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LAUTITE AND CADMIUM-RICH SPHALERITE FROM THE ROSS MINE, HISLOP TOWNSHIP, ONTARIO

T. T. CHEN[1] AND J.E. DUTRIZAC[2]
Mineralogy[1] and Metallurgical Chemistry[2] Sections, Mineral Sciences Laboratories, CANMET, Department of Energy, Mines and Resources, Ottawa, Ontario K1A 0G1

Abstract

Lautite and cadmium-rich sphalerite were identified in a single ore vein from the Ross mine, Hislop Township, Ontario; this is the first reported Canadian occurrence of lautite. Lautite, $(Cu,Ag)_{0.97}As_{1.00}S_{0.98}$, occurs as irregular or needle-like crystals in galena. Cadmium-rich sphalerite occurs as irregular zones bounded by galena and calcite; the highest cadmium content detected by microprobe analysis is 9.0 wt %.

Sommaire

Nous avons identifié de la lautite et une sphalérite riche en cadmium dans un seul filon de minerai de la mine Ross, canton de Hislop, Ontario. C'est la première fois qu'on signale de la lautite au Canada. On trouve la lautite, $(Cu,Ag)_{0.97}As_{1.00}S_{0.98}$, en cristaux difformes ou aciculaires inclus dans la galène. La sphalérite cadmifère se présente en zones irrégulières bordées de galène et de calcite. Les analyses à la microsonde indiquent une teneur maximum de cadmium dans la sphalérite de 9 pour cent (en poids).

(Traduit par la Rédaction)

Introduction

Lautite (CuAsS) was originally described from Lauta, near Marienberg, Saxony, where it occurs with native arsenic, tennantite, proustite, chalcopyrite, galena and barite (Palache *et al.* 1944). The mineral has been found in only a few other localities, *e.g.*, the Gabe Gottes mine, Alsace-Lorraine, France (Marumo & Nowacki 1964), Isérables, Wallis, Switzerland (Hügi *et al.* 1967) and the Hechtsberg quarry, Kinzigtal, Germany (Otto 1974).

Cadmium is a common trace constituent in sphalerite. Although synthetic CdS forms a complete solid-solution series with ZnS at high temperature (Charbonnier & Murat 1974), naturally occurring sphalerite with more than 1.0 wt. % Cd is rare and has been noted in only a few deposits, *e.g.*, Bernic Lake, Manitoba (Cd 17.6 wt. %; Černý & Harris 1978) and Pay Khoy, northern Urals, U.S.S.R. (Cd. 2.5 wt. %; Yushkin *et al.* 1975).

Lautite had not been reported previously from Canada. This mineral, associated with a cadmium-rich sphalerite, was recently identified at the Ross mine, Hislop Township, Ontario; this report summarizes studies on these two minerals.

Sample Description

The Ross mine, about 18 km southeast of Matheson and 1 km north of Holtyre, Hislop Township, Ontario, is situated in steeply folded Keewatin lavas and Timiskaming sediments intruded by stocks of syenite and granite. The general geology and mineralogy of this deposit have been described by Prest (1956) and Jones (1944). Although galena and sphalerite occur throughout the mine, lautite-bearing galena was found only in the upper workings of the No. 12 vein; galena from eight other active stopes was investigated but found to be lautite-free. The cadmium-rich sphalerite seems to be associated only with the lautite-bearing galena. The sample investigated consists of several irregular crustifications of silicates (innermost), calcite, sphalerite and a major galena mass. The zones are generally 1–3 mm thick, whereas the galena is at least 10 mm across and contains numerous triangular pits, cleavages and fractures in curved alignment suggestive of a deformation fabric. Chalcopyrite, nickeline, silicates, calcite and tetrahedrite–tennantite occur as inclusions in the galena; chalcopyrite, pyrite, marcasite, gypsum, nickeline, rammelsbergite and electrum are included in the silicate zone. Gypsum fills interstices between galena, sphalerite and calcite. The association of nickel arsenides with lautite-bearing galena seems to be characteristic and could serve as a guide to this rare mineral at the Ross mine.

Results and Discussion

Lautite

Lautite is found as small (20–140 μm) irregular to needle-like crystals in galena (Fig. 1).

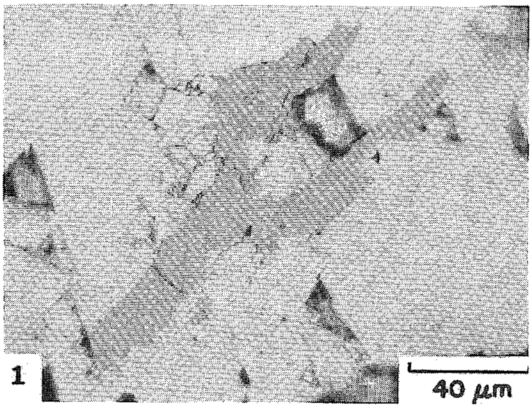

FIG. 1: Needle-like lautite (dark grey) in galena (light grey); oil immersion.

