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THE CRYSTAL STRUCTURE OF NIKISCHERITE, $NaFe^{2+}_6Al_3(SO_4)_2(OH)_{18}(H_2O)_{12}$, A MINERAL OF THE SHIGAITE GROUP

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ABSTRACT

The crystal structure of nikischerite, $NaFe^{2+}_6Al_3(SO_4)_2(OH)_{18}(H_2O)_{12}$, rhombohedral, *a* 9.347(1), *c* 33.000(7) Å, *V* 2497(3) Å^3, *Z* = 3, $R\bar{3}$, has been refined to an *R* index of 6.4% using 444 observed reflections measured with Mo*K*α X-radiation. The structure of nikischerite consists of planar $[AlFe^{2+}(OH)_6]$ sheets of octahedra that are intercalated with $(Na\{H_2O\}_6)$ octahedra, (SO_4) tetrahedra and (H_2O) groups, all units being linked by hydrogen bonds. Nikischerite is isostructural with shigaite, $NaMn^{2+}_6Al_3(SO_4)_2(OH)_{18}(H_2O)_{12}$, and motukoreaite, ideally $NaMg_6Al_3(SO_4)_2(OH)_{18}(H_2O)_{12}$.

Keywords: nikischerite, crystal structure, chemical formula, hydrogen bonding, shigaite, motukoreaite.

SOMMAIRE

Nous avons affiné la structure de la nikischerite, $NaFe^{2+}_6Al_3(SO_4)_2(OH)_{18}(H_2O)_{12}$, rhomboédrique, *a* 9.347(1), *c* 33.000(7) Å, *V* 2497(3) Å^3, *Z* = 3, $R\bar{3}$, jusqu'à un résidu *R* de 6.4% en utilisant 444 réflexions observées, mesurées avec rayonnement Mo*K*α. La structure est faite de feuillets planaires d'octaèdres $[AlFe^{2+}(OH)_6]$ intercalés avec des octaèdres $(Na\{H_2O\}_6)$, des tétraèdres (SO_4) et des groupes (H_2O), toutes ces unités étant liées par liaisons hydrogène. La nikischerite possède la même structure que la shigaïte, $NaMn^{2+}_6Al_3(SO_4)_2(OH)_{18}(H_2O)_{12}$, et la motukoréaïte, dont la formule idéale est $NaMg_6Al_3(SO_4)_2(OH)_{18}(H_2O)_{12}$.

(Traduit par la Rédaction)

Mots-clés: nikischerite, structure cristalline, formule chimique, liaisons hydrogène, shigaïte, motukoréaïte.

INTRODUCTION

Nikischerite is a sulfate mineral discovered at the Huanuni tin mine, Dalence Province, Oruro Department, Bolivia, and recently described by Huminicki *et al.* (2003). The chemical composition, ideally $NaFe^{2+}_6Al_3(SO_4)_2(OH)_{18}(H_2O)_{12}$, rhombohedral symmetry and cell dimensions indicate that nikischerite is isostructural with shigaite, ideally $NaMn^{2+}_6Al_3(SO_4)_2(OH)_{18}(H_2O)_{12}$ (Cooper & Hawthorne 1996), and motukoreaite, ideally $NaMg_6Al_3(SO_4)_2(OH)_{18}(H_2O)_{12}$ (Rius & Plana 1986). As part of our current general interest in sheet structures (Cooper & Hawthorne 1996, Hawthorne & Schindler 2000, Hawthorne & Sokolova 2002, Hawthorne *et al*. 2002), we have refined the crystal structure of nikischerite and report the results here.

EXPERIMENTAL

X-ray data collection

The material used in this work is from the Huanuni tin mine, Dalence Province, Oruro Department, Bolivia, and was obtained from Mr. Tony Nikischer. The crystal used in the measurement of the X-ray intensity data, an irregular fragment 0.12 × 0.14 × 0.20 mm, was mounted on a Siemens *P*4 automated four-circle diffractometer equipped with a SMART 1K CCD detector and Mo*K*α X-radiation. A total of 13291 reflections over the range $3 \le 2\theta \le 60°$ was collected according to the procedure described by Cooper & Hawthorne (2001) using 0.5° framewidths (diffraction spots were large and misshapen) and 120 s frames; this

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total is well in excess of the number of reflections in the Ewald sphere, and afforded considerable redundancy. The unit-cell dimensions (Table 1) were refined by least-squares using the positions of 1273 reflections with $I > 10\ \sigma I$. The data were corrected for absorption using SADABS, reducing R(int) to 4.5%. Reflections were corrected for Lorentz, polarization and background effects, and then reduced to structure factors; of the 1622 unique reflections, 644 were classed as observed ($|F_o| > 4\sigma F$) (essentially no data were observed above 40° 2θ).

