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X-RAY DIFFRACTION PARAMETERS IN VERY LOW-GRADE METAMORPHISM SEEN IN THE "LIGHT" OF TEM

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ABSTRACT

Methods based on X-ray diffraction commonly used to decipher diagenetic / low-grade metamorphic conditions are revised and evaluated according to our current knowledge of related geological processes obtained via transmission electron microscopy. A lack of evident qualitative changes in phyllosilicates, including their mineral chemistry, from deep diagenetic to low-epizone conditions explains the scarcity of valid grade criteria. Throughout this range of diagenetic-metamorphic conditions a progressive increase in the crystalline domain size together with a decrease in the number of defects are the only significant changes to be observed. Therefore indices related to crystallinity still remain the most successful methods based on the crystal-chemical characteristics of phyllosilicates.

Keywords: Crystallinity indices, polytypes, basal spacings, chemical composition, phillosilicates, low-grade metamorphism, TEM.

INTRODUCTION

The diagenetic and metamorphic processes that take place at temperatures lower than those of greenschist facies give rise to rocks characterised by a lack of chemical and textural equilibrium and minerals with a very small grain size, forming intergrowths at such a small scale that they cannot be recognized under light microscopy. In addition, in clastic lithologies there is commonly an absence of changes in the mineral paragenesis, making it difficult or impossible to apply the criteria normally used for higher grades, based on the petrogenetic grid of mineral association equilibria or on true geothermometers.

For many years, geologists working on rocks formed under such conditions have therefore searched for alternative criteria. In many cases these criteria are based on the crystal-chemical aspects of phyllosilicates, such as the Kübler Index (KI) or the so-called b_0 parameter, more appropriately known nowadays as the *b* parameter. Due precisely to their defective and metastable nature, the phyllosilicates of such rocks have been a promising field of study with regard to the phenomena englobed under the concept of Real Structures.

Nevertheless, the very characteristics that make them interesting pose the main limitation to performing a crystal-chemical study using the most powerful techniques, such as single-crystal X-ray diffraction or the different types of spectroscopy, which require monomineral samples. The most widely used tool has therefore traditionally been powder diffraction and, in recent years, transmission electron microscopy (TEM). The use of TEM has allowed the criteria developed by powder diffraction to be confirmed, qualified or completed.

EVOLUTION OF A CLAY MATERIAL WITH AN INCREASE IN THE DIAGENETIC-METAMORPHIC GRADE

The literature dealing with the mineralogy of burial diagenesis has traditionally been dominated by the formation of illite from smectite through mixed-layers. The necessary simplification of the scientific problems involved in this study has too often made researchers overlook the fact that other materials present in sediments, such as kaolinites, detritic micas and chlorites, carbonates and interstitial fluids, also play an essential role in rock genesis. Nonetheless, it is now well known that newly formed illites inherit many textural and chemical characteristics from the original smectites during the course of their evolution in a range of temperatures of about 200 ºC (Fig. 1). This circumstance can be accounted for due to Ostwald's rule, which governs most low-temperature mineral processes (Morse and Casey, 1988). According to this rule, under low-temperature conditions, systems evolve towards phases similar to the original ones, so that the driving force of the reaction is minimal. Evidently, such phases are metastable and they slowly approach equilibrium through successive processes termed Ostwald steps.

