

# CONTRIBUTIONS TO ECONOMIC GEOLOGY, 1923-24.

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## PART I. METALS AND NONMETALS EXCEPT FUELS.

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### ILSEMANNITE AT OURAY, UTAH.

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By FRANK L. HESS.

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#### THE DEPOSIT AT OURAY.

##### LOCATION AND GEOLOGIC CONDITIONS.

A deposit of molybdenum in soluble form near Ouray, Utah, was noted in a report published by the United States Geological Survey in 1920,<sup>1</sup> but no chemical or other study of the material found there had then been made. A study has since been made by the Geological Survey, and further publication on the deposit therefore seems desirable.

Ouray is a small settlement and trading post on the north side of Duchesne River at its junction with Green River, in Uintah County, northeastern Utah. (See Fig. 1.) It is reached by auto stage from Watson, about 40 miles to the southeast, the station at the end of a narrow-gage railroad connecting with the Denver & Rio Grande Western Railroad at Mack, Colo. The country is a desert.

Along its lower course the Duchesne has formed flats about a mile wide, above which, on its southwest side, bluffs and cliffs made up of beds of sandstone and shale of the Bridger formation (middle Eocene) rise to a height of more than 200 feet. Over the surface above the bluffs is spread a layer, 10 feet thick, of well-rounded pebbles of quartzite, a large part of which are 4 to 6 inches in diameter. The gravels show that the top of the bluff once formed the bed of a meandering stream, probably the Green, of which it is now a greatly eroded terrace. At its highest part the top of the bluff is narrow and slopes southwestward to low hills

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<sup>1</sup> Hess, F. L., Molybdenum: U. S. Geol. Survey Mineral Resources, 1917, pt. 1, pp. 913-914, 1920.

in which are numerous outcrops of thin beds of sandstone carrying more or less malachite and many plant remains.

Beds of shale form the greater part of the bluffs, and those near the top carry many turtle bones. Between the beds of shale lie beds of sandstone, which range in thickness from a few inches to

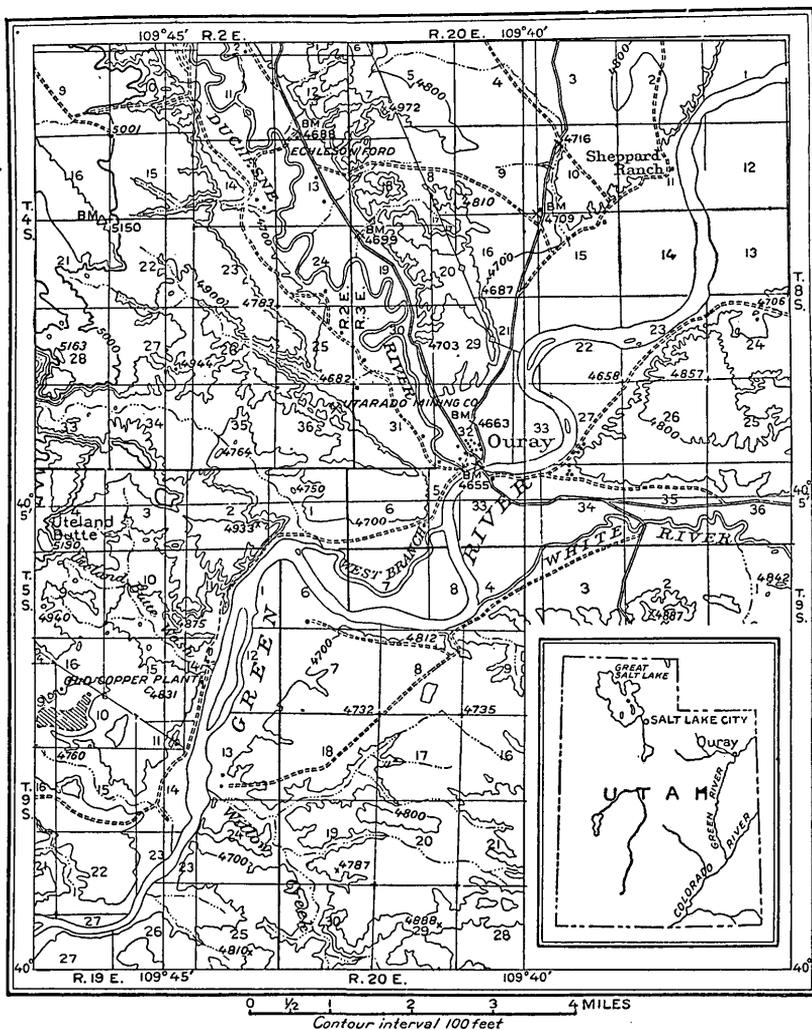
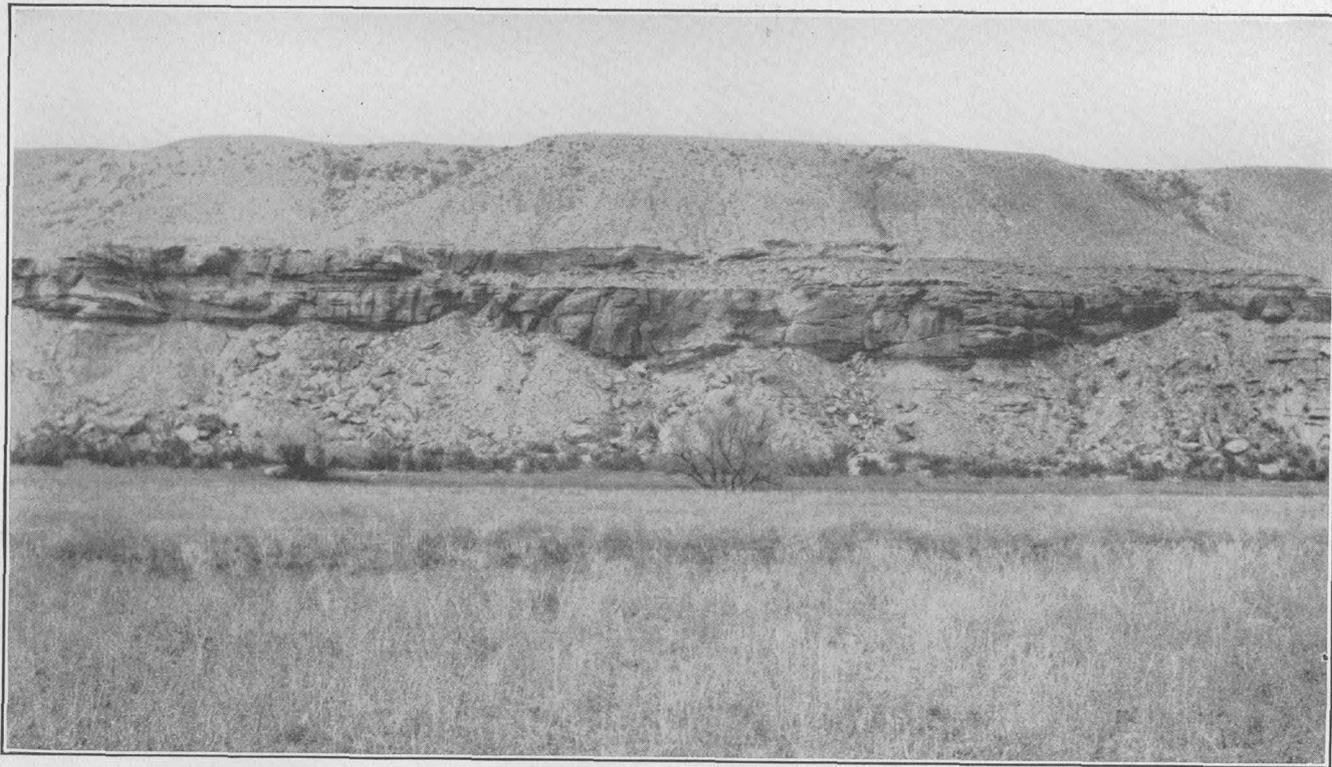


