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OCCURRENCE AND GENESIS OF RARE ARSENATE AND PHOSPHATE MINERALS AROUND PIZZO CERVANDONE, ITALY/SWITZERLAND

ABSTRACT. — Physical and X-ray data from a number of rare minerals (mostly arsenates) such as cafarsite, asbecasite, and chernovite, from the region around the Pizzo Cervandone on the Swiss-Italian border, are presented. The genesis of these minerals, many of which have not been previously described from Italian territory, is explained as the result of the « remobilisation » of an old (Hercynian) Cu-As-ore deposit in the center of the area. Such a remobilisation process has been previously postulated to account for the occurrence of sulphosalt minerals (Pb-Cu-Ag-As sulphides) in the dolomitic rocks at Binntal to the north of the region (in particular at Lengenbach). All the minerals described in this paper are new to Italian territory.

RIASSUNTO. — In questo lavoro descriviamo una regione attorno al Pizzo Cervandone, sul confine italo-svizzero, tra Binntal (Svizzera) e la Val Devero (Italia). Questa regione è diventata nota dopo il ritrovamento di una serie di minerali rari e, a volte, unici (in prevalenza arseniati) come la Cafarsite, l'Asbecasite, la Chernovite, il Clorotilo-Mixite, ecc. di cui vengono riportati i dati fisici e quelli risultanti dall'esame ai raggi X, ecc.

Tali minerali (compreso il Nb-Rutilo) rappresentano, tutti, specie nuove per il territorio italiano.

La genesi di questi minerali è spiegata come conseguenza dei processi di rimozione di un antico (Erciniano) deposito minerale di Cu-As esistente nel centro della zona.

L'esistenza di un tale processo di rimozione era stata postulata precedentemente nel tentativo di spiegare il ritrovamento di un gran numero di straordinari minerali del tipo solfosali (soprattutto solfoarseniuri di Pb, Cu, Ag) nelle rocce dolomitiche più a nord (Binntal, in special modo Lengenbach).

ZUSAMMENFASSUNG. — In dieser Arbeit wird eine mineralogisch sehr ungewöhnliche Region beschrieben, die sich rund um den Pizzo Cervandone entlang der Grenze zwischen Binntal (Schweiz) und Valle Devero (Italien) erstreckt. Das Gebiet ist bekannt geworden durch das Vorkommen einer Anzahl von seltenen und einzigartigen Mineralien (meist Arsenat- resp. Arsenit-Mineralien), wie etwa Cafarsit, Asbecasit, Chernovit, Chlorotil-Mixit, etc., von welchen physikalische, kristallographische, röntgenographische Untersuchungsergebnisse mitgeteilt werden. Die Entstehung dieser ungewöhnlichen Mineralien wird auf Remobilisationsprozesse einer hercynischen Kupfer-Arsen-Erzlagerstätte zurückgeführt, die im Zentrum der Region liegt. Die Existenz solcher Remobilisationsvorgänge war in einer früheren Arbeit postuliert worden, um die Entstehung einer grossen Zahl von höchst ungewöhnlichen Sulfosalz-Mineralien (Blei-Kupfer-Silber-Arsensulfide) im Dolomit des weiter nördlich gelegenen Binntales (speziell Lengenbach) erklären zu können.

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RÉSUMÉ. — Dans cette oeuvre nous décrivons une région autour du Pic Cervandone, à la frontière italo-suisse, entre Binntal (Suisse) et la Vallée Devero (Italie). Cette région est devenue connue après la découverte d'une série de minerais rares et parfois uniques (les plus souvent des arsénites) tels que la Cafarsite, l'Asbecasite, la Chernovite, le Clorotilo-Mixite, etc. dont sont rapportées les caractéristiques physiques et celles qui résultent de l'examen aux rayons X, etc.

De tels minerais (y compris le Nb-Rutil) représentent tous des espèces nouvelles pour le territoire italien.

La genèse de ces minerais est expliquée comme la conséquence de procès de déplacement d'un ancien (Erciniano) dépôt mineral de Cu-As existant au centre de la zone.

L'existence d'un tel procès de déplacement avait été postulée précédemment dans la tentative d'expliquer la découverte d'un grand nombre de minerais extraordinaires du type sulfosels (surtout des sulfoarséniures de Pb, Cu, Ag) dans les roches dolomitiques plus au nord (Binntal, en particulier Lengenbach).

