Atti Soc. Tosc. Sci. Nat., Mem., Serie A, **95** (1988)
pagg. 51-62, figg. 4, tabb. 3

V. Duchi (*), A. Minissale (**), M. Paolieri (*)

A GEOCHEMICAL CONTRIBUTION TO THE METALLOGENY OF THE BOTTINO-GALLENA Pb-Ag-Zn-SULPHIDES ORE-BODIES FROM APUANE ALPS, NORTHERN TUSCANY, ITALY

Abstract — The present study deals with the Pb-Zn-Ag deposits of Bottino-Gallena area (Apuan Alps). The distribution of Zn, Pb, Cu and Ag in the mineralized veins, as well as in both the wall and country rocks, suggests a syntectonic lateral secretion origin for the ore deposition. The main evidence of this is in the low Zn, Pb and subordinately Ag and Cu contents in the wall rock of the main mineralized area when compared with nearby sterile areas. Furthermore the silica distribution all around the mineralized quartz veins is clearly well below the regional background. All this excludes contributions from epithermal deep seated fluids.

Riassunto — *Contributo geochimico alla metallogenesi dei giacimenti a solfuri di Pb-Ag-Zn dell'area Bottino-Gallena nelle Alpi Apuane (Toscana, Italia).* Il confronto incrociato tra i tenori degli elementi maggiori e degli elementi metallici Pb, Zn, Ag e Cu nelle rocce incassanti i principali filoni dell'area mineralizzata di Bottino-Gallena, sia rispetto al *clark* calcolato nell'area della valle del Giardino suggerisce che la mineralizzazione si sia formata per secrezione laterale, senza apporti di fluidi idrotermali.

Key words — Geochemistry, Metallogeny, Lateral secretion, Tuscany.

Introduction

The Apuan Alps are a small area located in north-west Tuscany near the Tyrrhenian sea (Fig. 1). The region is famous for the «Carrara» marble, which still represents the most important product of quarry activity. In addition, many minor mining activities were developed in the last century for the production of iron, manganese,

(*) Dipartimento di Scienze della Terra, Università di Firenze, Via La Pira 4, 50121 Firenze.
(**) C.N.R. Centro Studi per la Mineralogia e la Geochimica dei Sedimenti, Via La Pira 4, 50121 Firenze.

lead, zinc, copper, mercury, pyrite and barite (CARMIGNANI *et al.*, 1972). Most of these mines (Fig. 1) have been exhausted. The origin of many ores is still under debate. According to BERGMANN (1969) most of

