

Article

High and Low Temperature Gold Mineralizations in the Fe–Cu–Zn Sulfide Deposits of Corchia Ophiolite, Northern Italian Apennine

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Abstract: Gold has been found in the Cyprus-type volcanogenic massive sulfide ore (VMS) deposits of Corchia ophiolite (Parma province, Italy) in the Cantiere Donnini, Speranza and Pozzo mining sites. At Cantiere Donnini and Speranza, the mineralization occurs at the contact between pillow lava and sedimentary rocks. The Pozzo mineralization is hosted by a serpentinite. Concentrations of gold up to 3070 ppb have been reported for the Cantiere Donnini and up to 6295 ppb in the Pozzo mine. According to the field relationships, gold composition, mineralogical assemblage and sulfur isotope data, we can conclude that two different types of gold mineralization have been recognized in the Corchia ophiolite: (1) formed at low temperature in submarine environment (Cantiere Donnini and Speranza) and (2) formed at high temperature in the oceanic mantle (Pozzo) by segregation of an immiscible sulfide liquid.

Keywords: gold; VMS deposits; Corchia ophiolite; Italy

1. Introduction

Several historical Cu–Fe–(Zn) ore deposits, classified as Cyprus-type volcanogenic massive sulfide ore (VMS) by [1,2], have been described in the ophiolites of the Northern Italian Apennines, geographically located in the regions of Emilia-Romagna and Liguria. These mines are famous among the economic geologists and archeologists, because they have been known as a source of copper since

the Bronze Age and because some of them possibly were active as far back as 3500 B.C. [3]. Between the Middle Age and the 18th century, copper was extracted sporadically. Copper became a major commodity during the Industrial Era, and from 1850 to 1910, a number of new deposits were discovered and intensively mined. After some years of decline, mining activities started again and lasted until the early seventies, when all the mines were definitively abandoned.

The presence of gold minerals associated with these sulfide deposits has been recently reported, for the first time, by [1]. In particular, in the Corchia ophiolite, located in the province of Parma, the gold minerals were found in the Donnini and Pozzo mining sites [1,4]. In this contribution, we report geological, mineralogical and geochemical information of the Corchia sulfide deposits, with the aim of better understanding the origin of these gold mineralizations associated with Cyprus-type VMS deposits.

2. Geological Background of the Northern Apennine Ophiolite and the Associated Sulfide Deposits

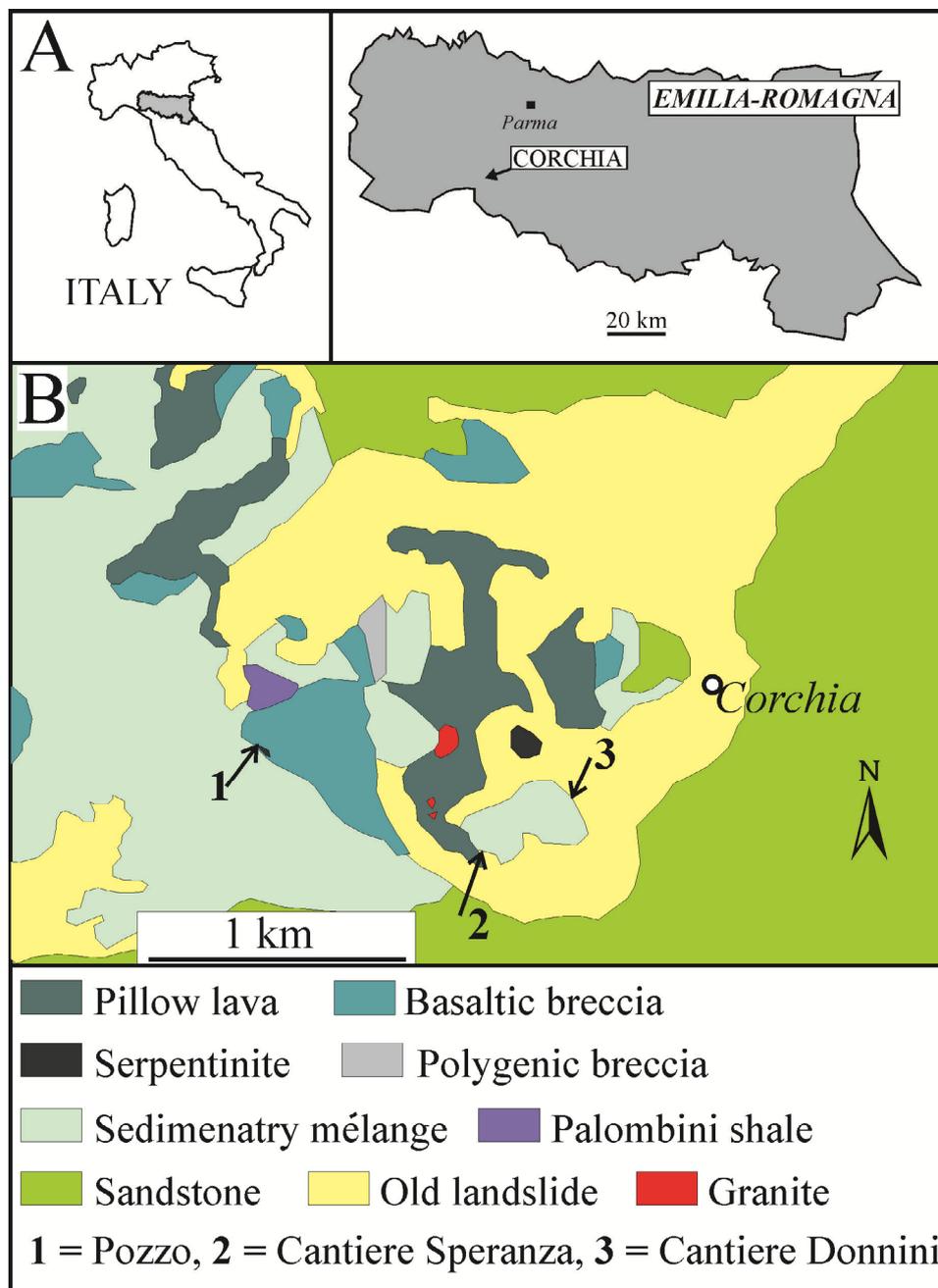
The Northern Apennine ophiolites are considered to be the remnants of the Ligurian Tethys. According to the interpretation by [5], the Ligurian Tethys represents the Jurassic analogue of modern ultraslow-spreading oceans. The formation and evolution of the Northern Apennine ophiolites, proposed by [5], comprise: (a) the rifting (continental) stage, characterized by the extension of the continental lithosphere and tectonic exhumation of lithospheric mantle; (b) the drifting (transition) stage, characterized by the inception of asthenosphere partial melting and mid-ocean ridge basalt (MORB) melt percolation through the overlying mantle lithosphere; and finally; and (c) the spreading (oceanic) stage, characterized by failure of the continental crust, sea-floor exposure of mantle tectonites and discontinuous MORB extrusion. The Northern Apennine ophiolites are strongly dismembered and tectonized. However, their stratigraphy has been recognized and reconstructed [5]. It consists of: (1) mantle tectonite, composed of partially to totally serpentinized peridotite; (2) gabbroic rocks; (3) pillow lava; and (4) a sedimentary cover of chert and limestone. The sheeted dyke complex is missing.