FIGURE 1.—Map of the vicinity of Ouray, Utah, and outline map showing location of Ouray.

35 feet. Even the thickest beds of sandstone are lenticular, pinching out altogether or swelling to a considerable thickness within short distances. The shale is soft, and that which lies below the surface is nearly black, but it weathers into loose light-gray, pink, and green clay, rounding the hills in which it predominates. The beds have a low dip, between south and east. Joints in the shale



BLUFF OF SHALES AND SANDSTONE ON SOUTHWEST SIDE OF DUCHESNE RIVER  $1\frac{1}{2}$  MILES NORTHWEST OF OURAY, UTAH.

Shows the discontinuity of the sandstone beds.



MOLYBDENUM-BEARING SANDSTONE IN OPEN CUT 2 MILES NORTHWEST OF OURAY, UTAH.

The hem of the man's coat touches the sandstone.

carry more or less yellow or brown iron oxide and gypsum, and along the joints the sandstone is bleached.

#### DISCOVERY OF THE DEPOSIT.

In 1916 a prospector, E. B. Curtis, found an ocherous coating along cracks in shale cropping out near the base of the bluff in a cove about 2 miles west-northwest of Ouray. The color of this coating made him think that it might be carnotite, but on digging farther he found a black sandstone, 8 to 12 inches thick, which became dark blue when exposed to the air. Another prospector, Moses Moore, of Ouray, to whom Mr. Curtis showed the material, thought that the black color was due to chalcocite and attempted to pan that mineral from a piece of the sandstone, but he found to his surprise that when the powdered rock was wet the water turned a fine deep blue, and he could find no chalcocite. He reported that he tried the blue solution as a dye on both cotton and silk and that he found it dyed the silk a fast blue. Mr. Moore interested Henry J. Arnold and through him Dr. W. A. Bell, of Denver, in the material, samples of which were sent to several assayers, who reported that the blue color was caused by cobalt or by some other substance. Samples were also sent to dyers, one of whom responded that his firm used "no molybdenum dyes," and this reply furnished the first knowledge of the element that caused the color. In April, 1917, Mr. Arnold sent a specimen of the molybdenum-bearing sandstone to George W. Stose, of the United States Geological Survey, and in May I visited the property.

The prospectors followed the sandstone for 60 feet by an open cut, which at this distance reached a depth of 15 feet, so that a tunnel was there begun, which at the time of my visit was 10 feet under cover. Even in the short distance it was followed the sandstone was of irregular thickness. (See Pl. II.) Its thickness in the face of the tunnel, about 70 feet from the point where it was first cut, was 3 feet, about four times its thickness at the beginning of the open cut. The sandstone here was black, appearing almost asphaltic, but on drying it became much lighter colored, was streaked parallel to the bedding, and only a part of it showed the blue color of molybdenum. In a letter dated March 15, 1922, Mr. Arnold says that this prospect tunnel was afterward driven 140 feet farther and that the sandstone there was 5 feet thick. The molybdenum disappeared 75 feet from the portal.

#### CHARACTER OF THE ROCKS.

Some of the ocherous coatings of the cracks in the shale, both above and below the sandstone, were of a yellow color that suggested molybdite, but molybdenum was found in only one or two specimens,

though a number were collected and tested. A few pieces of float fossil wood were coated with a thin greenish-yellow substance carrying vanadium, probably the mineral psittacinite, a vanadate of lead and copper. The origin of the petrified wood is uncertain, and no vanadium has been found in the sandstone.

