

The Ba-Fe-pyrite deposit of Buca della Vena, Apuan Alps, Italy

MARCO BENVENUTI, PIERFRANCO LATTANZI, GIUSEPPE TANELLI
Dipartimento di Scienze della Terra dell'Università, Via La Pira 4, 50121 Firenze

GIANNI CORTECCI
Dipartimento di Scienze della Terra dell'Università, Via S. Maria 53, 56100 Pisa

ABSTRACT. — The ore deposit of Buca della Vena is one of the currently active Ba-Fe-pyrite deposits, occurring in a NE-SW mineralized belt in the Southern Apuane Alps (NW Tuscany, Italy).

The deposit is closely associated to Middle-Upper Triassic calcareous levels interbedded in the upper portion of a silicoclastic complex (Scisti di Fornovolasco formation), which was metamorphosed in the greenschist facies during the Tertiary Apenninic orogeny. The paleogeographic environment defined by the host rocks marks the transition from a silicoclastic near-shore sedimentation to the instauration of the Norian hyperhaline platform of the Grezzoni formation.

The main ore body is represented by a near-concordant, 200 m-long, 1 to 20 m-thick lens, to which minor discordant/replacement bodies are associated. The main mineralogy consists of barite, hematite, magnetite and pyrite, with subordinate sphalerite and galena. The most relevant macroscopic texture is a banded alternance of barite and iron minerals, often folded and faulted. Microscopic observations provide further evidence of metamorphic deformation and/or recrystallization of both barite and iron minerals.

Sulfur isotope compositions ($\delta^{34}\text{S}_{\text{CDT}}$) vary between -13.0 and $+6.5$ for mil for pyrite, and between $+12.7$ and $+19.7$ for barite. Such data are compatible with a main source of sulfur from Triassic marine sulfate, which underwent bacterial reduction to sulfide in a restricted basin. Sr-isotope data (BARBIERI et al., 1982) suggest on the other hand that Sr (and by inference, Ba) in barites is essentially of continental origin.

The deposit of Buca della Vena is interpreted as a sedimentary-diagenetic Middle-Upper Triassic mineralization, formed in a coastal lagoonal domain, where mixing of marine sulfate, partly reduced to sulfide, and of Ba (and Fe?) released from continental weathering occurred. During the Apenninic orogeny, the mineralization was metamorphosed, deformed and partly remobilized.

Key words: metallogeny, mineralogy, Apuane

Alps, Ba-Fe ox-py mineralization, sedimentary-metamorphic origin.

RIASSUNTO. — Il giacimento di Buca della Vena è uno dei depositi a baritina-ossidi di Fe-pirite che attualmente vengono coltivati nelle Alpi Apuane.

Le mineralizzazioni sono strettamente associate ai livelli carbonatici presenti nella parte sommitale di un complesso prevalentemente filladico del Trias-Medio-Sup. (Scisti Fornovolasco). Il corpo minerario principale è rappresentato da una lente sub-concordante, alla quale sono associati minori corpi discordanti.

I minerali principali sono rappresentati da barite, ematite, magnetite e pirite, associati a minori quantità di galena e sfalerite, nonché tracce di numerosi e rari minerali: solfosali, wolframati, vanadati, ossosolfuri, etc.

La più rilevante tessitura macroscopica è rappresentata da una alternanza di bande millimetriche o centimetriche di barite ed ossidi di ferro frequentemente piegati e fogliettati. Le osservazioni microscopiche evidenziano ulteriormente fenomeni di deformazione metamorfica e ricristallizzazione subiti dal corpo minerario principale.

La composizione isotopica dello zolfo ($\delta^{34}\text{S}_{\text{CDT}}$) varia fra $+12.7$ e $+19.7$ per la barite. Tali dati sono compatibili con una sorgente principale dello zolfo da solfato marino triassico, che ha subito una riduzione batterica a solfuri in un bacino ristretto. I dati isotopici sullo stronzio (BARBIERI et al., 1982) suggeriscono del resto che lo Sr sia essenzialmente di origine continentale.

Il deposito di Buca della Vena è interpretato come una mineralizzazione sedimentaria diagenetica di età triassica medio-sup., formatosi in un dominio lagunare costiero, successivamente metamorfosato, deformato e parzialmente mobilizzato durante l'orogenesi Apenninica.

Parole chiave: metallogenesi, mineralogia, Alpi Apuane, mineralizzazione a Ba-Fe-pirite-ossidi, origine sedimentario-metamorfica.

