ATTI
DELLA
SOCIETÀ TOSCANA
DI
SCIENZE NATURALI
RESIDENTE IN PISA

MEMORIE - SERIE A
VOL. LXXXVI - ANNO 1979

ARTI GRAFICHE PACINI MARIOTTI - PISA - 1979

INDICE

Atti Soc. Tosc. Sci. Nat., Mem., Serie A, **86** (1979)
pagg. 127-165, ff. 4, tab. 1, tt. 2.

A. Dallegno (*), G. Gianelli (**), P. Lattanzi (*), G. Tanelli (*)

PYRITE DEPOSITS OF THE GAVORRANO AREA, GROSSETO

Abstract — The pyrite deposits of the Gavorrano area, SW Tuscany, have for a long time represented one of the most important mining centres of pyrite throughout the world. The ore occurs as massive, high-grade bodies located either at the contact between an Upper Trias limestone (' Calcare cavernoso ') and a quartzitic-phyllitic complex (Trias-Paleozoic?) or at the contact between the above-mentioned rocks and a Neogenic (4.9 m.y.) granitic stock.

Contact metamorphic phenomena around the intrusion are rather limited; a pressure of the order of 500 bars and a temperature reaching 530°C are inferred. A later metasomatic event produced the emplacement of very limited amounts of skarn. Finally, there was a stage of hydrothermal alteration.

The mineralogy of the ore bodies is quite simple, pyrite being the only important mineral. Trace amounts of pyrrhotite, hematite, magnetite, chalcopyrite, sphalerite, galena, tetrahedrite, stibnite, cassiterite, marcasite and covellite are present. The main minerographic feature is the occurrence and distribution of textural relics in pyrite, revealed by structural etching.

The various genetic hypotheses for these deposits are reviewed and discussed. It is felt that more detailed geochemical data than those available nowadays are required for a complete understanding of the genesis and emplacement of the ore. However, the attitudinal features, characteristics and distribution of the textural relics in pyrite and the absence of significant metasomatic skarn occurrence seem to indicate that the granitic intrusion has metamorphosed and remobilized pre-existing ore bodies. Some doubt is thus cast on the classic pyrometasomatic post-granite genetic model. Possible mechanisms of primary ore concentration are discussed.

Riassunto — *I depositi di pirite della zona di Gavorrano* (*Grosseto*). Il deposito di pirite di Gavorrano ha rappresentato, per molti anni, un centro minerario per l'estrazione di pirite tra i più importanti del mondo. Il minerale si trova in corpi massicci, ad alto tenore di FeS_2, al contatto tra il Calcare cavernoso e le formazioni

---

(*) Istituto di Mineralogia, Petrografia e Geochimica, Centro CNR per la Mineralogia e la Geochimica dei sedimenti, Via Lamarmora 4, I-50121 Firenze, Italy.

(**) Istituto Internazionale per le Ricerche Geotermiche, CNR, Via del Buongusto n. 1, I-56100 Pisa, Italy.

This work was financially supported by CNR - Progetto Finalizzato Geodinamica, U.O.: G. Tanelli, Pub. No. 264.

epimetamorfiche quarzitico-filladiche del Trias o del Paleozoico, oppure al contatto tra tutte queste formazioni ed una intrusione granitica neogenica. I fenomeni di metamorfismo di contatto attorno all'intrusione sono piuttosto limitati; per essi sono state dedotte una pressione dell'ordine di 500 bar e temperature fino a 530°C. A questo evento seguirono un metamorfismo allochimico con produzione di limitate masse di skarn ed una alterazione idrotermale. La mineralogia del giacimento è molto semplice, in quanto la pirite è l'unico minerale importante: sono presenti, in tracce, pirrotina, ematite, magnetite, calcopirite, blenda, galena, tetraedrite, antimonite, cassiterite, marcasite e covellite.

La caratteristica minerografica più importante delle piriti è la presenza di strutture relitte a « bassa cristallinità » evolventi verso cristalli idiomorfi. Queste strutture caratterizzano la pirite posta al contatto della intrusione granitica. La pirite dei corpi minerari più lontani dall'intrusione non presenta tali strutture relitte. Il riesame di tutte le varie e contraddittorie ipotesi sulle origini dei giacimenti di Gavorrano, alla luce dei nuovi dati stratigrafici e giacimentologici, fa ritenere poco probabile il classico modello pirometasomatico. Vengono discussi altri modelli alternativi, basati sulla esistenza di eventi metallogenici precedenti l'intrusione granitica di Gavorrano. In particolare le caratteristiche giaciturali, la presenza e la distribuzione spaziale della pirite con strutture relitte, nonché l'assenza di significative manifestazioni a skarn di sostituzione, sembrano indicare che l'intrusione granitica ha metamorfosato e parzialmente mobilizzato dei corpi minerari preesistenti.

Key words: morphology, attitude, minerography; hornfels, skarn; stratigraphy; metamorphism; metasomatism; genetic model.

Foreword

The sulphide ore bodies of Gavorrano (Grosseto, Italy) represented one of the most important mining centres of pyrite in the world. Since 1898 a total of about 24,500,000 metric tons of ore has been mined, with an average grade of 46% sulphur and 41% iron. Other metals are present in trace amounts: Cu, Pb, Zn, As (about 0.2%), Co (0.01%), Ag (about 6 g per ton), Au (0.05 g per ton) and locally some Sn (up to 0.06-0.16%).

The mined ore bodies consist of massive pyrite in a quartz-carbonate gangue, mostly occurring at the contact between metamorphic-sedimentary rocks (phyllite, quartzite and limestone) and a Neogenic granitic stock. Other ore minerals are scarcely more than impurities.

Nowadays the Gavorrano deposits are nearly exhausted, the proven reserves being less than 1,000,000 tons.

The ore is now mined from three massive pyrite bodies, called ' Rigoloccio ', ' Massa Boccheggiano ' and ' Valmaggiore '.

Mining first developed, at an elevation of 200 m a.s.l., at ' Fontevecchia ', south of the village of Gavorrano, in correspondence to an outcrop of the limonitic caprock (fig. 1a). Other sulphide concentrations were then discovered along the western side of the granite stock, from 'Rigoloccio' to 'Valmaggiore' and exploited down to 200 m b.s.l.. Only small mineralizations occur along the eastern side of the intrusion, in the limonitic caprock of 'Monticello'; minor amounts of fluorite, marcasite, barite, realgar and stibnite were also reported. Both at the northern and southern ends of the granite stock ('Fonte della Anguilla' and 'Fonte di Ravi'), quartz-chalcedony veins contain galena, sphalerite, chalcopyrite and pyrite in uneconomic amounts.

Data on the attitude of the ore bodies can be found in: LOTTI (1877, 1901-2, 1907, 1910, 1928, 1930), TOSO (1912), DE LAUNAY (1913), SAPPA (1921), POMPEI (1927), DE WIJKERSLOOTH (1930a, 1930b, 1934), TURACCHI (1954), TREFZGER (1954), CAVINATO (1961), ARISI-ROTA & VIGHI (1971), LEONARDELLI (1975).

Petrological contributions are from SAVI & MENEGHINI (1851), VOM RATH (1873), MAROCCHI (1897), MARTELLI (1909), MARINELLI (1961), BARBERI et al. (1971). The crystallographic characteristics of the pyrite from Gavorrano were described by AZZINI (1929); wollastonite occurring at the intrusive contact was studied by GIANNOTTI (1924); FORNASERI (1941) describes the berthierite from the 'Ravi Marchi' mine. More detailed studies on the minerography of the opaque minerals come from ARNOLD (1973) and NATALE (1974). Geochemical contributions are from MINGUZZI (1947), MINGUZZI & TALLURI (1951), TALLURI (1953), GARAVELLI (1962) who studied the distribution of the minor elements (especially Au, Ni, Co) within iron sulphides, the iron content of sphalerite and the chemistry of igneous and metamorphic rocks. Some sulphur isotope studies on sulphides and sulphates were carried out by CAGLIOTI et al. (1960) and ANCARANI-ROSSIELLO et al. (1962).

Earlier studies on the genesis of the Gavorrano sulphide deposits propose contradictory models, according to which they are either epigenetic and linked to the Neogenic intrusion (LOTTI, 1910; 1928; TOSO, 1912; DE LAUNAY, 1913; DE WIJKERSLOOTH, 1930a; CAVINATO, 1961; MARINELLI, 1961; ARISI-ROTA & VIGHI, 1971; JENKS, 1975), or sedimentary-metamorphic (BODECHTEL, 1965; ARNOLD, 1973; NATALE, 1974; ZUFFARDI, 1974). We shall discuss these models in more detail later on.

Despite the abundance of the literature a comprehensive report on the geological, attitudinal, mineralogical, textural and geochemical data had still to be presented. This work is aimed at providing the necessary background to eventual more detailed geochemical and mineral studies.

Geological background

a) *Regional geology*

Four main units are present in the Gavorrano mining zone, as in the neighbouring areas of southern Tuscany. These are, from bottom to top: 1) a phyllitic-quartzitic metamorphic complex; 2) the ' Tuscan unit ', made up of calcareous and sandy formations (Upper Triassic to Oligocene); 3) the ' Liguridi ' and ' Subliguridi ', consisting of flysch-type formations (Cretaceous to Eocene); 4) the ' Neoautochthon ', represented by post-orogenic sediments (Abbate et al., 1970; Giannini et al., 1971; Dallan-Nardi & Nardi, 1972).

There is a general agreement in considering the ' Liguridi ' and ' Subliguridi ' units as nappes overthrusting the lower units. On the contrary, differing opinions have been expressed on the relationship between the Tuscan Unit and the underlying phyllitic-quartzitic metamorphic complex. The metamorphic complex, in which low-grade parageneses are present, underlies a carbonate sequence beginning with the Norian ' Calcare Cavernoso ' (' Burano Formation ' of some AA.); the contact was considered as a Triassic transgression by Lotti (1910) and De Launay (1913). Both assign the phyllitic complex to the Permian. Recently some Authors (Trevisan, 1955; Signorini, 1966; Vighi, 1966; Bortolotti et al., 1970; Giannini et al., 1971; Arisi-Rota & Vighi, 1971), on the basis of the occurrence of dolostone and anhydrite lenses within the phyllitic-quartzitic complex, have considered it stratigraphically contiguous without hiatuses to the ' Calcare cavernoso ', assigning both formations to the Upper Trias. On the other hand, De Wijkerslooth (1930b, 1934) regards the quartzites and phyllites as the regional basement (' Tuscanide 1 ') of uncertain (Permo-Carboniferous to Triassic) age, whereas the overlying carbonate sequence would represent an allochthonous unit (' Tuscanide 2 '). This allochthonist model has been resumed recently by Baldacci et al. (1967) and Dallan & Nardi (1972), who describe the ' Calcare cavernoso ' as the base of a regional ' Tuscan nappe '. Seismic, borehole and drilling data from the Larderello-Travale geothermal field (BALDI et al., 1978; BATINI et al., 1978; GIANELLI et al., 1978) revealed the occurrence of tectonic wedges between the 'Calcare cavernoso' and the phyllitic complex. These results could support the allochthonist model.

The age and structure of the quartzitic-phyllitic complex have also been the subject of debate. In the older literature the various formations constituting the complex had been grouped together under the broad term of 'Verrucano sensu lato' (see, e.g., GIANNINI et al., 1971) and considered Triassic (TREVISAN, 1955). Recently (see, e.g., AZZARO et al., 1976; BAGNOLI et al., 1978, FRANCESCHELLI, 1978) a distinction has been introduced between the upper quartzite levels, referred to the Triassic 'Verrucano stricto sensu' (i.e. 'Quarziti di Monte Serra') and the underlying phyllites with quartzite and evaporite levels ('Filladi di Boccheggiano' of the 'Boccheggiano Group'). The latter were considered post-Hercynian by COCOZZA et al. (1974).

BAGNOLI et al. (1978), however, provide evidence of relics of a pre-Alpine metamorphic event and suggest that the complex would be pre-Sudetian. Owing to the lack of paleontologic and palynologic data, the question is still open to debate. According to GIANELLI & PUXEDDU (1979), the 'Boccheggiano Group' was formed in a sedimentary, low-Eh marine environment, characterized by the concurrent deposition of dolomite, sulphates and sulphides and by a basic volcanism, with re-sedimentation of its products. The 'Filladi di Boccheggiano' formation is characterized by the widespread occurrence of iron oxides and sulphides as thin levels lying parallel to the main schistosity plane. Economic pyrite concentrations (e.g., at Niccioleta) are associated with the dolomite-anhydrite lenses of the formation. Other important deposits (e.g., at Boccheggiano and Gavorrano) are located at the contact with the overlying 'Calcare cavernoso'.

