

# Genplesite, $\text{Ca}_3\text{Sn}(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , a new mineral of the fleischerite group: first occurrence of a tin sulfate in nature

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**Abstract:** The new mineral genplesite,  $\text{Ca}_3\text{Sn}(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , the first natural tin sulfate, is found in cavities in massive chalcopyrite ore at the Oktyabr'skoe Cu-Ni-Pd-Pt deposit (Oktyabr'sky mine), Talnakh, Norilsk district, Siberia, Russia. It is a late-stage hydrothermal mineral associated with greenalite, chamosite, pectolite, ferroactinolite, calcite and fluorapatite. Genplesite occurs as equant, short prismatic or thick tabular hexagonal crystals up to 0.5 mm and crystal clusters up to  $0.6 \times 1.2$  mm. The major crystal forms are  $\{100\}$  and  $\{001\}$  whereas  $\{102\}$  and  $\{101\}$  are minor. Genplesite is transparent, colourless, with vitreous lustre. It is brittle, the Mohs hardness is *ca.* 3. Cleavage is not observed, the fracture is conchoidal.  $D_{\text{meas}} = 2.78(1)$ ,  $D_{\text{calc}} = 2.773 \text{ g} \cdot \text{cm}^{-3}$ . Genplesite is optically uniaxial (–),  $\omega = 1.597(2)$ ,  $\epsilon = 1.572(2)$ . The IR spectrum is reported. The chemical composition (wt%, electron microprobe data,  $\text{H}_2\text{O}$  calculated for 3 molecules per formula unit, *pfu*) is: CaO 28.67,  $\text{Al}_2\text{O}_3$  0.11,  $\text{GeO}_2$  0.50,  $\text{SnO}_2$  24.20,  $\text{SO}_3$  27.25,  $\text{H}_2\text{O}_{\text{calc}}$  18.34, total 99.07. The empirical formula calculated on the basis of 17 O *apfu* is:  $\text{Ca}_{3.01}(\text{Sn}_{0.95}\text{Ge}_{0.03}\text{Al}_{0.01})_{\Sigma 0.99}\text{S}_{2.01}\text{O}_8(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ . Genplesite is hexagonal,  $P6_3/mmc$ ,  $a = 8.5139(2)$ ,  $c = 11.1408(3) \text{ \AA}$ ,  $V = 699.37(1) \text{ \AA}^3$  and  $Z = 2$ . The strongest reflections of the powder X-ray diffraction pattern [ $d$ ,  $\text{Å}$  ( $I$ )( $hkl$ )] are: 7.38(68)(100), 4.259(46)(110), 3.503(15)(201), 3.383(100)(112), 2.616(13)(203), 2.493(14)(212), 2.249(14)(302) and 2.130(17)(105, 220). Genplesite is a member of the fleischerite group. Its crystal structure was solved from single-crystal X-ray diffraction data ( $R = 0.016$ ). The major building unit of the structure is a column consisting of isolated  $\text{Sn}^{4+}(\text{OH})_6$  octahedra and trimers of edge-sharing  $\text{CaO}_2(\text{OH})_4(\text{H}_2\text{O})_2$  polyhedra. Adjacent columns are interconnected *via*  $\text{H}_2\text{O}$  molecules and  $\text{SO}_4$  tetrahedra. Genplesite is named in honour of Gennadiy N. Plesin (b. 1963), a mine surveyor at the Oktyabr'sky mine and an amateur mineralogist who found the mineral.

**Key-words:** genplesite; new mineral; tin sulfate; fleischerite group; ettringite group; crystal structure; Oktyabr'skoe deposit; Norilsk.

## 1. Introduction

This paper is devoted to the first natural sulfate with species-defining tin. It was found in a late-stage hydrothermal assemblage related to sulfide ores of the huge Oktyabr'skoe Cu–Ni–Pd–Pt deposit, operated by the Oktyabr'sky mine, in the Norilsk district, Krasnoyarsk Krai, Siberia, Russia. This new member of the fleischerite group was named genplesite (Cyrillic: генплесит) in honor of Gennadiy Nikolaevich Plesin (born 1963), a mine surveyor at the Oktyabr'sky mine and an amateur mineralogist who has made a significant contribution to the mineralogy of ore deposits of the Norilsk district. In particular, he collected and provided samples that became the holotypes of three mineral species, ferrotrochilinite

(Pekov *et al.*, 2013a), ferrovaleriite (Pekov *et al.*, 2013b) and genplesite described herein.

Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2014-034). The type specimen of genplesite is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 94618.

## 2. Occurrence and general appearance

Many publications are devoted to the famous Oktyabr'skoe deposit. The general description of the deposit, its ores and mineralogy can be found in Genkin *et al.* (1981) and Gorbachev (2006).

