

A first occurrence of gersdorffite in the Peloritani Mts. (Sicily N.E.)

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ABSTRACT. — Gersdorffite and tetrahedrite occur in association with quartz and carbonate gangue in vein mineralization from the Mts. Peloritani (N.E. Sicily). These phases were studied using X-ray, electron microprobe and optical methods. The gersdorffite found for the first time in the Mts. Peloritani proved to have a 6.44 % Sb content as well as minor amounts of Fe, Co and Cu; the tetrahedrite is a ferroan variety (4.66 % Fe). The mineral assemblages are very similar to nearby Cu, Sb, Ag sulphide and complex sulphosalts deposits which are regarded as hydrothermal in origin. X-ray data confirm that this gersdorffite has a $P2_13$, low-temperature ordered structure as expected from the likely depositional conditions of the ore deposits in the area.

Key-words: Sicily, Peloritani Mts., ore minerals, gersdorffite, tetrahedrite.

PRIMA SEGNALEZIONE DI GERSDORFFITE NEI MONTI PELORITANI (SICILIA)

RIASSUNTO. — Viene segnalata per la prima volta la presenza di gersdorffite nei M. Peloritani (Sicilia N.E.). La mineralizzazione a gersdorffite e tetraedrite in ganga quarzosa-carbonatica (siderite ed ankerite) appare filoniana discordante. Lo studio è stato condotto mediante microscopia ottica in luce riflessa, diffrattometria di polveri a RX e microsonda elettronica. La gersdorffite si distingue per l'elevato contenuto in Sb (6.44 %), come pure per minori Fe, Co e Cu, mentre la tetraedrite presenta un 4,66 % di Fe. La paragenesi è ampiamente confrontabile con analoghe vicine mineralizzazioni a solfuri e solfosali di Cu, Sb e Ag considerate di origine idrotermale. I dati dell'analisi a Raggi X confermano per questa gersdorffite un gruppo spaziale $P2_13$ in pieno accordo con le condizioni mineralogiche dell'area esaminata.

Parole chiave: Sicilia, M. Peloritani, minerali metalliferi, gersdorffite, tetraedrite.

Introduction

X-ray diffraction, electron-microprobe and optical studies were carried out on gersdorffite

observed for the first time in the Peloritani Mts. area, of N.E. Sicily. The only previous known determination of a gersdorffite mineralization in Italy being the one by ARTINI (1903). The gersdorffite is found in Cu-Pb-Zn-As-Sb vein deposits in the Zilli area, south of the village of Fiumedinisi (near Messina), on the eastern flanks of the Peloritani Mts. The Zilli vein system is considered to be continuation of the « S. Carlo » Sb-Cu-Ag mineralization, a system of unconfined fissure veins, steeply dipping or almost vertical, cutting Paleozoic phyllites and also containing (less commonly) scheelite associated with sulphides and complex Sb-Cu-Pb (Ag-Fe) sulphosalts. Further information on the deposit is provided by DONATI et al. (1978) and TRISCARI et al. (1982).

Experimental methods

The mineralogy and paragenesis of the deposits were studied by reflected light microscopy and X-ray powder diffractions using $CuK\alpha$ and $CoK\alpha$ radiation. Chemical (electron microprobe) analysis was carried out using a Cambridge Microscan V instrument operated with an accelerating voltage of 15 KV. Pure metals were used as standard except for Fe and S where pyrite was used as standard. Results presented are mean values of eight analyses, for each one, four ten seconds counts were recorded, and the data then averaged, corrected for background and deadtime, as well as for atomic number and fluorescence effects using the computer program of DUNCOMB et al. (1969). The reflectance was measured using a Reichert Spectral Microphotometer with a Zeiss WTiC standard approved by the Commission on

Ore Microscopy. Microhardness was measured using a Vickers diamond pyramid indenter employing a load of 100 gr.