Introduction

The Apuane Alps (NW Tuscany - Italy) have been the seat, since the first millennium B.C., of mining activity, exploiting the famous white marble of Carrara, and a number of Ba-Fe-pyrite, Fe-Mn, Cu-Fe, Pb-Zn-Cu(Ag) and Hg deposits (SIMI, 1855; ZACCAGNA, 1932; CARMIGNANI et al., 1972; CIPRIANI & TANELLI, 1983; TANELLI, 1983).

in the southern portion of the mountain group, along a mineralized belt extending SW-NE from Valdicastello to Fornovolasco (fig. 1). Till the second world war, these deposits were exploited almost exclusively for iron minerals, whereas subsequently the main economic interest has been represented by barite, utilized in heavy muds for oil drilling. Total production of the three mines,

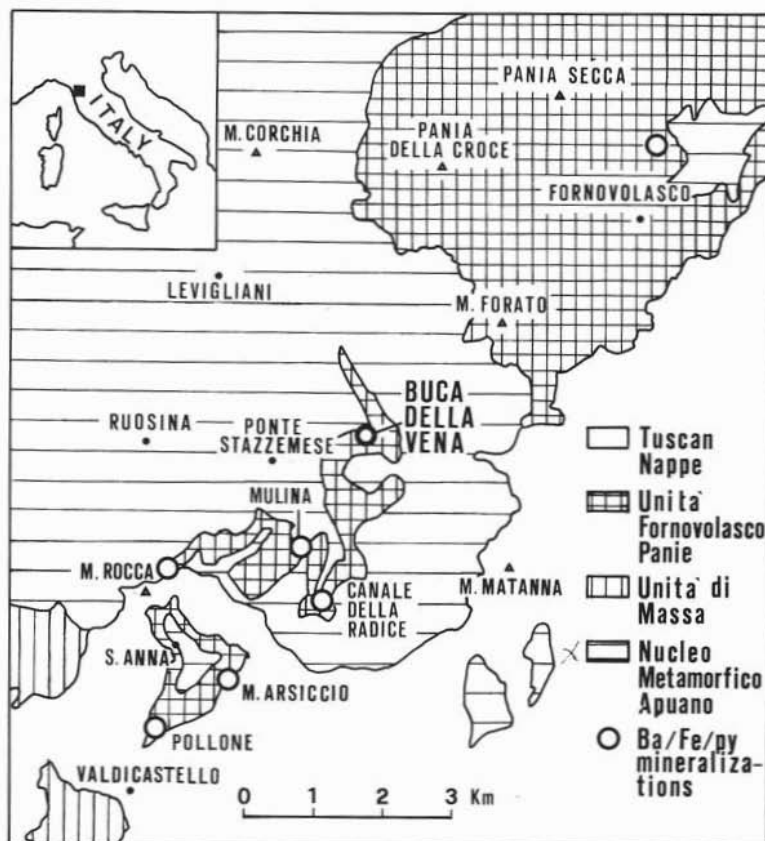


Fig. 1. Geological sketch map and Ba-Fe-pyrite mineralizations of southern Apuane Alps.

The deposits of the Apuane Alps are currently the target of a research project carried out in the Universities of Firenze, Pisa and Perugia in the framework of the National Project MPI «Metallogenesi e inventario delle risorse minerarie italiane» (previous contributions: CORTECCI et al., 1985; CIARAPICA et al., 1985).

Today, the only deposits mined are the Ba-Fe-pyrite mineralizations at Pollone, Monte Arsiccio and Buca della Vena, localized

operated by the companies EDEM and SIMA, has been in the recent years in the order of 15,000 t/yr concentrate (89-98 % BaSO_4). Other significant byproducts are mixed barite-iron oxides ores (5,000 to 10,000 t/yr), utilized as concrete in building nuclear power plants, and a minor production of pyrite, utilized for sulfuric acid and for abrasives.

The deposits have been interpreted either as the result of epigenetic replacement of

carbonate rocks by granite-affiliated fluids during the Tertiary Apenninic orogeny (CARMIGNANI et al., 1976), or as sedimentary-diagenetic Triassic concentrations, metamorphosed and partly remobilized during the Apenninic orogeny (TANELLI, 1983; CIARAPICA et al., 1985; CORTECCI et al., 1985). A syndimentary origin has been recently supported also by ORBERGER et al. (1985) and ORBERGER & SAUPÉ (1985), who however have suggested a Silurian-Devonian age for the host rocks, and therefore for the mineralizations (see below).

detailed facies analysis of the main sedimentary formations in the region. They have recognized three main paleogeographic domains, to which correspond five principal tectonic units:

- domain of «Spezidi» (tectonic units: Unità di Massa and North Nappe);
- domain of «Apuanidi» (Nucleo Metamorfico Apuano and Unità di Fornovolasco-Panie);
- domain of «Tuscanidi» (South Nappe, corresponding to the Tuscan Nappe of the previous literature).

