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MINERALS OF Au, Ag AND U IN VOLCANIC-ROCK-ASSOCIATED MASSIVE SULFIDE DEPOSITS OF THE NORTHERN APENNINE OPHIOLITE, ITALY

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ABSTRACT

Ore samples from five copper sulfide deposits associated with Jurassic ophiolites in the Northern Apennine belt of Italy were found to contain gold, acanthite or argentite (Ag_2S), and freibergite $(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$. These precious-metal minerals are part of a complex assemblage of microscopic to submicroscopic (<10 μm) accessory phases, including uraninite, barite, galena, smithsonite, siderite, a La–Ce carbonate and a Sn hydroxide, attributable to the rare mineral hydroromarchite $Sn_3O_2(OH)_2$. The textures of the sulfide host are indicative of metal deposition in a range of conditions, involving initial precipitation from hot, metal-charged solutions (syngenesis), followed by post-depositional replacement of biological material and resedimentation of clasts, at low temperature (epigenesis). Syngenetic gold is Ag-rich and associated with uraninite in Fe–Cu-rich ore. The fineness of native gold increases by loss of Ag into secondary Ag_2S during seafloor weathering of the sulfides. Freibergite forms during recrystallization of sphalerite in massive Zn–Fe ore. Hydroromarchite occurs in massive Zn–Fe ore, closely related with late deposition of siderite and secondary pyrite, possibly due to the action of neutral to basic and reducing waters flushing through the ore in the initial stages of seafloor diagenesis. The widespread evidence for seafloor resedimentation and for biogenic-activity-driven reworking of the sulfides suggests a transition from proximal VMS to a more distal type of deposit formed by resedimentation processes in a dynamic tectonic environment. This scenario seems to be consistent with the interpretation of the Jurassic Ligurian ocean as a narrow basin in the early stage of its opening, having its modern analogue in the Red Sea.

Keywords: gold, freibergite, uraninite, hydroromarchite, VMS-type deposit, Jurassic ophiolite, Northern Apennine, Italy.

SOMMAIRE

Nous documentons, dans des échantillons de minerai provenant de cinq gisements de sulfures de cuivre associés à la ceinture ophiolitique de l'Appenin Nord, en Italie, d'âge jurassique, la présence d'or, d'acanthite ou d'argentite (Ag_2S), et de freibergite $(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$. Ces minéraux de métaux précieux font partie d'un assemblage complexe de phases accessoires microscopiques à submicroscopiques (<10 μm) comprenant uraninite, barite, galène, smithsonite, sidérite, un carbonate de La–Ce et un hydroxyde d'étain, attribuable à la hydroromarchite, $Sn_3O_2(OH)_2$, minéral rare. Les textures de l'hôte sulfuré témoignent d'une déposition des métaux sur un intervalle de conditions, d'abord une précipitation initiale à partir de solutions porteuses de métaux à température élevée (syngenèse), et ensuite un remplacement tardif de matériaux biologiques et de resédimentation de fragments à basse température (épigenèse). L'or syngénétique est riche en argent et associé à l'uraninite dans un minerai riche en Fe–Cu. La pureté de l'or natif augmente par perte de l'argent et formation de Ag_2S secondaire suite au lessivage sous-marin des sulfures. La freibergite apparait au cours de la recristallisation de la sphalérite du minerai Zn–Fe massif. La hydroromarchite est présente dans ce minerai à Zn–Fe, étroitement lié à la déposition tardive de la sidérite et de la pyrite secondaire, peut-être à cause de la circulation dans l'amas sulfuré d'eaux réductrices dont le pH variait de neutre à basique durant les stades initiaux de diagenèse des sulfures. L'évidence répandue de resédimentation sur les fonds marins et de recyclage biogénique des sulfures fait penser à une transition de la partie proximale d'un gisement de type VMS à un faciès plus distal, formé par resédimentation dans un milieu tectonique dynamique. Ce scénario concorderait avec l'interprétation d'un bassin océanique ligurien d'âge jurassique assez étroit dans son stade précoce d'ouverture, ayant comme analogue moderne la mer Rouge.

(Traduit par la Rédaction)

Mots-clés: or, freibergite, uraninite, hydroromarchite, gisement de type VMS, ophiolite jurassique, chaîne de l'Appenin Nord, Italie.

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INTRODUCTION

> "*...Que in venis inventis et que inveniri vel reperiri poterunt in terris Medolae et Bochaxoli, ex quibus aurum, argentum, ramum, stagnum, plumbum, ferrum vel aliquod metallum de predictis haberi, percipi et extrahi poterit…*"
>
> From the contract with miners,
> drawn up by Sir Guglielmino
> of the late Matteo da Montecuccolo,
> on June 11th, Anno Domini 1343
> (Violi Guidetti 1968).

The citation reported above, dating from the late Middle Ages, is likely the oldest written document to proclaim the significance of base- and precious-metal mineral resources in the province of Modena, Emilia Romagna (Fig. 1). However, the first discovery of copper in the Northern Apennine is probably lost in the mist of time. The dating of prehistoric stony and wooden tools recovered from old mining sites of Eastern Liguria supports this conclusion, unequivocally indicating that copper mining was active about 2000 years B.C., in the Bronze Age (Galli & Penco 1996, Pipino 2003, and references therein). After several centuries of changing fortune, it was only with the advent of the Industrial Era that systematic exploitation of the deposits was undertaken. This activity yielded more than 1.5 Mt of ore with an average grade of 2–7% Cu between the 1850 and 1910 (*i.e.*, Galli & Penco 1996). Thereafter, mining activity declined until the so-called "Autarchy" in 1936, when several copper mines were reopened as a consequence of the international embargo that forced the Italian government to take advantage of any internal resource (Moretti 1937). The economic life-span of most deposits came to an end after World War II, and definitely in the early seventies, when the last mines were closed at Libiola (Eastern Liguria), Vigonzano and Ferriere (Emilia Romagna). Mining sites are now completely abandoned. Today, the collapsed galleries, open pits and ruins of old plants are the only witnesses of the past prosperity.

Despite their economic importance over time, the copper deposits of the Northern Apennine are poorly defined with regard to mineralogy and bulk composition of the sulfide ore. In particular, there is only sporadic information concerning the occurrence of gold and silver in the literature. Ancient and recent documents indicate that silver and gold were occasionally recovered in some copper mines of Eastern Liguria (Galli & Penco 1996, Pipino 2003, and references therein). However, as far as we know, only the occurrence of native silver in the Libiola mine has been documented in the scientific literature (Galli 1959, 1964).

In this work, we report the results of a mineralogical investigation of samples from five sulfide deposits, which were previously found to be the sites of geochemical anomalies in Au and Ag. The study of a great number of polished sections, using electron-microscope and electron-microprobe techniques, has revealed that Au and Ag occur as extremely fine grains (<10 μm) of gold and freibergite disseminated in the sulfide ore. These minerals are part of a complex assemblage of microscopic to submicroscopic accessory minerals, including uraninite, barite, galena, smithsonite, siderite, an unidentified La–Ce carbonate, and a Sn hydroxide corresponding to the rare mineral hydroromarchite.

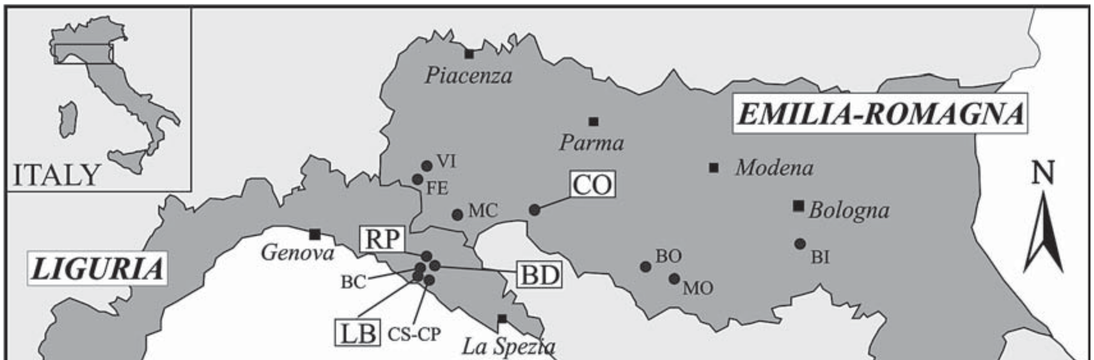

FIG. 1. Geographic location of 13 old copper mines in the Northern Apennine of Emilia Romagna and Liguria (Italy). Stratiform ores: BD: Monte Bardeneto, RP: Reppia, BC: Monte Bianco, CO: Corchia. Stratabound ore: LB: Libiola. Stockwork ore: VI: Vigonzano, FE: Ferriere, MC: Monte Castello, BO: Boccassuolo, MO: Montecreto, BI: Bisano, CS: Casali, and CP: Campegli. The deposits with Au–Ag–U mineralization are highlighted. The Reppia mines include two stratiform and one stockwork deposit (see Fig. 3).

