

Abundance and significance of Cu, Mn and Zn in the sulfides and host rocks from the hydrothermal mineralization of the Tolfa Mountains (Latium, Central Italy)

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ABSTRACT. — Cu, Mn and Zn of 29 samples of sulfide minerals (mainly pyrite) from the hydrothermal Pliocene vein mineralization of the Tolfa Mountains volcanic district have been measured. Abundances of these elements have also been measured in selected host rocks and travertines from the same area.

Hydrothermal pyrites of the stage II of mineralization show ranges of Cu (44-315 ppm), Mn (8-185 ppm) and Zn (33-424 ppm) contents that are similar to those of stage-III pyrites not associated with other sulfide phases (31-659 ppm, 4-211 ppm and 37-207 ppm, respectively), suggesting that the parent solutions had close contents of these elements. Pyrites associated with other sulfide phases exhibit the highest Cu and Zn contents.

The relationships among the trace elements in the hydrothermal pyrites studied suggest that the contents of Cu, Mn and Zn increased in these sulfides with evolution of the mineralizing process. This rules out that the solutions of stage III of the mineralization were the same as those of stage II, although at a more advanced step of evolution.

Volcanic pyrites show similar contents of Cu, Mn and Zn to those of hydrothermal pyrites, but there are inverse correlations between Cu and Mn, Zn respectively, thus indicating a different behavior of these elements under both magmatic and hydrothermal conditions.

Disseminated pyrites in the unaltered flysch show contents of Cu, Mn and Zn close to hydrothermal pyrites and, however, higher than those of sedimentary pyrites, thus indicating that they were deposited or reequilibrated their trace-element contents with hydrothermal fluids.

The Cu contents in the hydrothermally-altered flysch rocks are greater than those of corresponding unaltered rocks, indicating enrichment by the hydrothermal fluids. The positive correlation between

Cu and K in these rocks suggests accommodation of Cu in K-bearing phases. Unlike Cu, Mn shows a reverse pattern, indicating leaching of this element during alteration. Zn shows no substantial variation of content in the rocks with alteration.

Gossans are enriched in Cu and Zn, but not in Mn with respect to ironstones from the same area. This suggests a possible use of Cu and Zn as pathfinders in the oxidation zone for prospection of sulfide ores.

Finally, unlike Mn and Zn that show quite similar contents in both the sedimentary and hydrothermal carbonates, Cu shows lower contents in these latter, likely because it is preferentially partitioned into the silicate phase.

Key words: geochemical prospection, trace elements, sulfide ores, hydrothermal mineralization, pathfinder elements.

RIASSUNTO. — È stata eseguita la determinazione delle abbondanze di Cu, Mn e Zn in campioni di solfuri, rocce sedimentarie, vulcaniti e travertini del distretto vulcanico dei Monti della Tolfa.

Le piriti idrotermali del II e del III stadio di mineralizzazione non associate con altri solfuri mostrano livelli di concentrazione dei tre elementi considerati che non differiscono significativamente (Pirite del II stadio: Cu 44-315 ppm; Mn 8-185 ppm; Zn 33-424 ppm. Pirite del III stadio: Cu 31-659 ppm; Mn 4-211 ppm; Zn 37-207 ppm). Le piriti associate con altri solfuri sono invece caratterizzate da più elevati contenuti di Cu e Zn.

Le relazioni tra gli elementi in traccia contenuti nelle piriti idrotermali indicano che le concentrazioni di Cu, Mn e Zn sono andate aumentando con il procedere del processo di mineralizzazione; viene pertanto dedotto che le soluzioni idrotermali del II e III stadio differivano significativamente

per le loro rispettive caratteristiche chimico-fisiche.

I contenuti di Cu, Mn e Zn trovati nelle piriti idrotermali ed in quelle di origine vulcanica non mostrano differenze significative, tuttavia, poiché in queste ultime piriti la correlazione di Cu e Mn con lo Zn è negativa, se ne deduce che il comportamento geochemico dei tre elementi nell'ambiente magmatico è stato diverso.

Le piriti disseminate nel flysch hanno contenuti di Cu, Mn e Zn simili a quelli trovati per le piriti idrotermali e comunque sempre significativamente più alti di quelli misurati nelle piriti di origine sedimentaria. Ciò suggerisce una qual certa dipendenza genetica delle piriti contenute nel flysch dai fluidi mineralizzanti.

Il processo di alterazione idrotermale del flysch ha determinato un arricchimento in Cu, inoltre, poiché questo elemento è positivamente correlato con il K, se ne deduce che potrebbe essere essenzialmente ospitato nelle fasi minerali contenenti, per l'appunto, potassio. Il Mn risulta essersi significativamente impoverito durante l'alterazione idrotermale del flysch, mentre il contenuto di Zn non è variato significativamente. Le concentrazioni di Cu e Zn nei cappellacci di ossidazione dei solfuri sono significativamente superiori rispetto a quelle trovate per gli accumuli di ossidi idrati di Fe di natura sedimentaria. Ciò suggerisce un potenziale uso del Cu e dello Zn nella prospezione geochemica dei depositi di solfuri.

