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Interstratified Clay Minerals

**Origin, Characterization &
Geochemical Significance**

Edited by
**Saverio Fiore
Javier Cuadros
F. Javier Huertas**

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**Origin, Characterization &
Geochemical Significance**

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Edited by Saverio Fiore, Javier Cuadros and F. Javier Huertas



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Identification and characterization with microscopic methods

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1. Basics of electron microscopy

Electron microscopy includes a wide spectrum of techniques, which differ according to the kind of signal recorded, between the several signals produced as a consequence of the interaction of the electrons with the sample. The two basic branches are Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). In the first one both transmitted and diffracted electrons are used and the physical path of these electrons from the source to the detector system is broadly equivalent to that in an optical microscope (Figure 1). In the second one the beam scans the sample and different kinds of signals produced by the interaction of the electrons with each point of the sample are used to build an image, which, depending on the specific signal, has different meanings. Even if theoretically possible, a universal electron microscope is not usual, therefore TEM and SEM are clearly separated techniques, even from the time of preparation of the sample. When an SEM apparatus is optimized to produce the best possible microscopic chemical analyses it is named electron microprobe (EMPA or EPMA).

Generally speaking, resolution in SEM images is not sufficient to give significant information about very fine-grained materials, as is the case of interstratified minerals, with the exceptions of some textural relationships with other minerals and chemical compositions. Therefore most of this chapter is devoted to TEM with the exception

of the final part in which the use of chemical data of interstratified minerals is presented independently of the kind of microanalysis used.

The geometry of the path of the electron beam in TEM is equivalent to that of the light rays in an optical microscope (Figure 1). The obvious difference is the kind of lens employed to focalize the rays, however such difference has two important implications. The first one is that the focal length of electron lenses is not fixed, but may be continuously adjusted; as a consequence, various characteristics of the images may be easily modified with the pertinent electronic automatized instructions. The second one is a significant consequence of the above possibility, and is that the back focal plane of the objective lens may be brought to become the final image, instead of the intermediate image, as usual in optical microscopy. In all microscopes a diffraction pattern is produced in the back focal plane of the objective lens and the interference of the diffracted beams produces the image. Therefore the electrons can follow two different paths after the first projective lens, generating either an image or a diffraction pattern, and the change from one to the other path is instantaneous at the push of a button (Figure 1).

In addition to these two possibilities, one of the signals produced by the electrons is X-rays, which contain information about the chemistry of the sample. These X-rays are recorded and employed to obtain chemical analyses in TEM, SEM and EMPA. There-

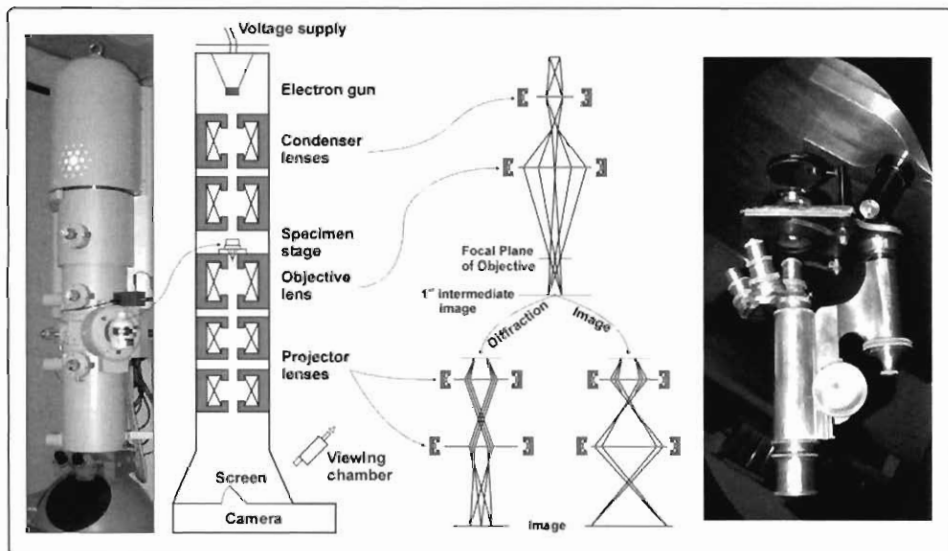


Figure 1. Column of a transmission electron microscope (left) and path of the rays valid for both electron and optical microscopes (right). The relative position of the radiation source, object and observing device is inverted in the electron and optical microscope. Two different paths of the electron beam after the first intermediate image, produced by different field strengths of the projector lenses, allow the projection on the image plane of 1) the back focal plane of the objective lens (diffraction pattern) or 2) the intermediate image. From Nieto (2008), with permission.

fore, a TEM apparatus is able to produce simultaneously, and from the same point of the sample, images, diffraction patterns and chemical analyses. Possibly, this variety of information, more than its high spatial resolution, is the main potential for the use of TEM in geology. Moreover, the possibility to take images at different scales enables users to characterize the textural relationships between clay minerals at low magnification (Figure 2a), while detailed specific aspects about each clay mineral phase can be observed and measured at high resolution: d-spacing, ordering, layer lateral variations, crystal edge terminations, defects, coherent domain transformations, etc. (Figure 2b).

