

REPLACEMENT OF WOLFRAMITE BY SCHEELITE WITH OBSERVATIONS ON THE FLUORESCENCE OF CERTAIN TUNGSTEN MINERALS

FRANK R. VAN HORN, *Case School of Applied Science.*

In September 1929, while on a rather hurried visit to the tin mines and china clay deposits of Cornwall, England, Captain M. T. Taylor of the East Pool Mine near Camborne, gave the writer a specimen that was very interesting and somewhat unusual. It came from a characteristic "lode fissure or crush conglomerate" at a depth of probably over 1500 feet. Of the twenty-two minerals listed by Ferguson and Bateman in "Geologic Features of Tin Deposits"¹ as occurring in Cornish mines, the specimen contains eight and, in addition, a ninth which they do not mention, namely, pyrrhotite. Nor does MacAlister in his "Geologic Aspects of the Lodes of Cornwall"² mention the occurrence of this mineral. It was thought at first that the pyrrhotite might possibly be stannite which although a very rare mineral, seems to be more common in Cornwall than pyrrhotite. However, the mineral is quite strongly magnetic, and specimens of stannite from Redruth, Cornwall; Zeahan, Tasmania; and Oruro, Bolivia; which were examined, were not at all magnetic. The mineral occurs in very small particles but possesses all the characteristics of pyrrhotite. The nine minerals identified, in the probable order of their importance are: quartz, wolframite, scheelite, arsenopyrite, pyrrhotite, chalcopyrite, fluorite, chlorite and cassiterite.

The wolframite is partially or wholly altered or replaced by pinkish scheelite, and the alteration seems to have taken place at right angles to the cleavage planes (010) and not parallel which would be easier, and this may be due to cross fractures in the vein along which calcareous solutions have circulated. In all places the wolframite is surrounded by the pinkish mineral. In some cases just a small particle of wolframite remains in the center of the grain, and in others the pink mineral, which is believed by the writer to be practically all scheelite, has completely replaced the wolframite.

¹ Economic Geology, Vol. 7, 1912, pp. 209-262.

² Economic Geology, Vol. 3, 1908, pp. 363-380.

Figure 1 shows a large black mass of wolframite with pronounced clinopinacoidal cleavage (010). It also shows small seams of scheelite at right angles to the cleavage plane. Since the color of the scheelite in the specimen is pinkish, the color in the photograph is intermediate between that of the white quartz and the black wolframite. In the upper left hand corner is a mass of scheelite with three elongated plates of wolframite still unaltered.

Figure 2 is the reverse side of Figure 1, and in the lower left hand corner and upper center above the white quartz band, is to

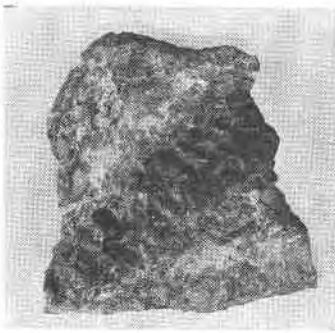


FIG. 1.

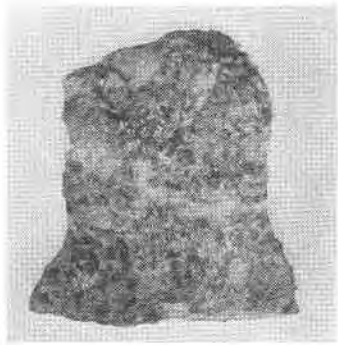


FIG. 2.

be seen especially well the black kernels of wolframite surrounded by grayish scheelite. The other six minerals on the specimen are not easily distinguishable in the photographs.

