Pararealgar and Alacranite from the Nishinomaki Mine, Gunma Prefecture, Japan

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Abstract   Pararealgar and alacranite are found in the arsenic ore from the Nishinomaki mine, Gunma Prefecture, Japan. The unit cell parameters calculated by powder X-ray diffraction data are $a=9.925(2)$, $b=9.695(2)$, $c=8.504(2)$ Å, $\beta=97.1(1)°$ for pararealgar, and $a=9.941(2)$, $b=9.398(2)$, $c=8.910(2)$ Å, $\beta=102.0(1)°$ for alacranite. Both minerals are yellow with resinous luster, and often occur as mixture on the surface of realgar. They may be formed secondarily under the exposing of realgar by sunlight.

Key words :   pararealgar, alacranite, realgar, Nishinomaki mine.

Introduction

During the examination of the Sakurai Mineral Collection, we recognized the specimen from the Nishinomaki mine labeled as pararealgar by late Dr. K. Sakurai. As the occurrence of pararealgar has not been known in Japan, we checked it by the powder X-ray diffraction method to confirm whether the label was correct or not. The result of experiment revealed that the examined materials are composed of realgar, pararealgar and alacranite.

Many phases of As_4S_4 or AsS composition are known as realgar, pararealgar, alacranite, and synthetic α-, β-, γ-, χ-AsS (Bonazzi *et al.*, 1995). However, the mineral name has been confused with the corresponding synthetic material. For instance, realgar is α-AsS (Bonazzi *et al.*, 1995; Strunz and Nickel, 2001) or it is β-AsS (Clark, 1970; Roland, 1972).

Pararealgar was firstly described in two realgar specimens from Mount Washington, Vancouver Island and the Gray Rock property, Lillooet district, British Columbia, Canada (Roberts *et al.*, 1980). It was misidentified as orpiment due to its appearance. Thin orange-yellow coating material on museum specimens of realgar was called as γ-phase, and it is able to form by exposing to infrared radiation (Hall, 1966). Now, γ-AsS is rec-ognized as pararealgar (Strunz and Nickel, 2001).

The α-phase associated with pararealgar from the original localities is corresponding to the high-temperature AsS synthesized by Roland (1972). The powder X-ray diffraction data closely resemble alacranite, which was named for the first locality, Mina Alacrán, Pampa Larga, Chile (Clark, 1970), by Popova *et al.* (1986). They reported the data of alacranite as a new mineral from the second locality, the Uson caldera, Kamchatka, Russia. Although they had proposed the ideal chemical formula of alacranite as As_8S_9, Burns and Percival (2001) have determined a new formula, As_4S_4, on the basis of their crystal structure analyses. Consequently, alacranite is considered as trimorphous with pararealgar and realgar.

The present work is for the description of pararealgar and alacranite as the first occurrence in Japan and for the consideration of the geneses of both minerals.

Occurrence

The Nishinomaki mine is one of the famous localities of realgar and orpiment in Japan, and also is known as the original locality of

Fig. 1. Mixture of pararealgar and alacranite (both are yellow) inverted from realgar (orange) in quartz vein (NSM-M30973). Field view: approximately 4×5 cm.

wakabayashilite (Kato *et al.*, 1970). The mine is situated about 30 km west of Takasaki City, Gunma Prefecture. The hydrothermal quartz veins including As-bearing minerals develop in altered Tertiary andesite. The exact collecting date of the examined specimen (NSM-M30973) is unknown, or we are unable to estimate the exposed time by sunlight. In the specimen yellow powdery material with resinous luster covers the aggregates of minute realgar grains associated with quartz (Fig. 1). Although a weak cleavage is rarely observed in grains supposed to be alacranite, it is difficult to distinguish between pararealgar and alacranite to the naked eye.