The Fe–Cu–Zn deposits associated with the Northern Apennine ophiolites occur at different stratigraphic levels in the ophiolite sequence, and five major structural types have been recognized: (1) stratiform ores occurring in the serpentinite breccia, covered by pillow lava; (2) stratiform ores located at the top of the volcanic pile, covered with sediments; (3) stratabound deposit inside the pillow basalt; (4) sulfide deposits related to hydrothermal veins cutting across serpentinite, gabbro and pillow basalt; and (5) small lenses of massive sulfide hosted in serpentinite, that possibly represent a fragment of oceanic mantle [6,7].

3. The Corchia Ophiolite and Description of the Associated Deposits

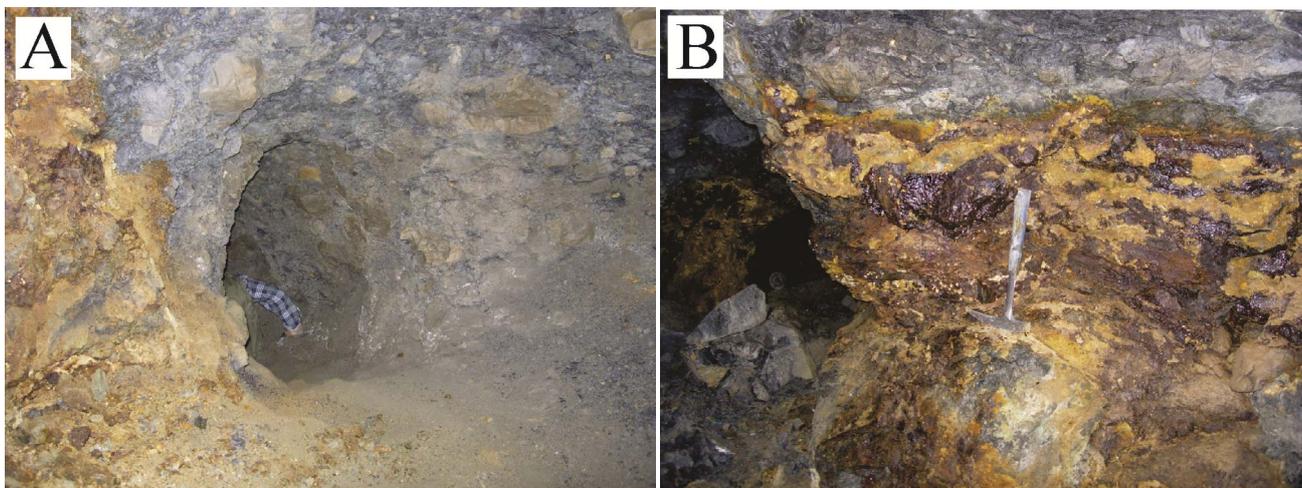
The Corchia ophiolite is located in the Emilia-Romagna region about 40 km southwest of Parma (Figure 1A). It consists of several fragmented blocks of pillow lava and serpentinite accompanied by basaltic and polygenic breccias (Figure 1B) embedded in sedimentary rocks, such as the Palombini shales and fragmented shales and sandstones.