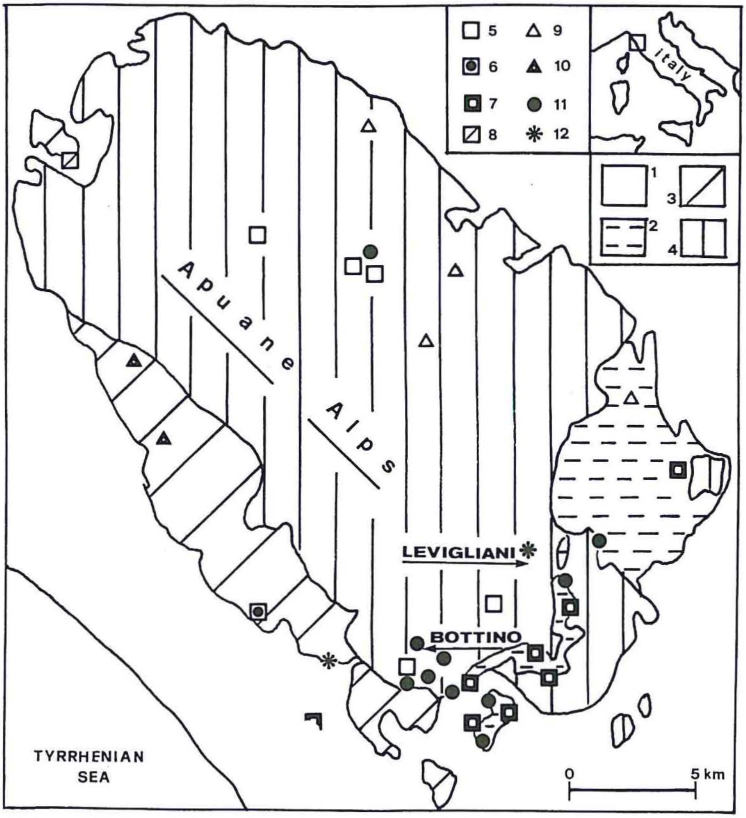

Fig. 1 - Sketch map of the Apuan Alps (after Cortecci et al., 1985) with the main mineralized areas. 1) «Tuscanid» and «Ligurid» nappes; 2) «Fornovolasco-Panie» unit; 3) «Massa» unit; 4) «Nucleo Metamorfico Apuano» unit; 5) Fe; 6) Fe (Mn, Cr); 7) barite-pyrite-Fe; 8) Mn; 9) Cu; 10) Cu (Fe); 11) Pb, Zn, Ag; 12) Hg.

the Apuan are exhalative Permo-Triassic deposits. A syngenetic origin was also proposed by NATALE (1974), CIARAPICA *et al.* (1983), TANELLI (1983) and CORTECCI *et al.* (1985). These authors suggest a Triassic sedimentary-diagenetic origin for the barite-iron oxide-pyrite ores of the Apuan Alps, with final enrichment during the metamorphic stage of the Apennine tectogenesis. On the contrary Carmignani *et al.* (1972; 1975; 1976) propose an epigenetic model, where the ore bodies are deposited from hydrothermal solutions related to hypothetical synkinematic granites.

The mineralogy, attitude and sulphide chemistry of the Pb-Ag-Zn deposits of Bottino (Benvenuti *et al.*, 1988) suggest a clear relation between the genesis of the mineralization and some tormalinolite levels embedded in the pre-Triassic phyllitic formations of the «Nucleo Metamorfico Apuano». These levels underwent, during the Apennine tectogenesis, multiple displacements and lamination (quartz veins) phenomena associated to a shear zone. In this context the present study tries to define the geochemistry of the main mineralized quartz veins, as well as the wall and country rocks in the Bottino-Gallena area.

Geological setting and mineralogy

The geological setting of Apuan Alps is highly complicated, as several metamorphic and sedimentary tectonic units from Paleozoic to Oligocene are piled up in narrow areas. The scarcity of recognizable fossils in the metamorphic formations make the stratigraphic and palaeogeographic reconstruction quite difficult.

According to Ciarapica and Passeri (1982), the lowermost geological unit is the «Nucleo Metamorfico Apuano», overlain by the metamorphic «Unità di Massa», in turn overlain by the weakly metamorphic «Unità di Fornovolasco Panie». Allochthonous sedimentary complexes («Tuscanidi» and «Liguridi») lie on top (Fig. 1).

The «Nucleo Metamorfico Apuano» formations occupy most of the study area (Fig. 2). From the bottom they are represented by phyllites («Lower Phyllites» formation), with interbedded basic metavolcanites; quartzites and phyllites («Upper Phyllites» formation), with interbedded acidic volcanites («Porfiroidi») and their sedimentary products («Scisti Porfirici»). Triassic evaporitic terrains («Grezzoni» formation) interposed locally with Triassic clastic sediments («Verrucano») lie over the phyllitic formations. The «Grezzoni» formation is followed by carbonatic («Marble») and clastic formation from Jurassic to Oligocene.

The metamorphic grade reached by the «Nucleo Metamorfico Apuano» is the greenschist facies, with temperature and pressure ranging respectively 300-400 °C and 300-400 MPa (Carmignani *et al.*, 1987.

