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THE TIN DEPOSIT OF MONTE VALERIO (TUSCANY): NEW FACTUAL OBSERVATIONS FOR A GENETIC DISCUSSION **

ABSTRACT. — All the Authors which were concerned with Monte Valerio supported pyrometasomatic or pneumatholitic-hydrothermal genetic processes, linked to the Mio-Pliocene acidic magmatic activity. The present Authors, on the basis of factual observations directly achieved and/or reported in the existing literature, suggest syn-sedimentary Tin deposition, followed by partial supergene remobilization, and assigne a very limited role (if any) to the Mio-Pliocene magmatism and metamorphism on Tin distribution.

RIASSUNTO. — Tutti gli Autori che si sono fino ad ora occupati di Monte Valerio ne sostengono una genesi pirometasomatica o pneumatolitiċo-idrotermale, connessa all'attività magmatica acida mio-pliocenica. Per parte nostra, sulla base di dati di osservazione rilevati sul terreno o ricavati dalla letteratura esistente, suggeriamo una genesi per deposizione sin-sedimentria, seguita da parziale rimobilizzazione supergenica, e riteniamo che il ruolo del magmatismo mio-pliocenico sulla distribuzione dello Sn nell'area di Monte Valerio sia stato assai limitato se non addirittura nullo.

RÉSUMÉ. — Tous les Auteurs qui jusqu'ici se sont interessés du gisement de Monte Valerio en soutiennent une gènese pyrometasomatique ou pneumatholitique-hydrothermale, en rapport avec l'activité magmatique acide mio-pliocene. De nôtre part, sur la base des données directement relevées sur le terrain ou tirées de la littérature existente, nous suggerons une gènese par dêpot sin-sedimentaire, suivie par une rémobilisation partielle supergènique; nous croyons par consequent que le rôle du magmatisme mio-pliocene sur la distribution du Sn dans l'aire de Monte Valerio a été très limité si non tout à fait inexistant.

1. - Foreword

Monte Valerio has been the largest Tin deposit of Italy. It was known since Etruscan times, and intensely exploited specially during World War Two. The original tonnage of exploited reserves (cut-off grade 0.3 % Sn) can be estimated about 1,000,000 ton crude ore, holding 4,000 tons of Tin. At present, reserves with higher grade than 0.3 % Sn are practically exhausted; large reserves with lower grade (0.1-0.2 % minimum) are very probably still available.

The most important paper (with a rich bibliography) on Monte Valerio is the one by STELLA (1955). The papers by GIANNINI (1955) and by BERTOLANI (1958) contain outstanding contributions to the geology and, respectively, to the petrology and ore microscopy of Campiglia area, in which Monte Valerio is included. The area of Campiglia in turn is a part of the sheet 119 (Massa Marittima)

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mapped by Lotti (1906) and re-mapped by Brandi, Dallan, Giannini, Lazzarotto, Mazzanti, Squarci, Taffi, Tongiorgi, Trevisan (1968).

Field work, for the present paper, was carried out by P. Zuffardi; laboratory studies mainly by I. Venerandi-Pirri; both are responsible for the conclusions.

2. - Geological outline

2.1. *Local situation*

The following terranes occur in Monte Valerio area (fig. 1):

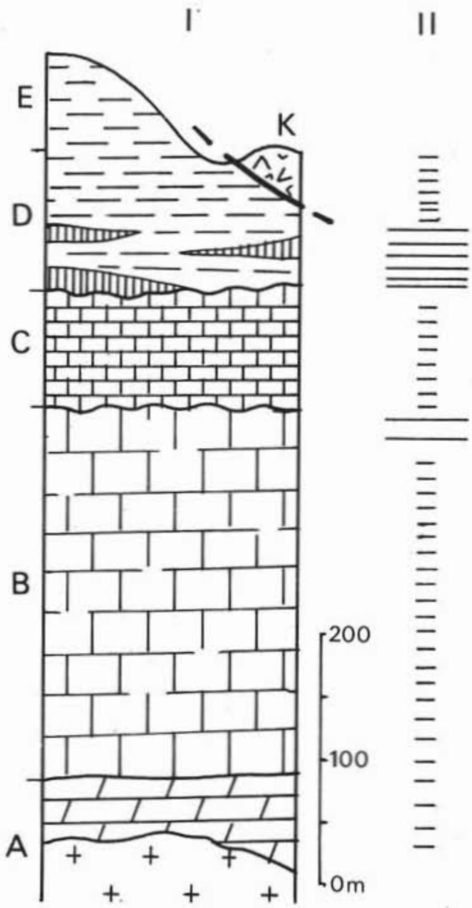


Fig. 1. — The stratigraphic column of Monte Valerio (I) and the distribution of Cassiterite along it (II). See point 2.1 for explanation of symbols.

A - Upper Triassic gray cristalline dolomite, blackish limestones, black shales.