The writer loaned the specimen to Mr. Frank L. Hess, Chief Engineer, Rare Metals and Non-Metals Division, United States Bureau of Mines, Washington, D.C., who examined both a polished specimen and thin section. Mr. Hess says: "The polished specimen shows that replacement has taken place. The section shows that very little of the replacement has been made by scheelite. It follows an earlier mineral which was probably rhodonite but which is now greatly altered. As you will see in the section, there is a little fluorite, and fluorite, scheelite and quartz are later than the rhodonite, though possibly a little of the scheelite is earlier." The writer is very grateful to Mr. Hess for his interest and assistance. As Captain Taylor had stated to the author that the pink mineral was scheelite, while Mr. Hess thought that only a small part consisted of that mineral, the writer recalled that among the

specimens which for years have been used to demonstrate the phenomena of fluorescence and phosphorescence under ultra-violet radiation, was one of scheelite from Atolia, California, which shows a bright light blue fluorescence, he therefore decided to test the Cornish specimen under the same conditions. The ultra-violet rays were produced by a high tension disruptive spark between iron terminals. The specimen in question showed the same beautiful bright blue fluorescence as the scheelite from Atolia, but with a darker blue color, so that the conclusion was drawn that practically all the pinkish mineral surrounding the wolframite was scheelite.

About this time, Mr. W. L. Lemcke, of Franklin, Pa., who had seen the abstract³ of the paper given by the writer at the Washington meeting of the Mineralogical Society of America, December 27, 1929, noted the somewhat qualified statement: "The wolframite is partially or wholly altered or replaced by a pinkish mineral which seems to consist, at least in part, of scheelite." Mr. Lemcke wrote to inquire if the specimen had been subjected to ultra-violet rays because "sometime ago, Mr. Paul Walther kindly presented me with a specimen of milky-white translucent quartz containing black, bladed wolframite altering to pale yellow scheelite, from Carrock Fell, Cumberland, England. Under the iron arc, some of the scheelite exhibited a bright light blue fluorescence, and some a bright dark blue fluorescence. Moreover, a specimen of pale pink scheelite from Fairbanks, Alaska, kindly presented to me by Mr. Lewis Reamer, exhibited a bright beautiful blue fluorescence under the iron arc." Mr. Lemcke loaned his Carrock Fell specimen to the writer for investigation and suggested that if I had not already done so, it might be worth while to test all the minerals of the scheelite group at my disposal. He also called my attention to investigations by De Rohden on the discovery of rare earths in scheelites which is thought to cause the fluorescent phenomena, and which will be discussed later. The writer is under great obligation to Mr. Lemcke for his interest and help.

Altogether the writer investigated fourteen specimens of scheelite, one of which was artificial calcium tungstate; and twenty-five specimens of ferberite, reinite variety of ferberite, wolframite and huebnerite, four of which contained scheelite and are there-

³ *American Mineralogist*, Vol. 15, No. 3, March, 1930, p. 120.

fore listed in two places. These specimens with localities and various observations together with their behavior under ultra-violet radiation are listed below.

SCHEELITES

Specimen No.	Characteristics	Locality	Fluorescence
1	Massive, pink with wolframite, quartz, arsenopyrite, pyrrhotite, chalcopyrite, fluorite, chlorite and cassiterite.	East Pool Mine, Camborne, Cornwall, England.	Bright dark blue. Wolframite negative.
2	Granular white.	Atolia, California.	Bright light blue.
3	Crystal, yellow.	Caldbeck Fell, Cumberland, England. ⁴	Bright light blue.
4	Crystal, yellow.	Kai, Japan.	Bright light blue.
5	Crystal, yellow, altering to reinite (Ferberite).	Kimbosan, Kai, Japan.	Bright light blue. Reinite negative.
6	Massive, yellow, with reinite.	Sannotake, Buzen, Japan.	Bright light blue. Reinite negative.
7	Granular, creamy, with stibnite.	Near Armidale, New South Wales, Australia.	Bright light blue.
8	Crystal, yellow, with iron tourmaline. Outside weathered cloudy, underside transparent yellow.	25 miles west of Cananea Sonora, Mexico.	Bright light blue on weathered surface, transparent yellow material absolutely none.
9	Aggregates of small crystals, greyish brown.	Zinnwald, Erzgebirge, Bohemia.	Crystals show none, but when powdered gave faint light blue.
10	Crystals, yellowish grey, with zinnwaldite and quartz.	Zinnwald, Erzgebirge, Bohemia.	Absolutely negative.

⁴ The locality of specimens 3, 12, and 13 are described by Paul Walther, *American Mineralogist*, vol. 5, No. 3, March 1920, pp. 54-57.

