# Arsenotučekite, $\mathrm{Ni}_{18} \mathrm{Sb}_{3} \mathrm{AsS}_{16}$, a new mineral from the Tsangli chromitites, Othrys ophiolite, Greece 

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#### Abstract

Arsenotučekite, $\mathrm{Ni}_{18} \mathrm{Sb}_{3} \mathrm{AsS}_{16}$, is a new mineral discovered in the abandoned chromium mine of Tsangli, located in the eastern portion of the Othrys ophiolite complex, central Greece. Tsangli is one of the largest chromite deposit at which chromite was mined since 1870. The Tsangli chromitite occurs as lenticular and irregular bodies. The studied chromitites are hosted in a strongly serpentinized mantle peridotite. Arsenotučekite forms anhedral to subhedral grains that vary in size between $5 \mu \mathrm{~m}$ up to $100 \mu \mathrm{~m}$, and occurs as single phase grains or is associated with pentlandite, breithauptite, gersdorffite and chlorite. It is brittle and has a metallic luster. In plane-polarized light, it is creamy-yellow, the bireflectance is barely perceptible and the pleochroism is weak. In crossed polarized reflected light, the anisotropic rotation tints vary from pale blue to brown. Internal reflections were not observed. Reflectance values of arsenotučekite in air ( $R \mathrm{o}, \mathrm{Re}^{\prime}$ in \%) are: $41.8-46.4$ at $470 \mathrm{~nm}, 47.2-50.6$ at $546 \mathrm{~nm}, 49.4-52.3$ at 589 nm , and $51.3-53.2 \mathrm{at} 650 \mathrm{~nm}$. The empirical formula of arsenotučekite, based on 38 atoms per formula unit, and according to the structural results, is $\left(\mathrm{Ni}_{16.19} \mathrm{Co}_{1.01} \mathrm{Fe}_{0.83}\right)_{\Sigma 18.03} \mathrm{Sb}_{3}\left(\mathrm{As}_{0.67} \mathrm{Sb}_{0.32}\right)_{\Sigma 0.99} \mathrm{~S}_{15.98}$. The mass density is $6.477 \mathrm{~g} \cdot \mathrm{~cm}^{-3}$. The simplified chemical formula is $\left(\mathrm{Ni}, \mathrm{Co}, \mathrm{Fe}_{18}{ }_{18} \mathrm{Sb}_{3}(\mathrm{As}, \mathrm{Sb}) \mathrm{S}_{16}\right.$. The mineral is tetragonal and belongs to space group $I 4 / \mathrm{mmm}$, with $a=9.7856$ (3) $\AA, c=10.7582(6)$ $\AA, V=1030.2(6) \AA^{3}$ and $Z=2$. The structure is layered (stacking along the $\mathbf{c}$-axis) and is dominated by three different Ni coordination polyhedral, one octahedral and two cubic. The arsenotučekite structure can be considered as a superstructure of tučekite resulting from the ordering of Sb and As. The name of the new mineral species indicates the As-dominant of tučekite. Arsenotučekite occurs as rims partly replacing pentlandite and irregularly developed grains. Furthermore, it is locally associated with chlorite. These observations suggest that it was likely precipitated at relatively low temperatures during: 1) the late hydrothermal stages of the ore-forming process by reaction of Sb - and As-bearing solutions with magmatic sulfides such as pentlandite, or 2) during the serpentinization of the host peridotite. The mineral and its name have been approved by the Commission of New Minerals, Nomenclature, and Classification of the International Mineralogical Association (number 2019-135).


Keywords Arsenotučekite • New mineral • Chromitite • Tsangli mine • Othrys • Ophiolite • Greece

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## Introduction

Recently, three new minerals, namely tsikourasite, $\mathrm{Mo}_{3} \mathrm{Ni}_{2} \mathrm{P}_{1+x}(x<0.25)$, grammatikopoulosite, NiVP, and eliopoulosite, $\mathrm{V}_{7} \mathrm{~S}_{8}$, were discovered in the heavy mineral concentrates from chromitite samples collected in the Othrys ophiolite, central Greece (Zaccarini et al. 2019; Bindi et al. 2020a, b). The Othrys ophiolite is structurally divided into west and east Othrys occurrences, which probably formed in different geotectonic environments. The western type includes formations, which are related to an extension regime, i.e. back-arc basin or mid-ocean ridge (MOR) (Barth et al. 2003, 2008; Barth and Gluhak 2009; Dijkstra et al. 2003), while the Othrys ophiolite from the eastern region is associated with a
supra-subduction zone setting (SSZ), as proposed by Barth and Gluhak (2009) and Magganas and Koutsovitis (2015).