Figure 1. (A) Geographical location of the Corchia ophiolite and (B) geological map of the Corchia ophiolite (modified after the Geological Map of Italy, Sheet 216, Borgo Val di Taro [8]) showing the location of the investigated deposits.



The contacts between serpentinite and basalt generally suggest thrusting of the mantle tectonite onto the volcanic pile. However, the stratigraphic succession from serpentinite to pillow lava and sediments can be observed only locally in small outcrops, located in the southeastern part of the Corchia ophiolite complex, where the ore deposits occur. The mineralization of Cantiere Donnini and Speranza are the most important deposits of the Corchia ophiolite (Figure 1). They were exploited from 1900 until 1943, when the mines were closed. They form several irregular lenses of massive sulfides, variable in size (up to 100 m), hosted by the contact between pillow basalt and marine sediments (Figure 2).

Figure 2. (A) and (B): underground view inside Cantiere Donnini mine, showing the contact between the mineralized lens and the marine sediments.



The ore body in Cantiere Donnini forms an irregular lens of massive sulfide that was originally exposed at the surface and, therefore, covered with a thick gossan. The massive sulfides comprise pyrite, chalcopyrite with accessory sphalerite, showing a detrital texture in which angular fragments of sulfides occur in a ground mass of quartz, calcite, chlorite and clay minerals [2]. Shells of microfossils replaced by sulfide and anomalous concentrations of Au and U are characteristic of this type of ore [1]. Gold and uraninite were found as microscopic inclusions in pyrite. The sulfide mineralization underwent post-depositional reworking by submarine debris flow and accumulation in a topographic depression, followed by burial under a Palombini shale olistostrome [6]. The Cantiere Speranza mineralization consists of a massive sulfide layer steeply inclined (about 70°–80°) southwards, probably extending more than 100 m along the strike and 40 m in depth, with a maximum thickness of about 5 m [9,10]. The ore assemblage is composed of pyrite and chalcopyrite with lenses of massive Zn–Fe ore, mainly sphalerite with accessory pyrite. The massive sphalerite displays a microscopic texture that represents replacement of radiolarian shells or bacterial colonies [1]. A great variety of microscopic and accessory minerals that accompany the Zn–Fe sulfide ore, such as acanthite, freibergite, siderite, smithsonite, Fe–Ca sulfate, barite and also the rare mineral, hydroromarchite, have been reported [1]. On the basis of the paragenesis, shape and stratigraphic position of the ore, it was possible to establish that these sulfide mineralizations formed in an ancient sea bed, representing the equivalent fossil of the so-called black smokers [6]. Another type of sulfide mineralization has been recognized in the Pozzo mine, located about one kilometer from the two mining sites mentioned above (Figure 1). In this area, serpentinites covered with sediments have been recognized (Figure 3A). The mineralization forms a lens of massive sulfide with a thickness of up to 1.5 m and with an extension of several tens of meters (Figure 3B). The massive sulfide is hosted by a block of strongly serpentinitized peridotite (Figure 3B). According to the data presented by [7], the sulfur isotope composition in the Donnini and Cantiere Speranza deposits show average value of 2.4‰ $\delta^{34}\text{S}$, whereas the average $\delta^{34}\text{S}$ ‰ composition in the Pozzo mine is 0.8. In Table 1, the main characteristics of the Corchia deposits have been listed.

Figure 3. (A) Field view of the contact serpentinite-sedimentary mélange of an unmineralized serpentinite, cropping out 300 m from the Pozzo mine and (B) external view of the Pozzo deposit, showing the contact between serpentinite and massive sulfide body.

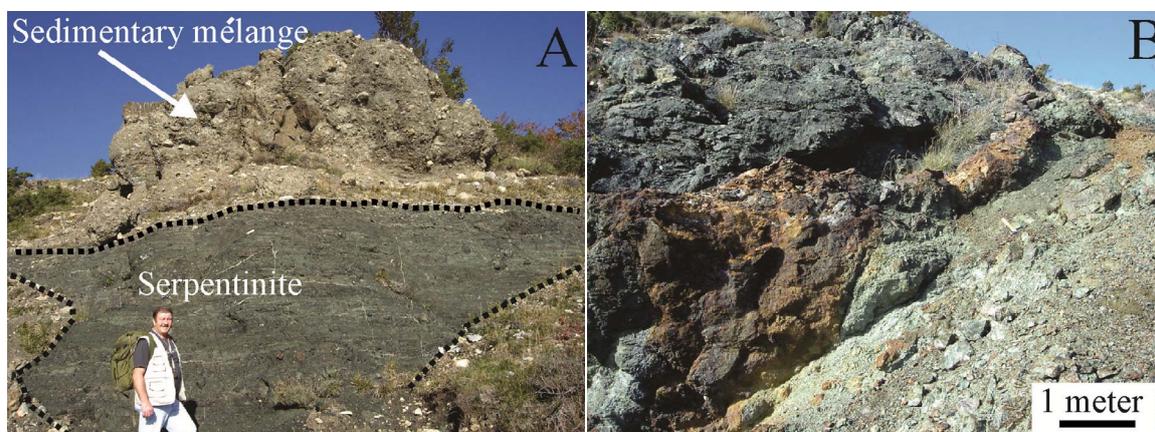


Table 1. Characteristics of the Corchia deposits.

