

Nickelsumcorite, $\text{Pb}(\text{Ni}, \text{Fe}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O}, \text{OH})_2$, a new tsumcorite-group mineral from Lavrion, Greece

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ABSTRACT

A new tsumcorite-group mineral, nickelsumcorite, $\text{Pb}(\text{Ni}, \text{Fe}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O}, \text{OH})_2$, the Ni-dominant analogue of tsumcorite and cobalttsumcorite, was found in the oxidation zone of a hydrothermal orebody containing gersdorffite and galena at the Km-3 mine, Lavrion, Attiki Prefecture, Greece. It is associated with annabergite, nickellotharmeyerite, nickelaustinite, gaspéite, calcite, dolomite, aragonite, quartz, goethite, cerussite, arseniosiderite, mimetite, oxyplumboroméite and Mn oxides/hydroxides. Nickelsumcorite occurs as open-work aggregates and interrupted crusts up to 3 mm × 5 mm in area and up to 0.2 mm thick. They typically consist of coarse radial spherulites or dense concentric nodules up to 0.15 mm in diameter. Bunches or hemispherical clusters of crude individuals and separate imperfect, elongated crystals (up to 0.02 mm long) are also observed. Nickelsumcorite is yellow, brownish-yellow, light brown or brown, with a yellow streak and a vitreous lustre. The Mohs hardness is ~4. The mineral is brittle; one direction of distinct cleavage is observed under the microscope. $D(\text{calc.}) = 5.02 \text{ g cm}^{-3}$. Nickelsumcorite is optically biaxial (-), $\alpha = 1.82(2)$, $\beta = 1.87(1)$, $\gamma = 1.90(1)$, $2V(\text{obs.})$ is large. The chemical composition (wt.%, electron-microprobe data, H_2O by difference) is CaO 2.79, PbO 28.12, MgO 0.30, CoO 0.15, NiO 17.39, ZnO 0.76, Mn_2O_3 0.57, Fe_2O_3 6.83, As_2O_5 38.17, H_2O 4.92, total 100.00. The empirical formula, calculated based on 10 O apfu, is $(\text{Pb}_{0.76}\text{Ca}_{0.30})_{\Sigma 1.06}(\text{Ni}_{1.39}\text{Fe}_{0.51}\text{Zn}_{0.06}\text{Mn}_{0.04}^{3+}\text{Mg}_{0.04}\text{Co}_{0.01})_{\Sigma 2.05}\text{As}_{1.99}\text{O}_{7.97}[(\text{H}_2\text{O})_{1.25}(\text{OH})_{0.78}]$. The strongest reflections in the powder X-ray diffraction pattern [$d, \text{Å}(I)(hkl)$] are 4.64(100)($\bar{1}11$), 4.47(41)($\bar{2}01$), 3.238(82)($\bar{1}12$), 3.008(60)(201), 2.859(41)(021), 2.545(79)($\bar{3}12, 112$), 2.545(79)($\bar{3}12, 112$) and 2.505(61)(220, $\bar{2}03$). The cation composition, powder X-ray diffraction data and IR spectrum show that nickelsumcorite belongs to the tsumcorite structure type. The new mineral is monoclinic, space group $C2/m$, $a = 9.124(8)$, $b = 6.339(3)$, $c = 7.567(7)$ Å, $\beta = 115.19(6)^\circ$, $V = 396.0(7)$ Å³ and $Z = 2$. Nickelsumcorite forms a solid-solution series with nickellotharmeyerite.

KEYWORDS: nickelsumcorite, new mineral, tsumcorite group, lead nickel arsenate, oxidation zone, Lavrion.

Introduction

THE tsumcorite group includes more than twenty natural monoclinic and triclinic arsenates, vanadates, sulfates and phosphates. Their general formula is $AM_2(\text{XO}_4)_2(\text{H}_2\text{O}, \text{OH})_2$ with species-defining

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$A = \text{Na, K, Ca, Pb}^{2+}, \text{Bi}^{3+}$; $M = \text{Mg, Co}^{2+}, \text{Ni}^{2+}, \text{Zn, Cu}^{2+}, \text{Al, Mn}^{3+}, \text{Fe}^{3+}$; $X = \text{P}^{5+}, \text{V}^{5+}, \text{As}^{5+}, \text{S}^{6+}$ (Krause *et al.*, 1998, 2001; Effenberger *et al.*, 2000; Back, 2014; Pekov *et al.*, 2014). The majority of these minerals, including both earlier known nickel members of the group, nickellotharmeyerite, $\text{Ca}(\text{Ni, Fe}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O, OH})_2$ and nickelschneebergite, $(\text{Bi, Ca})(\text{Ni, Co, Fe}^{3+})_2(\text{AsO}_4)_2(\text{OH, H}_2\text{O})_2$ (Krause *et al.*, 2001, 2002), occur in the oxidation zone of chalcogenide ores.