Infine il Cu è più abbondante nei carbonati di origine sedimentaria che non in quelli di origine idrotermale, mentre Mn e Zn non mostrano alcuna significativa differenza.

Parole chiave: prospezione geochemica, giacimentologia, elementi in traccia, solfuri, mineralizzazioni idrotermali.

Introduction

Previous papers (CALDERONI et al., 1985, 1986) showed the importance of studying the behavior and significance of elements such as Pb, Tl, Co and Ni in the sulfides and host rocks from the Tolfa Mountains area in order to ascertain the origin of the ores.

With this paper we have extended previous information by measuring Cu, Mn and Zn contents in the same samples, in order to test whether also these elements could be helpful in sulfide ore genesis studies. Cu and Mn were in fact used successfully by ROBERTS (1982) to distinguish types of mineral occurrences, and, in particular, those containing significant base-metal mineralization. Moreover, the study of the distribution of Cu, Mn and Zn among the various sulfide phases deposited during the same mineralizing cycle may help in understanding the behavior of these elements in ore-forming

hydrothermal systems, as indicated by other trace elements in previous papers (CALDERONI et al., 1985, 1986). This, in turn, may help in ore prospecting.

Geological setting

Geological information on the Tolfa vein mineralization and sampling locations were reported in full detail in previous papers (FIELD and LOMBARDI, 1972; FERRINI, 1975; BARBIERI et al., 1978; MASI et al., 1980; CALDERONI et al., 1985, 1986), and thus, here a concise review is only given. The Tolfa vein deposits can be referred to three stages of mineralization. During stage I calc-alkaline acidic magmas intruded into sedimentary terranes, forming garnet hornfels low in pyrrhotite. Rocks of this stage are rare, being represented by small blocks of garnet-bearing calcite (calcite I) scattered in the latter calcite (or calcite II) bodies, that, in turn, were formed during stage II by hydrothermal fluids upwelling along major faults through the flysch. Such fluids, following interaction with the flysch rocks that produced a metasomatized (sericite-chlorite rich) zone of few hundred meters of width around the faults, deposited small amounts of pyrite with minor sphalerite as disseminations in the calcite-II bodies. Finally, during stage III the mineralizing fluids laid down pyrite with minor galena and sphalerite in veinlets and small lenses within the altered flysch and between this and the calcite-II bodies. Scanty pyrite disseminated in the unaltered flysch rocks occurs at Rocaccia-Pozzi. Due to its occurrence this pyrite may be sedimentary in origin, although there is suggestion that it reequilibrated trace-element contents during the emplacement of a nearby small hypoabissal body (CALDERONI et al., 1986).

Analytical procedure

Sulfide samples were collected from dumps of three abandoned mines and purified to obtain concentrates by froth flotation, heavy liquid and magnetic separation. Concentrates were refined accurately under the binocular microscope up to > 98 % purity grade, then further checked by X-ray diffraction. Cu, Mn

and Zn abundances were determined by atomic absorption, following appropriate sample dissolution with routine technique.

Rock samples were examined to ensure that they were «unmineralized», then crushed and dissolved in a HF/HClO₄ mixture.

Results

The Cu, Mn and Zn contents in the sulfide minerals and host rocks analyzed are reported in tab. 1 and tab. 2, respectively.

a) Sulfide ore

Pyrites disseminated in the hydrothermal calcite II (pyrite I) (6 samples) show Cu, Mn and Zn contents ranging from 44 to 315 ppm ($\bar{x}$ = 111 ppm), from 8 to 185 ppm ($\bar{x}$ = 49 ppm) and from 33 to 424 ppm ($\bar{x}$ = 180 ppm), respectively.

Pyrites in veinlets and lenses scattered in the hydrothermally-altered flysch (pyrite II) (12 samples) show Cu, Mn and Zn contents ranging from 31 to 1,778 ppm (*) ($\bar{x}$ = 439 ppm), 4 to 211 ppm ($\bar{x}$ = 35 ppm) and 37 to 207 ppm (**) ($\bar{x}$ = 87 ppm), respectively. There is no difference among pyrites from the three mines. Pyrites associated with mixed sulfides generally show the highest Cu and Zn contents.

Pyrites disseminated in the unaltered flysch carbonates (4 samples) show Cu, Mn and Zn contents ranging from 101 to 184 ppm ($\bar{x}$ = 142 ppm), 15 to 260 ppm ($\bar{x}$ = 144 ppm) and 58 to 124 ppm ($\bar{x}$ = 88 ppm), respectively. Cubic pyrites show higher Mn contents than non-cubic pyrites.

Pyrites disseminated in the unaltered acidic volcanites (3 samples) show Cu, Mn and Zn contents ranging from 45 to 264 ppm ($\bar{x}$ = 144 ppm), 15 to 54 ppm ($\bar{x}$ = 31 ppm) and 85 to 423 ppm ($\bar{x}$ = 269 ppm), respectively.

