

Characterization and genetic inferences of arsenates, sulfates and vanadates of Fe, Cu, Pb, Zn from Mount Cervandone (Western Alps, Italy)

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ABSTRACT. — Mount Cervandone is among the most renowned mineral deposits in the Alpine chain and type locality of several very rare REE-arsenates. The present study allowed for the characterization and description of the assemblages of a number of arsenates, sulfates and vanadates of Fe, Cu, Pb, Zn that occur with a number of rare minerals of B, Be, As, Nb, Y, REE on the Italian slope of Mount Cervandone. The mineral deposits of Cervandone mainly occur in alpine quartz fissures and pegmatitic dikes. The pegmatitic dikes are hosted by very fine grained two-mica leucocratic gneisses. Locally the pegmatite dikes are cross cut by quartz veins. The assemblages reported in this study indicate that arsenates, sulfates and vanadates of Fe, Cu, Pb, Zn are mainly hosted in quartz veins and only occur sporadically in pegmatitic dikes. In the pegmatite dikes the Be, As, Y and REE minerals occur with higher frequency than in the quartz veins. During the Alpine event we account for a “scenario” where swarms of NYF (niobium, yttrium, fluorine) granitic pegmatites intruded the leucogranitic-aplites. It is unequivocal that the pegmatites show a strong NYF geochemical signature represented by the occurrence of an unique mineralogy.

Following these premises we expected that during the Alpine event As-enriched hydrothermal fluids circulating through pegmatite dikes allowed the

destabilization of accessory minerals hosted in these dikes and consequently the hydrothermal fluids assimilated light elements (Be, B, F), high field strength elements (Y, Nb, Ta) and rare earth elements (La, Ce, Nd, Th, U) and allowed the crystallization of several rare and exotic minerals.

KEY WORDS: *Arsenates, hydrothermal fluids, Mount Cervandone, NYF-pegmatites, quartz fissures, sulfates, vanadates.*

RIASSUNTO. — Il Monte Cervandone è uno dei principali depositi mineralogici presenti sulla catena Alpina e località tipo di numerosi arseniati di terre rare. Il presente studio ha permesso di caratterizzare e descrivere numerosi arseniati, solfati e vanadati di Fe, Cu, Pb, Zn che si rinvergono associati a rari minerali di B, Be, As, Nb, Y e REE sul versante italiano del Monte Cervandone. Il giacimento mineralogico del Cervandone è principalmente associato a fessure di quarzo di tipo alpino e filoni pegmatitici. I filoni pegmatitici sono ospitati in gneisses leucogranitici a due miche. Localmente i filoni pegmatitici sono intersecati da filoni quarzosi. Le associazioni mineralogiche riportate in questo studio indicano che gli arseniati, i solfati e i vanadati di Fe, Cu, Pb, Zn sono principalmente presenti nei filoni quarzosi mentre risultano essere sporadiche nelle pegmatiti. I minerali contenenti Be, As, Y and REE si rinvergono in concentrazioni più elevate nei filoni pegmatitici mentre sono presenti con minore frequenza nelle vene

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quarzose. Nel corso dell'evento alpino è possibile ricostruire uno scenario dove sciami di pegmatiti granitiche NYF (niobio, ittrio, fluoro) hanno intruso i leucograniti aptitici. Difatti è inequivocabile che le pegmatiti registrano una forte impronta geochemica a NYF determinata da una mineralogia assolutamente caratteristica.

Su queste premesse si può ritenere che durante l'evento alpino fluidi idrotermali arricchiti in arsenico siano circolati nei filoni pegmatitici permettendo la destabilizzazione di una serie di minerali accessori presenti in questi filoni e conseguentemente i fluidi idrotermali, avendo assimilato elementi leggeri (Be, B, F), elementi ad elevata forza di campo (Y, Nb, Ta) ed elementi delle terre rare (La, Ce, Nd, Th, U), hanno permesso la cristallizzazione di numerosi minerali rari.