1. Introduction

In order to explain the occurrence of a number of arsenic sulphosalt minerals in the Triassic dolomites of Binntal (southern Switzerland) it was suggested (GRAESER, 1965) that the arsenic was not primarily contained within the dolomite, but came from some extraneous source, presumed to be an extensive zone of Cu-As mineralisation which was found in granitic gneisses to the south.

This mineralised zone in the gneisses of the Binntal, around Pizzo Cervandone, consists of numerous secondary copper minerals, in particular malachite and azurite, accompanied by unaltered copper ores, for instance fahlore and chalcopyrite. A large number of rare arsenate and phosphate minerals are also present. Two of these, asbecasite and cafarsite (GRAESER, 1966), are new minerals. The purpose of the present work is to describe the range of minerals found in the Pizzo Cervandone region, and their relationship to each other.

2. The petrography of the granitic gneisses

Tectonically, the whole region belongs to the Monte Leone nappe, one of the lower Pinnidic (Simplon) nappes. The host rock of the mineralised zone is a light coloured, relatively coarse grained two-mica-gneiss. In thin section the rock appears homogeneous and equigranular. The slightly greenish white mica has been identified as phengite (GRAESER and NIGGLI, 1967). Biotite is abundant, green brown in colour, and forms narrow, strictly parallel layers. Potassium feldspar (mostly microcline) is common. Plagioclase ranges in composition from An_5 to An_{10} . Epidote (pistazite) is abundant and generally associated with biotite. Compared with similar gneisses of the Binntal region the rock is relatively rich in the accessory minerals zircon and apatite. The rock shows ortho character and is presumed to have formed under conditions of Alpine metamorphism from a normal granite of Hercynian age.

3. Mineralogical description

The region around the Pizzo Cervandone, on both sides of the Swiss-Italian border is rich in rare minerals. Table 1 lists the minerals found in the region, listed according to the STRUNZ (1970) crystallographic-chemical classification.

TABLE 1
Minerals from the Cervandone area

SULPHIDES	HALOGENIDES	OXIDES	CARBONATES
Chalcopyrite	Fluorite	Magnetite	Calcite
Tennantite		Hematite	Azurite
Pyrite		Quartz	Malachite
Molybdenite(2H)		Rutile	Synchisite
		Nb-rutile	
		Anatase	
		Aeschynite	
		Asbecasite	
MOLYBDATES	ARSENATES, PHOSPHATES	SILICATES	
Wulfenite	Xenotime	Titanite	
	Chernovite	Datolithe	
	Monazite	Epidote	
	Cafarsite	Tourmaline	
	Apatite	Tourmaline-Asbestos	
	Chlorotile-Mixite	Muscovite	
	Meta-Torbernite	Biotite	
	[Asbecasite]	Chlorites	
		Adularia	
		Albite	

Clearly, not all of these minerals have formed under the same conditions; it is possible to distinguish three mineral groups characterised by different origin and different age.

- I. Ore minerals from an old sulphide deposit, presumably of Hercynian age. To this group belong all the sulphide minerals and secondary copper carbonates.
- II. « Normal » fissure minerals, formed under conditions of Alpine metamorphism. All the silicates, oxides and some of the phosphates belong to this group.
- III. Minerals of unusual chemical composition, the origin of which is thought to be related to the « remobilisation » of the old Cu-As- sulphide deposit. This group includes all the arsenates (or arsenites) and a number of the phosphates. The intergrowth relationships between these minerals and those of group II suggests that the latter were deposited prior to the group III minerals.

The group III minerals are described in detail below. Of the minerals in groups I and II only those of particular interest will be mentioned.

The minerals of group I

The most interesting member of the group is the tennantite, which although for the most part altered to malachite and azurite, is fairly abundant. Spectroscopic analysis (GRAESER, 1965) has shown that the mineral is a relatively pure Cu-As-

fahlore (mole percentage tennantite approx. 85 %), with a small Sb content, traces of Bi, and by comparison with fahlore occurrences in the Binntal dolomites, poor in Ag and Zn. The tennantite occurs in veins of centimeter thickness associated with quartz, in the gneiss. Euhedral crystals have not been recorded. It is suggested that this mineral was the source of the As for the production of the As-sulphosalts of the Binntal dolomites.

