ON ALLOCLASITE, A Co-Fe SULPHARSENIDE

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ABSTRACT

Alloclasite is a cobalt-iron sulpharsenide, and the idealized formula for material in one sample from the type locality is $(Co_{0.75}\ Fe_{0.25})\ As_{1.0}\ S_{1.0}$. The material in this sample is orthorhombic with the space group $P22_12_1$ and cell constants: $a = 4.66$Å, $b = 5.61$Å, and $c = 3.40$Å ; Z = 2. Electron microprobe analyses and powder diffraction data are given for three natural and two synthetic samples.

INTRODUCTION

Alloclasite was first described by Tschermak (1866) as a bismuthian glaucodot from Oravicza, Hungary. Frenzel (1883) gives six analyses averaging 27.28% Bi (Palache *et al.* 1944, p. 325). Krenner (1929, *in* Palache *et al.* 1944) reexamined specimens from the type locality and concluded that alloclasite was a high cobaltian glaucodot.

Specimens from the type locality (Oravicza, Roumania**) were kindly provided by the United States National Museum (USNM 62855), and the Royal Ontario Museum (M 13000). An additional specimen from Westphalia (R 829) was provided by the USNM, and one from the Dogatani Mine in Japan by A. Kato.

Several attempts were made to synthesize the mineral alloclasite and two products with chemical composition close to the ranges of the natural material were produced.

PHYSICAL DESCRIPTION

The following morphological description of alloclasite is based on the only specimen displaying any development of crystal faces (USNM 62855). The specimen consists of a compact bundle of radiating crystals in a calcite gangue. These crystals are grown together parallel to the *b* crystallographic direction; they average 5mm in length and are 0.5 to 1.0mm across. One face of the pinacoid {010} is well developed on all of the crystals; (110) and $(\bar{1}10)$ faces are less perfectly developed. The faces

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** Before 1918 Oravicza was in Hungary.

are uneven resulting from lineage structure (Buerger 1934). This lineage structure is sufficiently coarse so as to permit cleavage fragments to be chosen from a single lineage for *x*-ray photographs. Wire gold is intergrown between the radiating crystals in a small amount.

No twinning, either macroscopic or microscopic is present in this specimen.

Alloclasite has the hardness and brittleness characteristic of the common sulpharsenide minerals. Fracture is irregular to subconchoidal and $\{010\}$ cleavage is poorly developed. The specific gravity measured on a single sample (USNM 62855) is 5.91 ± 0.02. The mineral is silver white in colour with a bright metallic lustre.

X-RAY DIFFRACTION STUDIES

Nickel-filtered copper radiation was used throughout the *x*-ray studies for both powder and single crystal photographs.

Powder photographs were taken with a Philips camera (diam. 114.6mm). The samples were crushed single crystals, or fragments chiseled from polished section surfaces after being analyzed by microprobe to verify their homogeneity.

The indexing of the *d*-spacings was based on the measured single crystal cell dimensions and was calculated by computer using an iterative least squares routine.

Only the specimen USNM 62855 yielded crystal fragments suitable for single crystal photographs. Weissenberg photographs taken with the *b* axis as the axis of rotation indicate orthorhombic symmetry with the following conditions: hkl, $0kl$, $h0l$, $hk0$, $h00$ present in all orders, $0k0$ present only with $k = 2n$; $00l$ present only with $l = 2n$. These criteria for non-extinction give the space group $P22_12_1$. The measured cell constants are: $a = 4.66$Å ± 0.02, $b = 5.61$Å ± 0.01, $c = 3.40$Å ± 0.02. This particular orientation of the unit cell was chosen in view of its close relation to the unit cell of arsenopyrite (Buerger 1936).

CHEMICAL COMPOSITION

All chemical analyses were carried out using an Applied Research Laboratories' AMX electron microprobe. A fixed voltage of 20kv and a sample current of approximately 0.03 micro-amps was used for all the elements. The sample current was checked periodically on the brass sample holder and was adjusted at the beginning of a series of analyses so that most of the measured counts would be below 5000 per second in order to reduce the dead time error to a minimum. Beam diameter averaged 1.5μm. The polished sections were coated with a vacuum-deposited layer of carbon.

Pulse height analysis was necessary to avoid interference of the sulphur $K\alpha$ peak with a third order cobalt peak.

Each analysis reported in this study is the result of a complete chemical analysis for Co, Fe, As, and S at a selected point. For each determination three ten-second counts were made at the point for each of the above elements. Ni was not detected in any of the samples.

Each set of three ten-second counts was averaged together and was corrected for background.

