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Very low-grade metamorphism in the Tuscan Nappe, Northern Apennines, Italy: relationships between deformation and metamorphic indicators in the La Spezia mega-fold

Rodolfo Carosi^{1,2}, Leonardo Leoni¹, Chiara Montomoli¹ and Franco Sartori¹

Abstract

The metamorphic grade of the Tuscan Nappe in the La Spezia region of the Northern Apennines (NW Italy) is investigated in shales and marls through mineral assemblages and "crystallinity" of illite and chlorite. In this area the Tuscan Nappe is involved in a regional-scale fold (up to 15 km long and 4–5 km wide), affected by different conditions of strain in the right way-up limb compared to the inverted limb or hinge zone. This geological setting allows exploration of the relationship between tectonic strain and assemblages/properties of clay minerals. Illite and chlorite "crystallinity" data point to middle anchizonal or to upper anchizonal conditions for the Tuscan Nappe, depending on whether the CIS or the Kübler's scale is applied; the metamorphic grade estimated using Kübler's scale seems more consistent with the paleo-thermal and structural evidence.

The most notable trend observed in the assemblages and properties of phyllosilicates from the different structural positions of the mega-fold is the disappearance of both illite/smectite mixed-layer minerals and intermediate Na/K-micas in the higher-strain zones; these phases are likely substituted by larger crystallites of discrete illite and paragonite. The differences in the "crystallinity" of illite and chlorite main populations over the different structural positions are, on the contrary, very small (on average 0.02° as $\Delta 2\Theta$), most of them being within error limits. However, such differences are systematic: there is a constant trend exhibiting mica and chlorite peaks slightly narrower in the most deformed zones than in the least deformed ones.

Keywords: Clay mineral assemblages, illite and chlorite "crystallinity", tectonic strain, La Spezia megafold, Tuscan Nappe, Northern Apennines.

1. Introduction

Crystal chemical changes affecting clay minerals in the transition from diagenesis to epizone have been extensively used to evaluate the conditions of very low-grade metamorphism in phyllosilicate-bearing rocks (Frey, 1987; Merriman and Peacor, 1999); among these, the changes referring to illite (IC) and chlorite (ChC) "crystallinity" are most widely applied. It is generally accepted that both these parameters are mainly influenced by temperature conditions (Merriman and Peacor, 1999), though other variables such as fluid pressure, tectonic strain, time, lithology, and mineral chemistry may play an additional role in their control (Frey, 1987). The effect and weight of these secondary factors is not yet completely clear. In particular, the relationships between IC (and ChC) and tectonic strain are still debated, in spite of the great efforts to produce a clearer picture of the matter (Arkai et al., 1997). Even more

scarce and less conclusive are the data concerning the relationships between strain and such mineralogical parameters as illite polytypism and clay mineral assemblage.

The relationships between IC and strain have been investigated on various scales by several researchers. Kübler (1967), Frey et al. (1973), Aldahan and Morad (1986), and Franceschelli et al. (1994) reported an improvement of illite "crystallinity" in tectonic shear zones, whereas Gutierrez-Alonso and Nieto (1996) found regional-scale inverse correlation between finite strain and white mica "crystallinity" indices. According to Merriman et al. (1995), in low-grade metamorphic terranes tectonic strain appears to play an important part in crystallization processes as grade increases from the anchizone to the epizone, with significant differences in crystal growth between illite and chlorite. Recently Árkai et al. (1997) studied two profiles traversing the Glarus overthrust (Swiss Helvetic Alps); they reported small-scale

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Fig. 1 Left: schematic stratigraphic column of the Tuscan Nappe in the La Spezia region: the formations investigated in the present study are marked by a star.

Right: Geological map of the La Spezia region showing the Tuscan Nappe formations folded into a W-facing, recumbent mega-anticline. Explanation: 1. Landslide deposits, slope debris and alluvium; 2. Ligurid Units; 3. Sub-Ligurid Unit (Canetolo Unit); 4. Macigno; 5. Tuscan Scaglia; 6. Maiolica and Chert; 7. Posidonomya Marl and Cherty Limestone; 8. Rosso Ammonitico Limestone and Angulati Limestone; 9. Massive Limestone; 10. Rhaetavicula contorta Limestone and Marl as well as Coregna Dolomite.

IC variations, without notable trends as a function of the distance from the thrust plane, in contrast to an apparent mean crystallite size decrease and lattice strain increase towards such a plane. Similar small-scale fluctuations were observed in ChC values, but the chlorite mean crystallite size and lattice strain were found to show a trend opposite to that of illite. The authors explained the different behaviour of the two phyllosilicates as due to syn- and post-overthrusting recrystallization affecting chlorite but not white K-mica.

Several authors investigated the role of strain on illite crystallinity on outcrop-scale folds (Flehmig and Langheinrich , 1974; Gruner, 1976; Teichmüller et al., 1979; Nyk, 1985) or on mega-scale folds (Roberts and Merriman, 1985; Leoni et al., 1992). Flehmig and Langheinrich, (1974) and Nyk (1985) found no correlation between values of the Kübler index and tectonic strain, whereas they observed increasing Flehmig indices (increasing "crystallinity") from the limbs towards the hinge. Gruner (1976) and Teichmüller et al. (1979) did not find any correlation between IC and deformation in single folds. Controversial are the conclusions drawn from the study of the tight Cwm Pennant anticline of Northern Wales; whereas Roberts and Merriman (1985) claimed the existence of a direct relationship between IC and tectonic strain (evaluated through the intensity of cleavage formation), Robinson and Bevins (1986) did not find this correlation for the same area. In contrast, a good positive correlation between IC and strain intensity was pointed out by Leoni et al. (1992) in a mega-fold (more than 1 km across and up to 3 km from the root to the hinge zone) developed in the Ligurian Apennines (NW Italy).