PAROLE CHIAVE: *Arseniati, fluidi idrotermali, monte Cervandone, pegmatiti NYF, fessure di quarzo, solfati, vanadati.*

INTRODUCTION

Mount Cervandone and the Swiss Wannigletscher (also named Cherbadung) are among the most renowned mineral deposits in the Alpine mountain chain. Several very rare REE arsenates including asbecasite (Graeser 1966), cafarsite (Graeser 1966), cervandonite-(Ce) (Armbruster *et al.* 1988), fetiasite (Graeser *et al.* 1994), gasparite-(Ce) (Graeser and Schwander 1987) and paraniite-(Y), (Demartin *et al.* 1994) were first described at these localities. The aforementioned mineralogy at Mount Cervandone and at Wannigletscher were extensively investigated in the past because of the very rare REE-arsenates which occur in this deposit and the mineralization was described as a typical example of alpine quartz type fissures (Albertini 1991; Graeser and Albertini 1995).

Arsenates, sulfates and vanadates of Fe, Cu, Pb, Zn occur with many other mineral phases which include arsenates and phosphates of Y, REE (rare earth elements), oxides of Y, Nb, Ta, REE, carbonates of Bi, REE and silicates of B, Be and Y that previous authors have described at Mount Cervandone and at Wannigletscher (Graeser and Stalder 1976; Albertini 1991; Graeser and Albertini

1995; Praeger and Crumbach 2004; Cuchet *et al.* 2005).

Field observations established the mineral deposit of Cervandone is mainly hosted in alpine quartz fissures and pegmatitic dikes. Based on these observations, this study expected to relate the formation of a number of rare minerals of B, Be, As, Nb, Y, REE, that occur with arsenates, sulfates and vanadates of Fe, Cu, Pb, Zn with the circulation of hydrothermal fluids. During the Alpine event As-enriched hydrothermal fluids, circulating through the pegmatite dikes, destabilized pre-existing accessory minerals contained in HFSE-rich (high field strength elements) pegmatites. These pegmatites with a NYF geochemical signature liberated Y, Nb, Ta and REE (La, Ce, Nd, Th and U). Low temperature hydrothermal fluids formed the quartz veins but also allowed the crystallization of several rare minerals.

ANALYTICAL METHODS

Sixty specimens containing arsenates, sulfates and vanadates of Fe, Cu, Pb, Zn from Mount Cervandone were observed under a stereomicroscope in order to describe of each mineralogical assemblage. Additionally, a number of samples were selected for chemical and/or diffraction data in order to characterize the specific mineral phases.

Mineralogical analyses were performed utilizing X-ray powder diffractometers and "JEOL" 5610 LV scanning electron microscope (SEM) equipped with a "Gresham" EDXS spectrometer. Powder diffraction data were collected with a "Panalytical X'Pert Pro" instrument operating at 40 kV and 40 mA with CuK α radiation at the Department of Earth Sciences of the University of Milano-Bicocca. Powder data for tyrolite were collected with a "Rigaku" DMAX III X-ray diffractometer operating at 40 kV and 40 mA with CuK α radiation at the Department of Structural and Inorganic Stereochemistry of the University of Milan. Diffraction peak intensities were measured in the 2 θ range 5-80° except for cornubite (range 5-110°); NIST Silicon 640c was used as an internal standard. Antlerite, linarite, mimetite, olivenite, pharmacosiderite, strashimirite and

vanadinite reflections were indexed to obtain unit-cell parameters. Brochantite- $2M_1$, cornubite and tyrolite unit cell parameters were refined with “Rietveld” method using “GSAS-EXPGUI” program (Larson and Von Dreele 2000; Toby 2001). Due the scarcity of material available for X-ray diffraction reliable cell parameters for duftite could not be obtained. The scarcity of material also precluded the collection of X-ray diffraction data of mottramite. Nevertheless mottramite and mimetite were characterized by means of electron microprobe analyses (EPMA) carried out at an accelerating voltage of 20kV, a filament current corresponding to 85 μ A, a beam diameter of 2 μ m (25 spot size) and count time of 60 s per point analysis. Quantitative analyses were performed on a polished section utilizing a series of natural standards (apatite for P; realgar for As; vanadinite for V and Pb) and synthetic metals (copper, iron and zinc).

All analyzed specimens were catalogued and deposited in the collections of the Museum of Natural History of Milan and of the Museum of Mineralogy of Padova.

