Clay-slate evolution. Onset of metamorphism

Fernando Nieto and Isabel Abad

Clay-slate evolution. Onset of metamorphism

Fernando Nieto[1], Isabel Abad[2]

[1]Departamento de Mineralogía y Petrología and IACT, Universidad de Granada-CSIC, Campus Fuentenueva s/n, Granada, 18002, Spain
(nieto@ugr.es)
[2]Departamento de Geología, Universidad de Jaén, Campus Las Lagunillas, Jaén, 23071, Spain

Introduction

A metamorphic rock is generally formed of a few minerals that are determined by the phase rule; these minerals are homogeneous in composition or nearly so, depending on pressure/temperature conditions. These rocks present chemical equilibrium and ordered textural characteristics, which respond to genetic processes. By contrast, a detrital sediment is an extremely heterogeneous material that presents many mineral types, each of which is heterogeneous itself. Neoformed and transformed phases begin to appear in addition to the detrital ones and, from a textural point of view, they are completely unordered.

The evolution from the former to the latter is well known and evident in a plethora of geological environments, but the opposite is a complex process poorly studied until recently and not yet entirely understood. This circumstance is due in part to its character as a transitional field, with different aims between sedimentologists and metamorphic petrologists, which has originated methodological problems. The objectives are more similar to those of metamorphic petrology, but the characteristic samples of this transitional field, close to those of clay materials, preclude the use of traditional methods such as optical microscopy and chemical analysis performed with the electron microprobe. This borderline character produced at first considerable nomenclatural confusion, which was not clarified until the works and meetings promoted by the IGCP 294 Project and the publication of the two perfectly complementary editions of Frey´s book (FREY, 1987 and FREY & ROBINSON, 1999). In any event, certain remnants of these "dark ages" of nomenclatural confusion can still be noted in non-specialized literature.

FREY (1987) emphasized a continuous transition between diagenesis and metamorphism, which in different contexts have been termed incipient metamorphism, very low-grade metamorphism, sub-greenschist facies, and so on. Such a bridge was absolutely necessary at that time and contributed to the comprehension of this field overall. Nevertheless, similarly to the manner in which the concept of relative space would not have been possible without the prior definition of absolute space, the use of the concept of a continuous transition between diagenesis and metamorphism has brought us at present to the consideration of significant genetic differences between burial diagenesis and metamorphism, related with the role of deformation in the genesis of a true metamorphic rock. In other words, currently it is finally known that a metamorphic mica can only be produced by metamorphism.

From diagenesis to metamorphism, clays evolve towards slates with a progressive substitution of primary bedding by tectonic foliation. Some of the more significant and widely investigated questions to explain the process have been schistosity genesis, mineral reactions, the change from heterogeneity to homogeneity, and the mechanisms for mineral transformations.

Evolution from heterogeneity to homogeneity

The decrease in the number of minerals and the evolution towards the homogeneous composition of a given mineral have been known facts since the first microchemical studies in the low-grade field (e.g. WYBRECHT et al., 1985). This process can be accounted for due to Ostwald's rule, which governs most low-temperature mineral processes (MORSE & CASEY, 1988). Mineral processes for rocks formed at or above temperatures corresponding to the greenschist facies are governed by the Phase's rule, in which the driving force is enough and reactions happen in one step from the reactant to the product. By contrast, when systems evolve according to Ostwald's rule, they change towards phases that are more chemically and structurally similar to the original ones, so that the driving force of the reaction is minimal. Consequently, such phases are metastable and they slowly approach the final product and equilibrium state through intermediate stages termed Ostwald steps. Rocks pass through a sequence of metastable states as they approach chemical equilibrium in the lithological sequence: mudstone and shale, slate, phyllite, and schist. The absence of equilibrium during the process produces chemical and grain-size heterogeneity and justifies the coexistence of diverse Ostwald steps. Two very significant consequences of the minimal driving force for the reactions are the importance of heterogeneous nucleation and topotactic relationships between mineral phases.

NIETO et al. (1996, Fig. 6) observed the coexistence of a R1 illite/smectite with 50% illite layers and an R>>3 with more than 90% illite layers. The coexistence of different thermodynamically incompatible illite/smectite mixed-layers in a few dozen nanometers indicates that the smectite/illite evolution is a process governed by Ostwald's rule, in which the different phases slowly approach equilibrium through steps that are progressively

less heterogenous and closer to the final stable phase, in this case a true metamorphic mica (Σinterlayer cations ≈ 1).