It is obvious from the above review that a clear relationship between strain and "crystallinity" has yet to be established. As suggested by Árkai et al. (1997), it seems likely that several factors may affect the action of strain on phyllosilicate properties including (i) the modal ratio and the physical and chemical differences between the phyllosilicates and the rock matrix (ii) the temperature of the rock mass during deformation (iii) the fluid/ rock ratio in the deforming medium (iv) the time relation of deformation and recrystallization.

The study presented here is aimed at assessing the metamorphic grade of the Tuscan Nappe of the Northern Apennines in the La Spezia region (NW Italy) as well as at investigating the relationships between strain and illite and chlorite "crystallinity" in a regional-scale fold affecting this tectonic unit. This fold, outcropping for 15 km along its axis and up to 4-5 km wide, is far greater than the mega-fold previously investigated by Leoni et al. (1992) and is supposed to have been more intensely deformed. Moreover, it shows significant differences in tectonic fabric between the inverted limb (and hinge zone) and the right way-up (normal) limb, suggesting greater amounts of strain in the former than in the latter (Montomoli, 1998). In order to investigate the relationships between deformation and illite and chlorite "crystallinity", samples were collected from three lithologically favourable formations in fold positions inferred to be significantly different as to the conditions and degree of strain.

Within the predominantly carbonate sequence of the Tuscan Nappe, the formations that best suit the need of a relatively high clay content are the "Rhaetavicula contorta Limestone and Marl" ("Calcari e Marne a Rhaetavicula contorta"), the "Posydonomia Marl" ("Marne a Posydonomia"), and the "Tuscan Scaglia" ("Scaglia Toscana").

2. Geological setting

The Northern Apennines represent a typical foldand-thrust belt made up of several tectonic units belonging to different paleogeographic and tectonic domains. In the Alpi Apuane region, where the relationship among tectonic units is best understood, the tectono-stratigraphic units, in ascending structural order, are: (1) the Tuscan metamorphic units, (2) the Tuscan Nappe, (3) the sub-Ligurid unit (Canetolo unit), and (4) the Ligurid units (Elter et al., 1975; Carmignani et al., 1978 and references therein).

The Tuscan metamorphic sequences consist of Triassic to Oligocene greenschist facies metasediments resting unconformably on a Paleozoic basement (Kligfield, 1979). The Tuscan Nappe is an allochthonous sheet of sedimentary rocks, ranging in age from Triassic to Oligocene, which now overlies the metamorphic sequences. The rocks of both the Tuscan Nappe and the metamorphic units belong to the Adriatic paleo-continental margin (Bortolotti et al., 1970). The sub-Ligurid unit (Canetolo unit) represents part of the sedimentary cover of the ocean-continent transitional area. The structurally highest Ligurid units, consisting of ophiolites and their deep-water sedimentary cover, are interpreted as remnants of an oceanic lithosphere, Jurassic to Early Paleocene in age (Elter et al., 1975).

In the La Spezia area the Tuscan Nappe is exposed below the Ligurid and the sub-Ligurid units in a SW-facing recumbent mega-anticline, which is characterized by a sub-horizontal axial plane and a N140E trending axis, that is plunging a few degrees to the north (Giammarino and Giglia, 1990). Such a mega-fold makes up the whole peninsula bordering the western side of the La Spezia gulf (Fig. 1). In this area the nappe is up to 3000 m thick (Abbate, 1969; Ciarapica and Passeri, 1980a, 1980b) and consists of Mesozoic to Lower Oligocene predominantly carbonate sediments followed by Oligocene-Lower Miocene siliciclastic flysch deposits. This succession records the evolution from shallow- to deep-water marine environments.

In ascending order the sequence is represented by Coregna Dolomite (Carnian), Rhaetavicula contorta Limestone and Marl (Norian–Rhaetian), Massive Limestone (Hettangian), Angulati Limestone (Upper Hettangian–Sinemurian), Rosso Ammonitico Limestone (Sinemurian– Pliensbachian), Cherty Limestone (Middle–Upper Lias), Posidonomya Marl (Aalenian–Callovian), Chert (Callovian–Kimmeridgian), Maiolica (Tithonian–Valanginian), Tuscan Scaglia (Upper Cretaceous–Oligocene), Macigno (Upper Rupe-



Fig. 2 Superposed foliations (S1 and S2) in the Posydonomia Marl (PM) formation (parallel nicols). S2 foliation is a crenulation cleavage, not associated with a significant synkinematic recrystallization.



Fig. 3 Microstructure of the S1 foliation in the Tuscan Scaglia (TS) formation from the hinge zone of the megafold (parallel nicols). S1 appears as a well developed, continuous foliation, highlighted by flattened clasts with quartz and calcite strain fringes. In the top left, interpenetration between adjacent clasts is evident.



