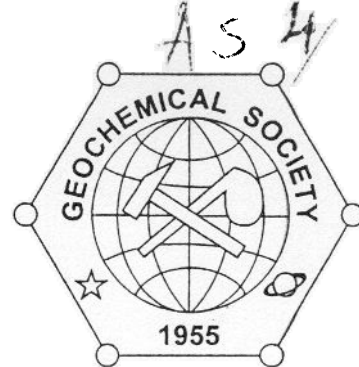




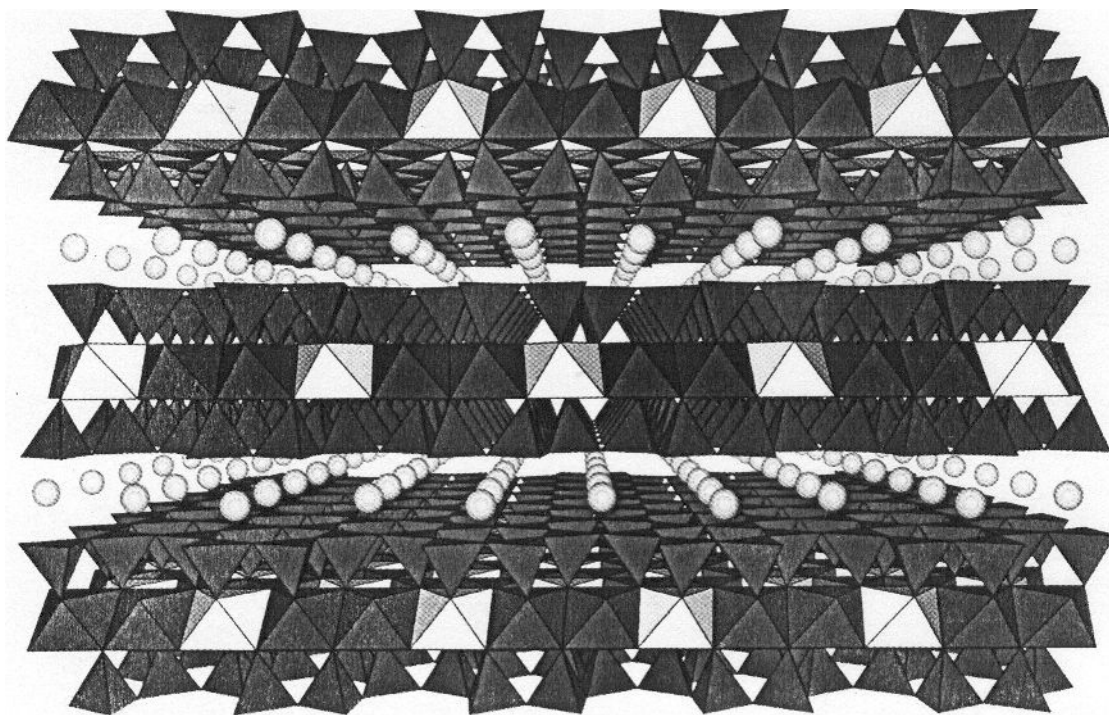
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**MICAS: CRYSTAL CHEMISTRY  
& METAMORPHIC PETROLOGY**

EDITORS:

ANNIBALE MOTTANA, FRANCESCO PAOLO SASSI,  
JAMES B. THOMPSON, JR., STEPHEN GUGGENHEIM



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**MICAS: CRYSTAL CHEMISTRY  
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*Editors*

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*Università degli Studi Roma Tre*  
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FRONT COVER: Perspective view of TOT layers in biotite down [100] ([001] is vertical), produced by *CrystalMaker*. Red tetrahedra contain Si or Al, green and white octahedra contain Mg and Fe, respectively, and yellow spheres represent the K interlayer cations. Courtesy of Mickey Gunter, University of Idaho, Moscow. [Data: S.R. Bohlen et al. (1980) Crystal chemistry of a metamorphic biotite and its significance in water barometry. *Am Mineral* 65:55-62]

BACK COVER: A view down [001] of lepidolite- $2M_2$ , showing tetrahedrally coordinated Si,Al (blue) joined with bridging oxygens (red thermal ellipsoids) in the T-layer and ordered, octahedrally coordinated Al (gray) and Li (yellow) in the O-layer. The interlayer cation is 12-coordinated K (green). Courtesy of Bob Downs, University of Arizona, Tucson. [Data: S. Guggenheim (1981) Cation ordering in lepidolite. *Am Mineral* 66:1221-1232]

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# 11 Phyllosilicates in Very Low-Grade Metamorphism: Transformation to Micas

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## INTRODUCTION

Phyllosilicates produced mostly by weathering of magmatic, metamorphic and sedimentary rocks are widespread in the surficial and near-surface zones of the Earth's crust. These phyllosilicates display very fine grain sizes, disordered crystal structures, and greatly varying chemical compositions, and they represent structurally and chemically metasable phases. They are subjected to heat during diagenesis and concomitant metamorphism, which provides a long-life source of energy for transforming the metastable phases into thermodynamically more stable phases through a long series of partly continuous, partly discontinuous reactions. The present review summarizes some major mineralogical aspects of these processes, with special reference to petrogenetic applications.

Forty years have passed since the first petrogenetic application of the illite structural changes for characterizing diagenetic processes in sedimentary basins (Weaver 1960). Weaver's "sharpness ratio" as well as Kübler's (1964, 1968) empirical illite "crystallinity" index, have been easy-to-use X-ray powder diffraction (XRD) measures of the manifold, inter-related changes that the hydrous, mica-like phyllosilicates experience during increasing burial.