Expanding our knowledge of the chemical composition of minerals and their possible evolution from diagenesis to low-grade metamorphism has been a difficult path due to their typically small grain size. ABAD et al. (2006) compiled a large set of analyses of dioctahedral micas corresponding to different sequences representative of diagenesis and low-grade metamorphism obtained by different techniques (SEM/EDX and TEM/AEM). All these data showed similar behaviour for the different sequences that could be explained by illitic ($\square K_{-1}$; $SiAl_1$), paragonitic (NaK_{-1}), and phengitic ($Mg+Fe$, Al^{VI}_{-1}; $SiAl^{IV}_{-1}$) substitutions. The latter is the main compositional vector, which determines the proportion of Si, Al, and Fe+Mg in dioctahedral micas. This substitution is responsible for the positive correlation between Si and Fe+Mg and the negative correlations between Al and Fe+Mg or Al and Si. There is also a certain influence of the ferrimuscovitic vector ($Fe^{3+} Al^{VI}_{-1}$), which produces contents higher in Fe and lower in Al than expected from only the phengitic substitution. There were no significant compositional differences among grades, except for high epizone (Kübler Index, KI< 0.2°2θ). Samples corresponding to this grade were characterized by the homogeneity of the mica composition and the reduction of the illitic component to low values. To determine whether the considerable scattering in chemical composition shown by all the samples corresponding to lower grades was due to differences among samples or represented heterogeneous mica compositions at the sample level, the chemical composition of one selected representative sample of each diagenetic or metamorphic grade was plotted (Fig. 1). With the sole exception of the high epizone sample, the compositional range displayed for the selected samples covered nearly the same range of mica compositions exhibited by all the studied samples (ABAD et al., 2006). Such a significant change in behaviour had previously been found in the Narcea micas by ABAD et al. (2003a), who showed that the effect of tectonic deformation is fundamental both in the approach to chemical equilibrium and in the development of a metamorphic texture. Micas from foreland samples (anchizone) were highly heterogeneous as a consequence of the absence of chemical equilibrium, including both illitic and muscovitic compositions, whereas micas from hinterland samples (high epizone) had evolved to homogeneous chemical compositions approaching the end-member muscovite. A significant textural change (Fig. 2) is accompanied by homogenisation of the chemical composition. Anchizone samples are usually characterised by a fine-grained matrix with micas formed by straight packets separated by low-angle boundaries; in contrast, the high epizone samples show a clear metamorphic texture with well-developed schistosity, well-differentiated phyllosilicate packets, lacking in defects, and oriented parallel to each other (NIETO & ABAD, 2003).
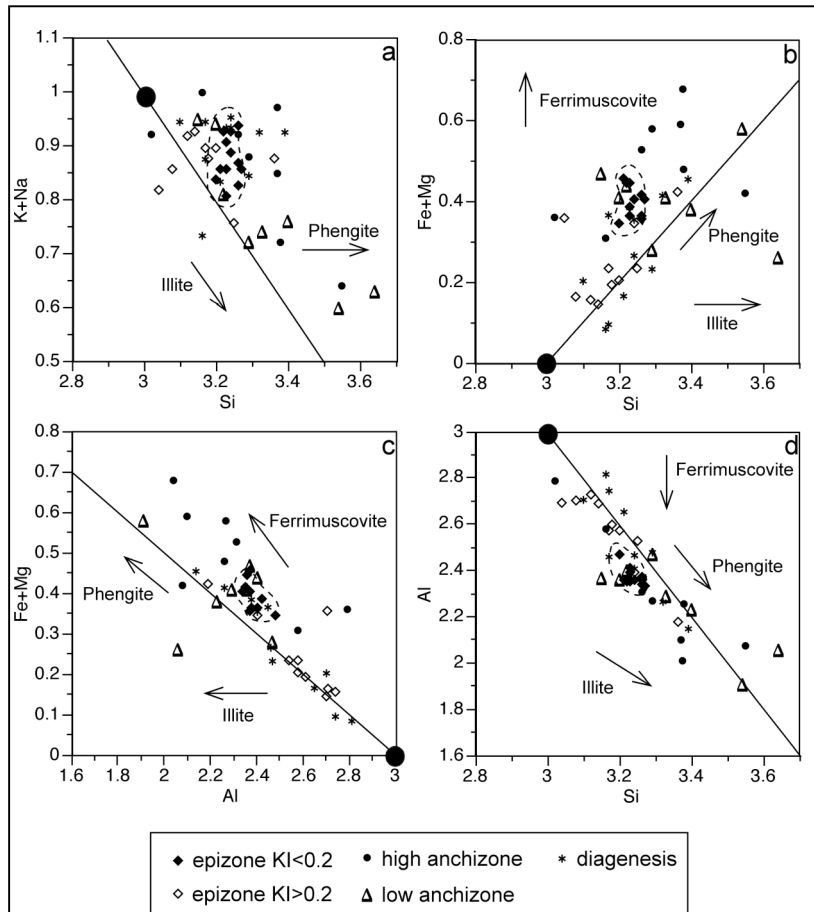

