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CONSISTENT MODELING OF THE XRD PATTERNS OF MIXED-LAYER PHYLLOSILICATES

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Abstract—The Markovian model of mixed-layering that has been used until now for the modeling of X-ray diffraction (XRD) patterns of 2:1 phyllosilicates describes the mixed-layer crystals as stacks of 'layer units' (LUs) that associate a 2:1 layer with an interlayer content. This model is not consistent when it is applied to a mixed-layer mineral (MLM) involving electrically charged layers, *i.e.* most of the mixed-layer phyllosilicates with 2:1 layers. Two consistent models can be proposed for these MLMs, which, instead of LUs, stack 'interlayer units' (IUs), composed of an interlayer content sandwiched between two half-layers. The IU-NPL model (interlayer units, non-polar layers) imposes non-polarity on the 2:1 layers resulting from the stack of these IUs, which implies restrictions on the succession of the IUs. In the other consistent model, the IU-PL one (interlayer units, polar layers), these restrictions are not imposed. These two models reproduce the Non-Polar 2:1 Layer Model and the Polar 2:1 Layer Model described by Altaner and Ylagan for illite-smectite mixed layering, and the second model corresponds to the stacks of $O_{0.5}$ T I′ T $O_{0.5}$ units described by Olives *et al*.

The present work points out the similarities and discrepancies of the calculated XRD patterns by using computer programs designed for the three models of mixed-layering (LU, IU-NPL and IU-PL) and for two- and three-component MLMs. Illustrations are provided for some I-S and I-S-V MLMs.

The IU-PL model leads to XRD patterns similar to those of the LU model. It is in agreement with lattice-energy calculations, expandability measurement, HRTEM imaging and NMR spectroscopy.

Key Words—2:1 Layer, Illite-smectite, Interlayer Unit, Layer Unit, Mixed Layer, Structural Determination, XRD Pattern.

INTRODUCTION

Classically, the structural determination of a mixed-layer mineral (MLM) is performed by the interpretation of its X-ray powder diffraction (XRD) patterns. The variety of the constituent layers excludes the use of a direct method (Fourier transform of the experimental XRD intensities) to determine the structural parameters which must be obtained by an indirect method: the comparison of the experimental XRD intensities with those calculated for a model of mixed layering.

Several works have been devoted to the development of the mathematical formalism of the diffracted intensities of MLMs, considering different numbers of components and different values for the reichweite, R, which characterizes the range of interaction between layers (Kakinoki and Komura; 1965, Reynolds, 1967; Drits and Sakharov, 1976). Although they consider stacks that could differ slightly in the nature of their external surfaces, all of them have been based on the same model of mixed layering: an MLM is a stack of electrically neutral units in which an electrically charged layer is associated with an inversely charged interlayer.

These formalisms have given rise to different computer programs: the widespread NEWMOD program (Reynolds, 1985), an unpublished program of Sakharov and Drits used in a lot of studies of two- and three-component systems (including Drits *et al*., 1997; Sakharov *et al*., 1999a), and, recently, MLM2C, for two-component MLMs, and MLM3C, for three-component MLMs (Plançon and Drits, 2000).

Referring to the agreement between the experimental and calculated intensities (see, for example, Drits *et al*., 1997), and to the reliability of the physical processes deduced from the evolution of the structural parameters, this model of mixed layering seems ratified.

Nevertheless, this problem deserves to be considered again, for at least two reasons. First, as explained previously by Plançon (2003) in a general case, such a model is not consistent when applied to mixed-layer phyllosilicates involving electrically charged 2:1 layers. And, second, numerous works have underlined that mixed layering can involve 2:1 layers for which the two tetrahedral sheets can be charged differently (polar layers).

The purpose of this paper is: (1) to explain why the model of mixed layering that has been used until now ('classical model') for the description of mixed-layer phyllosilicates is not consistent when it involves electrically charged 2:1 layers; (2) to describe two consistent alternative models of mixed layering which allow us to consider non-polar and polar 2:1 layers, respectively; (3) to sum up the main features of the computer programs that have been designed to calculate the theoretical intensities corresponding to these alternative models, for two- and three-component MLMs; (4) to provide comparisons of patterns calculated for the

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classical model and the two new models; (5) to understand why the inconsistent 'classical' model has nevertheless led to coherent physical conclusions, and (6) to point out the coherence of the new models with the data obtained using other techniques.

