

FLUORESCENT ANALYSIS

with Ultra Violet Rays

THE SHORTWAVE ULTRA-VIOLET LAMP IN SCHEELITE PROSPECTING

Magic Mineralight has located Scheelite worth over \$100,000,000. From the Arctic to the Antarctic—around the world through the United States, Canada, Mexico, South America, Africa, the East Indies, Australia and China—the magic black-light rays of Mineralight have uncovered fabulous hidden values of scheelite, ore of Tungsten. And other values too, in zinc mercury, zirconium, have rewarded Mineralight prospectors, to say nothing of the genuine satisfaction and pleasure its use has brought to mineralogists and collectors.

Mineralight short-wave ultra-violet lamps have a special filter which screens out most visible light but allows passage of the short ultra-violet rays. Used in darkness, these black light rays, as they are called, excite vivid color reponses from fluorescent objects, such as mineral ores mentioned above, as well as many other types of fluorescent and phosphorescent materials.

PROSPECTING FOR SCHEELITE

Without the help of Mineralight, scheelite is extremely difficult to locate because of the wide variety of rocks in which it appears. Ordinarily, it is found close to a limestone-granite contact, but often these contacts are hard to locate. Every type of ore should be carefully examined with a Mineralight. The 400 display specimens of scheelite in the office of the Ultra-Violet Products, Inc., illustrate the wide variety of rocks in which scheelite is found. The greatest number of samples are in limestone—then garnet, quartz, granite, epidote, gneiss, magnetite and also ores associated with gold, copper, silver, iron and molybdenum.

The fluorescent colors which indicate the presence of scheelite are blue, blue-white, cream and a golden yellow.

The pure form of calcium tungstate fluoresces a bright blue. The crystals are hard and the edges well defined. The appearance of the ore in daylight may be a white to orange grey, but the bright blue-white fluorescence indicates the lack of impurities in the scheelite.

Scheelite usually forms in small crystals disseminated through the rock. These vary from the size of a pin head to the size of a silver dollar. Sometimes it forms in solid veins, stringers or chunks, but the small disseminated spots are the most common.

Some scheelite fluoresces a white color. This type of ore is usually a true calcium tungstate, especially if the fluorescent areas are hard and well defined. If the crystals are soft and can be powdered with the fingernail it indicates the presence of more calcium than tungsten and the assays will probably be low.

The golden yellow fluorescence of scheelite is a definite indication that some impurity exists in the scheelite. Usually this is molybdenum but it may be copper, (cupro-scheelite) iron, manganese, etc. The combination of calcium tungstate and calcium molybdate is most frequently found. This ore is usually called powellite and may or may not have value. If the calcium tungstate predominates the crystals will be hard, with well defined edges and an apparent depth to the crystals. If the fluorescent spots smear upon rubbing, powder under pressure of the thumb nail or are more of a coating than a well defined crystal, it is likely that the amount of tungsten present is small or lacking. All scheelite which fluoresces yellow should be checked by assay much more carefully than the scheelite fluorescing blue or blue-white. A great many profitable mines are operating on golden yellow scheelite because the amount of impurities is small, but the yellow color does indicate an impurity which must be carefully checked and analyzed before development of the property.

FLUORESCENT LIGHT USED IN MOLYBDENUM ASSAY

A new method of evaluating certain tungsten deposits on the site of discovery, which will assist in the minerals war production program, has been developed by the U. S. Geological Survey, and an improved method of

accurate chemical determination of molybdenum in tungsten ores has also been perfected. Both are procedures for estimating the molybdenum content of scheelite, a common domestic mineral of tungsten. In the past the presence of molybdenum in scheelite has been detected only by testing in assay laboratories. One of the Survey's new testing methods, a fluorescence method, may be used in the field with results sufficiently accurate to permit a better appraisal of the ore.

The intensive search for tungsten, begun by the Survey in 1938, has met with success, although considerable scheelite with undesirable molybdenum content has been encountered. Most of the scheelite in the contact-metamorphic deposits of the Western states contains at least a trace of molybdenum, and in many localities as much as half a per cent. As commercial scheelite concentrates containing more than 0.4 per cent of molybdenum are subject to a price penalty, these methods of testing will be useful to persons engaged in developing, mining, or milling scheelite ores.

