

**Revised: 7Feb 2019; Revised 5 Apr 2019**

## **Ognitite, NiBiTe, a new mineral species, and cobaltian maucherite from the Ognit ultramafic complex, Eastern Sayans, Russia**

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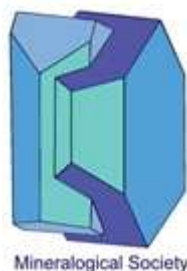
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## Abstract

We describe the new species ognitite, NiBiTe, and a cobaltian variety of maucherite, hitherto unreported; both were discovered in the Ognit ultramafic complex of Neoproterozoic age in Eastern Sayans, Russia. The mean composition of ognitite ( $n = 7$ ) is: Ni 17.05, Fe 0.07, Cu 0.14, Pd 0.14, Te 32.53, Bi 49.64, total 99.57 wt.%, corresponding to:  $(\text{Ni}_{1.11}\text{Cu}_{<0.01}\text{Fe}_{<0.01}\text{Pd}_{<0.01})_{\Sigma 1.13}\text{Bi}_{0.90}\text{Te}_{0.97}$  ( $\Sigma$  atoms = 3 *apfu*). Ognitite is trigonal, space group  $P3m1$  [ $R1 = 0.0276$  for 81 reflections with  $F_o > 4\sigma(F_o)$ ]. The unit-cell parameters derived from the single-crystal X-ray diffraction data are:  $a = 3.928(1)$  Å,  $c = 5.385(1)$  Å,  $V = 71.95(4)$  Å<sup>3</sup>, with  $Z = 1$ . The  $c:a$  ratio is 1.37. The X-ray powder-diffraction data obtained on the same fragment used for the single-crystal study are:  $a = 3.9332(4)$  Å,  $c = 5.3920(6)$  Å,  $V = 72.24$  (1) Å<sup>3</sup>. Ognitite exhibits the brucite-type structure with edge-sharing NiTe<sub>3</sub>Bi<sub>3</sub> octahedra forming sheets parallel to (0001). It is related to melonite, but is distinct compositionally (by the extreme Bi-enrichment; melonite and its synthetic analogue contain  $<0.4$  Bi *apfu*) and structurally: Bi and Te are ordered at two distinct sites, leading to the loss of the center of symmetry in ognitite.

At more than 9 wt.% Co, or  $\sim 2$  *apfu* Co, the core of cobaltian maucherite [(Ni,Co)<sub>11</sub>As<sub>8</sub>] in a zoned crystal, which is surrounded by Co-depleted orcelite, far surpasses the norm ( $\leq 1$  and up to 3.9 wt.% Co). The unit-cell parameters of the Co-rich maucherite are:  $a = 6.85(2)$  and  $c = 21.83(5)$  Å, which are based on results of synchrotron micro-Laue diffraction.

The host rock consists of serpentine, clinocllore (Mg# 95–97) and skeletal chromite. We favor the metastable crystallization of fluid-saturated globules of a sulfide-arsenide melt to explain the anomalous compositions of ore minerals at Ognit. These anomalies seem consistent with rapid cooling in a fluid-enriched system, possibly related to late-stage degassing of the magma, as reflected in a prominent metasomatic aureole at the contact with the enclosing gneissic rocks.

**Keywords:** ognitite; NiBiTe; new mineral species; cobaltian maucherite; zonation in arsenides; rapid cooling; Ognit complex; nickel-cobalt mineralization; ultramafic rocks; Eastern Sayans; Russia.

## Introduction

We document the occurrences and properties of two minerals of nickel, *i.e.* ognitite and cobaltian maucherite, discovered in the Ognit ultramafic complex, in Eastern Sayans, Russia. Ognitite has been approved as a valid species (No. 2018-006a) by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA). The name ognitite (огнитит) recalls the Ognit complex, in which the new mineral occurs.

Ognitite ( $\text{Ni}_{1.1}\text{Bi}_{0.9}\text{Te}$ ) has a distinctly bismuthian composition; besides, it differs structurally from melonite. With an ideal composition  $\text{NiTe}_2$ , melonite generally contains no more than 0.25 atoms of Bi per formula unit (*apfu*), and exceptionally up to 0.4 *apfu* in complex solid solutions that also involve Pt and Pd (Barkov *et al.*, 2017a, and references therein). Such an enrichment reflects the incorporation of substantial levels of the merenskyite ( $\text{PdTe}_2$ ) and moncheite ( $\text{PtTe}_2$ ) components (e.g., Garuti and Rinaldi, 1986). However, ognitite shows a striking Bi enrichment without those two components.

The cobaltian maucherite represents a novel variety, unusual and hitherto unreported. Maucherite, ideally  $\text{Ni}_{11}\text{As}_8$ , is one of the principal carriers of Pd in various Ni–Cu–PGE (platinum-group element) deposits. We report a major enrichment of cobalt in the core of a zoned grain. At more than 9 wt.% Co, or roughly 2 *apfu* Co, this composition far surpasses what is normally encountered:  $\leq 1.2$  wt.% Co (e.g., Fleet, 1973a; Wagner and Lorenz, 2002; Makovicky and Merlino, 2009) and, occasionally, up to 3.1–3.9 wt.% Co (Petruk *et al.*, 1971; Gritsenko and Spiridonov, 2008; Raič *et al.*, 2015).

We seek to establish the circumstances that could have led to the mineralogical anomalies observed. In addition, we describe a characteristic zonation, hitherto unreported, in Ni–(Co) arsenides at Ognit. Our findings extend knowledge of the pattern of behavior and extent of solid solution, and provide a useful insight into the ore-forming environments leading to Cu–Ni–PGE mineralization in ultramafic complexes.

## Background information

As noted, melonite and its synthetic analogue normally contain  $< 0.4$  *apfu* Bi (Barkov *et al.*, 2017, and references therein). Maucherite generally contains between 18 and 265 ppm Pd

(Gervilla *et al.*, 2000). In experiments, the extent of Pd-enrichment increases with decreasing temperature, to attain 5.5 at.% Pd at 450°C (Gervilla *et al.*, 1994). Elevated contents, up to 1.5–1.8 wt.% Pd, are known in grains of maucherite from the Sudbury and Noril'sk complexes, Canada and Russia, respectively (Cabri and Laflamme, 1976; Gritsenko and Spiridonov, 2008). In addition, maucherite is one of principal arsenides deposited from melts rich in As under experimental and natural conditions (Prichard *et al.*, 2013). Arsenic-rich melts segregated experimentally *via* immiscibility from sulfide melts are capable to scavenge efficiently the initially dissolved PGE, especially Pd (Fleet *et al.*, 1993; Makovicky *et al.*, 1990, 1992). Elevated contents of Cu (and S), up to ~5 wt.% each, were documented in grains of maucherite from metamorphosed Cu-Ni ores of the Noril'sk complex, Russia (Gritsenko and Spiridonov, 2008).

