Horomanite, $(Fe,Ni,Co,Cu)_9S_8$, and samaniite, $Cu_2(Fe,Ni)_7S_8$, new mineral species from the Horoman peridotite massif, Hokkaido, Japan

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Horomanite and samaniite are found in the interstices among grains of silicate minerals in lherzolite from the Horoman peridotite massif, Samani-cho, Hokkaido, Japan. The mean analytical data for the horomanite, as determined by electron-probe micro-analysis (EPMA), are Cu: 0.43, Fe: 41.82, Ni: 23.76, Co: 0.52 and S: 33.29 for a total of 99.82 wt%. The empirical formula is $(Fe_{5.77}Ni_{3.12}Co_{0.07}Cu_{0.05})_{\Sigma 9.01}S_{8.00}$. Crystallographic data for the horomanite acquired by X-ray single-crystal (precession) and powder (Gandolfi) diffraction methods. They revealed a tetragonal symmetry, space group *P*4/*mmm*, a = 8.707 Å, c = 10.439 Å, V = 791.4 Å^3, and Z = 4.

The mean chemical composition of samaniite obtained by EPMA is Cu: 16.90, Fe: 34.60, Ni: 15.48, Co: 0.16, and S: 32.87 for a total of 100.01 wt%. The empirical formula is $Cu_{2.08}(Fe_{4.84}Ni_{2.06}Co_{0.02})_{\Sigma 6.92}S_{8.00}$. The crystallographic data for samaniite, which were obtained by X-ray single-crystal and powder-diffraction methods, are tetragonal symmetry, space group $P4_2/mnm$, a = 10.089, c = 10.402Å, V = 1058.9Å3, and Z = 4.

Keywords: Horomanite $(Fe,Ni,Co,Cu)_9S_8$, Samaniite $Cu_2(Fe,Ni)_7S_8$, Sugakiite, Horoman peridotite massif, Cu-Fe-Ni sulfide

INTRODUCTION

During the study of sulfide minerals associated with ultramafic rock, some ore minerals were discovered; Ni-bearing pyrrhotite and isocubanite in ultramafic xenoliths from the Ichinome-gata, Akita Prefecture, Japan (Kitakaze et al., 1999), and magnetite, pentlandite, troilite, heazlewoodite, bornite, talnakhite, 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 of 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 and Ohnenstetter, 2002; Raghavan, 2004). Mineral Y was described as a new mineral and named sugakiite by (Kitakaze, 2008). Regarding the mineral X $[(Fe,Ni,Co,Cu)_9S_8]$ and mineral Z $[Cu_2(Fe,Ni)_7S_8]$, the crystallographic and optical properties are here reported as new minerals, horomanite and samaniite, respectively.

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OCCURRENCE

Sulfide aggregates are composed of horomanite, samaniite, sugakiite and 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 horomanite is intimately associated with sugakiite and/or samaniite (Figs. 1A–1D), and in some cases, is associated with copper, bornite and talnakhite, which are exsolution products of *Iss* (solid solution between isocubanite and mooihoekite at high temperature) in the system Cu-Fe-S. Samaniite and sugakiite sometimes occur as lamellae in horomanite (Figs. 1A–1C).