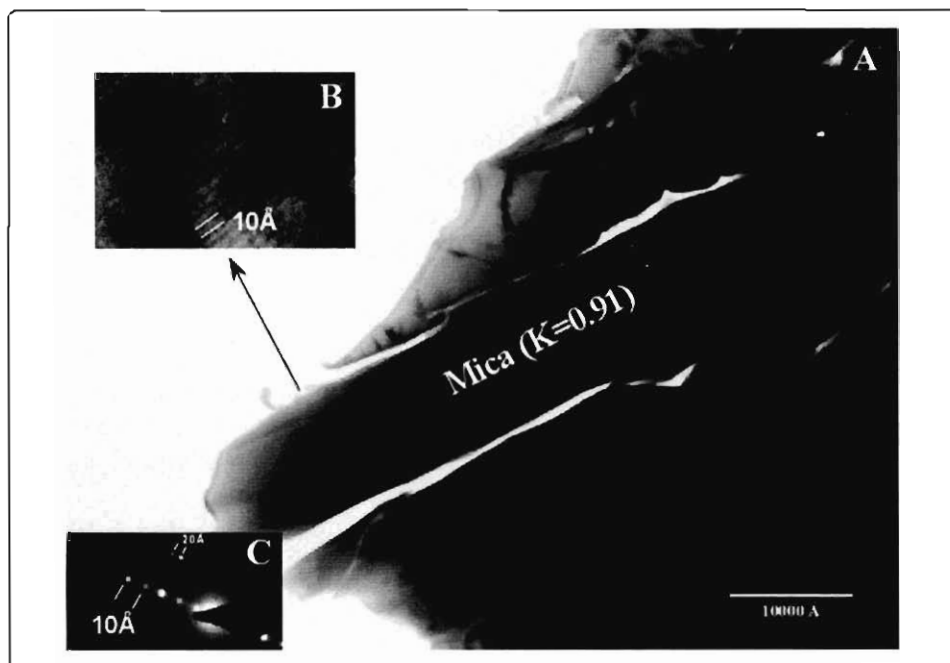


Figure 2. A: TEM textural image showing a large grain of detrital mica. B: Lattice-fringe image of the mica grain with the typical mottled texture, crystalline perfection and d-spacing of 10Å. C: SAED pattern of the same grain that indicates a 2M polytype. AEM analyses show a high K content in the interlayer (near 1 atom per formula unit). Modified from Arroyo *et al.* (2007), with permission.

1.1 Electron diffraction

Electron diffraction follows the same basic principles of X-ray diffraction (XRD) and is able to produce similar information, but from a very small area. Two significant differences between electrons and X-rays have notable consequences in the use of electron diffraction. 1) The diffracting power of electrons is some orders of magnitude higher than that of X-rays, therefore a diffraction pattern can be viewed in real time (the diffraction signal does not need to be accumulated during certain time). 2) The typical wavelength of electrons is about 0.02-0.03 Å, much smaller than those of X-rays (~1.5

Å for CuK α), therefore the Ewald sphere for electrons has a very large radius and its surface is an approximation to a plane so that it is possible that many points of the reciprocal lattice are simultaneously on the Ewald sphere, without any additional motion of the crystal. Adequate orientation of the crystal can produce a diffraction pattern of an entire crystalline level (Figure 2c).

1.2 Preparation of samples

In principle, the ways of sample preparation for TEM are as varied as the kind of samples and the nature of the problem to be investigated. Nevertheless, it is possible to summarize those more frequently used in geology in three basic methods.

(1) The most frequently used is ion milling. This way of sample preparation has been so important in mineralogy that the major use of TEM in geology was linked to the development of such technique. The main reason is that the procedure allows extracting the TEM sample from a thin section similar in nature to those routinely used in petrographic research. Therefore textural information is preserved (e.g., Figures 2 and 5). A metal ring is glued to the sample with its hole on the area to be studied. The thin section needs to be prepared with heat-sensitive resin. In this way, after cutting around the metal ring, this may be extracted with the attached piece of rock, after gentle heating. The metal with the attached sample is placed in an ion/atom beam of Ar, which polishes the centre of the ring until producing a hole. Numerous electron transparent areas are produced around this hole.

(2) The simplest mode of preparation is to deposit a very fine powder of the sample onto a metal grid. The grid is covered with a fine carbon or formvar film. Contrary to ion milling, this procedure destroys the physical integrity of the sample; consequently, information about textural relationships between grains is lost. It is very useful and frequently employed when a set of high-quality microanalyses (chemical characterization) of each mineral phase is desired. Moreover, this technique is often used to study the shape and morphology of distinct clay mineral phases, including mixed-layer clays (Figure 3).

(3) The star preparation mode in bio-medical sciences, ultramicrotomy, is also frequently used in geology to produce ultra-thin sections. It allows producing specimens of well-controlled thickness. The main disadvantages of this technique are the loss of information about textural relationships and the fact that the sample needs to be perfectly free of hard minerals. Therefore, its use for clay fractions has been frequent (Figure 9 below was produced following this procedure). The usual routine is to encase the powdered sample in a resin to produce a piece of solid plastic containing the clay particles in the desired orientation. Small slices of the piece are then cut to the desired thickness using a diamond knife.

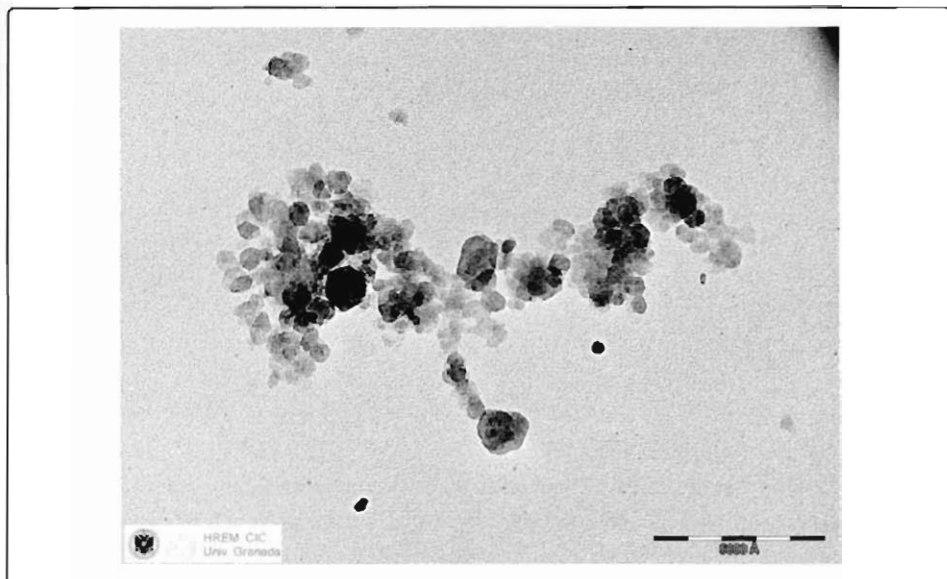


Figure 3. TEM photograph showing the morphology of kaolinite/smectite particles. Irregular anhedral morphology, typical of smectite, coexists with hexagonal shapes in the most kaolinitic grains (sample from Cuadros et al, 2009). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

1.3 Analytical electron microscopy (AEM)

Each chemical element produces a set of characteristic X-ray emissions when it is excited by a high-energy source of electrons. The intensity of the emission is proportional to the concentration of the element in the sample. Therefore the measure of the intensity of a significant level of energy provides information about the proportion of the analyzed element in the sample. In thick samples (SEM and EMPA techniques) the so called ZAF (atomic number, absorption, fluorescence) correction is required; however, in thin samples, such correction is neither necessary nor possible (Figure 4), as the exact thickness of the sample at a given point is unknown. This fact is at the same time the main simplifying factor and the main limitation of microanalysis with TEM.

