Per. Mineral. (2005), *74*, 1, 1-10 http://go.to/permin

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY, ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on *Environment, Archaeometry* and *Cultural Heritage*

Transformation mechanism of lamellar to lath-shaped illite/smectite: observation by SEM

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Submitted, June 2003 - Accepted, September 2004

ABSTRACT. — During investigation of the diagenetic processes which occurred in the «varicoloured» clay-shale formation along the italian Apennines strip, a lithofacies characterised by the presence of lath-shaped smectite/illite interstratification has been encountered in a zone affected by tectonic stresses; the occurrence area is located along the Sangro river valley, at the border between central and southern Italy.

Detailed SEM observations have evidenced that the clay particles show a morphological transition from flakes to laths. The change occurs via: (i) flattening and thinning of precursor wavy lamellae; (ii) formation of lath aggregates (where the laths are oriented at 60°/120° to each another) that are preserving the original flake contours; (iii) disaggregation of such aggregates into isolated disoriented laths.

Microanalytical EDAX data indicate only slight chemical changes associated with the morphotype transition, mainly concerning Mg and Al contents that are increasing-decreasing, respectively, whereas changes of Si and K amounts were not surely detectable.

Although there are some questions to be clarified (as reaction kinetics, thermal history and role of water content), the observed morphotype transformation is interpreted as a solid-state splitting mechanism, probably influenced by mechanical stresses due to tectonic events and associated chemical changes.

KEY WORDS: *smectite/illite interstratification, lamellar-to-lath morphotype transformation, solid-state splitting, tectonic stress.*

RIASSUNTO. — Nel corso di ricerche su processi diagenetici verificatesi nelle formazioni di argille-argilliti «varicolori» lungo l'Appennino italiano, è stata individuata una litofacies caratterizzata dalla presenza di un interstratificato smectite/illite con morfologia listiforme delle particelle; essa si trova in una area interessata da tettonizzazione e localizzata lungo la valle del fiume Sangro, al bordo centro-meridionale della penisola italiana.

Osservazioni dettagliate al SEM hanno evidenziato che la morfologia delle particelle argillose presenta una trasformazione da lamellare a listiforme. La transizione avviene per gradi: (1) appiattimento e assottigliamento delle lamelle originarie ondulate; (2) formazione di aggregati di particelle listiformi orientate reciprocamente a 60°/120°, che preservano i contorni delle lamelle originarie; (3) disgregazione di questi aggregati e isolamento delle particelle listiformi, che assumono orientamenti a caso.

Dati microanalitici EDAX indicano che le variazioni chimiche associate alla transizione

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morfologica delle particelle argillose sono lievi e riguardano principalmente il contenuto di Al e Mg, che aumenta-diminuisce rispettivamente; invece, non sono risultate significative le variazioni dei contenuti di Si e K.

Sebbene restino da chiarire alcuni aspetti (come la cinetica di reazione, la storia termale e il contenuto di acqua della formazione argillosa), la trasformazione morfologica osservata viene interpretata come un meccanismo di sfaldatura allo stato solido, probabilmente influenzato da azioni meccaniche causate da eventi tettonici e da modificazioni chimiche ad essi associate.

PAROLE CHIVE: *interstratificato illite/smectite, trasformazione morfologica lamellare-listiforme, sfaldatura allo stato solido, azioni tettoniche.*

INTRODUCTION

The layer silicates contained in the fine fraction of sediments evolve during burial diagenesis and anchimetamorphism (literature review in Chamley, 1989; Frey, 1987; Frey and Robinson, 1999; Peacor, 1992). Illitization of smectite via smectite/illite (S/I) interstratification(s) is a major process in such prograde evolution, and has been a focus for clay mineral research. The main processes suggested for the S-to-I transformation are: solid-state smectite illitization, dissolution of smectite and crystallization of illite, and neoformation (Srodon, 1987). The S-to-I regeneration occurs depending upon various factors: initial lithology, sedimentation «milieu», burial conditions and tectonic history. Other factors which control the reaction are temperature, pressure, K-availability, pore-fluid chemistry, permeability, fluid-rock ratio and residence time. Temperature is considered the major factor, whereas time is the least understood one (Velde and Vasseur, 1992): its duration has been estimated only through mathematical modelling approach (Elliott and Matisoff, 1996). Several factors are continuous, other are recognised as discontinuous; some mentioned works indicates that illitization of smectite is kinetically rather than thermodinamically controlled.