The three new minerals were found in the abandoned chromium mine of Agios Stefanos, located in the west area of the Othrys complex. Due to the promising mineralogical results, an additional amount of chromite was collected from the Tsangli mining area located in the east domain of the Othrys complex. It was studied by a combination of chemical analysis and X-ray diffraction techniques.

An additional new mineral was then discovered and approved by the Commission of New Minerals, Nomenclature and Classification of the International Mineralogical Association (number 2019-135). The simplified chemical formula of the new mineral is $(\mathrm{Ni}, \mathrm{Co}, \mathrm{Fe})_{18} \mathrm{Sb}_{3}(\mathrm{As}, \mathrm{Sb}) \mathrm{S}_{16}$ and it has been named arsenotučekite to indicate the As-dominant tučekite, as previously proposed for arsenohauchecornite, the As-hauchecornite (Gait and Harris 1980; Grice and Ferguson 1989). Holotype material is deposited in the collections of the Natural History Museum, London (catalogue number BM 2020,1).

## Geological background, description of the chromitite and chromite composition

Arsenotučekite has been found in massive chromitite which was collected from the Tsangli mining area located in the east Othrys ophiolite, central Greece (Fig. 1a, b). The Othrys ophiolite is a remnant of the Tethys Ocean, which extended between Eurasia and Gondwanaland in the Jurassic.

The geological history of the Othrys ophiolite is still debated and several models have been proposed for its origin. In particular, the east Othrys ophiolite is considered to have formed in the island arc of a SSZ geo-dynamic setting (Barth and Gluhak 2009; Magganas and Koutsovitis 2015). In contrast, the west Othrys ophiolite represents a section of MOR-type oceanic lithosphere formed along a paleotransform fault (Rassios and Konstantopoulou 1993; Dijkstra et al. 2003).

The Othrys ophiolite is strongly tectonically overprinted and fragmented, but an almost complete stratigraphy was recognized. It comprises a mantle peridotite, ultramafic and gabbroic cumulates, sheeted dikes, pillow lavas and a sedimentary cover (Rassios and Konstantopoulou 1993; Bortolotti et al. 2008; Koutsovitis 2012).

Although the mantle rocks of the Othrys ophiolite show characteristics of MOR and SSZ geodynamic settings, the occurrence of chromitites was reported in both of the mantle peridotites. The Othrys peridotites consist of fertile plagioclase lherzolites in the western part of the complex and of depleted harzburgites in the eastern domain. They represent residual rocks characterized by a different degree of partial melting.


Fig. 1 Location of the Othrys complex in Greece (a), general geological map of the Othrys ophiolite showing location of the Tsangli chromium mine (b) and detailed geology of the Tsangli area (c), (modified after Rassios and Smith 2001; Economou and Naldrett 1984)

The studied sample was collected from the Tsangli mining area located in the eastern portion of the Otrhys complex, about 40 km North-East of the Domokos village (Fig. 1b) and 1 km North-East of the Eretria village (Fig. 1c).

The sample that hosts arsenotučekite is a massive chromite host in an altered mantle peridotite. The chromitite contains interstitial $\mathrm{Ni}-\mathrm{Cu}-\mathrm{Fe}$ sulfides, such as pentlandite, and subordinate pyrrhotite and chalcopyrite (Economou and Naldrett 1984). The serpentinized peridotites are over- and underlain by schist, covered in turn unconformably by Cenomanian limestone (Economou and Naldrett 1984) (Fig. 1c). Conglomerates are widespread in the mining area (Fig. 1c).

