

# NIKISCHERITE

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## A NEW MINERAL FROM THE HUANUNI TIN MINE, DALENCE PROVINCE, ORURO DEPARTMENT, BOLIVIA

Danielle M. C. Huminicki and Frank C. Hawthorne  
Department of Geological Sciences, University of Manitoba  
Winnipeg, Manitoba, Canada, R3T 2N2

Joel D. Grice  
Research Division, Canadian Museum of Nature,  
PO Box 3443, Station D, Ottawa, Ontario, Canada, K1P 6P4

Andrew C. Roberts  
Geological Survey of Canada, 601 Booth Street  
Ottawa, Ontario, Canada K1A 0E8

John L. Jambor  
Department of Earth and Ocean Sciences, University of British Columbia,  
Vancouver, British Columbia, Canada V6T 1Z4

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### ABSTRACT

Nikischerite, ideally  $\text{NaFe}_{0.85}^{2+}\text{Al}_3(\text{SO}_4)_2(\text{OH})_{18}(\text{H}_2\text{O})_{12}$ , is a new mineral from the Huanuni tin mine, Dalence Province, Oruro Department, Bolivia. It occurs as small micaceous plates (to 4 mm) that form isolated radiating balls and aggregates that reach nearly 1 cm across in thin seams. Associated minerals are pyrite, pyrrhotite, siderite and cronstedtite in a brownish clay matrix. Nikischerite has a platy habit with the form {001} dominant; no twinning was observed. Crystals are typically Georgian green (RHS #139B), somewhat darker at the external edges of the aggregates, occasionally approaching grayish white at the core of the balls. They have a dull-to-greasy luster, a pale grayish green streak, and they do not fluoresce under longwave or shortwave ultraviolet light. The crystals have a Mohs hardness of 2, are crumbly with an irregular fracture, and have perfect cleavage parallel to {001}. The strongest five reflections in the X-ray powder-diffraction pattern are  $[d(\text{\AA}), I, hkl]$ : 10.98(100)(003); 5.539(60)(006); 3.674(50)(009); 2.425(30)(036); 1.932(30)(03.12); the refined cell dimensions for a trigonal cell with  $R\bar{3}$  space-group symmetry are  $a = 9.352(7)$ ,  $c = 33.08(4)$  Å,  $V = 2505(4)$  Å<sup>3</sup>,  $a:c = 1:3.537$ ,  $Z = 3$ . The density was measured using heavy liquids; the observed and calculated values are 2.33(2) and 2.30 g/cm<sup>3</sup>. In transmitted light, nikischerite is

colorless to gray and is uniaxial negative with  $\omega = 1.560(1)$ ,  $\epsilon$  is indeterminate; it is non-pleochroic. Electron-microprobe data for nikischerite are  $\text{SO}_3 = 13.54$ ,  $\text{Al}_2\text{O}_3 = 14.35$ ,  $\text{FeO} = 43.59$ ,  $\text{Na}_2\text{O} = 2.43$ ,  $\text{H}_2\text{O}(\text{calc.}) = 35.06$ , sum = 108.97 weight %; the corresponding unit formula [based on 38 anions with  $(\text{OH}) = 12$  and  $(\text{H}_2\text{O}) = 12$ ] is  $\text{Na}_{0.85}\text{Fe}_{0.85}^{2+}\text{Al}_{3.04}\text{S}_{1.83}\text{O}_8(\text{OH})_{18}(\text{H}_2\text{O})_{12}$ , where the OH and H<sub>2</sub>O groups were assigned from knowledge of the crystal structure; the infrared spectrum indicates the presence of both OH and H<sub>2</sub>O in the structure. The mineral is named for Anthony (Tony) J. Nikischer, geologist and mineral dealer.

### INTRODUCTION

Three years ago, Tony Nikischer (Excalibur Mineral Company) forwarded a specimen to one of us for identification. The mineral turned out to be new to Science, and its characterization is reported here. The new mineral is named after Anthony (Tony) J. Nikischer (born 1949), owner of the Excalibur Mineral Company, both for discovering the mineral, but more so for the help that he has given to the academic mineralogical community for many years by supplying rare minerals for scientific study.