Such transformation has also been recognised in hydrothermal environments (Inoue *et al.*, 1992; Ylagan *et al.*, 2000) or in contact metamorphism (Leoni *et al.*, 1984); furthermore, in atmospheric (surface) conditions during wetting/drying cycles (Andreoli *et al.*, 1989). Eberl *et al.* (1993) have observed low-temperature illitization of smectite under high-pH conditions in laboratory; experimental illitization of smectite have been obtained in K-rich solutions (Mosser-Ruck *et al.*, 2001).

Controversial opinions have been presented on the effects of tectonic shear strain on phyllosilicates transformation under conditions of incipient metamorphism (Arkai *et al.*, 2002). Also the fabric may influence smectite/illite diagenesis (Howard, 1987).

As a matter of fact, the mechanisms of smectite-to-illite conversion are still matter of debate, especially the formation of metastable lath-shaped morphotypes.

SEM, HRTEM and STEM investigations (Inoue, 1986; Lindgreen *et al.*, 1991 and 1992; other references therein) have revealed dramatic morphology changes of evolving S/I interstratified phases: flakes, laths and hexagons. The changes of morphology reflect changes in stability; lath-like crystals represent a metastable morphotype. In some instances, it has been observed that they are gradual, with co-existence of different shapes (Clauer *et al.* 1990; Eberl, 1993; Inoue, 1986; Keller *et al.*, 1986; Pollastro, 1985; Varajao and Meunier, 1995; Whitney and Velde, 1993), a situation to be expected in a system where the phase changes are slow.

S/I laths have been observed in fault zones where conditions may favour faster transformation processes (Varajao and Meunier, 1995); the changes of shape can occur abruptly as a consequence of sudden mechanical stresses/tectonisation (see review in Arkai *et al.*, 2002). Differences in morphology are also related to porosity and permeability of the hosting rocks (Niu *et al.*, 2000).

During investigation of diagenetic sequences which occur in the «varicoloured» clay-shale formation of the italian Apennines (Granata, 1991), a lithofacies characterised by lath-shaped smectite/illite has been encountered in a zone affected by tectonic stresses; the occurrence area is located along the Sangro river valley, at the border between central and southern Italy.

The paper presents the results of detailed observations by scanning electron microscopy (SEM), and of chemical micro-analyses (EDAX) of lamellar and lath-shaped clay particles in order to gain insights into the mechanism of the recognised flake-to-lath morphotype transformation.

Geological setting and lithofacies mineralogy

The so-called «argille varicolori» («varicoloured» clays-shales) are widely distributed along the Italian Apennines as allochtonous sediments (Fig. 1). Paleogeographical evidences indicate lateritic degradation of carbonate platforms as source areas, and deep basins as the depositional environments (D'Argenio *et al.*, 1975).

In central-southern Italy, the «varicoloured» clays-shales show mineral zoning as a consequence of varying source materials, diagenetic processes and tectonisation events (Belviso *et al.*, 1977; Del Prete *et al.*, 1979;