It is apparent that an understanding of the nature of this contact is of prime importance in interpreting the genesis of the ore. On the other hand, the study of the mineralizations may help in shedding some light on the stratigraphic and tectonic problem.

b) *Geology of the Gavorrano area*

Figures 1a and 1b show the geologic setting of the Gavorrano mining area, which is located in a horst limited by Mio-Pliocenic normal faults. Three main sets of faults occur, striking N-S, NE-SW and NW-SE. A granite intrusion occupies the northernmost part of the horst (ZIA, 1954; BERTINI et al., 1969 and ARISI-ROTA & VIGHI, 1971).

Stratigraphic sequence

All the Tuscan, 'Liguridi' and 'Subliguridi' terranes, as well as the phyllitic basement and the 'Neoautochthon' are found in this area. The oldest fossil-bearing formation is the Rhaetian 'Calcare a Rhaetavicula' of the Tuscan Unit. Below this formation the reconstruction of the stratigraphic sequence is problematic, because of metamorphic overprint and tectonic dislocations that affect the area.

According to LOTTI (1901-2, 1910, 1928), upper Triassic terranes, consisting of alternating schists and limestones, underlie without hiatus the Rhaetian 'Calcari grigi dolomitici' (= 'Calcare Rhaetavicula') and the 'Calcare cavernoso'. These calcareous schists are reported along the NW side of the intrusion; the shallowest ore bodies ('Massa Praga', 'Unione', etc.) of the area are associated with these rocks. Andalusite-bearing schists, found both on the northern and southern margins of the granite stock ('Fonte dell'Anguilla' and 'Fonte di Ravi' respectively) are considered by Lotti to be the oldest (Permian) formation of the area.

The same rocks were assigned by DE WIJKERSLOOTH (1934) to the basement ('Tuscanide 1'), while the calcareous schists are referred, along with the overlying 'Calcare cavernoso', to the overthrusting 'Tuscanide 2' complex.

MARINELLI (1961), SIGNORINI (1966) and ARISI-ROTA & VIGHI (1971) assign the schists of Fonte dell'Anguilla and Fonte di Ravi to the 'Formazione filladica di Boccheggiano', while the calcareous

---

Fig. 1 - Geological sketch map of the Gavorrano area (a) and cross-section A-B (b) (Slightly modified version of map by ARISI ROTA & VIGHI, 1971).
1) tourmaline-rich microgranite; 2) granite; 3) alluvium and debris (Quaternary); 4) 'Neoautochthon' (Neogene-Quaternary); 5) 'Liguridi s.l.'; 6) 'Subliguridi'; 7) 'Marne a Posidonomya' (Dogger); 8) 'Calcare selcifero' (Middle to Upper Lias); 9) 'Rosso ammonitico' (Sinemurian); 10) 'Calcare massiccio' (Hettangian); 11) 'Calcare a Rhaetavicula' (Rhaetian), partly metamorphosed (dotted area); 12) 'Calcare cavernoso' (Upper Trias-Norian?), partly metamorphosed (dotted area); 13) metamorphosed quartzites of 'Verrucano s.s. (?)'; 14) metamorphosed quartzitic phyllites of the 'Formazione filladica di Boccheggiano' (Paleozoic?); 15) borehole; 16) fault; 17) strike and dip; 18) trace of the geologic cross-section.

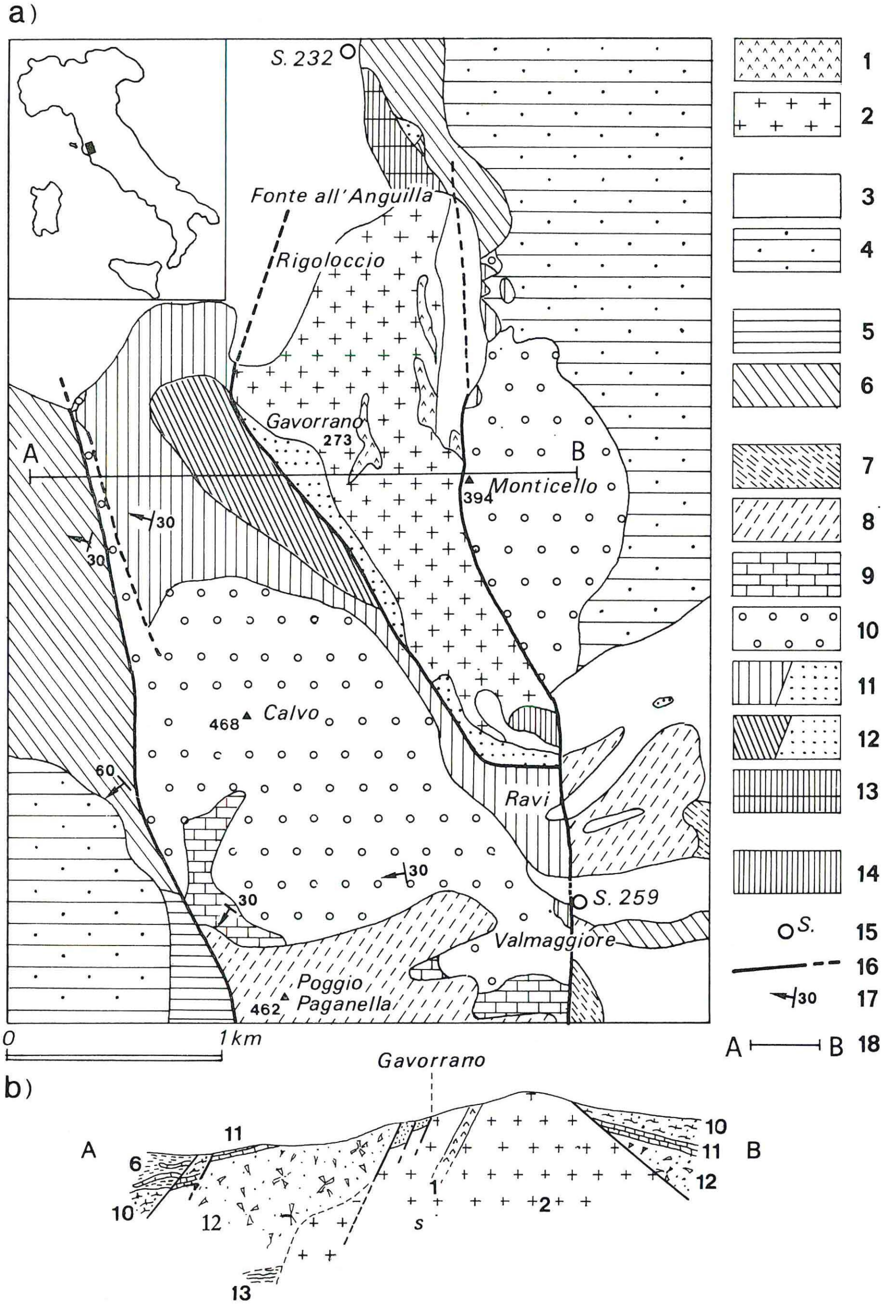

a)
S. 232
Fonte all'Anguilla
Rigoloccio
Gavorrano
273
A
B
Monticello
394
30
30
468
Calvo
60
Ravi
30
30
S. 259
Valmaggiore
Poggio
462
Paganella
0
1 km
1
2
3
4
5
6
7
8
9
10
11
12
13
14
S.
15
16
30
17
A B 18
b)
Gavorrano
A
6
11
10
12
13
1
2
s
10
11
B
12

Fig. 1

schists are considered the lowermost transitional member of the 'Calcare cavernoso' formation.

We made a detailed examination of the phyllites and quartzites outcropping north and south of the Gavorrano intrusion. Underground sampling was made at levels of —110, —130 and —200 m, in the mine tunnels crossing the 'Massa Boccheggiano' and 'Valmaggiore' stocks. Cores from two boreholes (Fig. 1a) north of Rigoloccio (n. 232) and south of Ravi (n. 259) were also examined.

Borehole n. 232 reveals that, under marly dark-gray limestones referrable to Rhaetian 'Calcare a Rhaetavicula', a dolostone with interbedded shaly and sulphate (anhydrite and gypsum) levels is present. These formations overlie quartzites with minor phyllitic levels. Similar rocks outcrop at 'Fonte dell'Anguilla' (Fig. 1a), are also present in borehole n. 259 and are possibly also in contact with the pyrite body of 'Valmaggiore'. These quartzites show a granoblastic inequigranular or seriate texture; the clasts are mainly represented by quartz, with minor fragments of phyllite, tourmalinite and red porphyries. Strained quartz fragments with undulate extinction are partially recrystallized in a finer polygonal aggregate owing to thermal metamorphism; nevertheless, the original texture of the rock is still recognizable. 'Tourmalinite' and 'red porphyry' clasts permit a correlation of these rocks with the Triassic 'Verrucano' ('Quarziti di Monte Serra'; RAU & TONGIORGI, 1974; BAGNOLI et al., 1978).

Hornfelses deriving from quartzitic phyllites and metagraywackes constitute the deepest level of borehole n. 232 and outcrop near Ravi (Fig. 1a). Moreover, these rocks form the bedrock of the 'Massa Boccheggiano' and 'Valmaggiore' sulphide stocks. Despite intense recrystallization and the growth of biotite and porphyroblastic andalusite, textural relics show that the original rocks were fine-grained quartzitic phyllites, graphitic schists and metagraywackes; primary minerals include quartz, chlorite, albite, sericite, ilmenite, sphene and minor apatite, tourmaline and zircon; at least two S-surfaces can be recognized; texture is granoblastic equigranular. These features permit us to refer the rocks to the 'Boccheggiano Group' described by BAGNOLI et al. (1978).

The local stratigraphic sequence is summarized as follows: below the 'Calcare cavernoso' formation a discontinuous 'Verrucano stricto sensu' horizon overlies the 'Filladi di Boccheggiano'.

We could not find the 'calcareous schists' reported previously by several authors; it is not clear whether they represent a discontinuous lowermost member of the 'Calcare cavernoso' formation or, rather, the calcareous schist of the 'Filladi di Boccheggiano' formation.

Magmatism and contact metamorphism

According to MARINELLI (1961), the Gavorrano intrusion is a quartz-monzonite with minor tourmaline-rich microgranite, porphyry and aplitic dykes; BARBERI et al. (1971) classify the main stock as granite. Its radiometric K/Ar age is 4.9 m.y. (BORSI et al. 1967). The intrusion is related to Mio-Pliocenic crustal magmatism whose intrusive bodies are as a rule characterized by shallow emplacement and a fast cooling rate. The thermal gradient around the intrusion probably decreased rapidly outwards (BARBERI et al., 1971). The most likely ascending pathway for the magma may be located more or less just under the town of Gavorrano, possibly at the intersection of two fault systems, one Apenninic (NW-SE) and the other anti-Apenninic (NE-SW). The magma mainly rose along Apenninic directions, with limited laccolithic expansion at the northern and southern ends, intruding the sedimentary rocks as far as the lowermost member of the Tuscan Unit (i.e., the 'Calcare cavernoso'). The area was then affected by faults related to the cooling and shinking of the igneous mass. The sedimentary cover at the time of the intrusion might have been represented by the Tuscan sequence and the overlying Ligurian nappes. The maximum overall thickness may be estimated at 2000-2500 m, which corresponds to a lithostatic pressure in the range of 0.5-1.0 kbar. Owing to the shallow depth of intrusion and to the presence of fractures, tectonic overpressures are not considered and from now on we shall assume that $P_{fluid} = P_{lithostatic} = 500$ bars.

The original contact between granite and country rocks is generally faulted, so that the width of the contact metamorphic aureole cannot be evaluated with precision; however, according to MARINELLI (1961) it does not exceed 200-300 m, in agreement with the estimated steepness of the thermal gradient around the granite. Apart from the basement and the 'Calcare cavernoso', the only formation affected by thermal metamorphism is possibly the Rhaetian ' Calcare a Rhaetavicula ', as ZIA (1954) included in this formation some graphitic schists (i.e., ' Calcari neri ' of Zia) at Fonte dell'Anguilla which contain biotite and diopsidic pyroxene of thermal metamorphic origin.

Contact metamorphism is present only for some tens of metres from the granite, as indicated by porphyroblastic andalusite or biotite flakes of up to 1-3 mm. At the intrusive contact the assemblage quartz+muscovite+K-feldspar+andalusite is widely represented as the thermometamorphic product in both the Triassic Verrucano and the quartzite and phyllite of the ' Filladi di Boccheggiano '. At 500 bars this assemblage shoud be in equilibrium (in the system K_2O-Al_2O_3-SiO_2-H_2O) at temperatures around 530°C (CHATTERJEE & JOHANNES, 1974; SKIPPEN, 1977).

