

## Elyite from the Mizuhiki Mine, Fukushima Prefecture, Japan

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**Abstract** Elyite from the Mizuhiki mine, Fukushima Prefecture, is found as fibrous crystal groups in tiny vugs of limonitic ore composed of supergene galena and chalcopyrite. This is the first occurrence of this mineral in Japan. The averaged chemical analysis by EPMA gave PbO 80.49, CuO 6.71, SO<sub>3</sub> 7.70, H<sub>2</sub>O (by difference) 5.10 wt%, yielding the empirical formula Pb<sub>3.99</sub>Cu<sub>0.94</sub>(SO<sub>4</sub>)<sub>1.07</sub>[O<sub>0.73</sub>(OH)<sub>6.28</sub>]<sub>7.01</sub> on the basis of total cations = 6 in anhydrous part. The X-ray single crystal study indicated elyite to be monoclinic  $P2_1/c$  with  $a = 14.244(1)$ ,  $b = 11.536(1)$ ,  $c = 14.656(1)$  Å,  $\beta = 100.45(1)^\circ$ .

**Key words:** elyite, Mizuhiki mine, plumbonacrite, galena.

### Introduction

Elyite is a rare hydrous sulfate of lead and copper, Pb<sub>4</sub>Cu(SO<sub>4</sub>)(OH)<sub>8</sub>, and firstly described from Ward, Nevada, USA, where it was found with langite, serpierite and supergene galena in voids of oxidized sulfide ore (Williams, 1972). Subsequently, the occurrences of elyite have been reported from the Rauris Valley, Austria (Schebesta, 1984), Plombieres, Belgium (De Geyter *et al.*, 1987), Grube Churfurst Ernst, Germany (Stieglitz & Metz, 1989), Badenweiler, Schwarzwald, Germany (Schlomann & Steen, 1990 b) and Freiamt, Schwarzwald, Germany (Schlomann & Steen, 1990 a). During mineralogical survey for old mines in Minami-Aizu area, the third author has recognized violet fibrous mineral on white scaly mineral coating vug walls in limonitic ore from the Mizuhiki mine. The X-ray and chemical studies have proved it to be elyite.

Though Williams (1972) assigned the space group  $P2_1/a$  from rotation and Weissenberg photographs, a few diffraction peaks were indexed contradictorily to the  $a$ -glide plane, i.e. (102), (302), (30 $\bar{2}$ ), (10 $\bar{3}$ ), (50 $\bar{2}$ ) and (50 $\bar{3}$ ).

This paper is for the description of the occurrence of elyite and for the discussion on the crystallography.

### Occurrence

In Minami-Aizu, Fukushima Prefecture and neighboring Kuriyama Village area, Tochigi Prefecture, numerous and small scale ore deposits are developed

along metasomatized limestone which is a constituent of Jurassic accretionary complex intruded by later granitic rocks. Among them the ore deposit of the Mizuhiki mine (N37°42', E139°31'15'), Tateiwa Village, Minami-Aizu, Fukushima Prefecture, is located at about 30 km SW of Aizu-Tajima station, Aizu Railway Co. (Fig. 1). The ore bodies composed of nearly pure galena are lenticular or irregular mass of 1.3 m in average width and 10 to 40 m in length (Fukushima Prefecture Office, 1954; Odani & Baba, 1961). Mine works were operated for silver, lead and zinc, and the activities have already ceased about 20 years ago (Fukushima Prefecture Office, 1964).

The studied material collected from the dump by E.H. in 1990 is a piece of limonitic ore composed of goethite, and partially altered galena and chalcopryrite. In this ore many vugs are observed and their walls are covered by aggregates of minute calcite crystals and white scaly mineral. The X-ray powder diffraction pattern of this mineral is very similar to that of plumbonacrite (Olby, 1966) whose existence in nature is considered to be uncertain (Fleischer & Mandarino, 1995). Elyite rarely occurs as radiating aggregates of fibrous crystals less than 1 mm long on plumbonacrite-like mineral (Fig. 2). It is light violet in color