By the fluorescent method, the molybdenum content of scheelite can be estimated visually in the field by any good observer equipped with an ultra-violet lamp. This method is based on the discovery that the fluorescence color of scheelite is directly related to the proportion of molybdenum contained in the crystal lattice of the mineral. In general, concentrates that are not penalized for molybdenum can be made from any scheelite that fluoresces distinctly blue; those that fluoresce white are borderline cases containing roughly from 0.35 to 1.0 per cent molybdenum; and scheelite that fluoresces distinctly yellow contains more than 1 per cent.

Occasionally a form of calcium carbonate will fluoresce and resemble scheelite very closely. When the calcium carbonate is a blue-white it is usually pale and does not have the luster of scheelite. It is often in the form of a coating, has the appearance of a fine grained substance and lacks the crystal structure of scheelite. Sometimes it phosphoresces and this definitely proves it cannot be scheelite. In a few rare instances Calcium carbonate has a golden color similar to scheelite but in these cases it is soft and smears upon rubbing.

The filter on the Mineralight Lamp passes a very small amount of blue-purple light. This light is reflected from the rock that is being examined. It will be a dark purple or blue that varies according to the natural color of the rock being examined. A white rock will reflect blue and a dark rock will reflect purple. This reflection should not be confused with fluorescence.

Scheelite never fluoresces green, red or pink. Also, for all practical purposes, it never phosphoresces. The fluorescence disappears instantly when the Mineralight is turned off. *Scheelite responds only to short-wave ultra-violet light, not to the long-wave.*

THERE ARE SEVERAL TUNGSTEN ORES

Tungsten never occurs free in nature and is found in relatively few minerals. Of the fourteen known tungsten-bearing minerals, the only four of commercial importance are Ferberite, FeWO_4 ; Wolframite, $(\text{Fe}, \text{Mn})\text{WO}_4$; Hubnerite, MnWO_4 ; and Scheelite, CaWO_4 . In each of these tungsten is the principal constituent. Scheelite and wolframite are the world's most important tungsten ore minerals. Ferberite is the principal tungsten mineral in Colorado's most productive deposits. Hubnerite is seldom

found in commercial ore bodies. The United States is unique in that it alone of the tungsten-producing countries produces more scheelite and ferberite than wolframite.

CHARACTERISTICS OF SCHEELITE

Scheelite, calcium tungstate (CaWO_4), contains 80.6 per cent WO_3 when pure and is the principal tungsten ore mineral in California. The mineral is white, yellowish-white, or else colored in light shades of yellow, brown, green, and red. The streak is white, and freshly broken surfaces show a characteristic greasy luster. Other characteristics are hardness, 4.5 to 5; specific gravity, 5.9 to 6.1; tenacity, brittle; cleavage, perfect; and fracture, uneven. Crystallizing in the tetragonal system, its habit is octahedral and tabular; it can also occur in regular masses with columnar structure and in granular massive forms. *Scheelite is characterized by its bright, light blue fluorescence under ultra-violet light.* The use of the ultra-violet lamp for recognition of scheelite is common as an aid in ore grade control and to check mill efficiency.

Ferberite, wolframite, and hubnerite form an isomorphous series between iron tungstate and manganese tungstate and are generally termed the wolframites. These are all heavy (sp. gr. from 7.2 to 7.5) and have a hardness of about 5. They range in color and streak from black to reddish brown. All have a sub-metallic luster. They have perfect cleavage in one direction and uneven fracture. Their crystal system is monoclinic, and bladed or lamellar cleavage masses are common. None of these minerals fluoresce under ultra-violet light, although scheelite is commonly associated with them.

The presence of tungsten in a mineral can be determined by the formation of a lemon-yellow residue when the powdered mineral is placed in concentrated hydrochloric acid and boiled. The residue thus formed can be subjected to two distinctive tests: (1) it is soluble in ammonia; (2) tin or zinc added to the above residue in hydrochloric acid solution will turn the residue a deep blue color.

