

Cobalt pyrite ores in the upper Martello Valley (Alto Adige, Northern Italy)

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ABSTRACT. — The pyrite-rich polymetallic stratiform mineralization occurring at Rifugio Borromeo in the upper Martello Valley (Alto Adige, Northern Italy) is closely linked to two adjacent, but lithologically different horizons (quartzites and chlorite-bearing phyllites) in the phyllites of Venosta Valley Austroalpine basement.

The microprobe analyses show the presence in both horizons of a pyrite very rich in Co and As; moreover, according to the analytical data, the more complex mineralization (Fe-Cu-Zn-Pb-Co-As-Ni-Ag-Bi-Te-Sb-Au) of the chlorite-bearing phyllite horizon presents Ag-Sb-Te-bearing galena, cobaltiferous ullmannite ($(\text{Ni}_{0.43}\text{Co}_{0.57})(\text{As}_{0.04}\text{Bi}_{0.01}\text{Sb}_{0.95})\text{S}_{1.08}$) and hedleyite ($(\text{Bi}_{1.31}\text{Te}_{0.69})$), a term of the tetradymite-tellurobismutite series).

The polymetallic paragenesis rich in Co and the high Co/Ni ratio of the pyrites suggest a volcano-sedimentary origin for the mineralization.

Key words: Austroalpine, Val Venosta phyllite, volcano-sedimentary sequence, sulfide geochemistry, Co-pyrite.

RIASSUNTO. — La mineralizzazione polimetallica stratiforme a prevalente pirite affiorante presso il Rifugio Borromeo in alta Val Martello (Alto Adige, Nord Italia) è concentrata in due livelli limitrofi litologicamente distinti (quartziti, filladi cloritiche) delle filladi austroalpine della Val Venosta.

Le analisi alla microsonda hanno messo in evidenza in entrambi i livelli una pirite molto ricca in Co e As, e nella più complessa mineralizzazione (Fe-Cu-Zn-Pb-Co-As-Ni-Ag-Bi-Te-Sb-Au) dell'orizzonte a filladi cloritiche una galena ricca in Ag, Sb e Te, ullmannite cobaltifera ($(\text{Ni}_{0.43}\text{Co}_{0.57})(\text{As}_{0.04}\text{Bi}_{0.01}\text{Sb}_{0.95})\text{S}_{1.08}$) e hedleyite ($(\text{Bi}_{1.31}\text{Te}_{0.69})$), un termine della serie tetradymite-tellurobismutite).

La paragenesi polimetallica ricca in Co e l'alto rapporto Co/Ni delle piriti suggeriscono un'origine vulcano-sedimentaria della mineralizzazione.

Parole chiave: Austroalpino, filladi della Val Venosta, sequenza vulcano-sedimentaria, geochimica dei solfuri, pirite cobaltifera.

Introduction

This paper deals with the cobalt pyrite rich ores cropping out around Rifugio Borromeo in the upper Martello Valley (Alto Adige, Northern Italy, fig. 1) and already mined in 1540 for copper, silver and gold (WOLFSTRIGEL-WOLFSKRON M.R.V., 1903). The mineralization appears of stratiform type, included within the Venosta Valley phyllite formation pertaining to the Austroalpine crystalline basement. The phyllite formation displays significant features from both metallogenetic (OMENETTO P., BRIGO L., 1974; BRIGO L., 1976; BRIGO L., OMENETTO P., 1978) and geotectonic (GREGNANIN A., PICCIRILLO E.M., 1972, 1974) viewpoints. GREGNANIN A. (1980) assigned to the formation an Upper Ordovician/Devonian sedimentation age with Hercynian metamorphic overprint. In the area the metamorphic assemblages show transition from greenschist to amphibolite (kyanite and/or staurolite) facies.

