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SUGAKIITE, $Cu(Fe,Ni)_8S_8$, A NEW MINERAL SPECIES FROM HOKKAIDO, JAPAN

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Abstract

Sugakiite is found in the interstices among grains of olivine in the Horoman peridotite massif, Hokkaido, Japan. The mean analytical data (and range) for the mineral, as determined by electron-probe micro-analysis (EPMA), are Cu: 6.95 (6.21–7.91), Fe: 43.27 (42.75–44.03), Ni: 16.10 (15.25–17.02), Co: 0.18 (0.10–0.28), S: 33.04 (32.66–33.61), for a total of 99.54 (98.63–100.80) wt%. The empirical formula is $Cu(Fe,Ni)_8S_8$. Crystallographic data for the mineral were acquired by X-ray single-crystal (precession) and powder (Gandolfi) diffraction methods. They reveal a tetragonal symmetry, space group $P4_2/mnm$, a 10.566 Å, c 9.749 Å, V 1088.4 Å^3, and $Z = 4$. The mineral is a product of high-temperature metasomatic adjustments after peridotite crystallization, and corresponds to $CuFe_6Ni_2S_8$ synthesized at 850°C by the dry method. Sugakiite is named in honor of Asahiko Sugaki (b. 1923), of the University of Tohoku, specialist in phase equilibria in sulfide systems.

Keywords: sugakiite, Cu–Fe–Ni sulfide, unknown mineral X, unknown mineral Z, metasomatic adjustments, Horoman peridotite massif, Japan.

Sommaire

La sugakiïte a été découverte dans les interstices parmi les grains d'olivine du massif péridotitique de Horoman, Hokkaido, au Japon. Les données analytiques et les intervalles entre maximum et minimum, tels que déterminés par analyses avec une microsonde électronique, sont: Cu: 6.95 (6.21–7.91), Fe: 43.27 (42.75–44.03), Ni: 16.10 (15.25–17.02), Co: 0.18 (0.10–0.28), S: 33.04 (32.66–33.61), pour un total de 99.54 (98.63–100.80)% (base pondérale). La formule empirique est $Cu(Fe,Ni)_8S_8$. Les données cristallographiques ont été acquises par précession d'un monocristal et par diffraction sur poudre (méthode de Gandolfi). Elles révèlent une symétrie tétragonale, groupe spatial $P4_2/mnm$, a 10.566 Å, c 9.749 Å, V 1088.4 Å^3, et $Z = 4$. Le minéral résulterait d'ajustements métasomatiques à température élevée suite à la cristallisation de la péridotite. Il correspond au composé $CuFe_6Ni_2S_8$ synthésisé à 850°C à sec. La sugakiïte est nommée en l'honneur de Asahiko Sugaki (né en 1923), de l'Université de Tohoku, spécialiste en équilibres de phases des systèmes sulfurés.

(Traduit par la Rédaction)

Mots-clés: sugakiïte, nouvelle espèce minérale, sulfure de Cu–Fe–Ni, minéral méconnu X, minéral méconnu Z, ajustements métasomatiques, massif péridotitique de Horoman, Japon.

Introduction

During the study of sulfide minerals associated with ultramafic rocks, some ore minerals were discovered: Ni-bearing pyrrhotite and isocubanite in ultramafic xenolith from Ichinome-gata, Akita Prefecture, Japan (Kitakaze *et al.* 1999), and magnetite, pentlandite, troilite, heazlewoodite, bornite, talnakhite, native copper and unknown minerals (X, Y and Z) in lherzolite from the Horoman peridotite massif, Samani-cho, Samani-gun, Hokkaido, Japan (Kitakaze 1998, 2006). The chemical compositions of the unknown minerals X $[Fe,Ni,Co,Cu)_9S_8]$, Y $[Cu(Fe,Ni)_8S_8]$ and Z $[Cu_2(Fe,Ni)_7S_8]$ were already reported (Kitakaze 1998, 2006), but without their crystallographic and optical properties. The minerals X, Y and Z were not reported or observed in synthetic experiments in the system Cu–Fe–Ni–S (Peregoedova *et al.* 1995, Peregoedova & Ohnenstetter 2002, Raghavan 2004). Regarding the mineral Y, $Cu(Fe,Ni)_8S_8$, the crystallographic and optical properties are here reported as a new mineral, sugakiite.