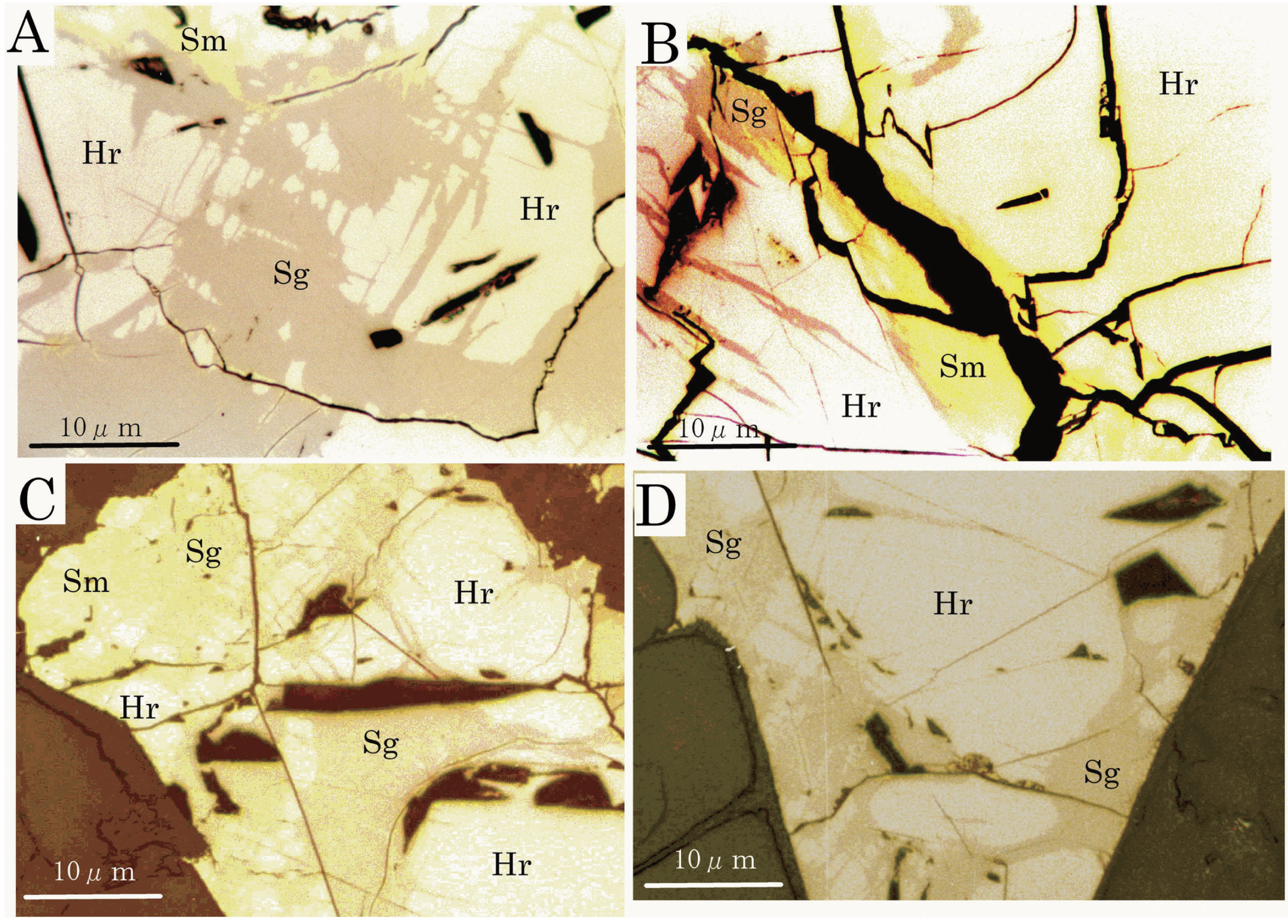

Figure 1. Photomicrographs of horomanite (Hr), and samaniite (Sm). (A) intimately associated with sugakiite (Sg), (B) lamellae of samaniite and sugakiite in horomanite, (C) horomanite in association with samaniite and sugakiite, (D) granular form of horomanite in sugakiite.

