

## NISNITE, Ni<sub>3</sub>Sn, A NEW NICKEL MINERAL SPECIES FROM THE JEFFREY MINE, ASBESTOS, QUEBEC

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### ABSTRACT

Nisnite, ideally Ni<sub>3</sub>Sn, was found during a re-examination of heazlewoodite crystals in rodingite samples from the Jeffrey mine, Asbestos, Quebec. It occurs as bronze-colored metallic, striated, blocky and square to rectangular tabular crystals of up to 100 μm in length, with groupings of ≤1 mm growing on heazlewoodite. Crystal groupings exhibit a boxwork-like habit. Reflectance measurements in air gave 43.2 (470 nm), 49.1 (546 nm), 53.2 (589 nm), and 59.0% (650 nm). Minerals closely associated with nisnite are chromite, diopside, grossular, heazlewoodite and shandite. The mineral is cubic,  $P4/m\bar{3}2/m$ , with unit-cell parameter refined using powder-diffraction data:  $a$  3.7349(6) Å,  $V$  52.10(3) Å<sup>3</sup>,  $Z = 1$ ,  $D_{\text{calc}} = 9.41$  g/cm<sup>3</sup>. The average results of five and three electron-microprobe analyses on separate crystals gave Ni 57.88, Sn 40.17, sum 98.05 wt.% and Ni 59.24, Sn 41.00, sum 100.24 wt.%, corresponding to Ni<sub>2.98</sub>Sn<sub>1.02</sub> on the basis of 4 *apfu*. The structure has been refined to an  $R$  index of 0.008% on the basis of 30 unique reflections. The structure of nisnite contains 12-coordinated Sn atoms (12 Ni) and 12-coordinated Ni atoms (8 Ni and 4 Sn). Among the three synthetic Ni<sub>3</sub>Sn phases known, nisnite corresponds to the **ccp** structure that has been synthesized at high pressure and high temperature.

*Keywords:* new mineral species, Ni<sub>3</sub>Sn, nisnite, rodingite, ophiolite, polymorph, synthetic compound, Jeffrey mine, Asbestos, Quebec.

### SOMMAIRE

Nous avons découvert la nisnite, de formule idéale Ni<sub>3</sub>Sn, au cours d'un ré-examen de cristaux de heazlewoodite dans des échantillons de rodingite provenant de la mine Jeffrey, à Asbestos, Québec. Elle se présente en cristaux carrés ou rectangulaires striés, métalliques, de couleur bronze, atteignant 100 μm en longueur, en groupes de ≤1 mm développés sur la heazlewoodite. Ces groupes ont une morphologie réticulaire en boîte. La réflectance mesurée dans l'air donne 43.2 (470 nm), 49.1 (546 nm), 53.2 (589 nm), et 59.0% (650 nm). Lui sont étroitement associés chromite, diopside, grossulaire, heazlewoodite et shandite. Il s'agit d'un minéral cubique,  $P4/m\bar{3}2/m$ , avec un paramètre réticulaire  $a$  affiné à partir du spectre de diffraction X sur poudre égal à 3.7349(6) Å [ $V$  52.10(3) Å<sup>3</sup>,  $Z = 1$ ,  $D_{\text{calc}} = 9.41$  g/cm<sup>3</sup>]. Les résultats de cinq et trois analyses avec une microsonde électronique sur deux cristaux sont: Ni 57.88, Sn 40.17, pour un total de 98.05%, et Ni 59.24, Sn 41.00, pour un total de 100.24% (poids), ce qui correspond à Ni<sub>2.98</sub>Sn<sub>1.02</sub> sur une base de quatre atomes par formule unitaire. Nous en avons affiné la structure, jusqu'à un résidu  $R$  de 0.008% en utilisant 30 réflexions uniques. La structure de la nisnite contient des atomes de Sn à coordinence 12 (avec 12 Ni) et des atomes de Ni à coordinence 12 (avec 8 Ni et 4 Sn). Parmi les trois polymorphes de Ni<sub>3</sub>Sn connus, la nisnite correspond à la structure **ccp**, synthétisée à pression et température élevées.