In this paper we describe a new mineral species belonging to this group, nickeltsumcorite (Cyrillic: никельцумкорит), $\text{Pb}(\text{Ni, Fe}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O, OH})_2$, the Ni-dominant analogue of tsumcorite, $\text{Pb}(\text{Zn, Fe}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O, OH})_2$ and cobalttsumcorite, $\text{Pb}(\text{Co, Fe}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O, OH})_2$, and the Pb-dominant analogue of nickellotharmeyerite (Table 1). The type specimens of the new mineral were collected by us in 2012 in dumps from the old

Km-3 mine in the Lavrion mining district, Attiki Prefecture, Greece. This mine, famous as a source of numerous, spectacular, and probably the World-best specimens of annabergite, is located ~ 2.5 km west of the city of Lavrion, near the “Km 3” milepost on the road from Lavrion to the village of Agios Konstantinos.

The new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2013–117). The type specimen of nickeltsumcorite is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, catalogue number 94317. Note that a mineral phase closely related (perhaps analogous) to nickeltsumcorite was reported briefly as coming from the Clara mine, Schwarzwald, Baden-Württemberg, Germany, as “a nickel analogue of cobalttsumcorite”. For this

TABLE 1. Comparative data for nickeltsumcorite and closely-related tsumcorite-group arsenates.

Mineral	Nickeltsumcorite	Tsumcorite	Cobalttsumcorite	Nickellotharmeyerite
Formula	$\text{Pb}(\text{Ni, Fe}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O, OH})_2$	$\text{Pb}(\text{Zn, Fe}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O, OH})_2$	$\text{Pb}(\text{Co, Fe}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O, OH})_2$	$\text{Ca}(\text{Ni, Fe}^{3+})_2(\text{AsO}_4)_2(\text{H}_2\text{O, OH})_2$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$	$C2/m$	$C2/m$
$a, \text{Å}$	9.124	9.12–9.16	9.097	9.005
$b, \text{Å}$	6.339	6.32–6.35	6.313	6.205
$c, \text{Å}$	7.567	7.57–7.61	7.555	7.411
$\beta, ^\circ$	115.19	115.1–115.5	115.08	115.31
$V, \text{Å}^3$	396.0	395–401	393.0	374.4
Z	2	2	2	2
Strongest lines of the powder	4.64–100 4.47–41	4.66–90 3.244–100	4.656–87 4.462–96	3.393–55 3.182–76
XRD pattern:	3.238–82	3.021–60	3.243–100	2.962–100
$d, \text{Å} - I, \%$	3.008–60 2.859–41 2.730–54 2.545–79 2.505–61	2.863–90 2.742–70 2.573–50 2.540–40	3.010–58 2.868–50 2.733–47 2.538–40	2.816–66 2.703–66 2.538–75 1.697–53
Density, g cm^{-3}	5.02 (calc.)	5.2–5.4	5.31 (calc.)	4.45 (calc.)
Optical data				
α	1.82	1.87–1.91	1.92 (calc.)	1.80
β	1.87	1.89–1.93	1.94	1.81
γ	1.90	1.92–1.96	1.98	1.87
Opt. sign, 2V	(–) large	(+) 67–83°	(+) 70°	(+) 40°
References	this work	Geier <i>et al.</i> (1971); Tillmanns and Gebert (1973); Krause <i>et al.</i> (1998)	Krause <i>et al.</i> (2001)	Krause <i>et al.</i> (2001)

phase monoclinic symmetry was mentioned and the approximate proportions of the *M* cations (Ni:Co:Cu:Fe \approx 1:0.48:0.27:0.14) are reported without providing any other data (Kolitsch *et al.*, 2004).

Occurrence and general appearance

The Lavrion mining district is situated \sim 50 km southeast of Athens and is famous for the exploitation of lead-silver ores during ancient times. Several types of mineralization occur in the Lavrion district, including porphyry, breccia-type, skarn, skarn-free carbonate replacement and vein-type ores (Voudouris *et al.*, 2008; Bonsall *et al.*, 2011; Baziotis and Mposkos, 2011). Mineralization is related to Miocene granitoids and occurs at several places such as in Plaka, Kamariza (Hilarion, Clemence, Jean Baptiste, Serpieri and Christiana deposits), as well in the 3rd kilometre (Km-3 mine), Esperanza and Sounio mines. Carbonate-replacement and vein Pb-Zn-Ag \pm Au ore deposits in Kamariza were the most economically significant in the Lavrion district, being dominated by sulfides and sulfoarsenides (pyrite, pyrrothite, arsenopyrite, chalcopyrite, galena, sphalerite, gersdorffite, marcasite), native metals (Au and Bi), Sn-In-bearing sulfides (petrukite, stannite), sulfosalts and sulfobismuthides of Ag, Bi, Cu, Pb, As and Sb (tetrahedrite-group minerals, bournonite, boulangerite, stephanite, pyrrargyrite, semseyite, enargite, bismuthinite derivatives, lillianite homologues, matildite, emplectite and wittichenite). Quartz, fluorite, calcite and sericite are gangue minerals. Oxidation and re-distribution of the elements of the primary ore has resulted in the formation of an extended supergene ore zone (Marinos and Petrascheck, 1956; Katerinopoulos and Zissimopoulou, 1994).