The mineral is light grey with moderate bireflectance from pink or brown to blue, and with distinct anisotropism from bluish grey to light greyish brown in oil. The optical properties are similar to those of enargite.

As can be seen from Table 1, the composition of lautite from the Ross mine is fairly uniform; in addition to major Cu, As and S, minor amounts of Ag and Sb substitute for Cu and As, respectively. Hg, Fe, Zn and Bi were not detected. The average electron microprobe analysis corresponds to $(Cu,Ag)_{0.97}(As,Sb)_{1.00}S_{0.98}$. A lautite specimen from Lauta, Marienberg, Saxony (National Mineral Collection No. 14870) was found to have an average composition corresponding to $Cu_{1.01}As_{1.00}S_{0.95}$ (Table 1). The slightly low total for lautite from the Ross mine is probably due to the small size of the lautite grains; the departure in molar ratios from the ideal 1:1:1 is possibly caused by the use of standards that do not exactly duplicate the lautite matrix. In general, however, the analyses indicate a composition of CuAsS with little departure from stoichiometry, in agreement with the study of Maske & Skinner (1971). The higher silver contents of lautite from the Ross mine indicate that (Cu,Ag) substitutions can be relatively important in lautite from silver-rich environments. The minor substitution of Sb for As is consistent with the phase studies of Luce *et al.* (1977).

X-ray diffraction study of Ross mine lautite was difficult because of its small grain-size. The Gandolfi patterns obtained with a 57.3 mm diameter camera inevitably showed galena lines and a few weak lautite lines: 3.10(m), 2.98(m, overlaps galena), 2.06(w), 1.90(m), 1.74(m, overlaps galena, 1.64(w) and 1.61(w). Comparison of these lines with the data for lautite from the type locality (Table 2) together with the optical and microprobe analyses confirms the occurrence of this mineral in the Ross mine. The cell dimensions calculated for the Ross mine lautite, assuming the space group $Pna2_1$, are *a* 11.4, *b* 5.5 and *c* 3.7Å, in close agreement with the values given in Table 2 and by Craig & Stephenson (1965).

Some confusion surrounds the powder-diffraction data available for natural and synthetic lautite. The original data listed in JCPDS 12–755 were indexed according to $P2_12_12_1$; this space group is now known to be incorrect (Craig & Stephensen 1965, Marumo & Nowacki 1964). A calculated pattern (25–1179) has been given in the JCPDS file for natural lautite, but the calculated intensities often differ significantly from the measured values. Maske & Skinner (1971) correctly identified the lautite space group as $Pna2_1$, but to provide a consistent basis of comparison with JCPDS 12–755, they indexed their data for synthetic lautite using the

TABLE 1. ELECTRON MICROPROBE ANALYSES OF LAUTITE

	Ross Mine, Ontario								Lauta, Marienberg, Saxony					
	Weight percent													
	1	2	3	4	5	6	7	Av.	1	2	3	4	5	Av.
As	44.3	42.7	45.0	44.3	43.8	43.6	44.2	44.0	44.2	44.2	44.4	44.6	44.6	44.4
S	18.2	18.4	18.7	18.6	18.6	18.8	19.1	18.6	18.2	18.3	18.2	18.1	17.9	18.1
Cu	37.1	37.2	34.7	35.1	36.3	35.9	35.2	35.9	38.3	38.0	38.3	37.7	38.1	38.1
Ag	n.d.	0.2	1.0	1.0	0.1	0.6	0.4	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sb	0.2	0.6	0.4	0.3	0.6	0.2	0.1	0.3	0.1	0.1	0.1	0.1	0.1	0.1
Total	99.8	99.1	99.8	99.3	99.4	99.1	99.0	99.3	100.8	100.6	101.0	100.5	100.7	100.7
	Atomic ratios													
(As,Sb)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
S	0.96	1.00	0.97	0.98	0.98	1.01	1.01	0.98	0.96	0.96	0.96	0.95	0.94	0.95
(Cu,Ag)	0.99	1.02	0.92	0.95	0.97	0.98	0.94	0.97	1.02	0.01	1.02	1.00	1.01	1.01

Analytical conditions; standards: enargite ($CuK\alpha$,$AsK\alpha$,$SK\alpha$), argentopyrite ($AgL\alpha$) and chalcostibite ($SbL\alpha$); EMPADR VII correction program (Rucklidge & Gasparrini 1969); 20kV.

