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# Kyanite-bearing early Alpine metapsammite in the Larderello Geothermal Region (Italy) and its implications to Alpine metamorphism and Triassic paleogeography*

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**Abstract**

Detailed petrological studies on cuttings and core samples from the Larderello wells reveal the existence of two types of Verrucano: the first (Verrucano LR), characterized by metamorphic partial recrystallization, the preservation of sedimentary features and a metamorphic grade reaching the pyrophyllite stability field, closely resembles the classical Verrucano of the Monti Pisani; the second (Verrucano HR), defined by strong recrystallization, overprinting of sedimentary features and a metamorphic grade reaching the kyanite and chloritoid stability fields, resembles the Verrucano of the Massa Unit. On the basis of mineralogical data the two Verrucano types represent a single prograde metamorphic complex. The two Verrucano types repeatedly alternate as a consequence of tectonic movements during the Tortonian compressional phase. The decreasing frequence of marble levels from the Verrucano HR to LR and the metamorphic grade of the HR comparable to that of the Massa Unit, indicate that the Verrucano sediments in the Larderello region were deposited in different parts of a single internal (western) Triassic basin.

Transitional types were also found between the evaporitic levels of the Triassic Burano Formation and the clastic members of the Verrucano LR. A structural study reveals two main Alpine schistosities and traces of a weak, late crenulation cleavage. The climax of metamorphism (appearance of kyanite) was reached after the end of the first folding phase.

*Keywords:* Verrucano, Alpine metamorphism, Pyrophyllite, Kyanite, paleogeography, Northern Apennines.

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## Introduction

The Northern Apennines consist of various tectonic units piled onto one another during the Alpine orogeny. The lower and intermediate tectonic units (Tuscan Nappe and Tuscanid I) show a gradual decrease of the degree of coalification (Reutter et al., 1980) and of illite crystallinity (Cerrina Feroni et al., 1983) from the internal (SW) towards the external (NE) zone. The coalification patterns have been explained by the existence of a thermal paleogradient higher than the present one, indicating that the entire edifice of nappes piled up and then moved towards the external zones after the main thermal event (Reutter et al., 1980). Likewise, the illite crystallinity patterns led Cerrina Feroni et al. (1983) to postulate an increasingly deep tectonic level for the Tuscan Nappe from the external towards the internal parts of the chain. Similar conclusions were reached for the variation of the metamorphic grade in the Tuscanid I Unit by Di Pisa et al. (1985).

The early Alpine clastic sediments known as "Verrucano Group" or "Triassic Verrucano" outcrop discontinously throughout the Northern Apennines (Fig. 1). According to Rau & Tongiorgi (1974) these sediments belong to the paleogeographic unit known as the Massa Unit l.s. The appearance of kyanite in the Verrucano of the Massa Unit s.s. (Apuan Alps), reported by Bonatti (1938) and the presence of the pair kaolinite-pyrophyllite in the Al-rich rocks of the Verrucano of South Tuscany (Azzaro et al., 1976; Melani, 1984) indicate a wide variation of the metamorphic grade for the Verrucano throughout the Northern Apennines. Up to now it was difficult to reconcile the lack of kyanite in the Verrucano of South Tuscany with the increase of metamorphic grade from NE to SW, indicated by the results of Reutter et al. (1980) and Cerrina Feroni et al. (1983).

Recent geological studies (Gianelli et al., 1978; 1979; 1981; Batini et al., 1983) carried out on deep drilling data from the Larderello geothermal field revealed the existence of a complex of tectonic slices between the metamorphic basement and the overlying Cenozoic-Mesozoic units.

Many levels of the Triassic Verrucano belong to this complex. Four of the wells reported in Fig. 2 were examined in greater detail: Sperimentale 1 Serrazzano (SS), Serrazzano 16 (S 16), CPC 1 (CP) and Monteverdi 5 (M 5).

These new petrologic data show that the Verrucano quartzites and phyllites underwent an Alpine prograde metamorphism reaching the kyanite stability field. In many cases complete recrystallization took place, making it very difficult to distinguish between the Verrucano and comparable levels of the Paleozoic Buti Group.

The recent discovery of many tourmalinites and pink quartz pebbles, the lack of thin hematite strings in some metamorphic levels previously assigned to the Buti Group (Gianelli et al., 1978; Batini et al., 1983) and the analogies of