Background for each element was measured frequently during a series of analyses by counting on samples containing none of the element sought, and was checked before and after a series of analyses by deflecting the spectrometers off wavelength.

The following standards were used throughout the series of analyses: for cobalt: Co metal (100% Co), for iron: pyrite (46.5% Fe), for arsenic and for sulphur: arsenopyrite (45.1% As and 20.4% S).

Corrections for absorption, backscatter (atomic number), and fluorescence were calculated using the procedure outlined by Smith (1965) and an iterative computer program developed by Rucklidge (1967) and extensively modified by Scott (personal communication).

Radcliffe (1966) has shown that with the present instrumentation, errors arising from peak shifts for Co, Fe, and As could amount to as much as ± 1.5% of the amount present. This peak shift error is necessarily inherent in all the analyses presented in this study. Care was taken not to change the wavelength settings on the spectrometers during the analyses. Peak shift errors are reduced by using standards similar to the unknowns.

The composition of the arsenopyrite used as a standard for As and S for the probe analyses was determined using the equation relating arsenic content to d_{131} as given by Morimoto & Clark (1961; the equation is misprinted in the original paper), $d_{131} = 1.6006 + 0.00098x$ where x is the atomic percent of arsenic in the arsenopyrite. For this arsenopyrite sample $d_{131} = 1.6332 \pm 0.0008$Å; the composition is:

Element	Atomic %	Weight %
As	32.5 ± 0.8	45.1 ± 1.1
S	34.2 ± 0.8	20.4 ± 0.5
Fe	33.3	34.5

Experience with analyses done on the electron microprobe used in this study indicates that any absolute value reported is correct to within

± 3% of the amount present. Because of the nature of the instrument and the method of analysis a higher degree of accuracy (± 0.5% of the amount present) may be used when comparing analyses done together at the same time under the same conditions; thus relatively small chemical variations may be detected although the absolute composition is less accurately known.

The electron microprobe analyses are given in Table 1.

ANALYSES AND CELL CONTENTS

The chemical formulae and least squares refined unit cell parameters (based on x-ray powder data) for natural and synthetic alloclasite are given in Table 2. The difficulty of obtaining reliable density data for these samples other than USNM 62855 precluded the calculation of precise chemical formulae. Consequently all formulae are calculated so that the metal atoms sum to 1.0. For this reason the discussion of metal atom deficiencies or excesses with respect to non-metal atoms is impossible except for USNM 62855 for which the calculations given in Table 3 are made. Thus the molecular formula derived from the analysis is $(Co_{0.72}Fe_{0.24})As_{0.99}S_{0.98}$. The indicated ideal cell content is $2[(Co_{0.75}Fe_{0.25})As_{1.00}S_{1.00}]$ giving a calculated density of 5.997 which is in reasonable agreement with the measured value of 5.91.

TABLE 1. ALLOCLASITE : ELECTRON MICROPROBE ANALYSES

Sample No.	Co *	Fe *	As *	S *	SUM	Values of x in $(Co_xFe_{1-x})AsS$
USNM 62855	25.4	8.4	44.3	18.7	96.8	0.74
USNM R829	23.6	9.1	45.5	20.9	99.1	0.71
Dogatani	23.3	7.7	47.3	20.7	99.0	0.74
M 13000	28.5	4.0	44.9	17.8	95.2	0.87
Synthetic samples						
Cpm -a	30.1	4.1	51.2	11.2	96.6	0.88
Cpm -b	30.5	4.1	47.0	15.6	97.2	0.88
R-1 -a	24.3	4.2	49.2	15.2	92.9	0.85
R-1 -b	23.5	3.8	48.1	16.0	91.4	

* Corrected for background, instrument drift, absorption, backscatter, and fluorescence.

MINERAL SYNTHESIS

Synthetic $CoAs_2$ was prepared by heating a stochiometric mixture of Co and As, sealed under vacuum in quartz tubing at 400°C for 4 days. The sample was removed, thoroughly ground, resealed and reheated at 700°C for 2 days to bring the reaction to completion.

The FeS_2 used in these experiments was prepared by finely grinding a large clean single crystal of pyrite from Elba. This pyrite was spectroscopically analyzed and was found to contain insignificant quantities of elements other than Fe and S.