In Mg- and Fe-bearing phyllites the significant assemblage found near the intrusive contact is quartz+muscovite+chlorite+cordierite+biotite. Extrapolation from the experimental data of SEIFERT (1970) would place the equilibrium Mg-chlorite+muscovite+quartz = Mg-cordierite+phlogopite at about 480°C at 500 bars pressure; in an Fe-bearing system this temperature will be somewhat lower.

The contact granite-carbonate rocks is characterized by a more complex situation. Thermometamorphic silicate assemblages along this contact have been described by several authors (MARTELLI, 1909; LOTTI, 1910; GIANNOTTI, 1924; BARBERI et al., 1971). The minerals reported are garnet, epidote, spinel, wollastonite, diopside, olivine (forsterite), scapolite, quartz, calcite and vesuvianite. The extent of these occurrences is, as in general for thermometamorphic phenomena in the area, quite limited. ARISI-ROTA & VIGHI (1971) point out that, where these silicates are present, the contact granite-limestone is barren.

The only report of metasomatic phenomena is a quite vague mention by TREFZGER (1954) who describes the occurrence, at Vignaccio, of calc-silicate masses ' similar to the Swedish skarns '. Metamorphism is considered by BARBERI et al. (1971) to have been essentially isochemical.

We have examined the granite-' Calcare cavernoso ' contacts occurring at the surface just west of the town of Gavorrano and, underground, at the —200 m level of the ' Massa Boccheggiano ' pyrite body. Other underground contacts are unfortunately no longer accessible. The only recognizable thermometamorphic effect in the surface contacts is the recrystallization of the limestone, with up to 1 cm growth of calcite and dolomite crystals. No silicate levels are found. Two different situations were encountered at the —200 m level.

Sometimes a dolomitic marble occurs at the contact; in other places a calc-silicate hornfels with some skarn occurrence is observed a few metres from the contact. The dolomitic marble consists of centimetric calcite and dolomite crystals. Recrystallization effect sharply wanes ten metres from the contact. Mineralized patches occur in the dolomitic marble. Sphalerite is the major sulphide here, with minor pyrite and chalcopyrite. Pyrrhotite and galena are present only as inclusions in pyrite and sphalerite respectively. The FeS content in sphalerite ranges from 2.6 to 4.3 moles % (GREGORIO et al., 1980). Vugs lined by calcite, dolomite, quartz and pyrite are also present. The contact with the granite is characterized by the presence of pyrite, chalcopyrite and minor galena, in a chlorite-quartz-carbonate gangue.

The calc-silicate hornfels appears to be essentially a forsterite marble, the stable primary mineral assemblage being: forsterite+ calcite$\pm$dolomite. This assemblage is stable (in the system CaO-MgO-SiO_2-H_2O-CO_2, when $P_{CO_2}+P_{H_2O}=P_{tot}=500$ bars and both $CaCO_3$ and $MgCO_3$ activities are fixed by the calcite-dolomite miscibility gap) only above 400°C, no matter what the X_{CO_2} is in the fluid (SKIPPEN, 1974). Accessory minerals include spinel, plagioclase and scapolite. The only opaque mineral is represented by widespread traces of pyrite as subhedral single grains.

The contact granite/calc-silicate hornfels is marked by a 1-2 m band consisting of major diopside, garnet, dolomite and calcite towards the hornfels and of epidote, tremolite, diopside, scapolite, calcite, garnet and typical granite minerals towards the igneous rock Much thinner (few cm) veins of endoskarn with the same mineral assemblages cut the granite a few m from the contact. The band may be regarded as a 'reaction skarn' (in the sense given by BURT, 1977) where exchange phenomena of Ca and Mg towards the intrusive, and of Si and Al towards the hornfels, took place. Diopside and tremolite-bearing exoskarn veins penetrate the calc-silicate hornfels a few meters from the contact. Calcite, dolomite, ilvaite, garnet, idocrase, wollastonite, chlorite, scapolite, K-feldspars and plagioclase are also present.

Minor quantities of needle-like hematite partly transformed in magnetite are strictly associated with ilvaite. Hexagonal pyrrhotite replaced by monoclinic and/or marcasite plus mottled pyrite, associated with traces of chalcopyrite, is also present.

The mode of occurrence and banded texture in the hand specimen, along with the development of centimetric crystals of diopside, tremolite and calcite, permit us to classify these veins as 'replacement skarns' (in the sense of BURT, 1977).

The boundary between the calc-silicate hornfels and the skarn is characterized by a narrow (few tenth of mm) band where phlogopite and tremolite ($\pm$ actinolite) develop. Tremolite forms outwards and is diffused within the marble in equilibrium with serpentine minerals. These zoned mineral assemblages suggest a prograde K, Mg (plus Al and Si) metasomatism towards the marbles and a Ca metasomatism towards the skarn. The occurrence of idocrase and ilvaite would indicate a fluid of low X_{CO_2} (see BARTHOLOMÈ & DIMANCHE, 1967; KERRICK et al., 1973; OLESCH, 1978). The presence of wollastonite also supports this idea, since high X_{CO_2} values imply the formation of wollastonite at very high temperature (600° to 700°C - GREENWOOD, 1967), which is not in agreement with the temperature of 530°C inferred from the mineral assemblages in the pelitic rocks (see above).

Away from the intrusive, forsterite-bearing marbles grade into a quartz-calcite-dolomite marble. Owing to the overlapping with skarn occurrences and the extreme narrowness of the aureole, a distinct prograde sequence cannot be recognized. Either tremolite or diopside could represent the markers of intermediate steps between forsterite-lacking and forsterite-bearing marbles. Moreover, the quartz content of the low-grade rocks seems too low to account for all the forsterite found in the high-grade paragenesis. Thus some silica was probably introduced during metamorphism. The forsterite being widespread, fine-grained and not related to any apparent pathway for infiltration, the mechanism most likely for the introduction of the silica is diffusion. These 'calc-silicate hornfels' would then grade into 'reaction skarn'. Occurrence of some metres of forsterite-bearing 'reaction skarn' is typical at the contact between acidic intrusives and magnesian limestones (PERTSEV, 1974; BURT, 1977).

The area of Gavorrano was the seat of a widespread hydrothermal activity, with retrograde phenomena affecting the high-temperature parageneses. Forsterite and diopside are often altered into serpentine, tremolite, chlorite and talc; vein minerals including quartz, adularia, epidote, sulphides and locally calcite, albite and tremolite are found extensively as late-stage products. Epidote and adularia are commonly found as hydrothermal minerals in the present-day geothermal fields, generally in the range 250-300°C (SEKI, 1972; MUFFLER & WHITE, 1969). At Rigoloccio, hydrothermal activity has also extensively affected both the granite and pyrite body, with production of goethite and clay minerals, including halloysite, which suggests a maximum temperature around 175°C (ROY & OSBORN, 1954) for the final stage. The higher-temperature mineral assemblages indicate a nearly neutral or slightly basic hydrothermal fluid, whereas the appearance of clay minerals at lower temperatures points to lower pH values (see BROWNE & ELLIS, 1970).

In conclusion, the conditions during thermal metamorphism at Gavorrano may be summarized as follows: the pelitic and calcareous rocks were metamorphosed at the contact, at a temperature reaching 530°C, which sharply decreased across a steep thermal gradient. Pressure was about 500 bars. Metamorphism was essentially isochemical, as the metamorphic assemblages seem to reflect the original rock compositions. Mobilization of non-volatile components was limited to diffusion exchange between carbonate and silica-bearing rocks. A later metasomatic event produced the emplacement of very limited amounts of a diopsidic skarn, from fluids characterized by low CO_2 contents. Relatively low contact temperatures and limited thermometamorphic effects support MARINELLI's (1961) contention that the intrusive rock, when emplaced, was already in an advanced stage of cooling. The area was subsequently affected by late stage hydrothermal activity, possibly developing at low pressure and decreasing temperature from 300° to 170°C.

ATTITUDE AND COMPOSITION OF THE ORE BODIES

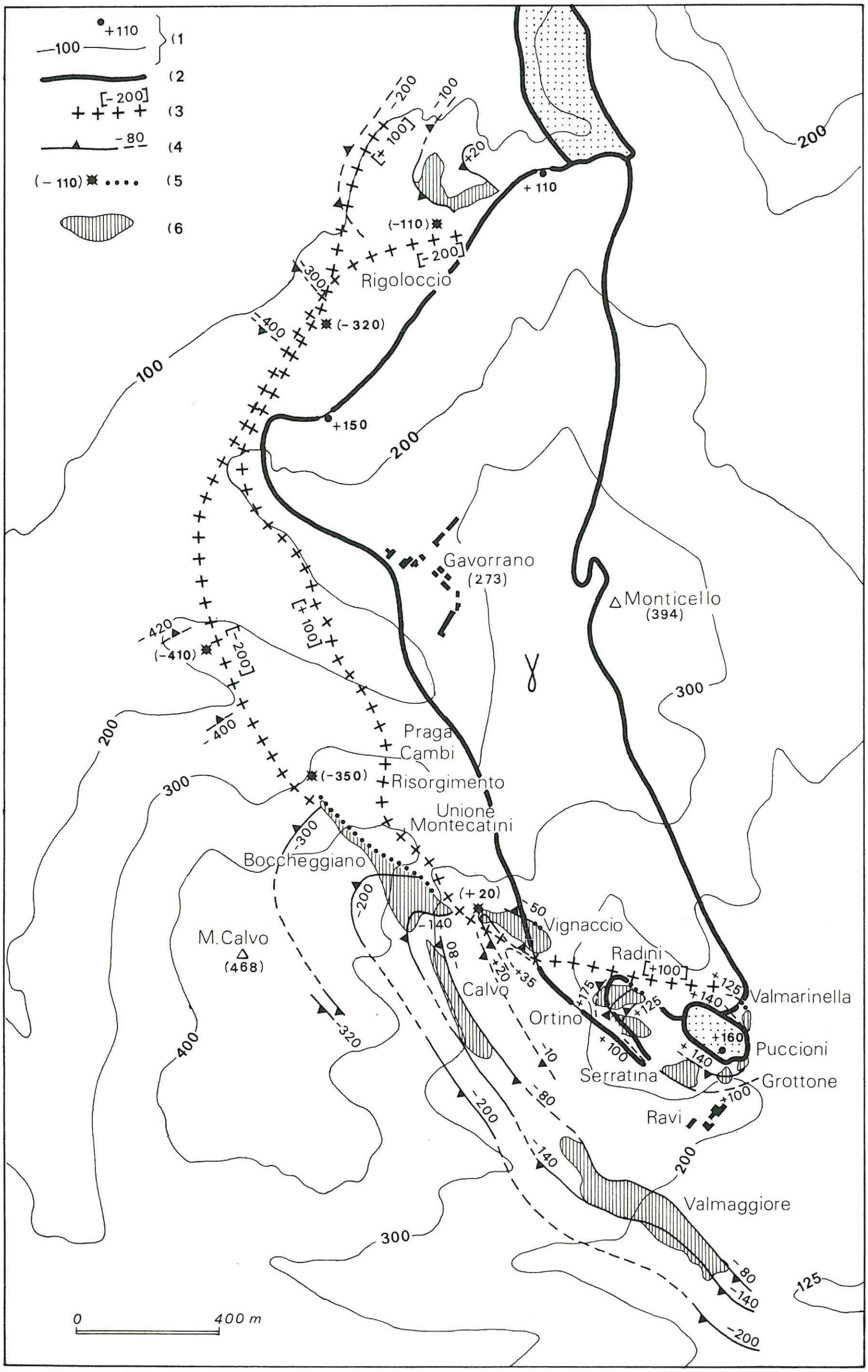
The ore bodies exploited so far at Gavorrano are massive pyrite stocks with little quartz-calcite gangue. Figures 2 and 3 show their shape and structure, as deduced from the literature and mining companies' reports, as well as from our own observations. Figure 2 also reports the contour lines of the top of the quartzitic-phyllitic complex and of the granite.