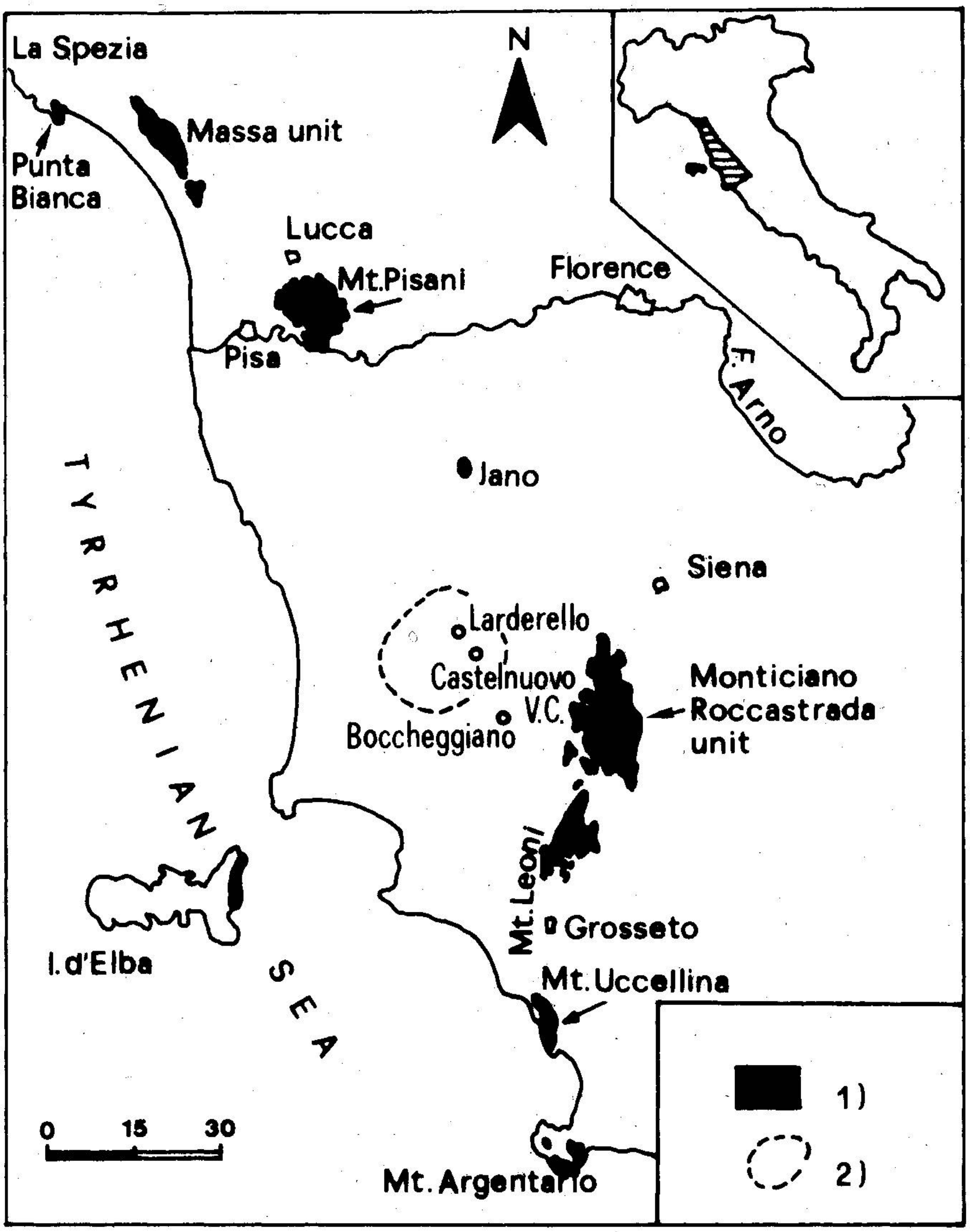



*Fig. 1* Location of the main Tuscan Verrucano outcrops cited in this paper. 1. Verrucano outcrops. 2. Larderello region.

these rocks with the metamorphic Verrucano of the Massa Unit suggest that they are more likely to belong to the Triassic Verrucano. However, the striking similarity between many samples of the Larderello Verrucano and analogous lithotypes of the Buti Group do not entirely rule out that some of the studied core samples belong to the Paleozoic. The present paper defines and describes

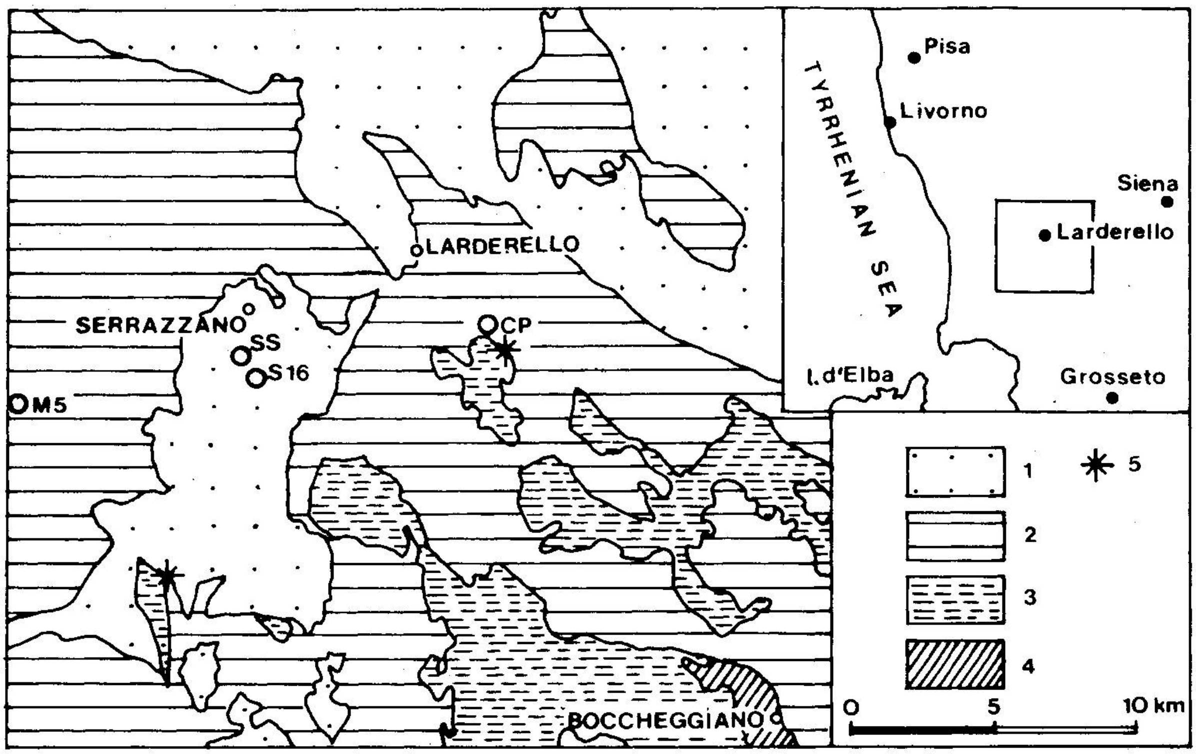



*Fig. 2* Geological sketch map of the Larderello region and location of the studied wells. 1. Neogene sediments. 2. Ligurids. 3. Tuscan Nappe. 4. Boccheggiano Formation s. l. 5. Small outcrops of Verrucano. Open circles: studied wells. For symbols see text.

the different varieties of Verrucano in the Larderello region, in order to reach a better understanding of the Alpine metamorphism and the Triassic paleogeography of Tuscany, and a more accurate reconstruction of the deep structural setting in the Larderello geothermal field.

## Geological outline

Surface geology and deep structural setting of the Larderello region has already been dealt with in the literature (see MAZZANTI, 1966; LAZZAROTTO, 1967; LAZZAROTTO & MAZZANTI, 1976; BATINI et al., 1983). The following tectonic units can be recognized, from the top downwards:

1. Quaternary travertine and alluvium
2. Autochthonous Mio-Pliocene sediments (maximum thickness 1100 m)
3. Allochthonous flysch units known as "Ligurids", characterized by high diagenesis to incipient metamorphism (Lower Cretaceous-Upper Eocene) (max. thickness 2500 m)
4. Tuscan Nappe (max. thickness 1400 m): "Macigno" and "Scaglia" Formations (Cretaceous-Lower Miocene), cherty and carbonate formations (Upper Trias-Malm) and basal anhydrite and dolostone of the Burano Formation (Trias). The entire Tuscan Nappe shows an incipient metamorphism.

5. Metaconglomerate, quartzite and phyllite of the Verrucano Group (Trias) of low metamorphic grade.
6. A complex of tectonic slices of the above-described Jurassic–Triassic formations and of the Permo–Carboniferous Supergroup and the Filladi Inferiori Group (see below).
7. Rocks of the Tuscan Crystalline Supergroup (Buti, Filladi Inferiori and Micaschist Groups) and gneiss (Devonian–Precambrian (?); see PUXEDDU et al., 1984 and related references). These rocks, showing a low-to-medium metamorphic grade, underwent a late Alpine contact metamorphism described in more detail by DEL MORO et al. (1982).