Tungsten deposits have been formed under widely different conditions of temperature and pressure, but they characteristically occur in or near the more acid igneous rocks. Most of the commercial primary occurrences are in veins or replacement bodies which are near igneous intrusions. Because of the high specific gravity of the important tungsten minerals and their resistance to weathering, they are readily concentrated in placer deposits. Thus the wolframite placers of China have been the world's principal source of tungsten.

Vein tungsten deposits are normally quartz-rich and commonly contain both scheelite and wolframite, but the important deposits at Atolia, San Bernardino County, contain scheelite as the only tungsten mineral. These Atolia veins are narrow and roughly parallel and occur in an area about 2 miles long and 500 feet wide. The ore was deposited in open fissures and is classified as epithermal. The Atolia veins, which contain the largest bodies of high-grade scheelite known in the United States, are the source of the scheelite in the nearby placer deposits. One of these placer deposits is known as the Spud Patch.

The Bishop district, Inyo County, is one of the few areas of the world where scheelite occurs in commercial quantities in contact metamorphic deposits. The Pine Creek mine, west of Bishop, contains the largest reserve

of tungsten ore in the United States and also produces molybdenum, copper, silver, and gold. It has been the state's principal tungsten producer in recent years. The ore bodies are in a garnet-diopside tactite zone between granite and marble. Scheelite is the only tungsten mineral.

Since 1905, tungsten deposits in California have yielded a total of nearly 40,000 short tons of 60 percent WO_3 concentrates. This represents nearly one-third of the total United States production. In 1948, California mines shipped 1767 short tons of concentrates, which was 44.1 percent of the nation's total of 4005 tons. Nevada and North Carolina followed California in that order. Domestic production of tungsten has averaged about 40 percent of the total domestic requirements. China, Korea, Brazil and Bolivia are major world producers.

The milling of tungsten ore is complicated by the sliming of the naturally brittle tungsten minerals. Flotation in addition to gravity concentration aids recovery but does not eliminate the slime losses completely.

Tungsten concentrates are chemically treated to produce sodium tungstate, tungstic acid, tungstic oxide, or ammonium paratungstate. These can be reduced to tungsten powder by either carbon or hydrogen in a controlled hydrogen atmosphere at temperatures from 1300°F. to 1900°F. Ferrotungsten can be prepared from the powder by a thermite-reaction process. Either ferrotungsten or the powder can be used in the manufacture of alloy steels. Because of its high melting point, tungsten is never melted during processing. The powder-metallurgy techniques were developed to produce tungsten in a usable form.

USES OF TUNGSTEN

Tungsten is one of the major alloying elements used in steel manufacturing. Another very important use is for filaments in incandescent electric lamps and radio tubes.

Tungsten is used principally in the manufacture of the "high-speed" steels. These steels retain their hardness even at red heat and are particularly useful for metal-cutting tools. The common alloy is the "18-4-1" type, which contains 18 per cent tungsten, 4 per cent chromium, and 1 per cent vanadium, plus 0.65 to 0.75 per cent carbon. In addition to cutting tools, other products made from tungsten steels include hacksaw, razor, and knife blades, armor plate, armor-piercing projectiles, and drawing-dies for wire manufacture.

Tungsten is used in the manufacture of cemented tungsten carbide, the hardest artificial substance in common use. Stellite, a non-ferrous cobalt-chromium tungsten alloy, is very hard and corrosion resistant; it is used for the same purposes as the "high-speed" steels.

Tungsten in rod, wire, or disc form is one of the few metals used commercially in a very pure state. Such industrial tungsten usually has a purity of 99.95 per cent, although minute amounts of impurities are added for special applications. Because of its high melting point (3400°C.), low vapor pressure, high tensile strength, and ductility, tungsten is used as filaments for incandescent electric lamps and radio tubes. This uses only small amounts of tungsten, but as yet there is no adequate substitute.

Tungsten compounds are used in dyes and paints, for

fluorescent materials in X-ray photography, and as coloring agents in the manufacture of porcelain and stained papers.