In the first two decades after the introduction of the illite "crystallinity" concept, it was applied to metamorphic petrogenetic studies in certain areas of Europe (especially to the external fold and thrust belts of the European Alps, Variscides, etc.). These studies were the starting point of important further developments which include: awareness of the phyllosilicate transformations during deep burial in sedimentary basins (Hower et al. 1976; Inoue et al. 1990; Amouric and Olives 1991; Lanson and Champion 1991; Lindgreen and Hansen 1991; Eberl 1993; Huang et al. 1993; Whitney and Velde 1993; Huggett 1995; Elliott and Matisoff 1996; Nieto et al. 1996; Dong et al. 1997), and recognition of the nature of interstratified clay minerals (see Reynolds and Hower 1970). Moreover, using the theory of X-ray powder diffraction (e.g., Klug and Alexander 1974), it became evident that the mysterious increase in "crystallinity" (i.e., the supposed increase of periodic order of the crystal structure of illite) with increasing depth is actually caused, first of all, by the increase in mean crystallite size [i.e., the mean size of crystal domains that scatter X-rays coherently (Weber et al. 1976; Dunoyer de Segonzac and Bernoulli 1976; Árkai and Tóth 1983; Merriman et al. 1990; Nieto and Sanchez-Navas 1994; Drits et al. 1997)]. Crystallite size, especially at lower (diagenetic) grades, seems to be strongly controlled by the numbers of swelling interstratified layers.

In the 1980s, reviews and textbooks by Kisch (1983) and Frey (1987) summarized the illite "crystallinity" concept mostly from a petrogenetic point of view. Subsequently, the illite "crystallinity" method has been increasingly and extensively applied all over the world as an empirical metamorphic petrological tool (for outstanding examples, see Merriman and Frey 1999). Simultaneously, studies to understand the mineral structural,

chemical and rock-textural changes have been published in increasing number. The vast amount of new data that has accumulated in the last two decades on low-temperature metamorphism and late diagenesis inspired a recent review: "Low-Grade Metamorphism," edited by Martin Frey and Doug Robinson (1999). Substantial parts in it, especially the chapter written by Merriman and Peacor (1999), deal with mineralogical aspects.

The summaries cited above are mainly petrologic. The present review focuses on mineralogical aspects and problems relating to phyllosilicate-transformation processes in the low-temperature realm, mainly on the basis of results achieved during the last 10-15 years. Special attention is also paid to emphasize the unresolved problems, controversies, future studies, and new approaches.

In the present paper, some terms are used with reference to the different diagenetic and metamorphic realms or stages. To avoid ambiguity, these terms, and the meaning with which they are used in the present paper, are listed below. The explanations of these terms are in agreement with the definitions of the Study Group, "Very Low-Grade Metamorphic Rocks" of the IUGS Subcommittee on Systematics of Metamorphic Rocks (SCMR):

*Diagenesis (sensu lato)*: all the chemical, mineralogical, physical and biological changes undergone by the sediment after its initial deposition and during and after its lithification, exclusive of surficial alteration (weathering) and metamorphism. These processes occur under conditions of pressure and temperature that are usual at the Earth's surfaces and in the outer part of the Earth's crust.

*Very low-grade metamorphism*: alterations producing mineral assemblages in the fields of the zeolite, prehnite-pumpellyite, prehnite-actinolite and pumpellyite-actinolite facies. In other words, it is metamorphism of lower grade than greenschist (and blueschist) facies. Recently, this realm has been called also subgreenschist facies.

*Diagenetic zone* (or more precisely, *diagenetic illite "crystallinity" zone*): after Kübler (1964, 1968), the diagenetic zone is a pre-metamorphic stage defined by illite "crystallinity" (IC) values greater than  $0.42 \Delta^{\circ}2\theta$  as measured on the  $<2 \mu\text{m}$  fraction of clay-rich, normal clastic rocks under conditions that correspond to the recommendations on sample preparation, X-ray diffraction settings and interlaboratory standardization as summarized by Kisch (1991).

*Anchizone*: after Kübler (1964, 1968), a transitional zone between the diagenetic zone and the epizone as defined by IC mean values between 0.42 and  $0.25 \Delta^{\circ}2\theta$ . [Kaolinite and/or dioctahedral illite/smectite interstratified clay mineral with more than about 10% expandable layers are absent in normal clastic rocks, but they may persist in carbonate rocks, and in organic matter-rich, Na-rich and K-poor shales.]

*Epizone*: after Kübler (1964, 1968), an advanced stage of metamorphism determined by IC mean values of less than  $0.25 \Delta^{\circ}2\theta$ . [Note that this definition is totally different from that originally given by Grubenmann for low-grade rocks.]

## MAIN METHODS OF STUDYING LOW-TEMPERATURE TRANSFORMATIONS OF PHYLLOSILICATES

Diagenetic and very low-grade metamorphic rocks are commonly polyphase, fine-grained aggregates for which, usually, there are no means for perfect grain separation of a given phase. Consequently, significant progress in the study of these aggregates was obtained mostly by using those methods which do not need a physical separation of mineral species: first of all, XRD and transmission electron microscopy (TEM).

## XRD techniques

The main aspects are outlined below.

Standardization aspects. They include: (1) sample preparation [separation of the required <2- $\mu$ m SED (spherical-equivalent diameter) grain-size fraction], (2) measuring conditions and (3) international calibration of the illite "crystallinity" measurements (Kisch 1990, 1991; Krumm and Buggisch 1991; Krumm et al. 1994; Warr and Rice 1994). Although significant results were achieved, correlation with Kübler's original boundaries requires further consideration, especially because of the originally rather poorly-defined nature of the diagenetic, anchi- and epizones as based on illite "crystallinity." In other words, the technical (methodological) aspects are rather clear, whereas the metamorphic petrological interpretations must be handled with great care and caution.