Field occurrence

This occurrence of gersdorffite lies in a small group of discordant veins, mainly quartzitic in composition, that form part of a vein system cutting Hercynian phyllites of the so-called Mandanici Unit. This unit is regarded as part of the Calabro-Peloritan arc, considered a complex overthrusting structure; has a medium-low metamorphic grade and it chiefly consists of phyllites, garnet and/or chloritoid phyllites, quartzites, metabasites and crystalline limestones (AMODIO MORELLI *et al.*, 1976; BONARDI *et al.*, 1982; FERLA, 1982 a, b). The deposits of the Peloritani Mts were once considered to be late magmatic in nature, but nowadays are generally considered as strata bound ores (FERLA, 1982 b), which have been secondarily mobilized by relatively recent hydrothermal activity. On the Peloritani Mts the tectonic sedimentary character of some of these deposits is still recognizable in a few areas, where small primary Pb, Cu, Zn deposits of simple composition were worked over the last few decades. The genesis of the sulphide ores locally appears to be spatially and temporally bound to the presence of basic metavolcanics in the hercynian phyllites of the Mandanici Unit (ATZORI *et al.*, 1973; FERLA, 1982 a, b). These primary strata-bound deposits, have been reworked by late tectonic events, that in the investigated area involved hydrothermal activity by which discordant veins ore bodies were deposited. The veins are between 5 and 30 cm wide, chiefly quartzitic in composition, with ankerite-siderite gangue. The average strike is NNE-SSW; these veins outcrop at an height of about 250 m above sea level in the Zilli area, south of the village of Fiumedinisi some 25 Km south of Messina.

Mineralogy

The main vein system consists of gersdorffite and associated tetrahedrite; gangue minerals are quartz, siderite and ankerite. Next to the surface, secondary alteration

products are observed: limonite, malachite and azurite. Gersdorffite in reflected light is seen as cubic idiomorphic masses and euhedral crystals with typical (100) cleavage observable as characteristic triangular pits. All sections studied showed evidence of intense cataclastic deformation. In some sections very rare calcopyrite was observed, always well rounded, quite often bordered by an encircling rim of covellite, and always contained within the quartz. The early formed phase is gersdorffite and a second episode of mineralization has brought the tetrahedrite which in part replaces the gersdorffite. It seems that the tetrahedrite is also associated with intense cataclastic phenomena; the substituting tetrahedrite is mainly present in the mylonitic zones. Both phases occur together and sometimes the tetrahedrite contains distinct euhedral cubes of gersdorffite (fig. 1 and fig. 2).

The gersdorffite has been affected by repeated episodes of clastic deformation.

Euhedral crystals of gersdorffite show fracturing and penetration by tetrahedrite veinlets. Following the characteristic (100) cleavage, the mechanical stresses have reduced the gersdorffite to an aggregate of irregularly shaped grains; late quartz with undulose extinction fills the main veins. Only tetrahedrite has been affected by an intense alteration to covellite; where covellite is observed within gersdorffite it occurs only as an alteration of tetrahedrite. Some parts of the veins show an abundance of chalcopyrite with tiny euhedral crystals of pyrite diffusely scattered, also in the form of strings and curved lines. Tetrahedrite shows a grey-white colour and takes a good polish, sometimes with a very light brownish tint: it is completely dark under crossed nicols.

Gersdorffite also polishes well: it is white in colour, sometimes with a very light yellowish tint. Zoning has not been observed in this locality. All sections studied are clearly isotropic. Although RAMDOHR (1980) reports that slight compositional variations in gersdorffite can be ascribed to submicroscopic intergrowth with chloantite, this mineral has not been observed optically or in XRD analysis.

Reflectance measurements on tetrahedrite fall in the range 30.3-32.5 % at 589 nm.

