

THE 12TH GEORGE BROWN LECTURE

Clay crystal-chemical adaptability and transformation mechanisms

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ABSTRACT: Chemical and mineralogical transformations of phyllosilicates are among the most important in diagenetic environments in all types of rocks because they can exert a large control on the processes taking place in such environments and/or provide constraints for the conditions in which phyllosilicate transformation occurred. Dissolution-precipitation and solid-state transformation are usually the two mechanisms proposed for such reactions depending on the crystal-chemical and morphological similarities between parent and neoformed phases together with knowledge of the environmental conditions. These two mechanisms, however, may be at both ends of the spectrum of those operating and many transformations may take place through a mixture of the two mechanisms, generating observable elements that are characteristic of one or the other. In the present literature, the boundaries between the two mechanisms are not clear, mainly because dissolution-precipitation is sometimes defined at nearly atomic scale. It is proposed here that such small-scale processes are considered as a solid-state transformation, and that dissolution-precipitation requires dissolution of entire mineral particles and their dissolved species to pass into the bulk of the solution. Understanding the reaction mechanisms of diagenetic transformations is an important issue because they impinge on geochemical conditions and variables such as cation mobility, rock volume, fabric changes, rock permeability, stable isotope signature and phyllosilicate crystal-chemistry.

I propose that, in the lower range temperatures at which clay mineral transformations take place, energy considerations favour solid-state transformation, or reactions that involve the breaking of a limited number of bonds, over dissolution of entire grains and precipitation of crystals of the new phase. Large morphological changes are frequently invoked as evidence for a dissolution-precipitation mechanism but changes in particle shape and size may be achieved by particle rupture, particle welding or by hybrid processes in which dissolution-precipitation plays a minor role.

Past and recent studies of phyllosilicate transformations show chemical and structural intermediates indicating a large crystal-chemical versatility, greater than is commonly recognized. These intermediates include tetrahedral sheets of different composition within TOT units (termed polar layers), dioctahedral and trioctahedral domains in the same layer, and 2:1 and 1:1 domains also within the same layers. The existence of such intermediate structures suggests that the reaction mechanisms that generated them are within the realm of the solid-state transformation processes.

KEYWORDS: clay mineral transformation, dissolution-precipitation, mixed-layer clay minerals, solid-state transformation.

Phyllosilicates are among the most important minerals in a wide range of environments and rock types because they can exert a large control on geochemical processes. Phyllosilicates are likely to play this major role in the control of chemical and

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mineralogical processes, even if they are not the most abundant phases, because of their high surface-to-volume ratio, which generates a large mineral-fluid contact surface (Table 1). In addition, their chemical and mineralogical transformations provide constraints for the environmental conditions that cause these processes (“transformation” is used throughout the text as meaning mineralogical or polytype change, without link to a reaction mechanism, unless explicitly stated). Mixed-layer clay minerals are the typical intermediates of such transformations and, as they contain both the initial and new components of the phyllosilicate transformation, it is possible to assess the direction in which the environmental conditions change, provided that it can be established which is the initial and which is the new phyllosilicate component in the mixed-layer phase. Mixed-layer clays are particularly useful in revealing superimposed processes due to major changes in the environmental conditions. For example, retrograde diagenesis of authigenic illite and detrital chlorite and muscovite resulting in illite-smectite (I-S) and chlorite-smectite indicates sediment exhumation and/or invasion of cool, diluted fluids (Zhao *et al.*, 1999).

Dissolution-precipitation and solid-state transformation are usually the two mechanisms proposed for phyllosilicate reactions, whether they take place via mixed-layer phases or not. The interpretation of the intervening mechanism is based on the crystal-chemical and morphological similarities between parent and neofomed phase. There are very compelling cases supporting both mechanisms as HRTEM images show crystal continuity between the original and newly formed layers (e.g. Banfield & Murakami, 1998) indicating a solid-state transformation and spiral growth of illite or illite-rich I-S crystals indicating growth from solution (e.g. Kuwahara *et al.*, 1998). If direct evidence from

the transforming phases is not sufficient, the environmental conditions are invoked to interpret the transformation mechanism. Increasing temperature and fluid-to-rock ratio are considered to increase the likelihood of dissolution-precipitation (Altaner & Ylagan, 1997).

The determination of the transformation mechanism of clay minerals is typically complex but the issue is important for understanding the evolution of diagenetic systems. The reaction mechanism is likely to influence geochemical conditions and variables such as cation mobility, cation concentration in pore fluids, rock volume, fabric changes, rock permeability, stable isotope signature and phyllosilicate crystal-chemistry. Solid-state transformation probably alters the physical conditions of the rock and the chemistry of the surrounding fluids to a limited extent but dissolution-precipitation may induce significant changes, of which some may be transient and some lasting. In addition, the reaction mechanism provides information on the energetics of interactions between the crystal lattice (including composition, structure, defects, etc.), mineral surface, water and dissolved species. Such information may be difficult to unravel at this stage of our knowledge but continued investigation of reaction mechanisms, the conditions under which they take place and possible micro-scale modifications of such conditions should produce results that can be systematized and result in the establishment of the relative energy barriers necessary to destabilize phyllosilicate phases through several mechanisms. This task can be aided by the use of computer models. The rapid development of calculations using increasingly larger atomic clusters brings us closer to the possibility of generating realistic models including several types of energy interactions over large volumes of atoms. In the present paper, some

TABLE 1. Surface area of some clay minerals and other common minerals, as determined from naturally occurring samples.

	Calcite	Feldspar	Quartz	Chlorite	Kaolinite	Mica and illite	Goethite	Smectite and vermiculite
Surface area (m ² g ⁻¹)	1–2 [‡]	2 [^] –8	3 [^] –5 [‡]	3 [#]	10–30 [*]	15–85 [*]	60–340 ^L	700–760 [†]

[‡] Røgen & Fabricius (2002); [^] Hlavay *et al.* (1978); ^{||} Altaner (1986); [#] Sondi & Pravdić (1998); ^{*} Newman (1987); ^L Houben & Kaufhold (2011); [†] Laird (1990)

considerations is given to the mechanism of clay transformations and the evidence of complex intermediate phyllosilicate structures is reviewed. These complex clay structures indicate or suggest reactions taking place through a solid-transformation mechanism.

CONSTRAINTS ON THE DEFINITION OF SOLID-STATE TRANSFORMATION

When considered in the abstract, dissolution-precipitation and solid-state-transformation appear as very distinct mechanisms but, as we focus on specific clay reactions, the border between the two may blur. Thus, it would be advisable to constrain their definition in the context of clay transformations. Some authors have defined transformation taking place at the atomic and layer scale as dissolution and crystallization (Ahn & Peacor, 1986; Li *et al.*, 1997), which I believe is not correct. A dissolution process would require the complete break up of a large volume of the solid and the diffusion of the species into the bulk of the solution, where the major interaction is with free water molecules and other freely-moving species. Crystallization from solution should require that the species taking part in the process are retrieved from the bulk of the solution. This definition of dissolution-crystallization is similar to that of Altaner & Ylagan (1997), and it applies to the discussion in this contribution. Such a mechanism cannot take place in confined volumes such as within the crystal lattice or in the interlayer of expanding clays, where the entire cycle of breaking of bonds, atom diffusion and formation of new bonds takes place necessarily within very short distances because (1) the forces dominating physical and chemical interactions are those from the solid and (2) because the small amounts of fluid involved do not allow for any building up of “dissolved species”. In these confined conditions, species that detach from the crystal lattice can diffuse away, leave the mineral particle and pass into solution. Alternatively, these detached species can be involved in the creation of a new structural unit either by creating new bonds with the solid or with other species within the interlayer. Such a process is more appropriately termed a recombination or rearrangement of atoms than dissolution and crystallization, and it falls within the realm of solid-state transformation as defined in the following paragraph.