TABLE 2. ALLOCLASITE : CHEMICAL AND REFINED X-RAY DATA FOR NATURAL AND SYNTHETIC SAMPLES

Sample number	Number of analyses	Formula *	Refined cell dimensions in Å		
			a	*b*	*c*
USNM 62855 †	1	$(Co_{0.74}Fe_{0.26})_{1.00}As_{1.01}S_{1.00}$	4.641	5.606	3.415
USNM R 829 †	1	$(Co_{0.71}Fe_{0.29})_{1.00}As_{1.08}S_{1.15}$	4.662	5.606	3.415
Dogatani	1	$(Co_{0.74}Fe_{0.26})_{1.00}As_{1.20}S_{1.23}$	—	—	—
M-13000 †	1	$(Co_{0.87}Fe_{0.13})_{1.00}As_{1.02}S_{0.95}$	4.631	5.605	3.430
Synthetic samples					
Cpm	2	$(Co_{0.88}Fe_{0.12})_{1.00}As_{0.94}S_{0.61}$	4.727	5.660	3.348
R-1	2	$(Co_{0.85}Fe_{0.15})_{1.00}As_{1.19}S_{0.89}$	4.783	5.700	3.319

* In all formulas Co + Fe is set equal to 1.00.

† Powder data for these samples is based on probe-analyzed monomineralic samples chipped out of polished sections.

TABLE 3. ALLOCLASITE : ANALYSIS AND CELL CONTENTS

	1	2	3	4	5
Co	25.4	0.262	0.004445	1.4468	1.50
Fe	8.4	0.087	0.001504	0.4894	.50
As	44.3	0.458	0.006113	1.9896	2.00
S	18.7	0.193	0.006019	1.9590	2.00
	96.8	1.000			

1 : Final analysis.

2 : Analysis reduced to unity.

3 : Atomic proportions (values in column 2 divided by the appropriate atomic weights).

4 : Number of atoms in the unit cell obtained by multiplying the values in column 3 by the molecular weight. $M = (V \times D)/(1.66) = 325.6$.

5 : Ideal cell contents.

A mixture of composition $FeS_2.3CoAs_2$ was sealed under vacuum in quartz tubing and heated to 1150°C for 10 hours. The run was cooled to 600°C in 4 hours and then air-quenched to room temperature in 10 minutes. This mixture reacted to produce morphologically pseudo-tetragonal grey crystals (0.5 x 0.5 x 3.5mm) designated R-1, as well as sulphur-bearing arsenic crystals and a small amount of an arsenic-bearing sulphur liquid.

A dry fusion of bulk composition $FeS_2.CoAs_2.CuFeS_2$ was heated to 1150°C for 6 hours under vacuum in quartz tubing and air-quenched to room temperature in 5 minutes. The $CuFeS_2$ was added in the form of finely ground chalcopyrite as a flux to promote chemical reaction. The product consisted of a number of small (0.1mm in length) sharp dentritic crystals of a silver-white mineral in an essentially chalcopyrite groundmass. The crystals were designated Cpm.

Both R-1 and Cpm have chemical compositions close to those of naturally occurring alloclasite, but the unit cell has a different space group.

Single crystal Weissenberg photographs of R-1 taken with *b* as the axis of rotation indicate orthorhombic symmetry with the following conditions : hkl present in all orders, $0kl$ present only with $k + l = 2n$, $h0l$ present only with $h + l = 2n$, $hk0$ present in all orders, $h00$ present only with $h = 2n$, $0k0$ present only with $k = 2n$, $00l$ present only with $l = 2n$ (?). These criteria for non-extinction give the space group *Pnnm*. The measured cell constants are : $a = 4.80Å \pm 0.02$, $b = 5.68Å \pm 0.01$, $c = 3.33Å \pm 0.01$.

DISCUSSION

The alloclasite specimen USNM 62855 from Oravicza, Hungary, the type locality, is associated with white cleavable calcite and a small amount of intergrown wire gold. This assemblage is what might well be expected to form in a low-temperature, late stage hydrothermal vein; Petruk (personal communication) describes a very similar occurrence of alloclasite (in calcite with native silver and cobalt-nickel sulpharsenides) from the Silverfields mine at Cobalt, Ontario. Sample R-829 consists of fine grained alloclasite in fine grained quartz (silicified, recrystallized metamorphic rock). The specimen from the Dogatani mine in Japan consists of alloclasite with glaucodot and danaite in a drusy quartz vein; the sulpharsenide minerals were not all formed at the same time, or presumably from the same mineralizing solutions.