X-ray Crystallography

We prepared seven yellow fragments collected from different portions of the specimen. The powder X-ray diffraction patterns were obtained using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered Cu $K\alpha$ radiation. In these
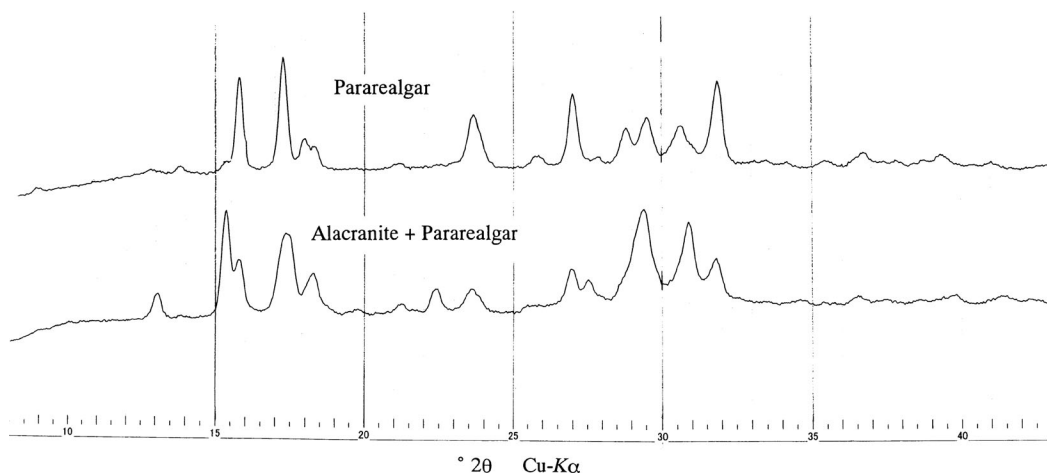

Fig. 2. The powder X-ray diffraction patterns of pararealgar and a mixture of pararealgar and alacranite.

Table 1. X-ray powder diffraction data for pararealgar.

Nishinomaki mine				Mount Washington copper deposit		
I	d_{obs}	d_{calc}	h k l	I	d	h k l
7	9.84	9.85	1 0 0			
2	6.89	6.91	1 1 0			
8	6.37	6.37	0 1 1			
80	5.59	5.59	1 1 $\bar{1}$	91	5.56	1 1 $\bar{1}$
100	5.13	5.13	1 1 1	100	5.14	1 1 1
25	4.93	4.92	2 0 0	29	4.90	2 0 0, 0 2 0
21	4.84	4.85	0 2 0			
3	4.19	4.20	0 2 1			
47	3.75	3.75	1 1 $\bar{2}$	78	3.75	1 1 $\bar{2}$
10	3.45	3.47	1 1 2	27	3.44	1 1 2, 2 2 0, 2 0 $\bar{2}$
		3.45	2 2 0			
		3.42	2 0 $\bar{2}$			
60	3.30	3.30	2 2 $\bar{1}$	50	3.299	2 2 $\bar{1}$
4	3.19	3.18	0 2 2	3	3.184	0 2 2
32	3.10	3.11	3 1 0	33	3.105	2 2 1
		3.10	2 2 1			
40	3.02	3.04	3 1 $\bar{1}$	51	3.025	2 0 2
		3.02	2 0 2			
33	2.92	2.92	1 3 $\bar{1}$	30	2.905	1 3 $\bar{1}$, 2 1 2
		2.89	2 1 2			
70	2.80	2.81	3 1 1	71	2.795	2 2 $\bar{2}$
		2.79	2 2 $\bar{2}$			
5	2.53	2.53	1 1 3, 1 3 $\bar{2}$	18	2.525	2 3 1
		2.52	2 3 1			
12	2.45	2.46	4 0 0	28	2.445	3 0 2
		2.45	3 0 2			
4	2.38	2.39	4 1 0	11	2.377	3 1 2
		2.37	3 1 2			
10	2.29	2.30	3 3 0	30	2.278	2 2 $\bar{3}$
		2.28	1 4 $\bar{1}$, 2 2 $\bar{3}$			
4	2.20	2.21	2 3 2	11	2.208	2 3 2
		2.20	4 2 0			
				2	2.106	1 3 $\bar{3}$, 0 4 2
12	2.07	2.08	1 4 $\bar{2}$, 2 4 1	6	2.069	4 2 1
		2.07	4 2 1, 1 1 $\bar{4}$			
15	2.04	2.04	4 2 $\bar{2}$, 1 3 3	22	2.030	2 0 $\bar{4}$
		2.03	2 0 $\bar{4}$, 1 4 2			
15	1.971	1.974	3 1 3	16	1.976	3 1 3
		1.971	1 1 4			
10	1.865	1.865	4 2 2	11	1.862	3 3 $\bar{3}$
		1.863	3 3 $\bar{3}$			
5	1.745	1.748	2 5 1	6	1.744	2 5 1
		1.743	5 2 1			
12	1.719	1.720	2 3 $\bar{4}$	10	1.710	4 0 $\bar{4}$
10	1.687	1.687	4 3 $\bar{3}$	11	1.682	5 3 0

a=9.925, b=9.695, c=8.504 Å, β=97.1°
This study

JCPDS 33-127
a=9.929, b=9.691, c=8.503 Å, β=97.06°
Roberts *et al.*, 1980

Table 2. X-ray powder diffraction data for alacranite and synthetic α-AsS.