It is usually the case that transformation processes, even in the solid state (i.e. mineral particles are preserved), involve structural changes within the layers. Montmorillonite cis-vacant layers are transformed into illite trans-vacant layers (Drits *et al.*, 1996; Cuadros & Altaner, 1998), which requires a reorganization of the relative positions of hydroxyls and octahedral cations. Similarly, kaolinite layers, with B- or C-vacant octahedral positions, are transformed into dickite layers, with alternating B- and C-vacant positions (Bailey, 1980; Shutov *et al.*, 1970; Brindley *et al.*, 1986). These and other changes require a simultaneous rearrangement of a group of atoms, in such a way that it is difficult or impossible to envisage solid-state transformation as a mechanism in which the anionic lattice is rigidly preserved and cations diffuse in and out of it. In their detailed analysis of the structural, chemical and stable isotope issues related to the mechanism of smectite illitization, Altaner & Ylagan (1997) also concluded that a solid-state transformation requires unlocking of a group of atoms in the structure to allow for the observed structural reorganization and changes in the oxygen isotope ratios. Altaner & Ylagan (1997) proposed two models, “reacting polyhedra”, in which the changes affect specific tetrahedra and octahedra in the layers, and “reacting interlayers” (Fig. 1), where the two tetrahedral sheets across the interlayer space undergo atom rearrangement (the authors termed this model local “dissolution and reprecipitation”, although they defined it as a solid-state process). Thus, a solid-state transformation is a reaction process that involves rearrangement of a group of atoms, usually coupled with the loss, addition, or both, of ions that diffuse in and out of the crystal through the interlayer space. These rearrangements are sequential and may spread within the lattice in various modes (laterally within layers, parallel to the c^* axis, etc.). The mechanism could operate through a series of events in which each triggers the next. For example, one Al atom from the octahedral sheet could displace a Si atom from a tetrahedral position, which would then move into the interlayer and become a SiO_4H_4 species. Such a transition would trigger further chemical and/or structural changes in a limited volume around the area because the empty octahedral position is unstable and prompts reorganization of the atoms that may include further loss of silica and changes in the relative positions of hydroxyls and vacancies (Cuadros &

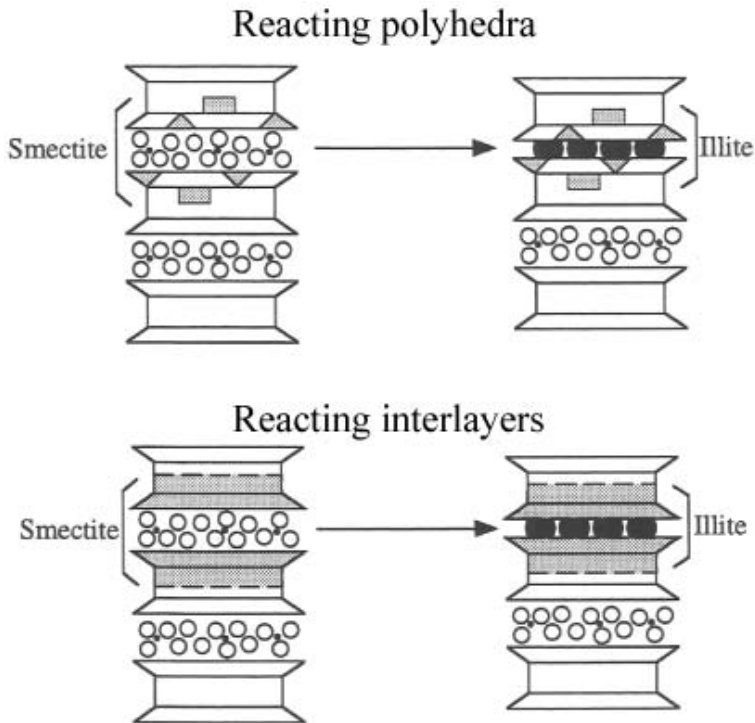


FIG. 1. Models of solid-state transformation of I-S proposed by Altaner & Ylagan (1997). The grey areas correspond to the part of the structure that is undergoing chemical and structural changes. Figure from Altaner & Ylagan (1997, fig. 5). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

Altaner, 1998). The changes can spread laterally in the *ab* plane, taking place at both sides of the interlayer space, where atom diffusion is easier. In this proposed mechanism, diffusion takes place (1) within the interlayer, that is frequently hydrated and where, in any case, energy requirements for diffusion are lower than within a 3D crystal lattice, (2) within a group of atoms that is in the process of (instantaneous) rearrangement, and (3) between immediate crystallographic sites, although the latter may not be necessary as atom rearrangement may be prompted by reacting species in the interlayer space or at layer edges.

Altaner & Ylagan's (1997) model of reacting interlayers is very appealing because it places the centre of reaction in the interlayer of smectite, which results in two important advantages, (1) diffusion of species in and out of the crystal is facilitated and (2) it explains the formation of polar layers in I-S (where illite and smectite units correspond to T-interlayer-T units, rather than

TOT units; i.e. the limits between smectite and illite layers are the octahedral sheets, which introduces "polarity" in the TOT units because in some of them one of the T sheets is smectitic and the other illitic: Lagaly, 1979; Güven, 1991). The polar layer model is in fact useful for other mixed-layer phases as it explains best their XRD characteristics (Cuadros, 2010).

At the same time that the above mechanism is taking place within the crystals, the edges of the crystals can experience changes driven by surface stabilization, such as loss or addition of rows of atoms to minimize the surface of the crystal. In this case, if the involved species are lost to or retrieved from the solution, and if the extent of the process is sufficiently large, the mechanism would be more properly defined as dissolution and precipitation (specifically, the above examples would be termed partial dissolution and overgrowth). Alternatively, if the number of atom layers involved in the process is limited and the species do not pass into the bulk

of the fluid but rather they break off from the surface, diffuse along it and link to it again in new places, the mechanism would be more properly called a solid-state transformation.

