

Nestolaite, $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$, a new mineral from the Little Eva mine, Grand County, Utah, USA

A. V. KASATKIN^{1,*}, J. PLÁŠIL², J. MARTY³, A. A. AGAKHANOV^{4,5}, D. I. BELAKOVSKIY⁵ AND I. S. LYKOVA⁵

¹ V/O "Almazjuvelirexport", Ostozhenka Street, 22, block 1, 119034, Moscow, Russia

² Institute of Physics ASCR, v.v.i., Na Slovance 2, CZ–182 21, Prague 8, Czech Republic

³ 5199 East Silver Oak Road, Salt Lake City, Utah, UT 84108, USA

⁴ Faculty of Geology, St Petersburg State University, Universitetskaya Nab. 7/9, 199034 St Petersburg, Russia

⁵ Fersman Mineralogical Museum of the Russian Academy of Sciences, Leninsky Prospekt 18-2, 119071 Moscow, Russia

[Received 4 December 2013; Accepted 21 January 2014; Associate Editor: S. Krivovichev]

ABSTRACT

Nestolaite (IMA 2013-074), $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$, is a new mineral species from the Little Eva mine, Grand County, Utah, USA. It is named in honour of the prominent Italian mineralogist and crystallographer Fabrizio Nestola. The new mineral was found on sandstone matrix as rounded aggregates up to 2 mm across and up to 0.05 mm thick consisting of tightly intergrown oblique-angled, flattened to acicular crystals up to 30 μm long and up to 7 μm (very rarely up to 15 μm) thick. Nestolaite associates with cobaltomenite, gypsum, metarossite, orschallite and rossite. The new mineral is light violet and transparent with a white streak and vitreous lustre. The Mohs hardness is 2½. Nestolaite is brittle, has uneven fracture and perfect cleavage on {100}. The measured and calculated densities are $D_{\text{meas.}} = 3.18(2) \text{ g/cm}^3$ and $D_{\text{calc.}} = 3.163 \text{ g/cm}^3$. Optically, nestolaite is biaxial positive. The refractive indices are $\alpha = 1.642(3)$, $\beta = 1.656(3)$, $\gamma = 1.722(6)$. The measured $2V$ is $55(5)^\circ$ and the calculated $2V$ is 51° . In transmitted light nestolaite is colourless. It does not show pleochroism but has strong pseudo-absorption caused by high birefringence. The chemical composition of nestolaite (wt.%, electron-microprobe data) is: CaO 28.97, SeO₂ 61.14, H₂O (calc.) 9.75, total 99.86. The empirical formula calculated on the basis of 4 O a.p.f.u. (atoms per formula unit) is $\text{Ca}_{0.96}\text{Se}_{1.02}\text{O}_3 \cdot \text{H}_2\text{O}$. The Raman spectrum is dominated by the Se–O stretching and O–Se–O bending vibrations of the pyramidal SeO₃ groups and O–H stretching modes of the H₂O molecules. The mineral is monoclinic, space group $P2_1/c$, with $a = 7.6502(9)$, $b = 6.7473(10)$, $c = 7.9358(13) \text{ Å}$, $\beta = 108.542(12)^\circ$, $V = 388.37(10) \text{ Å}^3$ and $Z = 4$. The eight strongest powder X-ray diffraction lines are [d_{obs} in Å (hkl) (I_{rel}): 7.277 (100)(100), 4.949 (110)(37), 3.767 (002)(29), 3.630 (200)(58), 3.371 (020)(24), 3.163 ($\bar{2}02$)(74), 2.9783 ($\bar{1}21$)(74) and 2.7231 (112)(31). The crystal structure of nestolaite was determined by means of the Rietveld refinement from the powder data to $R_{\text{wp}} = 0.019$. Nestolaite possesses a layered structure consisting of $\text{Ca}\Phi\text{--SeO}_3$ sheets, composed of edge-sharing polyhedra. Adjacent sheets are held by H bonds emanating from the single (H₂O) group within the sheets. The nestolaite structure is topologically unique.

KEYWORDS: nestolaite, new mineral, chemistry, Raman spectroscopy, powder X-ray diffraction, crystal structure, Little Eva mine, Utah.

Introduction

NATURAL selenites, i.e. minerals having a $[\text{SeO}_3]^{2-}$ group as the defining-species anion, are relatively rare. To date, 27 such minerals are

* E-mail: anatoly.kasatkin@gmail.com
DOI: 10.1180/minmag.2014.078.3.02

known and, amongst them, only five are molecular water-bearing selenites without additional anions, fitting Subdivision 04.JH in the Strunz classification: ahlfeldite $(\text{Ni,Co})\text{SeO}_3 \cdot 2\text{H}_2\text{O}$, chalcomenite $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$, clinochalcomenite $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$, cobaltomenite $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ and mandarinioite $\text{Fe}_2^{3+}\text{Se}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$. In this work a new mineral of this mineral subgroup is reported – nestolaite, ideally $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$, which was found underground at the Little Eva mine, Yellow Cat district, Grand County, Utah, USA.