Improvement of the "crystallinity" concept and measurements by deconvolution of the XRD line-profiles, to separate partly or totally overlapping peaks (Stern et al. 1991; Lanson and Besson 1992; Velde and Lanson 1993; Robinson and Bevins 1994; Hillier 1995; Wang et al. 1995; Schmidt and Robinson 1997). With the help of these rather sophisticated deconvolution approaches, the diffraction effects of intimately intergrown phases or certain components of a given phase can be separated. However, the results of these approaches strongly depend on the assumptions required for the method's use. In addition, correlation between the full width at half maximum (FWHM) values obtained in this way and Kübler's original IC scale (on which the petrogenetic applications are still based), may lead to conflicting conclusions.

Introduction of chlorite "crystallinity" (ChC) measurements, and correlation of ChC scales with that of IC, metabasite mineral facies, coal rank, etc. (Árkai 1991). The applicability of ChC for indicating grades in metaclastic rocks were statistically shown by Árkai et al. (1995b). The use of ChC was extended to meta-igneous rocks by Árkai and Sadek Ghabrial (1997) and Árkai et al. (2000).

Calculation of mean crystallite size, lattice strain and frequency distributions of crystallite sizes from the same XRD line-profiles used for "crystallinity" determinations. In addition to the application of the Scherrer equation, two single-line methods were used: the variance method of Wilson (1963) (Árkai and Tóth 1983; Nieto and Sánchez-Navas 1994), and the Voigt method of Langford (1978) in combination with single-line Fourier analysis (Árkai et al. 1996, 1997, 2000; Warr 1996; Jiang et al. 1997; Li et al. 1998). Simultaneously, numerous efforts were made to apply the multi-line size/strain analysis of Warren and Averbach (1950) (called Bertaut-Warren-Averbach analysis) (Eberl et al. 1987, 1990, 1996, 1998; Eberl and Srodon 1988; Lanson and Kübler 1994; Warr and Rice 1994). In the 1990s, some PC programs were written especially for phyllosilicate studies using single- and multi-line analyses [e.g.; the Krumm (1994) WINFIT<sup>®</sup> program and its updated versions and the Mudmaster<sup>®</sup> program of Eberl et al. (1996)]. These programs also estimate crystallite-size frequency distributions, which, in turn, have been used to interpret the processes of crystallization and recrystallization (Eberl and Srodon 1988; Eberl et al. 1990). Despite the great efforts made, these calculations rely on various mathematical assumptions and approximations. They also need "ideal" crystals for instrumental corrections and provide only apparent or (at best) semiquantitative estimates of crystallite sizes. This was shown by Árkai et al. (1996), who compared the applicability of most of these XRD-based methods on a natural sample series ranging from deep diagenesis to the epizone (for further details, see Árkai et al. 1997).

The relatively simple, quick, cheap and easy-to-use XRD-based "crystallinity"

methods have been, and surely will continue to be, basic tools for regional studies for a long time—especially when investigations of large sample-sets are required owing to the natural variability of the geological rock formations.

It is commonly assumed in XRD “crystallinity” studies that the  $<2\text{-}\mu\text{m}$  SED grain-size fraction is composed predominantly of authigenic (newly-formed, metamorphic) crystallites of the phyllosilicate mineral species. “Crystallinity” indices may then be considered representative of the diagenetic-metamorphic process the rock has experienced. Note, however, that the amount of the  $<2\text{-}\mu\text{m}$  fraction decreases with increasing grade—at epizonal (greenschist facies) conditions the amount of the  $<2\text{-}\mu\text{m}$  fraction is usually subordinate and is not representative of the rock as a whole. Actually, “crystallinity” values represent rough, weighted-average information on the structural state of the investigated phyllosilicate as found in the given grain-size fraction. Comprehensive studies show that, even for pelitic-silty-marly rocks (for which the method was originally developed), various proportions of newly-formed and inherited (detrital) varieties of white K-rich micas and chlorite commonly occur in “clay” separates. In addition, more than one authigenic generation may be present as a result of polymetamorphism and lack of homogenization.

### TEM techniques

In contrast to XRD methods that may introduce sample preparation artifacts (see Jiang et al. 1997; Li et al. 1998), TEM integrated with selected-area electron diffraction (SAED) and energy dispersive spectrometry (analytical electron microscopy, AEM) measurements, provides direct, *in situ* observations on rock microtextures, crystallite size distributions, lattice imperfections of crystallites and interstratification (see the extensive reviews by Peacor 1992 and Merriman and Peacor 1999). TEM observations on selected portions of thinned (ion-milled) whole rock samples contradict the “fundamental particle” theory of Nadeau et al. (1984a,b,c; summarized recently by Nadeau 1998). The observations show that phyllosilicate domains with interstratified structures form coherent boundaries, and therefore, “MacEwan-type crystallites” do exist in quasi-undisturbed rocks (Peacor 1998). In addition, AEM studies may provide reliable mineral-chemical data on the phases devoid of any external or internal impurities.