ENERGY CONSIDERATIONS

This contribution addresses clay mineral transformation in the typical range of physico-chemical conditions in which they take place, from surface alteration to low-grade metamorphism (thus below 250–300°C; Worden & Burley, 2003) and hydrothermal systems where maximum temperatures are similar to those of low-grade metamorphism. The following energy considerations are intended for the above minerals and range of conditions, although they may be also applicable to others. According to the above constraints on the definition of the reaction mechanisms, dissolution-precipitation involves the breaking of all bonds in the parent mineral or, at least, all those required to dissolve the mineral grains (some species may pass into solution with the preservation of some cation–oxygen bonds from the solid). Solid-state transformation requires the breaking of a much more limited number of bonds. Clay mineral transformations involve major to no chemical changes, as well as major to limited structural changes. The transformation of smectite into illite, for example, preserves the majority of the chemical components and the same TOT structure, although the surface-to-volume ratio and hydration energy are largely different, and the density of lattice defects can be also very different. The transformation of kaolinite into dickite involves no chemical changes and a limited structural modification (arrangement of vacancies in the octahedral sheet). Density of lattice defects and surface-to-volume ratio are not intrinsic characteristics of one and the other polytype, as indicated by the existence of high-crystallinity kaolinite such as the Keokuk specimen (Kameda *et al.*, 2005), kaolinite from burial series that develops together with dickite (personal data) and other examples (Kogure *et al.*, 2010), although most kaolinites do have lower crystallinity than most dickites. In these and other cases of clay transformation, a dissolution-precipitation mechanism requires the breaking of many bonds that are formed again in the product phase. Is such a process energetically efficient? This question needs to be set against the total energy requirements in a solid-state transformation. Both mechanisms

require diffusion of species. For dissolution-precipitation, the species have to travel away from the reacting surface. For solid-state transformation a limited number of ions or species have to travel in and out of the crystal lattice, but (1) the interlayer space of clay minerals, frequently hydrated, is a channel for ion transport, and (2) the typically small crystals and the existence of multiple crystal defects reduce the path that ions have to travel within the interlayer and the corresponding energy barrier. It may be considered that displacing entire layers with respect to their neighbours in certain transformations would require a large amount of energy in a model consisting of sliding rigid layers. However, the displacement may take place in a different way, for example as the 2-D propagation of the displacement of atoms. There are possible mechanisms of clay transformation in the solid state that appear to be more energy conservative than dissolution-precipitation. Thus, I propose that dissolution-precipitation requires the larger energy input in order to take place.

In my opinion, this interpretation is supported by some observations. One of them is that dissolution-precipitation of clays is frequently reported (e.g. Inoue & Kitagawa, 1994) and deemed more likely in hydrothermal environments (Altaner & Ylagan, 1997). Conceptually, the link between hydrothermal environments and dissolution-precipitation is established in the literature mainly based on the high water-rock ratio that favours rock dissolution, as the fluids are less likely to achieve saturation, and thus high permeability systems as sandstones and high-porosity hydrothermal environments are made akin in terms of promoting dissolution-precipitation (Inoue & Kitagawa, 1994; Altaner & Ylagan, 1997). However, such may not be exactly the case because an important factor that promotes dissolution-precipitation in hydrothermal systems is the high temperature that supplies the greater amount of energy necessary for the breaking of a larger number of chemical bonds. Other facts that may support that dissolution-precipitation requires larger energy input than solid-state transformation are changes observed only at the end of illitization series in shales, where the temperatures in the sequence were highest, such as release of ^{40}Ar (Clauer & Chaudhuri, 1996) and changes in O isotope composition of the clay (Lynch *et al.*, 1997; contrary to what the authors state, see their Fig. 5). These changes can be interpreted as a transition from solid-state transformation to dissolution-precipitation in the deepest stage.

Such an interpretation is consistent with the fact that, for a specific reaction, the slope of the increase of the rate constant with temperature depends on the activation energy, and thus on the mechanism of the reaction (Lasaga, 1998). In other words, considering several processes with their corresponding activation energy, as the activation energy increases so does the difference between rate constants at low and high temperature. Lasaga (1998) presents such variations for activation energies and temperatures typical of mineral processes, from 5 to 40 kcal/mole and from 0 to 200°C. At low temperatures, the low-activation energy reactions or mechanisms are faster (more rigorously, they have greater rate constants), whereas at high temperature, the high-activation energy mechanisms are faster. The high temperature provides the energy to overcome the higher activation energy barrier of a process that then becomes faster than the process with a low activation energy. For this reason, it can be expected that some mineral reactions take place through different mechanisms (which have different activation energies) at different temperatures (Lasaga, 1998). If, as I propose, dissolution-precipitation is more energetically demanding than solid-state transformation, it would be reasonable to expect that the latter mechanism is the more frequent of the two in the lower range of temperature conditions.

MORPHOLOGICAL CHANGES AND TRANSFORMATION MECHANISM

Large morphological changes between the original and final clay mineral are frequently invoked as evidence for a dissolution-precipitation mechanism. Such changes include particle shape (outline, surface-to-volume ratio, aspect ratio, etc.) and size. The use of morphological changes to interpret the transformation mechanism requires a detailed and quantitative approach in which morphological features are tested against the possible mechanisms (Cuadros & Altaner, 1998) and particularly against crystal growth habits (Inoue & Kitagawa, 1994). The reason is that morphological differences may be achieved by particle rupture, particle welding or by hybrid processes in which dissolution-precipitation plays a minor role. For example, changes in the outline of a particle can take place by dissolution-precipitation at the edges only. Morphological changes in the kaolinite-to-dickite transformation

series in burial diagenesis have been at times interpreted as indicating dissolution-precipitation (e.g. Ehrenberg *et al.*, 1993; Beaufort *et al.*, 1998). However, grains of kaolin during the kaolinite transformation into dickite in burial diagenesis frequently display a progressive thickening of laminae in vermicular aggregates that can be interpreted as the result of the merging of the laminae (Fig. 2). Not only can laminae be joined but also packs of them can merge face-to-face or edge-to-edge (Fig. 2c), with more drastic changes in size and shape of the resulting grains. Some authors have indeed interpreted that the reaction takes place through a solid-state mechanism (e.g. Shutov *et al.*, 1970; Brindley *et al.*, 1986; both are mainly based on spectroscopic data).

Setti *et al.* (2005) studied morphological changes of I-S from a clay-shale formation in the Apennines. From their article, it appears that smectite was transformed into I-S in an area affected by tectonic stress. SEM images show flakes (interpreted as the precursor material) break up into laths that progressively separate from each other. Flakes and laths have different chemical composition with differences that do not point clearly towards smectite illitization, and there are no XRD data to indicate mineralogical changes. In any case, the study shows a drastic change in morphology caused by the splitting of flakes. Similar morphological changes from predominantly flake-like to increasingly lath-like are described in smectite illitization (e.g. Nadeau *et al.*, 1985; fig. 4 in Worden & Morad, 2003; Ylagan *et al.*, 2000) and the study by Setti *et al.* (2005) introduces the possibility that in some cases such changes take place via a similar splitting of the original smectite flakes. In the TEM observation of the flakes of some smectites or smectite-rich I-S, it is possible to discern that the flakes are an aggregation of laths (Fig. 3 in this article; Güven, 1988). Güven (1974) described abundant laths in bentonites of smectite composition. Although he could not perform chemical analysis in his TEM work, it is likely that the laths were smectite. These observations suggest the possibility that the illitization of smectite with lath fine-texture may be accompanied by the separation of the laths. The laths could exist in the smectite and their presence enhanced by accretion of flakes, the coalescence of parallel laths that come together face-to-face and the separation of these laths as they become thicker and more rigid. A similar process of particle break-up may