Fig. 1. Chemical diagrams illustrating the homogeneity *vs.* heterogeneity of K-dioctahedral micas on the basis of only one selected sample representative of each grade of metamorphism (KI) (from ABAD et al., 2006, with permission).
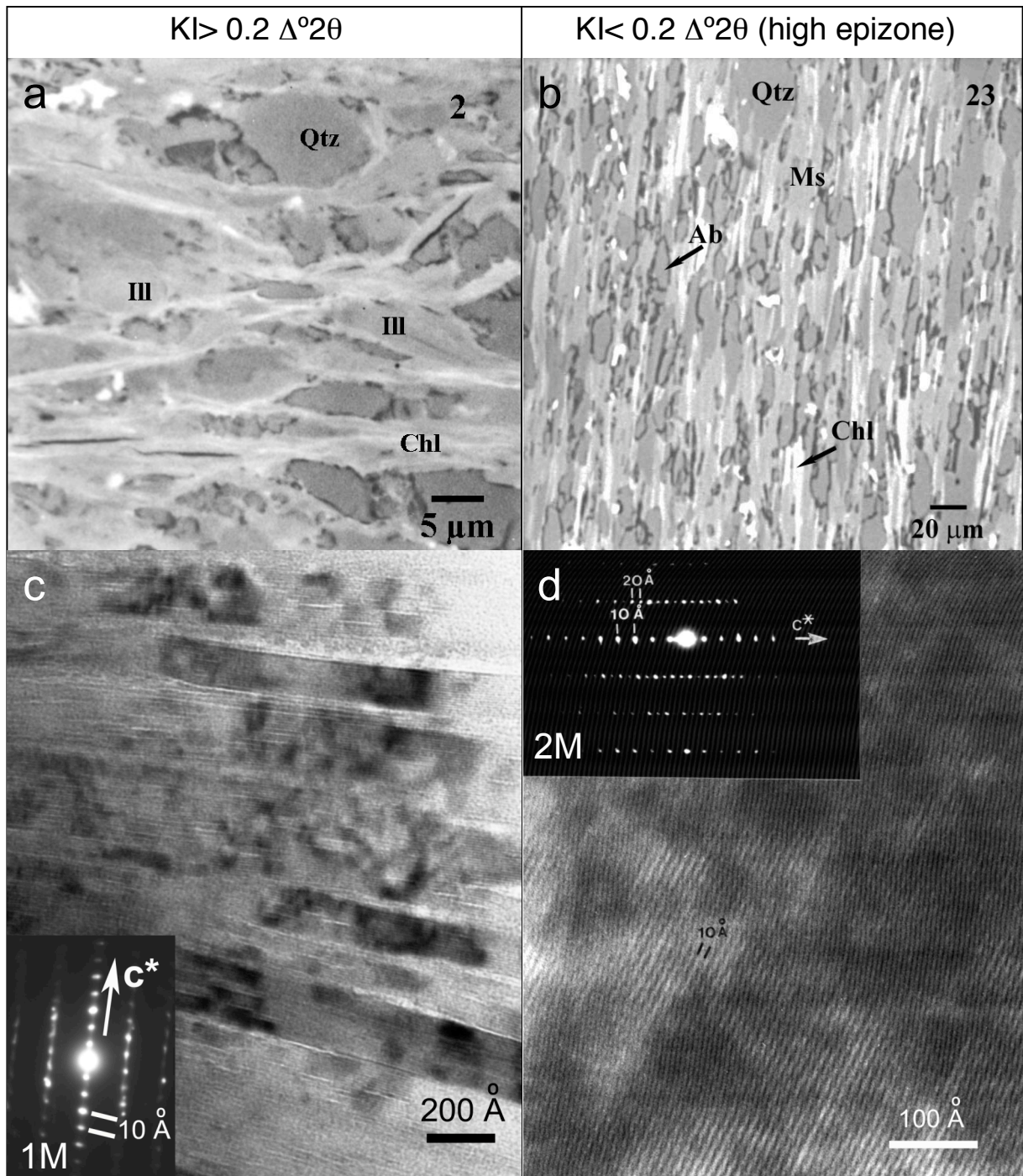
Fig. 2. Typical representative textures of mica-rich parts of metapelites at backscattered electron scale (up) and lattice fringe scale (down): a) Sample from Narcea Antiform, anchizone; b) Sample from Narcea Antiform, epizone; c) Sample from Ossa-Morena Zone, deep diagenesis; d) Sample from Puncoviscana Formation, epizone. Insets (Fig. 2c and d) present electron diffraction patterns showing the corresponding mica polytype. (From ABAD et al., 2006, with permission).

From X-rays to TEM

The most widely used tool for the study of these rocks has traditionally been powder X-ray diffraction (XRD) with the use of criteria based on the crystal-chemical aspects of phyllosilicates, such as the Kübler Index (KI) or the **b** parameter. However, in recent years, the use of high-resolution transmission electron microscopy (HRTEM) has also provided the means to check the criteria developed by powder diffraction and to understand their physical meaning. The first clear conclusion has been to confirm most of the knowledge obtained during decades of XRD analyses. Such knowledge in some cases has been clarified in points not totally understood and finally completed in some aspects impossible to attain by XRD, particularly regarding textural questions and internal differences at the sample level.