Two different structural settings (see also Fig. 3) are encountered:

a) Some ore bodies are found at the contact between the granite and the country rocks, whether they be ' Calcare cavernoso ' or the phyllitic-quartzitic complex. The main sulphide production derives from this type of ore. The ' Rigoloccio ' concentrations are found north of Gavorrano, while south of this town an apparently continuous producing horizon is represented by the stocks of ' Massa Praga ', ' Cambi ', ' Risorgimento ', ' Massa Boccheggiano ', ' Unione ', ' Montecatini ', ' Vignaccio ' and by the smaller ' Radini ', ' Ortino ' and ' Val Marinella ' occurrences. A remarkable variety of attitudinal features can be observed in these bodies: roughly lenticular masses (' Rigoloccio '), massive stocks dismembered by fractures that become increasingly complex towards the intrusive contact (' Massa Boccheggiano '), metasomatic masses (' Vignaccio '), filling veins (' Unione ', ' Risorgimento '). The latter extend locally (' Massa Praga ', ' Cambi ') into the granite itself, which in turn contains at the contact up to 70% disseminated pyrite (LOTTI, 1910, 1928; TOSO, 1912; DE WIJKERSLOOTH, 1934; TREFZGER, 1954; TURACCHI, 1954; ARISI-ROTA & VIGHI, 1971). The ore is mined nowadays at ' Rigoloccio ' and ' Massa Boccheggiano ' only.

b) Some massive pyrite, roughly lens-shaped bodies occur at the contact between the Triassic ' Calcare cavernoso ' and the quartzitic-phyllitic complex and do not show any direct relationship with the igneous rock. This producing horizon includes the ore bodies of ' Calvo ', ' Grottone ', ' Serratina ' and ' Puccioni ', now exhausted, and ' Valmaggiore ', still exploited (LOTTI, 1910, 1928; TOSO, 1912; DE WIJKERSLOOTH, 1934; TREFZGER, 1954; ARISI-ROTA & VIGHI, 1971).

Fig. 2 - Location of the pyrite ore bodies directly overlying the metamorphic complex (i.e., ' Filladi di Boccheggiano ' and ' Verrucano s.s. '). Based on cartography of the mining company.
1) topographic contour lines (in m a.s.l.). The level of the individual points on the surface are also indicated (solid circles); 2) geologic boundaries on the topographic surface: granite (γ), ' Verrucano s.s. ' and ' Filladi di Boccheggiano ' (dotted areas); 3) underground contour lines of the granite; 4) underground contour lines of the top of the metamorphic complex (in m); 5) depth of the contact granite-metamorphic complex-' Calcare cavernoso ' (or pyrite bodies); 6) contact surfaces between the metamorphic complex and the ore bodies.



+110
100
(1
(2
[-200]
(3
-80
(4
(-110)
(5
(6
Rigoloccio
Gavorrano
(273)
Monticello
(394)
Praga
Cambi
Risorgimento
Unione
Montecatini
Boccheggiano
M.Calvo
(468)
Vignaccio
Radini
Valmarinella
Calvo
Ortino
Puccioni
Serratina
Grottone
Ravi
Valmaggiore
0
400 m

Fig. 2

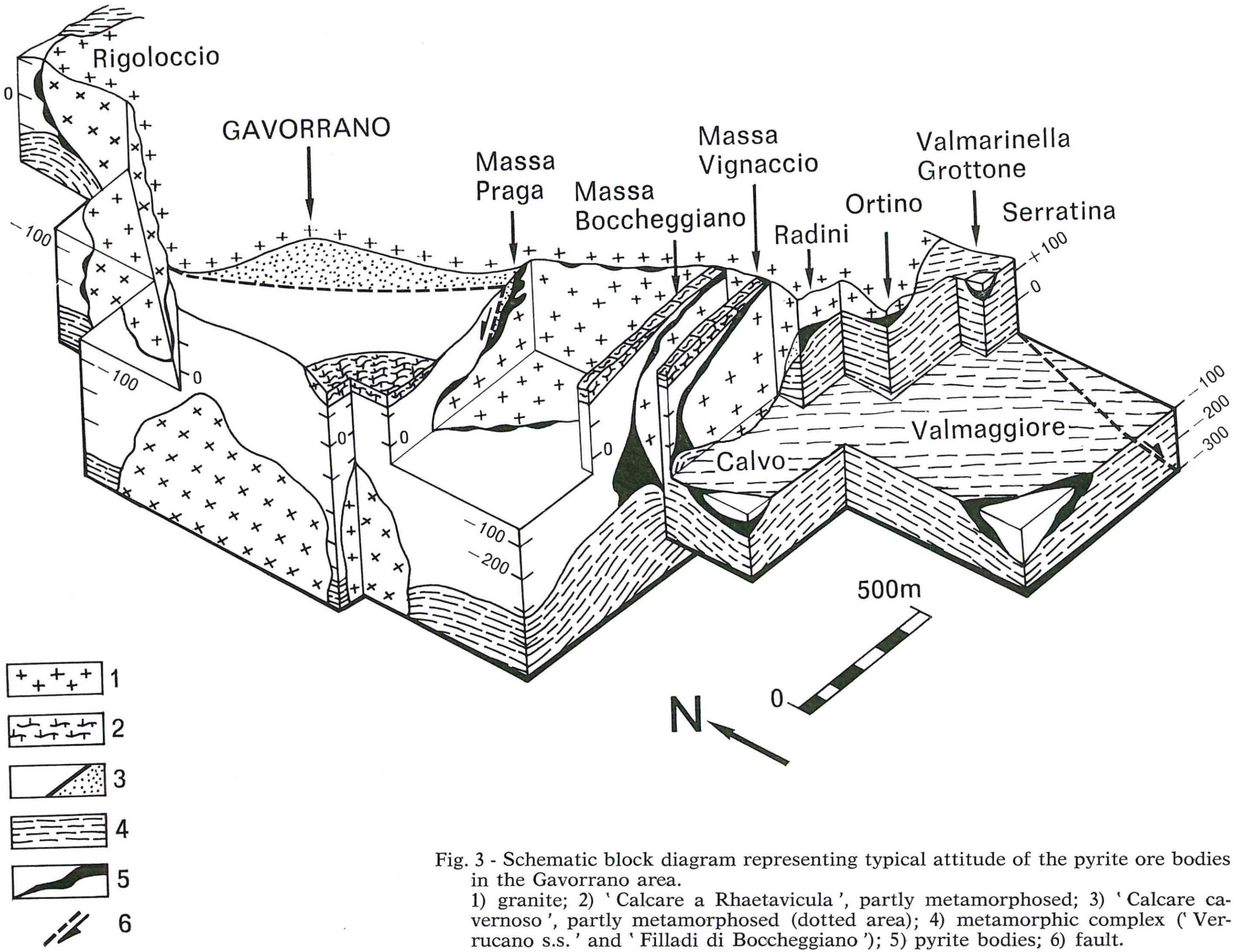


Fig. 3 - Schematic block diagram representing typical attitude of the pyrite ore bodies in the Gavorrano area.
1) granite; 2) ' Calcare a Rhaetavicula ', partly metamorphosed; 3) ' Calcare cavernoso ', partly metamorphosed (dotted area); 4) metamorphic complex (' Verrucano s.s. ' and ' Filladi di Boccheggiano '); 5) pyrite bodies; 6) fault.

The sulphide stocks being mined at present will now be described in detail.

I) *Rigoloccio* - The producing levels are now about 45 m b.s.l. and consist of lens-shaped pyrite bodies dipping steeply and lying between the 'Calcare cavernoso' and the granite. At present the ore-limestone contact is not exposed. Late-stage hydrothermal alteration affected both the granite and the pyrite, producing clay beds (montmorillonite, illite, kaolinite, endellite, with some siderite) and iron hydroxide (mainly goethite) beds, interlayered with pyrite (FURIERI et al., in prep.). Even iron hydroxide was mined occasionally. Unaltered pyrite is associated with a quartz-sericite gangue. The sulphur contents of the ore are up to 52%, in agreement with the absence of any other sulphide than pyrite (Table 1). Chemical ($KMnO_4 + H_2SO_4$ 1:1, or concentrated HNO_3) or electrolytic etching showed that the pyrite crystals are zoned, the core being formed by roundshaped grains, surrounded by octahedral and cubic rims (Plates 1a, b and c).

II) *Massa Boccheggiano* - Mining nowadays is developed around 200 m b.s.l., at the bottom of a pyrite stock in contact with the 'Calcare cavernoso', the phyllitic complex and the intrusion (Fig. 4). Several dykes of aplite and porphyric granite cut both the granite and country rocks (MARINELLI, 1961).

The phyllites and quartzites are transformed into hornfelses, but textural relics permit us to assign them to the 'Filladi di Boccheggiano'. The 'Calcare cavernoso' is strongly recrystallized and up to about ten metres from the contact it appears as a dolomitic marble; some calc-silicate hornfels and skarn are also present at the granite-limestone contact (see previous section). A detailed sampling of ores and host rocks was made from —185 down to —204 m. Table 1 summarizes the mineralogy and petrography of the rock types found at 'Massa Boccheggiano'.

The ore body of Massa Boccheggiano consists of massive pyrite, showing a coarse- to fine-grained, sometimes cataclastic, structure. Fractures in the pyrite are often filled by calcite, dolomite and, less commonly, by a little galena. Vugs lined by crystals up to several cm are not uncommon. Locally the cataclastic structure grades into tectonic breccias, made up of coarse pyrite fragments in a fine-grained pyrite matrix. These breccias are related to faults and fractures dismembering the stock. Displacement of these faults is

MINERAL	RIGOLOCCIO	MASSA BOCCHEGGIANO						VALMAGGIORE
		Main orebody	Orebody-granite contact	Carbonate lens at orebody-granite contact	Dolomitic marble	calc-silicate hornfels	Skarns	
Pyrite	▬	▬	▬	▬	▬	▬	▬	▬
Magnetite			▬				▬	▬
Hematite				▬			▬	▬
Pyrrhotite			▬		▬		▬	▬
Marcasite			▬ ?				▬	▬
Chalcopyrite			▬	▬	▬		▬	▬
Sphalerite			▬ ▬	▬	▬			
Galena		▬	▬	▬	▬			
Tetrahedrite				▬				
Chalcocite				▬				
Covellite				▬				
Other ore minerals	Goethite		Cassiterite Goethite, melnikovitic pyrite					Stibnite, melnikovitic pyrite
Gangue and non-ore minerals	Quartz, siderite, sericite, clay minerals	Calcite, dolomite (quartz)	Quartz (calcite, dolomite)	Calcite, dolomite, muscovite, chlorite	Calcite, dolomite, quartz, chlorite	Forsterite, calcite, dolomite, spinel, plagioclase, scapolite, serpentine, sericite, chlorite, talc, epidote	Diopside, tremolite, feldspars, garnet, ilvaite, wollastonite, idocrase, scapolite, chlorite, epidote, zoisite, flogopite, actinolite, calcite and dolomite	Calcite, dolomite, (quartz, siderite, muscovite, chlorite, epidote)
Textural relics in pyrite	Zoned textures with anhedral cores	Rare, ill-defined growth textures	Abundant and varied (see text)	Low - crystallinity core	Absent	Absent		Rare

Table 1 - Mineralogy of the ore bodies and contact metamorphic rocks at Gavorrano. Bar thickness roughly represents the relative abundance of the mineral for each association. Paragenetic sequence is shown approximately by the position of the bar, from left (early) to right (late).

