

Why are clay minerals small?

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ABSTRACT: The most abundant silicates formed under the Earth's 'normal' surface conditions, *i.e.* clay minerals, are always of small grain size. Under the same conditions, other mineral species such as carbonates, sulphates and oxides may form much bigger crystals. The reason why phyllosilicates formed in soils or in weathered rocks are always of small grain size is not related to the low-temperature-pressure conditions but rather to particular aspects of their crystal structure. Many recently published works describe the order-disorder cation distribution in the tetrahedral and octahedral sheets and the crystal defects in the layer stacks. Related to the Periodic Bond Chains (PBCs) theory, these data suggest that the size and the shape of clay crystallites could depend on the amount of crystal defects in the three axes of symmetry [100], $[\bar{1}10]$ and $[\bar{1}\bar{1}0]$. The accumulation of crystal defects poisons the crystal growth along one, two or three PBCs. Then, nucleation becomes less energy-consuming than crystal growth and favours the formation of numerous smaller crystals rather than fewer bigger ones.

KEYWORDS: crystal growth, crystal defects, order-disorder, polymerization, illite, smectite.

Clay minerals are ubiquitous on Earth, both in the continents and on the ocean floors. In particular, they are concentrated in geological formations where water-rock interactions are active. Their crystal structure and chemical composition are a response to the destabilization of minerals formed in higher pressure-temperature conditions when altered in different types of environments including soils, weathered rocks, geothermal systems, burial diagenetic series, etc.

It is remarkable that, whatever their origin, the most abundant silicates forming in the Earth's surface conditions are always of small grain size while other mineral phases (oxides, hydroxides, carbonates) are not necessarily so. This leads to the question: why are clay particles so small while in other conditions such as those prevailing in metamorphic or magmatic rocks, phyllosilicates are of much larger crystal size? In other words, why is the growth of clay minerals limited to a few micrometers or nanometers?

The present paper attempts to find an answer to this question using a critical analysis of published works describing the order-disorder and crystal defects in the phyllosilicates. For simplicity here we will use the term 'crystallite' for single-crystal bodies and 'particles' for composite ones (see definitions in Meunier *et al.*, 2000).

GENERAL CHARACTERISTICS OF CLAY MINERALS

Characteristics of clay minerals: thin and resistant

Assuming a circular shape, a montmorillonite crystallite 1 μm in diameter, having 10 coherently stacked layers, exhibits (001) and (*hk*0) faces of which the surface areas are $785 \times 10^3 \text{ nm}^2$ and $3.1\text{--}4.7 \times 10^3 \text{ nm}^2$, respectively. The area of the crystallite edges is 200 times less than a single (001) face. However, in spite of its very small thickness, the crystallite presents a physical coherence (spatial continuity of the crystal lattice) in the *a-b* plane which determines its mechanical properties. It is

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remarkable that the coherence of the lattice structure in the a - b plane is preserved even at the scale of a single layer (a 2/1 single layer is ~ 0.65 nm thick). The experiments conducted by Nadeau *et al.* (1984) showed that the physical delamination (*i.e.* separation of individual 2:1 layers) does not alter the internal structure of the isolated smectite layers since they are able to continue to diffract X-rays when mechanically stacked in new particles. This phenomenon was assigned the term ‘interparticle diffraction’. These experiments led to the ‘fundamental particle concept’. In spite of the fact that the effects of interparticle diffraction have been re-examined and strongly reduced in some particular cases (Kasama *et al.*, 2001), we continue to believe that the smectite layer structure is highly resistant to fragmentation. This is explained by a specific property: its flexibility. Using molecular dynamics, Sato *et al.* (2001) calculated that a single layer fractures under a stress of >0.8 GPa. Below this value, any pressure bends the crystal lattice by modification of the Si–O–Si angle in the tetrahedral sheets.

The surface area of the (001) faces and the thickness of the clay crystallites are measurable using atomic (AFM) or scanning (SFM) force

microscopes (see Nagy & Blum, 1994, for a review of these techniques). However, most of studies published recently concern clay species exhibiting euheedral, rather thick (several nanometers) crystallites such as illite or kaolinite (Nagy, 1994; Zbik & Smart, 1998). Finding thin smectite crystallites is difficult. A recent attempt by Bickmore *et al.* (2002) showed that measurements of the specific surface area (SSA) for three kaolinite standards using AFM agree to within 4% with those obtained using the BET method (Brunnauer, Emmett & Teller): adsorption of N_2 on clay layers. The AFM technique provides very useful information which is not given by the BET method: the statistical distribution of SSA values for individual crystallites and, hence, frequency. The distributions obtained are coherent with a log-normal law and the modes vary from 20 to $30 \text{ m}^2 \text{ g}^{-1}$ for the three specimens. Such data are fundamental for crystal growth studies. Moreover, for clay minerals which are composed of layers of constant thickness in the dehydrated state, it is possible to calculate their number in crystallites of known thickness. However, this technique does not indicate if defects alter the layer stacking along the c direction.

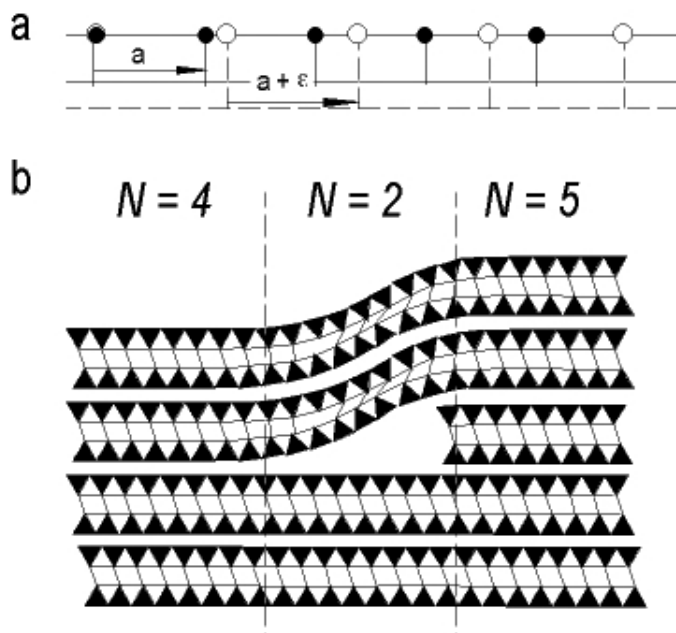


FIG. 1. The crystal defects in clay minerals: (a) in the a - b plane (from Ferrage, 2004); (b) in the c^* direction. N : number of coherently stacked layers.