The sandstone in which the molybdenum is found is rather fine grained and soft. A section examined is made up of basaltic or andesitic volcanic ash and quartz sand in more or less equal parts. The larger grains of sand and ash are from 0.3 to 0.6 millimeter (0.012 to 0.024 inch) in diameter. The cement is chalcedony, opal, and gypsum, and the rock contains innumerable tiny balls and aggregates of pyrite or marcasite, or both. The larger balls are 0.015 millimeter (0.0006 inch) in diameter, but most of the particles are very much smaller.

Efforts to trace the outcrop of the bed southeastward showed it uncertainly for about 300 feet, to a point where it seemed to pinch out. Immediately northwest of the original prospect tunnel the bed, if present, is covered by shale. In a wash about a quarter of a mile northwest of the tunnel (up the dip) there is a bed of sandstone, 30 feet thick, that seems to occupy the same relative position, but its weathered outcrops showed no sign of molybdenum.

The beds of sandstone are so discontinuous that it is difficult to find a datum plane from which to measure, but a fairly continuous sandstone, 15 feet thick, lies 175 feet above the molybdenum-bearing bed, as determined by repeated barometric measurements. Another less regularly bedded sandstone, 12 to 15 feet thick, lies 100 feet above the molybdenum-bearing bed. The 30-foot bed a quarter of a mile west of the tunnel has the same stratigraphic relation as the known molybdenum-bearing bed to the more regular upper bed.

Farther southeast along the bluff molybdenum is said to have been found for a distance of about 1,600 feet<sup>2</sup> but apparently as molybdite and not as the blue molybdenum mineral. Prospect pits were sunk on the southwest side of the ridge at several points, but apparently no molybdenum was found. The only discovery of the blue mineral was that in the original working.

Some of the samples of the blue molybdenum-bearing sandstone first taken are said to have yielded on assay more than 4 per cent of molybdenum, but several samples taken later with a view to extracting the molybdenum are said to have indicated a content of less than 1 per cent. The molybdenum is very unevenly distributed through the sandstone, and when the rock is first mined its molybdenum content can not be determined, either by its color or weight or by any other easily distinguished characteristic. Samples of sandstone that ap-

<sup>2</sup> Letters from Henry J. Arnold, E. B. Curtis, and Moses Moore.

peared to be as black as molybdenum-bearing rock taken from other parts of the same bed became light gray when dry and gave no indication of molybdenum, and a black sandstone from adjoining claims that was bleached along the cracks proved, on examination at the Geological Survey, to contain no molybdenum.

#### MOLYBDENUM MINERALS IN THE SANDSTONE.

The molybdenum-bearing mineral is evidently the substance that makes the sandstone black, its color when first mined, and that, as it dries, changes its color to blue, in tints ranging from light gray-blue to indigo or consisting of indigo spots in a gray-blue rock.

In many specimens no molybdenum-bearing mineral of definite form is visible to the unaided eye, nor even with the highest-powered binocular microscope adapted to examining rough surfaces. A blue substance coats the grains of sand, but it shows no structure. The solubility of the molybdenum mineral makes it impracticable if not impossible to cut thin sections for study under the microscope. A little of the blue mineral was preserved in one section, but it appeared merely as a stain. If a piece of this sandstone is placed in water the molybdenum-bearing mineral immediately begins to color the water—at first greenish blue, then dark indigo-blue. If a piece of the sandstone is partly immersed the water is drawn up into and through the rest of it by capillary attraction, and when the water evaporates a blue substance, apparently ilsemannite, is formed in mammillary crusts on the upper surface of the piece of sandstone.

When a piece of the sandstone has dried after mining and the moisture it contained is brought to its surface, a mineral is crystallized there in straight or curled fibers. Many of these fibers are blue, the tint varying from light gray-blue to dark blue, almost indigo. Some specimens are covered with tiny dark-blue crystals, which are visible only on close inspection; on other specimens the crystals or fibers may be half an inch long. W. T. Schaller, of the United States Geological Survey, examined some of this material and reported as follows:

The samples of sandstone from Ouray, Utah, collected by Frank L. Hess have been carefully tested to determine the presence of any molybdenum mineral other than the water-soluble material. If the powdered rock is treated with considerable water to leach out the soluble material and then with dilute sulphuric acid and carefully washed until no more water-soluble material is left, the insoluble residue is free from any molybdenum compound. Not a trace of any sulphide mineral containing molybdenum could be found in the sandstone. It is therefore concluded that the sandstone carries molybdenum only in the form of secondary compounds, soluble in water. The action of pure water on some of the soluble salts had a tendency to form and precipitate insoluble, probably basic compounds, which retained, probably mechanically, some molybdenum. The addition of a small quantity of sulphuric acid keeps all these salts in solution.

The water-soluble salts in the sandstone are so intermingled that it is not possible to separate any one of them in a pure state. The most homogeneous sample that could be collected consisted of the pale-blue fibers, the analysis of which is given in the second table below.

The analysis of a sample of the sandstone richest in secondary salts is as follows:

*Analysis of sandstone from Ouray, Utah.*

	Percent- age.	Percent- age minus insoluble material.
Insoluble in water.....	81.79	.....
Molybdenum oxide (MoO <sub>3</sub> ) <sup>a</sup> .....	.70	3.83
Alumina (Al <sub>2</sub> O <sub>3</sub> ).....	1.13	6.18
Ferrous oxide (FeO) <sup>b</sup> .....	1.62	8.88
Manganese oxide (MnO).....	.01	.07
Nickel oxide (NiO).....	.01	.09
Lime (CaO).....	.....	.....
Magnesia (MgO).....	.14	.78
Sulphur trioxide (SO <sub>3</sub> ).....	5.29	29.04
Water (H <sub>2</sub> O), by difference.....	9.31	51.13
	100.00	100.00

<sup>a</sup> Total molybdenum as MoO<sub>3</sub>.