The intensity ratio of the X-ray radiation from a couple of elements may be converted to the corresponding concentration ratio by means of a proportionality factor. This analytical technique, therefore, produces the element ratios but not their absolute concentrations. This is an intrinsic limitation of the technique, motivated by the lack of information about the thickness of the sample at the analyzed spot. Usually, a mineral formula is calculated from element ratios, assuming some normalization criterion.

The main advantage of microanalysis with TEM is that the volume excited is limited to the beam diameter, contrary to what happens in SEM and EMPA (Figure 4), so that the spatial resolution is much greater.

1.4 Lattice images vs. structure images

Spence (1981) defined a structure image as "...that restricted set of electron lattice images which may be directly interpreted to some limited resolution in terms of specimen's projected structure ...". Such structure image would allow interpreting the various shades of grey in the image in terms of different groups of atoms and interatomic distances. Nevertheless, the same author completed the paragraph in the following terms: "...At the time of writing the author is not aware of the existence of any experimental atomic resolution structure images". To our knowledge, 30 years later the situation has changed little and real structure images are exceptions, largely confined to the realm of utopia, or the product of image treatment by means of electron crystallography software. Therefore, most mineralogical interpretations are obtained from lattice images, which may be one-dimensional (lattice fringes) or bidimensional, if they contain information about crystallographic periodicity at least in two directions. Lattice fringes are very popular in clay mineral studies and particularly useful for interstratified minerals, due to the planar character of phyllosilicates. In some particularly favorable cases the components of the interstratification may be recognized and consequently the layer proportion and stacking order can be identified at a local level (Figure 5). This local character of the identification brings about a significant difference in relation to XRD, with consequences even on the very concept of stacking order. The term Reichweite, R, is used to express probability, in other words, it has a statistical meaning, perfectly compatible with the nature of XRD information, but in HRTEM it is used with a strict meaning of real succession of layers in a short layer sequence. The Reichweite nomenclature is therefore inappropriate for specific layer sequences as observed by TEM. This is why some authors have made some attempts to adopt a specific terminology to understand layer sequence ordering as seen by TEM. Bauluz *et al.* (2000) suggested the symbol In, where n is the number of illite-like layers (I) associated with a given smectite-like layer (S); i.e., layers of IS are denoted as an I1 unit, ISI as an I2 unit, etc. A similar classification (symbol Mn)

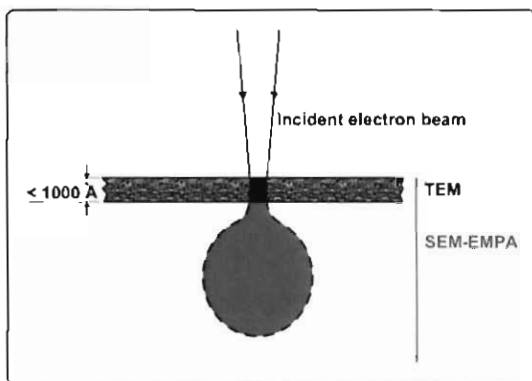


Figure 4. Electron-excited areas for thick (grey area) and thin (black area) samples. From Nieto (2008), with permission.

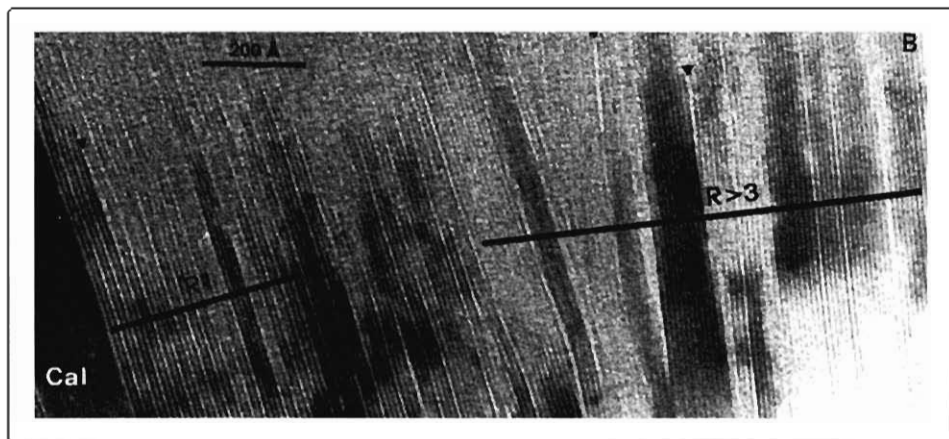


Figure 5. Lattice fringe image showing well-defined individual packets of R1 and R>3 I/S mixed-layer. Data obtained from ion-milled samples without anti-collapse treatment (from Nieto *et al.*, 1996). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

was applied to TEM images by Murakami *et al.* (2005). More research is necessary to find the adequate agreement between XRD- and TEM-defined ordering and to clarify the terms to be applied for each type of order in TEM images.