(Traduit par la Rédaction)

*Mots-clés:* nouvelle espèce minérale, Ni<sub>3</sub>Sn, nisnite, rodingite, ophiolite, polymorphe, composé synthétique, mine Jeffrey, Asbestos, Québec.

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## INTRODUCTION

An investigation by one of us (LH) of micro minerals associated with crystals of heazlewoodite ( $\text{Ni}_3\text{S}_2$ ) from the Jeffrey mine in Asbestos, Les Sources RCM, Estrie (up until recently, Shipton Township, Richmond County), Quebec, Canada, led to the discovery of many minerals new to the locality and a natural occurrence of  $\text{Ni}_3\text{Sn}$ . Eight specimens of heazlewoodite from the Horváth collection were carefully examined at high magnification (up to  $100\times$ ). Five minerals intimately associated with heazlewoodite were submitted for identification by X-ray diffraction at the Canadian Museum of Nature. Three were determined to be shandite,  $\text{Pb}_2\text{Ni}_3\text{S}_2$ , laurionite,  $\text{Pb}(\text{OH})\text{Cl}$ , and theophrastrite,  $\text{Ni}(\text{OH})_2$ , new for the Jeffrey mine, and two are unknowns, one hereby described as nisnite. Nisnite is the third new species described from the locality after spertiniite (Grice & Gasparrini 1981) and jeffreite (Grice & Robinson 1984).

The Jeffrey mine, once the largest producer of chrysotile asbestos in the world, was developed on a major asbestos deposit that was operated continuously from the late 1800s to 2001. It is part of an important ophiolitic belt in southern Quebec that formed early in the sequence of orogenic events that created the Appalachian Mountain Range (Grice & Williams 1979). The locality is particularly well known to collectors for its spectacular specimens of grossular and vesuvianite, which occur in rodingites.

Nisnite is named after its main constituents, nickel (Ni) and tin (Sn). The mineral and its name were approved by the Commission on New Minerals Nomenclature and Classification (CNMNC), IMA (2009–083). Type specimens are preserved at the Canadian Museum of Nature with catalogue number CMNMC 86097, and the Natural History Museum, London as BM 2010,121.

## OCCURRENCE

Nisnite is a rare mineral at the Jeffrey mine, which was confirmed by a re-examination of heazlewoodite specimens from the Canadian Museum of Nature mineral collection, which were found to be devoid of nisnite crystals. It occurs as intricate, boxwork-like clusters,  $<1$  mm in diameter, composed of crystals oriented at  $90^\circ$  to one another. All heazlewoodite specimens studied were from a rodingite dike and invariably associated with green grossular, diopside and chromite. In addition to the Ni-bearing minerals already mentioned, awaruite, cubanite, maucherite, nickeline and taenite also occur in rodingite dikes.

Specimens with heazlewoodite were obtained in 1977 and were in the Horváth collection until their re-examination in connection with a project on the mineralogy of the Jeffrey mine (Horváth & Spertini 2008, 2009). The specimens were originally collected

by miners and sold to mineral dealers, so the exact provenance within the mine is not known.

## PHYSICAL AND OPTICAL PROPERTIES

Crystals of nisnite are highly reflective, of bronze color, metallic, striated, blocky and square to rectangular, tabular and up to  $100\ \mu\text{m}$  in size where blocky (Fig. 1). Striations were observed by scanning electron microscopy (Fig. 2) on  $\{100\}$  and are parallel to the direction of elongation of the crystal. The hardness could not be measured owing to the minute size of the crystals, but they were observed to be brittle. No cleavage or fracture was observed on the crystals. The small size of the crystals also prevented a density measurement, but the calculated density, based on the structure determination, is  $9.41\ \text{g}/\text{cm}^3$ .