THE DIFFERENT MODELS OF MIXED LAYERING

The model used to date for the structural description of mixed-layer phyllosilicates

Apart from its external surfaces, an homogeneous 2:1 phyllosilicate crystal can be described by the stack of electrically neutral 'layer units' (LUs) composed of a negatively charged 2:1 layer plus its positive compensating charge (which can be either a network of cations surrounded or not by water or organic molecules, or a hydroxide sheet as in chlorite). Figure 1a is a schematic representation of a MacEwan crystal in which two-dimensional networks of cations are the compensating charges of 'high charge' (HC) 2:1 layers. This could be an illite (I) crystal, with a 2:1 charge c of ~0.9 e^- per half unit-cell. Figure 1b describes an homogeneous particle in which 'low-charge' (LC) 2:1 layers are compensated by networks of glycolated cations. This could be a smectite (S) crystal, in its ethylene glycol (EG) saturated state, with Ca exchangeable cations ($c \approx 0.3$ e^-). Figure 1a,b shows the LUs chosen for each of these crystals.

The model of mixed layering that has been used to date (LU model) stacks the LUs. Figure 1c illustrates a fragment of an I-S MacEwan crystal according to this model.

Reasons why the LU model is not consistent when it involves differently charged layers

The intrinsic inconsistency of the LU model was described in a general case by Plançon (2003). It occurs in mixed layering involving layers which are charged differently. Consider Figure 1c. As expected, the interlayer content between the HC layers is a network of K cations; and between LC layers, a network of Ca cations surrounded by EG molecules. Unexpectedly, the interlayer content between an HC and an LC layer is not unique and depends on the 'first' layer. If HC-LC is the sequence, the interlayer is that of the HC layer whereas

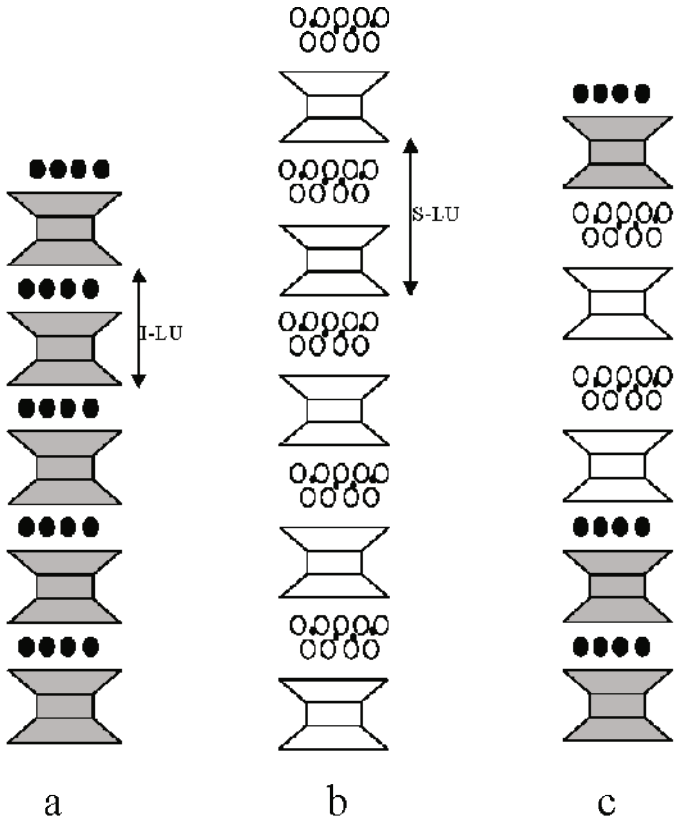


Figure 1. Layer-unit (LU) description of stacks of electrically charged layers: (a) fragment of a MacEwan illite crystal: the high-charge layers are represented in a gray color, the K ions are filled ellipses. I-LU is an illite layer unit for this crystal; (b) fragment of an EG-Ca smectite crystal: the low-charge layers are represented by a white color, the compensating charge is represented as EG molecules (open ellipses) surrounding Ca cations (dots); S-LU is a smectite layer unit for this crystal; (c) a fragment of an illite-smectite crystal in the LU model of mixed layering: stack of illite and smectite LUs.