However, TEM and related methods are comparatively expensive and extremely time-consuming. They require the careful selection of adequate sample parts [mainly by scanning electron microscopy (SEM) and electron microprobe (EMP)], and therefore—despite the great advantages listed above—they are (and presumably will remain) inadequate for studying the large number of samples that is required for regional petrological studies. The XRD-based calculations are less time-consuming and less expensive than the TEM measurements. In addition, XRD gives a more representative weighted average of the whole rock or its selected fraction, as compared to the TEM observations because X-rays provide information about a considerable larger number of crystals. (For illustrative purposes, consider that X-rays irradiate a sample surface of ca.  $3\text{ cm}^2$  in the interval of  $6\text{-}13^\circ 2\theta$ . The surface is covered with crystals of  $1\text{ }\mu\text{m}$  average grain-size, 1:10 to 1:20 elongation ratio and  $200\text{-}\text{Å}$  average crystallite thickness amounting to ca.  $10^9$  to  $10^{10}$  particles. The number of the direct TEM thickness measurements is on the order of  $10^2$  to  $10^3$ . Therefore, the crystallite population analysed by XRD is approximately  $10^7$  times larger than that of TEM observations.)

Obviously, the joint application of XRD and TEM methods is highly recommended: it may provide mineralogically well established petrogenetic information on low-grade changes in phyllosilicates. Examples of such comprehensive studies were available in the literature in the late 1980s, with many more appearing more recently (Eberl et al. 1987,

1990; Merriman et al. 1990, 1995; Srodon et al. 1992; Árkai et al. 1996, 2000; Jiang et al. 1997; Li et al. 1998; Warr and Nieto 1998). The main results of these studies are given briefly below.

### MAIN TRENDS OF PHYLLOSILICATE EVOLUTION AT LOW TEMPERATURE

As a result of detailed XRD and TEM studies carried out on sedimentary basins and on the outer thrust and fold zones of orogenic belts, the framework and main aspects of the structural changes and interrelated chemical changes of phyllosilicate aggradational processes are now fairly well understood (see the review of Merriman and Peacor 1999). These changes are usually described with reference to two main trends. For both trends the starting materials are, in sedimentary and early diagenetic conditions, low layer-charge smectites [either (or both) of detrital origin or/(and) crystallized from aqueous solution]. It is commonly accepted that the occupancy of the octahedral sites and the types of hydrated cations in the interlayer are controlled mainly by the chemistries of the enclosing fluids and reacting solid phases.

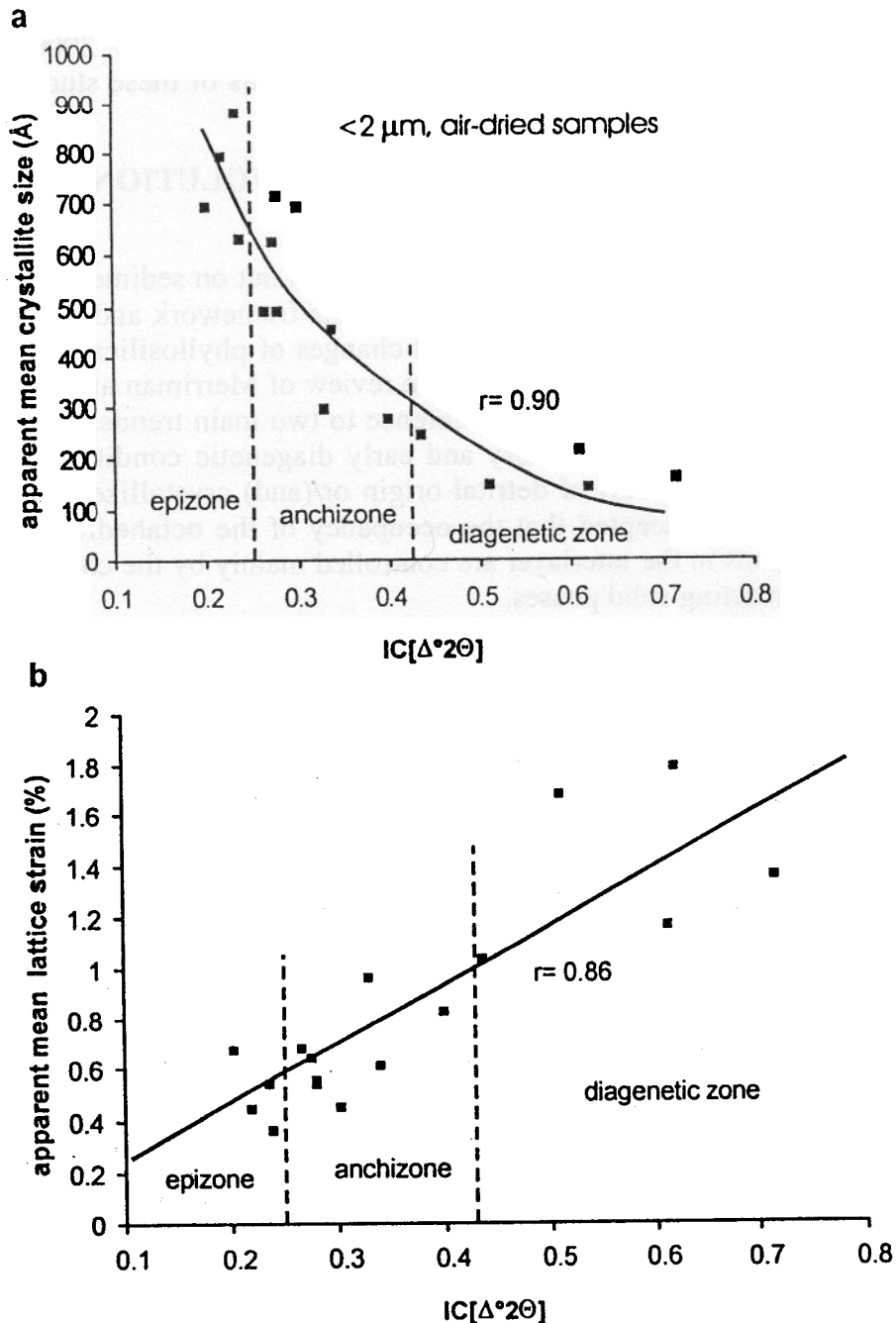
The two progressive trends, ranging from early (shallow) diagenesis to the so called epizone (i.e., the low-grade or greenschist facies metamorphism) are:

- (1) dioctahedral smectite → illite/smectite interstratified clay mineral → illite → dioctahedral white K-rich mica (muscovite);
- (2) trioctahedral smectite (or vermiculite) → chlorite/smectite or chlorite/vermiculite irregular and regular interstratifications → chlorite.