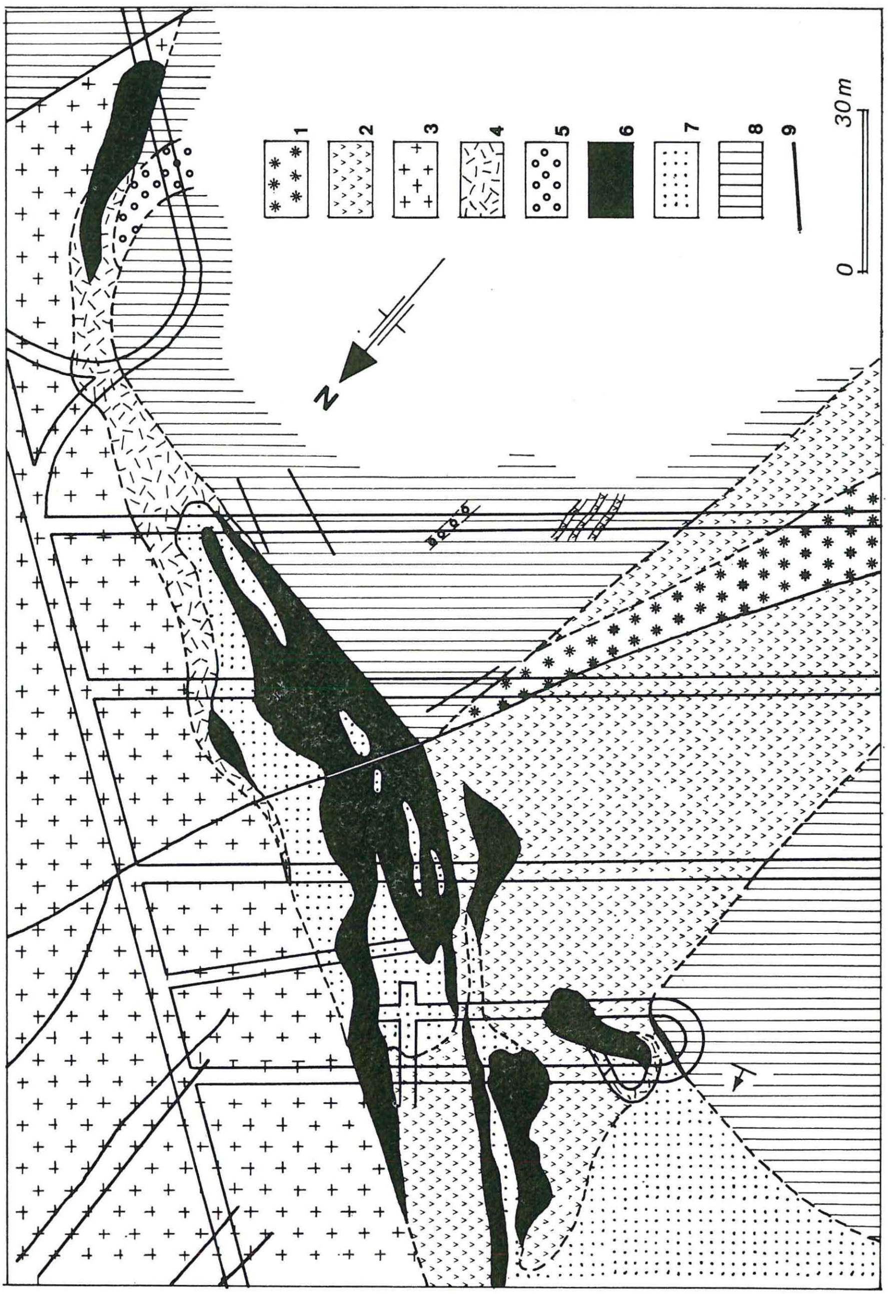


Fig. 4 - Map of the SE part of the —200 level in the Massa Boccheggiano mine. Based on cartography of the mining company. 1) aplite; 2) tourmaline-rich microgranite; 3) granite; 4) calc-silicate hornfels and skarn; 5) quartz vein; 6) pyrite; 7) metamorphosed limestone ('Calcare cavernoso'); 8) hornfels ('Filladi di Boccheggiano'); 9) fractures.

minor, nor do they appear to be aligned along any particular direction. Apart from these occurrences the stock is remarkably high-grade, with little gangue and not other sulphides than pyrite. Pyrrhotite, locally in sizable concentrations, was reportedly encountered during earlier mining works. The contacts with phyllites and limestone are generally sharp, wall rock replacement being limited to the hand specimen scale. Structural etching on pyrite revealed only ill-defined growth textures.

Ore features at the granite-ore body contact are somewhat different with respect to the main pyrite stock. An abundant quartz gangue is present; pyrite shows inclusions of pyrrhotite and minor sphalerite, the latter containing chalcopyrite blebs. Textural evidence indicates, however, that some sphalerite is younger than the pyrite: in this case a little galena is emplaced at the pyrite-sphalerite contact; sphalerite contains 3.1 to 4.3 moles % FeS (GREGORIO et al., 1980). Pseudomorphs of magnetite after hematite also occur, mainly as inclusions in pyrite. Minor aggregate of melnikovitic pyrite, associated with goethite, are locally present. Cassiterite has been found locally in the quartz gangue. Structural etching on pyrite revealed many interesting textures. The general trend is to an increase in size and euhedrality of the crystals from a low-crystallinity or anhedral core to coarser, subhedral to euhedral crystals. We may observe a) framboid-like aggregates grading to ringshaped clusters of larger crystals (Plate 1e). These aggregates should not be defined as true 'framboids' (cfr. typical pictures of these, e.g., in LOVE & AMSTUTZ, 1966; LOVE et al., 1971), in that the single grains are less closely packed and of markedly different sizes; their overall aspect is definitely less 'raspberry-like' than that of the true 'framboids'; b) zonal accretion of a single crystal with recurrent sequences of alternating microcrystalline pyrite and surfaces of euhedral crystals (Plates 2b, c, d and f). Sometimes structure etching reveals that the outermost rim of otherwise euhedral crystals consist of low-crystallinity pyrite (Plate 2f); c) cores of radial aggregates of pyrite needles that possibly developed after acicular marcasite (Plate 2e).

In the NW part of the —200 m level, near the ore body-granite contact, pyrite partly includes a carbonate lens, made up essentially of calcite. The contact with the ore is marked by the occurrence of muscovite, chlorite, calcite concretions and several opaque minerals: sphalerite, galena, chalcopyrite and minor tetrahedrite, hematite, chalcocite and covellite are present with the pyrite. Euhedral pyrite crystals show hematite inclusions and are often in turn surrounded by chalcopyrite. Ring-like aggregates of subhedral pyrite crystals whose size increases from the core outwards are typical of this occurrence. The core itself is often occupied by tetrahedrite or calcite that apparently replaces the sulphosalt (Plate 1d). Sphalerite and galena show mutual boundary relationships; they appear to be younger than pyrite and chalcopyrite, the latter often being present as inclusions in the sphalerite. The FeS content of the sphalerite ranges from 2.1 to 6.0 moles %. Structural etching on pyrite revealed for many grains a colloform, low-crystallinity core (Plate 1, f, g, h; Plate 2a).

III) *Valmaggiore* - A lens-shaped body is mined at Valmaggiore at the phyllites-'Calcare cavernoso' contact, from —80 down to —160 m. The stock dips NW-SE and strikes SW; thickness ranges from 2 to 30 m. The bedrock is represented by hornfelses deriving from the 'Filladi di Boccheggiano'; the metamorphic grade is remarkably lower than that noted at 'Massa Boccheggiano'.

The contact is sharp and concordant. The bedrock is only weakly mineralized; pyrite crystals, completely enclosed in quartz, are aligned parallel to the main schistosity.

The roof contact with the 'Calcare cavernoso' is not well exposed; replacement of the limestone by the ore, if any, is not apparent.

The gangue mainly consists of calcite and dolomite, with minor quartz and siderite; muscovite, chlorite and epidote are also present at the contact with the hornfelses. Apart from pyrite, other ore minerals (pyrrhotite, magnetite, hematite, chalcopyrite, stibnite and marcasite) rarely occur.

Overall ore grade is however slightly lower with respect to 'Massa Boccheggiano' and 'Rigoloccio'. The pyrite features are quite similar to those found in the main stock at 'Massa Boccheggiano': fine- to coarse-grained masses of subhedral crystals, with fractures filled by gangue minerals. Replacement of the latter by pyrite is also observed. Structure etching on pyrite revealed rare and rather poor textural relics. The magnetite is pseudomorphic after bladed hematite and is associated with siderite; the blades often display a rhombohedral or triangular array (Plate 2, g) which may suggest the previous existence of hematite lamellae replacing siderite along cleavage planes, as proposed by DE WIJKERSLOOTH

(1930a). The pyrrhotite forms lamellar aggregates extensively altered into marcasite and pyrite; unaltered pyrrhotite is present as small inclusions in pyrite. Minor chalcopyrite fills the intergranular spaces between the pyrite crystals. Another locally observed phenomenon is the late growth of melnikovitic pyrite, which takes places starting in the fractures and intergranular spaces of earlier pyrite crystals, with development of banded textures (Plate 2, h). The X-ray scanning images revealed no compositional difference between the layers forming the concretional texture.

Concluding remarks

The most significant features of the ore bodies may be summarized as follows:

a) the ore bodies are massive, mostly coarse-grained, high-grade, low-gangue; as pointed out by JENKS (1975), if they are a product of replacement, it must have been a remarkably complete one;

b) the contacts with the bedrock (phyllites) are sharp and roughly concordant; the occurrence of pyrite breccias was ascribed by DE WIJKERSLOOTH (1934) to the overlapping of the pyrite-forming process with the final stages of the tectonic activity that thrust the 'Tuscanide 2' onto the phyllites. However, these pyrite breccias seem rather to be linked to local fault systems; in fact, they have not been observed at the ore-phyllite contact;

c) the proximity of the intrusive is characterized by a marked change in the attitude and mineralogy of the ore bodies. The ore occurs as veins, metasomatic masses, disseminations into granite. The gangue is more abundant and more siliceous. Pb and Zn minerals are concentrated here, especially where limestone is also present. Textural relics into pyrite are also more abundant and more significant near the intrusive contact; they become increasingly rarer and poorer as they move away from it.

ORE GENESIS

Previous theories

A genetic interpretation of the Gavorrano ore bodies was first proposed by LOTTI (1901-2, 1910, 1928). Based on the occurrence of disseminated pyrite in the granite, in locally sizable concentrations, he proposed a magmatic segregation origin for the mineralization. This hypothesis was later reconsidered by CAVINATO (1961).

According to TOSO (1912), the pyrite bodies penetrating the granite might represent the product of replacement of calcareous masses by ore-forming fluids ascending along the granite-limestone contacts, producing ore bodies mostly in a vein-like attitude. TOSO thus referred the genesis of the mineralization to 'vaporous emanations related and subsequent to the granite, ascending through fractures in the schists of the basement' which 'metasomatically affected the schistous and cavernous limestones'. The last witnesses of these endogenous processes would be represented by the CO_2 and H_2S-bearing thermal springs of Bagni di Gavorrano and Caldana (NW and south of Gavorrano respectively). This pyrometasomatic model was subsequently accepted and re-elaborated by TREFZGER (1954), MARINELLI (1961), ARISI-ROTA & VIGHI (1971) and others. In particular, MARINELLI (1961), though the main point of interest was the intrusion itself rather than the ore occurrence, stated that 'pyrite is never found as a primary mineral in any type of magmatic rock of the Gavorrano intrusion' and that this mineral makes its appearance subsequent to the magmatic crystallization related to autometamorphism or albitization phenomena. Moreover, the mineralized veins cutting the thermometamorphic rocks of the aureole are later than the metamorphism and then subsequent to the intrusion. Thus, according to MARINELLI, the ore-forming process is pneumatolythic to frankly hydrothermal. We think that this classic pyrometasomatic model requires at least a critical examination, in the light of the following facts: a) a clearcut metasomatic character is observed only in the bodies nearest to the intrusive; b) as will appear from a later discussion, a simple pyrometasomatic model would hardly account for the textural relics in pyrite; c) the extent of metasomatic phenomena in the contact aureole is frankly limited. It seems rather unlikely that pyrometasomatic activity would have resulted in the emplacement of several million tons of sulphide, without producing any sizable skarn mass. We recall that elsewhere in southern Tuscany, from a quite similar genetic environment (T = 450°C, pressure of a few hundred bars, presence of fracture), important skarn occurrences are encountered along with sulphide and oxide mineralizations (TANELLI, 1977, 1978).

DE WIJKERSLOOTH (1930a, 1930b, 1934) proposed a general model in which the ore deposits of Tuscany are related to the overthrusting planes of the Mio-Pliocenic tectonic activity. Siderite deposits, originated during the first stages of the Apenninic orogeny from early-orogenic basic magmas (ophiolites), would have been subsequently transformed into iron oxides by dynamic and thermal metamorphism and, in turn, into local iron sulphides by sulphur-bearing fluids of granitic affiliation. To support his thesis De Wijkerslooth interprets the occurrence of hematite lamellae in triangular and rhombohedral arrays as evidence for hematite formation along cleavage surfaces of pre-existing siderite rhombohedra. He also finds examples of pyrite pseudomorphosis after hematite in the Ritorto deposit, 20 km north of Gavorrano. The sulphidation of the ores would have been mainly post-kynematic with some exceptions, e.g., at Gavorrano, as demonstrated by the occurrence of laminated and brecciated pyrite. Here the tectonic activity would correspond to the overthrusting of the 'Tuscanide 2' over the phyllites. Magnetite, hematite and siderite showing textural relationships which possibly support De Wijkerslooth's hypothesis were also observed by us. However, it should be noted that a) De Wijkerslooth's palinspastic interpretation of the Apenninic ophiolites is clearly out-of-date; b) we have not found any positive evidence at Gavorrano that supports his tectonic model; c) siderite is present only in trace amounts in all deposits of southern Tuscany.