### **Geological setting and ore-mineral associations**

Both ognitite and cobaltian maucherite occur in dunite in zones of disseminated Cu–Ni–PGE sulfide mineralization in the Ognit (or Medek) dunite–wehrlite complex of Neoproterozoic age, located at the southern margin of the Siberian Craton, Irkutskaya (Irkutsk) oblast, Russia (Figs. 1a, b). The Ognit complex belongs to a suite of dunite – peridotite – pyroxenite complexes, namely Shumikha, Kingash, Golumbei, Tartai, Ognit, Zhelos, Tokty-Oi and Malyi Zadoi, associated with the Yoko–Dovyren complex in the Baikal–Patom zone. These complexes formed in a continental margin setting in the East Siberian metallogenic province (e.g., Mekhonoshin *et al.*, 2013; Tolstykh *et al.*, 2014). They give a radiometric age in the range 731–710 Ma, which is close to the range reported for the Franklin Province in northwestern Canada, 725–710 Ma, and thus consistent with the inferred breakup of Rodinia in Neoproterozoic time (Gladkochub *et al.*, 2006; Ernst *et al.*, 2012; Tolstykh *et al.*, 2014).

The Ognit complex is a relatively small ultramafic body  $\leq 1.5$  km in length at the contact of granodiorite and gneiss. It is mostly composed of dunite, wehrlite, and olivine pyroxenite. The core-like zone is essentially dunitic; elements of large-scale layering are recognized in the complex (Fig. 1b). A notable feature is the development of a pronounced zone of metasomatic alteration, especially at the southeastern contact.

The ultramafic rocks of the Ognit complex are variably serpentized; they are composed of a serpentine-group mineral, clinocllore and calcic amphiboles (actinolite and tschermakite).

Chromite, including skeletal grains of low-Al compositions (Figs. 2a, 3, Table 1), and magnetite are common accessories. The ore zones consist of sulfides ( $\leq 3$  modal %), mainly pentlandite and chalcopyrite, subordinate troilite and cubanite, rare heazlewoodite, pyrite, bornite, mackinawite, secondary chalcocite, covellite, violarite, valleriite and, occasionally, sphalerite and molybdenite. Less common to rare species of ore minerals include orcelite, maucherite, cobaltite–gersdorffite, altaite, hessite, Se-bearing galena, shandite, parkerite, native silver and Ag–Au alloy (Ag-dominant), auricupride, awaruite, native copper, graphite, and native bismuth (Shvedov and Barkov, 2017).

Two associations of platinum-group minerals (PGM) exist in the Ni–Cu–PGE zones at Ognit. The first includes species rich in Ir–Ru–Os: Ru–Os disulfides (laurite–erlichmanite series), Ru–Os diarsenides (anduoite–omeiite) and sulfarsenides (platarsite – osarsite – ruarsite). These PGM, crystallizing relatively early, exhibit a close affinity to primary grains of base-metal sulfides. The second association is late, more diverse, and mainly consists of Pd-rich PGM: palladium bismuthotellurides and antimonides, such as phases of the type Pd(Bi,Te,Sb)<sub>1+x</sub>, merenskyite, michenerite, mertieite-II and stibiopalladinite, naldrettite, polarite, urvantsevite, froodite, palladogermanide [Pd<sub>2</sub>Ge: cf. IMA 2016-086] and unnamed Pd<sub>2+x</sub>Cu<sub>1-x</sub>(Sb,Sn) (Shvedov and Barkov, 2017).

### Analytical methods

Compositions of ognitite were established *via* wavelength-dispersive spectrometry (WDS) using a JEOL JXA-8900L electron microprobe, at 20 kV, 50 nA, and with a 5- $\mu$ m beam size at McGill University, Montreal, Canada. The following lines and standards were used: K $\alpha$  and CoNiAs (for Ni), K $\alpha$  and metallic iron (Fe), K $\alpha$  and CuFeS<sub>2</sub> (Cu), K $\alpha$  and CoNiAs (Co), L $\alpha$  and Pd<sub>3</sub>HgTe<sub>3</sub> or metallic Pd (Pd), M $\beta$  and metallic Pt (Pt), L $\alpha$  and PbTe (Te), M $\alpha$  and Bi<sub>2</sub>Te<sub>3</sub> (Bi), M $\alpha$  and PbTe (Pb), K $\alpha$  and Bi<sub>2</sub>S<sub>3</sub> (S), L $\beta$  and CoNiAs (As), and L $\beta$  and pure Sb (Sb). The PRZ corrections were applied. The counting periods were 150 s. for As, 60 s. for Pd, Pt, Co, Sb and Pb, and 20 s. for Ni, Fe, Cu, Te, Bi and S. Levels of minimum detection are: 0.01 (S and Co), 0.02 (Fe), 0.03 (Ni), 0.04 (Cu, Pd, Pt, Pb and As), 0.05 (Sb), 0.06 (Te), and 0.08 wt.% (Bi).

The Co-rich maucherite and associated minerals (chromite, clinocllore and serpentine) were analyzed with a JEOL JXA-8200 microprobe at the E.F. Stumpfl laboratory, University of Leoben, Austria. The analytical conditions (WDS with a  $\leq 2$ - $\mu$ m beam) used for the zoned

maucherite grain were: 20 kV, 10 nA, and 20-s. counting times for the peak and 10 s. for the backgrounds. The following lines and standards were used: NiK $\alpha$  (pentlandite), FeK $\alpha$ , SK $\alpha$  (pyrite), AsL $\alpha$ , CoK $\alpha$  (skutterudite), BiM $\alpha$ , TeL $\alpha$  (synthetic Bi<sub>2</sub>Te<sub>3</sub>), and SbL $\alpha$  and SbL $\beta$  (Sb<sub>2</sub>Te<sub>3</sub>). The detection limits expressed in ppm are: 100 for As and S, 150 for Ni, Fe and 600 for Co, Sb, Bi and Te. Levels of Sb, Bi and Te were below the detection limit.