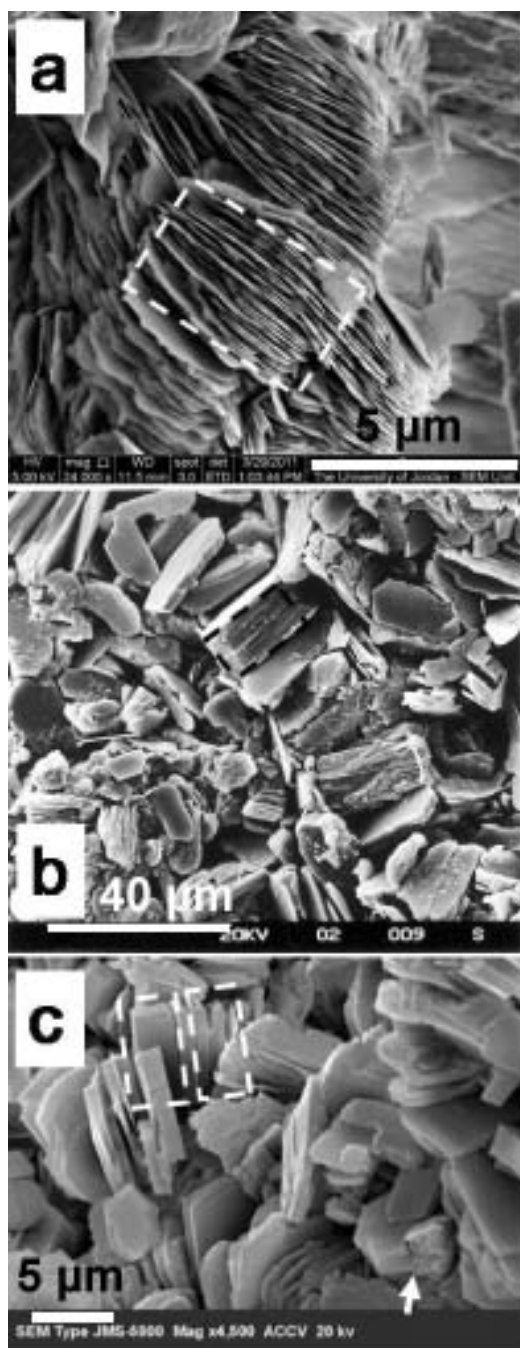


FIG. 2. SEM micrographs of kaolin samples. (a) Kaolinite of unknown origin, from FEI Image Gallery (www.fei.com/.../Kaolinite-Clay-2659.aspx); (b) dickite from the “varicoloured” clay-shale in the Apennines, from Veniale *et al.* (2002); (c) dickite from Recôncavo Basin, Brasil, from De Bona *et al.* (2008). The rectangles mark packets of laminae that can be interpreted to merge together with burial and generate thicker laminae and, finally, a single block. In (c) the arrow indicates the possible lateral merging of two packs of particles.

(Besson *et al.*, 1993) as well as that of I-S subjected to illitization by Fe reduction in wetting-and-drying cycles (Huggett & Cuadros, 2010). Mineralogical and structural changes taking place in wetting-and-drying cycles most certainly occur via mechanical rearrangements and chemical changes in the solid state (Eberl *et al.*, 1986; Besson *et al.*, 1993; Hugget & Cuadros, 2010), and yet they can produce drastic modifications of particle size.

The above possibilities do not exclude the dissolution-precipitation mechanism in cases where illite laths are generated. For example, Small *et al.* (1992) described illite laths and ribbons precipitated from gels or solution at 250 °C and above in synthesis experiments with no smectite precursor.

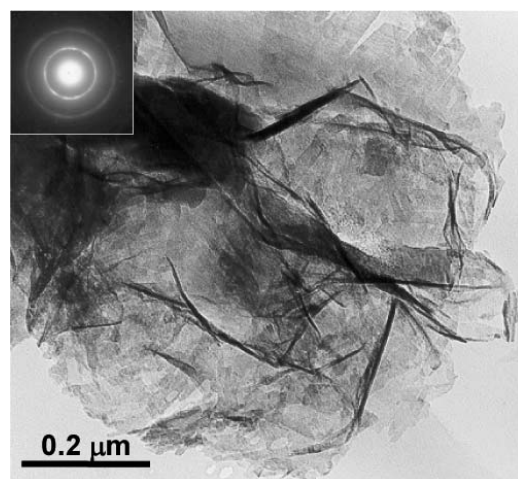


FIG. 3. TEM photograph of flakes of I-S (~25% illite) made up of superimposed laths, and the corresponding SAED pattern showing the random orientation of the individual layers. From de la Fuente *et al.* (2000, fig. 7c). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

take place in the reorganization of layer stacking driven by wetting-and-drying cycles of smectite. It is reported that the particle size of K- or Cs-smectite subjected to such processes is reduced

Laverret *et al.* (2006) showed SEM pictures of sandstone illite originated from kaolin, most probably through dissolution-precipitation. In this illite, laths and flakes are physically related. Laverret *et al.* (2006) interpreted the two particle types as two generations. However, a close inspection of their SEM pictures shows the several possibilities that laths merge into flakes, flakes break up into laths or laths grow from flakes. Ylagan *et al.* (2000) interpreted hydrothermal (85–220°C) I-S in bentonite, where laths are abundant in the intermediate I-S stages, as originated by dissolution-precipitation from smectite or from volcanic ash.

FORMATION OF MIXED-LAYER CLAY MINERALS FROM NON-PHYLLOSILICATE PHASES

It is acknowledged that mixed-layer phases may not have a phyllosilicate precursor. Although this fact does not affect the discussion of the clay transformation (rather than clay formation) mechanism, it is an important issue to bear in mind and is connected with the variability of clay crystal-chemistry. Mixed-layer I-S has been synthesized from volcanic glass (Šucha *et al.*, 1998; de la Fuente *et al.*, 2002) and synthetic gels (Güven & Huang, 1991); I-S can form from alteration of pyroclastics in supergene conditions (Berggaut *et al.*, 1994) or from volcanic glass in hydrothermal systems (Lanson & Champion, 1991; Altaner & Ylagan, 1997); in submarine hydrothermal systems, I-S has been interpreted to precipitate from hydrothermal fluids (Alt & Jiang, 1991), talc-smectite (or kerolite-smectite) has been described to precipitate from hydrothermal fluids within chimneys (Dekov *et al.*, 2008), and chlorite-smectite to replace basalt (Shau & Peacor, 1992). Accordingly, mixed-layer clays are not purely an intermediate stage in a process of transformation from one phyllosilicate to another, but they hold their own range of (meta-) stability derived from the surrounding physico-chemical conditions, the reaction mechanisms and the rates of these reaction mechanisms. Mixed-layer clay minerals are thus probably more frequent products of alteration of non-phyllosilicate phases than is recognized because of the difficulty of identifying them properly, especially at sub-millimetre and microscopic scales.

There are few papers that deal with the formation mechanism of mixed-layer clays with no phyllo-

silicate precursors. It can be argued that the mechanisms of alteration producing end-member or mixed-layer clays should be the same and there is no reason to deal with them separately. Thus a full discussion of such mechanisms should include both categories of products, which would widen substantially the scope of this paper. Rather than doing this, it can be indicated briefly that both mechanisms, dissolution-precipitation and solid transformation, have been described to produce mixed-layer clays with no phyllosilicate precursor. Examples of dissolution-precipitation are those of Altaner & Ylagan (1997), Šucha *et al.* (1998), Alt & Jiang (1991) and Dekov *et al.* (2008) mentioned above. Berggaut *et al.* (1994) imply a precipitation mechanism in surface alteration conditions. The large atom reconfiguration required from transformation of non-phyllosilicate phases in the solid state can take place on a very small scale, at the surface or within the precursor mineral, where the atoms and forces involved derive mainly from the solid, rather than the fluid. Such is most probably the reaction mechanism operating in cases where the morphology of the original grains is maintained after the transformation (de la Fuente *et al.*, 2000), and where alteration of different crystallographic planes in a single grain produces different clay minerals (Proust *et al.*, 2006). Güven & Huang (1991) imply a precipitation mechanism (they use the expression “edge-wise overgrowth”) for the formation of some of their I-S products, which have lath morphology, from synthetic gel. Such may well be the case due to the high temperature used (300°C). However, it is intriguing that although their gels had illitic composition the products were smectite or I-S, instead of illite. They interpret this result as due to the heterogeneity of the gel composition. If such was the case, the implication would be that the reaction products were strongly affected by the local chemistry of the gel grains, which seems to indicate that reactions took place in the immediate vicinity of the grains or in the grains.

