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An attempt to correlate HRTEM and XRD determination of coherent scattering domain size of illite-smectite interstratification using «illite crystallinity»

by

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Dédié à Bernard Kübler,
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Thank you Bernard

Abstract.–JABOYEDOFF M., † KÜBLER B., STADELMANN P., and THÉLIN Ph., 2001. An attempt to correlate HRTEM and XRD determination of coherent scattering domain size of illite-smectite interstratification using «illite crystallinity». *Bull. Soc. vaud. Sc. nat. 87.4*: 305-319.
The relationships among the Kübler Index (KI), coherent scattering domain thickness, and HRTEM data are examined, using careful modeling of X-ray diffraction (XRD) patterns of air dried, glycolated, and heated samples of interstratified illite-smectite (I-S) from a stylolitic marly limestone. The XRD spectra are decomposed assuming that I-S consists of illite particles can be separated along expandable interlayers; there are also small amounts of two discrete phases mica phases and maybe pyrophyllite. The values obtained for coherent diffraction domain thickness of I-S are compatible with results obtained by HRTEM.

Keywords : Kübler Index, HRTEM, XRD, decomposition method, I-S.

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Résumé.–JABOYEDOFF M., † KÜBLER B., STADELMANN P. et THÉLIN Ph., 2001. Essai de corrélation entre les déterminations par HRTEM et XRD de la dimension des domaines de diffraction des interstratifications illite-smectite. *Bull. Soc. vaud. Sc. nat. 87.4*: 305-319.
La cristallinité de l'illite (IC) ou index de Kübler permet d'évaluer la dimension moyenne des domaines cohérents de diffraction d'illite faiblement interstratifiée avec de la smectite. Sur la base d'une interprétation sommaire de l'IC, il est possible de réaliser des décompositions plus fines des profils de diffraction séchés à l'air, glycolés et chauffés. La procédure de décomposition des spectres de diffraction est systématique et s'appuie sur des simulations du programme Newmod. Elle a été appliquée à la fraction argileuse d'un échantillon de calcaire stylolitique. Les résultats sont d'une remarquable cohérence avec ceux provenant de la microscopie électronique à transmission.

L'accord entre les deux méthodes (microscopie et diffraction) laisse supposer que les pics de diffraction mesurés par la cristallinité de l'illite sont composés de contributions provenant d'un interstratifié illite-smectite, dont une partie a pu se cliver le long des couches gonflantes introduites artificiellement lors de la préparation de l'échantillon. De plus une composante de micas détritiques est présente. Un pic de pyrophyllite a dû être ajouté pour obtenir une bonne correspondance entre résultats expérimentaux et simulations, sa présence restant conjecturale.

Mots-clés: Index de Kübler, HRTEM, diffraction X, méthode de décomposition, I-S.4

Résumé étendu.–Dès la fin des années 50, les transformations successives des smectites en minéraux argileux (minéraux de très petite taille $<2\times10^{-3}$ mm) du type interstratifiés illite – smectite (I-S), puis en illite a été documentée dans le cadre de la prospection pétrolière. Le degré de cette transformation augmente généralement, avec l'enfouissement des sédiments à quelques exceptions près. Ces transformations minéralogiques font, de façon schématique, disparaître les argiles en feuillets de type «mica de charges faibles», qui ont la possibilité de gonfler par absorption d'eau au sein même de leurs structures en lamelles, et les «métamorphosent» en argiles non gonflantes de charge plus élevée. Ces transformations modifient souvent les formes et les tailles des argiles.

Idéalement, si l'enfouissement augmente suffisamment, et par conséquent également la température, ou si les sédiments sont impliqués dans une orogenèse, les transformations aboutissent à des phengites qui sont des micas riches en silicium et dont les tailles sont observables à l'œil nu.

L'illite s.l. correspond à un stade intermédiaire entre les I-S et la phengite; elle peut contenir jusqu'à 5% de couche de smectite (S). Elle peut se définir comme un mica mal cristallisé de la fraction granulométrique des argiles, qui contient encore quelques couches gonflantes. Notons que pour les minéralogistes, l'illite s.s. est un minéral pur qui ne gonfle pas, mais qui est une des composantes des interstratifiés I-S, ce qui est cohérent avec la terminologie I-S. Celle-ci distingue en effet les feuillets gonflants (smectite) des feuillets non gonflants au sein même des empilements. Très tôt les études dédiées aux I-S et à leurs transformations furent principalement abordées par la méthode de diffraction des rayons X (XRD) sur poudres orientées.

L'augmentation en température des sédiments provoque la diminution de la capacité des I-S à absorber des molécules d'eau, ce qui s'exprime par la diminution d'épaisseur des feuillets. La diffraction des rayons-X montre alors une migration de certains pics de diffraction qui caractérisent ces espacements. La migration cesse lorsque la transformation atteint le stade illite s.l. L'espacement entre les feuillets est alors d'environ 10 Å (10^{-9} m). A ce stade, les pics de diffraction sont larges et s'effilent avec l'augmentation de la température, ce qui signifie que l'épaisseur des domaines cohérents de diffractions augmente (nombre de feuillets qui peuvent diffracter de façon cohérente, c'est-à-dire parallèle) et que les dernières couches gonflantes disparaissent des illites s.l. La mesure de la largeur des pics de diffraction à 10 Å, que l'on appelle communément à tort «la cristallinité de l'illite (CI)» permet de suivre l'augmentation de «taille» des illites s.s. La CI, appelée aussi «Kübler Index», diminue donc avec l'augmentation de l'intensité du métamorphisme.

Cette méthode a été mise au point de 1964 à 1967 par Bernard Kübler, décédé le 16 septembre 2000; raison pour laquelle cet article, auquel il a participé, lui est dédié. Bernard Kübler a appliqué cette méthode dans la prospection pétrolière; elle permettait de mettre en évidence les zones stériles qui se trouvent au-delà de la fenêtre à huile, c'est-à-dire des roches ayant subi des conditions de température, durant une période suffisamment longue, pour lesquelles la stabilité des hydrocarbures exploitables est dépassée.