SOURCES OF ULTRA-VIOLET RADIATION

Sunlight is the only natural source of ultraviolet radiation, these rays are invisible and are commonly called "black light" they are shorter than visible radiations. Upon passing the rays of the sun through a quartz prism it is noted that the sunlight is separated into the various colours of red, orange and indigo. However, there are radiations longer than the red and invisible. These longer rays are called "infrared" radiations and are the wave-lengths responsible for heat effects. The ultraviolet radiations lie at the other end of the visible spectrum and have no heating effect, but they have a chemical action (actinic effect) on the skin. They form vitamin D and cause tan.

Wave-lengths are measured in Angstrom units, and one Angstrom unit equals approximately 4 billionths of an inch. This unit of measurement is not one of intensity or amount, but is the measurement of the wave-length. It is the wave-length that determines the effect of radiations

Ultraviolet wavelengths are generally considered to be those lying between 136 Angstrom and 4,000 Angstrom units. While this first figure is technically correct the light of transmission of quartz tubing is generally considered the lower range of ultraviolet radiation. This is approximately 1,800 Angstrom units.

Ultraviolet radiations may be divided into two classes:

1. "Short" ultraviolet radiations.—These rays are located at 136 to 3,000 Angstrom units. They are not found in sunlight and can be secured only from artificial sources. It is the ability of the "short" ultraviolet rays to create fluorescent effects which make them so valuable in the detection of scheelite. They also have a bactericidal effect; form vitamin D and cause sunburn.

2. "Long" ultraviolet radiations.—These radiations lie in the range of 3,000 to 4,000 Angstrom units. They have a fluorescent effect on a few minerals, but not on scheelite and create brilliant fluorescence in many chemicals and dyes.

ACTIVATORS

Fluorescence in many minerals is due to the presence of some impurity. This impurity is usually so small that it can be determined only by the use of the spectrograph. These impurities which cause fluorescence of a non-fluorescing mineral are termed *activating agents*, or *activators*. For example, calcite under normal conditions does not fluoresce but should a minute amount of manganese be present the calcite will fluoresce red. The brilliance of the red fluorescence will vary with the percentage of manganese present. Should the percentage of manganese be less than 1 percent or more than 5 percent it will not act as an activator, and therefore there will be no fluorescence.

The presence of uranium in various rocks will act as an activator, but the fluorescence will be green.

