ART. XLIX.—*On Roscoelite;* by W. F. HILLEBRAND and H. W. TURNER, with a note on its chemical constitution by F. W. CLARKE.

ANALYSIS AND COMPOSITION, BY W. F. HILLEBRAND.

THE rare mineral roscoelite has greatly needed reëxamination in order to reconcile the discrepancies between the analyses of Roscoe and Genth and to establish a satisfactory formula for this supposed vanadium mica. To the kindness of Mr. G. W. Kimble of Placerville, Cal., I am indebted through Mr. H. W. Turner for specimens from the Stockslager mine, from which a limited amount of fairly pure material was picked out. This was then laboriously purified by the aid of Thoulet's solution, the result being a very nearly pure product weighing only 1·2 grams and having after drying at 100° C. a density of 2·97 at 20° C.

Notwithstanding the small amount, it was possible by the exercise of care to make fairly satisfactory analyses.

With regard to the methods employed little need be said except as to the determination of the condition of the vanadium. For this purpose decomposition was effected by rather dilute H_2SO_4 in sealed tubes, the greatest care being taken to expel every trace of air from the powder and acid and to seal the tube during passage of a current of CO_2. Otherwise it is impossible to prevent oxidation of a considerable part of the V_2O_3. In one case, unfortunately, the air cannot have been fully expelled, for the solution after decomposition was blue instead of green and much less oxygen was required in titration than when the color was green.

The contents of the tube, still warm, were poured into fairly hot freshly boiled water and titrated rapidly. Iron and vanadium were then reduced by H_2S gas, the latter boiled out in a current of CO_2, and titration repeated on the hot liquid. The solution was then boiled with ammonia, the precipitate fused with Na_2CO_3, leached with water, and the residue again fused with Na_2CO_3 and leached to remove the last of the vanadium. This residue was then fused with $KHSO_4$,* dissolved in dilute H_2SO_4, boiled first with H_2S and then in a current of CO_2, and the liquid titrated for total iron. The solution held titanium which was then estimated colorimetrically.

The first of the titration results gave the effect of all iron, assuming its existence as FeO, and of all vanadium that might

* Any slight trace of vanadium remaining will impart a bright yellow color to the cold $KHSO_4$ fusion, a test which proved useful more than once during the analysis.

exist in a lower state of oxidation than V_2O_5. The second gave all iron as FeO and all vanadium as V_2O_4. Deduct from both the figure for FeO and the remainder gives that for vanadium. In this way two very concordant results were obtained for total vanadium as V_2O_4 which were supplemented by tests on portions used for other constituents, but only one was obtained for the vanadium as it exists in the mineral, a second being vitiated by evident oxidation during decomposition in the tube. As a check, however, a fresh sample of unpurified mineral was similarly treated and it was found that fully nine-tenths of the vanadium existed as V_2O_3, a result confirming the single test on the purified material which showed 93·5 per cent as V_2O_3. It is not impossible that slight oxidation had taken place even in these cases, and I feel justified in assuming with Genth that the vanadium should be considered wholly as V_2O_3.

In the other portions analyzed the vanadium was likewise titrated in V_2O_4 condition, but only after separation from iron, titanium and aluminum by fusion with Na_2CO_3, extraction with water and separation of dissolved alumina by ammonium carbonate. A second fusion of the residue and of the precipitated alumina was necessary in order to extract all the vanadium. These numerous manipulations render the figures for Al_2O_3 perhaps the least trustworthy of all, but the average given is probably not far from correct.

The iron is assumed to be present as FeO; and the titanium to belong to a foreign mineral, since a test on unpurified material gave much more, namely, 1·50 per cent TiO_2, without accompanying increase in FeO, which latter observation seems to exclude ilmenite as the source of the titanium.

Both the iron and magnesium are supposed to belong to the roscoelite, since they were found by Genth in nearly the same amounts and no recognizable iron or magnesium minerals were noticed in the purified powder.

For comparison, the mean of Roscoe's analyses and that one of Genth's considered by himself to be his best are also given in the table on the following page.

Very marked differences are apparent in the three analyses by different chemists. If titanium was present in the material analyzed by Genth and Roscoe, as is very probable, their high results for alumina are in great part at least accounted for. It is inconceivable how Genth obtained his value for water by ignition, since the mineral oxidizes when heated in air. In fact the oxidation in one of my own analyses, after allowing for loss of water as ascertained by direct weight, was almost what theory requires for the oxidation of V_2O_3 to V_2O_5 and of FeO to Fe_2O_3, or 5·14 per cent instead of 5·27 per cent. It

may fairly be assumed that his water was weighed directly after expulsion by ignition of the powder. Roscoe's figures for water, if not for moisture, must be affected by error, probably arising from the unsuspected oxidation of vanadium.