Fig. 4 Microstructure of the S1 foliation in the Tuscan Scaglia (TS) formation from the normal limb of the megafold (parallel nicols). S1 is only highlighted by feeble dark solution seams around clasts, while strain fringes appear poorly developed.

lian–Upper Oligocene). The presence of Massive Limestone in the Tuscan Nappe of the investigated zone is a controversial subject. According to Ciarapica and Passeri (1980a, 1980b) and Fazzuoli et al. (1985) this formation, which is well developed in the more eastern outcrops of the Tuscan Nappe, is completely lacking in the La Spezia area.

The La Spezia mega-fold shows the opposite direction of tectonic transport to that of other Northern Apennines structures, most of which are E-verging. The interpretation of this particular regional-scale fold is much debated and several tectonic models have been proposed. Some of these regard the structure as a post-collisional extensional feature that overprints an earlier Apennine thrust event (Elter, 1960; Giammarino and Giglia, 1990; Carmignani and Kligfield, 1990; Carter et al., 1991; Carter, 1992). Others explain the structure as an early compressional feature (Federici and Raggi, 1975; Reutter et al., 1978), which may be related with an important backthrust surface (Bernini, 1991; Bernini et al., 1991, 1997).

As already pointed out, the La Spezia structure shows evidence of greater strain in both the inverted limb and the hinge zone than in the normal limb (Montomoli, 1998). At the mega-scale the following features are apparent: (a) a strong lamination affects the inverted limb, whereas it is feeble or absent in the normal one; (b) sheared zones are relatively common in the inverted limb, but occur sporadically in the normal limb; (c) syntectonic veins are very frequent in the hinge zone, but are relatively rare in other parts of the fold.

Information on the metamorphism of the Tuscan Nappe in the La Spezia area is scarce. Reutter et al. (1980), who investigated the distribution of vitrinite reflectance in clastic formations from several units of the Northern Apennines, reported high anchizone/low epizone conditions for the Macigno of this zone. Cerrina Feroni et al. (1983) found rather contrasting IC values in "Rhaetavicula contorta Limestone and Marl" and in "Tuscan Scaglia" formations of the La Spezia megafold. Illite "crystallinity" indicates high anchizonal conditions (average IC index: $0.26 \circ \Delta 2\Theta$) in the "Rhaetavicula contorta Limestone and Marl", whereas late diagenetic conditions (average IC index: 0.44 $^{\circ}\Delta 2\Theta$) were indicated in the "Tuscan Scaglia". However, Cerrina Feroni's study (Cerrina Feroni et al., 1983) only refers to a small number of samples, collected with no record of their position in the mega-structure; furthermore, in the same study IC measurements were exclusively performed on ethylene glycol-solvated specimens and never were calibrated with respect to Kübler's (1990) or to Warr and Rice (1994) standards. More reliable are the preliminary data

on the same formations presented by Montomoli (1998), who suggests a strong control of metamorphic indicators by the deformation.

3. Strain pattern and deformation mechanisms

Recent works combining new geological surveys with meso- to micro-structural analyses (Montomoli, 1998; Montomoli, 2002; Carosi et al., 2002) provide a picture of the deformation history of the La Spezia structure more complex than that previously suggested (Giammarino and Giglia, 1990; Carter, 1992). The area shows evidence of three deformation events, all of them resulting in the development of folds with associated axial plane foliations. The most prominent deformation features are associated with an early phase (D1) which produced micro-, meso-, and mega-scale F1 folds, characterized by gently dipping axial planes and by different geometries which appear rheologically controlled. Montomoli (1998, 2002) and Montomoli et al. (2001) interpret this phase as related with the Northern Apennine main collisional event, which would also be responsible for the development of the whole La Spezia mega-structure. The F1 folds are associated with an S1 axial plane foliation, whose morphology varies in relation with lithology. According to the scheme proposed by Passchier and Trouw (1996), it may be classified as a spaced foliation varying from rough to stylolytic in the more competent, mainly calcareous lithologies, whereas it is a continuous foliation in the less competent, essentially pelitic lithologies. In these latter the S1 foliation is characterized by the growth of the mineral assemblage: quartz + calcite \pm albite \pm illite \pm chlorite + opaque minerals (iron oxides or sulfides), while in the former (carbonate-rich rocks) the cleavage surfaces appear to have been chiefly affected by pressure-solution processes, followed by a minor growth of illite.

The D1 phase was followed by a weaker D2 deformation, which produced steeply dipping F2 folds, a few meters to some hundred meters wide, with an associated S2 axial plane foliation. In the pelites the S2 foliation has the characters of a crenulation cleavage, not associated with a significant synkynematic recrystallization (Fig. 2). This phase has been interpreted as having developed during the late stages of the main collisional event.

The D2 phase was followed by a late, weak phase, referred to as D3 by Montomoli (1998; 2002), who interpreted it as equivalent to the second deformation phase commonly recognized by the previous authors (Giammarino and Giglia, 1990; Carmignani et al., 1991, 1992, 1993; Carter, 1992). This phase produced cylindrical F3 folds, a few meters wide, characterized by horizontal to gently dipping axial planes, associated with a discrete crenulation cleavage with no crystal growth. The D3 phase is probably related to the final stages of the Tuscan Nappe exhumation (Montomoli, 1998; Montomoli, 2002; Montomoli et al., 2001; Carosi et al., 2002).

The dominant deformation mechanism active during the main D1 phase is pressure solution, with subordinate intracrystalline deformation, indicated by the undulose extinction of quartz grains and the deformation twinning of calcite crystals (Burkhard, 1993).