As said above, the scarcity of microfaunas in the phyllitic formations (both «Lower» and «Upper»), as well as in the metavolcanites («Scisti Porfirici») has led to different evaluations of their age. Con-

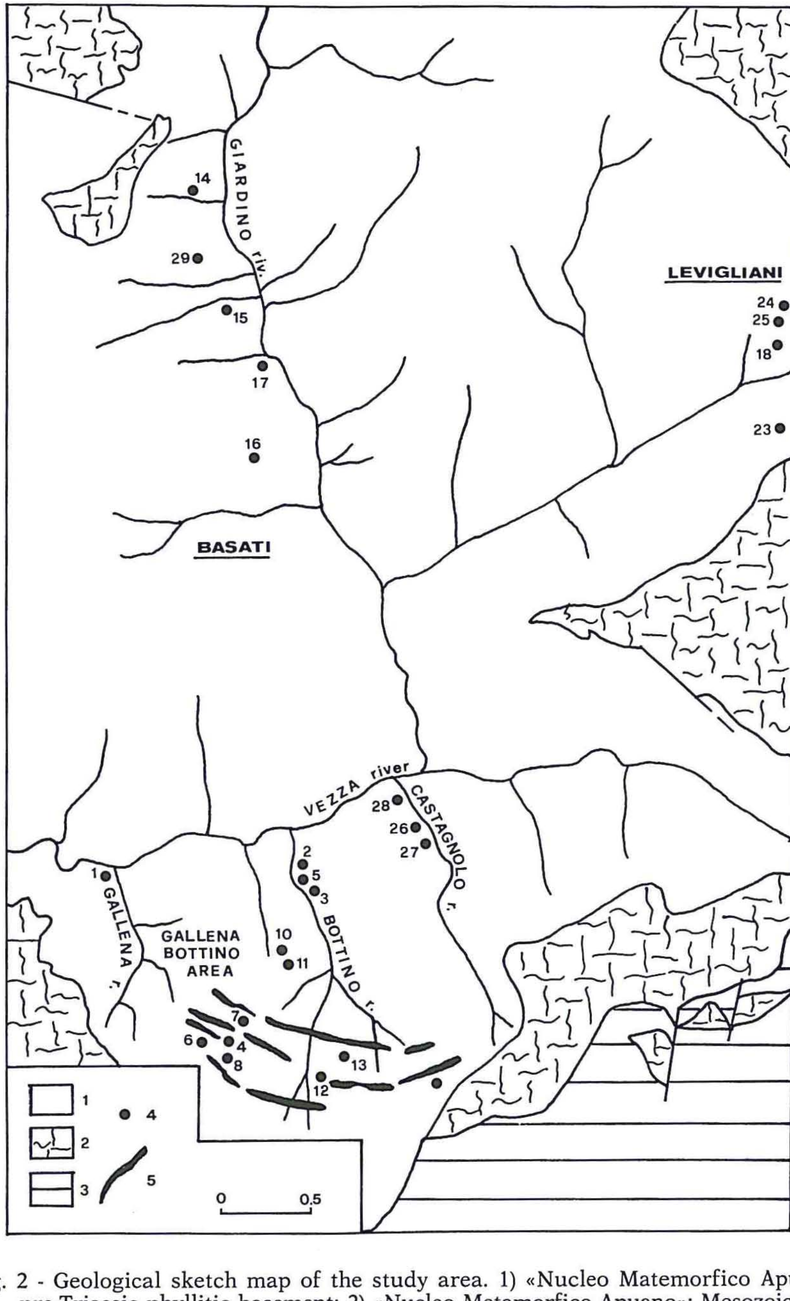

Fig. 2 - Geological sketch map of the study area. 1) «Nucleo Matemorfico Apuano»: pre-Triassic phyllitic basement; 2) «Nucleo Metamorfico Apuano»: Mesozoic cover formations; 3) Non metamorphic formations in «Tuscan» series; 4) sampling points; 5) mineralized quartz veins.

sidered Permo-Carboniferous (e.g. BARBERI and GIGLIA, 1966), in 1972 some dolomitic layers («Dolomie ad Ortoceras») embedded in the «Upper Phyllites» formation have been interpreted as Silurian, although as olistolites in the Carboniferous formations. More recently BAGNOLI *et al.* (1979) and PUXEDDU *et al.* (1984), in a review on the Tuscan crystalline basement, suggest a Siluro-Devonian pre-Sudetian age for both the «Upper» and «Lower» phyllites and related metavolcanites.