Finally, sphalerite disseminated in calcite II (sphalerite I) shows a much higher Cu content than pyrite I, while sphalerite TM-22, occurring in veinlets cutting calcite-

II bodies (sphalerite II), is enriched in Mn relative to coexisting pyrite II TM-13.

b) Host rocks

Unaltered flysch rocks (5 samples) show Cu, Mn and Zn contents ranging from 13 to 28 ppm ($\bar{x}$ = 37 ppm), 445 to 983 ppm ($\bar{x}$ = 694 ppm), and 22 to 64 ppm ($\bar{x}$ = 48 ppm), respectively. Altered flysch rocks (5 samples) show Cu, Mn and Zn contents ranging from 16 to 52 ppm ($\bar{x}$ = 37 ppm), 11 to 384 ppm ($\bar{x}$ = 142 ppm) and 17 to 140 ppm ($\bar{x}$ = 69 ppm), respectively. Samples from Hill-520 show a much higher Mn content than the others. Cu, Mn and Zn contents in the travertines (12 samples) range from 6 to 29 ppm ($\bar{x}$ = 12 ppm), 71 to 1,615 ppm ($\bar{x}$ = 398 ppm) and 19 to 256 ppm ($\bar{x}$ = 71 ppm), respectively.

Travertines from II Bagnarello and those from I Montirozzi show the highest Mn and Zn contents, respectively. Gossan samples from two mines show much higher Cu ($\bar{x}$ = 186 ppm) and Zn ($\bar{x}$ = 1,158 ppm) contents than ferruginous deposits unrelated to ores (ironstones) ($\bar{x}$ = 24 Cu ppm and 117 Zn ppm). On the contrary, Mn contents are not diagnostic of the two rock-types.

Calcite I displays a Cu, Mn and Zn content quite close to that of calcite II (7 samples); both rock-types ranging overall from 7 to 22 ppm ($\bar{x}$ = 12 ppm), 338 to 3,298 ($\bar{x}$ = 976 ppm) and 12 to 303 ppm ($\bar{x}$ = 79 ppm), respectively.

Finally, unaltered volcanites (4 samples) show Cu, Mn and Zn contents ranging from 9 to 15 ppm ($\bar{x}$ = 13 ppm), 167 to 523 ppm ($\bar{x}$ = 329 ppm) and 66 to 88 ppm ($\bar{x}$ = 78 ppm), respectively. On the contrary, altered volcanites (6 samples) display comparatively lower contents.

Discussion

Cu, Mn and Zn in the sulfides

The low contents of Cu, Mn and Zn displayed by most of the Tolfa pyrites may suggest that pyrite is not associated with major amounts of Cu+Pb+Zn sulfide ores in agreement with geologic evidence (FERLINI, 1975) and literature data from other similar deposits (e. g., FRIEDRICH and CHRISTENSEN, 1977; TAYLOR and SYL-

(*) Excluding sample TM-13 that shows a high Cu content.

(**) Excluding samples TM-13, TM-15 and TM-16 that show very high Zn contents.

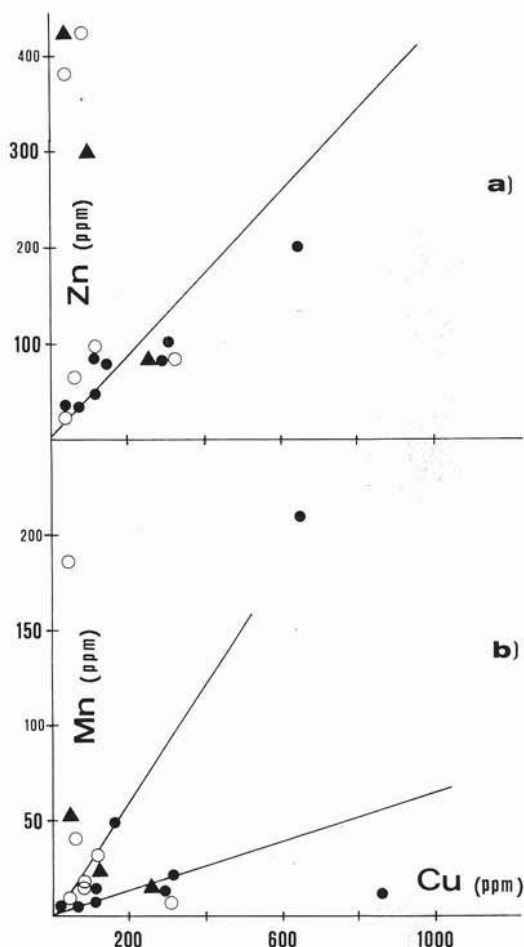


Fig. 1. — a) Cu vs. Zn and b) Cu vs. Mn in the hydrothermal pyrites from the Tolfa Mountains mineralization. Open and solid circles represent pyrite-I and pyrite-II samples, respectively. Volcanic pyrites from the same area (black triangles) are shown for reference.

VESTER, 1982; ROBERTS, 1982; DUCHESNE et al., 1983). It seems in fact reasonable that low contents of trace elements in pyrite likely reflect low contents of these elements in the ore-forming solutions, and, only to minor extent, the physico-chemical conditions of these fluids. In this view it is convincing that samples TM-13, TM-15 and TM-16 that are associated with other sulfide phases show the highest Cu and Zn contents.