Order-disorder and crystal defects in clay minerals

Clay mineral structures have long been recognized to be partially or totally disordered at various scales. According to Brindley & Brown (1980), the order-disorder in clay structures can be classified as follows: disorder in the cation distribution in the tetrahedral, octahedral or interlayer sheets; disorder in the layer stacking; disorder in mixed-layered structures; and lattice disorder due to finite crystal size.

The profile of the X-ray diffraction (XRD) peaks depends on the coherent diffracting domain size or CSDS (see Moore & Reynolds, 1989). A coherent scattering domain in a given crystallographic direction is the part of the crystallite which exhibits no interruption in the spatial periodicity of the atomic distribution in that direction. If an atom or line of atoms in a structure is slightly misplaced, *i.e.* at a non-regular interval, the periodicity is interrupted (Fig. 1a). This is a defect which limits the CSDS in the *a-b* plane. The greater the number of crystal defects, the lower the CSDS. Consequently, the intensity of the (*hkl*) diffraction peaks (particularly the (*h00*) and (*0k0*) ones) decreases while their full width at half maximum (FWHM) intensity increases. For example, the presence of defects in the *c** stacking direction decreases the number of layers in the coherent scattering domains. The layers in the left and right parts of Fig. 1b are stacked regularly, while they are deformed and not perfectly stacked in the middle one. In that case, the presence of a crystal defect reduces the size of the coherent scattering domain to 2. Plançon (2001) reviewed recent progress in the analysis of long- and short-range order-disorder by modelling XRD patterns and comparing this approach with various spectroscopic methods such as infrared, Mössbauer or extended X-ray absorption fine structure (EXAFS).

We will focus the following discussion on the 2:1 phyllosilicates which exhibit a negative charge on the unit layer.

CRYSTAL DEFECTS IN THE *c* DIRECTION

Layers of constant thickness (polytypes): stacking faults

According to the periodicity along the *c** stacking direction, different polytypes have been determined

for various mineral species: 1*M* or 2*M* for micas, 1*Ia*, 1*Ib* for chlorites, *etc.* However, screw dislocations emerge on the (001) faces, indicating the presence of crystal defects which interrupt the periodicity in the *c** direction (Fig. 2). Whatever the polytype, the periodicity may be interrupted by stacking faults (Nespolo, 2001, and references therein). The most commonly encountered stacking defect in clay minerals is the non-rational rotation between facing layers (stacking fault), *i.e.* a non-symmetric rotation according to the stacking scheme. The periodicity in the *c** direction is respected in large domains for most of the high-temperature phyllosilicates while stacking faults are more frequent for the low-temperature clay minerals such as illite (Yoder & Eugster, 1955) and of course, smectites. When the periodicity in the *c** direction is erased by non-rational rotations between adjacent layers in a stack, the crystallites are considered to be turbostratic, a totally disordered polytype. Turbostratism is easily detected using X-ray or electron diffraction (Fig. 3): (1) XRD of randomly oriented powders – the intensity of the *hk* bands decrease, and broad and asymmetrical peaks are formed. The profile of the (20;13) peak may be used to calculate the degree of turbostratism. The demodulation of the two (20*l*) and 13*l*) peaks into a two-dimensional band is due to turbostratic displacements. A completely turbostratic structure produces a single asymmetrical (20; 13) band typical of smectite (Reynolds, 1992). (2) Electron diffraction patterns obtained from single crystallites give circles (conical diffraction) or parts of circles instead of dots (Méring, 1975).

Layers of variable thickness (mixed layers): deformed layer

Interstratification is very common in clay minerals: layers of different types are found stacked in the same crystallite. Mixed-layer minerals (MLMs) exhibit specific rational or non-rational series of diffraction bands, depending on whether their crystal structure is regular or not. Non-rational series are observed for randomly ordered or ordered but not regular mixed-layer minerals. The XRD patterns are significantly different from those of pure, single-layer type species (Brindley & Brown, 1980). The most commonly encountered MLMs in soils are illite-smectite (I-S) or chlorite-smectite (C-S) or kaolinite-smectite (K-S). The MLMs frequently exhibit specific crystal defects due to lateral change of

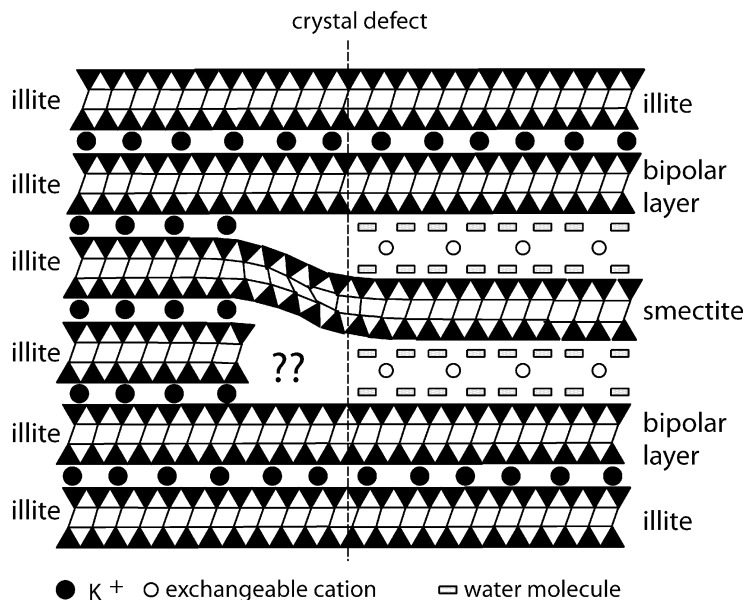


FIG. 2. Example of crystal defect in the c^* direction inside an illite-smectite mixed-layer mineral (from Lanson & Meunier, 1995).

some layers as depicted in Fig. 2, as a result of which, some layers are deformed.