Two mineralized horizons are observable within a 80 m-thick, ENE-WSW/SSE 40°-50° trending phyllitic sequence, here referred to as the « Borromeo Series ». The graphite- and chlorite-bearing phyllites with minor garnet and kyanite, showing frequent intercalations of grey and white quartzite layers upwards and, at the top, feldspar-rich gneisses, are closely associated with garnetiferous phyllites, approximately in the middle portion of the Venosta Valley phyllite formation. The upper and lower ore-bearing horizons are respectively represented by grey-

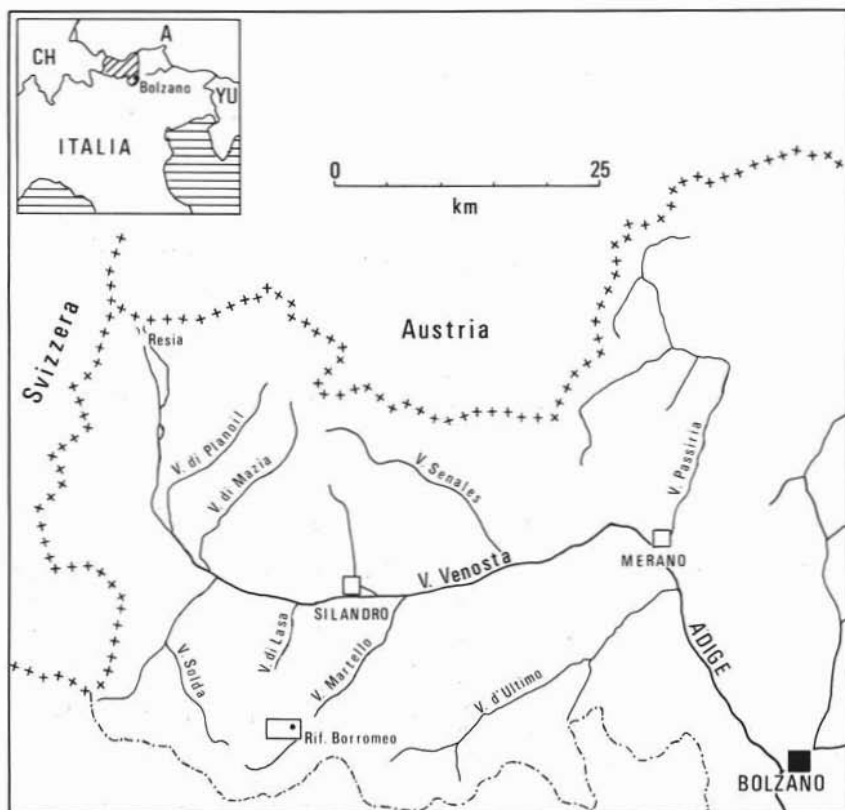


Fig. 1. — Location map of ore-bearing Rifugio Borromeo sequence in the upper Martello Valley.

green microcrystalline quartzites (thickness, 1m) and by poorly graphitic, chlorite-muscovite phyllites (thickness, 3m).

Chemical analyses of mineralized whole rocks and electron microprobe analyses of some peculiar sulfides were carried out together with current microscopic investigation.

Experimentals

The chemical analyses of mineralized whole rocks were carried out at Laboratorio Geominerario - SIMUR (Novazza, Bergamo) and were obtained as follows: Ba, Nb, Sn, Sr, V, Zr, Ti by ICP, S by iodometric titration, F by ISE (Ion-Selective-Electrode), P_2O_5 and Ge by colorimetric method, and the other elements by AAS. Accuracy is 1-2 % for major elements and between 5 and 10 % for minor. The analytical precision has been checked by international standards.

The electron microprobe analyses of some ore minerals were obtained using ARL-SEMQ instrument (Istituto di Mineralogia, Modena University) operated at 20 Kv, 10 nA probe current, defocused beam (spot size = 1 μ m), with on-line data reduction by

ZAF correction method (Magic IV; COLBY, 1968). Natural chalcopyrite and galena were used as standards for Fe, Pb, S, and synthetic standards for Co, Ni, As, Bi, Te, Sb, Ag, Cd.

Analytical data

The two mineralized horizons show different ore paragenesis:

— in the *upper quartzite horizon*, dominant pyrite and sphalerite appear to be concentrated in some mm- to dm-thick beds parallel to the schistosity. The enclosing quartzite is characterized by schistose fabric due to orientation of muscovite and slightly pleochroic chlorite in the fine-grained quartz matrix. Apatite, zircon and tourmaline are present in accessory amounts. The rim, the center or the whole crystal of porphyroblastic to idioblastic pyrite (ϕ : 0.08-1 mm) is frequently anisotropic. In the granular aggregates, anisotropic pyrites show random