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it is that of the LC layer if LC-HC is considered. Moreover, the interlayer content is necessarily one of these two, whereas it could be expected to be something else, with an intermediate compensating charge. The LU model is thus intrinsically inconsistent.

Alternative consistent models for the mixed layering of electrically charged layers

The models described below concern any type of mixed layering involving layers differently charged (if not so, there is no difference between the models, according to Plançon, 2003). Because I-S is so often considered in the literature, it is chosen here to illustrate the concepts.

As explained by Altaner and Ylagan (1997), the chemically distinct units in I-S could be interstratified interlayers (*i.e.* *c* unit-cell boundaries at the middle of each octahedral sheet), with low-charge tetrahedral sheets surrounding hydrous, expandable interlayers and high-charge tetrahedral sheets surrounding anhydrous, non-expandable interlayers.

This model of mixed layering, in which crystals are not described as stacks of LUs, but as stacks of 'interlayer units' (IUs) made up of an interlayer content sandwiched between two half-layers, allows for a short-range compensation of charges. There is only one type of interlayer content for a given couple of surrounding half-layers.

If the 2:1 layers are 'made' to be symmetrical (Non-Polar 2:1 Layer model of Altaner and Ylagan, 1997), four IUs should be involved (Figure 2a). These IUs are the HC-HC IU (I_1), the HC-LC IU (I_2), the LC-LC IU one (I_3) and the LC-HC IU (I_4). I_4 is symmetrical to I_2, and they both have an interlayer content different from that of I_1 and I_3, with an interlayer charge that realizes the electroneutrality of the IU. This is the first consistent model which imposes restrictions on the succession of the IUs (*i.e.* on the junction probabilities; *e.g.* I_1 cannot be followed by I_3 or I_4). This model will be referred to here as IU-NPL (IU model with non-polar 2:1 layers). Like the LU model, it allows us to describe MLMs built up of non-polar 2:1 layers and to consider an interlayer charge intermediate between the HC and LC layers.

If the non-polarity of the layers is not imposed, as proposed by several authors (Sudo *et al.*, 1962; Altaner *et al.*, 1988; Jakobsen *et al.*, 1995), a second consistent model can be considered (Figure 2b). It requires only two IUs (the I_1 and I_3 IUs of the IU-NPL model). The 2:1 layers themselves can then be either HC or LC for both halves, but also HC for one half and LC for the other. This model will be called IU-PL (IU model with polar 2:1 layers).

For both of these models that involve IUs, it is necessary to complete the stacks of IUs, on both basal surfaces, by an 'external surface' (ES) composed of a half-layer with whatever type of charged cover. Figure 2c proposes some possible ESs.

The qualifiers, 'two-component' MLM, 'three-component' MLM , and so on, are unambiguous for the LU model: a component is a LU, with its own content and its own *d* value. For example, a three-component EG I-S-V MLM (V for vermiculite) is made up of illite-LUs with a ~10.0 Å *d* value, EG smectite-LUs with a ~16.9 Å *d* value and EG vermiculite-LUs with a ~14.1 Å *d* value. A straightforward inference should consider an IU model of phyllosilicate containing four IUs as a 'four-component' MLM, but it is not that simple. For example, the piece of crystal described in Figure 2a contains two types of layers (HC and LC), four IUs (I_1, I_2, I_3 and I_4) and there are three *d* values (the HC-LC and LC-HC *d* values being the same). For reasons that will be detailed below, the XRD patterns of most phyllosilicates are much more sensitive to the *d* value of the units than to the layer contents. In the next part the term '*n* component' MLM (*n* being 2 or 3) will be applied to an MLM containing *n* *d* values. Figure 2a represents a three-component MLM.

Formalism and computer programs for the modeling of the XRD intensities of the IU models of mixed layering

The formalism for the modeling of the XRD intensities for each of the two IU models of mixed layering was described by Plançon (2003).

Three computer programs have been designed to calculate the intensities of: (1) the two-component IU-PL model; (2) the three component IU-PL model; and (3) the IU-NPL model that describes a three-component MLM but also a two-component one if the I_2 and I_4 *d* values are either the I_1 *d* value or that for I_3.