	Cantiere Donnini and Speranza	Pozzo
Geology	Contact pillow-sedimentary rocks	Serpentinite
Ore minerals	Pyrite, chalcopyrite, sphalerite, magnetite	Chalcopyrite, pyrite, magnetite, sagenite, molybdenite
Textures	Massive, detrital, biogenic	Massive
Average $\delta^{34}\text{S}\%$	2.4	0.8
Major gangue minerals	Quartz, chlorite, carbonates, clay minerals	Serpentine, chlorite

4. Methodology

Three samples from Pozzo mine and one from Cantiere Donnini have been analyzed for gold and the six platinum group elements (PGE) by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) after Ni-sulfide preconcentration at Genalysis Laboratory Services Pty Ltd., Western Australia. The results are listed in Table 2.

Gold minerals were investigated microscopically on 40 polished thick and thin sections representing 10 samples, under reflected light at 250–500 \times magnifications and using the electron microscope. The gold minerals were analyzed by electron microprobe with a Superprobe Jeol JXA 8200 at the Eugen F. Stumpfl Laboratory at Leoben University (Austria). Grains bigger than 5 μm were quantitatively analyzed, whereas the smaller ones were only qualitatively analyzed. The electron microprobe was operated by Energy Dispersive X-ray Spectroscopy (EDS) for qualitative analyses and Wavelength Dispersive X-Ray Spectrometry (WDS) for quantitative analyses modes, at 20 kV accelerating voltage and 10 nA beam current. During the acquisition of quantitative analyses, the counting times for peak and background were 20 and 10 s, respectively. The analysis of S, Cu, Ni and Fe was carried out using the $K\alpha$ lines, Ag using $L\alpha$ and Au using $M\alpha$. The following analyzing crystals were used: PETJ for S, PETH for Au and Ag and LIFH for Fe, Ni and Cu. Gold–silver alloy, chalcopyrite and millerite were used as reference material. Selected analyses have been reported in Table 3.

Table 2. Concentration of Au and platinum group elements (PGE) (ppb) in the deposits of Corchia.

Sample	Au	Os	Ir	Ru	Rh	Pt	Pd
COPO 1B	2171	4	5	8	0	7	8
COPO 2B	1569	6	6	9	3	13	11
COPO 3B	6295	3	3	8	0	8	10
CO 23	989	0	2	6	2	20	13

Notes: COPO = Pozzo, CO = Cantiere Donnini.

Table 3. Selected analyses of gold from the Pozzo mine.

wt %	Au	Ag	Fe	Ni	Cu	S	Total
copo1b 1	88.69	12.13	0.38	0	0.04	0.07	101.31
copo1b 1	87.15	11.8	0.95	0	0.9	0.55	101.33
copo1b 1	88.29	11.68	0.29	0.03	0.26	0.47	101.01
copo1b 1	86.16	11.53	1.26	0	0.51	0.05	99.5
copo1b 1	85.67	11.51	0.98	0	0	0.79	98.96
copo1b 1	86.47	12.04	0.87	0.02	0.04	0.13	99.56
copo1b 3	86.49	11.43	0.7	0	0.51	0.08	99.21
copo1b 3	88.05	11.64	0.34	0.01	0.29	0.39	100.72
copo1b 3	86.2	11.59	0.5	0	0.14	0.75	99.18
copo1b 3	85.23	11.96	0.96	0	1.22	0.14	99.52
copo1b 5	87.31	11.51	0.3	0.02	0.84	0.24	100.22
copo1b 5	87.31	11.61	0.88	0	0.56	0.14	100.51
copo1b 5	86.62	11.73	0.53	0.31	0.78	0.06	100.02
copo1b 5	86.94	11.52	0.71	0	0.34	0.15	99.65
copo2b 1	87.45	11.55	1.57	n.a.	1.12	n.a.	101.69
copo2a 2	86.59	11.56	0.36	n.a.	0.37	n.a.	98.88
copo2a 2	87.43	10.83	0.74	n.a.	0.64	n.a.	99.65
copo2a 2	87.47	11.37	0.43	n.a.	0.59	n.a.	99.86
copo2a 2	85.51	9.81	1.23	n.a.	1.74	n.a.	98.28
copo2b 2	83.19	12.22	2.25	n.a.	2.51	n.a.	100.17
copo2b 3	85.33	13.21	1.23	n.a.	2.05	n.a.	101.83
copo2b 3a	84.02	11.97	1.53	n.a.	2.45	n.a.	99.97
copo2b 4	84.17	12.69	1.18	n.a.	1.90	n.a.	99.94
copo2b 4	83.45	12.75	1.32	n.a.	1.90	n.a.	99.42
copo2b 5	85.23	12.29	1.37	n.a.	1.63	n.a.	100.51
copo2b 5	84.89	11.52	1.67	n.a.	2.70	n.a.	100.78
copo2b 5	84.44	12.28	1.31	n.a.	1.95	n.a.	99.98
copo2b 6	83.86	11.92	1.02	n.a.	2.07	n.a.	98.87
copo3b 1	87.80	9.48	1.23	n.a.	0.33	n.a.	98.84
copo3b 1	87.83	10.18	1.12	n.a.	0.24	n.a.	99.37
copo3b 1	89.59	9.94	1.48	n.a.	0.13	n.a.	101.15
copo3b 1	89.97	9.96	1.35	n.a.	0.31	n.a.	101.59
copo3b 2a	85.77	9.32	2.52	n.a.	2.86	n.a.	100.48
copo3b 2a	87.53	9.89	2.53	n.a.	2.94	n.a.	102.90
copo3b 2c	89.37	8.26	1.33	n.a.	2.16	n.a.	101.13
copo3b 3	86.15	9.99	1.49	n.a.	2.49	n.a.	100.12
copo3b 4b	88.04	9.71	0.78	n.a.	1.15	n.a.	99.68