The new mineral honours the prominent Italian mineralogist and crystallographer Fabrizio Nestola (born 1972), Associate Professor of Mineralogy at the Department of Geosciences, University of Padua, Italy. Fabrizio Nestola is particularly known for his contribution to the mineralogy of diamonds and the study of crystal structures of minerals under high-pressure conditions. In 2012 he obtained the largest ever grant from the European Research Council for the study of the inclusions in diamonds and for the research and description of new minerals. To date, Fabrizio Nestola has been the author or co-author of more than 130 publications, including 12 descriptions of new mineral species (see, for example, Nestola *et al.* (2009a,b, 2012), two of which come from Utah – manganoblödite and cobaltoblödite (Kasatkin *et al.*, 2013).

The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2013-074). The type specimen is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia under registration number 4417/1.

Occurrence

Specimens containing nestolaite were collected underground at the Little Eva mine, Yellow Cat District, Grand County, Utah, USA ($38^\circ 50' 17''\text{N}$, $109^\circ 31' 35''\text{W}$) in 1999 by one of the authors (JM).

The Little Eva mine belongs to a group of deposits near Thompsons, Grand County, Utah which have been worked intensively for U and V during the 1940s–1970s. The ore ranged in grade from a fraction of a percent to 10% V_2O_5 and up to 0.4% U_3O_8 (Stokes, 1952). The mineralization was developed in the Salt Wash member of the Jurassic Morrison formation. The Salt Wash Member forms the lower part of the Morrison

formation and is composed dominantly of interstratified units of sandstone and claystone. The sandstone forms either a stratum composed of a single lenticular bed 30–600 cm thick or strata composed of many lenticular beds which may have a total thickness of >2.4 m. Strata between the sandstone units consist of dominantly grayish and reddish mudstones and claystones with minor sand lenses. Sandstone comprises ~58% of volume, mudstone ~41% and limestone about 1% (Newman, 1962). The ore deposits in the Salt Wash member are generally tabular masses that appear to be localized in the thicker parts of sandstone lenses. Within a mineralized layer, high-grade concentrations of U and V minerals occur in masses or pods associated commonly with carbonaceous material (Newman, 1962).

In addition to U and V as key ore elements, the Morrison formation also contains Se. Newman (1962) reports that the Se content of the sandstone of the Salt Wash member may be as large as 15 ppm, though the average concentration of Se in sandstone seems to be <1 ppm. After the mining operations in the Little Eva mine stopped in 1979, primary Se minerals exposed during the workings, such as native Se and ferroselite, underwent supergene oxidation resulting in the formation of nestolaite.

The mineral is very rare and associates with cobaltomenite, gypsum, metarossite, orschallite and rossite. Other minerals occurring in the general assemblage in the mine include andersonite, ansermetite, calciodelirioite (Kampf *et al.*, 2012), calcite, carnotite, ferroselite, huemulite, lasalite, martyite, melanovanadite, nashite

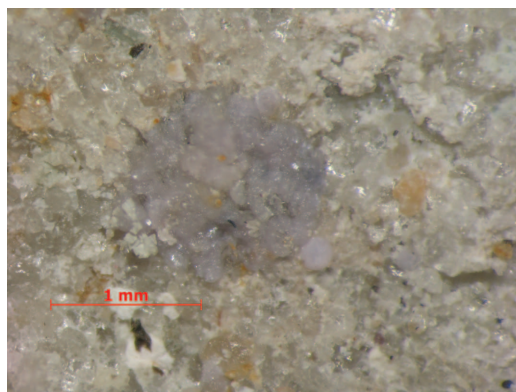


FIG. 1. Light violet, rounded aggregate of nestolaite on a sandstone matrix in association with white orschallite intimately intergrown with gypsum.

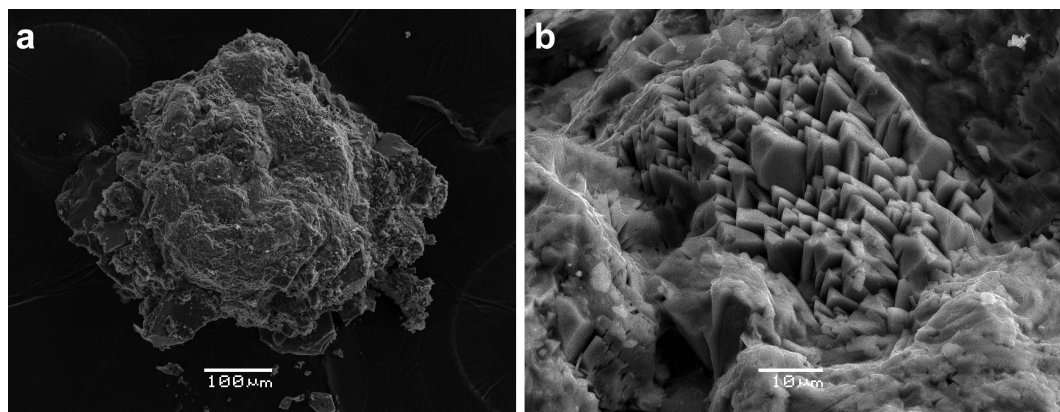


FIG. 2. Scanning electron microscopy images of nestolaite: (a) general view of a rounded aggregate, (b) fragment showing a close-up of the crystals.

