ART. XXIX.--The Chemical Composition of Molybdic Ocher;
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ART. XXIX.—*The Chemical Composition of Molybdic Ocher;* by WALDEMAR T. SCHALLER.[*]

Summary.—It is shown that the natural molybdic ocher, called molybdite, is not the trioxide of molybdenum, as stated in the literature, but a hydrous ferric molybdate with the formula, $Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O$.

The composition of natural molybdic ochre is given in all the text books on Mineralogy as agreeing in composition with the artificial product, molybdenum trioxide, MoO_3, which may be obtained by oxidizing the natural sulphide, molybdenite. So far as the writer is aware, but one analysis was ever made of the natural ocher, and while that suggested the desirability of further examination, such has never been made. This is doubtless due to the fact that whereas the yellow molybdic ocher is very widespread in its occurrence, it seldom occurs in sufficient quantity and of such purity as to warrant any chemical investigation. The writer was fortunate enough to receive a sample of supposed autunite from the Foote Mineral Company which, on investigation, was found to be molybdic ocher. As the mineral occurs in a pure state some qualitative tests were made and it was found that beside the molybdenum, considerable ferric iron and water were present. The material was then examined under the microscope and found to be pure and especially free from limonite. Some artificial crystals of MoO_3 were prepared, and on comparing the two substances under the microscope, such differences were found in their properties as to indicate that the mineral examined was not molybdite, but a new species,—a hydrated ferric molybdate. The investigation thus opened was extended, and through the generosity of several people, it has been possible to make analyses of the natural molybdic ocher from four different localities, and to show that the natural ocher is not MoO_3 but $Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O$.

A summary of the literature on molybdite is so well given by Hintze that only such points as bear directly on the question at hand will be mentioned. Owen[†] described a deep yellow iron molybdate from Nevada City, California, and W. J. Taylor[‡] described a similar occurrence from Heard County, Georgia, but neither article contained quantitative data of any value. Owen found 35 per cent Fe_2O_3, but Genth[§] in a later publication, made a determination on the same mineral and obtained 24·3 per cent Fe_2O_3. He says, "That which could

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[*] Published by permission of the Director of the U. S. Geological Survey.
[†] Proc. Ac. Phila., vi, 108, 1852.
[‡] This Journal, xix, 429, 1855.
[§] Ibid., xxviii, 248, 1859.

be scratched off the quartz was not quite pure and contained a trace of limonite . . . . . The sample examined gave 24·3 per cent of sesquioxide of iron, some of which was *certainly* mechanically mixed with it." Yet it would necessitate a mixture of nearly one-third limonite to give 24·3 per cent Fe_2O_3, while according to Genth, the sample only "contained a trace of limonite." The analytical result was correct, but the interpretation wrong. The sample doubtless contained a trace of limonite, as the 24·3 per cent is slightly higher than the figure required for the formula $Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O$, which gives 22 per cent Fe_2O_3.

Physical Properties.—The mineral has a fibrous structure and also forms radiating groups. Its color is yellow and the lustre often silky. All of the fibers examined gave parallel extinction. The double refraction is strong and the direction of elongation is always an axis of minimum elasticity. The pleochroism is strong but is masked by the very strong absorption. Normal to the elongation of the fibers, the transmitted light is pale yellow, parallel to the elongation the color is a much stronger yellow. The absorption parallel to the elongation is so strong that thick fibers frequently appear almost black and opaque. These same properties are mentioned by Lacroix* for molybdite from Corsica.

Crystals of MoO_3, prepared by roasting molybdenite in an open crucible, show very decided differences in their physical properties from those of the natural mineral. They are not fibrous but platy and are colorless, non-pleochroic and show no difference in absorption in different directions.

Chemical Analyses.—The largest sample obtained comes from Westmoreland, New Hampshire, and was very kindly furnished from the Brush Collection of Yale University by Prof. Wm. E. Ford. Nearly a gram of material was obtained and this was divided into portions of a quarter gram weight. Macroscopically, the specimen looks more earthy and not so finely crystallized as those from some of the other localities, but under the microscope, the material, with its characteristic optical properties, was seen to be homogeneous, free from limonite, and to contain a small quantity of molybdenite scales. The first figure given for the water content, 16·98 per cent, was obtained by weighing the water direct, using the method of glass tubes as advocated by Penfield. The other two figures represent the loss up to 200°, at which temperature all of the water of the mineral is given off. The residue was dissolved in HCl, and after filtering off the insoluble matter, the iron was precipitated by ammonia, filtered off, dissolved in HCl, and reprecipitated and weighed, while hydrogen sulphide was passed

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*Min. de France, iii, 8.