2. Application to interstratified clay minerals

The extensive application of TEM to diagenesis and very-low grade metamorphism studies in the last 2 decades has permitted to enhance the characterization of mixed-layer clay minerals. First of all these studies have allowed checking the criteria developed by powder diffraction and to understand their physical meaning. The most important advances are related with the textural relationships between the several interstratified clay minerals and their internal physical characteristics at the coherent domain dimension level. The study of textural relationships of mixed-layer clays by TEM has not been as difficult as the observation of their structural aspects. In the case of textural relationships, the large amount of low magnification images and SAED and AEM data available have facilitated the goal. By contrast, to obtain high quality HRTEM images is complicated by the easy damage of some mixed-layer clay minerals, their variable orientation in a small area, high amount of heterogeneities and variations in thickness. Mixed-layer illite/smectite (I/S) minerals have been the most extensively studied by TEM because of their relevance, abundance and relative ease to obtain high quality images. A great amount of work, producing good images, has also been performed in mixed-layer chlorite/smectite (C/S) minerals, but the number of studies in this case has been lower due to the comparatively minor presence of these phases in geological samples. In other mixed-layer clay minerals it is particularly difficult to obtain HRTEM images due to the excessive damage caused to the component

layers, as is the case of kaolinite/smeectite (K/S) interstratified clay minerals (Figure 6).

An essential problem in HRTEM investigation of mixed-layer I/S minerals is the dehydration and collapse of expandable interlayers under the high vacuum of the electron beam. This makes the distinction between smectitic and illitic interlayers, and thus, between smectite and illite in I/S mixed-layers, very difficult, if not impossible. In fact images showing I/S mixed-layers were absent in all the published photographs of initial studies of samples of diagenetic sequences, where such

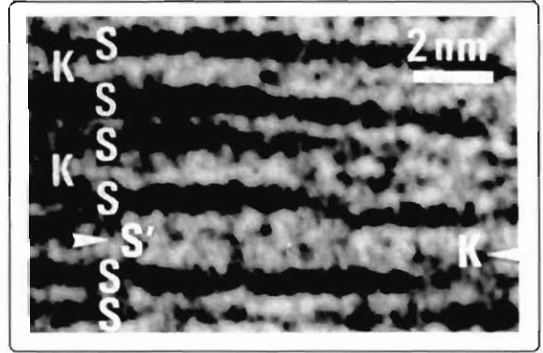


Figure 6. Lattice fringe images of interstratified kaolinite-smeectite layer sequences showing poor definition of the fringes. Arrows indicate the lateral transition between smectite and kaolinite. S: 10 Å smectitic interlayers. S': 12.5 Å smectitic interlayers. K: 7.2 Å kaolinitic interlayers (modified from Amouric and Olives, 1998). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

interstratified minerals were present according to XRD. However, layer collapse does not always occur, and sometimes differences in contrast between smectite and illite layers can be observed in the lattice fringe images (e.g., Figure 5). Guthrie and Veblen (1989a, 1989b and 1990) showed that smectitic and illitic interlayers could not be distinguished from one another in routine underfocus photographs, but only in overfocused images. Recent improvements in imaging and sample preparation techniques have addressed the collapse problem. Nevertheless, ambiguities may be still present due to specimen orientation and microscope focus. This is the reason why we present swelling and anti-collapse treatments below. In the case of C/S mixed-layer the collapse of the expandable layers is an advantage, as their contraction to 10 Å allows the easy visual distinction between the 14 Å chlorite layers and the collapsed 10 Å smectite and/or vermiculite layers (Figure 7).

2.1 Swelling and anti-collapse treatments

L.R. WHITE RESIN TREATMENT. Stucki and Tessier (1991) found LR White resin useful in helping to avoid complete collapse of smectite under high vacuum. Later on, Kim *et al.* (1995) developed a procedure to treat the specimens before ion-milling. In this procedure, which allows the distinction between smectite and illite interlayers in TEM, great care is taken to avoid direct contact with water during sample preparation in order to avoid expansion of smectite and consequent sample damage. Sticky wax-backed thin-sections are prepared with surfaces normal to bedding, and first examined by optical microscopy. The selected areas are

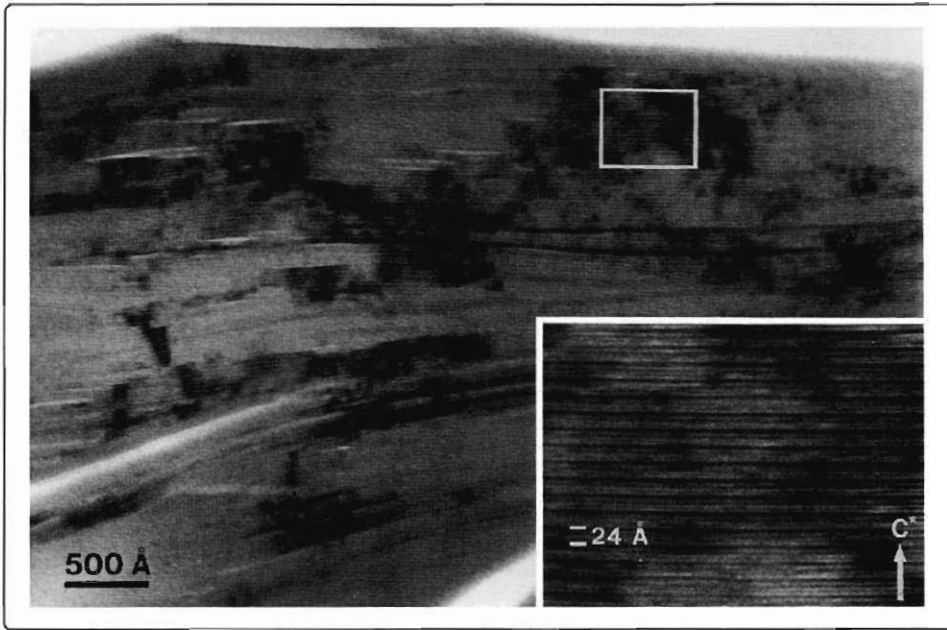


Figure 7. TEM image showing packets of corrensite more than 1000 Å thick. Bottom-right: lattice-fringe high resolution image with a periodicity of 24 Å due to a regular interstratification between 10 Å collapsed smectite and 14 Å chlorite layers (from Shau *et al.*, 1990). Reproduced with kind permission of Springer Verlag, publisher of *Contributions to Mineralogy and Petrology*.