ANALYSES OF ROSCOELITE.

Amount used.	Hillebrand. ·3000*g.*	·2531*g.*	·2635*g.*	·1560*g.**	·2038*g.*	Mean.	Genth.	Roscoe.	
SiO_2	45·30	45·04				45·17	47·69	SiO_2	41·25
TiO_2	·77		·77		·80	·78		V_2O_5	28·60†
V_2O_3	23·90	24·00		24·09	24·06	24·01	20·56	Al_2O_3	14·14
Al_2O_3		11·74	11·34			11·54	14·10	Fe_2O_3	1·13
FeO	1·59			1·65	1·57	1·60	1·67	Mn_2O_3	1·15
MgO	1·64					1·64	2·00	CaO	·61
K_2O		10·41	10·32			10·37	7·59	MgO	2·01
Na_2O		·13	none			·06	·17	K_2O	8·56
Li_2O		ft. tr.				ft. tr.	tr.	Na_2O	·82
H_2O below 105° C.	·40					·40		Water	1·08
								Moisture	2·27
H_2O 105–280° C.	·17		4·29			·17	4·96 ign.		101·62
H_2O above 280° C.						4·12			
Fl						none			
						99·86	98·76		

From the column of means of my own analyses the following ratios are obtainable:

SiO_2	·753
V_2O_3	·159
Al_2O_3	·113
FeO	·022
MgO	·041
K_2O	·110
H_2O	·229

The entire absence of manganese and of calcium in my own and Genth's samples tends to confirm the suspicion that Roscoe's material was far from pure. It is to be remarked, however, that my figures for vanadium agree quite closely with his and differ widely from Genth's.‡

Discrepancies of this kind are not necessarily to be ascribed to faulty analyses. It is well enough known that in any one

* 4·94 per cent oxygen used for complete oxidation instead of 5·27 needed for all V as V_2O_3 and Fe as FeO.

† Equivalent to 23·59 per cent V_2O_3.

‡ This agreement is probably more apparent than real for the reason that Roscoe's figure would be materially lowered by regarding the iron of his analysis as FeO instead of Fe_2O_3 in conformity with my analysis.

species of mica various molecules must sometimes be assumed to exist in different proportions and the general formula for such a species can only be arrived at by comparison of a series of analyses of different varieties. Hence, in view of the lack of any simple ratios, the deduction of a definite and final formula from my data is not justifiable. Further analyses are needed of new and very pure material from other locations even if these be not far removed from the source of the present material. Nevertheless, in the hands of an expert very unpromising data may often be made to afford positive indications, and that this is true in the present case the following discussion by Professor F. W. Clarke clearly shows.

CHEMICAL CONSTITUTION OF ROSCOELITE, BY F. W. CLARKE.

The ratios given in the foregoing new analysis, used directly, lead to the following empirical formula for roscoelite:

$$H_{458}K_{220}Fe_{22}Mg_{41}Al_{226}V_{318}Si_{753}O_{2724}.$$

Here H to K, and Mg to Fe are as 2 to 1. Between O and Si, however, the ratio is not simple, and lies below the orthosilicate and above the trisilicate proportion. Since in many micas the groups SiO_4 and Si_3O_8 are replaceable, that suggestion may be followed out here; and then the formula reduces to

$$R'_{678}R''_{63}Al_{226}V_{318}(SiO_4)_{536}(Si_3O_8)_{71}.$$

From this expression, applying Clarke's mica theory, the mineral may be regarded as a molecular mixture of the three compounds

1.	2.	3.
$SiO_4 \equiv FeK$	$Si_3O_8 \equiv KH_2$	$SiO_4 \equiv KH_2$
$Al—SiO_4 \equiv MgH$	$Al—Si_3O_8 \equiv KH_2$	$Al—SiO_4 \equiv V$
$SiO_4 \equiv MgH,$	$Si_3O_8 \equiv Al,$	$SiO_4 \equiv V,$

in the ratio 21 : 22 : 159, or nearly 1 : 1 : 8. Upon reducing the analysis to 100 per cent, after throwing out the TiO_2 and the water lost below 280° as extraneous, we get the following comparison between the results found and the theoretical composition.