The Km-3 mine orebody, which includes mainly galena-gersdorffite-rich veins crosscutting brecciated marble along a detachment fault, resembles the Ni-Au ores at Kamariza (e.g. the Clemence mine). In addition to galena and gersdorffite, the mineralization at Km-3 mine includes rammelsbergite, nickeline and safflorite (Baumgartl and Burow, 2002) and vaesite, millerite and ullmannite as inclusions in gersdorffite and galena (Voudouris, unpublished data). Nickelsumcorite is a supergene mineral formed in the oxidation zone of the hydrothermal orebody at the Km-3 Mine. The primary assemblage included quartz, carbonates (mainly calcite), gersdorffite (a source of Ni and As for nickelsumcorite and associated nickel arsenates), galena (the major

source of Pb for supergene minerals), pyrite, sphalerite and a Pb-Sb sulfosalt (presumably boulangerite; it is completely replaced by aggregates of lead and calcium minerals of the roméite group and various arsenates). Nickelsumcorite is associated closely with other Ni oxysalt minerals, namely annabergite, nickellotharmeyerite, nickel-austinite, gaspéite and an Ni-dominant serpentine-group member, presumably pecoraite (Table 2). Other associated supergene minerals are calcite, dolomite (including Ni-bearing varieties), aragonite, quartz, goethite, cerussite, arseniosiderite, mimetite, oxyplumboroméite (bindheimite), a Ca-rich roméite-group mineral (hydroxycalcioroméite?) and unspecified, black, manganese oxides/hydroxides. This mineral assemblage occurs in cavities and pores of a partially oxidized Ni-Pb-As-Sb-bearing ore. The richest aggregations of nickelsumcorite are observed close to altered nests of gersdorffite and galena, typically with relics of the latter surrounded by cerussite rims. The new mineral forms crusts and open-work aggregates (Fig. 1) up to 2 mm across (some interrupted crusts are up to 3 mm \times 5 mm in area) and up to 0.1 mm, rarely 0.2 mm thick. They overgrow calcite, dolomite, gaspéite, quartz, goethite, Mn oxides/hydroxides or roméite-group minerals. Aggregates of nickelsumcorite consist typically of coarse radial spherulites or dense concentric nodules (Figs 1 and 2a–d) up to 0.05 mm, rarely 0.15 mm, in diameter. In some cases their surface is formed by divergent crystals (Fig. 2c). Bunches or hemispherical clusters of crude individuals (Fig. 2e), separate crystals or thin crystal crusts of the new mineral (Fig. 2f) are also observed. Nickelsumcorite crystals (up to 0.01 mm, rarely 0.02 mm long) are elongated, sometimes flattened and lath-like. They are imperfect, typically split, divergent, sometimes showing fan-shaped forms (Figs 2c,e,f).

Physical properties and optical data

Nickelsumcorite is transparent in tiny individuals and translucent in aggregates. Its colour is yellow, brownish-yellow, light brown or brown. The streak is yellow. The lustre is vitreous. The Mohs hardness is \sim 4. The mineral is brittle. One plane of distinct cleavage is observed under the microscope (supposedly it is cleavage on {001}, by analogy with tsumcorite), the fracture is uneven. Density could not be measured because of the paucity of pure material for volumetric methods and lack of heavy

TABLE 2. Chemical composition of nickeltsumcorite (1) and associated supergene nickel minerals nickellotharmeyerite (2), nickelaustinite (3), annabergite (4), Ni serpentine (5) and gaspéite (6–8) from the Km-3 mine, Lavrion.^a

Constituent	Mineral							
	1	2	3	4	5	6	7	8
	Wt.%							
CaO	2.79 (2.02–4.54)	7.65	17.60			1.14	1.88	1.07
PbO	28.12 (23.47–30.74)	15.74	9.98					
MgO	0.30 (0.00–0.79)	0.78	0.96	1.85	0.72	4.35	9.31	9.05
CoO	0.15 (0.00–0.37)			0.10	0.08	0.12	0.26	0.49
NiO	17.39 (14.22–20.03)	20.56	25.65	32.33	46.63	36.45	40.95	33.98
ZnO	0.76 (0.32–1.32)	0.46	1.12	0.45	6.20	17.01	4.39	15.42
Mn ₂ O ₃	0.57 (0.34–1.05)	5.36	0.35	0.12**	0.05	1.65**	3.60**	0.44**
Fe ₂ O ₃	6.83 (4.34–9.86)	1.10	0.04	1.11**	5.60	0.56**	0.12**	
SiO ₂					31.81			
As ₂ O ₅	38.17 (37.24–39.19)	43.32	41.82	38.86				
H ₂ O(calc)*	4.92	5.63	2.48	25.18	8.91			
CO ₂ (calc)*						38.72	39.49	39.55
Total	100	100	100	100	100	100	100	100
	Formula coefficients							
Ca	0.30	0.67	0.87			0.02	0.04	0.02
Pb	0.76	0.38	0.12					
Mg	0.04	0.10	0.07	0.26	0.07	0.12	0.26	0.25
Co	0.01			0.01	0.00	0.00	0.00	0.01
Ni	1.39	1.47	0.96	2.52	2.36	0.56	0.61	0.51
Zn	0.06	0.03	0.04	0.03	0.29	0.24	0.06	0.21
Mn	0.04	0.36	0.01	0.01	0.00	0.03	0.06	0.01
Fe	0.51	0.07	0.00	0.09	0.27	0.01	0.00	
Si					2.00			
As	1.99	2.01	1.01	1.97				
C						1.01	0.99	1.00
O	7.97	8.05	4.23	7.85	5.26	3	3	3
OH ⁻	1.25	0.55	0.77		3.74			
H ₂ O	0.78	1.40		8.15				