Specimen No.	Characteristics	Locality	Fluorescence
11	Massive, greenish grey, with molybdenite and hornblende.	Clifton District, Tooele County, Utah.	Negative.
12	Pale yellow altering from wolframite with quartz.	Carrock Fell, Cumberland, England. ⁴	Bright light blue. Wolframite bright dark blue.
13	Pale yellow altering from wolframite with gruenlingite (Bi_4TeS_3) and quartz.	Carrock Fell, Cumberland, England. ⁴	Bright light blue. Wolframite bright dark blue.
14	Artificial white CaWO_4 .	Cleveland Wire Works, General Electric Co., Cleveland, Ohio.	Bright light blue.

WOLFRAMITES

For a classification and discussion of the various tungstates of iron and manganese, one should consult "Tungsten Minerals and Deposits" by Frank L. Hess.⁵

Specimen No.	Characteristics	Locality	Fluorescence
1	Ferberite.	Tirpersdorf, Saxony.	Negative.
2	Ferberite, var. Reinite.	Same as scheelite No. 5.	Negative.
3	Ferberite, var. Reinite.	Same as scheelite No. 6.	Negative.
4	Wolframite.	Same as scheelite No. 12.	Bright dark blue.
5	Wolframite.	Same as scheelite No. 13.	Bright dark blue.
6	Wolframite.	Same as scheelite No. 13.	Bright dark blue.

⁵ *Bulletin* 652, U. S. Geological Survey, Washington, D. C., 1917.

Specimen No.	Characteristics	Locality	Fluorescence
7	Wolframite, with quartz.	Near Goldyke, Paradise Range, Nye Co., Nevada.	Very intense bright dark blue in cracks.
8	Wolframite.	Upper Lead, South Dakota.	Intense bright light blue.
9	Wolframite.	Upper Lead, South Dakota.	Less intense bright light blue.
10	Wolframite or dark huebnerite.	Lawrence Co., South Dakota.	In spots bright light blue.
11	Large crystal wolframite with zinnwaldite and quartz.	Zinnwald, Erzgebirge, Germany.	In spots weak light blue.
12	Large crystal wolframite.	Same as No. 11.	Faint, light blue, almost negative.
13	Crystal wolframite.	Same as No. 11.	Same as No. 12.
14	Crystal wolframite.	Same as No. 11.	Same as No. 12.
15	Crystal wolframite.	Altenberg, Erzgebirge, Germany.	Same as No. 12.
16	Wolframite with arsenopyrite, chalcopyrite, and quartz.	Cornwall, England.	Negative.
17	Same as No. 16.	Same as No. 16.	Same as No. 16.
18	Wolframite with quartz.	Borestown, New Brunswick, Canada.	Negative.
19	Wolframite or dark huebnerite.	Bolivia.	Very little.
20	Wolframite or dark huebnerite. Fresh cleavage pieces.	Bolivia.	Negative.
21	Wolframite.	Llallagua, Bolivia.	Negative.
22	Huebnerite with quartz.	Minnesota Gulch, near Silverton, Col.	Negative.

Specimen No.	Characteristics	Locality	Fluorescence
23	Same as No. 22.	Same as No. 22.	Negative.
24	Huebnerite.	Near Deadwood, South Dakota.	Negative.
25	Huebnerite with quartz.	Redlicht District, Esmeralda Co., Nev.	Strong bright light blue.

An inspection of the results shows that fluorescence is the rule among the scheelites but that in the crystals from Zinnwald it is practically absent or very weak (Nos. 9, 10). The same was true with No. 11. On the other hand the phenomenon is the exception among the wolframite minerals, only eight out of twenty-five specimens showing any indication of color change. It is, however, to be noted that the specimens of wolframite from Zinnwald show the fluorescence better than the scheelites from the same locality. None of the specimens showed any phosphorescence after the source of the excitation was removed.