Moreover the average contents of Cu, Mn and Zn of Tolfa pyrites, being distinct from those of pyrites of high temperature occurrences (see in DUCHESNE et al., 1983)

because of the low Cu mean, and differing also from those of pyrites from shales because of the low Mn mean, suggest that the ores studied formed at relatively low temperature and in an environment that is not sedimentary. This is in agreement with field and geochemical evidence that in fact show the mineralization is epithermal and in particular temperature was $< 250^{\circ}\text{C}$ during the main stages (MASI et al., 1980; AZZARO and LOMBARDI, 1977).

Comparison of Cu, Mn and Zn contents in pyrite I and pyrite II shows that both generations of pyrite display similar ranges, thus reflecting comparable levels of such elements in the mineralizing fluids.

Fig. 1 shows the relationships between Cu and Zn, and Cu and Mn in the ores studied. Let's notice the positive correlation between Cu and Zn exhibited by most pyrites II, this correlation lacking on the contrary for those pyrites associated with other sulfide phases (not reported in the figure). As these latter phases are of later deposition than pyrite (CALDERONI et al., 1985), there is evidence that the highest Cu and Zn contents are a peculiar feature of the latest pyrites. We have not tested the manner of Cu and Zn incorporation in pyrites TM-13, TM-15 and TM-16, but according to ROBERTS (1982) these elements, unlike Mn that likely substitutes for Fe in the pyrite lattice, occur as submicroscopic inclusions and/or occlusions of chalcopyrite and sphalerite. However, whatever be the form of occurrence of Zn and Cu in the Tolfa pyrites, if we assume that the different samples of pyrite represent the ores precipitated from the mineralizing solutions at different steps of the hydrothermal process, there is a suggestion that the contents of Cu and Zn increased in pyrites with evolution of the process. To test the validity of this suggestion, the contents of Cu have been plotted against those of Ni from the same samples, as Ni content generally increased throughout the mineralizing cycle from early to late pyrites (CALDERONI et al., 1986). From fig. 2 it is apparent that there is an overall positive correlation between the two elements in most pyrite-I samples. The same pattern is also exhibited by pyrite II, but, unlike pyrite I, the slope of the regression line changing

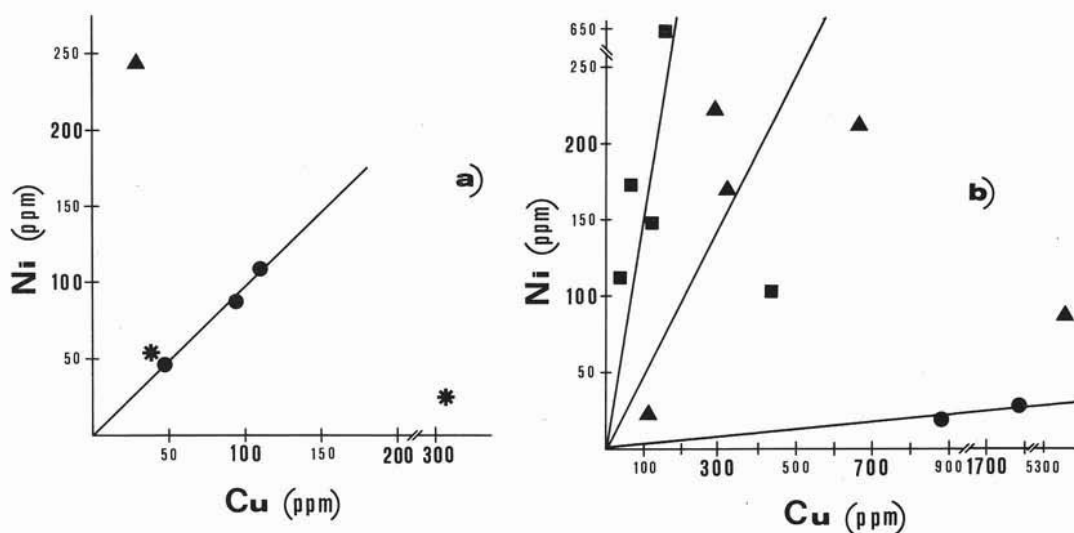


Fig. 2. — Cu vs. Ni in pyrite I (a) and pyrite II (b) from the Tolfa Mountains mineralization. Samples from Hill-520, « Iron Mine », Roccaccia-Pozzi and S. Lucia creek are shown by solid circles, triangles, squares and asterisks, respectively.

according to the mine considered. This may suggest that the physico-chemical conditions of the ore-forming fluids of stage III at the three mines were different, while, on the contrary, they were roughly similar during stage II, at least at Hill-520 and Santa Lucia-creek mines. It may be interesting that the Ni/Cu ratios are similar for pyrite II from the « Iron Mine » and Roccaccia-Pozzi, and however higher than those of pyrites from Hill-520. This may be related to the different type of main sulfide ore deposited in the two groups of deposits. In fact, while galena dominates at Hill-520, pyrite was the main sulfide phase deposited at « Iron Mine » and Roccaccia-Pozzi.

As a whole, the general positive correlation between Cu and Ni observed in most pyrites of both stage II and stage III supports that Cu, but also Zn because of its positive correlation with Cu, acted as incompatible in stage-III pyrites, thus producing Cu- and Zn-progressively enriched solutions up to deposition of other sulfide phases. Likely the partition coefficient of this pair of elements between the solution and pyrite would approach that typical for equilibrium conditions. Conversely those few pyrite samples that formed along with other sulfides, could be reflective of disequilibrium conditions.