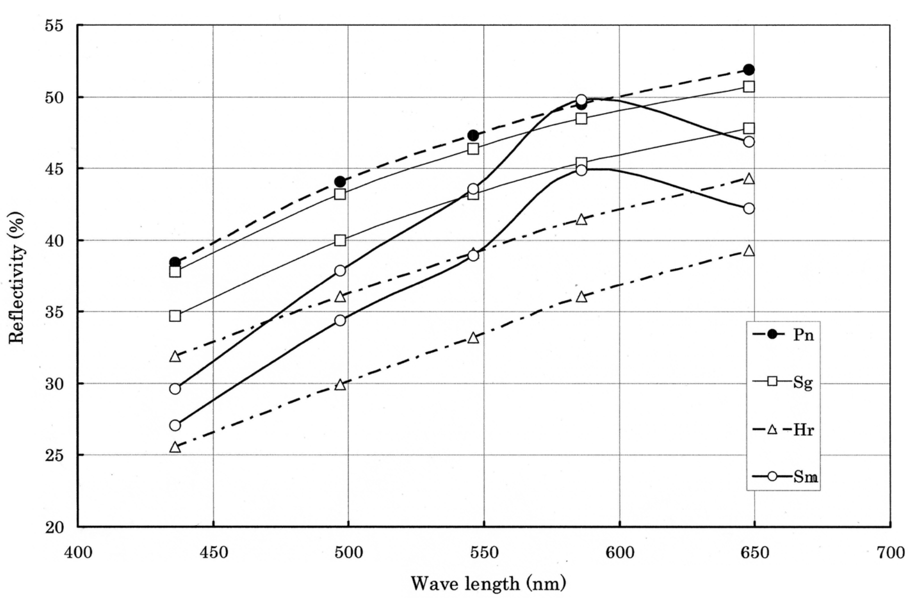

Figure 2. Reflectance spectra of horomanite (Hr), samaniite (Sm), sugakiite (Sg) and pentlandite (Pn) from the Horoman peridotite massif.

Table 1. Representative chemical compositions of horomanite from the Horoman peridotite massif

	1	2	3	4	5	6	7	8	9	10	11	12	13
Weight %													
Cu	0.80	0.14	0.18	0.89	0.56	0.51	0.69	0.56	0.10	0.20	0.27	0.29	0.78
Fe	43.77	43.61	42.89	42.34	42.17	42.43	41.76	41.86	42.20	41.12	41.19	40.89	40.80
Ni	21.31	22.32	22.42	22.71	23.07	23.38	23.64	24.00	24.18	24.27	24.37	24.73	24.94
Co	0.44	0.44	0.83	0.43	0.53	0.50	0.51	0.52	0.63	0.39	0.41	0.62	0.36
S	33.27	33.50	33.43	33.05	32.99	33.49	33.58	33.31	33.70	33.19	33.06	33.20	33.29
Total	99.59	100.01	99.75	99.42	99.32	100.31	100.18	100.25	100.81	99.17	99.30	99.73	100.17
Atomic %													
Cu	0.57	0.10	0.13	0.64	0.40	0.36	0.49	0.40	0.07	0.14	0.19	0.20	0.56
Fe	35.55	35.24	34.75	34.51	34.40	34.24	33.73	33.84	33.87	33.55	33.60	33.22	33.02
Ni	16.47	17.16	17.28	17.61	17.91	17.95	18.16	18.45	18.46	18.84	18.91	19.11	19.20
Co	0.34	0.34	0.64	0.33	0.41	0.38	0.39	0.40	0.48	0.30	0.32	0.48	0.28
S	47.08	47.16	47.20	46.91	46.88	47.07	47.23	46.91	47.12	47.17	46.98	46.99	46.94
Atomic ratio ($\Sigma=17$)													
Cu	0.10	0.02	0.02	0.11	0.07	0.06	0.08	0.07	0.01	0.02	0.03	0.03	0.10
Fe	6.04	5.99	5.91	5.87	5.85	5.82	5.73	5.75	5.76	5.70	5.71	5.65	5.61
Ni	2.80	2.92	2.94	2.99	3.04	3.05	3.09	3.14	3.14	3.20	3.22	3.25	3.26
Co	0.06	0.06	0.11	0.06	0.07	0.07	0.07	0.07	0.08	0.05	0.05	0.08	0.05
S	8.00	8.02	8.02	7.98	7.97	8.00	8.03	7.97	8.01	8.02	7.99	7.99	7.98

