

## Rambergite from the Hirogawara mine, Urayama, Chichibu City, Saitama Prefecture, Japan

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**Abstract** Rambergite is found in fissures of manganese ore at the Hirogawara mine, Urayama, Chichibu City, Saitama Prefecture, Japan. It occurs as pale orange prismatic hexagonal crystals up to 0.5 mm long and thin crusts composed of very fine acicular crystals. Electron microprobe analyses gave no other elements except Mn and S, and the empirical formula is  $Mn_{1.01}S_{0.99}$  on the basis of total ions=2. Lattice parameters obtained with a Gandolfi camera are  $a=3.972$ ,  $c=6.426$  Å and  $V=87.80$  Å<sup>3</sup>. Some of prismatic crystals of rambergite have changed to greenish black alabandite. Rambergite formed as a later stage hydrothermal mineral under low temperature condition.

**Key words:** rambergite, alabandite, Hirogawara mine

### Introduction

Rambergite is a hexagonal dimorph of alabandite, the cubic MnS. Although an occurrence of a hexagonal MnS mineral was first reported by Baron and Debyser (1957) from clay beds in the sediments at Landsortsdjupet in the Baltic Sea, there are no detailed description on this mineral after that. They indicated hexagonal MnS to be  $\beta$ -phase (now  $\gamma$ -phase according to the later nomenclature). In 1995 Kalinowski and Eriksson proposed rambergite as a new mineral found from tremolite skarn at Garpenberg Norra, Dalarna, Sweden to the CNMMN of IMA. After the approval, a complete description has not been published but the mineral name, rambergite was released by Kalinowski (1996). In 1997 Böttcher and Huckriede also reported  $\gamma$ -MnS (rambergite) from anoxic laminated sediments in the central Gotland Deep (Baltic Sea). During the study on manganese minerals from the Hirogawara mine, Urayama, Chichibu City, Saitama Prefecture, we have found rambergite as orange minute crystals and thin crusts in fissures of manganese ore. The

present paper deals with the first occurrence of this mineral in Japan.

### Occurrence

There are many small-scale manganese deposits in Jurassic accretionary complex around Urayama area in Chichibu City. The Hirogawara mine, where is the most upper reaches of Urayama river, was mined for manganese ore composed of mainly rhodochrosite. The ore specimens collected at the outcrop (Fig. 1) consist of very fine rhodochrosite and quartz in association with caryopilite and kellyite. Rhodochrosite also occurs as many thin veins in the ore. In the thin veins aggregates of minute apatite grains, switzerite-metaswitzerite (Yamada et al., 2003), wiserite, gageite and rambergite are observed. Rambergite occurs as minute crystals up to 0.5 mm long (Fig. 2) and as thin crusts composed of fine acicular crystals (Fig. 3). The crystal is transparent and pale orange in color with vitreous luster and forms typical hemimorphic dihexagonal-pyramidal. In spite of the same forms



Fig. 1. Outcrop of manganese ore deposit at the Hirogawara mine.



Fig. 2. Photomicrograph of rambergite crystal.

greenish black crystals have been replaced by alabandite structure (Fig. 4). Rambergite and/or alabandite often include such Ni-Co-Sb sulfides as siegenite and tučekite.

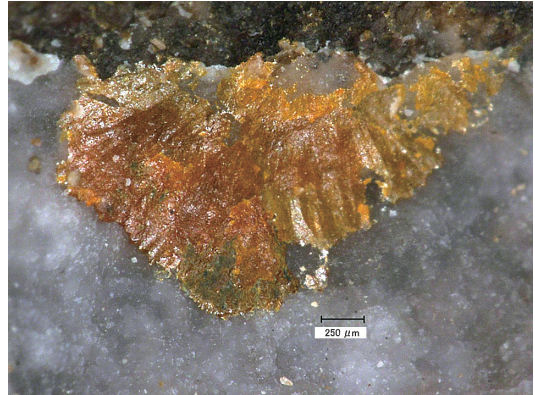


Fig. 3. Photomicrograph of thin crust composed of fine rambergite crystals.

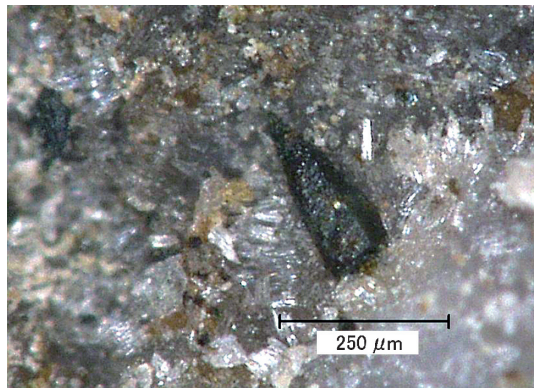


Fig. 4. Photomicrograph of alabandite pseudomorph after rambergite.

### X-ray Crystallography

The X-ray diffraction pattern of rambergite was obtained by using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered Cu- $K\alpha$  radiation. This diffraction pattern is demonstrated with that of rambergite from Sweden (Table 1). The unit cell parameters calculated as hexagonal cell are as follows:  $a=3.972$ ,  $c=6.426$  Å and  $V=87.80$  Å<sup>3</sup>. The parameters are comparable with those of rambergite from Sweden,  $a=3.975$ ,  $c=6.433$  Å and  $V=88.03$  Å<sup>3</sup> (Kalinowski, 1996). The synthetic equivalent of rambergite can be obtained from a reaction of H<sub>2</sub>S gas with MnCl<sub>2</sub> solution (ICDD 40-1289; Martain and Troemel, 1989).