Fig. 2 Digital images in reflected plane polarized light $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ and BSE image (d) showing arsenotučekite from the chromitite of Tsangli. Abbreviations: atc $=$ arsenotučekite, epx = epoxy, $\mathrm{chr}=$ chromite, $\mathrm{chl}=$ chlorite, $\mathrm{pn}=$ pentlandite, $\mathrm{btp}=$ beithauptite


Following the procedure described by Ifandi et al. (2018), chemical analyses of the spinels obtained on chromitite yielded the following compositional range: $\mathrm{Cr}_{2} \mathrm{O}_{3}$ (43.39$51.14 \mathrm{wt} \%), \mathrm{Al}_{2} \mathrm{O}_{3}$ (15.26-22.32 wt\%), MgO (11.77$14.08 \mathrm{wt} \%$ ), and FeO (13.56-16.31 wt\%). $\mathrm{Fe}_{2} \mathrm{O}_{3}$, calculated on the basis of the spinel stoichiometry, ranges from 3.46 to

Table 1 Reflectance values of arsenotučekite

| $\boldsymbol{\lambda}$ (nm) | Ro | R'e |
| :--- | :--- | :--- |
| 400 | 38 | 38.9 |
| 420 | 39 | 41 |
| 440 | 40 | 43.1 |
| 460 | 41.1 | 45.4 |
| $\mathbf{4 7 0}$ | $\mathbf{4 1 . 8}$ | 46.4 |
| 480 | 42.5 | 47.5 |
| 500 | 44.1 | 49.1 |
| 520 | 45.6 | 50.3 |
| 540 | 46.9 | 51.1 |
| $\mathbf{5 4 6}$ | $\mathbf{4 7 . 2}$ | $\mathbf{5 1 . 4}$ |
| 560 | 48 | 51.6 |
| 580 | 49 | 52.1 |
| $\mathbf{5 8 9}$ | $\mathbf{4 9 . 4}$ | $\mathbf{5 2 . 3}$ |
| 600 | 49.8 | 52.5 |
| 620 | 50.3 | 52.7 |
| 640 | 51 | 53.1 |
| $\mathbf{6 5 0}$ | $\mathbf{5 1 . 3}$ | $\mathbf{5 3 . 2}$ |
| 660 | 51.5 | 53.3 |
| 680 | 52.1 | 53.7 |
| 700 | 52.4 | 53.8 |

Values required by the Commission on Ore Mineralogy (COM) are given in bold
$6.92 \mathrm{wt} \%$. Minor elements are MnO ( $0.00-0.09 \mathrm{wt} \%$ ), ZnO ( $0.00-0.08 \mathrm{wt} \%$ ), $\mathrm{V}_{2} \mathrm{O}_{3}(0.08-0.19 \mathrm{wt} \%)$ and $\mathrm{NiO}(0.10-$ $0.23 \mathrm{wt} \%$ ). The $\mathrm{TiO}_{2}$ content is low ( $0.04-0.16 \mathrm{wt} \%$ ), and consistent with most mantle-hosted podiform chromitites.

Previous investigations had shown that the Tsangli chromitites contain several platinum group minerals (PGM), including laurite, erlichmanite, alloys in the Os-Ir-Ru system, irarsite, ruasrsite, osarsite, sperrylite and merenskyite (Tsikouras et al. 2016). Most of the discovered PGM have a magmatic origin and only few of them were re-worked and altered during the serpentinization (Tsikouras et al. 2016).

## Samples and experimental

Concentrate specimens of heavy minerals were prepared from samples of massive chromitite weighing ca. 10 kg . The


Fig. 3 Reflectance data (reflectance values plotted versus wavelength) for arsenotučekite

Table 2 Chemical compositions (WDS analyses) and calculated mineral formulae of arsenotučekite