These three programs allow us to consider various distributions of thickness for the crystals (or 'particles', Plançon, 2002).

Data to compare the calculated XRD intensities for the IUs and LU models

Since most of the previous studies of phyllosilicate mixed layering have examined the I-S minerals or the I-S-V minerals, these MLMs have then also been chosen for the comparisons. The illustrations of calculated intensities, which are potentially infinite, will be restricted here to a few examples that underline the features of the two new models.

All the calculations have been performed with the atomic coordinates and *d* values given by Moore and Reynolds (1989), with $(Si_{3.6}(Al,Fe)_{0.4})(Al_{1.5}Mg_{0.5})O_{10}(OH)_2$ for the 2:1 layer of illite and $(Si_4)(Al_{1.7}Mg_{0.3})0_{10}(OH)_2$ for the smectite one. A uniform distribution of crystal thickness between 3 and 12 layers (*i.e.* between 2 and 11 IUs) has mostly been used.

For both PL and NPL IU models, the external surfaces have been chosen to be identical to those of the LU model. These surfaces are different from that chosen in NEWMOD, *i.e.* 2:1 layers. Thus, it is the model of mixed layering, and only this model, that

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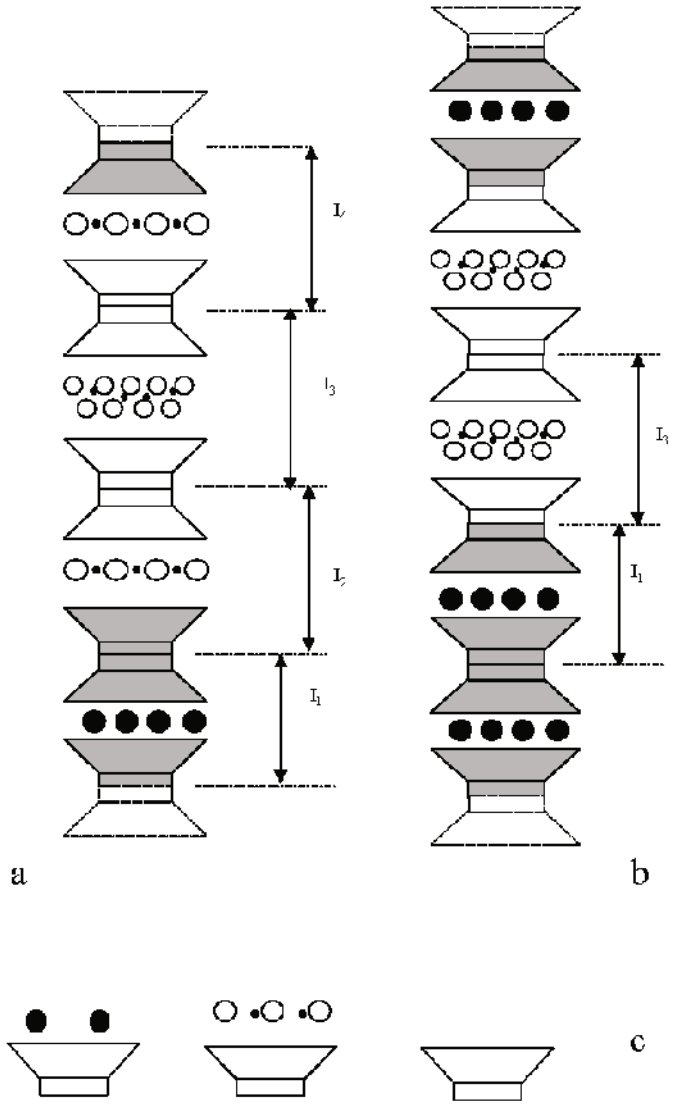


Figure 2. Interlayer unit (IU) description of stacks of electrically charged 2:1 layers: (a) fragment of an illite-smectite MacEwan crystal in the IU-NPL model of mixed layering: four interlayer units (IUs). The I_2 and I_4 units, which have half a 2:1 HC layer on one side and half an LC layer on the other, can have an interlayer content different from the I_1 and I_3 units. Restrictions exist in the succession of these units so that 2:1 layers are symmetrically charged. (b) Fragment of an illite-smectite crystal in the IU-PL model of mixed layering: two interlayer units (I_1 and I_3 IUs of the IU-NPL model of mixed layering), without restriction in the way in which these units follow one another. Some 2:1 layers are asymmetrically charged. (c) Some possible external surfaces for the top and bottom of the crystals.

differs in the following comparisons, except for the case in which the effect of a change of external surfaces is discussed.