The Pb-Zn-Ag ores of Bottino-Gallena consist of a quartz vein system outcropping from Gallena creek to Castagnolo creek (Fig. 2). The veins are associated with the phyllitic paleozoic terrains, and most of them appear to be related to tormalinite levels. Mineralogy consists mainly of galena and sphalerite, pyrite, chalcopyrite, arsenopyrite, pyrrotine with local sulphosalts including tetrahedrite. Gangue minerals are mostly quartz with minor calcite, siderite, tourmaline, ankerite and fluorite (BENVENUTI *et al.*, 1988).

GEOCHEMISTRY

Twenty five samples of Paleozoic phyllites, five of which were collected at increasing distance from the main quartz vein in the Bottino area, and six samples from mineralized quartz veins, have been analyzed (Tab. 1, Tab. 2 and Fig. 2). Zn, Pb, Cu and Ag have been determined with A.A. spectrophotometry and A.A. spectrophotometry with graphite furnace, in solutions from $HF+HClO_4$ etching, excepting for Ag, which has been determined in solutions from aqua regia etching.

The main constituents of the 16 samples of phyllites in Table 1 have been determined to evaluate the background value in the area. Silica, Ti, Al, Fe, Mn, Ca and K have been determined by X-ray fluorescence; Mg and Na with A.A. spectrophotometry. Table 2 reports the regional background for both the metals studied and the main components in the phyllitic formations. Table 3 reports the average metal values in each single sampling area (Bottino, Gallena, Castagnolo, Levigliani and Giardino in Fig. 2).

The following are the results

Zn - The mean value in the study area ($\bar{x}=97.1$ ppm in Tab. 2) is

TABLE 1. - *Chemical analyses for samples collected in the study area (Fig. 2).*

n.	area	type	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	LOI	Zn^1	Pb^1	Cu^1	Ag^2	tot.
1	Gallena	ph	71.01	1.15	11.73	1.85	2.84	0.07	1.56	1.68	4.97	0.66	2.47	56	3.6	19.2	0.012	99.99
2	Bottino	ph	74.97	0.77	12.77	1.40	2.00	0.02	1.13	0.15	2.75	2.00	2.04	52	3.5	4.4	0.009	100.00
3	»	ph	67.84	0.60	16.74	2.69	1.60	0.05	1.25	0.13	2.75	3.57	2.79	129	4.2	6.4	0.020	100.01
4	»	qv												40	0.8	7.7	0.012	
5	»	qv												159	4.2	31.4	0.008	
6	Gallena	ph	67.71	0.85	14.83	3.04	2.60	0.02	1.58	0.19	4.49	1.89	2.79	102	5.4	12.3	0.075	99.99
7	»	ph	63.88	0.78	17.42	1.97	3.72	0.03	2.43	0.12	4.49	2.14	3.02	102	5.1	18.2	0.065	100.00
8	»	qv												218	357.0	4.2	2.400	
10	Bottino	qv												101	14.6	16.7	0.062	
11	»	ph	77.36	0.67	12.77	0.87	0.28	0.02	0.23	0.13	5.26	1.62	0.79	20	3.2	8.1	0.060	100.00
12a	»	qv												4900	430.0	40.0	2.250	
12b	»	qv												17200	1133.0	26.2	1.700	
12c	»	qv												490	145.5	18.7	0.320	
13	»	ph												6	2.3	1.9	0.055	
14	Gallena	ph	60.61	0.97	14.18	2.11	4.36	0.18	3.39	3.74	0.85	2.74	6.85	197	8.0	11.7	0.062	99.92
15	Giardino	ph	56.26	1.11	15.98	2.48	4.96	0.12	2.70	4.26	5.47	1.44	5.27	99	3.6	11.0	0.010	100.05
16	»	ph	61.12	0.93	18.14	3.17	4.32	0.05	2.73	0.18	3.39	2.77	3.08	99	3.0	15.3	0.020	99.88
17	»	ph	73.33	0.82	12.85	1.25	3.04	0.05	0.90	0.70	2.88	1.74	2.43	61	3.2	4.9	0.030	99.99
18	Levigliani	ph	73.19	0.32	14.23	0.96	1.36	0.03	0.61	0.10	0.20	3.21	5.72	48	4.5	12.1	0.010	99.93
23	»	ph												11	6.0	3.6	0.010	
24	»	ph	75.99	0.15	7.39	1.88	2.14	0.11	1.17	4.50	0.15	2.00	4.55	19	11.9	3.1	0.020	100.03
25	»	pf	66.36	0.43	17.93	3.43	0.54	0.05	0.60	0.11	0.22	5.44	4.72	64	64.0	16.2	0.010	99.83
26	Castagnolo	ph	70.26	0.58	14.38	1.87	2.40	0.06	1.45	0.52	4.53	2.10	1.87	162	17.9	10.6	0.030	100.02
27	»	ph	61.96	0.71	15.57	2.13	4.90	0.10	2.90	1.23	2.50	4.11	3.90	161	16.4	26.0	0.100	100.01
28	»	ph	70.84	0.58	13.98	1.71	2.36	0.04	1.38	0.44	4.28	2.46	1.82	193	4.9	9.5	0.020	99.89
29	Giardino	ph												112	4.7	7.7	0.010	