Dès les années 70, les axes de recherches qui concernent la transformation des I-S en illite ont souvent porté sur des problèmes tels que:

– La simulation des spectres de diffraction orientés
– La compréhension des mécanismes de transformation
– L'imagerie des I-S au microscope électronique à transmission (MET)
– La comparaison des résultats XRD - MET

Toutes ces questions ne possèdent pas de nos jours de réponses définitives. Il n'existe en effet pas de modèle satisfaisant de transformation, principalement parce que les milieux de transformation des I-S sont variés et que les mécanismes changent en fonction des caractéristiques du milieu. Pourtant la question centrale est de savoir si les transformations se produisent par dissolutions-cristallisations successives ou par des transformations à l'état «solide» (dissolution à l'échelle cristalline). Il est vraisemblable que ces deux modes de transformation coexistent à des degrés divers. Si cette question n'est pas encore tranchée, c'est en partie à cause des observations XRD qui ont toujours montré une perte progressive des couches gonflantes des I-S. Avec un mécanisme de dissolution, on s'attendrait à un changement sans transition de la smectite à l'illite. La réponse se trouve peut-être dans le fait qu'on ne sait pas très bien distinguer entre monocristal et cristaux adjacents avec des surfaces cohérentes pouvant être confondues avec une continuité intra-cristalline. Cette remarque souligne le rôle important des énergies de surfaces.

Les images et études MET ont permis de montrer que des I-S existaient effectivement, mais qu'il était difficile de connaître leur nature chimique et de distinguer notamment la charge des surfaces et des inter-couches gonflantes (S) des I-S. La comparaison détaillée des résultats XRD et MET n'a pas été jusqu'à présent concluante pour ces raisons. On ne sait pas très bien si l'on mesure exactement les mêmes paramètres par les deux méthodes. De plus les XRD moyennent l'observation alors que le MET fournit des résultats à l'échelle atomique.

Les I-S sont-ils de simples empilements de cristaux d'illite s.l. pure au sens des minéralogistes, dont les interfaces auraient un comportement de couches gonflantes similaire aux smectites, ou faut-il considérer que les I-S sont des minéraux à part entière?

Cette question reste encore d'actualité, non seulement parce que le statut des I-S et de leurs transformations restent en partie incompris, mais aussi parce que lorsqu'on analyse des minéraux naturels, dans la plupart des cas les minéraux ne proviennent pas d'une seule source, par exemple on trouvera dans un échantillon des illites s.l. et des micas détritiques, les datations radiométriques attestant généralement de ces mélanges. Il n'est donc pas simple d'élucider leurs relations, ceci d'autant plus, que lorsque le métamorphisme augmente, les second disparaissent au profit des premières. C'est la raison pour laquelle il faut essayer de trouver une interprétation commune aux images MET et aux résultats XRD, et de mettre en évidence les différentes composantes des systèmes.

Le présent article rapporte un résultat partiel, qui met en évidence la possibilité de concilier les résultats XRD analysés à l'aide de simulations et les résultats MET. Ils tendent à montrer que les épaisseurs de I-S estimées à partir de la décomposition de diffractogrammes en utilisant des simulations XRD sont compatibles avec les observations d'image MET. Ceci tend à montrer que les observations XRD restent une source d'information valable pour l'étude des transformations des I-S.

Introduction

The Kübler index (KI) was developed during the 1960's as an empirical indicator of incipient metamorphism (Kübler 1967). KI is the illite 10-Å X-ray diffraction (XRD) peak full width at half maximum (FWHM) measured on air-dried (AD) XRD patterns of < 2 μm clay size fractions. It has been used to quantify progressive metamorphic reactions of subgreenschist facies pelitic rocks (Kübler 1984; Merriman and Frey 1999). KI characterizes interstratified illite-smectite (I-S) with a low smectite layers content (%S). For convenience, the term KI is used as metamorphic descriptor, while when the subject is about XRD, the FWHM of the 10-Å peak will be named Illite Width (IW), independently of the sample treatment. The IW measured on air-dried (IWAD) XRD patterns is equivalent to the illite Kübler Index (KI=IWAD). The IW depends on two main factors, the thickness or the number of layer N of the coherent scattering domain (CSD), the proportion of swelling interlayers (%S) within the I-S and of course of the presence of different illite or I-S populations. Lattice strain is also important, but the lack of model including both expandable layers and lattice strain does not allow a fine comparison of this effect between XRD and HRTEM methods. Furthermore, the expandable layers effect is greater than strain effect.

I-S may be considered as stacked packets of consecutive illite layers separated by swelling interlayers, where the illite packets correspond to the fundamental particles of Nadeau *et al.* (1984, 1985). This interpretation reconciles the MacEwan crystallite and fundamental particle concepts (Moore and Reynolds 1997, p. 180; Altaner and Ylagan 1997; Meunier *et al.* 2000). Fundamental particles are in crystallographic continuity along c^* direction, within the I-S or the MacEwan particles (Veblen *et al.* 1990; Dong and Peacor 1996) and possess swelling interfaces (Altaner *et al.* 1988). N and %S are linked to the fundamental particle mean layer number (N_{fp}) by the relationship $N_{fp}=N/(1+ (N-1)\times(\%S/100))$ (Srodon *et al.* 1990, 1992). N_{fp}, which is used to quantify low-grade metamorphic conditions, generally increases as metamorphic grade increases (Eberl and Srodon 1988; Eberl *et al.* 1987, 1990; Jaboyedoff *et al.* 2001). The ordering of the layer stacking in I-S increases as well. The ordering means that the type of a neighbor layer depends on its own type. For example, the ordering R = 1 (R: Reichweite, see Moore and Reynolds 1997) for I-S containing %S < 50% indicates that all smectite layers S have illite layers as neighbour on both sides, this means that no SS sequence can be found. For R = 3 all smectite layers are involved in ISII sequence indicating that %S ≤ 25%. R = 0 means that a layer has no effect on the type of its neighbour.

The XRD signal is produced by several crystallites, whereas high-resolution transmission microscope (HRTEM) observations are selective. As XRD methods usually show, most HRTEM studies indicate that I-S consist of two-component interstratified minerals (AHN and PEACOR 1986a, AHN and BUSECK 1990, SRODON *et al.* 1990, AMOURIC and OLIVES 1991). Often the comparison between HRTEM and XRD estimates of N or %S leads to incompatible results for small CSDs (AHN and PEACOR 1986b, BARONNET 1997, LI *et al.* 1998). However if only the interlayers are counted by HRTEM, %S values are similar to those obtained by XRD methods (SRODON *et al.* 1990, DONG *et al.* 1997).

