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WITH SEVEN PLATES.

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ART. III.—*On the Chemical Composition of Parisite and a new occurrence of it in Ravalli Co., Montana*; by S. L. PENFIELD and C. H. WARREN.

RECENTLY Mr. Lazard Cahn of New York sent to the Mineralogical Laboratory of the Sheffield Scientific School for identification, several specimens from Montana, showing crystals of an unusual appearance. These proved to be the rare mineral parisite, hitherto observed only in small amount at the original locality, the emerald mines of the Muso Valley, United States of Columbia; sparingly at Ober Arö, Langesundfiord, Norway;* and quite recently the mineral has been found at Narsásuk in Southern Greenland. A brief note on its occurrence at the latter locality was made by Gust. Flink in the report of a trip made there during the summer of 1897.

Not only does a new occurrence of parisite and the peculiar habit of the crystals deserve notice, but the chemical composition of the mineral has never been determined with certainty, and, therefore, analyses have been made for the purpose of determining this important character. It is with pleasure that we express to Mr. Cahn our thanks for a generous supply of the material from Montana for analysis.

The parisite crystals from Montana are supposed to have come from near Pyrites, Ravalli County, and occur in a fine-grained, loosely coherent, white material, which can be readily crushed to a powder with the finger nail. The matrix consists essentially of silica, alumina, calcium and a little alkali, and has the appearance of a decomposed rhyolite or trachyte, but its exact nature has not been more definitely determined. Through this white material crystals of pyrite and parisite are scattered, generally isolated, but at times the parisite has grown over and partly or completely surrounded the pyrite crystals. The pyrite is crystallized in pyritohedrons modified by small faces of the cube and octahedron, and the crystals vary in size from microscopic up to 3^{mm} in diameter. The average size of the parisite crystals is about 1^{mm} in diameter by 10^{mm} in length. They are quite numerous, so that from four to ten individuals may be seen on a surface of ten square centimeters of the matrix. The habit which they generally present is that of a horizontally striated hexagonal shaft, made up of steep pyramids in oscillatory combination and terminated at the ends by distinct, somewhat enlarged pyramids. The accompanying figure, which represents a portion of the shaft and one termination, gives a fair idea of the development of the crystals. The faces which are most prominent in forming the shaft are those of the pyramid *o* ($20\bar{2}1$) in oscillatory combination. Measurements over the reëntrant and salient angles

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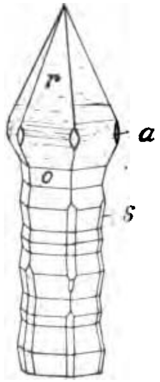
* Brögger, Zeitschr. Kr., xvi, 650, 1890.

could be made with the reflecting goniometer and are given in an accompanying table. Some of the edges of the pyramid *o* are truncated by a pyramid of the second order *s* $(11\bar{2}1)$, also in oscillatory combination, but, as shown in the figure, this form generally is not continuous throughout the whole length of the shaft nor is it present on all the edges. The pyramid which finally terminates the crystals is *r* $(20\bar{2}3)$. This is generally quite distinct, although its middle edges are somewhat rounded by a system of fine horizontal striations. The prism of the second order *a* $(11\bar{2}0)$, represented in the figure, is always small and frequently wanting. The prism of the first order, *m* $(10\bar{1}0)$, was not observed as a distinct face, although the oscillatory combination of the upper and lower pyramidal faces often gave rise to striated, rounded, surfaces which approximate in position to the faces of this prism. Occasionally the shafts taper to a point without the enlarged pyramid. Of the forms observed, *a* $(11\bar{2}0)$, *r* $(20\bar{2}3)$, *o* $(20\bar{2}1)$, *s* $(11\bar{2}1)$ and *m*? $(10\bar{1}0)$, the prism *a* is new. The angles which were measured are given below, together with the values calculated from the vertical axis established by Des Cloizeaux,* $c = 3{\cdot}2891$.



	Measured.	Calculated.
$a \wedge a = 11\bar{2}0 \wedge \bar{1}2\bar{1}0 =$	59° 54′	60° 00′
$r \wedge r = 20\bar{2}3 \wedge 02\bar{2}3 =$	55 25	55 25½
$r \wedge r = 20\bar{2}3 \wedge \bar{2}023 =$	137 22	136 54
$s \wedge s = 11\bar{2}1 \wedge 11\bar{2}\bar{1} =$	17 23	17 18
$o \wedge o = 20\bar{2}1 \wedge 20\bar{2}\bar{1} =$	13 10	14 00

For the chemical analysis the best material that could be obtained was secured by picking out the crystals from the matrix by hand, and rubbing them between the fingers to remove any loosely adhering material. The crystals enclosed, as has been said, a little pyrite and were not very firm, consequently some siliceous material was deposited in the cracks. These impurities amount to about six per cent. The material was of a nearly uniform yellowish brown color.

The method of analysis was as follows: Carbon dioxide was obtained by dissolving the mineral in hydrochloric acid and collecting the gas evolved in weighed potash bulbs. For fluorine, another portion of material was fused with sodium carbonate and a weighed amount of silica, and the fluorine separated and estimated by the Berzelius method as modified by Penfield and Minor.† The earths were separated from calcium by repeated precipitations with ammonia, and they were then converted into oxalates, ignited, and weighed as

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* Min., ii, p. 162, 1874.