TABLE 1
*Chemical analyses of some mineralized samples of quartzite (Bq)
 and chlorite-bearing phyllite (Bcl) horizons*

	Bq-1	Bq-2	Bq-3	Bcl-1	Bcl-2	Bcl-3	Bcl-4	Bcl-5	Bcl-6	Bcl-7
SiO ₂	86.96	41.60	47.07	58.23	51.16	29.32	80.31	78.71	72.04	58.55
Al ₂ O ₃	2.58	0.64	0.86	6.77	10.48	14.97	6.45	6.74	13.02	19.55
TiO ₂	0.19	0.04	0.06	0.35	0.58	0.73	0.46	0.48	0.29	0.75
Fe ₂ O ₃	2.24	30.08	28.13	20.36	23.53	34.93	6.14	6.17	2.21	8.01
MgO	0.53	0.14	0.22	2.48	3.74	6.95	1.05	1.05	1.96	1.89
CaO	0.01	0.03	0.01	0.09	0.14	0.08	<0.01	0.03	0.06	0.31
Na ₂ O	0.07	0.03	0.02	0.07	0.11	0.20	0.06	0.08	0.57	0.35
K ₂ O	0.45	0.09	0.06	0.43	0.61	0.50	0.63	0.93	3.40	4.79
MnO	0.02	0.01	0.01	0.08	0.11	0.16	0.15	0.05	0.02	0.15
P ₂ O ₅	0.02	0.02	0.03	0.08	0.11	0.11	0.05	0.05	0.07	0.17
S	0.13	24.06	21.71	6.70	5.85	7.80	0.03	0.06	0.07	0.20
Cu	31	365	144	22400	16350	6812	250	108	16	56
Zn	133	34540	40690	713	585	1337	88	58	61	83
Pb	27	2431	2585	450	578	219	15	8	43	31
Co	233	417	273	276	251	941	153	130	84	105
Ni	2	3	1	39	31	40	4	5	9	44
As	11	189	157	17	30	232	119	236	7	24
Sb	<0.5	9.4	11.3	1.1	0.9	1.9	<0.5	0.7	<0.5	<0.5
Bi	1.1	17.8	17.1	19.4	26.6	87.8	0.9	1.6	0.6	0.2
Sn	<30	<30	<30	202	304	263	<30	<30	<30	<30
Mo	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3
Au	<0.1	<0.1	<0.1	0.4	0.2	0.2	<0.1	<0.1	<0.1	<0.1
Ag	1	10	9	19	14	6	0.4	0.4	0.1	0.0
Ge	3.9	2.7	2.5	2.7	4.2	2.7	2.5	3.2	2.0	5.7
Cd	<1	156	164	13	10	4	<1	<1	<1	<1
V	13	10	9	40	63	85	35	38	21	104
Be	<1	<1	<1	<1	<1	<1	<1	<1	2	3
Nb	4.2	2.7	1.6	6.6	10.6	12.4	7.0	7.8	4.3	13.5
Zr	46	48	64	22	51	154	95	102	55	74
Li	6	2	3	34	49	65	21	24	38	38
Cr	4	<1	<1	25	41	48	24	22	12	84
Ba	3637	272	49	59	274	383	3098	198	258	492
Sr	40	11	7	13	18	16	64	13	44	83
F	134	73	59	443	705	966	474	492	932	822