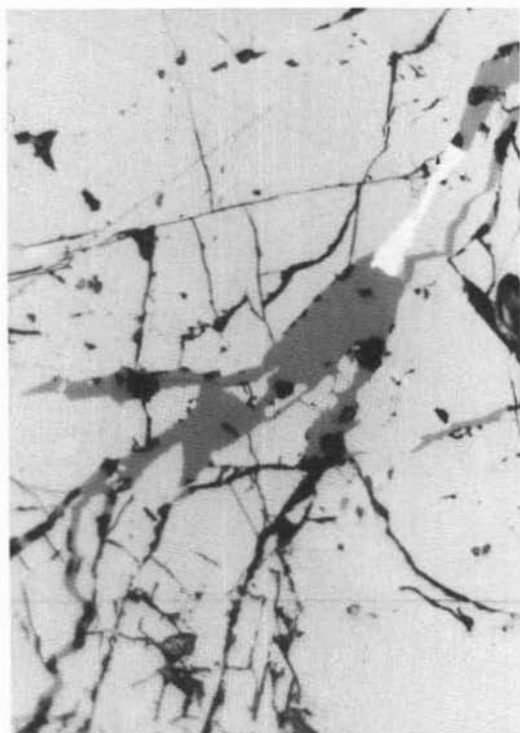


Fig. 1. — Chalcopyrite (*bright white*) in a tetrahedrite veinlet (*grey*), crossing gersdorffite (*white*). P.P.L. 400 x.

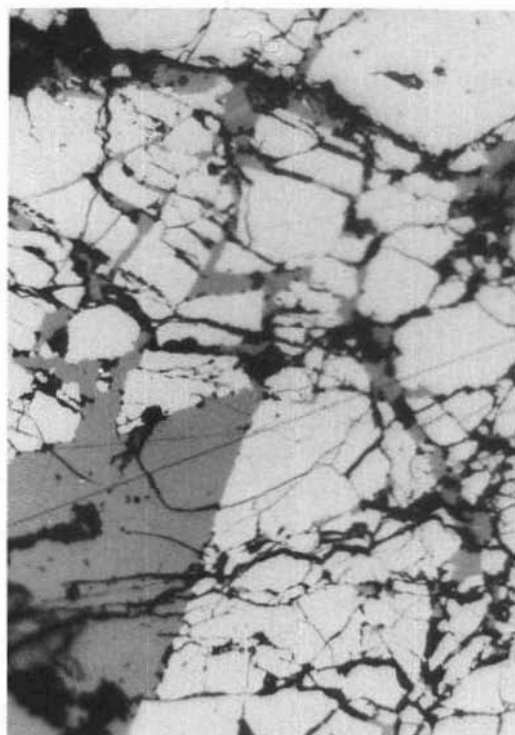


Fig. 2. — Euhedral gersdorffite crystals (*white*) with substituting tetrahedrite. P.P.L. 400 x.

Reflectance measurements on gersdorffite fall in the range 44.8-47.0 % at 589 nm.

These values, while in good agreement with data from GALOPIN et al. (1972) (Tetrahedrite 30.7 - Gersdorffite 47.5), VAUGHAN et al. (1978) (Tetrahedrite 30-30.5 - Gersdorffite 46.3-53.8), PICOT et al. (1982) (Tetrahedrite 32.6 - Gersdorffite 45.4), show significantly lower values for gersdorffite than the IMA/COM data, perhaps because of measurement of material of different composition. In fig. 3 are shown the spectral reflectance curves (air) for tetrahedrite and for gersdorffite. VHN values vary in the range 275-322 for tetrahedrite and 634-717 for gersdorffites, both at 100 gr load. Published data are: GALOPIN et al. (1972) (Tetrahedrite 328-367 and gersdorffite 665-743), VAUGHAN et al. (1978) (Tetrahedrite 285-322 and gersdorffite 520-907). The COM data for gersdorffite, refer to synthetic material (the material reported also in J.C.P.D.S. card 12-705 and the values (782-

835) are slightly different to those observed in this work. Several X-ray powder diffraction patterns were run for tetrahedrite and for gersdorffite. The results are given in table 1 and 2. From the observed d values, cell parameters were calculated following the cell refinement program of PREWITT modified by COPLEY (1975).

The unit cell edge measured was $a_0 = 10.377 \text{ \AA}$ for tetrahedrite and $a_0 = 5.694 \text{ \AA}$ for gersdorffite.

Gangue minerals are quartz and the carbonates siderite and ankerite; quartz veins often show included fragments of the host rock (phyllite).

