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HAWLEYITE, ISOMETRIC CADMIUM SULPHIDE, A NEW MINERAL*

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ABSTRACT

A new mineral identical with isometric cadmium sulphide has been found in the Hector-Calumet mine, Galena Hill, Yukon Territory. The mineral occurs as a fine-grained, bright yellow, earthy coating on sphalerite and siderite, in vugs and along late fractures. Geochemical and mineralogical evidence, together with laboratory studies, suggest that the mineral has been deposited from meteoric waters. The name hawleyite is given to this new mineral in honor of J. E. Hawley, Miller Research Professor, Queen's University, Kingston; Ontario.

Hawleyite is isometric, with space group $F\bar{4}3m$, $a = 5.818 \pm 0.005 \text{ \AA}$, and a sphalerite-type structure. Assuming a cell content of $4[\text{CdS}]$, the calculated specific gravity is 4.87.

INTRODUCTION

In 1954, while investigating the lead-zinc-silver deposits in the Keno-Galena Hill area of the Yukon one of the authors (R.W.B.) collected a specimen of sphalerite richly coated with a bright yellow mineral. The specimen was submitted to the X-ray Laboratory, Geological Survey of Canada, for identification of the yellow mineral.

The x-ray powder pattern of the mineral was found to match the pattern of $\beta\text{-CdS}$, the isometric polymorph of cadmium sulphide. A survey of the literature revealed that this compound has not been reported as occurring in nature.

The new mineral is named hawleyite in honor of Professor J. E. Hawley of Queen's University, Kingston, Ontario, who has contributed greatly to Canadian mineralogy as a mineralogist and teacher.

IDENTIFICATION (R.J.T.)

The specimen consists of a mixture of massive siderite and coarsely-crystalline sphalerite, with a bright yellow coating. A microscopic examination revealed that the coating was composed of a bright yellow mineral,

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now named hawleyite, admixed with lesser amounts of fine-grained sphalerite and siderite. The grain-size of the hawleyite was so small that individual grains could not be discerned.

Some of the admixed sphalerite and siderite was removed by brushing the coating through a 325-mesh screen, but a sample of hawleyite suitable for quantitative chemical analysis and specific-gravity determination could not be obtained. A partly purified sample was analyzed semi-quantitatively by *x*-ray spectrography and found to contain 50–70 per cent cadmium, 5–10 per cent zinc, and less than 5 per cent iron. Selenium could not be detected, indicating that less than 0.05 per cent is present.

Several *x*-ray powder photographs of hawleyite were taken using a camera with a diameter of 57.54 mm., and nickel-filtered copper radi-

TABLE 1. HAWLEYITE, β -CdS; X-RAY POWDER PATTERN
Isometric $F\bar{4}3m$; $a = 5.818 \text{ \AA}$, $Z = 4$

| <i>I</i> (Cu) | <i>d</i> (meas) | <i>hkl</i> | <i>d</i> (calc) | <i>I</i> (Cu) | <i>d</i> (meas) | <i>hkl</i> | <i>d</i> (calc) |
|---------------|-------------------|------------|-------------------|---------------|--------------------|------------|--------------------|
| 10 | 3.36 \AA | 111 | 3.36 \AA | 1 | 1.298 \AA | 420 | 1.301 \AA |
| 4 | 2.90 | 200 | 2.91 | 3 | 1.186 | 422 | 1.188 |
| 8 | 2.058 | 220 | 2.057 | 3 | 1.120 | 333, 511 | 1.120 |
| 6 | 1.753 | 311 | 1.754 | $\frac{1}{2}$ | 1.028 | 440 | 1.028 |
| 1 | 1.680 | 222 | 1.680 | 2 | 0.985 | 531 | 0.983 |
| 2 | 1.453 | 400 | 1.454 | $\frac{1}{2}$ | 0.918 | 620 | 0.920 |
| 3 | 1.338 | 331 | 1.335 | $\frac{1}{2}$ | 0.887 | 533 | 0.887 |

ation. The observed intensities and measured spacings of the hawleyite pattern are listed in Table 1, together with the spacings calculated from a lattice constant of 5.818 \AA . The observed intensities and measured spacings of the *x*-ray patterns of artificial β -CdS published by Milligan (1934) and Ulrich & Zachariasen (1925) are reproduced in Table 2. The close agreement between the patterns of Tables 1 and 2 clearly establishes the identity of the natural and artificial materials.