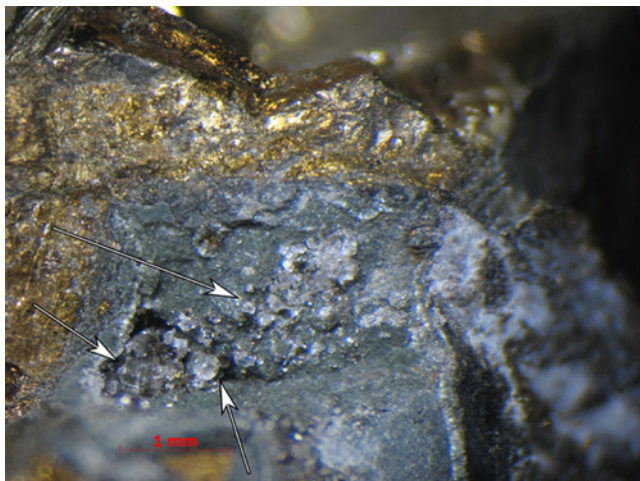


Fig. 1. Numerous transparent, colourless crystals of genplesite (marked with arrows) on greenalite crust in a cavity in massive chalcopyrite. Field of view 5.8 mm. Photo: I.V. Pekov & A.V. Kasatkin.

Specimens bearing the new mineral were collected by G. N. Plesin in March 2013 at the No. 1 shaft (level –750 m) of the Oktyabr'sky mine, Talnakh city, Norilsk district.

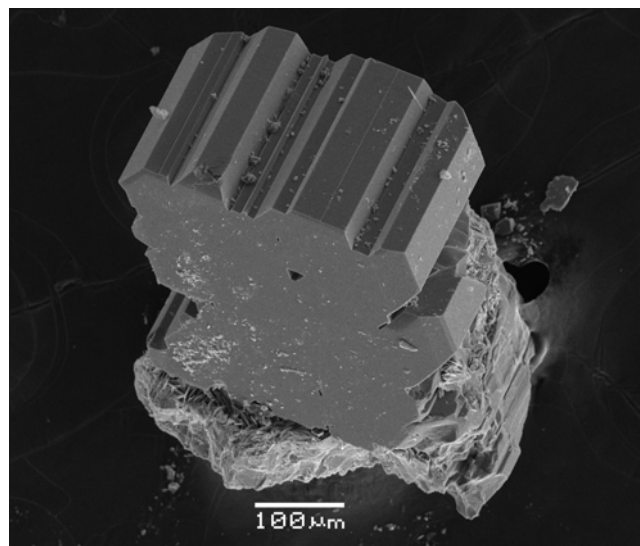
Genplesite was found in the cavernous part (about 0.3 m across) of a massive chalcopyrite body located at the contact between a rich mooihoeekite–chalcopyrite ore and gabbro-dolerite with embedded chalcopyrite. The new mineral occurs on greenish-grey greenalite crystalline crusts lining walls of roundish caverns (up to 1 cm in diameter) in a massive chalcopyrite (with subordinate pentlandite) ore (Fig. 1). Some genplesite crystals were observed on brown chamosite spherulites overgrowing greenalite crusts. Other minerals found in these cavities are pectolite, ferroactinolite, calcite and fluorapatite.

Genplesite occurs as hexagonal, equant, short prismatic or thick tabular crystals. Their major forms are the hexagonal prism  $\{100\}$  and the pinacoid  $\{001\}$ ; the hexagonal dipyrnidal faces  $\{102\}$  and  $\{101\}$  were observed on some crystals (Figs. 2 and 3). Crystal forms were determined after observations under scanning electron microscope. Gear-like parallel intergrowths of crystals are typical (Figs. 2a and 3c). Genplesite crystals are up to 0.5 mm across, gear-like parallel intergrowths are up to  $0.6 \times 1$  mm and crystal clusters are up to  $0.6 \times 1.2$  mm in size.

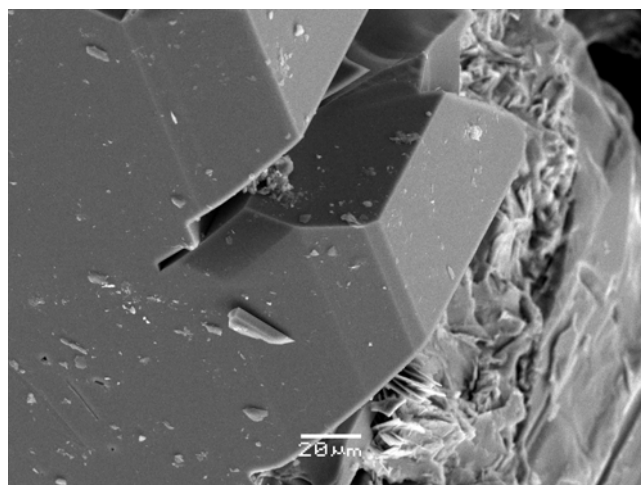
### 3. Physical properties

Genplesite is transparent, colourless, with a white streak and a vitreous lustre, brittle, with a Mohs hardness of *ca.* 3. No distinct cleavage or parting were observed and the fracture is conchoidal. Density measured by flotation in heavy liquids (bromoform + dimethylformamide) is 2.78(1) and the density calculated using the empirical formula is  $2.773 \text{ g} \cdot \text{cm}^{-3}$ .