Note that biotite does not form as an end product of this prograde evolution of trioctahedral phyllosilicates. In normal pelites, biotite usually crystallizes by mineral reactions of muscovite plus chlorite at higher temperatures, between ca. 400 and 450°C; in greywacke-type clastic rocks biotite appears at the expense of K-rich feldspar and chlorite at considerably lower temperatures (ca. 300-350°C) (Winkler 1979; Bucher and Frey 1994; Árkai et al. 1995a).

The above mentioned prograde series are characterized by the following mineral or crystal structural changes:

- decrease in the proportions of swelling interstratified layers (smectitic and vermiculitic);
- increase of ordering of interstratification in the di- and trioctahedral series (with Reichweite values of  $R = 0 \rightarrow R = 1 \rightarrow R > 1$  in illite/smectite and randomly interstratified chlorite/smectite → corrensite → corrensite/chlorite);
- increase in the illite and chlorite crystallite mean size, i.e., the mean size of domains that scatter X-rays coherently (Fig. 1a);
- decrease of various lattice imperfections of illite and chlorite that cause lattice strain, e.g., layer terminations, etc. (Fig. 1b);
- rather regular prograde changes of polytypes  $Ad$  (or  $1Md$ ) →  $(1M)$  →  $2M_1$  of illite-muscovite (Velde and Hower 1963; Maxwell and Hower 1967; Hoffman and Hower 1979; Walker 1993; Dalla Torre et al. 1994; Dalla Torre and Frey 1997), although the existence of the  $1M$  polytype in sedimentary and under incipient metamorphic conditions has been questioned recently by Grubb et al. (1991) and Dong and Peacor (1996);
- in chlorites, polytype I (mostly  $Ib$ ) is restricted to lower temperatures, whereas at higher grades (i.e., at anchi- and epizonal metamorphic conditions) polytype  $Iib$  predominates (Bailey and Brown 1962; for critical reviews see also Walker 1993; Schmidt and Livi 1999).



**Figure 1.** Relations between illite crystallinity (IC) and mean crystallite size (a) and lattice strain (b) as calculated from XRD line-profiles by the modified Voigt method. Data from Árkai et al. (1996, 2000), Jiang et al. (1997) and Li et al. (1998).

The above structural changes are primarily related to mineral-chemical changes, and the main trends are as follows: (1) an increase of net negative layer charge and consequently, an increase of positive interlayer charge caused mainly by the increasing substitution of Al for Si in tetrahedral sites and increasing order of occupancy in the octahedral sites, including the take up of cations from the interlayer or from outside the crystallite; and (2) stabilization of the interlayer by predominantly  $\text{K}^+$ , subordinately  $\text{NH}_4^+$  and  $\text{Na}^+$  substitutions, in 2:1 layer silicates or by increasingly ordered brucite-like layers in chlorite.

In the last few years, contrasting results (and opinions) concerning the mineral-chemical features of illite and chlorite and their precursor phases have been published.



These results often led to conflicting mineralogic and petrogenetic interpretations. Some features of this "hot topic" are discussed below.

### CURRENT PROBLEMS IN STUDYING PHYLLOSILICATE EVOLUTION AT THE LOWER CRYSTALLITE-SIZE LIMITS OF MINERALS

Although the main trends of phyllosilicate evolution are fairly well known, there are numerous less well understood aspects that may significantly influence the petrogenetic interpretation of the mineral-structural and mineral-chemical features. The common sources of these problems are related mainly to the fact that, especially in near-surface and diagenetic conditions, the size of coherent crystallites (in the basal-normal direction) is very close or equal to the size of the unit cell. These particles exhibit extremely high specific surface areas and surface free energies. Thus, the determination of their original (*in situ*) properties is rather difficult, often impossible, taking into account the resolution of the AEM. Because of the extreme instability of these finely dispersed particles, most XRD results characterize the interaction between the object and the researcher (sample preparation problems) rather than the original characteristics of the particles. The perfect separation of pure monomineralic fractions from these very fine-grained mineral aggregates is practically impossible. Consequently, our knowledge of the mineral chemistry of these phyllosilicates is based mainly on the interpretation of data obtained from mixtures of mineral phases or from "fortunate," more or less monomineralic, occurrences of a given mineral. However, the genetic relations of these latter occurrences generally strongly differ from those of common sedimentary rocks and their incipient metamorphic equivalents. Some of the open questions related to these specific features are discussed below.