Like pyrite II, also pyrite I shows a positive correlation between Cu and Zn in all samples, except two that are particularly enriched in Zn relative to Cu. These latter were likely deposited in disequilibrium, perhaps in connection with precipitation of sphalerite, that crystallized simultaneously with pyrite during stage II.

Fig. 1 b shows positive Cu-Mn correlations in most samples of both pyrite I and pyrite II, except for those displaying the highest contents. These latter may reflect disequilibrium conditions. The lower Mn/Cu ratio of pyrite II relative to pyrite I suggests that stage-III solutions were depleted in Mn relative to Cu with respect to those of stage II. The reason of this fact is not known.

As whole, since the Cu, Mn and Zn contents of the Tolfa pyrites likely paralleled the variations of content of these elements in the mineralizing fluids, it is apparent that the parent solutions of pyrite-II were not those of pyrite-I, but at a more advanced stage of evolution of the ore-forming process. This is because pyrite II displays no higher contents of these elements than pyrite I (tab. 1) as to be expected if stage-II and stage-III fluids would belong to the same descent line. This view is in full agreement with the conclusions of previous

TABLE 1
Cu, Mn and Zn contents of the sulfide minerals from the Tolfa Mountains
 a) Sulfide in calcite I, calcite II and hydrothermally-altered flysch
 b) Sulfides in unaltered flysch carbonates
 c) Sulfides in unaltered volcanites

Formation	Sample	Locality	Mineral	Cu(ppm)	Mn(ppm)	Zn(ppm)
calcite I	TM- 1	"Iron-Mine"	pyrrhotite	281	43	109
	TM- 2	Hill-520	pyrite I	113	32	95
	TM- 3	Hill-520	pyrite I	93	17	424
	TM- 4	Hill-520	pyrite I	45	8	33
	TM- 5	"Iron-Mine"	pyrite I	57	41	67
calcite II	TM- 6	S.Lucia Creek	pyrite I	315	8	81
	TM- 7	S.Lucia Creek	pyrite I	44	185	383
	TM- 8	Roccaccia-Pozzi	sphalerite I	1,880	117	-
	TM- 9	Roccaccia-Pozzi	sphalerite I	941	483	-
	TM-10	"Iron-Mine"	pyrite II	320	23	102
altered flysch	TM-11	"Iron-Mine"	pyrite II	659	211	207
	TM-12	"Iron-Mine"	pyrite II	293	14	84
	TM-13	"Iron-Mine"	pyrite II	5,176	54	11,221
	TM-14	"Iron-Mine"	pyrite II	107	9	85
	TM-15	Hill-520	pyrite II	1,778	22	20,147
	TM-16	Hill-520	pyrite II	879	13	2,963
	TM-17	Roccaccia-Pozzi	pyrite II	31	2	39
	TM-18	Roccaccia-Pozzi	pyrite II	151	47	74
	TM-19	Roccaccia-Pozzi	pyrite II	117	14	48
	TM-20	Roccaccia-Pozzi	pyrite II	64	4	37
	TM-21	Roccaccia-Pozzi	pyrite II	430	11	105
	TM-22	"Iron-Mine"	sphalerite II*	5,628	282	-
b) sulfides in unaltered flysch carbonates						
	TM-23	Roccaccia-Pozzi	(cubic)pyrite	103	260	124
	TM-24	Roccaccia-Pozzi	(cubic)pyrite	180	245	83
	TM-25	Roccaccia-Pozzi	(globular)pyrite	184	54	58
	TM-26	Roccaccia-Pozzi	(pentagon-dodecahedral)pyrite	101	15	85
c) sulfides in unaltered volcanites						
	TM-27	Tolfa	pyrite	45	54	423
	TM-28	Allumiere	pyrite	264	15	85
	TM-29	Allumiere	pyrite	123	25	300

* coexisting with pyrite TM-13

studies dealing with Pb, Tl, Co and Ni distribution in the same ores (CALDERONI et al., 1985, 1986).

Unlike hydrothermal pyrites, pyrites from volcanic rocks show inverse correlations between Cu and Zn, and Cu and Mn (fig. 1)

despite the ranges of these elements are similar in both groups of sulfides. If these differences are not fortuitous, suggesting that under magmatic conditions the Mn-Zn pair is antagonistic of Cu competing for accomodation in pyrite, the use of Cu/Zn