The pressure solution mechanism is attested by characteristic micro-structures which are more or less conspicuous in relation to the structural position in the megafold. In the inverted limb and hinge zone they include the flat surfaces between major grains and foliation planes, the solution seams of insoluble material concentrated around the grains and the interpenetration of adjacent clasts. In these micro-structural positions, re-deposition or crystallization of dissolved material mainly occurred in strain shadows around rigid objects such as detrital quartz and microfossils (Fig. 3).

In the normal limb, pressure solution is attested by feeble dark solution seams around rigid objects and poorly developed strain fringes (Fig. 4).

Quantitative measurements of the strain variation in a selected stratigraphic level over the various parts of the megafold would have been desirable, but they have proved to be impracticable, essentially because of the scarcity of reliable markers. An attempt to estimate the finite strain in the Tuscan Scaglia formation along the fold profile by applying the "center-to-center" method (Fry, 1979) did not produce reliable results both because of the inhomogeneous distribution of the centers of the strain markers (quartz grains and microfossils) and the heterogeneity of rock composition. Therefore the strain distribution can be only qualitatively inferred from some microstructural features. Among them, the spacing of the S1 foliation is particularly indicative; in a given lithotype this foliation is better developed and much more closely spaced in the hinge zone and the inverted limb than in the normal limb. The number of foliation planes per unit area is about two times greater in the former than in the latter structural position. The major amount of shortening in the inverted limb and hinge zone is also attested by a greater length and continuity of solution seams, by better developed strain fringes and by a greater frequency of clasts showing interpenetration effects in the direction perpendicular to the foliation (compare Fig. 3 with Fig. 4).

4. Sampling and analytical methods

For the present study the following three formations, belonging to the Tuscan Nappe sequence, have been selected on the basis of their favourable lithology: "Rhaetavicula contorta Limestone and Marl", "Posydonomia Marl", and "Tuscan Scaglia".

The first one is known as "Rhaetavicula contorta Limestone and Marl" in the oldest literature (Capellini, 1862; Zaccagna, 1935; Federici and Raggi, 1975) and on Italian Geological Survey sheet 95, but was renamed "La Spezia Formation" by Ciarapica and Passeri (1980a, 1980b). In the present paper the name used in the map of the Italian Geological Survey is maintained and the formation will be hereafter referred to as RcLM formation. It consists of limestone beds alternating with marly layers, rich in bivalve and gastropod shells (lower member), and thin black limestones alternating with fine-grained dolomites or black marls (upper member).

The Posidonomya Marl (hereafter referred to as PM formation) is mostly made up of greenishgrey marls and clayey marls which alternate with subordinate beds of a brownish marly limestone or a grey to pink limestone; these sediments are considered to have been deposited in a pelagic environment near to the carbonate compensation depth.

The Tuscan Scaglia (hereafter referred to as TS formation) consists of varicoloured shales and marls alternating with subordinate beds of micritic limestones and calcarenites; these sediments are also interpreted as deep pelagic deposits. The Tuscan Scaglia is also referred to as Scisti Policromi (Polychrome Shales) (Abbate, 1969; Ciarapica and Passeri, 1980a).

A suite of 67 samples was collected from the clay-rich beds of the three formations. For each formation sampling was carried out on both limbs of the mega-anticline, wherever possible (RcLM formation), or on both the normal limb and the hinge zone (PM and TS formations).

These samples were analysed for bulk mineralogy on randomly oriented powders of whole rock, while the $<2 \,\mu m$ fraction mineralogy was investigated both on oriented aggregates and randomly oriented powders, using standard X-ray powder techniques on a Philips PW 1710 automatic diffractometer equipped with a long finefocus Cu tube. The $<2 \,\mu m$ ("clay") fraction was prepared by sedimentation from powders obtained after gentle grinding of rock chips for short times; this avoided appreciable comminution of clastic phyllosilicates and their inclusion in the clay fraction. No preliminary treatment has been applied to remove carbonates, which are more or less common in all the collected samples, or organic matter, present in significant amounts in some samples from the RcLM formation. These treatments were avoided since they may have deleterious effects on the small-sized phyllosilicates.

The illite and chlorite "crystallinity" indices (half-height peak width expressed as $\Delta 2\Theta$ of the basal reflections) were measured on experimental XRD patterns collected on the $<2 \mu m$ fraction samples sedimented on glass slides. Care was taken to avoid thin slides: the amount of clay on each slide was at least 3mg/cm² (Lezzerini et al., 1995). Whenever peak intensity was high enough, both (001) and (002) reflections were measured for mica as well as for chlorite and the relative parameters referred to as $IC_{10\text{\AA}}$ and $IC_{5\text{\AA}}$, and $ChC_{14\text{\AA}}$ and $ChC_{7Å}$, respectively (indices of reflections will be hereafter referred to 1-layer polytypes). For mica, the measurements were performed on air-dried specimens (AD) and also after ethylene glycol solvation (EG); for chlorite only measurements on air-dried specimens were effected, after a preliminary survey showed that no change occurs in the basal peaks in response to glycolation. For "crystallinity" measurements each sample was run at the following instrumental setting: CuKa Ni-filtered radiation; 40 kV; 20 mA; slits: 1/ 2° divergence and scatter, 0.2 mm receiving; continuous scanning; scan speed: $0.25^{\circ} 2\Theta$ per minute; time constant: 4 s. Experimental profiles were analysed using Krumm's WINFIT program (Krumm, 1996), that determines the crystallinity by first subtracting the background from the raw data, then operating the peak fitting through an asymmetrical Pearson VII function. Single peak fits of the 14 Å, 10 Å and 7 Å profiles have been carried out; in contrast, the 5 Å peak was fitted simultaneously with all the other peaks in the angular range 16-19.5 °20, because in some raw XRD patterns it appeared partially overlapped by a large band which extended to the chlorite (003) reflection. Although these peaks are slightly asymmetrical, their fitting was performed through a symmetrical Pearson VII function in order to reduce the number of parameters to be refined. Various peak-fitting trials, in which $K\alpha_2$ wavelength was retained, were performed; this produced suitable fitted profiles, on which the "crystallinity" was measured. Experimental data were then converted to calibrated CIS data using the procedure and standards (SW1, SW2, SW4, SW6, and MF1) of Warr and Rice (1994) and applying the calibration equation: $IC_{CIS} = IC_{Pisa} \times 1.09 + 0.05 (^{\circ}\Delta 2\Theta)$; ($R^2 = 1.0$; $\sigma = 3.5\%$; Leoni, 2001). This regression equation, obtained for the $IC_{10Å}$ parameter, was also applied to the calibration of $IC_{5Å}$ as well as $ChC_{14Å}$ and $ChC_{7Å}$ values.