The mineral is opaque with a metallic luster, and is bronze-colored in reflected light. Reflectance data over the range 400 to 700 nm were obtained in air using a Zeiss Axiotron microscope. A Crystal Structures (Lanham) superstage was employed to level the specimen and standard prior to measurement with a J&M Tidas diode array spectrometer. Measurements were made in air relative to a Zeiss WTiC standard using Cavendish Instruments Onyx software at intervals of 0.823 nm from 400 to 700 nm, following the procedure described by Stanley *et al.* (2002). The reflectance data and color values of nisnite are listed in Tables 1 and 2, respectively.

## CHEMICAL COMPOSITION

The chemical composition of nisnite was determined using a JEOL 733 electron microprobe, using an accelerating voltage of 20 kV, a beam current of 20 nA and a focused beam ( $\sim 2\ \mu\text{m}$ ). We used the following standards: SnL $\alpha$ : cassiterite, NiK $\alpha$ : pentlandite. The following elements were sought but not detected: S, Al, Ti, Cr, Mn, Fe, Co, Cu, Zn, As, Ag, Sb and Pb. Analytical results for two grains of nisnite are presented

TABLE 1. REFLECTANCE DATA FOR NISNITE, MEASURED IN AIR

$\lambda$ nm	R avg %	$\lambda$ nm	R avg %
400	39.0	560	50.4
420	40.2	580	52.3
440	41.4	<b>589</b>	<b>53.2</b>
460	42.6	600	54.4
<b>470</b>	<b>43.2</b>	620	56.3
480	43.9	640	58.1
500	45.3	<b>650</b>	<b>59.0</b>
520	46.8	660	59.8
540	48.5	680	61.4
<b>546</b>	<b>49.1</b>	700	63.0

The standard wavelengths (COM) are shown in bold.

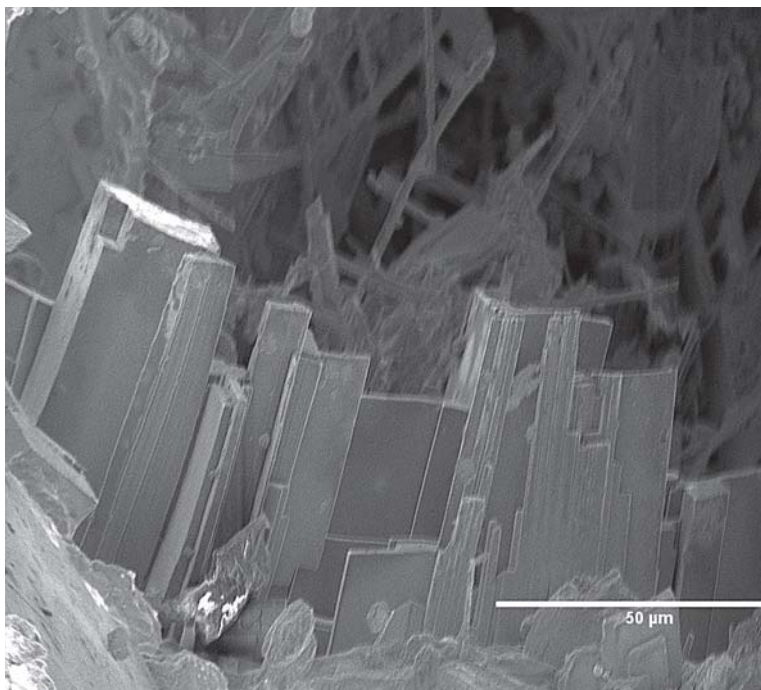


FIG. 1. Nisnite: SEM image of a group of nisnite crystals showing the different habits, from platy to elongate and blocky.