TABLE 2
Cu, Mn and Zn contents of «unmineralized» rocks from the Tolfa Mountains

Sample	Locality	Rock-type	Cu(ppm)	Mn(ppm)	Zn(ppm)
TM-30	Mt.Paradiso	unaltered flysch carbonate	27	929	60
TM-31	Roccaccia-Pozzi	" "	28	983	51
TM-32	Roccaccia-Pozzi	" "	25	609	43
TM-33	Roccaccia-Pozzi	" "	19	445	64
TM-34	Roccaccia-Pozzi	" "	13	502	22
TM-35	Hill-520	hydrothermally-altered flysch	40	384	133
TM-36	Hill-520	" "	47	243	30
TM-37	S.Lucia Creek	" "	52	27	140
TM-38	S.Lucia Creek	" "	16	11	17
TM-39	Roccaccia-Pozzi	" "	29	46	27
TM-40	Roccaccia-Pozzi	garnet-bearing calcite I	7	907	12
TM-41	Roccaccia-Pozzi	calcite II	7	344	29
TM-42	Roccaccia-Pozzi	calcite II	9	403	39
TM-43	S.Lucia Creek	calcite II	10	665	303
TM-44	S.Lucia Creek	calcite II	22	338	117
TM-45	Hill-520	calcite II	13	981	15
TM-46	Hill-520	calcite II	19	873	73
TM-47	"Iron-Mine"	calcite II	7	3,298	44
TM-48	North of Tolfa	unaltered ignimbrite	9	388	75
TM-49	North of Tolfa	" "	13	167	66
TM-50	Tolfa	unaltered lava dome	15	240	84
TM-51	Tolfaccia	" " "	14	523	88
TM-52	Allumiere	slightly altered ignimbrite	6	38	12
TM-53	Allumiere	strongly altered ignimbrite	6	6	16
TM-54	Allumiere	" "	9	4	13
TM-55	Tolfaccia	slightly altered lava dome	15	87	83
TM-56	Allumiere	kaolin	9	115	54
TM-57	Tolfa	kaolin	5	22	9
TM-58	"Iron-Mine"	gossan	148	82	1,451
TM-59	Hill-520	gossan	224	122	865
TM-60	Tolfa	ironstone	32	14	62
TM-61	Bagnarello	ironstone	15	582	171
TM-62	I Montirozzi	travertine	12	1,615	19
TM-63	I Montirozzi	"	8	1,486	20
TM-64	La Ficoncella	"	6	71	28
TM-65	La Ficoncella	"	9	215	20
TM-66	Il Bagnarello	"	29	322	217
TM-67	Il Bagnarello	"	10	289	256
TM-68	Il Bagnarello	"	8	81	51
TM-69	I Bagni	"	13	214	65
TM-70	I Bagni	"	10	179	72
TM-71	I Bagni	"	14	88	44
TM-72	I Bagni	"	12	104	33
TM-73	Pian Sultano	"	10	107	25

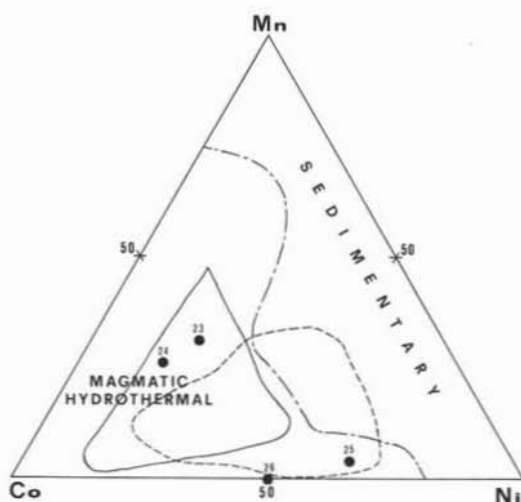


Fig. 3. — Co-Ni-Mn diagram showing the position of the Tofla pyrites from the unaltered flysch with respect to fields of sedimentary and magmatic-hydrothermal pyrites (UDUBASA, 1984). The fields of pyrite I and pyrite II are also shown for reference.

and Cu/Mn ratios for discriminating between pyrites of magmatic and hydrothermal origin in ore-genesis studies may be suggested.

Finally, the lack of any difference in Cu, Mn and Zn contents between pyrites from the unaltered and altered flysch rocks suggest a common origin for all these ores. However, as the ranges of these elements are higher than those of sedimentary pyrite (e.g., FRIEDRICH and CHRISTENSEN, 1977; STRAUSS *et al.*, 1981 and as observed by us in pyrite nodules occurring in Apennine flysch: 11-12 Cu ppm, 10-18 Mn ppm and 37-40 Zn ppm, unpublished data), it is suggested that the pyrites disseminated in the unaltered flysch had either a hydrothermal origin or reequilibrated their trace-element contents with hydrothermal fluids, in agreement with the conclusions carried out on the basis of Pb, Tl, Co and Ni in the same ores (CALDERONI *et al.*, 1985, 1986). In particular plotting Co, Ni and Mn contents of the pyrites of the unaltered flysch on a ternary diagram (fig. 3) (UDUBASA, 1984), it is seen that these samples fall out of the field of sedimentary pyrites, being on the contrary within the fields of both pyrite I and pyrite II. Moreover, as it is also apparent that the cubic pyrites are Mn-richer than the non-cubic ones, and these

latter are closer to the hypoabyssal body that might be to some extent indirectly responsible for the formation or trace-element reequilibration of these pyrites, there is suggestion that the Mn content of pyrites disseminated around a magmatic body depends on the distance from the intrusion.

Cu, Mn and Zn in the host rocks

While the unaltered flysch shows average Mn content quite similar to that of marine limestones, the average Cu and Zn contents are comparatively higher (WEDEPOHL, 1974), likely reflecting the relatively high detrital component of the rocks analyzed (FERRINI and MASI, in preparation).