The distribution of CIS-scale-normalized IC and ChC values in the three formations is shown as histograms in Figs. 5, 6, 8 and 9 and discussed in paragraphs 5.2.1 and 5.2.2. Only for the sake of a more reliable assessment of the Tuscan Nappe's metamorphic grade, the $IC_{10\text{\AA}}$ values were also calibrated with respect to the standard rock slab series provided by Kübler (samples 32, 34, 35). Conversion of our IC_{10Å} data to the Kübler scale was achieved by applying the calibration equation: $IC_{Neuchâtel} = IC_{Pisa} \times 1.08 + 0.01 (^{\circ}\Delta 2\Theta); (R^2 =$ 0.98 $\sigma = 5\%$; Leoni, 2001). These Kübler-scalenormalized IC_{10Å} data, which are about 0.04° (as $\Delta 2\Theta$) smaller than the CIS-scale-normalized values, are not reported throughout most of the paper; only in the discussion, their average value in the PM formation is given and used in connection with the assessment of the Tuscan Nappe's metamorphic grade.

Composition of calcite coexisting with dolomite was determined in 7 samples from the RcLM formation. Microanalyses were carried out on carbon-coated polished thin sections using a X-ray energy-dispersive system (EDAX PV 9900) attached to a Philips 515 scanning electron microscope (SEM). The general analytical conditions were: acceleration voltage, 15 kV; excitation current, 20 mA; beam spot size (and selected area of analysis), 0.5 µm; counting time, 100 s. Standard minerals used were: diopside, calcite, and Fe-poor dolomite (FeO 0.50 wt%). Data were corrected by applying the ZAF correction program proposed by Mikledust et al. (1978) and processed through a PV SUPQ program, which gives mineral compositions recalculated to a 100% content on a CO_2 -free basis.

5. Results and discussion

5.1. Petrography and mineral assemblages

Samples collected in the RcLM formation consist of grey to black marls, which have a composition dominated by carbonates (chiefly calcite, in some cases accompanied by dolomite), associated with important amounts of quartz and clay minerals. K-feldspar and plagioclase occur as widespread, but minor components; accessory minerals are apatite and pyrite. In addition, traces of gypsum, probably of secondary origin, appear in few samples. The clay minerals are mainly illite and chlorite; in the fold's normal limb some samples with small amounts of illite/smectite mixed-layer minerals and intermediate sodium potassium micas (Jiang and Peacor, 1993; Merriman and Peacor, 1999) have been found.

Within the same specimen, white K-mica, chlorite, quartz and calcite occur both as detrital (usually in moderate amounts) and D1-metamorphic minerals. K-feldspar and plagioclase are detrital minerals; almost pure albite, observed in sporadic small grains, is the only newly formed feldspar.

The materials collected in the PM formation are greenish-grey clayey marls, whose bulk mineralogy is similar to that observed in the RcLM formation; the main differences with respect to this latter are a significantly lower content of calcite, very rare occurrence of kaolinite (observed only in small amounts in two samples), and the total absence of any mixed-layer mineral or intermediate Na/K-mica. The PM formation does not show any difference in mineralogical composition in the different structural positions.

Samples from the TS formation are shales, grey, green or red, characterized by the following bulk mineralogy: calcite (scarce), quartz, clay minerals, feldspars (traces); the most common accessory mineral is hematite. The clay mineral assemblage is dominated by illite and chlorite, followed by intermediate sodium potassium micas and illite/smectite mixed-layer minerals; the presence of very small amounts of paragonite is doubtful.

The mineralogy of the TS formation is clearly differentiated over the two structural positions of the hinge and the normal limb. Mixed-layer minerals and intermediate Na/K-micas, which are present in significant amounts in the normal limb, completely disappear in the hinge, possibly replaced, at least in part, by the small amounts of paragonite (whose identification, however, is not certain).

5.2. IC and CHC data

5.2.1. Illite "crystallinity"

The distribution of air-dried $IC_{10Å}$ and $IC_{5Å}$ values in the three formations is shown as histograms in Figs 5 and 6 respectively; IC average values and standard deviations are given for both the airdried (AD) and the ethylene glycol-solvated (EG) samples.