| Chemical constituents, as measured (wt\%) |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | S | As | Sb | Ni | Co | Fe | Total |
| TS1-10an10 | 25.50 | 2.50 | 20.29 | 46.39 | 3.22 | 2.71 | 100.62 |
| TS1-10an9 | 25.81 | 2.67 | 19.13 | 46.95 | 2.93 | 2.86 | 100.36 |
| TS1-11an13 | 25.01 | 3.13 | 20.41 | 46.73 | 3.54 | 2.11 | 100.92 |
| TS1-13an16 | 25.49 | 2.68 | 20.05 | 47.87 | 2.95 | 1.65 | 100.69 |
| TS1-19an20 | 25.36 | 3.32 | 18.33 | 48.05 | 2.13 | 2.49 | 99.67 |
| TS1-19an21 | 25.66 | 3.18 | 19.21 | 48.02 | 2.22 | 2.78 | 101.08 |
| TS1-21an23 | 25.57 | 2.11 | 20.96 | 47.42 | 2.87 | 1.89 | 100.81 |
| TS1-21an24 | 25.44 | 2.39 | 20.34 | 47.25 | 2.92 | 1.88 | 100.21 |
| TS1-21an26 | 25.61 | 2.86 | 19.84 | 47.49 | 2.84 | 1.98 | 100.62 |
| TS1-7an2 | 25.63 | 2.29 | 20.58 | 47.12 | 3.31 | 2.18 | 101.10 |
| TS1-9an5 | 25.78 | 3.33 | 18.88 | 48.05 | 3.20 | 1.99 | 101.22 |
| TS1-35an18 | 25.76 | 2.63 | 19.62 | 47.07 | 3.20 | 2.62 | 100.90 |
| Chemical constitutents, normalised (at\%) |  |  |  |  |  |  |  |
|  | S | As | Sb | Ni | Co | Fe | Total |
| TS1-10an10 | 42.10 | 1.77 | 8.82 | 41.84 | 2.90 | 2.57 | 100 |
| TS1-10an9 | 42.40 | 1.88 | 8.28 | 42.13 | 2.62 | 2.70 | 100 |
| TS1-11an13 | 41.41 | 2.22 | 8.90 | 42.28 | 3.19 | 2.01 | 100 |
| TS1-13an16 | 42.05 | 1.89 | 8.71 | 43.14 | 2.65 | 1.56 | 100 |
| TS1-19an20 | 41.95 | 2.35 | 7.99 | 43.43 | 1.92 | 2.36 | 100 |
| TS1-19an21 | 41.98 | 2.23 | 8.27 | 42.92 | 1.98 | 2.61 | 100 |
| TS1-21an23 | 42.23 | 1.49 | 9.11 | 42.79 | 2.58 | 1.80 | 100 |
| TS1-21an24 | 42.19 | 1.69 | 8.88 | 42.81 | 2.64 | 1.79 | 100 |
| TS1-21an26 | 42.20 | 2.01 | 8.61 | 42.75 | 2.55 | 1.87 | 100 |
| TS1-7an2 | 42.13 | 1.61 | 8.91 | 42.32 | 2.96 | 2.06 | 100 |
| TS1-9an5 | 42.05 | 2.32 | 8.11 | 42.82 | 2.84 | 1.86 | 100 |
| TS1-35an18 | 42.23 | 1.84 | 8.47 | 42.14 | 2.85 | 2.47 | 100 |
| Calculated mineral formulae (apfu) ${ }^{\text {a }}$ |  |  |  |  |  |  |  |
|  | S | As | Sb | Ni | Co | Fe | Total |
| TS1-10an10 | 16.00 | 0.67 | 3.35 | 15.90 | 1.10 | 0.98 | 38 |
| TS1-10an9 | 16.11 | 0.71 | 3.14 | 16.01 | 0.99 | 1.03 | 38 |
| TS1-11an13 | 15.74 | 0.84 | 3.38 | 16.07 | 1.21 | 0.76 | 38 |
| TS1-13an16 | 15.98 | 0.72 | 3.31 | 16.39 | 1.01 | 0.59 | 38 |
| TS1-19an20 | 15.94 | 0.89 | 3.03 | 16.50 | 0.73 | 0.90 | 38 |
| TS1-19an21 | 15.95 | 0.85 | 3.14 | 16.31 | 0.75 | 0.99 | 38 |
| TS1-21an23 | 16.05 | 0.57 | 3.46 | 16.26 | 0.98 | 0.68 | 38 |
| TS1-21an24 | 16.03 | 0.64 | 3.38 | 16.27 | 1.00 | 0.68 | 38 |
| TS1-21an26 | 16.04 | 0.77 | 3.27 | 16.25 | 0.97 | 0.71 | 38 |
| TS1-7an2 | 16.01 | 0.61 | 3.39 | 16.08 | 1.12 | 0.78 | 38 |
| TS1-9an5 | 15.98 | 0.88 | 3.08 | 16.27 | 1.08 | 0.71 | 38 |
| TS1-35an18 | 16.05 | 0.70 | 3.22 | 16.01 | 1.08 | 0.94 | 38 |

${ }^{\text {a }}$ calculated based on 38 atoms per formula unit
processing and recovery were carried out following the procedure described elsewhere (Tsikouras et al. 2016; Ifandi et al. 2018; Zaccarini et al. 2019; Bindi et al. 2020a, b). The heavy minerals were embedded in epoxy, and ground and polished for mineralogical investigation.