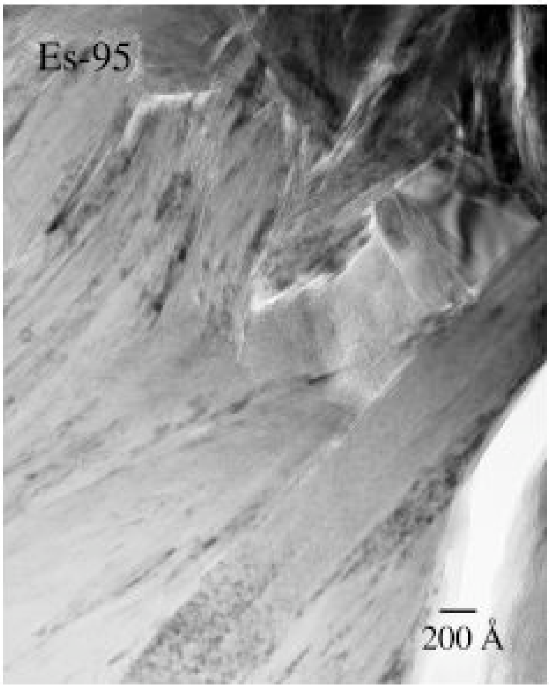

Figure 1. Lattice-fringe image showing arrays of wavy, discontinuous and anastomosing packets of illite.

In the smectite→muscovite evolution, mixed-layers are very obvious steps. However, it should not be forgotten that, after the disappearance of the last smectite layers and up until the formation of a true metamorphic mica, there is still a long temperature pathway in which illite or other phengitic and muscovitic micas, with unequilibrated compositions, are new intermediate steps.

Data obtained by lattice fringe images over the last two decades have revealed that the evolution through the anchizone and start of the epizone occurs with a gradual decrease in the defective nature of the rock-forming phyllosilicates and a progressive increase in their grain size (Merriman and Peacor, 1999). Notwithstanding, this evolution lacks qualitative changes from the disappearance of the last smectite layers, during diagenesis, up until the formation of a "true" metamorphic rock in deep epizone. The term "true" metamorphic rock is used here to designate a rock formed by well-differentiated phyllosilicate packets that are lacking in defects (Fig. 2), orientated parallel to each other, have a main metamorphic cleavage and that normally reach a size recognisable even under light microscopy.

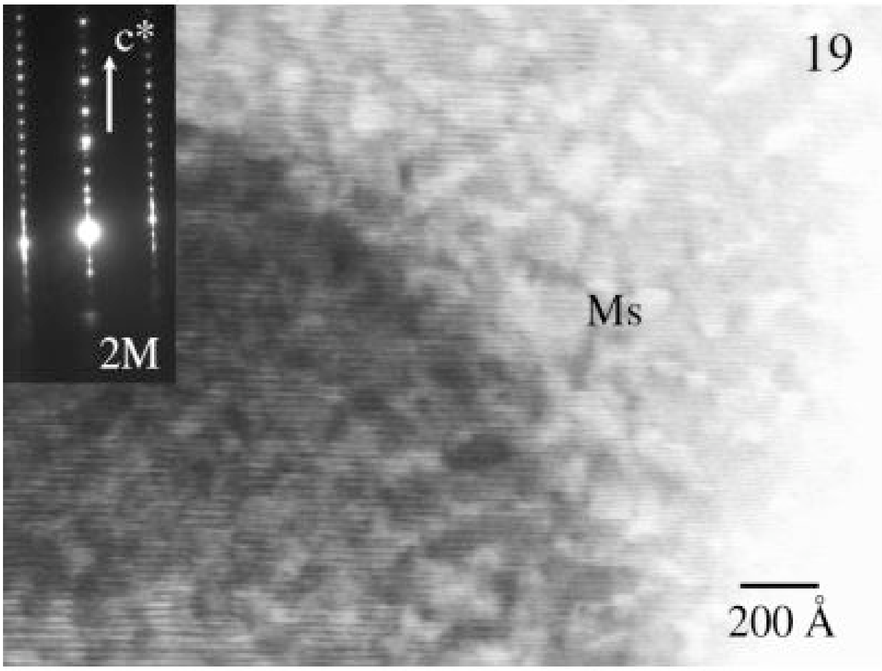

Figure 2. TEM image of 2M muscovite crystal with a thickness of over 1500 Å. This perfectly crystalline texture is characteristic of greenschist facies metamorphic rocks.