TEM observations by AHN & PEACOR (1986) on the Gulf Coast sequence (Mexico), the type sequence used for decades for studies on mudstones, demonstrated the genesis of thin, small illite packets (in fact illite/smectite

mixed-layers) from smectite with variable orientation. These illite packets increase in size until they coalesce with increasing depth; that is, with the advance of burial diagenesis. The change in mineral composition implies a gain in Al and K and the concomitant release of Fe, Mg, and Si. LEE et al. (1985) also proposed the genesis of chlorite in the Gulf Coast sequence as a subproduct. The excess Mg and Fe in octahedral layers associated to smectite segregated into disordered units of a trioctahedral phase, which finally became an ordered trioctahedral phase upon recrystallization.

TEM images of diagenetic samples show a characteristic texture dominated by packets of wavy, discontinuous and anastomosing layers of smectite and illite (see NIETO et al., 1996 and ABAD et al., 2003b). Newly formed illites inherit many textural and chemical characteristics from the original smectites during their evolution in a range of temperatures around 200 ºC. From deep diagenesis to low epizone conditions, the phyllosilicate matrix of clastic rocks is formed by straight packets up to several hundred Å thick of illite-chlorite intergrowths formed by small, slightly unoriented, crystals (ABAD et al., 2001). The few defects present are primarily edge dislocations. By contrast, TEM images corresponding to epizone conditions are characterised by defect-free crystals of muscovite, more than 1000 Å thick and usually a sharp 2M-layer electron-diffraction pattern (ABAD et al., 2001 and DO CAMPO & NIETO, 2003).

In general, data obtained by lattice-fringe images over the last two decades have revealed that evolution through the anchizone to the beginning of the epizone occurs with a progressive increase in the crystalline domain size of the rock-forming phyllosilicates together with a decrease in the number of defects (MERRIMAN & 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 high epizone conditions (Fig. 3).
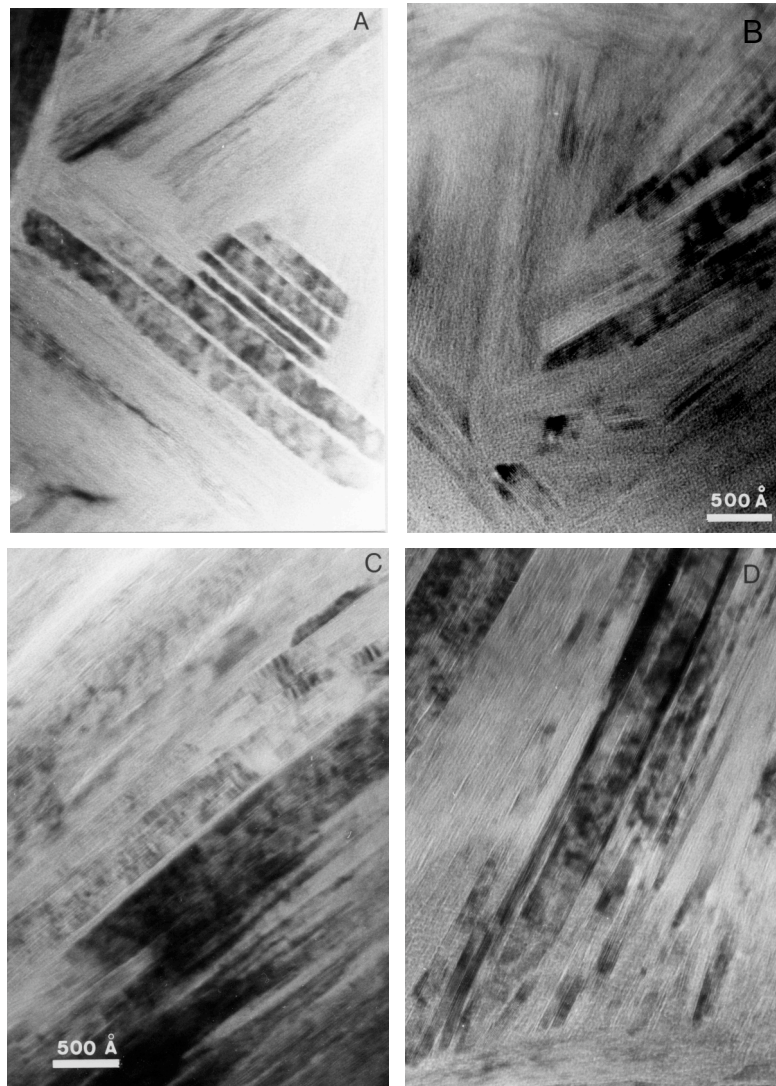

Fig. 3. TEM images belonging to the Alconera Unit. The images, corresponding to different grades (A: diagenesis; B-C: anchizone; D: epizone) show the lack of qualitative differences among them, (from NIETO & ABAD, 2003, with permission).

The absence of evident qualitative changes in phyllosilicates, including their mineral chemistry, from deep diagenetic to low epizone conditions implies the lack of valid grade criteria for this range. This justifies the development and use of alternative criteria for decades. Below we succinctly review as an example the geothermometry of chlorites, phyllosilicate polytypes, and the Kübler Index.

