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Crystallinity distribution and crystallinity – b_0 relationships in white K-micas of Verrucano metasediments (Northern Apennines, Italy)

by *Marcello Franceschelli*[1], *Leonardo Leoni*[2] and *Franco Sartori*[2]

Abstract

The "crystallinity" distribution and the relationship between "crystallinity" and b_0 in white K-micas from pelitic and psammitic metasediments of Triassic Verrucano sequences of the Northern Apennines are examined. The mica "crystallinity" index, i.e. the (001) peak width at half height measured in degrees $\Delta 2\Theta$, shows an appreciable dispersion of values, even within an individual outcrop. However, when outcrops are grouped according to metamorphic grade established on the basis of the occurrence of kaolinite, pyrophyllite and kyanite, and average "crystallinity" index values are considered, a clear trend in the "crystallinity" distribution becomes apparent. Average "crystallinity" values decrease (the "crystallinity" increases) from the "kaolinite + pyrophyllite + quartz" zone ($\Delta 2\Theta = 0.33°$) through the "pyrophyllite + quartz" zone ($\Delta 2\Theta = 0.28°$) to the "kyanite + quartz" zone ($\Delta 2\Theta = 0.26°$).

The b_0 parameter of Verrucano white K-micas is positively correlated with the "crystallinity" values of the micas. This relation is so evident that micas characterized by high b_0 values ($b_0 > 9.040$ Å) have diffraction patterns showing an incipient $K\alpha_1$–$K\alpha_2$ splitting of the (060) peak as a consequence of their high "crystallinity". The close relationship between b_0 and "crystallinity" suggests that in low or very low grade metamorphic processes the latter may be influenced by the octahedral sheet composition.

Keywords: Mica "crystallinity", b_0 determination, chemical composition, X-ray diffraction, Verrucano rocks, Northern Apennines, Italy.

Introduction

Since the work of Weaver (1960) and Kübler (1968) the "crystallinity" of fine-grained white K-micas has been related to progressive evolution of sediments from diagenesis to early stages of metamorphism. It is now recognized that, apart from instrumental conditions, several factors like temperature, fluid pressure, stress, time, lithology and mineral chemistry may affect the mica "crystallinity" values (Frey, 1987). However, the actual role and weight of these factors is not yet clear. In particular the relationships between mica chemistry and mica "crystallinity" are not fully understood. It is well established that increasing K-content in illite leads to better illite "crystallinity" (Riedel, 1966; Weaver and Beck, 1971; Brauckmann, 1984; Hunziker et al., 1986), but the influence of the octahedral sheet composition still represents a controversial point. According to Esquevin (1969), in the diagenesis zone an increase of the Mg content in the octahedral sheet promotes a better illite "crystallinity", while during low grade metamorphism the Mg-rich micas are prevented from enhancing their degree of "ordering" by the heterogeneity of the charge deficit distribution within the silicate layer.

In the present study "crystallinity" distribution and "crystallinity" relationships with b_0 (assumed to be an estimate of the Mg + Fe_{tot} content) have been examined in white K-micas from a large number (110) of samples of Verrucano metasediments from the Northern Apennines (Italy). The aim of this investigation is to document the progressive modification of mica "crystallinity" in sedimentary sequences affected by very low grade metamorphism, in which a mineral zonation had been already recognized (Franceschelli et al., 1986), as well as to provide data for a better understanding of the relationships between mica composition and mica "crystallinity".

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Regional setting

The Verrucano rocks, mainly quartzites, phyllites, metapsammites and metaconglomerates, form the clastic sedimentary sequences representing the basal quartz-arenite assemblage of the Alpine geosyncline in the Tuscan Domain of the Northern Apennines (CASSINIS et al., 1979). These sequences of Middle to lower Upper Triassic age, outcrop in discontinuous patches from Punta Bianca (Eastern Liguria) to Monte Argentario (Southern Tuscany) (Fig. 1).