The fissure minerals. Group II

This group comprises, as noted above, all the silicate and oxide minerals and a number of the phosphates. The arsenite mineral, asbecasite, which is listed as an oxide in the STRUNZ (1970) classification, will be treated here as an arsenate. Of the oxides, two, Nb-rutile and aeschynite, are uncommon.

Nb-rutile occurs in yellow crystal aggregates up to 1 cms across. Microprobe analyses have yielded a maximum Nb content of 1.5 wt %. The cell parameters are practically identical with those of ordinary rutile ($a_0 = 4.593$, $c_0 = 2.964$ Å). In habit and appearance the mineral is practically indistinguishable from normal rutile.

Aeschynite. The occurrence of this mineral in the Alps has only been recently described (SOMMERAUER et al., 1972). It occurs in the Cervandone region as small crystals (up to 5 mm) of a brown-red colour. Debye-Scherrer and single crystal X-ray studies have shown that the mineral shows no signs of metamict alteration, unlike most members of this series. The cell parameters of the Cervandone aeschynite are as follows:

$$\begin{aligned} a_0 &= 5.185 \text{ \AA} \\ b_0 &= 10.925 \text{ \AA} \\ c_0 &= 7.531 \text{ \AA} \end{aligned} \quad \text{Space group } D_{2h}^{16} - \text{Pbnm}$$

The arsenate and phosphate minerals. Group III

Apart from the common members, apatite, monazite, xenotime, etc., this group includes a number of interesting, and to a certain degree, unique minerals. Two, cafarsite and asbecasite proved to be new mineral species (GRAESER, 1966), whilst chernovite has been described from only one other locality (GOLDIN et al., 1967).



Chernovite is a yttrium arsenate which forms an isomorphous solid solution series with the yttrium phosphate xenotime, YPO_4 (GRAESER et al., 1973). The members of this series found around the Pizzo Cervandone show a variability in chemical composition from about 60 % to more than 80 % chernovite molecule. In the only other recorded occurrence of this mineral, in the Urals (GOLDIN et al., 1967), it was described as being present only as minute crystals less than 1 mm in length. In the Cervandone chernovite occurs as crystals up to 2 mm across of pseudo-octahedral habit. The colour varies from lemon-yellow (slightly altered material) to bright green for fresh specimens. With increasing substitution of phosphate for arsenate the refractive index of the mineral increases,

concomitantly the cell parameters enlarge, hence a simple and rapid estimation of the molar percentage of $YAsO_4$ is possible. Optical and crystallographic data for a chernovite sample with the highest As content found in the region (82 mol% $YAsO_4$) are tabulated in table 2 (data from GRAESER et al., 1973).

TABLE 2
Optical and X-ray data of chernovite (82 % $YAsO_4$ mol, SG 1053)

$a_0 = 7.09 \text{ \AA}$	strongest lines in powder diagram :		
$c_0 = 6.32$	hkl	d in \AA	I *
$c/a = 0.8914$	200	3.56	100
Space gr. $D_{4h}^{19} - 14_1/amd$	112	2.673	90
	220	2.509	40
Refractive index:	312	1.830	80
	400	1.776	20
$n_0 = 1.783 (Na_D)$	424	1.120	40

* Relative intensities, estimated by eye

Chernovite is commonly associated with Nb-rutile, magnetite, asbecasite and cafarsite, etc.

Cafarsite $Ca_6Mn_2Fe_4Ti_3[OH/(AsO_4)_3]_4$ cubic $T_h^2 - Pn3$

This arsenate was first described as a new mineral by GRAESER (1966). The original material consisted of two damaged brown nodules. The mineral has since been found in excellent crystalline form (IMHOFF, personal communication). Crystals of this new sample generally show combinations of octahedral and hexahedral faces, with the former predominand; often a pentagondodecahedral face is present. The drawing of fig. 1 is based on optical goniometer measurements of one of the crystals

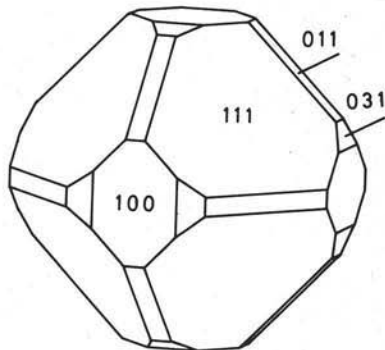


Fig. 1. — Cafarsite - idealized crystal drawing. The crystal shows the combination of octahedron, hexahedron, and a pentagondodecahedron $\{310\}$.

supplied by Imhof. The indices of the pentagondodecahedron form were calculated to be $\{310\}$. Besides this common cafarsite habit crystals showing only octahedral, or hexahedral, or rarely, only pentagondodecahedral faces, occur. The largest cafarsite crystals found hitherto reach up to 3 cms across and almost 50 g in weight (fig. 2).