<sup>b</sup> Total iron as FeO.

The analysis of a selected sample of the pale-blue fibers is as follows:

*Analysis of pale-blue fibers in sandstone from Ouray, Utah.*

	Percent- age.	Percent- age minus insoluble material.
Insoluble in water.....	7.06	.....
Molybdenum oxide (MoO <sub>3</sub> ) <sup>a</sup> .....	2.06	2.22
Ferrous oxide (FeO) <sup>b</sup> .....	10.95	11.78
Alumina (Al <sub>2</sub> O <sub>3</sub> ).....	3.07	3.30
Magnesia (MgO).....	1.54	1.66
Sulphur trioxide (SO <sub>3</sub> ).....	25.09	27.00
Water (H <sub>2</sub> O), by difference.....	50.23	54.04
	100.00	100.00

<sup>a</sup> Total molybdenum as MoO<sub>3</sub>.

<sup>b</sup> Total iron as FeO.

The optical properties of the blue fibers indicate that they belong to the halotrichite-pickeringite group. Some fibers have parallel extinction; others have moderate extinction angles. Elongation is Z. Birefringence very weak, not over 0.005. Maximum index of refraction about 1.490.

The chemical composition of the blue fibers agrees approximately with that of halotrichite, although the R<sub>2</sub>O<sub>3</sub> (Al<sub>2</sub>O<sub>3</sub>) is very low. But it is not known how the MoO<sub>3</sub> functions, whether as an acid or as a base. There is probably also more or less melanterite present, which, if deducted, would raise the Al<sub>2</sub>O<sub>3</sub> ratio.

In conclusion:

1. The sandstone contains no molybdenum mineral as such of any kind. The water-soluble material, blue in color, is probably halotrichite containing a small percentage of MoO<sub>3</sub>.

2. The sandstone contains no original or sulphide molybdenum mineral.

3. The molybdenum is distributed through the sandstone in the same way as the secondary sulphates are distributed. The material collected is not suitable for a study of the mineral ilsemannite.

This molybdenum-bearing halotrichite may be reproduced by repeatedly dissolving the efflorescence on the sandstone and recrystallizing it by allowing the solution to be drawn through the specimen by capillarity and thus compelling the dissolved mineral to re-form on the surface. With it is an apparently amorphous blue mineral that answers the descriptions given by Höfer for ilsemannite. As usually happens, other iron sulphates and possibly other aluminum sulphates perhaps crystallize at the same time and are mixed with the halotrichite.

The blue molybdenum minerals are, however, probably not original minerals of the rock, for when first mined the sandstone is black, not blue, and it becomes blue only after it is exposed to the air and its moisture has begun to evaporate noticeably. What the black mineral is we do not know, nor do we know much about the apparently amorphous blue mineral.

Molybdite, the yellow iron molybdate, forms in small quantity on a few of the specimens as they are dried and is found in some of the ochreous iron oxide along cracks in the rock. Where a little brown iron oxide is mixed with the molybdite this ochreous deposit is so nearly like it in color that the presence of molybdenum can be determined only by tests. The ochreous coating generally contains no molybdenum, but it creeps from the sandstone into cracks in the shale and is apparently the material found southeast of the original opening.

That so soluble a mineral should be found in porous sandstone in a country in which, though a desert, there are occasional heavy rains, is explained by the facts that the sandstone is lenticular, that it slopes downward from its outcrop, and that it is inclosed in shales that do not readily allow the solutions in it to escape. What may have been the origin of the molybdenum in the sandstone can only be conjectured, though there are some significant facts at hand. There are no igneous rocks in the vicinity and no known metallic veins. Across the ridge to the southwest of the deposits and extending for several miles more or less parallel to Green River are copper deposits in sandstone, but the copper was probably deposited with the sandstone, and the deposits are younger than the molybdenum-bearing sandstone. No molybdenum has been reported from these deposits or from any other place in the region.

The facts that the molybdenum is in a readily soluble form, that it is found only in a sandstone from which water is prevented from escaping by the inclosing shale, and that there seems to be no possible local source of molybdenum indicate that it was deposited with the sandstone.

Traces of molybdenum are found in the carnotite of the sandstones in the McElmo formation (Cretaceous?) of Colorado and Utah, but nowhere in visible quantities. The metals in the carnotite deposits were probably precipitated by decaying vegetable matter from very weak solutions in a very shallow but broad lake.

The conditions when the Bridger sandstone and shale were deposited were apparently somewhat similar to those that prevailed when the McElmo formation was deposited, but no signs of fossil vegetation were found in place either in or adjacent to the molybdenum-bearing sandstone. Here, too, probably a salt of the metal was collected in shallow water, into which it had drained from decaying veins, probably as a complex sulphate. The lenticular form of the sandstone shows very uneven deposition of sediments, and into these sediments molybdenum-bearing solutions probably soaked, the water then evaporated, and the molybdenum was later sealed in the sand by mud that afterward hardened into shale as the sand was cemented to sandstone. If the deposit was made in this manner it may have been originally much larger, and other lenses of molybdenum-bearing sandstone may also have been formed.

The molybdenum found was probably concentrated from the sandstone up the dip (to the northwest), and much of it has been lost by erosion. Other similar deposits may be found at the same horizon, but they will be found in just such pocketed parts of the sandstone. The outcrops will all be leached, and if the sandstone dips downward the molybdenum may be preserved in its buried part; but if the sandstone rises from the outcrop it will probably be entirely washed free from molybdenum by moving underground waters.

Unless some of the less soluble molybdate should remain in the outcrops prospecting for the molybdenum-bearing sandstone must be work that offers little promise.