(Kampf *et al.*, 2013), native Se, natrozippeite, pascoite, pyrite, schröckingerite, sherwoodite and uraninite.

Physical and optical properties

Nestolaite occurs as light violet, rounded aggregates (up to 2 mm across and up to 0.05 mm thick) on the surface of sandstone blocks (Figs 1, 2a). These aggregates consist of tightly intergrown oblique-angled, flattened to acicular crystals up to 30 μm long and up to 7 μm (very rarely up to 15 μm) thick. Some crystals are coarse, distorted, twisted, slightly divergent, or skeletal (Fig. 2b). Nestolaite is transparent, has a white streak and a vitreous lustre. It is not fluorescent in ultraviolet radiation or when exposed to cathode rays. Its Mohs hardness is

2½. Nestolaite is brittle, has an uneven fracture and perfect cleavage on {100}. The density of nestolaite measured by flotation in heavy liquids ($\text{CHBr}_3 + \text{CH}_2\text{I}_2$) is 3.18(2) g/cm^3 and the calculated density (by X-ray diffraction) is 3.163 g/cm^3 .

Optically, nestolaite is biaxial positive. The refractive indices are $\alpha = 1.642(3)$, $\beta = 1.656(3)$, $\gamma = 1.722(6)$. The measured $2V$ is $55(5)^\circ$ and the calculated $2V$ is 51° . In transmitted light nestolaite is colourless. It does not show pleochroism but has strong pseudo-absorption caused by high birefringence. In crossed nicols acicular crystals show positive elongation. Many crystals show straight extinction. The crystals oriented parallel to the optical axis plane show that the angle between the direction of the crystal elongation and Z is $4(2)^\circ$.

TABLE 1. Chemical composition (wt.%) of nestolaite.

	Mean ($n = 5$)	Range	SD
CaO	28.97	27.30–30.86	1.47
SeO ₂	61.14	59.36–62.93	1.49
H ₂ O*	9.75		
Total	99.86		
Formula calculated on the basis of 4 O a.p.f.u.			
Ca	0.96		
Se ⁴⁺	1.02		
H ₂ O	1		

* H₂O content was calculated by stoichiometry

Chemical composition and chemical properties

Preliminary chemical analyses using a CamScan 4D electron microprobe in energy-dispersive spectroscopy mode (20 kV, 3 nA and a beam diameter of 5 μm) showed the presence of Ca, Se and O in the mineral. No other elements with atomic numbers higher than 8 were observed. Further chemical analyses (5) were obtained using a JEOL Superprobe 733 scanning electron microscope equipped with an INCA wavelength-dispersive spectrometer. Operating conditions were as follows: accelerating voltage 20 kV, beam current 20 nA, beam diameter 1 μm . The following standards were used: diopside (Ca) and synthetic CdSe (Se). H_2O was not determined directly because of the scarcity of pure material. The H_2O content was calculated by stoichiometry and confirmed by the crystal-structure refinement and Raman spectroscopy. The latter also shows the absence of CO_2 in the mineral. Analytical data are given in Table 1. The empirical formula (calculated on the basis of 4 O a.p.f.u.) is

$\text{Ca}_{0.96}\text{Se}_{1.02}\text{O}_3 \cdot \text{H}_2\text{O}$. The ideal formula is $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$, which requires CaO 30.25, SeO_2 60.00 and H_2O 9.75, total 100.00 wt%.

The values of the Gladstone-Dale compatibility index [$1 - (\text{K}_\text{p}/\text{K}_\text{c})$] (Mandarino, 1981) for nestolaite are: 0.003, using the calculated density; and 0.008, using the measured density. Both values are rated as superior.

Nestolaite is insoluble in water but dissolves easily in both diluted and concentrated HNO_3 .

Raman spectroscopy

The Raman spectrum of nestolaite (Fig. 3) was recorded on a Thermo Scientific DXR Raman Microscope interfaced with an Olympus microscope (objective $\times 50$) in the 50–6400 cm^{-1} spectral region with $\sim 5 \text{ cm}^{-1}$ spectral resolution. The power of the frequency-stabilized single mode diode laser (532 nm) impinging on the sample was set to 5 mW (10 s exposure, accumulation of 64 scans). The spectrometer was calibrated by a software-controlled (Omnic 8) calibration procedure using multiple Ne emission lines (wavelength calibration),

TABLE 2. X-ray powder diffraction data for nestolaite.

