ILSEMANNITE AND JORDISITE

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Abstract

Ilsemannite, a molybdenum mineral of uncertain composition, was identified in Oregon for the first time by the writer in 1939, in an ore specimen from the Kiggins mine on the Oak Fork of the Clackamas River. The occurrence is different from any previously described in that the ilsemannite is associated with cinnabar, the latter being of good enough grade to permit profitable mining during periods of high prices.

The ilsemannite occurs as a coating and alteration product of a fine-grained, black, sectile, submetallic material. Chemical and x-ray analyses of the original black material prove it to be an amorphous molybdenum disulfide. It is recommended that the name "jordisite," suggested by Cornu in 1909, be used for this material. Höfer and other writers have assumed ilsemannite was derived from wulfenite, other molybdates, or molybdenite.

Jordisite, possibly because of its amorphous state, alters more readily to ilsemannite than does molybdenite. This, together with the relative scarcity of jordisite in mineral deposits, probably accounts for the few known occurrences of ilsemannite in molybdenum districts.

INTRODUCTION

The Kiggins mine on the Oak Fork of the Clackamas River, located about 50 miles southeast of Portland, Oregon, has been a small intermittent producer of quicksilver. In 1939, when the writer was engaged as geologist in charge of developing this property, he had an opportunity to collect several interesting suites of minerals from the mine. One of the gangue minerals associated with the cinnabar was identified as ilsemannite. Laboratory work later confirmed this field identification. A further study of the ilsemannite showed that it occurred as a coating on a black sectile material from which it was obviously derived. As the origin of ilsemannite has never been satisfactorily explained, a study of this material was undertaken in the hope of obtaining further information leading toward the solution of the problem.

Acknowledgments

Data for this paper were obtained in part from the chemical analyses made by Mr. K. C. Peer of San Francisco, and Mr. H. C. Frye of the Department of Chemistry, University of Oregon, and from the x-ray diffraction photographs obtained under the direction of Dr. J. D. H. Donnay of The Johns Hopkins University and Mr. A. J. Kaufmann, Jr., of the U. S. Bureau of Mines, Albany, Oregon. Two spectrographic analyses were made by Mr. T. C. Matthews of the Oregon State Department of Geology and Mineral Industries. The writer also wishes to acknowledge financial assistance from the Graduate School of the University of Oregon which helped defray the expense of some of the analyses.

ILSEMANNITE

Andesites, probably of Miocene age, form the country rock in the region of the Kiggins mine. They are highly fractured, the most prominent trend of fractures being N. 45° W. Veins filling these fractures and related fissures contain cinnabar in commercial amounts. Calcite, pyrite, and stilbite are the principal gangue minerals.

The ilsemannite is found as veinlets and irregular lenses or pods closely associated with the cinnabar. Although ilsemannite is found in small amounts in many places in the mine, the richest occurrence is in the main tunnel (adit #1), 45 to 60 feet from the portal. Here the ilsemannite is in a calcite vein which varies in dip from 60° N. E. to almost vertical, and extends in a N. 45° W. direction along the adit. An underhand stope 6 feet deep, was put down on the calcite vein at this point and showed a concentration of both cinnabar and ilsemannite on the footwall.

Stilbite frequently occurs as a fissure filling with well-developed comb structure, the subhedral crystals often exceeding 5 cm. in length. In addition, fine-grained stilbite is intimately mixed with cinnabar, in the calcite veins. This close association of stilbite and cinnabar, although not common in quicksilver mines, is not anomalous since both minerals are characteristic of low temperature, epithermal deposits. The ilsemannite when first found has a dark blue-black color and often stains the calcite light blue. On exposure to sunlight the ilsemannite turns blue-green and fades. Some of the mineral was furnaced along with the cinnabar and the calcined product emerged a purplish pink in color. Ilsemannite is soluble in water, first producing a greenish blue solution which later deepens to a typical molybdenum blue.