GEOLOGICAL SETTING

The copper deposits of the Northern Apennines are characterized by the Cu- to (Zn,Cu)-rich mineral assemblages (Bertolani 1952, 1953, 1959, 1962) typical of hydrothermal ophiolite-hosted VMS deposits worldwide (Galley & Koski 1999). Their ophiolite hosts (the "Ligurides") are considered to be remnants of the oceanic crust underlying the western limb of the Jurassic Tethys (Piccardo *et al.* 2002, and references therein). These ophiolites have an anomalous stratigraphy compared with Tethyan ophiolites in the Eastern Mediterranean domain (*i.e.*, Barrett & Spooner 1977, Abbate *et al.* 1980). A detailed study of several stratigraphic sections in Eastern Liguria (Barrett 1982) indicates the lack of either a true sheeted dike complex or of a well-developed cumulus transition-zone. In the Ligurian ophiolites, Middle Jurassic gabbroic rocks intrude the old (Proterozoic to Permian) subcontinental lithosphere (serpentinized lherzolite and serpentinite) or lie as thin layers over it. Upper Jurassic MORB-type pillow lava is usually very thin (<200 m) or absent, whereas pelagic sedimentary units may rest directly on the mantle basement. Erosion of serpentinite and pillow basalt on the seafloor generated thick horizons of ophiolitic breccia that accumulated in topographic depressions, directly over serpentinite or lava flows. Pelagic sedimentation started in the Upper Jurassic with deposition of various types of cherts containing Mn-ore deposits (Bonatti *et al.* 1976), and continued with the Calpionella limestone, Palombini shale (Lower Cretaceous), and Lavagna shale (Upper Cretaceous), up to deposition of M. Gottero Flysh (Paleocene). According to Lemoine *et al.* (1987), an extensional detachment fault developed along the Europe–Adria plate boundary, and allowed the mantle to be exposed at the ocean floor and to be eroded over a long time, prior to outflow of pillow basalt or deposition of pelagic sediments (Gianelli & Principi 1977). The scenario envisaged, characterized by a rugged topography on the seafloor, with the mantle tectonite exposed at high points and with a limited extrusion of basalt and formation of thick breccia deposits along valleys and fault scarps, is consistent with formation of the Ligurian ophiolites during the early stages of opening of an ocean basin located to the west of the Jurassic Tethys (Barrett 1982), possibly an analogue to the modern Red Sea basin (Piccardo *et al.* 2002).

On the basis of morphology and stratigraphic position of the sulfide deposits in Eastern Liguria, Ferrario & Garuti (1980) have distinguished four major types of ores: 1) stratiform deposits in ultramafic breccia occurring at the top of the mantle tectonite, invariably covered by pillow lava, 2) stratiform deposits in basalt breccia, occurring at the top of the pillow lava unit, in contact with the sedimentary cover, 3) stratabound deposits inside the pillow lava unit, and 4) stockwork veins, cutting across various units of the ophiolite sequence, including the mantle tectonite, the massive gabbro, and the pillow basalts. According to these authors, stratiform sulfide ores of type 1 and 2 formed at the seafloor by exhalative and sedimentary processes preceding and following the emplacement of pillow basalt. The restriction of stratabound sulfide ore inside the pillow lava sequence is found only at the Libiola mine. The general lack of biogenic features and redeposition structures led Ferrario & Garuti (1980) to suggest that sulfide deposition may have occurred below the seawater–basalt interface, syngenetic with the emplacement of the host pillow-lava. The stockwork ores consist of a network of veins cross-cutting the ophiolite rocks, containing low- to high-grade disseminated sulfide. The veins (usually up to 30–50 cm in thickness) are intimately intermixed with the country rock, the structure suggesting hydraulic explosion, in some cases. The stratigraphic position of the stockwork systems suggests distinct hydrothermal convective cells at different stages during opening of the Ligurian oceanic basin.

Results of the chlorite geothermometry (Zaccarini *et al.* 2003) are consistent with the inferred environment of deposition of the deposits. Chlorite from stratiform ores gave temperatures between 50 and 298°C (average 170°C), with 85% of the values clustering in the range of 100–200°C. In contrast, the highest temperatures were obtained from the stratabound and the stockwork ores; they vary in the range 85–360°C (average 255°C), with more than 90% of data plotting between 200 and 310°C.

ANALYTICAL METHODS

Bulk-rock analysis for Au, Ag, and U were performed at the Actlabs Laboratory, Thornhill, Ontario, Canada. Polished sections obtained from samples with relatively high concentrations of Au, Ag, and U were investigated by electron-microscope and electron-microprobe techniques at the Department of Earth Sciences and CIGS (Centro Interdipartimentale Grandi Strumenti) of the University of Modena and Reggio Emilia. Several grains containing the above metals were located by scanning the polished sections at approximately 500× magnification with a Philips XL 40 Scanning Electron Microscope (SEM), operated in back-scattered electron (BSE) mode, at an accelerating voltage of 20–30 kV and a beam current of 10–20 nA. The composition of the grains was first determined qualitatively by energy-dispersion spectrometry, and then quantitatively by wavelength-dispersion spectrometry, using an ARL–SEMQ instrument equipped with both EDS and WDS spectrometers. Quantitative analysis was performed at 20 kV and 20 nA, using counting times as short as 20 and 5 seconds for peak and backgrounds, respectively. These analytical conditions allowed qualitative identification of grains of less than 0.2 μm, and quantitative analysis of grains as small as 2 μm. The $K\alpha$ X-ray lines were used for Mn, Fe, Co, Ni, Cu, Zn, and S, $L\alpha$ lines for Ag, Sn, Cd, As, Sb, and *M*α line for Au. Synthetic $Au_{70}Ag_{30}$, Ag_2S, NiAs, CoAsS, FeS_2, $CuFeS_2$, ZnS, CdS, SnO_2 were used as reference materials.

LOCATION AND DESCRIPTION OF SAMPLES

Preliminary chemical analyses indicated the existence of significant concentrations of Au, Ag, and U in samples from the stratiform and the stratabound ores, whereas all of the stockwork veins were found to be depleted in these metals (Table 1). Figure 2 shows that stratiform deposits, in general, are enriched in Au, and four samples from Monte Bardeneto and Reppia II plot in the "Auriferous" field in the Au – Ag – (Cu + Zn + Pb) diagram of Hannington *et al.* (1999).

Monte Bardeneto and Reppia (*Eastern Liguria*)

At Monte Bardeneto and Reppia I (Fig. 3), the sulfide ore occurs in an ultramafic breccia composed of serpentinite with minor fragments of sandstone and micritic limestone. The ore ranges from fairly massive (~20 wt% total S) at the contact with the hanging-wall pillow lava, in high-grade disseminated sulfide (<10 wt% total S) toward the serpentinite footwall. The Au–U anomalies were observed in the massive ore containing subordinate amounts of sandy matrix composed of quartz, calcite, chlorite, and siderite. In these samples, pyrrhotite and chalcopyrite are early phases, and both are overgrown by pyrite and magnetite, with accessory sphalerite. The pyrrhotite is the monoclinic variety (Fe_7S_8), and contains significant amounts of Ni and Cu, but Co is close to the detection

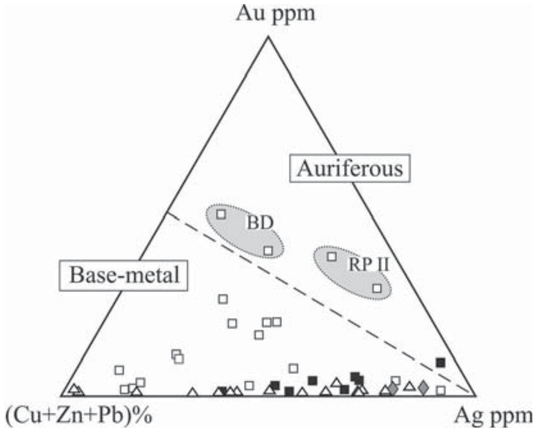

FIG. 2. Plot of bulk-sulfide composition in terms of Au – Ag – (Cu + Zn + Pb) according to the classification of Hannington *et al.* (1999). Open square: stratiform deposits of Monte Bardeneto, Reppia I and II, and Cochia; filled square: stratabound deposit of Libiola; diamond: massive Zn–Fe ore of Corchia; triangle: stockwork veins. Au-rich samples from BD (Monte Barnedeto) and RP (Reppia II) are marked with dashed line. See text for explanation.