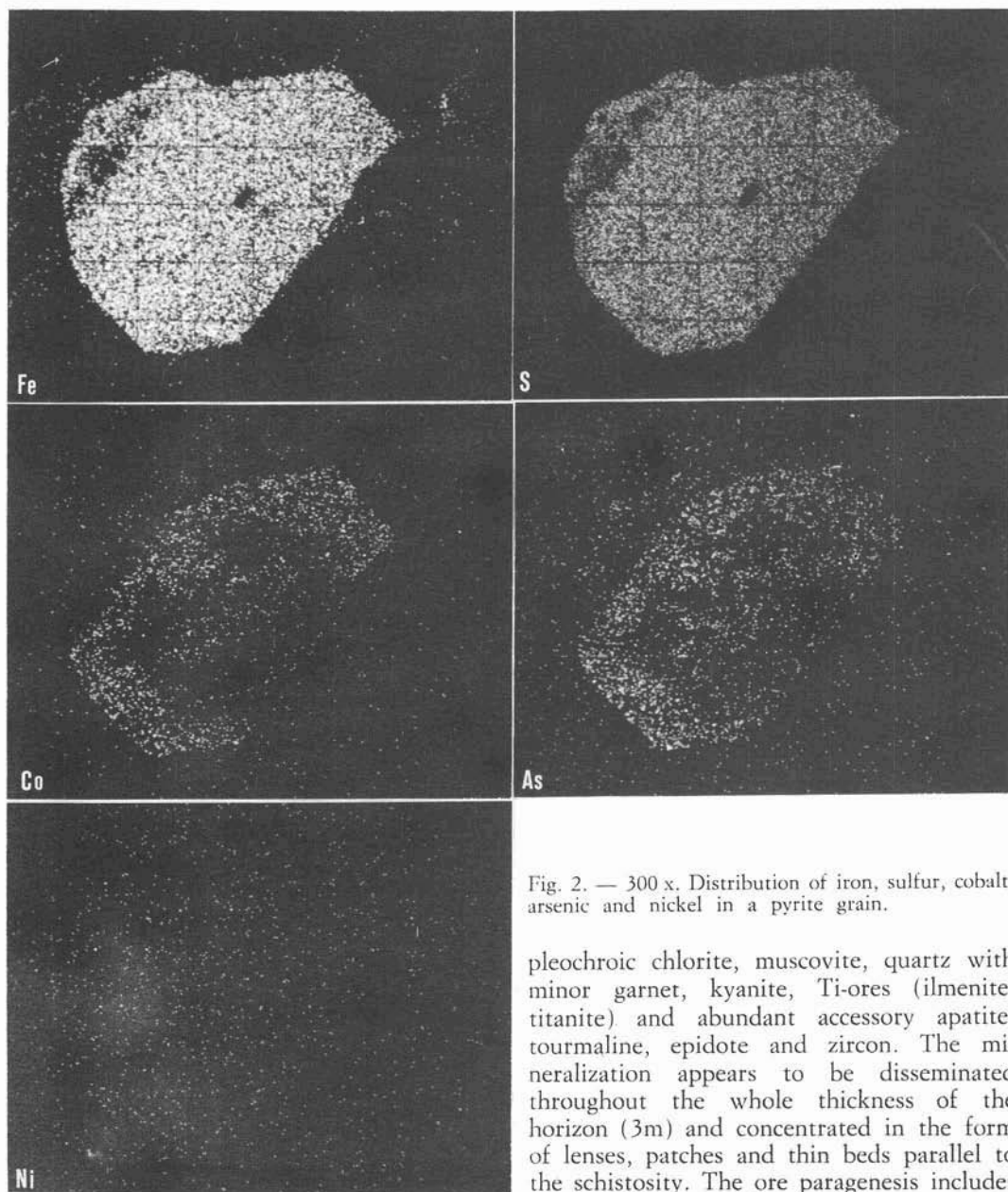


Fig. 2. — 300 x. Distribution of iron, sulfur, cobalt, arsenic and nickel in a pyrite grain.

distribution. Inclusions-free sphalerite pertains to medium iron-bearing type, locally with red internal reflections. Traces of pyrrhotite and chalcopyrite are also visible;

— in the *lower mineralized horizon*, pyrite and chalcopyrite prevail in a slightly folded phyllite matrix composed of strongly

pleochroic chlorite, muscovite, quartz with minor garnet, kyanite, Ti-ores (ilmenite-titanite) and abundant accessory apatite, tourmaline, epidote and zircon. The mineralization appears to be disseminated throughout the whole thickness of the horizon (3m) and concentrated in the form of lenses, patches and thin beds parallel to the schistosity. The ore paragenesis includes pyrite (coarse crystals, irregularly anisotropic, and granular aggregates), pyrrhotite, abundant chalcopyrite with « Oleanderblatt » - type twins, and minor sphalerite and galena. In the galena there are inclusions of native bismuth, ullmannite and of a Bi(Ag)-telluride of tetradyomite-tellurobismuthite series. There are some very rare arsenopyrite (linked to more graphitic intercalations) and very fine gold inclusions.