#### SOURCE OF THE MOLYBDENUM.

The molybdenum seems to have come from some original deposit that was weathering down at the time the sandstone was formed and was moved by water to its present location. The source could not have been very far away, else the molybdenum would have been dissipated before it reached its present position. It seems hardly possible that it could have been as far away as the main part of the Uinta Mountains, which are 20 miles or more distant in a direct line and considerably farther by a meandering stream channel. The deposit may have been in some outlying spot, perhaps in a hill now worn away and covered by sediment, close to the present resting place of the molybdenum. The original mineral from which the ilsemannite was derived is equally unknown but will be considered farther on in this paper.

Deposits of ilsemannite in sedimentary rocks, such as that at Ouray, must continue rare because the conditions required for their deposition and preservation are peculiar.

#### ORIGIN OF THE NAME ILSEMANNITE.

The name ilsemannite was proposed by Hans Höfer<sup>3</sup> in 1871, in honor of J. C. Ilsemann,<sup>4</sup> who published the results of a study of molybdenite in 1787. The specimens described by Höfer were obtained from Herr Kroeller, administrator of the wulfenite-bearing mines of Bleiberg, Carinthia. They were largely aggregates of small crystals of barite. Höfer says:

Between these [crystals] is the blue-black to black, mostly earthy to cryptocrystalline mass which becomes bluer the longer it is exposed to the air. It is soluble in water and shows itself as molybdate of molybdic oxide. I could find no other minerals, even with a lens; only one piece shows a bit of galena 6 lignes [0.048 inch] across.

A part of the mineral aggregate was powdered and boiled with distilled water; the resulting solution was in the beginning a deep, dark green-blue, in the course of an hour becoming a rich deep blue, reminding one of the color of the sulphate of copper treated with ammonia. \* \* \* The dark-blue mineral forms, after evaporation of the water, cohering lumps in which there are only small aggregates of indistinct crystals.

Gypsum was an accompanying mineral. The parallelism to the Ouray mineral between the black mineral and the solution—at first greenish-blue, then blue—is striking. Höfer made qualitative tests of the material, but no quantitative analysis. He says:

So far as known, no other molybdenum compounds give such an intense blue when dissolved in water as does the molybdate of molybdic oxide, so that there can be no question that the mineral under discussion is this salt. \* \* \* It is known that the chemical formula for this is  $\text{MoO}_2 \cdot 4\text{MoO}_3$ , according to Berzelius. It may also be noted that in many of the pieces tested free sulphuric acid was found.

Höfer has apparently given the name ilsemannite to two different substances—a black material, original in the specimens, and a blue material formed from it—and he knew positively the composition of neither. He concluded that ilsemannite, the blue mineral, is  $\text{MoO}_2 \cdot 4\text{MoO}_3$  because it looks like a substance said to have that formula. In the present article the term ilsemannite is applied to the blue apparently amorphous molybdenum mineral. 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 ( $\text{CaSO}_4$ ) has to gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

<sup>3</sup> Ilsemannite, ein natürliches Molybdänsalz: Neues Jahrb., 1871, pp. 566-570.

<sup>4</sup> Versuche ueber die Molybdäna und das Wasserbley von Altenberg: Chemische Annalen von D. Lorenz Crell, vol. 1, pp. 407-414, 1787.

## KNOWN OCCURRENCES OF ILSEMANNITE.

Lindgren and Ransome<sup>5</sup> found ilsemannite on specimens obtained from a vein on the Anaconda property, near Cripple Creek, Colo. The specimens consisted

of coarse quartz with comb structure, growing on a black, fine-grained mixture of pyrite, molybdenite, and zinc blende, with a very small amount of galena and traces of copper and tellurium (Hillebrand). Upon exposure to the air and sun the quartz turns yellow or green and finally a deep Prussian blue color. \* \* \* The blue substance, which dissolves in water and is associated with some ferrous sulphate, also contains a large amount of molybdenum and probably is the rare mineral ilsemannite \* \* \* [and] here it appears as a direct production of oxidation of molybdenite.

I have examined the specimen of this material that Lindgren and Ransome transmitted to the United States National Museum but have been unable to find molybdenite in it. The specimen is spongy and rough and contains tiny crystals of pyrite which are partly covered by an efflorescence of sulphates and might readily be mistaken for tiny flecks of molybdenite if molybdenite was expected.

In 1907 Lindgren<sup>6</sup> noted blue stains on the rock in the dump of the Mogul tunnel, Spencer Mountain, near Eldora, Boulder County, Colo., which he thought to be ilsemannite.

In 1915 Ball<sup>7</sup> noted the occurrence of ilsemannite at Bamford, Queensland, thus:

Ilsemannite \* \* \* was observed at the Dog, Enright and Thompson's, and Northern United as slight stains in the vug kaolin [in pipes] and in the crystalline molybdenite-bearing quartz on the dumps. It was, however, noticed in quantity only at the Gillian and Bridge, where it occurs in vugs among interpenetrating crystals of quartz. It is an earthy substance, shading off from light turquoise-blue into blue-black, and is soluble in cold water, the solution readily reacting for molybdenum. This mineral has not previously been recorded from Queensland.

The molybdenite obtained from these workings is crystallized in quartz, individual crystals being 1½ inches in diameter and radiating in structure. Its oxidation has given rise to the rare molybdate of molybdenum, ilsemannite, which occurs as a blue incrustation among the quartz crystals.