Hawleyite has a sphalerite-type structure with space group $F\bar{4}3m$. The lattice constant, $a = 5.818 \pm 0.005 \text{ \AA}$, was calculated from the powder pattern. Assuming a cell content of 4[CdS], the calculated specific gravity of the mineral is 4.87.

OCCURRENCE (R.W.B.)

The Hector-Calumet mine, from which the hawleyite was obtained, is the largest and most productive of the lead-zinc-silver mines in the Keno-Galena Hill area, Yukon Territory. This mineral district is in the central Yukon 35 miles northeast of Mayo and some 220 miles due north

TABLE 2. ARTIFICIAL β -CdS; X-RAY POWDER PATTERN
Isometric $F\bar{4}3m$; $a=5.820$ Å, $Z=4$

| Ulrich & Zachariasen (1925) | | <i>hkl</i> | (Milligan 1934) | |
|-----------------------------|------------------------------|------------|-----------------|-----------------|
| <i>I</i> (Cu) | <i>d</i> (meas) ¹ | | <i>I</i> (Cu) | <i>d</i> (meas) |
| 5 | 3.35 Å | 111 | 10 | 3.36 Å |
| 1 | 2.93 | 200 | 3 | 2.90 |
| 5 | 2.062 | 220 | 10 | 2.06 |
| 5 | 1.758 | 311 | 9 | 1.756 |
| $\frac{1}{2}$ -1 | 1.683 | 222 | 1 | 1.683 |
| 1 | 1.452 | 400 | 1 | 1.456 |
| $2-2\frac{1}{2}$ | 1.337 | 331 | 2 | 1.335 |
| $1\frac{1}{2}$ | 1.303 | 420 | 1 | 1.302 |
| $2\frac{1}{2}$ | 1.191 | 422 | 3 | 1.189 |
| $2\frac{1}{2}$ | 1.122 | 333, 511 | 3 | 1.121 |
| 2 | 1.033 | 440 | 2 | 1.026 |
| $3\frac{1}{2}$ | 0.985 | 531 | 2 | 0.982 |
| 1 | 0.971 | 442, 600 | | |
| $2\frac{1}{2}$ | 0.922 | 620 | | |
| $1\frac{1}{2}$ | 0.888 | 533 | | |
| 1 | 0.879 | 622 | | |

¹ Spacings calculated from the θ values of Ulrich & Zachariasen.

of Whitehorse. The district is served by an all weather road from Whitehorse and by Canadian Pacific Airlines.

The consolidated rocks underlying the area are mainly sediments belonging to the Yukon group of Precambrian or Paleozoic age. They consist of sericitic, chloritic, and graphitic schists, phyllites, and quartzites. Conformable sills and lenses of greenstone occur throughout the sediments.

The lead-zinc-silver vein deposits of Keno and Galena Hills occur in brecciated fault zones and sheeted zones. Two types of veins are recognized; an early vein type consisting of quartz, pyrite, and arsenopyrite, and a late vein type mineralized with siderite, galena, sphalerite, and argentian tetrahedrite. Both types may occur separately. The early type, however, may be fractured and contain minerals of the second type.

The veins near the surface are highly oxidized. The depth of oxidation varies but is seldom less than 50 feet. The minerals found in the oxidized zone include limonite, various manganese oxides, calcite, gypsum, smithsonite, cerussite, anglesite, quartz, azurite, malachite, and oxides of arsenic and antimony.

A marked feature of the veins in both the primary and oxidized parts,

is the presence of numerous vugs and open spaces in which excellent crystals of galena, sphalerite, siderite, calcite, gypsum, and quartz abound.