The thickness of a smectite layer varies with its hydration state; the amount of deformed layers in I-S or C-S MLMs increases with the smectite content. If all the smectite layers are in the same

hydration state (1.25 nm or 1.5 nm for one or two water layers, respectively), then the crystal structure is that of two-component MLMs. Consequently, the corresponding XRD patterns present relatively narrow diffraction maxima. However, if some of the smectite layers are in one hydration state (two

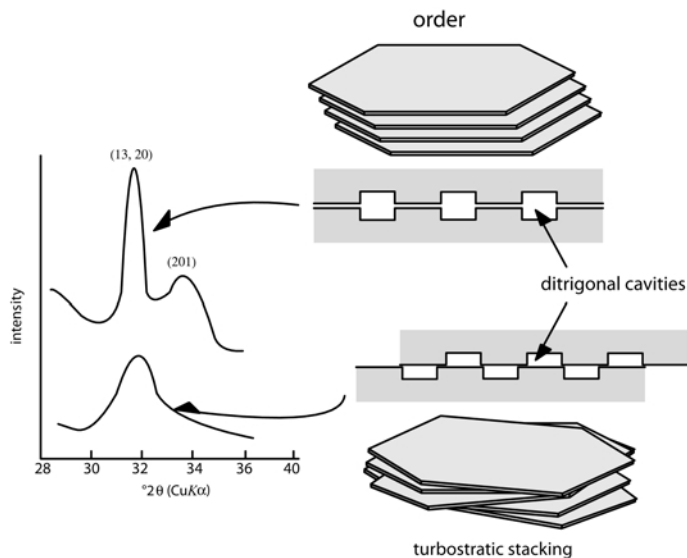


FIG. 3. Schematic representation of stacking order and turbostratic stacking in phyllosilicates with the corresponding (20;13) XRD bands (modified from Méring, 1975). Detailed explanations are given in the text.

water layers for example) and the others in another (one water layer), the crystal structure is that of three-component MLMs. Consequently, the diffraction maxima are strongly broadened and displaced (Drits *et al.*, 1997). However, the crystal structures typical of the 2- or 3-component MLMs are not perfectly coherent with most of the natural samples because the distribution of charged sites inside individual smectite layers induces the variation of its hydration state (Fig. 4). In that case, the fit of the XRD peak profile shows that the MLM behaves as the sum of domains limited by the deformation of the layers, *i.e.* crystal defects (Ferrage, 2004; Ferrage *et al.*, 2005).

CRYSTAL DEFECTS INSIDE THE LAYER

Order-disorder within the tetrahedral sheet

The composition of the tetrahedral sheets varies from 0 to ~1 Al-for-Si substitution for Si₄O₁₀

depending on the clay mineral species. The phenomenon of Al avoidance (Löwenstein's rule) is considered to control the Al-Si ordering because Al-O-Al linkages are 'not allowed'. This is obviously easier for clays having low Al/Si ratios. There is enough room for Al tetrahedra to avoid nearest neighbouring even if they are randomly distributed inside the sheet. With increasing Al/Si values, avoidance of Al-O-Al links requires long-range ordering. Ordering should be controlled by interactions between tetrahedral sites that are not nearest neighbours (Dove *et al.*, 1996). Until now, systematic studies of order-disorder in phyllosilicates have been presented only for high-temperature dioctahedral micas (Palin *et al.*, 2001, 2003; Palin & Dove, 2004). Of course, the conclusions of these works cannot be applied directly to low-temperature smectites or illite, but some points are potentially interesting for such minerals: (1) even in high-temperature muscovite (tetrahedral sheet: Al/Si = 1/3), the probability of the existence of the 0Al-3Si configuration is not zero. (It is clear that it should

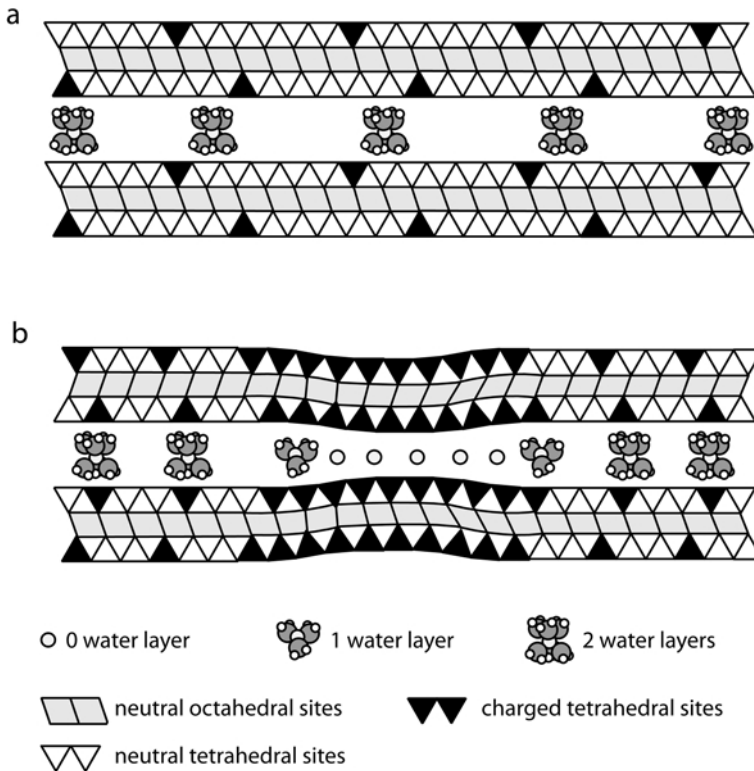


FIG. 4. Variation of the d_{001} thickness of smectite due to different hydration states for a given relative humidity. (a) Homogeneous distribution of the layer charge. (b) Heterogeneous distribution (from Ferrage, 2004).

increase in illite and smectite which has a lesser degree of Al-for-Si substitution.); (2) in phengites (micas in which ionic substitutions, i.e. the layer charge, originate both in the tetrahedral and octahedral sheets), there are interactions between the cation distributions in tetrahedral and octahedral positions; (3) simulations of a dilute Al-for-Si

substitution system such as phengitic micas showed that Al–O–Al linkages are avoided because Al^{3+} cations are dispersed. However, there is no requirement for long-range order.

A typical Al^{3+} cation distribution in the tetrahedral sheet of phengite is given in Fig. 5. From the above, one can extrapolate some consequences for clay