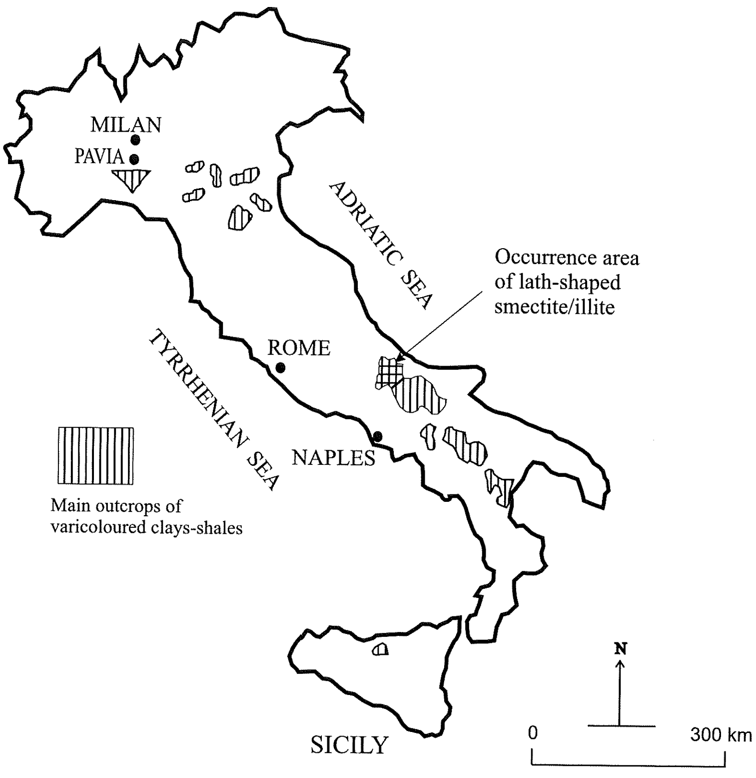

Fig. 1 – Occurrences of varicoloured clays-shales along the italian Apennines strip.

Granata, 1991). The lithofacies not affected by tectonization are characterised by a mineralogical assemblage with dominant smectite (up to 70-80%), whereas randomly interstratified smectite/illite predominates in the areas affected by diagenetic processes and/or low-intensity tectonic stresses; in some occurrences (higher-tectonised zones), illite and chlorite are present, but chlorite may be partly detrital. Authigenic dickite may also be present (see recent review in Veniale *et al.*, 2002).

MATERIALS AND METHODS

The samples representative of the lithofacies containing lath-shaped smectite-illite were selected from those collected by Belviso *et al.* (1977) and Del Prete *et al.* (1979). Scanning Electron Microscopy (SEM) observations (Fig. 2) and Energy Dispersive Analysis of X-ray (EDAX) microanalyses (Fig. 3) have been performed on air-dried specimens (obtained from natural samples by splitting, to give fresh fracture surfaces) submitted to cryo-lyophilisation to avoid artifacts due to sudden dehydration when inserted in the vacuum chamber of the electron microscope. Specimen surface was coated with a thin gold-film. The used apparatus (Cambridge Stereoscan 250) is coupled with an EDAX micro-analytical device. The EDAX spectra (spot analyses) were obtained with a beam of 2000 Å (maximum) diameter; operating conditions are given with the EDAX spectra (Fig. 3). The peak intensities are not to be taken as the percentages of the elements they represent, but rather as relative amounts of elements in different analysed spots.

RESULTS

Detailed SEM observations on tens of specimens have evidenced various particle morphotypes: flakes with irregular borders, and laths either as aggregates or discrete particles. The micrographs in fig. 2 are representative of the full range of observed morphotypes.

Flakes are characterized by wavy aspect, irregular rounded shape, curled edges and varying thickness, e.g. thinner at the border (fig. 2, A-1 and A-2). Single laths are characterised by high length/width ratio, their dimension ranging from 1-2 µm (length) to 0.05-0.10 µm (width): fig. 2-B, C, D and E.

A transition sequence has been recognised from flake to lath via different steps:

(i) flattening and thinning of the wavy flakes (fig. 2, A-1) which are considered as precursor; BSE image (fig. 2, A-2) shows that the particle borders are lighter with respect of the core (it could be due either to thinner thickness or to different chemical composition);

(ii) formation of discrete laths arranged in a rather regular manner (sub-parallel sets intersecting at angles of 60°/120° to each another) inside of the precursor flakes, that preserve their primary contours (fig. 2-C);

(iii) disaggregation of the lath aggregates giving rise to frayed and denticular edges (fig. 2-E, left);

(iv) splitting out of the lath aggregates into separate random-oriented laths (fig. 2-D and 2-E, right).