TABLE 2. COLOR VALUES FOR NISNITE

	C illuminant	A illuminant
x	0.335	0.47
y	0.334	0.41
Y %	50.3	51.7
$\lambda d$ nm	582	591
Pe %	11.4	16.6

TABLE 3. THE COMPOSITION OF NISNITE

	CMN (n = 5)	Std. Dev.	NHM (n = 3)	Std. Dev.
Ni wt. %	57.88	0.227	59.24	0.150
Sn	40.17	0.415	41.00	0.063
Total	98.05		100.24	
Ni <i>apfu</i>	2.98		2.98	
Sn	1.02		1.02	
Total	4.00		4.00	

The formula is calculated on the basis of 4 atoms per formula unit (*apfu*).  
CMN: Canadian Museum of Nature; NHM: Natural History Museum.

in Table 3. The slightly low results for the grain labeled CMN are the result of measurements made on an unpolished surface. The ideal formula for nisnite requires 59.73 wt.% Ni and 40.27 wt.% Sn.

An intensive search for possible substituting elements showed nisnite to have no chemical variability and to be essentially pure  $\text{Ni}_3\text{Sn}$ . The chemical analyses done on nisnite helped distinguish the specimen from the mineral auricupride ( $\text{Cu}_3\text{Au}$ ), which has a similar X-ray diffraction pattern and was initially considered to be a potential match.

#### X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

The X-ray powder-diffraction pattern was collected with a Bruker AXS D8 Discover microdiffractometer equipped with a 2D Hi-Star area detector operated with a GADDS system,  $\text{CuK}\alpha_1$  radiation, at 40 kV and 40 mA and a sample-to-detector distance of 12 cm. The instrument was calibrated according to a statistical procedure (Rowe 2009). A cell refinement from measured powder-diffraction data was done by indexing the diffraction maxima by comparison with the calculated powder-pattern of synthetic  $\text{Ni}_3\text{Sn}$  (ICSD #105353). The X-ray-diffraction data for both nisnite and its synthetic analog are presented in Table 4.

The single crystal of nisnite used for structure determination is a cube measuring 80  $\mu\text{m}$  on a side. Intensity data for this small crystal were found to be quite strong owing to the high scattering power. Intensity data were collected on a fully automated Bruker *P4* four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated  $\text{MoK}\alpha$  radiation and a 4K APEX CCD detector mounted at 6 cm distance from the crystal. Integrated intensities were collected up to  $2\theta = 60^\circ$ ,

using 30 s frame counts and a frame width of  $0.2^\circ$ . Data pertinent to the intensity-data collection are given in Table 5. The unit-cell parameters for the single crystal were refined using 744 indexed reflections.

Reduction of the intensity data, structure determination and structure refinement were done with the SHELXTL (Sheldrick 1990) package of computer programs. Data reduction included corrections for background, scaling and Lorentz-polarization factors. An empirical absorption correction (SADABS, Sheldrick 1998) was applied. The structure refined to an amazing value of  $R$ , 0.008. The merging  $R_{\text{int}}$  for the dataset (731 reflections) decreased from 0.126 before

TABLE 4. NISNITE: X-RAY POWDER-DIFFRACTION DATA

<i>l</i> obs	<i>d</i> obs	<i>l</i> calc*	<i>d</i> calc**	<i>d</i> synth*	<i>h k l</i>
27	3.728	19	3.735	3.738	1 0 0
22	2.639	14	2.641	2.643	1 1 0
100	2.155	100	2.156	2.158	1 1 1
45	1.8667	44	1.8674	1.8690	2 0 0
10	1.6706	6	1.6703	1.6717	2 1 0
6	1.5245	4	1.5248	1.5260	2 1 1
25	1.3202	19	1.3205	1.3216	2 2 0
3	1.2457	3	1.2450	1.2460	3 0 0
2	1.1811	2	1.1811	1.1821	3 1 0
22	1.1266	18	1.1261	1.1271	3 1 1

\* calculated with ATOMS V6.0 using atom coordinates of synthetic  $\text{Ni}_3\text{Sn}$  (Cannon 1984) from ICSD #105353.

\*\* calculated from XRPD cell refinement with  $a = 3.7349(6)$  Å,  $V = 52.10(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $\text{CuK}\alpha$  radiation. Values of  $d$  are expressed in Å.