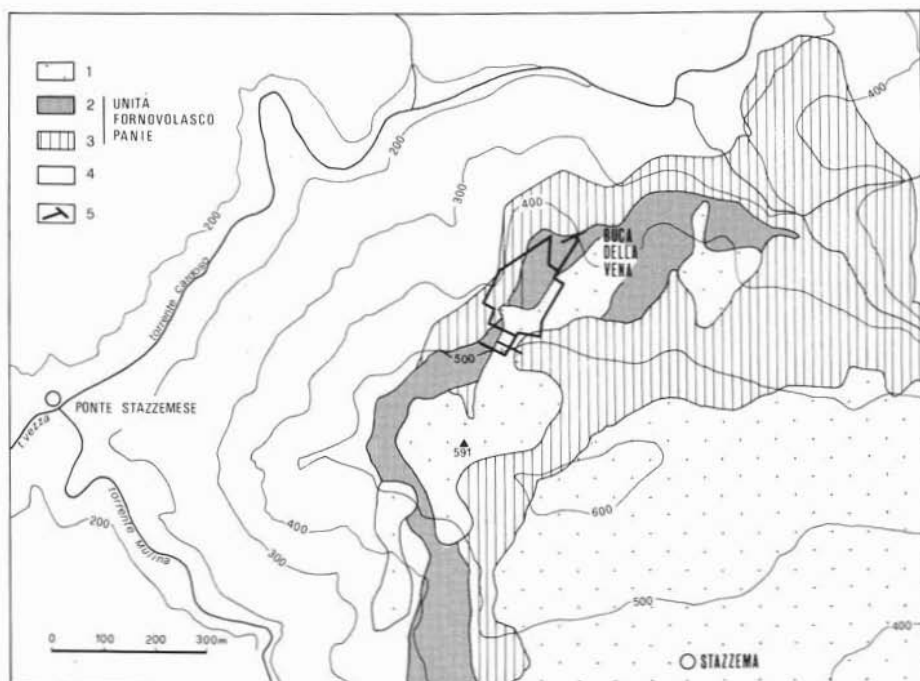


Fig. 2. — Geological map of the area of Buca della Vena. - 1 = alluvium and debris; 2 = dolomitic breccias; 3 = Scisti di Fornovolasco; 4 = Nucleo Metamorfico Apuano; 5 = projection of the main underground works (cf. fig. 4).

Geological setting

The stratigraphic and structural setting of the zone of Stazzema, to which the area of Buca della Vena belongs, and in general of the Apuane Alps, is quite complicate, and not unanimously established. CIARAPICA & PASSERI (1982) and CIARAPICA et al. (1985) — to whom the reader is referred for further details and literature — have recently suggested an interpretation of the geology of the Apuane Alps based chiefly on the

These units were overthrust during the Apenninic orogeny (Mid- to Late Tertiary), which is also responsible for a greenschist metamorphic imprint on all units, except the geometrically uppermost North Nappe and South Nappe.

In the area of Buca della Vena (fig. 2), the geometrically lowermost unit is constituted by terrains of the Nucleo Metamorfico Apuano (Paleozoic to Oligocene). They are unconformably overlain by an epimetamorphic

complex, about 100 m thick, made up by greenish sericitic-quartzitic-chloritic phyllites, with tourmaline-bearing quartzo-arenitic intercalations, and roughly lens-shaped calcareous levels (« Calcare metallifero » of ZACCAGNA, 1932), to which are typically associated the Ba-Fe mineralizations. Overlying this complex there is a dolomitic, sometimes brecciated, unit, correlated by SUPPA (1982) to the lowermost subfacies of the Norian « Grezzoni delle Panie » (CIARAPICA & PASSERI, 1982), whereas CARMIGNANI et al. (1976) assigned it to the Calcare Cavernoso Formation of the Tuscan Nappe. This dolomitic unit is only weakly mineralized near its bottom contact with the phyllitic complex.

The main facies of the phyllitic complex of Buca della Vena is made up by millimetric alternances of granoblastic quartzitic layers, and of lepidoblastic chloritic-sericitic-quartzitic layers. The main schistosity, trending NNE-SSW and dipping SE, is well displayed. The characteristic metamorphic assemblage is quartz-sericite-chlorite-muscovite-albite.

The quartzo-arenitic subfacies consists of quartz and idiomorphic tourmaline in a chlorite-sericite matrix. The carbonate levels, especially present in the uppermost portion of the complex, are represented by white schistous marbles, calc-schist, calcareous dolomitic breccias, and most often by recrystallized dolomitic limestones. These are widely fractured, with fissure infillings of calcite, pyrite and dolomite. The metamorphic overprint has mostly cancelled the original sedimentary features; in places, structures recognizable as load casts may be seen at the roof contact with the embedding phyllites. The calcareous levels may also occur as lenses interlayered in the ore bodies, displaying boudinage-like structures (fig. 3) and being laminated and dismembered.

The general features of the phyllitic complex of Buca della Vena allow to correlate it with the Scisti di Fornovolasco Formation, which represents, according to CIARAPICA & PASSERI (1982) and CIARAPICA et al. (1985), the lowermost member of the Unità di Fornovolasco-Panie. The formation is strongly tectonized, and its stratigraphy is not easily reconstructed. The basal portion consists of quartzitic milonites, which may represent the tectonized epimetamorphic equivalent of the « Porfiroidi »

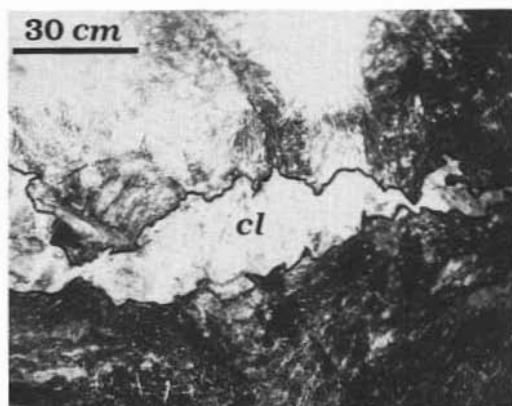


Fig. 3. — Boudinage-like structure of calcareous lenses (cl) within the ore body.