	Found.	Reduced.	Calculated.
SiO_2	45·17	45·88	45·52
TiO_2	·78	----	----
V_2O_3	24·01	24·39	24·64
Al_2O_3	11·54	11·73	11·62
MgO	1·64	1·66	1·72
FeO	1·60	1·63	1·55
K_2O	10·37	10·53	10·81
H_2O, 280°—	·57	----	----
" 280°+	4·12	4·18	4·14
	99·80	100·00	100·00

This comparison, based on the ratio 21 : 22 : 159, is as satisfactory as could be expected.

Of these component molecules, the first represents the normal phlogopite type: the second is a trisilicate alkaline biotite; and the third, which forms 74·5 per cent of the whole mass, is a muscovite in which two-thirds of the aluminum have been replaced by vanadium; in short, a vanadium muscovite. Ordinary muscovite is $Al_3(SiO_4)_3KH_2$; and whether a corresponding $V_3(SiO_4)_3KH_2$ exists, can be determined only by analyses of roscoelite from other localities, and so learning its range of variation. That vanadium may replace aluminum is shown by the fact that Piccini has prepared true vanadium alums. That roscoelite is essentially a vanadium muscovite seems to be fairly well established. As for the molecule $Al_2(Si_3O_8)_3K_2H_4$, its existence is indicated in some other micas; and in Simmler's "helvetan" it seems to be the dominant molecule.

The Occurrence of Roscoelite, by H. W. Turner.

According to H. G. Hanks,* at one time State mineralogist of California, attention was first called to roscoelite by Dr. James Blake at a meeting of the San Francisco Microscopical Society, July 2d, 1874. The specimens then exhibited were from the Stockslager† mine, which is about 1^{klm} southwesterly from Lotus on Granite Creek in Eldorado County.

At a meeting of the California Academy of Sciences held July 20, 1874, Dr. Blake presented specimens of the same mineral, which he then supposed to be a chromium mica.

At a meeting of the California Academy held August 2, 1875,‡ Dr. Blake read a paper on roscoelite. Samples sent by him to Dr. Genth of Philadelphia were found to contain vanadium. The mineral was named by Blake in honor of Professor Roscoe of Manchester, England, who had made vanadium a special study. Dr. Blake calls attention to the fact that Dr. Hall found vanadium widely diffused in many rocks, generally associated with phosphorus. According to Hanks the Stockslager vein from which the roscoelite obtained by Dr. Blake was taken, is small and not continuous, varying from two inches to a foot in thickness and running nearly parallel with Granite Creek. Associated with the quartz is calcite, and there are at least two varieties of iron sulphide present, probably pyrite and chalcopyrite. Hanks states further that the gold occurs only with the roscoelite and is

* Second Ann. Rep. State Mineralogist of California, pp. 263–4, 1880–2.

† According to Lindgren (see Economic Sheet of the Placerville folio of the Geol. Atlas of the U. S.) this name should be spelled as above, but Hanks spells it *Stuckslager*.

‡ Proceedings Cal. Acad., vol. vi, p. 150, 1875.

found interstratified with the roscoelite laminæ in pieces from the value of one dollar to the minutest microscopic particles. He also states that from four to five hundred pounds of roscoelite were obtained by the miners, all of which was wasted in extracting the gold.

Mr. George W. Kimble of Placerville, California, for many years county surveyor, has furnished the California material analyzed by Dr. Hillebrand as well as other specimens. In these specimens the roscoelite is in part embedded in quartz and probably contemporaneous in formation with the quartz, and in part fills little cracks in the quartz and therefore somewhat later.

There are given below four localities where roscoelite has been found, according to Mr. Kimble, to whom the author is indebted for the following information about the occurrence of the mineral at these localities.

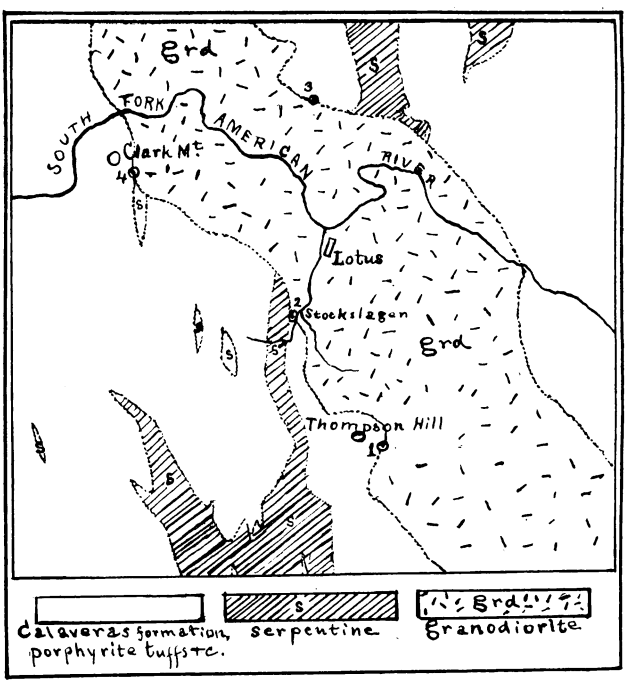

FIG. 1. Geological map copied from the Placerville folio, showing roscoelite localities. Geology by W. Lindgren.