TABLE 2

Electron microprobe analyses of core (c) and rim (r) of pyrite grains in quartzite

Grain n°	Σ wt. chemical composition									
	Fe		Co		As		Ni		S	
	c	r	c	r	c	r	c	r	c	r
1	46.83	47.12	0.08	0.02	0.02	0.07	0.04	0.07	51.95	51.75
2	46.52	46.90	0.16	0.08	0.04	0.01	0.12	0.00	51.27	51.61
3	47.65	47.73	0.11	0.06	0.01	0.03	0.00	0.82	50.56	49.96
4	47.49	47.09	0.06	0.22	0.00	0.07	0.04	0.07	52.53	52.49
5	47.98	47.23	0.11	0.42	0.00	0.11	0.07	0.00	51.89	51.94
6	47.47	46.92	0.00	0.06	0.03	0.10	0.00	0.03	52.26	51.55
7	46.81	44.19	0.11	2.52	0.04	1.50	0.00	0.65	52.22	50.26

TABLE 3

Electron microprobe analyses of core (c) and rim (r) of pyrite grains in chlorite-bearing phyllite

Grain n°	Σ wt. chemical composition									
	Fe		Co		As		Ni		S	
	c	r	c	r	c	r	c	r	c	r
1	43.57	45.09	2.66	1.55	1.26	0.52	0.00	0.00	52.49	52.83
2	46.86	45.76	0.06	1.04	0.00	0.39	0.04	0.04	53.02	52.77
3	47.14	44.58	0.15	3.00	0.17	2.50	0.00	0.19	52.53	49.72
4	44.80	47.85	2.04	1.90	0.85	0.12	0.00	0.02	52.29	50.09

TABLE 4

Electron microprobe analyses of sphalerite grains in quartzite

Grain n°	Σ wt. chemical composition					Total
	Zn	Cu	Fe	Cd	S	
1	61.20	0.05	7.17	0.25	32.60	101.27
2	61.91	0.02	6.93	0.27	32.68	101.81
3	58.46	0.14	9.57	0.28	32.16	100.61
4	60.72	0.02	7.18	0.24	32.79	100.95
5	59.95	0.00	8.13	0.25	32.87	101.20
6	61.64	0.01	6.24	0.26	32.61	100.76
7	59.50	0.00	6.94	0.29	32.38	99.11
Mean	60.48	0.03	7.45	0.26	32.58	100.81

Table 1, referred to whole rock chemical analyses of mineralized samples, shows that the Bq-quartzites and Bcl-chlorite-bearing phyllites are different for major elements and for Cu, Zn, Pb, Cd, Bi, Ni, Sn, Au, F.

The ore minerals from the paragenetic assemblages of both horizons, which have been subjected to microprobe analyses are

the following: pyrite, sphalerite, galena, Bi(Ag)-telluride and ullmannite.

Pyrite

The results of the analyses carried out at the cores and the rims of several pyrite grains from the two mineralized horizons are shown in table 2 and 3. It is possible to observe:

- significant contents of Co and As (in positive correlation) particularly in the chlorite-bearing phyllite horizon;
- low and localized contents of Ni;
- non-homogeneous distribution of the considered elements, with low (or absent) up to high contents in the whole grain, often in central or in marginal areas of the grain. There is a direct relationship between elements concentration and anisotropy (fig. 2);
- Co/Ni ratio with values > 2 in the quartzite and > 10 in the chlorite-bearing phyllites.

Sphalerite

The sphalerite data contained in table 4 and 5 indicate a homogeneous and uniform distribution of the components. The difference between the two mineralized horizons is particularly emphasized by the higher contents of Cd and Cu in the sphalerite of chlorite-bearing phyllites.

Galena

Tables 6 and 7 show the electron microprobe analyses of some galena grains of the two mineralized horizons. Galena of the upper quartzite horizon is characterized by high Ag- and Sb-contents, attributable to either submicroscopic inclusions of silver-carriers (probably freibergite) or to a solid solution in PbS. Galena of the chlorite-bearing phyllite horizon, at time stoichiometric, appears to be irregularly enriched in Ag, Sb and Te. Here, too, these enrichments are to be referred either to submicroscopic inclusions of one or more Ag-bearing minerals or to solid solution. The absence of Bi could be explained by distinctive mineral assemblages, associated to galena in the form of native Bi (particularly abundant) and a