Table 3. Cont.

at %	Au	Ag	Fe	Ni	Cu	S
copo1b 1	78.67	19.65	1.19	0.00	0.11	0.38
copo1b 1	73.72	18.23	2.83	0.00	2.36	2.86
copo1b 1	77.15	18.64	0.89	0.09	0.70	2.52
copo1b 1	75.88	18.54	3.91	0.00	1.39	0.27
copo1b 1	74.50	18.28	3.01	0.00	0.00	4.22
copo1b 1	76.85	19.54	2.73	0.06	0.11	0.71
copo1b 3	77.29	18.65	2.21	0.00	1.41	0.44
copo1b 3	77.35	18.67	1.05	0.03	0.79	2.10
copo1b 3	75.50	18.54	1.54	0.00	0.38	4.04
copo1b 3	74.05	18.97	2.94	0.00	3.29	0.75
copo1b 5	76.90	18.51	0.93	0.06	2.29	1.30
copo1b 5	76.45	18.56	2.72	0.00	1.52	0.75
copo1b 5	76.16	18.83	1.64	0.91	2.13	0.32
copo1b 5	77.31	18.71	2.23	0.00	0.94	0.82
copo2b 1	74.38	17.94	4.71	n.a	2.96	n.a
copo2a 2	78.65	19.17	1.15	n.a	1.04	n.a
copo2a 2	78.19	17.69	2.33	n.a	1.79	n.a
copo2a 2	78.39	18.61	1.37	n.a	1.63	n.a
copo2a 2	75.59	15.83	3.82	n.a	4.76	n.a
copo2b 2	68.63	18.40	6.55	n.a	6.42	n.a
copo2b 3	71.01	20.08	3.62	n.a	5.29	n.a
copo2b 3a	70.68	18.39	4.54	n.a	6.39	n.a
copo2b 4	71.69	19.74	3.55	n.a	5.02	n.a
copo2b 4	71.16	19.85	3.97	n.a	5.01	n.a
copo2b 5	72.51	19.09	4.11	n.a	4.30	n.a
copo2b 5	70.63	17.50	4.91	n.a	6.96	n.a
copo2b 5	71.84	19.08	3.94	n.a	5.15	n.a
copo2b 6	72.53	18.82	3.10	n.a	5.55	n.a
copo3b 1	79.49	15.67	3.91	n.a	0.92	n.a
copo3b 1	79.05	16.74	3.54	n.a	0.68	n.a
copo3b 1	79.02	16.01	4.61	n.a	0.37	n.a
copo3b 1	79.00	15.97	4.18	n.a	0.85	n.a
copo3b 2a	71.15	14.12	7.37	n.a	7.36	n.a
copo3b 2a	70.80	14.60	7.22	n.a	7.38	n.a
copo3b 2c	77.14	13.02	4.05	n.a	5.79	n.a
copo3b 3	73.42	15.55	4.47	n.a	6.57	n.a
copo3b 4b	78.54	15.81	2.46	n.a	3.19	n.a