The next known description was that of A. L. du Toit<sup>8</sup> of a deposit in the Hlatimbe Valley, a tributary of that of the Umkomaas, in Impendhle County, Natal, South Africa. The deposit is in the Indian sandstone, a bed about 18 feet thick, of which the uppermost part is soft and medium grained and contains glittering fragments of quartz, and the lowest 4 or 5 feet is harder and coarser grained, carrying pebbles of vein quartz an inch in diameter. Between the

<sup>5</sup> Lindgren, Waldemar, and Ransome, F. L., *Geology and gold deposits of the Cripple Creek district, Colo.*: U. S. Geol. Survey Prof. Paper 54, pp. 123-124, 1906.

<sup>6</sup> Lindgren, Waldemar, *Some gold and tungsten deposits of Boulder County, Colo.*: *Econ. Geology*, vol. 2, pp. 457-458, 1907.

<sup>7</sup> Ball, L. C., *The wolfram, molybdenite, and bismuth mines of Bamford, North Queensland*: *Queensland Geol. Survey Pub.* 48, pp. 30, 48, 49; 1915.

<sup>8</sup> On a unique occurrence of molybdenum in Natal: *South African Jour. Sci.*, vol. 13, pp. 153-156, 1916.

grains there is some kaolin, a product of the decomposition of feldspar. The two parts are separated by a slightly uneven surface, along which lie lenses of thinly laminated black shale. Above the sandstone is an oil shale, and below it is a mudstone. Two dark carbonaceous masses occur in the lower bed within a distance of 60 feet. Many spherical masses of pyrite, from half an inch to 2 inches in diameter, are scattered through the sandstone. On the outcrop some molybdate and some ilsemannite are found. On the walls of a prospect tunnel there were incrustations of aluminite (a hydrous aluminum sulphate containing some iron), part of which was colored blue by molybdenum. No analysis of the material is mentioned, but the presence of pyrite indicates that it may be either halotrichite or a closely related mineral. In considering the origin of the ilsemannite, Du Toit says that the rock gave, on analysis, silica ( $\text{SiO}_2$ ), 88.8; alumina ( $\text{Al}_2\text{O}_3$ ), 0.8; sulphur (S), 4.4; iron (Fe), 2.9; molybdenum (Mo), 1.1; alkalis, 0. From this he deduces that the rock contains 6.53 per cent of pyrite or marcasite and 1.85 per cent of molybdenite. The incrustations of aluminite (?) show that the rock contains aluminum sulphate. The quantity of alumina reported in the analysis is sufficient to combine with all of the sulphur that is not taken up by the iron, and although part of the alumina may be combined in clay probably not all the sulphur that is uncombined as pyrite belongs to the molybdenum. Du Toit says that minute scales of molybdenite were seen with a microscope, but in view of the difficulties of determining opaque minerals under an ordinary microscope it seems possible that some other opaque mineral may have been mistaken for molybdenite. He thinks the origin of the molybdenum may be connected with a sill of basalt 100 feet above. The general resemblance between the deposit in Natal and that at Ouray is striking.

In 1916 F. W. Horton<sup>9</sup> and F. B. Laney collected samples of a deep-blue water dripping from vein No. 21 in the Lucania tunnel, near Idaho Springs, Colo., which, on analysis by R. C. Wells, of the United States Geological Survey, proved to be a strong solution of ilsemannite. Wells published no conclusions as to the composition of the mineral, but the results of his analysis are as follows:

*Analysis of mine water from vein 21, Lucania tunnel, Idaho Springs, Colo.*

Substance.	Grams per liter.	Substance.	Grams per liter.
Molybdenum trioxide ( $\text{MoO}_3$ ).....	7.98	Magnesium (Mg).....	0.73
Molybdenum dioxide ( $\text{MoO}_2$ ).....	Trace.	Sodium (Na).....	.26
Ferrous iron ( $\text{Fe}^{++}$ ).....	2.01	Potassium (K).....	.14
Ferric iron ( $\text{Fe}^{+++}$ ).....	1.75	Sulphate ( $\text{SO}_4$ ).....	18.26
Aluminum (Al).....	.27	Chlorine (Cl).....	.17
Calcium (Ca).....	.59	Hydrogen (of free acid).....	.13

The specific gravity at 25° was 1.031.

<sup>9</sup> Molybdenum; its ores and their concentration, with a discussion of markets, prices, and uses: Bur. Mines Bull. 111, pp. 15-16, 1916.

The fact that the water gave only a trace of molybdenum dioxide shows that it did not contain molybdenum as  $\text{MoO}_2 \cdot 4\text{MoO}_3$ . The quantity of the sulphate radicle is sufficient to combine with the  $\text{MoO}_3$  as  $\text{MoO}_3 \cdot \text{SO}_3 + x\text{H}_2\text{O}$  and with the other bases present, so that the molybdenum is possibly present as a sulphate.

One of the first specimens obtained from the deposit near Ouray was analyzed by Schaller.<sup>10</sup> Of this specimen 9.5 per cent was soluble in cold water. His analysis is given below.

*Analysis of ilsemannite-bearing rock obtained near Ouray, Utah.*

	Percent- age.	Ratio.	Ratio after deducting melanter- ite.
Substances insoluble in water.....	90.50	.....	.....
Substances soluble in water:			
Ferrous oxide ( $\text{FeO}$ ).....	.99	0.014	.....
Molybdic oxide ( $\text{MoO}_3$ ).....	2.37	.017	0.017=1
Molybdous oxide ( $\text{MoO}_2$ ).....	Trace.	.....	.....
Sulphur trioxide ( $\text{SO}_3$ ).....	2.64	.033	.019=1
Water ( $\text{H}_2\text{O}$ ), by difference.....	3.50	.194	.097=5

From these ratios Schaller obtained the formula  $\text{MoO}_3 \cdot \text{SO}_3 \cdot 5\text{H}_2\text{O}$ . He believed that the blue color was given by the trace of  $\text{MoO}_2$ .