^aEach oxide content given for the nickeltsumcorite (1) represents the average value from 6 spot analyses of the holotype sample. Ranges are in parentheses. An empty cell means that the concentration of the element is below its detection limit (bdl) or, for CO₂ and H₂O, was not calculated. Contents of other elements with atomic numbers higher than carbon are bdl in all analyses. Formulae are calculated on the following bases: nickeltsumcorite and nickellotharmeyerite – 10 O apfu = [O + OH + H₂O = 10]; nickelaustinite – 5 O apfu = [O + OH = 5]; annabergite – 16 O apfu = [O + H₂O = 16]; Ni serpentine – 9 O apfu = [O + OH = 9]; gaspéite – 3 O apfu. *Calculated by total difference. **Recalculated for MnO or FeO.

liquids of required density. The density calculated using the empirical formula is 5.02 g cm⁻³.

Nickeltsumcorite is optically biaxial (–), $\alpha = 1.82(2)$, $\beta = 1.87(1)$, $\gamma = 1.90(1)$ (589 nm). $2V(\text{obs.})$ is large, $2V(\text{calc.}) = 74^\circ$. The tiny size and imperfection of single crystals prevented us obtaining more precise values of refractive indices and $2V(\text{obs.})$ for nickeltsumcorite. Dispersion of optical axes was not observed. Under the microscope, the mineral is yellowish-brown and non-pleochroic.

Infrared spectroscopy

The infrared (IR) absorption spectrum of nickeltsumcorite was obtained for a powdered sample mixed with anhydrous KBr and pelletized. The pellet was analysed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm⁻¹ with 16 scans. The IR spectrum of a pure KBr disc was subtracted from the overall spectrum. The spectrum is close to that of tsumcorite (Fig. 3).

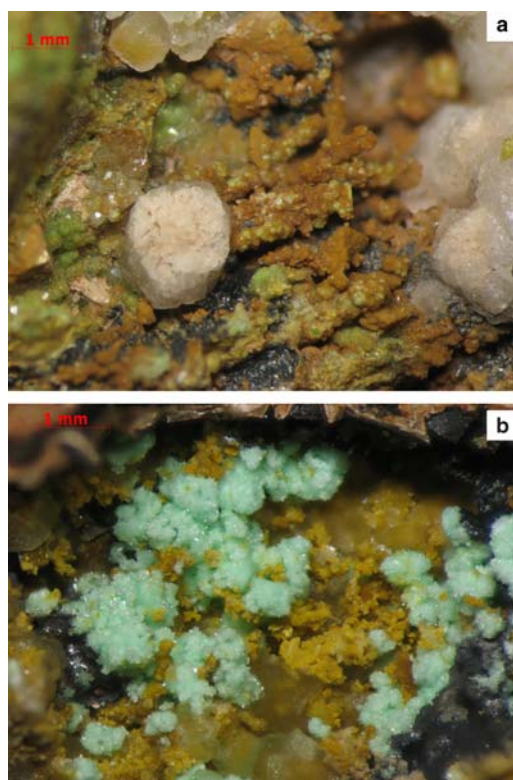


FIG. 1. Morphology of nickeltsumcorite: (a) light brown crusts formed by small nodules of nickeltsumcorite on green gaspéite and black crusts consisting of goethite and Mn oxides/hydroxides, with colourless and white calcite; (b) open-work brownish-yellow aggregates of nickeltsumcorite with light green annabergite, colourless calcite and black crusts of goethite and Mn oxides/hydroxides. FOV: (a) 7.1 mm, (b) 5.7 mm. Photos: I.V. Pekov and A.V. Kasatkin.