ph = phyllite; qv = quartz vein; pf = «Porfiroide»; Zn, Pb, Cu and Ag are in ppm.
(1) Analytical data after HF + $HClO_4$ etching; (2) Analytical data after aqua regia etching.

TABLE 2. - *Chemical data for samples collected at increasing distance from a mineralized vein in the Bottino area (sample CD in Fig. 2), compared with the regional background in the phyllite formations.*

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	LOI	Zn[1]	Pb[1]	Cu[1]	Ag[2]	tot.
quartz vein	58.43	0.08	2.43	3.30	11.44	0.08	4.17	4.84	0.07	0.52	12.63	6262	990	11.9	3.90	98.61
0.5 m	67.47	0.75	16.21	0.59	3.54	0.15	1.00	0.69	1.08	3.84	4.29	4506	100	10.8	0.45	100.06
1.2 m	58.80	0.88	18.63	2.37	4.20	0.26	1.63	1.27	1.83	3.78	5.89	375	13	7.6	0.16	99.54
2.5 m	51.16	1.04	24.25	4.10	4.56	0.15	2.80	0.18	2.45	4.54	4.28	104	12	12.0	0.09	99.60
5.0 m	53.14	1.18	24.31	4.00	3.00	0.12	2.58	0.29	1.19	5.60	4.25	43	7	8.9	0.03	99.66
background	68.03	0.71	14.40	5.05		0.06	1.62	1.13	3.07	2.49		97	7	11.0	0.03	

(1) Analytical data after HF + $HClO_4$ etching;
(2) Analytical data after aqua regia etching.

TABLE 3. - *Statistical parameters for the phyllitic formations for individual areas.*

SITE		x̄ (ppm)	s	Cv (%)
Bottino (4)	Zn	90.0	59.0	52.0
	Pb	3.8	0.5	13.0
	Cu	9.6	8.1	84.9
	Ag	0.02	0.02	100.1
Gallena (4)	Zn	114.0	59.0	52.0
	Pb	5.5	1.8	33.0
	Cu	15.4	3.9	25.0
	Ag	0.05	0.03	53.0
Giardino (4)	Zn	92.5	22.0	24.0
	Pb	3.6	0.8	21.0
	Cu	9.7	4.5	46.0
	Ag	0.02	0.01	53.0
Levigliani (4)	Zn	35.4	24.6	69.0
	Pb	7.5	3.9	52.0
	Cu	8.8	6.5	74.0
	Ag	0.01	0.01	43.0
Castagnolo (3)	Zn	172.0	18.0	10.0
	Pb	13.1	7.1	54.0
	Cu	15.4	9.2	60.0
	Ag	0.05	0.04	87.0

In brakets are reported the number of samples considered.

similar to the values in the Bottino ($\bar{x}=90$ ppm), Gallena ($\bar{x}=114$ ppm) and Giardino ($\bar{x}=92$ ppm) areas (Tab. 3). The Levigliani samples have low Zn content ($\bar{x}=35$ ppm); the Castagnolo samples are anomalously high ($\bar{x}=172$ ppm). Comparing the mean values in the mineralized area it is interesting to note that the Bottino samples, which are from the most mineralized area show the lowest mean value ($\bar{x}=90$ ppm) compared with the Castagnolo samples ($\bar{x}=$ 172 ppm), where there are no mineralized veins.