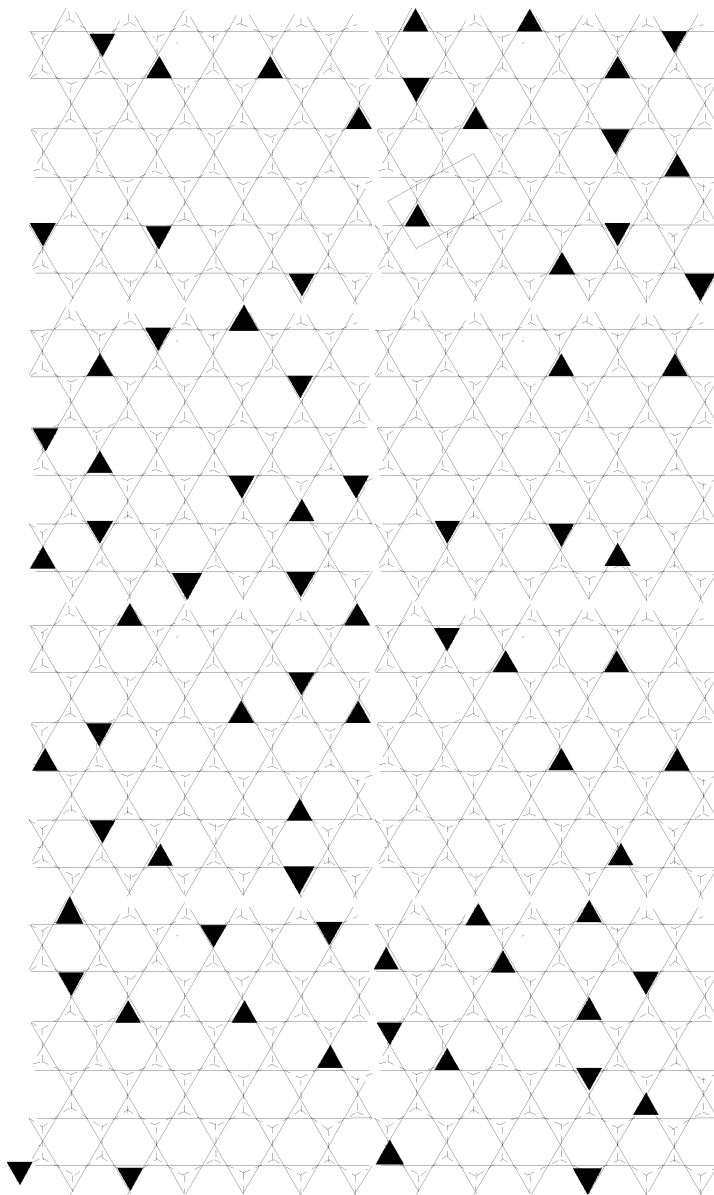


FIG. 5. Typical Al^{3+} cation (black triangles) distribution in the tetrahedral sheet of phengite using Monte Carlo simulation (from Palin *et al.*, 2003).

minerals in the illite-to-smectite composition range. Indeed, their tetrahedral structure is similar to that of phengites (no long-range order) with fewer Al-for-Si substituted sites (Fig. 6).

Order-disorder in dioctahedral sheets

The main octahedral cations are Al^{3+} , Fe^{3+} , Mg^{2+} , Fe^{2+} and Mn^{2+} . According to spectroscopy data, the distribution of Fe^{3+} cations in dioctahedral smectites was shown to be randomly ordered, ordered or segregated (Fig. 7). Order is ruled by the limitation of neighbouring possibilities for 2 cations of the same element. These distribution modes have been simulated using inverse Monte Carlo calculations (Cuadros *et al.*, 1999; Sainz Diaz *et al.*, 2001; Vantelon *et al.*, 2001, 2003). The presence of a divalent cation in place of a trivalent

one locally creates a negative charge in the octahedral sheet. This negative charge modifies the electrical equilibrium with the surrounding oxygens. A charge imbalance diffuses inside the tetrahedral sheets to the basal oxygens forming the outer surfaces of the 2:1 layer. Consequently, the distribution of the divalent cations in the octahedral sheet controls the position of the compensating cations in the interlayer zone. Order or disorder in the octahedral sites can cause specific site occupancy in the interlayer sites.

Order-disorder in the interlayer zone

Considering dioctahedral 2:1 phyllosilicates, the layers are negatively charged by heterovalent cation substitutions either in the tetrahedral sheets (Al^{3+} for Si^{4+}) or in the octahedral sheets (R^{2+} for R^{3+}).

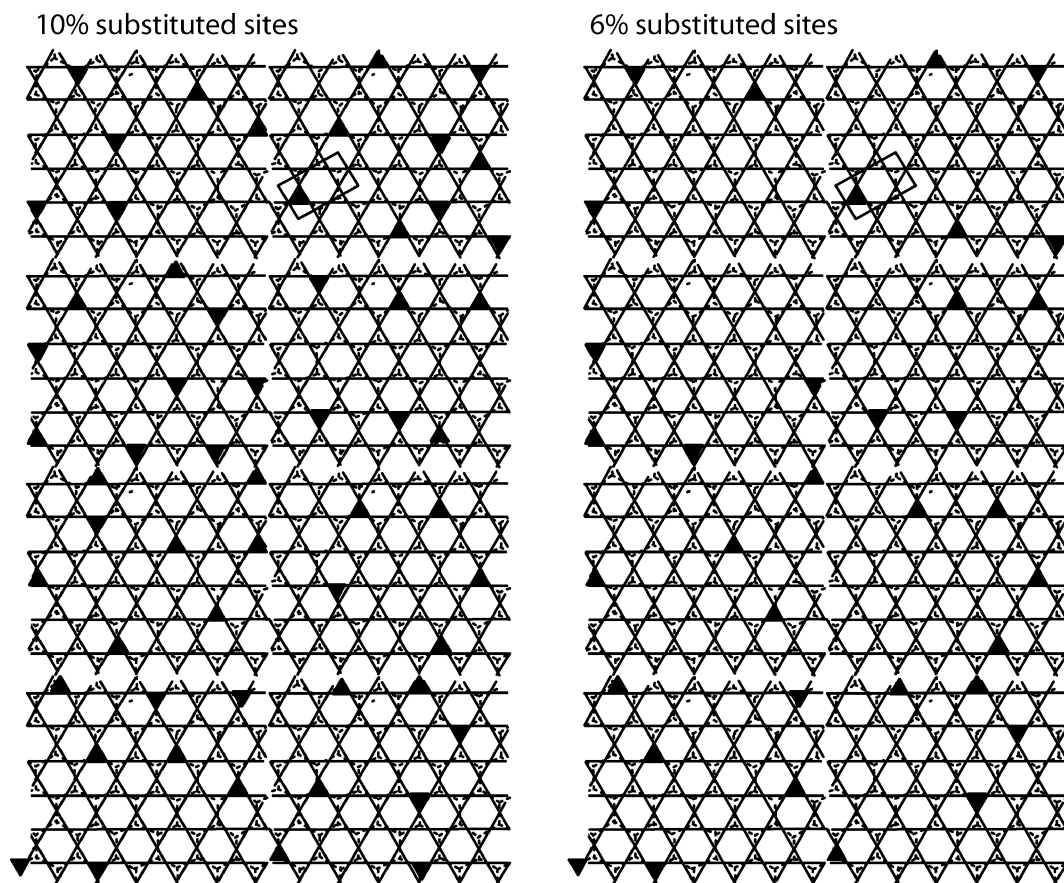


FIG. 6. Possible distribution patterns of Al^{3+} cations (black triangles) in the structure of the tetrahedral sheet according to different Al/Si ratios without long-range order.

