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A. Dini, P. Orlandi

COLORADOITE (HgTe), FROM BUCA DELLA VENA MINE, APUAN ALPS, TUSCANY, ITALY

Abstract - The first italian occurrence of the extremely rare mercury telluride coloradoite (HgTe) is reported from the Buca della Vena mine, Apuan Alps, Tuscany. The studied samples show fine and distinct sub-millimetric, tetrahedral or more complex black crystals of coloradoite on calcite. Chemical composition and cell parameter are very similar to those of coloradoite from other localities in the world and with synthetic phase. The presence of this rare telluride at Buca della Vena within an unusual mineral assemblage (Fe-Ba ore deposit), is probably due to a short lived increase in fTe_2, reflecting a finite and local tellurium supply in the vein cavities.

Key words - Coloradoite, tellurides, Buca della Vena mine, Apuan Alps,Tuscany, Italy.

Riassunto - *La Coloradoite (HgTe) della miniera di Buca della Vena (Alpi Apuane, Toscana, Italia).* Viene segnalato il ritrovamento di coloradoite, un raro tellururo di mercurio, nelle cavità di vene di calcite nella miniera abbandonata di barite e ossidi di ferro di Buca della Vena, Alpi Apuane. La coloradoite si presenta in cristalli ad abito tetraedrico o più complesso di colore nero. È la prima volta che vengono osservati cristalli ben formati di questo minerale. I dati chimici e diffrattometrici coincidono con quelli di coloradoiti di altre località e con il composto sintetico. La presenza di questo raro tellururo in un giacimento di Ba-Fe è singolare, e probabilmente riflette un temporaneo aumento della fTe_2, connesso ad una locale e limitata disponibilità di tellurio all'interno delle cavità.

Parole chiave - Coloradoite, tellururi, miniera di Buca della Vena, Alpi Apuane, Toscana, Italia.

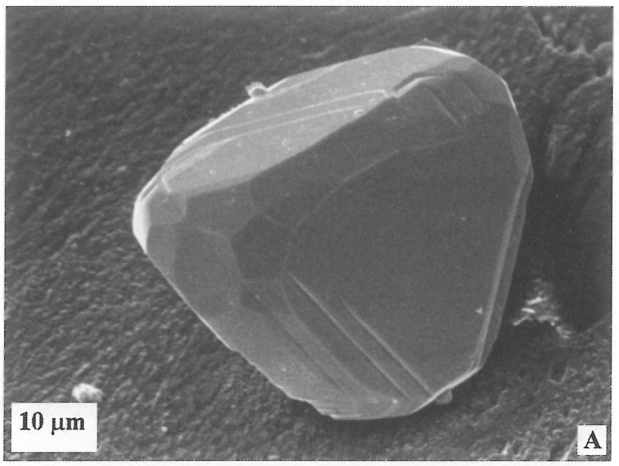
Introduction

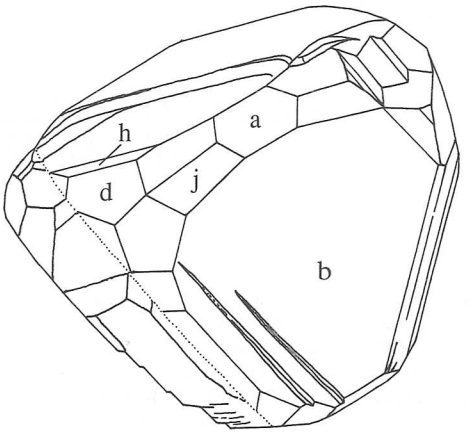
Coloradoite (HgTe) and temagamite (Pd_3HgTe_3) are the only two mercury tellurides present in nature; they are extremely rare and occur only as accessory minerals in some Au-Ag-Cu ore deposits.
Coloradoite was first identified by Genth (1877) in some gold deposits of Boulder County, Colorado. It was than identified in some other localities: Kirkland Lake and Hemlo districts, Ontario, Canada (Thompson, 1949); Kalgoorlie district, Western Australia (Markham, 1960); Emperor mine, Fiji Islands (Ahmod *et al.*, 1987); Ashanti mine, Ghana (Bowell *et al.*, 1990); Commoner mine, Zimbabwe (Twemlow, 1984). In all these localities coloradoite occurs, together with other Ag and Au tellurides, as black, brittle, millimetric microgranular metallic masses. Well formed crystals were never found in all these localities.
The present note describes the first occurrence of distinct crystals of coloradoite within the cavities of calcite veins, in the barite-pyrite-iron oxides deposit of Buca della Vena, Apuane Alps, Tuscany, Italy.