Genplesite is optically uniaxial (–),  $\omega = 1.597(2)$ ,  $\varepsilon = 1.572(2)$  (589 nm). Under the microscope it is colourless and non-pleochroic.



a



b

Fig. 2. Parallel intergrowth of genplesite crystals (a) and its magnified fragment (b). Genplesite overgrows greenalite crust. Scanning electron microscope (secondary electrons) image.

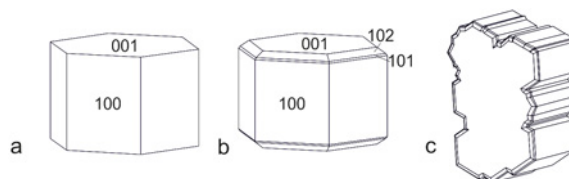


Fig. 3. Genplesite crystals (a–b) and their parallel intergrowth (c).

### 4. Infrared spectroscopy

Absorption bands in the IR spectrum of genplesite (Fig. 4) and their assignments are ( $\text{cm}^{-1}$ , s – strong band, w – weak band, sh – shoulder): 3520 sh, 3451 s, 3365 s (O–H stretching vibrations of  $\text{H}_2\text{O}$  molecules and OH groups), 1663, 1550 sh (H–O–H bending vibrations of  $\text{H}_2\text{O}$  molecules; splitting of the band is due to the bifurcation

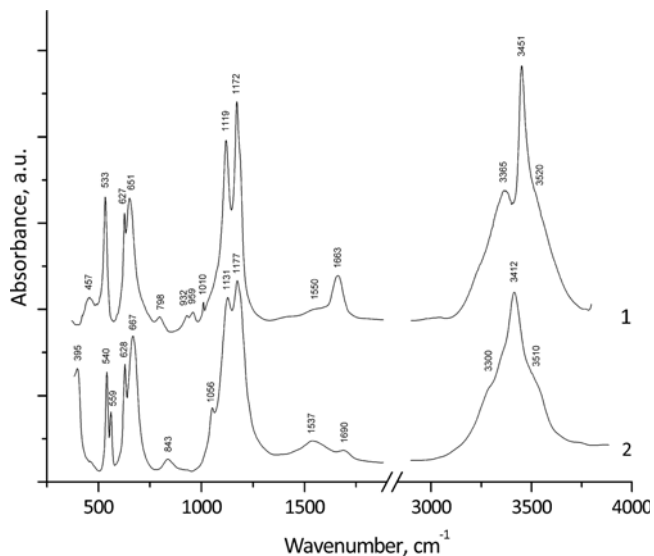


Fig. 4. IR spectra of genplesite (1) and schaurteite from Tsumeb, Namibia (2, after Chukanov, 2014).

of the H-bond formed by the H<sub>2</sub>O molecule; see footnote to Table 5), 1172 s, 1119 s [ $\nu_3(F_2)$  – asymmetric stretching vibrations of SO<sub>4</sub><sup>2-</sup> anions], 1010 w ( $\nu_1(A_1)$  – symmetric stretching vibrations of SO<sub>4</sub><sup>2-</sup> anions), 959 w, 932 w, 798 w (Sn...O–H bending vibrations), 651, 627 ( $\nu_4(F_2)$  – bending vibrations of SO<sub>4</sub><sup>2-</sup> anions), 533 (Sn–O stretching vibrations), 457 (possible librational vibrations of H<sub>2</sub>O molecules). The presence of  $\nu_1(A_1)$  at 1010 cm<sup>-1</sup> corresponding to the nondegenerate S–O stretching mode, as well as the splitting of the band  $\nu_3(F_2)$  of the SO<sub>4</sub> group (the doublet 1119 + 1172 cm<sup>-1</sup>) reflect some distortion of SO<sub>4</sub> tetrahedra.

Three bands of O–H stretching vibrations in the range 3300–3600 cm<sup>-1</sup> correspond to three normal modes (O–H stretching mode of the OH group and in-phase and out-of-phase stretching modes of the H<sub>2</sub>O molecule).

Characteristic bands of BO<sub>3</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> groups are absent in the IR spectrum of genplesite.