DESCRIPTION OF THE MINERALIZATION

The investigated area of Mount Cervandone includes steep rock walls and a talus field between “Bandiera” peak and “Canalino Ferrari”. In this area swarms of sub-horizontal and parallel dikes with pegmatitic texture outcrop for several meters along the central body of Mount Cervandone. These pegmatitic dikes are hosted by very fine grained two-mica leucocratic gneisses related to the “Mount Leone-Arbola” nappe (Dal Piaz 1975). These dikes have decimetric thickness and are composed of coarse vitreous quartz, K-feldspar and greenish micas (probably muscovite). Sporadic pegmatitic dikes contain fractured black tourmaline prisms and contorted mica flakes embedded in vitreous “smoky” quartz exhibiting boudinage-like textures. Locally the pegmatite dikes are cross cut by quartz veins up to several decimeters in thickness. The quartz veins are generally subvertical, discordant with respect to the foliation of the gneissic host rock and frequently contain open fissures lined with quartz crystals.

Along the north-east flank of “Bandiera” peak a mineralogical deposit occurring in quartz veins was investigated. This deposit includes large alpine type quartz fissures that may contain museum quality specimens. Smoky quartz crystals coated by dodecahedral and octahedral crystals of cafsarsite were collected. A number of accessory mineral phases were also collected and they include weathered, brownish masses of tennantite, agardite-(Y), asbecasite, chernovite-(Y), gasparite-(Ce), rutile and minor anatase. Along the endocontact of the quartz vein with the two-mica leucocratic gneisses, a number of arsenates, sulfates and vanadates of Fe, Cu, Pb, Zn occur. Four characteristic assemblages were observed and include:

brochantite- $2M_1$ (Fig. 1) + cerussite + duftite + linarite + olivenite (Fig. 3) + strashimirite (Fig. 4)

antlerite + brochantite- $2M_1$ + cyanotrichite + K-feldspar + muscovite

pharmacosiderite + chrysocolla + “fibrous” olivenite

tyrolite + chrysocolla + black tennantite + amorphous yellow earthy As, Bi, Cu unnamed phase.

Around the main quartz vein tiny millimetric quartz veins sporadically contain vanadium- and bismuth-bearing mineralization and the following assemblages were also observed:

earthy, yellow brown bismutite + cerussite + galena + mimetite

mottramite (Fig. 2) + vanadinite + hematite + anglesite

Another mineral deposit, currently under investigation, is located along the central body of Mount Cervandone. This deposit includes a swarm of sub-horizontal and parallel pegmatite dikes. These dikes also contain decimetric cavities that are genetically related to the quartz veins that intersect the pegmatite dikes. A number of Be-As-Y-REE minerals were observed and they include asbecasite, cervandonite-(Ce), crichtonite-senaite group minerals, gasparite-(Ce) and xenotime-(Y). Tennantite masses are present in small amounts and are typically rimmed by azurite, chrysocolla and malachite; minor anatase and rutile were also identified. In this deposit cornubite was the only copper arsenate observed and occurs associated with quartz and K-feldspar.



Fig. 1 – SEM image shows platy tabular crystals of brochantite-2M₁ (dark in the picture) to 0.3 millimeters in length. Brochantite-2M₁ is associated with elongated prismatic crystals of linarite to 0.5 millimeters in length. Both brochantite-2M₁ and linarite lie on microcrystals of cerussite.

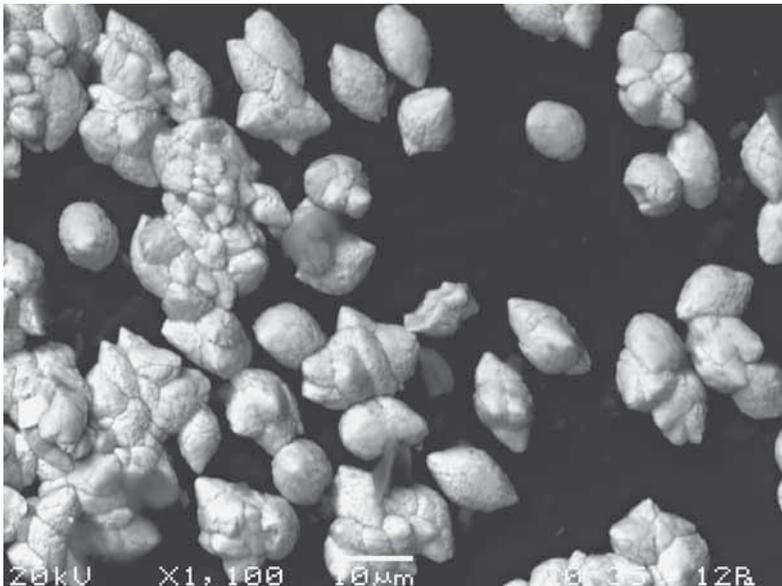


Fig. 2 – SEM image shows unusual dipyramid crystals with rounded edges of mottramite up to 0.04 millimeters in length. Mottramite crystals are covered by thin crusts of opal.