The thickness of the above formations vary widely. The values given are the maximum thicknesses reported in the literature for the Larderello region. The real thickness of the various units cannot be estimated because of tectonic repetitions and stretching. A rough idea of their thicknesses can, however, also be obtained from the stratigraphic logs of Fig. 3.

## Lithology

Many lithotypes were recognized in the Verrucano samples from the Larderello region and they can easily be compared with those described by RAU & TONGIORGI (1974) and TONGIORGI et al. (1977) for the Monti Pisani. Two main groups of samples can be recognized: they are characterized by a relatively low (LR) or high (HR) degree of metamorphic recrystallization. The different lithotypes are:

### VERRUCANO LR:

1. Pink and white, coarse-to-medium grained, poorly sorted, quartz pebble metaconglomerate ("Anageniti Grossolane" and "Anageniti Minute"), sometimes containing tourmalinite.
2. Fine-grained quartzite ("Quarziti Verdi") derived from mature well-sorted near-shore sandy sediment.
3. Fine-grained greenish grey phyllite ("Scisti Verdi") derived from alternating clay and sandy to silty levels.
4. Very fine-grained red to violet, black or grey-whitish hematite-rich phyllite ("Scisti Violetti") with sporadic grey-violet, silty intercalations.

Only in well CPC 1 at 1213 m depth (for this and all other wells depth is referred to ground-level) were pure marbles encountered, associated with green quartzite and phyllite of the Verrucano LR. Some small outcrops of Verrucano slices near Castelnuovo belong to the Verrucano LR.

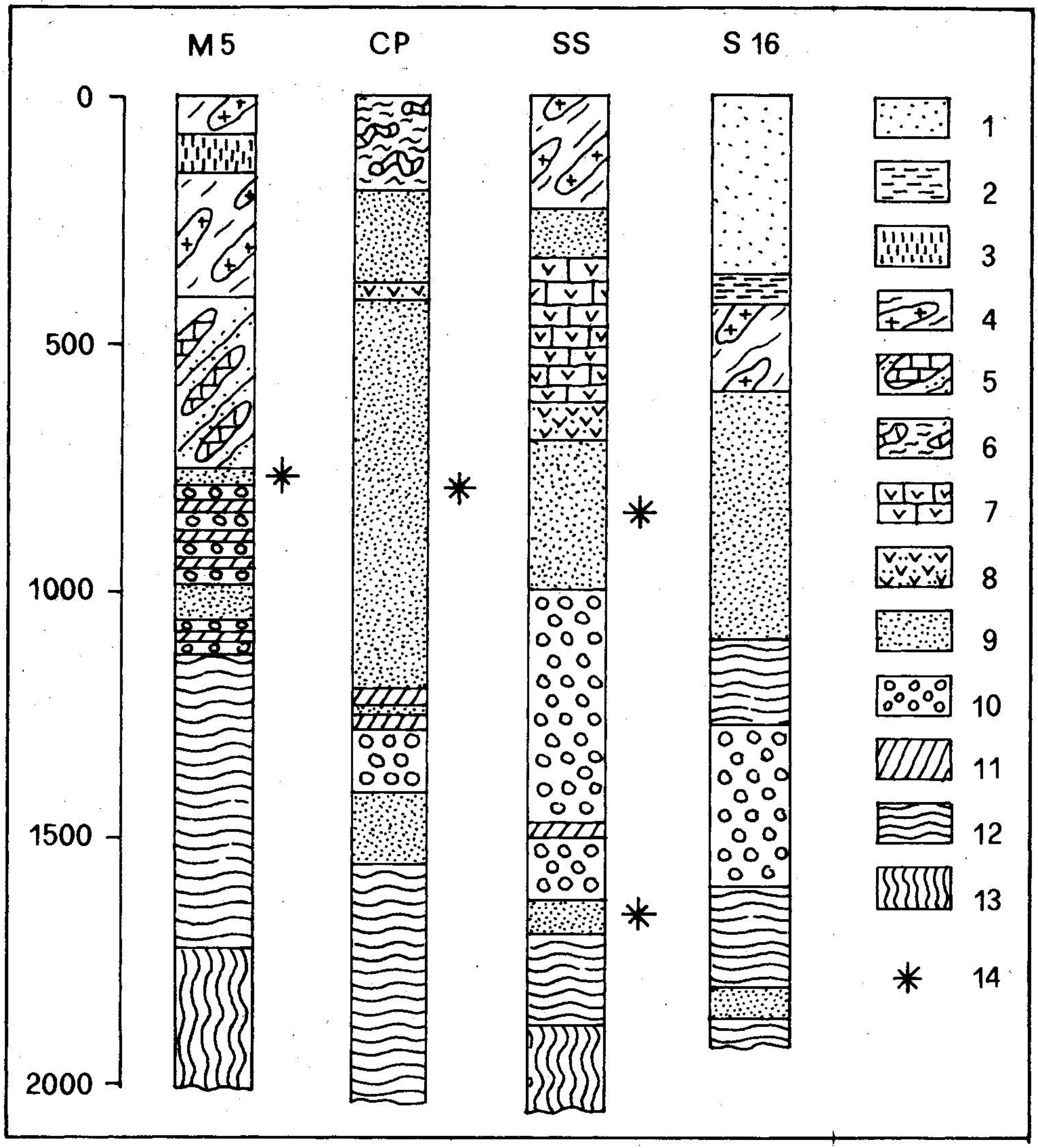



*Fig. 3* Stratigraphic logs of the wells. Monteverdi 5 (M 5), CPC 1 (CP), Sperimentale 1 Serrazzano (SS) and Serrazzano 16 (S 16). 1. Neogene sediments (Lower-Middle Pliocene). 2. Neogene sediments (Upper Miocene). 3. Lanciaia Formation (Middle-Upper Paleocene - Middle Eocene). 4. Palombini shales (Lower Cretaceous). 5. Calcareous marly flysch (Upper Cretaceous). 6. Canetolo complex (Paleocene-Upper Eocene). 7. Burano Formation (cavernous limestone) (Trias). 8. Transitional clastic evaporitic levels (Trias). 9. Verrucano Formation - Type LR (Trias). 10. Verrucano Formation - Type HR (Trias). 11. Marble levels (Trias ?). 12. Filladi Inferiori Group. 13. Micaschist Group. 14. Anhydrite-bearing Verrucano levels. Due to discontinuous coring, the contacts between the various formations are approximations.

