types must be consistent with the chemical data reported previously. Velde & Brusewitz (1986) showed from the chemical compositions of different I-S series, both from bentonites and shales, that the smectite component consistently has a montmorillonitic composition, with only octahedral substitutions. Meunier & Velde (1989), using data from several I-S mineral sequences in shales and bentonites from diagenetic series, hydrothermal areas or metasomatic environments, have shown that the charge of this smectite component ranges from 0.30 (low-charge) to 0.60 (high-charge) per $O_{10}(OH)_2$ and that the illite component has a fixed composition $K_{0.9}Si_{3.3}Al_{0.7}R_{1.8}^{3+}R_{0.2}^{2+}O_{10}(OH)_2$. One may note in Table 1 that the chemical compositions obtained by other methods for the illite end-member (Lanson & Velde, 1992; Środoń *et al.*, 1992) are similar to the one determined by Meunier & Velde (1989). This layer charge is different from that of true micas: 0.9 instead of 1.0 per Si_4O_{10} . The homogeneity of the illite end-member composition through the natural formations studied indicates that the I-S series results from the

addition of illite layers whose compositions are controlled by intensive variables. In other words, the I-S series must be considered as resulting from the formation and/or growth of illite layers having a fixed composition. Again, this fixed composition illite may be a simplified description of nature's variability as lower illite layer charge (0.75 per Si_4O_{10}) was determined in I-S from diagenetically altered shales by Drits *et al.* (1997a) by fitting the experimental XRD profiles.

Because of the presence of the third component, the actual nature of the expandable end-member is more complex than apparently indicated by its chemical composition. The XRD studies using the Li-saturation test (Greene-Kelly, 1953) have revealed a 'beidellitic' behaviour in I-S mixed-layers (Howard, 1981; Sato *et al.*, 1996) and, consequently, the existence of expandable inter-layers limited by substituted tetrahedral sheets. The existence of such expandable layers having tetrahedral substitutions is consistent with ^{29}Si NMR data obtained by Altaner *et al.* (1988). However, the mean structural formulae proposed by these authors for illite and smectite end-members ($Si_{3.19}Al_{0.81}$ and $Si_{3.66}Al_{0.34}$, respectively) remain speculative because they were calculated assuming the existence of only two components (illite and low-charge smectite) in the I-S stacking. Actually, the discrepancy observed by Altaner *et al.* (1988) between the composition determined by NMR and other techniques could be reduced, if not explained, by using two expandable components, one with low-charge and octahedral substitution (montmorillonite) and the other with a high-charge induced by tetrahedral substitutions (vermiculite). This description is reminiscent of that of Kerns & Mankin (1968) who have shown previously that most expandable layers are octahedrally substituted low-charge, whereas less expandable layers are tetrahedrally substituted.

TABLE 1. Chemical compositions of the illite end-member of I-S mixed-layers expressed as ionic proportions per $O_{10}(OH)_2$. The oxidation state of Fe ions is arbitrarily determined with respect to the electrical neutrality.

Reference	Si	^{IV}Al	^{VI}Al	^{VI}Fe	Mg	K
Meunier & Velde (1989)	3.30	0.70	1.80	0.05	0.15	0.90
Lanson & Velde (1992)	3.25	0.75	1.75	0.10	0.15	0.90
Środoń <i>et al.</i> (1992)	3.20	0.80	1.85	0.05	0.10	0.90

Crystal growth during the illitization process

Size and shape of I-S mixed layers. From the study of I-S series originating from burial diagenesis, hydrothermal activity, and metasomatism, it is now established that, in most cases, the shape and size of I-S crystals change with increasing temperature. For example, Inoue *et al.* (1987) have shown that the R0 and R1 I-S crystals are flaky and lath-shaped, respectively. Additionally, the morphological ratio (length/width) of the laths decreases with increasing diagenesis towards more isotropic (pseudo-hexagonal shaped) crystals (Lanson & Champion, 1991; Inoue & Kitagawa, 1994). Statistical analyses have shown that this morphological change is accompanied by an increase in average size, and that crystal or fundamental particle size distributions are approximately log-normal in shape and steady-state when plotted in reduced coordinates (Eberl *et al.*, 1990; Lanson & Champion, 1991; Šucha *et al.*, 1993). Such a morphological evolution is incompatible with a pure solid-state transformation mechanism, as evoked by Shutov *et al.* (1969) or Bethke & Altaner (1986), and was interpreted at one time as resulting from a specific dissolution-recrystallization process, namely Ostwald ripening (OR) (Eberl & Środoń, 1988; Inoue *et al.*, 1988). However, it should be noted that the OR process cannot account for a mineral transformation, such as I-S illitization, and that none of the OR physico-chemical conditions are satisfied during diagenesis. Indeed, four conditions have to be satisfied in OR (Baronnet, 1982, 1991; Lanson & Champion, 1991): (1) isothermal system in space and time; (2) only one solid phase is stable in the system; (3) closed system (isochemical conditions); and (4) the solution is weakly supersaturated with respect to the solid phase.