Chemical analysis

The crystal used in the X-ray intensity-data collection was mounted in a plastic disk, polished, carbon-coated and analyzed. Electron-microprobe analysis was done on a CAMECA SX–50 electron microprobe in wavelength-dispersion mode. Beam conditions for all elements were 15 kV, beam current of 20 nA, and a spot diameter of 5 μm. Counting times for all element peak and background determinations were 20 s and 10 s, respectively. The analytical data were reduced and corrected using the (φρz) method (Pouchou & Pichoir 1984, 1985). The crystals were analyzed with the following standards: albite (Na), fayalite (Fe), kyanite (Al) and anhydrite (S). The chemical composition given in Table 2 is the mean of eighteen determinations. The unit formula was calculated on the basis of 38 anions assuming 18 (OH) groups and 12 H_2O groups, as derived from the refined structure.

Crystal-Structure Refinement

All calculations were done with the SHELXTL PC (Plus) system of programs; R indices are of the form given in Table 1. The atom coordinates for all non-hydrogen atoms in shigaite (Cooper & Hawthorne 1996) were used to initiate the refinement. Full-matrix least-squares refinement of all variables with anisotropic-displacement parameters for all atoms converged to an R index of 6.4%. Final positions of the atoms and displacement factors are given in Table 3, and selected interatomic distances and angles are given in Table 4. Observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 1. MISCELLANEOUS INFORMATION FOR NIKISCHERITE

a (Å)	9.347(1)	crystal size (mm)	0.12 x 0.14 x 0.20
c	33.000(7)	radiation	Mo$K\alpha$
V (Å^3)	2497(3)	No. of reflections	13291
α (°)	90	No. in Ewald sphere	7621
β	90	No. unique reflections	1622
γ	120	No. $\|F_o\| > 4\sigma F$	444
Sp. Gr.	$R\bar{3}$	R_{merge} %	4.5
Z	3	R_1 ($\|F_o\| > 4\sigma$) %	6.4
D_{meas} * (g/cm^3)	2.32(2)	wR_2 (F_o^2) %	6.7
D_{calc} (g/cm^3)	2.3		

$R = \Sigma(|F_o|-|F_c|) / \Sigma|F_o|$

$wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{½}$, $w = 1 / \sigma F_o^2$

Description of the Structure

The structure of nikischerite, Na Fe^{2+}_6 Al_3 $(SO_4)_2$ $(OH)_{18}$ $(H_2O)_{12}$, is isostructural with that of shigaite, Na Mn^{2+}_6 Al_3 $(SO_4)_2$ $(OH)_{18}$ $(H_2O)_{12}$ (Cooper & Hawthorne 1996). The <*S*–O> distance of 1.51(2) Å in nikischerite (Table 4) is in accord with the grand <*S*–O> distance of 1.473 Å for all well-refined sulfate minerals (Hawthorne *et al.* 2000). There is one unique *Fe* site that is occupied by Fe, and the <*Fe*–OH> distance of 2.14 Å (Table 4) shows the Fe to be divalent. There are two distinct *Al* sites, *Al*(1) and *Al*(2), each coordinated by six OH anions in an octahedral arrangement. The unit formula derived from the electron-microprobe analysis (Table 2) shows an excess of 0.55 Fe *apfu* over that required to fill the *Fe* site. There is a possibility that this excess of Fe is in the trivalent state and occurs at the *Al*(1) or *Al*(2) sites (or both). However, both the <Al–OH> distances, 1.91 and 1.92 Å (Table 4), and the final equivalent isotropic-displacement parameters (Table 3) indicate the *Al*(1) and *Al*(2) sites to be occupied only by Al. Hence the excess Fe present in the unit formula of Table 2 is presumably an artifact of the instability of this mineral in the beam of the electron microprobe.