VERRUCANO HR:

1. White-to-pink, fine-to-coarse grained phyllitic quartzite.
2. Greyish-black to grey-whitish, hematite-rich, sometimes greenish, quartzitic phyllite, containing scattered millimetric pink quartz pebbles. Sporadic occurrence of tourmalinites was observed. Types 1 and 2 of the Verrucano HR could represent the more metamorphosed and recrystallized equivalents of the previous four types described (Verrucano LR).
3. Thin grey-whitish, micaceous, siliceous marble intercalations (probably of stratigraphic nature) are also present at many levels.

## Microstructural features

The structural study was carried out on hand specimens and thin sections of core samples from three deep wells, SS, S 16, CP. Cuttings only were available for well M 5.

Two main schistosities, $S_1$ and $S_2$, were identified. Sometimes $S_2$ is crenulated by a third surface, $S_3$. These three surfaces show a great variety of morphological characters, depending on the lithology and position of the samples in the well.

Schistosity $S_1$ is the most penetrative deformation surface. It occurs more frequently in phyllitic quartzite in which later deformation phases did not induce a complete textural reorganization. In more pelitic fine-grained rocks the $S_1$ surface is transposed and totally obliterated. In the phyllitic quartzite $S_1$ is evidenced by a preferred orientation of sheet silicates and by flattening and elongation of quartz crystals. Sometimes $S_1$ is defined by a metamorphic layering made up of alternations of quartzitic and phyllitic layers.

Schistosity $S_2$ is usually very distinct, closely spaced, and sometimes parallel to $S_1$. The surface $S_2$ is defined by alignments of muscovite and chlorite flakes. In the fine-grained rocks $S_2$ dominates over $S_1$ and viceversa in the coarse-grained rocks.

Schistosity $S_3$ was observed in a few samples only, as a weak crenulation of $S_2$, locally producing a pervasive surface.

## Mineralogical and petrological data

The mineralogical study of the metamorphic minerals was based on optical and X-ray data. The results obtained are summarized and presented graphically in Fig. 7.

The petrological data have revealed the existence of two main populations, which partially overlap. The first (LR) is characterized by weak recrystallization, locally giving a blastopsammitic texture, still preserved sedimentary fea-

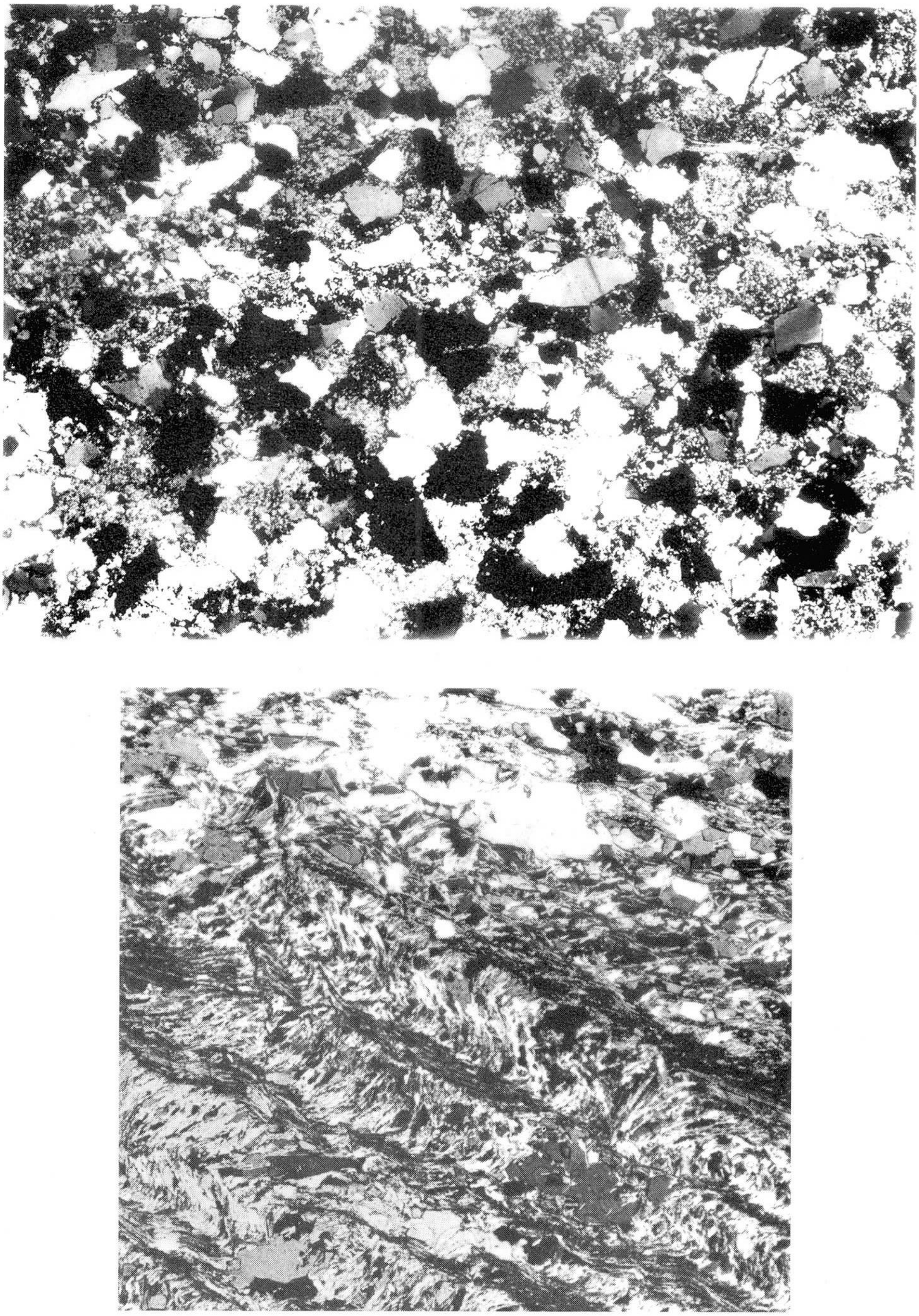


*Fig. 4* Photomicrographs of samples from Verrucano LR. Crossed polars, × 40. a) Metapsammite of sample SS 881 m. Note the weak recrystallization of the rock, characterized by a microcrystalline matrix. b) Quartzitic phyllite of sample SS 802 m, showing $S_1$ and $S_2$ schistosities at high angle.