We also employed scanning-electron microscopy (SEM) and energy-dispersive analysis (EDS), using a MIRA 3 LMU (Tescan Ltd.) system combined with INCA Energy 450+ XMax 80 (Oxford Instruments Ltd), at the Institute of Geology and Mineralogy, Novosibirsk, Russia. The reflectance measurements on ognitite were carried out using a WTiC standard at the Natural History Museum, London, UK.

Single-crystal X-ray diffraction data were collected on the ognitite specimen using an Oxford Diffraction Xcalibur diffractometer equipped with an Oxford Diffraction CCD detector, with graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ).

The X-ray powder diffraction data were obtained on the same fragment of the ognitite grain used for the single-crystal study with an Oxford Diffraction Xcalibur PX Ultra diffractometer fitted with a 165 mm diagonal Onyx CCD detector and using copper radiation [CuK $\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ )]. The working conditions were 40 kV and 40 nA with 3 hours of exposure; the detector-to-sample distance was 7 cm. The program *CrysAlis* RED (Oxford Diffraction, 2006) was used to convert the observed diffraction rings to a conventional powder-diffraction pattern. The least squares refinement gave the unit-cell values listed below.

We also provide results of synchrotron X-ray Laue microdiffraction measurements at beam line 12.3.2 of the Advanced Light Source (ALS), Berkeley, California, USA. A polychromatic X-ray beam (5–24 keV) was focused to approximately  $2 \times 2 \text{ \mu m}^2$  (FWHM) with Kirkpatrick–Baez mirrors. Laue diffraction patterns were collected with a PILATUS 1M area detector in reflection geometry, with the sample inclined  $45^\circ$  to the primary beam, and the area detector was set to  $90^\circ$ . The Laue diffraction patterns were collected with raster scanning across the entire sample area. The patterns were indexed and analyzed using XMAS v.6 (Tamura, 2014). An energy scan (10–20 keV, 10 eV step size) was performed on single reflections to determine the lattice parameters.

### Occurrence, physical and optical properties, and composition of ognitite

Ognitite forms a single homogeneous grain ( $80 \times 30\text{-}40 \mu\text{m}$ ) hosted by chalcopyrite; it is anhedral, irregularly shaped, and occurs next to a small grain of native bismuth (Figs. 4a, b). The new species is metallic and opaque; its color and streak are metallic black (powder). The value of its density (calc.) is  $8.75 \text{ g}\cdot\text{cm}^{-3}$ .

Under reflected light, ognitite is creamy white. It is slightly to distinctly bireflectant with a pleochroism from creamy white to slightly lighter creamy white. Ognitite is slightly to distinctly anisotropic. Internal reflections were not observed. Reflectance values of ognitite (WTiC standard, in air) are listed in Table 2.

Representative compositions of ognitite are given in Table 3. Other elements (Co, Pt, Sb, Pb, As, and S) were also sought, but not detected. The mean composition (and ranges for seven point analyses,  $n = 7$ ) are: Ni 17.05 (16.91-17.15), Fe 0.07 (0.02-0.16), Cu 0.14 (0.08-0.26), Pd 0.14 (0.09-0.16), Te 32.53 (31.79-33.67), Bi 49.64 (48.27-50.31), total 99.57 (99.01-100.07) wt.%. Minor Pd is thus present. Results of two independent methods of microprobe analyses (WDS and SEM/EDS) are in excellent agreement; they yield essentially the same empirical formula:  $(\text{Ni}_{1.11}\text{Cu}_{<0.01}\text{Fe}_{<0.01}\text{Pd}_{<0.01})_{\Sigma 1.13}\text{Bi}_{0.90}\text{Te}_{0.97}$ , calculated on the basis of a total of 3 *apfu*. A minor extent of Ni-for-Bi substitution is thus implied. Examples of Ni – Bi substitution are known in some compounds:  $\text{LaNi}_{4.7-x}\text{Bi}_x\text{Al}_{0.3}$  with  $x=0.1, 0.2, 0.3$  (Yilmaz *et al.*, 2012) and  $\text{Bi}_{2-x}\text{Ni}_x\text{Sr}_2\text{CaCu}_2\text{O}_y$  with  $x=0, 0.05, 0.1, 0.2$  (Özkurt, 2012). In addition, a mean electron number lower than 83 at the Bi site of ognitite is consistent with the inferred presence of a lighter element (presumably Ni) at the *1b* position. The ideal formula of ognitite is NiBiTe, which requires Ni 14.85, Bi 52.87, and Te 32.28, for a total of 100 wt.%.

An initial study of the ognitite grain was done using synchrotron micro-Laue diffraction followed by a monochromator energy scan, results of which indicate that is a single phase, apparently untwinned, with  $a = 3.925(5) \text{ \AA}$  and  $c = 5.381(7) \text{ \AA}$ . These patterns were indexed and analyzed using XMAS v.6 (Tamura, 2014).

Ognitite is trigonal; its space group is  $P3m1$ . The unit-cell parameters derived from the single-crystal X-ray diffraction data are:  $a = 3.928(1) \text{ \AA}$ ,  $c = 5.385(1) \text{ \AA}$ ,  $V = 71.95(4) \text{ \AA}^3$ , with  $Z = 1$ . The  $c:a$  ratio calculated from the unit-cell parameters is 1.37.

The X-ray powder-diffraction data (Table 4), obtained on the same fragment as used for the single-crystal study, are:  $a = 3.9332(4) \text{ \AA}$ ,  $c = 5.3920(6) \text{ \AA}$ , and  $V = 72.24(1) \text{ \AA}^3$ .

### Crystal structure of ognitite

A small fragment ( $0.040 \times 0.050 \times 0.060 \text{ mm}^3$ ) was handpicked from the ognitite grain (Figs. 4a, b) and examined with an Oxford Diffraction Xcalibur single-crystal diffractometer equipped with an Oxford Diffraction CCD detector, with graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The collected data were integrated and corrected for standard Lorentz and polarization factors with the *CrysAlis* RED package (Oxford Diffraction, 2006). The program ABSPACK in *CrysAlis* RED (Oxford Diffraction, 2006) was used for the absorption correction. Details of the selected crystal, data collection, and refinement are given in Table 5. The calculated value of R-factor is  $R1 = 0.0276$  for 81 reflections with  $F_o > 4\sigma(F_o)$ .