Whether the mixed-layer clay forms by crystallization from solution or by reorganization of atoms on or within a solid, hydrated matrix, the alternation of layers with different chemical composition is a remarkable phenomenon. Wang & Xu (2006) proposed a model of crystallization that can shed light into mixed-layer formation without a phyllosilicate precursor. They propose that the composition of each individual layer at the moment of its deposition depends on the saturation degree of the

solution with respect to each layer type, the affinity for the attachment of each structural component onto a preceding layer and the strain generated by the stacking of layers of different composition. The interplay of these factors generates perturbations, of random or perfect periodicity, that correspond to random and ordered mixed-layering. This model can be translated to a solid-state transformation mechanism, where the cations in the solid are arranged into a mixed-layer structure due to two possible reasons: (a) the formation of one or several layers of each type results in a relative enrichment of the surrounding solid towards the composition of the other layer type, which then starts to form instead; (b) the cations in the solid are most stably arranged in a mixed-layer phase because layers of two different compositions are more stable than one single layer type of intermediate composition.

VERSATILITY OF CLAY CRYSTAL-CHEMISTRY

One of the marks of the solid-state transformation mechanism should be the existence of intermediate chemical compositions and complex structures containing elements of the original and final phase within layers or at similar level. These features are difficult to recognize because of the intrinsically complex signature that they produce and because it may be not be easy to define the level at which the chemical heterogeneity exists, whether it is within layers, within crystals or in separate crystals. However, studies have shown the existence of some such complex structures, as shown below in this section. In some cases, these complex structures are a direct indication of a solid-state transformation whereas in other cases they simply suggest it as the more likely transformation mechanism. Independently of the reaction mechanism, these complex intermediate structures are extremely interesting, as they show the large crystal-chemical adaptability of clays and they set the boundaries of possible (stable or metastable) clay structures.

Three-component mixed-layer systems

The development of XRD-pattern modelling techniques has provided a deep insight into the complexity of mixed-layer systems (e.g. Ferrage *et al.*, 2011). The analysis of I-S has shown a diversity of arrangements of illite and smectite layers within

single samples and the existence of 3-layer components. Examples of the latter include illite-vermiculite-smectite (where there are illite layers, high-charge smectite or vermiculite layers and low-charge smectite layers) and kaolinite-illite-vermiculite. Such structures are best interpreted as an intermediate stage in a solid-state transformation process, as indeed has been the case (Drits *et al.*, 1997). In a solid-state transformation there can be layers of several types due to preservation of layers from a former phase, to intermediate stages in the transformation of layers and to superposition of a transformation process (due to a change of physico-chemical conditions) on another not yet finished. It is more difficult to see the reason why a precipitating phase would produce up to three layer types. The kaolinite-illite-vermiculite mentioned above corresponds to a weathering process (from illite to kaolinite), and the illite-vermiculite-smectite to a prograde diagenetic process (from smectite to illite). The vermiculite layers are in both cases an intermediate stage of the transformation. In the illite-vermiculite-smectite series, the proportion of the vermiculite-type layers is very small compared with those of the other two components (Drits *et al.*, 1997), as would be expected in layers of a transient nature. It needs not to be considered that entire physical layers have this vermiculite nature; vermiculite may actually exist in portions of the layers where partial tetrahedral substitution has taken place (on both sides of the interlayer, following the polar layer concept). Mixed-layer systems with three (or more) components could provide great insight into their crystal-chemistry and the reaction processes. Unfortunately, at this stage, their investigation requires detailed and time-consuming XRD modelling and is complicated by the increasing uncertainty of the models as they incorporate an increasing number of variables (i.e. more types of layers and possible layer combinations in the diffracting crystallites).

Kaolinite-smectite

The transformation of smectite into kaolinite via kaolinite-smectite (K-S) takes place through the progressive loss of the tetrahedral sheet of smectite layers (Fig. 4), followed by changes in the octahedral sheet and remaining tetrahedral sheet (Dudek *et al.*, 2006). The main evidence for the sequential transformation is obtained from the

combination of XRD and thermogravimetric data (TG). The loss of tetrahedra generates areas with a TO structure (kaolinite-like areas) within the TOT layers. Within the kaolinite-like areas the hydroxyl content corresponds to that of kaolinite (larger than that of smectite), although no further chemical changes have taken place. If these areas are small, the layers do not collapse to $\sim 7 \text{ \AA}$ d -spacing and maintain a smectitic character (Fig. 4). Thus, at the beginning of the transformation, XRD indicates a lower kaolinite content than TG (Fig. 5). Towards the end of the transformation, however, TG indicates a lower kaolinite content than XRD (Brindley *et al.*, 1983; Dudek *et al.*, 2006). The reason is probably that the layers at the end of the crystallites are the last to transform into kaolinite, as suggested by HRTEM observation of kaolinite crystals terminating in smectite layers (Ma & Eggleton, 1999). As the crystals in the oriented mounts on which the XRD study is performed are not perfectly parallel and in perfect contact, only a fraction of the external surface of the particles generates coherent diffraction and thus XRD detects only this fraction, overestimating the proportion of kaolinite. Thermogravimetry, however, detects

hydroxyl loss in all layers and thus records a higher smectitic content. Transformation via dissolution-precipitation would have generated identical TG and XRD results (straight line in Fig. 5) as smectite grains would dissolve entirely and complete kaolinite crystals grow from solution.

Further evidence for the kaolinite-like patches is obtained from TG (Dudek *et al.*, 2006). As dehydroxylation of K-S takes place, dehydroxylation events can be identified and assigned to kaolinite ($\sim 450^\circ\text{C}$) and smectite ($\sim 620^\circ\text{C}$). However, a dehydroxylation event is observed at intermediate temperature ($\sim 550^\circ\text{C}$), assigned to smectite dehydroxylation in the areas next to the kaolinite-like patches. The dehydroxylation temperature in these areas is lower than that of normal smectite because the open structure allows loss of the hydroxyls more easily. The relative weight loss of the intermediate dehydroxylation event (Fig. 6) has a maximum at $\sim 50\%$ kaolinite content, which is consistent with the above model, because at this stage the perimeter of the kaolinite-like patches is at its maximum. As kaolinitization progresses further the kaolinite-like patches merge and their total perimeter becomes smaller. The

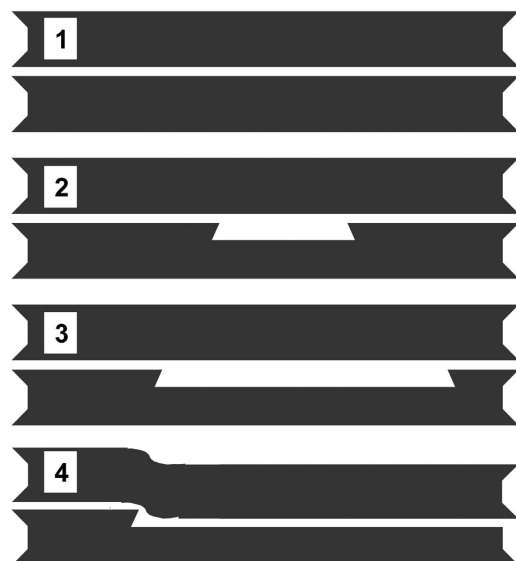


FIG. 4. Sequence of loss of tetrahedra from TOT layers in smectite kaolinitization. The layer collapses to $\sim 7 \text{ \AA}$ d -spacing only after the area without tetrahedra is sufficiently large. The kaolinitic part of the structure in steps 2 and 3 can be detected with TG but not with XRD. Figure from Cuadros (2010).