The $Fe\phi_6$ octahedra (ϕ: unspecified anion) form a dioctahedral sheet similar to that in gibbsite, and the Al atoms in shigaite occupy the remaining octahedra in the sheet: $[Al\ Fe^{2+}\ (OH)_6]^{1+}$ (Fig. 1). Interstitial Na is coordinated by six (H_2O) groups in an octahedral arrangement. The hydrogen atoms were not resolved in this study, but by analogy with shigaite (Cooper & Hawthorne 1996), the interstitial species form a sheet of composition $\{Na\ (H_2O)_6\ \{H_2O\}_6\ (SO_4)_2\}$ (Fig. 2) that is linked by a network of hydrogen bonds, accounting for the perfect {001} cleavage in nikischerite.

Related structures

Nikisherite, Na Fe^{2+}_6 Al_3 $(SO_4)_2$ $(OH)_{18}$ $(H_2O)_{12}$, is the Fe^{2+} analogue of shigaite, Na Mn^{2+}_6 Al_3 $(SO_4)_2$ $(OH)_{18}$ $(H_2O)_{12}$ (Peacor *et al.* 1985, Cooper & Hawthorne

TABLE 2. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA* (*apfu*) FOR NIKISCHERITE

SO_3	13.54	S	1.83
Al_2O_3	14.35	Al	3.04
FeO	43.59	Fe^{2+}	6.55
Na_2O	2.43	Na	0.85
H_2O_{calc}	(35.06)	OH	18
Total	102.97	H_2O	12

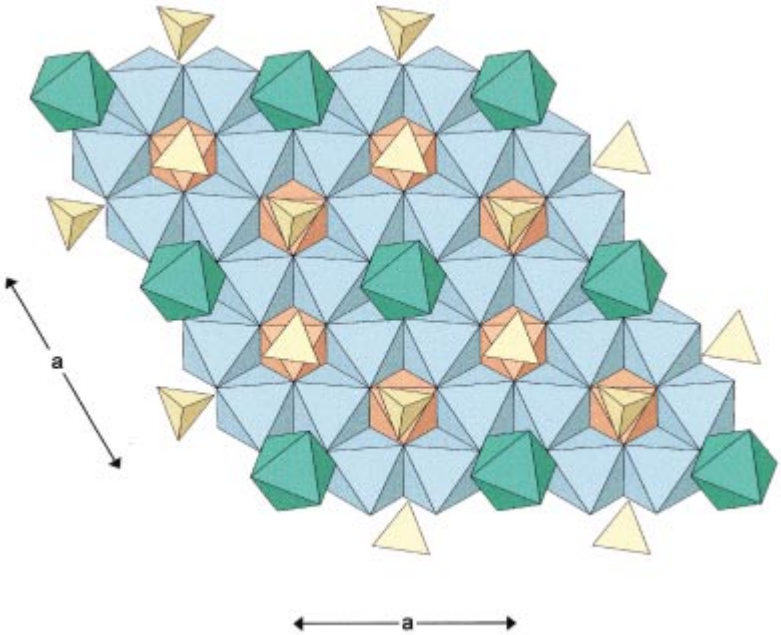

FIG. 1. The structural unit in nikischerite projected down [001]; $Fe^{2+}\phi_6$ octahedra are shown in blue, $Al\phi_6$ octahedra are shown in orange, $Na\phi_6$ octahedra are shown in green, and SO_4 tetrahedra are shown in yellow.

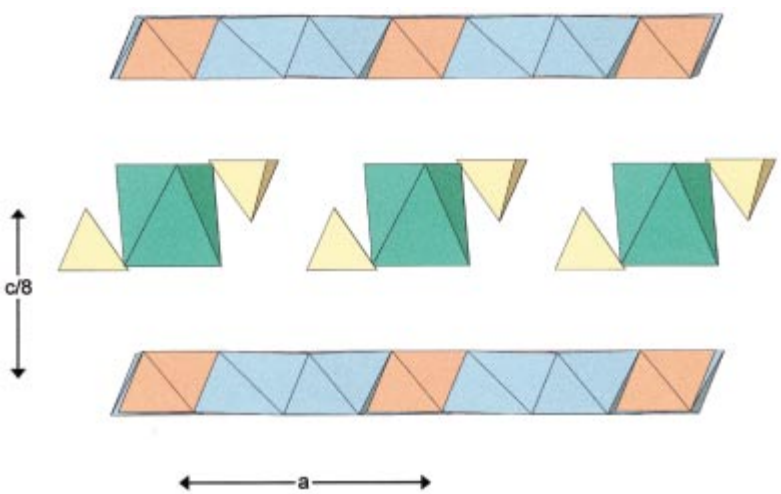

FIG. 2. The crystal structure of nikischerite projected onto (010); legend as in Figure 1.