Table 2. Representative chemical compositions of samaniite from the Horoman peridotite massif

	1	2	3	4	5	6	7	8	9	10	Average	σ
Weight %												
Cu	16.37	16.78	16.88	17.31	16.08	17.44	17.80	16.41	17.33	16.63	16.90	0.52
Fe	32.81	33.15	33.55	33.90	34.41	34.81	35.00	35.72	35.80	36.85	34.60	1.22
Ni	17.90	17.04	16.51	15.75	16.12	15.09	14.01	14.96	13.92	13.47	15.48	1.37
Co	0.14	0.15	0.15	0.16	0.19	0.11	0.19	0.14	0.13	0.28	0.16	0.05
S	32.82	32.84	32.80	32.78	32.93	32.97	32.75	32.95	32.90	32.93	32.87	0.07
Total	100.04	99.96	99.89	99.90	99.74	100.42	99.75	100.18	100.08	100.16	100.01	0.20
Atomic %												
Cu	11.84	12.14	12.22	12.54	11.64	12.56	12.91	11.83	12.52	11.99	12.20	0.38
Fe	27.00	27.29	27.65	27.94	28.34	28.53	28.88	29.31	29.41	30.23	28.46	0.97
Ni	14.02	13.35	12.94	12.35	12.63	11.76	11.00	11.68	10.88	10.52	12.11	1.09
Co	0.11	0.12	0.12	0.12	0.15	0.09	0.15	0.11	0.10	0.22	0.13	0.03
S	47.04	47.09	47.07	47.05	47.24	47.06	47.06	47.08	47.09	47.05	47.08	0.06
Atomic Ratio ($\Sigma=17$)												
Cu	2.01	2.06	2.08	2.13	1.98	2.14	2.19	2.01	2.13	2.04	2.08	0.07
Fe	4.59	4.64	4.70	4.75	4.82	4.85	4.91	4.98	5.00	5.14	4.84	0.16
Ni	2.38	2.27	2.20	2.10	2.15	2.00	1.87	1.99	1.85	1.79	2.06	0.18
Co	0.02	0.02	0.02	0.02	0.03	0.02	0.03	0.02	0.02	0.04	0.02	0.01
S	8.00	8.01	8.00	8.00	8.03	8.00	8.00	8.00	8.01	8.00	8.00	0.01

APPEARANCE AND PHYSICAL PROPERTIES

Horomanite

The macroscopic appearance of horomanite reveals an alloy with a white in color with a yellowish tint, and a metallic luster. Horomanite has the following physical properties: micro-indentation hardness: VHN_{50} in the range 125–145 (mean 135) kg/mm^2, brittle tensile strength, observed cleavage, and uneven fracture. Its density could not be measured, because of its small grain-size. The calculated density is 6.44 g/cm^3, with an ideal formula $Fe_6Ni_3S_8$ and $Z=4$.

Table 1. (Continued)

	14	15	Average	σ
Weight %				
Cu	0.21	0.30	0.43	0.26
Fe	40.31	39.97	41.82	1.08
Ni	25.30	25.75	23.76	1.19
Co	0.41	0.77	0.52	0.13
S	33.05	33.26	33.29	0.21
Total	99.28	100.05	99.82	0.46
Atomic %				
Cu	0.15	0.21	0.31	0.19
Fe	32.90	32.39	33.92	0.85
Ni	19.64	19.85	18.33	0.92
Co	0.32	0.59	0.40	0.10
S	46.99	46.95	47.04	0.11
Atomic ratio (Σ=17)				
Cu	0.03	0.04	0.05	0.03
Fe	5.59	5.51	5.77	0.14
Ni	3.34	3.37	3.12	0.16
Co	0.05	0.10	0.07	0.02
S	7.99	7.98	8.00	0.02

Samaniite

The macroscopic appearance of samaniite revel an alloy with a yellowish white in color and a metallic luster. Its 23 micro-indentation hardness is VHN_{50} in the range 120–140 (mean 130) kg/mm^3. The fracture is uneven and tenacity is brittle. No cleavage is observed. The density could not be measured, because of its small grain-size. The calculated density is 4.89 g/cm^3, with an ideal formula, $Cu_2Fe_5Ni_2S_8$ and Z = 4.