(Paleozoic felsic volcanites) of the « Nucleo Metamorfico Apuano ». According to ORBERGER et al. (1985) and ORBERGER & SAUPÉ (1985), the schists hosting the mineralizations at Buca della Vena, Pollone and Monte Arsiccio, are the metamorphic equivalent of sandy-shaly sediments, characterized by strong anomalies in B and Ba. By chemical comparison with similar rocks dated elsewhere, the above authors suggest a Silurian-Devonian age for these schists. However, paleontological findings (CIARAPICA & ZANINETTI, 1983) indicate an Upper Ladinian to Carnian age for the calcareous levels occurring in the uppermost portion of the formation. Therefore, the Scisti di Fornovolasco, or at least their uppermost member, may be interpreted as Middle to Late Triassic near-shore clastic sediments, preceding the instauration of the Norian hyperhaline platform of the Grezzoni Formation. The transition apparently took place as repeated limited transgressive cycles, represented by the carbonatic intercalations, interrupting the dominantly clastic sedimentation. The tourmaline-bearing facies is of difficult interpretation. The idiomorphic habitus of tourmaline seems to preclude a clastic derivation of this mineral; it might be the metamorphic derivative of locally B-rich sediments (cf. ORBERGER et al., 1985).

Structure, texture and mineralogy of the ore body

The main ore body exploited at Buca della Vena is represented by a barite $\pm$ iron

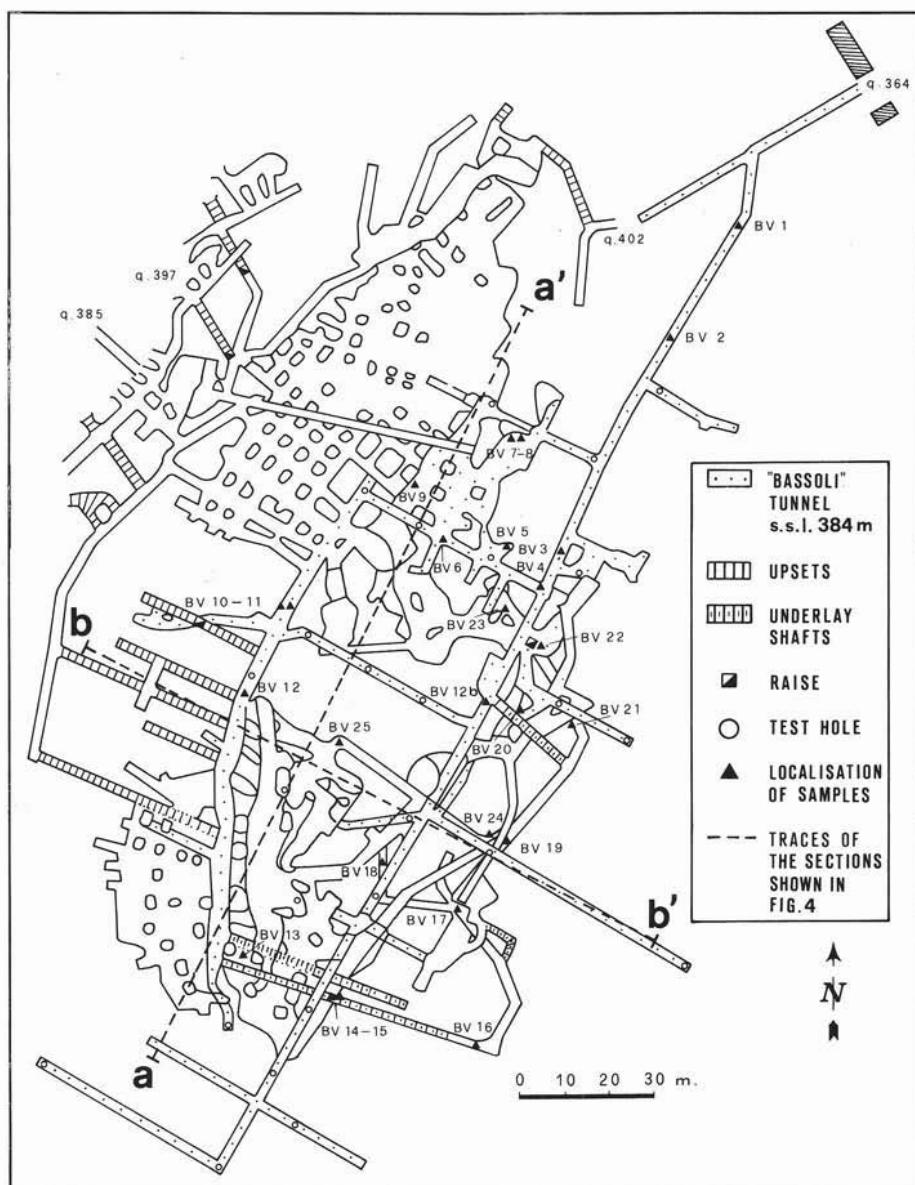


Fig. 4. — Map of the mining works at Buca della Vena. - $a-a'$, $b-b'$ = traces of sections in fig. 5.

oxides $\pm$ pyrite lens, which has been explored by mining works between the elevations of 347 and 414 m a.s.l. Current mining activity takes place in the south-eastern section of the ore body, where it appears to be truncated by a NE-SW sub-vertical fault.