Nishinomaki mine				synthetic a-AsS			alacranite			alacranite	
I	d_{obs}	d_{calc}	h k l	I	d	h k l	I	d	h k l	d_{calc}	h k l
30	6.77	6.76	1 1 0	10	6.76	1 1 0	40	6.89	1 1 0	6.746	1 1 0
100	5.76	5.76	1 1 1̄	80	5.75	1 1 1̄	90	5.91	1 1 1̄	5.751	1 1 1̄
70	5.02	5.01	1 1 1	40	5.01	1 1 1	80	5.11	1 1 1	5.000	1 1 1
38	4.85	4.86	2 0 0	20	4.85	2 0 0				4.863	2 0 0
				20	4.69	0 2 0	30	4.87	0 2 0	4.683	0 2 0
10	4.15	4.14	0 2 1	20	4.15	0 2 1	10	4.25	0 2 1	4.125	0 2 1
23	3.95	3.93	1 1 2̄	70	3.93	1 1 2̄	70	4.05	1 1 2̄	3.927	1 1 2̄
4*	3.44	3.45	1 1 2	10	3.44	1 1 2				3.441	1 1 2
				5	3.39	2 2 0				3.373	2 2 0
37*	3.31	3.32	2 2 1̄	10	3.33	2 2 1̄	30	3.38	2 2 1̄	3.311	2 2 1̄
20	3.19	3.20	0 2 2	80	3.20	0 2 2	50	3.291	0 2 2	3.190	0 2 2
				70	3.08	3 1 1̄				3.086	3 1 1̄
85	3.05	3.07	3 1 0				100	3.064	3 1 0	3.064	3 1 0
				100	3.01	1 3 0				2.973	1 3 0
				30	2.95	2 0 2				2.954	2 0 2
58	2.88	2.88	1 3 1̄, 2 2 2̄				90	2.950	2 2 2̄	2.875	2 2 2̄
				100	2.89	1 3 1̄				2.870	1 3 1̄
38*	2.81	2.82	1 1 3̄	60	2.82	1 1 3̄	20	2.903	1 1 3̄	2.819	1 1 3̄
				10	2.76	3 1 2̄				2.776	3 1 2̄
2	2.74	2.73	3 1 1	10	2.74	3 1 1				2.727	3 1 1
							30	2.707	3 2 1̄**	2.680	3 2 1̄
				30	2.53	1 1 3				2.538	1 1 3
							20	2.606	1 3 2̄	2.532	1 3 2̄
8	2.51	2.50	2 2 2	20	2.50	2 2 2				2.498	2 2 2
				5	2.47	0 2 3				2.468	0 2 3
				10	2.44	4 0 0	20	2.419	4 0 0	2.431	4 0 0
				30	2.39	2 2 3̄				2.377	2 2 3
							20	2.346	0 4 1	2.261	0 4 1
8	2.26	2.26	3 3 1̄							2.258	3 3 1̄
		2.25	3 3 0	20	2.25	3 3 0	10	2.286	3 3 0	2.249	3 3 0
				20	2.21	4 2 1̄				2.191	4 2 1̄
5	2.18	2.18	0 0 4							2.178	0 0 4
				20	2.17	1 1 4̄				2.166	1 1 4̄
				20	2.15	2 0 4̄				2.163	2 0 4̄
							20	2.166	4 2 0	2.158	4 2 0
							30	2.224	1 3 3̄	2.147	1 3 3̄

Table 2. (continued).

Nishinomaki mine				synthetic a-AsS			alacranite			alacranite	
I	d_{obs}	d_{calc}	h k l	I	d	h k l	I	d	h k l	d_{calc}	h k l
				1	2.11	2 4 1̄	20	2.136	0 4 2	2.062	0 4 2
										2.094	2 4 1̄
				5	2.01	1 1 4	20	2.017	4 2 1	2.010	4 2 1
										1.991	1 1 4

C 2/c ?
a=9.94, *b*=9.40, *c*=8.91 Å,
β=102° This study

JCPDS 25-57
C 2/c
a=9.92, *b*=9.48, *c*=8.91 Å,
β=101.83° Roland, 1972

JCPDS 42-537
C 2/c
a=9.89, *b*=9.73, *c*=9.13 Å,
β=101.84° Popova *et al.*, 1986
**: not permitted by space group

C 2/c
a=9.943, *b*=9.366, *c*=8.908 Å,
β=102.007° Burns & Percival, 2001
D-values are calculated by the unit cell.