Schaller also examined specimens of ilsemannite from Saxony and Carinthia, furnished by Col. Washington A. Roebing, and found that each gave a strong reaction for sulphate. The water-soluble part of the Carinthian specimen contained a trace of ferrous iron, but no ferric iron could be detected. A second water leach of the specimen gave a blue solution in which only a minute trace of ferrous iron could be found.<sup>11</sup> Ferrous-iron minerals (melanterite, halotrichite, and possibly others) seem to be usually very intimately mixed with the blue ilsemannite.

Schaller further says:

The iron in the water leach may be in a condition that will not readily give the normal reaction for iron, so that the failure to get the reaction by an ordinary test does not necessarily show that the water contains no iron. E. Dittler, of Vienna, in a letter to me, says that he obtained no reaction for iron (either ferrous or ferric) in a water solution of ilsemannite, although the solution contains much iron. Dittler suggests that ilsemannite may be a "colloidal complex" consisting essentially of iron and sulphate—not combined, however, as in melanterite—in which molybdenum plays a necessary but perhaps relatively small part as a coloring agent. The iron, present in some "complex" form, may be functioning as an acid.

It is questionable whether molybdenum sulphate has been made artificially. Many writers on chemistry in the nineteenth century

<sup>10</sup> Schaller, W. T., Ilsemannite, hydrous sulphate of molybdenum: Washington Acad. Sci. Jour., vol. 7, pp. 417-420, 1917.

<sup>11</sup> Personal communication from W. T. Schaller.

mentioned without doubt its artificial production. Michaelis<sup>12</sup> reports that hydrous and anhydrous sulphates were made by Shulz-Sellac and Anderson, but later writers either do not describe the sulphates or mention them doubtfully.<sup>13</sup>

In 1918 H. F. Yancey<sup>14</sup> took up the problem of the composition of the blue molybdenum mineral found at Ouray. He boiled some of the sandstone and evaporated the solution to dryness. An analysis of the residue gave the following results:

*Analysis of water-soluble salts in sandstone from Ouray, Utah.*

Silica (SiO <sub>2</sub> )	0.98	Magnesium oxide (MgO)	1.36
Alumina (Al <sub>2</sub> O <sub>3</sub> )	10.62	Sulphur trioxide (SO <sub>3</sub> )	38.48
Ferrous oxide (FeO)	9.58	Molybdic oxide (MoO <sub>3</sub> )	23.85
Titania (TiO <sub>2</sub> )	Trace.	Chlorine (Cl)	0.17
Calcium oxide (CaO)	1.24		

The analysis shows nearly enough SO<sub>3</sub> to combine with the molybdenum (as MoO<sub>3</sub>.SO<sub>3</sub>) and the alumina, but not enough to combine with the iron, magnesium, and calcium, which are probably present, at least much the larger part of each, as sulphate. Nor does Yancey find a basis for the old formula for ilsemannite, MoO<sub>2</sub>.4MoO<sub>3</sub>, though he believes much more MoO<sub>2</sub> is present than the traces found by Schaller or in the mine water by Wells. Yancey boiled the sandstone for 20 minutes and dried at 105° C. the residue left by evaporation of the solution. He then separated the molybdenum, presumably the quadrivalent from the hexavalent, by ether and hydrochloric acid. The effect of these modes of treatment is uncertain, and the results can hardly be accepted as determining the radicles present.

George Teagarden, working on a vein in the Sunburst level, near Georgetown, Colo.,<sup>15</sup> found rock that stained the hands like ink. This stain was supposed to be caused by ilsemannite, and it is said that it had been found also in the Bard Creek mine some years before.

The veins of Spencer Mountain, Boulder County, those cut by the Lucania tunnel, and those of the Sunburst level and the Bard Creek mine are all in the same general group, and one would expect to find other deposits in an area so large and with so many veins, but none were found by P. G. Worcester,<sup>16</sup> who studied the Colorado molybdenum deposits.

<sup>12</sup> Michaelis, A., in Graham-Otto's Ausführliches Lehrbuch der Chemie, vol. 2, p. 1181, 1881.

<sup>13</sup> Watt's Dictionary of chemistry, vol. 3, p. 433, 1892. Péchard, Molybdène: Traité de chimie minérale (Moissan, Henri), p. 707, 1905. Roscoe and Schorlemmer do not mention molybdenum sulphate.

<sup>14</sup> Chem. and Met. Eng., vol. 19, pp. 186-190, 1918.

<sup>15</sup> Salt Lake Min. Rev., Aug. 1, 1920, quoting the Georgetown Courier.

<sup>16</sup> Molybdenum deposits of Colorado: Colorado Geol. Survey Bull. 14, 1919.

C. W. Cook<sup>17</sup> has recently described an occurrence of ilsemannite 4 miles west of Gibson, Shasta County, Calif., where molybdenite is found with pyrite in boulders of aplite. At many places in this locality the molybdenite has been altered to molybdite, and at places where it has not been completely altered a bluish zone appears around the nucleus of molybdenite. This zone is plainly a result of the staining of the quartz and feldspar by ilsemannite or some like substance.

At the time of the examination of the property, something over 100 tons of ore had been removed, according to reports, and some of this ore was still on the ground at the railroad awaiting shipment. This broken rock had been exposed to the action of the atmosphere for several months, and many pieces had been completely discolored blue on the surface, giving them an entirely different appearance from that of the freshly broken rock. It would seem, therefore, that the alteration of the molybdenite to ilsemannite had been relatively rapid.

There is "a bronze-brown to violet-brown to blue" tarnish on the molybdenite, which Cook thinks is probably molybdenum dioxide, insoluble in water. He thinks that

subsequent oxidation to a hexavalent form would result in a change of color from brown to blue, but still insoluble in water. Further oxidation, with an increase in the relative amount of the trioxide, and hydration would then transform this insoluble blue compound into the soluble blue compound ilsemannite. Finally complete oxidation to the trioxide, on combination with iron, would yield the yellow compound molybdite.