During Alpine orogenesis the Verrucano sediments underwent deformations and modifications under very-low-grade metamorphic conditions. On the basis of the regional distribution of some Al-silicates, FRANCESCHELLI et al. (1986) recognized the following four metamorphic zones: 1) "kaolinite + quartz" zone; 2) "kaolinite + pyrophyllite + quartz" zone; 3) "pyrophyllite + quartz" zone; 4) "kyanite + quartz" zone. According to FRANCESCHELLI et al. (1986) the four metamorphic zones correspond to temperatures ranging from 300 to about 450 °C at pressures between 3 and 5 kbar.

Within very-low-grade metamorphism these thermal conditions represent a rather wide range. Owing to the large variety of lithology, also the bulk chemistry of Verrucano rocks cover a wide spectrum of compositions, characterized by different degrees of Al-saturation (FRANCESCHELLI et al., 1989). It is therefore evident that Verrucano metasediments offer the opportunity of investigating the "crystallinity" evolution and the "crystallinity" relationships with b_o (i.e. with octahedral composition) of white K-micas in a wide range of temperatures and chemistry at the onset of metamorphism.

Sample selection and analytical techniques

Samples analyzed in the present study were collected from Verrucano sequences belonging to the three higher-grade metamorphic zones identified by FRANCESCHELLI et al. (1986). No samples from the "kaolinite + quartz" zone (so far reported only from drill holes; FRANCESCHELLI et al., 1986) have been considered. Moreover great care was taken in avoiding samples where more than one muscovite type is evident. In fact during Alpine orogenesis the Verrucano rocks underwent polyphasic deformation; three major folding phases, associated with development of S1, S2 and S3 axial plane schistosities have been recognized (FRANCESCHELLI et al., 1986). Generally only S1, and subordinately S2, schistosities are associated with mineral growth. This means that three different muscovite types may coexist within the same specimen: detrital muscovite, metamorphic S1 muscovite and metamorphic S2 muscovite. Since the presence of detrital and late-phase metamorphic micas can be easily detected in thin section on the basis of microstructural relationships, samples characterized mainly by S1 muscovites were selected.

Furthermore, special attention was paid to the presence of other sheet silicates with a first basal reflection close to that of white K-micas, i.e. pyrophyllite and paragonite. Pyrophyllite never caused serious problems; when present this mineral occurs only in small amounts, giving X-ray diffraction patterns characterized by a low first basal peak, always distinct from the strong mica reflection. On the contrary the presence of paragonite in significant amounts resulted to be a highly disturbing factor in the accuracy of illite "crystallinity" measurement; in this study samples from paragonite-containing rocks were then carefully avoided.

The Kübler "crystallinity" index (half-height peak width expressed as $\Delta 2\Theta$) has been measured with a Philips PW 1793 automatic diffractometer. Measurements were performed on the < 2 µm fraction sedimented on glass slides. Care was taken to avoid thin slides (FREY, 1988). The instrumental conditions were as follows: CuK_α Ni-filtered radiation, divergence and receiving slit width = $(^1/_2)°$, focusing slit width = 0.2 mm, goniometer rotation speed = $^1/_4$°/min., chart speed = 4 cm/min., time constant = 4.

The values of "crystallinity" index were calibrated with respect to those of Kübler's laboratory using his standards.

The non-metamorphic/anchimetamorphic ($\Delta 2\Theta$ = 0.42°) and anchimetamorphic/epimetamorphic ($\Delta 2\Theta$ = 0.25°) boundaries proposed by KÜBLER (1984) were assumed.

On the same specimens the mica polytypes were identified by the MAXWELL and HOWER (1967) method.

