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WITH FIVE PLATES.

NEW HAVEN: EDITOBS.

1876. St of the substance to the Microscopical Society and at the Academy of Sciences of California in September, I made the general statement that it was a potash-mica, containing 23 per cent chromic oxide and traces of lithia. It was not until I had sent a specimen of the mineral to Dr. Genth to analyze that the presence in it of vanadium was discovered, and to him is due the entire credit of having first detected the true character of this interesting mineral. I have availed myself of the action of nitrohydrochloric acid on the mineral to prepare a considerable quantity of vanadic compounds for physiological experiment, as this affords about the easiest method of obtaining vanadic acid, although it is impossible thus to extract all the vanadium from the mica.

ART. V.—On some American Vanadium Minerals; by F. A. GENTH.

1. Roscoelite.

I am indebted to Dr. James Blake of San Francisco, California, for a small quantity of the very interesting mineral, which he called "Roscoelite," in honor of Professor Roscoe, whose important investigations have put vanadium in its proper place among the elements.

Roscoelite occurs in small seams, varying in thickness from r_{s}^{1} to r_{s}^{1} of an inch in a decomposed yellowish, brownish or greenish rock. These seams are made up of small micaceous scales, sometimes $\frac{1}{2}$ of an inch in length, mostly smaller and frequently arranged in stellate or fan-shaped groups. They show an eminent basal cleavage. Soft. The specific gravity of the purest scales (showing less than one per cent of impurities) was found to be 2.938; another specimen of less purity gave 2.921. Luster pearly, inclining to submetallic. Color dark clove-brown to greenish-brown, sometimes dark brownish-green.

Before the blowpipe it fuses easily to a black glass, coloring the flame slightly pink. With salt of phosphorus gives a skeleton of silicic acid, a dark yellow bead in the oxidizing flame, and an emerald-green bead in the reducing flame. Only slightly acted upon by acids, even by boiling concentrated sulphuric acid; but readily decomposed by dilute sulphuric acid, when heated in a sealed tube at a temperature of about 180° C., leaving the silicic acid in the form of white pearly scales, and yielding a deep bluish-green solution. With sodic carbonate it fuses to a white mass. The roscoelite, which I received for investigation was so much mixed with other sub-

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stances, such as gold, quartz, a feldspathic mineral, a dark mineral and very minute quantities of one of orange color, that it was impossible to select for analysis material of perfect purity. For this reason I have delayed the publication of my results, which were obtained over one year ago, in the hope of being able to repeat my analyses with better and purer specimens; but I now give the results of my analyses because there is no prospect of getting any more of this mineral, as will be seen from a letter of Dr. Blake, dated San Francisco, April 5th, 1876, in which he says, that the mine in which it occurs cannot be worked any farther until a tunnel has been run, and that it is quite uncertain when this will be done.

Although by no means perfect, my results approach the truth and give a fair idea of the composition of the mineral, even if the evident admixture of other minerals, varying in the different samples analyzed, from about one to perhaps over twelve per cent, does not permit one to calculate the atomic ratio of the constituents and establish the constitution of this species. There is especially an uncertainty with reference to the quantities of silicic acid, alumina and potassa which belong to the roscoelite, or which may have been introduced by admixtures of feldspathic and other minerals, as will appear from the results given below, which show that the mineral, when decomposed with sulphuric or dilute hydrofluoric acid generally gives only about six per cent of potassa, while fusion with calcic carbonate and ammonic chloride yields from eight to nine per cent. Some of these uncertainties could have been removed, if a larger quantity of the mineral had been at my disposal.

Particular attention was paid to the correct determination of the vanadium and the form in which it exists in the roscoelite.

The separation of vanadium is attended with great difficulties, and I have not found any of the methods of separation to give fully reliable results. This is in part owing to the incomplete precipitation of the vanadic acid, and in part to the impossibility of washing the precipitates completely without loss of vanadium. It was therefore always determined by the only method which I found to give fully reliable results—by titration with potassic permanganate.