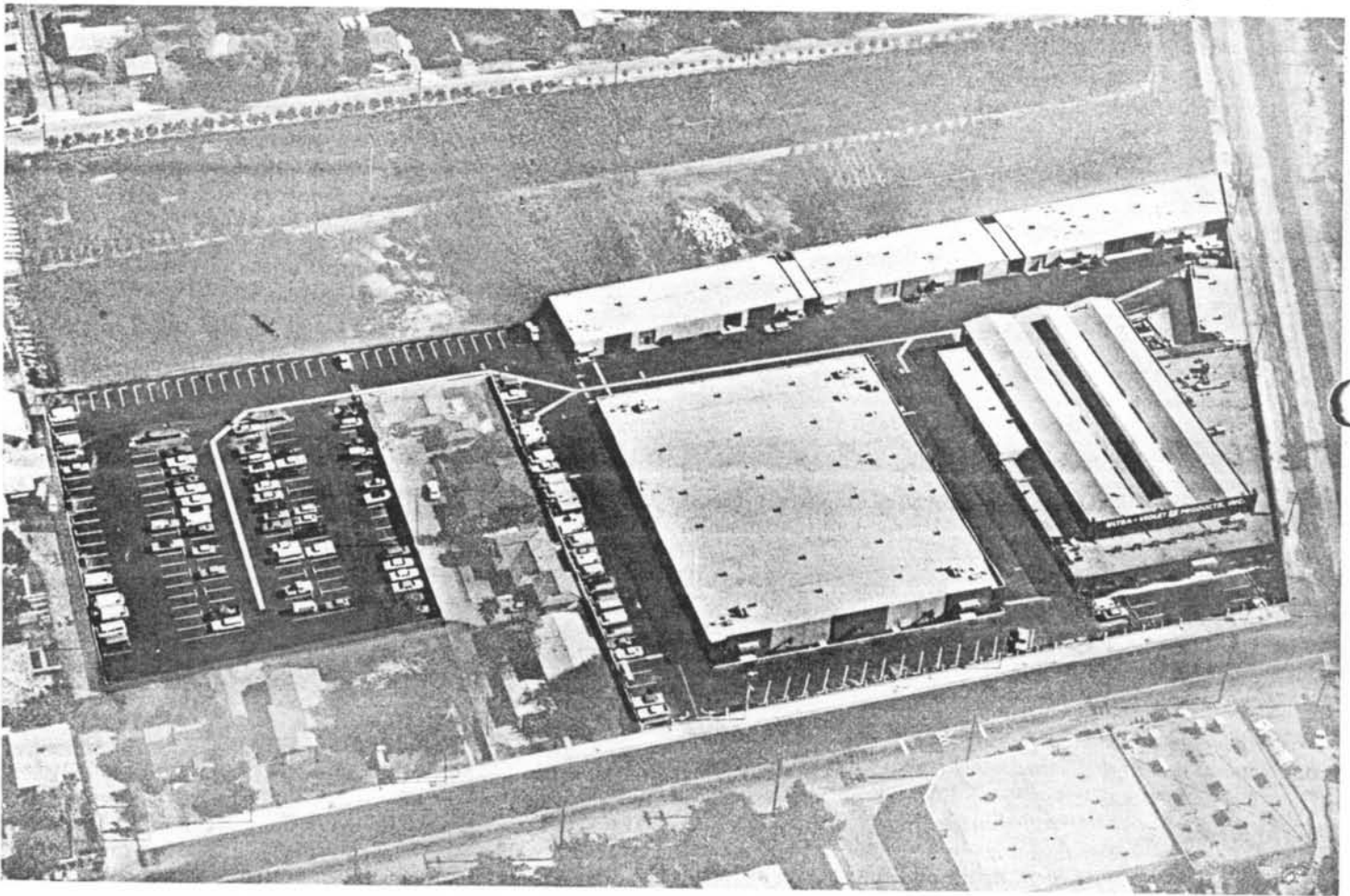
There are numerous cases, where it is almost impossible to determine the reason for the fluorescence of a mineral. To date all activators have not been identified. In some instances the fluorescence may be due to variable molecular arrangement. It must be kept in mind that the

entire field of fluorescent mineralogy is so new that in only a few cases are the reasons fully understood for the fluorescent response to ultraviolet radiation. A mineral may be listed as fluorescent, but actually it may fluoresce due to a coating of fluorescent nature, on the other hand a fluorescent mineral may be present as a mixture, or disseminated inclusion throughout the mass.

The colour of any mineral cannot be correlated with the colour of its fluorescence, some colorless varieties of the same mineral will often show different intensities and colours of fluorescence, depending on the source of the ultraviolet radiations, location and other variables. However, general characteristics will remain the same.

THIS BULLETIN CONTAINS EXCERPTS
FROM THE FOLLOWING ARTICLES

1. *A Review of Fluorescence as applied to Minerals, with special reference to Scheelite*, by John W. Vanderwilt—*Mining Technology*, March, 1946.
2. *Fluorescent Light Used in Molybdenum Assay*—*Engineering and Mining Journal*, September, 1942.
3. *Mineral Information Service*, Volume 3, No. 6, June 1, 1950, published by Division of Mines, Department of Natural Resources, Ferry Building, San Francisco 11, California.
4. Various publications, Ultra-Violet Products, Inc., South Pasadena, California.
5. *Identification and Qualitative Chemical Analysis of Minerals*, by Orsino C. Smith, A.B., A.M., published by D. VanNostrand Company, Inc., 250 Fourth Ave., New York 3, New York.
6. *Detection of Scheelite by Ultra-violet Radiation*, by D.C. McLaren—*Canadian Mining Journal*, August 1943.



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