The number of layers in CSDs obtained by HRTEM studies generally agrees with N values from KI studies, estimated by the Scherrer equation or related methods (MERRIMAN *et al.* 1990; NIETO and SANCHEZ-NAVAS 1994, MERRIMAN *et al.* 1995, ÁRKAI *et al.* 1996, DALLA TORRE *et al.* 1996, JIANG *et al.* 1997). Some discrepancies may arise where data derived from HRTEM measurements on whole-rocks are compared with XRD data from < 2 μm size fractions (WARR and NIETO 1999).

The purpose of this paper is to show that by using IW values measured on both AD and ethylene-glycol (EG) patterns, it is possible to model the raw XRD data with a set of simulated XRD patterns that agree with N values measured from HRTEM images, by careful decomposition of XRD patterns using a quick and simple approach.

MATERIALS AND METHODS

Sample description

The studied sample is a stylolitic marly limestone from the Couches Rouges of the Préalpes Médianes Rigides nappe in the northwest Swiss Alps (ESCHER *et al.* 1997; see JABOYEDOFF and THÉLIN (1996) for sample location: Dreveneuse). In this unit the KI values increase toward the southeast from diagenetic to anchizonal values (JABOYEDOFF and THÉLIN 1996). The studied sample underwent deep diagenetic conditions. The clay minerals are located with quartz within stylolites, which are about 10 μm thick. The total XRD rock analysis indicates approximately 75% calcite 15 % quartz and 10 % clays and ~1% albite (JABOYEDOFF and THÉLIN 1996). The clay fraction is mainly composed of illite (including I-S with I% > 90%), with small quantities of chlorite and a small amount of smectitic material, kaolinite is suspected but not proved (note that in the paper JABOYEDOFF and THÉLIN (1996) a large amount of kaolinite was erroneously reported for this sample D4). The clay mineralogy of the < 2 μm size fraction presents more clays.

XRD Methods

The sample was first treated with 2M HCl for 20 minutes, followed by washing and dilution to a pH of 5.6. The <2 μm size fraction was obtained by centrifugation. The clay suspensions were then exposed to a 1M $CaCl_2$ solution two times during 24h. XRD data were collected with a Rigaku horizontal powder diffractometer (18.5 cm radius, Cu$K\alpha$ radiation, nickel filter, 0.5° divergent and scatter slits, 0.15 mm receiving slit and two Soller slits of 5°). Operating conditions were 40 kV and 30 mA using 0.01° steps and 1 second count times. For these conditions the anchizone limits are 0.18° and 0.36°Δ2θ Cu$K\alpha$, corresponding to the standards limits epizone-anchizone of 0.25° and anchizone-diagenesis of 0.42°Δ2θ Cu$K\alpha$ defined by KÜBLER (1967), (KISCH 1991).

The IW measurements of XRD patterns from EG and heat-treated specimens, corrected for instrumental broadening, permit determination of N and %S. Corrected IW values are plotted on a graph of IWAD versus IW, measured on glycolated XRD spectra (IWEG), from which isolines of mean N, mean of %S and N_{fp} are included. Around two hundred Newmod© simulations (REYNOLDS and REYNOLDS 1996) are necessary to create this chart (JABOYEDOFF *et al.* 2001). Assuming that the swelling interlayers are smectite, they can be considered to contain 2 planes of water (2w) for the AD specimen and 2 planes of ethylene-glycol (2g) for the EG specimen, and none for the heated specimen. IW2w-IW2g plots were established for R = 0, R = 1 and R = 3 I-S (fig. 1) (JABOYEDOFF *et al.* 2001, JABOYEDOFF *et al.* 1999). These plots can be used to determine *N* and %S on natural samples of I-S by making measurements of IWAD and IWEG (fig. 1). The peak broadening caused by lattice strain are not taken into account by this method. The results of the method described above can be used to compare calculated XRD patterns directly with experimental ones. To obtain acceptable fitting of all three patterns types, the initial N and %S results are refined.

To use the plots described above, the instrumental broadening must be corrected. The corrected IW (IW_c) is calculated by using the geometric mean of gaussian and lorentzian correction as the following expression: $IWc= ((IW-IW_i) \times (IW^2-IW_i^2)^{0.5})^{0.5}$ (BALASINGH *et al.* 1991), where IW_i is the instrumental broadening value. Using powdered mica (from U.S. Department of Commerce; National Bureau of Standards Washington, DC 20234, labeled Standard Reference Material 675 Mica Powder) assumed to be composed of perfect crystals, IW_i is estimated to 0.09 °Δ2θ Cu$K\alpha$. Because no interlayer ordering higher than R = 1 is observed in the Alpine area studied (JABOYEDOFF and THÉLIN 1996), we use a R = 1 plot.

The results obtained by the plot shown in figure 1 can be refined by decomposition of XRD peaks assuming additional mineral components: (1) a detrital component (pure mica) which was supported in the studied lithologies

by $^{39}Ar/^{40}Ar$ ages older than the stratigraphic age and by SEM images (JABOYEDOFF and COSCA 1999); and (2) a neoformed component (I-S) which evolves toward illite with increasing incipient regional metamorphism (JABOYEDOFF and THÉLIN 1996, JABOYEDOFF *et al.* 2000). To compare results, the simulations are folded with the instrumental profile estimated using the 10 Å peak of the mica powder standard.