From late diagenesis to low epizone conditions, the phyllosilicate matrix of clastic rocks is formed of straight packets of the rock-forming phyllosilicates, separated by low-angle boundaries, with the few defects present primarily being edge dislocations (Fig. 3). Throughout this transition, the most apparent texture is unchanged (Fig. 4) and, if the quantitative aspects such as the number of defects and packet size are not taken into account, the lattice-fringe images are indistinguishable (López Múnguira and Nieto, 2000). Moreover, the chemical composition of dioctahedral micas is extremely variable at the sample level, combining several exchange vectors, among which the illitic substitution is significant (Fig. 5). These wide compositional ranges do not change among the samples representative of the different grades. There is no homogenisation of the composition, with disappearance of the illitic exchange vector, until metamorphism, primarily by the effect of tectonic stress, is capable of developing the afore-mentioned "true" metamorphic rock (Abad *et al.*, 2003b).

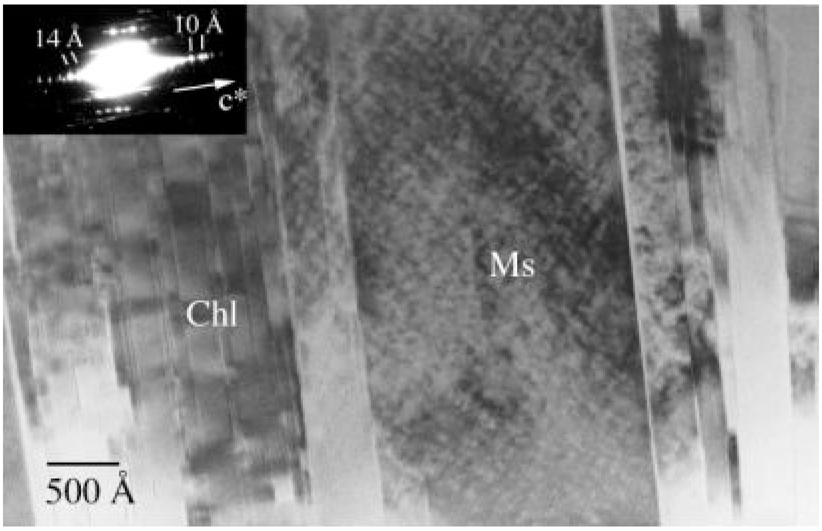

Figure 3. Lattice-fringe image corresponding to an anchizonal sample with chlorite and muscovite packets.