With respect to the alteration processes that affected the flysch rocks during the ore emplacement Cu, Mn and Zn show quite different behaviors. In fact, while the Cu contents in the altered flysch are greater than those of corresponding unaltered rocks, indicating that the hydrothermal solutions carried some Cu, on the contrary the Mn contents decrease in the altered rocks, suggesting leaching by the fluids and, finally, Zn shows no substantial change in the two groups of rocks, pointing out that this element was virtually immobile during alteration.

Fig. 4 illustrates the relationships between the three elements analyzed and K, the content of which increased in the metasomatized relative to unaltered limestone because of hydrothermal formation of silicate phases such as sericite and subordinatedly K-feldspar. In particular it is apparent that there is a positive correlation between Cu and K in most altered rocks, suggesting that Cu entered the lattice of K-bearing phases. A positive correlation exists also between Zn and K only for lower contents, suggesting that at higher levels Zn was not linked only to K-phases. Finally, the lack of any correlation between Mn and K in the rocks analyzed is explained by removal, instead of addition, of the former element by altering fluids.

The hydrothermal calcites and travertines show lower Cu contents than limestones from the same area, indicating that during mobilization and reprecipitation of calcium

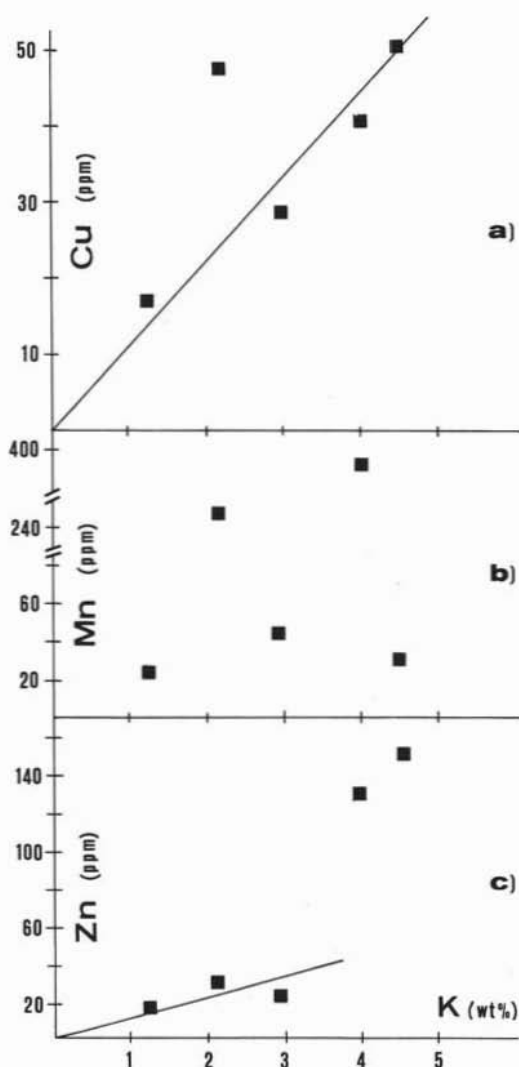


Fig. 4. — a) K vs. Cu; b) K vs. Mn and c) K vs. Zn in the hydrothermally-altered flysch rocks from the Tolfa Mountains.

carbonate not all Cu was made available, likely because at Tolfa this element could enter other hydrothermal phases (e.g. silicates), as it is suggested by the K-Cu correlation. On the contrary the hydrothermal processes did not alter significantly the Mn and Zn contents of hydrothermal carbonates with respect to limestones, the contents of these elements being roughly equal in both rock-types.

Alteration of volcanic rocks resulted in a pronounced depletion of Mn, and subordi-

nately of Zn and Cu, all these elements thus being released to ground water.

Finally, it is noticed that supergene alteration of the ores formed gossans enriched in both Cu and Zn, but not in Pb (CALDERONI et al., 1985) relative to ironstones from the same area. Such a feature can be tentatively explained with the findings of a previous study (CALDERONI et al., 1984) concerning the chemistry of water involved in supergene alteration at Tolfa and constraints on the mobility of Cu, Pb and Zn. From this study it is resulted that the composition of Tolfa gossans is that compatible with an aqueous medium low in $[Cl^-]$, very low in $[SO_4^{2-}]$ at $pH < 7$ and with a $[CO_2 \text{ tot.}] \leq CO_2$ of the atmosphere. The enrichment in Cu and Zn displayed by the studied gossans hints a possible use of these two elements as pathfinders in the oxidation zone for prospection of sulfide ores, the same being unworthy for Mn and Pb.

Conclusions

The analytical data presented in this paper indicate that the Cu, Mn and Zn contents of the hydrothermal pyrites from the Pliocene vein mineralization of Tolfa, as they do not show significant differences, do not make possible an unbiased evaluation of the various mineralizing stages. This suggests that the parent solutions of the ores should have close levels of these elements. However, as the pyrites associated with other sulfide phases, that are of late segregation than pyrite, exhibit the highest Cu and Zn contents, and more generally there are positive relationships among the trace elements studied in most Tolfa pyrites, it is suggested that the contents of Cu, Mn and Zn increased in these latter sulfides with evolution of the mineralizing process. Therefore there is a strong suggestion that the parent solutions of the main stages of the mineralization (i.e. stage II and stage III) were different, despite the contents in the related pyrites are similar.