For each formation the distribution is analyzed both in the whole data set, that is in the mega-fold as a whole (Figs. 5a and 6a), and in two sub-sets of data, which refer to sample groups col-





 \bar{x} = average value; σ = standard deviation; AD = values from air-dried slides; EG = values from ethylene glycol-solvated slides; n = number of examined samples. "RcLM" Form. = "Rhaetavicula contorta Limestone and Marl" formation; "PM" Form. = "Posidonomya Marl" formation; "TS" Form. = "Tuscan Scaglia" formation.





Fig. 7 Examples of raw and deconvoluted (through the WINFIT program of Krumm, 1996) X-ray diffraction patterns in the range 16–20° 2 Θ of two TS shale samples. (a) Sample from the mega-fold's normal limb, containing significant amounts of an intermediate sodium potassium mica: the first peak (at about 17.70° 2 Θ) corresponds to the illite (002) reflection, the large band centered around 18.25° 2 Θ is due to the intermediate Na/K-mica, the last peak (at about 18.70° 2 Θ) corresponds to the chlorite (003) reflection. (b) Sample from the mega-fold's hinge zone, where no intermediate mica is present: it is evident the absence of any diffraction effect between the illite (002) and chlorite (003) peaks.

lected in the megastructure's most deformed (Figs. 5b and 6b) and less deformed (Figs. 5c and 6c) zones, respectively.

Considering the whole mega-fold, $IC_{10\text{\AA}}$ presents average values distinctly different in the three formations (Fig. 5a); the largest value (IC_{10Å}) = $0.48^{\circ} \Delta 2\Theta$) characterizes the TS formation, where a bimodal distribution is apparent. This pattern is clearly related to the presence, within the whole sample set, of two different sample populations, having quite distinct $IC_{10Å}$ values. The samples from the more deformed zones are characterized by low values of the index, and hence by higher "crystallinities" of mica (Fig. 5b), whereas in the samples from the less deformed zones the index is comparatively high (Fig. 5c). A similar pattern seems to characterize the RcLM samples, which exhibit a relatively large $IC_{10\text{\AA}}$ average value (IC_{10Å} = $0.35^{\circ} \Delta 2\Theta$), associated with a large standard deviation; also in this formation, significantly different IC_{10Å} values over the different structural positions are evident.

In contrast, PM formation shows a strictly unimodal distribution, characterized by the smallest average "crystallinity" index (IC_{10Å} = $0.31^{\circ} \Delta 2\Theta$) and standard deviation ($\sigma = 0.02$) values (Fig. 5a). Ethylene glycol solvation does not produce any significant effect in the samples from this formation, while it results in a distinct sharpening of the mica (001) peak in samples from the other two formations, mostly in those from the lower strain zones. This pattern has been interpreted as due to the small amounts of illite/smectite mixed layer minerals, which are present in these formations within the megastructure's normal limb, but lacking in the other zones.

However, in terms of data from glycolated mounts (EG values of Fig. 5), relatively large differences persist between the different formations and between the different structural positions. Such differences, which can not be ascribed to any swelling component, are chiefly explainable on the basis of the distribution of intermediate sodium potassium micas (Jiang and Peacor, 1993). As for illite/smectite, these phases accompany the illite main population in the TS and RcLM formations, though only within the normal limb. Their first order-basal peak completely overlaps the 10-A reflection of illite, greatly contributing to its broadening. On the contrary, their second order reflection appears partially separated from illite 5-A peak and may be fully resolved from the latter through application of the curve fitting/peak deconvolution WINFIT program (Krumm, 1996). This is clearly shown in Fig. 7, where examples of raw and deconvoluted X-ray diffraction patterns in the range $16-20^{\circ} 2\Theta$ are given for two TS shale

samples. Figure 7a, which refers to a sample from the megastructure's normal limb, show a broad band connecting and partially overlapping illite (002) and chlorite (003) reflections. Application of the fitting program resolves the cluster of diffraction effects into sharp illite and chlorite peaks and a broad band, centered around 4.86 Å (18.25° 2 Θ), which is due to intermediate Na/K-micas. Figure 7b, which refers to a sample from the megastructure hinge, illustrates the case of a clay mineral assemblage lacking any mixed layer phase or intermediate Na/K-mica: illite (002) and chlorite (003) peaks are sharp and well-resolved even in the raw diffraction curve.

Since the illite (002) peak is virtually free of any effect of interference by mixed-layer minerals and may be stripped of the intermediate Na/Kmica contribution (when present) through fitting programs, the IC5Å values appear significantly smaller than those of $IC_{10\text{\AA}}$ and slightly different in the various formations and the various structural positions (Fig. 6). In most cases the difference between average IC_{5A} values from the higher strain zones (inverted limb and hinge) and average $IC_{5\text{\AA}}$ values from the lower strain zones (normal limb) is only 0.02 $^{\circ}\Delta 2\Theta$, close to the error limits; in TS formation such a difference rises to a value of 0.05 ° $\Delta 2\Theta$. However, these small deviations are systematic, with more narrow mica peaks in the more deformed zones than in the less deformed ones.

Another significant observation on $IC_{5\text{\AA}}$ is that the width of the second order peak constantly appears narrower than that of the first order reflection, even where no mixed-layer mineral nor intermediate Na/K-mica occurs (that is all over the PM formation and within the most deformed zones of the other formations). This feature has been also observed by Warr (1996) in XRD profiles of the higher-grade metamorphic samples (IC_{10Å} about 0.3 $^{\circ}\Delta 2\Theta$ or lower); it is regarded as deriving in part from the combined effect of the Lorentz-polarization factor and structure factor, which has a different impact on the two peaks, in part it may be a consequence of a strong size grading of the clay specimen (Warr, 1996; Krumm and Buggish, 1991).