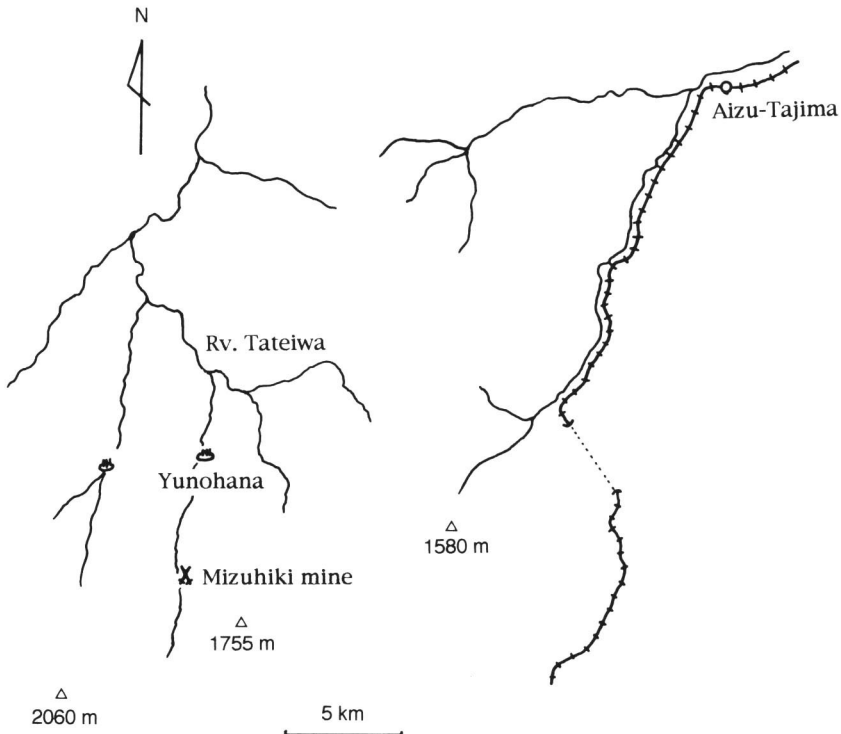


Fig. 1. The index map of the Mizuhiki mine.



Fig. 2. Photomicrograph of elyite crystal (purple) on plumbonacrite-like mineral. Field view, approximately  $6 \times 4$  mm.

with silky luster. Under the microscope crystal shows straight extinction in elongated direction. It is transparent with distinct pleochroism from deep pinkish purple in direction parallel to polarizer to pale purple in direction perpendicular to polarizer.

### Chemical Composition

Six microprobe measurements for Cu, Pb and S were made by employing JEOL JXA-8800 electron probe microanalyser. No other elements of higher atomic number than Na are detected. Standard materials are chalcopyrite for Cu and anglesite for Pb and S. Owing to the minuteness  $H_2O$  is estimated by difference. In Table 1 the figures of average and ranges of the present material are compared with original one (Williams, 1972). The empirical formula derived from the average is  $Cu_{0.94}Pb_{4.00}(SO_4)_{1.07}[O_{0.73}(OH)_{6.28}]_{7.01}$  on the basis of total cations = 6 in anhydrous part. Lower  $H_2O$  than the ideal formula,  $CuPb(SO_4)(OH)_8$ , may be considered by measurement error due to too slender crystal against diameter of operating electron beam.

Table 1. Chemical analyses of elyite. Abbreviations: 1, average analysis of elyite from the Mizuhiki mine; 2, average analysis of elyite from Ward, Nevada, USA (Williams, 1972); 3, recalculated to 100% of analysis 2; 4,  $\text{Pb}_4\text{Cu}(\text{SO}_4)(\text{OH})_8$ .

wt%	1	Ranges	2	3	4
PbO	80.36	79.11–82.38	81.65	79.41	79.40
CuO	6.71	6.15– 6.99	7.98	7.76	7.07
SO <sub>3</sub>	7.70	7.52– 7.92	7.10	6.90	7.12
H <sub>2</sub> O	5.10		6.1	5.93	6.41
Total	100		102.83	100	100
Atomic ratios on the basis of total cations=6 in anhydrous part					
Pb	3.99			4.00	4
Cu	0.94			1.10	1
S	1.07			0.97	1
H	6.28			7.40	8

### X-ray Studies

The selected crystal for X-ray studies has tabular form confirmed to be optically single phase under the microscope. The single crystal study was made by using Rigaku AFC7R four-circle diffractometer with graphite monochromatized Mo K $\alpha$  radiation. This indicated that the present elyite has monoclinic symmetry with the unit cell parameters,  $a = 14.244(1)$ ,  $b = 11.536(1)$ ,  $c = 14.656(1)$  Å,  $\beta = 100.45(1)^\circ$ . Both of  $b$  and  $c$  are approximately twice of those of original unit cell parameters,  $a = 14.248(2)$ ,  $b = 5.768(2)$ ,  $c = 7.309(2)$  Å,  $\beta = 100^\circ 26'(1')$ , proposed by Williams (1972). The X-ray powder diffraction data were obtained by Gandolfi camera using Cu/Ni radiation as given in Table 2, in which those of the material from Ward was compared. The indices are decided after judging from the intensities of reflections obtained for the single crystal.