No tests to show the composition of the ilsemannite are mentioned, and apparently none were made, nor do any tests seem to have been made to see whether the rock contained any other original molybdenum mineral than molybdenite.

Near the head of Death Valley, in Nevada, E. S. Larsen<sup>18</sup> examined a deposit of molybdenite containing much pyrite and some copiapite (hydrous iron sulphate), which, like the halotrichite of Ouray, Utah, and the aluminite (?) of Hlatimbe Valley, Natal, was colored blue by molybdenum. The molybdenum-bearing copiapite suggests that the deposit may contain ilsemannite, though none was found. The blue color disappeared when the mineral was exposed to the hot sun and thus partly dehydrated, but on the next morning it would again have become blue by hydration during the night.

#### GENERAL CONCLUSIONS.

The short review of the reports on known deposits of ilsemannite just given shows that at only two known places—one near Gibson, Calif., and the other at Bamford, North Queensland—is molybdenite

<sup>17</sup> A new occurrence of ilsemannite: *Am. Jour. Sci.*, 5th ser., vol. 4, pp. 50-52, 1922.

<sup>18</sup> Personal communication.

unquestionably present with the ilsemannite, unless it can be supposed that ilsemannite colors the copiapite at the head of Death Valley. At Bleiberg, Carinthia, there is a deposit of wulfenite (lead molybdate), but there is no indication that it is being altered to ilsemannite, and as wulfenite is itself a mineral of the oxidized zone, both minerals are probably formed from the same original mineral. At three places soluble sulphate minerals are stained blue by molybdenum.

The beautiful blue color of solutions of ilsemannite and of the stains left by them on the white quartz or the light-colored granite that is commonly associated with molybdenite is so striking that if a description of a molybdenite deposit by a competent observer contains no mention of ilsemannite it probably is either not present or is present in insignificant quantity.

Though rather extensive studies of molybdenum deposits have been made<sup>10</sup> and hundreds of deposits have been described and many others examined, yet the few deposits considered in this paper are the only ones in which ilsemannite has been noted. It seems evident, therefore, that if ilsemannite is formed from molybdenite or wulfenite it is probably formed only under unusual conditions, and the mere association of molybdenite with pyrite and other easily oxidizable sulphides does not sufficiently explain its formation, for these sulphides occur in all known deposits of molybdenite.

In the mines of Boulder and Gilpin counties, Colo., in which ilsemannite is found, as in the numerous deposits of wulfenite in the United States and other countries, no original molybdenum mineral

<sup>10</sup> The following works are among the broader studies of molybdenum deposits:

*Australia:*

- Andrews, E. C., The molybdenum industry in New South Wales: New South Wales Geol. Survey Mineral Resources, vol. 24, 199 pp., 1916.  
 Ball, L. C., The wolfram, molybdenite, and bismuth mines of Bamford, North Queensland: Queensland Geol. Survey Pub. 48, 78 pp., 1915.  
 Cameron, W. E., Wolfram and molybdenite mining in Queensland: Queensland Geol. Survey Rept. 188, 13 pp., 1904.  
 Hills, Loftus, Tungsten and molybdenum, pt. 1, 32 pp., pt. 2, 14 pp. Tasmania Geol. Survey Mineral Resources, No. 1, 1916.

*Canada:*

- Gwillim, J. C., Molybdenite in Nova Scotia, Quebec, Ontario, and British Columbia: Canada Munition Res., Final Rept., November, 1915, to March, 1919, pp. 108-133, 1920.  
 Parsons, A. L., Molybdenite deposits of Ontario: Ontario Bur. Mines Twenty-sixth Rept., pp. 275-313, 1917.  
 Walker, T. L., Report on the molybdenum ores of Canada, 64 pp., Canada Dept. Mines, Mines Branch, 1911.

*France and its colonies:*

- Lacroix, A., Minéralogie de la France et de ses colonies, 5 vols., 1893-1913.

*Norway:*

- Falkenberg, B. O., Norske Molybdengrubber: Teknisk Ukeblad, vol. 68, pp. 6-11, 1921.

*United States:*

- Horton, F. W., Molybdenum, its ores and their concentration, with a discussion of markets, prices, and uses: Bur. Mines Bull. 111, 132 pp., 1916.  
 Worcester, P. G., Molybdenum deposits of Colorado: Colorado Geol. Survey Bull. 14, 131 pp., 1919.

from which the oxidation minerals may have been formed has yet been found.

F. Cornu,<sup>20</sup> in reporting the results of a search for the parent mineral of ilsemannite, states that the black mineral from which ilsemannite is formed with water is a colloidal molybdenum sulphide ( $\text{MoS}_2$ ), which he calls jordisite. His material was obtained from Himmelsfuerst, a little south of Freiberg, Saxony. Cornu's short notice is almost wholly lacking in necessary details and leaves much to be desired. It does not convince one that his material was really a sulphide of molybdenum. Such a mineral as that he supposed to exist might occur not only in complex sulphide veins, such as those of Himmelsfuerst and the Gilpin-Boulder County mineral belt, but here and there in deposits of molybdenite.

The evidence is not conclusive as to the composition of ilsemannite, though it seems to me, as it does to Schaller, more probably a molybdenum sulphate than a molybdyl molybdate.

Ilsemannite, like wulfenite, is probably formed from some unknown mineral, perhaps a sulphide.

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<sup>20</sup> Natürliches Kolloides Molybdänsulfid (Jordisit): Zeitschr. Chem. Ind. Kolloide, vol. 4, p. 190, 1909.