Geological setting and occurrence

The Buca della Vena mine exploited, until 1990, a small iron ore deposit, hosted in the metamorphic complex of the Apuan Alps; the ore bodies were constituted by barite, magnetite, hematite and subordinately pyrite lenses, located at the contact between Liassic-upper Triassic carbonatic formations (marbles and dolomite), and phyllitic formations of uncertain age (Paleozoic - Trias).
According to Carmignani *et al.* (1976), ore bodies in Buca della Vena mine should be the result of a metasomatic replacement of carbonatic rocks by hydrothermal fluids; on the contrary, Cortecci *et al.* (1985) suggest a singenetic theory that explain the genesis of this deposit with a metamorphic, fluids involving, remobilization of a Triassic sedimentary proto-ore deposit. Nevertheless all these authors are in agreement on the main role played by tectono-metamorphic alpine event (27-8 Ma) in the definition of the actual structural arrangement, mineralogical association and geochemical features of the ore deposit.
Carbonatic host rocks, ore bodies and some large carbonatic rocks lenses embedded into the ore bodies, are crossed by centimetric calcite veins. Veins within the phyllites are more rare and cut the main foliation. Such distribution is due to the brittle behaviour of the former rocks in respect to the ductile phyllites. The extensional character of some of these veins is outlined by their particular distribution as well as the growth of fiber like aggregates of quartz, calcite and barite, disposed at high angle to the vein walls. In this way we can tentatively attribute the formation of the veins and their minerals at the post-peak extensional stage of the tectono-metamorphic alpine event (Carmignani and Kligfield, 1990). Coloradoite, together with many other rare minerals, such as apuanite, versiliaite, derbylite, stibivanite, dessauite, beryl, etc., was found in small cavities widespread inside the calcite veins (Orlandi and Checchi, 1986).
Coloradoite occur as tetrahedral, pseudo-octahedral

Dipartimento di Scienze della Terra, Università di Pisa - Via S. Maria, 53 - 56126 - Pisa.





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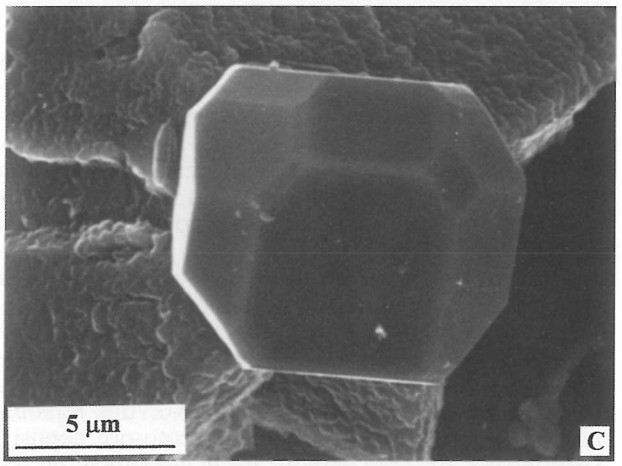