Comparisons of the XRD calculated intensities for the IU-PL and LU models

Do noticeable differences exist between the calculated powder XRD intensities if IUs are stacked instead of LUs? This is the fundamental question that requires the use of the IU-PL and LU models of mixed layering. Figure 3 illustrates part of the answer in the simple case of a two-component EG I-S MLM with $Si_{3.6}Al_{0.4}$ for the illite tetrahedral sheets (Si-Al substitution). For the LU model, the chosen stacking parameters are: a proportion W_I of illite LU = 70%, and a junction probability p_{SS} for an S LU to be followed by an S LU = 0 (maximum possible degree of ordering, MPDO). For the IU-PL model, the same parameters apply to the IUs. The *d* values are 10.0 Å for illite (IU and LU), and 16.9 Å for the EG-Ca-smectite (IU and LU). With these data, the intensity distributions for the IU-PL model and the LU model are almost the same: on this scale the two curves superimpose. This conclusion is valid whatever the stacking parameters.

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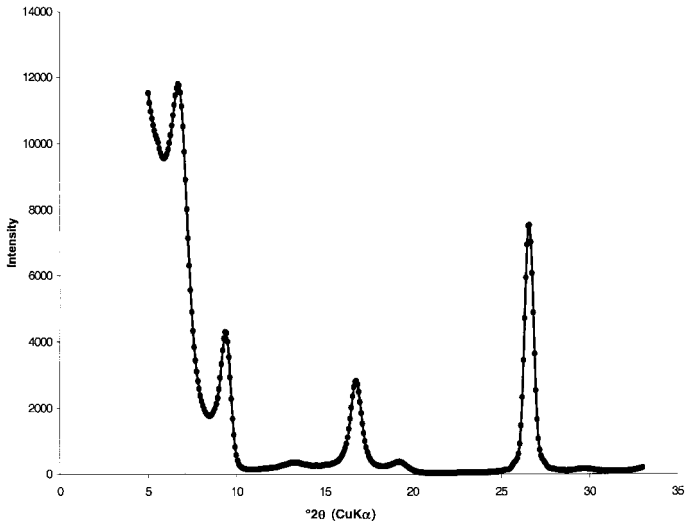


Figure 3. Comparison of LU (dots) and IU-PL (thin line) XRD modeling for a two-component EG I-S MLM, $W_I = 0.70, p_{SS} = 0$. The tetrahedral charge of illite comes from Si-Al substitution ($Si_{3.6}Al_{0.4}$). The two intensity distributions cannot be seen on this scale.

Two reasons explain the absence of noticeable difference in the intensity distributions. First, it must be observed that, for identical stacking parameters, the two models lead to absolutely identical successions of interlayer contents, and that the structural differences exist only for the layers that are surrounded by interlayer spaces of different natures. These 2:1 layers are polar in the IU-PL model, and non-polar in the LU model. It remains to be seen why these different polarities of the 2:1 layers have a negligible influence on the diffracted intensities. In the present case, the charge of the tetrahedral sheets comes from Si-Al substitution. For XRD, atoms and ions contribute to the intensity by their diffusion factor. But, Si^{4+}, Al^{3+} and Mg^{2+} have approximately the same diffusion factors. Consequently, as long as the atomic substitutions involve only these ions, all 2:1 layers contribute to diffraction in approximately the same way, whatever the global charge of the layers and their possible polarity due to the asymmetry of the substitutions.

The same calculation has then been repeated (W_I = 0.7, p_{SS} =0), but with an illite layer in which the same tetrahedral charge comes from Si-Fe substitution ($Si_{3.6}Fe_{0.4}$). The results are presented in Figure 4. The intensity distributions for the IU-PL and LU models are then noticeably different because Si^{4+} and Fe^{3+} have quite different diffusion factors.