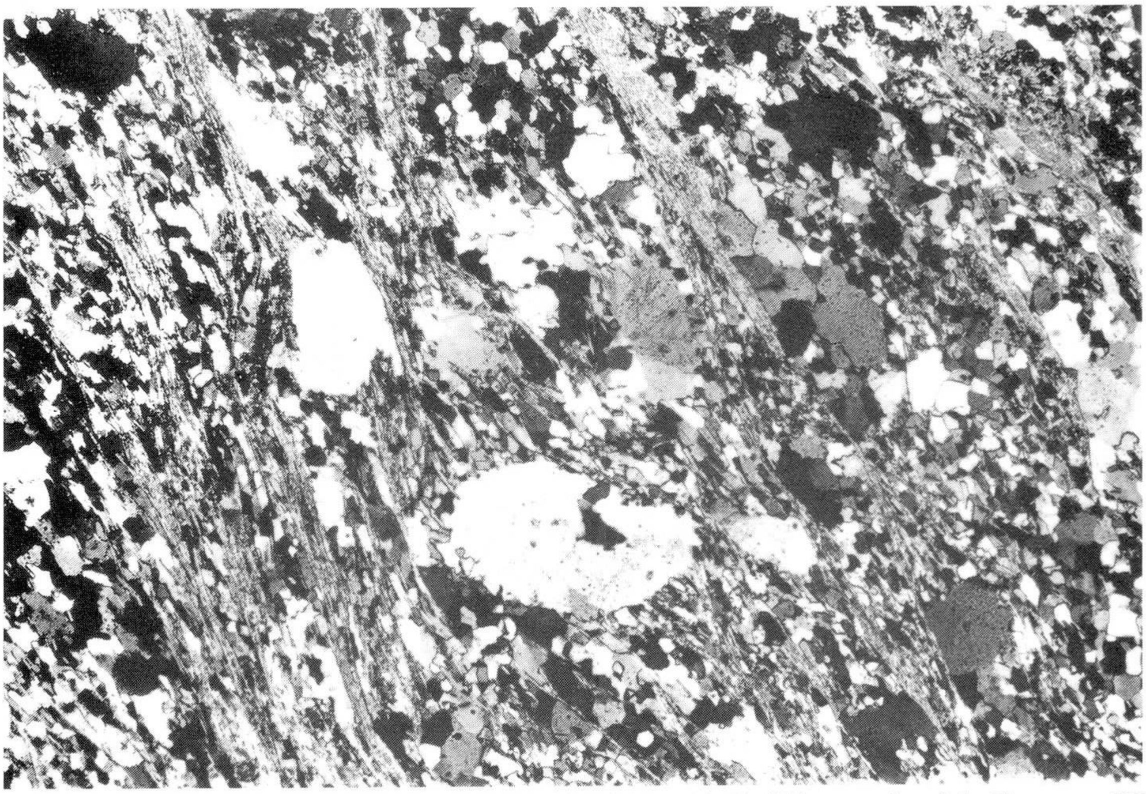


*Fig. 5* Photomicrograph of sample SS 1298 m. Crossed polars, × 40. Phyllitic quartzite of the Verrucano HR. Note the greater textural reorganization compared to the Verrucano LR, producing a granoblastic texture in the matrix of quartz-rich layers. The $S_1$ schistosity is defined by preferred orientation of sheet silicates.

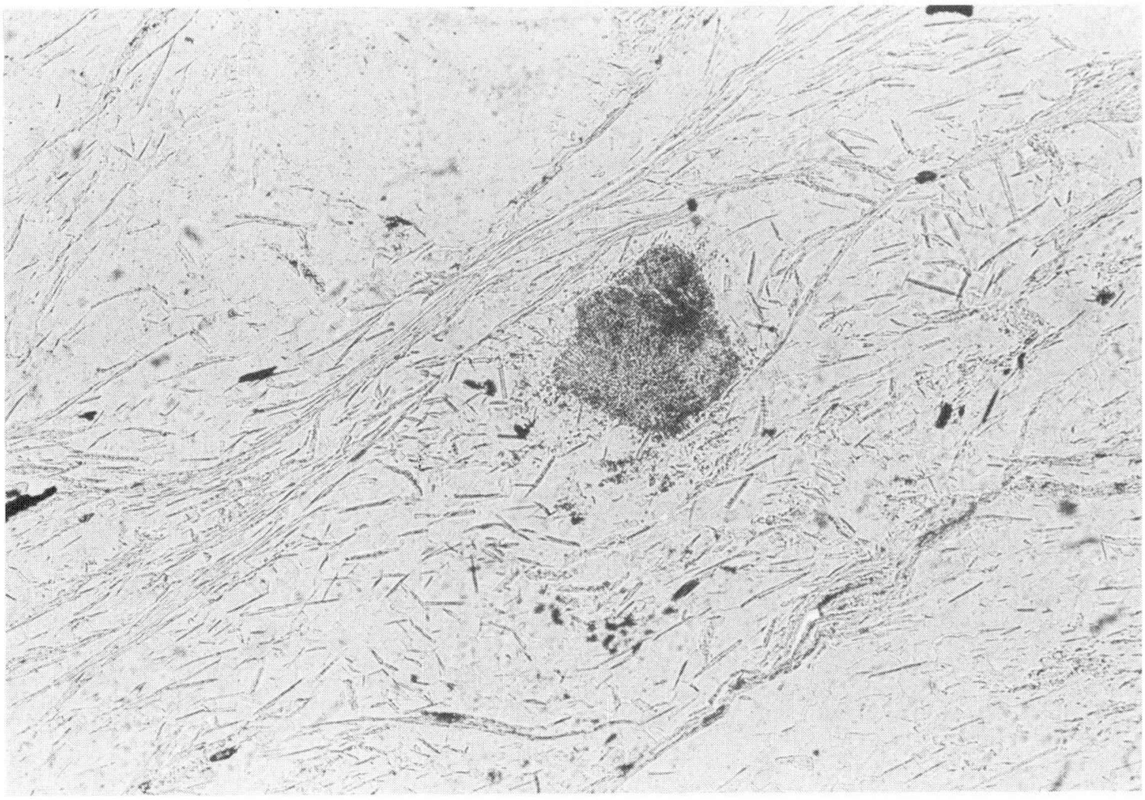


*Fig. 6* Photomicrograph of sample SS 1300 m. Crossed polars, × 40. Presence of tourmalinite in the Verrucano HR.

tures, clasts that are clearly distinguishable from the surrounding matrix (see Fig. 4) and sporadic occurrence of pyrophyllite. This type is almost identical to the Verrucano of the Monti Pisani. The second HR (see Fig. 5) underwent strong recrystallization with a grano-lepidoblastic texture, partial and sometimes complete effacement of any sedimentary feature and sporadic occurrence of kyanite. This type closely resembles the kyanite-bearing, strongly recrystallized Verrucano of the Massa Unit.

The Verrucano rocks consist of variable amounts of newly formed metamorphic phases and relict detritic minerals, often still recognizable in spite of Alpine recrystallization (particularly in the Verrucano LR). The modal percentages of these two kinds of minerals are a function of lithotype and metamorphic grade. Detritic minerals, mainly quartz, muscovite and tourmaline (in tourmalinites: see Fig. 6) are pre-tectonic with respect to the $S_1$ schistosity, whereas the metamorphic minerals are syn- or post-tectonic.