Although the statistical tests ( $|E^2 - 1| = 0.756$ ) suggested an acentric space-group, the crystal structure was initially refined starting from the atomic coordinates of melonite,  $\text{NiTe}_2$  (Peacock and Thompson, 1946) and using the program SHELXL-97 (Sheldrick, 2008). Given the observed larger unit-cell volume of ognitite (*i.e.*,  $71.95 \text{ \AA}^3$ ) compared to melonite (*i.e.*,  $66.93 \text{ \AA}^3$ ; Peacock and Thompson, 1946), the site-occupancy factor at the crystallographic sites was allowed to vary (Ni *vs* structural vacancy at the  $1a$  site, and Bi *vs* Te at the  $2d$  site) using scattering curves for neutral atoms taken from the *International Tables for Crystallography* (Wilson, 1992). After several cycles of anisotropic refinement, a final  $R1 = 0.0795$  was achieved, but the atomic displacement parameter at the  $2d$  position was abnormally high and asymmetric, thus suggesting a split into two positions. The introduction of two partially occupied (50%) positions (one partially occupied by Bi and one partially occupied by Te) led the  $R1$  index to 0.0608. At this stage, given the indication coming from the normalized structure-factors, we decided to try to solve the structure in the non-centrosymmetric space-group  $P3m1$ , which allows the separation of the  $2d$  position into two positions,  $1b$  and  $1c$ . The new refinement ( $R1 = 0.0276$ ) showed that Bi and Te are completely ordered at  $1b$  and  $1c$ , respectively, with Bi being likely replaced by 0.03 Ni (according to the refined mean number of electrons at the site). The Te-Ni and Bi-Ni bond distances vary accordingly: the Te-Ni distance ( $2.575 \text{ \AA}$ ) is identical to that observed in melonite ( $2.575 \text{ \AA}$ ; Peacock and Thompson, 1946), whereas the Bi-Ni distance ( $2.696 \text{ \AA}$ ) is in agreement with those observed in parkerite,  $\text{Ni}_3\text{Bi}_2\text{S}_2$  ( $2.64\text{-}2.86 \text{ \AA}$ ; Fleet, 1973b).



Ognitite exhibits a brucite-type structure (Fig. 5a, b). The edge-sharing  $\text{NiTe}_3\text{Bi}_3$  octahedra form sheets parallel to (0001); the sheets are linked by van der Waals interactions.

Atom coordinates, site occupancies, and equivalent isotropic displacement parameters are given in Table 6. Selected bond-distances are given in Table 7.

Ognitite is thus related to melonite; however, it differs compositionally (i.e., the marked Bi-enrichment) and structurally, because atoms of Bi and Te are ordered at two specific sites, leading to the loss of the center of symmetry in the crystal structure, corresponding to a variant of the  $\text{CdI}_2$ -2H structure-type. An additional characterization of kitkaite ( $\text{NiTeSe}$ ; Häkli *et al.*, 1965) is likely required to check whether it also belongs to that structure-type.

### Cobaltiferous maucherite and zoning in Ni-(Co) arsenides

As noted, the anomalously Co-rich variant of maucherite occurs in the core of a zoned grain (Figs. 2b, 6a, 6b). The rim, composed of orcelite, is essentially devoid of Co (<0.1 wt.%), in contrast to the core zone, which contains ~8 to 10 wt.% Co (or 1.7–2.0 Co *apfu*: Table 8, #1–6). At least in some cases, the quantitative SEM/EDS method is preferable in analyzing narrow zones or tiny phases. Indeed, the SEM/EDS composition (#6, Table 8) is somewhat closer to the ideal stoichiometry; nevertheless, the WDS results obtained (Table 8, #1–5) are consistent.

Our results of the synchrotron micro-Laue diffraction followed by a monochromator energy scan yielded the following cell parameters for the Co-rich maucherite at Ognit:  $a = 6.85$  (2) and  $c = 21.83(5)$  Å. Thus, these data agree well with those known for the “normal” phase of maucherite (Co-free; Fleet, 1973a).

The orcelite rim corresponds to  $\text{Ni}_5\text{As}_2$  (Table 8, #7). The structure of orcelite [ $\text{Ni}_{5-x}\text{As}_2$ ;  $x = 0.25$ ] represents a distorted variant of the  $\text{Pd}_5\text{Sb}_2$  structure (Bindi *et al.*, 2014).

As noted, the Co-rich maucherite–orcelite crystal is hosted by a matrix of fine intergrowths of serpentine and clinochlore (Figs. 2a, b). Five grains of serpentine (WDS data) yielded the composition  $(\text{Mg}_{2.69-2.74}\text{Fe}_{0.09-0.11}\text{Al}_{0.02-0.08}\text{Cr}_{0-0.02}\text{Mn}_{<0.01}\text{Ni}_{<0.01})_{\Sigma 2.83-2.90}\text{Si}_{2.03-2.08}\text{O}_5(\text{OH})_4$  (calculated for O = 7 *apfu*). The Mg# index [ $100\text{Mg}/(\text{Mg} + \text{Fe}^{2+} + \text{Mn})$ ] is high: ~97.

Compositions of six grains of clinochlore analyzed (WDS) in this sample are uniformly rich in Mg, and in Cr, with 2.93–3.21 wt.%  $\text{Cr}_2\text{O}_3$ , and correspond to  $(\text{Mg}_{4.57-4.70}\text{Fe}_{0.21-0.24}\text{Mn}_{<0.01}\text{Ni}_{\leq 0.01})_{\Sigma 4.80-4.96}\text{Al}_{1.0}(\text{Si}_{3.00-3.09}\text{Al}_{0.73-0.80}\text{Cr}_{0.22-0.25}\text{Ti}_{\leq 0.01})_{\Sigma 4.01-4.10}\text{O}_{10}(\text{OH})_8$  (for O = 14

apfu). Their values of the Mg# index are correspondingly high: up to ~96.

The skeletal grains of chromite associated with the zoned grain of Co-rich maucherite–orcelite (Fig. 2a) are weakly magnesian, with Mg# in the range 17–22, and are low in aluminum ( $\leq 6.5$  wt.%  $\text{Al}_2\text{O}_3$ ); they display very high values of Cr# [ $100\text{Cr}/(\text{Cr} + \text{Al} + \text{Fe}^{3+})$ ]: 85–92 (Table 1). In addition, elevated levels of Ti (0.7–1.4 wt.%  $\text{TiO}_2$ ), V ( $\leq 0.3$  wt.%  $\text{V}_2\text{O}_3$ ), Mn (0.9–1.0 wt.% MnO), and Zn (0.5–0.7 wt.% ZnO) are present. The chromite grains have a narrow rim of virtually pure magnetite (Fig. 3, Table 1, #10).