Table 3 Wyckoff positions, atom coordinates and isotropic displacement parameters $\left(\AA^{2}\right)$ for arsenotučekite

| Atom | Wyckoff | $x / a$ | $y / b$ | $z / c$ | Uiso |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Ni1 | $4 c$ | 0 | 0.5 | 0 | $0.0394(4)$ |
| Ni2 | $16 m$ | $0.14285(8)$ | $0.14285(8)$ | $0.38158(10)$ | $0.0399(3)$ |
| Ni3 | $16 m$ | $0.17361(11)$ | $0.17361(11)$ | $0.13537(12)$ | $0.0538(3)$ |
| Sb1 | $4 d$ | 0 | 0.5 | 0.25 | $0.0426(3)$ |
| Sb2 | $2 a$ | 0 | 0 | 0 | $0.0400(3)$ |
| As | $2 b$ | 0 | 0 | 0.5 | $0.0327(6)$ |
| S 1 | $16 l$ | $0.3447(4)$ | $0.1711(4)$ | 0 | $0.0652(7)$ |
| S 2 | $16 n$ | 0 | $0.2440(3)$ | $0.2507(3)$ | $0.0603(7)$ |

Quantitative chemical analyses of arsenotučekite were obtained using a JEOL JXA-8200 electron probe microanalyser, operating in WDS (wavelength dispersive X-ray spectrometry) mode. Major and minor elements were determined at 20 kV accelerating voltage and 10 nA beam current, with 20 s as counting time for the peaks and 10 s for the backgrounds. The beam diameter was about $1 \mu \mathrm{~m}$ in size. For the WDS analyses, the following lines and diffracting crystals were used: $\mathrm{S}=K \alpha$, PETJ, As $=L \alpha$, TAP, $\mathrm{Sb}=L \alpha$, PETJ, and $\mathrm{Fe}, \mathrm{Co}, \mathrm{Ni},=K \alpha$, LIFH. The following reference materials were selected: skutterudite (Co, As), stibnite ( $\mathrm{Sb}, \mathrm{S}$ ), millerite ( Ni ), and pyrite ( Fe ). The same instrument was used to obtain back-scattered electron (BSE) images.

Reflectance measurements were made using a J \& M TIDAS diode array spectrometer attached to a Zeiss Axiotron microscope. Measurements were made in air relative to a WTiC standard.

Single-crystal X-ray analysis was done on a crystal fragment hand-picked from the polished section under a reflected light microscope. The crystal (about $35 \mu \mathrm{~m}$ in size) was carefully washed in acetone several times. It did not show any visible other phase attached to the surface. The analysis was carried out using a Bruker D8 Venture Photon 100 CMOS diffractometer system, using graphitemonochromatized Mo $K \alpha$ radiation $(\lambda=0.71073 \AA$ ). X-ray powder diffraction data were not collected owing to the small size of the grain and the limited material available.

## Physical and optical properties

More than 50 grains of arsenotučekite were identified in the studied polished sections. Arsenotučekite forms anhedral to subhedral grains and ranges in size from $5 \mu \mathrm{~m}$ to rarely up to about $100 \mu \mathrm{~m}$ (Fig. 2a-d). It occurs as single phase grains (Fig. 2a) but was also associated with chlorite (Fig. 2b),

Table 4 Calculated Xray powder diffraction pattern for arsenotučekite [only Icalc $>5 \sigma$ (Icalc) are reported], the strongest reflections are given in bold