"Chlorite Geothermometry"

The lack of suitable parameters to evaluate temperature in low-grade conditions made popular the so-called "Chlorite Geothermometry" during the 80s and 90s. The commonest method was based on a fully empirical calibration, which related the composition of chlorites formed in the geothermal field of Los Azufres (Mexico) with the temperature directly measured in the field (CATHELINEAU & IZQUIERDO, 1988). Low-temperature chlorite is usually intergrown and interlayered with smectitic, vermiculitic, and mica layers and packets. This is an intrinsic characteristic of minerals formed in low-temperature conditions and, logically, tends to decrease with metamorphic grade. The mathematical consequence of such contaminations is a decrease in total octahedral population and a consequent increase in Si. A relationship between these chemical parameters of a contaminated chlorite and temperature is logical, but it is not a geothermometer (ESSENE & PEACOR, 1995). The users of the chlorite geothermometry claimed that only uncontaminated analyses of chlorite had been considered. Nevertheless, uncontaminated analyses are impossible in the case of interlayers and very difficult in the case of intergrowths. In fact, the "small" contents in interlayer cations of "clean" chlorites, usually mentioned by the authors of that work, are perfectly compatible with levels of contamination by smectitic layers in a proportion of around 5 or 10%, for instance. A very simple calculation verifies that the differences taken into account by the "geothermometer" may be perfectly compatible with such minimal contamination. In fact, DE CARITAT et al. (1993) analysed the consistency between different chlorite geothermometers and concluded that "no single chlorite geothermometer performs satisfactorily over the whole range of natural conditions". Surprisingly, many papers that present temperature data calculated using chlorite "thermometry" cite DE CARITAT et al. (1993) in *support* of the method.

LÓPEZ-MUNGUIRA et al. (2002) presented the compositional data of chlorites in basic rocks, whose corresponding temperature calculated using "chlorite geothermometry" was absolutely incompatible with the diagenetic grade of the clastic rocks in which the volcanic rocks were interbedded. That diagenetic grade had been established from clay mineralogy employing XRD and TEM methods (LÓPEZ MUNGUIRA & NIETO, 2000). Furthermore, the chemical composition of the basic-rock chlorites was apparently compatible with a proportion of smectite layers ranging from 20 to 2%, as a result of the assumption that the octahedral population should be exactly 6 a.p.f.u.. Nevertheless, XRD methods and lattice-fringe images demonstrated that these chlorites were pure with no smectite layers. Therefore, when contamination is really absent, the genuine composition of chlorite is not related with temperature. Instead, a perfect correlation between the MgO content of the basic rocks and all the chemical parameters of chlorites was found. According to XIE et al. (1997), the Mg content of a basic rock determines the Mg proportion in chlorite and the latter, through crystal-chemical constraints, determines the rest of the cation proportions in chlorite.

Phyllosilicate polytypes

The presence or absence of certain given polytypes of phyllosilicates is another traditional criterion to assign metamorphic grade in incipient metamorphism. X-ray diffraction was the traditional and most commonly used technique to investigate polytypes, but now the stacking sequence in mica and chlorite polytypes can be directly determined using TEM methods. One of the advantages is that TEM allows the polytype to be easily determined *in situ* by the use of selected electron diffraction patterns (SAED). HRTEM also allows the determination of stacking sequence at the layer level, but it requires images with a resolution better than 4 Å and perfect orientation of the sample.

The most common polytype in dioctahedral micas in diagenesis and very low-grade metamorphism is the $2M_1$. It can be accompanied by variable amounts of the $1M_d$ polytype (Fig. 4); coherently with previous XRD data, the TEM data indicate that the disordered polytype tends to be absent with increasing grade. DONG & PEACOR (1996) recognized short-range order in the stacking sequences, concluding that the $2M_1$ polytype is the most stable one in all conditions and suggested that the identification of the $1M_d$ polytype could be the result of the characteristic misorientation of small packets in diagenetic rocks. The $1M_1$ polytype is scarce and is not present as an intermediate stage between the 2M and the $1M_d$ polytypes in most samples. PEACOR et al. (2002) found evidence for high Mg contents of 1M illite and concluded 1M polytypism is absent in normal prograde diagenetic sequences.

Complex multilayer sequences, which can be interpreted in terms of high-order polytypes, have also been described in micas (ABAD et al., 2002, 2003b; DO CAMPO & NIETO, 2003; LÓPEZ-MUNGUIRA & NIETO, 2000) as well as in chlorites (DO CAMPO & NIETO, 2003; LÓPEZ-MUNGUIRA et al., 2002).