## Discussion and conclusions

We have described two highly unusual species of Ni ore minerals found in mineralized zones in the Ognit ultramafic complex, Eastern Sayans, Russia. The anomalously high level of Bi in ognitite [ $\text{Ni}_{1.1}\text{Bi}_{0.9}\text{Te}$ ] evidently cannot be explained by incorporation of the merenskyite and moncheite components in solid solution (Table 3). There is no evidence that the proximity to granodiorite (Fig. 1b) is an important factor, as there is no evidence of assimilation of xenoliths. And efforts to synthesize the phase NiBiTe in long-duration experiments at 200°, 400° and 600°C were not successful; the bismuth present in the charge crystallized to Bi +  $\text{Bi}_2\text{Te}$  (Barkov *et al.*, 2017a). Thus, we suggest that special conditions were important to stabilize the markedly Bi-enriched ognitite structure instead of that of common melonite.

The uniqueness of the Co-rich variant of maucherite also implies the existence of strongly atypical conditions. The high values of Mg# (95–97) of serpentine and clinochlore reflect the highly magnesian compositions of primary grains of olivine and pyroxene crystallized in the primitive ultramafic cumulates. We propose that the skeletal texture of the associated grains of chromite (Fig. 2a) indicates difficulties in their nucleation. They could well provide an indication of rapid cooling in the system, possibly related to the degassing of the magma at an advanced stage of crystallization of the complex, reflected in the prominent metasomatic aureole at the contact (Fig. 1b). Effects of supercooling and metastable crystallization were observed in the Pados-Tundra ultramafic complex, Kola Peninsula, Russia (Barkov *et al.*, 2016, 2017), for example.

We thus appeal to a mechanism of metastable crystallization to explain the anomalous compounds at Ognit. An elevated fluid pressure could have existed in the ore-forming system. The anomalously bismuthian composition of ognitite could well represent a late-crystallizing

phase formed in a fluid-saturated environment from a droplet of residual melt enriched in Ni, Bi, and Te. These elements are incompatible in the host chalcopyrite, as are Ag and Pb, present in the coexisting hessite and altaite. The shared boundary with native Bi (Figs. 4 a, b) is consistent with various occurrences of native elements and alloys (i.e., native silver, Ag–Au alloy, auricupride, awaruite, native copper, and graphite), which indicate the existence at Ognit of reducing conditions (Shvedov and Barkov, 2017).

These conditions point to a likely stability-field at Ognit of the reduced form,  $\text{As}^{3+}$ , rather than  $\text{As}^{5+}$ , which seems to be typical of mantle-related serpentinites (Hattori *et al.*, 2005). The Ni-rich arsenides, including their grains with their original shapes, are quite common accessory phases in the ore zones at Ognit; these formed from droplets of As-rich melts (Shvedov and Barkov, 2017). The documented occurrences of Ni arsenides thus reflect arsenide saturation of the sulfide liquid (cf., Piña *et al.*, 2014); an initial content of  $\geq 0.1$  wt.% As is considered sufficient to ensure saturation in an arsenide (Fleet *et al.*, 1993). The zonation is documented in the grain composed of the Co-rich maucherite in the core and Co-depleted orcelite in the rim (Figs. 2b; 6a, 6b). In other layered complexes, zoned grains of Ni-Co-(PGE) sulfarsenides are developed instead (e.g., Barkov *et al.*, 1999).

If the equilibrium crystallization is postulated at Ognit, results of experimental studies are then applicable. The melting point of synthetic  $\text{Ni}_5\text{As}_2$  (orcelite equivalent) is  $998^\circ\text{C}$ ; the upper thermal stability limit of  $\text{Ni}_{11}\text{As}_8$  (maucherite) is  $830^\circ\text{C}$  (Yund, 1961; Singleton and Nash, 1987). These values suggest that orcelite is expected to crystallize before maucherite if they coexist under normal conditions. In contrast, we observe that the Co-enriched maucherite occurs in the core; thus, it presumably nucleated first and before the orcelite phase developed in the rim. If so, we can reasonably propose that the incorporation of Co increases, to a notable extent, the melting point of  $\text{Ni}_{11}\text{As}_8$ , in contrast to the effect observed from the incorporated Pd (cf., Gervilla *et al.*, 1994). This possibility requires an experimental confirmation, however. The Co analogue of maucherite does not seem to have been reported, and thus likely was not obtained by synthesis. However, synthetic  $\text{Co}_5\text{As}_2$  (space group  $P6_3cm$ ; i.e., prototype of  $\text{Pd}_5\text{Sb}_2$ ), related to orcelite, exists in the system Co–As, in which it is a high-temperature phase; it undergoes a disproportionation transformation to  $(\alpha\text{-Co}) + \beta\text{-Co}_2\text{As}$  at  $867^\circ\text{C}$  (Ishida and Nishizawa, 1990, and references therein). Note that the orcelite phase is essentially devoid of Co in the rim, in spite of the existence of the cobalt analogue of orcelite. This feature also implies that Co was

preferentially incorporated into maucherite as the early phase, a reflection of relatively high temperature of its crystallization.

## Acknowledgements

The catalogue number of the ognitite single crystal is 3292/I at the Museo di Storia Naturale of the University of Firenze, Italy. We are grateful to an anonymous referee, Drs. Peter Leverett, Anna Vymazalová, Irina Galuskina, Roger Mitchell, and to the editorial staff for their valuable comments.

This research required access to beamline 12.3.2 at the Advanced Light Source, which is a DOE Office of Science User Facility under contract #DE-AC02-05CH11231.

A.Y.B. gratefully acknowledges a partial support of this investigation by the Russian Foundation for Basic Research (projects #RFBR 16-05-00884 and # RFBR 19-05-00181).

C.J.S. acknowledges Natural Environment Research Council grant NE/M010848/1 “Tellurium and Selenium Cycling and Supply”.