TABLE 1. RANGES OF VARIATION OF Au, Ag, AND U IN THE COPPER SULFIDE DEPOSITS OF THE NORTHERN APENNINE

Type of deposit and locality	GPS coordinate	No.	Ore type	Au ppm	Ag ppm	U ppm
Type 1) Stratiform sulfide ore in serpentinite breccia covered with pillow basalt						
Monte Bardeneto	N 44° 20' 376, E 09° 29' 400	8	massive Py-Po-Cp-Sp	0.03-2.64	0.03-1.4	1.3-3.9
Reppia I	N 44° 22' 905, E 09° 27' 451	3	massive Py-Po-Cp-Sp	0.08-0.76	0.03-1.8	1.1
Type 2) Stratiform sulfide ore in basalt breccia covered by sediments						
Reppia II	N 44° 23' 228, E 09° 27' 392	4	massive Py-Cp-Sp	0.34-1.35	0.7-1.3	1.1
Corchia (Cantiere Donini)	N 44° 28' 678, E 10° 02' 010	4	massive Py-Cp-Sp	0.03-3.07	3.9-13	2.5-3.5
Corchia (Cantiere Speranza)	N 44° 28' 488, E 10° 02' 000	2	massive Sp-(Py)	0.03-0.06	81-130	n.d.
Type 3) Stratabound sulfide ore in pillow basalt						
Libiola	N 44° 18' 240, E 09° 26' 938	4	massive Py-Cp-Sp	0.34-0.85	5.2-9.5	4.4-5.4
		3	stringer Py-Cp-Sp	<0.02	1.1-1.9	4.2-8.9
Type 4) Stockwork veins cross-cutting ophiolite rocks (serpentinite, gabbro, basalt)						
ten different mining sites in Eastern Liguria and Emilia Romagna		25	low-grade Py-Cp-Sp	0.03-0.141	0.3-11	n.d.

No.: number of samples, n.d.: not detected. Symbols: Py: pyrite, Po: pyrrhotite, Cp: chalcopyrite, Sp: sphalerite.

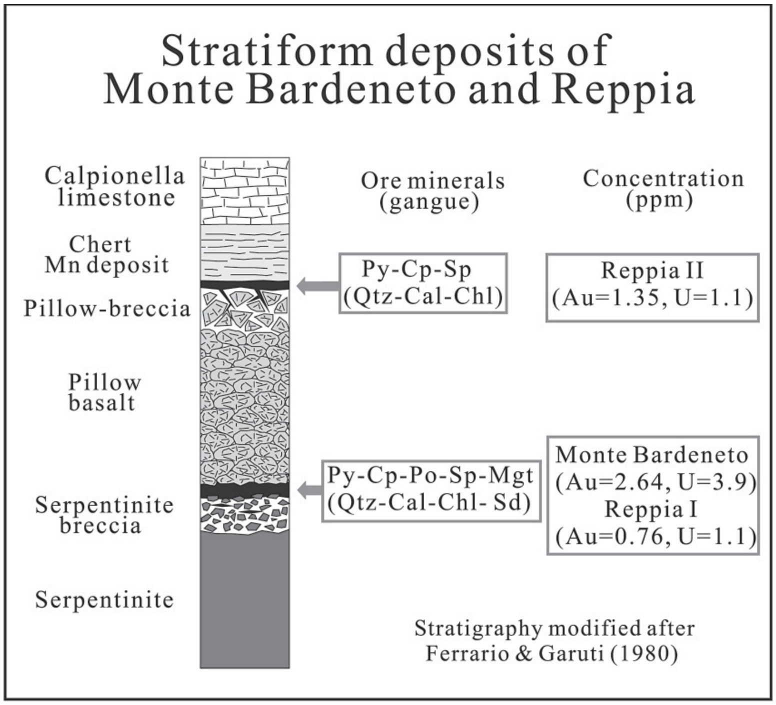

FIG. 3. Stratigraphic relations of the stratiform sulfide deposits of Monte Bardeneto, Reppia I and Reppia II (Eastern Liguria). A small stockwork-type system occurs below the stratiform ore at Reppia II. Maximum concentrations of Au and U are given. Abbreviations: Py: pyrite, Cp: chalcopyrite, Sp: sphalerite, Po: pyrrhotite, Mgt: magnetite, Qtz: quartz, Cal: calcite, Sd: siderite, and Chl: chlorite.

limit (Table 2). Pyrite is also Ni-rich, with Co/Ni less than 1 in general. Sphalerite contains variable amounts of Fe (7.63–10.6 wt%) and up to 5.6 wt% Cu. Textures predominantly reflect the replacement of biogenic material, and bacteria-induced or bacteria-controlled precipitation of sulfides (framboids, corona-like and filament aggregates) are predominant (Figs. 4A, B). Rock fragments and minerals that do not pertain to the hydrothermal-biogenic assemblage (*i.e.*, chromian spinel, serpentine, clay minerals) occur in the sulfide and the gangue, possibly representing detrital material and products of alteration of the ultramafic breccia. Large crystals of zircon of probable detrital origin also have been observed embedded in the carbonate matrix of the sulfide ore.

The stratiform deposit Reppia II (Fig. 3) is hosted inside pillow breccia at the top of the pillow lava unit, in upper contact with chert, passing upward into the Calpionella limestone. The ore forms a tabular body of fine-grained massive sulfide (20–25 wt% total S) in contact with the sediments and becomes disseminated downward. Gold anomalies were encountered in the massive ore, consisting predominantly of pyrite, along with subordinate chalcopyrite and accessory pyrrhotite and sphalerite in a gangue of calcite, quartz, chlorite, siderite, clay minerals and sand-size fragments of basalt and chert. The pyrite mainly occurs as framboids and replacement of organic matter (algae, shells). In contrast with Monte Bardeneto and Reppia I, it is characterized by high Co contents and extremely high Co/Ni values (Table 2).

Corchia (*Emilia Romagna*)

The stratiform sulfide ore of Corchia (Fig. 5) contains two distinct types of mineralization characterized by very different Au–Ag–U proportions. The orebody exposed in the "Cantiere Donini" consists of massive pyrite and chalcopyrite with accessory sphalerite. Anomalous concentrations of Au and U were found with minor Ag in sulfide samples of detrital texture and containing abundant relics of shells replaced by pyrite, in a gangue of quartz, calcite, chlorite and clay minerals (Figs. 4C, D). Pyrite is enriched in As, Co and Ni, with Co/Ni > 1 (Table 2). Examination of the results of a chlorite geothermometry study (unpubl.

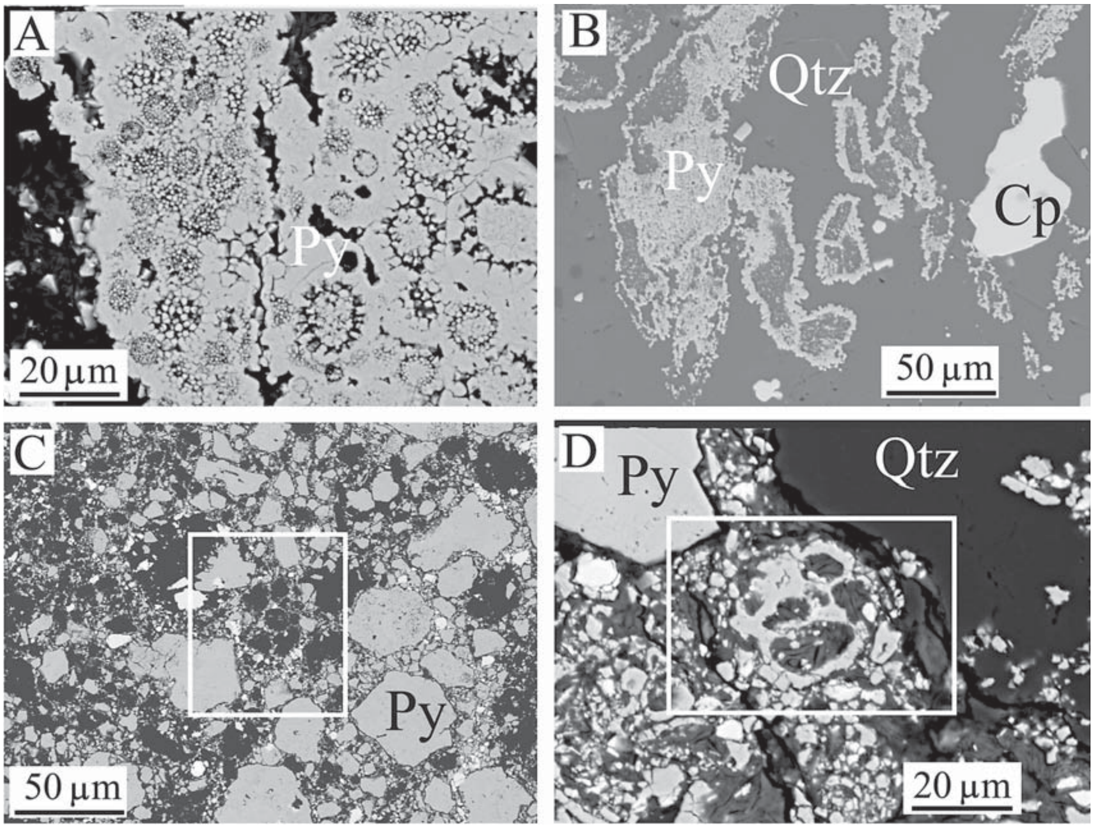

FIG. 4. BSE images of biogenic features in stratiform sulfide deposits of the Northern Apennine ophiolites. A) Pyrite framboids (Monte Bardeneto). B) Pyrite replacing relics of algae or bacterial materials (Monte Bardeneto). C and D) Shells of foraminifera replaced by pyrite (and chalcopyrite) in accumulated clasts of sulfide (Corchia, Cantiere Donini). Symbols: Py: pyrite, Cp: chalcopyrite, Qtz: quartz.

data of Zaccarini *et al*. 2003) shows two distinct groups of temperatures, 180–320°C and 130–90°C, possibly indicating two separate generations of chlorite in the samples of detrital sulfide.