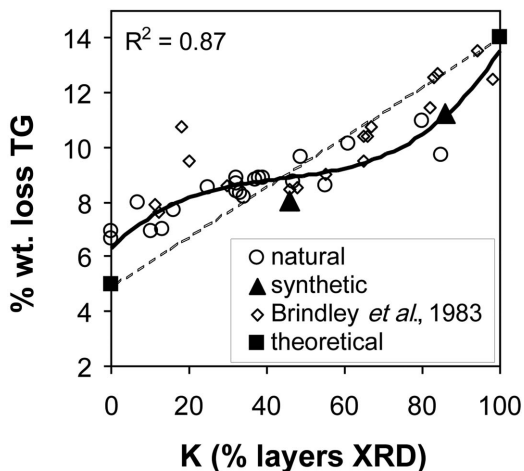


FIG. 5. Plot of dehydroxylation weight loss of K-S versus their kaolinite layer content as measured using XRD. The natural-sample data points (circles) are from Dudek *et al.* (2006) and the curve corresponds to the best fit for them; the synthetic-sample data points are from Dudek *et al.* (2007). The departure from the straight dot-line indicates a complex transformation mechanism in which loss of tetrahedra and layer collapse do not take place at the same time. Figure from Cuadros (2010).

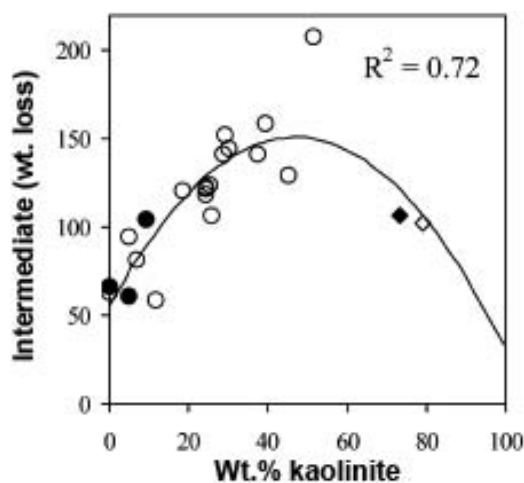


FIG. 6. Relative weight loss of K-S during dehydroxylation at a temperature intermediate between those of kaolinite and smectite, versus kaolinite content from XRD analysis in K-S. Plot from Dudek *et al.* (2006, fig. 12). Reproduced with kind permission of the Mineralogical Society of America, publisher of *American Mineralogist*.

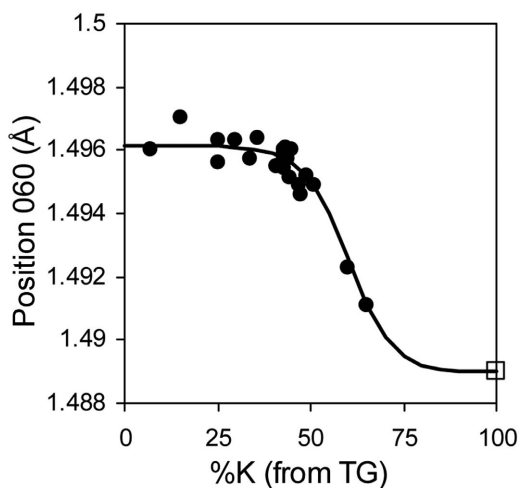


FIG. 7. Position of the (060) peak from XRD of K-S samples versus their kaolinite content from TG. The position of the (060) peak is a proxy for Mg and Fe content in the octahedral sheet. Figure from Cuadros *et al.* (2009, fig. 5). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

chemical changes in the octahedral sheet take place when the transformation into kaolinite, as detected with TG, has progressed to 50% and above, i.e. when a large proportion of the tetrahedral sheet at one side of the layers has been stripped (Cuadros *et al.*, 2009). The changes in the chemistry of the octahedral sheet are indicated by the change in the position of the (060) peak (a proxy for octahedral composition; Fig. 7). This is reasonable because at that stage the large loss of tetrahedra causes the hybrid structure that has been generated to become unstable (Cuadros *et al.*, 2009).

There is HRTEM evidence for the existence of lateral transformation of smectite layers into kaolinite layers in K-S by stripping of one tetrahedral sheet (Amouric & Olives, 1998; Ryan & Huertas, 2009). Together with this mechanism, the generation of kaolinite layers within the interlayer space of smectite also appears as a possibility (Amouric & Olives, 1998; Ryan & Huertas, 2009). The mechanism of smectite to kaolinite conversion by stripping of one of the tetrahedral sheets of smectite has been supported also based on the overall chemistry of the sediments (Hughes *et al.*, 1993) and the preservation of Fe and Mg in kaolinitic layers (Hughes *et al.*, 1993; Dudek *et al.*, 2006, 2007; Cuadros & Dudek, 2006; Ryan & Huertas,

2009). Aspandiar & Eggleton (2002) and Ryan & Huertas (2009) describe the transformation mechanism as a dissolution-precipitation of individual layers or a few of them within the K-S crystals. However, for the reasons indicated above, such process should rather be considered a solid-state transformation mechanism.

Diocahedral to trioctahedral transformation

Traditionally, it has been considered that there is a compositional gap between diocahedral and trioctahedral structures, i.e. there is no continuum in the composition of the octahedral sheet between the two groups. The compositional gap has been supported by compilation of the chemical composition of numerous samples. In the case of 1:1 structures (serpentine and kaolin groups), the rock and water chemistry conditions that cause the formation of di- and trioctahedral phases are so divergent that it is indeed very difficult for these phases to occur together. It is possible that clays of different octahedral character are generated in the same place due to microscopic environmental control. For example, hydrothermal alteration of basalt can produce simultaneously serpentine from

the alteration of olivine and kaolinite from the alteration of feldspar. However, because the control is operating at a very local scale and there is a steep gradient of the chemical conditions, it is difficult for an intermediate di-trioctahedral structure to form. In the case of the transformation of a preexisting 1:1 phase into another of different octahedral character, there must be a large change in the $(\text{Mg} + \text{Fe}^{2+})/\text{Si}$ activity ratio to move between the high values favourable for the formation of trioctahedral 1:1 clay minerals and the low values required by the dioctahedral 1:1 counterparts. This change in $(\text{Mg} + \text{Fe}^{2+})/\text{Si}$ ratio necessarily passes through intermediate values that promote the formation of 2:1 clay minerals. Thus, transformation of 1:1 clays by changing chemical conditions will probably result in the destruction of the original 1:1 structure by the formation of intermediate 2:1 layers and thus no 1:1 dioctahedral phase can form.