However, it remains that the smallest, smectite-richest, crystals disappear, or transform, whereas large illite-rich and illite crystals grow (Varajao & Meunier, 1995). To refine this global scheme it is necessary to take into account the heterogeneity of the clay fraction. This heterogeneity, which is implicit in the Markovian statistics used to model I-S (Drits, 1985), may be described schematically using the mathematical decomposition of diffraction patterns (Lanson & Champion, 1991). In particular, the illitic clay fraction can be described as being composed of crystal sub-populations that differ in their expandability properties on ethylene glycol

solvation such as I-S, poorly crystallized illite (PCI) and well-crystallized illite (WCI). Each of these sub-populations is composed of crystals having different thicknesses and/or compositions (% illite). The authors' model of morphological and compositional transformations of I-S during burial diagenesis is shown schematically in Fig. 2. All these transformations are governed mainly by the growth of illite layers having a fixed composition on both I-S and illite crystals, whereas the smallest I-S and illite crystals are dissolved. One may note that even though this growth process seems predominant, it does not preclude a partial solid-state illitization of I-S.

Fundamental particle/crystal thickness-composition relationships. Three parameters can be used to describe the coherent stacking of I-S: (1) the mean thickness of fundamental particles (T_{fp}) stacked to form MacEwan crystallites; (2) the average number of 2:1 layers in MacEwan crystallites (N , T_{cry}); and (3) the average proportion of swelling interlayers (EXP) in MacEwan crystallites. These three parameters are interdependent, as shown by Środoń *et al.* (1990, 1992) and Drits *et al.* (1998a). Only two of them are necessary to characterize I-S crystals if these parameters are determined using a similar weight for all observations, i.e. if crystallite volume is used to weight-average TEM measurements.

To determine the parameters above, several methods are available: (1) counting layers on high resolution TEM (HRTEM) lattice fringe images to measure T_{cry} (Środoń *et al.*, 1990); (2) Pt-shadowing to measure T_{fp} (Nadeau *et al.*, 1984a) or T_{cry} (Inoue & Kitagawa, 1994); (3) direct measurement of T_{fp} from the Bertaut-Warren-Averbach (BWA) analysis of XRD patterns collected on I-S intercalated with high molecular weight polyvinylpyrrolidone (PVP-10; Eberl *et al.*, 1998); (4) calculation of T_{fp} and of the average number of fundamental particles building up MacEwan crystallites using the fixed cation content (Środoń *et al.*, 1992; Eberl & Blum, 1993); and (5) determination of the coherent scattering domain size (CSDS, N) and of the illite content (EXP) from XRD patterns. This can be performed either by trial-and-error comparison with simulated profiles or, in favourable cases, by using simplified methods such as peak position-FWHM (full width at half maximum intensity) plots (Lanson & Velde, 1992; Lanson *et al.*, 1996). However, the most reliable procedure to determine both N and the illite content from XRD patterns is to determine at first the CSDS distribution from the