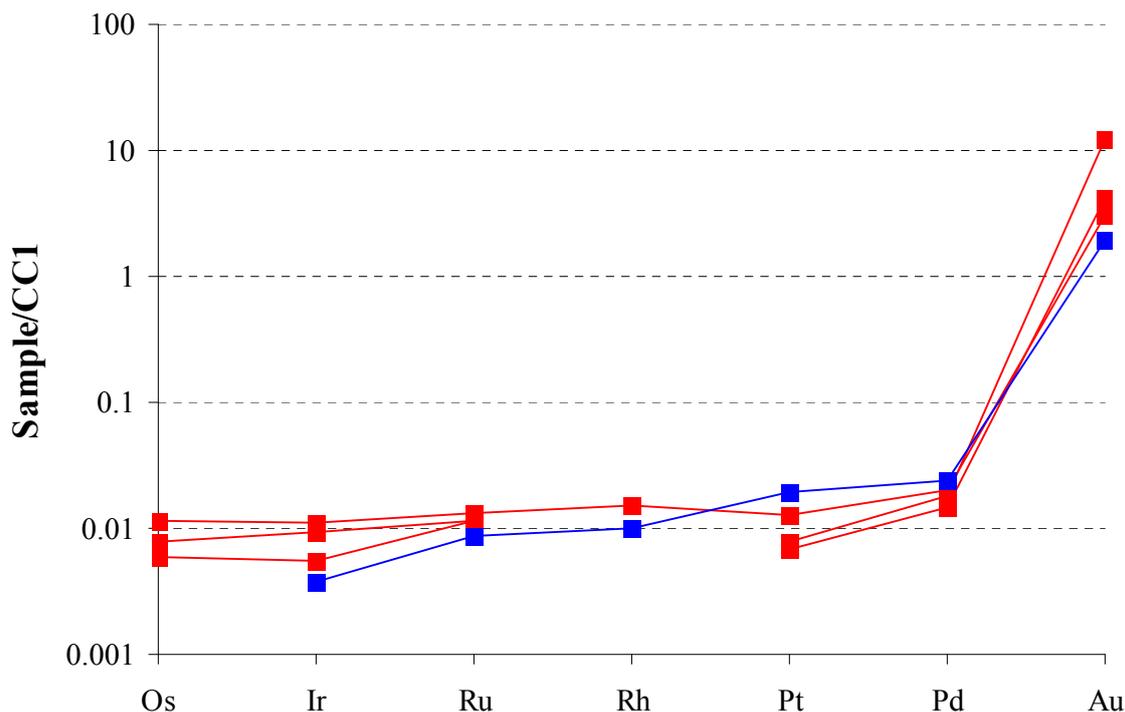
Note: n.a. = not analyzed.

5. Results

Whole rock analyses presented in this study indicate that the concentration of gold in the Pozzo mine is significant, ranging from 1569 to 6295 ppb (Table 2). The amount of gold found in the Cantiere Donnini and Speranza is comprises between 300 up to 3070 ppb (Table 2 and data from [1]).

The PGE concentration (Table 2) is always very low (up to 48 ppb of total PGE). Chondrite-normalized Au and PGE patterns of Cantiere Donnini and Speranza and Pozzo massive sulfides (Figure 4) are generally flat with respect to PGE, as is typical for un-mineralized mantle peridotite formed in supra-subduction zone ophiolites ([11] and reference therein). Gold, on the other hand, is enriched up to ten times, compared to the chondrite (Figure 4).

Figure 4. Chondrite-normalized patterns of massive sulfide from Cantiere Donnini (blue square) and Pozzo (red square) mining sites. Normalization values are from [12].



As previously reported by [1], the gold minerals found in the Cantiere Donnini and Speranza are randomly distributed and occur as minute grains (less than 10 μm), generally with a rounded and irregular shape. Therefore, most of them have been only qualitatively analyzed. They have mostly been found associated with detrital minerals (Figure 5A) and rarely associated with sulfide (Figure 5B). On the contrary, the gold minerals found in the Pozzo mine are more evenly distributed (Figure 6A), forming crystals with a size from 2 up to 40 μm . Few grains have a size of 100 μm . Their shape varies from rounded blebs and irregular to polygonal grains. They always were found associated with massive sulfide, mostly included in chalcopyrite (Figure 6A) and sometimes in pyrite. They occur also in contact with molybdenite (Figure 6B) and magnetite (Figure 6C). Selected optical images of gold grains are presented in Figure 7. The composition of the analyzed grains has been plotted, as at %, in the ternary diagram Au–Ag–(Fe + Cu) presented in Figure 8. According to this diagram, the gold grains plot in two fairly distinct populations. The grains analyzed in the Cantiere Donnini and Speranza mine display a higher content of gold (from about 80 up to about 100 at %), whereas in Pozzo, minerals the concentration of gold are comprised between about 60 to 80 at %.

Figure 5. Backscatter electron images of gold grains from Cantiere Donnini: (A) detrital gold in the clastic accumulate sulfide and (B) small bleb of gold included in pyrite. Scale bar is 10 μm. Abbreviations: Au = gold, Chp = chalcopyrite, Qz = quartz, Py = pyrite.

