ART. XLVII.—*Chemical Composition of Hulsite and Paigeite*,* by WALDEMAR T. SCHALLER.

Introduction.

IN the April number of this Journal for 1908† in conjunction with Mr. Adolph Knopf, who discovered these minerals in Alaska, I published a description of two new borates, hulsite and paigeite. These borates contained both ferrous and ferric iron, magnesia, and a small amount of water. The boric acid was determined by distillation with methyl alcohol and subsequent weighing as lime borate. Only a single determination of the B_2O_3 was given for each mineral. As, however, both analyses footed up well and the ratios, moreover, were fairly close to simple numbers, no doubt was entertained as to the correctness of the results given.

Shortly after, Prof. Clarke informed us that the method of determining boric acid in minerals was being investigated by two students of Prof. Edgar F. Smith, of the University of Pennsylvania. On entering into communication with Prof. Smith, we were enabled to have the boric acid content of both new minerals redetermined by methods devised by E. T. Wherry and W. H. Chapin.‡ It was found that the values first obtained were erroneous, being much too high.§ On again examining the minerals, therefore, to account for the deficiency, tin was found to be present in appreciable quantity in both minerals. It therefore became necessary to revise and extend the original analyses in order to definitely fix the composition of these minerals.

Notes on Chemical Examination.—These borates, having very similar composition, contain ferrous and ferric iron, magnesia, tin, water, boric acid, and there are in addition present in the HCl solution of the sample, silica, alumina and lime, derived from the gangue.

After considerable work performed on these two minerals, the results herein presented were obtained, but the unsatisfactory character of the determinations is fully recognized. A complete revision of all the chemical data is highly desirable, but for this pure material, free from any interfering gangue, is

* A brief abstract of a much fuller paper which is to appear in a forthcoming Bulletin of the U. S. Geological Survey.

† Knopf, A. and Schaller, W. T., Two New Boron Minerals of Contact Metamorphic Origin, this Journal (4), vol. xxv, p. 323, 1908.

‡ Determination of Boric Acid in Insoluble Silicates, Jour. American Chem. Soc., vol. xxx, p. 1687, 1908.

§ This Journal (4), vol. xxv, p. 323, 1908.

necessary, and for the complete elucidation of the problem considerable material must be available.

The present investigation was carried out under two great disadvantages, namely, (1) paucity of material, and (2) the unavoidable presence of considerable gangue in the samples. For the hulsite samples, free from magnetite, less than a gram was available, while several grams of paigeite, as pure as possible, had to suffice. Various questions developed only after some of the analyses had been completed, so that additional material was often needed but could not be had. It was found, too, that the different samples of each mineral varied somewhat in composition due to the different quality and quantity of the gangue and also to isomorphous replacements in the minerals themselves. All these points, developed as the analyses progressed, served to render the results obtained unsatisfactory to the analyst.

Analyses of hulsite.

Three different samples of hulsite were obtained and analyzed, the first two being the ones given in the original paper. Sample No. 1 consisted of about half a gram of magnetite-free hulsite, which was partially analyzed, only ferrous and ferric iron, magnesia, and the insoluble matter being determined. Sample No. 2 was about a gram of material, consisting of a mixture of hulsite and magnetite with but a few per cent of insoluble gangue. Tin was not determined in either of these samples and the value for boric acid given below for sample No. 2 was furnished by Wherry and Chapin.* Sample No. 3 was obtained by reexamining all the available material and picking out a small amount of non-magnetic hulsite mixed with considerable gangue. The relatively large amount of the gangue that was soluble in acid complicated the discussion of the results.

Only the average of the analyses of samples Nos. 1 and 2 are repeated below, the fuller data being given in the original paper.

Average analyses of samples Nos. 1 and 2, hulsite.

	No. 1.	No. 2.
FeO	33.27	34.44
MgO	10.17	8.48
Fe ₂ O ₃	17.83	27.64
B ₂ O ₃	----	10.44
H ₂ O	----	1.66
Insol.	10.00	2.24
SnO ₂	not det.	not det.

From the analysis of sample No. 3, the ratio of B₂O₃ to Fe₂O₃ is found to be 3:2. From this ratio the amount of magnetite

* Loc. cit.

present in the above sample No. 2 can be calculated. The amount of ferric iron belonging to the borate being thus determined, the amount belonging to the magnetite is found, and deducting the proper amount of FeO to form $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, the ratios reduce to the figures given beyond, which represent the composition of the magnetite-free hulsite.

The results obtained for the analyses of sample No. 3 are given below. Though considerable insoluble gangue was present, magnetite was entirely absent. The results shown under 1a were made on a small sample of still impurer material and is chiefly of value for the determination of the tin, as the value confirms the other figures given for tin. The ammonia precipitate for sample 1a was not determined, as it was used for various qualitative tests and the calcium precipitate was accidentally lost. The figures given under 1a are not taken into the average. The higher value for the boric acid under columns 1 and 2 is taken in the average instead of the mean of the two values, as the second determination given is believed to be low.