Kübler Index

Lattice-fringe images allow the direct recognition and measurement of phyllosilicate packets. Numerous attempts have been made to interpret the physical meaning of the Kübler Index (KI), beginning with the seminal paper by MERRIMAN et al. (1990). WARR & NIETO (1998) compared TEM and XRD data of four pelitic rocks corresponding to the international standards of WARR & RICE (1994). They interpreted the measurement of mean thickness and thickness distributions of crystallites by the XRD approach in the light of TEM images. All the literature agrees that the KI quite faithfully reflects the evolution of the thickness of the phyllosilicate packets. MERRIMAN & PEACOR (1999) have summarized current knowledge on this relationship; their figure 2.19 indicates that the sizes predicted by Scherrer's equation are very close to those found by various studies, despite differing regarding the means of defining what a coherent domain in a lattice-fringe image is. This difference in criteria and the wide dispersion of sizes at the sample level are the reasons for the differences in detail between the various published papers regarding the limits of the anchizone in terms of size of the crystalline domain. Therefore, the KI can be considered a good statistical indicator of the wide range of sizes present in a very low-grade pelite, once the initial methodological problems were overcome by means of the proposal for standardization by WARR & RICE (1994).
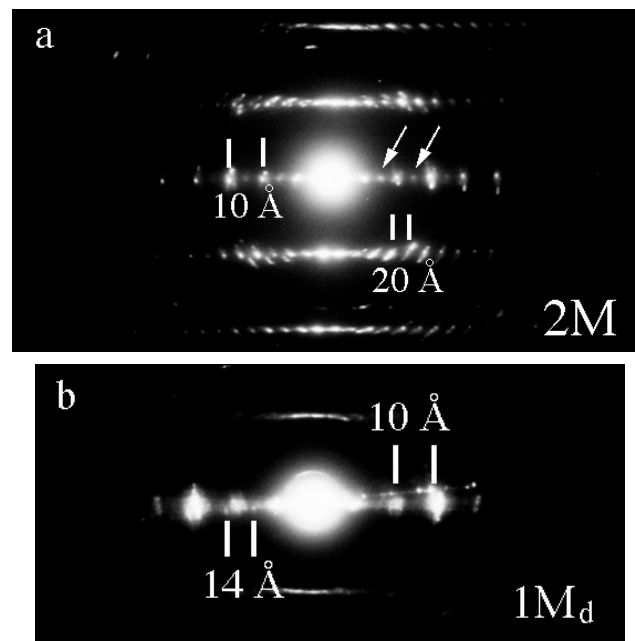

Fig. 4. SAED corresponding to the most common polytypes in micas of diagenesis and very low-grade metamorphism: (a) 2M polytype, the general (non-basal) reflections indicate 20 Å periodicity. In some cases, low intensity "forbidden" spots due to dynamic effects (see arrows) allow this periodicity to be detected in the basal reflections as well; (b) $1M_d$ polytype from mica. The 14 Å periodicity corresponds to chlorites. These two phyllosilicates frequently coexist in these environments. (From NIETO & ABAD, 2003, with permission).

Very low-grade metamorphism in geotectonic contexts
ROBINSON & BEVINS (1989) proposed the term "diastathermal metamorphism" for very low-grade metamorphic terranes in extensional settings. They based this proposal on a variety of observations related with P-T-t paths incompatible with crustal thickening models, such as the absence of structural features typical of collision settings with an increase in thermal gradient combined with an absence of high-pressure phases. The very low-grade types of metamorphism, which these authors considered, have an anticlockwise pattern to the P-T-t paths, in contrast to the classic P-T-t path for sub-greenschist metamorphism, characterized by a clockwise pattern.
MERRIMAN & FREY (1999) described the differences among the patterns of very low-grade metamorphism in metapelitic rocks in accretionary, alpine, and extensional geotectonic contexts. MERRIMAN (2005) has made regional comparisons among clay mineral assemblages generated in different geotectonic settings. Clay assemblages and microfabrics found in extensional basins were compared with those found in convergent basin settings. Extensional back-arc basins, characterised by high heat-flow (>35 ºC/km), tend to have a great range of transformed clay minerals (K-, K/Na- and Na-micas, pyrophyllite, and chlorite/mica intergrowths) and K-micas are usually dioctahedral with **b** cell dimensions of <9.01 Å. In contrast, low heat-flow basins (convergent margins) have less diverse transformed clay mineral associations of K-white mica and chlorite and K-micas are phengitic with **b** cell dimensions >9.02 Å. In conclusion, clay mineral assemblages and the **b** cell dimension of K-white mica can be used to infer the geotectonic settings of sedimentary basins (MERRIMAN, 2005).

Current state of knowledge

The greatest successes of the numerous TEM studies carried out in the 80s and 90s was the recognition and identification of diverse phases of mineral genesis throughout a given geological evolution. The co-existence of neoformed and detrital phases was successfully predicted by traditional diffractometry. The co-existence of minerals growing under diverse conditions of pressure and temperature in a clockwise P-T-t evolution was predictable, but impossible to approach via powder XRD; now they are well-established facts using electron microscopy techniques (e.g. DALLA TORRE et al., 1996). Similarly, the existence of retrograde processes superimposed to the normal prograde evolution is a currently acknowledged and demonstrated fact (NIETO et al., 1994, 2005). In general, the use of SEM, TEM, and AEM has allowed scientists to fill the gaps in textural and mineral chemistry due to the very small grain size and defective nature of very low-grade metamorphic rocks.