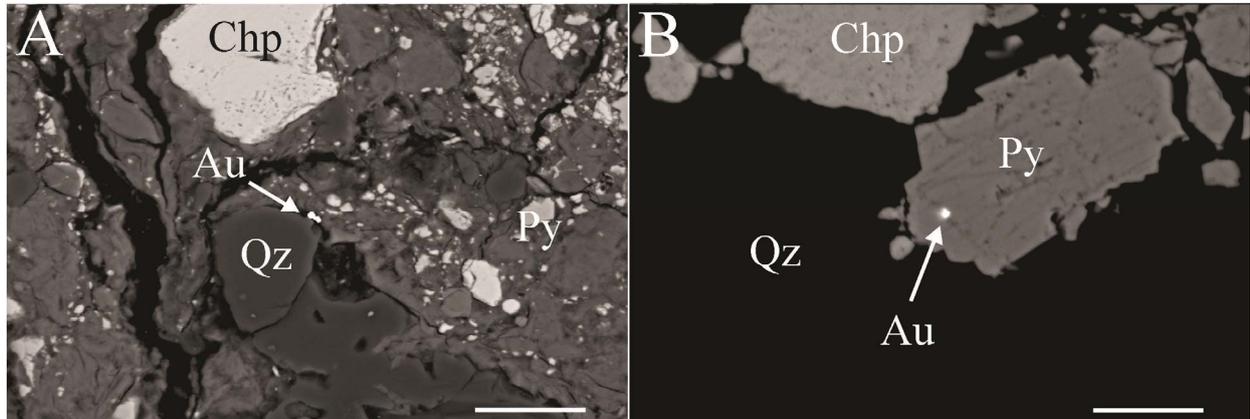


Figure 6. Backscatter electron images of gold (white grains) from the Pozzo mine: (A) several small gold blebs included in chalcopyrite; (B) gold associated with molybdenite; and (C) gold rimmed by magnetite. Abbreviations: Mgt = magnetite, Chp = chalcopyrite, Mol = molybdenite, Chl = chlorite.

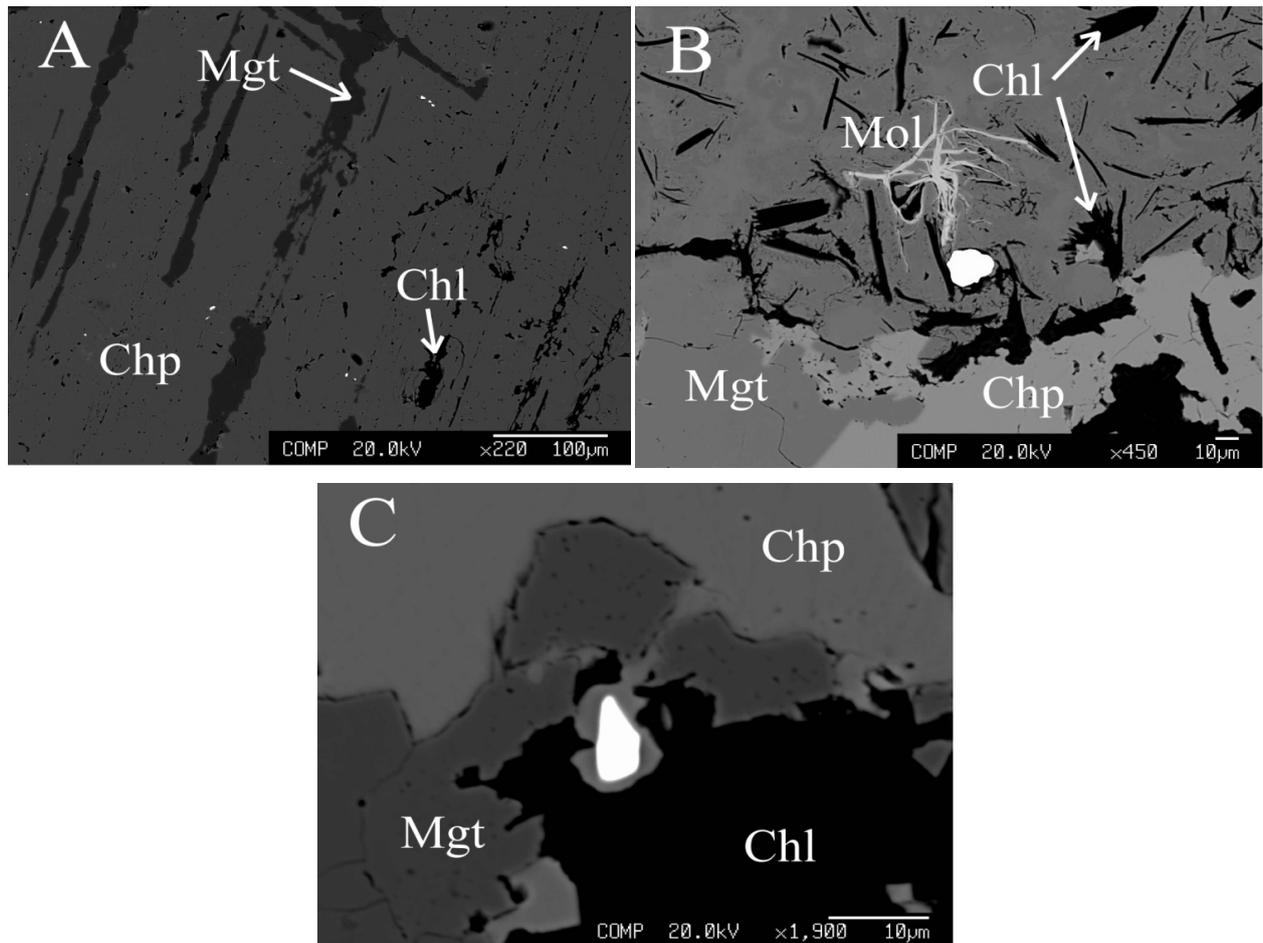


Figure 7. Photomicrographs (reflected light) images of gold grains from the Pozzo mine: (A) gold grains included in chalcopyrite. One of the grains is in contact with magnetite (gray) and (B) gold included in pyrite. Scale bar is 20 μm .