The main metamorphic minerals of the Verrucano LR are quartz, muscovite, pyrophyllite, chlorite and carbonates, with accessories such as apatite, zircon and tourmaline. Quartz is the most common mineral, together with muscovite; it appears elongated, parallel to the $S_1$ surface. Muscovite forms lepidoblastic blades parallel to both $S_1$ and $S_2$ schistosities. X-ray data indicate the presence of only $2M_1$ muscovite, with variable celadonite contents ($b_o = 8.999–9.050$ Å).

The crystallinity index of K-white mica is always below $2\theta = 0.30$.

Chlorite is parallel to muscovite and belongs to an Mg–Fe variety.

The carbonates are widespread and represented by calcite and dolomite in variable combinations.

Pyrophyllite was recognized on the basis of the first basal reflections at 9.16, 4.58 and 3.05 Å.

Except for an increase in grain size, all these minerals are present with the same features in the Verrucano HR.

Some minerals, however, have so far been found in the Verrucano HR only: paragonite, kyanite and chloritoid. Paragonite was identified by reflections at 9.67, 4.82, 3.21 Å in two samples of the Verrucano HR from well SS.

Kyanite was found in two samples from well SS and in many cuttings from well M5. It is worth noting the coexistence of kyanite and pyrophyllite in the sample SS 1300 m. Kyanite postdates $S_1$ and predates $S_2$.

Chloritoid was observed in cuttings from well M5. It forms the typical fan-shaped to radiating aggregates and crystallized between the $S_1$ and $S_2$ development.

## PT conditions of metamorphism

The sequence pyrophyllite - pyrophyllite + kyanite - kyanite observed throughout the Larderello Verrucano samples may be evidence of an original prograde metamorphism beetween the Verrucano HR and LR, although the contact between these two types in the wells is sharp. The repeated tectonic alternations between Verrucano LR and HR were produced during the last compressional phase dated as Tortonian by BOCCALETTI et al. (1980). The peak metamorphism deduced from the crystallization of kyanite and chloritoid between the first two folding phases, was reached before the complex tectonic overthrusting of the two Verrucano types.

In order to estimate PT conditions at the peak of the Alpine metamorphism, we compared the observed mineral assemblages with the stability fields determined for the system $Al_2O_3$ - $SiO_2$ - $H_2O$ in theoretical and experimental studies (see Fig. 8) (ALTHAUS, 1966; KERRICK, 1968; THOMPSON, 1970; HEMLEY et al., 1980).

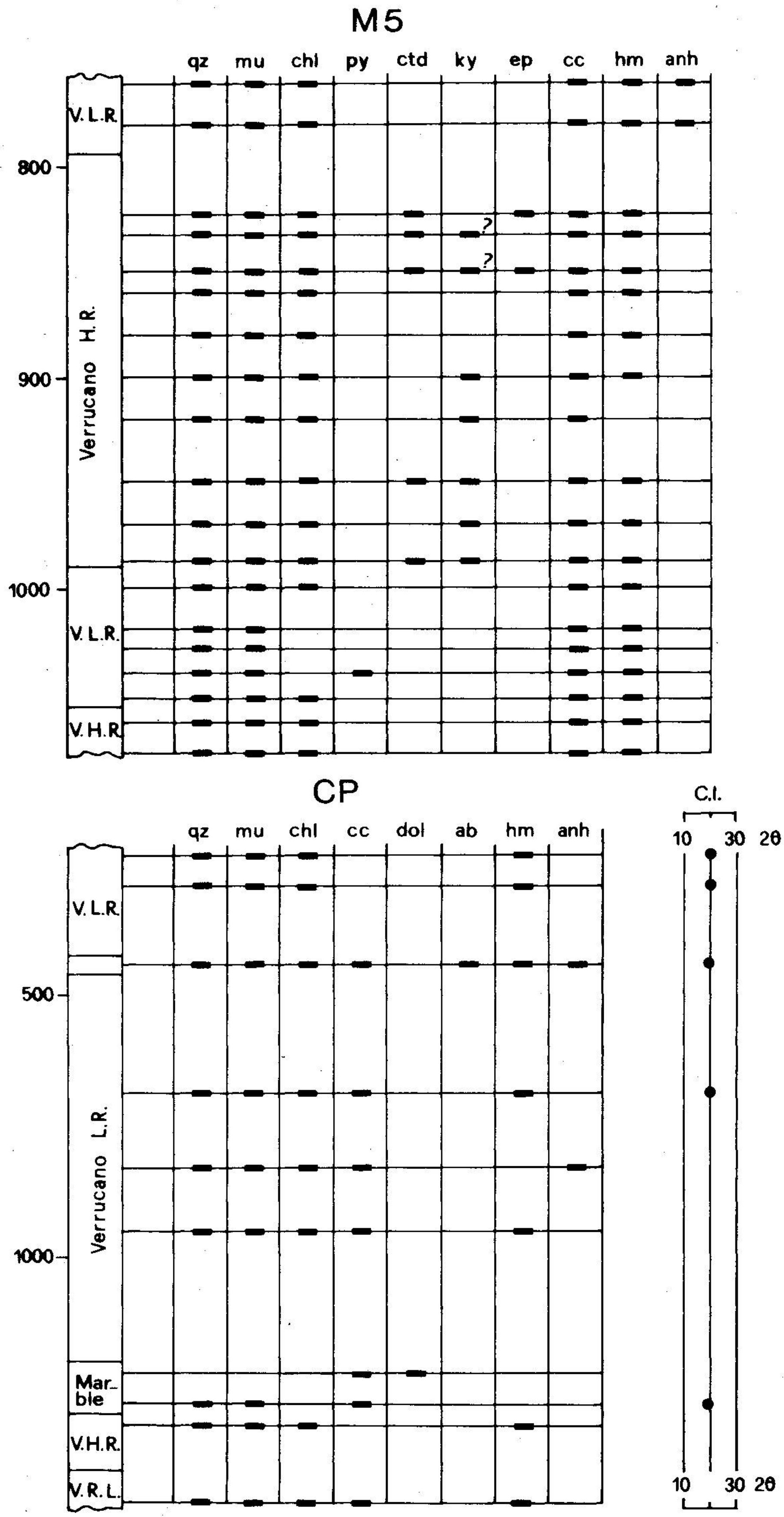
Some differences of opinion exist with regard to the lower limit of the pyrophyllite stability field. THOMPSON (1970) gives the following values for the first appearance of pyrophyllite: T = 325 °C for 1 Kb, T = 345 °C for 2 Kb and T = 375 °C for 4 Kb, for $P_{H_2O} = P_{total}$. HEMLEY et al. (1980) obtained T = 273 °C for 1 Kb. In the Verrucano LR samples we found pyrophyllite alone, whereas in the Verrucano HR samples we observed both coexisting pyrophyllite + kyanite and kyanite alone.