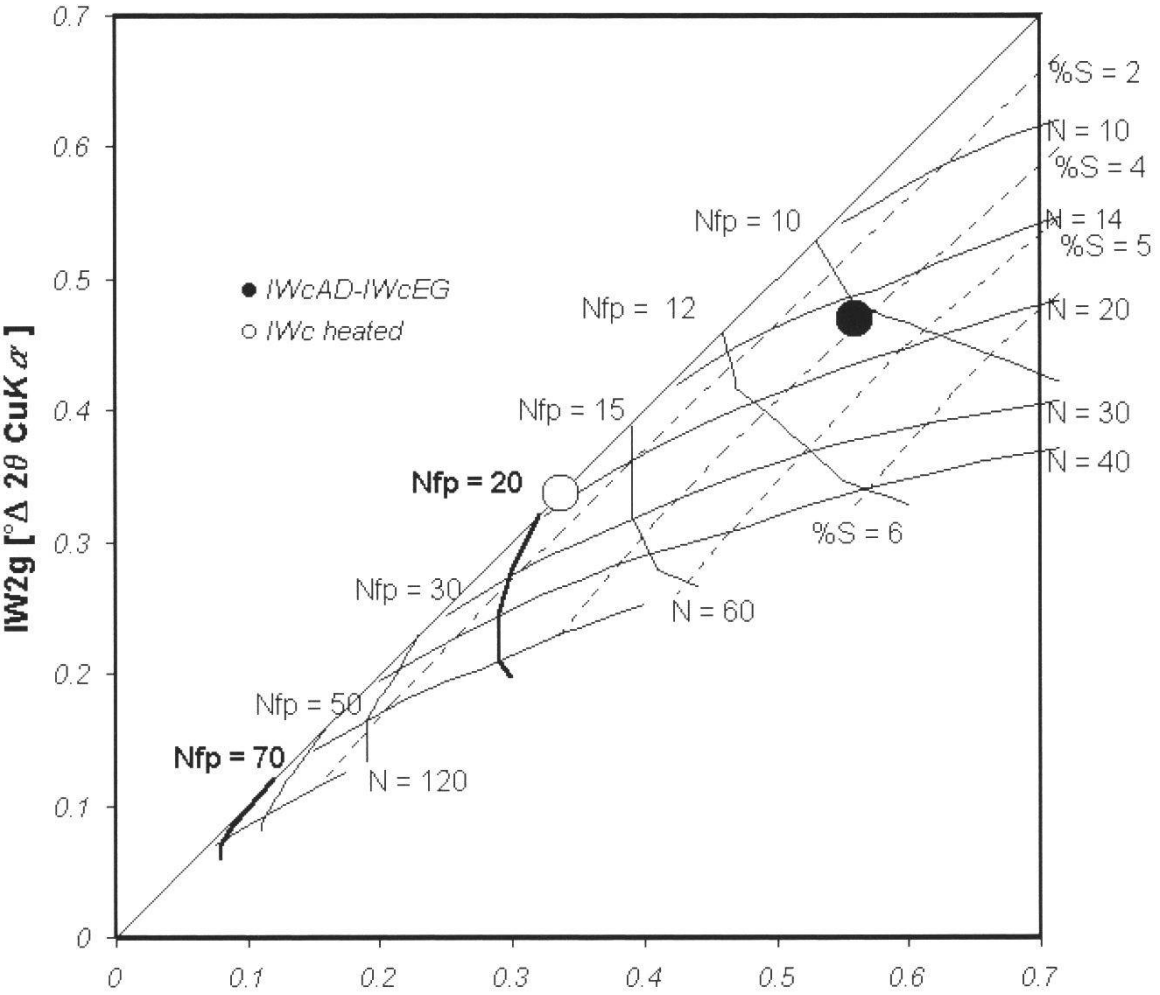

Figure 1.–Plot of illite width corrected (IW_c) for I-S containing 2 water planes (IW2w) versus IW_c for I-S containing 2 ethylene-glycol interlayers (IW2g), assuming R = 1 ordering (JABOYEDOFF *et al.* 2001). The black spot represents the IW_cAD and IW_cEG values for the studied sample and the white spot represents the IW_c for a heated sample, assuming that heated specimen is equivalent to 0% S and N is then determined using IW2w = IW2g. Anchizone limits without instrumental effect are 0.10° and 0.30° 2θ Cu$K\alpha$.

The following default Newmod parameters were used: *d* value for dioctahedral mica = 9.98 Å; dioctahedral smectite with 2 EG planes = 16.9 Å; dioctahedral smectite with 2 water planes = 15 Å; Cu$K\alpha$ radiation; Ca = exchange cation. The following adjusted parameters were used: divergent slit 0.5°, goniometer radius 18.5 cm, sample length 2.8 cm, 2 Soller slits of 5°;

illite chemistry is set to $K_{0.9}$ ($Al_{1.9}$, $Fe_{0.1}$) ($Si_{3.2}$, $Al_{0.8}$) O_{10} $(OH)_2$; smectite chemistry to $Ca_{0.17}$ ($Al_{1.66}$, $Fe_{0.1}$, $Mg_{0.24}$) (Si_4) O_{10} $(OH)_2$. Pyrophyllite was simulated using a $d(001)$ of 9.2 Å and the amount of interlayer K set to 0.

HRTEM Techniques

HRTEM analysis was performed on ion-thinned sections of the stylolites. Thin disks of limestone were mounted on a copper ring, thinned by abrasion, and then beveled by ionic bombardment. Lattice fringe images were obtained using a Hitachi HRTEM at 150 kV and 30 µA with a cold field emission source (CIME-EPFL Lausanne). The lattice fringe images were obtained near Scherzer optimal defocus.

The number of 10 Å layers was measured in each CSD observed using HRTEM. The boundaries of particles were determined based on the following features: layer stacks limited by low-angle boundary, i.e. > 2°, limit above which XRD layers are not diffracting coherently (Guthrie and Reynolds 1998). Strong differences in image intensity or rupture of periodicity were also used to delimit boundaries (fig. 2).

Results

The IW of the 10 Å XRD peak measured on the three types of treated samples of the <2 µm size fraction are: 0.61° (air-dried), 0.52° (glycolated) and 0.39° $\Delta 2\theta$ Cu$K\alpha$ (heated). After removal of the instrumental effect the IWs are 0.56°, 0.47° and 0.34° $\Delta 2\theta$ Cu$K\alpha$, respectively. Using the method outlined above, it indicates a sample comprised of 96% illite layers (it means one swelling layer for 25 layers), a mean N of 16 layers and N_{fp} = 10 (fig. 1), which indicates that on average for any 3 I-S crystallites only 2 contain one smectite interlayer. The result for heated patterns gives a number of layer N superior around 20, it was not considered for the decomposition, because the whole profiles fitting was not accurate enough, furthermore the XRD peak shape changes with heating (the base is larger and the top sharper). Decomposition of XRD patterns using Newmod simulations was done assuming the following:

1. Some of the I-S particles can be cleaved to isolated fundamental particles of approximately 10 pure illitic layers during sample treatment (e.g. Ahn and Peacor 1986a).
2. Some detrital mica consisting of a mean of twenty-five 10 Å layers is present.