Analyses of sample No. 3, hulsite.

	1a	1	2	3	Average
FeO	----	----	----	27.71	27.71
MgO	3.62	----	4.13	4.45	4.29
CaO	----	7.98	9.82	9.54	9.11
Fe_2O_3	----	----	----	----	15.21
Total iron as Fe_2O_3 ..	----	----	46.30	45.67	----
SnO_2	6.13	6.85	7.15	7.20	7.07
B_2O_3	----	9.20	8.27	----	9.20
Insoluble	27.42	19.92	17.52	18.44	18.63
H_2O , CO_2 , SiO_2 , Al_2O_3 ..	----	----	diff.	----	8.78
					100.00

From the figures given above for the average analysis the ratios were calculated with the following values:

Ratios of analysis of sample No. 3, hulsite.

FeO	.385	}	10.47
MgO	.107		
Fe_2O_3	.095		2.02
SnO_2	.047		1.00
B_2O_3	.131		2.79

The analyses of samples No. 2 of paigeite, as given beyond, give an indication of the amount of calcium oxide which may be derived from the gangue. For 15 per cent insoluble matter the calcium oxide content is about 4 per cent. If this ratio remains fairly constant, there should be, in the above analysis of hulsite sample No. 3, about 5 per cent of lime obtained from the gangue. This would leave approximately somewhat

less than 4 per cent CaO which may belong to the borate mineral. Assuming this to be so, the ratio of (FeO, MgO, CaO) to Fe_2O_3 would become 11.9:1 or nearly 12:1. From the analysis of sample No. 3, given above, we obtain for the formula of hulsite, then, either $10\frac{1}{2}\text{RO} \cdot 2\text{Fe}_2\text{O}_3 \cdot \text{SnO}_2 \cdot 3\text{B}_2\text{O}_3 + ?\text{H}_2\text{O}$, or regarding the 4 per cent of CaO as belonging to the mineral, the formula $12\text{RO} \cdot 2\text{Fe}_2\text{O}_3 \cdot \text{SnO}_2 \cdot 3\text{B}_2\text{O}_3 + ?\text{H}_2\text{O}$.

Discussion of Formulæ of Hulsite.

From the results of the analyses of the three samples of hulsite, as just given, there are derived the following partial formulæ for the mineral.

Partial Formulæ for Hulsite.					
	RO	Fe_2O_3	SnO_2	B_2O_3	H_2O
From Sample No. 1	13.2	2.0	--	--	--
" 2	12.4	2.0	--	3.0	1.9
" 3	10.5	2.0	1.0	2.8	-- or
" 3	12.0	2.0	1.0	2.8	--

From this compilation, incomplete as it is, the most probable formula derivable from the results obtained is $12\text{RO} \cdot 2\text{Fe}_2\text{O}_3 \cdot 1\text{SnO}_2 \cdot 3\text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ or $(\text{Fe}, \text{Mg})_{12}\text{Fe}_2\text{SnB}_6\text{H}_4\text{O}_{31}$. In considering the relations of the various elements, it becomes almost impossible to consider hulsite as a borate of iron (ferrous and ferric), tin and magnesia, as the bases are present in overwhelming amount. Therefore, the ferric iron may be considered as present as an acid, playing the same rôle as the borates. On this assumption the above formula may be written: $\text{R}''_6(\text{BO}_3)_6 \cdot [\text{R}''_3[\text{Sn}(\text{OH})]''' \text{H}_3(\text{FeO}_3)_3]$. The tin in hulsite is in a condition which is so easily soluble in dilute acid that it seems more probable to regard it as present as some form of stannic acid. The presence, however, of stannic acid, in combination with boric and possibly some iron acid, leads to a complicated subject on which it is best to, at present, pass by.

Analyses of Paigeite.

For paigeite, three different samples were prepared and analyzed. The amount of gangue varied slightly, but no such large variations in the amount were encountered as with hulsite. Sample No. 1 was the sample on which the first analyses were made. Tin was not determined in it, and the value given for B_2O_3 is the one determined by Wherry and Chapin. The average of the analyses is:

FeO	44.48
MgO	1.44
Fe_2O_3	16.72
H_2O	2.03
B_2O_3	9.83
Insol.	15.65

The other two samples were prepared from the specimens at hand, sample No. 2, consisting of finely-ground material, for which reason the value for FeO may be somewhat low. Sample No. 3 consisted of coarser material, otherwise very similar in character to that of No. 2.

Analyses of the second sample yielded the following results :

Analysis of sample No. 2, paigeite.				
FeO -----	40.82	----	----	40.82
MgO.....	2.02	2.01	2.10	2.04
CaO	4.28	4.31	3.81	4.13
Fe ₂ O ₃	18.19	19.34	18.48	18.67
Total iron as Fe ₂ O ₃ ..	63.54	64.69	63.83	----
SnO ₂	3.15	3.14	3.26	3.18
B ₂ O ₃	9.10	----	----	9.10
Insoluble	16.18	15.74	16.38	16.10
SiO ₂ , Al ₂ O ₃ , H ₂ O ----	by difference			5.96
				<hr/> 100.00

Considering all the lime as resulting from the solution of the gangue, the ratios deduced from the above analyses are :

Ratios of analyses of sample No. 2, paigeite.		
FeO	.567	} 29.4
MgO	.051	
Fe ₂ O ₃	.117	5.6
SnO ₂	.021	1.0
B ₂ O ₃	.130	6.2
H ₂ O.....	----	----

From these ratios the formula, incomplete in regard to the water content, is 29.4RO.5.6Fe₂O₃.1SnO₂.6.2.B₂O₃. + ? H₂O.