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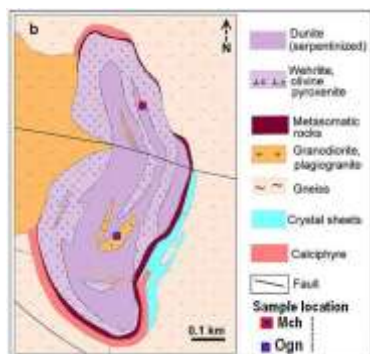
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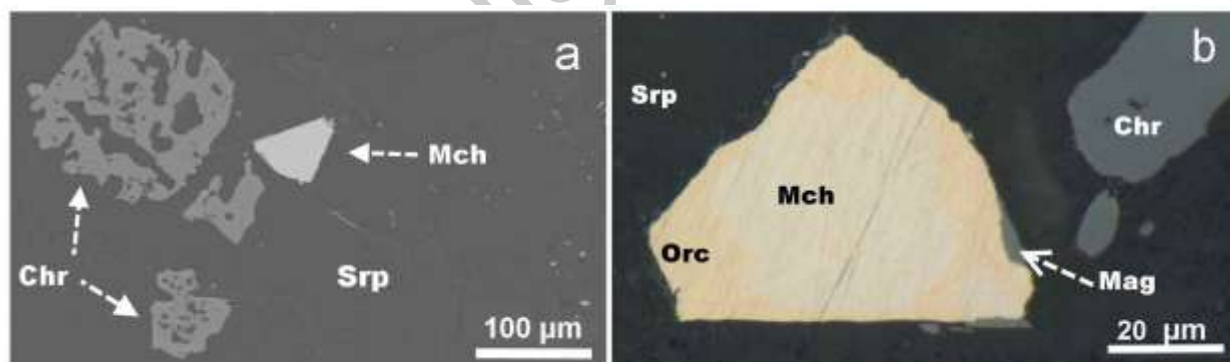
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Figs. 1 (a, b). The location of the Ognit complex in the Russian Federation (a) and geological map of the Ognit complex, Eastern Sayans, Russia, based on various sources (Mekhonoshin *et al.*, 2014, and references therein; Oleshkevich *et al.*, unpubl. data, etc.). The sample location is shown for ognitite (labeled Ogn) and Co-rich maucherite (Mch).



Figs. 2 (a, b). A back-scattered electron (BSE) image (a) and reflected light microphotograph (b) showing the zoned grain of maucherite (Mch) – orcelite (Orc), associated with skeletal grains of chromite (Chr), hosted by fine intergrowths of serpentine (Srp) and clinocllore; Mag is secondary magnetite.



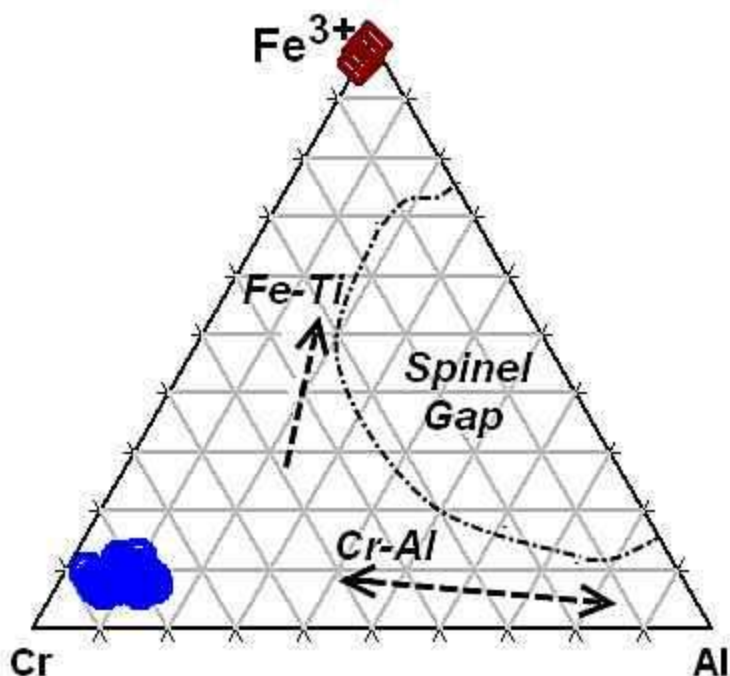
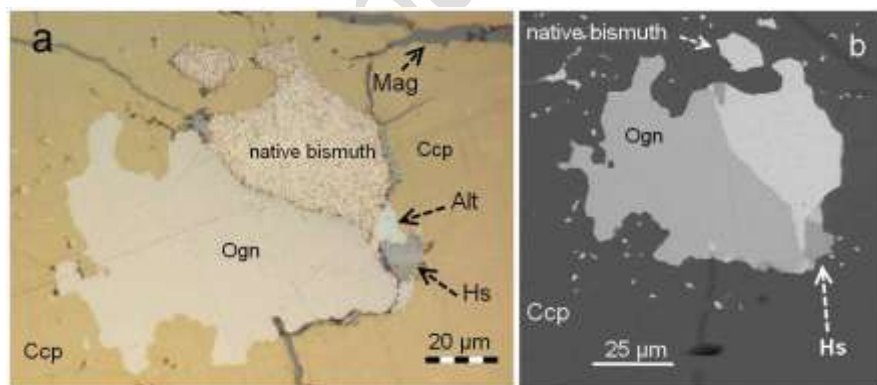


Fig. 3. Compositions of skeletal grains of chromite and associated magnetite zones (shown by blue and brown symbols, respectively) from the Ognit complex in terms of the Cr – Fe<sup>3+</sup> – Al plot (atomic %). The positions of Fe–Ti and Cr–Al trends and the miscibility gap are quoted after Barnes and Roeder (2001).



Figs. 4a, b. Reflected light microphotograph (a) showing the ognitite grain (Ogn), which is hosted by chalcopyrite (Ccp), and is associated with native bismuth, hessite (Hs), altaite (Alt), and also with late veinlets of magnetite (Mag). Fig. 4b is a BSE image showing ognitite (Ogn) and associated grains, complementary to those shown in the optical photograph in Fig. 4a.