The $(\text{Mg} + \text{Fe}^{2+})/\text{Si}$ formation conditions of 2:1 di- and trioctahedral phyllosilicates are closer to each other and there are numerous examples of coexistence of both types of clays, particularly smectite, and of transformation of one type into the other in areas with heterogeneous rock and water chemistry or where water chemistry has experienced changes. Most smectite compositions show a chemical gap between di- and trioctahedral specimens although some specimens have intermediate compositions even on a microscopic scale (Grauby *et al.*, 1993). Whether such particles are aggregates of di- and trioctahedral crystals, mixed-layer phases or have octahedral sheets with both di- and trioctahedral domains has to be investigated using XRD and spectroscopic methods (Grauby *et al.*, 1993; Huertas *et al.*, 2000). Amouric *et al.* (1995) interpreted EDX analyses at the HRTEM scale (10 nm) of individual crystals of Fe^{2+} -Al 1:1 clay from intermediate to purely trioctahedral composition to correspond to a transformation series where Fe^{2+} progressively substituted Al homogeneously in all the octahedral sheets. Their analyses certainly rule out the existence of separate phases although it is possible that the substitution took place through mixed-layering.

Deocampo *et al.* (2009) studied the $<0.1 \mu\text{m}$ fraction of clays from the Olduvai palaeolake, where volcanic ash had been originally deposited in a freshwater lake and generated Al- and Fe-rich dioctahedral smectite. Evaporation reduced the size of the lake and caused increased salinity in the

centre of the lake, where the dioctahedral clay was altered in two parallel transformations towards I-S and trioctahedral clay. There is no correlation between the extent of both transformations, indicating that illitization and Mg enrichment did not take place at the same time. The detailed analysis of the (060) XRD peaks of the clays and of their chemical composition showed that the (060) peaks had 2–3 components (Fig. 8) corresponding to the following phases: dioctahedral Al-rich ($61.64\text{--}62.16^\circ 2\theta$), dioctahedral Fe-rich ($60.95\text{--}61.52^\circ 2\theta$), and Mg-rich of intermediate

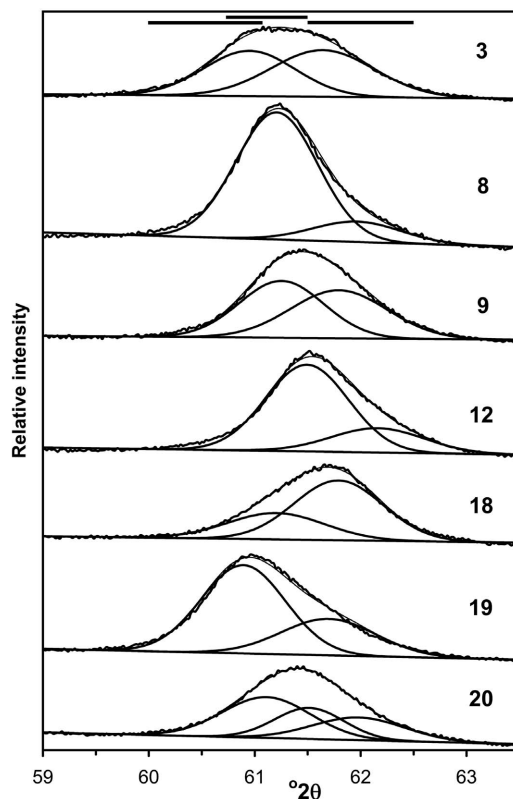


FIG. 8. X-ray diffraction (060) peaks of I-S samples of mixed di- and trioctahedral character from the Olduvai (Tanzania) hypersaline palaeolake. The three bars at the top mark, from left to right, the range of 2θ where the maxima of purely trioctahedral, nontronite and montmorillonite smectites are found. The peaks have several components of which the one in the left corresponds to a phase with intermediate di-trioctahedral character except in sample 3, where it corresponds to a nontronite. Figure modified from Deocampo *et al.* (2009).

di-trioctahedral character ($60.89\text{--}61.25^\circ 2\theta$). The position of the individual peak components could be reproduced carrying out deconvolution and curve fitting of the (060) peaks at varying starting conditions, and there was a good match between the chemistry of the samples and the relative abundance of the above phases. The position of the maximum of the (060) peak in the Mg-rich phase indicated that dioctahedral and trioctahedral environments coexisted within the coherent diffraction domain of individual layers (Deocampo *et al.*, 2009). The domains could be small but segregated from each other, or they could be evenly distributed in the layer with a homogeneous distribution of cations. The analysis of octahedral cation groups (metal-metal-vacancy and metal-metal-metal, in di- and trioctahedral environments) using IR spectroscopy showed it to be compatible with a random distribution of cations (Mg, Fe, Al) across the octahedral sheet of the phase of intermediate character (Deocampo *et al.*, 2009). Whether or not this is the case, this study described a hybrid structure in which dioctahedral and trioctahedral domains coexist in the same layer.

Mixed-layering between dioctahedral and trioctahedral phases

Clay mineral transformations most frequently preserve the chemical signature of the octahedral sheet. Thus, montmorillonite is diagenetically transformed into illite, both dioctahedral minerals, whereas saponite is transformed into trioctahedral chlorite. In the same fashion, alteration of chlorite or trioctahedral mica produces trioctahedral vermiculite. This is a reasonable fact because the chemistry of the two components is similar and because of structural reasons related to the polarity of the layers (uneven distribution of layer charge across TOT units). In the polar layer concept, the octahedral sheets are shared by T units of expanding (low-charge) and non-expanding (high-charge) character. If both layer end-members are di- or trioctahedral, the shared O units can be transformed from the one to the other with limited changes, such as minor chemical variations, cation ordering and cis-trans vacancy location. However, a transformation between a dioctahedral and a trioctahedral O unit requires major chemical changes. If the layers are polar, how are these chemical changes incorporated in the octahedral sheets of mixed-layer minerals of di- and trioctahedral

end-members? What is the structural arrangement of divalent and trivalent cations within these octahedral sheets? If such structural arrangement involved coexisting di- and trioctahedral domains, this fact may be a cause of instability that explains why such mixed-layer systems are scarce.

Even though scarce, there are descriptions of mixed-layer systems with di- and trioctahedral components. Aldega *et al.* (2009) found evidence for one such system in the investigation of volcanoclastic material deposited and partially altered in a karstic environment. The volcanic material contained large phlogopite crystals (mm size) and microscopic crystals embedded in the glass matrix. XRD analysis of the fine phlogopite in the matrix showed it to be mixed-layered with smectite, with only <5% smectite layers. The coarse phlogopite did not show signs of alteration in the XRD study, although SEM-EDX analysis showed alteration in frayed edges (Fig. 9). Such alteration was too small to be detected with XRD. However, the finer phlogopite, with greater surface/volume ratio had experienced further alteration, observable with XRD. The altered phlogopite investigated with SEM-EDX showed an *in-situ* transformation of portions of the phlogopite flakes, with a drastic Mg and K loss towards clay of beidellitic composition (Fig. 9). The overall picture is of alteration of phlogopite via mixed-layering, limited in volume but intense where it takes place, resulting in the massive loss of Mg. Such a process can be explained by the intense water flux in the karstic system and the solubility of Mg, which is readily flushed away. The opening of the phlogopite layers takes place at a lower rate than their chemical transformation after they become expandable.