After the separation from the other elements, the vanadic acid was reduced by hydrosulphuric acid into $\nabla_2 O_4$, which, after the excess of hydrosulphuric acid had been expelled by continued boiling, was re-oxydized into $\nabla_2 O_4$ by the permanganate. I have satisfied myself by numerous experiments that, no matter whether only a very minute quantity of sulphuric acid is present, or a very large excess, the $\nabla_2 O_4$ is completely oxidized into $\nabla_2 O_4$ by this process.

For the determination of the state of oxydation of the vana-AM. JOUR. SCI.-THIRD SHEIRS, VOL. XII, NO. 67.-JULY, 1876.

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dium in the roscoelite, a quantity of the mineral was dissolved in dilute sulphuric acid in a sealed tube at a temperature of about 180° C., and was titered after cooling; the liquid was then reduced by hydrosulphuric acid, and after boiling off the excess of the latter, it was again titered. From the quantity of oxygen required for oxidation in both cases it was found that vanadium in the mineral is present as $V_0O_{11} = 2V_0O_3$, V_2O_3 .

The determinations of the other elements were made by the usual methods.

The finely-powdered mineral was dried (unless otherwise stated) for two days over sulphuric acid, and the different samples gave the following results:

(a.) Purest scales.—The analysis was made by dissolving one portion in sulphuric acid and determining in this the quantity and state of oxidation of the vanadium, the silicic acid and insoluble impurities. The latter were left behind in dissolving the silicic acid in sodic carbonate and gave 0.85 per cent; a second portion was decomposed by sodic carbonate and nitrate, and a third for the determination of the alkalies by J. L. Smith's method. The $V_{\bullet}O_{+1}$ given below is the mean of the two determinations. (b.) Another sample, not quite as pure as a, was analyzed by fusion. (c.) Still more contaminated with impurities, was analyzed by dissolving in dilute sulphuric acid in a sealed tube, &c., $c\alpha$ is the result of this analysis, $c\beta$ after deducting 11.45 per cent of impurities. (d.) Another sample was decomposed by dilute hydrofluoric acid; the analysis was unfortunately lost excepting the determinations given below; the material for this analysis had not been dried over sulphuric acid. (e.) This sample was dried over sulphuric acid for several weeks; a portion, which was decomposed by sulphuric acid, gave 5.37 per cent insoluble silicates, 0.28 per cent of gold and 43.24 per cent of silicic acid; the $\nabla_{0}O_{11}$ was determined by difference. The results given below were obtained by decomposing the mineral by fusion.

		a	Ь	ca	cβ	d	e
Insoluble silicates,							
quartz, gold, &c.		[0.85]		11.45		8 ·91	[5 · 6 0]
SiO ₂	=	47.69	47.82	43.46	48.60		46 81
Al ₂ Ū ₃	=	14.10	12.60	10.22	11.76		15.78
FeO	=	1.67	3·3 0	2.03	2.27		1.28
MgO	=	2.00	2.43	1.74	1 . 95		2.31
CaO	=	trace	trace	0.50	0.23	.	trace
Na ₂ O (trace Li ₂ O)	=	0.18	0.33	0.30	0.34	\$ 5.96	0 .6 0
K.Ŭ	==	7.28	8.03	5.35	5 9 8	10.00	8.89
$\begin{array}{c} \mathbf{K}_{2}\mathbf{O}\\ \mathbf{\nabla}_{6}\mathbf{O}_{11} \end{array}$	=	22. 02	21.36	20.20	22.92	<i>.</i>	20.16
Ignition		4.96	5.13	5.32	5.95	6.34	8.87
				_ 			
		100.22	101.00	100.87	100.00		100.00

A mineral, very similar in composition and perhaps a compact impure variety of roscoelite is found associated with the scales. It has the appearance of a massive dark green chlorite or that of some varieties of serpentine. The analysis was made by fusion, &c., and gave:

SiO,	== 46.09	Na ₂ O	= 0.18
Al ₂ Ō ₃ FeO	= 17.46	K2O	== 8.66
FeO	<u> </u>	V ₆ O ₁₁ Ignition	== 17.23
MgO	= 2·18	Ignition	= 6.82
-		-	
			10 0·42

2. Prittacinite, a new hydrous vanadate of lead and copper.

In a paper on American Tellurium and Bismuth minerals, read before the American Philosophical Society at the meeting of August 21st, 1874 (Proc. Am. Phil. Soc., xiv, 223-231), I mention, on the authority of Mr. P. Knabe, a siskin-green pulverulent mineral from the "Iron Rod Mine," Silver Star District, Montana, as a new "Tellurate of lead and copper." I had at that time no opportunity to examine into the merits of this mineral, having mislaid the small sample which he had sent me. On receiving a copy of my paper, Mr. Knabe furnished me with several specimens, which gave me a sufficient quantity of fair material for an analysis. A qualitative examination proved it to be a hydrous vanadate of lead and copper and not a tellurate.