Figs. 4 and 5 show, respectively; the horizontal schematic projection of the mining

works, and the schematic partly projected vertical sections of the main ore body, as reconstructed from company reports. The 200 m-long, NNE-SSW trending lens dips southeastward between 15° and 30° , with a variable thickness from 1-2 to 15-20 m. The lens crops out in a limited area in the north-western slope of the hill of Stazzema, and extends along the dip for about 80 m,

progressively thinning out southeastward, where, as said above, it is abruptly terminated by a fault.

The ratios barite : iron oxides : pyrite in the extracted ore are in the order of 2:2:1. Total production from 1968 to present adds up to about 130,000 tons; the proven reserves are rather limited (less than 50,000 tons).

In the central and southeastern zones, the ore, mostly consisting of barite $\pm$ iron oxides, is chiefly associated to the calcareous-dolomitic intercalations, whereas in the southwestern and northern sections the host rock is mainly represented by quartzitic phyllites, and the ore mostly consists of barite $\pm$ pyrite.

contact ore body-carbonatic rocks.

The main ore minerals at Buca della Vena are barite, hematite, magnetite and pyrite, with minor galena, sphalerite and siderite; gangue is mostly represented by the host-rock minerals (calcite, dolomite, quartz, albite, mica, chlorite). A host of less common and rare minerals (fig. 12) were described by MELLINI et al. (1979, 1981, 1983), MERLINO & ORLANDI (1983) and CHECCHI & ORLANDI (personal communication, 1984).

Under the microscope, barite appears as granoblastic aggregates, typically showing 120° triple joints, in places intergrown with metamorphic phyllosilicates. Microscopic textures involving iron minerals are more complex. Magnetite occurs as subhedral,

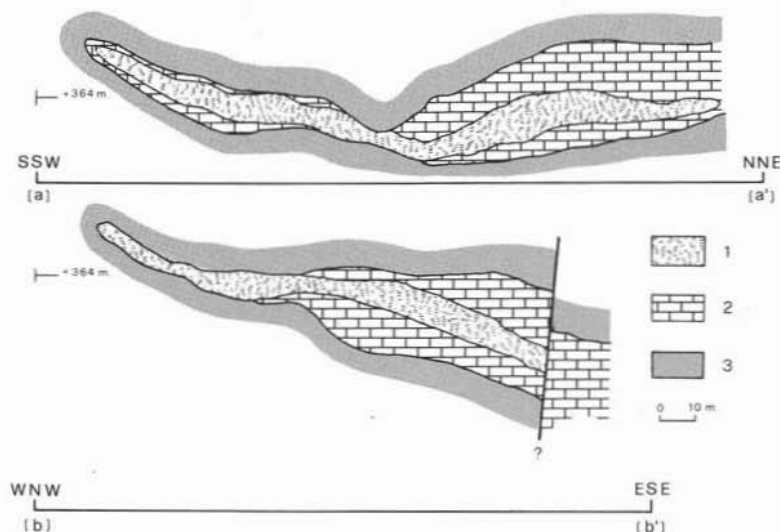


Fig. 5. — Schematic partly projected vertical sections through the main ore body at Buca della Vena. Vertical scale same as horizontal scale. - 1 = ore body; 2 = calcareous levels; 3 = schists.

The most relevant macroscopic texture of the ore is a banded texture of alternating barite and iron minerals (fig. 6), with a remarkable lateral continuity, roughly concordant with the wallrock contact, in places folded or dissected by short-thrust faults, or else disrupted by structures which may be reminiscent of load casts. Massive bodies, either of barite or of iron minerals, are also present. Limited discordant masses, with signs of wall-rock replacement, may occur in association with fractures or faults at the

partly fractured porphyroblasts, which may include more or less rounded blebs (remnants?) of hematite, which in turn replaces magnetite up to the development of pseudomorphs (figs. 7, 8). Hematite is also present as idiomorphic lamellae and needles (fig. 9), which may form intergrowths with sericite, displaying characteristic « roll textures » around porphyroblasts of magnetite (fig. 10). Pyrite occurs in two distinct generations, the earlier being represented by aggregates of minute crystals, which, upon structure



Fig. 6. — Folded banded texture between barite and pyrite.

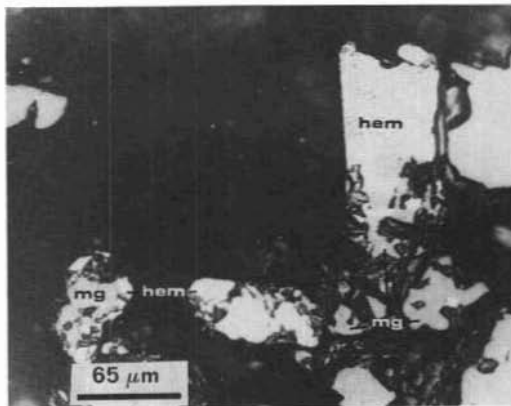


Fig. 8. — Pseudomorphic replacement of hematite (*hem*) after magnetite (*mg*).