The IR spectrum of the new mineral is similar to that of its Ge-analogue schaurteite Ca<sub>3</sub>Ge(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>·3H<sub>2</sub>O (Fig. 4). The main differences between IR spectra of these sulfates are observed in the ranges of O–H stretching (3300–3600 cm<sup>-1</sup>) and M–O stretching (530–560 cm<sup>-1</sup>) vibrations of the M<sup>4+</sup>(OH)<sub>6</sub> octahedra (M = Sn, Ge).

## 5. Chemical composition

The chemical composition of genplesite was determined using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University), with an acceleration voltage of 20 kV and a beam current of 15 nA; the electron beam was rastered over an area of 10 × 10 μm to minimize damage to the unstable, highly hydrated mineral. The following standards were used: CaWO<sub>4</sub> (Ca), Al<sub>2</sub>O<sub>3</sub> (Al), Ge (Ge), SnS (Sn), and FeS<sub>2</sub> (S). Contents of other elements with

Table 1. Powder X-ray diffraction data for genplesite.

$I_{\text{obs}}$	$d_{\text{obs}}, \text{\AA}$	$I_{\text{calc}}^*$	$d_{\text{calc}}, \text{\AA}^{**}$	$hkl$
68	7.38	56	7.373	100
12	6.15	9	6.148	101
11	5.587	5	5.570	002
11	4.446	8	4.445	102
46	4.259	44	4.257	110
15	3.503	12	3.500	201
100	3.383	100	3.382	112
4	3.319	1	3.317	103
6	3.076	5	3.074	202
8	2.787	3, 6	2.787, 2.785	210, 004
3	2.705	1	2.704	211
13	2.616	15	2.616	203
6	2.604	4	2.606	104
14	2.493	20	2.492	212
2	2.459	1	2.458	300
3	2.402	3	2.400	301
2	2.330	3	2.331	114
14	2.249	22	2.249	302
8	2.227	8, 6	2.229, 2.222	213, 204
17	2.130	6, 24	2.133, 2.128	105, 220
6	2.050	9	2.050	303
1	2.013	0.5	2.011	311
5	1.971	9	1.970	214
2	1.920	1	1.920	312
2	1.908	2	1.907	205
1	1.858	1	1.857	006
4	1.844	5	1.843	304
3	1.819	4	1.819	401
2	1.800	3	1.801	106
3	1.751	5	1.750	402
3	1.742	6	1.740	215
3	1.702	6	1.702	116
11	1.692	6, 19	1.692, 1.691	320, 224
2	1.659	5	1.658	206
4	1.650	1, 8	1.651, 1.648	403, 314
1	1.620	1	1.619	322
2	1.610	4	1.609	410
1	1.593	0.5	1.592	411
10	1.547	15, 4	1.546, 1.545	412, 216
3	1.483	7	1.482	306
2	1.462	3	1.461	207
2	1.447	4	1.446	324
2	1.427	2	1.426	502
3	1.420	5	1.419	330
3	1.394	0.5, 3, 2	1.393, 1.393, 1.393	420, 414, 008
2	1.384	2, 0.5	1.383, 1.382	421, 217
5	1.376	7, 4	1.375, 1.375	332, 316
1	1.352	2	1.352	422
1	1.325	1	1.324	118
1	1.317	0.5	1.315	511
2	1.305	3, 0.5	1.305, 1.304	423, 415
2	1.289	2	1.288	512
2	1.230	1, 3	1.230, 1.229	505, 600
2	1.217	7	1.216	416
2	1.206	1, 4	1.205, 1.205	431, 407
1	1.197	2	1.196	514
2	1.184	2	1.184	432

\* For the calculated pattern, only reflections with intensities  $\geq 0.5$  are given;

\*\* for the unit-cell parameters calculated from single-crystal data.

Table 2. Crystal data, data collection information and structure refinement details for genplesite.

Formula	Ca <sub>3</sub> Sn(SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O
Formula weight	587.15
Temperature, K	293(2)
Radiation and wavelength, Å	MoKα; 0.71073
Crystal system, space group, Z	Hexagonal, P6 <sub>3</sub> /mmc, 2
Unit cell dimensions, Å	<i>a</i> = 8.5139(2) <i>c</i> = 11.1408(3)
<i>V</i> , Å <sup>3</sup>	699.37(3)
Absorption coefficient μ, mm <sup>-1</sup>	3.318
ρ <sub>calc</sub> for the ideal formula, g·cm <sup>-3</sup>	2.788
<i>F</i> <sub>000</sub>	580
Crystal size, mm	0.14 × 0.14 × 0.22
Diffractometer	Xcalibur S CCD
θ range for data collection, °	2.76–34.77
Index ranges	−13 ≤ <i>h</i> ≤ 13, −13 ≤ <i>k</i> ≤ 13, −17 ≤ <i>l</i> ≤ 17
Reflections collected	17960
Independent reflections	613 ( <i>R</i> <sub>int</sub> = 0.0367)
Independent reflections with <i>I</i> > 2σ( <i>I</i> )	590
Structure solution	direct methods
Refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>
Number of refined parameters	35
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0162, <i>wR</i> 2 = 0.0414
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0178, <i>wR</i> 2 = 0.0420
Weighting parameters <i>a</i> , <i>b</i>	0.0183, 0.4311
GoF	1.255
Largest diff. peak and hole, e/Å <sup>3</sup>	0.325 and −0.783