1996), and motukoreaite, $Na_{0.6}$ $(Al_{3.4}\,Mg_{5.6})$ $(SO_4)_{1.3}$ $(CO_3)_{0.7}$ $(OH)_{18}$ $(H_2O)_{12}$, ideally Na Mg_6 Al_3 $(SO_4)_2$ $(OH)_{18}$ $(H_2O)_{12}$, an important phase in altered submarine basalts (Rodgers *et al.* 1977, Zamarreño *et al.* 1989).

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TABLE 3. ATOM POSITIONS AND DISPLACEMENT FACTORS FOR NIKISCHERITE

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Fe	–0.0007(4)	0.3341(4)	0.16683(7)	0.020(2)	0.020(2)	0.024(1)	0.001(2)	0.001(2)	0.010(2)	0.022(2)
Al(1)	0	0	0.1651(4)	0.017(3)	0.017(3)	0.042(8)	0	0	0.009(2)	0.026(4)
Al(2)	1/3	2/3	1/6	0.023(6)	0.023(6)	0.015(11)	0	0	0.012(3)	0.020(6)
Na	0	0	0	0.052(10)	0.052(10)	0.046(17)	0	0	0.026(5)	0.050(9)
S	2/3	1/3	0.0383(3)	0.034(3)	0.034(3)	0.035(6)	0	0	0.017(2)	0.034(3)
O(1)	1/3	2/3	0.0069(7)	0.057(11)	0.057(11)	0.001(20)	0	0	0.026(6)	0.038(10)
O(2)	0.603(2)	0.160(2)	0.0543(4)	0.084(13)	0.021(8)	0.031(9)	0.001(6)	0.004(8)	0.019(8)	0.049(8)
OH(1)	0.565(2)	0.132(2)	0.1379(4)	0.024(9)	0.018(8)	0.019(8)	–0.003(7)	–0.014(7)	0.008(7)	0.021(7)
OH(2)	0.203(2)	0.101(2)	0.1351(4)	0.024(9)	0.036(9)	0.023(10)	0.001(8)	–0.004(8)	0.022(8)	0.025(7)
OH(3)	0.231(2)	0.467(2)	0.1357(4)	0.025(9)	0.014(8)	0.035(10)	–0.003(7)	0.001(8)	0.015(7)	0.023(7)
OW(1)	0.127(2)	0.425(2)	0.0564(5)	0.052(11)	0.052(11)	0.071(12)	0.013(9)	0.005(9)	0.032(9)	0.056(9)
OW(2)	0.212(2)	0.178(2)	0.0505(5)	0.045(11)	0.051(10)	0.067(12)	0.011(10)	0.007(9)	0.014(9)	0.059(9)

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN NIKISCHERITE

Fe–OH(1)a	2.13(2)		Al(1)–OH(1)a	x3	1.91(2)
Fe–OH(1)b	2.10(2)		Al(1)–OH(2)	x3	1.92(2)
Fe–OH(2)b	2.16(2)		<Al(1)–OH>		1.91
Fe–OH(2)c	2.15(2)				
Fe–OH(3)	2.14(1)		Al(2)–OH(3)	x6	1.92(1)
Fe–OH(3)c	2.16(1)				
<Fe–OH>	2.14		Na–OW(2)	x6	2.49(2)
S–O(1)d	1.49(3)				
S–O(2)	x3 1.51(2)				
<S–O>	1.51				

a: 2/3–*x*, 1/3–*y*, 1/3–*z*; b: –*y*, *x*–*y*, *z*; c: 2/3+*y*–1, 1/3+*y*–*x*, 1/3–*z*; d: 1–*x*, 1–*y*, –*z*.

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