A volcano-sedimentary origin, with subsequent metamorphic overprint, was proposed for the iron deposits of southern Tuscany by Bodechtel (1965). Primary hematite-pyrite Permo-Triassic deposits would have been thermally metamorphosed during the Mio-Pliocenic emplacement of the granitic stocks. This metamorphic effect would have been especially strong at Gavorrano. This model relies mainly on the strata-bound character of most ore-bodies; Bodechtel finds evidence for Permo-Triassic volcanism in some occurrences of porphyroids in the Tuscan basement; metamorphic imprint on the ores would be demonstrated by the transformations hematite — magnetite and pyrite — pyrrhotite near the intrusive contacts. In this respect we point out that a) the muskhetovitization process is observed not only in the deposits related to Triassic formations but in the post-Triassic ones as well (e.g., Ritorto and Fenice Capanne); b) pyrrhotite occurrence is neither clearly nor univocally related to the proximity of intrusives. The mineralogical changes reported by Bodechtel may well be ascribed to chemical, rather than to thermal, variations (Corsini et al., 1975). This does not mean, of course, that a volcano-sedimentary origin must be ruled out. Recent observations, however, suggest a Silurian-Devonian, rather than Permo-Triassic, age for the Tuscan porphyroids (which are part of the 'Buti Group' of BAGNOLI et al., 1978). The metallogenic significance of this volcanism has, at any rate, still to be demonstrated.

Synsedimentary genetic models have also been proposed: regional and thermal metamorphism would have affected and partially remobilized primary Triassic deposits of evaporitic (JENKS, 1975) or sabkha (ZUFFARDI, 1974) origin. JENKS (1975) notably believes that the Gavorrano deposits (namely, 'Massa Boccheggiano', to which his description seems to refer) are the result of a complete remobilization process, producing 'discordant and epigenetic' ore bodies.

Bearing of textural relics in pyrite on ore genesis

Studies on textural relics revealed by structural etching on pyrite have recently been considered to support a sedimentary-metamorphic origin of the deposits. ARNOLD (1973) described textural relics entirely similar to our findings. The author interpreted the microcrystalline, framboidal and/or colloform textures of the cores of euhedral crystals as witnesses, only partially erased by later metamorphic events, of a primary low-temperature crystallization of pyrite. In particular, Arnold studied a number of samples from Gavorrano and Niccioleta, claiming evidence for *in situ* thermometamorphic recrystallization of a primary low-crystallinity pyrite. He rules out any significant remobilization process. We think that, at Gavorrano, this picture can logically be referred to the bodies farthest from the intrusion, although no mention is made by Arnold about the exact location of his samples. NATALE (1974), in his otherwise exhaustive study of pyrite from several Tuscan deposits, could examine a few samples only from Gavorrano, finding meager evidence for textural relics. While stressing the preliminary character of his results, he tentatively concluded that Gavorrano represents the most metamorphosed deposit, where all but a few primary textural features have been cancelled out by thermal metamorphism.

The characteristics and spatial distribution of textural relics we observed at Gavorrano seem to require a rather complex interpretation. Framboidal and/or colloform textures of pyrite have for a long time been considered as results of low temperature processes. In particular, the presence of organic matter was believed to be essential in the formation of framboids, some of which can be considered as microfossils (see TRUDINGER, 1976, for a discussion and a comprehensive reference list). During the last ten years, experimental evidence has been produced (BERNER, 1969; FARRAND, 1970) to demonstrate that the formation of framboids from purely inorganic processes and at temperatures up to 250°C (SUNAGAWA et al., 1971) is also possible. CHEN (1978) ascribes to chemical precipitation the colloform and framboidal textures of pyrite from the Caribou deposits, New Brunwick. Development of framboids seems to depend on the mechanism of formation of pyrite. The latter may be precipitated directly from the solution, or else involve, as a first step, the formation of an iron monosulphide turning subsequently into greigite and eventually pyrite (see BERNER, 1971 and RICKARD, 1975, with references). SWEENEY & KAPLAN (1973) believe that the spherical textures that developed upon transformation of the first-formed monosulphide into greigite, are the basis for the formation of framboids. During the greigite-pyrite transformation these spherical textures may either be preserved of evolve to framboids, owing to internal nucleation of pyrite crystallites. Sweeney & Kaplan obtain framboidal structures in an aqueous medium at 85°C, while in absence of water the spherical texture inherited from greigite is preserved up to 400°C. No framboids at all are observed by RICKARD (1975) in pyrite directly precipitated from the solution, without the intermediate iron sulphide steps. Finally, framboidal and/or colloform textures may be the result of fast precipitation of crystallites from supersaturated solutions (ROEDDER, 1968; FARRAND, 1970; ARNOLD, 1976). Farrand found that the originally formed framboids generally evolve to larger single crystals if not isolated from the solution. ARNOLD (1976) suggests that an increase of temperature (e.g., upon metamorphism) tends to transform these low-crystallinity textures into more stable configurations, that is, mosaic crystal ('paracrystal' of Arnold) and eventually monocrystals. Pyrite is notoriously a refractory mineral, so that in a rapidly evolving system relics of the intermediate steps will be preserved and revealed by structure etching of the final pyrite crystal. On the contrary, little trace of the previous stages will be found when the system was able to completely re-equilibrate into the most stable configuration.

In this context, we propose the following interpretation of the observed textures and of their spatial distribution at Gavorrano: near the intrusion pyrite was remobilized and reprecipitated from supersaturated solutions, producing low crystallinity ('framboidal' and ' colloform ') textures; some marcasite might also have formed. The temperature being relatively high, there was a quick evolution of these low crystallinity forms towards coarser and subhedral crystals. The transformation, however, took place in a rapidly changing environment, where equilibrium was not fully attained. This resulted in a partial preservation of the intermediate steps; our ' framboid-like aggregates ' might represent the first evolution of originally formed ' true ' framboids. Several episodes of precipitation and recrystallization seem to have occurred, as demonstrated by the repeated alternance of low-crystallinity and euhedral pyrite layers. On the contrary, no remobilization took place away from the intrusive; pyrite bodies were only affected by thermal metamorphism, resulting in a recrystallization of pyrite as coarse individuals. The environmental conditions being relatively homogeneous, complete equilibrium was attained, with near total erasement of any earlier texture. We might point out that the ore where abundant textural relics were found appears to have been remobilized, whereas those bodies, where no such textures are observed, might well have pre-existed the granite. At any rate, formation of both types of pyrite from a common process seems to be precluded.

Geochemical data

The limited geochemical data available so far makes a small contribution towards the genetic interpretation of the Gavorrano deposits. MINGUZZI & TALLURI (1951) determined spectrographically the Co (60 to 114 ppm) and Ni (absent) contents of three pyrite samples. The same authors point out that a very high Co/Ni ratio is characteristic of all Tuscan pyrites (*). Pyrites of magmatic-hydrothermal origin are believed to show, as a rule, higher Co/Ni ratios than those formed in a sedimentary environment (FLEISCHER, 1955). However, the metamorphic overprint on sedimentary pyrite may result in a substantial increase of the Co/Ni ratio (ITO, 1971). In general, genetic interpretations of the content of these metals in pyrite require a careful study of the geochemical environment as a whole (LOFTUS-HILLS & SOLOMON, 1967; VAUGHAN, 1976).

Some sulphur isotope data were obtained in the early '60's

(*) Additional data have been recently supplied by H. DILL (Mineral. Dep. 14, 57-80; 1979). Ni content of pyrite from Gavorrano ranges from 10 to 50 ppm; Co content from 10 to 438 ppm.

(CAGLIOTI et al., 1960; ANCARANI-ROSSIELLO et al., 1962). Apart from any consideration of the formal presentation of these data, contrasting interpretations were offered for the origin of the sulphur (from a basic magma; from reduction of evaporitic sulphates). At any rate, the data must be critically re-evaluated in the light of further progress in this field, as a warning against simplistic applications of sulphur isotopes as source indicators (OHMOTO, 1972; OHMOTO & RYE, 1979).

Final remarks

It is apparent that further specific geochemical and mineralogical studies, in part under way, are required to develop an articulated genetic model for the Gavorrano deposits. However, we think that, in the light of the literature and of the new data presented here, the most satisfactory model is that of pre-existing mineralizations, metamorphosed and partially remobilized by the Mio-Pliocenic granitic stock. The interaction between the granite and these pre-existing ores resulted in two different situations: the bodies further from the intrusion were affected only by thermometamorphic phenomena, while the ones nearest the intrusion were remobizilized and re-emplaced, producing a variety of attitudinal features: filling veins, metasomatic masses, occurrence of pyrite, both disseminated and in veins, in the granite. 'Massa Boccheggiano' appears to be a composite body: the lowermost part, farthest from the intrusion, may represent the primary concentration, while near the contact and possibly in the upper parts (unfortunately no longer accessible), attitudinal and mineralogical features of a metasomatic postintrusion emplacement are apparent. The ore bodies were then affected by tectonic collapse due to the cooling and shrinking of the igneous stock.

Hypotheses on the source of the elements and the origin of the pre-existing ore are so far merely speculative. In this respect, attitude and mineralogy of the ore bodies themselves are of little help. Tentative interpretations may be presented on the basis of the various paleogeographic and paleotectonic models of Tuscany. We may consider the following models: a) if, at least at Gavorrano, no overthrusting of the Tuscan Unit over the phyllites is assumed, and the contact is considered to be a Triassic transgression over the Paleozoic basement, the paleogeographic reconstruction by ZUFFARDI (1974) may suggest the Triassic origin of the Valmaggiore-type ore bodies from a sabkha-like environment. A sabkha origin has actually been proposed for the 'Calcare cavernoso' formation (PASSERI, 1975). On the contrary, JENKS (1975) ruled out the existence of a Triassic sabkha environment, relying on the alleged absence of nearshore sediments. However, the Triassic 'Verrucano s.s.' formation, which also occurs in the Gavorrano area, may be regarded as consisting of continental to nearshore clastic sediments. Jenks' interpretation possibly arises from the confusion, that still existed then, as to the exact stratigraphy and structure of the Tuscan formations underlying the 'Calcare cavernoso'; b) sulphate-evaporitic deposits are not found in the Gavorrano area, except for tiny levels in the 'Calcare cavernoso', so that origin of sulphides in an evaporitic basin seems rather unlikely to have occurred here; c) in considering a volcano-sedimentary origin (BODECHTEL, 1965), it must be noted that Triassic rift volcanism is known from northern Tuscany (RICCI & SERRI, 1975) and the Filladi di Boccheggiano contain meta volcanic levels (BAGNOLI et al., 1978); d) the ores might well be epigenetic, but pre-granite. The diffuse occurrence of thin concordant sulphide and oxide levels in the 'Filladi di Boccheggiano' has already been reported. We consider that pre-intrusive hydrothermal convective phenomena, possibly localized around Apenninic dislocations, have remobilized and redeposited these mineralizations, mainly at the limestone-phyllite contacts (cfr. MARINELLI, 1963). With respect to a 'pyrometasomatic' emplacement, this concentration process could reasonably have developed at lower temperatures and over a larger time span. This would give a batter account for the partial strata-bound character of the ore bodies; concomitant skarn formation would not be required and wall rock alteration effects, and thus evidence for metasomatism, would have been rather limited. The heat flow responsible for the activation of the convection cell might well derive from the deep-seated granite itself, prior to its upwelling and emplacement. The role played by granite in the ore formation could then have been that of a driving force for the convective process, while the source of both the oreforming fluids and the elements has to be sought elsewhere.

The presence of Pb, Zn and Sn minerals practically near the intrusive contacts may suggest a direct magmatic affiliation of these elements. However, owing to the higher mobility of Pb and Zn with respect to Fe, the former elements could have been selectively and completely remobilized from the primary ores, being redeposited near the limestone-granite contacts. It this respect, we point out the occurrence of the quartz-Cu-Pb-Zn sulphide vein of Fonte dell'Anguilla, in close spatial relationship with the pure pyrite of Rigoloccio.

ACKNOWLEDGEMENTS

The authors wish to thank Drs. F. Arisi Rota, A. Leonardelli and B. Burtet Fabris, of RIMIN S.p.A., who contributed in various degrees with their stimulating discussions and supply of maps. Thanks are also extended to the staff of SOLMINE S.p.A. for the assistance during visits to the mines and to Prof. P. Natale, Politecnico of Torino, for his helpful suggestions on structural etching of pyrite.

REFERENCES

ABBATE E., BORTOLOTTI V., PASSERINI P. & SAGRI M. (1970) - Introduction to the geology of the Northern Apennines. In: (G. SESTINI, ed.) Development of the Northern Apennine Geosyncline. *Sed. Geol.*, **4**, 207-215.

ARNOLD M. (1973) - Etude préliminaire des sulfures des gisements de Niccioleta et de Gavorrano. *C.R. Acad. Sci. Paris*, **276**, sér. D, 445-447.