Fig. 3 – SEM image shows aggregates of olivenite composed of platy tabular microcrystals to 0.02 millimeters in length. Above in the middle, a group of laminar crystals of strashimirite to 0.02 millimeters in length are associated.

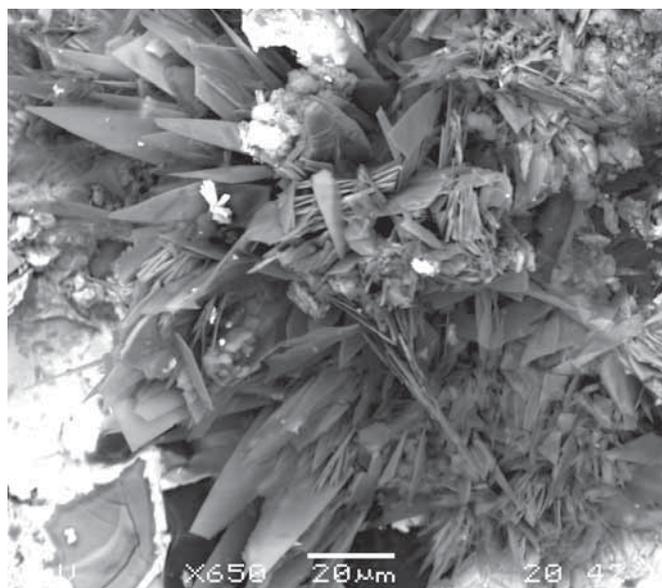


Fig. 4 – SEM image shows an aggregate of laminar crystals of strashimirite. The very thin crystals of strashimirite to 0.02 millimeters in length evidence typical acute terminations.

DISCUSSION

Previous authors explained that the enrichment of arsenic- and copper-bearing minerals was facilitated by the circulation of hydrothermal fluids after the remobilisation of an old Cu-As (Hercynian) ore deposit during the Alpine event (Graeser 1965; Graeser and Roggiani 1976).

It is unequivocal that As-rich hydrothermal fluids contributed to the formation of this deposit but the genetic inferences should also take into consideration the presence of a complex and exotic mineralogy including many Be-As-Y-REE minerals. Field observations identified swarms of pegmatitic dikes composed of quartz + K-feldspar + micas and occasionally black prisms of tourmaline. These dikes are strongly deformed and contorted but they are generally concordant with the foliation of the fine-grained two-mica leucocratic gneiss. Alpine type quartz veins are subvertical, cross cut the gneissic foliation and often intersect the pegmatite dikes allowing the formation of quartz cavities, frequently containing Be-As-Y-REE minerals. The assemblages reported in this study indicate that arsenates, sulfates of Fe, Cu, Pb, Zn are mainly hosted by quartz veins while these minerals are sporadically distributed in the pegmatite dikes. Vanadium- and bismuth-bearing minerals are associated with minor secondary quartz veins and do not appear to be related with the major As-mineralization. In the pegmatite dikes the Be, As, Y and REE minerals occur with frequency higher than in the quartz veins. However As-bearing minerals like asbecasite, cafarsite and tennantite can also be present in pegmatitic dikes.

During the Alpine event we account for a "scenario" where swarms of NYF (niobium, yttrium, fluorine) granitic pegmatites (Černý 1990a; Černý 1990b) intruded the leucogranitic-aplites. It is unequivocal that the pegmatites show a strong NYF geochemical signature represented by the occurrence of an unique mineralogy that includes: aeschynite-(Y), agardite-(Y), niobian-anatase, cervandonite-(Ce), chernovite-(Y), crichtonite-senaite group minerals, fergusonite-(Y), fluorite, gadolinite-(Y), monazite-(Ce), parniite-(Y), niobian-rutile, synchysite-(Ce), and xenotime-(Y) (Graeser and Stalder 1976; Albertini 1991; Graeser and Albertini 1995).

Field observations have also identified the two-mica fine grained leucocratic gneisses of Mount Cervandone, in which the pegmatites are hosted, can be described as metamorphosed leucogranitic-aplitic rocks.