TABLE 5. NISNITE: DATA COLLECTION AND STRUCTURE REFINEMENT INFORMATION

Space group (no. 221)	$P4/m\bar{3}2/m$
Unit-cell parameter $a$ (Å)	3.7344(7)
Unit-cell volume $V$ (Å <sup>3</sup> )	52.08(3)
$\mu$ (mm <sup>-1</sup> )	33
Measured reflections	416
Unique reflections [all > $4\sigma(F)$ ]	30
Ideal unit-cell contents	1[Ni <sub>3</sub> Sn]
$R$ (int $F^2$ )	0.020
$R$ (merging [ $I$ ])	0.014
Goodness of fit on $F^2$	1.43
$R_1$ index for observed data	0.008
$wR_2$ index for observed data	0.019

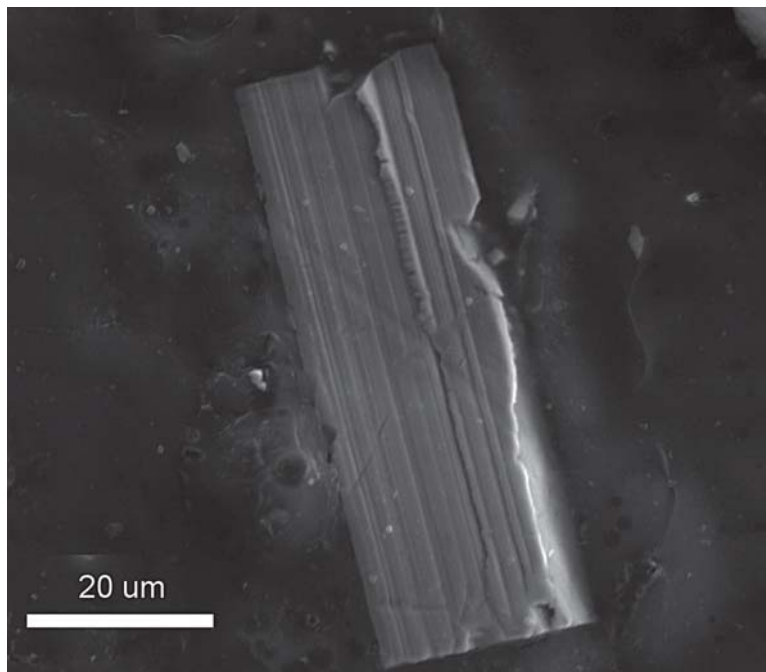


FIG. 2. Nisnite: SEM image of unpolished crystal of nisnite showing striations along  $\{100\}$ .

the absorption correction to 0.023 after the absorption correction, which is a significant improvement even on such a small crystal.

In the final least-squares refinement, all atom positions were refined with anisotropic displacement-factors. The weighting scheme is inversely proportional to  $\sigma^2(F)$ . The addition of an isotropic extinction-correction did not improve the refinement. In the last stage of refinement, there were electron residuals of +0.34 and -0.61 e<sup>-</sup>/Å<sup>3</sup>. The final positional coordinates and anisotropic displacement-parameters are given in Table 6. Tables listing the observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, on the MAC web site [document Nisnite CM49\_651].

#### Description of the structure

There are three synthetic Ni<sub>3</sub>Sn phases: low-temperature  $\alpha$ -Ni<sub>3</sub>Sn,  $P6_3/mmc$ , is a **hcp** structure (Lyubimtsev *et al.* 2002), high-temperature  $\beta$ -Ni<sub>3</sub>Sn, above 917 °C,  $F4/m\bar{3}2/m$ , is a **fcc** structure (Schubert *et al.* 1956), and high-pressure and high-temperature Ni<sub>3</sub>Sn,  $P4/m\bar{3}2/m$ , a **ccp** structure. Cannon (1984) synthesized the phase at 900–1200°C and 65 kbar. Nisnite corresponds to a **ccp** structure (Fig. 3). In such a structure, each atom is 12-coordinated. The larger atom, Sn (radius 1.41 Å), is surrounded by 12 Ni atoms, and each Ni (radius 1.15 Å) is surrounded by eight atoms of Ni and four atoms of Sn. All bond lengths are 2.6406(5) Å, which is slightly longer than the sum of covalent radii (2.56 Å).