According to Giannini (1955) they are not outcropping and have been found in depth by drilling; their base is not visible; proved thickness is about 50 m.

Maybe some bedded crystalline grayish limestones underlying the massive white marbles of complex B and included in it according to the official geologic maps, should be predated and included in complex A; a good example is visible at the western base of Monte Spinosa.

This hypothesis was also forwarded, at least in dubitative form, by Lotti (1910) and by Merciai (1936).

The transition from A complex to B complex seems to be conformable.

B - Lower Liassic massive, whitish and gray limestones, turning to white massive marbles in depth and in the proximity of the Tertiary granites of Botro ai Marmi. They are some hundred meters thick (300 or more?).

Their composition is monotonous along their whole thickness except the upper 20 meters: pink, somewhat silicic limestone lenses are frequent in the latter section. The pink colour is connected to diffused presence of haematite-goethite (often pseudomorphous after cubic pyrite) all along the beds (not only at their exposed surfaces). This fact speaks for an early, syn-diagenetic, weathering of pyrite and consequent deposition of Fe ox.

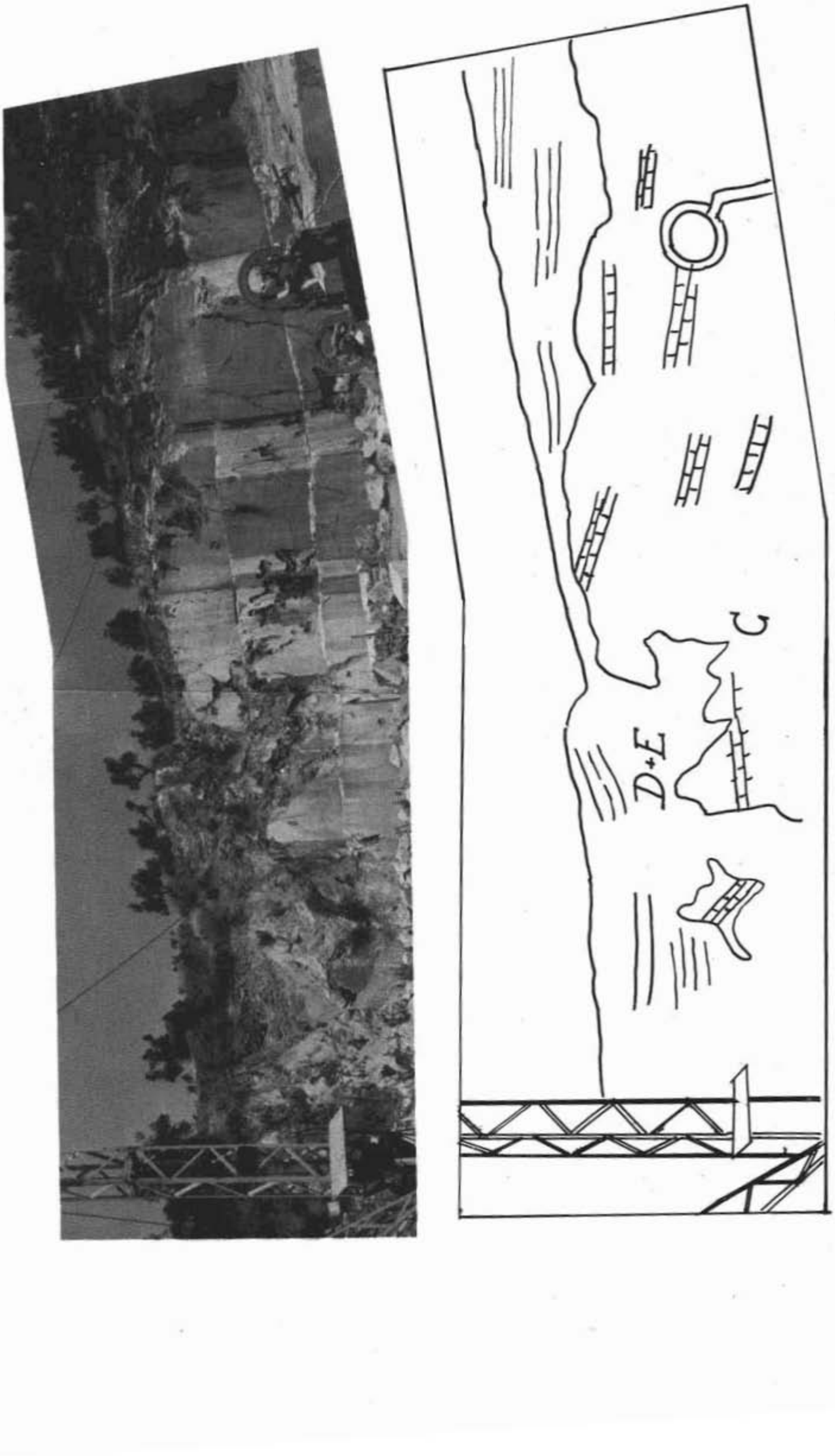


Fig. 2. — Photo and scheme of a front in a quarry at Monte Peloso.
Symbols: C: « Ammonitic Red Limestones »; D+E: jaspers of the D+E complex.