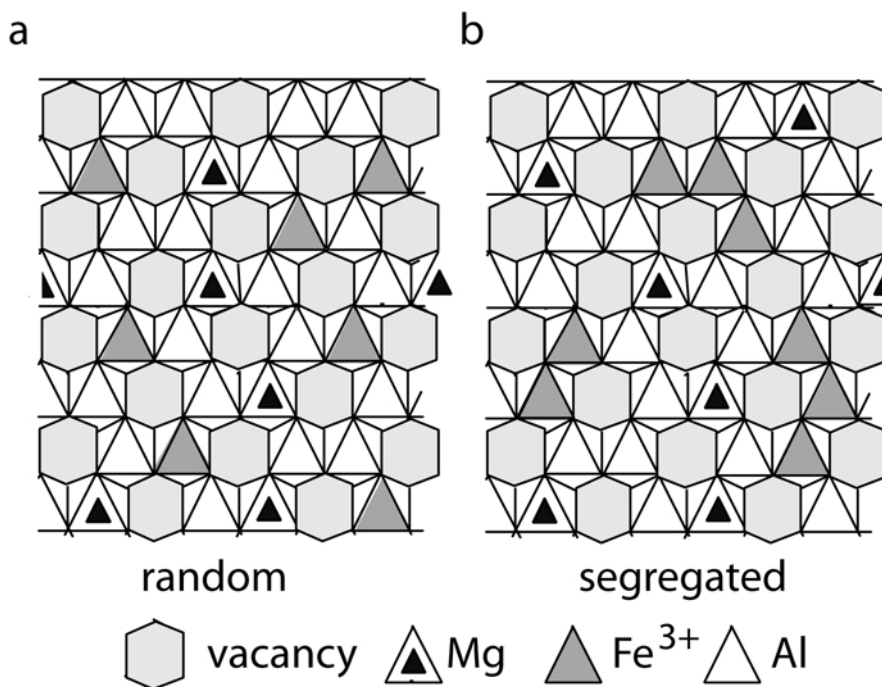


FIG. 7. Variable degree of order-disorder in dioctahedral sheets of smectites (from Vantelon *et al.*, 2003): (a) random distribution; (b) segregated distribution.

In the mica family (muscovite, phengite), the negative charge is -1 per $O_{10}(OH)_2$. It is homogeneously distributed on the surface of the 2:1 layers, i.e. 1 for each hexagonal cavity. Consequently, the compensating interlayer cations (K^+ , Na^+ , NH_4^+) occupy all the hexagonal cavities; they are periodically distributed on the layer surface. This is not the case for phyllosilicates when the layer charge is <-1 per $O_{10}(OH)_2$.

The location of the negative charge at the surface of the layer depends on the location of the cation substitutions within the 2:1 lattice. The Al^{3+} ionic substitution for Si^{4+} in the tetrahedral sheet creates under-saturated valency in the three basal oxygens surrounding the Al^{3+} ions. The negatively charged sites on the layer surface are punctual. On the contrary, octahedral substitutions induce a more diffuse valency under-saturation for a large number of basal oxygens because the charge imbalance is diffused through two more layers of ions in the structure. Therefore, the attractive force on the interlayer cations is more site-specific for tetrahedral substitutions and reduces the number of hydration layers around cations (Laird, 1996, 1999).

If, for simplicity, one considers only the

negatively charged hexagonal cavities where inter-layer cations are attracted whatever the location of the negative charge in the 2:1 layer, several distribution types are theoretically possible for phyllosilicates, the layer charge of which is less than that of micas, i.e. randomly ordered, ordered or clustered (Fig. 8). In spite of technical difficulties in obtaining a statistical representation of the distribution of the interlayer cations, it seems clear that the lower the layer charge, the greater the degree of disorder of charged sites. For a given layer charge, several distribution types are theoretically possible, as shown in Fig. 8a,b. Assuming that the crystallite morphology is related to the degree of order-disorder of interlayer cations, low-charge smectites should exhibit two types of crystal shape: allomorph platelets or elongated hexagonal-shaped laths. This appears to be the case for montmorillonite (octahedral substitution) and beidellite (tetrahedral substitution), respectively.

In summary, analyses of the degree of order-disorder of clay crystal structures could help us to answer the following questions: why are clay mineral particles always small? Why are some clay minerals allomorphic in shape? In other words,

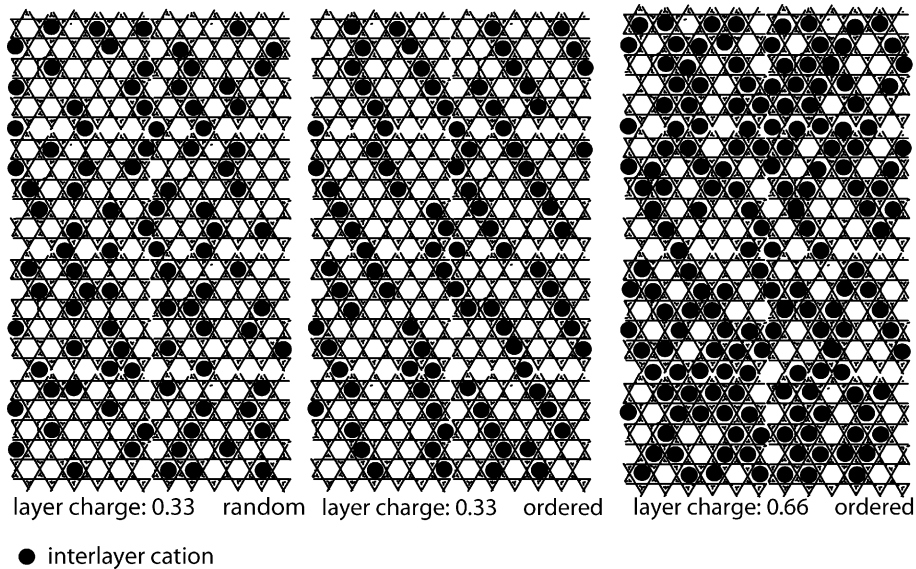


FIG. 8. Some possible interlayer cation distributions for different layer charges (LC) per $\text{O}_{10}(\text{OH})_2$. (a) LC = 0.33, random distribution; (b) LC = 0.33, ordered distribution; (c) LC = 0.66, ordered distribution.

how may the degree of order-disorder influence crystal growth processes?