Following these premises we expected that during the Alpine event As-enriched hydrothermal fluids circulating through pegmatite dikes allowed the destabilization of accessory minerals hosted in these dikes and consequently the hydrothermal fluids assimilated light elements (Be, B, F), high field strength elements (Y, Nb, Ta) and rare earth elements (La, Ce, Nd, Th, U) and allowed the crystallization of several rare and exotic minerals of B, Be, As, Nb, Y and REE.

CONCLUSIONS

Mineralogical and field studies, performed in collaboration with the Natural Park "Veglia-Devero", allowed the characterization of a number of arsenates, sulfates and vanadates of Fe, Cu, Pb, Zn that occur on the Italian slope of Mount Cervandone. Several arsenates, sulfates and vanadates which represent the first descriptions for Mount Cervandone and Wannigletscher were identified (Tab. 1) and a number of arsenates and sulfates only previously reported at Wannigletscher were also characterized (Tab. 2). (Schmutz *et al.* 1982; Meisser and Ansermet 1993; Kolitsch 1998).

Further studies are needed to address the distribution of Be-As-Y-REE minerals and describe in more detail the mineralogical sequences that occur in pegmatite dikes and quartz veins of the Mount Cervandone-Wannigletscher region. We will also expect to recognize and identify relict mineralogy represented by Nb-Ta oxides, allanite or gadolinite group minerals in the pegmatites, in order to account for the hydrothermal overprint during the Alpine event that destabilized and caused the partial to complete dissolution of accessory phases contained in the NYF pegmatitic dikes.

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TABLE 1 – Arsenates, sulfates and vanadates representing the first occurrences at Wannigletscher and at Mount Cervandone. Linarite, mimetite, olivenite and vanadinite cell data agree with those reported in Strunz and Nickel, (2001).

Minerals	Mineral description and assemblage	Cell parameters	Notes
Duftite	Occurs as grass green coatings and globular aggregates. SEM images reveal the mineral is composed of fibrous-radiated mammillary aggregates. Duftite is associated with brochantite- $2M_1$, cerussite, linarite, olivenite and strashimirite.	Main diffraction d_{obs} peaks correspond to 3.318 (34), 2.952 (100), 2.653 (8), 2.561 (12), 2.409(10), 2.084 (4), 1.867 (8), 1.753 (4), 1.659 (3), 1.489 (3), Å.	A refinement of the unit cell of duftite was not feasible due the scarcity of material available. SEM-EDS analyses excluded Ca presence and avoided a possible confusion with β -duftite, an intermediate Ca-rich member of the duftite-conichalcite series (Guillemin, 1956; Kharisun <i>et al.</i> , 1998).
Linarite	Forms vitreous, brilliant, dark blue elongated prismatic crystals, to 1 millimeter in length. Linarite is associated with brochantite- $2M_1$, cerussite, duftite, olivenite and strashimirite.	$a = 9.692(3)$ Å $b = 5.649(2)$ Å $c = 4.688(2)$ Å $\beta = 102.70(2)^\circ$ $V = 500.85$ Å ³	
Mimetite	Forms coatings of submillimetric yellowish, pale-green hexagonal prisms associated with bismutite, cerussite, galena and quartz.	$a = 10.244(1)$ Å $c = 7.456(1)$ Å $V = 677.60$ Å ³	Electron microprobe analyses (EPMA) revealed PbO (75.1 wt%), As ₂ O ₅ (20.1 wt%), P ₂ O ₅ (2.8 wt%), Cl (2.4 wt%).
Mottramite	Occurs as yellowish thin coatings on quartz. SEM images reveal the coatings are composed of microcrystals, 0.05 millimeters in length, cone-shaped which actually are dipyramids with rounded edges. Mottramite is associated with anglesite, hematite, quartz and vanadinite.		The scarcity of material precluded the collection of X-ray diffraction data. Electron microprobe analyses (EPMA) revealed PbO (54.6 wt%), V ₂ O ₅ (20.4 wt%), CuO (16.8 wt%), As ₂ O ₅ (3.1 wt%), P ₂ O ₅ (0.8 wt%), ZnO (0.5 wt%).
Olivenite	Forms millimetric olive-green aggregates. SEM images show the aggregates to consist of platy tabular microcrystals, 0.02 millimeters in length. Olivenite is associated with brochantite- $2M_1$, cerussite, duftite, linarite and strashimirite.	$a = 8.243(3)$ Å $b = 8.621(3)$ Å $c = 5.943(1)$ Å $V = 422.37$ Å ³	
Vanadinite	Forms yellow-brownish millimetric hexagonal elongated prismatic crystals with dipyramidal terminations. Vanadinite is associated with anglesite, hematite, mottramite and quartz.	$a = 10.305(3)$ Å $c = 7.377(2)$ Å $V = 678.51$ Å ³	