### Discussion

The secondary minerals of hydrous sulfate and/or carbonate of lead and copper (in  $\text{Pb} \geq \text{Cu}$ ) are plotted in  $[\text{SO}_4]-[\text{CO}_3]-[\text{OH}]$  diagram (Fig. 3). Among them the ideal chemical composition of chenite,  $\text{Pb}_4\text{Cu}(\text{SO}_4)_2(\text{OH})_6$ , is most close to that of elyite with relation of  $(\text{SO}_4) \rightleftharpoons 2(\text{OH})$  substitution. This mineral is found in association with caledonite, linarite, leadhillite, and susannite (Paar *et al.*, 1986). In this diagram, the present assemblage of elyite and “plumbonacrite” exists at most  $[\text{SO}_4]$ - and  $[\text{CO}_3]$ -poor side. Rarity of elyite formation is derived from such limited condition. That is, on the following equation:

Table 2. X-ray powder data for elyite. Abbreviations: 1, Mizuhiki mine, Fukushima Prefecture, Japan; 2, Ward, Nevada, USA (Williams, 1972).

I	1				2				
	d <sub>obs.</sub>	d <sub>calc.</sub>	h k l	I/I <sub>0</sub>	d	h k l	I/I <sub>0</sub>	d	h k l
W	8.01	8.00	1 1 $\bar{1}$						
S	7.21	7.21	1 1 1, 0 0 2	99	7.19	0 0 1		2.62	3 0 4
VS	7.00	7.00	2 0 0	100	7.00	2 0 0		2.62	4 2 2
W	5.96	5.98	1 0 2					2.57	5 1 $\bar{3}$
W	4.61	4.62	2 0 2	11	4.61	2 0 1		2.55	5 2 $\bar{1}$
S	4.47	4.50	0 2 2					2.51	5 2 2
M	4.15	4.45	2 2 0	25	4.46	2 1 0		2.45	2 4 2
W	3.99	4.00	2 2 $\bar{2}$					2.44	1 0 $\bar{6}$ , 5 0 $\bar{4}$
M	3.63	3.63	1 3 $\bar{1}$ , 3 0 2	21	3.63	3 0 1		2.39	1 4 3
VW	3.49	3.49	2 1 3					2.33	3 4 $\bar{2}$
W	3.41	3.41	3 2 1					2.33	6 0 0
W	3.34	3.40	4 0 $\bar{2}$	17	3.40	4 0 $\bar{1}$		2.31	4 0 4, 0 3 5
VW	3.19	3.21	1 1 4	31	3.34	1 0 2		2.26	3 4 2
W	3.14	3.14	3 0 $\bar{4}$	32	3.14	3 0 $\bar{2}$		2.25	1 2 $\bar{6}$
VS	3.08	3.09	1 2 4	29	3.08	1 1 2		2.20	4 4 2
S	3.05	3.07	3 2 2	30	3.05	0 1 2		2.18	1 4 4, 6 2 $\bar{2}$
VS	2.99	2.99	4 2 0, 2 0 4	73	2.995	4 1 0		2.16	6 2 0
M	2.93	2.95	4 0 2	8	2.970	2 1 $\bar{2}$		2.14	6 0 4
VS	2.88	2.93	4 2 2	12	2.930	4 1 $\bar{1}$		2.12	3 4 4
M	2.79	2.89	1 2 4	37	2.884	0 2 0		2.11	3 4 3
M	2.78	2.88	0 4 0					2.10	2 3 5
M	2.76	2.78	4 0 4	18	2.772	4 0 $\bar{2}$		2.08	2 4 4
S	2.66	2.77	2 1 5					2.06	4 4 2
		2.76	3 2 4					2.05	2 1 7
		2.68	0 4 2					2.04	5 0 4
		2.67	2 4 0					2.01	5 0 $\bar{6}$ , 6 2 $\bar{4}$
		2.66	1 4 $\bar{2}$ , 2 2 4	11	2.663	1 2 $\bar{1}$ , 2 2 0		2.00	4 4 4
								1.94	3 4 4
								1.92	5 2 4
								2.011	5 0 $\bar{3}$ , 6 1 $\bar{2}$