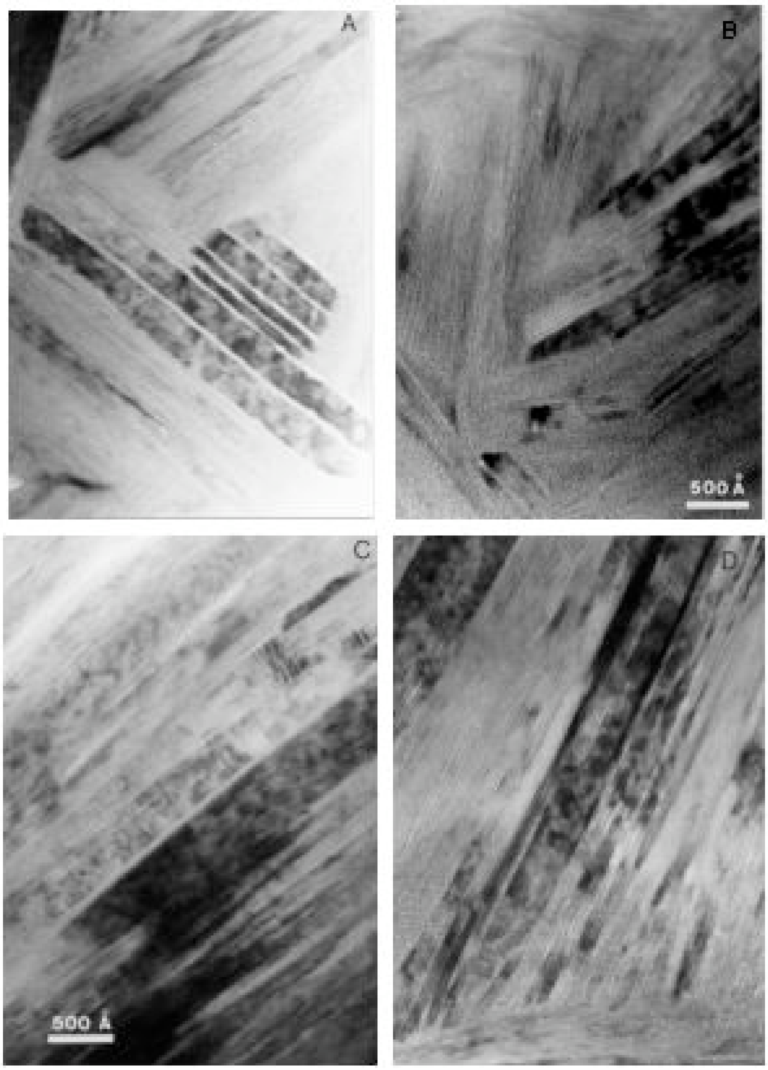

Figure 4. TEM images belonging to the Alconera Unit. The images, corresponding to different grades (A: diagenesis; B-C: anchizone; D: epizone) show the lack of qualitative differences among them.

CRYSTAL-CHEMICAL CONSEQUENCES

Below, the various crystal-chemical parameters and criteria normally used are interpreted in the light of the model outlined in the section above.

Basal spacing of micas and chlorites

These parameters depend on the chemical composition of each phyllosilicate. Some chemical parameters are more decisive than others, such as the degree of paragonitization and phengitization in micas (Guidotti *et al.*, 1992) or the Al content in chlorites (Rausell Colom *et al.*, 1991). Since powder diffractometry measurements can be routinely performed, there is a long tradition of using them for the diagenesis-metamorphism transition, although it has been scarcely successful in terms of predicting the metamorphic grade. Until very recently it was unknown whether these parameters were unable to reflect chemical changes or these changes simply did not exist. Modern microanalytical techniques using back-scattered imaging in SEM and transmission electron microscopy (AEM) have revealed that the basal spacing of each sample is an average of those corresponding to many crystals with markedly different chemical compositions covering ranges that do not vary with the metamorphic grade (Fig. 5) (López Múnguira and Nieto, 2000; Abad *et al.*, 2003b).

Other characteristics based on the chlorite composition

The basal spacing, together with the *b* parameter and the basal intensity ratios, allows a good approximation to the chemical composition of chlorite (Nieto, 1997; Shata and Hesse, 1998). Nonetheless, these compositional data based on powder diffraction have not been successful at predicting the metamorphic grade either. However, the so-called chlorite geothermometry based on EMPA data has become very popular since it was first proposed by Cathelineau in 1988. De Caritat *et al.* (1993) strongly questioned the coherence of the data obtained by the various chlorite geothermometers available up to that time. Essene and Peacor (1995) justified the compositional differences of chlorites as being due to the different degrees of contamination by dioctahedral phyllosilicate layers according to the metamorphic grade. López Múnguira *et al.* (2002) have claimed that the *genuine composition* of chlorites in basic rocks, that is, when the contamination by smectite layers or other phyllosilicates is completely absent, exclusively depends on the Mg contents of the rock, which is in agreement with the proposal by Xie *et al.* (1997). Moreover, if the system is richer in Fe than in Mg, the smectite layers may be absent in the diagenetic and metamorphic evolution of the chlorite. Therefore, the use of the chlorite composition with the aim of using it as a geothermometer, based on the indirect effect of the proportion of smectite layers, should be approached very cautiously.