atomic numbers higher than carbon are below detection limit. H<sub>2</sub>O was not determined because of the scarcity of material and its content was calculated on the basis of the structural data (see below), for 3 H<sub>2</sub>O molecules per formula unit (*pfu*).

The chemical composition of genplesite (average of 4 spot analyses; wt%, with ranges/standard deviations in parentheses) is: CaO 28.67 (28.49–28.84 / 0.15), Al<sub>2</sub>O<sub>3</sub> 0.11 (0.04–0.16/0.06), GeO<sub>2</sub> 0.50 (0.35–0.63/0.13), SnO<sub>2</sub> 24.20 (24.02–24.45/0.19), SO<sub>3</sub> 27.25 (27.06–27.53/0.20), H<sub>2</sub>O<sub>calc</sub> 18.34, total 99.07 wt%.

The empirical formula calculated on the basis of 17 O *apfu* is Ca<sub>3.01</sub>(Sn<sub>0.95</sub>Ge<sub>0.03</sub>Al<sub>0.01</sub>)<sub>Σ0.99</sub>S<sub>2.01</sub>O<sub>8</sub>(OH)<sub>6</sub>·3H<sub>2</sub>O. The idealized formula is Ca<sub>3</sub>Sn(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>·3H<sub>2</sub>O, which requires CaO 28.65, SnO<sub>2</sub> 25.66, SO<sub>3</sub> 27.28, H<sub>2</sub>O 18.41, total 100.00 wt%.

The Gladstone-Dale compatibility index 1−(*K<sub>p</sub>*/*K<sub>c</sub>*) is −0.016 (superior) if *D<sub>meas</sub>* is used or −0.019 (superior) if *D<sub>calc</sub>* is used.

## 6. X-ray crystallography and crystal structure

Powder X-ray diffraction data of genplesite (Table 1) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image plate detector (radius 127.4 mm) using Debye-Scherrer geometry, CoKα radiation (rotating anode with Vari-MAX microfocus optics), 40 kV, 15 mA, 15 min exposure. The angular resolution of the detector was

0.045 2θ (pixel size 0.1 mm). The data were integrated using the software package Osc2Tab (Britvin *et al.*, 2017).

The hexagonal unit-cell parameters refined from the powder data are: *a* = 8.518(1), *c* = 11.149(2) Å and *V* = 700.6(3) Å<sup>3</sup>.

Single-crystal X-ray diffraction study of genplesite was carried out using an Xcalibur S diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. The measured intensities were corrected for Lorentz, background, polarization and absorption effects. Data reduction was performed using CrysAlisPro Version 1.171.35.21 (Agilent Technologies, 2012). The structure was solved by direct methods and refined using the SHELX-97 software package (Sheldrick, 2008) to *R* = 0.016 for 590 independent reflections with *I* > 2σ(*I*). Hydrogen atoms were located from the difference Fourier electron-density maps and refined freely. Both H atoms form O–H...O hydrogen bonds; moreover, the H bond formed by the H<sub>2</sub>O molecule could be considered as bifurcated due to the presence of an O(4) (in the H<sub>2</sub>O molecule) – O(2) distance of 3.0051(15) Å, confirmed by the IR spectroscopy data. The crystal data and the experimental details are presented in Table 2, atom coordinates and displacement parameters in Table 3, selected interatomic distances in Table 4, hydrogen-bond geometry in Table 5 and bond-valence calculations in Table 6.

The crystal structure of genplesite (Fig. 5a) is typical for fleischerite-group minerals (Table 7). Its major building unit is a column parallel to [001], which consists of isolated Sn<sup>4+</sup>(OH)<sub>6</sub> octahedra and trimers of edge-sharing CaO<sub>2</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> polyhedra (Fig. 5b). Neighbouring columns are interconnected by Ca-centred polyhedra sharing oxygen atoms of H<sub>2</sub>O molecules O(4) and through SO<sub>4</sub> tetrahedra, sharing three O vertices O(2) with Ca-centred polyhedra (Fig. 5a). The O(1) apical vertices of the SO<sub>4</sub> tetrahedra are H-bonded to the O atoms of the H<sub>2</sub>O molecules (Table 6). According to Pushcharovsky *et al.* (1998), the structural formula of genplesite could be given as <sup>3</sup><sub>∞</sub>[Ca<sub>3</sub><sup>[8]</sup>Sn<sup>0</sup>S<sup>t</sup>O<sub>8</sub>(OH)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>].