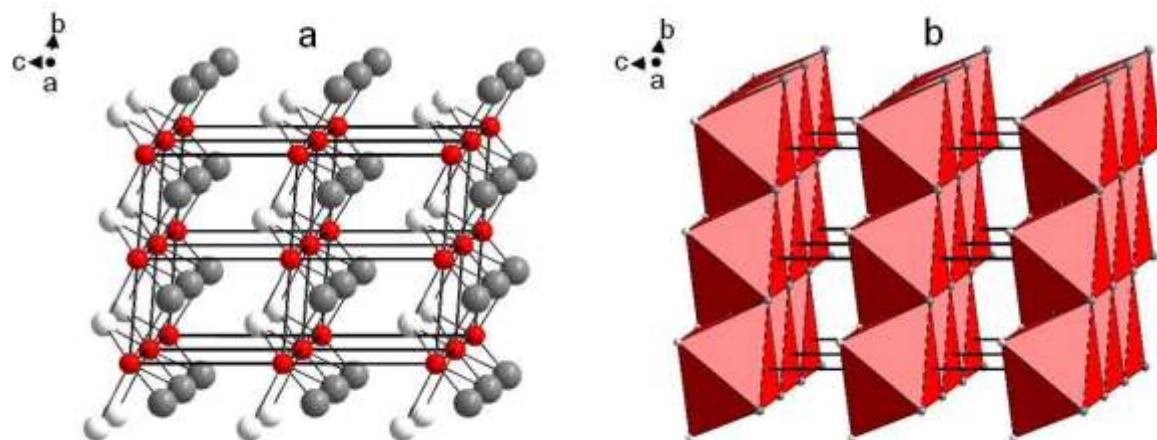


Fig. 5. The crystal structure of ognitite. On the left (a), balls and sticks representation: red, white and grey spheres refer to Ni, Te and Bi, respectively; on the right (b), polyhedral representation. The unit-cell and the orientation of the Figures are outlined.



6	0.81	3.76	57.81	0.17	32.71	27.07	6.27	0.94	3.24	0	0.62		
100.69													
7	1.15	6.47	55.07	0.27	31.42	26.18	5.83	0.88	4.35	0.04	0.62		
100.86													
8	1.16	5.19	55.91	0.16	32.27	27.18	5.65	0.92	3.37	0.02	0.74		
100.29													
9	1.15	5.91	56.33	0.15	31.22	26.64	5.09	0.89	3.99	0.08	0.54		
100.77													
10(R)	0.28	0.03	0.41	0.04	92.23	29.74	69.44	0.06	1.06	0.30	0		101.36

#	Ti	Al	Cr	V	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mn	Mg	Ni	Zn	Mg#	Cr#	Fe <sup>3+#</sup>
1	0.019	0.14	1.68	0.005	0.14	0.80	0.030	0.17	0	0.013	17.0	92.2	7.1
2	0.037	0.20	1.54	0.006	0.18	0.81	0.027	0.19	0.001	0.012	17.9	88.8	9.5
3	0.026	0.17	1.60	0.008	0.18	0.80	0.029	0.18	0	0.016	17.2	90.5	9.1
4	0.027	0.22	1.53	0.006	0.19	0.77	0.028	0.21	0	0.016	20.5	87.3	9.6
5	0.023	0.21	1.54	0.006	0.20	0.76	0.027	0.21	0	0.019	21.0	88.0	10.4
6	0.022	0.16	1.63	0.005	0.17	0.81	0.028	0.17	0	0.016	16.8	91.2	8.6
7	0.030	0.27	1.51	0.007	0.15	0.76	0.026	0.23	0.001	0.016	21.9	85.1	7.9
8	0.031	0.22	1.57	0.005	0.15	0.81	0.028	0.18	0.001	0.019	17.3	87.8	7.8
9	0.030	0.24	1.56	0.004	0.13	0.78	0.026	0.21	0.002	0.014	20.3	86.5	6.9
10	0.008	0	0.01	0.001	1.97	0.94	0.002	0.06	0.009	0	6.0	91.1	99.3

Note: Results of WDS analyses are listed in weight %. R\* (#10) refers to a rim zone of skeletal grain of chromite. Zero means below detection limit. FeO(t): all Fe is expressed as FeO. FeO(c) and Fe<sub>2</sub>O<sub>3</sub> (c) are values calculated on the basis of stoichiometry and charge balance. The bottom part of the table shows the compositions recalculated on the basis of stoichiometry per four oxygen atoms. The index Mg# is 100Mg/(Mg+Fe<sup>2+</sup>+Mn); Cr# is 100Cr/(Cr + Al), and Fe<sup>3+#</sup> is 100Fe<sup>3+</sup>/(Fe<sup>3+</sup> +Cr + Al).

Table 2. Reflectance values for ognitite

$\lambda$ nm	R <sub>max</sub> %	R <sub>min</sub> %	$\lambda$ nm	R <sub>max</sub> %	R <sub>min</sub> %
400	52.0	51.0	560	55.5	55.1
420	52.2	51.3	580	56.3	56.0
440	52.5	51.6	589 (COM)	56.7	56.4
460	53.0	52.1	600	57.0	56.8
470 (COM)	53.2	52.4	620	57.7	57.5
480	53.4	52.6	640	58.5	58.3

500	53.9	53.2	650 (COM)	58.9	58.7
520	54.4	53.8	660	59.2	59.0
540	54.9	54.4	680	60.0	59.8
546 (COM)	55.1	54.6	700	60.8	60.6

Note: These values were measured in air; the standard used is WTiC.

Table 3. Compositions of ognitite from the Ognit complex

#	Ni	Pd	Fe	Cu	Bi	Te	Total
1	17.03	0.09	0.05	0.12	48.27	33.67	99.23
2	16.91	0.15	0.05	0.13	49.68	32.10	99.01
3	17.07	0.14	0.03	0.09	49.92	32.35	99.60
4	17.06	0.14	0.02	0.08	49.68	32.77	99.75
5	17.00	0.16	0.08	0.14	50.31	31.79	99.48
6	17.15	0.11	0.16	0.26	49.95	32.44	100.07
7	17.15	0.16	0.12	0.19	49.64	32.59	99.85
8	17.05	0.14	0.07	0.14	49.64	32.53	99.57
9	17.17	0	0	0	49.68	33.16	100.01
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1	1.10	0.003	0.003	0.007	0.88	1.00	
2	1.11	0.005	0.003	0.008	0.91	0.97	
3	1.11	0.005	0.002	0.005	0.91	0.97	
4	1.11	0.005	0.001	0.005	0.90	0.98	
5	1.11	0.006	0.005	0.009	0.92	0.95	
6	1.10	0.004	0.010	0.015	0.90	0.96	
7	1.11	0.006	0.008	0.011	0.90	0.97	
8	1.11	0.005	0.005	0.009	0.90	0.97	
9	1.11	0	0	0	0.90	0.99	

Note: Analyses #1–7 are results of WDS analyses listed in weight %. Composition #8 is mean result of the seven point analyses (WDS). Analysis #9 pertains to results of an SEM/EDS analysis. Other elements (Co, Pt, Sb, Pb, As and S) were sought (WDS), but not detected. The bottom part of the table shows the compositions recalculated on the basis of three atoms per formula unit.