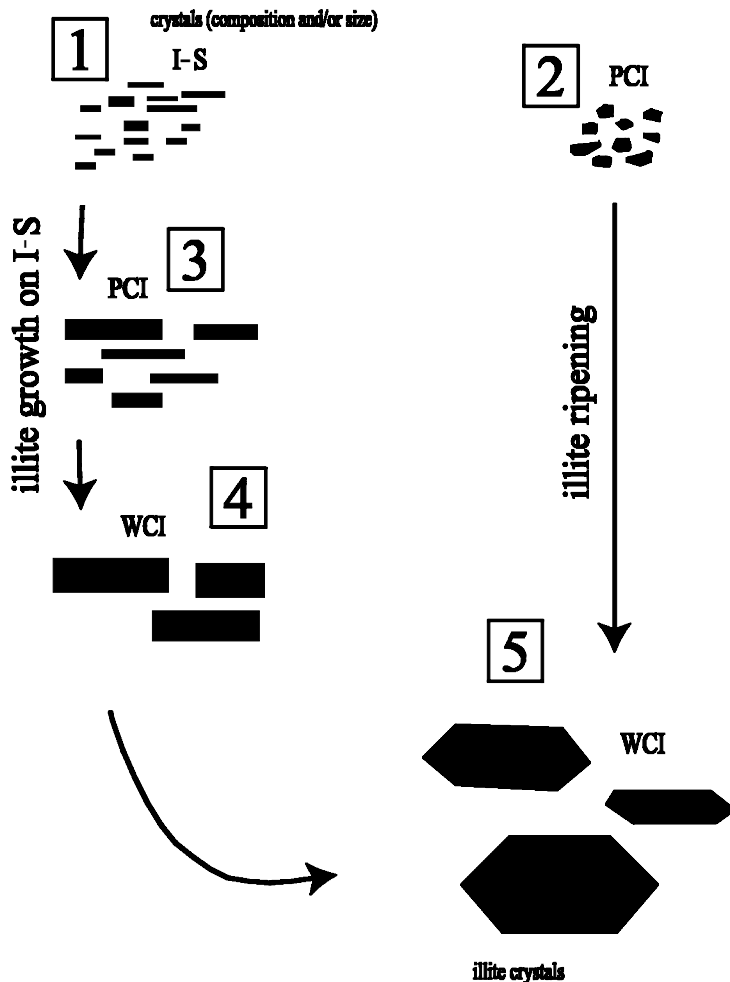


FIG. 2. Schematic representation of the morphological evolution (size and shape) of I-S mixed-layers and illite during late-stage diagenesis. Five groups may be distinguished according to morphological and XRD parameters (see text for details). I-S, PCI and WCI refer to the XRD parameters of illitic clays (Lanson *et al.*, 1998) and represent I-S MLM, poorly crystallized illite and well-crystallized illite sub-populations, respectively. The arrows indicate the processes which transform the small particles into larger, more illitic ones with increasing diagenetic conditions.

BWA analysis of XRD patterns obtained from K-saturated, heated I-S samples, and then the illite content by fitting the complete XRD profiles obtained on air-dried and/or ethylene glycol-solvated preparations of the same I-S samples (Drits *et al.*, 1998a).

Few papers are devoted to the statistics of fundamental particle and crystal thicknesses vs.

illite content using direct measurement techniques (Środoń *et al.*, 1992; Inoue & Kitagawa, 1994; Dong & Peacor, 1996). All these authors consistently show a steady thickening of I-S crystals/fundamental particles with increasing illite content. A CSDS increase, along the *c*-axis, was related to the decrease of FWHM measured on I-S XRD patterns (Lanson & Velde, 1992) in shales and

sandstone diagenetic series, even though this latter parameter is also controlled by factors such as interstratification effects, instrumental effects, strains or distortions within crystals, and stacking faults in addition to crystallite size. Lanson *et al.* (1998), using more than 700 decompositions of XRD patterns of I-S from diagenetic shales and sandstones, have shown that FWHM and the position of the elementary bands do not vary independently. This indicates that the illite content of ordered I-S crystals (Fig. 2, groups 1 and 3) increases simultaneously with the CSDS and that illite average CSDS (Fig. 2, groups 2, 4, and 5) increases with increasing diagenetic conditions as shown by the increase of T_{cry} and T_{fp} (Drits *et al.*, 1997c, 1998a).

DISCUSSION

Structure of expandable layers and of crystal interfaces

As discussed above, an accurate structural model for I-S must answer the following question: how can I-S minerals having a montmorillonite + illite bulk chemical composition display swelling properties similar to that of beidellite? Or, how is it possible to distribute electric charges and interlayer cations to have a global composition of a montmorillonite + illite mixture and, simultaneously, a heterogeneous swelling behaviour? A possible model is proposed in Fig. 3 where the expandable layers of the MacEwan crystallites are of two types thus inducing a heterogeneous swelling behaviour. The first type is low-charge and presents a montmorillonitic character with mostly octahedral sheet charge, whereas the second type has a high-charge vermiculite-like character with predominant tetrahedral sheet charge. The interlayer region defined by two interfaces of the second type remains expandable as long as not saturated with K^+ or NH_4^+ .

