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LAROSITE, A NEW COPPER-LEAD-BISMUTH SULPHIDE

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ABSTRACT

A new mineral, larosite, $(Cu_{17.7}Ag_{3.3})(Pb_{1.0}Bi_{1.0})S_{13}$, was found in an assemblage of sulphides and silver in a sample from the Foster mine in the Cobalt area, Ontario. The mineral is rare and occurs as small acicular crystals in a chalcocite-stromeyerite assemblage. It is anisotropic and weakly pleochroic in reflected light, and its reflectance at 546nm is $R_{min.}$ 29.7–30.1 and $R_{max.}$ 31.2–32.0. The powder pattern was indexed on an orthorhombic cell with $a = 22.15$, $b = 24.03$, $c = 11.67Å$, and $Z = 10$. The strongest x-ray diffraction reflections are at 3.206, 2.917, 2.846, 2.471 and 1.982Å. The calculated specific gravity is 6.18. This mineral has a similar mode of occurrence and a similar metal : sulphur ratio to betekhtenite, $Cu_{21}Pb_2S_{14}$.

INTRODUCTION

During the course of a broad study of ores in the Cobalt area in Ontario, a new copper-lead-bismuth sulphide mineral was found in a sample from the Foster Mine, Cobalt, Ontario. The sample had been stored in the G.S.C. collection, and was kindly supplied to the writer by Dr. J. L. Jambor, G.S.C. The optical properties, chemical composition, and x-ray diffraction pattern of the mineral were determined in the Mineral Sciences Division of the Mines Branch at Ottawa, and the mineral was named larosite in recognition of Mr. LaRose, one of the discoverers of silver ore at Cobalt. The mineral and mineral name were approved by the IMA Commission on New Minerals and Mineral Names. Dr. Akira Kato, National Science Museum, Ueno Park, Tokyo, Japan, indexed the x-ray diffraction pattern and suggested a unit cell when the mineral data were circulated by the Commission. His indexing and proposed cell are given here, with his consent.

MODE OF OCCURRENCE

Larosite occurs as acicular to flame-like crystals in an assemblage of chalcocite and stromeyerite * in the central portion of a layered vein

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* Figure 138 in Petruk *et al.* 1971.

about 1 inch wide. The mineral is rare and the crystals are small with the largest being about 25 microns wide and 300 microns long. The layered vein was described by Petruk *et al.* (1971, Fig. 137), but the description is repeated here because it is considered that the mode of occurrence has a bearing on the stability of the mineral. The outer layers of the vein (*i.e.* layers nearest the wall rock) consist of intimately intergrown native silver, bornite, acanthite, and chalcopyrite. The central layer consists of chalcocite, stromeyerite, and larosite. This central layer also contains inclusions of arsenopyrite, of chalcocite with exsolved galena (Fig. 139 in Petruk *et al.* 1971), and of tetrahedrite intergrown with a copper-rich polybasite (1-1-1). These inclusions occur near the outer edge of the central layer and were referred to as an intermediate layer by Petruk *et al.* (1971). The bulk composition of the chalcocite with exsolved galena is similar to that of phase A of Craig & Kullerud (1968) and is considered to represent the unmixed products of phase A. The name polybasite (1-1-1) refers to the small-cell polybasite according to the usage proposed by Harris *et al.* (1965). The compositions of the polybasite (1-1-1) and of the tetrahedrite are reported by Petruk *et al.* (1971).

OPTICAL PROPERTIES

Larosite is whitish buff in reflected light and is moderately anisotropic. Its anisotropic colours are grey and greenish buff. The mineral is weakly pleochroic, and its reflectance, measured according to the method described by Petruk *et al.* (1969) by using a silicon standard, is given in Table 1. The Vickers microhardness, measured with a 25-gram load, varies from 87 to 124 kg/mm^2 for 10 measurements with a mean of 106 kg/mm^2.

TABLE 1. REFLECTANCE OF LAROSITE

Wavelength nm	$R_{max.}$ Range	$R_{min.}$ Range
470	32.2–32.7	31.0–31.7
546	31.3–32.0	29.7–30.1
589	30.5–31.7	29.1–30.0
650	30.3–32.0	29.1–30.0

CHEMICAL COMPOSITION

The results of two electron microprobe analyses, determined on different crystals at two different times, are given as Analysis 1 and Analysis 2 in Table 2. The analyses were performed with a Material Analysis Company (MAC) Model 400 electron microprobe using Cu, Ag, Bi, and synthetic PbS as standards for Analysis 1, and Ag, synthetic CuS and PbS and bismuthinite as standards for Analysis 2. The data were processed with the computer program of Rucklidge (1967). Analysis 1 gives the composition $(Cu_{17.7}Ag_{3.3})(Pb_{1.0}Bi_{1.0})(S_{13.1})$, and Analysis 2 $(Cu_{17.6}Ag_{3.4})(Pb_{0.9}Bi_{1.1})(S_{14.3})$. These compositions recalculated in terms of Cu_2S, Ag_2S, PbS, and Bi_2S_3, give the formula $(Cu,Ag)_{21}(Pb,Bi)_2S_{13}$. Larosite has a somewhat similar elemental ratio to betekhtinite, $(Cu,Ag,Fe)_{21}Pb_2S_{14}$, but contains significant amounts of silver and bismuth, and less copper and lead (Schüller & Wohlman 1955, Mukanov *et al.* 1960, Markham & Otteman 1968).