removed from the thin-section via attached washers, thinned in an ion mill and carbon coated. Specimens prepared with this technique are perfect to study both textural relationships between clay mineral packets (due to the preservation of the original texture of the sample) and detailed lattice-fringe images where smectitic interlayers do not collapse totally and maintain a spacing greater than 10 Å (Figure 8). This method has been successfully applied in many HRTEM observations (e.g., Bauluz *et al.*, 2000, 2002; Yan *et al.*, 2001; Tillick *et al.*, 2001; Arroyo *et al.*, 2007) with the consequent improvement in the quality of the TEM images. Using this technique, Bauluz *et al.* (2000) showed bidimensional images (Figure 8) with continuous cross fringes, which indicate coherent stacking relationships between smectite and illite layers. Such coherence demonstrates that I/S interstratified minerals are real mineral phases and not a simple physical juxtaposition of individual layers. Kim *et al.* (1995) recommended that LR White resin-impregnated I/S minerals are imaged under overfocus conditions.

***n*-ALKYLAMMONIUM TREATMENT.** Another technique to obtain a permanent expansion of smectitic interlayers is the intercalation of *n*-alkylammonium ions before the TEM study of the sample (Bell, 1986; Vali and Köster, 1986; Vali and Hesse, 1990). In this procedure ultramicrotomed thin-sections are prepared

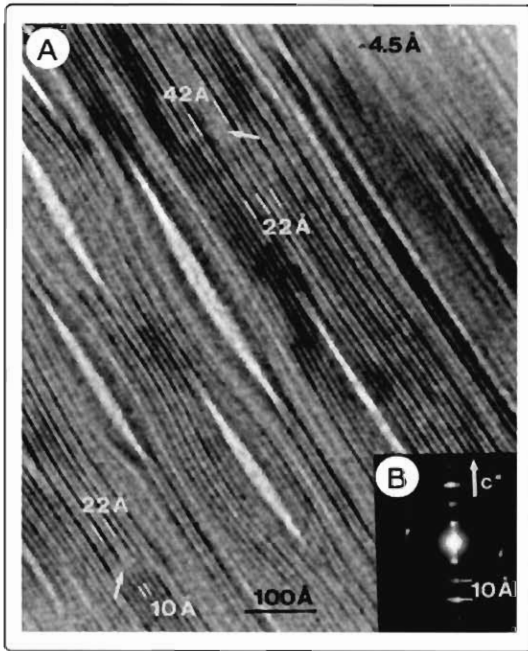


Figure 8. A: Lattice-fringe image of a sample treated with LR White resin showing I/S mixed-layer with non-collapsed smectitic interlayers (12 Å) and illitic interlayers (10 Å). In the top right part of the image, 4.5 Å cross-fringes continuous across 00l fringes, can be seen (bidimensional image). B: SAED pattern displaying highly ordered 00l reflections with a 10 Å spacing (modified from Bauluz *et al.*, 2000). Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

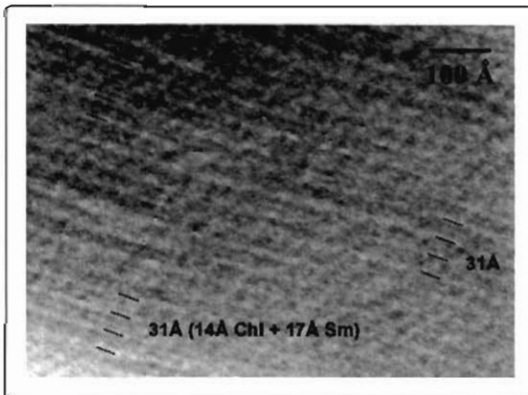


Figure 9. Lattice fringe image of chlorite/smectite treated with octylammonium ions, showing a 31 Å regular interstratification in a thick packet, where the smectitic interlayers expanded to 17 Å.

to obtain lattice-fringe images of interstratified clay minerals, mostly I/S but also C/S (Figure 9) (Arroyo *et al.*, 2006a). Due to the intercalation of n-alkylammonium ions (n_c : 6-18), expandable interlayers retain layer spacings between 10 and 30 Å. The degree of expansion depends on and increases with the length of the alkyl chain (n_c) and the layer charge of the expandable component. In the literature there are two ways to prepare the specimens to be studied by TEM. Some authors (Vali and Köster, 1986; Ghabru *et al.*, 1989; Malla *et al.*, 1993; Laird and Nater, 1993; Cetin and Huff, 1995) intercalate the n-alkylammonium ions previous to the preparation of the ultra-thin sections, following the procedure of Ruelicke and Köhler (1981). Others (Vali and Hesse, 1990, 1992; Vali *et al.*, 1994; Kelly Sears *et al.*, 1998; Shata *et al.*, 2003; Arroyo *et al.* 2006a, 2006b) chose to intercalate the n-alkylammonium ions in prepared ultra-thin sections to prevent problems related with the pre-expansion of the interlayers. Malla *et al.* (1993) showed that samples prepared with the first procedure had a highly disintegrated layer organization and spacings larger than expected from XRD studies. They concluded that these problems might be due to a pre-expansion and mild degradation produced by the n-alkylammonium ions before the preparation of the ultra-thin sections.

The alkylammonium technique allows an easy observation of the expandable layers in lattice-fringe images of mixed-layer clays thanks to the high expansion of the interlayer and can be used to study the expandability of even illite-rich I/S ($R \geq 3$) (Shata *et al.*, 2003). It can be also very helpful in the identification of differences of layer charge of the expandable interlayers of samples with heterogeneous clay mineralogy (Arroyo *et al.*, 2006a, 2006b). The main disadvantage of this technique is the loss of the original sample texture, precluding the study of textural relationships between clay mineral phases. Moreover, due to the large range of d-spacing values that expandable interlayers can have and to some problems that can appear with expandable illite, we strongly recommend a previous complete characterization by means of XRD with the n-alkylammonium method prior to the TEM study.