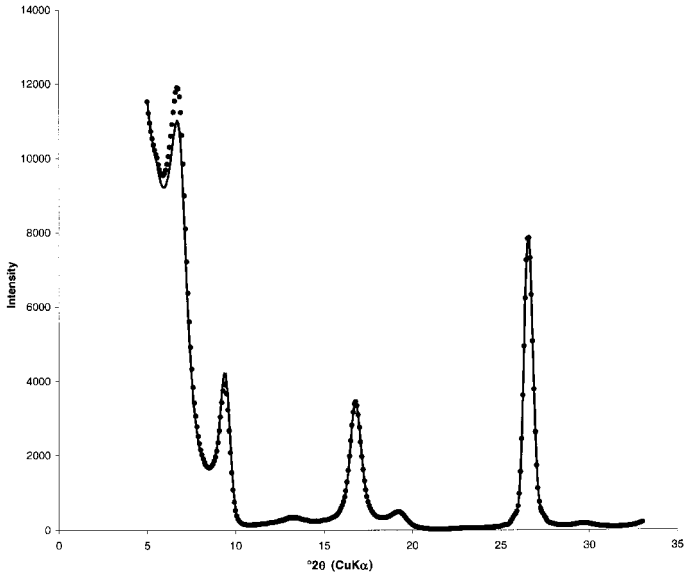


Figure 4. Comparison of LU (dots) and IU-PL (thick line) modeling for a two-component EG I-S MLM, $W_I = 0.70, p_{SS} = 0$. The tetrahedral charge of illite comes from Si-Fe substitution ($Si_{3.6}Fe_{0.4}$).

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Comparisons of the XRD calculated intensities for the two-component IU-PL and IU-NPL models

Are the two IU models of mixed layering very different for two-component MLMs? Figure 5 illustrates the same EG I-S MLM as above, considering only two *d* values (10.0 and 16.9 Å) in the stacks for the IU-NPL model, *i.e.* with the hypothesis that the HC-LC interlayer and the LC-HC interlayer should behave in the same way, either (1) like the HC-HC interlayer, with K compensating cations, and a 10.0 Å *d* value, or (2) like the LC-LC interlayer, with EG Ca compensating cations, and a *d* value of 16.9 Å.

For a two-component I-S MLM, the IU-PL and IU-NPL models produce rather different intensity distributions. In fact, the IU-NPL models produce stacking sequences different from those generated by the IU-PL model. The choice of a K interlayer content for the HC-LC IU of the IU-NPL model reinforces the apparent illite contribution, compared to the IU-PL model, and, reciprocally, the choice of EG Ca as interlayer content reinforces the apparent contribution of smectite. Thus the IU-NPL model, which is intended to describe a three-component MLM, is rather rigid when used for a two-component MLM.

Comparisons of the XRD calculated intensities for the three-component IU-PL and IU-NPL models

An important feature of the IU-NPL model is to predict implicitly the existence of three-component MLMs, because the HC-LC interlayer content should be different from that of the HC-HC and that of the LC-LC. For example, if HC-HC is I and LC-LC is S, HC-LC could be vermiculite-like. With this hypothesis, the two IU models can also be compared for a three-component I-S-V MLM (Figure 6). For the IU-NPL model, the EG I-S MLM has been chosen again ($W_I = 0.75$, $p_{SS} = 0.50$), with the above-mentioned assumption that the HC-LC and LC-HC IU models vermiculite ones (*d* value = 14.2 Å). The corresponding parameters for its description as a three-component MLM (Plançon, 2003) are then $W_I = 0.625$, $W_S = 0.125$, $p_{SS} = 0.50$, $p_{SV} = 0.50$, $p_{VS} = 0.25$, $p_{VV} = 0.333$. These structural parameters have been introduced in an I-S-V IU-PL model. For three-component MLMs, the two IU models provide noticeably different results. For two-component MLMs, as well as for three-component MLMs, the IU-NPL model is then rather rigid and does not allow all the varieties of stacking sequences that potentially exist with the IU-PL.