5.2.2. Chlorite "crystallinity"

The distribution of $ChC_{14\text{\AA}}$ and $ChC_{7\text{\AA}}$ in the three formations is shown in histograms of Fig. 8 and Fig. 9. Since ethylene glycol treatment does not appear to appreciably influence the two indices, averages have been calculated only for air-dried (AD) values. In the whole mega-fold, both $ChC_{14\text{\AA}}$ and $ChC_{7\text{\AA}}$ exhibit a distribution which closely conforms to the trend shown by $IC_{5\text{\AA}}$ (and,





for PM formation, also by $\rm IC_{10 \AA}$), i.e., the values recorded in the most deformed zones are always slightly smaller (on average, 0.02 $^\circ\Delta 2\Theta$) than those from the least deformed ones.

As with illite, the index measured on the second order basal reflection is always smaller than that measured on the first, the two parameters showing a good linear correlation (ChC_{7Å} = (ChC_{14Å} \cdot 0.985) – 0.027; r = 0.85); this feature is probably to be ascribed to the same effects indicated for mica reflections.

5.3. Calcite–Dolomite geothermometry

The occurrence of calcite-dolomite-bearing assemblages in 7 samples from the RcLM formation allows the thermal conditions which affected the Tuscan Nappe in La Spezia area to be estimated using carbonate thermometry. Despite the uncertainties inherent in the method (Turner, 1981), its application has been regarded as worthwhile in order to check the temperatures estimated by Montomoli et al. (2001) within the "Macigno" formation through fluid inclusion analysis.

The amounts of $MgCO_3$ in calcite have been determined in crystals coexisting with dolomite. In these crystals the contents of $FeCO_3$ and $MnCO_3$ are always below detection limits (<0.05) mol%); therefore no correction for the iron and manganese contents is necessary for application of the Bickle and Powell's (1977) equation. The data collected are plotted as a frequency distribution diagram in Fig. 10, in which a temperature scale is also reported. This scale has been calculated from Bickle and Powell's (1977) equation, assuming a lithostatic pressure of 2.5 kb (P_{tot} = P_{H2O}) as suggested by the thickness of the Tuscan Nappe's overburden at the time of the metamorphic peak (Carmignani et al., 1992). The distribution of MgCO₃ contents clearly shows that the probable metamorphic temperature ranges from 250 to 315 °C. The observed scatter of temperatures may be partially due to analytical errors and/or it may partially reflect re-equilibration effects during cooling. From Fig. 10 it is evident that, within the limits of the method, no clear separation of values between the normal limb and inverted limb (or hinge zone) can be pointed out. This suggests that the mega-fold's various structural elements have been affected by roughly the same thermal conditions.

If the overall average MgCO₃ content is assumed, a mean temperature of 294 ± 15 °C is derived, that is a value in good agreement with that proposed by Montomoli et al. (2001). Using fluid inclusion analyses of quartz crystals from syntectonic veins of Macigno, these authors determined a temperature value of 280 °C for the end of the D1 tectonic phase. This is also in full agreement with the metamorphic conditions suggested by the vitrinite reflectance data, which point to the anchizone/epizone boundary (Reutter et al., 1980).

6. Discussion

It is obvious that establishing the metamorphic grade of the Tuscan Nappe through illite and chlorite "crystallinities" requires use of data not affected by interferences by associated mixed-layer minerals and/or intermediate Na/K-micas. Therefore only data from PM samples have been applied to this purpose. On the basis of the CIS scale (Warr, 1996), that adopts the same values of Kübler's scale (Kübler, 1984, 1990) for the diagenesis zone/anchizone and anchizone/epizone transitions (0.42 and 0.25° $\Delta 2\Theta$, respectively), the average IC index value of this sample set ((AD) $IC_{10\text{\AA}}$ = 0.31 ° $\Delta 2\Theta$; Fig. 5) suggests middle anchizonal conditions for "Posidonomya Marl" (PM) formation. The same metamorphic grade can be reasonably ascribed to the other formations owing to the small difference in their structural depths (see Fig. 1). This grade matches only approximatively the metamorphic conditions suggested by the geothermometric data. In fact, if we assume for the anchizone the temperature range indicated by most metamorphic petrologists, that is $\sim 200 \,^{\circ}\text{C}$ to ~300 °C (Kisch, 1987; Merriman and Frey, 1999), the temperature derived in the present work through carbonate thermometry (~ 290 °C) and by Montomoli et al. (2001) through fluid inclusion analysis (280 °C) would rather suggest an upper anchizonal grade, not far from the conditions of the boundary anchizone/epizone. This grade would be also expected on the basis of both the structural features (deformation mechanisms and cleavage fabrics) of the Tuscan Nappe in the La Spezia area, and the data on vitrinite reflectance collected by Reutter et al. (1980) on the Macigno formation. In our opinion such inconsistency is most likely due to the inadequacy of the CIS scale to work as a precise indicator of metamorphic grade. The problem is discussed at length in a paper by Leoni (2001), who essentially points out that the CIS scale is an excellent tool for inter-laboratory calibration of IC data, but it would require an appropriate resetting of the boundary values of the anchizone to work also as a precise indicator of the metamorphic grade. Probably these limits ought merely to be shifted towards higher values of 0.04 $^{\circ}\Delta 2\Theta$ (Leoni, 2001). When the Kübler-scale-normalized data are considered,

an average IC_{10Å} value of 0.27 ° $\Delta 2\Theta$ (AD value) is obtained for PM formation; the subsequent application of Kübler's illite "crystallinity" boundary limits (Kübler, 1984, 1990) would shift the PM formation metamorphic grade towards the anchizone/epizone boundary, that is in the upper anchizonal grade, which is much more consistent with the geothermometric and structural evidence.