into the combined ammoniacal filtrates until the characteristic red color was produced. The solution was then acidified with H_2SO_4 and after heating on the steam bath, to allow the molybdenum sulphide to settle, it was filtered through a Gooch crucible. This was then dried, and the sulphide changed into the trioxide at a low heat and weighed to constant weight. The filtrate from the molybdenum sulphide was made alkaline with ammonia, hydrogen sulphide again passed into the solution, which was then re-acidified with H_2SO_4 and a small amount of molybdenum which had escaped precipitation in the first case recovered. The filtrate, on testing, showed no more molybdenum. Neither was any residue found on evaporating it to dryness and tests that were made showed the absence of calcium and magnesium. The weighed iron oxide was fused with sodium bisulphate and determined volumetrically with a result that agreed with the gravimetric determination. The results obtained are as follows:

	1	2	3	Av.	Ratio	
H_2O	16·98	17·95	17·93	17·62	7·43	7½
Fe_2O_3...	21·08	21·07	....	21·08	1·00	1
MoO_3...	57·02	57·49	58·55	57·69	3·04	3
Insol....	4·66	....	....	4·66		
				101·05		

The average analysis, with the insoluble matter deducted and reduced to 100 per cent, is compared with the figures calculated for $Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O$.

	Analysis	Calculated
H_2O	18·28	18·57
Fe_2O_3	21·87	22·01
MoO_3	59·85	59·42
	100·00	100·00

Partial water determinations were made on two samples as follows, the amount of water being represented by the loss in weight, the crucible being heated at the temperature given till six hours further heating produced no difference in weight.

Total loss up to 110° = 14·04%
" " " " 125° = 15·50
" " " " 185° = 17·64
" " " " 200° = 17·93

This shows that of the total seven and a half parts of water, 5·92, or six parts, are given off at a little above 100°, while a higher temperature is required to drive off the remainder.

For the material from the other localities,* the quantity was so small that exact values cannot be expected, but the analyses all show a general agreement with the calculated values. The samples analyzed are as follows:

No. 1 is from Telluride, Colorado, and is from the sample furnished by the Foote Mineral Company, of Philadelphia.

No. 2 was very kindly furnished by Prof. A. J. Moses, of Columbia University, who states that the sample is probably from California, though the locality is not known for certain. Two samples were sent, one yellow, which was seen to be pure, and one brown, which was seen under the microscope to consist of a mixture of the pure yellow mineral and limonite. This sample at once suggested that it was similar to that analyzed by Owen, who obtained 35 per cent Fe_2O_3. It also showed the ease with which a mechanical mixture of molybdite and limonite could be detected under the microscope. The opaque brown limonite was scattered through some of the yellow molybdite, and caused it to appear almost opaque, besides which there were numerous patches of earthy limonite. The brown sample was not analyzed.

No. 3 is from Renfrew, Ontario, and was very kindly furnished by Prof. C. Palache, of Harvard University. Most of the material is massive and earthy appearing, though seen under the microscope to consist of minute fibrous crystals. The material did not look promising, but analysis showed values agreeing well with the other. Owing to an accident, only the iron and molybdenum could be determined. These values are not given. On one of the specimens sent by Prof. Palache, there was a small amount of the finely crystallized fibrous material which seemed to be very pure. This was scraped off and analyzed, and though only about fifty milligrams were available, the results given under No. 3 were obtained.

The methods of analyses were like those mentioned with the analyses of the New Hampshire material. By heating in a closed tube, to obtain the water, some of the molybdenite which was usually mixed with the mineral doubtless oxidized to the oxide, thus increasing the amount of molybdenum present. The results obtained are:

	No. 1 Colorado	No. 2 California	No. 3 Ontario
H_2O	15·8	15·4	15·5
Fe_2O_3	19·0	15·8	17·3
MoO_3	59·3	47·7	55·7
Insol.	[5·9]	24·0	9·4
	100·0	102·9	97·9

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*The characteristic optical properties of the ferric molybdate were also determined on specimens from Stanhope, New Jersey; Gold Creek, Deer Lodge Co., Montana; Aldfield Township, Pontiac Co, Quebec.

Deducting the insoluble matter and reducing the analyses to 100 per cent, we obtain:

	No. 1	No. 2	No. 3	Calc.
H_2O	16·8	19·5	17·5	18·6
Fe_2O_3	20·2	20·0	19·6	22·0
MoO_3	63·0	60·5	62·9	59·4
	100·0	100·0	100·0	100·0

The ratios give:	Fe_2O_3	:	H_2O	:	MoO_3.
Anal. 1,	1·0	:	7·3	:	3·4
Anal. 2,	1·0	:	8·6	:	3·3
Anal. 3,	1·0	:	7·8	:	3·5

The analyses agree sufficiently well to show that the mineral is uniform in composition and the analysis of the material from New Hampshire serves to establish its formula.