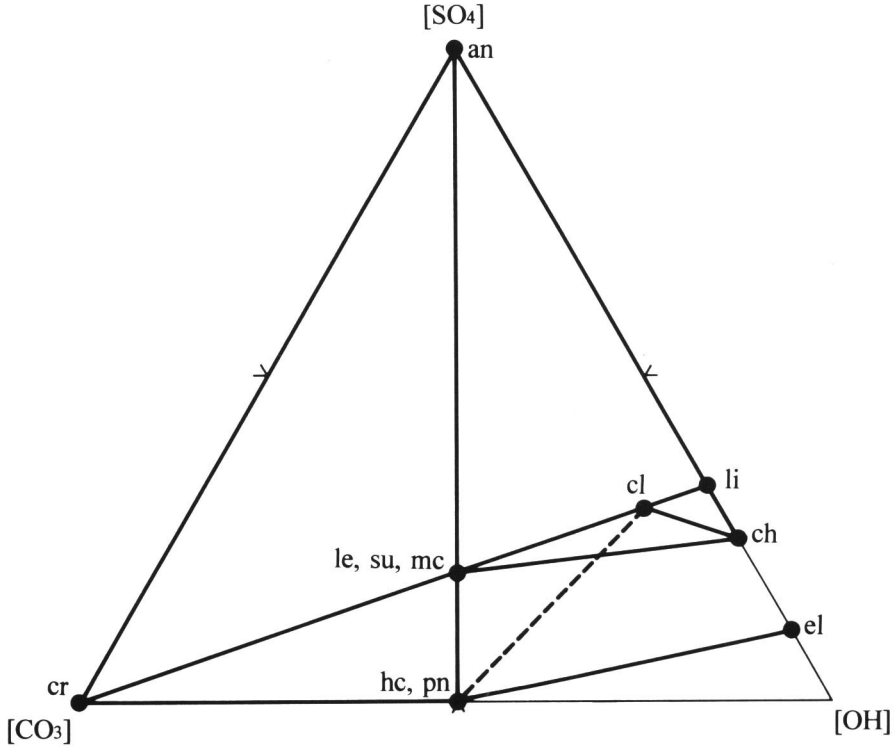
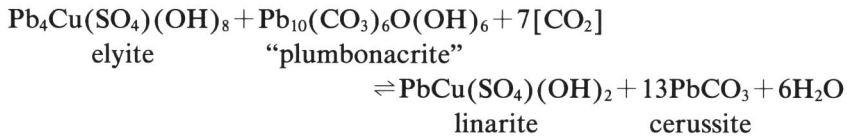


Fig. 3.  $[\text{SO}_4]$ - $[\text{CO}_3]$ - $[\text{OH}]$  diagram. Symbols: an (anglesite);  $\text{PbSO}_4$ , cr (cerussite);  $\text{PbCO}_3$ , el (elyite);  $\text{Pb}_4\text{Cu}(\text{SO}_4)(\text{OH})_8$ , ch (chenite);  $\text{Pb}_4\text{Cu}(\text{SO}_4)_2(\text{OH})_6$ , li (linarite);  $\text{PbCu}(\text{SO}_4)(\text{OH})_2$ , cl (caledonite);  $\text{Pb}_5\text{Cu}_2(\text{CO}_3)(\text{SO}_4)_3(\text{OH})_6$ , le (leadhillite), su (sunnite), mc (macphersonite);  $\text{Pb}_4(\text{CO}_3)_2(\text{SO}_4)(\text{OH})_2$ , hc (hydrocerussite);  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ , pn (plumbonacrite);  $\text{Pb}_{10}(\text{CO}_3)_6\text{O}(\text{OH})_6$ . Mineral assemblages are indicated by heavy solid lines and dashed line (uncertain).



the left side assemblage is considered to be rarer than the right side assemblage represented as the products under the ordinary oxidized condition in chalcopyrite-bearing galena ore.

The original space group,  $P2_1/a$  (Williams, 1972) is not correct because of appearance of diffraction peaks indicating the absence of  $a$ -glide plane, that is  $(102)$ ,  $(302)$ ,  $(30\bar{2})$ ,  $(10\bar{3})$ ,  $(50\bar{2})$  and  $(50\bar{3})$  indexed for the smaller lattice in Table 2 of his own report. In our X-ray single crystal study, we have recognized the extinction rules of  $(h0l)$  with  $l = \text{even}$ , and of  $(0k0)$  with  $k = \text{even}$ . Therefore, the possible space group is selected as  $P2_1/c$ .

Judging from the reflections in single crystal study, the present elyite is elongated on [010] and tabular on [100]. Williams (1972), however, has indexed the tabular face to be  $c\{001\}$  by the goniometric measurement. After the crystal structure analysis being now in progress, we will discuss in detail on these crystallographic problem.

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