*: Intensity is enhanced by admixed pararealgar

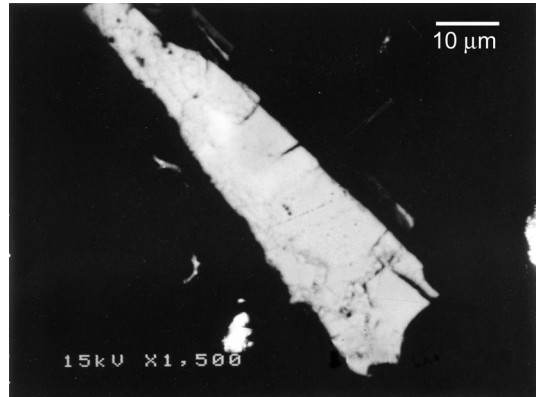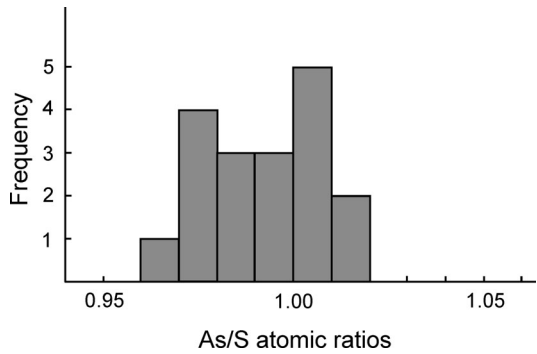
Fig. 3. The Back-scattered Electron Image of a supposed alacranite fragment.

Fig. 4. The frequency of As/S ratio of 18 chemical analyses for As_4S_4-minerals.

Table 3. Chemical composition for As_4S_4.

	Wt.%	Atom %
As	69.60	49.93
S	29.87	50.07
Total	99.47	

patterns three assemblages, 1) pararealgar, 2) pararealgar+realgar, and 3) pararelagar+alacranite were recognized (Fig. 2). Although the powder X-ray diffraction pattern of the present pararealgar resemble that of pararealgar from Mount Washington copper deposit (Roberts *et al.*, 1980) (Table 1), the alacranite studied here differs in the diffraction pattern from the original one from Uzon Caldera, Kamchatka (Popova *et*

al., 1986). The d-spacing in X-ray diffraction pattern of alacranite from Japan is similar to that of the synthetic α-AsS (Roland, 1972) or the calculated d-spacing based on the unit cell parameters determined by Burns and Percival (2001) who solved the crystal structure of alacranite collected from the seafloor around Lihir Island, Papua New Guinea (Table 2). The unit cell parameters of the present pararealgar and alacranite are: $a=9.925(2)$, $b=9.695(2)$, $c=8.504(2)$ Å, $\beta=97.1(1)°$, and $a=9.941(2)$, $b=9.398(2)$, $c=8.910(2)$ Å, $\beta=102.0(1)°$, respectively.

Chemical Composition

Chemical analyses were made using Link Systems energy dispersive X-ray spectrometer (QX-2000) for the specimen of pararelagar+alacranite mixture. In this specimen we analyzed cleavable fragments to be considered as alacranite (Fig. 3). The detected elements are only As and S, and As/S ratio is from 0.97 to 1.02 for eighteen analyses (Fig. 4). The average of the ratio is 0.996. However, the figure is not valid for the chemical composition of alacranite due to the lack of fully characterization. The closest analysis to the average is demonstarated in Table 3.

Consideration on Geneses

According to the experimental result by Roland (1972), α-AsS now corresponding to alacranite inverts to realgar under about 240°C. Namely, he proposed that α-AsS is a high-temperature phase. On the other hand, Migdistov and Bychkov (1998) have reported that alacranite forms at the temperature between 50 and 75°C at Uzon caldera, Kamchatka. In the case of the present specimen, it is considered that the alacranite was formed under low temperature, because of its typical appearance indicating secondary formation. The phase relation between pararealgar and alacranite has been unknown, but it is probable that the both minerals were formed from realgar under the moderate condition such as the ex-

posing by sunlight around room temperature.

The association of alacranite and realgar has been confirmed experimentally (e.g. Roland, 1972), and described as natural occurrences at Uzon caldera (Migdistov and Bychkov, 1998) and at the seafloor around Lihir Island (Burns and Percival, 2001). The present assemblage with alacranite and pararealgar is the second example after the first report from Mina Alacrán by Clark (1970). Therefore, we consider that realgar inverts easily into other two As_4S_4 polymorphs through exposing by sunlight under the moderate conditions as follows; realgar→alacranite→pararealgar.

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