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Occurrence

Sulfide aggregates are composed of sugakiite, the unknown minerals X and Z, and native copper in lherzolite of the Horoman peridotite massif. The grains are anhedral, 0.05–0.1 mm across, filling interstices of olivine, clinopyroxene and orthopyroxene aggregates in the lherzolite.

The sugakiite is intimately associated with minerals X and Z (Figs. 1A, B), and in some cases, is associated with native copper, bornite and talnakhite, which are exsolution products of *Iss* in the system Cu–Fe–S (Figs. 1C, D). Sugakiite and mineral Z commonly occur as lamellae along the cleavage of mineral X, which is thought to be formed after the crystallization of the lherzolite (Figs. 1A, B). Therefore, sugakiite is produced during a lower-temperature re-equilibration and formed later than mineral X.

Appearance and Physical Properties

The macroscopic appearance of sugakiite reveals an alloy with reddish yellow color and a metallic luster. Sugakiite has the following physical properties: micro-indentation hardness: VHN_{50} in the range 130–170 (mean 145) kg/mm^2, brittle tensile strength, no observed cleavage, and uneven fracture. Its density could not be measured, because of its small grain-size. The calculated density is 4.71 g/cm^3, with an empirical formula $Cu(Fe_6Ni_2)_8S_8$ and Z = 4.

Optical Properties

Under reflected light, the mineral is a creamy-white in color with a reddish tint, but without internal reflections. Pleochroism is not observed, but there is very weak anisotropy (dark gray to faint light gray). The polished surface of sugakiite is easily tarnished to a brownish gray color in air after 72 h. The reflectance values in air are 25.6–31.9% (436 nm), 29.9–36.1% (497 nm), 33.2–39.1% (543 nm), 36.1–41.5% (586 nm) and 39.3–44.3% (648 nm). The reflectance in oil was not measured.

Chemical Data

Analysis of the chemical composition of sugakiite was performed by electron-microprobe micro-analysis (JEOL JXA 8800, wavelength-dispersion mode, 20 kV, 10 nA, beam diameter of 2 μm). The standards used in the analysis are natural chalcopyrite (Cu$K\alpha$, Fe$K\alpha$ and S$K\alpha$), synthetic NiS (Ni$K\alpha$), and synthetic CoS (Co$K\alpha$). Silver was found to be lower than the detection limit (0.1 wt%). The analytical results are given in Table 1. Comparison of the atomic proportions in sugakiite with those of minerals X, Z, and pentlandite from the Horoman peridotite massif are shown in Figure 2. The difference in the composition of these minerals is clarified in this figure. It is possible that the mineral exhibits a limited solid-solution in terms of Cu content, present over an interval of 0.75 to 0.97 *apfu*. Accordingly, the simplified formula is $Cu(Fe,Ni)_8S_8$.

Crystallography

Grains of sugakiite were selected from the polished surface under a binocular microscope; one grain was used for the single-crystal study, and the other for the powder-diffraction study. Single-crystal X-ray studies were carried out using the precession method and provided the following data; tetragonal symmetry with space group $P4_2/mnm$, *a* 10.566(5) Å, *c* 9.749(8) Å, *V* 1008.4(14) $Å^3$ and Z = 4. X-ray powder-diffraction (XRD) data (Gandolfi camera, Cu$K\alpha$) are presented in Table 2 along with data for synthetic $CuFe_6Ni_2S_8$. The cell dimensions were determined from the powder-diffraction data. Diffraction planes (*hkl*) were determined from the precession photographs.

Synthetic sugakiite, $CuFe_6Ni_2S_8$, was synthesized by the evacuated silica glass-tube method at 850°C, using pure Cu, Fe and Ni metals and sulfur. The optical properties and X-ray powder data of the synthetic product are in good accordance with those determined for naturally occurring sugakiite.