In considering the mode of formation of the hydrous ferric molybdate, it may be well to call attention to the fact that the interaction of molybdic acid, $H_2MoO_4.H_2O$, on limonite may be written so as to yield a product with a formula that is identical with the new formula and exactly balances the equation; $2Fe_2O_3.3H_2O+6(H_2MoO_4.H_2O) = 2(Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O)$.

Pyrognostic Properties.—On heating the mineral in a closed tube abundant water is easily given off and the mineral becomes a dark olive color which on further heating again becomes lighter in color. On heating the mineral in a crucible, the color changes are very marked. At first, the yellow mineral darkens and becomes a dark gray, appearing almost black and with a slight olive tint, then it becomes a light yellow again, and on further heating changes to a deep orange color. If the mineral now be allowed to cool, the orange changes to yellow and back to orange again on reheating. If the dark colored material be allowed to cool, it retains its dark gray color and on reheating passes through yellow to the orange. On heating for some time at a higher temperature, the mineral, on cooling, becomes a permanent bright green. By further heating all of the molybdenum is volatilized and the dark red ferric oxide remains. The mineral is readily soluble in hydrochloric acid, and dissolves slowly in ammonia, taking on a brown color (probably due to the separating ferric hydroxide). After a while, all the molybdenum of the mineral goes into solution, leaving the insoluble ferric hydroxide.

Artificial ferric molybdate.—Chemical dictionaries mention but two hydrous ferric molybdates, neither of which is crystalline, and which approximate in formula to $Fe_2O_3.4MoO_3.7H_2O$, and $Fe_2O_3.5MoO_3.16H_2O$. On adding a solution of ammonium molybdate to an excess of a solution of a ferric salt, no precipitate is formed, but on reversing the process and adding the ferric salt to the ammonium molybdate, a voluminous yellow precipitate appears. A precipitate thus prepared was air-dried for about a week and analyzed with the following result:

		Ratio
Fe_2O_3	15·9	1·0
MoO_3	61·6	4·3
H_2O (by diff.)	22·5	12·5
	100·0	

These results are between those of the two salts above quoted. It was found, however, that a large amount of free molybdic acid contaminated the material and the impossibility of air-drying the non-crystalline mass sufficiently accounts for the high water content. It is therefore believed that neither of the two salts above mentioned and described in chemical dictionaries has any existence, but that they are mixtures of a salt of the formula $Fe_2O_3.3MoO_3+n(3H_2O)$ with molybdic acid and water.

A preliminary experiment of heating precipitated ferric hydroxide and molybdic acid in the correct molecular proportions with an excess of water in a glass bomb failed to give any result. After heating to about 150° for several hours, there was no indication of any reaction and on higher heating the bomb exploded.

An attempt was next made to crystallize the yellow amorphous precipitate. The precipitate was heated with water in a glass bomb up to 180°–200° for several days, and when examined, was found to consist of a mass of fine yellow crystals and a greenish amorphous mass. By shaking up the tube, the green part settled very quickly, while the minute yellow crystals settled so slowly that a nearly perfect separation of the two products could be made. The yellow crystalline part was examined under the microscope and found to consist of three products, all crystallized. The most abundant salt occurs in minute pale yellow tablets of quadratic outline and sometimes with an octagonal shape suggesting combinations of the cube and octahedron, and which seem to be isotropic. They were too small to test for interference figures. The second most abundant salt occurs in pale yellow fibrous prisms and also in radiated fan-shaped masses that show the characteristic absorption of the natural mineral, and are probably to be identified with it. The third salt also occurs in prisms which, however, are not fibrous, do not show any absorption, and seem to be colorless. They may be molybdic acid, but the first two salts are probably hydrated ferric molybdates. It is the writer's intention to continue the study of the artificial formation of these salts, especially to obtain, in a state of purity, that one which corresponds in composition to the natural mineral.

Occurrence of natural MoO_3.—The existence of the trioxide of molybdenum as a natural mineral has not been demonstrated, and what is commonly believed to be MoO_3 is shown to be a hydrated ferric molybdate, $Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O$. There is also the possibility that the hydrous oxide $MoO_3.2H_2O$, or molybdic acid, has a natural occurrence. If either of these should be shown to exist, the name molybdite should be applied to the species and the salt $Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O$ should receive a different name; but until it is shown conclusively that an oxide of molybdenum does exist in nature, the name molybdite must be retained for the hydrated ferric molybdate.