The orebody exposed in the "Cantiere Speranza" consists of pyrite + chalcopyrite with workable lenses of massive Zn–Fe ore, mainly sphalerite with accessory pyrite. Two samples of massive sphalerite were studied. They consist of fine-grained sphalerite (<20 μm) spotted with interstitial patches of quartz and calcite. Locally, sphalerite consists of closely packed spheroids (up to 100 μm in diameter) coated with a thin shell of silica (Figs. 6A, B, C), possibly representing replacement of radiolarian shells or bacterial colonies. The boundaries with the interstitial quartz–calcite patches are characterized by coarse recrystallization of sphalerite, commonly intermixed with idiomorphic pyrite. The quartz–calcite patches contain minute fringes of pyrite intergrown with siderite, smithsonite, barite, a Fe–Ca sulfate, and the rare mineral hydroromarchite (see below). The sphalerite is Fe-rich, containing up to 14.6 wt% Fe, with minor Cu, Cd and As. The idiomorphic pyrite is Co-rich, whereas the pyrite fringes are Co-poor and enriched in Cu, Zn, As, and Ag (Table 2).

Libiola (*Eastern Liguria*)

The sulfide deposit of Libiola (Fig. 7) consists of a suite of massive sulfide lenses (25–35 wt% S) stacked one on the other at the top of a huge dome of pillow basalt, underlain by gabbro and serpentinite. At the footwall of massive orebodies, the sulfide "infiltrates" among pillows and pillow-breccia fragments, giving rise to an interstitial ore (<10 wt% S) that grades downward into a network of millimetric veins, filling cracks and fissures within completely chloritized basalt (stringer ore). Seven samples representative of the massive and stringer ore were studied. Geochemical data (Table 1) indicate Au and Ag enrichment, up to 0.85 and 9.5 ppm, respectively, in the massive ore;

both types have high U contents, varying between 4.2 and 8.9 ppm. The sulfide assemblage is dominated by pyrite and chalcopyrite with subordinate sphalerite and pyrrhotite, in a gangue of quartz, calcite and chlorite. The sulfides lack the typical biogenic features observed in stratiform deposits; pyrite framboids are common, however. Ilmenite, rutile, and titanite occur in the chlorite gangue of the stringers. The pyrite has a generally lower content of Co and Ni, and thus differs from that of the stratiform deposits.

PARAGENESIS AND COMPOSITION

The mineral carriers of Au, Ag, and U are gold, Ag_2S (undetermined argentite or acanthite), freibergite, Ag-bearing pyrite, and uraninite, accompanied by accessory barite, galena, smithsonite, an unidentified La–Ce carbonate and Fe–Ca sulfate, and the rare Sn mineral hydroromarchite. Native silver described from Libiola (Galli 1959, 1964) was not observed in our samples, although we cannot exclude that some grains qualitatively determined as Ag_2S are actually native silver (see below). Selected results of electron-microprobe analyses of the precious minerals and the relevant accessory phases are presented in Tables 3 to 5. The composition of uraninite is presented as EDS spectra in this paper.

TABLE 2. SELECTED RESULTS OF ELECTRON-MICROPROBE ANALYSES OF PYRITE, PYRRHOTITE AND SPHALERITE IN Au–Ag–U-MINERALIZED SAMPLES FROM COPPER SULFIDE DEPOSITS OF THE NORTHERN APENNINE OPHIOLITES

	Fe	Ni	Co	Mn	Cu	Zn	Cd	Ag	S	As	total
d.l.	0.07	0.03	0.03	0.08	0.12	0.17	0.09	0.07	0.02	0.10	
Monte Bardeneto											
Po	59.9	0.18	0.05		0.13				39.6		99.86
Po	60.1	0.05	0.05		0.18				39.7		100.08
Py	46.4	0.71	0.09						53.2		100.40
Sp	10.6			0.12	5.65	51.1			34.0		101.47
S	7.63			0.09	0.12	58.4			33.9		100.14
Reppia I and II											
Po (I)	59.6	0.59	0.10		0.33				39.0		99.62
Py (I)	46.6	0.04	0.05						53.9		100.59
Py (I)	46.9	0.25	0.14						52.9		100.19
Py (II)	45.8	0.05	1.61						52.9		100.36
Py (II)	46.1	0.09	0.97		0.47				52.3		99.93
Corchia, Cantiere Donini (Fe-Cu ore)											
Py cl.	45.9	0.06	0.54		0.08				52.4	0.10	99.08
Py cl.	44.0	0.19	1.55		0.12				52.9	0.45	99.21
Py cl.	44.6	0.03	1.14		0.83				52.8	0.10	99.50
Corchia, Cantiere Speranza (Zn-Fe ore)											
Sp m.	6.58				0.34	60.1	0.12		32.8	0.12	100.06
Sp m.	14.6				2.22	47.8	0.25		34.8	0.16	99.83
Po inc.	59.7	0.03	0.41		0.12				39.5		99.76
Py id.	45.5	0.03	0.73						52.3	0.17	98.73
Py fr.	44.7				0.34	0.49		0.83	53.6	0.52	100.48
Py fr.	44.1				0.31	1.12		0.59	52.0	0.30	98.42
Libiola (massive ore)											
Py	45.8	0.12	0.09	0.09					53.8		99.90
Sp	4.75			0.14	3.53	58.2	0.13		33.2		99.95
Sp	1.21			0.18	0.22	64.6	0.11		32.6		98.92

Symbols: Po: pyrrhotite, Py: pyrite, Sp: sphalerite. Abbreviations: cl.: clastic ore, m.: massive ore, inc.: included in Sp, id.: idiomorphic, fr.: fringes, d.l.: detection limit.

Gold (*Au,Ag,Cu*)

All the samples of Fe–Cu sulfide ore examined were found to contain discrete grains of gold, from 0.2 to

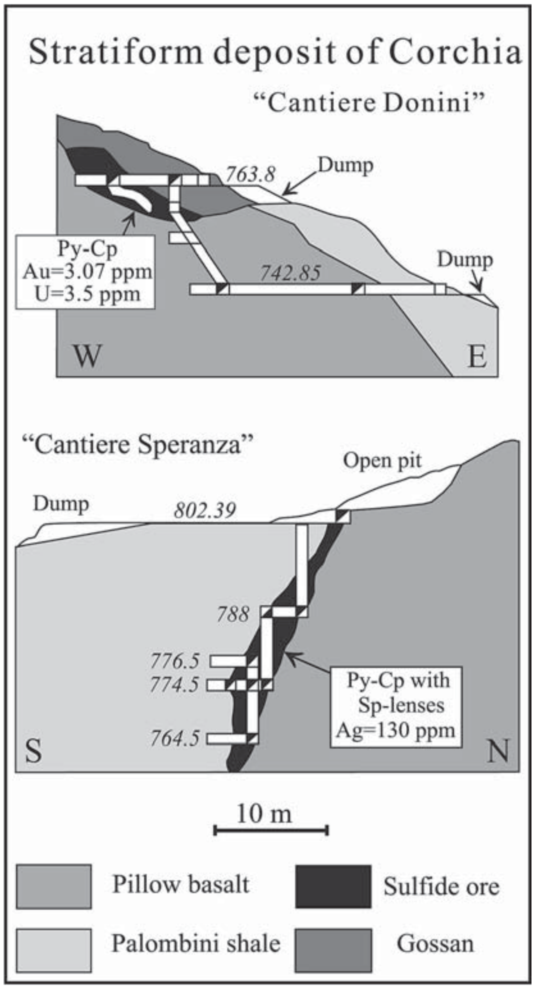

Fig. 5. Corchia mine (Emilia Romagna): vertical sections across the Fe–Cu ore deposit (Cantiere Donini), and the Fe–Cu–Zn ore deposit (Cantiere Speranza). Maximum concentrations of Au, U, and Ag are given. Numbers in italics are heights above the sea level, in meters. Redrawn after the "Società Industriale Mineraria del Rame", internal report on the state of work at the first of May, 1928.