It is generally accepted that dioctahedral and trioctahedral *smectites* form two distinct groups during sedimentation. This initial distinction is decisive during the whole range of phyllosilicate evolution, disregarding the mechanisms of aggradation. Although considerable deviations from ideal di- or trioctahedral compositions are common, there are no continuous transitions between the two basic structural groups. By contrast, there are only sporadic direct observations on the nature of (hydrated) interlayer cations of smectites from pelitic sediments and sedimentary rocks. Recently, in addition to the predominating hydrated  $\text{Ca}^{2+}$  and  $\text{Na}^+$ , the presence of  $\text{K}^+$  has also been postulated (Buatier et al. 1992; Freed and Peacor 1992; Masuda et al. 1996; Merriman and Peacor 1999). In addition,  $\text{NH}_4^+$  content is generally disregarded in analysing the chemistry of smectites, and also of other phyllosilicates. However,  $\text{NH}_4^+$ , made available by early alteration of organic matter finely dispersed in sediments, may be fixed in the interlayer, causing special problems when interpreting illite "crystallinity" and cell dimensions of dioctahedral white micas in evolved rocks.

Mineral-chemical estimates drawn indirectly from bulk clay-mineral analyses often differ significantly from direct AEM observations. As a consequence, controversial views were published on net negative charge and interlayer occupancy of *illite layers in Illite/smectite (I/S) interstratified clay minerals*. Originally, Hower and Mowatt (1966) extrapolated 0.75 K p.f.u. (i.e., per  $\text{O}_{10}(\text{OH})_2$ ) for end member illite, using bulk chemical and XRD data on interstratified I/S. Srodon and Eberl (1984), using a similar estimation technique, postulated that an early type of illite layer with ca. 0.55 K p.f.u. formed in smectite-dominant random interstratified I/S and a late 1 K p.f.u.-type illite was found in the ordered IIS type I/S. They supposed that both types of layers were preserved also in the evolved I/S and illites, similarly to the preservation of octahedral layers throughout the entire interstratified series. Thus, according to Srodon and Eberl (1984), solid phase transformation rather than dissolution and crystallization is the ruling mechanism in

phyllosilicate evolution. Nadeau and Bain (1986) concluded that illite layers in I/S do not have a unique value but a range of 0.5-0.9 p.f.u. layer charge with a mean of 0.76. By contrast, Eberl and Srodon (1988) and Srodon et al. (1992) determined a unique layer charge of 0.9-0.89 p.f.u. for illite of I/S of various origin. These latter conclusions were based on the fundamental particle theory of Nadeau et al. (1984a,b,c), using XRD and TEM data for calculating the I/S proportions. Considering XRD, TEM, AEM and other analytical data, Ransom and Helgeson (1993) concluded that the layer charge of illite or illitic layers may vary between 0.5 and 0.9 p.f.u. Dioctahedral aluminous illite and smectite form two separate solid solutions. Thus, there is no mutual solid solution corresponding to interstratified I/S. Cautiously selected data have shown that limited dioctahedral-trioctahedral and dioctahedral-vacancy compositional variations may occur in both minerals. Thus, in contrast to the wide overlaps plotted by gross (bulk) analyses of clay minerals (i.e., impure samples), smectite and illite occupy more restricted and differing compositional planes.

It is evident that, in addition to smectitic interstratifications (the effect of which on illite "crystallinity" have been frequently eliminated by glycolation and/or deconvolution of the basal reflections), the various contents of interlayer K may considerably affect illite "crystallinity." Recent issues prove that most probably, the amount of K should increase with increasing grade (temperature) (Hunziker et al. 1986; Livi et al. 1997).

The values of FWHM of illite basal reflections may be significantly modified not only by the quantity of interlayer K, but also by the kind, mixtures and proportions of the interlayer cations. This feature may eventually lead to erroneous petrogenetic interpretations. Therefore, rock samples that contain *paragonite* and/or *margarite* either forming discrete, sometimes intimately intergrown phases or interstratifications, should be excluded from the "crystallinity" studies (Frey 1987). However, the detection of these phases/components depends on the amounts of illite, paragonite and margarite. Routine, serial XRD studies may easily overlook very small portions of Na- or Ca-rich mica, which, in turn, may cause considerable peak-broadening and shift in IC. At higher anchizonal and epizonal grades, paragonite (and also margarite) usually forms separate phases, the identification of which is much easier than that of the interstratified K/Na-rich micas. At these grades, equilibrium solid solution of Na in muscovite and K in paragonite is extremely limited (for extensive reviews see Guidotti et al. 1994a,b). By contrast, at diagenetic and lower anchizonal grades metastable *K/Na-rich micas* were described by Li et al. (1994) and Livi et al. (1990, 1997). On the basis of poorly developed, intermediate basal reflections, Frey (1969) originally determined that these micas were ordered paragonite/phengite interstratifications, which according to recent, integrated TEM/AEM and XRD studies, actually correspond to cation-disordered homogenous mica of intermediate composition (Li et al. 1994). Livi et al. (1997) dispute the proof of these homogenous mixed micas of intermediate composition. These nanometre-scale Na/K-rich micas together with eventual brammalite evolve to discrete muscovite, paragonite and margarite through the anchizone to the epizone (Livi et al. 1997).

According to recent studies (see Drits et al. 1999), *NH<sub>4</sub>-rich illite (tobelite)* may be frequently found in metapelites, especially in metaclastic, marly rocks rich in interdispersed organic matter. The spacing of the first basal reflection of tobelite (10.3 Å) is nearly the same as that of illite-muscovite (~10 Å). Thus, considering nonproportional quantities of these minerals, their discrimination by XRD alone is unrealistic. The relation of tobelite to illite is unknown at present: they may form a solid solution, although no data exist on their mixing properties. One may speculate that metastable mixing could occur similarly as the Na/K micas characterized above. Consequently, homogenous, metastable K-NH<sub>4</sub>-rich illite or mica, or random ordered

illite/tobelite may form as well. The contribution of an  $\text{NH}_4$ -bearing phase or component to illite or muscovite should significantly influence the shape of the basal reflections, and may cause a small but systematic increase in FWHM that, in turn, may lead to petrogenetic misinterpretations. Although the identification of  $\text{NH}_4^+$  being present in subordinate quantities in illite and muscovite is practically impossible by conventional XRD analytical methods, infrared adsorption (IR) and Fourier transform infrared (FTIR) spectroscopy may help to identify and locate  $\text{NH}_4^+$  for simple modal compositions. The evaluation of  $\text{NH}_4$ -rich illite and its significance in diagenesis and incipient metamorphism is perhaps one of the greatest challenges that researchers will face in the near future. For this, electron energy loss spectroscopy (EELS) is the obvious method of choice (Livi and Abad 2000).