I_{obs}	d_{obs}	d_{calc}	I_{calc}	h	k	l	I_{obs}	d_{obs}	d_{calc}	I_{calc}	h	k	l
100	7.277	7.259	89	1	0	0	1	2.0326	2.0335	11	$\bar{3}$	2	1
22	5.033	5.025	33	0	1	1	3	2.0154	2.0162	5	1	3	1
37	4.949	4.941	65	1	1	0	2	1.9445	1.9450	2	$\bar{1}$	3	2
6	3.884	3.880	2	$\bar{1}$	0	2	1	1.9301	1.9302	4	$\bar{2}$	3	1
3	3.780	3.777	3	1	1	1	1	1.9104	1.9111	1	2	3	0
29	3.767	3.767	40	0	0	2	*15	1.9013	1.9005	22	$\bar{1}$	1	4
58	3.630	3.630	55	2	0	0	1	1.8828	1.8831	3	$\bar{4}$	0	2
24	3.371	3.372	4	0	2	0	3	1.8356	1.8344	9	$\bar{4}$	1	1
*	3.347	3.363	25	$\bar{1}$	1	2	8	1.7968	1.7950	2	3	0	2
13	3.292	3.288	4	0	1	2	13	1.7867	1.7854	13	$\bar{3}$	2	3
74	3.163	3.157	76	$\bar{2}$	0	2	1	1.7294	1.7346	3	3	1	2
74	2.9783	2.9743	100	$\bar{1}$	2	1	1	1.7134	1.7126	1	$\bar{1}$	3	3
2	2.8606	2.8591	2	$\bar{2}$	1	2	2	1.6878	1.6859	2	0	4	0
31	2.7231	2.7269	46	1	1	2	8	1.6737	1.6748	8	0	3	3
20	2.6839	2.6866	34	2	1	1	2	1.6607	1.6590	2	$\bar{2}$	3	3
9	2.5125	2.5123	12	0	2	2	2	1.6455	1.6469	47	3	3	0
4	2.3519	2.3532	7	0	1	3	2	1.5808	1.5845	1	3	2	2
2	2.3109	2.3045	2	$\bar{2}$	2	2	5	1.4887	1.4878	4	$\bar{5}$	1	2
21	2.2840	2.2775	18	3	1	0	1	1.4638	1.4686	<1	$\bar{2}$	3	4
1	2.2119	2.2113	1	2	2	1	1	1.4195	1.4193	4	5	1	0
1	2.1619	2.1541	2	0	3	1	3	1.2887	1.2856	3	1	2	5
2	2.0806	2.0807	3	$\bar{1}$	2	3	1	1.2719	1.2701	1	$\bar{3}$	1	6

3–70°2 θ , $\text{CuK}\alpha$ radiation, 0.01° per step, counting time 0.5 s per step (accumulations of 20 scans).

* due to quartz present in the specimen. d_{hkl} in Å.

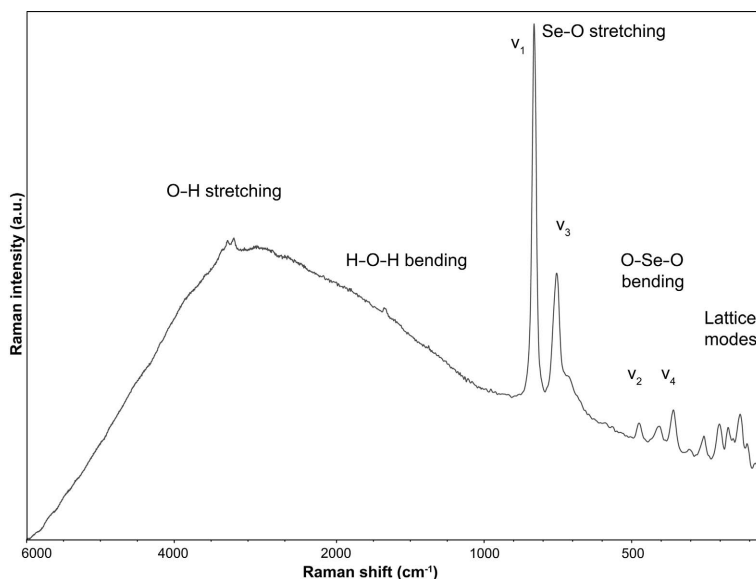


FIG. 3. Raman spectrum of nestolaite with the important vibration regions highlighted.

multiple polystyrene Raman bands (laser frequency calibration) and standardized white light sources (intensity calibration). Spectral manipulation, such as background correction and band-component

analysis, was performed with *Omnic 8* software. The interpretation of the spectrum follows those by Peercy (1970), Torrie (1972) and Mička *et al.* (1994, 1996).

TABLE 3. Crystal data and statistics for the Rietveld refinement of the structure of nestolaite.