| $h$ | $k$ | $l$ | $d \mathrm{calc}$ | Icalc |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 0 | 1 | 7.239 | 9 |
| 1 | 1 | 0 | 6.92 | 7 |
| 1 | 1 | 2 | 4.247 | 33 |
| 2 | 2 | 0 | 3.4597 | 56 |
| 3 | 1 | 0 | 3.0945 | 85 |
| 2 | 2 | 2 | 2.9098 | 37 |
| 2 | 1 | 3 | 2.7738 | 5 |
| 3 | 1 | 2 | 2.6823 | 81 |
| 3 | 2 | 1 | 2.6316 | 6 |
| 1 | 1 | 4 | 2.5068 | 42 |
| 2 | 0 | 4 | 2.3569 | 96 |
| 4 | 1 | 1 | 2.3176 | 7 |
| 3 | 3 | 0 | 2.3065 | 15 |
| 4 | 0 | 2 | 2.2269 | 10 |
| 4 | 2 | 0 | 2.1881 | 75 |
| 3 | 2 | 3 | 2.1641 | 6 |
| 3 | 1 | 4 | 2.03 | 38 |
| 5 | 0 | 1 | 1.9255 | 11 |
| 4 | 0 | 4 | 1.8097 | 100 |
| 5 | 1 | 2 | 1.8075 | 5 |
| 3 | 3 | 4 | 1.7508 | 91 |
| 4 | 4 | 0 | 1.7299 | 47 |
| 4 | 2 | 4 | 1.6973 | 18 |
| 6 | 0 | 0 | 1.6309 | 54 |
| 5 | 3 | 2 | 1.6021 | 16 |
| 2 | 2 | 6 | 1.5919 | 8 |
| 3 | 1 | 6 | 1.5514 | 13 |
| 4 | 3 | 5 | 1.4478 | 6 |
| 0 | 0 | 8 | 1.3448 | 20 |
| 6 | 2 | 4 | 1.3412 | 13 |
| 7 | 3 | 0 | 1.2849 | 7 |
| 7 | 3 | 2 | 1.2498 | 7 |
| 3 | 1 | 8 | 1.2333 | 7 |
| 7 | 1 | 4 | 1.2305 | 11 |
| 6 | 4 | 4 | 1.2115 | 21 |
| 8 | 2 | 0 | 1.1867 | 7 |
| 7 | 3 | 4 | 1.1594 | 6 |
| 6 | 6 | 0 | 1.1532 | 8 |
| 4 | 2 | 8 | 1.1457 | 15 |
| 8 | 0 | 4 | 1.1135 | 6 |
| 8 | 3 | 3 | 1.091 | 5 |
| 4 | 4 | 8 | 1.0617 | 14 |
| 6 | 0 | 8 | 1.0376 | 16 |
| 8 | 4 | 4 | 1.0134 | 13 |
| 9 | 3 | 4 | 0.9631 | 7 |

pentlandite, breithauptite (Fig. 2c, d) and gersdorffite. It is brittle and has a metallic luster.

Table 5 Selected bond distances ( $\AA$ ) for arsenotučekite

| Ni1-S1 | $2.261(3)(\times 4)$ |
| :--- | :--- |
| Ni1-Sb1 | $2.6896(1)(\times 2)$ |
| Ni2-S2 | $2.217(2)(\times 2)$ |
| Ni2-S1 | $2.226(3)(\times 2)$ |
| $\mathrm{Ni} 2-\mathrm{As}$ | $2.3519(11)$ |
| $\mathrm{Ni} 2-\mathrm{Ni} 3$ | $2.5465(15)$ |
| $\mathrm{Ni} 2-\mathrm{Ni} 2$ | $2.548(2)$ |
| $\mathrm{Ni} 2-\mathrm{Ni3}$ | $2.6828(18)$ |
| $\mathrm{Ni} 3-\mathrm{S} 2$ | $2.213(2)(\times 2)$ |
| $\mathrm{Ni} 3-\mathrm{S} 1$ | $2.219(3)(\times 2)$ |
| $\mathrm{Ni} 3-\mathrm{Ni} 2$ | $2.5465(15)$ |
| $\mathrm{Ni} 3-\mathrm{Ni} 2$ | $2.6828(18)$ |
| $\mathrm{Ni} 3-\mathrm{Sb} 2$ | $2.8095(15)$ |
| $\mathrm{Ni} 3-\mathrm{Ni} 3$ | $2.913(3)$ |
| $\mathrm{Sb} 1-\mathrm{S} 2$ | $2.505(3)(\times 4)$ |
| $\mathrm{Sb} 1-\mathrm{Ni} 1$ | $2.6896(1)(\times 2)$ |
| $\mathrm{Sb} 2-\mathrm{Ni} 3$ | $2.8095(15)(\times 8)$ |
| As-Ni2 | $2.3518(11)(\times 8)$ |

In plane-polarized light, the color is creamy-yellow (Fig. $2 \mathrm{a}-\mathrm{c}$ ), the bireflectance is barely perceptible and the pleochroism is weak. In crossed polarized reflected light, the anisotropic rotation tints vary from pale blue to brown. Internal reflections were not observed.