Name

The name honors Emeritus Professor Asahiko Sugaki (b. 1923), of Tohoku University, Sendai, Japan, an economic geologist and sulfide mineralogist; he is mainly known for his studies of phase relation in sulfide systems.

This naming of this new mineral as sugakiite was approved by the committee for New Minerals and Mineral Names of the International Mineralogical Association (IMA #2005–033). The type material is deposited at the Tohoku University Museum.

Relation to Other Species

The chemical composition of sugakiite is similar to that of pentlandite, but the Cu content of pentlandite is normally less than 1 wt%, and pentlandite is cubic, whereas sugakiite is tetragonal. Sugakiite corresponds to the ideal composition $CuFe_6Ni_2S_8$ (Table 2), synthesized using the evacuated-glass-tube method at 850°C. However, Peregoedova & Ohnenstetter (2002) did not find sugakiite in a phase equilibrium study of the system Cu–Fe–Ni–S at 860°C, but rather found a continuous solid-solution series between *Iss* and $(Ni,Fe)_3S_2$ at a constant S content of 47 at.%. Sugakiite has a distinct composition with respect to the solid-solution range observed in that study. Accordingly, the mineral is determined to be stable at temperatures lower than 860°C.

TABLE 1. REPRESENTATIVE CHEMICAL COMPOSITIONS OF SUGAKIITE FROM THE HOROMAN PERIDOTITE MASSIF, HOKKAIDO, JAPAN

	1	2	3	4	5	6	7	8	Average	σ
Cu wt%	7.91	6.21	6.58	6.95	7.20	7.43	6.74	6.88	6.99	0.73
Fe	43.23	43.65	43.74	44.03	42.94	43.03	42.75	42.75	43.27	0.34
Ni	15.25	17.02	16.71	15.98	15.95	15.78	16.19	15.93	16.10	0.48
Co	0.10	0.13	0.16	0.28	0.21	0.16	0.19	0.12	0.17	0.01
S	32.70	33.39	33.61	33.24	32.87	32.87	32.66	32.95	33.04	0.18
Total	99.19	100.40	100.80	100.48	99.17	99.27	98.53	98.63	99.57	0.40
Cu at.%	5.71	4.42	4.66	4.95	5.19	5.35	4.89	4.98	5.02	0.52
Fe	35.51	35.32	35.24	35.65	35.23	35.28	35.29	35.20	35.34	0.22
Ni	11.92	13.10	12.81	12.31	12.45	12.31	12.72	12.48	12.51	0.40
Co	0.08	0.10	0.12	0.21	0.16	0.12	0.15	0.09	0.13	0.01
S	46.78	47.06	47.17	46.88	46.97	46.94	46.96	47.25	47.00	0.33
Cu *apfu*	0.97	0.75	0.79	0.84	0.88	0.91	0.83	0.85	0.85	0.09
Fe	6.04	6.00	5.99	6.06	5.99	6.00	6.00	5.98	6.01	0.04
Ni	2.03	2.23	2.18	2.09	2.12	2.09	2.16	2.12	2.13	0.07
Co	0.01	0.02	0.02	0.04	0.03	0.02	0.03	0.02	0.02	0.00
S	7.95	8.00	8.02	7.97	7.98	7.98	7.98	8.03	7.99	0.06

