Dufrenoysite and marumoite from the Okoppe Mine, Japan

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Abstract. Dufrenoysite and marumoite (IMA 1998-004) from high sulfidation-type epithermal Cu-Pb-Zn disseminated-massive sulfide deposits of the Okoppe mine, Japan are reported based on their chemical compositions and powder XRD patterns. Marumoite from Okoppe is the second occurrence.

Keywords. Dufrenoysite, marumoite, jordanite, Okoppe mine, high sulfidation type, epithermal

1 Introduction

High sulfidation-type epithermal Cu-Pb-Zn disseminated-massive sulfide deposits of the Okoppe mine are located in Ohma Town, Shimokita-gun, Aomori Prefecture, northern Japan. There are two localities of jordanite in Japan; the Yunosawa mine also in Aomori Prefecture in addition to the Okoppe mine. Tsugaruite and gratonite are observed from the Yunosawa mine, and some of Pb-As-S sulfosalt minerals from the Okoppe mine are here reported. Arsenic is one of characteristic elements enriched in hydrothermal solution in back-arc basin (e.g., Fouquet et al., 1991), which is different from that in oceanic ridges.

2 Occurrence

The deposits of the Okoppe mine are embedded in the altered dacitic to andesitic rocks of the “Green Tuff” of middle to late Miocene age. Argillic alteration of pyrophyllite, kaolinite, sericite and less chlorite is dominated in the deposits whereas propylitic and smectite alteration occurs far from them.

The ores are composed of pyrite, enargite, chalcopyrite, barite and small amounts of jordanite, wurtzite, and covellite. Some of Pb-As-S sulfosalt minerals also occur as acicular crystals of lead-gray color associated with jordanite-barite (J type) or pyrite (P type). Hydrothermal activity here in a back-arc basin (Japan Sea) is characterized by low pH and Ba-, As-, Pb-rich solutions.

Table 1: Chemical compositions for dufrenoysite, marumoite and baumhauerite

	1	1'	2		2'	3	3'	4	4'	5	6
Wt.%											
Pb	55.08	53.75 ~ 57.09	51.82		51.64 ~ 52.09	57.42	57.20	47.5	51.38	47.1	50.92
Ag	0.12	0.03 ~ 0.27	0.13		0 ~ 0.26					1.4	0.44
Tl	0.17	0 ~ 0.36	0.14		0 ~ 0.26			0.8		0.5	0.83
As	20.99	20.15 ~ 21.98	22.75		22.46 ~ 23.12	20.89	20.68	27.9	24.77	26.8	23.42
Sb	0.14	0.04 ~ 0.29	1.37		1.10 ~ 1.64						0.28
S	23.12	22.65 ~ 23.56	23.25		23.06 ~ 23.35	22.55	22.12	24.6	23.85	23.9	23.46
total	99.62		99.46			100.86	100	100.8	100	99.7	99.35
Atomic Proportions											
Pb	14.74		12.42	31.74		15.76	16	10.7	12	10.9	30.91
Ag	0.06		0.06	0.15						0.6	0.51
Tl	0.04		0.04	0.09				0.2		0.1	0.51
As	15.54		15.08	38.54		15.86	16	17.4	16	17.3	39.30
Sb	0.06		0.56	1.42							0.46
S	40		36	92		40	40	36	36	36	92

1; Dufrenoysite from the Okkope mine, Aomori Prefecture.
2; Marumoite from the Okkope mine, Aomori Prefecture.
3; Dufrenoysite from Binntal, Switzerland (Palache et al., 1946).
4; Baumhauerite from Binntal, Switzerland (Pring et al., 1990).
5; Baumhauerite-2a from Binntal, Switzerland (Pring et al., 1990).
6; Marumoite from Binntal, Switzerland (Ozawa, personal communication).