3. Analytical electron microscopy

3.1 Previous considerations

Chemical composition of interstratified minerals may be obtained with both TEM and SEM, although in the latter case the grain size needs to be sufficiently large to reach the limited SEM spatial resolution. Therefore, this section is devoted to the interpretation of results obtained using the two methods. Some considerations, specific for each method, are necessary.

In SEM, an EDX spectrum may be easily obtained both from a chip of rock or from a thin section. Both of them are able to give qualitative information about the elements present in the analysed grain; however only data obtained on thin sections are free from topographical effects and may be confidently used with a quantitative character. The popular tridimensional images obtained with secondary electrons from a chip of the studied material offer a wonderful picture of the textural relationships between minerals; a spectrum can be easily obtained and apparently quantified, but one should resist the temptation of giving any quantitative meaning to such chemical data. Microanalysis in SEM uses a very similar routine to Electron Microprobe, hence all the basic rules of this technique must be respected if one wants to obtain quantitative analyses, regarding preparation of samples (polished thin sections) and interpretation of spectra (ZAF correction).

In TEM, spatial resolution is obviously better. However, as this technique is usually employed on very fine-grained materials, contamination with other phases may also occur. The best way to avoid, or at least reduce, such problem is to check the analysed areas previously in electron diffraction mode to ensure that only one crystallographic pattern is present in the area. The best analytical results are obtained on individual clay particles dispersed on a carbon coated metallic grid (Cu is usually employed, but Au is recommend if Na will be analyzed).

An additional problem is alkaline cation loss (Van der Pluijm *et al.*, 1988). This problem may be present to a certain extent in SEM, but in TEM the problem becomes such that the real quantity of K and/or Na may be reduced even to a half, rendering the data useless. According to Van der Pluijm *et al.* (1988) the problem may be reduced using scanning transmission electron microscopy instead of a fixed beam; both beam size and scanning window should be as large as possible. This is one of the reasons why a clay particle on a grid in a horizontal position (c parameter parallel to the beam) produces much better results than in the usual vertical position (c parameter normal to the beam) in ion-milled samples. Also, it is important to obtain two different spectra, one at short time (15-30 seconds) for alkaline elements and the other at longer time (100-200 seconds) for the rest of the elements (Nieto *et al.*, 1996).

3.2 Interpretation of results from SEM and TEM

Chemical data need to be normalized to a mineral formula. Normalization is based on some known characteristics of the mineral as total number of cations, the sum of some cations or, more frequently, number of oxygen atoms (equivalent to the number of positive charges). When the formulas of the components of interstratified minerals have similar characteristics, due to a similar basic structure (e.g., I/S), this normalization is not more problematic than for the basic components. However, if the components correspond to different structural models (e.g., C/S or kaolinite/smectite) it is impossible to have a rational normalization criterion unless a given proportion between components is assumed. In most cases this proportion is unknown. In such cases the use of ratios between elements rather than absolute values may be helpful. As an example, do Campo and Nieto (2005) could perfectly distinguish the combination of chlorite with three other components and identify chlorite as the major component (Figure 10), using data both from SEM and TEM. A rational selection of chemical ratios is important for a better discrimination.

The above example reveals that identification of the components of mixed-layer minerals is possible in most cases. Nevertheless, chemical composition only cannot be considered a powerful tool to determine the proportion between components, or, even less, the type of stacking order of the interstratified layers. Arroyo (2010) obtained a set of high-quality microanalyses for different I/S phases. The plot of data in an MR3-2R3-3R2 diagram (Velde, 1985) (Figure 11) showed clear different chemical ranges between R1 I/S, R3 I/S and illite, but also significant overlapping between them. In conclusion, the interpretation of chemical data should be supported in all cases by a detailed XRD study. If more than one kind of layer stacking order coexist within the samples, as is the most frequent case, ordering identification for individual grains is not always guaranteed.

A significant contribution of microanalysis to the knowledge of chemical composi-

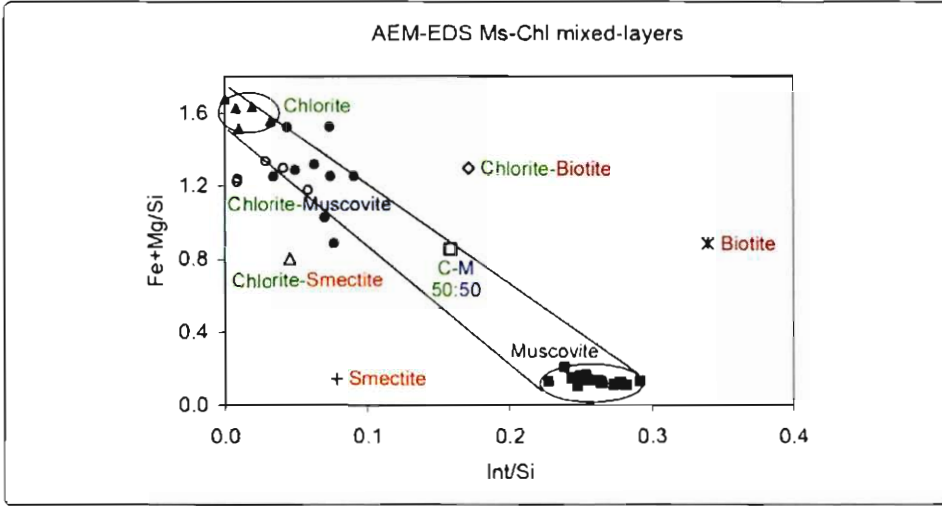


Figure 10. Chemical variations of muscovite, chlorite and mixed-layer muscovite-chlorite (AEM - solid circles and SEM - open circles) on the $(\text{Na} + \text{K} + \text{Ca})/\text{Si}$ vs. $\text{Fe} + \text{Mg}/\text{Si}$ diagram. Representative analyses of biotite and smectite, and 0.5/0.5 mixtures of muscovite-chlorite (square), chlorite-smectite (triangle) and biotite-chlorite (diamond) are included as a reference (modified from do Campo and Nicro, 2005). Reproduced with kind permission of the Mineralogical Society, publisher of *Clay Minerals*.

tion of interstratified minerals is the study of heterogeneity between grains. All analytical methods based on the analysis of the whole sample or granulometric fractions are unable to recognize differences between individual grains. Cuadros *et al.* (2009) used TEM to complete previous studies on the transformation process from smectite to kaolinite. Even if a clear relationship between kaolinite/smectite proportion and chemical composition had been established by X-ray fluorescence, AEM analyses of individual particles showed results perfectly compatible with the global compositions of the samples, but with very significant differences within each sample. Differences among particles were coherent with different proportions of smectite and kaolinite, indicating that the chemical variation found is mainly the consequence of different degrees of kaolinitization. Such result is coherent with the previous model (Dudek *et al.*, 2006) describing progressive destruction of one of the tetrahedral sheets; the different particles are affected by different degrees of transformation, which produces variable chemical compositions.