If this is true, the pink silicic lenses may be considered as evidences of sin-diagenetic oxidizing environments possibly related to paleo-currents.

The boundary between formation B and the overlying formations C has the geometric and stratigraphic characters of an emersion surfaces: f.i.: the boundary surface is oblique to stratification; the basal beds of C sometimes occupy hollows of B and are placed side by side to the massive limestones. These features have been described also by GIANNINI (1955).

C - Middle (partially Upper?) Liassic thinly bedded marly limestones, disconformably overlying formation B. They are pinkish, at places silicified, with

Fig. 3. — Another section in the same front of fig. 2; the lower part (smooth vertical surfaces) is made of thinly bedded « Ammonitic Red limestones »; the upper part (rough, irregular surfaces) is (mainly) made of jaspers. The regular bedding of limestones and some karstic cavities in them are evident. A piece of limestone, embedded in jasper, is visible at the extreme left side of the photo.

interbedded pinkish silicic lenses close to the base; they are gray and flint nodules bearing in the middle and upper section.

The thickness of the whole complex in Monte Valerio area is about 100 meters. An evident emersion surface, partially coated with a thick quarzitic crust, separates formation C from the overlying formation D. Features interpretable as connected to (partial) emersion and — in general — to basin instability (obliquity of boundary surfaces to bedding planes; slumping, quick eteropic changes) occur also inside the same formation C.

GIANNINI (1955) calls « Red Ammonitic limestones » the lower section of this complex, and « Gray flinty limestones » the upper one.

D+E - A huge (300-400 meter thick) inclusive sequence ranging from Lower

Fig. 4 and Fig. 5. — Evidences of erosion surfaces (Fig. 4) and syn-sedimentary deformations (Fig. 5) in the « Ammonitic Red Limestones » in a creek, close to Sassetta.

Jurassic to Paleogene unconformably [1] overlie Complex C. It is foundamentally made up of variegated, more or less silicified slates; lenses of marbles, of marly

(1) It is difficult to establish if the unconformity is stratigrafic or is tectonic, and connected to differential settling of the tyo complexes, that have so different plasticity.

and/or silicified limestones, of jaspers and (particularly in the lowermost 50 meters) of ferruginous quartzites are occasionally interbedded in the lower section (complex D). They are still less frequent in the upper one (complex E), the topmost part of which includes lenses of nummulitic breccias.

The lower section, on the basis of its fossil content, is considered to be equivalent to the « Posidonomya marls » formation of other part of Tuscany and the upper one to the « Scaglia Rossa » (= Red Scale) also called « Polichronous Slates » on the basis of their most evident characters.

To put a boundary in between complex D and complex E is however very problematic in Monte Valerio area; it is not so uncertain in other parts of the region, as it will be said in section 2.2.1.

Fig. 6. — A front in a small quarry on the S-E side of Monte Calvi, showing syn-diagenetic deformations in « Ammonitic Red limestones ».

The ferruginous quartzitic lenses of Lower Jurassic deserve some attention: thay are lenticular and isooriented in plan, with long axes nearly parallel to the bed dips.

They occur at different levels, and pass laterally either to lesser and lesser silicified beds or to silicic Iron-Manganese hydroxide lenticular concentrations.

Their thickness is about 1 meter, the maximum thickness (6-8 meters) pertaining to a quartzitic lense occurring at the base of the complex. Short apophyses, specially along their foot-walls, are not uncommon.

We interpret them as « hard grounds »; this is in contrast with the existing literature, that explain them either as primary sediments or deriving from metasomatic-hydrothermal processes.

Moreover, it has to be pointed out that the ferruginous quartzitic lenses are quite different from the jaspers, either on the lithological/structural standpoint and — in our opinion — on the genesis: is fact, whichever their origin (volcanic? organogenic?), the jaspers are primary sediments.

K - A small klippen, made of Upper Triassic brecciated dolomitic limestones, covers the Lower Jurassic complex in S. Barbara region (West of Monte Valerio). Its surface extent is very limited and it should not be worth mentioning, if not because of the significance it can have for palinspastic/paleogeographic reconstructions.

2.2. *Correlations with the regional geology*

2.2.1. *The regional sedimentary sequence*

Monte Valerio area is a small section (about 3.5 sq. km) of the Campiglia region, that is a triangular area of about 70 sq. km, made up of various autochtonous terranes, ranging from Trias to Oligocene, intruded by a number of Alpidic magmatic rocks.

It is surrounded by recent sediments and/or volcanic flows and, at places, covered by alloctonous (mainly clayey) terranes.