The b_o parameter has been calculated from the mica (060, $\bar{3}31$) spacing using the (211) quartz reflection as an internal standard. Measurements were performed on randomly oriented samples of the < 2 µm fraction prepared by filling the sample-holder from above against a glass slide. For some specimens the measurement of (060, $\bar{3}31$) spacing was repeated on rock slices cut perpendicular to the foliation, as recommended by SASSI and SCOLARI (1974). This procedure largely eliminates the problems connected with the overlapping of the (060) reflection by the strong ($\bar{3}31$) reflection of the $2M_1$ muscovite (SASSI and SCOLARI, 1974; FREY et al., 1983). No significant difference between the values obtained by the two procedures was ob-

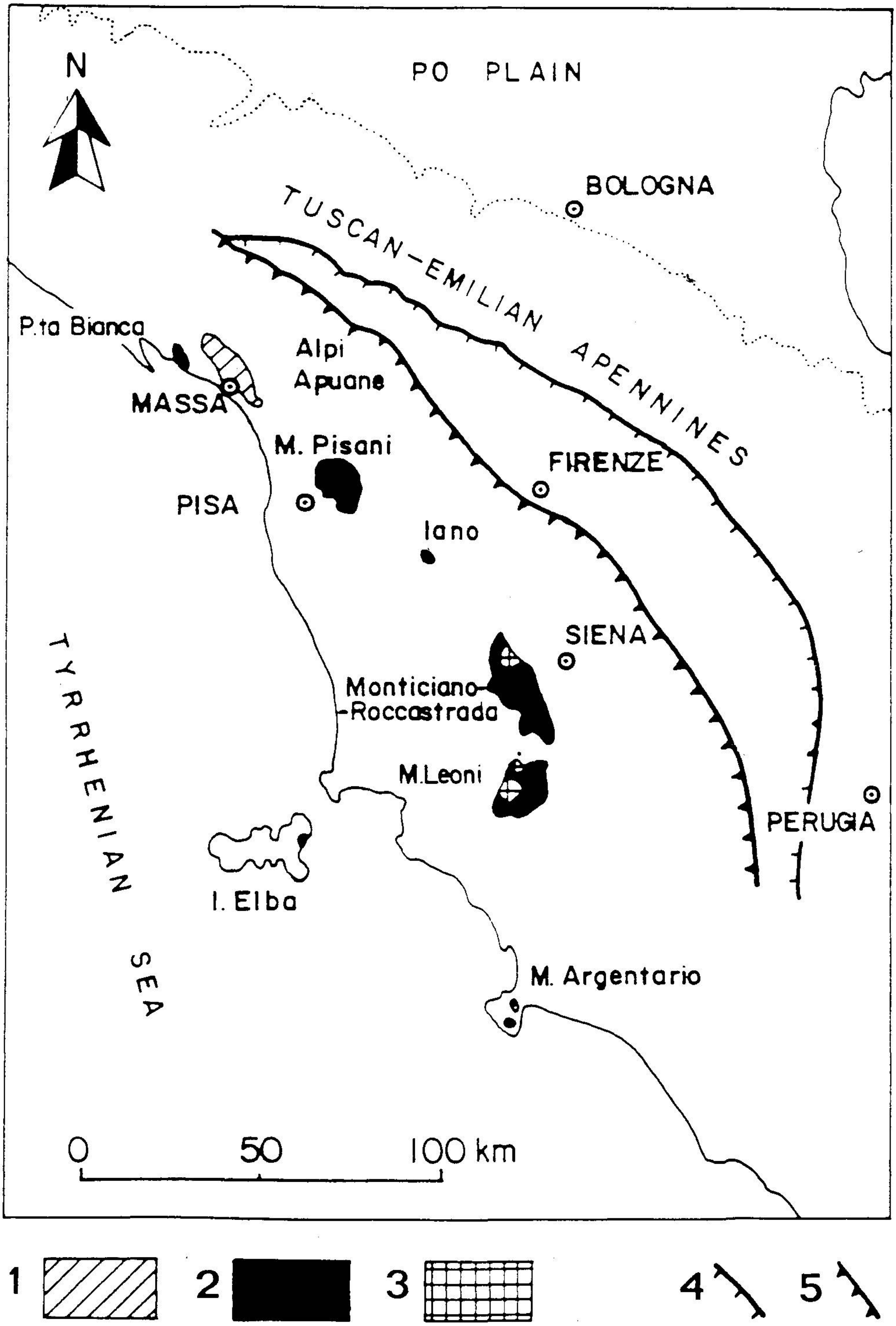

Fig. 1 Sketch map of Verrucano metamorphic zonation in the Northern Apennines and geographical distribution of sampled outcrops. (1) "kyanite + quartz zone"; (2) "pyrophyllite + quartz zone"; (3) "kaolinite + pyrophyllite + quartz zone"; (4) front of the Tuscan Nappe; (5) front of the Cervarola Flysch.

served, and conventional powder diffractometry has been regarded as giving sufficiently reliable results.