ARNOLD M. (1976) - Quelques aspects de la cristallogenèse des bisulfures de fer à basse température. *Mém. h. sér. Soc. Géol. France*, **7**, 227-231.

ARISI ROTA F., VIGHI L. (1971) - Le mineralizzazioni a pirite e a solfuri misti. In: La Toscana meridionale. *Rendiconti Soc. Ital. Mineral. Petrol.*, **27**, 370-420.

ANCARANI-ROSSIELLO L., BETTINALI C., FAINA G. (1962) - Sulla composizione isotopica dello zolfo nelle piriti della Maremma Toscana e dell'Isola d'Elba. *Per. Mineral.*, **31**, 369-373.

AZZARO E., COCOZZA T., DI SABATINO B., GASPERI G., GELMINI R. & LAZZAROTTO A. (1976) Geology and Petrography of the Verrucano and Paleozoic Formations of the Southern Tuscany and Northern Latium. In: FALKE H. (ed.) - The continental Permian in Central, West and South Europe, 185-195. Reidel Publishing Co., Dordrecht.

AZZINI F. (1929) - Le piriti di Gavorrano e Ravi. *Atti Soc. Tosc. Sc. Nat. Mem.*, **40**, 51-69.

BAGNOLI G., GIANELLI G., PUXEDDU M., RAU A., SQUARCI P. & TONGIORGI M. (1978) - The Tuscan Paleozoic; a critical review. In: M. TONGIORGI editor: « Report on the Tuscan Paleozoic basement ». C.N.R., rapporto interno del Sottoprogetto Energia Geotermica, P.F. Energetica, Pisa.

BALDACCI F., ELTER P., GIANNINI E., GIGLIA G., LAZZAROTTO A., NARDI R. & TONGIORGI M. (1967) - Nuove osservazioni sul problema della Falda Toscana e sulla interpretazione dei flysch arenacei tipo « Macigno » dell'Appennino settentrionale. *Mem. Soc. Geol. It.*, **6**, 199-211.

BALDI P., BERTINI G., CELATI R., RIDOLFI A. & SQUARCI P. (1978) - Inventario dei pozzi sterili e studio delle cause di non produttività con particolare riferimento a quelle relative alla bassa permeabilità. Unpublished report, ENEL, CNR - Pisa.

BARBERI F., INNOCENTI F., RICCI C. A. (1971) - Il magmatismo. In: La Toscana Meridionale. *Rend. Soc. Ital. Mineral. Petrol.*, **27**, 169-210.

BARTHOLOMÈ P. & DIMANCHE F. (1967) - On the parageneses of ilvaite in italian skarns. *Ann. Soc. Géol. Belge Bull.*, **90**, 533-564.

BATINI F., BURGASSI P. D., CAMELI G. M., NICOLICH R. & SQUARCI P. (1978) - Contribution to the study of the deep lithosperic profiles: « Deep » reflecting horizons in Larderello-Travale Geothermal Field. Atti 69° Congr. Soc. Geol. It., Perugia, Ottobre 1978.

BERNER R. A. (1969) - The synthesis of framboidal pyrite. *Econ. Geol.*, **64**, 383-384.

BERNER R. A. (1971) - Principles of chemical sedimentology. Mc Graw-Hill, New York, 240 pp.

BERTINI M., CENTAMORE E., JACOBACCI A. & NAPPI G. (1969) - Note illustrative alla Carta Geol. d'Italia, Fo. 127 « Piombino ». Serv. Geol. It., Roma.

BODECHTEL J. (1965) - Zur Genesis der Eisenerze der Toskana und der Insel Elba. *N. Jb. Mineral. Abh.*, **103**, 147-162.

BORSI S., FERRARA G. & TONGIORGI E. (1967) - Determinazione con il metodo K/Ar della età delle rocce magmatiche della Toscana. *Boll. Soc. Geol. It.*, **86**, 403-410.

BORTOLOTTI V., PASSERINI P., SAGRI M. & SESTINI G. (1970) - The miogeosynclinal Sequences. In: G. SESTINI ed. « Development of the Northern apennine geosyncline ». *Sed. Geol.*, **4**, 341-444.

BROWNE P. R. L. & ELLIS A. J. (1970) - The Ohaki-Broadlands Hydrothermal Area, New Zealand: mineralogy and related geochemistry. *Amer. Jour. Sc.*, **269**, 97-131.

BURT D. M. (1977) - Mineralogy and petrology of skarn deposits. *Rend. Soc. Ital. Mineral. Petrol.*, **33**, 859-874.

CAGLIOTI V., BETTINALI C., GIARDINI-GUIDONI A., MELE A. (1960) - Isotopic abundance of some native sulphur and sulphide minerals. In: CNEN, Summer course on nuclear geology, Varenna, 202-213.

CAVINATO A. (1961) - Giacimenti minerari. UTET, Torino, 686 pp.

CHATTERJEE N. D. & JOHANNES W. (1974) - Thermal stability and standard thermodynamic properties of synthetic $2M_1$-muscovite. *Contr. Mineral. Petrol.*, **48**, 89-114.

CHEN T. T. (1978) - Colloform and framboidal pyrite from the Caribou deposit. New Brunswick. *Can. Mineral.*, **16**, 915.

CORSINI F., LATTANZI P., TANELLI G. (1975) - Contenuto in Fe delle blende del giacimento a solfuri di Cu, Pb e Zn di Fenice Capanne (Massa Marittima, Toscana): condizioni ambientali di formazione. *Rend. Soc. Ital. Mineral. Petrol.*, **31**, 351-364.

COCOZZA T., GASPERI G., GELMINI R. & LAZZAROTTO A. (1974) - Segnalazione di nuovi affioramenti paleozoici (Permo-Carbonifero?) a Boccheggiano e tra Capalbio e i Monti Romani (Toscana Meridionale-Lazio Settentrionale). *Boll. Soc. Geol. It.*, **93**, 47-60.

DALLAN NARDI L., NARDI R. (1972) - Schema stratigrafico e strutturale dell'appennino settentrionale. *Mem. Acc. Lunigianese Sc. 'G. Capellini'*, **42**, 1-212.

DE LAUNAY L. (1913) - Gites minéraux et metallifères. v. I, 350-353, Paris.

DE WIJKERSLOOTH P. (1930a) - The mineralization of the Tuscan Mountains in connection with their tectonic evolution. *Proc. Konink. Akad. Wetensch. Amsterdam*, **33**, 557-565.

DE WIJKERSLOOTH P. (1930b) - Der Deckenbau Süd-Toskanas. *Proc. Konink. Akad. Wetensch. Amsterdam*, **33**, 1189-1200.

DE WIJKERSLOOTH P. (1934) - Bau und Entwicklung des Apennins besonders der Gebirge Toskanas. Geologisch Instituut. Amsterdam, 426 pp.

FARRAND M. (1970) - Framboidal pyrite precipitated synthetically. *Mineral. Dep.*, **5**, 237-247.

FLEISCHER M. (1955) - Minor elements in some sulfide minerals. *Econ. Geol.*, **50**, 970-1024.

FORNASERI M. (1941) - Berthierite nella miniera Marchi di Ravi (Gavorrano). *Rend. Soc. Ital. Mineral.*, **1**, 59.

FRANCESCHELLI M. (1978) - The phyllites of the Boccheggiano Formation (Southern Tuscany). Petrographic outlines. In: M. TONGIORGI editor: « Report on the Tuscan Paleozoic basement », Pisa, 67-70.

FURIERI A., LATTANZI P., TANELLI G. - Fenomeni di alterazione idrotermale nel giacimento a pirite di Rigoloccio (Toscana). In preparation.

GARAVELLI C. L. (1962) - Contenuto in Fe e temperatura di formazione di blende italiane. *Atti Soc. Tosc. Sci. Nat.* (A), **69**, 52-96.

GIANELLI G. & PUXEDDU M. (1979) - Some observation on the genesis of ore deposits and associated evaporites in southern Tuscany. Atti 69° Congr. Soc. Geol. It., Perugia, Ottobre 1978, in press.

GIANELLI G., PUXEDDU M. & SQUARCI P. (1979) - Structural setting of Larderello-Travale geothermal region. Atti 69° Congr. Soc. Geol. It., Perugia, Ottobre 1978, in press.

GIANNOTTI C. (1924) - Wollastonite nella formazione granitica di Gavorrano. *Atti Soc. Tosc. Sci. Nat. Proc. Verb.*, **33**, 37-41.

GIANNINI E., LAZZAROTTO A. & SIGNORINI R. (1971) - Lineamenti di stratigrafia e tettonica. In: « La Toscana meridionale ». *Rendiconti Soc. Ital. Mineral. Petrol.*, **27**, 33-168.

GREENWOOD H. J. (1967) - Wollastonite: stability in H_2O-CO_2 mixtures and occurrence in a contact metamorphic aureole near Salmo. B.C., Canada. *Am. Mineral.*, **52**, 1669-1680.

GREGORIO F., LATTANZI P., TANELLI G. (1980) - Contributo alla definizione degli ambienti di formazione dei giacimenti toscani di Niccioleta, Boccheggiano, Gavorrano e Campiano: studio della sfalerite. *Rendiconti Soc. It. Mineral. Petrol.*, **36** (in press).

ITO S. (1971) - Quoted in Mukherjee A. (1976) - Ores and metamorphism: temporal and genetic relationships. In: K.H. WOLFF ed., Handbook of stratabound and stratiform ore deposits. *Elsevier, Amsterdam*, **4**, 215.

JENKS W. E. (1975) - Origin of some massive pyritic ore deposits of Western Europe. *Econ. Geol.*, **70**, 488-498.

KERRICK D. M., CRAWFORD K. E., RANDAZZO A. F. (1973) - Metamorphism of calcareous rocks in three roof pendants in the Sierra Nevada, California. *Jour. Petrol.*, **14**, 303-325.

LEONARDELLI A. (1975) - Toscana: Pirite e solfuri misti. In: Memoria illustrativa della carta mineraria d'Italia, G. Castaldo & G. Stampanoni eds., Servizio Geol. d'Italia, Roma.

LOFTUS-HILLS G. & SOLOMON M. (1967) - Cobalt, nickel and selenium in sulfides as indicators of ore genesis. *Mineral. Dep.*, **2**, 228-242.

LOVE L. G. & AMSTUTZ G. C. (1966) - Review of microscopic pyrite from the Chattanooga shale. *Fortschr. Miner.*, **43**, 273-309.

LOVE L. G., CURTIS C. D., BROCKLEY H. (1971) - Framboidal pyrite: morphology revealed by electron microscopy of external surface. *Fortschr. Miner.*, **48**, 259-264.

LOTTI B. (1877) - Sulla geologia del Gruppo di Gavorrano. *Boll. R. Com. Geol. d'Italia*, **8**, 53-63.

LOTTI B. (1901-2) - Sul giacimento di pirite di Gavorrano in Toscana. *Rass. Mineraria*, **15-16**, 16 pp.

LOTTI B. (1907) - Osservazioni sulla memoria di L. de Launay « La métallogénie de l'Italie. *Boll. R. Com. Geol. d'Italia*, **38**, 3-23.

LOTTI B. (1910) - Geologia della Toscana. *Mem. descritt. Carta geol. d'Italia*, **13**, Roma, 484 pp.

LOTTI B. (1928) - I depositi dei minerali metalliferi. Ed. *L'Industria Mineraria*, Roma.

LOTTI B. (1930) - Sui rapporti genetico-tettonici del giacimento di pirite dell'Isola del Giglio con quello di Gavorrano. *La Min. Ital.*, **14**, 206-209.

MARINELLI G. (1961) - L'intrusione terziaria di Gavorrano. *Atti Soc. Tosc. Sc. Nat.* (A), **68**, 117-194.

MARINELLI G. (1963) - L'énergie géothérmique en Toscane. *Ann. Soc. Géol. Belg. Bull.*, **85**, 417-438.

MAROCCHI E. (1897) - Studio sul granito di Gavorrano. *Atti Soc. Tosc. Sc. Nat. Mem.*, **15**, 171-187.

MARTELLI A. (1909) - Ricerche petrografiche e chimiche sulle formazioni granitiche di Gavorrano. *Atti R. Acc. Lincei, Rend.*, **18**, (12).

MINGUZZI C. (1947) - Dosatura spettrografica dell'oro in piriti italiane. *Atti Soc. Tosc. Sc. Nat.* (A), **54**, 210-243.

MINGUZZI C. & TALLURI A. (1951) - Indagini e considerazioni sulla presenza e sulla distribuzione di costituenti minori nelle piriti. *Atti Soc. Tosc. Sc. Nat.* (A), **58**, 89-102.