The procedure of adjustment was stopped when the three different calculated patterns (AD, EG, heated) lead to an accurate matching of all three

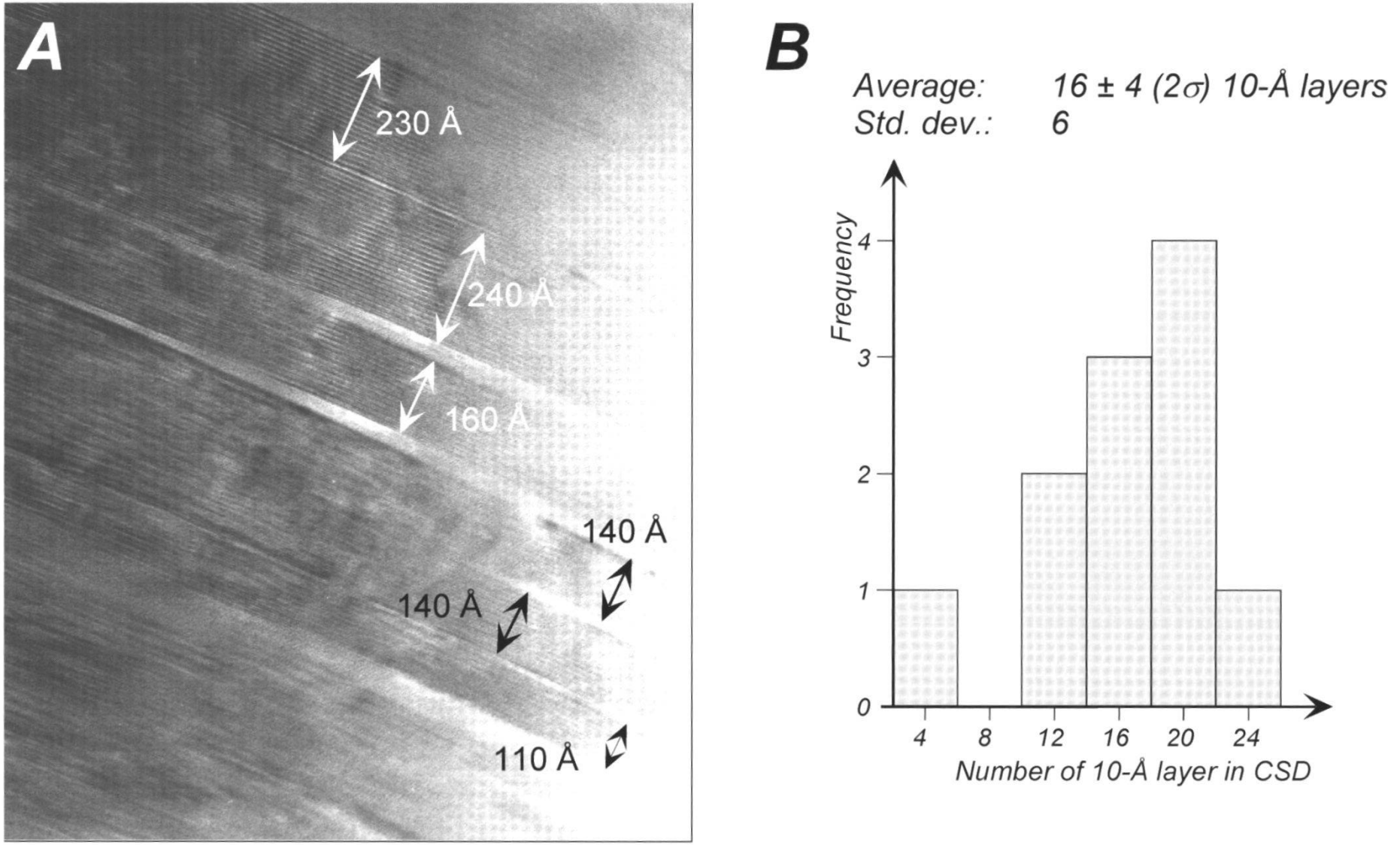

Figure 2.–HRTEM lattice fringe image of I-S from the studied sample. Several representative thicknesses are indicated. The histogram lists the frequency of different thicknesses of CSDs.

treated patterns with the same mineral components in identical proportions. The goodness of fit was estimated visually, considering the background as an important parameter. The best-fit solution was for 68% I-S containing 96% I with N= 6-26 (equally distributed, average = 16), 13% pure illite with N= 2-18 (equally distributed, average = 10) and 9% of a mica with N= 15-35 (equally distributed, average = 25) (fig. 3). The pure illite may correspond to the