OPTICAL PROPERTIES

Horomanite

Under reflected light, the mineral is a white in color with a yellowish tint, but without internal reflections. Pleochroism is very weak (white with yellowish tint to white). There is weak anisotropy (dark-gray to slightly light-gray). The reflectance values in air are 34.7–37.8% (436 nm), 40.0–43.2% (497 nm), 43.2–46.4% (543 nm), 45.4–48.5% (586 nm) and 47.8–50.7% (648 nm). The reflectance in oil was not measured.

Samaniite

Samaniite is a yellowish white in color, but without internal reflection under reflected light. Pleochroism is weak (yellowish white to pale yellowish white). There is weak anisotropy (dark gray to light gray). The reflectance values in air are 27.1–29.6% (436 nm), 34.4–37.9% (497 nm), 38.9–43.6% (543 nm), 44.9–49.8% (586 nm) and 42.2–46.9% (648 nm). The reflectance in oil was not measured.

Reflectance spectra of horomanite, samaniite, pentlandite and sugakiite from the Horoman peridotite massif are shown in Figure 2.

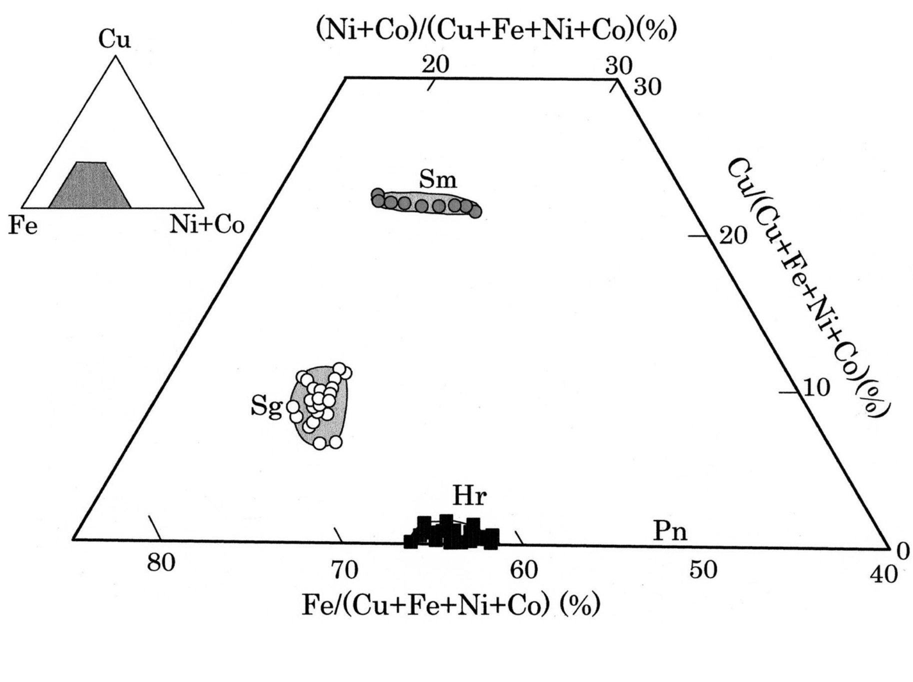

Figure 3. Compositions for horomanite (Hr), samaniite (Sm), sugakiite (Sg) and pentlandite (Pn), plotted according to atomic ratio in terms of Cu-Fe-(Ni + Co).