Secondary alteration products observed are malachite, azurite and limonite. In the nearby locality of « S. Carlo » a much bigger vein system with the same strike directions and gangue minerals, studied by DONATI et al. (1978) and TRISCARI et al. (1982), show the following assemblage (in order of decreasing abundance): tetrahedrite, chalc-

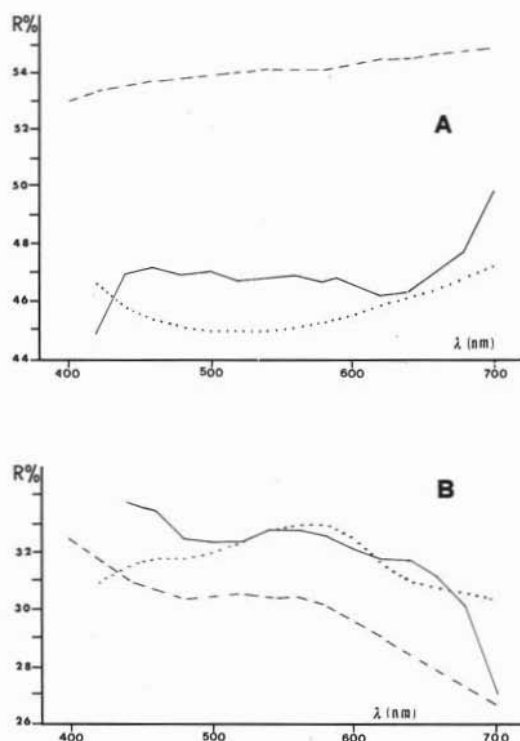


Fig. 3. — Spectral Reflectance Curves (AIR) for gersdorffite (A) and tetrahedrite (B); Standard Zeiss WTiC.

----- (IMA/COM)
 Picot et al., 1982
 — This work.

pyrite, bournonite, stromeyerite, bismuthinite, galena, pyrite, sphalerite, pentlandite, covellite, arsenopyrite, boulangerite, jamesonite, argentite, digenite as well as secondary products as malachite, azurite, goethite and limonite.

Discussion

The formula of gersdorffite is NiAsS , it is cubic $P2_13$. KLEMM (1965) observed that Fe and Co can substitute for Ni, and PALACHE et al. (1944) noted that Sb can also substitute for As giving the variety corynite, although this has been recently proved to be only an Sb bearing gersdorffite (BAYLISS, 1982a) so that use of this varietal name is unnecessary. The cell size of gersdorffite from the examined locality is similar to the cell size of 5.69 Å

TABLE 1
 Values of d obs. and d calc.; cell edge parameters for the examined tetrahedrite

hkl	$1/I_0$	d obs.	d calc.
002	6	5.206	5.188
022	15	3.676	3.669
222	100	2.998	2.995
123	10	2.776	2.773
004	18	2.598	2.595
033	11	2.449	2.446
024	5	2.323	2.320
224	6	2.119	2.118
134	8	2.037	2.035
125	8	1.897	1.894
044	35	1.835	1.834
035	4	1.781	1.779
006	3	1.730	1.729
116	6	1.684	1.683
026	3	1.645	1.640
226	13	1.566	1.564
444	3	1.498	1.497
055	4	1.468	1.467
127	3	1.411	1.412
008	3	1.297	1.297
118	3	1.278	1.277
356	3	1.242	1.240
129	3	1.119	1.119
039	3	1.094	1.093
448	4	1.057	1.059

Zillli's tetrahedrite $a_0 = 10.377$

for synthetic stoichiometric NiAsS (YUND, 1962): it is noticeable that previous literature reports show that the parameter of natural gersdorffites range from 5.60 Å (PEACOCK et al., 1940) to 5.731 Å (OLSHAUSEN, 1925). The crystal structures known for gersdorffites ($P2_13$, $P2_13$, $P1$) were well described by BAYLISS et al. (1967, 1968) and BAYLISS (1966, 1982b) and the reader is referred to the work of YUND (1962) and BAYLISS (1982b) for relevant literature. In his study, BAYLISS (1969) of more than a dozen gersdorffites and related minerals, noticed that gersdorffite with small cell sizes commonly occurs with calcite and sulphides such as pyrite and pyrrhotite, while gersdorff-