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR SUGAKIITE AND A RELATED PRODUCT OF SYNTHESIS

Sugakiite			Synthetic material		
I	*d*(obs) Å	*d*(calc) Å	*I*	*d*(obs) Å	*hkl*
74	3.061	3.105	70	3.065	103
32	2.975	2.979	30	2.978	113
30	2.93	2.931	25	2.930	320
14	2.804	2.806	15	2.805	321
16	2.683	2.677	15	2.685	213
33	2.641	2.641	35	2.642	400
17	2.519	2.511	15	2.52	322
17	2.432	2.437	15	2.439	004
19	2.391	2.388	19	2.392	303
23	2.315	2.317	25	2.315	114
18	2.222	2.218	20	2.224	332
100	2.072	2.072	100	2.072	510
17	2.047	2.050	17	2.051	403
16	2.032	2.027	16	2.034	511
19	2.004	2.004	19	2.004	304
20	1.977	1.977	20	1.978	333
38	1.962	1.962	40	1.964	520
42	1.954	1.950	40	1.953	005
22	1.936	1.939	25	1.937	432
83	1.804	1.802	85	1.804	215
85	1.793	1.791	85	1.795	404
14	1.761	1.761	13	1.762	600
14	1.737	1.737	13	1.738	610
15	1.711	1.710	15	1.712	611
15	1.617	1.619	15	1.612	443
Unit-cell parameters	*a* (Å)	10.566(5)		10.569(7)	
	c (Å)	9.749(8)		9.751(9)	

The synthetic material has the composition $CuFe_6Ni_2S_8$.

A copper-bearing pentlandite from the Talnakh mine, in Russia, containing 5.8 wt% Cu, 42.7 wt% Fe, 15.3 wt% Ni and 36.2 wt% S, was described by Mitenkov *et al.* (1970); however, no crystal data were reported. The chemical composition of sugakiite is very similar to that of their material. Sugakiite may thus be present at the Talnakh mine.

Sugakiite has a composition similar to that of unknowns X and Z; however, XRD powder patterns for the three minerals are different. Mineral X is tetragonal with a different space, group than that of sugakiite. Mineral Z is tetragonal, and its space group is the same as that of sugakiite, but the XRD pattern and cell dimensions are distinctly different (A. Kitakaze, unpubl. data). Therefore, sugakiite is determined to be a different species than minerals X and Z; the compositions in Figure 2 are distinctly separate, and solid solutions between these minerals are not observed.

Argentopentlandite, $Ag(Fe,Ni)_8S_9$, has a similar composition to sugakiite, where Ag is dominant, replacing Cu in the chemical formula of sugakiite. However, sugakiite is tetragonal, whereas argentopentlandite is cubic.