Absorption bands and their assignments (cm^{-1} ; s – strong band, w – weak band, sh – shoulder) are 3610w, 3244, 2800sh (O–H-stretching vibrations; see Discussion), 1944w (O–H-stretching vibrations of acidic OH-groups), 1645 (H–O–H bending vibrations of H_2O molecules), 1080w, 1020w (presumably $\text{Fe}^{3+}\cdots\text{O–H}$ bending vibrations), 870 sh, 812 s, 802 s (asymmetric As–O stretching vibrations of AsO_4^{3-} anions), 680sh, 578w, 464s, 425, 400sh [lattice modes possibly involving (Ni, $\text{Fe}^{3+})\cdots\text{O}$ stretching vibrations and librational modes of H_2O molecules]. Bands of C-, N- and B-bearing groups are absent in the IR spectrum of nickeltsumcorite, as well as bands corresponding to As^{3+}O_3 anions.

Chemical data

The chemical composition of nickeltsumcorite and associated Ni minerals (Table 2) was studied using a Tescan VEGA-II XMU electron microprobe (digital scanning electron microscope with an Oxford INCA Wave 700 wavelength dispersive spectrometer), with an acceleration voltage of 20 kV, a beam current from 150 to 800 pA and spot size of 157–180 nm in diameter. The following standards, MgO (Mg), wollastonite (Ca, Si), Co (Co), Ni (Ni), Zn (Zn), PbTe (Pb), Mn (Mn), Fe (Fe) and InAs (As) were used. H_2O was not analysed because of paucity of pure material; its presence was confirmed by IR spectroscopy.

The empirical formula of the holotype nickeltsumcorite (#1 in Table 2) calculated based on 10 O apfu is $(\text{Pb}_{0.76}\text{Ca}_{0.30})_{\Sigma 1.06}(\text{Ni}_{1.39}\text{Fe}_{0.51}^{3+}\text{Zn}_{0.06}\text{Mn}_{0.04}^{3+}\text{Mg}_{0.04}\text{Co}_{0.01})_{\Sigma 2.05}\text{As}_{1.99}\text{O}_{7.97}[(\text{H}_2\text{O})_{1.25}(\text{OH})_{0.78}]$. The OH/ H_2O ratio was calculated from the charge balance. For notes on the valence states of Fe and Mn and their role in nickeltsumcorite as well as other tsumcorite-group minerals see the Discussion. As our electron microprobe study of different samples from the Km-3 mine showed, nickeltsumcorite forms a solid solution series with Mn-enriched nickellotharmeyerite; the Pb:Ca ratio in the series varies from $\text{Pb}_{99}\text{Ca}_1$ to $\text{Ca}_{69}\text{Pb}_{31}$.

X-ray crystallography

A single-crystal X-ray diffraction (XRD) study of nickeltsumcorite could not be carried out because of the absence of suitable crystals; the mineral was observed only as aggregates consisting of tiny, divergent individuals (Fig. 2). Powder XRD data collected with a STOE IPDS II diffractometer equipped with an image plate area detector, using the Gandolfi method (MoK α radiation; detector-to-sample distance = 200 mm) are given in Table 3. Unit-cell parameters calculated from the powder XRD data by analogy with isostructural tsumcorite (see Discussion and Tables 1 and 3) are $a = 9.124$ (8), $b = 6.339$ (3), $c = 7.567$ (7) Å, $\beta = 115.19$ (6) $^\circ$, $V = 396.0$ (7) Å 3 and $Z = 2$.

Discussion

In spite of the absence of single-crystal diffraction data and a direct crystal structure determination, we consider that nickeltsumcorite is undoubtedly a nickel analogue of tsumcorite and cobalttsumcorite (Table 1). The crystal chemistry of the tsumcorite