Pb - The distribution of Pb is similar to that of Zn. The Castagnolo samples ($\bar{x}=13$ ppm) and Levigliani ($\bar{x}=7.5$ ppm) are anomalously high when compared with the background ($\bar{x}=6.3$ ppm). In the mineralized areas of Bottino and Gallena, on the contrary, the Pb content in the country rock is very low ($\bar{x}=3.8$ and 5.5 ppm respectively).

Cu and Ag - These elements show an irregular behavior with respect to Zn and Pb. However the lowest values are still those in the Bottino area.

Of course the quartz vein samples (qv in Tb. 1) are the most enriched in the area in all metals. However, it is interesting to note in sample no 12 that Ag is mostly linked to the centre of the quartz vein (samples 12a), while Pb and Zn are enriched in the phyllitic wallrock (samples 12b and 12c).

The already pointed low metal contents in the phyllite samples from the mineralized Bottino-Gallena area compared to the rest of samples in the study area, suggest a local origin for the ore deposition, without large circulation of deep hydrothermal fluids. Five phyllites samples at increasing distance (0.5, 1.25, 2.5 and 5 metres) from the main quartz vein in the Bottino area have been analyzed to confirm this hypothesis. Table 2 shows the analytical results for these samples (CD in Fig. 2). The vein is made up (after X-ray diffraction) of quartz and siderite, ankerite and micas in lesser amount.

Figure 3, where the dispersion pattern for the main constituents are shown, clearly demonstrates that the silica content around the

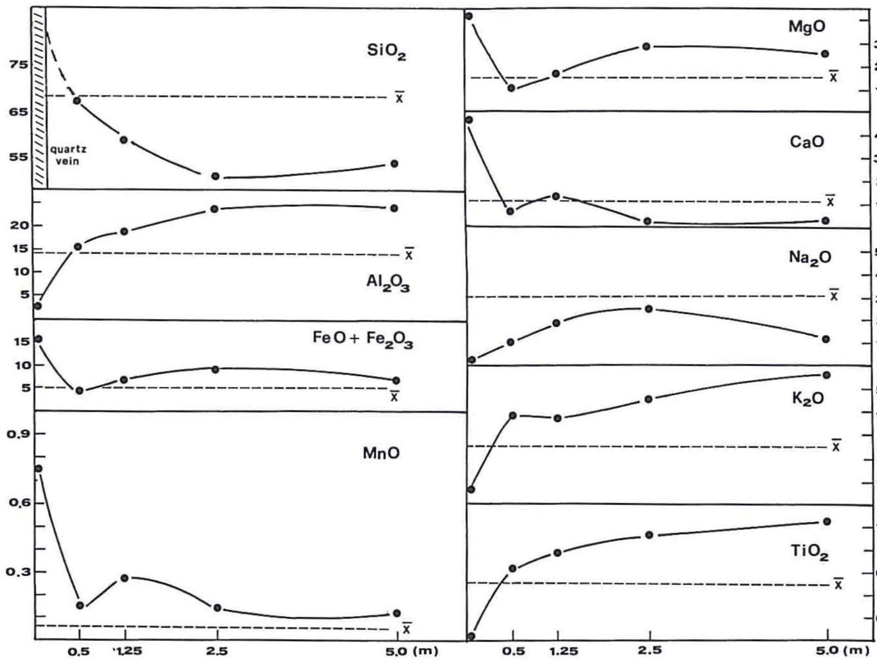

Fig. 3 - Distribution pattern for the main components (in %) of CD samples in Fig. 2. The background values ($\bar{x}$ are reported for comparison. (See text).

quartz vein (53.14% at 5 m) is well below the regional background (68.03%). The apparent relative low silica value of the vein sample in Fig. 3, which is lower than the regional mean value, is caused by the abundant carbonates in the matrix. The loss of ignition (LOI) lowers about 25-30% the true silica value. The dotted line for silica in Figure 3 points to the theoretical values. The remaining is due to sulphides, oxides and alteration minerals, which is confirmed by the high Fe, Mn, Ca and Mg content in the vein sample.