TABLE 2

Values of $d_{obs.}$ and $d_{calc.}$; cell edge parameters for the examined gersdorffite

hkl	I/I ₀	d obs.	d calc.
110	16	4.023	4.026
111	8	3.287	3.287
200	61	2.843	2.847
210	100	2.544	2.546
211	47	2.323	2.324
220	17	2.013	2.013
300	4	1.894	1.898
310	5	1.799	1.800
311	42	1.716	1.716
222	7	1.643	1.643
320	15	1.579	1.579
321	18	1.521	1.521
400	3	1.422	1.423
410	3	1.381	1.381
411	4	1.342	1.342
420	4	1.274	1.273
421	9	1.243	1.242
332	4	1.214	1.214
422	4	1.162	1.162
510	2	1.116	1.116
511	12	1.096	1.095
520	8	1.858	1.857
521	6	1.040	1.039
440	8	1.007	1.006

Zill's gersdorffite $a_0 = 5.694$

fite with large unit cell size commonly occurs with siderite and arsenides such as skutterudite and safflorite; the presence of cobalt and iron being ubiquitous in arsenic rich environments. Of these accessory minerals, only siderite, which decomposes at 500°C, indicates any limitation to formation temperatures. The presence of only gersdorffite rules out temperatures higher than 700°C. Above that temperature it would be represented by niccolite and maucherite following the reaction



TABLE 3

Representative electron microprobe analyses of gersdorffite and tetrahedrite of the present study

Gersdorffite							
Ni	As	S	Sb	Fe	Co	Cu	Total
31.80	41.14	20.52	6.44	1.98	0.37	0.13	101.98
Tetrahedrite							
S	Cu	Sb	Fe	Ag	Zn	As	Total
24.19	39.14	29.07	4.66	0.33	2.30	0.23	99.92

(HAWLEY et al., 1961). These two other phases have not been observed in the assemblages from the locality studied and are not mentioned in other paragenetic sequences from the Peloritani Mts.

BAYLISS (1982b) also confirmed, through chemical analyses on thirteen gersdorffite samples, that Co content causes a decrease in the cubic unit cell, and As increases it. Furthermore as the (001) and (110) reflections may be used in space group differentiation (BAYLISS, 1969) the presence in this gersdorffite of the (110) reflection in all the examined specimens indicate a cubic $P2_13$ structure; the (001) was always looked for but never found.

Heating experiments at 500°C and 600°C carried out by the same author, indicate a crystal structure change with the loss of the (100) reflection first, and the (001) later. From these heating experiments it seems likely that the $P2_13$ form is the low-temperature, ordered phase.

Chemical analyses (electron microprobe) are shown in table 3. Ag, Zn, Au, Cd, Pb and Bi were also looked for in the gersdorffite and Au, Cd, Te, Pb, Bi in the tetrahedrite, but not found. In the gersdorffite chemical analyses showed a substitution of Ni by Co and Fe; it is worth also noting that the high Sb and Cu contents are probably related to the associate tetrahedrite. In the tetrahedrite particularly high values are found for Sb and Fe. The lesser commonly associated mineral phase showed normal characteristics and were quite similar to the mineral assemblages of the nearby deposits of «S. Carlo», the main difference consisting only in the presence of gersdorffite and a

lesser number of associated minerals. Both deposits have in common strike directions main minerals and similar gangues: chemical and physical data, as well as microscopic observations and the accessory phases observed for this mineralization of the Zilli area next to Fiumedinisi (Messina, Sicily), agree with the data of the previous workers: this first observed gersdorffite in the Peloritani

Mts., proved to be a low-temperature, ordered phase of space group $P2_13$.