In light of the TEM data now available, the lack of qualitative changes across a wide range of temperatures covering both sides of the anchizone boundaries has made it difficult to define really new metamorphic grade criteria. As the only features differentiating the samples corresponding to the distinct grades are quantitative, related to packet size and number of defects, it is not surprising to note the remarkably good performance of the Kübler and Árkai (Árkai, 1991) Indices.

Throughout this range, phyllosilicates are very far from chemical equilibrium and, moreover, the compositional ranges they define can be entirely equivalent for deep diagenesis and low epizone samples, for instance. Regarding the use of chemical compositions of phyllosilicates, VIDAL & PARRA (2000) successfully developed geothermobarometric methods for low-grade metapelites based on local equilibria for chlorite-phengite assemblages. The possible extension of these methods to very low-grade conditions may be one of the most promising tools to be monitored in the near future.

The introduction of TEM to diagenesis and very low-grade metamorphism research in the mid-80s represented the beginnings of true petrography and microchemistry for such very small-grained materials. Now their mean textural and chemical characteristics are known and the next frontier is to begin true crystallo-chemical research on the mineral phases in very low-grade rocks, using tools such as Electron Crystallography or EELS (Electron Energy-Loss Spectroscopy).

Acknowledgements

References

ABAD, I., NIETO, F. & GUTIÉRREZ-ALONSO, G. (2003a): Textural and chemical changes in slate-forming phyllosilicates across the external-internal zones transition in the low-grade metamorphic belt of the NW Iberian Variscan Chain.- Schweizerische Mineralogische und Petrographische Mitteilungen, 83, 63-80.

ABAD, I., NIETO, F., GUTIÉRREZ-ALONSO, G., do CAMPO, M., LÓPEZ-MUNGUIRA, A. & VELILLA, N. (2006): Illitic substitution in micas of very low-grade metamorphic clastic rocks.- European Journal of Mineralogy, 18, 59-69.

ABAD, I., NIETO, F., PEACOR, D.R. & VELILLA, N. (2003b): Prograde and retrograde diagenetic and metamorphic evolution in metapelitic rocks of Sierra Espuña (Spain).- Clay Minerals, 38, 1-23.

ABAD, I., NIETO, F. & VELILLA, N. (2001): The phyllosilicates in diagenetic-metamorphic rocks of the South Portuguese Zone, southwestern Portugal.- The Canadian Mineralogist, 39, 1571-1589.

ABAD, I., NIETO, F. & VELILLA, N. (2002): Chemical and textural characterisation of diagenetic to low-grade metamorphic phyllosilicates in turbidite sandstones of the South Portuguese Zone: A comparison between metapelites and sandstones.- Schweizerische Mineralogische und Petrographische Mitteilungen, 82, 303-324.

AHN, J.H. & PEACOR, D.R. (1986): Transmission and analytical electron microscopy of the smectite-to-illite transition.- Clays and Clay Minerals, 34, 165-179.

ÁRKAI, P. (1991): Chlorite crystallinity - An empirical-approach and correlation with illite crystallinity, coal rank and mineral facies as exemplified by Paleozoic and Mesozoic rocks of Northeast Hungary.- Journal of Metamorphic Geology, 9, 723-734.

CATHELINEAU, M. & IZQUIERDO, G. (1988): Temperature-composition relationships of authigenic micaceous minerals in the Los Azufres geothermal system.- Contributions to Mineralogy and Petrology, 100, 418-428.

DALLA TORRE, M., LIVI, J.T.K., VEBLEN, D.R. & FREY, M. (1996): White K-mica evolution from phengite to muscovite in shales and shale matrix melange, Diablo Range, California.- Contributions to Mineralogy and Petrology, 123, 390-405.

DE CARITAT, P., HUTCHEON, I. & WALSHE, J.L. (1993): Chlorite Geothermometry - A Review.- Clays and Clay Minerals, 41, 219-239.

DO CAMPO, M.D. & NIETO, F. (2003): Transmission electron microscopy study of very low-grade metamorphic evolution in Neoproterozoic pelites of the Puncoviscana Formation (Cordillera Oriental, NW Argentina).- Clay Minerals, 38, 459-481.

DONG, H. & PEACOR, D.R. (1996): TEM observations of coherent stacking relations in smectite, I/S and illite of shales: evidence for MacEwan crystallites and dominance of 2M1 polytypism.- Clays and Clay Minerals, 44, 257-275.

ESSENE, E.J. & PEACOR, D.R. (1995): Clay mineral thermometry: a critical perspective.- Clays and Clay Minerals, 43, 540-553.

FREY, M. (1987): Low temperature metamorphism.- Blackie, Glasgow, 351 p.