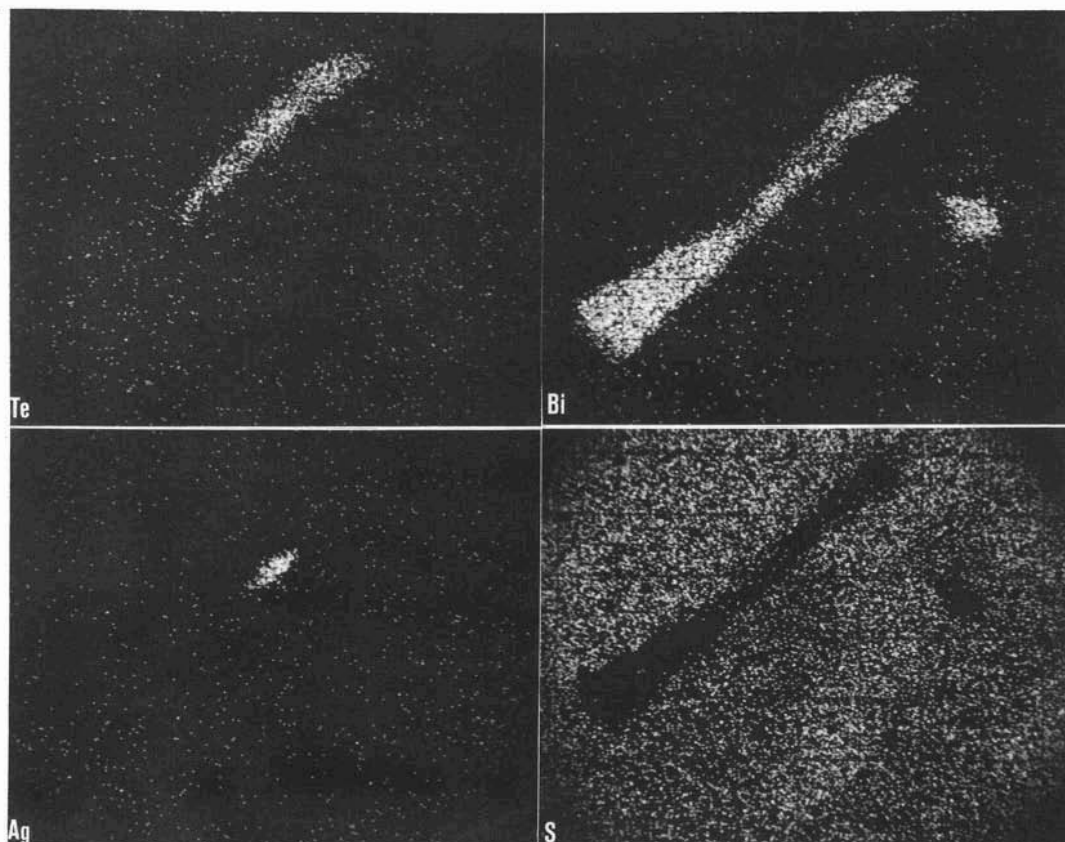


Fig. 3. — 2400 x. Distribution of tellurium, bismuth, silver and sulfur in hedleyite.

rarer Bi-telluride. This is most likely due to formation of new minerals resulting from a selective purification process linked to the recrystallization of galena.

Bi-telluride and ullmannite

The Bi-telluride corresponds approximately to the hedleyite composition ($\text{Bi}_{14}\text{Te}_6$). Electron microprobe analysis gives 79.45 % Bi and 19.28 % Te (total 98.73 wt%) corresponding to $(\text{Bi}_{14.31}\text{Te}_{5.69})$. Fig. 3 shows that Bi-telluride is associated to native Bi, including a native silver grain and is itself included in Te- and Ag-rich galena.

Electron microprobe analysis of a Co-rich ullmannite gives 15.15 % Co, 12.61 % Ni, 55.37 % Sb, 15.92 % S, 1.24 % Bi and 1.39 % As (total 101.23 wt%) corresponding to the formula $(\text{Ni}_{0.43}\text{Co}_{0.53})(\text{As}_{0.04}\text{Bi}_{0.01}\text{Sb}_{0.95})\text{S}_{1.03}$. Fig. 4 shows ullmannite associated with pyrite and gangue minerals.

Conclusions

The two mineralized horizons of the Borromeo series differ according to their lithology, composition and geochemical characters.

