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Vittorio Duchi, Stefano Santoni

Metamorphism and Metal Mobilization in Calcareous Rocks from Campiglia Marittima Mineralized Area. Nota I

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Geochimica. — *Metamorphism and Metal Mobilization in Calcareous Rocks from Campiglia Marittima Mineralized Area.* Nota I di VITTORIO DUCHI (*) e STEFANO SANTONI (*), presentata (**) dal Socio G. CAROBBI.

RIASSUNTO. — Su novantadue campioni di rocce della formazione carbonatica liassica della Serie Toscana di Campiglia Marittima sono state condotte determinazioni sul contenuto di Ca, Mg, Mn, Fe, Cu, Zn mediante spettrofotometria di assorbimento atomico.

In questa area sono note mineralizzazioni ad ossidi e idrossidi di ferro, a cassiterite e a solfuri misti associati a silicati di skarn; queste mineralizzazioni si ritrovano in una formazione della Serie Toscana nota come «calcare massiccio». Una parte di questa formazione (marmi) è stata metamorfosata da una intrusione quarzo-monzonitica a cui queste mineralizzazioni sono associate.

Sono state studiate le variazioni del contenuto dei metalli tra i marmi e il calcare massiccio non metamorfosato ed è stato evidenziato che durante il processo termometamorfico il contenuto dei metalli pesanti nella roccia tende a diminuire.

È stata fatta una stima approssimata dell'importanza quantitativa di tale mobilizzazione ed ipotizzata una relazione alle mineralizzazioni. Infine si è proposto un modello schematico della mobilizzazione dei metalli attraverso soluzioni acquose riscaldate dalla intrusione.

INTRODUCTION

Although of moderate economic importance, the mineralizations of Campiglia Marittima (southwestern Tuscany, Italy, Fig. 1) are mineralogically interesting. Indeed they are related to a calcalkaline intrusion and occur in a formation of the Tuscan sequence known as "calcare massiccio", widely outcropping in the area and which partly underwent thermal metamorphism.

This work was aimed at the study of the distribution of Ca, Mg, Mn, Fe, Cu, and Zn in the liassic formations of "calcare massiccio", "calcare rosso ammonitico", and "calcare selcifero" belonging to the Tuscan sequence, in relation to mineralizations. In particular we have studied the metal contents in the metamorphosed portion ("marbles") of "calcare massiccio" and in the unmetamorphosed one of the same formation, in order to better understand if a connection does exist between metamorphism and minerogenesis.

GEOLOGICAL SETTING AND PREVIOUS WORK

The hills of Campiglia Marittima are a positive structure bordered east and west by two normal faults striking N-S and NW-SE. The area is also crossed by two fractures, evidenced as lineations on a regional scale by Boccaletti *et al.* (1977), striking NE-SW and along which mainly horizontal displa-

(*) Istituto di Mineralogia, Petrografia e Geochimica, Via Lamarmora 4, Firenze.
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cements occurred (Fig. 1). The folds and the transcurrent faults which interest the formation outcropping in the area (belonging to the Tuscan and Ligurian sequences, Giannini, 1955) are related to the compressional appenines tectonics, while the normal faults seem younger and related to the general post-Tortonian tensional tectonics of southern Tuscany (Elter *et al.*, 1975).

According to Borsi *et al.* (1967) and Barbieri *et al.* (1967) 5.7 m.y. ago a quartz-monzonite intrusion, which outcrops only at Botro ai Marmi, was intruded. It caused the thermal metamorphism of a great portion of the " calcare massiccio " formation. Later (5.0–4.3 m.y. ago) quartz-monzonite and femic (diopsidic)-monzonite porphyries were intruded, the latter only Southeast of Valle dei Lanzi. Then quartz-latite lavas were emplaced (4.7 m.y. ago) Northwest of Botro ai Marmi and hydrothermal activities mineralized the wall rock of the femic-monzonite porphyries.

The mineralizations of the area were studied by Stella (1938, 1955), Bertolani (1958), Goswani (1962), Bartholomé, and Evrard (1970), Bernardini *et al.* (1974), Corsini and Tanelli (1974), Gregorio *et al.* (1977), Tanelli (1977). They may be distinguished as follows:

a) cassiterite and limonite mineralizations, near Mt. Valerio (southern portion of the map in Fig. 1);

b) iron (mainly oxides and hydroxides) mineralizations of S. Antonio–Mt. Rombolo–Mt. Spinosa;

c) skarn-sulphide mineralizations (hedenbergite-johannsenite, manganiferous ilvaite, epidote, Fe—Cu—Zn—Pb sulphides), mainly associated with femic-monzonite porphyries and involving the area between Valle dei Lanzi and Valle del Temperino.