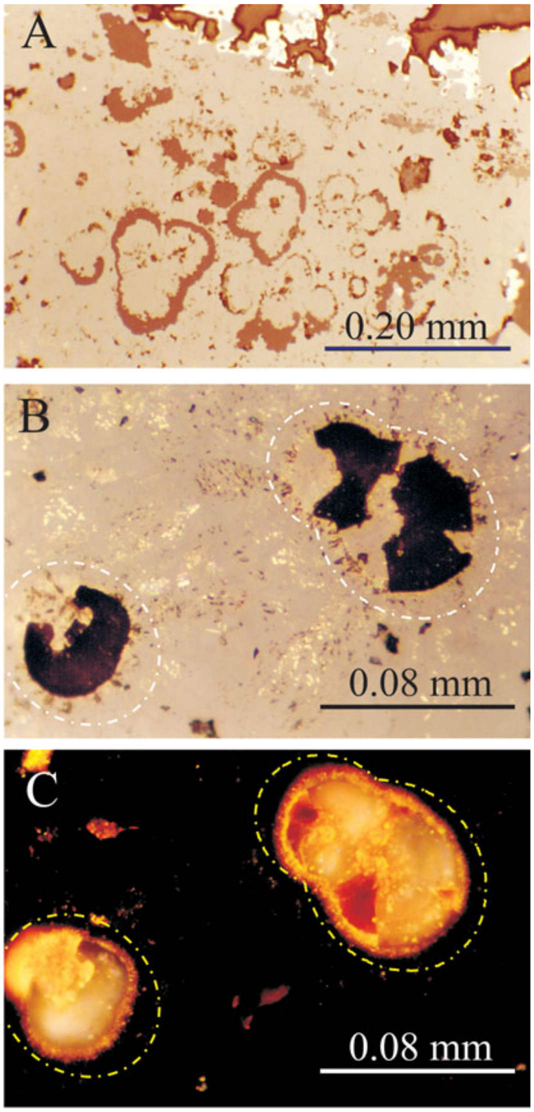

FIG. 6. Reflected-light images of biogenic features in lenses of massive sphalerite from Cantiere Speranza (Corchia). A) Closely packed spheroids coated with silica, possibly representing replacement of bacterial colonies (plane-polarized light). B) Individual spheroids partially substituted by silica (black) in sphalerite (grey) (plane-polarized light). C) The same as B) (crossed nicols); note the internal reflections in sphalerite from the core of the spheroids.

10 μm in size, disseminated in the sulfide and gangue minerals. In the stratiform deposits of Monte Bardeneto and Reppia I, gold commonly occurs included in pyrrhotite (Fig. 8A). At Corchia (Cantiere Donini), gold occurs as very irregular grains in the quartz – chlorite – clay matrix of the sulfide debris (Fig. 8B), or is found included in detrital pyrite. Polygonal crystals of gold were also encountered disseminated in the quartz–calcite gangue of the massive sulfide of Reppia II (Fig. 8C). At Libiola, several grains of gold were found included in chlorite forming the gangue of the sulfide ore (Fig. 8D). Electron-microprobe data (Table 3) indicate that gold varies in composition from almost pure Au to a composite alloy containing significant amounts of Ag, Cu, and traces of Fe. A plot of the compositions in the Au – Ag – (Cu + Fe) diagram shows that the gold from Libiola is the richest in Ag and Cu (Fig. 9). In contrast, gold grains from the stratiform deposits of Monte Bardeneto, Reppia and Corchia are characterized by high Au/(Ag + Cu) values, and some compositions can be considered pure gold (>98 wt% Au) with only trace amounts of other metals.

Argentite or acanthite (*Ag_2S*)

An Ag sulfide corresponding to Ag_2S (argentite or acanthite) is common in the clastic Fe–Cu sulfide ore of Corchia (Cantiere Donini), where it occurs as irregular flakes and tufts associated with the silicate matrix. Furthermore, the mineral occurs in the Zn–Fe ore of Cantiere Speranza, finely disseminated in the quartz–calcite matrix of the massive sphalerite. Generally, the grains are less than 3 μm in size, and therefore only one reliable electron-microprobe analysis could be made, from the grain in Figure 10A. Other grains (<2 μm) were found attached to the rim of euhedral

TABLE 3. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF GOLD FROM THE NORTHERN APENNINE COPPER SULFIDE DEPOSITS

		Au	Ag	Cu	Fe	total
d.l.		0.11	0.07	0.13	0.08	
		Corchia, Cantiere Donini (Fe–Cu ore)				
1	in Qtz-Chl	95.8	1.06	1.64	0.09	98.59
2	in Py	89.7	5.53	2.09	1.23	98.55
3	in Chl	91.2	2.23	2.84	0.89	97.16
		Libiola				
1	in Chl	71.7	16.9	9.00	1.23	98.83
2	in Chl	72.6	13.9	11.1	0.98	98.58
3	in Chl	78.8	11.5	9.66		99.96
		Reppia II				
1	in Qtz	98.6	0.33	0.13	0.78	99.84
2	in Py	97.0	0.40	0.24	1.33	98.97
		Monte Bardeneto				
1	in Po	97.4	1.25	0.33		98.98
2	in Po	99.0	1.58	0.27		100.85
3	in Po	97.5	1.48	0.70		99.68
4	in Po	95.8	1.29	1.44		98.53

Symbols: Qtz: quartz, Chl: chlorite, Py: pyrite, Po: pyrrhotite. The compositions are expressed in wt%; d.l.: detection limit.

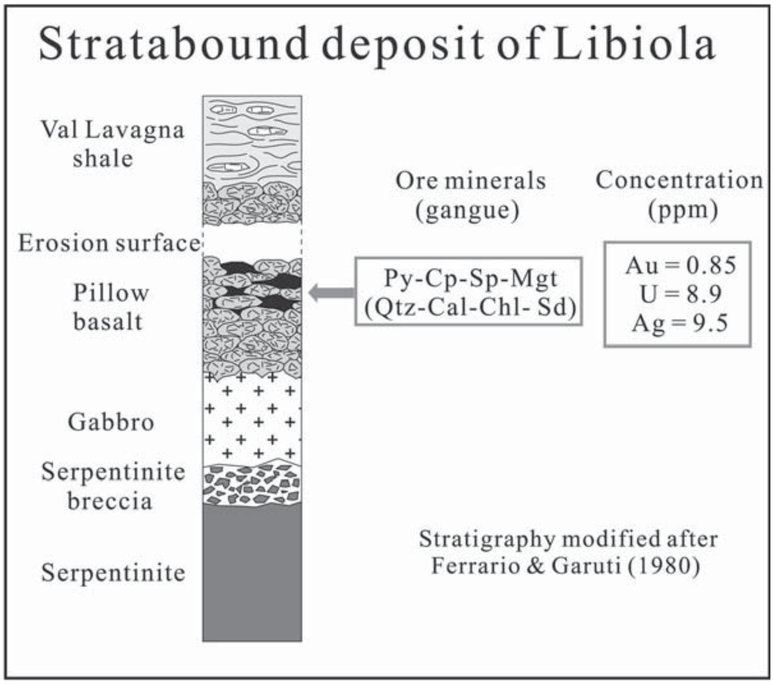

FIG. 7. Stratigraphic relations of the strabound sulfide deposit of Libiola. The sulfide deposit is cut by an erosion surface. The top of pillow basalt is in contact with sediments. Maximum concentrations for Au, U, and Ag are given. Sd: siderite; other symbols as in Figure 2.

crystals of pyrite in the Fe–Cu sulfide ore of Reppia II and Libiola. They were classified as Ag_2S on the basis of EDS spectra. Some doubt does exist that the grains might be native silver, however, the detected sulfur possibly being due to spurious fluorescence from the adjacent pyrite.

Freibergite, ideally $(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$

Freibergite was encountered only in the Zn–Fe ore of Cantiere Speranza (Corchia). Grains up to 20 μm are rather abundant, accounting for the high concentrations of Ag, up to 130 ppm reported in this type of ore. In contrast with the Ag sulfide, freibergite occurs included in sphalerite, typically associated with the coarse-grained, recrystallized rims that line the contact with the quartz and calcite (Figs. 10B, C). Freibergite may be associated with small crystals of chalcopyrite or pyrite that usually occur attached to the external boundary of the grains. The electron-microprobe analyses of ten different grains (Table 4) indicate a constant composition, represented by the average formula $(Ag_{5.5}Fe_{2.1}Cu_{4.3})_{\Sigma 11.9}(Sb_{4.0}As_{0.15})_{\Sigma 4.15}S_{12.8}$.

TABLE 4. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF FREIBERGITE FROM CORCHIA

	Ag	Fe	Cu	S	Sb	As	Total
d.l.	0.09	0.05	0.07	0.03	0.15	0.16	
1	31.22	5.67	14.45	21.05	26.13	0.61	99.13
2	30.48	5.50	14.39	21.09	27.50	0.59	99.55
3	31.50	5.57	14.33	22.00	27.31	0.61	101.32
4	30.48	5.48	14.39	21.20	26.89	0.59	99.03
5	31.08	5.59	13.78	21.25	26.10	0.57	98.37
6	31.64	5.99	14.16	20.97	27.20	0.61	100.57
7	28.49	6.13	14.19	21.28	28.72	0.53	99.34
8	31.77	6.06	14.00	20.67	26.67	0.59	99.76
9	31.93	6.12	14.09	21.38	27.36	0.59	101.47
10	28.33	5.94	12.80	21.46	29.77	0.66	98.96

The compositions are expressed in wt%; d.l.: detection limit.