Role of the nature of the crystal external surfaces on the XRD patterns

As shown by Sakharov *et al.* (1999b) the nature of the external surfaces of the crystals also plays a role in the XRD pattern. Figure 7 illustrates the effect of these external surfaces for an I-S MLM, $W_I = 0.7$, MPDO, IU-PL model. One curve corresponds to crystals whose external surfaces are those of the LUs, *i.e.* asymmetrical (without any compensating charge on one external surface, the whole compensating charge being on the other surface). The other curve corresponds to crystals with symmetrical external surfaces, without any compensating charge, *i.e.* 2:1 layer surfaces. Intensity differences exist, indicating that a change of external surfaces could explain small intensity discrepancies between experimental and modeled XRD patterns.

DISCUSSION

The main aim of the simulation of the XRD patterns of MLMs is the determination of the number, nature,

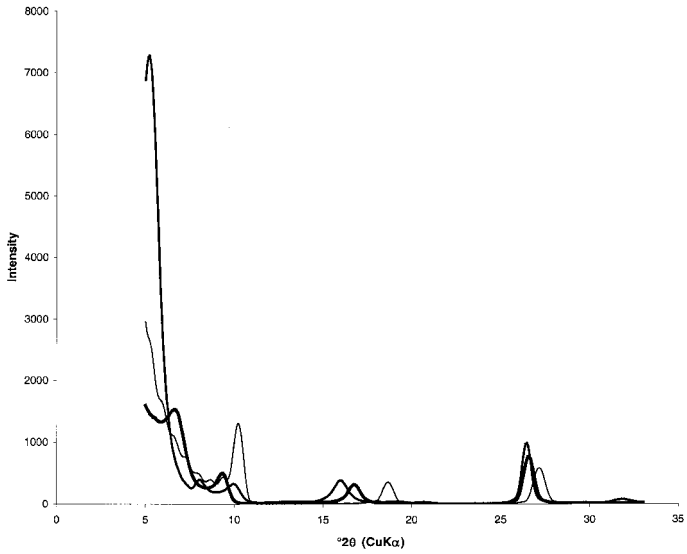


Figure 5. Comparison of IU-PL (thick line) and IU-NPL XRD models for a two-component EG I-S MLM, $W_I = 0.70$, $p_{SS} = 0$. For the IU-NPL models the *d* value of the HC-LC IUs is either the illite one (thinner line) or the smectite one (thicker line).

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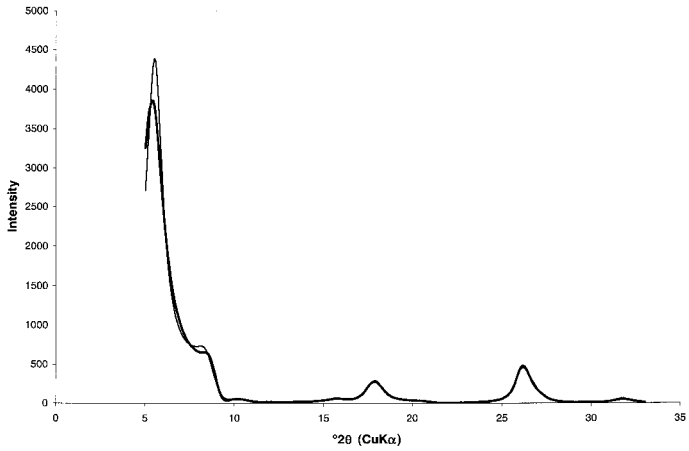


Figure 6. Comparison of IU-PL (thinner line) and IU-NPL (thicker line) XRD models for a three-component I-S-V MLM, $W_I = 0.625$, $W_S = 0.125$, $p_{SS} = 0.50$, $p_{SV} = 0.50$, $p_{VS} = 0.25$, $p_{VV} = 0.333$.

content and distribution of the interstratified units, taking into account the low sensitivity of XRD to local disorder (*e.g.* to the variation of chemical composition of the layers; the precise determination of this composition requires the use of other methods). In fact, similar diffraction effects may be simulated with various structural and probability parameters. And several different models may describe equally well the experimental XRD pattern (Sakharov *et al.*, 1999a, 1999b). Therefore, the conventional approach should be replaced by a new one if it provides new information about the crystallochemical features of the MLMs.