Table 4. Measured and calculated X-ray powder diffraction data ( $d$  in Å) for ognitite

$hkl$	$d_{\text{meas}}$	$I_{\text{meas}}$	$d_{\text{calc}}$	$I_{\text{calc}}$
001	5.39	10	5.3850	9
100	3.39	15	3.4017	12
011	<b>2.880</b>	<b>100</b>	2.8760	29
101			2.8760	71
002	2.697	10	2.6925	11
012	<b>2.110</b>	<b>30</b>	2.1112	13
102			2.1112	13
110	<b>1.968</b>	<b>30</b>	1.9640	28
111	-	-	1.8451	3
200	-	-	1.7009	2
021	<b>1.625</b>	<b>15</b>	1.6219	11
201			1.6219	5
013	<b>1.589</b>	<b>20</b>	1.5875	10
103			1.5875	4
112			1.5867	12
022	1.440	5	1.4380	3
202			1.4380	3
004	-	-	1.3463	2
113	-	-	1.3250	1
210	-	-	1.2857	1
121	1.252	10	1.2506	3
211			1.2506	8
203	1.237	10	1.2346	4
023			1.2346	2
122	-	-	1.1602	3
212	-	-	1.1602	3
300	-	-	1.1339	3
114	1.112	5	1.1104	6
123	-	-	1.0453	4
213	-	-	1.0453	2
032	-	-	1.0450	1
302	-	-	1.0450	1
015	-	-	1.0268	1
105	-	-	1.0268	2
131	-	-	0.9293	1
025	-	-	0.9099	2

*Note:* calculated diffraction pattern obtained with the atom coordinates reported in Table 6 (only reflections with  $I_{\text{rel}} \geq 1$  are listed). The strongest diffraction lines are given in bold.

Table 5. Data and experimental details for the selected ognitite crystal

Crystal data	
Ideal formula	NiBiTe
Crystal size (mm <sup>3</sup> )	0.040 × 0.050 × 0.060
Form	Block
Colour	Black
Crystal system	Trigonal
Space group	<i>P3m1</i>
<i>a</i> (Å)	3.928(1)
<i>c</i> (Å)	5.385(1)
<i>V</i> (Å <sup>3</sup> )	71.95(4)
<i>Z</i>	1
Data collection	
Instrument	Oxford Diffraction Xcalibur 3
Radiation type	MoKα (λ = 0.71073 Å)
Temperature (K)	293(3)
Detector to sample distance (cm)	6
Number of frames	348
Measuring time (s)	50
Maximum covered 2θ (°)	74.26
Absorption correction	multi-scan (Oxford Diffraction, 2006)
Collected reflections	1325
Unique reflections	167
Reflections with $F_o > 4\sigma(F_o)$	81
$R_{\text{int}}$	0.0286
$R_{\sigma}$	0.0347
Range of <i>h, k, l</i>	-6 ≤ <i>h</i> ≤ 6, -6 ≤ <i>k</i> ≤ 6, -6 ≤ <i>l</i> ≤ 9
Refinement	
Refinement	Full-matrix least squares on $F^2$
Final $R_1$ [ $F_o > 4\sigma(F_o)$ ]	0.0276
Final $R_1$ (all data)	0.0460
<i>S</i>	0.943
Number refined parameters	11
$\Delta\rho_{\text{max}}$ (e Å <sup>-3</sup> )	1.83
$\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	-1.01

Table 6. Atoms, site occupancy factors (s.o.f.), fractional atomic coordinates and anisotropic displacement parameters ( $\text{\AA}^2$ ) for the extracted ognitite crystal

Atom	s.o.f.	$x/a$	$y/b$	$z/c$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{\text{eq}}$
Ni	Ni <sub>1.00</sub>	0	0	-	0.0267	0.0267	0.031	0	0	0.0134	0.0283(
Bi	Bi <sub>0.97(2)</sub> Ni	$\frac{1}{3}$	$\frac{2}{3}$	0.72947(2)	0.0436	0.0436	0.063	0	0	0.0218	0.050(1
Te	Te <sub>1.00</sub>	$\frac{2}{3}$	$\frac{1}{3}$	0.2267(4)	0.033(	0.033(	0.022	0	0	0.0166	0.0295(

Table 7. Bond distances (in  $\text{\AA}$ ) in the structure of ognitite

Ni-Te ( $\times 3$ )	2.575(5)
Ni-Bi ( $\times 3$ )	2.696(5)
Ni-Ni	3.334(2)
Bi-Te	3.509(3)
Bi-Bi	3.928(2)
Te-Te	3.928(2)



Table 8. Compositions of cobaltian maucherite and associated orcelite in a zoned grain from the Ognit complex

#	Ni	Co	Fe	As	S	Te	Sb	Total
1	45.40	9.56	0.55	44.76	0.53	0.07	0.04	100.91
2	45.42	9.59	0.58	44.49	0.53	0.03	0	100.64
3	45.77	9.55	0.57	44.10	0.52	0.03	0.13	100.68
4	45.58	8.71	0.70	44.47	0.49	0	0.05	100.00
5	46.54	8.63	0.75	44.50	0.50	0.03	0.02	100.97
6	44.82	8.43	0.57	46.95	0.48	0	0	101.25
7	65.98	0	0.68	33.85	0	0	0	100.51

#	Ni	Co	Fe	As	S	Te	Sb	Ni+Co +Fe	As +S
1	9.42	1.98	0.12	7.27	0.20	0.006	0.004	11.51	7.48
2	9.44	1.98	0.13	7.24	0.20	0.003	0	11.55	7.45
3	9.51	1.98	0.12	7.18	0.20	0.003	0.013	11.61	7.38
4	9.54	1.82	0.15	7.30	0.19	0	0.005	11.51	7.48
5	9.64	1.78	0.16	7.22	0.19	0.003	0.002	11.58	7.41
6	9.31	1.74	0.12	7.64	0.18	0	0	11.18	7.82
7	4.98	0	0.05	2.00	0	0	0	5.03	2.00

Note: Results of WDS (#1–5) and SEM/EDS (#6, 7) analyses are listed in the top part of the table in weight %. Analyses #1–6 pertain to maucherite. Analysis #7 pertains to orcelite. Atomic proportions, shown in the bottom part, are based on a total of 19 atoms per formula unit (*apfu*) for maucherite, and on two *apfu* S for orcelite. Zero stands for not detected.