For the Verrucano LR the presence of pyrophyllite indicates temperatures in the broad range of 270 °C - 400 °C (for P = 4 Kb), but the transition to the assemblage pyrophyllite + kyanite suggests a more reliable temperature value close to the upper limit of 400 °C. For the Verrucano HR the presence of pyrophyllite + kyanite and kyanite alone suggests temperatures of about 400 °C - 450 °C (for P = 4 Kb). However, almost all the samples include at least one carbonate mineral, indicating the presence of $CO_2$ and $H_2O$ mixtures in the fluid phase during metamorphism. All the temperature estimates will consequently be slightly lower than the above values. For the pressure of the Alpine metamorphism a value of 4 Kb was assumed from the Si content of the Verrucano muscovites at Larderello and elsewhere in Tuscany (FRANCESCHELLI, unpublished data) and the pressure values estimated for the Verrucano of Elba by DESCHAMPS et al. (1983)

## Paleogeography of the Verrucano

Two important paleogeographic implications arise from the study of the Larderello Verrucano.

Firstly, comparisons of the Verrucano Group with the Burano Formation reveal the presence of intermediate facies with a gradual transition from clastic to evaporitic sedimentation. The Burano Formation is made up of anhydrite with levels of dolomicrite and calcareous dolostone, frequently brecciated. In the


M5
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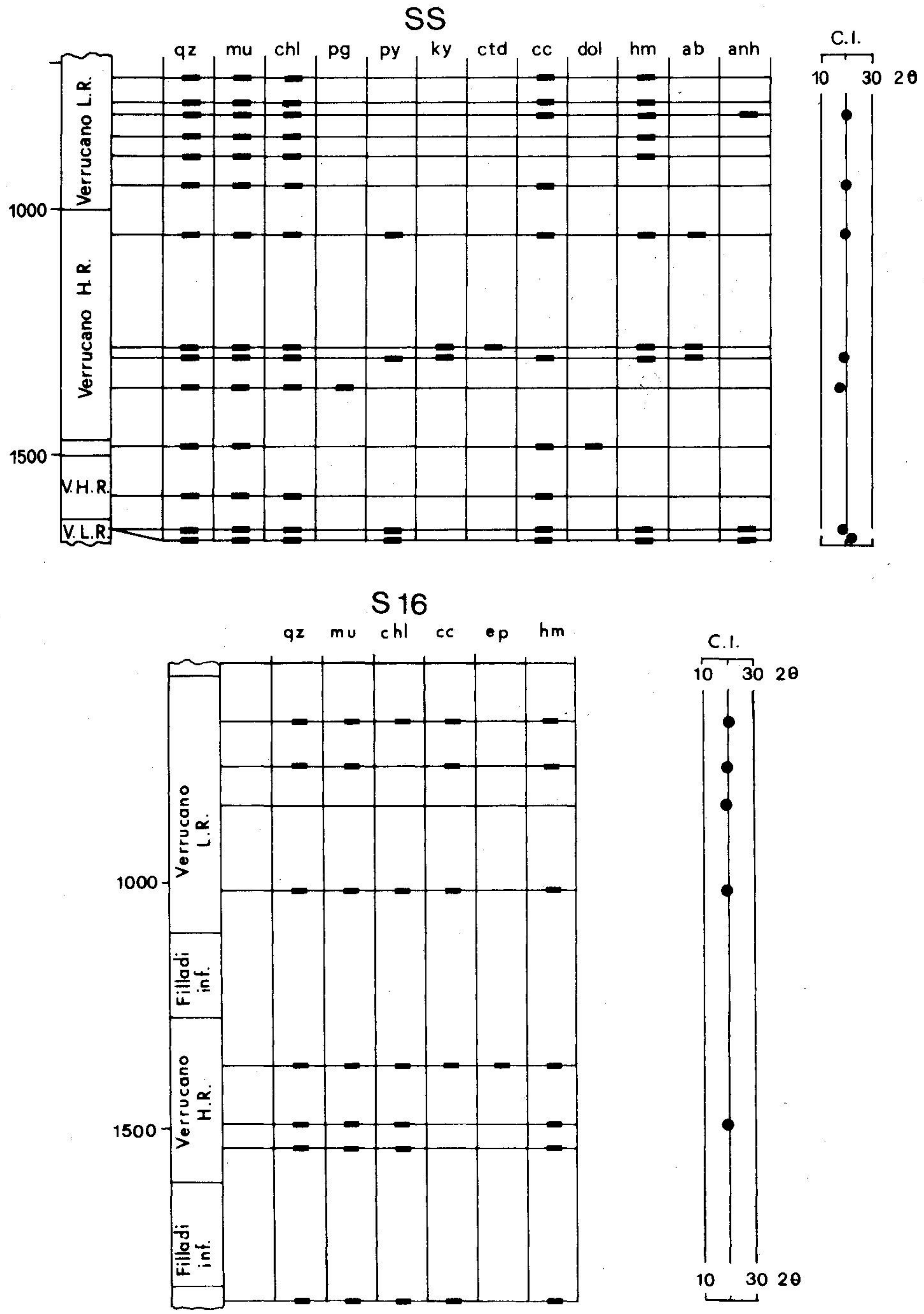


*Fig. 7* Metamorphic minerals and illite crystallinity index of studied samples. M 5; CP; SS; S 16. Mineral abbreviations are: qz: quartz; mu: muscovite; chl: chlorite; pg: paragonite; py: pyrophyllite; ky: kyanite; ctd: chloritoid; ep: epidote; ab: albite; cc: calcite; dol: dolomite; anh: anhydrite; hm: hematite; k: kaolinite; di: diaspore; stau: staurolite; a: andalusite; sill: sillimanite; w: $H_2O$.