The regional sequence includes, in addition to all terranes occurring in Monte Valerio area, also the Oligocene complex made of nummulitic breccias, and of the so-called « macigno » (= hard rock). Moreover, at places, a well developed, intensely quarried, jasper horizon is present nearly in the middle section of complex D + E, and (as proposed by Giannini, 1955) it may be considered as the key bed to separate D from E. Jasper age, consequently, should be Malm, according to that Author.

Unfortunately the jaspers horizon, even if at places fairly thick (up to some tens of meters), is not continuous all over the region: f.i., it is absent in Monte Valerio area.

The stratigraphic relations among these complexes are not so easy to be established: thick vegetation covers and masks large areas and consequently outcrops are generally poor and discontinuous. Fortunately some quarries, open in complexes B, C and in jaspers, help mapping, at places.

Additional interpretative hinderances arise from strong differences in competences of the different complexes; as a matter of fact some of them became rigid since an early diagenetic stages (limestones), others have been plastic during diagenesis and then became rigid (jaspers), others have always been, and still are, plastic (slates).

2.2.2. *Tectonic hypotheses*

All these difficulties taken into consideration, the previous literature inclines for a continuous and conformable deposition of the whole series from Trias to Oligocene. This statement howewer does not apply all over Campiglia region: f.i., Monte Valerio area, as it was discussed at point 2.1, shows evidences of emersions.

Another convincing emersion evidence is visible in a quarry recently open in Monte Peloso; here the jaspers of complex D+E overlie directly an eroded, karstified surface of the « Ammonitic Red », as it is shown in fig. 2 and 3.

Some features of « Ammonitic Red » visible along a creek, close to Sassetta, are also interpretable as indicative of emersion stages (fig. 4, 5).

Furthermore bedding irregularities of some « Ammonitic Red » and of some jaspers and their relationships to the country rocks speak for slumping and flowing during their diagenesis in local syn-sedimentary bottom trenches (fig. 6).

One is consequently induced to suggest that the Campiglia region was affected by syn-sedimentary tectonics, from upper Lower Lias to Malm, that caused at places (?) partial (?) emersions/subemersions: Monte Valerio is one, but not the only, of such areas.

Going deeper into the geology of this region is well beyond the purpose of this paper and of the same experiences of the Authors. They wish only to underlain that, on the prospectors' standpoint, the localization of other paleogeographic environments like or similar to the Monte Valerio area, could be of outstanding interest, specially if the genetic hypothesis, we are going to propose, is correct.

3. - Cassiterite occurrences

3.1. *Factual observations at the large scale*

a) Cassiterite non-commercial occurrences (below 0.3 % Sn: most frequently between 0.01 and 0.1 %) and/or positive geochemical anomalies are widespread in all terranes A, B, C, D. It has to be pointed out that also in the Triassic complex of Gavorrano and of Monte Argentario, traces of Sn were recently found (Burtet Fabris & Omenetto, 1975 and personal comunication by Omenetto).

b) Cassiterite commercial concentrations (more than 0.3 % Sn) occur either in strata-bound and in cross-cutting deposits.

1) The *strata-bound deposits* are located in two well defined sections of the stratigraphic sequence described at point 2.1; namely:

(I) the upper 10-20 meters of complex B;

(II) the lowest 50 meters of complex D.

2) *The cross-cutting deposits* occur along faults and fractures: they are fairly frequent in complex B, where they show the typical shapes and compositions of karstic concentrations. A small, limonite-cassiterite stockworck was exploited in complex D.

It is noterworthy that cassiterite cross-cutting industrial concentrations occur only in connection to the strata-bound industrial accumulations.

c) The strata bonds in strata-bound concentrations are still more evident, if they are investigated at the scale of the deposit.

1) Sn concentrations in section *b*-1) are located in two beds, each one having

1-2 meter thikness; the first at the very top of the complex, the second 5-7 meters below.
The pay-streaks, in both beds, are isooriented, lenticular, with long axes slightly oblique to the bed dips, and therefore they are more or less parallel to the ferruginous quartzitic lenses of complex D.
It is noterworthy that these pay-streaks coincide with the pink, somewhat silicic, limestone lenses described and discussed at point 2.1.B.
At places and in very confined portions of the pay-streaks (a few cubic meters) grade is very high (up to 70 % Sn): miners call them « massello calcareo » (limy small masses).

2) Sn concentrations in section *b*-2) are located inside the most silicic interbedded lenses.
« Massello » type concentrations are present also in them; they are called « massello pietra » (stony small masses) owing to their particular hardness and compactness.

d) Mio-Pliocene granite crops out 3 km North of Monte Valerio; it was reached, at 1130 m depth, by a drill-hole beneath the Sn ore deposit.
It is an aplitic, Tourmaline bearing granite in both cases. Some co-magmatic porphyries occur North of Monte Valerio; Cu, Pb, Zn bearing skarns are also present; they have been intensely explored and exploited.
The numerous explorations and samplings carried out close to the granite and to the porphyries and in the skarns, cleary demonstrated that there is no change in Sn content approaching them.
On the other hand, tourmaliniferous granites occur also in two other areas of Tuscany: the mining districts of Gavorrano (pyrite) and of Elba Island (complex Fe ores), but no Sn concentrations or, even, positive anomalies, are known in these areas.
One may thus assume that, on the stand-point of Sn distribution, Mio-Pliocene magmatism and allied metamorphism are ininfluential.
This sentence is evidently in contrast with the ancient genetic hypotheses, which attached particular importance to the presence of Tourmaline in the granite and in the Sn deposit.