Results and discussion

MICA POLYTYPISM AND "CRYSTALLINITY"

In the investigates samples, $2M_1$ is by far the most common polytype of white K-micas; only few samples show small amounts of the 1Md polytype. This indicates metamorphic conditions close to the anchizone/epizone boundary or the low-grade greenschist facies (FREY, 1987). This conclusion is supported by the absence or rare occurrence of detrital muscovite in the examined Verrucano rocks; according to HUNZIKER at al. (1986) some detrital micas can still be observed optically in rocks at the anchizone/epizone boundary or in the lower epizone, but completely disappear in samples from the middle epizone. Furthermore the Verrucano "crystallinity" index values (Fig. 2) again suggest anchizone/epizone boundary conditions.

Within these overall metamorphic conditions it is possible to detect a metamorphic zonation on the basis of the regional distribution of the "crystallinity" index values. In Fig. 2 histograms of the "crystallinity" index values for individual outcrops are reported; only the histogram g combines data from several outcrops. These histograms show that an appreciable dispersion of values exists within individual outcrops: Monte Argentario ($\Delta 2\Theta$ = 0.26°–0.38°), Monti Leoni ($\Delta 2\Theta$ = 0.26°–0.38°), Iano ($\Delta 2\Theta$ = 0.26°–0.36°), Monticiano-Roccastrada ($\Delta 2\Theta$ = 0.24°–0.36°), Punta Bianca ($\Delta 2\Theta$ = 0.26°–0.32°), Massa ($\Delta 2\Theta$ = 0.20°–0.34°), Monti Pisani ($\Delta 2\Theta$ = 0.20°–0.32°).

As will be discussed later, such a spread of values may be largely ascribed to the wide range of chemical compositions of micas within an individual outcrop and to the control exerted by this parameter on "crystallinity" values. On the other hand it seems unlikely that differences in lithology could play an important role, if it were not through the resultant differences in bulk rock chemistry. On account of Verrucano metamorphic grade, the two lithological factors pointed out by FREY (1987), that is differences in "crystallinity" due to detrital micas and differences in porosity and permeability controlling aggradation of illite, are in fact to be ruled out. According to KÜBLER (1968, 1984) and DUNOYER DE SEGONZAC (1970), the influence of these factors on illite "crystallinity" diminishes with increasing diagenetic of metamorphic grade and becomes negligible at the onset of the anchizone.

Notwithstanding the dispersion of values within most individual outcrops, a general trend of mica "crystallinity" distribution may be perceived if Verrucano samples are grouped according to their Al-silicate assemblages (FRANCESCHELLI et al., 1986). Histograms f to h of Fig. 2 show mica "crystallinity" index distributions within the three groups of sequences identified (each ot the "kaolinite + pyrophyllite + quartz" and "kyanite + quartz" zones is only represented by one outcrop, Monte Argentario and Massa, respectively). Even if differences between average "crystallinity" indices of the three groups are not significant at two-sigma level, comparison of the three histograms suggests a small shift of the "crystallinity" index distribution to lower values (which means higher mica "crystallinity") from the "kaolinite + pyrophyllite + quartz" zone (average "crystallinity" index: $\Delta 2\Theta = 0.33° \pm 0.07$ [2 σ]) through the "pyrophyllite + quartz" zone (average "crystallinity" index: $\Delta 2\Theta = 0.28° \pm 0.06$ [2 σ]) to the "kyanite + quartz" zone (average "crystallinity" index: $\Delta 2\Theta = 0.26° \pm 0.045$ [2 σ]).