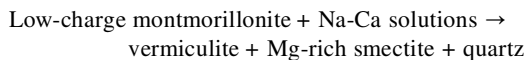
Finally, because illitization and crystal growth are concomitant, a structural model for I-S has to be compatible with the growth constraints. In particular, this model has to determine appropriate crystalline and chemical properties for the outer edges of the I-S crystal. It should be noted that in the proposed model the outer edges of I-S crystals are high-charge expandable ones, in agreement with the presence of such high-charge layers with exchangeable cations on the outside edges of

rectorite crystals deduced by Jakobsen *et al.* (1995) from NMR data. This is also in agreement with the evolution of I-S catalytic properties which are dependent on Al for Si tetrahedral substitutions on external basal surfaces as demonstrated by Johns & McKallip (1989).

The existence of high-charge expandable layers results from the formation of tetrahedral charges starting from a low-charge montmorillonitic material. Such a process was proven experimentally by Howard & Roy (1985) on a pure montmorillonite material (SWy-1). In the early diagenetic stages of shales and sandstones from Eocene formations in Japan, Sato *et al.* (1996) also described the formation of tetrahedral charges leading to the conversion of montmorillonite to beidellite. According to these authors the beidellitization of montmorillonite is the first step of the I-S illitization observed at greater depth. Two mechanisms can control the replacement of Si by Al in tetrahedral sheets: solid-state transformation or dissolution-precipitation (Altaner & Ylagan, 1997).

Solid-state transformation. The tetrahedral sheets of some montmorillonite layers are modified by the replacement of Si by Al. In such cases, total layer charge increases because a tetrahedral charge is added to the original octahedral one. The solid-state transformation produces high-charge bi-substituted layers similar to vermiculite ones. Such a process has been evidenced in diagenetically altered bentonite samples (Cuadros & Altaner, 1998).

Dissolution-precipitation. Quartz precipitates as some montmorillonite layers are dissolved (Howard & Roy, 1985; Whitney & Northrop, 1988). The chemical balance of this reaction also implies the crystallization of an Mg-rich component that was supposed to precipitate in the interlayer (Howard & Roy, 1985) or as a separate phyllosilicate phase (Meunier *et al.*, 1998). In the absence of any XRD evidence of brucite-like sheets, it is likely that the Mg-rich phase is a saponite or a stevensite (Mg-rich trioctahedral smectite), and that the complete reaction may be written:



This reaction is difficult to observe in diagenetically altered rocks because expandable layers are not differentiated, and because Mg-smectite may be replaced by a Ca-Mg-Fe²⁺ carbonate phase (dolomite or ankerite) if CO₂ is available in the system. Nevertheless, the formation of a beidellite +