3.2. *Factual observations at the micro-scale*

Observations at the microscopic scale of the strata-bound concentrations seem to have particular bearing on the genetic investigations.

a) Fig. 7 and 8 show structural/textural details of a « massello pietra » sample: they all suggest sedimentary deposition processes.

b) Paragenesis in strata-bound concentrations include essentially Cassiterite, Tourmaline, Quartz, Calcite, and minor quantities of Limonite, Ematite, Pyrolusite, Siderite, Pyrite, Chalcopyrite, Galena, Sphalerite as recognized by BERTOLANI, 1958. STELLA, 1955 quote the possible presence of acicular transparent Actinote;

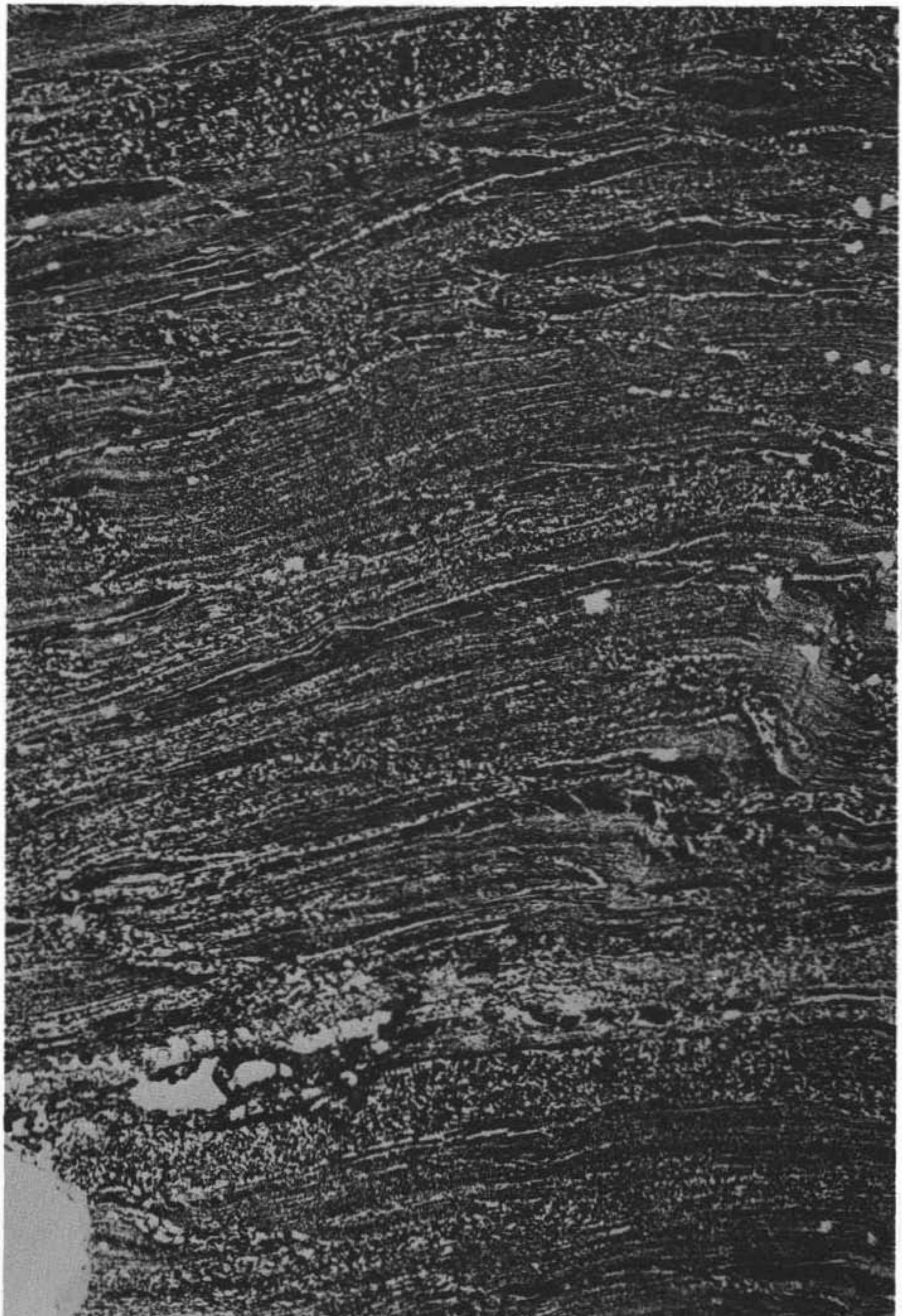
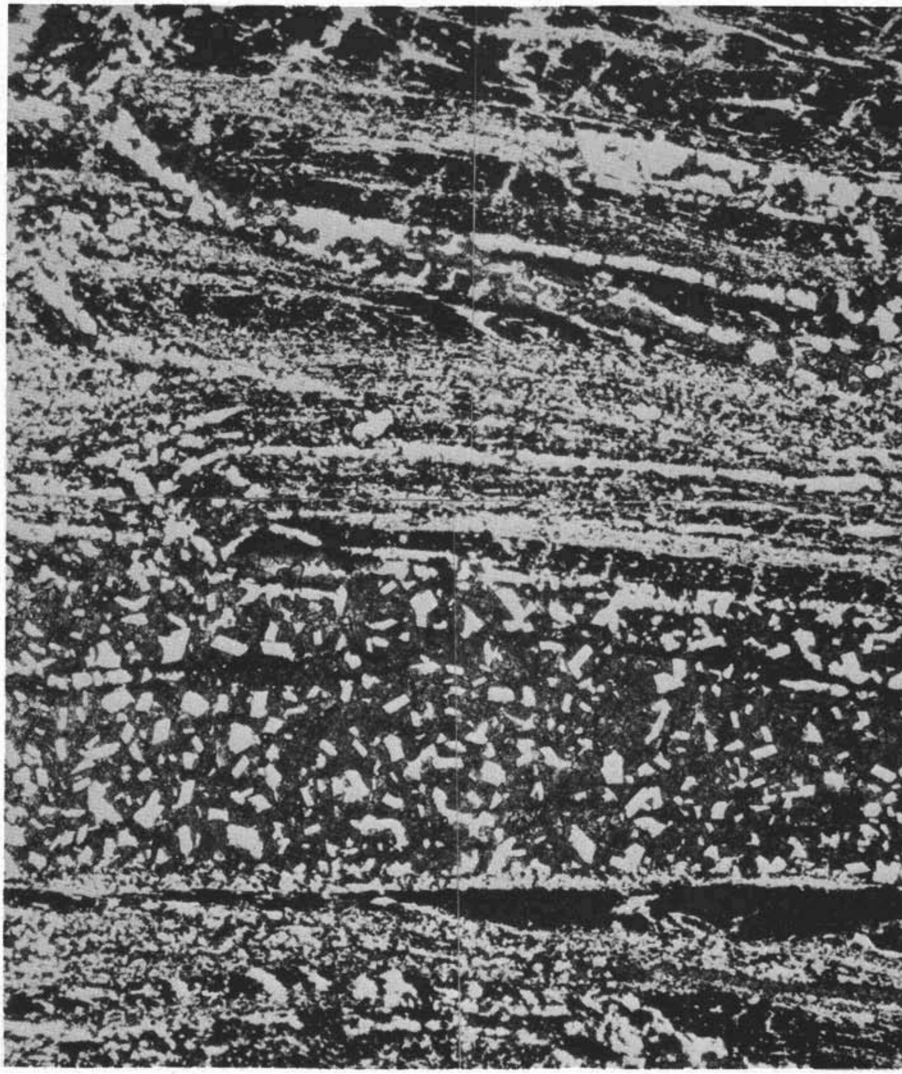
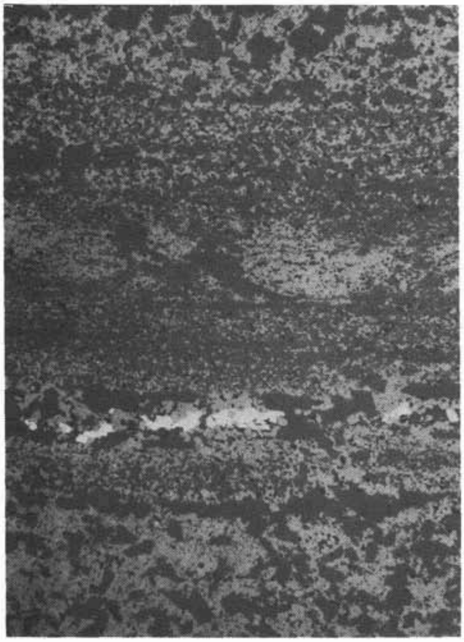


Fig. 7. — *Thin section of « Massello Pietra »*; 1 Nicol, X 8 (about). - Cassiterite is black; the white thin seams/veinlets and the smallest white specks are made of Quartz aggregates, holding Tourmaline: this latter is not visible at this enlargement. Quartz, in some seams, in evidently pseudomorphous after romboedral minerals (probably Calcite). The large white spots (specially



frequent in the central section of the right side and near the left lower corner) are vugs. These vugs were not produced during the preparation of the thin section (may be some ones!): they were present in the rock itself, and were stained or partially filled with Goethite; the cubic outline of most of them suggests the presence of an original idioblastic mineral (probably Pyrite) formed during diagenesis. Banded structure is the most stricking feature; other features which can be explained as produced by sedimentary/diagenetic processes, are also evident; f.i.: slumping (central part of the right side), squeezed diagenetic fractures (left side), cross and convolute bedding, load casts (upper sectiốn of this Fig. and in Fig. 8).