The dispersion diagram for the metals analyzed, and reported in Figure 4, shows that Zn, and to a lesser extent Pb and Ag are

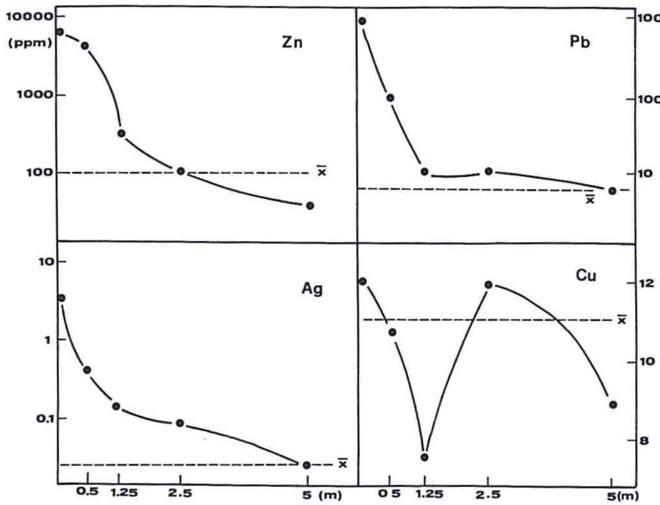

Fig. 4 - Distribution pattern for the study metals (in ppm) of CD samples in Fig. 2. (See text).

enriched in the quartz vein sample and show the same pattern as silica. The 5 m values for those elements are already below the regional background reported in Tab. 2. All this suggests that the metal deposition in the Bottino area is of local origin, due to the «squeezing» of wall rocks, and not due to deep rising fluids. The metal contents in the phyllite formations in the Bottino-Gallena area, which are the lower in the study area, points to the same conclusion.

Conclusions

The ore deposits in the Bottino-Gallena area seem to have a syntectonic origin. As already pointed in the introduction section, the

Apuan Alps have many types of mineralizations. Some of them, and in particular the barite-pyrite and barite-iron oxide-pyrite (e.g. the one described in BENVENUTI *et al.*, 1986), have been formed in the Ladinian-Carnian in a coastal logoonal environment of the «Grezzoni» formation. The Pb, Zn and Ag deposit of Bottino area seems to have a different genesis and probably a different metallogenic period. Taking into account the age of the «Lower» and «Upper» phyllite formations, some speculations about the period of the metamorphic event which could have fovoured the lateral secretion for the Bottino-Gallena deposits can be made. The principal metamorphic event recorded in the Apuan Alps is dated 27 Ma, others date 24, 20, 12 and 8 Ma (KLIGFIELD *et al.*, 1981; 1986). The ore deposition is probably connected to one or more of these apennine metamorphic events. The main clue of this hypothesis is in the conformity between ore-bodies and main schistosity. Anyway, an ercinic metamorphic event for the metals enrichment in the Bottino-Gallena area cannot be completely ruled out. In fact, relict preapennine schistosity planes are reported e.g. in GUNTHER and WALLBRECHER (1977). Furthermore, at least in the Bottino-Gallena area, the mineralization never crosses the Triassic «Grezzoni» formation, and this does not agree with an Apennine metamorphic phase.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. Tanelli, University of Florence, for the critical revision of the manuscript.

REFERENCES

BAGNOLI G., GIANELLI G., PUXEDDU M., RAU A., SQUARCI P., TONGIORGI M. (1979) - A tentative reconstruction of the Tuscan Paleozoic Basement. *Mem. Soc. Geol. Ital.*, **20**, 99-116.

BARBERI F., GIGLIA G. (1966) - La serie scistoso-basale dell'autoctono delle Alpi Apuane. *Boll. Soc. Geol. Ital.*, **84**, 41-92.

BENVENUTI M., LATTANZI P., TANELLI G., CORTECCI G. (1986) - The Ba-Fe-pyrite deposit of Buca della Vena, Apuan Alps, Italy. *Rend. Soc. Ital. Min. Petrol.*, **41**, 347-358.