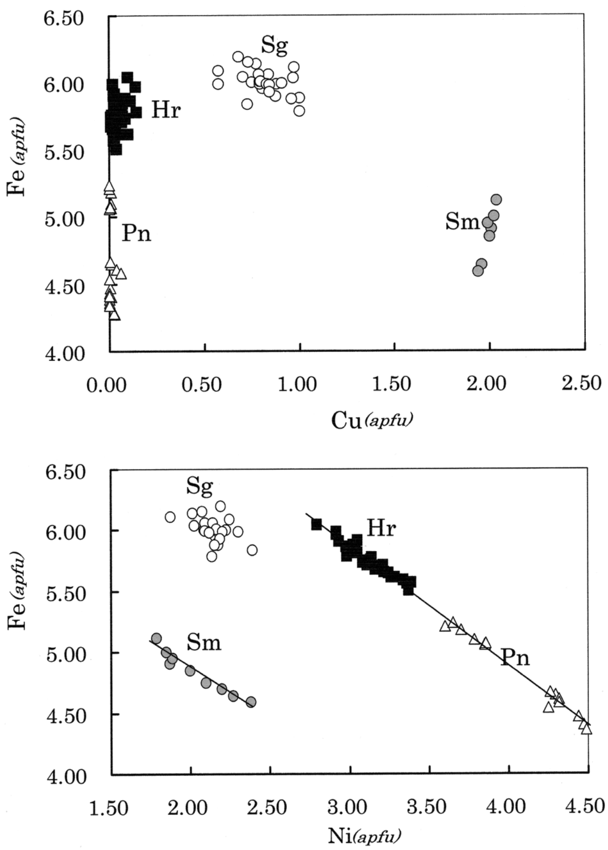

Figure 4. Cu-Fe and Ni-Fe plots for horomanite (Hr), samaniite (Sm), sugakiite (Sg) and pentlandite (Pn) from the Horoman peridotite massif.

Table 3. X-ray powder data for horomanite from the Horoman peridotite massif

I	*d*(obs)	*d*(calc)	*hkl*
10	6.160	6.157	110
5	5.225	5.220	002
2	4.479	4.477	102
2	4.351	4.354	200
4	3.983	9.981	112
3	3.121	3.121	212
100	3.080	3.078	220
32	2.955	2.953	221
5	2.752	2.753	310
5	2.536	2.537	302
6	2.435	2.435	312
2	2.354	2.353	321
1	2.191	2.192	322
5	2.176	2.177	400
4	2.132	2.131	401
3	2.051	2.052	330
4	2.014	2.014	331
25	1.984	1.984	323
4	1.957	1.958	412
51	1.947	1.947	420
5	1.914	1.914	421
60	1.825	1.824	422
54	1.805	1.805	413
2	1.685	1.685	511
1	1.598	1.598	521

Unit cell parameters: a = 8.707, c = 10.439Å

CHEMICAL DATA

Analysis of the chemical composition of horomanite and samaniite was performed by electron-microprobe microanalysis (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-$K\alpha$). Ag was found to be lower than the detection limit (0.1 wt%). No other element with atomic number >10 was detected.

The analytical results for horomanite and samaniite are given in Tables 1 and 2, respectively.

The mean analytical data for the horomanite are Cu: 0.43, Fe: 41.82, Ni: 23.76, Co: 0.52 and S: 33.29, for a total of 99.82 wt%. The empirical formula is $(Fe_{5.77}Ni_{3.12}Co_{0.07}Cu_{0.05})_{\Sigma 9.01}S_{8.00}$.

The chemical composition of samaniite are Cu: 16.90, Fe: 34.60, Ni: 15.48, Co: 0.16, and S: 32.87 for a total of 100.01 wt%. The empirical formula is $Cu_{2.08}(Fe_{4.84}Ni_{2.06}Co_{0.02})_{\Sigma 6.92}S_{8.00}$.