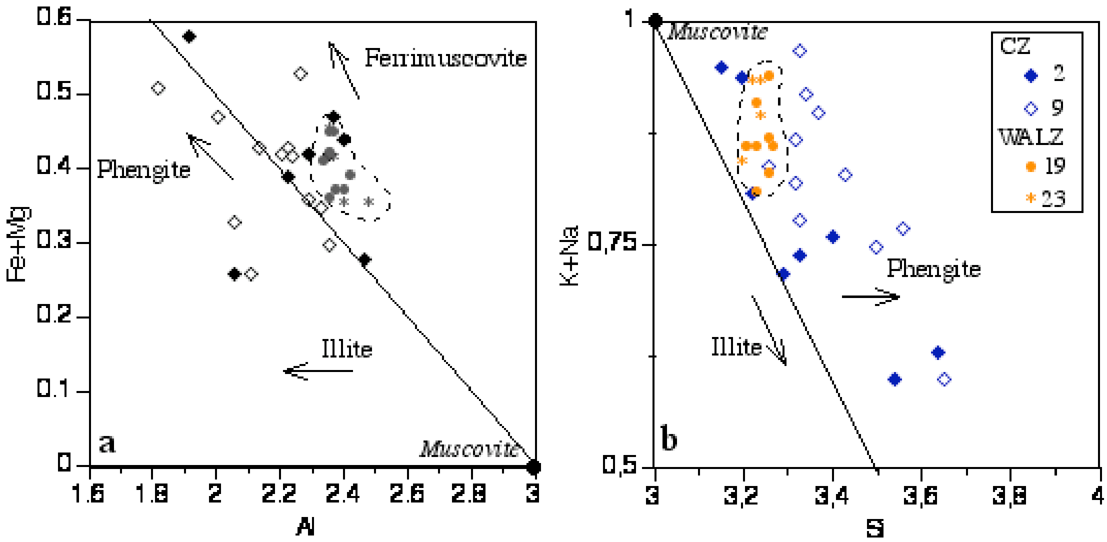

Figure 5. Diagrams showing the chemical composition of micas of the samples from the Narcea Antiform. The grey-orange symbols represent the WALZ samples (internal zone) and the black-blue symbols the CZ samples (external zone), the former with a higher metamorphic grade (modified from Abad *et al.*, 2003b).

The b parameter of white mica. Differences in accordance to pressure

The lateral dimension of the unit-cell of dioctahedral micas is primarily dependent on the degree of phengitization, although with the notable additional influence of the ferrimuscovitic vector (Guidotti *et al.*, 1989). Since, in its turn, the degree of phengitization depends on the pressure (Massonne and Schreyer, 1987), this parameter, known as b_0, has been widely used as a semiquantitative geobarometer in greenschist facies (Guidotti and Sassi, 1986).

Merriman and Frey (1999) have emphasized the importance of evaluating the gradient when identifying the geotectonic context in which the genesis of very low-grade rocks takes place, as compressive and extensional regimes can thus be differentiated. It is therefore primordial to define which tools are valid for evaluating pressure in very low-grade rocks. Abad *et al.* (2003a) have observed an excellent correlation between the *b* parameter and the phengitic content of micas in the Talas Ala Tau region (Central Asia). These two parameters can therefore be used to obtain a reliable estimate of the pressure of the metamorphic process.

For many years, studies on sequences affected by incipient metamorphism have focused on regimes with intermediate-pressure regional metamorphism. When Kisch (1987) correlated the distinct parameters used in evaluating incipient metamorphism, he noted that this correlation was based on intermediate gradients and was therefore not applicable to high- or low-pressure regimes.

Based on their own data on the Puncoviscan Formation (Argentina) and data from the literature on the Franciscan Formation (California), the Verrucano (Italy) and the Alpujarride Complex (Spain), do Campo and Nieto (2004) have proposed that the Kübler Index in rocks that have undergone a high-pressure stage can present high anchizone-low epizone data that are incompatible with other criteria indicating higher temperatures. This circumstance is due to the fact that the high-pressure stage generates micas with a smaller grain size than those produced in the high-temperature stage and these small grains are, obviously, the primary component of the <2 μm fraction.