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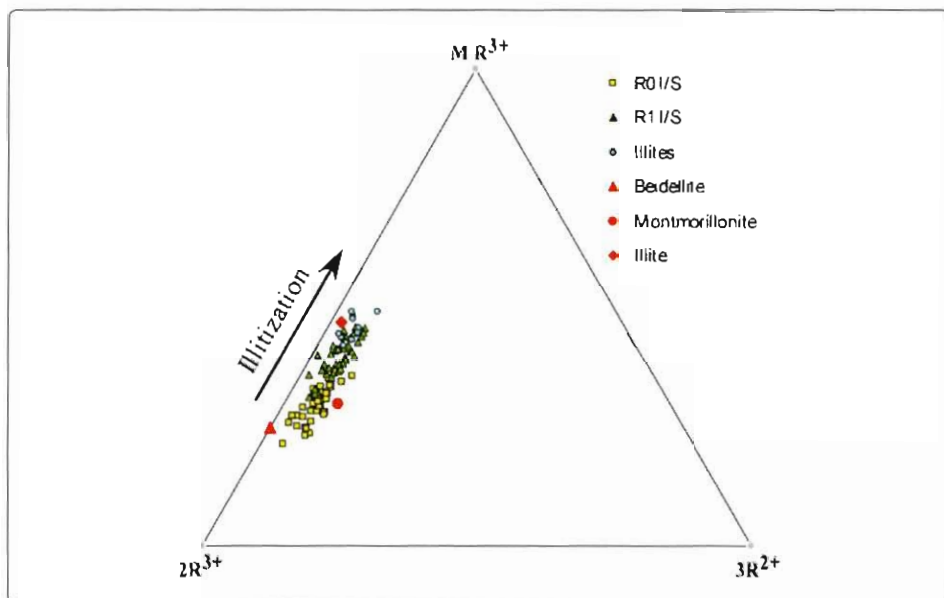


Figure 11. AEM chemical data of the smectite illitization process represented in an MR^{3+} - $2R^{3+}$ - $3R^{2+}$ diagram (Velde, 1985). MR^{3+} : $(Na^+ + K^+ + 2Ca^{2+})$, $2R^{3+}$: $(Al^{3+} + Fe^{3+} - MR^{3+})/2$, $3R^{2+}$: $(Fe^{2+} + Mg^{2+} + Mn^{2+})/3$. Symbols in red indicate theoretical compositions of discrete phases. Modified from Arroyo (2010).

References

- Amouric, M. and Olives, J. (1998) Transformation mechanisms and interstratification in conversion of smectite to kaolinite: an HRTEM study. *Clays and Clay Minerals*, **46**, 521-527.
- Arroyo, X., Aróstegui, J., and Nieto, F. (2006a) Characterization of the expandable component of mixed-layer chlorite/smectite by n-alkylammonium methods. A XRD-HRTEM-AEM study. *Fourth Mediterranean Clay Meeting*. Ankara, Turkey.
- Arroyo, X., Aróstegui, J., and Nieto, F. (2006b) Estudio comparativo mediante XRD-HRTEM-AEM del componente expansible de interstratificados I/S tratados con iones n-alkilamonio. *Macla*, **6**, 69-71.
- Arroyo, X., Aróstegui, J., and Nieto, F. (2007) TEM textural study of the illite/smectite evolution in marls from the Basque-Cantabrian Basin, Spain: Transition from R0 to R1 diagenetic stages of smectite illitization. *Seminarios de la SEM*, **3** (*Diagenesis and low-temperature metamorphism. Theory, methods and regional aspects*), 101.
- Arroyo, X. (2010) Evolución de las esmectitas e interstratificados I/S en la serie carbonatada del Cretácico Superior del Bloque Alavés. Implicaciones sobre el mecanismo de illitización durante la diagénesis. Ph.D. dissertation. Universidad del País Vasco. 252 pp.
- Bauluz, B., Peacor, D.R., and Gonzalez Lopez, J.M. (2000) Transmission electron microscopy study of illitization in pelites from the Iberian Range, Spain: layer-by-layer replacement? *Clays and Clay Minerals*, **48**, 374-384.
- Bauluz, B., Peacor, D.R., and Ylagan, R.F. (2002) Transmission electron microscopy study of smectite illitization during hydrothermal alteration of a rhyolitic hyaloclastite from Ponza, Italy. *Clays and Clay Minerals*, **50**, 157-173.