Elemental EDAX spectra obtained by spot analyses of flakes and laths (see representative examples in fig. 3) revealed Si, Al and K as major constituents; Mg is less represented, whereas Na, Ca and Ti are negligible.

The following main variation trends have been recognised:

flakes ⟶ laths

Al decreases
Mg increases

They suggest that a replacement of Mg for Al occurred, probably located within the octahedral sites; changes of Si and K contents are not surely detectable.

The relatively high amount of Fe may be related to Fe-oxy-hydroxide coatings of the

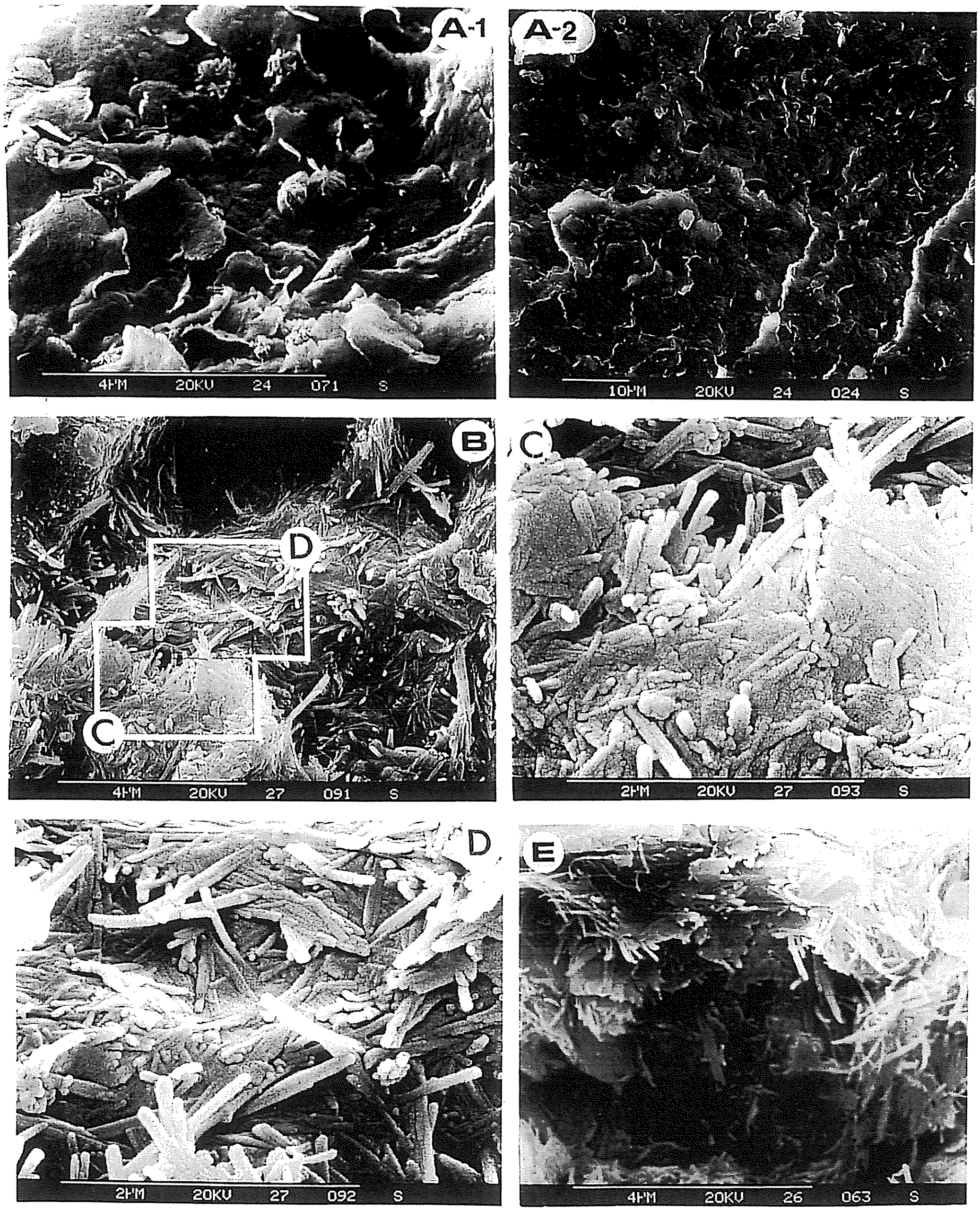

Fig. 2 – SEM aspects of the various particle morphotypes. A-1) Lamellar particles with wavy aspect and curled edges. A-2) Back-scattered electron (BSE) image showing light-coloured edges of the lamellar particles. B) Different steps of lath formation (see details in C and D). C) Remnants of precursor flaky particles constituted of aggregates of laths oriented at 60°/120° each other. D) Discrete laths assuming random orientation. E) *Left:* incipient stage of disaggregation of the lath aggregates (see also C) showing frayed edges; *Right:* splitting-out of the lath aggregates into random-oriented discrete laths (see also D).

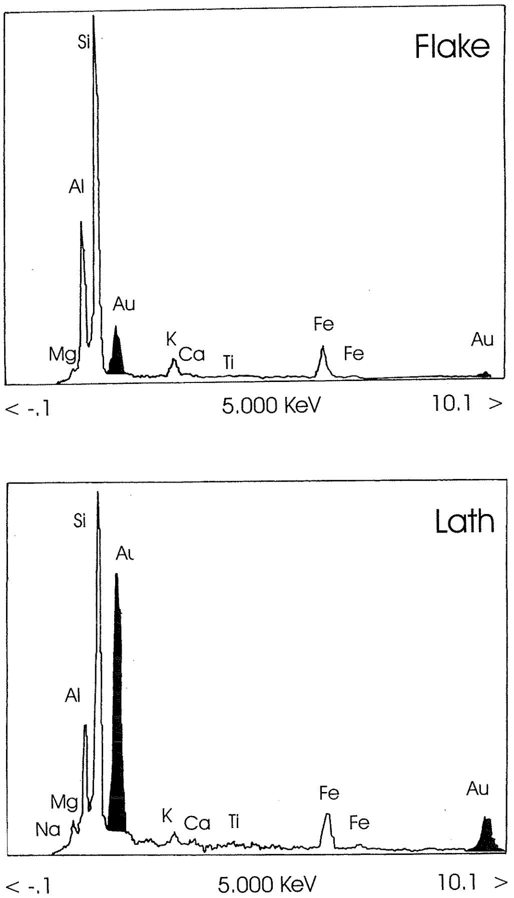

Fig. 3 – EDAX spectra of a flaky particle, and of lath aggregate.

clay particles, that accounts for the reddish-greenish colour of these «varicoloured» geomaterials.

DISCUSSION AND INTERPRETATION