Regarding the opposite environment, contact metamorphism, Abad (2002) has presented data revealing that the degree of recrystallization in rocks affected by contact metamorphism can be notably lower than that of rocks produced at equivalent temperatures in a regime of regional metamorphism.

Chlorite and mica polytypes

The variable presence of the diverse polytypes of phyllosilicates is another criterion traditionally used to assign metamorphic grade in incipient metamorphism. TEM allows the polytype to be determined *in situ* by the use of selected electron diffraction patterns (Figs. 6-7).

The data obtained clearly indicate that the 2M polytype is the most abundant in dioctahedral micas in rocks affected by very low-grade metamorphism (Fig. 6a). It can be accompanied by variable amounts of the $1M_d$ polytype, decreasing with the grade (Fig. 6b). The $1M_1$ polytype is scarce and does not represent an intermediate stage between the 2M and the $1M_d$ polytypes. In addition, complex multilayer sequences have been described (Fig. 7), which can be interpreted in terms of high-order polytypes in micas as well as in chlorites (López Múnguira and Nieto, 2000; do Campo and Nieto, 2004; Abad *et al.*, 2002, 2003b). However, the presence of a given polytype bears no relationship to specific textural positions or to particular compositions. Dong and Peacor (1996) recognized short-range order in the stacking sequences, concluding that the $2M_1$ polytype is the most stable one in all conditions. These authors even suggested that the identification of the $1M_d$ polytype could be the result of misorientation of small packets, characteristic of very low-grade rocks.

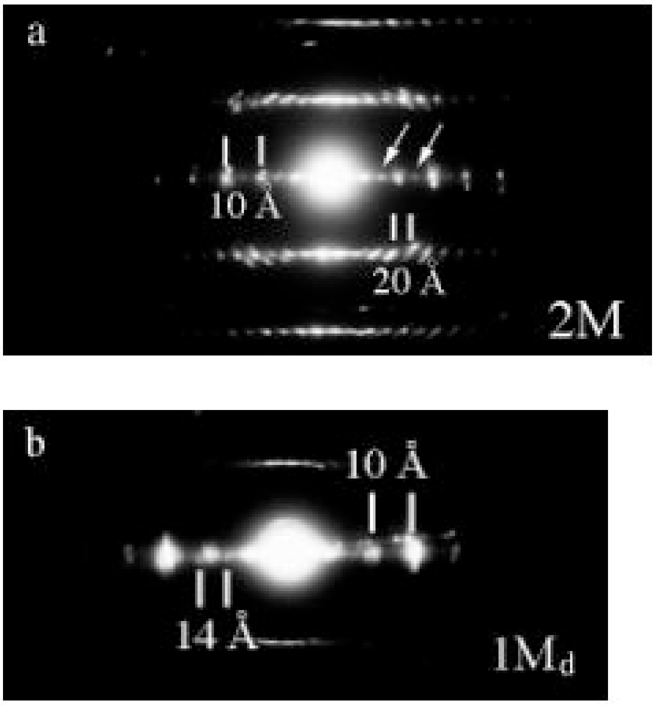

Figure 6. SAED corresponding to the most common polytypes in micas of diagenesis and very low-grade metamorphism: (a) 2M polytype, the general (non-basal) reflections indicate 20 Å periodicity. In some cases, low intensity "forbidden" spots due to dynamic effects (see arrows) allow this periodicity to be detected in the basal reflections as well; (b) $1M_d$ polytype from mica. The 14 Å periodicity corresponds to chlorites. This two phyllosilicates frequently coexist in these environments.