b_0 PARAMETER AND CHEMICAL COMPOSITION

As pointed out in previous studies (FRANCESCHELLI et al., 1986; BALDELLI et al., 1989), Verrucano white K-micas show a wide range in chemical composition. In the octahedral sheet Al varies from 2.62 to 3.67 a.f.u. (atoms per formula unit), (Mg + Fe^{2+}) ranges from 0.32 to 0.72 a.f.u., while the Fe^{3+} content may be as low as 0.05 up to 0.67 a.f.u. (BALDELLI et al., 1989). The interlayer sheet is commonly characterized by a cation deficiency, the sum (Na + K) ranging from 1.69 to 1.99 a.f.u. These micas show b_0 values in the range of 8.990–9.065 Å, which appear highly correlated with octahedral sheet compositions. If such compositions are expressed by their RM-values as defined by CIPRIANI et al. (1968), that is RM = 2 Fe_2O_3 + FeO + MgO (molar proportions), the following correlation is obtained: $b_0 = 8.982 + 0.499 \cdot RM$, $r = 0.88$, where r is the correlation coefficient (FRANCESCHELLI et al., 1989).

The relationships between b_0 and the "crystallinity" index are illustrated in Fig. 3. Notwithstanding the large spread of points most plots exhibit a well established trend. The "crystallinity" index appears to decrease when b_0 increases. This means that under the same metamorphic conditions the mica "crystallinity" becomes higher when the celadonitic and the ferrimuscovitic contents of the mineral increase. This relation is so evident that micas