Reflectance values in air ( $R$ in \%) requested by the Commission of Ore Mineralogy (COM) of arsenotučekite are ( $\mathrm{Ro}, \mathrm{Re}^{\prime}$ in $\%$ ) are: $41.8-46.4$ at $470 \mathrm{~nm}, 47.2-50.6$ at $546 \mathrm{~nm}, 49.4-52.3$ at 589 nm , and 51.3-53.2 at 650 nm . The reflectance values are reported in Table 1 and Fig. 3.


Fig. 4 The crystal structure of arsenotučekite. Black, grey and white circles refer to $\mathrm{Ni}, \mathrm{Sb}$ and S atoms, respectively. Grey globes refer to As atoms. The unit cell and the orientation of the structure are outlined


Fig. 5 The crystal structure of arsenotučekite down the $\boldsymbol{a}$-axis. It can be considered as a superstructure of tučekite resulted from the ordering of Sb and As along the $\mathbf{c}$-axis (alternation of rectangles with different shades of grey). Symbols as in Fig. 4. The unit cell and the orientation of the structure are outlined

Mass density was not measured because of the small amount of available material. The mass density, on the basis of the ideal chemical formula and unit-cell volume from single-crystal X-ray data, is $6.477 \mathrm{~g} \cdot \mathrm{~cm}^{-3}$. The calculated mass density is equal to $7.085 \mathrm{~g} \cdot \mathrm{~cm}^{-3}$, based on the empirical


Fig. 6 The crystal structure of arsenotučekite down the $c$-axis. Geometric relationships with the tučekite unit cell (light-grey dashed square) are reported. Symbols as in Fig. 4. The unit cell and the orientation of the structure are outlined
composition and unit-cell volume refined from single-crystal XRD data.

## Chemical composition and X-ray crystallography

Representative results of chemical analyses of arsenotučekite are listed in Table 2. The empirical formula of arsenotučekite, based on 38 atoms and according to the structural results (see below), is $\left(\mathrm{Ni}_{16.19} \mathrm{Co}_{1.01} \mathrm{Fe}_{0.83}\right)_{\Sigma 18.03} \mathrm{Sb}_{3}\left(\mathrm{As}_{0.67} \mathrm{Sb}_{0.32}\right)_{\Sigma 0.99} \mathrm{~S}_{15.98}$ and the simplified formula is $(\mathrm{Ni}, \mathrm{Co}, \mathrm{Fe})_{18} \mathrm{Sb}_{3}(\mathrm{As}, \mathrm{Sb}) \mathrm{S}_{16}$. The ideal formula is $\mathrm{Ni}_{18} \mathrm{Sb}_{3} \mathrm{AsS}_{16}$, which requires Ni $52.58 \mathrm{wt} \%$, $\mathrm{Sb} 18.17 \mathrm{wt} \%$, As $3.73 \mathrm{wt} \%$ and S $25.52 \mathrm{wt} \%$, in order to sum up to $100 \mathrm{wt} \%$.

Single-crystal X-ray diffraction intensity data were integrated and corrected for Lorentz and polarization factors and absorption using the software package APEX3 (Bruker 2016). A total of 678 unique reflections were collected. Given the similarity in unit-cell values and space groups, the structure was refined starting from the atomic coordinates reported for the $14 / \mathrm{mmm}$ crystal structure of arsenohauchecornite (Grice and Ferguson 1989) using the program Shelxl-97 (Sheldrick 2008).

The site occupancy factor at the $\mathrm{Ni}, \mathrm{Sb}$ and As sites was allowed to vary (Ni versus structural vacancy, Sb versus As ) using scattering curves for neutral atoms taken from Wilson (1992). Ni and Sb sites were found to be fully occupied by Ni and Sb , respectively. The mean electron number refined at the As site was $39.1 e^{-}$, in excellent agreement with the site population obtained from the chemical data (i.e., $\mathrm{As}_{0.65} \mathrm{Sb}_{0.35}$ ). At the last stage, with anisotropic displacement parameters for all the atoms, the structure was refined to $R 1=0.0562$ using 678 independent reflections. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 3. These data were used to calculate a theoretical X-ray powder diffraction pattern (Table 4). Selected bond distances are shown in Table 5.