The new mineral and mineral name have been approved by the

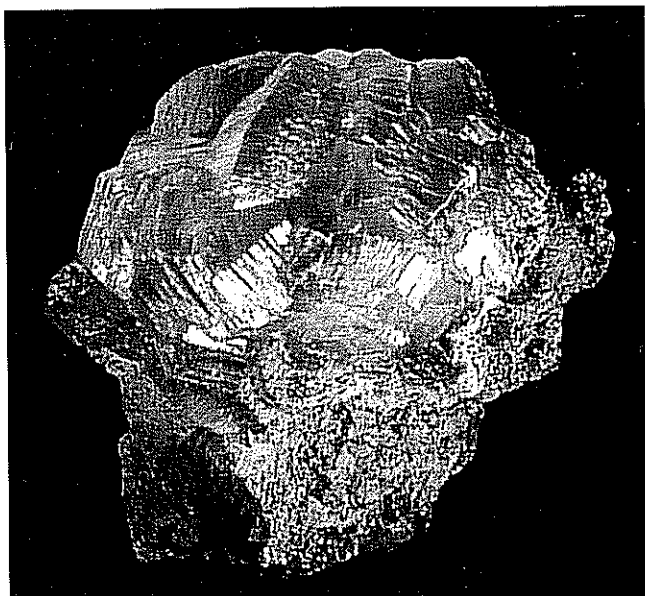


Figure 1. Nikischerite (georgian green) perched on a brown clay matrix, specimen is 1.5 cm across. Tony Nikischer specimen and photo.

Commission on New Minerals and Mineral Names of the International Mineralogical Association (2001-39). Type material has been deposited at the Canadian Museum of Nature (specimen number CMNMC 83499) and in the X-ray powder-mount reference collection in the X-ray diffraction laboratory at the Geological Survey of Canada, Ottawa, Ontario.

### PHYSICAL PROPERTIES

Nikischerite occurs as small micaceous plates (to 4 mm) that form radiating, irregular aggregates up to 1 cm across, and reach nearly 1 cm across in thin seams, perched on or penetrating a brown clay matrix (Fig. 1). The mineral has a platy habit with {001} cleavage surfaces dominant; no twinning was observed. Nikischerite is typically Georgian green (RHS # 139B), somewhat darker at the external edges of the aggregates, and occasionally approaching grayish white at the cores of the spherical aggregates. It has a dull to greasy luster and a pale grayish green streak; crystals do not fluoresce under longwave or shortwave ultraviolet light. Nikischerite is crumbly with an irregular fracture and a perfect cleavage parallel to {001}; Mohs hardness is 2. The density was measured with heavy liquids, giving a value of 2.33(2) g/cm<sup>3</sup>, and the calculated density for the ideal end-member composition is 2.30 g/cm<sup>3</sup>.

### OPTICAL PROPERTIES

In transmitted light, nikischerite is colorless to grayish white and non-pleochroic. The refractive index was measured in monochromatic light ( $\lambda = 590$  nm):  $\omega = 1.560(1)$ ;  $\epsilon$  could not be measured because of the extreme thinness of the crystals. Nikischerite is uniaxial negative.

### CHEMICAL COMPOSITION

Crystals were analyzed chemically with a Cameca SX-50 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, a beam size of 30  $\mu$ m and counting times on peak and background of 20 and 10 s, respectively. The following standards were used: anhydrite (S); kyanite (Al); fayalite (Fe); albite (Na).

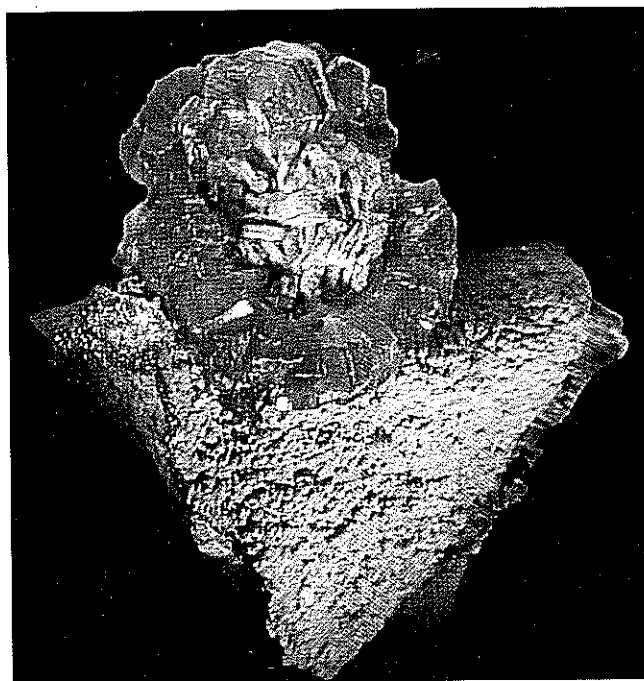


Figure 2. Nikischerite (georgian green) on a brown clay matrix containing grains and small aggregates of pyrite (yellow), specimen is 1.5 cm across. Tony Nikischer specimen and photo.