- Bell, T.E. (1986) Microstructure in mixed-layer illite/smectite and its relationship to the reaction of smectite to illite. *Clays and Clay Minerals*, **34**, 146-154.
- Cetin, K. and Huff, W.D. (1995) Characterization of untreated and alkylammonium ion exchanged illite/smectite by high resolution transmission electron microscopy. *Clays and Clay Minerals*, **43**, 337-345.
- Cuadros, J., Nieto, F., and Dudek, T. (2009) Crystal-chemical changes of kaolinite-smectite mixed-layer with progressive kaolinization as investigated by TEM-AEM and HRTEM. *Clays and Clay Minerals*, **57**, 742-750.
- do Campo, M. and Nieto, F. (2005) Origin of mixed-layered (R1) muscovite-chlorite in an anchizonal slate from Puncoviscana Formation (Salta Province, Argentina). *Clay Minerals*, **40**, 317-332.
- Dudek, T., Cuadros, J., and Fiore, S. (2006) Interstratified kaolinite-smectite: Nature of the layers and mechanism of smectite kaolinization. *American Mineralogist*, **91**, 159-170.
- Ghabru, S.K., Mermut, A.R., and Arnaud R.J.Sr. (1989) Layer-charge and cation-exchange characteristics of vermiculite (weathered biotite) isolated from a gray Luvisol in northeastern Saskatchewan. *Clays and Clay Minerals*, **37**, 164-172.
- Guthrie, G.D. and Veblen, D.R. (1989a) High-resolution transmission electron microscopy of mixed-layer illite/smectite: Computer simulation. *Clays and Clay Minerals*, **37**, 1-11.
- Guthrie, G.D. and Veblen, D.R. (1989b) High-resolution transmission electron microscopy applied to clay minerals. In *Spectroscopic Characterization of Minerals and Their Surfaces*, L.M. Coyne, S.W.S. McKeever, and D.E. Blake, eds., Symposia Series 415, American Chemical Society, Washington, D.C., 75-93.
- Guthrie, G.D. and Veblen, D.R. (1990) Interpreting one-dimensional high-resolution transmission electron micrographs of sheet silicates by computer simulation. *American Mineralogist*, **75**, 276-288.
- Kelly Sears, S., Hesse, R., and Vali, H. (1998) Significance of n-alkylammonium exchange in the study of 2:1 clay-mineral diagenesis, Mackenzie Delta-Beaufort Sea region, Arctic Canada. *The Canadian Mineralogist*, **36**, 1485-1506.
- Kim, J.-W., Peacor, D.R., Tessier, D., and Elsass, F. (1995) A technique for maintaining texture and permanent expansion of smectite interlayers for TEM observations. *Clays and Clay Minerals*, **43**, 51-57.
- Laird, D.A. and Nater, E.A. (1993) Nature of the illitic phase associated with randomly interstratified smectite/illite in soils. *Clays and Clay Minerals*, **41**, 280-287.
- Malla, P.B., Robert, M., Douglas, L.A., Tessier, D., and Komarneni, S. (1993) Charge heterogeneity and nanostructure of 2:1 layer silicates by high-resolution transmission electron microscopy. *Clays and Clay Minerals*, **41**, 412-422.
- Murakami, T., Inoue, A., Lanson, B., Meunier, A., and Beaufort, D. (2005) Illite-smectite mixed-layer minerals in hydrothermal alteration of volcanic rocks: II. One-dimensional HRTEM structure-images and formation mechanism. *Clays and Clay Minerals*, **53**, 440-451.
- Nieto, F. (2008) TEM in Geology. Basics and applications. In I. Subias, and B. Bauluz, Eds. *Instrumental techniques applied to Mineralogy and Geochemistry*, **5**, Sociedad Española de Mineralogía, Zaragoza. 21-42.
- Nieto, F., Ortega-Huertas, M., Peacor, D.R., and Aróstegui, J. (1996) Evolution of illite/smectite from early diagenesis through incipient metamorphism in sediments of the Basque-Cantabrian Basin. *Clays and Clay Minerals*, **44**, 304-323.
- Rühlicke, G. and Köhler, E.E. (1981) A simplified procedure for determining layer charge by the n-alkylammonium method. *Clay Minerals*, **16**, 305-307.

- Shata, S., Hesse, R., Martin, R.F., and Vali, H. (2003) Expandability of anchizonal illite and chlorite: Significance for crystallinity development in the transition from diagenesis to metamorphism. *American Mineralogist*, **88**, 748-762
- Shau, Y.-H., Peacor, D.R., and Essene, E.J. (1990) Corrensite and mixed-layer chlorite/corrensite in metabasalt from northern Taiwan: TEM/AEM, EPMA, XRD, and optical studies. *Contributions to Mineralogy and Petrology*, **105**, 123-142.
- Spence, J.C.H. (1981) Experimental high resolution electron microscopy. Clarendon Press, Oxford, 307 pp.
- Stucki, J.W. and Tessier, D. (1991) Effects of iron oxidation state on the texture and structural order of Na-nontronite gels. *Clays and Clay Minerals*, **39**, 137-143.
- Tillick, D.A., Peacor, D.R., and Mauk, J.L. (2001) Genesis of dioctahedral phyllosilicates during hydrothermal alteration of volcanic rocks: I. The Golden Cross epithermal deposit, New Zealand. *Clays and Clay Minerals*, **49**, 126-140.
- Vali, H. and Hesse, R. (1990) Alkylammonium ion treatment of clay minerals in ultrathin section: A new method for HRTEM examination of expandable layers. *American Mineralogist*, **75**, 1443-1446.
- Vali, H. and Hesse, R. (1992) Identification of vermiculite by transmission electron microscopy (TEM) and XRD diffraction. *Clay Minerals*, **27**, 185-192.
- Vali, H. and Köster, H.M. (1986) Expanding behaviour, structural disorder, regular and random irregular interstratification of 2:1 layer-silicates studied by high-resolution images of transmission electron microscopy. *Clay Minerals*, **21**, 827-859.
- Vali, H., Hesse, R., and Martin, R.F. (1994) A TEM-based definition of 2:1 layer silicates and their interstratified constituents. *American Mineralogist*, **79**, 644-653.
- Van der Pluijm, B.A., Lee, J.H., and Peacor, D.R. (1988) Analytical electron microscopy and the problem of potassium diffusion. *Clays and Clay Minerals*, **36**, 498-504.
- Velde, B. (1985) Clay Minerals: a Physico-Chemical Explanation of their Occurrence. Elsevier, Amsterdam & New York.
- Yan, Y., Tillick, D.A., Peacor, D.R., and Simmons, S.F. (2001) Genesis of dioctahedral phyllosilicates during hydrothermal alteration of volcanic rocks: II. The Broadlands-Ohaaki hydrothermal system, New Zealand. *Clays and Clay Minerals*, **49**, 141-155.