FREY, M. & ROBINSON, D. (1999): Low grade-metamorphism.- Blackwell Science, Oxford, 313 p.

LEE, J.H., AHN, J.H. & PEACOR, R. (1985) Textures in layered silicates: Progressive changes through diagenesis and low-temperature metamorphism.- Journal of Sedimentary Petrology, 55, 532-540.

LÓPEZ-MUNGUIRA, A. & NIETO, F. (2000): Transmission Electron Microscopy study of very low-grade metamorphic rocks in Cambrian sandstones and shales. Ossa-Morena Zone, South-West Spain.- Clays and Clay Minerals, 48, 213-223.

LÓPEZ-MUNGUIRA, A., NIETO, F. & MORATA, D. (2002): Chlorite composition and geothermometry: a comparative HRTEM/AEM-EMPA-XRD study of Cambrian basic lavas from the Ossa Morena Zone, SW Spain.- Clay Minerals, 37, 267-281.

MERRIMAN, R.J. (2005): Clay minerals and sedimentary basin history.- European Journal of Mineralogy, 17, 7-20.

MERRIMAN, R.J. & FREY, M (1999): Patterns of very low-grade metamorphism in metapelitic rocks. .-In: FREY, M. & ROBINSON, D. (eds.): Low-Grade Metamorphism. Blackwell Sci., 61-107.

MERRIMAN, R.J. & PEACOR, D.R. (1999): Very low-grade metapelites: mineralogy, microfabrics and measuring reaction progress.-In: FREY, M. & ROBINSON, D. (eds.): Low-Grade Metamorphism. Blackwell Sci., 10-60.

MERRIMAN, R.J., ROBERTS, B. & PEACOR, D.R. (1990): A transmission electron microscope study of white mica crystallite size distribution in a mudstone to slate transitional sequence, North Wales, UK.- Contributions to Mineralogy and Petrology, 106, 27-40.

MORSE, J.S. & CASEY, W.H. (1988): Ostwald processes and mineral paragenesis in sediments.- American Journal of Science, 288, 537-560.

NIETO, F. & ABAD, I. (2003): X-Ray Diffraction Parameters in Very Low-Grade metamorphism Seen in the "Light" of TEM.-In: PÉREZ RODRÍGUEZ J.L. (ed.): Applied Study of Cultural Heritage and Clays. CSIC, Biblioteca de Ciencias, 83, 363-376.

NIETO, F., MATA, M.P., BAULUZ, B., GIORGETTI, G., ÁRKAI, P. & PEACOR, D. R. (2005): Retrograde diagenesis, a widespread process on a regional scale. Clay Minerals, 40, 93-104.

NIETO, F., ORTEGA-HUERTAS, M., PEACOR, D.R. & ARÓSTEGUI, J. (1996): Evolution of illite/smectite from early diagenesis through incipient metamorphism in sediments of the Basque-Cantabrian Basin.- Clays Clay Minerals, 44, 304-323.

NIETO, F., VELILLA, N., PEACOR, D.R. & ORTEGA-HUERTAS, M. (1994): Regional retrograde alteration of sub-greenschist facies chlorite to smectite.- Contributions to Mineralogy and Petrology, 115, 243-252.

PEACOR, D.R., BAULUZ, B., DONG, H., TILLICK, D., & YAN, Y. (2002): Transmission and analytical electron microscopy evidence for high Mg contents of 1M illite: Absence of 1M polytypism in normal prograde diagenetic sequences of pelitic rocks.- Clays and Clay Minerals, 50, 757-765.

ROBINSON, D. & BEVINS, R.E. (1989): Diastathermal (extensional) metamorphism at very low grades and possible high grade analogues.- Earth and Planetary Science Letters, 92, 81-88.

VIDAL, O. & PARRA, T. (2000): Exhumation paths of high-pressure metapelites obtained from local equilibria for chlorite-phengite assemblages.- Geological Journal, 35, 139-161.

WARR, L.N. & NIETO, F. (1998): Crystallite thickness and defect density of phyllosilicates in low-temperature metamorphic pelites: a TEM AND XRD study of clay-minerals crystallinity-index standars.- The Canadian Mineralogist, 36, 1453-1474.

WARR, L.N. & RICE, A.H.N. (1994): Interlaboratory standardization and calibration of clay mineral crystallinity and crystallite size data.- Journal of Metamorphic Geology, 12, 141-152.

WYBRECHT, E., DUPLAY, J., PIQUÉ, A. & WEBER, F. (1985): Mineralogical and chemical evolution of white micas and chlorites, from diagenesis to low-grade metamorphism; data from various size fractions of greywackes (Middle Cambrian, Morocco).- Mineral Magazine, 4, 401-411.

XIE, X., BYERLY, G.R. & FERRELL, R.E. (1997): IIb trioctahedral chlorite from the Barberton greenstone belt: crystal structure and rock composition constraints with implications to geothermometry.- Contributions to Mineralogy and Petrology, 126, 275-291.