Compositional ranges of horomanite, samaniite, sugakiite and pentlandite from the Horoman peridotite massif sown in Figure 3. The difference in the composition of these mineral is clarified in this figure. It is possible that horomanite exhibits a limited a solid-solution in term of Fe content, preset over an internal of 5.51 to 6.04 *apfu* (Fig. 4). This trend is very similar to that of pentlandite. Cu and Co content of horomanite are lower than 0.08 and 0.11 *apfu*, respectively. Accordingly, the simplified formula for horomanite is $(Fe,Ni,Co,Cu)_9S_8$.

Samaniite also exhibits a limited solid-solution in terms of Fe content (4.59 to 5.14 *apfu*) that decreases with increasing Ni content. This fact indicates Fe that is substituted by Ni. Cu content of samaniite is 1.98 - 2.19 *apfu* and their variation is smaller than that of Fe and Ni contents (Fig. 4). Accordingly, the simplified formula of samaniite is $Cu_2(Fe,Ni)_7S_8$.

CRYSTALLOGRAPHY

Grains of horomanite and samaniite 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 for both minerals were carried out using the precession method. X-ray powder-diffraction (XRD) data (Gandolfi camera, Cu*K*α) of horomanite and samaniite are presented in Tables 3 and 4, respectively. Their cell dimensions were determined from the powder-diffraction data. Diffraction planes (*hkl*) were determined from the precession photographs.

Horomanite is tetragonal, space group *P*4/*mmm* with a = 8.707(1), c = 10.439(6) Å, V = 791.4(4) Å^3 and Z = 4 (Table 3). Whereas samaniite is tetragonal space group is $P4_2/mnm$ with a = 10.089(1), c = 10.402(8)Å, V = 1088.4 (14)Å^3 and Z = 4 (Table 4).

Table 4. X-ray powder data for samaniite from the Horoman peridotite massif

I	*d* (obs)	*d* (calc)	*hkl*
15	5.880	5.883	111
2	3.621	3.621	202
1	3.375	3.374	221
3	3.278	3.279	103
2	3.191	3.190	310
100	3.118	3.119	113
20	3.050	3.050	311
5	2.703	2.702	321
1	2.205	2.205	421
3	2.178	2.178	323
2	2.070	2.070	422
5	1.981	1.981	501
5	1.961	1.961	333
4	1.944	1.944	511
25	1.873	1.874	520
50	1.844	1.844	521
5	1.707	1.707	531
3	1.638	1.638	611
45	1.595	1.595	620

Unit cell parameters: a = 10.089, c = 10.402Å

NAME

The names, horomanite and samaniite, were derived from the locality, Horoman in Samani-cho, Samani-gun, Hokkaido, Japan. The mineral name and mineral data have been approved by the commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA #2007-037 and IMA #2007-038). The type materials are deposited at the Tohoku University Museum.

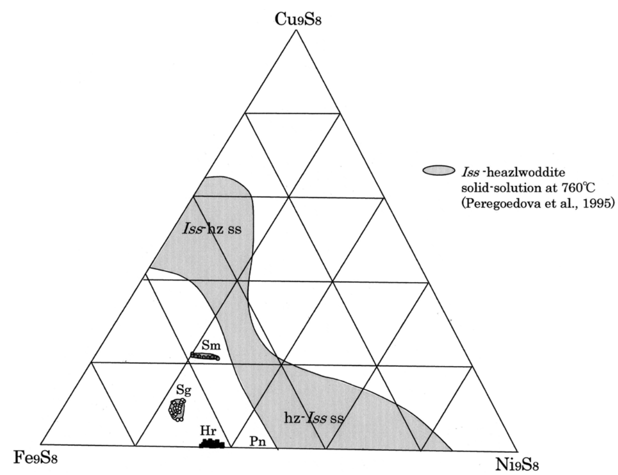

Figure 5. Compositions of horomanite (Hr), samaniite (Sm) and sugakiite (Sg), compared with the *Iss*-heazlewoodie solid-solution at 760 °C after Peregoedova et al.(1995).