Although ilsemannite is not a common mineral, there are several known occurrences of it. It was first described by Höfer (1871) from Bleiberg, Carinthia. Since then it has been described from more than a dozen localities, but in spite of this there is still uncertainty regarding its origin and chemical composition.

Hess (1925, p. 9) has shown that Höfer in his original discussion of ilsemannite confused two substances, one a black material and the other a blue substance derived from the first. Hess remarks, "The black mineral that forms with water first a greenish-blue and then a blue solution may be a different mineral having perhaps some such relation to ilsemannite as anhydrite (CaSO₄) has to gypsum (CaSO₄ $2H_2O$)." Strunz (1941) describes ilsemannite as amorphous, and corresponding to the so-called blue molybdenum oxide. Dana (1944, pp. 602–603) well summarizes the situation by stating, "Possibly several different substances are represented among the natural occurrences." In general, most mineralogists seem to have applied the name "ilsemannite" to any molybdenum compound or mixture which is water soluble and turns the solution a typical molybdenum-blue color.

No method was worked out whereby the very thin coating of ilsemannite, often existing only as a stain on other water soluble minerals like halotrichite, could be separated from them. Consequently chemical analyses of this material were not obtained.

Underneath the coating of soluble sulfates and ilsemannite there was discovered a black, submetallic, sectile mineral which was first thought to be metacinnabar. Microchemical tests, however, proved it to be a molybdenum compound rather than a mercury mineral. It is obvious that the ilsemannite is derived from this black mineral, since the ilsemannite occurs as bluish spots, coatings, or along cracks where there was opportunity for ready alteration.

Ilsemannite is usually considered to be a secondary mineral and there has been considerable uncertainty concerning the primary or earlier mineral from which it was derived. Höfer (1871) believed the Bleiberg ilsemannite to be derived from wulfenite, as no other molybdates were known from the locality, but he had no positive evidence and based his conclusions on the fact that a molybdenum-blue coloration may be obtained by the action of concentrated sulfuric acid on wulfenite. Cook (1922), in studying ilsemannite from Shasta County, California, suggested molybdenite as the source mineral. Likewise, Lindgren and Ransome (1906, p. 124) believed that ilsemannite from Cripple Creek, Colorado, was a direct product of the oxidation of molybdenite. Hess (1925, p. 16) concluded that, "Ilsemannite, like wulfenite, is probably formed from some unknown mineral, perhaps a sulfide." The fact that molybdenite deposits so seldom are accompanied by ilsemannite makes it doubtful that molybdenite is usually the source of ilsemannite.

A study of the black mineral in polished sections and in fragments indicates that it is not molybdenite. It lacks cleavage, is dull black except where scratched, and then it has a submetallic gray black to lead gray appearance. It is soluble in concentrated HNO₃, very slightly soluble in HCl and insoluble in H_2SO_4 and H_2O . In the Clackamas occurrence it was deposited about the same time as the cinnabar and later than the calcite and stilbite. Figure 1 shows veinlets of the black mineral following the rhombohedral outlines of the calcite.

CHEMICAL DATA

Because the Clackamas material is an intimate mixture of molybdenum minerals with quartz, cinnabar, stilbite, pyrite, opal, halotrichite, and

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calcite, separation for analysis is very difficult. Purification of the black mineral was accomplished first by removing the water-soluble minerals and then discarding all the other remaining minerals by hand-picking under the microscope. Two spectrographic analyses were made on this material, the first¹ showing Si and Ca greater than 10%; Al, Fe, Mo, ranging from 10% to 1%; Mg, As from 1% to 0.1%; Na, K, Mn, Ti, Ba, Sr, from 0.1% to 0.01%, and Cr, V, Cu, Bi, B, less than 0.01%. A second



FIG. 1. Jordisite veinlets (black) with rhombohedral pattern outlining calcite.

spectrographic analysis on slightly purer material² obtained Si as the major constituent; Mo from 20% to 10%; Fe from 6% to 3%; Al from 0.5% to 0.1%; and smaller amounts of Ca, Na, Ba, Cu, Mn, Ni, Sr, Ti, and V. The question raised by these analyses was whether the black mineral was a complex salt such as a silicomolybdate of iron or aluminum, or whether most of the reported elements were due to impurities that were not removed.