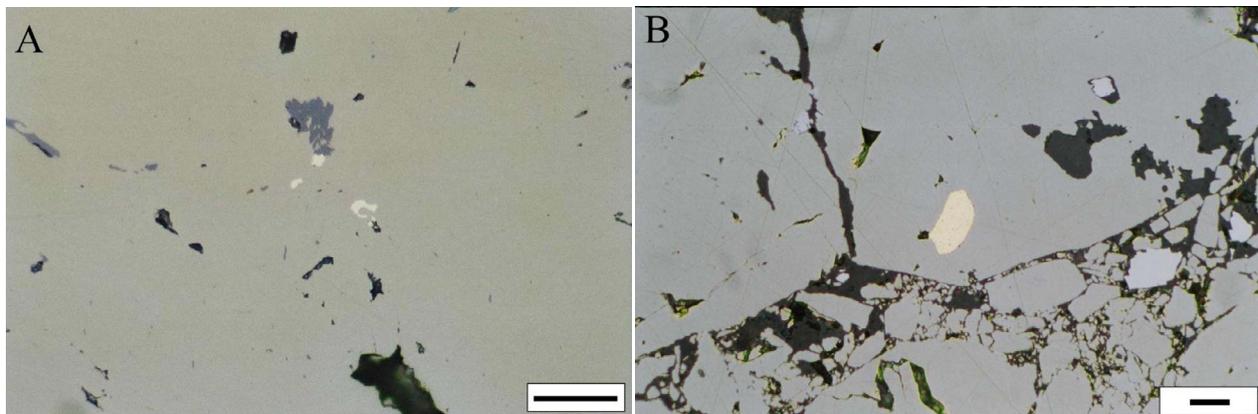
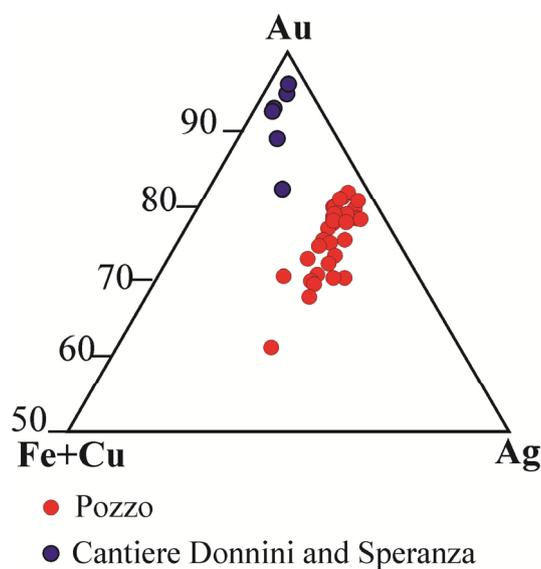


Figure 8. Composition of gold minerals, as at %, in the Au–Ag–(Fe + Cu) ternary diagram. Data of Cantiere Donnini and Speranza are from [1].



6. Concluding Remarks

Field relationships coupled with the geochemical and mineralogical data presented in this contribution suggest that two different types of gold mineralizations have been recognized in the Corchia ophiolite. According to the geochemical data reported by [1], these gold mineralization are not related with the presence of the mineralized quartz hydrothermal veins cutting across serpentinite, gabbro and pillow basalt described in the ophiolites of the Northern Italian Apennines, since they are gold barren. The gold minerals in the Cantiere Donnini and Speranza mines formed at low temperature in submarine environment by loss of Ag during submarine weathering in a way similar to that described for weathered gold nuggets in terrestrial placers and laterite hosted gold deposits [13]. These observations point to the weathering process as the major factor controlling the concentration of gold in these mineralizations and indicate that post-depositional processes of alteration were very active in the stratiform deposits. Gold enrichment has been previously reported from ophiolitic mantle rock, in

particular in the so-called listwanites [14]. Listwanites represents carbonatized peridotites and, according to the observation of [14], based on the investigation of ultramafic rocks in upper Proterozoic ophiolites from Arabia, Mali and Morocco, they can contain up to 10 ppm of gold. The model proposed by [14] implied a mobilization of gold at low temperature (less than 300 °C) by hydrothermal fluids enriched in CO₂ and Ca that produced a metasomatic reaction in the host peridotite. This reaction transformed the mantle peridotite in the listwanite, a rock mainly composed of Mg–Fe–Ca carbonates, with accessory quartz, serpentine, chlorite, fuchsite, Fe-oxides and chromite. The gangue minerals identified in the Pozzo mine mainly consist of serpentine and chlorite (Table 1); thus, this mineralogical paragenesis is not consistent with those described in the gold-bearing listwanite. Therefore, we can argue that the Pozzo mine represents the metamorphic product of a magmatic sulfide mineralization, probably formed at high temperature in the ophiolitic mantle and not during the hydrothermal stage, as also suggested by the sulfur isotope signature. Furthermore, According to this observation and with the available mineralogical data, we can argue that crystallization of gold in this mine started at high temperature, possibly during the formation of an immiscible sulfide liquid. However, this immiscible sulfide liquid was not able to trap and concentrate the PGE, despite the fact that these noble metals are strongly chalcophilic. The effects on the gold minerals produced by the metamorphic overprint are still not understood and need further investigation.

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