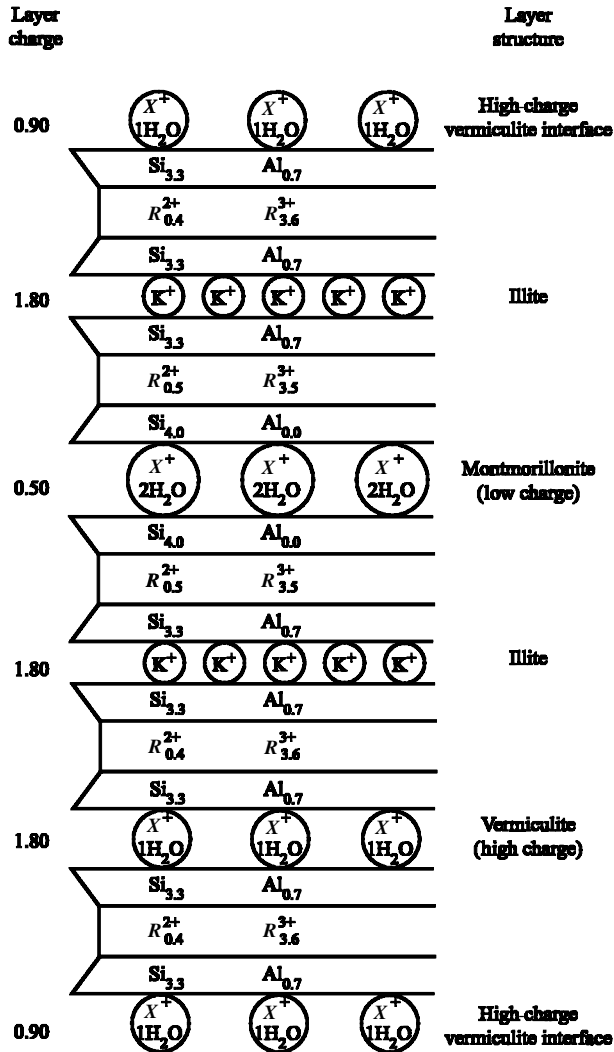


FIG. 3. Schematic representation of the distribution of charges in an I-S crystal using a three component structure: illite-montmorillonite-vermiculite. The whole stacking has an illite plus montmorillonite bulk chemical composition. When saturated with K or hydrated ions, the high-charge interlayers are either collapsed (illite) or partly expandable (vermiculite), respectively.

saponite assemblage has been observed experimentally by Yamada *et al.* (1991) and Yamada & Nakasawa (1993) during the hydrothermal alteration of synthetic beidellite-montmorillonite mixed-layers. Investigations of high enthalpy geothermal systems also show that montmorillonite is replaced systematically by a beidellite + saponite assemblage at temperatures >100°C (Beaufort *et al.*, 1995a,b).

A model for a possible growth mechanism accounting for the illitization of I-S crystals

The two-step process suggested by Howard (1981) and Whitney & Northrop (1988) for the illitization of I-S crystals results in a natural series from the overlap of two processes: I-S illitization and direct precipitation of illite, the I-S illitization

itself being a two-step process (Drits, 1985). The first step (vermiculitization) is the formation of the high-charge, tetrahedrally substituted layers and crystal interfaces from the original low-charge montmorillonite. This process is presumably a solid-state transformation with a low activation energy of ≈ 3 kcal/mol (Howard & Roy, 1985; Fig. 4a,b). The second step (growth of illite layers) is the addition of illite layers whose external interfaces behave as high-charge vermiculite if their charge is not compensated for by K^+ and/or NH_4^+ (Fig. 4c,d). In natural environments, the activation energy of this second reaction ranges from 25 to 30 kcal/mol according to the authors.

Figure 4 depicts the illitization of smectite crystals schematically, starting from a 100% montmorillonite crystal. The presence of both low- and high-charge expandable interfaces in the I-S crystals is the major difference with the fundamental particle model. The proposed model, based on the growth of illite layers on smectite and I-S crystals, explains the conversion from random to ordered interstratification observed in natural environments as shown by Shutov *et al.* (1969). Additionally, one may note that as diagenesis proceeds, the ordering increases because only illite layers are added on the outer interfaces of I-S crystals. At the same time the inner interlayers,