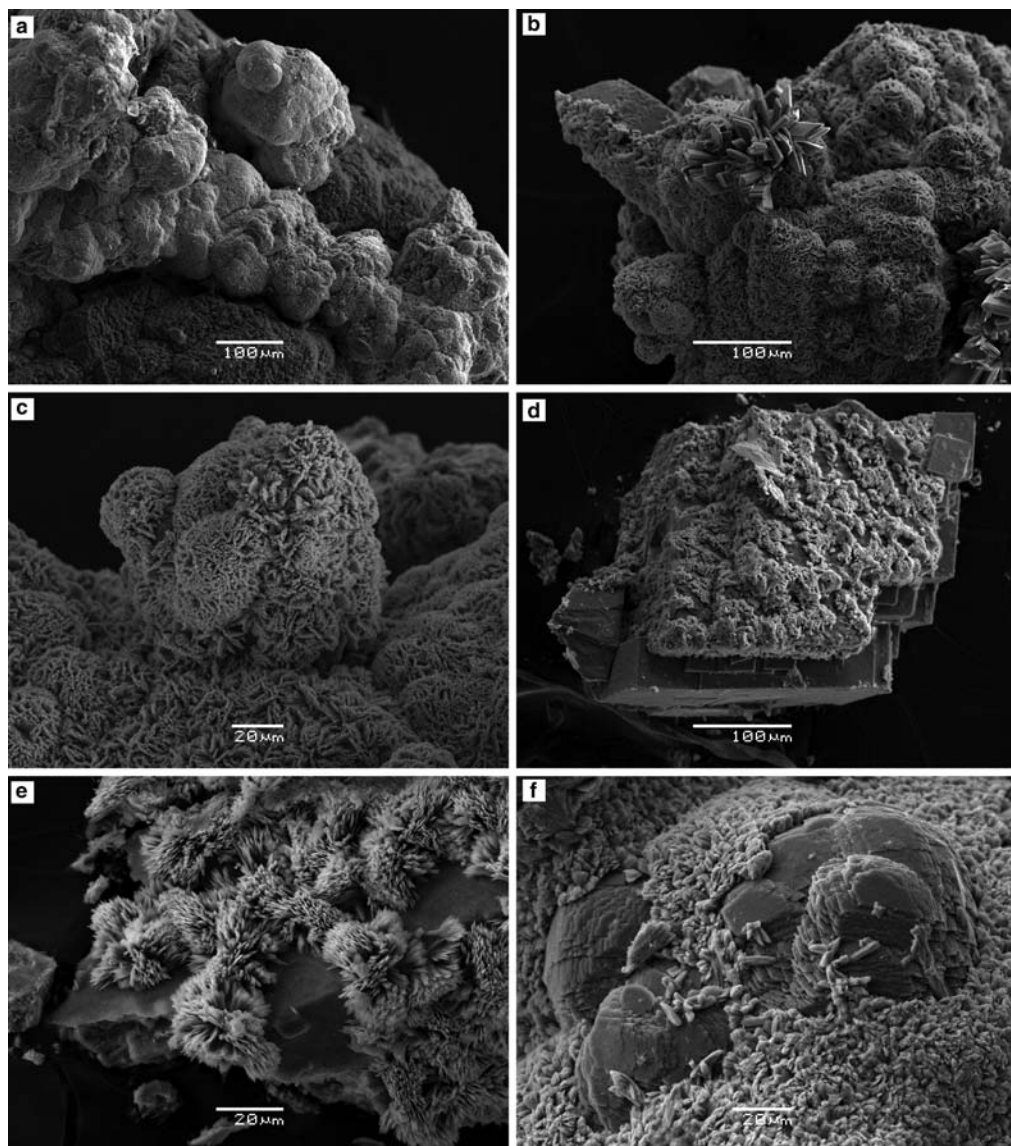


FIG. 2. Scanning electron microscope secondary electron images showing the morphology of nickeltsumcorite: (a) dense crust consisting of nodules on calcite; (b) crust of divergent crystals on quartz, with overgrowths of annabergite crystal clusters; (c) the same, an enlarged fragment; (d, e) aggregates of divergent crystals on dolomite; (f) crystals and crystal crusts on split rhombohedra of gaspéite.

group is well studied. Three related structure types are known for this group and the strict dependence of the structure type on the chemistry for arsenates, vanadates and phosphates has been elucidated (Krause *et al.*, 1998, 2001; Effenberger *et al.*, 2000). Members of the group belonging to these three chemical classes have the general formula

$AM_2(X^{5+}O_4)_2(H_2O,OH)_2$ with $A = Ca, Pb^{2+}, Bi^{3+}$; $M = (Me^{2+}: Mg, Co, Ni, Zn), Cu^{2+}, (Me^{3+}: Al, Mn, Fe)$; $X = P, V, As$. Copper is separated here from other bivalent M cations because of its specific role in the structures of these minerals; its presence causes the ordering of Cu and Me^{3+} (typically Fe) and, correspondingly, symmetry lowering from

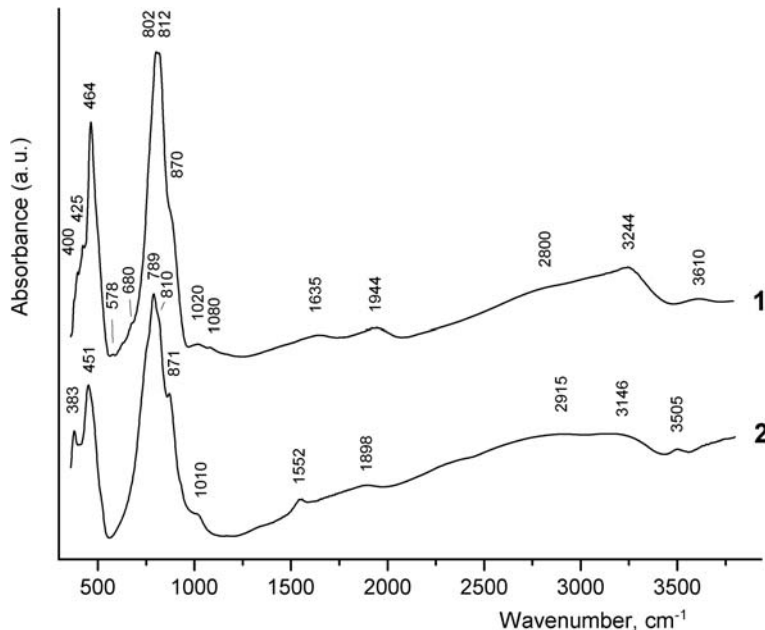


FIG. 3. The IR spectra of nickelsumcorite from Lavrion (1) and tsumcorite from the Tsumeb mine, Tsumeb, Otjikoto Region, Namibia (2). The spectra are shown with a vertical offset.