HOW CLAY MINERALS GROW

Phyllosilicate growth principles

As all minerals do, illites and smectites experience nucleation and crystal growth. According to the crystal growth theory of Hartman (1973), their structures can be described as a network of strong bond chains which are periodically distributed (Periodic Bond Chains or PBCs). These chains must have the following characteristics: they must divide the crystal into stoichiometric units; they must not have common bonds with neighbouring chains; and they must not be multiples of other chains. The growth faces of the crystal are observed to lie parallel to one or more continuous PBCs: flat faces F (2 PBCs), stepped faces S (1 PBC), kinked faces K (0 PBC). Phyllosilicates are characterized by huge F faces in the (001) planes. The (010), (110) and $(1\bar{1}0)$ faces are stepped faces. According to the dissolution experiments of Bickmore *et al.* (2001), the (100) and (130) faces which are parallel to zigzag PBCs behave chemically as intermediate between S and K faces (Fig. 9a). The growth processes govern the crystal habits of phyllosilicates. Therefore,

analysing the crystal shape may indicate how the mineral grows (Güven, 2001). Two parameters have to be taken into account: the aspect ratio (length/width) and the thickness in the c^* direction.

How are chemical elements incorporated into a growing PBC? This point is still the subject of speculation. However, the concept of 'building blocks' (Fig. 9b) seems to be consistent with the structure of the different PBCs (White & Zelazny, 1988). How these 'building blocks' are formed can be ignored for the moment. Assuming that they really exist, their incorporation in the PBCs of clay minerals such as illite, vermiculite or smectite should be associated with incorporation of the interlayer cations. Re-examining the distribution models of interlayer cations depicted in Fig. 8, one can see that the random model cannot allow any PBCs to develop. This could explain why the montmorillonite crystallites are always small and allomorph. On the contrary, because the distribution of interlayer cations in beidellite, vermiculite and illite is ordered, their crystallites may be euhedral. As interlayer occupancy is denser in illite than in vermiculite or beidellite, the three types of PBCs may develop and give hexagonal crystallites. When euhedral beidellite crystallites form elongated laths, only 1 PBC has grown.

Two processes may control the crystal growth in the c^* direction: layer nucleation on the (001) face

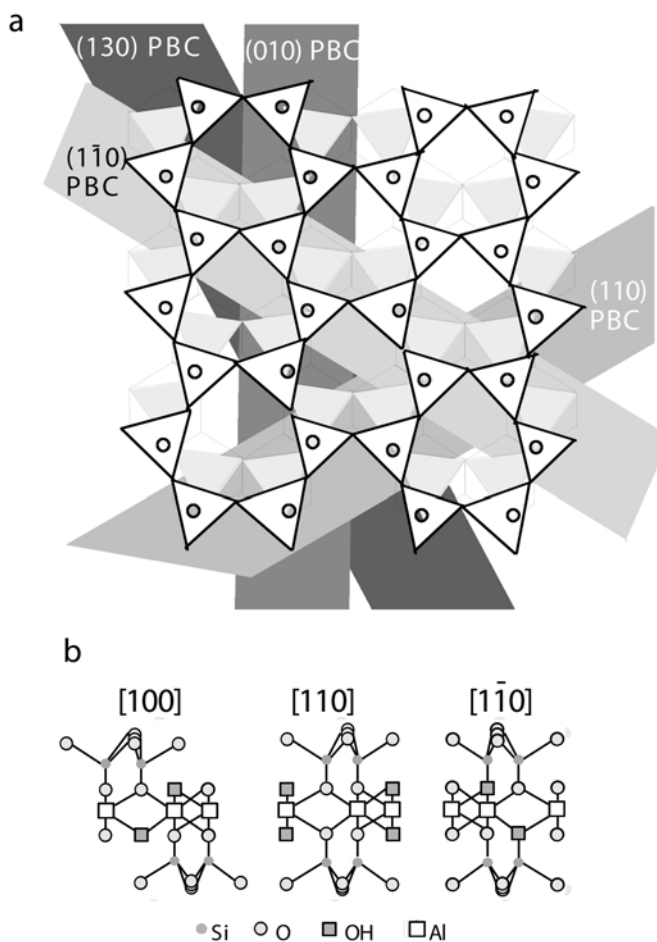


FIG. 9. The Periodic Bond Chains (PBCs) in phyllosilicates (from Bickmore *et al.*, 2001). (a) The different PBCs; (b) the 'building blocks' which are supposed to be incorporated in the PBCs (modified from White & Zelazny, 1988).

of the phyllosilicate or continuous incorporation of atoms or 'building blocks' on a spiral step originating from a screw dislocation emerging on the (001) face (Fig. 10a,b). The first one necessitates a greater degree of oversaturation to overcome the nucleation energy barrier. Spiral step growth is more sparing from an energy point of view. It has been shown, first on biotite crystals (Amelinckx, 1952), and in relation to polytype formation for phlogopites (Baronnet, 1972). Subsequently, it was also described in clay minerals using decoration techniques for kaolin group minerals (Sunagawa *et al.*, 1975; Sunagawa & Koshino, 1975) and for illite (Inoue & Kitagawa, 1994). Spiral growth steps have been observed even on elongated laths of illite.

Speculative interpretation of growth processes - crystal morphology relations

The clay minerals which commonly exhibit euhedral morphology typically belong to the kaolin and illite groups. These minerals have either none or a high layer charge. On one hand, the lack of interlayer charges eliminates the potential source of crystal defects related to a disordered distribution of interlayer cations. On the other hand, the high layer charges favour a regular occupancy of the hexagonal cavities by interlayer cations. On the contrary, smectites, with low charge and hence less regular distribution, are rarely euhedral except for beidellite or nontronite in certain circumstances. Montmorillonite is always

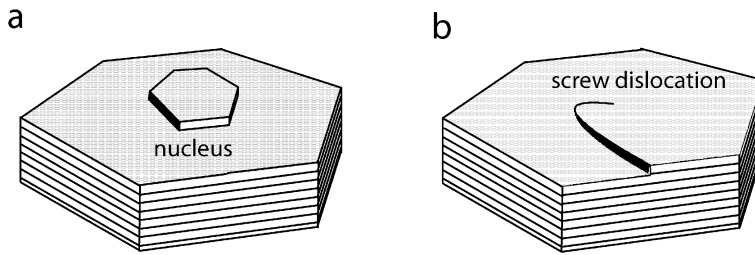


FIG. 10. The crystal growth processes. (a) Nucleation of a new layer on the outer surface of the clay particle. (b) Spiral growth originating from a screw dislocation.

allomorphic. Considering these observations, we must search for the common phenomenon which may control the morphology of either 1:1 or 2:1 phyllosilicates. Obviously, we have to consider at first the way that layers stack in euhedral crystals and particularly, how the structure of the interlayer zone controls the stacking.