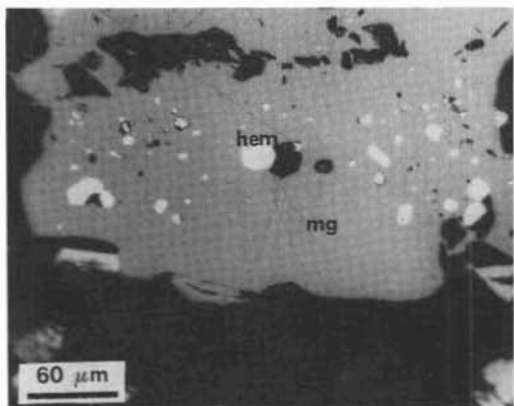


Fig. 7. — Magnetite (*mg*) porphyroblasts enclosing remnants of hematite (*hem*).

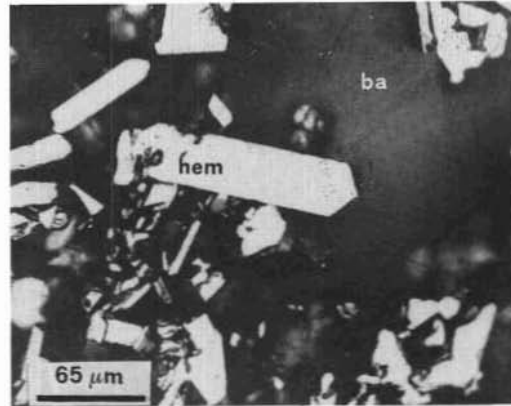


Fig. 9. — Idiomorphic hematite (*hem*) in barite (*ba*).

etching (NATALE, 1974), reveal multistage complex growth textures, very similar to those in pyrite from the Alpine Kieslager. The second generation is made up by euhedral to subhedral porphyroblasts, which at least in part appear to have grown by recrystallization of the earlier generation (fig. 11). Both types of pyrite may be deformed and fractured. Poikiloblastic textures between iron- and gangue minerals are quite diffuse (cf. also NATALE, 1974, fig. 1 b). Galena and sphalerite, present in small amounts only, occupy the intergranular spaces of the other ore minerals.

In general, the ore textures can be interpreted as the evidence of recrystallization and deformation processes (presumably me-

tamorphic) having affected the main ore minerals. The inferred paragenetic sequence (tab. 2) indicate a complex sequence of partial superposition of the main ore minerals — as evidenced also by the banded texture — suggesting local repeated variations of the physicochemical parameters, so that pyrite and/or hematite and/or magnetite and/or barite were in turn the stable minerals.

The mineral association at Buca della Vena, characterized by the widespread coexistence of barite and iron oxides, is not unique in stratiform barite ores, although less common of the typical $Ba \pm F \pm Pb \pm Zn$ association. Iron oxides occur as accessory minerals in the bedded barite ores of Nevada (PAPKE, 1984); partly banded

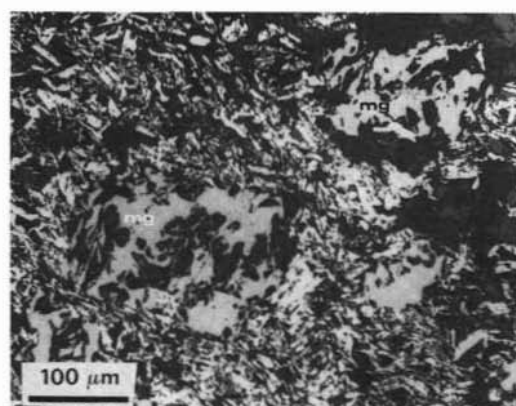


Fig. 10. — «Roll-texture» of hematite-sericite intergrowths around magnetite (mg) porphyroblasts.

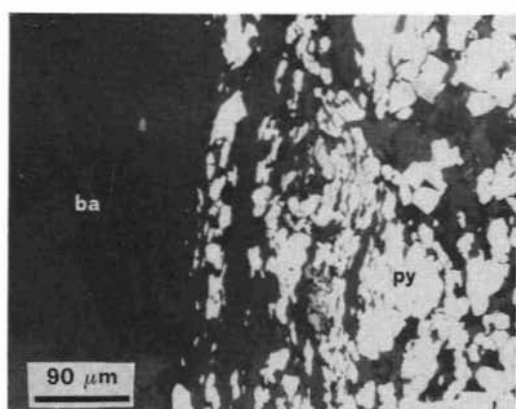


Fig. 11. — Pyrite (py) of the second generation, resulting from recrystallization of an earlier microcrystalline pyrite. Notice the gently folded alignment of the smaller pyrite crystals (center portion of the figure). The figure is the enlarged view of a banded sample of pyrite and barite (ba), such as seen in fig. 6.

hematite-barite ores accompanies the volcano-genic sulfide ores at Mount Lyell, Tasmania (WALSHE & SOLOMON, 1981); and LAZAR et al. (1980) describe syngenetic metamorphosed banded barite $\pm$ iron oxides and sulfides ore bodies closely associated to carbonate levels within chlorite-albite schists at Mount Bihor, Rumania.