TABLE 2. X-RAY POWDER DIFFRACTION DATA OF LAUTITE FROM LAUTA, MARIENBERG, SAXONY

hkl	d_{calc}	d_{meas}	I_{est}	*hkl*	d_{calc}	d_{meas}	I_{est}
200	5.678	5.70	3	221	2.055	2.057	4
110	4.914	4.90	1	420	1.966	1.966	1/2
201	3.129			321	1.905	1.904	8
310	3.109	3.105	10B	600	1.893	1.891	6
011	3.090			002	1.875	1.875	2
111	2.981	2.977	3	511	1.830	1.831	3
400	2.839	2.836	2	130	1.794	1.796	2
211	2.714	2.715	3	520	1.745	1.743	4
120	2.650	2.647	1/2	421	1.741		
410	2.518	2.515	2	230	1.730	1.730	1
220	2.457	2.459	3	601	1.690	1.688	2
311	2.393	2.395	1	330	1.638	1.636	4
320	2.212	2.212	1	031	1.635		
121	2.164	2.165	3	131	1.618	1.616	5
510	2.096	2.096	1	611	1.614		
411	2.090	2.091	2	312	1.606	1.606	2

114.6mm Debye-Scherrer camera; Co$K\alpha$ radiation (λ= 1.7902Å); *d* values corrected with Si standard (*a*= 5.43088Å). Indexed with *a*= 11.355, *b*= 5.450, *c*= 3.750Å, assumed space group $Pna2_1$.

$P2_12_12_1$ space group. Furthermore, there are some slight but potentially significant differences in *d* values less than 1.97Å between natural (JCPDS 12–755) and synthetic lautite. For these reasons it was considered worthwhile to redetermine the X-ray powder-diffraction pattern for lautite from the type locality. The results of this investigation are given in Table 2.

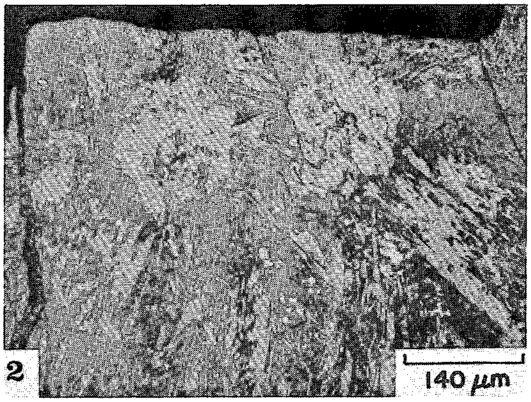

FIG. 2: Cadmium-rich sphalerites showing crude hexagonal or strip-like "patches" (light grey); etched with 1:1 HNO_3; oil immersion.

The lines were indexed assuming the space group $Pna2_1$ (Craig & Stephenson 1965); the calculated cell parameters are *a* 11.355 (5), *b* 5.450(2), *c* 3.750(2)Å. The *d* values and intensities correspond closely to those of natural lautite (JCPDS 12–755); it is not known why the calculated intensities (25–1179) are somewhat different. There is relatively poor agreement in *d* values < 1.97Å between the data for natural lautite and for the synthetic phase of Maske & Skinner (1971); the reasons for this are not obvious, as the two phases are similar in composition.

Cadmium-rich sphalerite

Although sphalerite occurs throughout the Ross mine, most of this is "normal" with respect to cadmium concentration: Zn 66.6, Cd 0.4, Fe 0.1, S 32.8 (wt.%) Cadmium-rich sphalerite (Cd > 1 wt.%) seems to be associated only with

TABLE 3. ELECTRON MICROPROBE ANALYSES OF CADMIUM-RICH SPHALERITE FROM THE ROSS MINE

	1	2	3	4	5	6	7	8	9	10	11	12
Weight percent												
Fe	4.3	6.9	5.9	2.8	2.9	11.5	2.7	1.9	10.3	5.1	13.7	5.9
Cd	6.9	5.8	5.8	7.0	7.6	5.6	6.7	6.1	9.0	6.2	4.7	1.8
Zn	55.2	55.8	56.3	57.6	57.1	50.3	57.8	59.2	50.4	56.3	48.7	59.6
S	32.7	32.3	32.5	32.3	32.5	32.5	32.5	32.3	31.6	32.3	32.4	32.7
Total	99.1	100.8	100.5	99.7	100.1	99.9	99.7	99.5	101.3	99.9	99.5	100.0
Atomic ratios (Fe + Cd + Zn = 1.00)												
Fe	0.08	0.12	0.10	0.05	0.05	0.20	0.05	0.03	0.18	0.09	0.24	0.10
Cd	0.06	0.05	0.05	0.06	0.07	0.05	0.06	0.06	0.08	0.06	0.04	0.02
Zn	0.86	0.83	0.85	0.89	0.88	0.75	0.89	0.91	0.74	0.85	0.72	0.88
S	1.04	0.98	1.00	1.01	1.02	1.00	1.02	1.01	0.95	1.00	0.98	0.99

Mn, In and Hg are less than 0.08 wt.%. Analytical conditions: 20kV; synthetic standards: (Zn,Fe)S with 4.75 wt.% Fe for Zn$K\alpha$, Fe$K\alpha$ and S$K\alpha$ lines, CdS for Cd$L\alpha$ line; EMPADR VII correction program.