SAMPLING AND ANALYTICAL PROCEDURES

Ninety-two samples of the liassic calcareous formations of the Tuscan sequence were collected near the mineralized zones in an area of about 20 sq. Km. Sixty-nine samples belong to "calcare massiccio" (from now on the metamorphosed portion of this formation will be referred to as " marbles "), twelve to " calcare rosso ammonitico ", and eleven to " calcare selcifero ", as listed in Table II (cfr. note II). The thick vegetation covering the area prevented us from following a regular grid of sampling. Thus the samples were collected along the few existing pathways and in faces of quarries, the latter mainly developed in the Mt. Rombolo–Mt. Calvi area. Location of samples is shown in Fig. 1.

The samples were pulverized and homogenized in agate mortar. Solubilization of the carbonate fraction as well as the metal hydroxides was obtained with 3 N HCl, using the procedure described by Bencini and Turi (1974). Ca, Mg, Mn, Fe, Cu, Zn were determined by atomic absorption spectrophotometry using a Perkin-Elmer Model 303 instrument equipped with a Hitachi recorder.

RESULTS

The lithological and chemical feature of samples are listed in Table II. Coefficients of correlation for Mg, Mn, Fe, Cu, Zn, and insoluble residue are shown in Table I (cfr. note II).

The significance of Fe vs. ins. res., Mn vs. ins. res., and Fe vs. Mn relations seems to be related to sedimentary processes. Indeed the pH of precipitation of transition metal hydroxides is relatively low, this being particularly true for Fe. Gibbs (1977) pointed out quantitatively that these metals are transported by rivers to the sea largely as metal hydroxide coatings and only in small amounts as ions. Only the latter may enter carbonate lattice during sedimentation so that in the presence of a hypothetically pure limestone (= without silicate fraction, i.e. HCl insoluble residue) the content of these metals is supposed to be very low. In any case all limestone contains some amount of argillacenous minerals to which the metal hydroxide coatings mainly bind. By acid treatment of calcareous rocks metals—either in carbonate lattice or as hydroxide coatings on argillaceous lattice—solubilize. Hence the close correlation between these elements and insoluble residue.

The correlation Cu vs. Zn does not seem to be related to sedimentary processes but is mainly caused by the strong correlation of Cu vs. Zn existing in P and T zones, as (will be better explained) in the following.

We have distinguished six zones of sampling in which metals show different distribution. In the following discussion of results we refer only to the " calcare massiccio " formation, since it is the only one of the three sampled formations affected by metamorphic processes and because its metamorphosed portion shows variations in the metal content with respect to the unmetamorphosed " calcare massiccio ".

"Calcare massiccio " of the A zone from West to East shows a gradual transition from " marbles " to the unmetamorphosed portion of the formation and it is barren.

Zone B is like zone A, but is intruded by the northern portion of the mineralized porphyries.

The center of skarn-sulphide mineralizations is localized in zone C where only " marbles " outcrop.

Zones P and T are intensely faulted and were not affected by metamorphism.

In zone S, cut by a great fault, " marbles " mainly outcrop; in thin section they show oriented recrystallization mosaics, probably due to the stresses originated by the fault.

DISCUSSION

The samples collected in zones P and T show positive anomalies for Cu and Zn and a greatly significant relationship between the two metals ($r = 0.912$). This may not be related to sedimentary processes. Indeed Zn and Cu contents of unmetamorphosed " calcare massiccio " from other outcroppings of the Tuscan sequence we have analyzed are lower and referable to the ones of " calcare massiccio " in zones A and B. From these results the anomalies for Cu and Zn appear to be related to the rising through fractures of hydrothermal mineralizing fluids in relation to the quartz-monzonite intrusion.

Beside metamorphism zone S seems to have undergone the same processes as those described above and shows an enrichment in Zn with respect to " marbles " of the unmineralized zones and to " calcare massiccio " itself.

Of the three zones just outlined zone P seems to be a particularly favorable p e r s p e c t i v e area for base metal deposits, also because of its closeness to the mineralized area of Mt. Valerio.

Analytical data suggested a comparison of zones A, B, and C, with respect to the geochemical behaviour of each metal in " marbles " and unmetamorphosed " calcare massiccio " (Fig. 2). We wish to state that subdivision between the metamorphosed portion of " calcare massiccio " and the unmetamorphosed one is a necessary attempt to divide a natural continuum. Fig. 2 indeed shows for " calcare massiccio " of zones A and B some variations in the metal content which do not seem to be related to different sedimentary facies but rather to the greater or lesser distance from Botro ai Marmi intrusive and mineralizations.