SEM observations (Fig. 2) have shown that the smectite/illite laths encountered in the investigated «varicoloured» clays-shales appear to have developed by «splitting open» of lath aggregates which constitute the early transformation stage of original smectite/illite lamellae. In fact, sets of parallel laths, intersecting at angles of 60°/120° to each other, constitute aggregates which are delimited by borders recalling those of the precursor lamellae. A sort of disintegration mechanism, like a cleaving process, may represent the initial stage of lath formation; in a later stage, these ordered lath arrangements had split into isolated randomly oriented laths, via fraying of the aggregate edges.

The laths constituting the oriented aggregates have strict crystallographic correlations, i.e. crystallographic planes-directions form the contacts between laths. Such a strict geometrical arrangement of the laths, resulting in new lattices, may be referred as a «reticular arrangement». Whether the laths are to be considered as twin individuals or as ribbons of unit-cell thickness is another question, because it was not possible to determine if the thinned flakes transformed into lath aggregates reached the thickness of «fundamental particles» (see Special Issue no. 6, 1998, of Canadian Mineralogist for discussion about the concept of «fundamental particle», its evolution and geological implications).

Some structural evolution did occur during the lath formation, probably due to a crystal-chemical re-arrangement that took place as a consequence of geochemical changes concomitant with tectonic stresses.