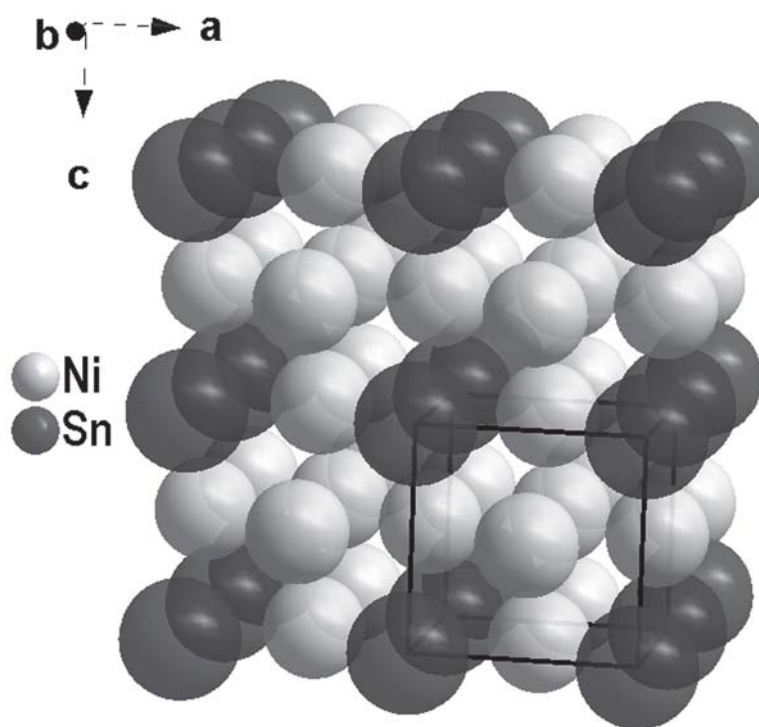


FIG. 3. The **ccp** crystal structure of nisnite with an inclined projection.

TABLE 6. NISNITE: COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS

Site	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
Ni	0	½	½	0.0098(3)	0.0089(2)	0.0089(2)	0	0	0	0.092(2)
Sn	0	0	0	0.0082(2)	0.0082(2)	0.0082(2)	0	0	0	0.008(2)



## DISCUSSION

Heazlewoodite occurs as late-stage, hydrothermal mineral in cavities on green grossular crystals intergrown with diopside. The crystallization of nisnite occurred fairly late in the paragenesis.

Comparative volumes (*i.e.* for  $Z = 1$ ) for the three synthetic  $\text{Ni}_3\text{Sn}$  polytypes are: low-temperature, ambient pressure **hcp**  $51.58 \text{ \AA}^3$ , high-temperature, ambient pressure ( $950^\circ\text{C}$ ) **fcc**  $53.46 \text{ \AA}^3$ , and high-temperature and high-pressure **ccp**  $52.23 \text{ \AA}^3$ . The expansion of the cell volume (a 3.6 % increase) at an elevated temperature is expected. Cannon (1984) expressed concern that his high-pressure phase has a larger volume than the hexagonal **hcp**, low-pressure form, and he tried at length to rationalize this observation. It is true that thermodynamically, this is “unreasonable” as he stated, but he only considered the pressure effect and mentioned nothing about the fact that his phase was produced at a high temperature. It is in fact perfectly reasonable that the higher temperature reverses, or at least modifies, the effect of the pressure, and the resulting cell volume is intermediate between the high- and low-temperature phases grown at ambient pressure conditions. Nisnite has a cell volume of  $52.08 \text{ \AA}^3$ , close to, but slightly smaller than that of the synthetic analogue. The rodingites at Jeffrey mine have been suggested to have formed at intermediate conditions of pressure and temperature [2.5–4.5 kbar,  $290\text{--}400^\circ\text{C}$ : Normand & Williams-Jones 2007]. The presence of nisnite in this rock type infers that the field of stability of the **ccp** polytype extends at least to the intermediate conditions stated and not only to high P–T regimes. The P–T conditions may have been even lower, as nisnite is the last mineral to precipitate. The lack of extensive experimental data on these polymorphs and the role played by hydrothermal fluids within the rodingite prevent us from elaborating further on the stability fields of  $\text{Ni}_3\text{Sn}$ .