Uraninite UO_2

Uraninite was observed in all samples, except for the Zn–Fe ore of Corchia. On BSE images, it appears as highly reflective, rounded grains of 0.2–2 μm included in pyrite (Fig. 11A). However, it was also observed as

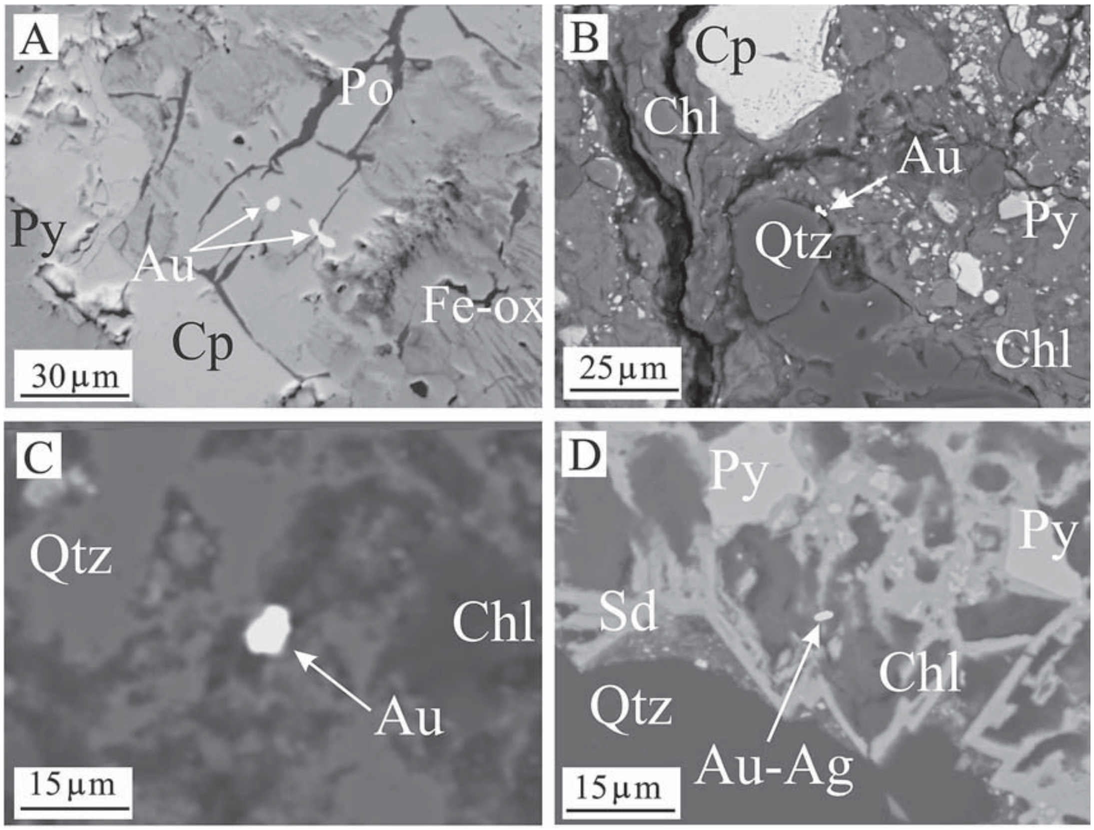

FIG. 8. BSE images of gold from stratiform sulfide deposits of the Northern Apennine ophiolites. A) Two gold grains included in pyrrhotite (Monte Bardeneto). B) Detrital gold in the clastic accumulated sulfide (Corchia, Cantiere Donini). C) Gold included in the quartz–chlorite gangue matrix of the massive sulfide ore (Reppia II). D) Silver-rich gold in the pyrite – chlorite – siderite assemblage in contact with the quartz gangue of massive sulfide (Libiola). Au–Ag: Ag-rich gold, Au: gold, Sd: siderite; other symbols as in Figure 5.

euhedral crystals associated with ilmenite in titanite-rich veins, within high-temperature chlorite (250°C), in the U-rich stringer ore of Libiola (Fig. 11B). Owing to the small size of the grains, spurious fluorescence from the including matrix interfered with quantitative electron-microprobe analysis. However, all of the grains seem to be essentially constituted by U and O in a proportion consistent with uraninite (Fig. 12).

Hydroromarchite $Sn_3O_2(OH)_2$

The mineral was identified on the basis of its chemical composition, deduced from results of several electron-microprobe analyses (Table 5). Although we are aware that a complete characterization is needed to confirm its mineralogical nature, the observed compositions perfectly fit those reported by Dunkle *et al*. (2003) for anthropogenic hydroromarchite. Hydroromarchite was encountered in Cantiere Speranza (Corchia mine) as part of a complex assemblage consisting of siderite, pyrite, smithsonite, barite, and an unidentified Fe–Ca sulfate associated with the interstitial quartz–calcite gangue of the massive Zn–Fe ore. Textural relations indicate that hydroromarchite coats pyrite or sphalerite (Fig. 13A), or may occur as small spots (50 µm) intermixed with pyrite inside sphalerite (Fig. 13B). Hydroromarchite also occurs included in siderite as isolated crystals (5–10 µm) characterized by their rectangular or rhombic section (Figs. 13C, D). Several grains of hydroromarchite were tested, and gave the same spectrum. Electron-microprobe analyses were made of eight large grains; the results reveal a rather constant composition, with only weak substitution of Fe and Zn for Sn (Table 5). The composition of the small grain shown in Figure 12B indicates that hydroromarchite in this context may be slightly enriched in Fe (anal. 8, Table 5).

Barite and other accessory minerals

Barite was identified by EDS qualitative analysis. The mineral is very common in all the samples examined, occurring as minute grains (up to 100 μm) disseminated in the quartz – calcite – chlorite – siderite gangue of the sulfide ores. It commonly occurs at the sulfide–gangue contact, but never within the primary sulfide minerals (pyrrhotite, pyrite, chalcopyrite, sphalerite). In the Zn–Fe ore of Corchia, barite is particularly abundant; in some cases, it occurs as large euhedral crystals (50 μm) included in siderite, which in turn is replaced by pyrite.

One polygonal grain (3.5 μm) of a La–Ce carbonate was found at the contact of quartz and pyrite, in the

TABLE 5. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF HYDROROMARCHITE FROM CORCHIA

	Sn	Fe	Zn	S	O	subtotal	H_2O	total
d.l.	0.05	0.07	0.17	0.11				
(§)	84.36	0.00	0.00	0.00	11.37	95.73	4.27	100.00
1	82.06	0.68	0.31	b.d.l.	11.33	94.38	4.27	98.65
2	83.88	0.64	0.54	b.d.l.	11.62	96.68	4.27	100.95
3	83.94	0.5	1.1	b.d.l.	11.73	97.27	4.27	101.54
4	84.67	0.61	1.17	b.d.l.	11.87	98.32	4.27	102.59
5	83.01	0.94	0.62	0.17	11.61	96.35	4.27	100.62
6	84.78	1.03	0.27	0.15	11.79	98.02	4.27	102.29
7	84.57	0.55	b.d.l.	b.d.l.	11.57	96.69	4.27	100.96
8	80.35	1.36	0.53	b.d.l.	11.35	93.59	4.27	97.86

(§): ideal composition of hydroromarchite; d.l.: detection limit; b.d.l.: below detection limit. Compositions are expressed in wt%.

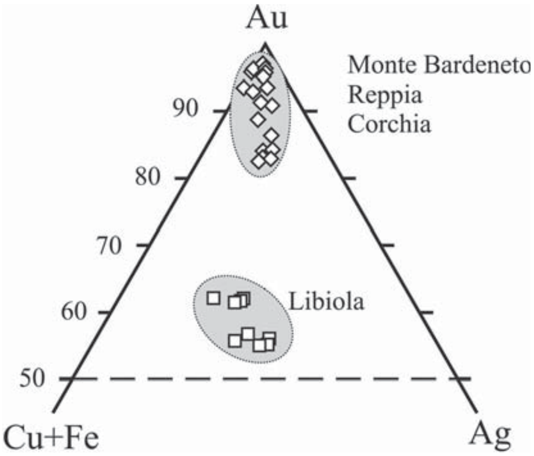

FIG. 9. Electron-microprobe-derived compositions of gold plotted on the Au – Ag – (Cu + Fe) diagram. Open square: stratabound deposit of Libiola, diamonds: stratiform deposits of Monte Bardeneto, Corchia, and Reppia. See text for explanation.