Thus the classical evolution scheme of (Ca-, Na-rich) smectite-illite/smectite-(K-rich) illite-(K-rich) muscovite should be replaced by a more complex multiphase/multicomponent model, in which K-rich smectite, Na-,  $\text{NH}_4$ - and Ca-rich illite and white mica also play significant roles.

Trends somewhat similar to those discussed above for dioctahedral hydrous phyllosilicates can be assumed also for the chemical and structural evolution of *trioctahedral hydrous phyllosilicates*, namely from *trioctahedral smectite* (commonly, saponite and iron saponite) through various (random or ordered) *interstratified chlorite/smectite (C/S)* and *chlorite/vermiculite (C/V)* to *chlorite*. Thus, for example, EMP analyses showed a continuous increase of  $^{\text{iv}}\text{Al}$  in the chlorite structure with increasing grade (temperature). This feature has been used as a geothermometer [Cathelineau and Nieva 1985; Cathelineau 1988; and many others (for a comprehensive review of chlorite geothermometers see De Caritat et al. 1993)]. By contrast, TEM/AEM studies showed that the chemistries of true chlorite stacks do not change systematically with grade (Jiang et al. 1994). Instead, the proportion of impurities providing swelling (smectitic) interstratifications decreases with increasing temperature, which, considering the chlorite + chlorite/smectite mixture as a whole (as EMP study does), may result in an increase of  $^{\text{iv}}\text{Al}$  content, simply on the basis of chemical differences between chlorite and smectite (see also Árkai and Sadek Ghabrial 1997; Schmidt and Livi 1999; Árkai et al. 2000).

In addition to the common, well-known evolution trend of trioctahedral phyllosilicates to chlorite, the appearance of *berthierine* in certain metasediments increases the complexity of the process (Mata et al. 2001). Berthierine, which (at least in moderate quantities) is easily overlooked by XRD when chlorite is dominant, has been observed by TEM/AEM. Further research is needed to establish bulk chemical constraints as well as the stability/metastability relations of chlorite and berthierine.

Mostly the effects of sample preparation techniques, i.e., the modifying effects caused by the interaction between researchers and objects, are real and involves debate between the theory of conventional "MacEwan crystallites" versus that of "fundamental particles" of interstratified clay minerals. The theory of fundamental particles elaborated by Nadeau and his co-workers (Nadeau et al. 1984a,b,c; Nadeau 1985; Nadeau and Bain 1986; Nadeau 1998) explains the XRD signatures of interstratified layers by interparticle diffraction. During sample preparation of clay fractions for XRD or TEM, particles of interstratified layers split along the weakest coherency, along which single-crystal-like illitic fundamental particles were attached to each other incoherently, in a turbostratic way, corresponding to a smectitic interlayer. These fundamental particles measured by TEM on separates prepared from dilute clay fractions of rocks were used to obtain conclusions on the chemistry of illite/smectite (Srodon et al. 1992) and has been preferentially applied in clay mineralogy during the last 15 years.

Veblen et al. (1990), Dong and Peacor (1996), and Peacor (1998) questioned the validity of the fundamental particles theory of Nadeau, on the basis of TEM data obtained from quasi-undisturbed whole-rock samples prepared by ion-milling. Their data proved coherency across smectite and illite interlayers and showed also incoherency within larger illitic stacks. As to their interpretation, sample preparation methods conventionally used to XRD and Pt-shadowing TEM techniques may create artifacts (i.e., fundamental particles as coherent crystallites). The relation of these fundamental particles to the crystallites (coherent domains) in the undisturbed rock matrix can and should be questioned and may at least be indirect.

Other aspects of mechanical sample preparation and separation on properties of clay-size phyllosilicates were presented by Jiang et al. (1997) and Li et al. (1998). They demonstrated that, in metapelitic whole-rock samples prepared by ion-milling, mean crystallite size of illite-muscovite measured by TEM on selected (authigenic) matrix portions may be 6 times larger than those obtained from the <2- $\mu\text{m}$  SED grain-size fractions directly by TEM, or indirectly, using the Scherrer equation or the modified Voigt method for XRD line-profile analysis. Not ruling out the possible contributions of other factors to this effect, it seems obvious that sample preparation may produce artifacts which could seriously modify the original features (in this case, crystallite size distributions) of phyllosilicates. Further clarification is needed in this respect.

### REACTION PROGRESS OF PHYLLOSILICATES THROUGH SERIES OF METASTABLE STAGES

Based on recent reviews (see e.g., Peacor 1992; Merriman and Peacor 1999), thermodynamic equilibrium can be attained in phyllosilicate-bearing rocks at around the onset of the epizone ( $\approx$  greenschist facies), i.e., at 300-350°C, according to rough estimates. These equilibrium states are documented by mineral-chemical, mineral-structural and rock textural features. In general, the ranges of isomorphic substitutions in coexisting minerals decrease, i.e., miscibility gaps increase with decreasing temperature (for micas, see Guidotti 1994a,b).