Stable isotope and fluid inclusion studies

A number of samples of barite and pyrite were analyzed for S-isotope compositions.

TABLE 1

Sulfur isotope compositions and apparent isotopic temperatures for pyrite and barite from Buca della Vena

SAMPLE	$\delta^{34}\text{S}_{\text{CDT}}$ per mil		ISOTOPIC TEMPERATURE* ($T \pm 15^\circ\text{C}$)
	pyrite	barite	
BV 1	+5.0		
BV 3		+19.2	
BV 8	-13.0	+12.7	213
BV 11	+0.5	+19.8	319
BV 13		+18.8	
BV 15		+19.2	
BV 16	+6.5		
BV 25		+19.5	
BVP 1	+0.6	+19.7	324
BVX	-10.5		

* Calculated according to OHMOTO & RYE (1979).

The minerals were separated by heavy liquids, magnetic and handpicking methods; the purity of the separates was checked under the binocular and by X-ray powder diffraction. Treatment and mass spectrometer analyses of the separates were carried out in the Laboratoire de Hydrologie et Géochimie Isotopique, Université de Paris Sud (Orsay). Routine analytical uncertainty is ± 0.2 per mil or better.

In table 1 are reported the analytical results expressed in the usual notation $\delta^{34}\text{S}$ vs. CDT, and the apparent isotopic temperatures from coexisting barite-pyrite pairs.

Pyrite shows a large spread of isotopic compositions (-13.0 to $+6.5$ per mil), whereas values for barite fall in a more restricted range ($+12.7$ to 19.7 per mil, averaging 18.4 ± 2.5 per mil). Roughly similar data were obtained for barite and pyrite from the deposits of Monte Arsiccio and Pollone (CORTECCI et al., 1985). Also, there is a good agreement with the S-isotope determinations on these deposits reported by ORBERGER et al. (1985).

The large spread of S-isotope compositions of pyrite is consistent with an origin of sulfide by bacterial reduction of marine sulfate. The occurrence of positive $\delta^{34}\text{S}$

values may be ascribed to progressive enrichment in ^{34}S in the residual sulfate, as it happens when sulfate reduction occurs in a restricted basin, partly closed to sulfate. Alternatively, the observed distribution of $\delta^{34}\text{S}$ values for pyrite might result from equilibrium precipitation under highly variable conditions of temperature and/or pH and/or Eh and/or $\delta^{34}\text{S}_{\text{SLS}}$ (fluid).

All but one $\delta^{34}\text{S}$ values for barite are rather homogeneous around +18 to +20 per mil, suggesting again marine sulfate as the most likely sulfur source. Middle-Upper Triassic marine sulfate has $\delta^{34}\text{S}$ values around +16 per mil (CLAYPOOL et al., 1980; cf. also, for Tuscany, CORTECCI et al., 1983) i.e. not dissimilar to most values of Buca della Vena barite. The slight enrichment of ^{34}S in the latter with respect to Triassic marine sulfate may be again explained as the result of bacterial reduction in a partly restricted basin. The only barite sample showing a lower $\delta^{34}\text{S}$ value may indicate contamination with ^{34}S -depleted sulfate: for instance, sulfate resulting from partial re-oxidation of the bacteriogenic sulfide.

The ore bodies at Buca della Vena show evidence of having suffered metamorphism, the peak conditions of which have been estimated, for the host rocks, at 465°C and 2 Kb (ORBERGER & SAUPÉ, 1985). The recorded apparent isotope temperatures for coexisting barite-pyrite pairs ($213^\circ \pm 15^\circ$ to $324^\circ \pm 15^\circ\text{C}$; table 1) may therefore represent temperatures of isotopic re-equilibration during metamorphism. We notice, however, that metamorphic isotopic equilibrium between sulfide and sulfate is only seldom attained, even under more drastic metamorphic conditions (see e.g. RICKARD et al., 1979; CORTECCI et al., 1983; WILLAN & COLEMAN, 1983). Notably, apparent isotope temperatures pairs for the deposit of Monte Arsiccio span from 140° to 530°C, and have been interpreted as evidence of isotopic disequilibrium (CORTECCI et al., 1985).

A number of barite samples were prepared as doubly polished thin plates for fluid inclusion studies. Unfortunately, only rare trails of very small inclusions, of clearly secondary origin and not amenable to meaningful microthermometric measurements, were

TABLE 2
Mineral association and inferred paragenetic sequence at Buca della Vena

	time
BARITE	-----
HEMATITE	-----
PYRITE	-----
MAGNETITE	-----
SPHALERITE	-----
GALENA	-----
QUARTZ	-----
SERICITE	-----
CHLORITE	-----
ALBITE	-----

Other minerals: allanite, anatase, apuanite ($\text{Fe}_{20}\text{Sb}_{14}\text{O}_{44}\text{S}_4$), beryl, bourbonite-seligmannite ($\text{PbCu}(\text{Sb,As})\text{S}_3$), calcite, chalcostibite (Cu_3SbS_3), cinnabar, derbylite ($\text{SbFe}_2\text{Ti}_3\text{O}_{13}\text{OH}$), dolomite, malachite, phlogopite, rutile, schafarzikite ($\text{Fe}_2\text{Sb}_4\text{O}_{16}$), siderite, spessartite, stibivanite (Sb_2VO_3), stibnite, stolzite (Pb_{10}O_4), tetrahedrite, vanadinite, versiliaite ($\text{Fe}_{12}\text{Sb}_{12}\text{O}_{32}\text{S}_2$), vivianite.