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

<i>h</i>	<i>k</i>	<i>l</i>	1			2		3	
			<i>d</i> (obs.)	<i>d</i> (calc.)	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
1	0	0	3.44	3.44	90	3.445	886	3.449	98
0	0	2	3.21	3.21	95	3.217	715	3.225	100
1	0	1	3.03	3.03	100	3.036	657	3.041	75
1	0	2	2.36	2.35	45	2.350	323	2.354	24
1	1	0	1.986	1.986	65	1.988	819	1.989	98
1	0	3	1.817	1.818	80	1.820	1000	1.823	60
2	0	0	1.720	1.720	12	1.721	180	1.723	9
1	1	2	1.689	1.689	47	1.691	627	1.693	61
2	0	1	1.662	1.661	10	1.663	168	1.665	9
2	0	2	1.517	1.516	8			1.520	2
2	0	3	1.342	1.342	25			1.345	13
2	1	0	1.300	1.300	4			1.303	8
2	1	1	1.275	1.274	5			1.277	8

1: Hirogawara mine, Chichibu, Japan (present study)

2: Garpenberg Norra, Sweden (Kalinowski, 1996)

3: Synthetic MnS (ICDD 40-1289)

Table 2. Chemical composition of rambergite, siegenite and tučekite.

	1	2	3	4	5
Mn	63.44	62.61	2.87	1.15	0.80
Co			26.00	6.10	5.85
Ni			31.57	44.86	46.61
As				0.64	4.27
Sb				22.20	15.87
S	36.29	36.17	38.93	24.84	25.94
Total	99.73	98.78	99.37	99.79	99.34
Total atoms	2	2	7	19	19
Mn	1.01	1.01	0.16	0.21	0.15
Co			1.38	1.06	0.99
Ni			1.68	7.83	7.92
As				0.09	0.57
Sb				1.87	1.30
S	0.99	0.99	3.79	7.94	8.07

1,2: rambergite, 3: siegenite, 4,5: tučekite

### Chemical Composition

Chemical analyses of the present rambergite and associated minerals were carried out using a Link Systems energy dispersive X-ray spectrometer (QX-2000) for Mn, Co, Ni, As, Sb and S (15 kV, 1 nA, 3  $\mu$ m beam diameter). The standard materials used were Mn for Mn, Co for Co, Ni for Ni, InAs for As, InSb for Sb, and pyrite for S,

respectively. Table 2 shows the representative analyses of rambergite, siegenite and tučekite. The empirical formula of the present rambergite is  $\text{Mn}_{1.01}\text{S}_{0.99}$  on the basis of total atoms=2. Although electron microprobe data have not been given for the Swedish rambergite, Kalinowski (1996) described only the empirical formula as  $(\text{Mn}_{0.950}\text{Fe}_{0.030}\text{Sb}_{0.004}\text{Zn}_{0.002}\text{Ag}_{0.002})_{\Sigma 0.988}\text{S}_{1.000}$ . The dark brown to black color of the Swedish ramber-

gite corresponds to its distinct Fe-content. On the contrary, the Hirogawara rambergite indicates pale orange color due to nearly pure MnS. It corresponds to the orange color of the synthetic rambergite (Martain and Troemel, 1989). Both of siegenite and tučekite are characterized by the Co-rich nature.

### Discussion

Although the detailed condition forming rambergite from Sweden has not been reported by Kalinowski (1996), the new mineral proposal data informs that rambergite was formed in late-stage mobilisation during skarn-forming processes under low  $f_{O_2}$  and high  $P_{Mn^{2+}}/P_{S_2}$  conditions (Kalinowski and Eriksson, 1995). Also, Böttcher and Huckriede (1997) reported that  $\gamma$ -MnS (rambergite) occurs in anoxic sea sediments rich in organic matter. The synthetic studies (e.g. Lei et al., 2005) indicated that  $\gamma$ -MnS was crystallized under lower temperature than  $\alpha$ -MnS (alabandite) and that  $\gamma$ -MnS was transformed irreversibly into the stable  $\alpha$ -MnS upon heating. The occurrence of rambergite from the Hirogawara mine supports the above reports, that is, rambergite crystallized under low temperature, but a

part of rambergite transformed to alabandite holding dihexagonal-pyramidal form due to increasing of temperature or other unknown factors.

### References

- Baron, G. and Debyser, J. (1957) Sur la presence dans des vases organiques de la mer Baltique du sulfure manganese b hexagonal. *Comptes rendu de l'Académie des sciences de Paris*, **245**, 1148–1150.
- Böttcher, M. E. and Huckriede, H. (1997) First occurrence and stable isotope composition of authigenic  $\gamma$ -MnS in the central Gotland Deep (Baltic Sea). *Marine Geology*, **137**, 201–205.
- Kalinowski, M. P. and Eriksson, L. (1995) Rambergite. IMA 1995–028.
- Kalinowski, M. P. (1996) Rambergite, a new polymorph of MnS with hexagonal structure. *Geological Förenings i Stockholm Förhandlingar*, **118**, A53–A54.
- Lei, S., Tang, K., Yang, Q., and Zheng, H. (2005) Solvothermal synthesis of metastable  $\gamma$ -MnS hollow spheres and control of their phase. *European Journal of Inorganic Chemistry*, **2005**, 1–5 (Published Online).
- Martain, L. and Troemel, M. (1989) *Institut für Anorganische chemie, Frankfurt, ICDD Grant-in-Aid*.
- Yamada, T., Takizawa, M., and Tange, K. (2003) Meta-switzerite in manganese ore deposit from Urayama, Chichibu City. *Mineralogical Society of Japan, Annual Meeting Abstracts*, **2003**, 198 (in Japanese).