At Tolfa the volcanic pyrites can be distinguished from the hydrothermal pyrites due to the inverse correlations occurring among the three elements studied, though the contents range similarly in both types of sulfides. This points out that Cu, Mn and

Zn behaved differently under hydrothermal and volcanic conditions.

Pyrites disseminated in the unaltered flysch show contents of Cu, Mn and Zn higher than sedimentary pyrites, but slightly towards the hydrothermal ones, thus indicating some interaction with hydrothermal fluids. Likely these latter brought some Cu to the altered flysch rocks, Cu entering mostly K-bearing phases of new formation. The mineralizing fluids were also responsible for Mn depletion in the altered rocks, while Zn levels were unaffected, this reflecting antithetic behaviors of the two elements during alteration.

The gossans of the Tolfa mineralization were found Cu- and Zn-enriched, but not in Mn relative to ironstones from the same area. This suggests a possible use of Cu and Zn as pathfinders in the oxidation zone for prospection of sulfide ores.

Finally, as hydrothermal carbonates and travertines are depleted in Cu relative to sedimentary carbonates, while Mn and Zn contents are comparable, it is apparent that hydrothermal remobilization of carbonate rocks may cause Cu fractionation, likely because this element enters silicates lattices.

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REFERENCES

- AZZARO E., LOMBARDI G. (1976) - *Logistics of an Instrumental Analysis of Complex Phyllosilicatic Parageneses*. *Thermanal* 76, Pragma, 57-64.
- BARBIERI M., FERRINI V., LOMBARDI G., PENTA A. (1978) - *Use of strontium in carbonates for the interpretation of the deep minerogenetic fluid circulation in the Tolfa Mts. (Rome)*. *Chem. Erde*, 37, 143-153.
- CALDERONI G., FERRINI V., PETRONE V. (1984) - *Hydrogeochemical modeling. Apparent controls on solution transport for Zn, Pb and Cu in the supergene zone of Tolfa Mountains volcanic district (Latium, central Italy)*. *Rendiconti Soc. It. Mineral. Petrol.*, 39, 429-438.
- CALDERONI G., FERRINI V., MASI U. (1985) - *Distribution and significance of Pb and Tl in the sulfides and host rocks from hydrothermal mineralization of the Tolfa Mountains (Latium, Central Italy)*. *Chem. Geol.*, 51, 29-39.
- CALDERONI G., FERRINI V., MASI U. (1986) - *Abundance and significance of Co and Ni in the sulfides and host rocks from the hydrothermal mineralization of the Tolfa Mountains (Latium, central Italy)*. *Periodico Mineral.* (in press).
- DUCHESNE J.C., ROUHART A., SCHOUMACHER C., DILLEN H. (1983) - *Thallium, Nickel, Cobalt and Other Trace Elements in Iron Sulfides from Belgian Lead-Zinc Vein Deposits*. *Mineral. Deposita*, 18, 303-313.
- FERRINI V. (1975) - *Studio geopetrografico del complesso vulcanico Tolfa-Cerite (Lazio). VII: Le mineralizzazioni a solfuri misti in un settore dei Monti della Tolfa*. Università di Roma, Istituto di Petrografia, Roma, p. 63.
- FIELD C.W., LOMBARDI G. (1972) - *Sulfur Isotopic Evidence for the Supergene Origin of Alunite Deposits, Tolfa District, Italy*. *Mineral. Deposita*, 7, 113-125.
- FRIEDRICH G.H.W., CHRISTENSEN S.M. (1977) - *Geochemical dispersion patterns associated with the lake Yindarlgooda sulphide mineralization, Western Australia*. *J. Geochem. Explor.*, 8, 219-234.
- MASI U., FERRINI V., O'NEIL J.R., BATCHELDER J.N. (1980) - *Stable Isotope and Fluid Inclusion Studies of Carbonate Deposits from the Tolfa Mountain Mining District (Latium, Central Italy)*. *Mineral. Deposita*, 15, 351-359.
- ROBERTS F.I. (1982) - *Trace element chemistry of pyrite: a useful guide to the occurrence of sulfide base metal mineralization*. *J. Geochem. Explor.*, 17, 49-62.
- STRAUSS G.K., ROGER G., LECOLLE M., LOPERA E. (1981) - *Geochemical and geologic study of the volcano-sedimentary sulfide crebody of La Zarza, Huelva province, Spain*. *Econ. Geol.*, 76, 1975-2000.
- TAYLOR G.F., SYLVESTER G.C. (1982) - *Analysis of a weathered profile on sulfide mineralization at Mugga Mugga, Western Australia*. *J. Geochem. Explor.*, 16, 105-134.
- UDUBASA G. (1984) - *Iron sulfides in sedimentary rocks. Some occurrences in Romania*. In: *Syngensis and Epigenesis in the Formation of Mineral Deposits* (Eds. A. Wanschkuhn et al.), Springer-Verlag, Berlin.
- WEDEPHOL K.H. (1974) - *Handbook of Geochemistry*. Springer-Verlag, Berlin.