$C2/m$ (the tsumcorite structure type) to $P\bar{1}$ (the structure type of gartrellite, $PbCuFe^{3+}(AsO_4)_2\{(H_2O)(OH)\}$). The presence of only bivalent cations at the M sites is needed for charge balancing the presence of only H_2O , without OH^- , causing a reorganization of the system of hydrogen bonding and, correspondingly, the transition from the tsumcorite structure type to that of helmutwinklerite, $PbZn_2(AsO_4)_2(H_2O)_2(P\bar{1})$. Note that thometzkeite, $PbCu_2(AsO_4)_2(H_2O)_2$, a Cu-rich but Me^{3+} -free mineral, also belongs to the helmutwinklerite structure type. Thus a structure type for arsenates, vanadates and phosphates in the tsumcorite group depends on ratios of the M cations, namely on the amounts of Me^{3+} and/or Cu^{2+} . The analysis of all known crystal-chemical data for these minerals make it possible to propose and substantiate a diagram showing the relationships between the chemical composition in part of the M cations and the structure type; see the triangle $Me^{3+}-Me^{2+}-Cu^{2+}$ (Fig. 4). The areas marked 1, 2 and 3 on this diagram belong to the tsumcorite type ($C2/m$, $Z=2$), helmutwinklerite type ($P\bar{1}$, $Z=4$) and gartrellite type ($P\bar{1}$, $Z=1$), respectively (Effenberger *et al.*, 2000).

Numerous studies, including systematic Mössbauer measurements, show the presence of

Fe and Mn in tsumcorite-group arsenates, vanadates and phosphates in the trivalent state and the absence of Fe^{2+} and Mn^{2+} in significant amounts (Krause *et al.*, 1998; Brugger *et al.*, 2000, 2002). For this reason, we consider all iron and manganese in nickelsumcorite as Fe^{3+} and Mn^{3+} (this is compatible with high-valency states of Fe and Mn in all associated supergene minerals containing these elements as species-defining constituents). Nickelsumcorite contains more than $1/4 Me^{3+}$ of all cations in the M sites (Table 2) and does not contain Cu in detectable amounts. Thus its composition belongs to the field corresponding to the tsumcorite structure type ($C2/m$, $Z=2$) in Fig. 4. By this reasoning we believe that nickelsumcorite is a representative of this structure type. Another argument for assigning nickelsumcorite to the tsumcorite structure type is the good correspondence between measured intensities of reflections in its powder XRD pattern with calculated intensities for structurally characterized tsumcorite (Table 3). Comparison with triclinic helmutwinklerite shows a poorer correspondence.

Further important evidence concerning the assignment of nickelsumcorite to the tsumcorite structure type follows from the analysis of its IR

TABLE 3. Powder X-ray diffraction data for nickelsumcorite and tsumcorite.

Nickelsumcorite			Tsumcorite		<i>hkl</i>
<i>I</i> _{meas}	<i>d</i> _{meas} , Å	<i>d</i> _{calc} , Å	<i>I</i> _{calc} *	<i>d</i> _{calc} *, Å	
14	6.89	6.847	13	6.851	001
15	4.94	5.028	5	5.022	110
100	4.64	4.671	100	4.670	111
41	4.47	4.477	31	4.479	201
22	4.12	4.128	12	4.125	200
6	3.620	3.629	5	3.626	111
8	3.438	3.455	5	3.460	202
17	3.420	3.424	10	3.426	002
82	3.238	3.249	87	3.250	112
23	3.126	3.169	21	3.165	020
60	3.008	3.013	59	3.011	201
41	2.859	2.876	57	2.873	021
54	2.730	2.741	50	2.740	311
79	2.545	2.566, 2.540	28, 33	2.567, 2.539	312, 112
61	2.505	2.514, 2.498	26, 19	2.511, 2.501	220, 203
28	2.316	2.336, 2.317	19, 8	2.335, 2.318	222, 113
8	2.239	2.239	6	2.239	402
5	2.223	2.213	1	2.218	202
14	2.197	2.184	14	2.181	221
9	2.170	2.165	3	2.167	313
6	2.061	2.064	7	2.063	400
7	2.042	2.047	2	2.044	130
9	2.011	2.016	12	2.018	403
12	1.908	1.901	14	1.901	113
15	1.896	1.892	9	1.894	204
9	1.861	1.852	9	1.852	023
21	1.823	1.828, 1.814	1, 8	1.828, 1.813	422, 222
2	1.765	1.775	1	1.777	314
33	1.716	1.721, 1.712	7, 11	1.720, 1.713	511, 004
29	1.695	1.701, 1.688	23, 5	1.702, 1.687	423, 332
8	1.623	1.624	12	1.625	224
8	1.606	1.611	2	1.610	133
7	1.595	1.598	5	1.597	510
16	1.553	1.551	12	1.549	421
6	1.505	1.507, 1.507	8, 8	1.506, 1.506	223, 402
4	1.488	1.492	4	1.493	603
5	1.475	1.476	2	1.475	601
4	1.467	1.468, 1.464	3, 2	1.469, 1.466	315, 405
6	1.440	1.438	6	1.436	042
3	1.427	1.431	1	1.430	511
7	1.377	1.371, 1.371	8, 8	1.370, 1.370	622, 332
11	1.361	1.365, 1.360	3, 3	1.364, 1.360	531, 225
10	1.350	1.350, 1.350	3, 2	1.352, 1.350	515, 623
4	1.339	1.338	3	1.337	243
2	1.293	1.297, 1.293	1, 2	1.296, 1.292	441, 442
2	1.284	1.283, 1.281	1, 1	1.282, 1.282	403, 605
5	1.271	1.271	2	1.270	713
7	1.256	1.257, 1.257	6, 4	1.257, 1.255	025, 440
3	1.245	1.247, 1.246, 1.242	2, 2, 1	1.245, 1.245, 1.242	151, 443, 115