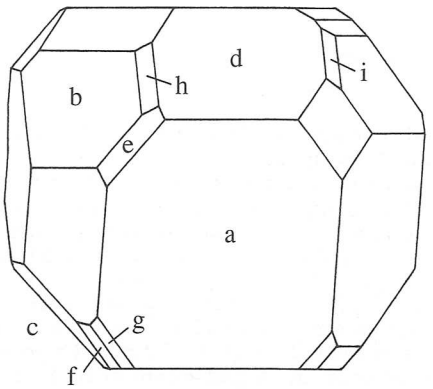

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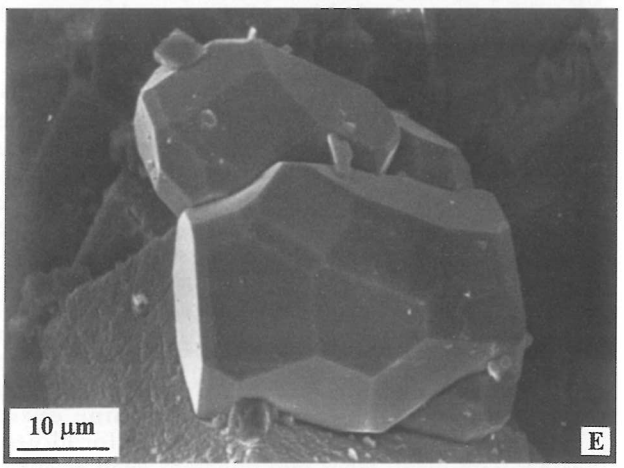

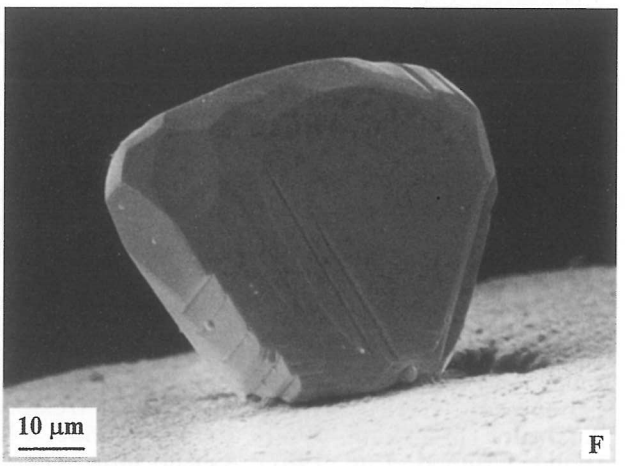

Fig. 1 - a) Twinned {111} coloradoite crystal with tetrahedral habit.
b) Coloradoite crystal drawing from fig. 1/a; a: {100}, b: {111}, d: {110}, h: {hhl} (probably {221}), j: {hkl} (probably {30 10 1})
c) Coloradoite complex crystal.
d) Coloradoite crystal drawing from Fig.1-c; a: {100}, b: {111}, c: {1$\bar{1}$1}, d: {110}, e: {211}, f: {2$\bar{1}$1}, g: {3$\bar{1}$1}, h: {221}, i: {2$\bar{2}$1}.
e) Coloradoite crystals aggregate.
f) A different view of coloradoite crystal of Fig. 1-a.

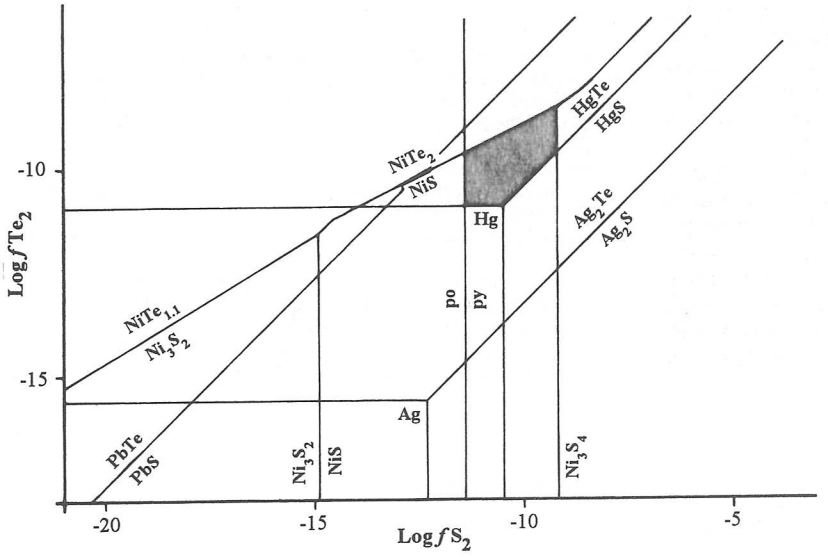

Fig. 2 - Stabilities of telluride and some sulfides as a function of the fugacities of S_2 and Te_2 at 300°C (after Afifi *et al.*, 1988a; modified). The shaded region represents the stability field for the coloradoite assemblage at Buca della Vena.