When I communicated this result to Mr. Knabe he gave me an interesting account of how he fell into his error. At the Uncle Sam's Lode, in Highland District, occurs with the tetradymite a siskin-green mineral, which has not yet been analyzed, but which appears to be a tellurate. It looks exactly like the pulverulent variety of the psittacinite from the Iron Rod Mine. When Mr. K. dissolved the latter in hydrochloric acid, the evolution of chlorine indicated the presence of a higher oxide; the solution precipitated with an excess of ammonic sulphide gave sulphides of lead and copper and a filtrate which, on addition of an acid, gave a black precipitate—vanadic sulphide—which he mistook for tellurous sulphide.

Psittacinite occurs in very thin cryptocrystalline coatings, sometimes showing a small mammillary or botryoidal structure, also pulverulent; color siskin-green, sometimes with a grayish tint, to olive-green. Before the blowpipe it fuses easily to a black shining mass. With fluxes gives the reactions of vanadium, lead and copper. Soluble in dilute nitric acid, the solution yielding on evaporation a deep red mass.

As it was impossible to get any of the mineral in a pure state, I had to use coatings with quartz attached to them, sometimes contaminated with a little limonite; but these admixtures could not influence the analysis farther than very slightly with reference to the amount of water which it contains.

The following are my results:

		a	Ь	C	đ	8
РЬО	=	41.36	50.17	42.89	27-12	42.38
CuO	=	14.84	1 6-66	14.72	9.75	15.03
V ₂ O ₅	=	14.64	19.05	15.87	9-96	15-77
H,O	=	7.42		not determin	ned	7.25
SiÒ,	=	15-13)	10.10)	15.57
Al,Ŏ,	=	1.29	ſ	8.83	ſ)
Fe ₂ O ₃	=	2.72	} 7.6 0	2.19	} 48 84	4.00
MgO)_	ot det.	1	0.65		00 ₽ ۲
CaO	<u>۲</u>		J	0.12	J	J

The oxygen ratio of PbO: CuO: $\nabla_{g}O_{5}$: $H_{g}O$ in the above analyses is in:

	a	=	2.97	:	2.89	:	6.41	:	6.28
	b	=	8.60	:	8.36	:	8.84	:	
	C	=	8.08	:	2-97	:	6.92	:	
	d		1.94	:	1.96	:	4.36	:	
	e	=	8.04	:	8.08	:	6-90	:	6•44
or	a	=	1	:	0.82	:	2.16	:	2.19
	b	=	1	:	0.88	:	2.31	:	
	C	=	1	:	0 -9 7	:	2-26	:	
	d	=	1	:	1.01	:	2-25	:	
	e	=	1	:	1	:	2•27	:	2.12

The average of the five analyses gives the ratio of

1	:	0.98	:	2.22	:	2.15
9	:	9	:	20	:	18

corresponding to-

3 (3 PbO, $\nabla_{\mu}O_{5}$) + (3 CuO, $\nabla_{\mu}O_{5}$) + 6 (CuO, $H_{\mu}O$) + 12 $H_{\mu}O$. giving the following percentage:

PbO CuO	=	53·15 18 ·9 5
		19.82
V ₂ O ¹ H ₂ O	=	8.28
		100.00

Psittacinite occurs, sometimes associated with gold, and small quantities of cerussite, chalcopyrite and limonite upon quartz, at several of the mines in Silver Star District, Montana, especially in the Iron Rod Mine and New Career Mine, and its occurrence in these mines is looked upon as a favorable indication, for, when it is met with, the vein becomes immediately or soon after rich in gold. This mineral has been called "psittacinite" from psittacinus, siskin- or rather parrot-green.

University of Pennsylvania, Philadelphia, May 16th, 1867.

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