1'; range
2'; range
3'; $Pb_{16}As_{16}S_{40}$
4'; $Pb_{12}As_{16}S_{36}$

Table 2: X-ray powder diffraction data for dufrenoysite

1				2			1				2		
d_{obs}	d_{calc}	*I*	*h k l*	*d*	*I*	*h k l*	d_{obs}	d_{calc}	*I*	*h k l*	*d*	*I*	*h k l*
7.69		9	B				2.405	2.402	10	3 3 1			
7.53	7.54	9	1 1 0	7.50	10	1 1 0	2.346	2.346	30	1 $\underline{10}$ 1	2.36	60	1 $\underline{10}$ 1
7.02	7.01	7	0 2 1				2.310	2.314	10	2 9 0			
6.71	6.72	7	1 2 0	6.81	20	1 2 0	2.262	2.263	15	1 9 $\bar{2}$			
5.81	5.80	7	1 3 0	5.99	10	1 3 0	2.239	2.241	16	3 6 0			
4.98	4.98	12	1 4 0	4.98	20	1 4 0	2.216	2.218	24	3 0 2	2.23	60	3 1 2
4.32	4.31	11	1 5 0				2.164	2.168	18	3 6 $\bar{1}$	2.16	20	2 $\underline{10}$ 0
4.26	4.27	42	1 4 1	4.27	20	1 4 1		2.161		3 6 1			
4.12	4.13	17	0 1 2	4.11	20	0 1 2	2.137	2.138	14	3 7 0			
3.945	3.942	23	2 0 0	3.93	10	2 0 0	2.090	2.091	20	0 0 4	2.09	30	2 $\underline{10}$ 1
3.894	3.897	31	2 1 0				2.066	2.068	44	3 7 1			
3.854		24	B					2.064		0 2 4			
3.805		48	B				2.033	2.035	34	3 8 0	2.03	30	1 1 $\bar{4}$
3.767	3.766	100	1 6 0	3.74	100	1 0 $\bar{2}$	2.027	2.028	27	2 9 $\bar{2}$			
3.681	3.684	23	1 0 2				1.972	1.971	20	4 0 0			
3.576	3.576	30	2 0 $\bar{1}$	3.56	50	2 0 1	1.955		13	B			
3.477		17	B				1.948	1.948	13	4 2 0			
3.437	3.438	21	1 6 $\bar{1}$				1.926	1.925	30	1 4 4			
3.401	3.401	25	1 3 $\bar{2}$	3.40	50	1 3 2	1.921	1.921	33	4 3 0			
3.334	3.330	36	1 7 0				1.907	1.908	16	3 7 $\bar{2}$	1.910	40	4 1 1
3.220	3.215	63	0 8 0	3.21	60	1 4 2		1.906		3 0 3			
3.125	3.125	36	2 4 $\bar{1}$				1.873	1.873	10	3 3 $\bar{3}$			
3.100	3.097	18	1 7 $\bar{1}$				1.855	1.854	15	2 8 3			
3.004	3.007	56	1 5 $\bar{2}$	3.00	90	1 5 2	1.850	1.848	15	2 1 $\bar{4}$			
2.899	2.902	34	2 6 0	2.90	50	2 6 0	1.832	1.831	13	1 6 $\bar{4}$			
2.868	2.861	21	2 1 $\bar{2}$				1.825	1.826	14	1 6 4	1.831	40	3 4 3
2.833	2.841	16	2 1 2					1.824		2 2 4			
2.790	2.791	23	2 2 2	2.80	40	0 0 3	1.808	1.811	13	2 3 $\bar{4}$			
2.763	2.760	30	0 7 2				1.793	1.794	18	3 $\underline{10}$ 1			
2.730	2.729	30	2 3 $\bar{2}$				1.787	1.787	17	3 5 3			
2.698	2.704	58	0 9 1	2.70	80	1 9 0	1.772	1.773	15	1 7 $\bar{4}$			
2.615	2.615	16	3 1 0				1.753	1.753	10	0 8 4			
2.572	2.572	20	0 $\underline{10}$ 0	2.58	10	1 2 3	1.741	1.742	20	3 6 3	1.746	10	3 6 3
2.486	2.491	10	3 1 1					1.741		4 3 2			
2.443	2.445	8	1 $\underline{10}$ 0	2.44	10	1 8 $\bar{2}$	1.703	1.703	14	4 7 $\bar{1}$			

1: Dufrenoysite + "baumhauerite (B)" from Okkope mine. ***a*** 7.885 (1), ***b*** 25.72 (1), ***c*** 8.365 (1) Å, $\boldsymbol{\beta}$ 90.4 (1)°
2: Dufrenoysite from Binntal, Switzerland (ICDD 10-453). ***a*** 7.88, ***b*** 25.85, ***c*** 8.41 Å, $\boldsymbol{\beta}$ 90.5°.

In polished sections, in plane-polarized light, the two minerals (dufrenoysite and marumoite) are weakly bireflectant, weakly pleochroic, and strongly anisotropic similar to jordanite.

Homogenization temperature of fluid inclusions in barite from the mine ranges from 300 to 170°C.

3 Chemical data

Chemical analyses were carried out by means of an electron microprobe using the following standards: synthetic PbS (Pb-Mα), Cu_3AsS_4 (As-Lα), ZnS (S-Kα), $AgBiS_2$ (Ag-Lα), $Cu_{10}Fe_2Sb_{1.4}As_{2.6}S_{13}$ (Sb-Lα) and lorandite (Tl-Lα). The analyses of jordanite give a composition $Pb_{14}(As,Sb)_6S_{23}$. The average of 15 analyses of Pb-As-S sulfosalt minerals associated with jordanite-barite (J type) is: Pb 55.08, Ag 0.12, Tl 0.17, As 20.99, Sb 0.14, S 23.12, total 99.62 wt.%, and those (6 analyses) associated with pyrite (P type) are: Pb 51.82, Ag 0.13, Tl 0.14, As 22.75, Sb 1.37, S 23.25, total 99.46 wt.%, shown in Table 1. The empirical formulae based on S = 5 and S = 92 are: $(Pb_{1.84}Ag_{0.01}Tl_{0.01})_{1.86}(As_{1.94}Sb_{0.01})_{1.95}S_{5.00}$ and $(Pb_{31.74}Ag_{0.15}Tl_{0.09})_{31.98}(As_{38.54}Sb_{1.42})_{39.96}S_{92.00}$, respectively. They can be simplified to $Pb_2As_2S_5$ and $Pb_{32}As_{40}S_{92}$, respectively.

4 X-ray crystallography

Powder XRD patterns for J- and P-type samples (Tables 2 and 3) were obtained but both samples are thought to be a mixture of dufrenoysite and a small amount of "baumhauerite", and that of "baumhauerite" or marumoite (IMA 1998-004) and a small amount of dufrenoysite, respectively. The cell parameters for defrenoysite refined from the data are: $a = 7.885(1)$, $b = 25.72(1)$, $c = 8.365(1)$ Å, and $\beta = 90.4(1)°$.

5 Discussion and conclusion

It is difficult to distinguish the powder XRD patterns of baumhauerite, baumhauerite-2a and marumoite, probably because they can easily form mixtures in the lattice order and a large single crystal is generally very rare. They seem to be complicated mixtures with lattice defects. It is concluded that two Pb-As-S sulfosalt minerals, dufrenoysite and marumoite occur to the exclusion of jordanite in the Okoppe mine, Japan as products of typical hydrothermal activity in a back-arc basin (Japan Sea).

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Reference

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