## 7. Discussion

Genplesite Ca<sub>3</sub>Sn<sup>4+</sup>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>·3H<sub>2</sub>O is a new member of the fleischerite group (Table 7), and is a tin analogue of schaurteite, Ca<sub>3</sub>Ge<sup>4+</sup>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>·3H<sub>2</sub>O, and despujolite, Ca<sub>3</sub>Mn<sup>4+</sup>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>·3H<sub>2</sub>O. All these minerals are hexagonal with the unit-cell parameters in the range 8.51–8.94 Å for *a* and 10.76–11.14 Å for *c*. Genplesite and schaurteite are isotopic (both crystallize in space group *P*6<sub>3</sub>/*mmc*), whereas other fleischerite-group members possess different space groups: despujolite and fleischerite crystallize in the space group *P*-62*c*, and mallestigitite crystallizes in the space group *P*6<sub>3</sub>. Origlieri & Downs (2013) noted that, although schaurteite and fleischerite are minerals from the same deposit, no significant Pb ↔ Ca

Table 3. Atom coordinates, displacement parameters ( $U_{\text{eq}}$ , in  $\text{\AA}^2$ ) and site multiplicities ( $Q$ ) for genplesite.

Site	$x$	$y$	$z$	$U_{\text{eq}}$	$Q$
Sn	0	0	0	0.00817(7)	2
Ca	0.30866(6)	0.15433(3)	1/4	0.01008(9)	6
S	1/3	2/3	0.52868(6)	0.00881(11)	4
O(1)	1/3	2/3	0.10438(18)	0.0166(4)	4
O(2)	0.47792(18)	0.23896(9)	0.07082(12)	0.0195(2)	12
O(3)	0.10624(8)	0.21249(16)	0.11835(10)	0.01105(19)	12
O(4)	0.50906(13)	0.49094(13)	3/4	0.0165(3)	6
H(1)	0.152(2)	0.304(5)	0.084(3)	0.031(8)*	12
H(2)	0.537(2)	0.463(2)	0.695(3)	0.050(11)*	12

\*  $U_{\text{iso}}$ .Table 4. Selected interatomic distances ( $\text{\AA}$ ) in the structure of genplesite.

Sn – O(3)	2.0477(11) $\times$ 6
Ca – O(2)	2.3542(13) $\times$ 2
– O(3)	2.4939(7) $\times$ 4
– O(4)	2.6159(10) $\times$ 2
S – O(2)	1.4687(13) $\times$ 3
– O(1)	1.482(2)
O(3) – H(1)	0.78(3)
O(4) – H(2)	0.74(3) $\times$ 2

Table 5. Hydrogen-bond geometry ( $\text{\AA},^\circ$ ) in the structure of genplesite.

$D - H \cdots A$	$D - H$	$H \cdots A$	$D \cdots A$	$\angle(D - H \cdots A)$
O(3) – H(1) $\cdots$ O(2)	0.78(3)	2.14(3)	2.8761(18)	157(3)
O(4) – H(2) $\cdots$ O(1)	0.74(3)	2.16(3)	2.834(2)	152(3)

Table 6. Bond-valence calculations for genplesite.

	Sn	Ca	S	$\Sigma$	H-bonding	$\Sigma$
O(1)			1.47	1.47	+0.17 $\times$ 3 $\rightarrow$ (O(4))	1.98
O(2)		0.35 $\times$ 2 $\downarrow$	1.52 $\times$ 3 $\downarrow$	1.87	+0.16 (O(3))	2.03
O(3)=OH	0.68 $\times$ 6 $\downarrow$	0.24 $\times$ 4 $\downarrow$ $\times$ 2 $\rightarrow$		1.16	–0.16 (O(2))	1.00
O(4)=H <sub>2</sub> O		0.17 $\times$ 2 $\downarrow$ $\times$ 2 $\rightarrow$		0.34	–0.17 $\times$ 2 $\rightarrow$ (O(1))	0.00
$\Sigma$	4.08	2.00	6.03			

Bond-valence parameters were taken from Brese & O'Keeffe (1991) for Sn–O, Ca–O and S–O and from Ferraris & Ivaldi (1988) for H-bonding.

substitution is observed. This could be explained by the stereochemical activity of lone electron pairs on  $\text{Pb}^{2+}$  cations in fleischerite, which disrupt the centrosymmetry of the whole structure (Origlieri & Downs, 2013).