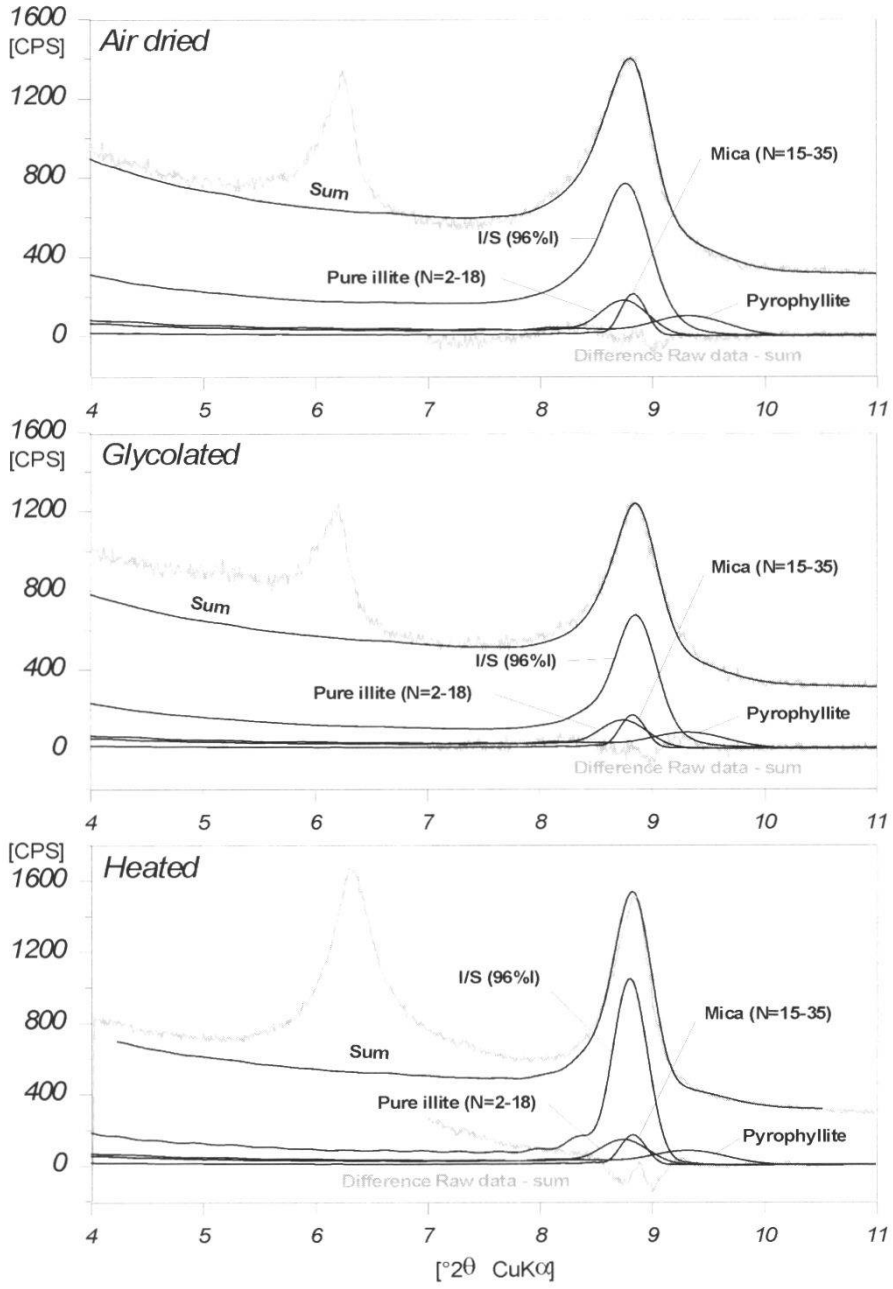

Figure 3.–Comparison of observed XRD patterns for the <2 μm size fraction of the studied sample with calculated XRD patterns for three different treatments (AD, EG, Heated). The sum of calculated patterns were convoluted with the instrumental profile. Because of this procedure and the use of the default *d* value of Newmod, we have shifted the AD pattern by 0.02° and the heated preparation by 0.04° to achieve a close match to peak positions. For the AD pattern, this small shift is acceptable, because it corresponds to 0.2 Å. Deformation of the sedimented slide due to heating can be the source of the discrepancy for the heated sample.

cleavage of the I-S, along swelling interlayer, into discrete fundamental particles during sample preparation. In order to obtain a good fit in the 9.3° 2θ area, we added a diffraction peaks corresponding to a hypothetical 10% pyrophyllite with N= 2-12. A pyrophyllite-like peak was used because the high angle side of the 10 Å peak does not change with the three different treatments indicating no expandable layer influence. The chlorite and the poorly crystallized expandable phase peaks are not simulated. The previous procedure does not mean that other solutions do not exist, but our results are supported by its coherency.

HRTEM lattice fringe images of 10 Å layers show cross-fringes indicating coherent layer stacking, with a partial $2M_1$ polytype stacking (fig. 4) affecting two to five consecutive layers, which was not clearly detected by XRD method. The mean thickness of N is 16 ± 4 (2σ) 10-Å layers, which is compatible with XRD results (fig. 2).

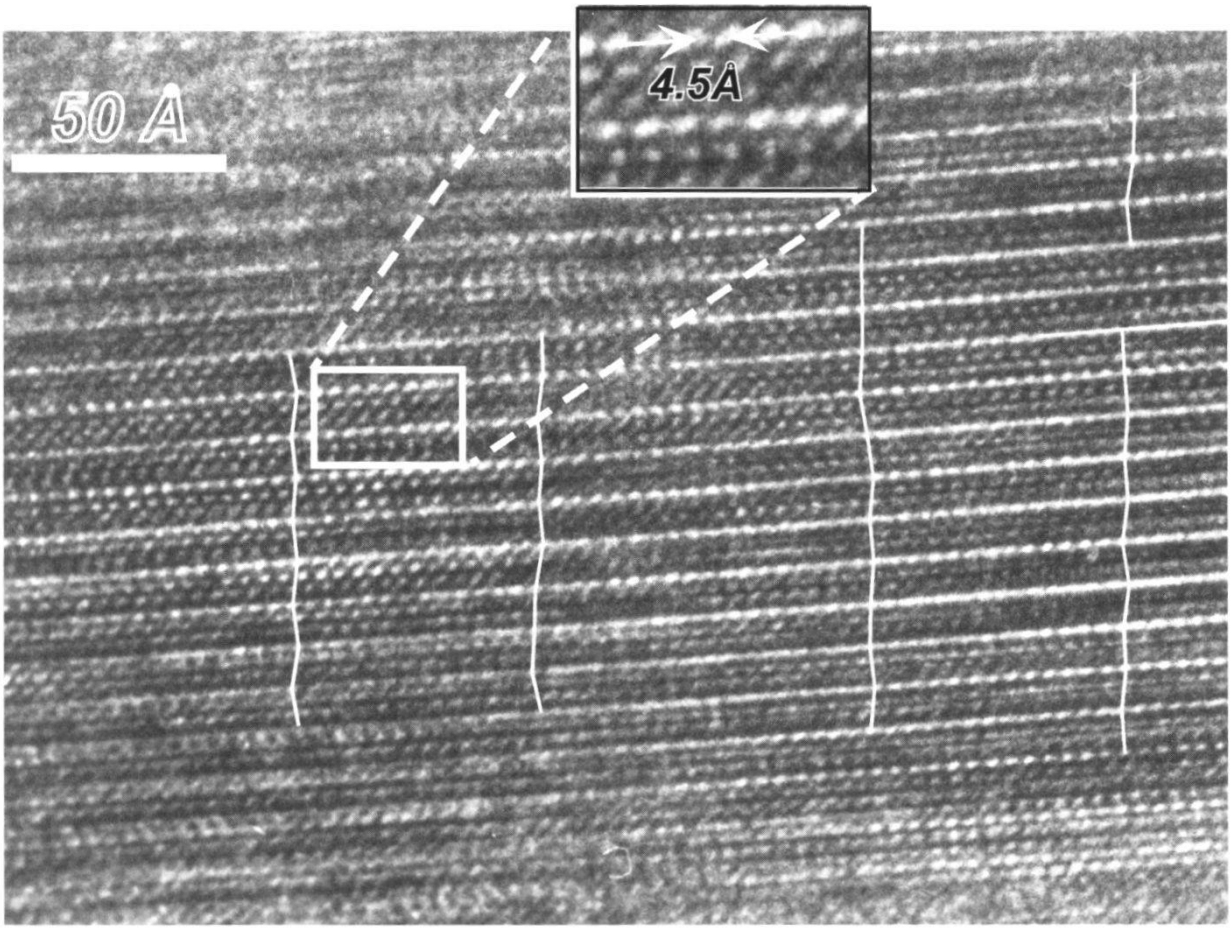

Figure 4.–Lattice fringe image of illite and I-S in the studied sample. The cross-fringes demonstrate the coherence of the stacked layers. Because of the 4.5 Å spacing in the bright strip (Ahn and Busek 1990) and by analogy with images of Amouric *et al.* (1981), the view must be along [1 $\bar{1}$ 0] or [1 $\bar{1}$ 0] of a $2M_1$ polytype. This ordering appears to be disturbed laterally by comparing the stack sequence (white breaks in the lines) and some defects may occur. The brighter spots are attributed to smectite interlayers.