and more complex crystals. Complex crystals frequently build irregular group (Fig. 1/e) while simple ones occur as single crystals sometimes twinned according to the plane (111), (Fig. 1/a, f). Drawings reported in Fig. 1/b and Fig. 1/d were copied from SEM photographs (Fig. 1/a, 1/c). Fig. 1/a represents a tetrahedral (111) twinned crystal; associated forms are {111}, {110}, {hkl} (probably {30 10 1}) and a {hhl} (probably {221}). Crystal in Fig. 1/c shows the combination of the following forms : {111}, {$\bar{1}\bar{1}\bar{1}$}, {100}, {110}, {211}, {$2\bar{1}\bar{1}$}, {$3\bar{1}\bar{1}$}, {221}, {$\bar{2}\bar{2}\bar{1}$}. Two circle goniometer measurements were not collected due to the small dimensions of crystals (10-50 μm). Indicization was carried out by comparison with crystal drawings obtained from SHAPE drawing program.
Studied samples are preserved in the Museo di Storia Naturale e del Territorio, University of Pisa, with the catalogue number 16385.

Mineral chemistry and X-ray data

Coloradoite was identified by means of SEM-EDS chemical analyses and X-ray powder diffraction pattern by Gandolfi camera (114.6 mm and Cu Kα radiation). Qualitative EDS analyses showed the presence of Hg and Te and the absence of other elements with a.n.>11; composition from semiquantitative analyses resulted comparable to that of the synthetic stoichiometric compound.
Cell parameter, refined by least squares method from x-ray powder diffraction pattern, resulted: a = 6.462(2) Å, in good agreement with the parameter of the stoichiometric HgTe synthetic compound (a = 6.4604 Å).
Coloradoite from Buca della Vena mine represents the pure term of the compound HgTe; chemical composition and cell parameter are very similar to those of most samples from various localities in the world, although a copper bearing coloradoite with a copper content of 12 wt % is known (Povarennykh, 1972).

Genetic considerations and conclusion

Coloradoite represents the unique Te mineral in the Apuan Alps; on the contrary mercury sulphide is very common in many mines from this area: cinnabar occurs in the mercury ore deposit of Ripa and Levigliani, and, as rare occurence, at the Pollone mine. Zincian metacinnabar and mercurian sphalerite were also found in the Levigliani mine (Dini *et al.*, 1995), while polhemusite was described from Monte Arsiccio mine (Costagliola *et al.*, 1990).
Cinnabar is also present at Buca della Vena mine in calcite veins similar to those where coloradoite was found, together with tetraedrite, millerite, pirite, ematite, calcite, quartz, and barite.
Previous paragenetic informations together with fS_2-fTe_2 phase diagrams for tellurides (Afifi *et al.*, 1988/a, b) were tentatively used to obtain the physical-chemical parameters during coloradoite growth. The results were compared with the numerous estimates available for this locality (Benvenuti *et al.*, 1986; Cortecci *et al.*, 1985).
Geothermometric data for many gold telluride deposits in the world indicate that temperature of tellurides deposition in veins was in general lower than 350°C, and tipically below 250°C (Ahmod *et al.*, 1987, Afifi *et al.*, 1988/b). At Buca della Vena isotopic temperatures for barite-pyrite pair span the 213°-324°C interval (Benvenuti *et al.*, 1986) while homogeneization temperature, obtained on beryl from the same veins falls between 270° and 310°C (Duchi *et al.*, 1993). On the basis of these data we chose the fS_2-fTe_2 phase diagram calculated at 300°C by Afifi *et al.* (1988a) to outline the stability field of coloradoite mineral

assemblage at Buca della Vena. In Figure 2 the shaded region represent the narrow field of existence of coloradoite associated with millerite and pyrite; fS_2 values (log fS_2 = -10, -11) are consistent with the available data from other barite-pyrite-Fe oxide ore deposits in the Apuan Alps.

The absence of coloradoite in the Ripa and Levigliani cinnabar deposits and its extreme rarity in Buca della Vena mine, indicates low amount of Te within the system and then prevailing fTe_2 values below the HgTe-HgS reaction (about log fTe_2 = -10 -11 at 300°C). When compared with the entire vein mineral assemblage the deposition of coloradoite at Buca della Vena mine is due to a short lived increase in fTe_2, probably reflecting a finite and local tellurium supply.

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