† This Journal, III, xlvii, p. 387, 1894.

oxides. The amount of cerium oxide, Ce_2O_3, was estimated by decomposing the ignited oxides (CeO_2, La_2O_3 and Di_2O_3) with sulphuric acid, to which some oxalic acid was added, and weighing the carbon dioxide liberated by the higher oxide of cerium, according to the equation, $2CeO_2+H_2C_2O_4=Ce_2O_3+2CO_2+H_2O$. The joint molecular weight of the cerium, lanthanum, and didymium oxides $(Ce, La, Di)_2O_3$ was estimated by converting a weighed quantity of the oxides into sulphates and was found to be 328·2. The results of the analyses are given beyond.

As the considerable amount of impurities in the Montana parisite rendered the calculation of the formula somewhat uncertain, an analysis of the mineral from Muso Valley was also made. Exceptionally pure material for this analysis was obtained from a fragment of a large crystal in the Brush collection. In this analysis it was found that the full amount of fluorine was not obtained by a single fusion with sodium carbonate and silica, and soaking out with water. By saving the residues and fusing them a second time with sodium carbonate and a slight addition of silica, about 0·5 per cent of fluorine was obtained. This precaution was not taken in the analysis of the Montana mineral and consequently the ratio of the fluorine in that analysis is a little low. The joint molecular weight of the cerium, lanthanum and didymium oxides was found to be 328·4. The results of the analyses are given below, together with the analysis by Damour and Deville* of the parisite from Muso.

	I. Warren. Montana.	Ratio.	II. Warren. Muso.	Ratio.	III. Damour and Deville. Muso.	Ratio.
Specific gravity,	4·128		4·302		4·358	
CO_2	22·93	·521	24·22	·550	23·48	·533
F	5·90	·310	6·82	·359	5·55	·292
Ce_2O_3	26·14	·166	30·67	·183	44·21	·187
$(La, Di)_2O_3$	28·46		29·74		18·00	
CaO	10·98	·196	10·70	·191	10·10	·180
Fe_2O_3 (pyrite ?)	·80		·20		101·34	
Na_2O	·69		·20		0= 2F=2·34	
K_2O	·19		.10		99·00	
H_2O	·26		102·65			
Gangue by difference.	6·13		0=2F=2·87			
	102·48		99·78			
0 = 2F	2·48					
	100·00					

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* C. R., lix, p. 270, 1864.

The ratios derived from the foregoing analyses are as follows:

	CO_2 :	F :	$(Ce, La, Di)_2O_3$:	CaO			
I.	·521 :	·310 :	·166 :	·196 =	3·00 :	1·79 :	0·96 : 1·13
II.	·550 :	·359 :	·183 :	·191 =	3·00 :	1·96 :	1·01 : 1·04
III.	·533 :	·292 :	·187 :	·180 =	3·00 :	1·65 :	1·05 : 1·01

The new analysis of the exceptionally pure material from Muso Valley gives a ratio approximating very close to 3 : 2 : 1 : 1. The material from Montana is not so pure, consequently the ratio is less satisfactory. The fluorine in the mineral doubtless caused some of the gangue material to go into solution, thus causing the calcium to be a little high; while the fluorine is evidently low, because, as previously stated, the precaution was not taken to repeat the fusion with sodium carbonate and silica in estimating that constituent. The ratio obtained by Damour and Deville agrees with those obtained from the new analyses except as regards fluorine. It is believed, however, that their method of estimating fluorine is open to criticism, since they made no direct determination of this element but, assuming that on dissolving the mineral in very dilute hydrochloric acid the fluorine separated out completely as the fluorides of calcium and cerium, they ascertained the weight of these fluorides, and considered fluorine as equal to the difference between this weight and that of the calcium and cerium derived from an analysis of the insoluble residue.

Excepting the defects in the analyses, evidently due to failures in estimating fluorine correctly, the ratios derived from the three analyses indicate conclusively that CO_2, F, $(Ce, La, Di)_2O_3$ and CaO are united in the proportion of 3 : 2 : 1 : 1. Representing the trivalent metals of the cerium group collectively by R, it is probable that fluorine is directly united with them to form a bivalent radical (RF), and that parisite is a double carbonate, $2(RF)CO_3 + CaCO_3$, or $(RF)_2Ca(CO_3)_3$.

As far as the proportions of the different constituents is concerned, either of the foregoing expressions is equivalent to the formula proposed by Groth† $(CaF)'(CeF)''Ce(CO_3)_3$. Groth based his formula upon the single analysis of Damour and Deville, previously cited, and was correct in assuming that the deficiency in fluorine was due to a failure to estimate that constituent correctly. It seems to us more reasonable to consider the fluorine as playing a single role, united with the Ce, La, and Di metals to form a bivalent radical (RF), than to adopt the formula of Groth where fluorine plays a double role, united with calcium to form a univalent radical (CaF) and with cerium to form a bivalent radical (CeF).

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* Tabellarische Uebersicht der Mineralien, 1898, p. 61.

Laboratory of Mineralogy and Petrography,
Sheffield Scientific School, April, 1899.