The specimen of hawleyite was obtained from a vuggy part of the primary zone of the Hector-Calumet mine. Similar occurrences of cadmium sulphide have been noted in other veins, but at the time of writing the examination of the ores is not complete, and it is not known whether or not all of the cadmium sulphide is hawleyite. Some may be greenockite.

ORIGIN

The geochemistry of the veins has not been worked out in detail but the mode of occurrence of the hawleyite suggests that it is a secondary mineral which has been deposited from meteoric waters in vugs and along late fractures.

Geochemical work shows that the sphalerite in the veins contains up to 1 per cent cadmium which undoubtedly replaces zinc in the sphalerite structure. Analyses of the meteoric waters show that zinc is present in amounts up to 2 parts per million. Cadmium was not detected, probably owing to its very low concentration in the waters. The waters are acid with a pH between 4 and 6. Sulphate (SO_4) is the principal anion, and some H_2SO_4 is present, accounting in part for the acid pH.

Analyses of the vein material show that the concentrations of zinc and cadmium in the oxidized parts are as much as 5 per cent lower than in the primary parts. These chemical facts in conjunction with mineralogical studies indicate that during the oxidation process the sphalerite is altered to limonite by the meteoric waters with consequent solution and transport of the zinc and probably the cadmium as sulphates.

Laboratory studies on the precipitation of cadmium sulphide from solutions of cadmium salts have been made by several investigators, and their results have a direct bearing on the origin of the hawleyite. Thus, Böhm & Niclassen (1924) first showed by *x*-ray diffraction that β -CdS is precipitated by H_2S from cadmium sulphate solutions. Their findings were confirmed by Ulrich & Zachariassen (1925) who prepared β -CdS for *x*-ray study by passing H_2S into a saturated solution of cadmium sulphate. Dana (1944, p. 230) reports incorrectly that Ulrich & Zachariassen prepared isometric CdS by heating CdS in sulphur vapor for two hours at 700–800°. Actually, Ulrich & Zachariassen prepared the hexagonal polymorph, α -CdS, by heating β -CdS in sulphur vapor. Milligan (1934) showed that β -CdS is formed at 30° C. when H_2S is passed through a 0.1 N solution of cadmium sulphate made acid by the addition of 1 c. c. of concentrated H_2SO_4 to 50 c. c. of solution. Milligan also found that

α -CdS is produced from 0.1 N solutions of cadmium nitrate, chloride, bromide, and iodide when treated in the same manner. These laboratory studies indicate clearly that hawleyite is the polymorph of cadmium sulphide which will be precipitated under reducing conditions from acidic sulphate solutions.

Considering the field facts and the knowledge that cadmium follows zinc closely in its geochemistry, it is logical to assume that in the zone of oxidation cadmium would be taken into solution by the meteoric waters which contain H_2SO_4 , and be transported downward into the zone of reduction. H_2S , generated by the action of H_2SO_4 on primary sphalerite and other sulphides, would reduce the cadmium sulphate and precipitate hawleyite (β -CdS) as shown by the laboratory studies.

Acidic sulphate solutions, from which the hawleyite polymorph of cadmium sulphide precipitates, are common in sulphide deposits, and it seems probable that hawleyite is more common than its very recent discovery would indicate. Much material, previously identified as greenockite by casual hand-specimen examination, may prove to be hawleyite when identified by x -ray diffraction.

REFERENCES

- BÖHM, J. & NICLASSEN, H. (1924): Über amorphe Niederschläge und Sole, *Zeits. anorg. Chem.*, **132**, 7.
- DANA, J. D. & E. S. (1944): *System of Mineralogy*, 1, ed. 7, by C. Palache, H. Berman and C. Frondel, New York.
- MILLIGAN, W. O. (1934): The color and crystal structure of precipitated cadmium sulphide, *J. Phys. Chem.*, **38**, 797-800.
- ULRICH, F. & ZACHARIASEN, W. (1925): Über die Kristallstruktur des α - und β -CdS sowie des Wurtzits, *Zeits. Krist.*, **62**, 260-273.