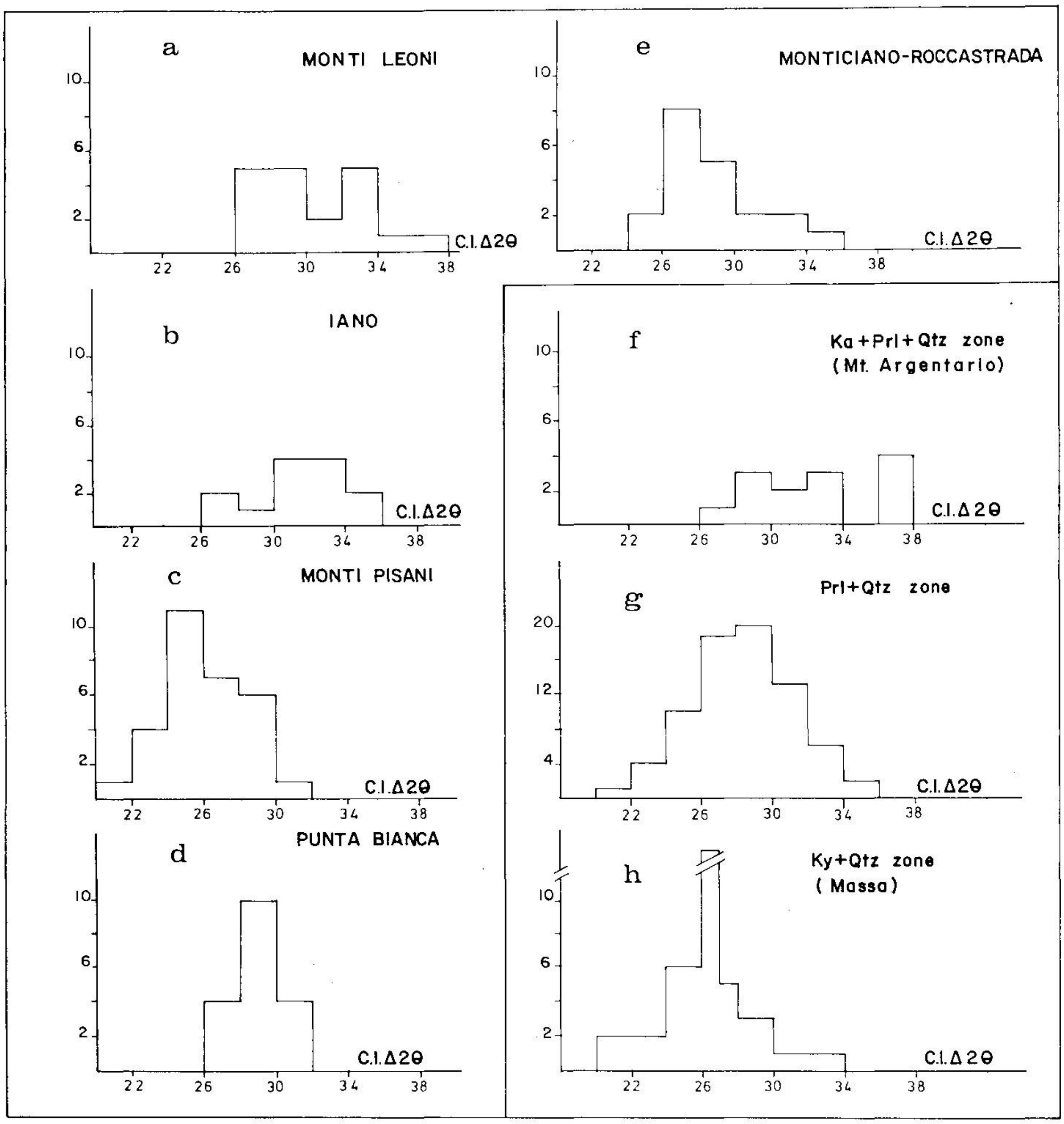

Fig. 2 Histograms showing the regional distribution of "crystallinity" index values ([001] peak width at half height measured in degrees $\Delta 2\Theta$) in Verrucano white K-micas. a–e are histograms for individual outcrops from the "pyrophyllite + quartz zone"; in f–h the data are arranged according to metamorphic zonation.

characterized by high b_0 values ($b_0 > 9.040$ Å) have diffraction patterns showing incipient $K\alpha_1$–$K\alpha_2$ splitting of the (060) peak as a consequence of their high degree of "ordering" (Franceschelli et al., 1989; Fig. 2).

Therefore it can be stated that the octahedral sheet composition is an important factor affecting mica "crystallinity" in the low-grade metamorphic processes. The way it affects mica "crystallinity" supported by our data is at variance with that pointed out by Esquevin (1969). He found a positive correlation between "crystallinity" and the Mg-content of Mg-rich illites from the diagenesis field, but observed that these minerals hardly improve their "crystallinity" during low-grade metamorphism. The data of Esquevin (1969) are to be considered as doubtful because of the parameter he used to distinguish between aluminous and magnesian illites, that is the intensity ratio I(002)/I(001). In fact Hunziker et al. (1986) showed that little confidence can be placed in the estimation of chemical composition of illites from their intensity ratios at 10 and 5 Å. On the other hand the b_0 parameter adopted in the present paper is generally considered as a proper tool to evaluate the octahedral sheet compositions of white K-micas (Frey et al., 1983 and literature cited therein).