Fig. 8. — *A detail from the upper section of Fig. 7* - Thin Section - 1 Nicol, X 30 (about) - The different compositions and textures of the various bands is clearly visible. Convolute bedding in the upper seams is evident. Specks (made of Quartz aggregate) with rombohedral outline (pseudomorphous after Calcite?) are frequent in a Cassiterite rich seam in the lower half of the photo. A Cassiterite accumulation with « scour and fill » texture occurs beneath it.



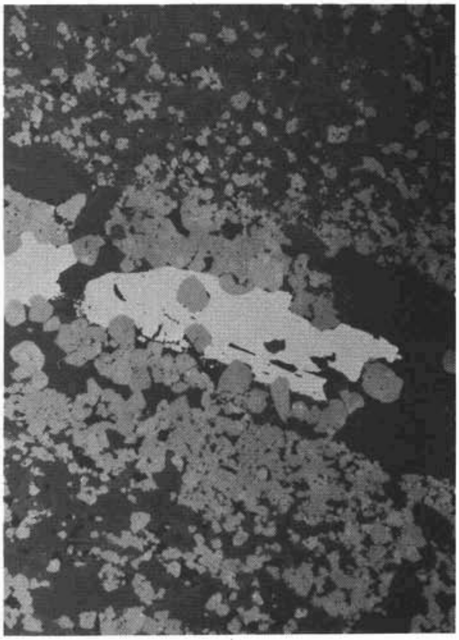


Fig. 9 (left) and Fig. 10 (right). — *Polished section of a detail of Fig. 7* - 1 Nicol, X 35 and X 140 respectively. - The white spots are Rutile; Cassiterite is pale gray; dark gray are silicatic gangue minerals (Quartz + Tourmaline). The parallel texture of the rock is evident in photo 9. Cassiterite seams (as it is shown in photo 10) are made of aggregates of mainly idiomorphous, slightly pleochroic crystals.

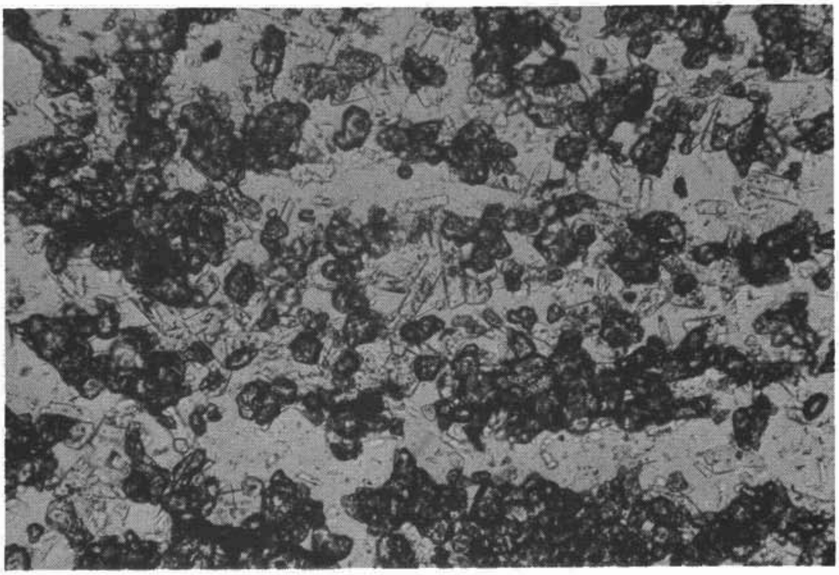


Fig. 11. — *A detail from Fig. 7* - Thin Section - 1 Nicol, X 200 (about). - The parallel textures of the rock is evident: alignments of Cassiterite aggregate grains (dark) alternate with Quartz seams, including colourless crystals of Tourmaline, having strong relief and random orientation.

we have not found it and incline to think that, more probably, those acicular crystals were Tourmaline, that occur abundantly, with this same feature, as described also in BERTOLANI, 1958, and it was determined also by us.

The presence of Rutile (see fig. 9, 10) is here reported for the first time.

c) The texture of « massello » is thinly bedded, with thin seams of practically pure Cassiterite passing to practically pure Tourmaline-Quartz seams (see fig. 11). Cassiterite occur as aggregates of equidimentional well sorted grains; their average diameter is 0.04 mm, ranging from 0.005 to 1.8; the largest crystals appear to be the product of coalescence and recrystallization.