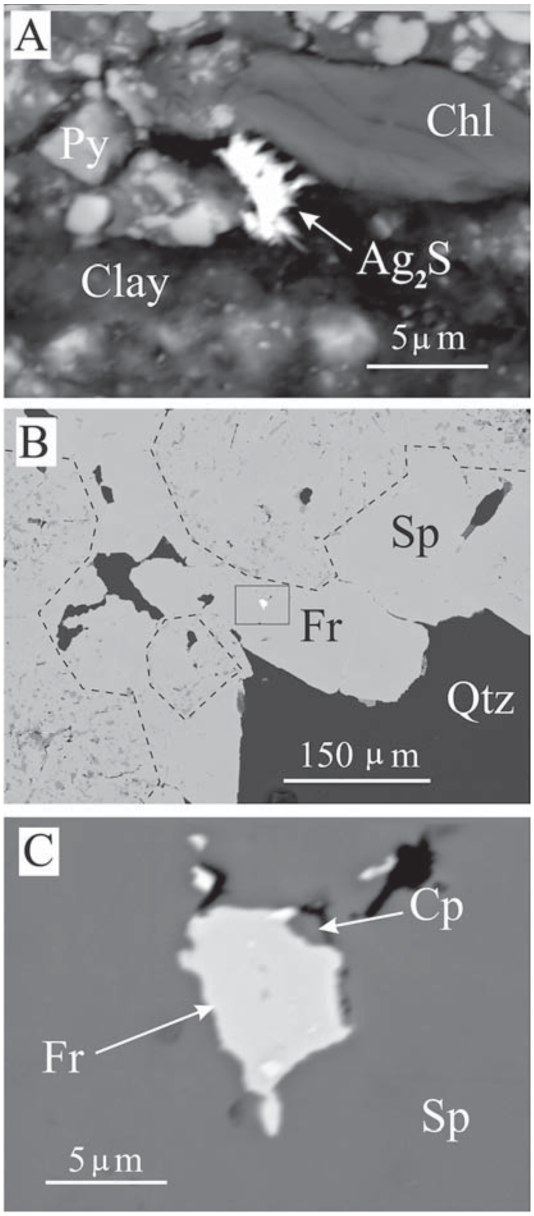

FIG. 10. BSE images of Ag-bearing minerals from Corchia. A) Irregular tuft of probably secondary argentite (Ag_2S) disseminated in the clay–chlorite matrix of the clastic accumulated sulfide (Cantiere Donini). B) Freibergite included in secondary recrystallized sphalerite at the boundary with patch of quartz. Dashed line marks the limit between recrystallized sphalerite and the spheroid-bearing sphalerite, in massive Zn–Fe ore of Cantiere Speranza. C) Enlargement of B) showing a small grain of chalcopyrite at the rim of freibergite. Clay: Fe-rich clay mineral with illite-type composition, Fr: freibergite; other abbreviations as in Figure 5.

auriferous sample of Reppia II. The mineral appears lead-grey in color, weakly anisotropic, with a sharp and dark extinction. A quantitative electron-microprobe analysis indicates high La:Ce ratio, with a recalculated formula $(La_{1.5}Ce_{0.6})_{\Sigma 2.1}(CO_3)_{2.9}\bullet 8H_2O$, possibly lanthanite.

A few grains of galena (2–5 µm) were encountered in the same auriferous sample from Reppia II. The grains are polygonal and occur included in pyrite, at the boundary with the quartz gangue. Qualitative EDS analyses indicate an ideal composition.

Smithsonite is particularly abundant in the argentiferous samples of Zn–Fe ore from Corchia. The mineral occurs as tufts and flakes (100 µm) associated with the pyrite–siderite assemblage in the quartz patches inside massive sphalerite (Fig. 13A).

Perfect rhomb-shaped crystals (5–20 µm) of an unidentified Fe–Ca sulfate also occur in the pyrite–siderite assemblage (Fig. 13C). The mineral seems zoned, with a Ca-rich core and a thin rim enriched in Fe.

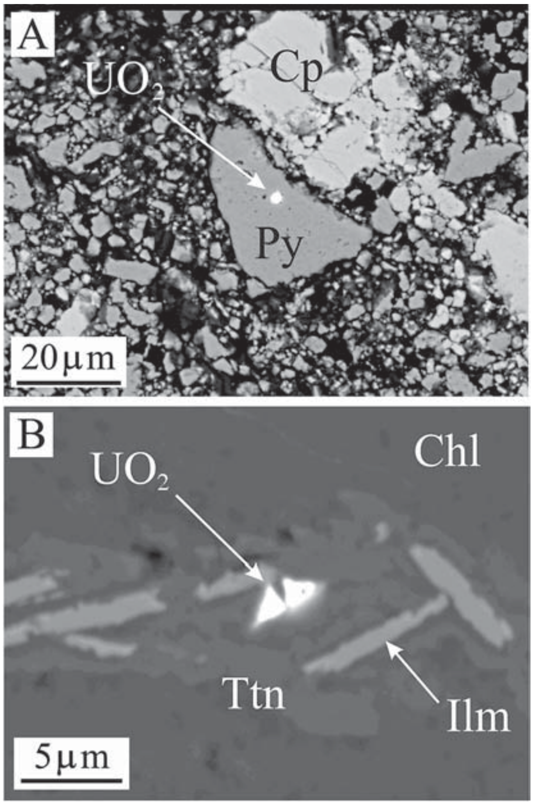

FIG. 11. BSE images of uraninite grains from stratiform sulfide deposits of the Northern Apennine ophiolites. A) Uraninite included in a pyrite fragment of the clastic accumulated sulfide (Corchia, Cantiere Donini). B) Two grains of uraninite in a titanite–ilmenite-rich vein cross-cutting the chlorite gangue of the stringer sulfide ore (Libiola). UO_2: uraninite, Ttn: titanite, Ilm: ilmenite; other symbols as in Figure 5.

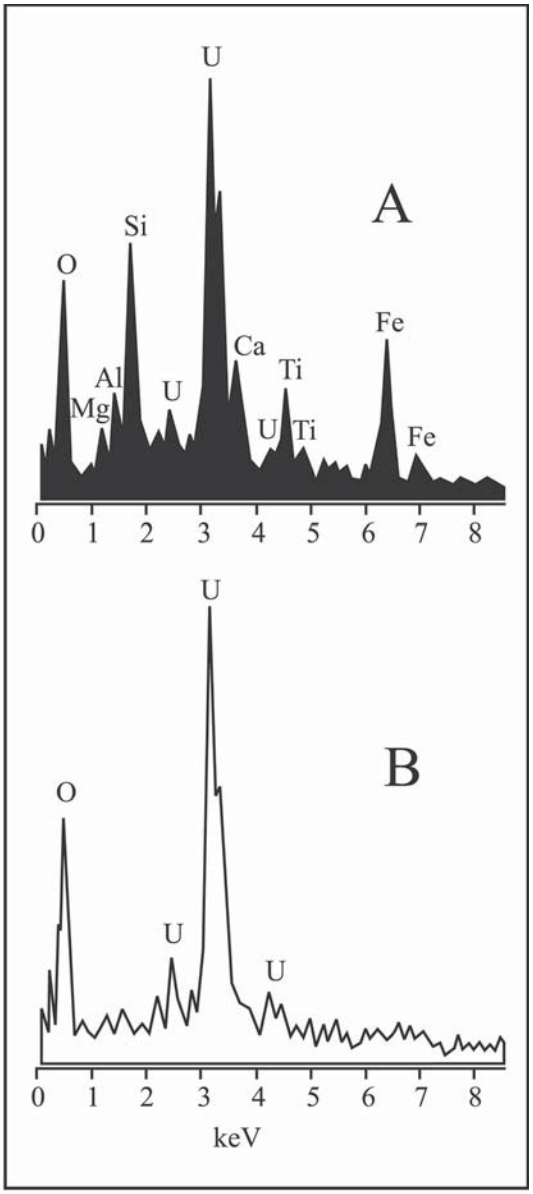

FIG. 12. EDS spectrum of the uraninite grain in Figure 11B compared with the spectrum of pure uraninite B). Note the spurious fluorescence of Ca, Ti, Fe, Si, Al, and Mg from the adjacent grains of chlorite and titanite.

A qualitative EDS analysis shows Ca, Fe and S as the only components, and suggests that the mineral may be a sulfate, possibly of the alunite or copiapite group.

DISCUSSION

In this paper, we have documented the presence of microscopic to submicroscopic grains of specific minerals disseminated in the ore–gangue assemblage, which accounts for the anomalous concentrations of Au, Ag and U detected in samples of the Northern Apennine sulfide deposits. Gold, uraninite, and minor Ag sulfide (argentite or acanthite) are the carriers of the metals in the Fe–Cu ore, whereas the marked Ag-anomaly in the Zn–Fe sulfide ore of Corchia is accounted for by freibergite and minor Ag_2S. The fact that the Au–Ag–U mineralization is restricted to the stratiform and stratabound ores, and seems absent in the subseafloor stockwork veins, suggests that the processes leading to the concentration of these metals occurred exclusively in the submarine environment. The textures of sulfides in the mineralized samples, as well as the paragenetic assemblage and composition of the Au, Ag and U minerals, are important indicators of ore genesis, as illustrated below.

The sulfide textures are indicative of metal deposition in a range of conditions, involving an initial precipitation from hot, metal-charged hydrothermal solutions venting at the seafloor (syngenesis), and a post-depositional biogenically driven reworking and clastic accumulation of sulfide debris in topographic lows (epigenesis). The results of chlorite geothermometry (Zaccarini *et al*. 2003) point to a temperature of about 360°C for primary deposition, and to a relatively low temperature (<100°C) for the epigenetic processes, possibly indicating an occurrence in the early stages of diagenesis, prior to or shortly after burial under lava flows or pelagic sediments.