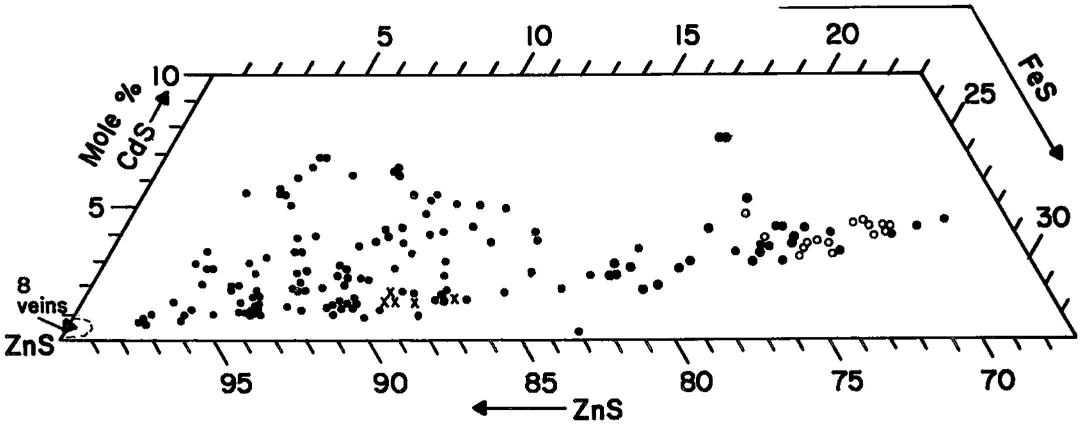

FIG. 3: Molar compositions of sphalerite samples from the Ross mine. "Normal" sphalerite from this mine is shown by the dashed line and "8 veins". The solid points are for cadmium-rich sphalerite associated with lautite-bearing galena. The open circles are the values for the "patches" and the crosses are the corresponding matrix compositions.

the lautite-bearing galena. This sphalerite generally occurs as a slightly concave zone, with the outer part separated by the galena and the inner part bounded by euhedral calcite. The sphalerite contains numerous minute inclusions of chalcopyrite, galena, pyrite, silicates and pits that increase in abundance towards galena. Numerous chalcopyrite and marcasite veinlets and cracks are present, and the cracks are roughly perpendicular to the concave outline. In polished thin section under transmitted light some of the sphalerite also shows color banding from yellow to reddish-yellow to dark brown. The inner bands adjacent to calcite are yellow and free of inclusions whereas the outer bands are dark brown with abundant inclusions. The sphalerite contains many light-colored "patches" which also proved to be cadmium-rich. The "patches" and the matrix sphalerite are optically similar but are readily resolved after etching with 1:1 HNO_3. The "patches" are irregular, mostly strip-like masses 5–75 μm long (Fig. 2) that seem to radiate towards the concave outline; a few of them have crude hexagonal shapes.

The cadmium-rich sphalerite was subjected to microprobe analysis. Some of the results are summarized in Table 3; all of the analytical data are displayed graphically in Figure 3. In contrast to the "normal" sphalerite in the Ross mine (Fig. 3), the cadmium-rich sphalerite is variable in composition over the following ranges (wt.%): Zn 48.2–66.1, Cd 0.4–9.0, Fe 1.0–15.8, S 31.6–33.9 (total 99.1–101.3%). The highest cadmium concentration observed was 9.0 wt. %. From Figure 3 it is hard to draw any conclusion about the effect of iron on the degree of cadmium substitution, although the Cd concentration commonly increases as the iron increases.

In one section the "patches" were sufficiently coarse to permit their analysis with minimal interference from the matrix sphalerite. Detailed analytical data are presented in Table 3 for both the "patches" (6 and 11) and the matrix (12). The "patches" are clearly cadmium-rich with respect to the surrounding matrix sphalerite, and have the compositional ranges (wt.%): Zn 48.7–51.3, Cd 3.8–5.6, Fe 11.5–14.7, S 31.6–32.9; their average composition is $(Zn_{0.73}Cd_{0.04}Fe_{0.23})S_{0.98}$, whereas that of the matrix is $(Zn_{0.88}Cd_{0.02}Fe_{0.10})S_{0.99}$.

The X-ray powder diffraction pattern (Gandolfi camera) of a crystal consisting mainly of "patches" is similar to that of synthetic sphalerite (JCPDS 5–566). The cell parameter calculated is 5.421(1)Å.

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