X-ray powder data for natural alloclasite and for synthetic material having the alloclasite composition are given in Table 4. This data shows that the alloclasite in samples USNM 62855 and R829 gives one type of powder pattern, that in sample M-13000 gives another type, and that in the synthetic material gives still another type. The alloclasite in Sample USNM 62855 and R829 can be readily indexed on an orthorhombic cell, space group $P22_12_1$. The unit cell is dimensionally related to that of arsenopyrite in Buerger's (1936) orthorhombic setting :

Arsenopyrite	*Alloclasite*
A	$a = A/2$
B	$b = B$
C	$c = C/2$
$Z = 8$	$Z = 2$

The alloclasite in sample M-13000 has 12 extra lines when indexed on the $P22_12_1$ cell and may represent an alloclasite polytype. Electron microprobe studies show that this sample has a uniform composition hence the extra lines in the powder pattern do not appear to be due to an admixed mineral phase.

The synthetic material can be indexed on an orthorhombic cell space group *Pnnm*, but the powder data for Sample R-1 has 3 extra lines even when indexed on this cell.

The composition of alloclasite in one sample from the type locality (sample USNM 62855) can be expressed by the formula $Co_{0.74}Fe_{0.26}AsS$, and in another sample (M-13000) by $Co_{0.87}Fe_{0.13}AsS$. It is not known whether a solid solution exists between these compositions because the alloclasite in these samples may be present in two different structural forms. Petruk (report in preparation) reports that alloclasite from Cobalt, Ontario has a variable composition that can be expressed by the formula $(Co_{0.65\text{-}0.89}\,Fe_{0.01\text{-}0.18}Ni_{0.0\text{-}0.28})AsS$, and that an alloclasite having the formula $Co_{0.80}Fe_{0.20}As_{1.17}S_{0.96}$ has the space group $P2 2 2_1$. The x-ray powder pattern that he reports for the $P222_1$ space group is similar to that for the specimen with space group $P22_12_1$ reported here. Petruk also reports an x-ray powder pattern for material of glaucodot composition that has some of the extra lines found in the powder pattern for sample M-13000.

Klemm (1965) shows a large cubic phase field in the CoAsS-FeAsS-NiAsS system along the CoAsS-NiAsS join and extending more than 50 mole percent towards FeAsS; this cubic field is based on synthetic data. The present study shows that the natural alloclasite and the synthetic material made during this study has a composition that corresponds to a composition for the cubic phase field, but the crystallography is

TABLE 4. ALLOCLASITE, X-RAY POWDER DATA

USNM 62855				USNM R829		M–13000		R–1		Cpm	
I	*d* meas	*d* calc	*hkl*	*I*	*d* meas	*I*	*d* meas	*I*	*d* meas	*I*	*d* meas
½	4.643	4.641	100								
						2	3.969				
						½	3.745				
								1	3.657		
3	3.575	3.575	110	2	3.587	9	3.570				
						2	3.531				
						9	3.273				
						2	3.110				
1	2.917	2.916	011								
								1½	2.865		
3	2.802	2.803	020	10	2.794	2	2.803	1	2.848		
10	2.750	2.757	101	8	2.755	10	2.754	10	2.727	10	2.732
						½	2.712				
						1	2.642	2	2.632		
						2	2.520	2	2.586		
9	2.469	2.469	111	6	2.471	7	2.471	10	2.460	10	2.460
5	2.401	2.399	120	4	2.406	5	2.396			4	2.424
						2	2.366				
½	2.321	2.321	200								
						2	2.270				
½	2.167	2.167	021								
1	2.143	2.144	210	1	2.134			½	2.207		
								3	2.053		
2	1.9632	1.9682	121	2	1.966	2	1.966	2	1.970	2	1.966
						1	1.885				
						1	1.867				
7	1.8165	1.8159	211	6	1.819	6	1.819	7	1.836	4	1.827
1	1.7879	1.7875	220			1	1.785	2	1.832		
2	1.7329	1.7334	130	3	1.734	1	1.733	1	1.767		
3	1.7069	1.7074	002					1	1.660	1	1.677
3	1.6393	1.6392	031 102	2	1.641	2	1.640	3	1.649	1	1.643
2	1.5833	1.5836	221 300	1	1.587	1	1.584	2	1.604		
2	1.5457	1.5456	131 112	1	1.545	1	1.546	1	1.559		
2	1.4901	1.4913	310	1	1.497	1	1.487	1	1.534		
¼	1.4556	1.4554	230 022			1	1.443				
2	1.3901	1.3911	122 040			1	1.397	2	1.374		
1	1.3361	1.3357	212								
½	1.2603	1.2604	032 321								
¼	1.2344	1.2349	222								
1	1.2166	1.2164	132								
½	1.1996										
2	1.1142										

different. Hence the natural alloclasite is indeed a separate mineral species.

Alloclasite has a narrow range of chemical composition from sample to sample and any one sample is entirely uniform in composition within the limits of detection of the electron microprobe.

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