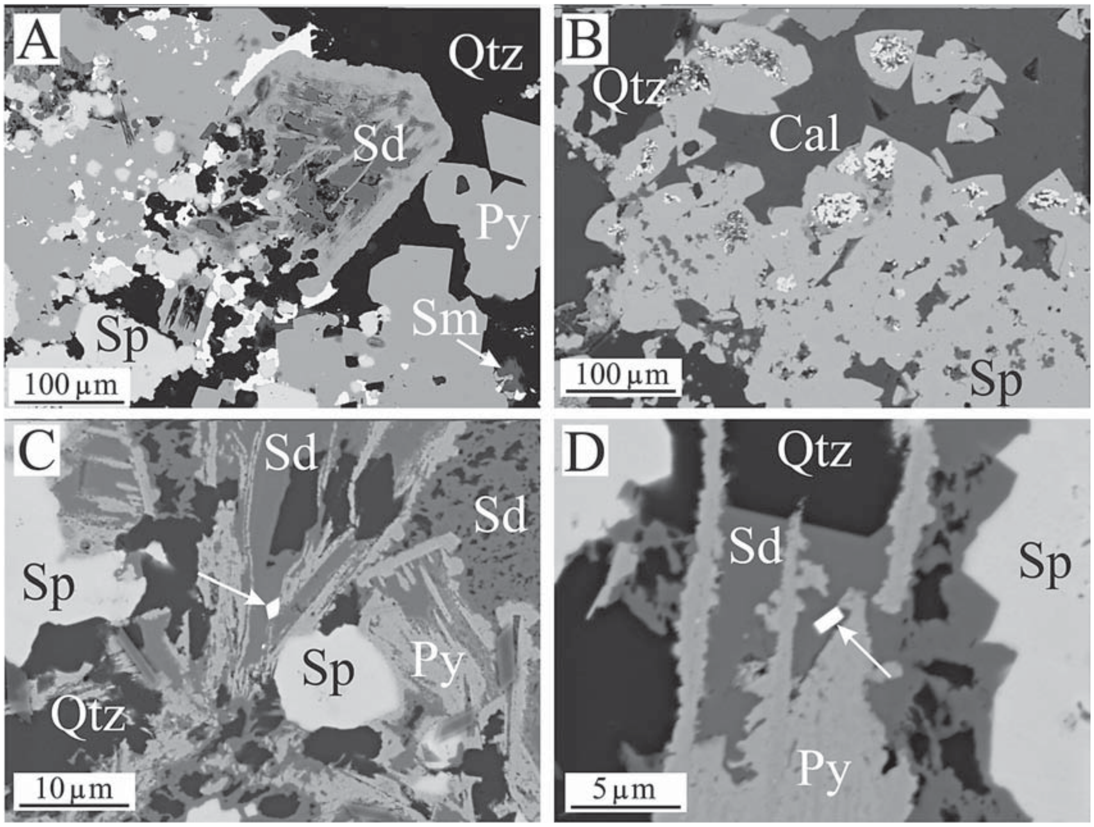

FIG. 13. BSE images of hydroromarchite from Cantiere Speranza (Corchia). A) Hydroromarchite (brilliant white) coats pyrite at the boundary with patch of quartz. B) Hydroromarchite spot in sphalerite intermixed with quartz and calcite. C and D) Euhedral crystals of hydroromarchite (indicated with arrow) intergrown with siderite in the pyrite–siderite assemblage developing at the boundary with quartz patch. The rhombic grey crystals in C (right and left lower corners) are an unidentified Fe–Ca sulfate. Sm: smithsonite; other symbols as in Figure 5.

The inclusion of gold in primary Fe-sulfides suggests that Au precipitation started in the high-temperature hydrothermal stage. Consistent with data from several VMS deposits (*i.e.*, Herzig *et al.* 1991), the primary hydrothermal gold is enriched in Ag and Cu, up to 16.9 and 11.1 wt% respectively, in contrast to the gold associated with the matrix of sulfide debris (Corchia), which is pure (>95 wt% Au). The pure gold is believed to have formed at a low temperature, by loss of Ag during submarine weathering, in a way similar to that described for weathered gold nuggets in terrestrial placers (Groen *et al.* 1990) and laterite-hosted gold deposits (Mann 1984). The occurrence of Ag_2S (argentite or acanthite) and possibly native silver (Galli 1959, 1964) in a replacement texture may account for the redeposition of silver removed from the primary Ag-rich gold by dissolution. Considered noteworthy is the fact that the Fe–Cu stratiform ores display an extremely wide variation of the Au content (0.03–3.07 ppm, Table 2) and preferentially contain gold of secondary origin. In contrast, the stratabound deposit of Libiola displays homogeneous Au concentrations (0.34–0.85 ppm, Table 2) and contains gold with predominant Ag–Cu-rich composition, consistent with limited submarine weathering of the sulfide ore. These observations point to the weathering process as the major factor controlling the concentration of gold in the Northern Apennine sulfide deposits, and indicate that post-depositional processes of alteration were more active in the stratiform deposits associated with the ophiolitic breccia than in the stratabound sulfide bodies within an accumulation of pillows.

The patterns of metal zoning commonly observed in ophiolite-hosted VMS deposits worldwide are characterized by the sequence Fe (pyrite), Fe–Cu (chalcopyrite, pyrite) plus Au and Fe–Zn–Ag (sphalerite, pyrite, acantite), and is believed to reflect a decrease in solubility of the metals with declining temperature (*i.e.*, Reed 1983, Lydon 1988). In this view, the Ag-rich Zn–Fe ore of Corchia probably formed at a lower temperature than the associated Fe–Cu ore. The slight increase in Au solubility with decreasing temperature below 230°C may explain the lack of primary gold in this type of ore (Large 1992). The Ag minerals do not appear to be syngenetic in origin. The mode of occurrence of freibergite and the Ag sulfide in the Zn–Fe ore suggests a timing of formation during the recrystallization of sphalerite, which may have taken place in the initial stage of ore diagenesis. The latest stages are characterized by circulation of relatively cool fluids throughout the Zn–Fe sulfide ore, leading to precipitation of carbonates (siderite, smithsonite), sulfates (barite, Fe–Ca sulfate), and hydroromarchite. Only a few natural occurrences of hydroromarchite have been reported in the literature, although the mineral has been recognized to be a common product of submarine corrosion of pewter artifacts (Ramik *et al.* 2003, Dunkle *et al.* 2003). Since no Sn-mineral precursor has ever been reported from the Northern Apennine copper deposits, a natural origin of the hydroromarchite from Corchia could be seriously challenged. However, the alternative hypothesis of an anthropogenic origin appears to be remote, since it would require Sn to have been introduced into the orebody from an external source, at some stage during the mining works. At present, we prefer to consider the hydroromarchite of Corchia as a natural phase deposited by the action of fluids (possibly connate seawater) circulating through the porous orebody, at some stage during diagenesis. These fluids were probably able to dissolve and redeposit sulfide minerals, in this way removing their trace elements (*e.g.*, Sn) and precipitating them as specific phases further away. The close association of pyrite and siderite places the conditions for the formation of hydroromarchite at Eh of –0.2 to –0.4 units and pH between neutral (pH = 7) and moderately basic ($8 < pH < 9$), compatible with the submarine environment.

There are no data concerning the abundance and distribution of U in ophiolite-hosted VMS (Galley & Koski 1999). However, uranium has been detected in modern hot springs at mid-oceanic ridges (Michard *et al.* 1983, Chen *et al.* 1986), where it is removed from seawater by reducing hydrothermal solutions venting at the seafloor (Klinkhammer & Palmer 1991). Uraninite formation involves the reduction of a soluble U^{6+} complex (possibly a carbonate complex) to the insoluble U^{4+} oxide, or some hydroxide precursor. Once formed, uraninite is stable under anoxic conditions, such as those occurring in the organic-matter-rich sulfide ores, and remains immobile during seafloor weathering. The almost homogeneous distribution of U in the Fe–Cu stratiform deposits of the Northern Apennines indicates that there was little or no remobilization of uranium subsequent to primary deposition. As is the case with Au, U is absent in the Zn–Fe ore, and would appear to be restricted to primary precipitation of pyrite at a relatively high temperature. The reason for such a behavior is not completely understood, but precipitation of uraninite may in some way be dependent on temperature, as the mineral is particularly abundant (up to 8.9 ppm U) in the stringer ore of the stratabound deposit of Libiola, for which the highest chlorite-based temperatures were obtained (Zaccarini *et al.* 2003).

CONCLUDING REMARKS

1) The historically reported recovery of Au and Ag from the copper sulfide deposits of the Northern Apennine ophiolites is supported by the presence of geochemical anomalies and by the occurrence of specific phases disseminated in the sulfide ore.

2) The concentration processes are closely related to the deposition and further evolution of the sulfide ore at the seafloor, probably including the early stages of ore diagenesis, prior to or shortly after burial of the deposits under the volcanic or sedimentary cover.

3) The numerous features observed in the stratiform deposits indicating biogenic replacement and clastic reworking of sulfide suggest a transition from VMS-type deposits, possibly proximal to black smoker fields, to more distal types, formed by resedimentation of sulfide in ophiolitic breccias, in a tectonically active geodynamic environment. This model seems to be consistent with the interpretation of the Jurassic Ligurian ocean as a narrow basin in the early stage of its opening (Barrett 1982), possibly having its modern analogue in the Red Sea embryonic ocean (Piccardo *et al*. 2002).

4) In this paper, we present the first documented occurrence of gold, freibergite, uraninite and hydroromarchite in the sulfide deposits of the Northern Apennine ophiolites.

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