The most detailed studies on chlorite "crystallinity" (ChC) are those of Arkai (Arkai, 1991; Árkai et al., 1995, 1996), who asserts that the ChC method is a tool as trustworthy as the IC method, though less sensitive than the latter for identifying differences in metamorphic grade (Árkai et al., 1995). In particular, chlorite "crystallinity" can be considered a useful complementary tool where the interpretation of illite "crystallinity" is hindered by disturbing factors. The anchizone ChC boundaries proposed by Árkai et al. (1995) were established by linear correlation between IC and ChC and based on IC boundaries of Kübler's scale; the values of these boundaries, appropriately re-calculated according to interlaboratory (Budapest-Neuchâtel) calibration equations, are 0.390–0.266 °Δ2Θ and 0.307–0.244 °Δ2Θ for ChC_{14Å} and ChC_{7Å} indices, respectively (measurements at low goniometer speed). Application of this scale to the chlorite indices of the present study produces results largely coincident with those given by IC Kübler's scale. In fact, the average values of $ChC_{14\text{\AA}}$ and $ChC_{7\text{\AA}}$ indices for PM samples, re-calculated according to interlaboratory (Pisa-Neuchâtel) calibration equation, are $0.27 \circ \Delta 2\Theta$ and $0.24 \circ \Delta 2\Theta$, respectively. These values are actually very close to the ChC limit established by Árkai et al. (1995) for the anchizone/epizone boundary.

Relative differences and trends in assemblages and properties of phyllosilicates from the different structural positions of the mega-fold must be taken into consideration to evaluate the influence of strain on crystal structural features of illite and chlorite. The most notable trend observed is the disappearance of both the mixedlayer minerals and the intermediate Na/K-micas in the higher-strain zones, where the latter phases are probably replaced by discrete illite and paragonite. Where mixed-layer minerals and intermediate micas are absent (as in PM formation) or their effect is resolved from the measured XRPD reflections (as in the cases of $IC_{5Å}$, $ChC_{14Å}$, and $ChC_{7Å}$ peaks), the differences in the "crystallinity" of illite main population as well as in the "crystallinity" of chlorite over the different structural positions are actually very small, most of them being within error limits. However such differences are systematic: there is a constant trend exhibiting mica and chlorite peaks slightly narrower in the most deformed zones than in the least deformed ones. This pattern is likely justifiable on the basis of the following considerations: (a) strain (and, subordinately, lithology) seems to be an important factor in the development of cleavage in the rocks sampled (all of which are anchizonal in grade), where a cleavage more closely spaced in the inverted limb and in the hinge zone of the megastructure than in the normal limb is observed; (b) according to Merriman et al. (1990)



Fig. 10 Frequency distribution of MgCO₃ contents (mol%) in calcite crystals coexisting with dolomite in 7 samples from RcLM formation. The temperature scale reported as a line graph below the histogram was calculated from the equation in Bickle and Powell (1977).

and Roberts et al. (1991) the increase of phyllosilicate crystallite size may be accelerated by cleavage development as cleavage contributes to the simultaneous dissolution and growth of larger crystals at the expense of the smaller ones; (c) mixed-layer minerals and intermediate Na/K-micas are the more unstable phases from equilibrium considerations (Jiang and Peacor, 1993; Velde, 1995; Merriman and Peacor, 1999); it is then obvious that such phases are the first to be dissolved to produce larger, homogeneous phyllosilicate crystallites; (d) in the present case study the input of strain energy into the sequence of rocks involved in the La Spezia mega-fold, already undergoing syntectonic very low grade crystallization, went on only to the stage of a full dissolution of mixed-layer minerals and intermediate Na/K-micas and a moderate acceleration of illite and chlorite growth rates.

7. Conclusions

1) In most cases the $IC_{10\dot{A}}$ index values measured on rocks of the Tuscan Nappe involved in the La Spezia megastructure are greatly influenced by the distribution of illite/smectite mixed-layer minerals and intermediate sodium potassium micas, which, in turn, are strongly controlled by the intensity of deformation. This explains the high scattering of values of the mica "crystallinity" index observed in the previous studies of this unit in the La Spezia area and the highly variable metamorphic grade that was inferred from them.

2) The CIS scale introduced by Warr and Rice (1994) and currently used by several workers represents an excellent tool for inter-laboratory calibration of clay mineral "crystallinity" data, but it would require an appropriate resetting of the anchizone boundary limits to work also as a precise indicator of metamorphic grade; in our opinion, a shift towards higher values of $0.04 \circ \Delta 2\Theta$ of both the anchizone's upper and lower limits would be adequate (Leoni, 2001).

3) In the La Spezia mega-fold the effect of tectonic strain on crystal structural features of illite and chlorite manifests itself as small-scale variations in IC and ChC as a function of structural position; in contrast, tectonic strain appears to promote the dissolution / recrystallization of illite/ smectite mixed-layer minerals and intermediate Na/K-micas.

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