Discussion and conclusion

The agreement between the three sets of calculated and observed XRD patterns supports the method of XRD peak decomposition. Furthermore, the good agreement between XRD and HRTEM determinations of N also supports this interpretation. We conclude that 13% of pure illite represents I-S that cleaved along expandable interlayers during the acid treatment considering that no mechanical breakage has occurred. The occurrence of detrital mica is confirmed by $^{40}Ar/^{39}Ar$ apparent ages and SEM observation (Jaboyedoff and Cosca 1999). The assumption of a pyrophyllite-like component is often necessary to model the region of deep diagenetic and anchizonal I-S samples. The bulge on the high angle side of the illite peak is possibly due to a change in structure factor, but is more likely due to the presence of poorly crystalline pyrophyllite (6 layers thick on average). Although pyrophyllite was not observed in HRTEM images, it is possible that some segregated layers of pyrophyllite occur. Also the probable presence of kaolinite, which exists in this location, may explain the pyrophyllite by the beginning of the reaction 1 kaolinite + 2 quartz = 1 pyrophyllite + 1 H_2O (Frey 1987).

The agreement between CSD thickness of I-S (N=16) obtained by XRD and HRTEM methods implies that during HRTEM analysis, smectite interlayers are dehydrated (N=16 including collapsed expandable layers) due either to ionic bombardment during the sample preparation or high vacuum conditions during analysis or both. This is supported by variable brightness of some interlayers as also seen by Guthrie and Veblen (1989). The $2M_1$ polytype affecting only few consecutive layers in I-S (fig. 4) seems to support a neoformation origin as previously observed by Ahn and Buseck (1990) or Amouric *et al.* (1981). Furthermore, the < 2 µm size fraction is usually dominated by neoformed minerals (Warr and Nieto 1998); this is confirmed by the evolution of the < 2 µm size fraction at a regional scale, indicating clearly a KI decrease with increasing metamorphic conditions (Jaboyedoff and Thélin 1996). $^{39}Ar/^{40}Ar$ ages support this assumption. XRD data may be compared consistently with the HRTEM data.

Further investigation should be done, especially concerning the detection of expandable interlayers in I-S with low %S content. The IW method, in spite of the few available data, agrees well with other methods of determining CSD size in I-S such as HRTEM. As described above, simulated XRD patterns may be used to reconcile HRTEM and XRD data in future studies, by assuming three components: detrital mica, I-S and cleaved I-S.

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REFERENCES

AHN J.H. and PEACOR D.R., 1986a. Transmission electron microscope data for rectorite; implications for the origin and structure of «fundamental particles». *Clays and Clay Miner. 34*: 180-186.

AHN J.H. and PEACOR D.R., 1986b. Transmission and analytical electron microscopy of the smectite-to-illite transition. *Clays and Clay Miner. 34*: 165-179.

AHN J. H. and BUSECK P.R., 1990. Layer-stacking sequences and structural disorder in mixed-layer illite/smectite; image simulations and HRTEM imaging. *Amer. Mineralogist 75*: 3-4.

ALTANER S.P. and YLAGAN R.F., 1997. Comparison of structural models of mixed-layer illlite/smectite and reaction mechanisms of smectite illitization. *Clays and Clay Miner. 45*: 517-533.

ALTANER S.P., WEISS C.A., and KIRKPATRICK R.J., 1988. Evidence from ^{29}Si NMR for the structure of mixed-layer illite/smectite clay minerals. *Nature 331*: 699-702.

AMOURIC M. and OLIVES J., 1991. Illitization of smectite as seen by high-resolution transmission electron microscopy. *Eur. J. Mineral. 3*: 831-835.

AMOURIC M., MERCURIOT G., and BARONNET A., 1981. On computed and observed HRTEM images of perfect mica polytypes. *Bull. Minéral. 104*: 298-313.

ÁRKAI P., MERRIMAN R.J., ROBERTS B., PEACOR D.R. and TOTH M., 1996. Crystallinity, crystallite size and lattice strain of illite-muscovite and chlorite: comparison of XRD and TEM data for diagenetic to epizonal pelites. *Eur. J. Mineral. 8*: 1119-1137.

BALASINGH C., ABUHASAN A. and PREDECKI P. K., 1991. Diffraction peak broadening studies in Al_2O_3 (wishker) composites. *Powder Diffraction 6*: 16-19.

BARONNET A., 1997. Silicate microstructures at sub-atomic scale. *C. R. Acad. Sci. (Paris) 324, série IIa*: 157-172.

DALLA TORRE M., LIVI K.J.T., VEBLEN D.R., and FREY M., 1996. White K-mica evolution from phengite to muscovite in shales and shale matrix melange, Diablo Range, California. *Contrib. Mineral. Petrol. 123*: 390-405.

DONG H. and PEACOR D.R., 1996. TEM observation of coherent stacking relations in smectite, I/S and illite of shales: evidences for MacEwan crystallites and dominance of 2M1. *Clays and Clay Miner. 44*: 257-275.

DONG H., PEACOR D.R., and FREED R.L., 1997. Phase relations among smectite, R1 illite-smectite and illite. *Amer. Mineralogist 82*: 379-391.

EBERL D.D. and SRODON J., 1988. Ostwald ripening and interparticle-diffraction effects for illite crystals. *Amer. Mineralogist* 73: 1335-1345.

EBERL, D.D., SRODON J., LEE M., NADEAU P.H. and NORTHROP H.R., 1987. Sericite from Silverton caldera, Colorado: correlation among structure, composition, origin, and particle thickness. *Amer. Mineralogist 72*: 914-934.

EBERL D.D., SRODON J., KRALIK M., TAYLOR B.E. and PETERMAN Z.E., 1990. Ostwald ripening of clays and metamorphic minerals. *Science 248*: 474-477.