Structural formula	Ca(SeO ₃)(H ₂ O)
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6502(9), 6.7473(10), 7.9358(13)
β (°)	108.542(12)
<i>V</i> (Å ³)	388.37(10)
<i>Z</i>	4
<i>D</i> _{calc.} (g/cm ³)	3.129
Temperature	298 K
Source; wavelength	X-ray tube; CuKα _{1,2} , (1.54056+1.54443) Å
Specimen	Powder in 0.3 mm glass capillary
Collection mode	θ–2θ scans; specimen rotation along φ axis
θ range for data collection (°), step size (°)	3 to 90, 0.01
Absorption correction, coefficient (mm ^{−1})	Cylindrical, 23.71
Rietveld refinement by <i>JANA2006</i> on <i>F</i> ²	
Profile function; asymmetry	Pseudovoigt; by divergence (Finger <i>et al.</i> , 1994)
Data/obs/restraints/parameters	6691/313/4/45
<i>R</i> _p , <i>R</i> _{wp}	0.0134, 0.0191
<i>R</i> _F , <i>R</i> _{Bragg}	0.0488, 0.0799
GOF, χ ²	1.61, 2.59
Δρ _{min} , Δρ _{max} (e/Å ³)	−0.85, 0.62
Weighting scheme	σ, based on measured s.u.'s

The spectrum is dominated by the Se–O stretching vibration of SeO_3 groups. Ideally, they are trigonal pyramidal (C_{3v}) symmetry, showing four fundamental vibration modes, of the A_1 (ν_1 and ν_2) and E (ν_3 and ν_4) symmetries. In the crystalline state the lowering of the real symmetry (site and factor group) leads to the splitting of the degeneracy of the E modes and thus leads to the split of the vibration bands. The vibration band with the highest intensity at $\sim 825 \text{ cm}^{-1}$ was attributed to the ν_1 Se–O stretching vibration. Such a large value for the stretching frequency matches the frequency observed for the SeO_3^{2-} ‘free’ anion in the solution (Torrie, 1972). The less intensive band at $\sim 750 \text{ cm}^{-1}$ was assigned to the split doubly-degenerated ν_3 Se–O stretching vibration. The bending O–Se–O modes occur at $\sim 470 \text{ cm}^{-1}$ (ν_2) and $410\text{--}370 \text{ cm}^{-1}$ (split ν_4), followed by the external, lattice modes in the lowest region.

Since nestolaite is a monohydrate, the O–H stretching frequencies are expected to occur in the spectrum. Raman spectrum shows their presence in the very characteristic spectral region between 3400 and 3200 cm^{-1} . According to the empirical relation given by Libowitzky (1999), the corresponding separation O...O distances of the H bonds are expected to be at around $2.7\text{--}2.8 \text{ \AA}$, which is a similar range to the values for O...O interatomic distances obtained from the Rietveld refinement (see Table 5). The H–O–H (ν_2) bending vibration of the H_2O molecules occurs at 1680 cm^{-1} .

X-ray crystallography and structure determination

Due to the small size of nestolaite crystals and unsuccessful attempts to obtain single-crystal data, a Rietveld refinement of the structure from in-house powder X-ray diffraction data was undertaken in order to prove the structural equality of the new mineral and the synthetic $\text{Ca}(\text{SeO}_3)(\text{H}_2\text{O})$ (Valkonen *et al.*, 1985).

Powder data were collected on a PANalytical Empyrean powder diffractometer equipped with a Cu X-ray tube and PIXcel^{3D} solid-state detector. The powder data were measured in capillaries (Debye-Scherrer focusing geometry, provided by a Göbel curved primary mirror), in the range $3\text{--}90^\circ 2\theta$ with step size $0.013^\circ 2\theta$ and a total counting time of 48 h by accumulation of repeated scans. Prior to the measurement, the diffractometer was calibrated against the LaB₆ standard

TABLE 4. Atom coordinates, displacement parameters ($\text{\AA}^2$) and bond-valence sums for the structure of nestolaite.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}	BV
Ca	0.098(5)	0.145(5)	0.354(4)	0.096(13)*							2.25(14)
Se	0.248(3)	0.6559(19)	0.492(3)	0.067(7)	0.074(11)	0.055(9)	0.095(11)	0.066(12)	0.060(9)	0.104(8)	4.1(2)
O1	0.264(6)	0.574(8)	0.699(3)	0.013(10)*							1.62(15)
O2	0.203(8)	0.437(4)	0.379(5)	0.013(10)*							2.10(15)
O3	0.063(4)	0.806(6)	0.460(6)	0.013(10)*							2.29(18)
O4	0.349(6)	0.103(10)	0.630(6)	0.03(2)*							0.29(4)

* refined with isotropic displacement parameter.