The minerals that form the kaolin group do not have any interlayer cations; the interlayer zone is structured by the hydrogen bonds between two adjacent 1:1 layers. The layer stacking is controlled by these electrical interactions which link the basal oxygens (tetrahedral sheet) of layer 1 to the OH groups (octahedral sheet) of the layer 2. Stacking disorder is due to rational rotations of $\pm 60^\circ$ between adjacent layers. Such rotations conserve the pseudo-hexagonal crystal lattice orientations, then the pseudo-hexagonal morphology (Fig. 11). This shape, typical of kaolinite platelets, is lost when it is formed in soils, particularly Oxisols, because some of the Al^{3+} cations are substituted by Fe^{3+} cations in the octahedral sheets (Muller *et al.*, 1995; Balan *et al.*, 1999). The presence of Fe^{3+} cations in place of Al^{3+} cations enlarges the b structural parameter locally. When multiplied by a great number of unit cells, the size difference induces the formation of crystal defects (Brindley *et al.*, 1986) and the crystallites become 'shapeless' (Petit & Decarreau, 1990).

Compared to micas, illite crystals are always smaller and their morphology more variable. Illite is found either as thin elongated laths ('hairy illite') or as hexagonal platelets. Because the lattice structure of the 2:1 units of both illite and mica is very similar, the cause of the contrasted morphologies could be related to the distribution of ions in the interlayer zone. In micas, each hexagonal cavity of the tetrahedral sheets is occupied by a monovalent cation (K^+ or Na^+). Consequently, the PBCs along the three axes of symmetry $[100]$, $[\bar{1}10]$

and $[\bar{1}\bar{1}0]$ are identical (Fig. 12a), and hence the isometric shape is favoured. On the contrary, some of the hexagonal cavities are vacant in illite crystallites. Thus, the facing PBCs of two adjacent 2:1 layers may be not regularly linked by a monovalent cation. This could be considered as a crystal defect. The elongated lath-shaped crystallite could result from the 'poisoning' of certain PBCs by the accumulation of crystal defects in their direction. Indeed, 'poisoning' is not only due to incorporation of impurities in a chemical sense; it can also be due to misaligned building bodies ('self-poisoning', Schilling & Frenkel, 2004).

According to Güven (2001), the growth is oriented in the $[100]$ direction for lath-shaped illites (Fig. 12b). One may assume that beidellites grow in a similar way, but because the vacancies are more numerous, the poisoning effect is greater and the crystallites therefore smaller (Fig. 12c). If these vacancies are randomly distributed, the poisoning effect should be identical, whatever the direction. Consequently, the crystallites must be shapeless, as is the case for montmorillonite.

Nucleation and crystal growth: possible competition

The environments favourable for the formation of clay minerals evolve typically towards fine-grained rocks (including soils). In other words, clay-rich materials are composed of a great number of small crystallites instead of a few large crystals. This is particularly the case for nearly monomineral ones such as bentonites which are almost pure clay deposits (montmorillonite or I-S). This simple observation leads one to suspect that nucleation is favoured compared to crystal growth. Indeed, because crystal growth is limited by the presence of crystal defects, nucleation is accelerated by the catalytic effects of the irregular surfaces of the pre-

existing solids. Two paths are available according to the degree of solution over-saturation: homogeneous or heterogeneous nucleation. Homogeneous nucleation happens when the degree of over-saturation necessary to overcome the energy barrier is reached abruptly. Then, nuclei precipitate directly in the solution. On the contrary, if the solution oversaturates slowly, then the nuclei form on the surfaces of pre-existing solids. They form first on the emerging crystal defects which locally furnish an excess of energy. This process requires less energy since the energy barrier is less than that for homogeneous nucleation (Fig. 13).

Heterogeneous nucleation is certainly the controlling factor in most of the altered or diagenetic rocks. For example, illite fibres are commonly observed growing on quartz or detrital mica surfaces in buried sandstones. Sometimes they grow on pre-existing diagenetic clay minerals such as kaolinite or dickite (Lanson *et al.*, 2002). The heterogeneous nucleation of metal-bearing phyllosilicates has been reproduced experimentally on different pre-existing solids: trioctahedral Co-clay on quartz (Manceau *et al.*, 1999), Zn-phyllosilicate on the edges of hectorite (Schlegel *et al.*, 2001) and Ni-phyllosilicate on the outer (001) faces of

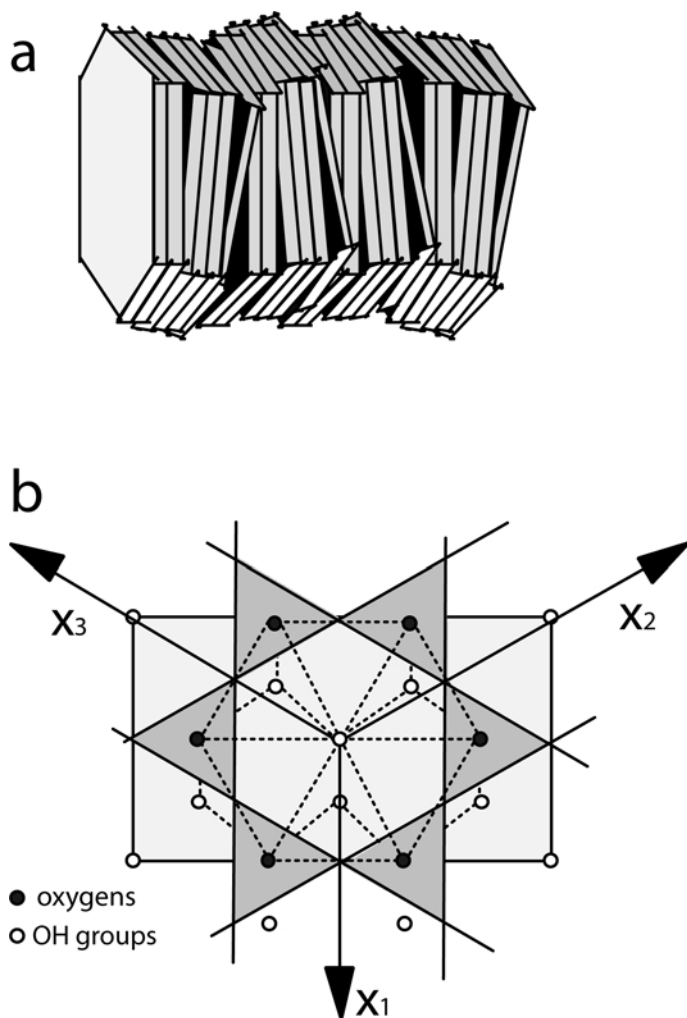


FIG. 11. The pseudo-hexagonal morphology of kaolinite crystallites is conserved in spite of disorder in the layer stacking. (a) Typical kaolinite crystallite in diagenetic environment ('booklet' morphology). (b) The three symmetry axes which allow rational rotations.

montmorillonite (Rainer *et al.*, 2002). It is deduced from these experiments that: (1) nucleation begins by the formation of a hydroxide on which silica is adsorbed; (2) the outer surfaces of non-phyllosi-

cate minerals (quartz) may catalyse the nucleation of phyllosilicates; (3) the edges as well as the (001) layer surfaces of pre-existing phyllosilicates may catalyse the nucleation.