Table 1. Chemical composition (wt.%) and unit formula\* (apfu) for nikischerite.

SO <sub>3</sub>	13.54	S	1.83
Al <sub>2</sub> O <sub>3</sub>	14.35	Al	3.04
FeO	43.59	Fe <sup>2+</sup>	6.55
Na <sub>2</sub> O	2.43	Na	0.85
H <sub>2</sub> O <sub>calc</sub>	(35.06)	OH	18
Total	102.97	H <sub>2</sub> O	12

Data were reduced using the  $\phi\rho\rho Z$  method of Pouchou and Pichoir (1985).

The analytical sums are uniformly high in all of the electron-microprobe analyses. We experimented with different beam diameters and beam intensities, and the analytical sums varied accordingly. However, we could never get sums around the ideal value of 100 weight % (inclusive of calculated H<sub>2</sub>O content). These results are in accord with previous results on the isostructural mineral shigaite, ideally Na Mn<sub>6</sub><sup>2+</sup>Al<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>18</sub>(H<sub>2</sub>O)<sub>12</sub>, in which the analytical sums were uniformly high (Cooper and Hawthorne, 1999). The crystal structure shows that some of the (H<sub>2</sub>O) in the structure is not bonded directly to a cation, but is held in the structure only by (weak) hydrogen bonds. It seems reasonable to suggest that some of this weakly bound (H<sub>2</sub>O) is lost when the sample is exposed to the electron beam in the vacuum of the electron microprobe; this may also lead to the removal of some (SO<sub>3</sub>) and Na (as was the case for shigaite). This would account for the high analytical total and the high value for FeO. It is notable that the refined site-scattering at the Fe site in the crystal structure of nikischerite (Huminicki and Hawthorne, 2002) is in accord with the ideal end-member formula of nikischerite. The mean of 18 analyses and the chemical formula are listed in Table 1. The chemical formula was calculated on the basis of 38 anions includ-

Table 2. X-ray powder-diffraction data for nikischerite.

$l_{\text{est}}$	$d_{\text{meas}}$ (Å)	$d_{\text{calc}}$ (Å)	$h$	$k$	$l$	$l_{\text{est}}$	$d_{\text{meas}}$ (Å)	$d_{\text{calc}}$ (Å)	$h$	$k$	$l$
100	10.980	11.027	0	0	3	3	2.287	2.287	2	2	3
60	5.539	5.513	0	0	6	* 20	2.176	2.176	0	3	9
3	4.677	4.676	1	1	0	* 30	1.932	1.929	0	3	12
* 20	4.311	4.305	1	1	3	3	1.872	1.871	1	2	14
* 50	3.674	3.676	0	0	9	5b	1.838	1.838	0	0	18
5b	3.035	3.048	2	1	1	* 5	1.747	1.745	4	1	3
"	"	3.010	1	2	2	* 10	1.707	1.708	0	3	15
3	2.892	2.890	1	1	9	* 10	1.560	1.559	3	3	0
* 10	2.700	2.700	0	3	0	* 5	1.544	1.543	3	3	3
* 25	2.624	2.622	0	3	3	3	1.519	1.519	0	3	18
* 30	2.425	2.425	0	3	6	* 10	1.497	1.500	3	3	6

114.6 mm Debye-Scherrer powder camera, Ni-filtered Cu radiation ( $\lambda_{\text{CuK}\alpha} = 1.54178 \text{ \AA}$ ).

Intensities estimated visually, b = broad line. Not corrected for shrinkage and no internal standard used.

\* = lines used for unit-cell refinement. Indexed on  $a = 9.352(7)$ ,  $c = 33.08(4) \text{ \AA}$ ,  $V = 2505(4) \text{ \AA}^3$ .

ing 18 (OH) groups and 12 (H<sub>2</sub>O) groups, as derived from solution and refinement of the crystal structure (Huminicki and Hawthorne, 2002).

#### X-RAY DIFFRACTION

The powder-diffraction pattern was recorded with a 114.6-mm Debye-Scherrer powder camera using Ni-filtered CuK $\alpha$  X-radiation. The X-ray powder-diffraction pattern is reported in Table 2, together with the experimental conditions and the refined cell dimensions. The crystal structure was determined in the space group R $\bar{3}$ , and details will be given elsewhere (Huminicki and Hawthorne, 2002).