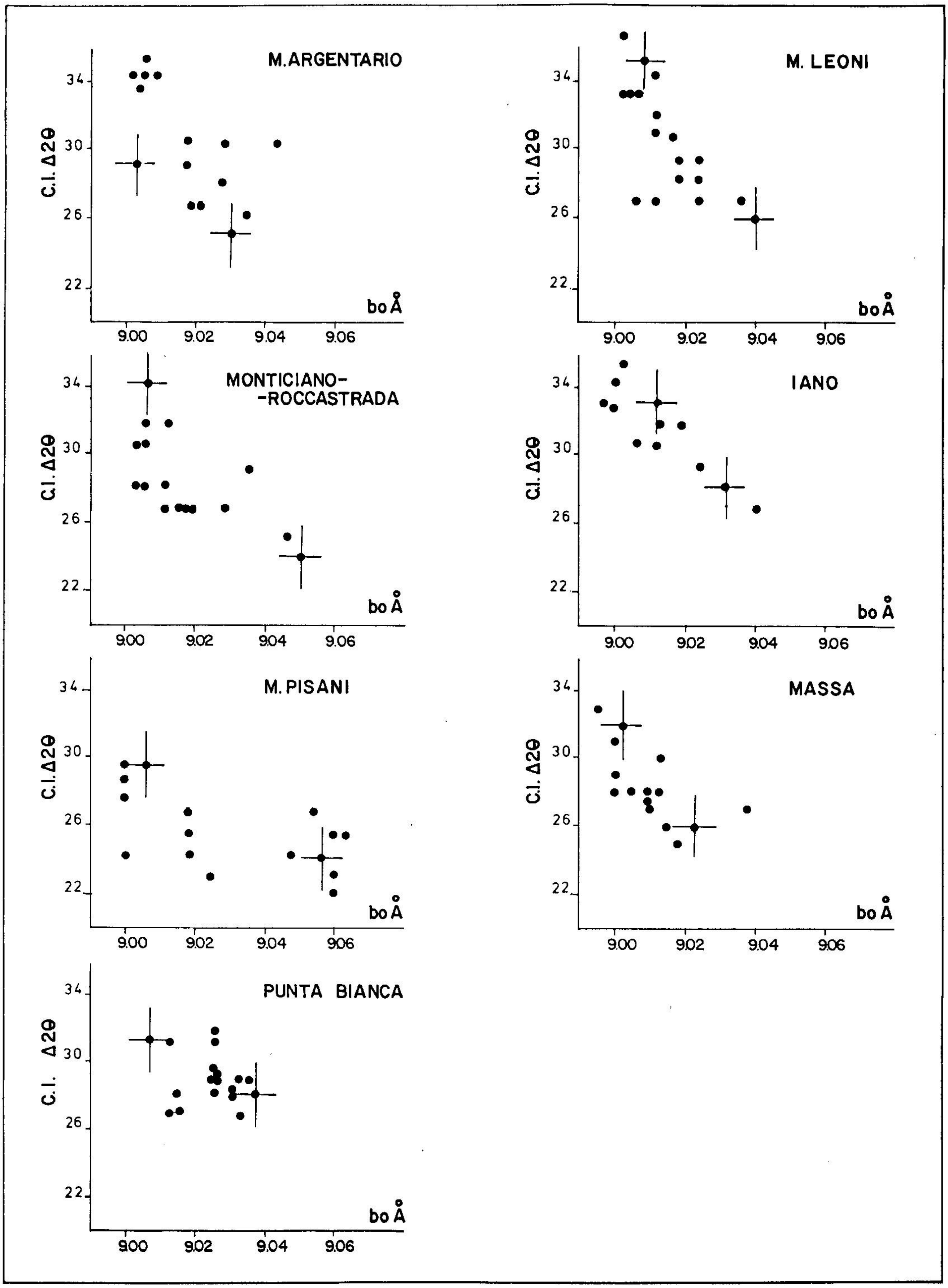

Fig. 3 Correlation of b_0 with "crystallinity" index (C.I.) values in Verrucano white K-micas (two-sigma standard deviations are plotted as bars).

Conclusions

The mineralogical data on Verrucano white K-micas presented here have given new informations on: (1) the influence of the octahedral sheet composition upon mica "crystallinity", and (2) the variation of metamorphic grade within the Verrucano sequences.

Octahedral sheet composition appears to play an important role in determing mica "crystallinity". In contrast to the results of ESQUEVIN (1969) it has been found that mica "crystallinity" increases with increasing celadonite and ferrimuscovite contents, even in the anchizone or in the low-grade greenschist facies. This would imply that for establishing variations of metamorphic grade only the "crystallinity" values from micas having the same (or nearly the same) composition should be compared. This condition could be met by selecting samples from chemically similar rocks. This severe constraint can be overcome by the practical approach of determining mica "crystallinity" index on a large enough sample population for each outcrop and for each metamorphic zone. As pointed out by FREY (1987) this procedure allows to avoid several pitfalls connected with the large number of factors affecting mica "crystallinity".

The data on Verrucano mica "crystallinity" distribution presented in this paper clearly support the reliability of such a practical approach. Despite the large range of mica octahedral sheet composition and the absence of any preliminary screening of samples on a bulk-chemistry basis, the analysis of the mica "crystallinity" distribution from large sample populations allows to confirm the metamorphic zonation of the Verrucano sequences already established by Al-silicate assemblages (FRANCESCHELLI et al., 1986).

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