ESCHER A., HUNZIKER J.C., MARTHALER M., MASSON H., SARTORI M. and STECK A., 1997. Geologic framework and structural evolution of the Western Swiss-Italian Alps. *In* Deep structure of the Swiss Alps, PFIFFNER O.A., LEHNER P., HEITZMANN P., MUELLER S. and STECK A. (Ed.), 1997. Results of the NRP 20: 205-221

FREY M., 1987. The reaction-isograd kaolinite + quartz = pyrophyllite + H2O, Helvetic Alps, Switzerland. *Schweiz. Mineral. Petrogr. Mitt. 67*: 1-11.

GUTHRIE G. D. and VEBLEN D.R., 1989. High-resolution transmission electron microscopy of mixed-layer illite/smectite; computer simulations. *Clays and Clay Miner. 37*: 1-11.

GUTHRIE G. D. and REYNOLDS R.C. Jr., 1998. A coherent Tem- and XRD-description of mixed-layer illite/smectite. *Can. Mineral. 36*: 11421-1434.

JABOYEDOFF M. and THÉLIN P., 1996. New data on the low-grade metamorphism in the Briançonnais domain of the Prealps, western Switzerland. *Eur. J. Mineral. 8*: 577-592.

JABOYEDOFF M. and COSCA M.A., 1999. Dating incipient metamorphism using $^{40}Ar/^{39}Ar$ geochronology and XRD modeling: an example from the Swiss Alps. *Contr. Mineral. Petrol. 135*: 93-113.

JABOYEDOFF M., KÜBLER B. and THÉLIN P., 1999. An empirical Scherrer equation for weakly swelling mixed-layer minerals, especially illite-smectite. *Clay Miner. 34*: 601-617

JABOYEDOFF M., KÜBLER B., SARTORI M. and THÉLIN P., 2000. Basis for meaningful illite crystallinity measurements: an example from the Swiss Prealps. *Bull. suisse Minéral. Pétrogr. 80*: 75-83.

JABOYEDOFF M., BUSSY F., KÜBLER B. and THÉLIN P., 2001. Illite crystallinity revisited. *Clays and Clay Miner. 49*: 156-167.

KISCH H. J., 1991. Illite crystallinity: recommendations on sample preparation, X-ray diffraction settings, and interlaboratory samples. *J. Metamorphic Geol. 9*: 665-670.

JIANG W.-T., PEACOR D.R., ÁRKAI P., TOTH M. and KIM J.W., 1997. TEM and XRD determination of crystallite size and lattice strain as a function of illite crystallinity in pelitic rocks. *J. Metamorphic Geol. 15*: 267-281.

KÜBLER B., 1967. La cristallinité de l'illite et les zones tout à fait supérieures du métamorphisme. Etages tectoniques, Colloque de Neuchâtel 1966, Edition de la Baconnière, Neuchâtel, Suisse: 105-121.

KÜBLER B., 1984. Les indicateurs des transformations physiques et chimiques dans la diagenèse, température et calorimétrie. *In* Thermométrie et barométrie géologiques, LAGACHE M. (Ed.), Soc. Franç. Min. et Crist., Paris: 489-596.

LI G., PEACOR D.R., BUSECK P.R. and ARKAI P., 1998. Modification of illite-muscovite crystallite-size distributions by sample preparation for powder XRD analysis. *Canad. Mineralogist 36*: 1435-1451.

MERRIMAN R.J. and FREY M., 1999. Pattern of very low-grade metamorphism in metapelitic rocks. *In* Low-Grade Metamorphism, FREY M. and ROBINSON D. (Ed.), Blackwell Science, Oxford: 61-107.

MERRIMAN R.J., ROBERTS B. and PEACOR D.R., 1990. A transmission electron microscope study of white mica crystallite size distribution in mudstone to slate transitional sequence, North Wales, UK. *Contrib. Mineral. Petrol.* 106: 27-40.

MERRIMAN R.J., ROBERTS B., PEACOR D.R. and HIRONS S.R., 1995. Strain-related difference in crystal growth of mica and chlorite: a TEM and XRD study of the development of metapelitic microfabrics in the Southern Uplands thrust terrane, Scotland. *J. Metamorphic Geol. 13*: 559-576.

MEUNIER A., LANSON B. and BEAUFORT D., 2000. Vermiculitization of smectite interfaces and illite growth as a possible dual model for illite-smectite illitization in diagenetic environments: a synthesis. *Clay Miner. 35*: 573-586.

MOORE D.M. and REYNOLDS R.C. 1997. *X-ray Diffraction and the Identification and Analysis of Clay Minerals.* Oxford Univ. Press, Oxford. 396 p.

NADEAU P.H., WILSON M.J., MCHARDY W.J. and TAIT J.M., 1984. Interstratified clays as fundamental particles. *Sciences 225*: 923-925.

NADEAU P.H., WILSO M.J., MCHARDY W.J. and TAIT J.M., 1985. The conversion of smectite to illite during diagenesis: evidence from some illitic clays from bentonites and sandstones. *Mineral. Mag. 49*: 393-400.

NIETO F. and SANCHEZ-NAVAS A., 1994. A comparative XRD and TEM study of the physical meaning of the white mica «crystallinity» index. *Eur. J. Mineral. 6*: 611-621.

REYNOLDS R.C. Jr. and REYNOLDS R.C. III, 1996. NEWMOD for Windows, a computer program for the calculation of one -dimensional diffraction patterns of mixed-layered clays. Reynolds, R.C., Jr., 8 Brook Dr., Hanover, New Hampshire.

SRODON J., ANDREOLI C., ELSASS F. and ROBERT M., 1990. Direct high-resolution transmission electron microscopic measurement of expandability of mixed-layer illite/smectite in bentonite rock. *Clays and Clay Miner. 38*: 373-379.

SRODON J., ELSASS F., MCHARDY W.J. and MORGAN D.J., 1992. Chemistry of illite-smectite inferred from TEM measurements of fundamental particles. *Clay Miner.* 27: 137-158.

VEBLEN D.R., GUTHRIE G.D. and LIVI K.J.T., 1990. High-resolution transmission electron microscopy and electron diffraction of mixed-layer illite/smectite: experimental results. *Clays and Clay Miner. 38*: 1-13.

WARR L.N. and NIETO F., 1998. Crystallite thickness and defect density of phyllosilicates in low temperature metamorphic pelites: a TEM and XRD study of clay-mineral crystallinity-index standards. *Can. Mineralogist 36*: 1453-1474.

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