Table 5. Comparison of crystallographic data, physical properties and optical properties of pentlandite, horomanite, sugakiite and samaniite from the Horoman peridotite massif

	Pentlandite	Horomanite	Sugakiite	Samaniite
	Cubic	Tetragonal	Tetragonal	Tetragonal
	$Fm3m$	$P4/mmm$	$P4_2/mnm$	$P4_2/mnm$
	$Fe_{4.5}Ni_{4.5}S_8$	$(Fe,Ni,Co,Cu)_9S_8$	$Cu(Fe,Ni)_8S_8$	$Cu_2(Fe,Ni)_7S_8$
a	10.038(1)	8.707(1)	10.566(5)	10.089(1)
c		10.439(6)	9.749(8)	10.402(1)
V	1011.4(3)	791.4(4)	1088.4(14)	1058.9(2)
c/a		1.1994	0.9227	1.0306
Density	5.07	6.45	4.76	4.89
Hardness	140-150	125-145	130-170	120-140
Refrectance				
436 nm	38.4	34.7-37.8	25.6-31.9	27.1-29.6
497 nm	44.1	40.0-43.2	29.9-36.1	34.4-37.9
546 nm	47.3	43.2-46.4	33.2-39.1	38.9-43.6
586 nm	49.5	45.4-48.5	36.1-41.5	44.9-49.8
648 nm	51.9	47.8-50.7	39.3-44.3	42.2-46.9

RELATION TO OTHER SPECIES

The chemical composition of horomanite is similar to that of Fe–rich pentlandite. The Fe/Ni ratio, of horomanite is more than 1.5, but that of pentlandite is normally less than 1.5 (Misra and Fleet, 1973), and pentlandite is cubic, whereas horomanite is tetragonal. X–ray powder patterns of both minerals are distinctly different. Therefore, horomanite and pentlandite are different species.

Horomanite and sugakiite are tetragonal, but horomanite is different in space group from sugakiite. The Cu content of horomanite is less than 0.80 wt%, whereas that of sugakiite ranges from 6.21 to 7.91 wt%. Therefore, horomanite and sugakiite are different species.

The chemical composition of samaniite is similar to that of pentlandite, but the Cu content of pentlandite is normally less than 0.80 wt%, but samaniite contained up to 16.08 wt% Cu. Samaniite is tetragonal, whereas pentlandite is cubic. These X–ray powder patterns are distinctly different.

Samaniite has a composition similar to that of sugakiite. But the Cu content of samaniite ranges from 16.08 to 17.33 wt%, whereas sugakiite has lower Cu content (6.21 to 7.91 wt% Cu). Samaniite is tetragonal, and its space group is the same of sugakiite, but the XRD pattern and cell dimensions are distinctly different. Therefore, samaniite is determined to be a different mineral species than sugakiite.

The horomanite, samaniite and sugakiite corresponds to the ideal compositions $Fe_6Ni_3S_8$, $Cu_2Fe_5Ni_2S_8$ and $CuFe_6Ni_2S_8$. However, Peregoedova and Ohnenstetter (2002) did not find horomanite, samaniite and sugakiite in a phase equilibrium study of the system Cu–Fe–Ni–S at 760 °C, but rather found a continuous solid–solution series between *Iss* and $(Ni,Fe)_3S_2$ at a constant S content of 47.0 at% (Fig. 5). Horomanite, samaniite and sugakiite have distinct composition with respect to the solid–solution range observed in that study (Fig. 5). Accordingly, the minerals are determined to be stable at temperatures lower than 760 °C.

Table 5 demonstrates the comparison of crystallographic data, physical properties and optical properties of horomanite, samaniite, pentlandite and sugakiite from the Horoman peridotite massif.

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

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