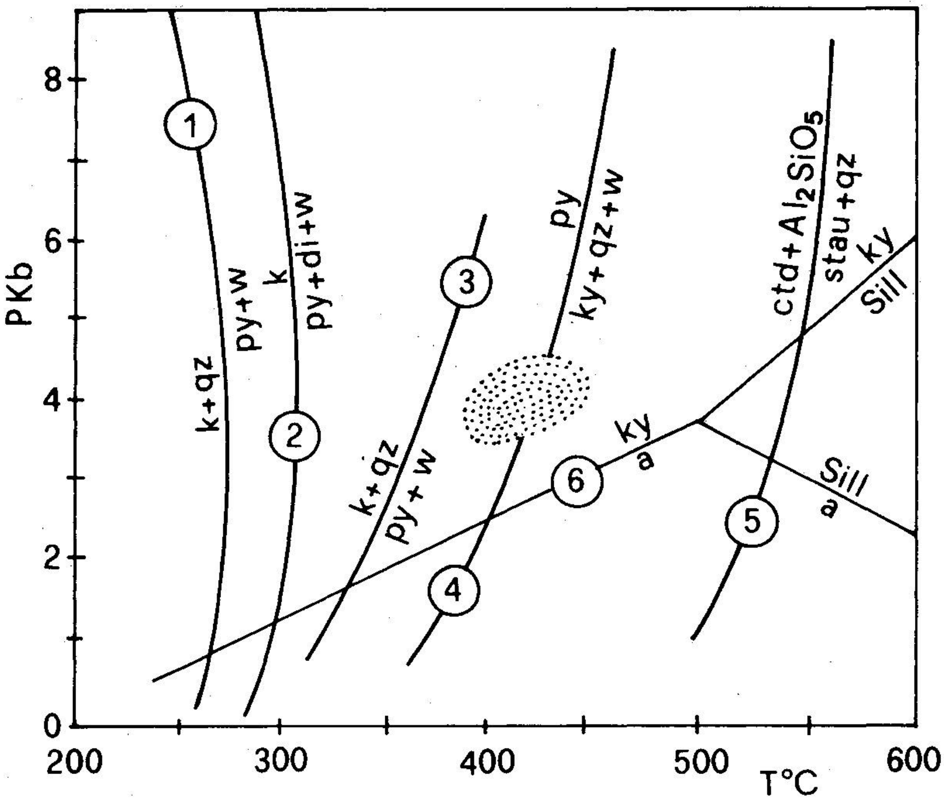


*Fig. 8* Inferred PT conditions of the Alpine metamorphism in the Larderello Verrucano (1, 2, 4 after HEMLEY et al. (1980); 3: after THOMPSON (1970); 5: after RICHARDSON (1968); 6: $Al_2SiO_5$ equilibria after HOLDAWAY (1971). Stippled area represents the inferred PT conditions of the Alpine metamorphism in the Larderello region. For mineral abbreviations see Fig. 7.

lower part of this formation sporadic thin intercalations of very fine-grained silty to sandy green phyllite are also present. Near its base this formation shows a gradual increase of clastic quartz. Below the tectonic surface dividing the Burano evaporite from the underlying Verrucano, the Larderello wells then cross transitional facies between the Burano Formation and Verrucano Group, characterized by repeated alternations of anhydrite, micaceous siliceous dolostone, sometimes with variable amounts of anhydrite, albite and hematite, violet and greenish phyllite ("scisti violetti" and "scisti verdi"), quartz pebble metaconglomerate ("anageneti") and green quartzite ("quartziti verdi"). The matrix of the clastic types is made up of quartz, sericite, and abundant anhydrite and carbonate. The transition to the highest part of the Verrucano sequence is marked by a gradual decrease in the anhydrite content. The above-described transition zone was probably affected at times by tectonic movements producing breccias in which elements of different lithotypes are surrounded by a matrix of carbonates, anhydrite, quartz and sericite.

In conclusion, the clastic contribution to the Verrucano sediments in the Triassic basin at Larderello was gradually replaced by chemical deposition of the

Burano evaporites. During the Alpine orogeny, the Burano Formation, with part of the basal transitional levels, was detached from the underlying Verrucano. The original stratigraphic transition from Verrucano to evaporite cannot, therefore, be observed because of this detachment.

The transitional levels rarely occur because they were crushed and scraped off by the overriding of the Tuscan Nappe onto the Verrucano substratum.

Another interesting feature of the Larderello Verrucano is the presence of some marble intercalations, mainly in the Verrucano HR.

The occurrence of relevant carbonatic levels was observed (see Fig. 1) in the Verrucano of the Massa Unit and of Punta Bianca (ELTER et al., 1966; FEDERICI and RAGGI, 1976; CIARAPICA and PASSERI, 1980), of Elba (DESCHAMPS, 1980, and DESCHAMPS et al., 1983) and of the Larderello region (this paper).

In other areas (Monti Pisani, Jano, Monti Leoni and Monti dell'Uccellina, Monticiano-Roccastrada area, Mt. Argentario; see Fig. 1), with the exception of the uppermost part showing passages to evaporitic sequences, thick carbonatic levels have not been recognized in the Verrucano (SIGNORINI, 1966; GELMINI, 1969; GIANNINI et al., 1971; GASPERI and GELMINI, 1973; RAU and TONGIORGI, 1974; GASPERI and GELMINI, 1975; AZZARO et al., 1976; PUXEDDU et al., 1979; BURGASSI et al., 1979; COSTANTINI et al., 1980).

This difference (presence or lack of important carbonatic levels) could represent a marker of the paleogeographic position of the Verrucano basins. This is supported by the following observation: the Verrucano containing marble levels generally shows a slightly higher metamorphic grade than the other Verrucano; a prograde metamorphic zoning from the internal (western) to the external (eastern) part of the Apennine belt has been reported by REUTTER et al. (1980), CERRINA FERONI et al. (1983), DI PISA et al. (1985). Consequently we suggest a more internal position for the marble-bearing and more metamorphic Verrucano in Tuscany.

At Larderello the decreasing frequency of marble levels and the decreasing metamorphic grade from Verrucano HR to LR, as well as the repeated tectonic alternations of the two types, indicate that the Verrucano forms a prograde metamorphic complex whose sediments were deposited in different parts (for the LR and HR) of the same internal Triassic basin.

## Concluding remarks

The geological conclusions that can be drawn from this study are:

1. Some levels with high metamorphic recrystallization, previously attributed to the Paleozoic Buti Group, belong instead to the Verrucano Group.
2. Mineralogical evidence shows that the Verrucano samples can be subdivided

into at least two mineral zones based on the sporadic occurrence of alumina-rich minerals:

a) pyrophyllite zone,

b) kyanite zone.

These zones, and the occurrence of kyanite + pyrophyllite-bearing samples indicate that the Verrucano of the Larderello region underwent a prograde regional metamorphism during the Alpine orogeny.

3. The discovery of kyanite in the Verrucano samples of the Larderello region reveals that in central-southern Tuscany (south of the Arno river), the Verrucano rocks reached a metamorphic grade comparable to the observed in the Verrucano of the Massa Unit (north of the Arno river). These new data allow us to interpret the variation of metamorphic grade for the Verrucano in Southern Tuscany and in the Larderello region in particular in the same way proposed by Reutter et al. (1980) for the lower tectonic units of the Northern Apennines.
4. The presence of intermediate facies between the Verrucano and the Burano Formation and, in particular, the occurrence of anhydrite-bearing Verrucano samples, are interpreted as evidence of a gradual transition from clastic to chemical sedimentation during the Triassic period in southern Tuscany.

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