In fact, aggregations of lath-shaped illite units with polycrystalline montmorillonite particles have also been observed (Güven, 1974); whether the laths have grown from the montmorillonite or are simply entangled with it, was still an open question. This kind of illite laths are extremely fragile and flexibile; they can easily break into fine laths under external stimulation, probably along preferential crystallographic directions corresponding to Al substitution for Si in the tetrahedral sheets (Gatineau, 1964); see also Jasmund *et al.* (1969); Mosser (1974) and Güven (2001).

As concerning the crystal-chemical changes related to flake-to-lath morphotype transformation encountered in the investigated «varicoloured» clays-shales, Mg is increasing within the laths, whereas Al is decreasing;

hence, from the crystal-chemical point of view, the morphotype transformation seems correspond to a somewhat retrograde pathway. Decrease of Al along certain structural directions may explain the preferential splitting of the precursor flakes into lath-shaped particles.

Veniale (1970) already mentioned the presence of some Mg in lath-shaped S/I particles constituting the «varicoloured» clays-shales formation in the Apennines of northern Italy, whereas Mg is absent in the lamellae particles.

Müller *et al.* (2000), investigating the structure transformations occurring in 2:1 dioctahedral layer silicates during dehydroxylation-rehydroxylation processes, have correlated the structural reactions to the original distribution of octahedral cations over cis- and trans-sites in the natural state, and to their migration during the dehydroxylation-rehydroxylation processes. These reactions can lead to noticeable changes of the unit cell parameters with relative displacement of adjacent layers; furthermore, a partial decrease in the particle size after dehydroxylation can occur, whereas a significant increase after rehydration can be the result of trapping H_2O molecules within the interlayer space.

Dehydration of Al-smectite as a function of temperature and depth in sedimentary basins have been investigated by chemical and thermodynamic model (Ransom and Helgeson, 1995). Dehydration of smectite can also be a stress-induced process (Fitts and Brown, 1993); the consequent freshening of pore solutions can influence the heterogeneous morphotype paths.

The intensity of the K-peak in the EDAX traces (Fig. 3) of the investigated clay particles roughly corresponds to about 4% K_2O (value obtained by comparison with mica standards), that indicates an illite content of about 1/3 within the S/I interstratification. In fact, the illite end-member is regarded as having 0.90 interlayer cations (mainly K^+) per half unit-cell (see review in Rosenberg, 2002): it corresponds to about 10% K_2O of the bulk chemical composition. Consequently, the K_2O content can be related to the percentage of illite layers using the ratio K/Kmax, where Kmax = 0.90, and K = the value for the sample.

Several authors (Eberl *et al.*, 1993; Inoue, 1986; Varajao and Meunier, 1995) have assumed such range (1/3 illite layers) suitable for the formation of metastable laths. Structural strain can be due to K-deficiency, which are compensated by increased Si/Al ratio in tethrahedral positions; random variations of these compositional parameters will account for local charge imbalance and structural «discrepancies» (Mosser-Ruck *et al.*, 2001).

After Eberl *et al.* (1993) the growth sequence S-to-S/I-to-I consists of three distinct zones: (i) primarily flake-like particles having more or less curled irregular borders (between 15 and 35% illite layers); (ii) growth of laths, sometimes oriented to each other at 60° or 120° (between 35 and 65% illite layers); and (iii) hexagonal shaped particle, mostly subhedral (between 65 and 85% illitic layers).

Velde and Vasseur (1992) have proposed different mechanisms, based on kinetic modelling, for the formation-transformation of S/I interstratification having different ratio of expandable layers; in fact, their structures differ considerably with respect to layer ordering and stacking, octahedral site occupancy, and particle morphology (flake versus lath). It is to mention that Ylagan *et al.* (2000), investigating the smectite illitization associated with hydrothermal alteration of volcanic rocks, have encountered a multi-step mechanism which is evidenced by abrupt changes in morphology, polytype and chemistry of the particles.