#### INFRARED SPECTROSCOPY

Experimental methods are identical to those reported by Roberts *et al.* (1994). The spectrum (Fig. 3) shows a broad absorption at  $\sim 3300 \text{ cm}^{-1}$  and a sharp weaker absorption at  $1663 \text{ cm}^{-1}$ , indicating the presence of (H<sub>2</sub>O) in the structure; the sharp absorptions at 3447 and possibly 3403  $\text{cm}^{-1}$  are compatible with the presence of (OH) in the structure.

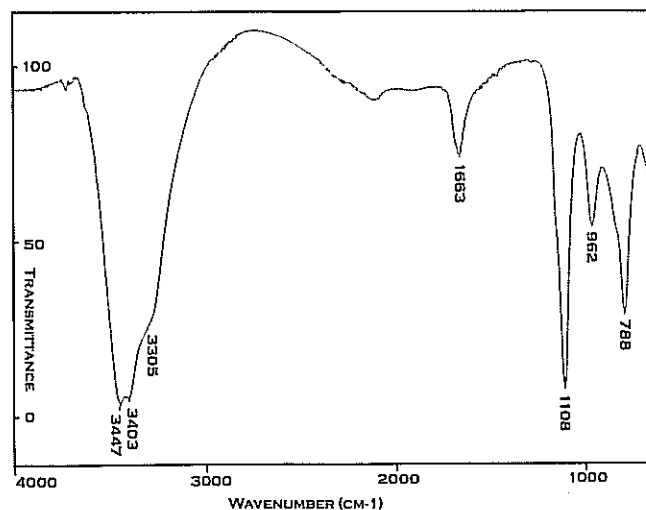


Figure 3. The infrared-absorption spectrum of nikischerite.

#### ASSOCIATED MINERALS

Both spherical aggregates and thin seams occur on or in a brownish clay matrix containing small grains of pyrite, occasional pyrrhotite and/or minor siderite and black cronstedtite. There are also heavily weathered samples of nikischerite perched on crystals of vivianite, but these samples were found several years ago in a different part of the mine, and were not observed *in situ*.

#### RELATED MINERALS

Nikischerite, ideally  $\text{NaFe}_6^{2+}\text{Al}_3(\text{SO}_4)_2(\text{OH})_{18}(\text{H}_2\text{O})_{12}$ , is the Fe<sup>3+</sup> analog of shigaite, ideally  $\text{NaMn}_6^{2+}\text{Al}_3(\text{SO}_4)_2(\text{OH})_{18}(\text{H}_2\text{O})_{12}$  (Cooper and Hawthorne, 1999), and motukoreaite, ideally  $\text{NaMg}_6\text{Al}_3(\text{SO}_4)_2(\text{OH})_{18}(\text{H}_2\text{O})_{12}$  (Rius and Plana, 1986). These three minerals are part of a large family of minerals and industrially important synthetic compounds that consist of positively charged  $[(M^{2+}, M^{3+})_n(\text{OH})_{2n}]$  sheets between which are intercalated both simple and complex anions in order to produce electroneutrality in the structure. The  $[M_n(\text{OH})_{2n}]$  sheet resembles that in brucite,  $\text{Mg}(\text{OH})_2$ , and the positive charge on the sheet is produced by substitution of trivalent cations (e.g., Fe<sup>3+</sup>, Al, Cr<sup>3+</sup>) for some of the divalent cations (Fe<sup>2+</sup>, Mn<sup>2+</sup>, Mg) while maintaining complete occupancy of the octahedrally coordinated sites within the sheet. Thus meixnerite, ideally  $\text{Mg}_6\text{Al}_2(\text{OH})_{18}(\text{H}_2\text{O})_4$ , is the simplest basic structure, and the minerals of the shigaite, hydrotalcite and manasseite groups are stuffed-interlayer derivatives.


#### ACKNOWLEDGMENTS

We thank Tony Nikischer (Excalibur Mineral Company) for bringing this mineral to our attention and supplying us with (ugly) specimens and information on its occurrence, and E. Moffat (Canadian Conservation Institute, Ottawa) for the infrared spectrum. This work was supported by a Canada Research Chair and Major Installation, Major Equipment, Major Facilities Access and Research Grants to FCH from the Natural Sciences and Engineering Research Council of Canada.

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