The more complex metalliferous paragenesis of chlorite-bearing phyllite (with prevailing Fe-Cu with subordinate Zn, Pb, Co, As, Ni, Ag, Bi, Te, Sb, Au) contrasts with the simpler paragenesis of quartzite (with prevailing Fe, Zn and minor Pb, Co, As, Ni, Cu, Ag, Sb). Both horizons have cobaltiferous pyrite in common. The Co content, higher in the lower horizon, is characterized by a non-homogeneous distribution, with frequent enrichment at the rims. Such enrichment at the idiomorphic pyrite grain rims (up to 4 % Co) is typical of Cu-Co deposits of sedimentary origin at Kamoto in Congo (BARTHOLOMÉ and KATEKESHA, 1971). BROWN and BARTHOLOMÉ

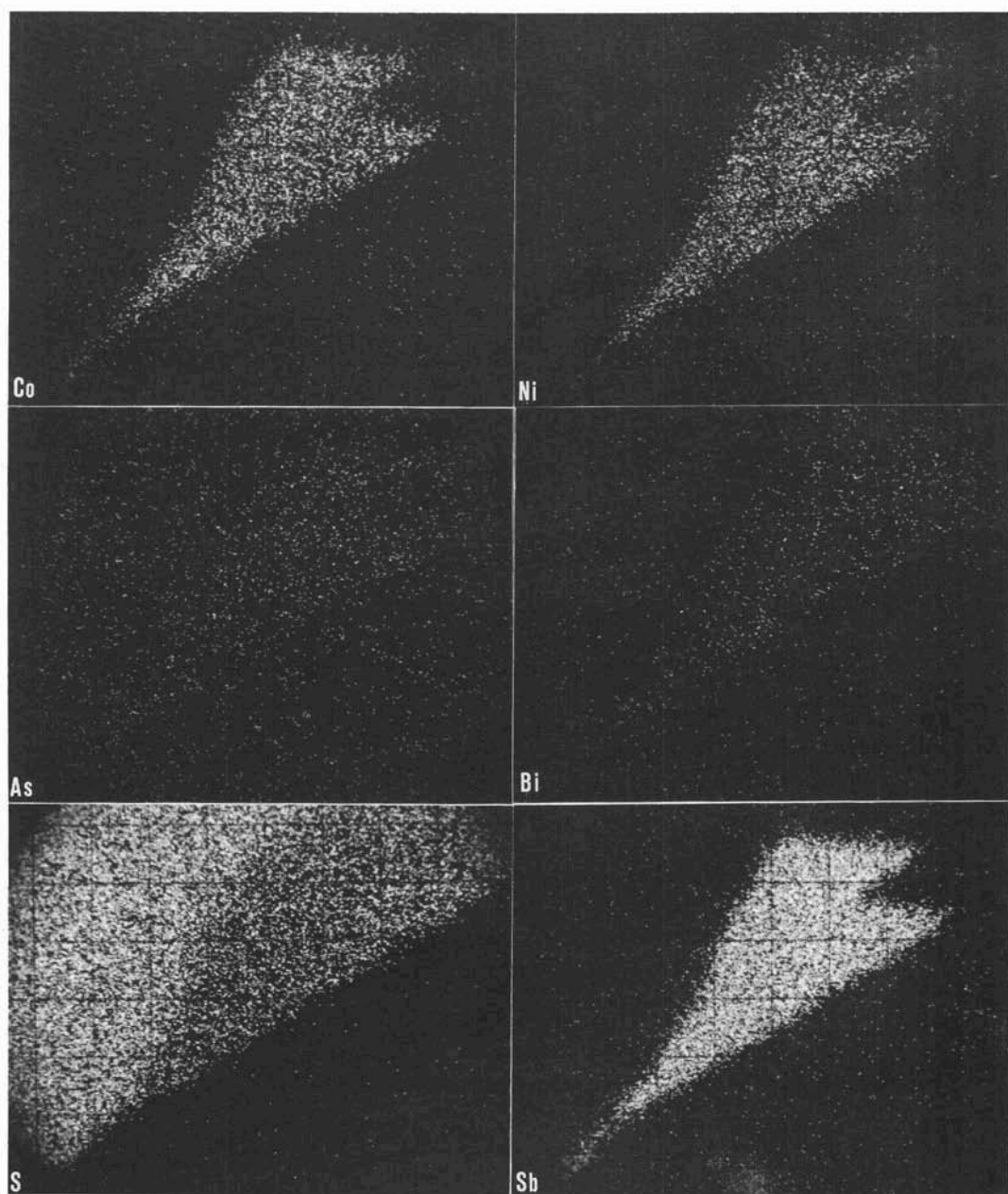


Fig. 4. — 2700 x. Cobalt, nickel, arsenic, bismuth, sulfur and antimony distribution in ullmannite.