The calculations of the XRD patterns of the LU and IU-PL models showed that they are not the same. For example, Figure 4 shows that the LU XRD pattern of an I-S where the tetrahedral sheets of illite have the $Si_{3.6}Fe_{0.4}$ composition differs from that obtained of the IU-PL XRD pattern. However, such a difference is not diagnostic. Calculations by Drits and Sakharov (pers. comm.) made in terms of the LU model show similar diffraction effects for the Fe-containing I-S and an Fe-free I-S with the same structural parameters but 0.3 additional water molecules (per unit-cell) in the smectite interlayers.

Quite similar patterns can also be obtained for the IU-NPL I-S model in Figure 6, and a LU-model with $W_I = 0.625$, $W_S = 0.125$, $p_{SS} = 0.5$, $p_{SV} = 0.5$, $p_{VS} = 0.15$, $p_{VV} = 0.333$ (Drits and Sakharov, pers. comm.). These examples emphasize that similar diffraction effects can occur with different structural parameters, demonstrating the limitations of the simulation of the experimental XRD patterns. The so-called multispecimen approach (Drits *et al.*, 1997; Sakharov *et al.*, 1999) should be applied to provide a reliable interpretation of the XRD patterns.

On the other hand, each of the LU, IU-PL and IU-NPL models has been considered here as equivalent to

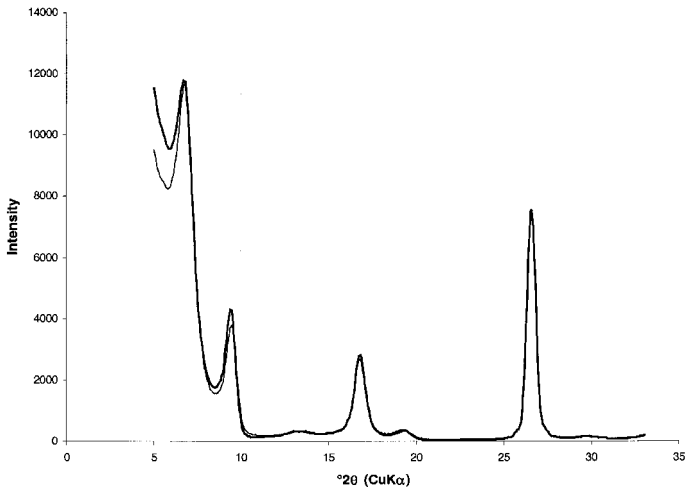


Figure 7. Role of external surfaces on the XRD models for a two-component EG I-S MLM, $W_I = 0.70$, $p_{SS} = 0$, IU-PL model, uniform distribution of MacEwan crystals thickness from 4 to 13 IUs. The external surfaces are either those of the LUs (thinner line) or those of 2:1 layers (thicker line).

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the corresponding mathematical formalism. However, many authors distinguish the models for the description of the actual I-S structures and the models for the simulation of the XRD patterns. For example, in Drits *et al.* (1997) the transformation of I-S and I-S-V was described in terms of transformation of smectite and illite interlayers in the IU-PL model although structural parameters were obtained by formalism based on the LU model. This concept is widely accepted by the clay community although this is only an approximation if one takes into account the huge structural and chemical heterogeneity of MLM.

As far as the self-consistency of the models is not considered, the approaches based on the LU and IU-PL models describe experimental XRD patterns equally well. Another question is how to interpret the structural and probability parameters obtained by XRD-pattern simulation.

The IU-PL model involves polar layers, as proposed by Sudo *et al.* (1962), and assumed, in the mechanisms of smectite illitization, by Altaner and Ylagan (1997) or Drits *et al.* (1997). Its validity is supported by a great number of results obtained by different techniques. For example, Olives *et al.* (2000) performed lattice-energy calculations to determine the structure of the I-S sequence which corresponds to the minimum energy. They considered stacks of different units and concluded that the minimum energy is obtained by stacks of $O_{0.5}$ T I′ T $O_{0.5}$ units, *i.e.* what is termed here as IUs. The IU-PL model is then in agreement with the lattice-energy calculation. It is also in agreement with expandability measurements and HRTEM imaging (*e.g.* Jiang *et al.*, 1990; Veblen *et al.*, 1990), and with NMR spectroscopy (Barron *et al.*, 1985; Altaner *et al.*, 1988; Jakobsen *et al.*, 1995).

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