The structure of arsenotučekite (Fig. 4) consists of alternating layers of Ni atoms and $\mathrm{S}, \mathrm{Sb}$ and As atoms, parallel to (001), at approximately one-eighth intervals of the $\mathbf{c}$ cell dimension. The structure is dominated by three different Ni coordination polyhedra, two of them are distorted cubes and the third is an octahedron. The Nil-octahedron has a plane of four S atoms parallel to (001) and two apical Sb atoms. Ni2 and Ni3 are 8coordinated distorted cubes. Although the latter two sites are similar, Ni2 exhibits a shorter mean bond distance than Ni 3 . Both of these polyhedra contain a nearly square plane of four atoms, which is a diagonal within the distorted cube.

As shown in Fig. 5, arsenotučekite structure can be considered as a superstructure of tučekite resulting from the ordering

Table 6 Members of the hauchecornite group

| Name | Chemical formula | $a(\AA)$ | $c(\AA)$ | Space group | References |
| :--- | :--- | :--- | :--- | :--- | :--- |
| arsenohauchecornite | $\mathrm{Ni}_{18} \mathrm{Bi}_{3} \mathrm{AsS}_{16}$ | 10.271 | 10.807 | $I 4 / \mathrm{mmm}$ | Gait and Harris (1980) |
| bismutohauchecornite | $\mathrm{Ni}_{9} \mathrm{Bi}_{2} \mathrm{~S}_{8}$ | 7.37 | 5.88 | $P 4 / \mathrm{mmm}$ | Just (1980) |
| hauchecornite | $\mathrm{Ni}_{9} \mathrm{BiSbS}_{8}$ | 7.3 | 5.402 | $P 4 / \mathrm{mmm}$ | Peacock (1950) |
| tellurohauchecornite | $\mathrm{Ni}_{9} \mathrm{Bi}(\mathrm{Te}, \mathrm{Bi}) \mathrm{S}_{8}$ | 14.64 | 10.87 | - | Gait and Harris (1980) |
| tučekite | $\mathrm{Ni}_{9} \mathrm{Sb}_{2} \mathrm{~S}_{8}$ | 7.174 | 5.402 | - | Just and Feather (1978) |
| arsenotučekite | $\mathrm{Ni}_{18} \mathrm{Sb}_{3} \mathrm{AsS}_{16}$ | 9.7856 | 10.7582 | $I 4 / \mathrm{mmm}$ | present work |

in the cubic polyhedra of Sb and As (alternation of rectangles with different shades of grey in Fig. 5), which have very different mean bond-lengths ( 2.810 and $2.352 \AA$, respectively). We show here that the unit cell of arsenotučekite is multiple of the $7.2 \AA \times 5.4 \AA$ tetragonal primitive cell of Just and Feather (1978) given for tučekite. Geometric relationships between the two cells are given in Fig. 6. The matrix to transform the cell of Just and Feather (1978) to the present one is |1-10/110/ 002|. It is very likely that tučekite also crystallizes in this space group.

Arsenotučekite does not correspond to any valid or invalid unnamed mineral (Smith and Nickel 2007). It is a new member of the hauchecornite group (Table 6), besides hauchecornite, bismutohauchecornite, tellurohauchecornite, arsenohauchecornite and tučekite (Gait and Harris 1980; Just 1980; Peacock 1950; Just and Feather 1978).

## Origin of arsenotučekite

Based on previous and our mineralogical descriptions, it is possible to propose a genetic model for arsenotučekite. Arsenotučekite was not observed as inclusions in the magmatic chromite grains. Instead, it occurs as rims partly replacing pentlandite and as irregularly developed grains, locally associated with chlorite. These observations suggest that arsenotučekite likely precipitated at relatively low temperatures and two possible scenarios are proposed.

Arsenotučekite formed during (i) the late hydrothermal stages of the ore-forming process by reaction of Sb - and Asbearing solutions with magmatic sulfides such as pentlandite or (ii) during the serpentinization of the host peridotite. The first hypothesis was also proposed for tučekite described in the Kanowna nickel mineralization, its type locality, hosted in metamorphosed mafic and ultramafic rocks of the West Australian Archaean shield (Just and Feather 1978). The second hypothesis is in agreement with the model proposed by Economou and Naldrett (1984) for the formation of the interstitial sulfide described in the Tsangli chromitites. These authors suggested that the sulfides precipitated from hydrothermal fluids, which were also possibly responsible for the
serpentinization of their host rocks. The source of the metals originates from the host rock.

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