The accompanying map, on the scale of about 1-150000, gives the exact localities where the roscoelite has been found. The Calaveras formation is largely of Carboniferous age, as may

also be the augite-porphyrite tuff associated with it. The serpentine is later than the Calaveras formation and earlier than the granodiorite, which is probably late Jurassic or early Cretaceous. It will be observed that all of the localities are at or near the contact of an intrusive granodiorite mass with the surrounding rocks, chiefly sediments and older lavas. This suggests that the mineral may be regarded as in some way due to the mineralizing solutions accompanying the intrusion of the granodiorite. However, the quartz veins clearly fill fractures which formed in the granodiorite and associated rocks after the consolidation of the granodiorite; consequently the deposition of the quartz and the associated gold and roscoelite must have been also subsequent to the consolidation of the granodiorite. The following are the localities reported by Mr. Kimble. They are all in Eldorado County, from 8 to 15^{klm} northwest of Placerville.

Locality 1. Thompson Hill on its northeast slope about 2·5^{klm} southeast of the Stockslager mine. — There are here fifteen or more small seams of quartz having a strike of north of west. As these seams pass through the contact of the granodiorite with the greenstone (augite-porphyrite?) they contain rich spots of gold and roscoelite. The seams of quartz pass on through the northeast point of Thompson Hill and come into the granodiorite again.

Locality 2. Stockslager mine on Granite Creek. — Mr. Lindgren informs me that the vein of the Stockslager mine is in a narrow wedge of metamorphic sediments of the Calaveras formation. Immediately east of this wedge is granodiorite, and immediately west is serpentine. Mr. Kimble states that there is here but one vein of quartz. This passes from the granodiorite into the narrow wedge of the Calaveras formation. It does not penetrate the serpentine. As previously stated, it was at this locality that by far the larger part of the roscoelite was obtained, including that analyzed by Dr. Hillebrand.

Locality 3. South slope of spur about 2·7^{klms} north of the village of Lotus.—In micaceous slate, which is part of a contact metamorphic zone of the Calaveras formation. The exact locality is about 500 feet east of the contact. It has never been demonstrated, but Mr. Kimble thinks that this quartz vein extends southeast into the granodiorite.

Locality 4. Clark Mountain on its east slope at the contact of the Calaveras formation and the granodiorite.—The occurrence here is identical with that at the Stockslager mine.

According to Kimble no roscoelite has ever been found where the seams are in granodiorite, and the latter is not altered; but some has been found at the contact of the quartz with serpentine in localities 2 and 4. All of the quartz seams at localities 1, 2, and 4 dip southwest and have pockets of gold.

Prof. Hanks* states that roscoelite was also found in Sec. 31, T. 11 N. Range 10 E, two miles from the Stockslager mine. This appears to be the Thompson Hill locality of Kimble, to whom, indeed, Prof. Hanks was probably indebted for his information. Hanks states that the roscoelite was found here in the bed rock of Big Red ravine in a dark-colored micaceous rock in small seams of quartz with calcite and gold.

The roscoelite from California shows a tendency to crystallize in little rosettes, so that individual scales of any size with the same optical orientation throughout are difficult to obtain. Some scales gave with convergent light a nearly uniaxial black cross, the hyperbolas opening but slightly on rotation, indicating a small axial angle. Like all other micas it is optically negative. The pleochroism as seen in thin foils is, c and b clove brown to greenish yellow brown, a light greenish yellow. In the scales of the powder analyzed no rutile needles or other inclusions were detected, but in the center of a rosette of roscoelite scales were found dark grains with a metallic luster. These grains are of sufficient size to have fallen with the heavy minerals during the process of separation with the Thoulet solution, and it is not likely that any of them have been included in the powder analyzed, although they were noted in the impure material before it had undergone the final separation. The grains show no crystal form and were not determined.

* Loco citato, p. 263.