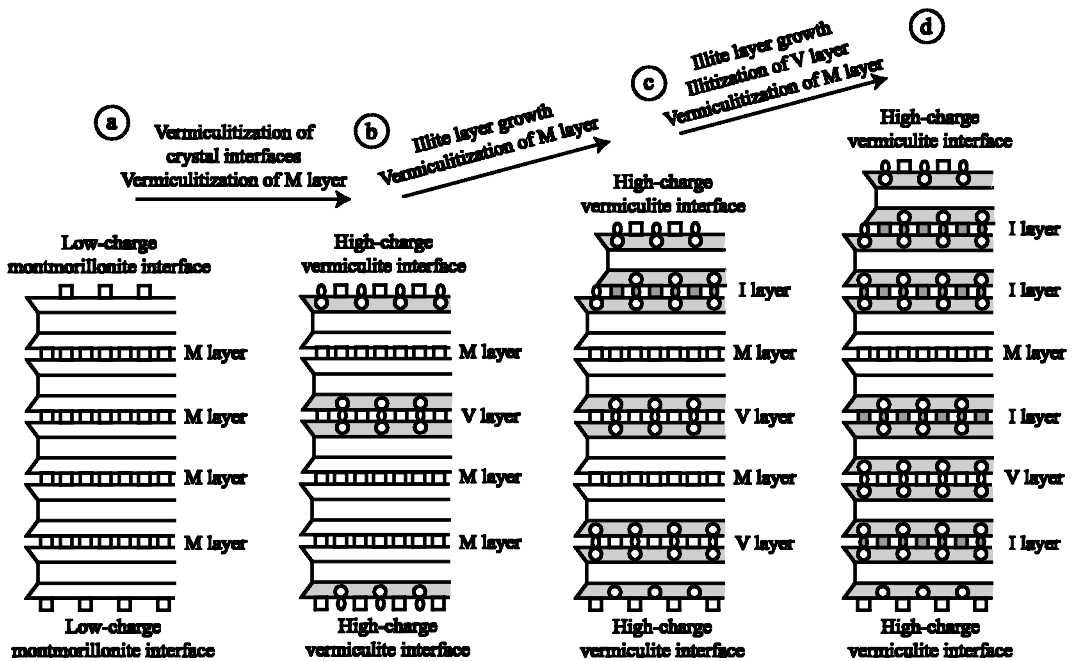


FIG. 4. Schematic representation of the illitization process by a two-step model relating the growth along the *c*-direction and the increase of illite content in the I-S series. For simplicity, growing illite layers are represented only on the upper interface (V: vermiculite layer; I: illite layer; M: montmorillonite layer). (a) The starting material is a 5-layer thick montmorillonite crystallite; octahedral charges are compensated by interlayer cations (squares). (b) The charge of outer edges of the crystal increases by tetrahedral substitutions (circles) transforming locally the low-charge montmorillonite into a high-charge vermiculite. The tetrahedral charges are compensated for by the addition of exchangeable interlayer cations (ovoids). The bulk chemical composition is controlled by the montmorillonite-illite tie-line (Meunier & Velde, 1989). Tetrahedral sheets with Al for Si substitutions are represented in grey. (c) Addition of an illite layer having both tetrahedral and octahedral charges, and vermiculitization of an internal montmorillonite layer. If not saturated with K^+ or NH_4^+ , this layer remains expandable. At the same time, the vermiculitization process transforms some montmorillonite layers inside the stacking. (d) The progressive addition of illite layers and the illitization of vermiculite layers in the stacking produces a series of I-S MLM in which the initial montmorillonite 'nucleus' is progressively illitized via a vermiculite intermediate.

originally with a low charge and octahedral substitutions, are progressively transformed in illite via a vermiculite intermediate, exhibiting a high-charge from tetrahedral substitutions. The vermiculitization of initial montmorillonite layers (Fig. 4a,b) may also account for the decrease of the turbostratic index described by Reynolds (1992) as illitization proceeds. Indeed, the vermiculite-to-illite layer conversion is similar to the process observed during wetting and drying of smectites in the presence of K^+ . This treatment permits the rotation of adjacent layers by a few degrees around the c -axis to reduce the three-dimensional stacking disorder (Mamy & Gaultier, 1975). The effect should be enhanced as the layer charge is greater than in the smectites usually subjected to this treatment.

The necessary condition for such a smectite illitization mechanism to work is that montmorillonite must be formed in the early diagenetic stages. Unfortunately, numerous diagenetic series studied have experienced an erosion cycle which removed the upper part of the sequence in which the formation of pure montmorillonite may occur. However, this process was shown in the Colorado river deltaic sedimentary formation by Jennings & Thompson (1987). Indeed, the mineralogical composition of the sediments, which is variable in the upper part of the sequence, becomes remarkably homogeneous at a depth corresponding to a temperature of $\sim 80^\circ\text{C}$. A 100% expandable new material of montmorillonitic chemical composition is formed.

Finally, one may note that the proposed conversion/growth model may explain why the completion of the illitization reaction is so slow; in other words, why it seems so difficult to reach the 100% illite limit. The inner interfaces, initially with a montmorillonite character, which are not involved in the vermiculite stage, become less and less accessible to K^+ and/or NH_4^+ as I-S crystals are growing in the ab plane. As a consequence, it is likely that these inner interlayers will remain expandable.

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APPENDIX: GLOSSARY

Layer

A layer is defined symmetrically on each side of the interlayer space, with the origin being located in the middle of the octahedral sheet. This may lead to the existence of polar 2:1 units (Güven, 1991; Altaner & Ylagan, 1997).