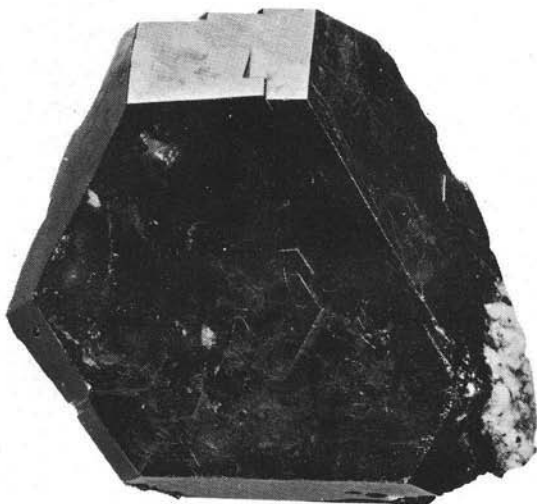


Fig. 2. — The largest cafarsite crystal found since its description as a new mineral. The octahedron edge visible in the photograph measures 25 mm. This sample shows strong predominance of the octahedron form.

The mineral is coloured dark brown to black, though small splinters are red translucent. The brown colour may be one reason why the mineral has gone unrecorded, it being confused with oxydised pyrite.

Table 3 lists the strongest reflections on a XRD powder pattern of fresh cafarsite.

TABLE 3

Powder data of cafarsite, Pizzo Cervandone (SG 1299)

hkl	d in Å	I	
111	9.17	40	
331	3.675	50	
510	3.140	60	
440	2.827	100	
530	2.747	80	$a_0 = 16.01 \pm 0.01 \text{ \AA}$
800	1.9995	40	
930	1.6857	60	

Cafarsite has been found in association with magnetite, malachite, tennantite, and asbecasite etc. Like chernovite it has been found in localities in Switzerland and Italy, though the best material is of Italian provenance.

Chlorotile-Mixite approx. $(\text{Cu,Fe})_2\text{Cu}_{12}[(\text{OH})_{12}(\text{AsO}_4)_6] \cdot 6\text{H}_2\text{O}$
hexagonal

Recent X-ray results (table 4) of a pale green powdery veneer that occurs on cafarsite has shown the presence of chlorotile-mixite. The data are at present insufficient to determine the mineral accurately as either chlorotile or mixite, the crystallographic data for the two minerals being very similar. It is hoped that final identification can be resolved once microprobe data on better crystallised material becomes available.

TABLE 4
X-ray data of chlorotile-mixite, Pizzo Cervandone

hkl	d in Å	I	
100	11.9	100	
111	4.450	60	$a_0 = 13.546 \text{ Å}$
211	3.546	70	$c_0 = 5.884$
002	2.935	60	$c/a = 0.434$
410	2.560	50	
321	2.455	80	

Meta-torbernite $\text{Cu}[\text{UO}_2/\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$ tetrag. $D_{4h}^7 - P4/nmm$

GRAESER (1972) noted the occurrence of this mineral in two restricted outcrops in the Swiss zone of the region. It is present as tiny, quadratic, tabular crystals (less than 1 mm across) of a brilliant green colour. It was anticipated that a solid solution series, analogous to that of chernovite-xenotime would be present. Careful study has shown however that only the pure phosphate mineral is present in the Cervandone region.

TABLE 5
Physical and crystallographic data of meta-torbernite, Cervandone region

	hkl	d in Å	I
$a_0 = 6.995$	110	4.98	100
$c_0 = 17.400$	200	3.50	80
$c/a = 2.487$	202	3.25	60
Space gr. $D_{4h}^7 - P4/nmm$	310	2.21	60
Refractive index :	304	2.047	70
$n_x = 1.626 \pm 0.002$ (N_D)	324	1.767	50
$2V_z = 0^\circ$ (+)			

Meta-torbernite occurs in association with black tourmaline (schorl), smokey quartz, albite, adularia, apatite and an unidentified bismuth mineral. Rarely, chernovite is also present. The presence of an uranium mineral in this region is also present. The presence of an uranium mineral in this region is unusual since the U content of the host Monte Leone gneiss is low.