Analyses of the third sample yielded the following results. The evidence having indicated that the gangue was considerably dissolved by the HCl, direct determinations of the silica and alumina were made.

Analysis of sample No. 3, paigeite.				
	1	2	3	Average
FeO -----	34.68	34.86	35.52	35.02
MgO -----	2.25	1.89	2.22	2.12
CaO -----	8.97	8.56	8.84	8.79
Fe ₂ O ₃ -----	14.69	14.84	15.18	14.90
Total iron as Fe ₂ O ₃ -----	53.22	53.57	54.62	----
SnO ₂ -----	2.77	2.86	2.76*	2.80
B ₂ O ₃ -----	----	6.71	7.16	6.94
Insoluble -----	18.62	18.81	18.29	18.57
SiO ₂ -----	3.28	2.78	3.25	3.10
Al ₂ O ₃ -----	2.51	2.41	2.09	2.34
H ₂ O, etc. -----	by difference			5.42
				100.00

* A fourth determination of SnO₂ gave 2.97 per cent.

In the ratios of the above analysis, the CaO , SiO_2 and Al_2O_3 are excluded as belonging with the insoluble matter to the gangue. As obtained from the average analysis, they are:—

Ratios of analysis of sample No. 3, paigeite.

FeO	·486	}	28·5
MgO	·056		
Fe_2O_3	·093		4·9
SnO_2	·019		1·0
B_2O_3	·099		5·2
H_2O	----		----

Like one of the hulsite analyses, the calcium oxide is considerably higher in sample No. 3 than in sample No. 2 and it seems as if some of the lime belonged to the borate. It would need only 1·57 per cent. of CaO to raise the ratio of $(\text{FeO} + \text{MgO} + \text{CaO})$ to SnO_2 from 28·5 : 1, as given above, to 30 : 1. This small amount of lime may, therefore, be considered as belonging to the borate. The ratios then obtained are 28·5 or 30·0 $\text{RO} \cdot 4 \cdot 9 \text{Fe}_2\text{O}_3 \cdot 1 \text{SnO}_2 \cdot 5 \cdot 2 \text{B}_2\text{O}_3 + ? \text{H}_2\text{O}$.

Discussion of Formulæ of Paigeite.

From the above three series of analyses, the following are the formulæ deduced for paigeite:

Formulæ for Paigeite.

	RO	Fe_2O_3	SnO_2	B_2O_3	H_2O
From sample No. 1	31·1	5·0	---	6·7	5·4
“ 2	29·4	5·6	1·0	6·2	---
“ 3 }	28·5	4·9	1·0	5·2	--- or
“ }	30·0	4·9	1·0	5·2	---

The average of the above shows that the most probable formula for paigeite and the one proposed for the mineral is: $30\text{FeO} \cdot 5\text{Fe}_2\text{O}_3 \cdot 1\text{SnO}_2 \cdot 6\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. While the above formula is complex and yields a rather high ratio of FeO to SnO_2 , there does not seem to be any other interpretation to the analyses. While not impossible that paigeite is a mixture of two or more closely related minerals, nothing but the unusual composition indicates such a mixture. The constant small percentage of tin oxide shows that the mineral is essentially different in ratios from the corresponding hulsite. The occurrence in wavy lamellar masses of fine radiating fibers, the intense shiny black color, the marked tendency as seen in thin sections for the individual fibers and masses to fray out at the ends into a

bunch of very thin fibers, all differentiate this mineral from hulsite, which never shows any indication of fibrosity.

An alternative interpretation of the composition of paigeite is that it is a mixture of hulsite and a fibrous borate. Subtracting from the formula of paigeite the necessary amounts to include all the tin with the hulsite, the following results are obtained :

Should future investigation prove this to be the case, then the material now called paigeite would consist of a mixture of 1 part hulsite and 3 parts of the borate $6\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$, to which the name of paigeite could then be referred. However, on the evidence at hand, it is most reasonable to regard paigeite as homogeneous and with the composition ascribed to it.

To repeat, the formulæ now proposed are, for hulsite, $12(\text{Fe}, \text{Mg})\text{O} \cdot 2\text{Fe}_2\text{O}_3 \cdot 1\text{SnO}_2 \cdot 3\text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and for paigeite, $30\text{FeO} \cdot 5\text{Fe}_2\text{O}_3 \cdot 1\text{SnO}_2 \cdot 6\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

Chemical Laboratory,
U. S. Geological Survey.