Montmorillonitic layer

Fully expandable layer (2 water layers or 2 ethylene glycol layers at 80% RH, whatever the interlayer cation, except for K^+ and NH_4^+). Most of the charge originates from the octahedral sheet. Total layer charge varies from 0.3 to 0.6 per $O_{10}(OH)_2$.

Vermiculitic layer

High-charge layer is partly expandable (1 water layer or 1 ethylene glycol layer at 80% RH) if the interlayer is not K^+ - or NH_4^+ -saturated. If so, the interlayer is collapsed to $\approx 10 \text{ \AA}$. In this paper the layer charge is assumed to be as high as that of illite: 0.9 per $O_{10}(OH)_2$, and to originate mostly from the tetrahedral sheets surrounding the interlayer space.

Illite

Non-expanding, dioctahedral, aluminous, potassium mica-like mineral that occurs in the clay size-fraction ($<4 \mu\text{m}$) (Środoń & Eberl, 1984). In the present article, illite is considered to have a fixed negative layer charge as well as a fixed distribution of this charge between octahedral and tetrahedral

sheet sites. This illite layer is characterized by the structural formula determined by Meunier & Velde (1989): $K_{0.9}Si_{3.3}Al_{0.7}R_{1.8}^{3+}R_{0.2}^{2+}O_{10}(OH)_2$, with an interlayer charge greater than that determined by Hower & Mowatt (1966) for 0% smectite clay fractions (0.75 per half unit-cell). Additionally, K^+ or NH_4^+ in oil shales are strictly unexchangeable (Williams & Ferrell, 1991; Lindgreen, 1994; Drits *et al.*, 1997b; Schroeder & McLain, 1998).

Illite-smectite

Mixed layer minerals (MLM) composed of illite-like and expandable layers whatever their stacking sequence. The expandability results from the presence of montmorillonitic and/or vermiculitic layers.

Illitic minerals

Clay size-fraction mineral assemblage dominated by discrete illite but still containing a significant proportion of highly illitic ($>90 \%$ illite) I-S (Środoń, 1984).

Stacking sequence

This sequence is statistically determined as a function of the ordering type which is characterized by the Reichweite (R) parameter (Jagodzinski, 1949). This parameter indicates how far a layer may influence the occurrence of another layer type in the stacking sequence. However, the R parameter alone does not allow the whole sequence to be described; this is determined by the relative

proportions of the different layer types and by the junction probabilities used to describe the influence of a sequence fragment on the nature of the next layer. It should be noted that the occurrence of a regular ISIS... sequence does not imply an R1 stacking, with or without maximum possible degree of order, such a sequence being possible in an R0 structure, for example.

MacEwan crystallite

The McEwan model provides a one-dimensional description of I-S along the c^* -direction. Layers of illite and smectite are pictured as intimately interlayered, stacked either as a random, as an ordered (even partially), or as a segregated sequence. Such a sequence of strictly parallel layers of different nature and/or thickness, acting as a coherent unit, scatters X-rays (Moore & Reynolds, 1989). The number of diffracting layers (N) indicates the coherent scattering domain size (CSDS). After K saturation and heating (Drits *et al.*, 1997c), the CSDS may be computed from the peak profile using a modified Scherrer or Bertaut-Warren-Averbach procedure (Drits *et al.*, 1997c, 1998a). This parameter may be derived by fitting the complete XRD profile by a trial-and-error approach (Drits & Tchoubar, 1990).

Crystal

Three-dimensional unit of strictly parallel layers that scatters X-rays coherently along the three axes. The periodicity along the three axes may be disrupted by crystal defects (turbostratism included). Three different layer types can be distinguished in I-S crystals: smectite, vermiculite, and illite. The crystal thickness (T_{cry}) is identical to the N value used by Reynolds (1985) for the CSDS.

Fundamental particles (FP)

Particles whose interfaces are capable of absorbing water and organic molecules and, as a consequence, behave as a smectite interlayer if two such particles are stacked. A smectite FP is 10 Å thick whereas thicker particles are illite FPs (Nadeau *et al.*, 1984b). Fundamental particles can be considered as sub-units of a MacEwan crystallite (Eberl & Środoń, 1988; Reynolds, 1992).

Particle

Super-unit composed of several crystals connected by coalescence or formed by epitaxial growth process. Crystal defects may interrupt the periodicity along any crystallographic axis.