Sassi *et al.* (1994) related the 3T polytype in dioctahedral micas to high-pressure conditions. Likewise, Jullien *et al.* (1996) found a relationship between the polytype range and the pressure in Li chlorites. Nonetheless, these relationships have also been seriously questioned (Mata *et al.*, 1998) –while some terranes appear to confirm some sort of relationship between polytypes and pressure (Puncoviscana Formation, do Campo and Nieto, 2004), others clearly do not support such a conclusion (Narcea Antiform, Abad *et al.*, 2003b). The possible relationship between polytypes and pressure is, therefore, still open to debate.

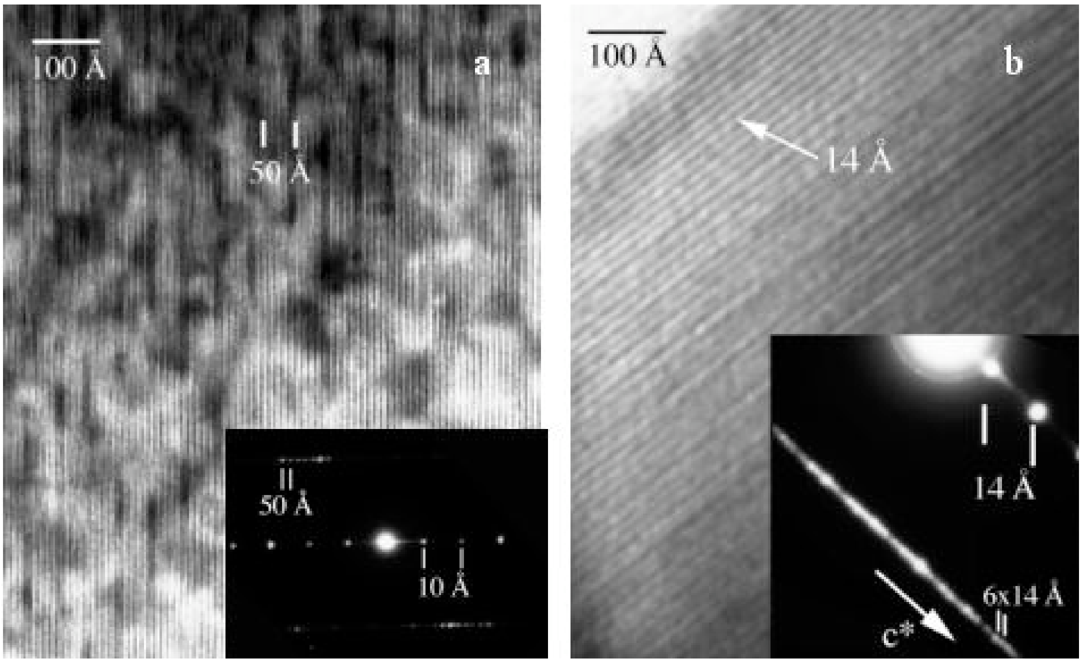

Figure 7. Examples of high-order stacking sequences: a) TEM image and electron diffraction of mica showing a 5 layer stacking sequence; b) Complex multilayer sequences in chlorite. The 6 layer superperiodicity is obvious only in electron diffraction.

The size of the crystalline domain

Since the seminal paper by Merriman *et al.* (1990), numerous studies have centred on the physical significance of the Kübler Index (KI) by comparing it with lattice-fringe images. Although they differ in details on questions such as the means of defining what a coherent domain in a lattice-fringe image is, all the literature agrees that the KI quite faithfully reflects the evolution of the thickness of the phyllosilicate packets (see, for instance, Abad *et al.*, 2001). Merriman and Peacor (1999) have summarised current knowledge on this relationship (Fig. 8), indicating that the sizes predicted by Scherrer's equation are very close to those found in samples. In addition, all the works that have performed a statistical study of the packet thickness coincide in that there is a very wide dispersion at the sample level; therefore, the size detected by X-ray diffraction data can be considered as a statistical indicator of the wide range of values found in each sample.

Given these conditions, attempts to obtain a more precise evaluation of the sizes based on methods of peak profile analysis have not significantly improved on the simple data from the KI. The differences in precision are well below the variation ranges at the sample level and are, in addition, strongly affected by experimental conditions.