TABLE 2 – *Arsenates and sulfates previously only reported at Wannigletscher and actually also occurring at Mount Cervandone. Antlerite cell data agree with Hawthorne et al. (1989). Brochantite-2M₁ cell data agree with those reported in literature (Cocco and Mazzi, 1959; Merlino et al., 2003). Cornubite cell refinement agree with the data reported by Sieber et al. (1984). Pharmacosiderite cell data agree with those reported in Strunz and Nickel (2001). Strashimirite cell data agree those reported in Mincheva-Stefanova (1968). Tyrolite cell refinement agree with the data reported by Krivovichev et al. (2005).*

Minerals	Mineral description and assemblage	Cell parameters	Notes
Antlerite	Occurs as greenish-blue aggregates to 1 centimeter. SEM images show single platy tabular crystals 0.05 millimeters in length. Antlerite is associated with brochantite-2M ₁ , cyanotrichite, white K-feldspar and muscovite.	$a = 8.268(1) \text{ \AA}$ $b = 6.053(1) \text{ \AA}$ $c = 11.998(2) \text{ \AA}$ $V = 600.47 \text{ \AA}^3$	
Brochantite-2M ₁	Forms vitreous, brilliant, emerald green, platy tabular crystals to 1 millimeter in length. SEM images show the brochantite-2M ₁ has “chisel” habit formed by acute prisms and cut by a basal pinacoid face. Brochantite-2M ₁ is associated with cerussite, duftite, linarite, olivenite and strashimirite.	$a = 13.164(3) \text{ \AA}$ $b = 9.864(5) \text{ \AA}$ $c = 6.117(3) \text{ \AA}$ $\beta = 103.95(4)^\circ$ $V = 770.89 \text{ \AA}^3$	
Cornubite	Occurs as millimetric dark green coatings and globular aggregates. SEM images reveal the mineral is composed of fibrous-radiated mammillary aggregates. Cornubite is associated with white K-feldspar and “smoky” quartz.	$a = 6.141(1) \text{ \AA}$ $b = 6.271(1) \text{ \AA}$ $c = 6.788(2) \text{ \AA}$ $\alpha = 93.15(1)^\circ$ $\beta = 111.49(1)^\circ$ $\gamma = 107.03(2)^\circ$ $V = 228.68(3) \text{ \AA}^3$	The morphology of cornubite resembles duftite, but cornubite is never associated with other copper, lead arsenates and sulfates.
Pharmacosiderite	Forms yellow-green thin coatings replacing tennantite and lining secondary reticulated cavities. SEM images show groups of cubic crystals with selective corroded faces. Pharmacosiderite is associated with pale blue chrysocolla and white “fibrous” prismatic olivenite.	$a = 7.965(1) \text{ \AA}$ $V = 505.31 \text{ \AA}^3$	SEM-EDS analyses excluded Ba presence (no solid solution with barium-pharmacosiderite).
Strashimirite	Forms radiated pale blue or whitish aggregates. SEM images reveal thin laminar crystals with acute terminations. Strashimirite is associated with brochantite-2M ₁ , cerussite, duftite, linarite and olivenite.	$a = 9.51(1) \text{ \AA}$ $b = 18.62(1) \text{ \AA}$ $c = 8.93(1) \text{ \AA}$ $\beta = 95.23(2)^\circ$ $V = 1573.70 \text{ \AA}^3$	
Tyrolite	Forms greenish, green-blue, millimetric platy laminar groups of crystals. Tyrolite is associated with chrysocolla and black metallic or brownish, if weathered, tennantite masses.	$a = 27.56(1) \text{ \AA}$ $b = 5.62 \text{ \AA}$ $c = 10.49 \text{ \AA}$ $\beta = 98.1(4)^\circ$ $V = 1608.56 \text{ \AA}^3$	

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