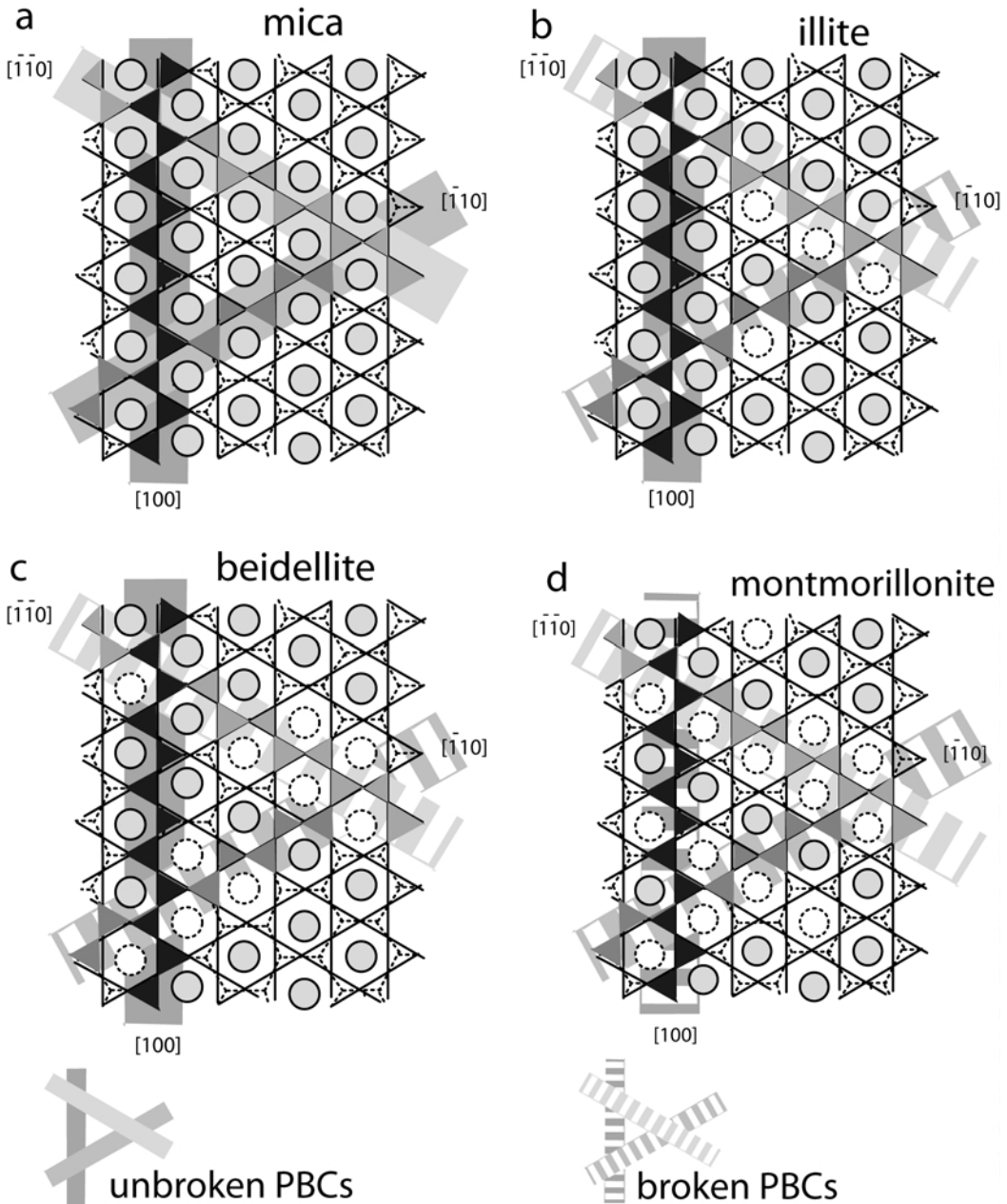


FIG. 12. Schematic representation of the relationship between the continuity of the PBCs in the three major crystallographic directions and the saturation state of the interlayer zone. (a) The three PBCs are continuous in a mica (a), only one in illite (b) and beidellite (c) and none in montmorillonite (d).

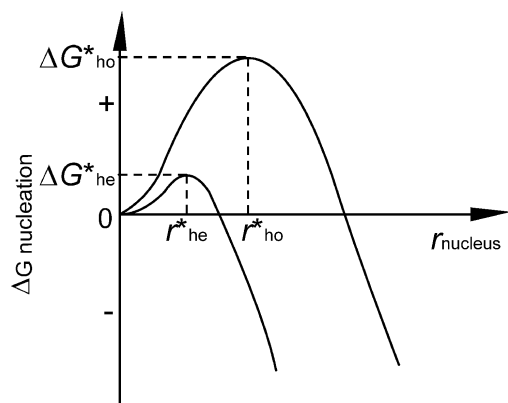


FIG. 13. Schematic representation of the critical energy (ΔC_{ho}^* and ΔG_{he}^*) and critical radius (r_{ho}^* and r_{he}^*) values for homogeneous and heterogeneous nucleation processes, respectively.

Numerous small crystals are formed instead of a few big ones because nucleation, particularly heterogeneous nucleation, consumes less energy than crystal growth. In this field of speculation, a possible reason could be that the growth of clay minerals is made difficult because of the presence of numerous crystal defects. The energy necessary for defective crystals to grow becomes too high, especially in low-temperature conditions. To overcome this energy cost requires higher temperature-pressure conditions as was shown by Nakasawa *et al.* (1992) who synthesized giant montmorillonite crystals with coesite and kyanite.

CONCLUSIONS

Clay minerals, because of their crystallochemical properties (incomplete interlayer occupation, hydration heterogeneity, turbostratism, etc.) are 'genetically' too defective to form large crystals. Whatever the physico-chemical conditions prevailing during their formation in soils, sediments, diagenetic formations or hydrothermally altered rocks, it seems that nucleation is always favoured over crystal growth. Of course, all clay species do not have the same density of crystal defects. The less defective ones may grow up to few tens of micrometres wide and may present usual phyllosilicate crystal faces (kaolinite or illite for instance). On the contrary, those which accumulate all the categories of crystal defects remain small and heteromorphous (montmorillonite). This re-opens old questions: are the more defective clays true

crystal species or intermediate forms of condensed matter such as quasi-crystals? Are the nuclei chemically identical to the mineral they give? Whatever the answers, most of the original chemical properties of clays are related to their small size and their significant crystal defect density.

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