observed. This scarcity of fluid inclusions, and specifically the lack of primary ones, in barite, may result from the annealing and recrystallization processes of this mineral demonstrated by the triple-joint granoblastic texture. CORTECCI et al. (1985) report a limited number of fluid inclusion data for barite from the vein mineralization at Pol-lone: temperatures of homogenization were in the order of 200°C, and salinities around 10 % wt. NaCl equivalent.

Ore genesis

The barite-iron oxide-pyrite deposit of Buca della Vena presents a number of characters common to the other Ba-Fe-pyrite deposits of Apuane Alps, which were interpreted by CORTECCI et al. (1985) and CIARAPICA et al. (1985) as evidence of pre-

metamorphic syngenetic origin of the mineralizations:

- the ore bodies show evidence at macro-, meso- and microscale of metamorphic deformation and/or recrystallization. To explain these features, CARMIGNANI et al. (1976) postulated the affiliation of the deposits with early-orogenic Apenninic plutonic rocks, the very existence of which remains however merely speculative;
- the control on the mineralization is markedly lithostratigraphic and not structural. Most of the ore is associated to the uppermost portion of the Scisti di Fornovolasco Formation (and in particular to the interbedded Ladinian-Carnian calcareous levels), which corresponds to a specific paleogeographic domain (a sub-domain of the Apuanidi, in the sense of CIARAPICA & PASSERI, 1982). The overlying Norian dolomitic formations are only weakly mineralized at their bottom contact with the Scisti di Fornovolasco, and the younger formations do not host any mineralization;
- although the metamorphism has affected the original textures, the presently observable dominantly stratiform and near-conformable morphology of the ore bodies, and their well-displayed rhythmic banded texture are in agreement with a synsedimentary formation of the ore. The minor discordant and/or replacement bodies may be ascribed to late-metamorphic remobilization.

We therefore conclude that Buca della Vena represents a metamorphosed and partly remobilized Middle- to Upper Triassic deposit (or, at least, preconcentration) coeval with the sedimentation and/or diagenesis of the host formation.

A question which remains open, is whether the primary mineral-forming event was strictly sedimentary, or, at least to some extent, hydrothermal-sedimentary. BERGMANN (1969) and CIARAPICA et al. (1985) appear to favour a hydrothermal-sedimentary genesis, relying on the existence of an almost coeval mafic volcanism in the Apuane area (although in a different paleogeographic domain, corresponding to the « Unità di Massa »: CIARAPICA & PASSERI,

1982). Without ruling out possible contributions from an endogeneous source to the mineralizations of Buca della Vena, we notice that such contributions are not necessary to explain the available field and geochemical evidence.

As outlined above, the uppermost portion of the Scisti di Fornovolasco Formation marks the transition from a dominantly nearshore sedimentation to the instauration of the hyperhaline platform of the Grezzoni Formation. The corresponding paleogeographic environment can therefore be depicted as a coastal lagoonal domain, characterized by concurrent and partly alternating clastic sedimentation, and transgressive marine hyperhaline-evaporitic episodes.

In such an environment, as demonstrated by FUCHS (1978, 1980), barite concentrations may form by migration and mixing, during diagenesis, of marine sulfate and surface waters carrying Ba released from weathering of continental rocks. A marine source of sulfate is consistent with S-isotope data, whereas a continental origin of Sr (and, by inference, Ba) in barites has been suggested by the Sr-isotope studies of BARBIERI et al. (1982). The source of iron remains more speculative: it could have been too derived from continental weathering, considering the mobility of this element in surface waters under appropriate pH/Eh conditions. At Buca della Vena, the observed predominance of pyrite in association with calcareous rocks, may reflect two different deposition environments: a more reducing environment, characterized by clastic sedimentation, where iron was precipitated by reaction with sulfide deriving from bacterial reduction of marine sulfate; and a more oxidizing environment, corresponding to the deposition of carbonate sediments, where iron was fixed as oxide. A bacteriogenic origin of sulfide sulfur is in agreement with the S-isotope data, and is further supported by the widespread occurrence of carbonaceous matter in the country schists.

Conclusions

The barite-iron oxide-pyrite deposit of Buca della Vena, as well as other similar deposits of Apuane Alps, is a sedimentary-

diagenetic Middle-Upper Triassic mineralization (or at least preconcentration) which suffered metamorphism and partial remobilization during the Tertiary Apenninic orogeny. The conclusion provides further evidence (cf. TANELLI, 1983) to the strata- and time-bound character of all major iron oxide and/or sulfide ($\pm$ Ba) deposits of the Tuscan metallogenic province, which appear to be linked to the uppermost portion of Paleo-

zoic(?) - Triassic silicoclastic formations, and to the bottom of overlying Upper Triassic dolomitic-evaporitic rocks.

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