Mg) On the average " marbles " of zones A and B are enriched in this element by about 30 %, while in zone C they show approximately the same content as " calcare massiccio " of zone B. This metal seems to have been mobilized by the intrusion from the triassic evaporite levels which are widespread in Tuscany although not outcropping in the area, and brought up in the overlying formation of the Tuscan sequence. Indeed a bore hole at Botro ai Marmi met magnesian inclusions in the quartz-monzonite (Ferrara, 1962); Barberi *et al.* (1967) described dolomitized levels in " marbles " at the contact with the intrusive.

Mn) The Mn contents in the zone A and B " marbles " decrease on the average by about 80 % with respect to " calcare massiccio ". The zone C " marbles " on the contrary show high Mn contents. Therefore this element seems to have been mobilized during metamorphism and conveyed toward the zone C, where it enriched " marbles " and probably played an important role in the development of the Ca—Si—Fe (Mn)-skarn. Zone C would have represented a very low pressure area during and after the thermal metamorphism, as the hydrothermal processes which occurred in it confirm.

Fe) The behaviour of this element is similar to that of Mn, on the average approximately 60 % of the original content of " calcare massiccio " being mobilized during thermal metamorphism. It was probably conveyed toward zone C although it contributed to iron mineralization and did not enrich the " marbles " of the zone because of its low mobility.

Cu) " Marbles " have on the average a Cu content 15 % lower than that of " calcare massiccio " we have excluded the Cu and Zn anomalous sample No. 56), showing a slight mobilization of this element during thermal metamorphism. The zone C samples, collected just around the chalcopyrite mineralization, have no anomalous Cu content, thus evidencing the difficulty with which Cu enters carbonate lattice.

Zn) In the barren zone A the average Zn content of " marbles " is about 30 % lower than that of " calcare massiccio ". Therefore Zn also seems to be mobilized during thermal metamorphism. "Marbles " in zone B are enriched with respect to Zn. This is because half of the samples have an abnormally high Zn content due to the nearby base metal mineralization. Excluding these samples from the average, the other " marbles " show the same rule verified in zone A; here also Zn decreases by about 30 % with respect to the zone B " calcare massiccio ". In zone C the trend of this element to be enriched in the proximity of base metal mineralization is still better evidenced, thus making Zn a valuable " pathfinder " in calcareous rocks.

Quantitative Importance of Mobilized Metals

The outcropping of metamorphosed " calcare massiccio " may be coarsely evaluated as about 10 sq. Km. According to Giannini (1955) and Bortolotti *et al.* (1970) the mean thickness of the formation in the area is about 250 m. Therefore 2,000–3,000 million cubic meters of rock have undergone thermal metamorphism, corresponding (using a consistent value for density of 2.5 g/cm^3) to 5,000–7,500 million metric tons. Considering the metal content variations which occurred during thermal metamorphism a coarse computation of the quantitative importance of metal mobilization may be attempted.

"Marbles " are enriched by approximately 750 ppm Mg with respect to " calcare massiccio ". Thus the intrusion seems to have brought up 3–5.5 million metric tons of this element. On the contrary " marbles " are lower in Mn content by about 400 ppm, a figure which results in a mobilization of 2–3 million metric tons. Likewise during thermal metamorphism 300 ppm of Fe were mobilized for an overall mobilization of 1.5–2 million metric tons. The slight decrease in Cu and Zn contents in " marbles " indicated the mobilization of some thousands of metric tons of these elements.

Therefore the quantities of Mg, Fe and Mn mobilized during thermal metamorphism are not negligible if minerogenetic processes are to be fully understood. On the contrary, the lower original Cu and Zn content of a very pure limestone like " calcare massiccio ", gives their mobilization during metamorphism a secondary importance.

Conclusion

The general trend we observed in this work on the liassic calcareous formations of the Tuscan sequence is that during thermal metamorphism heavy metal content decreases in the rock.

Mobilization of these metals probably occurred through aqueous solutions of connate (Belevtsev, 1970), acid-magmatic (through complexation of metals like Zn and Cu) and meteoric origin, heated by the quartz-monzonite intrusive. Belewzew *et al.* (1973) have shown such a form of mobilization to be effective.

In the area of Campiglia Marittima the mobilized heavy metals seem to have been conveyed toward zone C, which was a very low pressure area, and been redeposited according to their geochemical behaviour. Fe, for instance, was likely to contribute to oxide and hydroxide mineralizations and to a lesser extent to skarns; the more mobile Mn enriched skarns and " marbles " of zone C. Also Cu and Zn were probably conveyed toward zone C, even if the relatively low quantities mobilized prevent us from individuating the role played by them in the development of base metal mineralization.

Moreover, they stress the fact that Zn can be considered a " pathfinder " for base metal deposits in calcareous rocks.

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For editing reasons bibliographic references and tables of analytical data are reported in Note II.