The existence of two Ge members of the fleischerite group, namely fleischerite,  $\text{Pb}_3\text{Ge}(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , and schaurteite, demonstrates a strong affinity of fleischerite-type structures for  $\text{Ge}^{4+}$ . Genplesite also contains up to 0.6 wt%  $\text{GeO}_2$ .

The general formula of the fleischerite-group minerals is  $A^{2+}_3M(\text{TO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$  with species-defining  $A = \text{Ca}$  or  $\text{Pb}$ ,  $M = \text{Ge}^{4+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Sn}^{4+}$  or  $\text{Sb}^{5+}$ , and  $T = \text{S}^{6+}$  or  $\text{As}^{5+}$  (Table 7). In their structures, the heteropolyhedral columns formed by the  $A$ - and  $M$ -centred polyhedra are topologi-

cally the same as polyhedral columns found in the crystal structures of ettringite-group minerals, which have the general formula  $\text{Ca}_6M_2(\text{OH})_{12}R_{3-4} \cdot n\text{H}_2\text{O}$ , in which  $M = \text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{Mn}^{4+}$  or  $\text{Ge}^{4+}$  are species-defining cations,  $R = \text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{PO}_3\text{OH}^{2-}$  or  $\text{B}(\text{OH})_4^-$  are species-defining anions and  $n = 11-13$  (Pöllmann *et al.*, 1989; Pekov *et al.*, 2012; Chukanov *et al.*, 2016). In the crystal structures of ettringite-group minerals and isostructural synthetic compounds (all are hexagonal or trigonal, with  $P$  unit cells), the columns formed by the  $M(\text{OH})_6$  octahedra and trimers of edge-sharing Ca-centred polyhedra are connected with  $R$  anions by a complex system of H-bonds. In less hydrated fleischerite-group minerals, topologically similar columns are instead