At grades lower than the epizone, i.e., in the anchizone and diagenetic zone, increasing chemical heterogeneity can be observed, jointly with structural features also compatible with increasing disorder (decreasing crystallite size, increasing lattice strain and imperfections). All these features imply that phyllosilicates in diagenetic and very low-grade metamorphic conditions do not reflect thermodynamic equilibria. Instead, phyllosilicates in these rocks occur as metastable phases. Their crystallization is controlled not only by temperature, but also by kinetic factors, following the Ostwald Step Rule (Essene and Peacor 1995). An important statement has been made by these latter authors, using the pioneering conclusions of Lippmann (1981, 1982) on the thermodynamic status of clay minerals and a vast amount of TEM, AEM and microtextural features of diagenetic and low-temperature metamorphic phyllosilicates. Essene and Peacor (1995) have stated that these materials represent indeed high surface-energy and high free-energy (also high entropy) metastable phases between the equilibrium state end members, namely pyrophyllite and muscovite (or talc and chlorite). By mostly dissolution of metastable smectites other metastable phases crystallize (e.g., I/S, C/S or illite), instead of stable muscovite and chlorite. Thus, sequences of metastable phases may form and persist with increasing temperature. The related series of reactions that act during diagenesis and very low-grade metamorphism is strongly controlled by kinetic factors, in addition to temperature and pressure. Consequently, the structural and chemical characteristics of these metastable phases can not serve as a basis for geothermometers or geobarometers (that would require equilibrium states and

equilibrated mineral assemblages). These metastable phases are only qualitative indicators of the stages the investigated rock system has reached through a series of metastable mineral reactions.

### CONCLUDING REMARKS

All of the parameters used for characterizing the phyllosilicates in the very low-grade metamorphism (illite and chlorite "crystallinity" indices, mean crystallite size and lattice strain, proportion of swelling interstratifications, proportion of metastable and stable polytypes, and also the so called chlorite geothermometers elaborated on the basis of polytypes, chemistry of chlorite, etc.) are suitable tools for monitoring the reaction progress, but not for quantitatively estimating the temperature. However, surprisingly good and consistent correlations have been found between phyllosilicate characteristics, metabasite mineral facies and organic maturity parameters (for reviews see Kisch 1983, 1987; Árkai 1991; Merriman and Frey 1999). These rather strong correlations suggest that the kinetic factors that have acted in the various geological systems might be similar.

Evaluation of the advantages and disadvantages of XRD and TEM techniques shows that integrated application of these methods may provide mineralogically well established petrogenetic information on low-grade metamorphic changes of phyllosilicates. The often conflicting results, best exemplified by the long-lasting debates between the theories of "MacEwan crystallites" and "fundamental particles" reflect mainly the effects of sample preparation techniques applied, i.e., the modifying effects caused by the interaction between researchers and the materials in those cases, when the size of the investigated mineral particles is near or at the lower size limits of minerals.

Critically reviewing the recent mineralogical and petrological data on diagenetic and incipient metamorphic evolution paths of hydrous phyllosilicates, in the present paper we have focused the attention on the two, rather distinct evolutionary trends:

- dioctahedral smectite → random and/or ordered interstratified I/S clay mineral → illite → white K-rich mica (muscovite), and
- trioctahedral smectite → C/S (random and/or ordered: corrensite) → chlorite/corrensite → chlorite.

Because of the lack of relevant chemical and structural data on smectites from pelitic sediments and early diagenetic rocks, further research is needed to determine if the path toward and along one of these two series is pre-determined by the previously available (detrital or authigenic) smectites. In other words: do transitional dioctahedral-trioctahedral smectites exist in common sediments? Moreover or alternatively, are the fates of the two divergent prograde series controlled by local changes of the fluid and rock chemistries?

Phyllosilicate evolution in both prograde series is characterized by the decrease of swelling interstratifications, increase of ordering of interstratification, increase of mean crystallite size and decrease of lattice strain, and by formation of stable polytypes with increasing grade. These structural changes are accompanied by systematic changes in mineral chemistry, the main features are discussed in detail. Evolved mica and chlorite form through metastable phases produced by disequilibrium processes also controlled by kinetic factors. Therefore, all the methods, which are based on certain varying structural or chemical properties of these metastable phases, express only the stage the evolution process has reached during the reaction progress involving phyllosilicates. They are therefore inadequate for quantitative geothermometric and geobarometric purposes in the strict thermodynamic sense.

Contrary to the early, oversimplified views on phyllosilicate assemblages of very

low-grade metapelites, recent studies unequivocally show that metastable polytypes and phases including interstratified clay minerals are present also in anchizonal conditions, and diminish only approximately near to the onset of epizone (greenschist facies). Instead of the rather "clear" schemes of (Ca,Na)-bearing dioctahedral smectite  $\rightarrow$  I/S  $\rightarrow$  K-bearing illite  $\rightarrow$  muscovite, and trioctahedral smectite  $\rightarrow$  C/S  $\rightarrow$  chlorite, the effects of various interlayer cations like  $K^+$ ,  $Na^+$  and  $NH_4^+$  and the presence of berthierine should also be taken into consideration when illite and chlorite "crystallinity" indices are used.

All the aspects discussed in this review suggest that instead of using only a given specific method for a certain lithotype, the integrated use of all possible parameters from various lithotypes better monitor the metamorphic grade and may lead to more realistic petrogenetic interpretations. Such a complex, integrated approach may allow for the necessary screening of the applicability of various methods.

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