MUFFLER L. J. P. & WHITE D. E. (1969) - Active Metamorphism of Upper Cenozoic Sediments in the Salton Sea Geothermal Field and the Salton Trough, southeastern California. *Geol. Soc. Amer. Bull.*, **80**, 157-182.

NATALE P. (1974) - Relitti di bassa temperatura nelle piriti di alcuni giacimenti della Toscana. *Boll. Ass. Mineraria Subalp.*, **2**, 1-12.

OHMOTO H. (1972) - Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. *Econ. Geol.*, **67**, 551-578.

OHMOTO H. & RYE R. O. (1979) - Isotopes of sulfur and carbon. In: H.L. Barnes (ed.) Geochemistry of hydrothermal ore deposits. 2nd edition. Holt, Rinehart & Winston, Publ., New York, London. In press.

OLESCH M. (1978) - Obere thermische Stabilität von Vesuvian (Idocras) bis 2 kbar und Vesuvian+Quarz bis 5 kbar im System CaO-MgO-Al_2O_3-SiO_2-H_2O. *Fortschr. Mineral.*, **56**, (1), 99.

PERTSEV N. N. (1974) - Skarns as magmatic and as post-magmatic formations. *Internat. Geol. Rev.*, **16**, 572-582.

POMPEI A. (1927) - Giacimenti di pirite, di Fe e di fosfati. *Mem. per il Cong. Geol. Inter. di Madrid*, Ministero Econ. Naz., Roma.

PASSERI L. (1975) - L'ambiente deposizionale della formazione Evaporitica nel quadro della paleogeografia del Norico Tosco-umbro-marchigiano. *Boll. Soc. Geol. It.*, **94**, 231-268.

RAU A. & TONGIORGI M. (1974) - Geologia dei Monti Pisani a sud-est della Valle del Guappero. *Mem. Soc. Geol. It.*, **13**, 227-408.

RICCI C. A. & SERRI G. C. (1975) - Evidenze geochimiche sulla diversa affinità petrogenetica delle rocce basiche comprese nelle serie a facies Toscana. *Boll. Soc. Geol. It.*, **94**, 1187-1198.

RICKARD D. T. (1975) - Kinetics and mechanism of pyrite formation at low temperatures. *Am. J. Sci.*, **275**, 636-652.

ROEDDER E. (1968) - The noncolloidal origin of « colloform » textures in sphalerite ores. *Econ. Geol.*, **63**, 451-471.

ROY R. & OSBORN E. F. (1954) - The system Al_2O_3-SiO_2-H_2O. *Am. Mineral.*, **39**, 853-885.

SAPPA G. (1921) - Breve descrizione geologico-mineraria del giacimento di pirite di Gavorrano-Ravi. Abstr. in: *Boll. Soc. Geol. Ital.*, **40**, LXVIII-LXIX.

SAVI P. & MENEGHINI G. (1851) - Considerazioni sulla geologia stratigrafica della Toscana. In: Sir R.E. Murchison, Memorie sulla struttura geologica delle Alpi, degli Appennini e dei Carpazi. Firenze, Stamperia Granducale, 279-522.

SEIFERT F. (1970) - Low-temperature compatibility relations of cordierite in haplopelites of system K_2O-MgO-Al_2O_3-SiO_2-H_2O. *Jour. Petrol.*, **11**, 73-99.

SEKI Y. (1972) - Lower-grade stability limit of epidote in the light of natural occurrences. *J. Geol. Soc. of Japan*, **78**, 405-413.

SKIPPEN G. B. (1974) - An experimental model for low pressure metamorphism of siliceous dolomitic marble. *Am. J. Sci.*, **274**, 487-509.

SKIPPEN G. B. (1977) - Dehydration and decarbonation equilibria. In: Greenwood H.J., ed., Application of thermodynamics to petrology and ore deposits. *Mineral. Assoc. Canada Short Course Handb.* n. 2.

SIGNORINI R. (1966) - Il Verrucano della Toscana Meridionale. Atti Symposium sul Verrucano. *Soc. Tosc. Sc. Nat.*, Pisa, 55-71.

SUNAGAWA I., ENDO Y., NAKAI N. (1971) - Hydrothermal synthesis of framboidal pyrite. *Soc. Mineral. Geol., Japan*, **2**, 10-14.

SWEENEY R. E. & KAPLAN I. R. (1973) - Pyrite framboidal formation: laboratory synthesis and marine sediments. *Econ. Geol.*, **68**, 618-634.

TALLURI A. (1953) - Studio genetico e geochimico del giacimento di pirite di Ravi Marchi. *Rend. Soc. Min. It.*, **9**, 264-266.

TANELLI G. (1977) - I giacimenti a skarn della Toscana. *Rend. Soc. Ital. Mineral. Petrol.*, **33**, 865-893.

TANELLI G. (1978) - Non-porphyry skarn deposits of Tuscany (Italy). *Geol. Soc. Am. Abstr. Progr.*, **10**, 149-150.

TOSO P. (1912) - Sul modo di formazione dei principali giacimenti metalliferi aventi forma di irregolari ammassi o di strati, coltivati in Toscana ed in altre regioni d'Italia. *Boll. R. Com. Geol. d'Italia*, Ser. V, **3**, 113-233.

TREFZGER E. F. (1954) - Ueber die Schwefelkies Lagerstätten der Toskanischen Maremma. *N. Jb. Mineral. Mh.*, 73-95.

TREVISAN L. (1955) - Il Trias della Toscana e il problema del Verrucano Triassico. *Atti Soc. Tosc. Sc. Nat.* (A), **62**, 1-30.

TRUDINGER P. A. (1976) - Microbiological process in relation to ore genesis. In: Handbook of Strata-bound and stratiform ore deposits. K.H. Wolf, ed., *Elsevier, Amsterdam*, **2**, 135-190.

TURACCHI A. (1954) - Pirite e miniere di pirite della Maremma. *L'Ind. Min.*, **5**, 15-26.

VAUGHAN D. J. (1976) - Sedimentary geochemistry and mineralogy of the sulfides of Pb, Zn, Cu and Fe, and their occurrence in sedimentary ore deposits. In: K.H. Wolf ed., Handbook of stratabound and stratiform ore deposits, Elsevier, Amsterdam, **2**, 317-363.

VIGHI L. (1966) - Descrizione di alcuni sondaggi che hanno attraversato lenti anidritico-dolomitiche intercalate alle filladi triassiche (Verrucano) nei dintorni di Massa Marittima (Grosseto - Toscana). *Atti Symposium Verrucano, Tosc. Tosc. Sc. Nat.*, 72-95.

VOM RATH G. (1873) - Geognostisch-mineralogische Fragmente aus Italien. *V. Zeitschr. Deut. Geolog. Gesell.*, 4T, **25**.

ZUFFARDI P. (1974) - La metallogenesi italiana in relazione alla evoluzione del Mediterraneo. *Mem. Soc. Geol. It.*, **13**, 359-365.

ZIA R. (1954) - Carta geologica di Scarlino e Gavorrano (Grosseto). Edited by the 'Centro Studi Geologia Appennino C.N.R.', Pisa.

(*ms. pres. il 7 luglio 1979; ult. bozze l'1 ottobre 1979*).

PLATE

PLATE I

Plate 1 - Microphotographs of polished sections from Gavorrano, taken in reflected, plain-polarized light, parallel nicols, air except where noted.

a), b), c) Rigoloccio etched pyrite. Anhedral cores (not clear in the pictures) are followed outwardly by distintly euhedral cubic and octahedral rims.

d) (oil) Massa Boccheggiano. Cluster of pyrite crystals (white), increasing in size outwards. Core of the cluster is occupied by tetrahedrite (gray), partially replaced by carbonate gangue (black).

e) to h) Massa Boccheggiano etched pyrite. e) (oil): framboid-like aggregate of pyrite crystals. f) to h): low-crystallinity textural relics into large euhedral crystals. Black is gangue in all pictures.

PLATE I

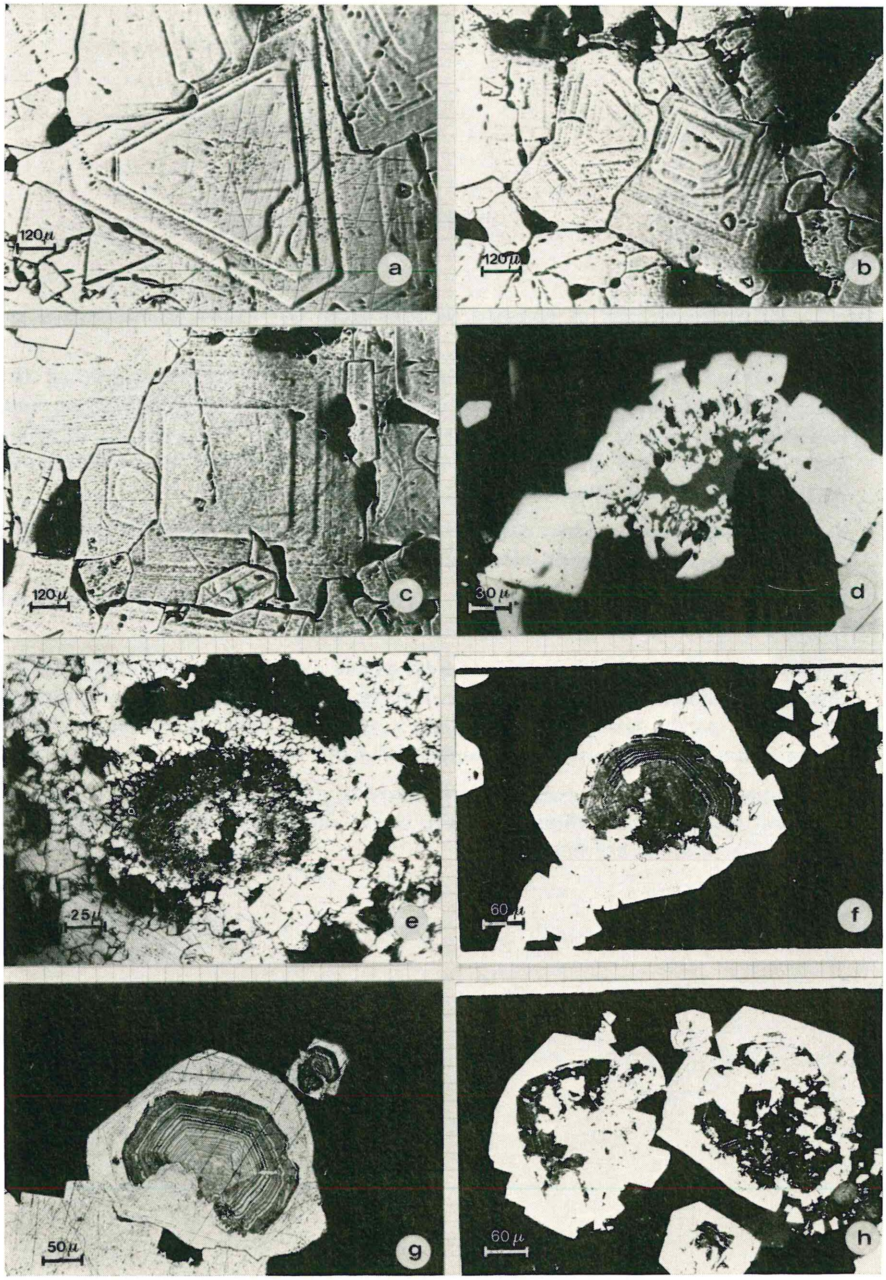


PLATE II

Plate 2 - Microphotographs of polished sections from Gavorrano. Conditions as in Plate 1.

a) to d) Massa Boccheggiano etched pyrite. Low-crystallinity textural relics are seen to develop into large euhedral crystals. Alternating microcrystalline and euhedral layers can be recognized, especially in b) and c). The presence of sphalerite inclusions (gray, indicated by arrows) should be noted in the outermost pyrite rim of d) (oil). Black is gangue in all pictures.

e) (oil) Massa Boccheggiano. Structural etching on pyrite reveals a needle-like aggregate, possible developed after marcasite.

f) Massa Boccheggiano. After etching, pyrite euhedral crystals are shown to be rimmed by late microcrystalline pyrite.

g) (oil) Valmaggiore. Magnetite (white-gray) pseudomorphic after hematic lamellae displaying triangular and rhombohedral arrays. The rest of the area is almost all siderite, partly dark gray, partly lighter, owing to internal reflections. Some pyrite (pure white) appears in the upper left-hand corner.

h) Valmaggiore. Banded textures of melnikovitic pyrite (medium gray to white). Euhedral pyrite is pure white. Magnetite (gray) and siderite (dark gray) are also present; black areas are holes.

PLATE II