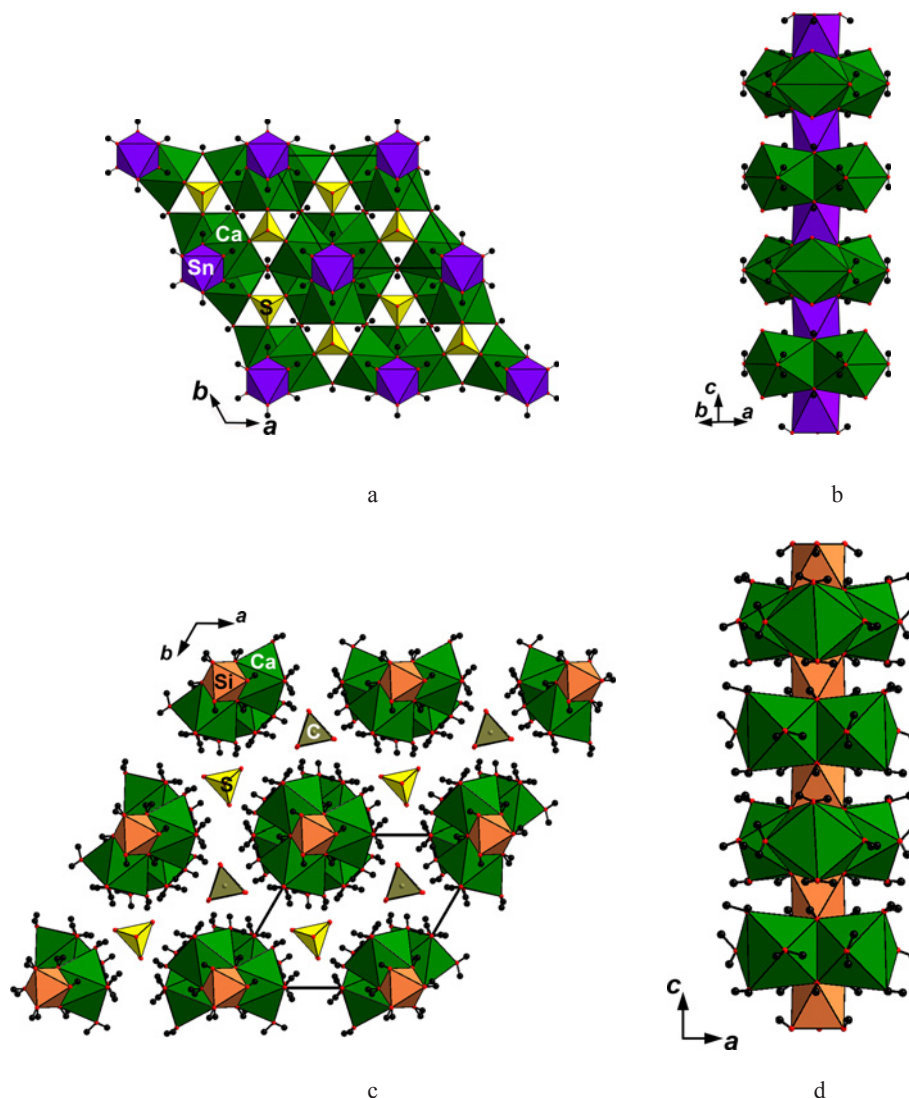


Fig. 5. The crystal structures of genplesite (a, b) and thaumasite (c, d: drawn after Effenberger *et al.*, 1983). Figures (a) and (c) show a general view of the structures projected on the  $ab$  plane; (b) the column formed by  $\text{Sn}(\text{OH})_6$  octahedra and trimers of  $\text{CaO}_2(\text{OH})_4(\text{H}_2\text{O})_2$  polyhedra in genplesite; (d) the column formed by  $\text{Si}(\text{OH})_6$  octahedra and trimers of  $\text{Ca}(\text{OH})_4(\text{H}_2\text{O})_4$  polyhedra in thaumasite. Hydrogen atoms are black circles. The unit cells are outlined.

directly linked *via*  $\text{SO}_4$  tetrahedra. This causes a significant difference in the  $a$  unit-cell parameter between ettringite-group minerals (10.8–11.3 Å) and Ca representatives of the fleischerite group (8.5–8.6 Å), whereas their  $c$  parameters do not differ essentially: 10.4–10.6 Å (or 21.0–21.9 Å for the ettringite-group minerals with a  $c$ -doubled unit cell) and 10.8–11.3 Å, respectively: see Table 7 and comparative data reported by Pekov *et al.* (2012) and Chukanov *et al.* (2016). Figure 5 depicts the above-mentioned features of the structure of genplesite as a fleischerite-group member, compared to the most widespread ettringite-group mineral thaumasite,  $\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4)\cdot 12\text{H}_2\text{O}$ .

Genplesite is a late-stage low-temperature hydrothermal mineral. No sign of influence of supergene processes was observed in this orebody situated at significant depth.

The sulfide ores of the Oktyabr'skoe deposit are relatively enriched in tin and sporadically contain Sn sulfides, cassiterite and numerous intermetallic compounds with species-defining Sn with Pd or Pt (Gorbachev, 2006). Thus the formation of tin minerals in the hydrothermal assemblages related to such ores is not unexpected.

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Table 7. Comparative data for fleischerite-group minerals.

Mineral	Genplesite	Schaurteite	Despujolsite	Fleischerite	Mallestigit
Formula	$\text{Ca}_3\text{Sn}(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$	$\text{Ca}_3\text{Ge}(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$	$\text{Ca}_3\text{Mn}^{4+}(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$	$\text{Pb}_3\text{Ge}(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$	$\text{Pb}_3\text{Sb}^{5+}(\text{SO}_4)_2(\text{AsO}_4)(\text{OH})_6 \cdot 3\text{H}_2\text{O}$
Crystal system	Hexagonal $P6_3/mmc$	Hexagonal $P6_3/mmc$	Hexagonal $P-62c$	Hexagonal $P-62c$	Hexagonal $P6_3$
$a$ , Å	8.514	8.525	8.54–8.56	8.89	8.938
$c$ , Å	11.141	10.80	10.76–10.81	10.86	11.098
$V$ , Å <sup>3</sup>	699	680	683	743	768
$Z$	2	2	2	2	2
Strong lines of the powder X-ray diffraction pattern: $d$ , Å – $I$ , %	7.38–68 4.259–46 3.503–15 3.383–100 2.493–14 2.249–14 2.130–17 2.78 (meas.)	7.40–50 4.26–70 3.49–50 3.34–100 2.579–50 2.239–50 2.129–60 2.65 (meas.)	7.40–60 4.26–80 3.34–100 2.570–60 2.129–80 2.025–60 2.46 (meas.)	7.681–50 3.619–100 3.437–60 2.800–50 2.635–80 2.214–60 1.889–60 4.59 (calc.)	7.74–25 6.35–44 3.655–100 3.481–80 3.175–31 2.675–62 2.235–35 4.91 (calc.)
Density, $\text{g} \cdot \text{cm}^{-3}$					
Optical data					
$\omega$	1.597	1.569	1.656	1.747	1.801
$\epsilon$	1.572	1.581	1.682	1.776	1.760
Optical sign	–	+	+	+	+
References	this work	Strunz & Tennyson (1967); Origlieri & Downs (2013)	Gaudefroy <i>et al.</i> (1968); Barkley <i>et al.</i> (2011)	Frondel & Strunz (1960); Otto (1975)	Sima (1998)

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