BENVENUTI M., LATTANZI P., TANELLI G. (1988) - Tormalinolite-associated Pb-Ag mineralization of Bottino-Gallena, Apuane Alpes, Italy. *Econ. Geol.* (submitted).

BERGMANN H. (1969) - Geologische und lagerstattenkundliche Unter suchungen in den sudwestliche Apuaner Alps (Toscana, Italien). *Doktoral Dissertation*, München, 1-78.

CARMIGNANI L., DESSAU G., DUCHI G. (1972) - I giacimenti minerari delle Alpi Apuane e le loro correlazioni con l'evoluzione del gruppo montuoso. *Mem. Soc. Geol. Ital.*, **11**, 417-431.

CARMIGNANI L., DESSAU G., DUCHI G. (1975) - Una mineralizzazione sintettonica: il giacimento di Valdicastello (Alpi Apuane). *Boll. Soc. Geol. Ital.*, **94**, 725-758.

CARMIGNANI L., DESSAU G., DUCHI G. (1976) - I giacimenti a barite, pirite e ossidi di ferro delle Alpi Apuane: studio mineralogico e strutturale. *Boll. Soc. Geol. Ital.*, **95**, 1009-1061.

CARMIGNANI L., GATTIGLIO M., KALIN O., MECCHERI M. (1987) - Guida alla escursione sul complesso metamorfico delle Alpi Apuane. In: «Summer school di Geologia e Petrologia dei Basamenti Cristallini», C.N.R. - Università di Siena.

CARMIGNANI L., GIGLIA G., KLIGFIELD R. (1978) - Structural evolution of the Apuan Alps: an example of continental margin deformation in the northern Apennines, Italy. *Journ. Geol.*, **86**, 478-504.

CIARAPICA G., PASSERI L. (1982) - Panorama sulla geologia delle Alpi Apuane alla luce delle più recenti ricerche. *Mem. Soc. Geol. Ital.*, **24**, 193-208.

CIARAPICA G., OLIVERO S., PASSERI L. (1983) - Evoluzione paleogeografica durante il Trias e giacimenti minerari nella Toscana a nord dell'Arno e nelle Liguria orientale. C.N.R. Progetto Finalizzato «Geodinamica».

CORTECCI G., LATTANZI P., TANELLI G. (1985) - Barite-iron oxide-pyrite deposits from Apuan Alps (Northern Tuscany, Italy). *Geol. Carpathica*, **36**, 347-357.

GUNTHER K., WALLBRECHER E. (1977) - Relations between superimposed fabric patterns and nappe movements in the tectonic units of the Apuan Alps (Northern Tuscany, Italy). *L'Ateneo Parmense*, **13**, 175-205.

KLIGFIELD R., CARMIGNANI L., OWENS W.H. (1981) - Strain analysis of a northern Apennine shear zone using deformed marble breccias. *Journ. Struct Geol.*, **3**, 421-436.

KLIGFIELD R., HUNZIKER J., DALLMEYER R.D., SCHAMEL S. (1986) - Dating of deformation phases using K-Ar and $^{40}Ar/^{39}Ar$ techniques: results from the northern Apennines. *Journ. Struct. Geol.*, **8**, 781-798.

NATALE P. (1974) - Relitti di bassa temperatura nelle piriti di alcuni giacimenti della Toscana. *Boll. Ass. Min. Subalpina*, **11**, 319-332.

PUXEDDU M., SAUPÈ F., DECHOMETS R., GIANELLI G., MOINE B. (1974) - Geochemistry and stratigraphic correlations: applications to the investigation of geothermal and mineral resources of Tuscany. *Chem. Geol.*, **43**, 77-114.

TANELLI G. (1983) - Mineralizzazioni metallifere e minerogenesi della Toscana. *Mem. Soc. Geol. Ital.*, **25**, 91-109.

VAI G.B. (1972) - Evidence of Silurian in the Apuan Alps (Tuscany, Italy). *Giorn. Geol.*, **38**, 349-372.

(ms. pres. il 20 novembre 1988; ult. bozze il 31 dicembre 1988)