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## REFERENCES

- CANNON, J. F. (1984): Effect of high pressure on the structures of  $\text{AB}_3$ -type layered compounds. (ICSD #105353). In *High Pressure Science and Technology III* (C. Homan, R.K. MacCrone & E. Whalley, eds.). *Mater. Res. Soc., Symp.* **22**, 113–116.
- GRICE, J.D. & GASPARRINI, E. (1981): Spertiniite,  $\text{Cu}(\text{OH})_2$ , a new mineral from the Jeffrey mine, Quebec. *Can. Mineral.* **19**, 337–340.
- GRICE, J.D. & ROBINSON, G.W. (1984): Jeffreyite,  $(\text{Ca}, \text{Ma})_2(\text{Be}, \text{Al})\text{Si}_2(\text{O}, \text{OH})_7$ , a new mineral species and its relation to the melilite group. *Can. Mineral.* **22**, 443–446.
- GRICE, J.D. & WILLIAMS, R. (1979): Famous mineral localities: the Jeffrey mine, Asbestos, Québec. *Mineral. Rec.* **10**, 69–80.
- HORVÁTH, L. & SPERTINI, F. (2008): Die Jeffrey Mine in Asbestos, Québec, Kanada. I. *Mineralien Welt* **19**(5), 42–67.
- HORVÁTH, L. & SPERTINI, F. (2009): Die Jeffrey Mine in Asbestos, Québec, Kanada. II. *Mineralien Welt* **20**(1), 64–83.
- LYUBIMTSEV, A., BARANOV, A.I., FISCHER, A., KLOO, L. & POPOV, B.A. (2002): The structure and bonding of  $\text{Ni}_3\text{Sn}$ . *J. Alloy Comp.* **340**, 167–172.
- NORMAND, C. & WILLIAMS-JONES, A.E. (2007): Physicochemical conditions and timing of rodingite formation: evidence from rodingite-hosted fluid inclusions in the JM Asbestos mine, Asbestos, Québec. *Geochem. Trans.* **8**:11.
- ROWE, R. (2009): New statistical calibration approach for Bruker AXS D8 Discover microdiffractometer with Hi-Star detector using GADDS software. *ICDD Powder Diffract. J.* **24**, 263–271.
- SCHUBERT, K., BURKHARDT, W., ESSLINGER, P., GUENZEL, E., MEISSNER, H.G., SCHUETT, W., WEGST, J. & WILKENS, M. (1956): Einige strukturelle Ergebnisse an metallischen Phasen. *Naturwiss.* **43**, 248–249.
- SHELDRIK, G.M. (1990): *SHELXTL, a Crystallographic Computing Package, revision 4.1*. Siemens Analytical Instruments Inc., Madison, Wisconsin.
- SHELDRIK, G.M. (1998): *SADABS User's Guide*. University of Göttingen, Göttingen, Germany.
- STANLEY, C.J., CRIDDLE, A.J., FÖRSTER, H.-J. & ROBERTS, A.C. (2002): Tischendorfite,  $\text{Pd}_8\text{Hg}_3\text{Se}_9$ , a new mineral species from Tilkerode, Harz Mountains, Germany. *Can. Mineral.* **40**, 739–745.

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