Assuming the polar layer model for this phlogopite-beidellite, which provides a clear definition of the expandable and non-expandable layers, the question arises of how the dioctahedral domains grow from the trioctahedral O units in the TOT layers. It is possible that the octahedral sheets next to an expanding interlayer change their chemistry immediately after the layer becomes expandable. In this case all polar TOT units would be purely dioctahedral in nature. Given the low extent of the alteration it is not possible to test this hypothesis by relating chemical and XRD data. Another possibility is that the chemistry of the octahedral sheets next to an expandable interlayer change progressively (although quickly) after the expansion took place. In this case, di- and trioctahedral environ-

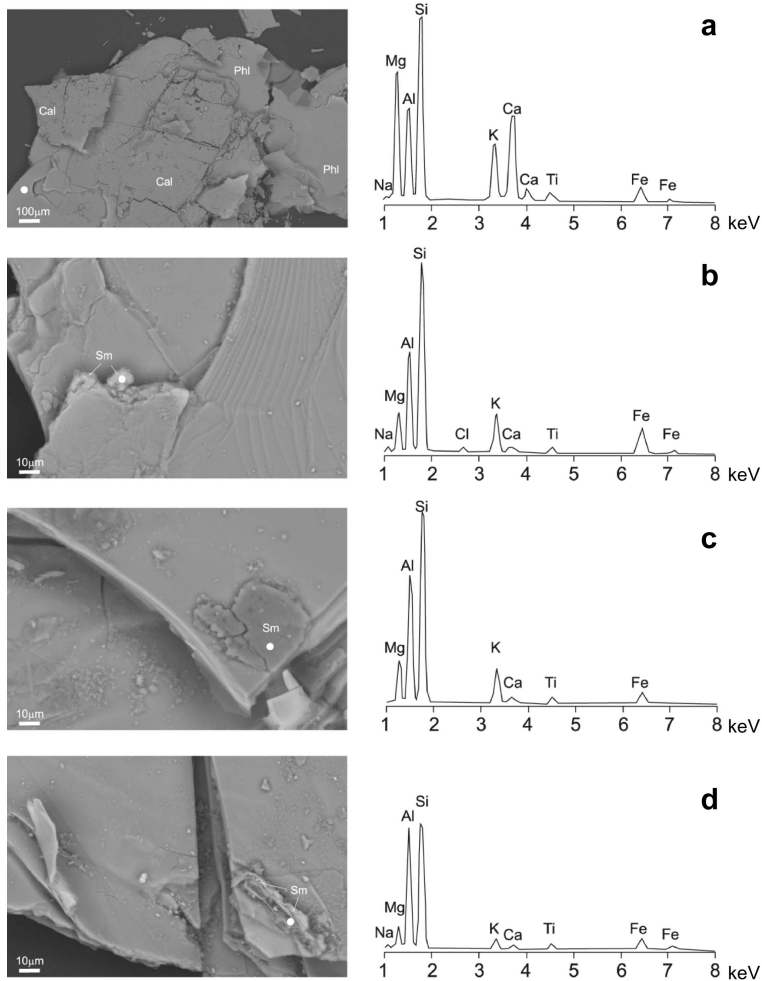


FIG. 9. SEM photomicrographs and EDS spectra of phlogopite (Phl) particles from a volcanic deposit altered in a karstic environment. The white dots indicate the location of the analyses, which show a progressive *in situ* alteration of phlogopite flakes to beidellite. The high Ca content in the top spectrum is due to precipitated calcite (Cal). Figure from Aldega *et al.* (2009, fig. 9). Reproduced with kind permission of the publishers of *American Journal of Science*.

ments would mix in some fashion within these O units. Aldega *et al.* (2009) interpreted that the most likely way in which the chemical process took place was by the loss of Mg and K and the addition of Al and Si from the dissolving glass in the matrix embedding the phlogopite grains.

Aoudjit *et al.* (1995) also described mixed-layering between a trioctahedral and a dioctahedral phase, in this case biotite-beidellite. The inter-stratified mineral resulted from the alteration of biotite in the saprolite in a well drained terrain

subjected to moist conditions (~1000 mm annual precipitation and average temperature of 11°C). They observed mixed-layering by HRTEM and analysed the chemistry of individual crystals using EDX. The chemical trend was the same as described above: loss of K, Fe and Mg, and increase of Al and Si. Ahn & Peacor (1987) described kaolinite-biotite mixed-layering in a hydrothermally altered schist (Craw *et al.*, 1982), using HRTEM and EDX. The kaolinite layers contained Fe, Mg and K, indicating a progressive

transformation and a hybrid nature as in the cases of K-S described above. Anh & Peacor (1987) observed most times pairs of kaolinite layers interstratified with the biotite layers and sometimes these layer pairs merged laterally into one biotite layer, which strongly suggests that the overall mechanism of the reaction involved the transformation of one biotite layer into two kaolinite layers by the incorporation of Al. In all the above studies, the key element that drives the transformation is the effective flushing of cations by abundant water in a well drained system or in a hydrothermal system. A similar case is described by Wilson (1966), where kaolinite pseudomorphs of biotite were found together with pristine biotite, was produced by alteration in a well drained terrain subjected to high precipitation. No mixed-layering between biotite and kaolinite was described but, independently of the mechanism of transformation of biotite into kaolinite, this is another example of alteration progressing heterogeneously between layers as in the examples above, or between neighbouring crystals as in Wilson's (1966) study.

The case of mixed-layering between di- and trioctahedral minerals described by Lee & Peacor (1985) is different from the above as it corresponds to prograde alteration, rather than retrograde alteration, within the mudstone to slate transition. They describe random illite-chlorite mixed-layering, where illite is dioctahedral and chlorite is trioctahedral and Fe-, Mg-rich. Their interpretation of such a rare system is that it is the product of transformation of Fe-Mg-rich smectite (presumably also with sufficient Al), where smectite follows the two routes of prograde transformation at the same time. Lee & Peacor (1985) considered the possibility that the illite and chlorite layers had similar octahedral composition, both with a di- and octahedral component. This is quite possible because their system contained similar proportions of illite (~40 mole %) and chlorite (~60%) and had areas with perfect alternation of layers, which implies that, according to the polar model, many of the TOT units had one T unit of illitic character and one T unit of chloritic character. As discussed above, the O unit could then have an intermediate di-, trioctahedral composition. Lee & Peacor (1985) observed that samples corresponding to a higher grade (greenschist facies) did not contain mixed-layering but independent packets of chlorite and illite (or muscovite). The higher temperature conditions, they argued, facilitates the segregation

of the two phases into a more stable system with lower crystal stress.

CONCLUSIONS

The above examples show that clay minerals display compositional and structural heterogeneities within layers, across TOT units (polar layers, kaolinite-like patches in smectite crystals) and within the *ab* plane (di- and trioctahedral domains). Sometimes the two types of heterogeneity are present (i.e. mixed-layering of di- and trioctahedral structures). When crystallites, rather than single layers, are considered, the possibilities of coexisting domains with different composition and structure multiply (e.g. 3-component mixed-layer mineral with di- and trioctahedral components, or with 2:1 and 1:1 sheet components), some of which have been described. Such complex structures suggest transformation in the solid state, even if the layers have to undergo significant atomic rearrangement, which can take place locally, in contact with a reduced amount of fluid confined within the mineral or at its very surface, and progress sequentially. Similar processes can affect grain morphology. Since solid-state transformation typically requires less bond disruption than dissolution-precipitation, I suggest that energy considerations indicate that the former is probably the faster and the more frequent mechanism in low-temperature environments.

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