¹ Analysis by Oregon State Department of Geology and Mineral Resources, T. C. Matthews, analyst.

² Analysis by Multiphase Laboratories, San Francisco, K. C. Peer, analyst.

Two small samples of the purified material were analyzed³ and the following was determined to be the composition of the material:

Silica (SiO_2)	57.0
Molybdenum sulfide (MoS ₂)	20.5
Iron sulfide (FeS ₂)	9.3
Alumina (Al ₂ O ₃)	1.2
Calcium compound (CaX)	0.6
Heavy metal sulfides (as HgS) also undetermined and traces	1.2
Total water	10.2
	100.0%

It was evident that the analyzed sample contained impurities of pyrite, stilbite, and cinnabar, so the presence of iron sulfide, alumina, calcium, and heavy metal sulfides was to be expected in the above analysis. The analysis indicated only a trace of sulfate sulfur, practically all of the sulfur appearing as sulfide sulfur. On distributing the sulfur between the iron and molybdenum, there was almost exactly the correct amount to yield the formula MoS_2 , making it evident that although the material did not have the properties of molybdenite it was a molybdenum disulfide.

It was found possible to make a satisfactory bromoform separation of the material, thereby removing almost all of the cinnabar, pyrite, and calcite. As a further check for the presence of molybdenum disulfide an analysis⁴ was made of some material purified in this manner. This showed only a trace of iron and when all the sulfide was applied to the molybdenum present it gave a ratio of 59.8% molybdenum to 40.2%sulfur, as compared with an ideal ratio of 60.0% to 40.0% for MoS₂, leaving no doubt that the compound is molybdenum disulfide.

X-RAY ANALYSIS

X-ray diffraction patterns were made on the material by Dr. J. D. H. Donnay and Mr. A. F. Rekus of The Johns Hopkins University. These exposures indicated the presence of considerable quartz which yielded the predominant pattern, and corroborated the chemical analysis. No additional match could be made from the weaker lines and a comparison with molybdenite from Haddam, Conn., and Ogden Mine, N. J., indicated that the black mineral was not molybdenite. Dr. Donnay⁵ made the interesting observation that colloidal matter might be present as indicated by several broad bands in some of the films. These

⁴ H. C. Frye, Dept. of Chem., Univ. of Oregon, analyst.

⁵ Personal communication.

³ Analysis by Multiphase Laboratories, San Francisco, K. C. Peer, analyst.

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results were confirmed by x-rays⁶ on material further purified by bromoform separation and the only pattern obtainable was that of quartz, with no evidence of the presence of any molybdenite. From these analyses it is concluded that the black mineral is an amorphous molybdenum disulfide.

JORDISITE

Cornu (1909) stated that ilsemannite is derived from a black powdery colloidal molybdenum sulfide which he called "jordisite." He gave no proof of this derivation nor did he describe jordisite. Hess (1925, p. 16) in commenting on this reference stated, "It does not convince one that his material was really a sulphide of molybdenum." So far as known no one has confirmed the occurrence of jordisite since Cornu's brief description. The present study on material from the Clackamas locality indicates that Cornu was correct in his statement that ilsemannite is derived from a black colloidal molybdenum sulfide, and although Cornu did nothing to establish the name "jordisite," the occurrence in Oregon should confirm the name as a valid one for the mineraloid. Furthermore, unlike the most common occurrence of molybdenite, jordisite appears to be a low temperature product as indicated by its association with cinnabar and zeolites. This, together with the relative rarity of jordisite, may explain the scarcity of ilsemannite in most molybdenite deposits. In those few cases where ilsemannite has been reported as associated with or derived from molybdenite, it is likely that some jordisite was also present.

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⁶ Diffraction pattern by U. S. Bureau of Mines, Albany, Oregon.

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