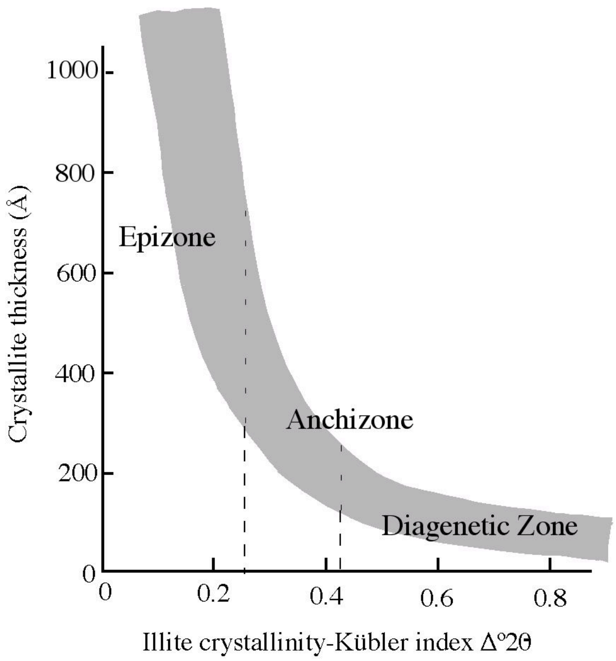

Figure 8. Transmision electron microscope (TEM) measured illite-muscovite crystallite thickness along c* plotted against the Kübler Index. Grey bands include various relationships based on different authors and ways of defining a coherent domain size in lattice-fringe images. (Modified from Merriman and Peacor, 1999).

CURRENT STATE OF KNOWLEDGE AND FUTURE DEVELOPMENT

The numerous TEM studies carried out in the 80s and 90s sought to fill the void regarding textural and mineral chemistry aspects due to the defective nature of very low-grade rocks. There is no doubt that the greatest successes have been related to the recognition and identification of diverse phases of mineral genesis throughout a given geological evolution. This aspect was predictable, but impossible to approach via powder diffraction. Currently, the existence of retrograde processes (Nieto *et al.*, 1994) and the co-existence of minerals growing under diverse conditions of pressure and temperature in a clockwise PTt evolution are well-established facts (Dalla Torre *et al.*, 1996). These can now be included with the co-existence of neoformed and detritic phases, which had been successfully predicted by traditional diffractometry.

Nevertheless, the confirmation of the lack of qualitative changes in a wide range of temperatures beginning before and ending after the anchizone boundaries has made it impossible to provide metamorphic grade criteria that are truly new with respect to the traditional ones based on X-ray diffraction. Throughout this range, phyllosilicates are very far from chemical equilibrium and, moreover, the compositional ranges they define can be entirely equivalent for a late diagenesis and low epizone sample, for instance. The only features differentiating the samples corresponding to the distinct grades are quantitative, related to the packet size and number of defects.

In the light of the TEM data now available, it is not surprising to note the remarkably good performance of the Kübler Index, particularly once the initial methodological problems were overcome by means of the proposal for standardization by Warr and Rice (1994). Notwithstanding, we should not forget the warning by Kisch in 1987 against automatically expanding its use to terranes with pressure gradients other than intermediate, now updated for high pressure (do Campo and Nieto, 2004) and contact metamorphism (Abad, 2002) rocks.

After the qualitative leap provided by the introduction of TEM to diagenesis and very low-grade metamorphism studies in the mid-80s, the next frontier is to carry out true crystal-chemical research on the mineral phases present in very low-grade rocks, similar to that normally used in higher grades for instance for amphiboles and pyroxenes. Given the impossibility of using the methods successfully applied to those grades, the most promising tools are Electron Crystallography (Dorset *et al.*, 1997), as an alternative to single-crystal methods, or EELS (Livi *et al.*, 2001), as an alternative to spectroscopic methods.

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