Since it seemed possible that the phenomena might be due to surface changes caused by alteration, such as oxidation to tungstite (WO_3), a specimen of tungstite on wolframite from Ponga, Oruro, Bolivia, was tested and both minerals gave absolutely no fluorescence. Mr. W. P. Sykes of the Research Laboratory of the Cleveland Wire Works of the General Electric Company kindly furnished the writer with a sample of artificial WO_3 and $CaWO_4$. The former gave no results while the latter showed the normal fluorescent color given by most scheelites. (See No. 14). Mr. Sykes stated that both artificial substances were pure. It, therefore, seems probable that all the eight wolframites which fluoresced were coated with a small amount of scheelite due to alteration or replacement similar to the specimen from the East Pool Mine, which was the original cause of this article, but in which the changes had gone farther, even to the complete alteration of the wolframite.

The writer had no specimens of cuproscheelite or cuprotungstite, powellite, or stolzite, which are the other members of the scheelite group, to investigate (wulfenite shows no color), and it is to be hoped that others who have these minerals will test them under

ultra-violet rays. With this in view, the Department of Mineralogy at the University of Michigan was asked to investigate their specimens, and Professor Walter F. Hunt, to whom my thanks are due, wrote as follows: "This afternoon I made the tests with the iron arc. As we do not seem to have tungstite in the museum, I could not run the test on that mineral. I tested scheelite from California; Dragoon Mts., Arizona; Idaho; Derbyshire; Kai, Japan; Schwarzenberg; Schlaggenwald; and a number from Zinnwald. All showed various shades of blue with the exception of those from Schlaggenwald and Zinnwald. Here most of the specimens gave negative results with the exception of one massive white specimen which gave a beautiful blue fluorescence. Apparently those from Zinnwald behave differently, as a rule, with the exception of that single specimen, and it is barely possible that the label as to locality is not correct in that case. None of the wolframites were affected with the exception of a wolframite pseudomorph after scheelite from Monroe, Conn., and here no doubt the blue was due to some unreplaced scheelite." In general, the results obtained by Dr. Hunt conform to those obtained by the writer.

Mention has already been made of an article by C. De Rhoden, "Sur La Phosphorescence Cathodique des Scheelites et des Alumines"⁶ He investigated seven scheelites under cathode rays and found them all to "phosphoresce," and that the colors of three of the seven were "persistent." I assume that all fluoresced under cathode rays and that three phosphoresced when the source of excitation was removed. He examined this "phosphorescent" (fluorescent?) light with a spectroscope and found bands, although not of the usual kind, indicating the presence of dysprosium and samarium in all seven scheelites. Terbium was found in five, europium in two, and praseodymium, neodymium, and erbium, in one specimen each. Three scheelites came from unknown localities, two from Marmolejo, Cordoba, Spain; one from Waipone, Otago, New Zealand, and one from Gangthal Salzburg, Austria. The writer had no specimens from any of De Rhoden's known localities, and is not sure that his phosphorescence under cathode rays is identical with the fluorescence under ultra-violet radiation, but it is very clear that De Rhoden believes that the phenomena observed by him on seven scheelites is due to the presence of the rare

⁶ *Annales de Chimie*, 9 serie, 3-4, 1915, pp. 338-366.

earths enumerated above. He further states that Cossa⁷ observed in scheelites from Traversella, Italy; Jumilla, Spain; and Meymac, France, the absorption spectrum bands of didymium, cerium and lanthanum, and that Cossa made artificial scheelite containing didymium which showed the same bands as the natural occurring specimens.

CONCLUSIONS

The writer has described the alteration or replacement of wolframite by scheelite from the East Pool Mine, Camborne, Cornwall, England, and has found that most scheelites fluoresce under ultra-violet radiation, and that some wolframites and huebnerites show the same phenomenon. It is suggested that in the last mentioned minerals this is caused by a slight alteration to scheelite. No explanation can be given why the scheelites Nos. 9, 10, and 11 do not show fluorescence unless we accept the explanation of De Rhoden, and assume that they do not contain the rare earths. It should also be remembered, however, that the artificial scheelite, No. 14, said to be pure CaWO_4 , fluoresces like most of the natural scheelites. The whole object of the latter part of this paper has been to record the results obtained and to stimulate further investigations on the subject and especially on the cause of the fluorescence of the various tungsten bearing minerals.

⁷ *C. R. Acad. Sc.*, Vol. **LXXXVII**, p. 377.