Tourmaline occurs as small transparent prismatic, sometimes zoned, often bi-ended crystals; the average lenght of their long axes is 0.02 mm, ranging from 0.003 to 0.1. Comparing Cassiterite and Tourmaline grain size, and taking into account their specific weights (7 and 3.1 respectively) it ensues that they are not « equivalent », in the dressing plant meaning.

4. - Discussion - Genetic hypotheses

We incline to attach great significance to the structure and texture of strata-bound Cassiterite deposits (3.2.*a*, 3.2.*c*), and to the topographic correlation between strata-bound and cross-cutting ore accumulations (3.1.*b*); the lack of correlation between Mio-Pliocene magmatism and cassiterite occurrences, inferred by us, at point 3.1.*d*, is — in our opinion — another important argument in the genetic discussion.

On these bases, we incline to curtail very much the role of Mio-Pliocene magmatism on the formation of Cassiterite accumulations and propose the following two-stages genetic scheme: (I) syn-sedimentary deposition of Cassiterite-Tourmaline in the time span from Trias to Dogger, with particular intensity in the uppermost fraction of Lower Lias and in Lower Dogger; (II) Post-Pliocene supergene partial remobilization, with consequent karstic and/or « sedimentary vein » accumulations.

Recrystallization, well visible in Cassiterite, may be diagenetic or may the (only) result of the (feeble) Mio-Pliocene metamorphism affecting Monte Valerio area.

The other factual observations listed in chapter 3 fit quite well this scheme: as a matter of fact, we explained the shapes, compositions and orientations of pay-streaks in Lower Lias and in Lower Dogger as sedimentary features (paleo-currents and, respectively, hard grounds).

Also the thinly bedded texture of « massello » (see point 3.2.*c*) can be interpreted as a sedimentary alluvial feature: in particular the non-equivalence of Cassiterite and of Tourmaline particles hindered mixed depositions and helped their separation, according to (slight) changes in current velocity, giving thus rise to different, practically mono-mineralic seams or lenses.

The same accessory presence of Rutile grains is in favour of alluvial deposition processes; on the other hand, the (occasional) presence of Sulfides suggests the intervention (even if scanty) of chemical metal transport and ore deposition.

The source of Cassiterite and Tourmaline is a troubling problem, on the basis of the data till now available. The limited roundness of Cassiterite and the perfect shape of Tourmaline particles suggest, in our genetic scheme, that the source should have been very close to the site of deposition.

It is difficult to go further in trying to unravel this problem; in a merely sedimentary alluvial scheme, the presence of a paleo-continent, just West of Tuscany, undergoing erosion during Mesozoic sedimentation, may be suggested, according to the paleogeographic recostruction of Central-Northern Italy by BOSELLINI, 1973, by HSÜ, 1971 and by COCOZZA and SCHÄFER, 1974; the Island of Elba, the deep section of Monte Argentario (and probably of some minor islands of central Tyrrhenian) can be considered residual parts of such a paleo-continent, and a more or less direct connection with the Corso-Sardic massive can be suggested.

It is well known that the presence of Cassiterite, even if in non conspicuous accumulations, is well known in Sardinian Hercynian basement, and has been recently enphasized with geochemical prospecting (MARCELLO, PRETTI, SALVADORI, 1977); it is not illogical to think that this same situation extended also in the supposed paleo-continent.

A more or less direct volcanic source could also be considered, taking into account that recently GIANNELLI & PUXEDDU (1979), BAGNOLI et alii (1978) proved the existence of volcanic activity in the Paleozoic terranes of Tuscany; the presence of hydrothermal sources, of strong hydrothermal alteration phenomena, the same presence of Mio-Pliocene granite and of conspicuous Plio-Pleistocene lava flows close to, or not far from, Monte Valerio area, could be interpreted as the recent prosecution of a more ancient, till now unknown, volcanism close to the area of Monte Valerio.

The boron content of Larderello hydrothermalism may be also significant, in this volcano-sedimentary scheme, in order to explain the presence of tourmaline.

4. - Conclusion

We don't expect to have solved the genetic problem of Monte Valerio; we think howewer that the factual observations described above are sufficient to suggest to let drop the pneumatolytic-hydrothermal model and to support a syn-sedimentary genetic scheme, in which alluvial concentration processes of ores/minerals coming from a close source had noteworthy importance.

This working hypothesis should be taken into consideration for future Cassiterite prospecting in Tuscany.

Aknowledgments. — We are indebted with Prof. M. BERTOLANI, of Modena University, who kindly supplied us with a sample of the, by now undiscoverable, « massello » and with some thin sections of his collection. We are also indebted with Dr. R. CRESPI, Dr. LIBORIO and Prof. A. GREGNANIN of Milan University for assistence in laboratory work; to Prof. I. URAS of Cagliari University, who revised the manuscript, for criticism and suggestions; to Mr. U. FEDERICI and F. GERVASONI, students in Milan University, for assistence in field work.

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