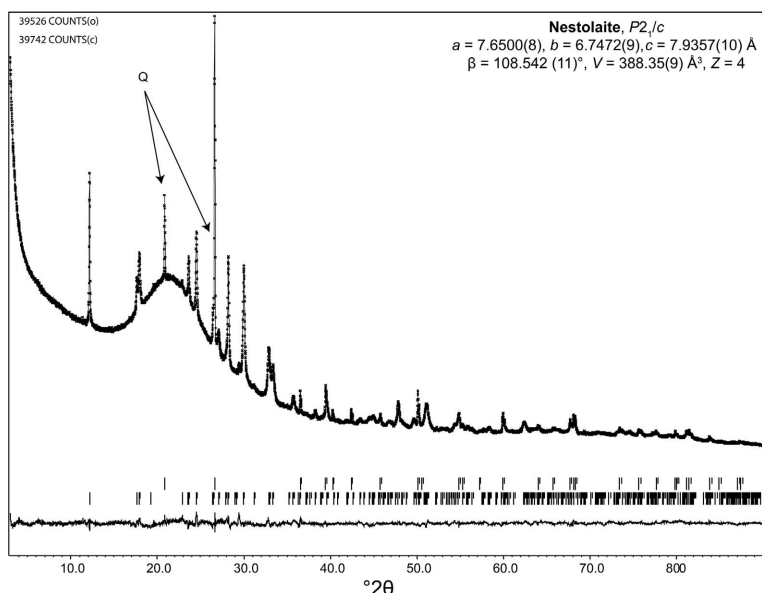


FIG. 4. The result of the Rietveld refinement, showing observed data (points), calculated profile (solid black line) and difference profile (below the data). The vertical dashes correspond to the Bragg peaks. Q = quartz admixture.

with the same settings. The unit-cell refinement was performed with the software *Celref* (LMPG suite of programs). The monoclinic unit-cell parameters refined from the powder data (Table 2) are $a = 7.655(8)$, $b = 6.750(7)$, $c = 7.944(8)$ Å, $\beta = 108.35(2)^\circ$ with $V = 389.5(7)$ Å³.

The Rietveld refinement was performed using the *JANA2006* program (Petříček *et al.*, 2006, 2014) with the structure model given for the synthetic phase by Valkonen *et al.* (1985) and the following variables: background, shift, *FWHM* function, unit-cell parameters, the asymmetry by divergence, anisotropic broadening, atomic coordinates and their displacement parameters. The refined values were corrected for correlations after Bérar and Lelann (1991). The final refinement plot is provided in Fig. 4. The unit-cell parameters obtained from the Rietveld refinement are, for the monoclinic space group $P2_1/c$, $a = 7.6502(9)$, $b = 6.7473(10)$, $c = 7.9358(13)$ Å, $\beta = 108.542(12)^\circ$, $V = 388.37(10)$ Å³ and $Z = 4$. The refinement converged with the final indices of agreement: $R_p = 0.0134$, $R_{wp} = 0.0191$, $R_F = 0.0488$, $R_{Bragg} = 0.0799$ and a GOF = 1.61. Other details for the refinement are given in Table 3. The atom positions and displacement parameters are given in Table 4; selected interatomic distances are given in Table 5. All atoms,

except Se, were refined with isotropic displacement parameters. The O atoms within the SeO_3^{2-} pyramidal group were refined with their displacement parameters constrained softly to the same U_{iso} value; a soft constraint was also applied to the Ca–O2 distance.

TABLE 5. Interatomic distances for the structure of nestolaite (Å).

Ca–O1 ⁱ	2.51(6)	O1–O2	2.60(5)
Ca–O2	2.11(5)	O1–O3	2.56(5)
Ca–O2 ⁱⁱ	2.83(5)	O1–O4 ^v	2.84(6)
Ca–O3 ⁱⁱⁱ	2.48(5)	O2–O3	2.86(6)
Ca–O3 ⁱⁱ	2.64(5)	O2–O3 ⁱⁱ	2.95(5)
Ca–O3 ^{iv}	2.23(6)	O2–O4 ⁱ	3.00(7)
Ca–O4	2.43(5)	O3–O3 ^{vii}	2.93(6)
<Ca–O>	2.46	O3–O4 ^{vi}	2.94(6)
Se–O1	1.70(4)		
Se–O2	1.71(3)		
Se–O3	1.69(4)		
<S–O>	1.70		

Symmetry codes: (i) $x, -y+1/2, z-1/2$; (ii) $-x, y-1/2, -z+1/2$; (iii) $x, y-1, z$; (iv) $-x, -y+1, -z+1$; (v) $-x+1, y+1/2, -z+3/2$; (vi) $x, y+1, z$.