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REFERENCES

- AMODIO MORELLI L. et al. (1976) - *L'arco calabro-peloritano nell'orogene appenninico-maghrebide*. Mem. Soc. Geol. Ital., 17, 1-60.
- ARTINI E. (1903) - *Note mineralogiche sulla Valsassina*. Atti Soc. Ital. Sc. Nat. Museo Civ. St. Milano, 42, 101-117.
- ATZORI P., SASSI P. (1973) - *The barometric significance of the Savona phyllites (M. Peloritani)*. Schweiz. Min. u. Petr. Mitt., 53/2, 243-253.
- BAYLISS P., STEPHENSON N.C. (1967) - *The crystal structure of gersdorffite*. Min. Mag., 36, 38-42.
- BAYLISS P., STEPHENSON N.C. (1968) - *The crystal structure of gersdorffite (III), a distorted and disordered pyrite structure*. Min. Mag., 36, 940-947.
- BAYLISS P. (1969) - *X-ray data, optical anisotropism, and thermal stability of cobaltite, gersdorffite and ulmannite*. Min. Mag., 37, 26-33.
- BAYLISS P. (1982a) - *A further crystal structure refinement of cobaltite*. Amer. Miner., 67, 1048-1057.
- BAYLISS P. (1982b) - *A further crystal structure refinement of gersdorffite*. Amer. Miner., 67, 1058-1064.
- BONARDI G., GIUNTA G., DE VIVO B., LIMA A., PERRONE V., ZUPPETTA A. (1982) - *Mineralizzazioni dell'arco calabro-peloritano. Ipotesi genetiche e quadro evolutivo*. Boll. Soc. Geol. Ital., 101, 141-155.
- COMMISSION ON ORE MICROSCOPY (1977) - *IMA/COM Quantitative Data File* (Editor N.F.M. Henry). Applied Mineralogy Group. Mineralogical Society, London.
- CRAIG J.R., VAUGHAN D.J. (1981) - *Ore microscopy and ore petrography*. J. Wiley & Sons, New York.
- DONATI G., STAGNO F., TRISCARI M. (1978) - *Ricerche sulle manifestazioni metallifere dei M. Peloritani. III) Giacimenti delle C.de S. Carlo, Montagne e vicini, presso Fiumedinisi (Messina)*. Atti Acc. Peloritana Pericolanti, Cl. Sc. Mat. Fis. Nat., 56, 177-238.
- DUNCOMB P., JONES E.M. (1969) - *Electron probe microanalysis: an easy to use computer program for correcting quantitative data*. Report n. 260, Tube Investigation Research Lab., Hinxton, Saffron, England.
- FERLA P. (1982a) - *Aspetti strutturali e composizionali delle sequenze cristalline prealpine nei M. Peloritani*. In «Guida alla Geologia della Sicilia Occidentale», Ed. Catalano R. e D'Argeo B., Società Geologica Italiana, Guide Geologiche Regionali.
- FERLA P. (1982b) - *Inquadramento geologico-petrografico delle mineralizzazioni metallifere nei M. Peloritani (Sicilia)*. Rendic. Soc. Ital. Min. Petr., 38, 1075-1091.
- GALOPIN R., HENRY N.F.M. (1972) - *Microscopic study of opaque minerals*. W. Heffer & Sons Ltd., Cambridge, England.
- HAWLEY J.E., STANTON R.L., SMITH A.Y. (1961) - *Pseudo-eutectic intergrowths in arsenical ores from Sudbury*. Canad. Miner., 6, 555-575.
- JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS (1974) - *Selected powder diffraction data for minerals*. Swarthmore, U.S.A.
- KLEMM D.D. (1965) - *Synthesen und Analysen in den Dreieck diagrammen FeAsS-CoAsS-NiAsS und FeS₂-CoS₂-NiS₂*. Neues Jahr. Abh., 103, 205-255.
- OLSHAUSEN S.K.V. (1925) - *Strukturuntersuchungen nach der Debye-Scherrer Method*. Zeit. Krist., 61, 463-514.
- PALACHE C., BERMAN H., FRONDEL C. (1944) - *The system of mineralogy - Vol. I*. Wiley Sons, New York.
- PEACOCK M.A., BERRY L.G. (1940) - *Röntgenographic observations on ore minerals*. Toronto Univ. Studies, Geol. ser., 44, 47-69.
- PICOT P., IOHAN Z. (1982) - *Atlas of ore minerals*. B.R.G.M. Elsevier Publ., Amsterdam.
- PREWITT C.T. (1974) - *A cell refinement program*. Dpt. Earth and Space Sciences, New York State University. Version of august 1975 modified by P.A. Cupley Cambridge, England.
- RAMDOHR P. (1980) - *The ore minerals and their intergrowths*. 2nd ed. Pergamon Press, Oxford.
- TRISCARI M., SACCÀ C. (1982) - *Scheelite at the «S. Carlo» Sb-Cu-Ag Mine, Fiumedinisi, Messina, Italy*. Miner. Petr. Acta, 26, 159-168.
- VAUGHAN D.J., CRAIG J.R. (1978) - *Mineral chemistry of metal sulphides*. Cambridge University Press, Cambridge, England.