(1972) report that the recrystallization under regional and/or local metamorphism may apparently homogenize some pyrite (Cu-Co deposits in the Zambian copperbelt) and they remark that preliminary studies suggest that genetic interpretations may be derived

from textures preserved in nonhomogeneous grains.

The significance of the Co/Ni ratio of pyrite as a geochemical parameter for the genetical interpretation of deposits, is still a controversial matter. In fact, according to

TABLE 5
*Electron microprobe analyses
of sphalerite grains in chlorite-bearing phyllite*

Grain n°	wt. chemical composition					Total
	Zn	Cu	Fe	Cd	S	
1	58.48	0.11	6.38	1.51	33.47	99.95
2	58.17	0.36	5.94	1.53	33.36	99.36
3	58.51	0.43	6.79	1.53	33.46	100.72
4	59.23	0.13	6.29	1.55	33.53	100.73
5	59.21	0.10	6.87	1.57	33.57	101.32
Mean	58.72	0.23	6.45	1.54	33.48	100.42

TABLE 6
*Electron microprobe analyses
of galena grains in quartzite*

Grain n°	wt. chemical composition					Total
	Pb	Ag	Te	Sb	Bi	
1	88.12	0.00	0.00	0.00	0.00	13.11
2	85.72	0.47	0.00	0.25	0.00	13.00
3	87.35	0.52	0.00	0.31	0.00	13.51
Mean	87.06	0.33	0.00	0.19	0.00	13.21

TABLE 7
*Electron microprobe analyses of galena grains
in chlorite-bearing phyllite*

Grain n°	wt. chemical composition					Total
	Pb	Ag	Te	Sb	Bi	
1	86.03	0.18	0.09	0.27	0.00	13.21
2	85.48	0.72	0.12	0.24	0.00	13.47
3	84.77	0.14	0.09	0.01	0.00	13.51
4	87.69	0.10	0.01	0.21	0.00	13.46
5	86.75	0.00	0.13	0.38	0.00	13.58
6	87.65	0.00	0.00	0.00	0.00	12.59
7	87.75	0.00	0.00	0.00	0.00	13.06
Mean	86.59	0.16	0.06	0.16	0.00	13.27

LOFTUS HILL and SOLOMON (1967) the < 1 Co/Ni ratio is typical of deposits of sedimentary or diagenetic origin in shales (with contents high in Co and Ni) and of those of probable volcanic origin associated with Zn and Pb ores (low contents in Co

and Ni); high Co contents may be related to volcanic processes. BRALIA et al. (1979), instead, in their studies on Tuscan pyrites considered values of Co/Ni > 5 up to 50 to be typical of volcanogenic pyrites. On the other hand CAMPBELL and ETHIER (1983) suggested that the genetic fields based on Co/Ni ratio of pyrite/pyrrhotite are incompletely defined and do not permit the genetic classification of Faro and Sullivan-type ore-bodies.

Co/Ni ratios in pyrites of the mineralizations studied in this work are often particularly difficult to assess because of the non-homogeneous Ni distribution (in many case Ni is absent or only locally concentrated). However, the values calculated are extremely variable, being lower for the quartzites (Co/Ni values > 2), and much higher for chlorite-bearing phyllites (Co/Ni > 10). According to BRALIA et al. (1979) these values, are typical of a volcanic-exhalative environment, whereas CAMPBELL and ETHIER's considerations do not allow a genetic classification.

Therefore, for a genetic interpretation of the Martello Valley mineralization, only the following parameters may be considered as particularly significant: the lithological association and the polymetallic paragenesis with abundant Co, which would suggest a volcano-sedimentary origin for the portion of Venosta Valley phyllite complex (including marine sediments and volcanic rocks) cropping out between the Pozzo, Madriccio and Peder Valleys, on the left side of the upper Martello Valley.

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