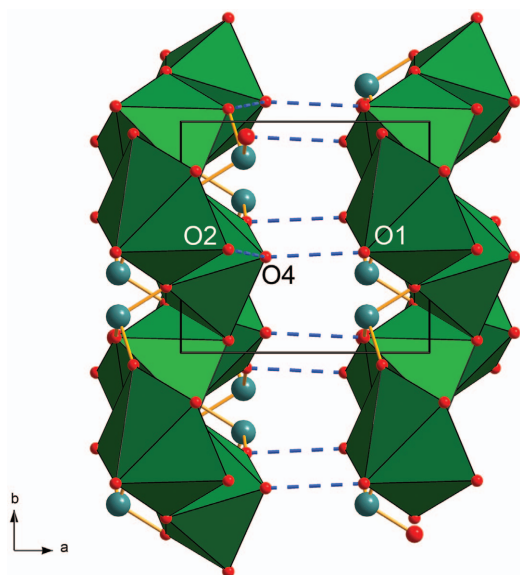


FIG. 5. The crystal structure of nestolaite viewed along *c*. The sheets of Ca-polyhedra (green) and SeO_3 groups (pyramidal) are linked by H bonds (dashed, in blue). Unit-cell edges are outlined.

Description of the crystal structure

The asymmetric unit of the nestolaite crystal structure (Table 4) contains one Ca site, occupied by the Ca^{2+} cation, one Se site, occupied by the Se^{4+} cation and four O sites. One of these O sites is occupied, according to the bond-valence analysis (Table 4), by the (H_2O) group. Nestolaite possesses a layered structure, which is composed of sheets of $\text{CaO-H}_2\text{O}$ edge-sharing polyhedra, also interconnected by the $(\text{SeO}_3)^{2-}$ groups (Figs 5, 6). The Ca^{2+} cation is [7]-coordinated within the sheet with the mean bond length $\text{Ca}-\Phi$ (where Φ is a miscellaneous ligand) of 2.46 Å (Table 5, Fig. 6). The Se^{4+} is stacked up towards the interlayer, which suggests that the lone electron pair is active. The adjacent structure sheets are linked by the H bonds (Fig. 5) emanating from the (H_2O) group (O4 atom) with one H bond accepted by the O1 atom (the bond valence sum indicates considerable undersaturation, see Table 5) with the corresponding O...O separation distances of ~ 2.8 Å, which is a reasonable value for the H-bond length. The second H bond is probably accepted by the O2 atom, with the O...O separation distance of ~ 2.6 Å.

The mechanism by which the Ca-polyhedra share edges to form six-membered rings, is very

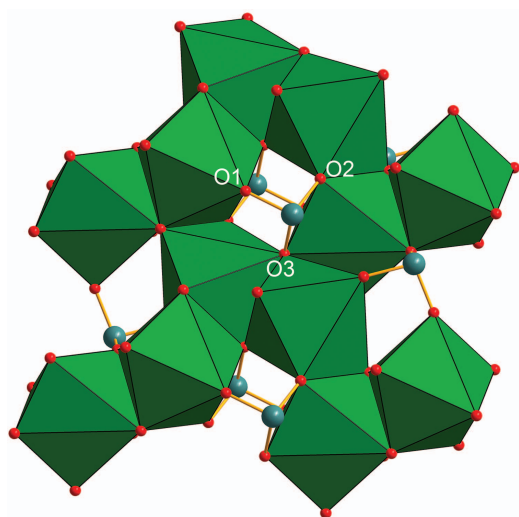


FIG. 6. A fragment of the sheet found in nestolaite. The polyhedra of [7]-coordinate Ca^{2+} ions share edges to form six-membered rings, additionally interconnected by the pyramidal SeO_3 groups.

similar to the structural order, which is also the case for the mineral hannebachite (Hentschel *et al.*, 1985; Schröpfer, 1973) that is, however, based on a different topology, representing a framework structure instead of sheets.

Acknowledgements

The authors are grateful to Ladislav Lapčák (Institute of Chemical Technology, Prague) and Igor V. Pekov (Moscow State University) for their help with Raman spectroscopic analysis and scanning electron microscopy images, respectively. The authors thank Vladislav V. Gurzhiy and an anonymous reviewer for their constructive comments that helped to improve the manuscript. This research was financially supported by the post-doctoral project 13-31276P of the Grant Agency of the Czech Republic to JP.

References

- Bérar, J.-F. and Lelann, P. (1991) Esds and estimated probable errors obtained in Rietveld refinements with local correlations. *Journal of Applied Crystallography*, **24**, 1–5.
- Finger, L.W., Cox, D.E. and Jephcoat, A.P. (1994) A correction for powder diffraction peak asymmetry due to axial divergence. *Journal of Applied Crystallography*, **27**, 892–900.