Lanson and Champion (1991) concluded that the smectite-to-illite transition (via metastable lath-like particles) is not one continuous reaction, but is accomplished by several reactions driven by minimisation of the surface free energy. This sequence is accomplished slowly in rocks subjected to burial diagenesis, but can occur abruptly as consequence of sudden mechanical stresses (tectonic events): see review in Arkai *et al.* (2002).

If some slip occurs along the boundary

planes of the aggregated laths, «splitting open» of the laths will occur; the reaction may be accelerated by wetting/drying cycles (Eberl *et al.*, 1993; Müller *et al.*, 2000). In fluid-rich or -deficient systems the rate and extent of reaction can be enhanced or inhibited, respectively, and the differences in reactivity related to the H_2O content can mediate the production of particles morphologies (Whitney, 1990; Small, 1994). Moreover, the geochemical system can be whether open (chemical migration) or confined (constant composition). It is to notice that «excess» interlayer water still remains an unsolved question, although it should be largely in form of neutral molecules, which may cause structural strain. Dehydration would create interlayer vacancies (in fact, K-smectite is a mixed layer of one water layers and dehydrated interlayers: Cuadros, 1997) and, thus, promote splitting into lath-shaped particles.

Relatively few data exist and rather controversial opinions have been presented on the effects of tectonic shear strain on phyllosilicate properties and behaviour under conditions of incipient metamorphism (for review, refer to Arkai *et al.*, 2002). Laboratory experiments at low pressure and temperature, equivalent to high diagenetic and very low-grade metamorphic conditions, have provided no direct evidence on the relationship between tectonic shear strain and phyllosilicate reaction progress. Our present knowledge has been accumulated in case studies carried out in fold and thrust belts.

It is evident that the response of phyllosilicates to strain depends on numerous physical and chemical factors, including kinetic ones: relative timing of reaction, fluid/rock ratio and fluid migration near the sliding planes. Dissolution-(re)crystallisation, grain-size reduction and grain-boundary deformation can be associated mechanisms. Phyllosilicate transformation can suffer appreciable retardation due to the presence of certain compounds in the circulating fluids; for instance, organic matter can influence the morphotype changes (Small, 1994). On the other hand, it seems plausible that frictional heating locally associated with short-live tectonic shear strain can promote reaction progress depending on the state of (dis)equilibrium reached during the transformation. Thus, the prograde or retrograde trend depends on the prevailing conditions which can be related to superposition or reset of additional effects (strain rate and differential stress). Such an overlap can result in heterogeneity of the reaction mechanisms and, consequently, in mixtures with varying morphotypes aspects.

CONCLUSIONS

The formation mechanisms of lath-shaped 2:1 clay minerals particles is still an intriguing problem. Structural factors coupled with somewhat chemical changes should pay a role in the cleaving («splitting open») process.

The stepwise transformation of lamellar smectite/illite particles into lath-shaped morphotype, as occurring in the «varicoloured» clays-shales formation from the central-southern Italy Apennines, has been visualised by detailed SEM observation. It seems that in the investigated geomaterials there is a close and reciprocal relationship between the lath growth and disintegration of the precursor smectite/illite flakes. Literature references do not report analogous documentation for such a pathway.

The observed lath-shaped smectite/illite particles are considered as a result of disintegration («splitting open») of lamellae particles (precursor) along preferential crystallographic directions. These directions would be the most fragile on the exposure to mechanical stresses, which have damaged the integrity of the oriented lath aggregates formed as early stage of the morphotype transformation. Such a mechanism may have been accompanied by wetting/drying cycles, likely to occur in «scaly» shales, which could have caused interstitial water fluxes and, consequently, changes in the geochemical environment. Loosely-bound hydrated interlayer K-ions may had dehydrated causing coalescence of the flakes, and of the incipient lath aggregates.

ACKNOWLEDGMENTS

The senior author (F.V.) is grateful to the Italian Consiglio Nazionale delle Ricerche (CNR) for supporting four months (November 1988-February 1989) of research at the Soil Division-CSIRO Land & Water Center, Adelaide (Australia) during which time most of the electron microscopy and microanalytical analyses were carried out; furthermore, to S. McLure of the same Electron Microscopy Service for his help and assistance with some of the lab work.

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