*Calculated from the structure data of Tillmanns and Gebert (1973).

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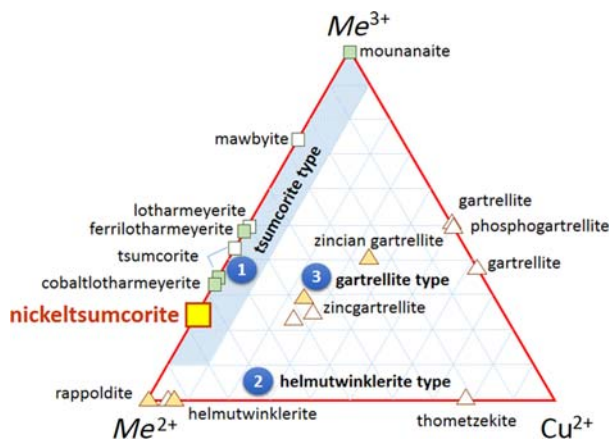


FIG. 4. The analysis of holotype nickeltsumcorite from Lavrion (yellow square) plotted on the Me^{3+} – Me^{2+} – Cu^{2+} triangular diagram of Effenberger *et al.* (2000), showing the relationships between the tsumcorite, helmutwinklerite and gartrellite structure types depending on the ratios of M cations in arsenates, vanadates and phosphates of the tsumcorite group with the general formula $AM_2(X^{5+}O_4)_2(OH, H_2O)_2$ ($A = Ca, Pb^{2+}, Bi^{3+}$; $M = (Me^{2+}: Mg, Co, Ni, Zn), Cu^{2+}, (Me^{3+}: Al, Mn, Fe)$; $X = P, V, As$). Copper is separated from other bivalent M cations because of its specific role in the structures of these minerals (see text). Type specimens are shown by empty signs while those of structurally investigated samples are shaded. Samples in areas 1, 2 and 3 belong to the tsumcorite type ($C2/m, Z = 2$), helmutwinklerite type ($P\bar{1}, Z = 4$) and gartrellite type ($P\bar{1}, Z = 1$), respectively (Effenberger *et al.*, 2000). The position of the holotype Lavrion nickeltsumcorite is on the line Me^{2+} – Me^{3+} because the mineral is Cu-free.

spectrum. As mentioned above, monoclinic tsumcorite-type and triclinic helmutwinklerite-type arsenates show significantly different systems of H bonds caused by differences in the H_2O/OH ratio as a result of the substitution $Me^{2+} + H_2O^0 \rightarrow Me^{3+} + OH^-$. These changes in the system of hydrogen bonding induce structural transformations that cause the transition from the tsumcorite structure type to that of helmutwinklerite. This phenomenon is well-studied using both structural and the IR spectroscopic data and has been discussed in detail in several papers (Krause *et al.*, 1998, 2001; Effenberger *et al.*, 2000; Brugger *et al.*, 2002). Differences in IR spectra of representatives of these structure types were clearly shown by Krause *et al.* (1998). In particular, IR spectra of minerals belonging to the helmutwinklerite and gartrellite structure types contain strong bands located above 3500 cm^{-1} , which correspond to weak hydrogen bonds, and strong, relatively narrow bands in the region of $1500\text{--}1600\text{ cm}^{-1}$ (H–O–H bending vibrations of H_2O molecules). These bands are very weak in the IR spectrum of nickeltsumcorite and weak to very weak in the spectra of other minerals belonging to the tsumcorite structure type.

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