- Hentschel, G., Tillmanns, E. and Hofmeister, W. (1985) Hannebachite, natural calciumsulfite hemihydrate, $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. *Neues Jahrbuch für Mineralogie, Monatshefte*, **1985**, 241–250.
- Kampf, A.R., Marty, J., Nash, B.P., Plášil, J., Kasatkin, A.V. and Škoda, R. (2012) Calciodelrioite, $\text{Ca}(\text{VO}_3)_2(\text{H}_2\text{O})_4$, the Ca analogue of delrioite, $\text{Sr}(\text{VO}_3)_2(\text{H}_2\text{O})_4$. *Mineralogical Magazine*, **76**, 2803–2817.
- Kampf, A.R., Hughes, J.M., Marty, J. and Brown, F. H. (2013) Nashite, $\text{Na}_3\text{Ca}_2[(\text{V}^{4+}\text{V}_9^{5+})\text{O}_{28}]\cdot 24\text{H}_2\text{O}$, a new mineral species from the Yellow Cat Mining District, Utah and the Slick Rock Mining District, Colorado: crystal structure and descriptive mineralogy. *The Canadian Mineralogist*, **51**, 27–37.
- Kasatkin, A.V., Nestola, F., Plášil, J., Marty, J., Belakovskiy, D.I., Agakhanov, A.A., Mills, S.J., Pedron, D., Lanza, A., Favaro, M., Bianchin, S., Lykova, I.S., Goliáš, V. and Birch, W.D. (2013) Manganoblödite, $\text{Na}_2\text{Mn}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$ and cobaltoblödite, $\text{Na}_2\text{Co}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$: two new members of the blödite group from the Blue Lizard mine, San Juan County, Utah, USA. *Mineralogical Magazine*, **77**, 367–383.
- Libowitzky, E. (1999) Correlation of O–H stretching frequencies and O–H...O hydrogen bond lengths in minerals. *Monatshefte für Chemie*, **130**, 1047–1059.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *The Canadian Mineralogist*, **19**, 441–450.
- Mička, Z., Němec, I., Vojtišek, P., Ondráček, J. and Hölsä, J. (1994) Crystal structure, thermal behavior, and infrared absorption spectrum of cobalt(II) hydrogen selenite dihydrate $\text{Co}(\text{HSeO}_3)_2\cdot 2\text{H}_2\text{O}$. *Journal of Solid State Chemistry*, **112**, 237–242.
- Mička, Z., Němec, I., Vojtišek, P. and Ondráček, J. (1996) Crystal Structure and infrared absorption spectra of magnesium (II) hydrogen selenite tetrahydrate, $\text{Mg}(\text{HSeO}_3)_2\cdot 4\text{H}_2\text{O}$. *Journal of Solid State Chemistry*, **122**, 338–342.
- Nestola, F., Guastoni, A., Cámara, F., Secco, L., Dal Negro, A., Pedron, D. and Beran, A. (2009a) Aluminocerite-Ce: a new species from Baveno, Italy: description and crystal structure determination. *American Mineralogist*, **94**, 487–493.
- Nestola, F., Guastoni, A., Bindi, L. and Secco, L. (2009b) Dalnegroite, $\text{Tl}_{5-x}\text{Pb}_{2x}(\text{As,Sb})_{21-x}\text{S}_{34}$, a new thallium sulphosalt from Lengenbach quarry, Binntal, Switzerland. *Mineralogical Magazine*, **73**, 1027–1032.
- Nestola, F., Cámara, F., Chukanov, N.V., Atencio, D., Coutinho, J.M.V., Contreira Filho, R.R. and Farber, G. (2012) Witzkeite: a new rare nitrate-sulphate mineral from a guano deposit at Punta de Lobos, Chile. *American Mineralogist*, **97**, 1783–1787.
- Newman, W. L. (1962) Distribution of elements in sedimentary rocks of Colorado Plateau –A preliminary report. Pp. 337–440 in: *Contributions to the Geology of Uranium 1959–1960*, United States Geological Survey Bulletin, **1107-F**, US Government Printing Office, Washington DC.
- Peercy, P.S. (1970) The Raman spectrum of $\text{NaH}_3(\text{SeO}_3)_2$. *Optics Communication*, **2**, 270–272.
- Petríček, V., Dušek, M. and Palatinus, L. (2006) JANA2006. *The Crystallographic Computing System*. Institute of Physics, Prague.
- Petríček, V., Dušek, M. and Palatinus, L. (2014) Crystallographic Computing System Jana 2006: general features. *Zeitschrift für Kristallographie*, **229**, 345–352.
- Schröpfer, L. (1973) Strukturelle untersuchungen am $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. *Zeitschrift für anorganische und allgemeine Chemie*, **401**, 1–14.
- Stokes, W. L. (1952) *Uranium – Vanadium deposits of the Thompsons Area Grand County, Utah*. Utah Geological and Mineralogical Survey Bulletin, **46**. Utah Department of Natural Resources, Salt Lake City, Utah, USA, 51 pp.
- Torrie, B.H. (1972) Raman and Infrared Spectra of Na_2SeO_3 , NaHSeO_3 , H_2SeO_3 , and $\text{NaH}_3(\text{SeO}_3)_2$. *Canadian Journal of Physics*, **51**, 610–615.
- Valkonen, J., Losoi, T. and Pajunen, A. (1985) Structure of calcium selenite(IV) monohydrate, $\text{CaSeO}_3\cdot \text{H}_2\text{O}$. *Acta Crystallographica*, **C41**, 652–654.