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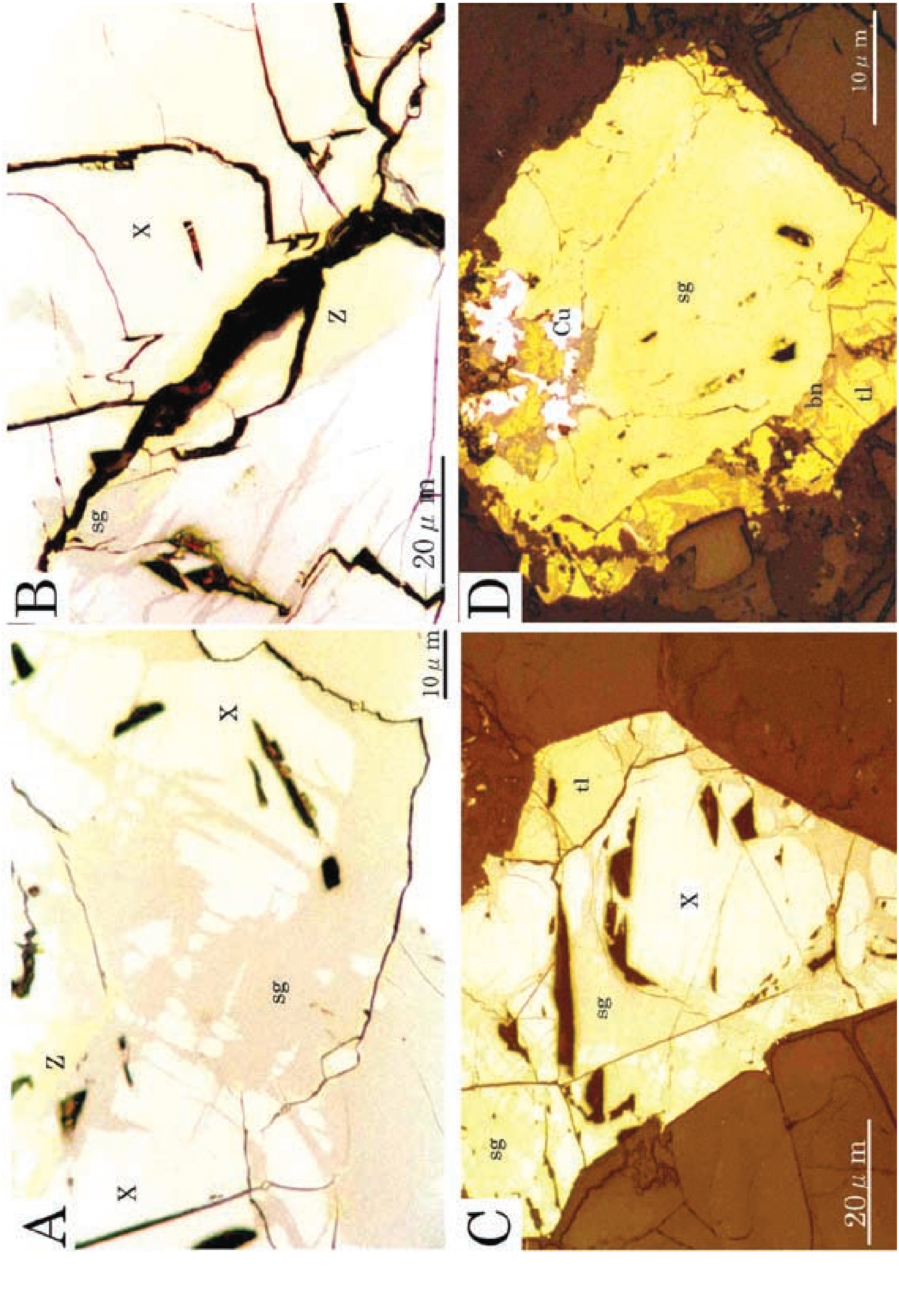
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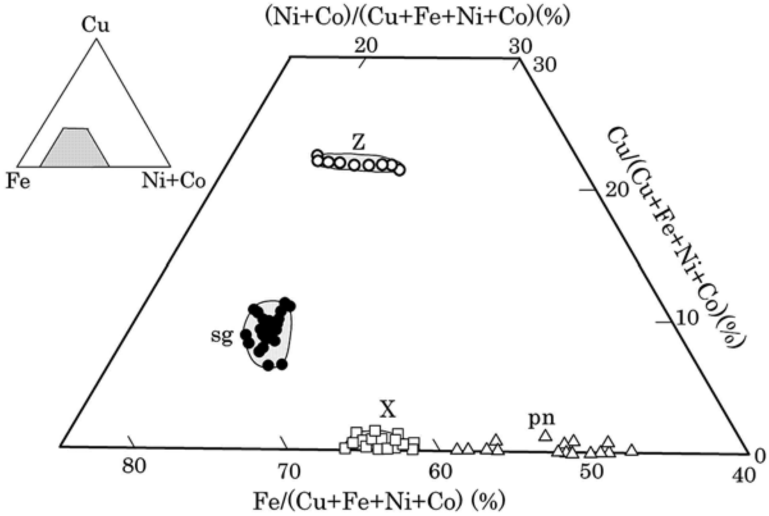

FIG. 2. Compositions of sugakiite (sg), unknown minerals X [$(Fe,Ni,Co,Cu)_9S_8$] and Z [$Cu_2(Fe,Ni)_7S_8$], and pentlandite (pn), plotted according to atomic ratio in terms of Cu – Fe – (Ni + Co).

FIG. 1. Photomicrographs of sugakiite from the type locality, the Horoman peridotite massif, in Hokkaido, Japan. A, B. Sugakiite (sg) intimately associated with lamellae along the cleavage of mineral X and mineral Z. C. Sugakiite in association with mineral X and talnakhite. D. Sugakiite associated with bornite (bn), talnakhite (td) and native copper (Cu).

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