Asbecasite $\text{Ca}_3(\text{Ti},\text{Sn})(\text{As}_3\text{BeSiO}_{10})_2$ ditrigonal $D_{3d}^4 - P\bar{3}c1$

Asbecasite (GRAESER, 1966) is relatively common throughout the region, occurring as aggregates of small intergrown lemon-yellow crystals. Good single crystals are rare. Those that have been found are always formed by a combination of two face-forms, rhombohedron ($10\bar{1}2$, indexing based on the ratio c/a as determined by XRD), and basal (0001), see fig. 3. The crystal structure has been determined by

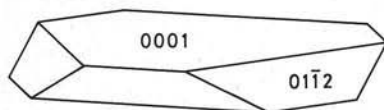


Fig. 3. — Asbecasite - idealized crystal drawing. The platy habit of the crystal is caused by the predominance of pinacoid {0001} over the rhombohedron.

CARNILLO et al. (1969); though the classification of the mineral is still under discussion; STRUNZ (1970) considered it to be an arsenite, whereas CODA (1969) is of the opinion that it should be considered to be a silicate.

The mineral is associated with colourless fluorite, cafarsite etc., and rarely with chernovite. Both Swiss and Italian localities have been recorded.

TABLE 6

X-ray and physical data of asbecasite, Cervandone region

$a_0 = 8.33 \text{ \AA}$	Powder diagram (only strongest reflections)		
$c_0 = 15.29$	hkl	d in Å	I
$c/a = 1.836$	111	4.030	50
Space gr. $D_{3d}^4 - P\bar{3}c1$	004	3.830	50
Refractive indices:	210	3.231	100
	300, 213	2.404	70
$n_0 = 1.86$ (n_{aD})	312	1.929	60
$n_E = 1.83$	410	1.746	50
$2V_X = 0-17^\circ$ (-)	411	1.571	50
		1.154	50

4. Genesis of the arsenate-phosphate (Group III) minerals of the Cervandone region

The extensive presence of a number of rare arsenate minerals of unusual chemical composition suggests that they have an origin different from that of the ordinary fissure minerals of the Cervandone region. The presence of extensive Cu-As mineralisation in the center of the area suggests that there is a correlation between the presence of the arsenate minerals and the arsenic deposit. The production and transportation of As bearing solutions from this deposit, due to the effects of Alpine metamorphism has already been postulated (GRAESER, 1965) to account for the presence of the large As mineralised zone in the dolomites

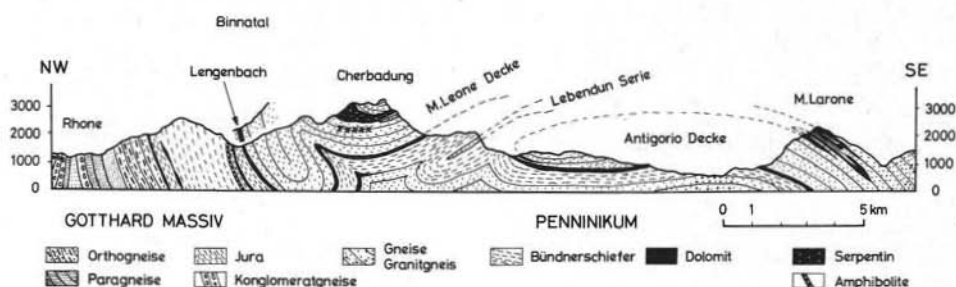


Fig. 4. — Geological section through the studied area. The localization of the Cu-As ore deposit is marked by crosses below Pizzo Cervandone (Cherbadung).

of Binnatal. It is suggested that the arsenate minerals in the gneiss are the products of the same process, the As becoming partially oxidised and redeposited as arsenate after the crystallisation of the ordinary fissure minerals. Arsenic transportation through the gneisses can be seen at the present day, for instance the existence of As rich spring water at the Alpe Veglia (Italy).

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