X-RAY DATA AND SPECIFIC GRAVITY

The *x*-ray diffraction powder pattern of larosite is different from that of betekhtinite and could not be indexed satisfactorily by personnel in the Mines Branch Laboratory. The pattern, using a 114.6 mm-diameter Debye-Sherrer powder camera, is given in Table 3. The indexing by Dr. Akira Kato, is based on an orthorhombic cell with $a = 22.15$, $b = 24.03$, $c = 11.67$Å and $Z = 10$. The cell and indexing are provisional. The specific gravity of larosite could not be measured because the mineral grains are too small. On the basis of the above cell data, the calculated specific gravity is 6.19 for Analysis 1, 6.31 for Analysis 2, and 6.18 for $(Cu_{17.7}Ag_{3.3})(Pb_{1.0}Bi_{1.0})S_{13}$. The last formula is probably the real composition for larosite.

TABLE 2. ELECTRON MICROPROBE ANALYSES OF LAROSITE

Element	Analysis 1 Wt.%	Analysis 2 Wt.%
Cu	49.7	48.3
Ag	15.6	15.6
Pb	9.0	8.5
Bi	8.9	9.6
S	18.5	19.8
Total	101.7	101.8

SYNTHESIS

L. J. Cabri of the Mines Branch attempted to synthesize larosite but preliminary runs failed to produce the mineral and, due to increased pressure of other work, the project was set aside. A mixture with the composition of $Cu_{17.5}Ag_{3.5}PbBiS_{15}$ was prepared and heated at 700°C. Because the resulting product contained several phases, it was annealed at various lower temperatures for different periods of time. A variety of new phases were obtained, and the material annealed at 300°C contained a phase whose *x*-ray diffraction powder pattern was somewhat similar to that of larosite. This phase contained copper, lead, bismuth, sulphur and more than 30% silver. These results indicate that it may be possible to prepare synthetic larosite, but the conditions for producing it have not yet been established.

DEPOSITIONAL CONDITIONS FOR LAROSITE

As mentioned above, larosite occurs in an assemblage of chalcocite and stromeyerite in the centre of a layered vein. The chalcocite-stromeyerite assemblage behaves as one mineral replacing tetrahedrite-polybasite (1-1-1) grains. Such a relationship suggests that the chalcocite-stromeyerite host was deposited as one mineral and subsequently unmixed into the chalcocite-stromeyerite assemblage. Published phase equilibrium data show that chalcocite and stromeyerite can co-exist only below $-67°C$ (Skinner 1966), and that they can unmix from a hexagonal close-packed phase at this temperature. Impurities may alter these conditions.

Larosite is present in the chalcocite-stromeyerite assemblage but it is not known whether the larosite is also an unmixed phase or an inclusion in the assemblage. The intergrowths and intimate association of larosite with the chalcocite-stromeyerite assemblage suggest unmixing but, even if larosite is an unmixed phase, its stability conditions cannot be defined because unmixing could have preceded, coincided with, or postdated the unmixing of chalcocite and stromeyerite.

The chalcocite-stromeyerite assemblage contains an inclusion of chalcocite with exsolved galena (Fig. 139 in Petruk *et al.* 1971). The bulk composition of this inclusion is similar to that of phase A of Craig & Kullerud (1967) and likely represents an unmixed product from such a phase. Since phase A is stable only between 486°C and 523°C the inclusion was likely deposited within this temperature range. Thus, it probably represents an early phase which was deposited from the same mineralizer that deposited larosite and the chalcocite-stromeyerite host. It is, therefore, interpreted that either larosite or its parent (high temperature polymorph) was deposited at some temperature below 500°C.

TABLE 3. X-RAY DIFFRACTION PATTERN FOR LAROSITE

I	$d_{\text{meas.}}$ Å*	$Q_{\text{meas.}}$*	$Q_{\text{calc.}}$	hkl**
1	3.832	0.0680	0.0677	430
			0.0681	103
1	3.689	0.0734	0.0727	052
			0.0730	023
			0.0740	531
1	3.407	0.0862	0.0861	541
1	3.311	0.0913	0.0914	323
5	3.206	0.0973	0.0964	631
9	2.917	0.1175	0.1175	004
6	2.846	0.1234	0.1230	731
1	2.769	0.1304	0.1306	800
4	2.555	0.1532	0.1536	831
2	2.503	0.1597	0.1600	802
6	2.471	0.1637	0.1636	344
1	2.391	0.1750	0.1754	524
1	2.260	0.1958	0.1960	534
1	2.249	0.1977	0.1967	803
			0.1985	591
2	2.173	0.2118	0.2118	833
4	2.162	0.2139	0.2125	464
			0.2146	293
1	2.044	0.2394	0.2391	0.10.3
10	1.982	0.2546	0.2541	265
			0.2538	6.10.1
			0.2547	10.5.1
			0.2550	824
1	1.762	0.3221	0.3215	10.0.4
			0.3230	6.12.0
1	1.667	0.3599	0.3600	13.3.0

* X-ray diffraction pattern obtained by Mines Branch Laboratory.
** Indexing by Dr. A. Kato.

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