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ART. XXXVI.—*Two New Boron Minerals of Contact-Metamorphic Origin*; by A. KNOPF and W. T. SCHALLER.

THE material upon which the following paper is based was gathered by one of the writers (Knopf) during the summer of 1907 while engaged in an investigation of the Alaskan tin deposits for the U. S. Geological Survey. The chemical and crystallographical work was performed in the laboratory of the Survey by Waldemar T. Schaller.

The Alaskan tin deposits of known economic importance are limited to the extreme western part of the Seward Peninsula, about 100 miles northwest of the city of Nome. They are genetically associated with granitic intrusives which have invaded limestones of Paleozoic age. Along the margins of the granitic bosses an intense pneumatolytic contact-metamorphism has frequently been produced and a considerable variety of minerals developed. The largest granite boss of the region is that of Brooks Mountain, and the most energetic contact action is displayed along its periphery. The granite has a coarse porphyritic habit, and consists of phenocrysts of orthoclase an inch in diameter, and of smoky quartz, half an inch in size, embedded in a coarse to fine-grained granular matrix of feldspar, quartz and biotite. Along the margin of this intrusive body, the granite is often strongly tourmalinized. No tin deposits are known to be associated with this particular granite, but a few miles to the south of it they occur in connection with a smaller intrusive.

On the northwest flank of Brooks Mountain a prospect cut has been opened on a showing of contact metamorphic minerals occurring in marmorized limestone 10 feet from the granite contact. Examination of this deposit showed that an unknown mineral, which subsequent investigation has shown to be a new boron mineral, was present in considerable abundance. We propose for it the name *hulsite*, in honor of Mr. Alfred Hulse Brooks, geologist in charge of the Division of Alaskan Mineral Resources. In the hand specimen brown-green vesuvianite, magnetite, hulsite and rarely brown garnet occur scattered through a matrix of coarse white calc-spar. Occasionally some fluorite is visible. The characteristic forms of vesuvianite are $a \{100\}$, $m \{110\}$, $f \{120\}$, $c \{001\}$, $p \{111\}$, $t \{331\}$. Less prominent, $h \{130\}$, $\delta \{113\}$, $\epsilon \{112\}$, $b \{221\}$ and others. Treated with fluorite mixture, it gives a distinct boron flame, and is therefore regarded as probably belonging to

the variety wiluite. The magnetite shows $o\{111\}$, $m\{311\}$ large with $a\{100\}$, $d\{110\}$ small. The hulsite is quite abundant and is sometimes intergrown with magnetite and vesuvianite. Its characteristic features are its strong submetallic luster, black color, good prismatic cleavage, and tendency toward a tabular development. Its surface weathering is entirely similar to that of magnetite, and on casual inspection the hulsite may easily be confounded with that mineral. The tabular individuals of hulsite vary in thickness from a fraction of a millimeter to over a centimeter in the maximum noted. Under the microscope few additional features appear. A small amount of diopside is found to be associated with the other minerals already enumerated. The hulsite is completely opaque and appears black in reflected light. The thin sections show that magnetite is often intimately intergrown with the hulsite, from which it is distinguished by its bright metallic reflection.

The other mineral, for which we propose the name *paigeite*, in honor of Mr. Sidney Paige of the Geological Survey, was found at two localities, at Brooks Mountain in loose blocks, and at Ear Mountain, 40 miles to the northeast, *in situ*. It is a lustrous coal-black mineral of foliated appearance. The material from Brooks Mountain was subjected to chemical analysis. A thin section of the matrix shows vesuvianite, calcite, hedenbergite, a small amount of biotite, and arsenopyrite in sporadic grains. Paigeite is abundant, and is often in capillary or trichite-like forms transfixing the various other associated minerals. It is opaque, and appears black in reflected light. Other contact-metamorphosed limestones, from the near vicinity from which the paigeite rock was collected, show the following combination of minerals: chondrodite, spinel, magnetite, and calcite; a fibrous green boron mineral resembling ludwigite, and galena; highly ferriferous sphalerite, galena, pyrrhotite, diopside, calcic plagioclase, fluorite and calcite.

At Ear Mountain a granite intrusion has produced an extensive development of contact-metamorphosed limestones, largely consisting of lime-silicate hornfels. Some of these are flecked with paigeite and chalcOPYrite. Under the microscope this variety of hornfels is seen to consist of a confused intergrowth of calcite, zonally banded tourmaline, pleochroic in tones of blue and brown, vesuvianite, fluorite and zoisite, with accessory phlogopite, chalcOPYrite, and magnetite. Paigeite fibers and matted aggregates are embedded in the various constituent minerals, especially in the tourmaline and calcite. With the paigeite-bearing hornfels is associated a tourmaline-scapo-

lite-pyroxene hornfels, which reacts chemically for chlorine. It is clear from the paragenesis of paigeite that it represents a fixation product of magmatic emissions rich in fluorine (and chlorine), boron, and iron.

Hulsite.

Hulsite always occurs crystallized; either as small crystals about 1^{mm} diameter, or as large tabular masses, extending several centimeters and showing the prismatic cleavage well developed. The crystals, while often complete, are always uneven, and the faces dull and rough, so that no measurements could be obtained from any of the natural faces. Inspection with a hand lens shows that these crystals are often rectangular in shape, and as hulsite is provisionally considered orthorhombic these rectangular prisms consist of three pinacoids. Sometimes the crystals are bounded by the prism faces, and the basal pinacoid, though it is not always possible to decide whether the prisms are natural crystal faces or those due to cleavage. Often one pair of prism faces becomes much larger than the other pair. The cleavage parallel to the prism is good and measurements of three such cleavage angles gave the values:

$$m \wedge m''' = 57^\circ 44', 57^\circ 38', 57^\circ 33'. \text{ Average value, } 57^\circ 38'.$$

Therefore assuming that hulsite is orthorhombic, the crystallographic elements become

$$a : b : c = .5501 : 1 : ?.$$

Forms $a \{100\}$, $b \{010\}$, $c \{001\}$, $m \{110\}$.

The crystals are often twinned, one individual being turned about 120° to the other, the two basal pinacoids remaining in the same plane. The crystals are also often grouped in parallel position, especially when the individual crystals are elongated parallel to a prism face. The following photomicrograph shows the characteristic appearance of hulsite crystals when grouped together (fig. 1).

The color of the mineral is black, and when free from enclosed magnetite has a greenish, brownish and sometimes a reddish tinge. Many of the smaller crystals are covered with a brownish coating, probably limonitic in character. Streak black, luster submetallic, but on the pure mineral inclining more to vitreous-like hornblende. Hardness about 3. Density 4.28. Cleavage good, prismatic $m \{110\}$. Readily soluble in HCl and HF, less so in other acids. Gives off water in a closed tube and before the blowpipe fuses quietly to a dull black slag and colors the flame slightly green. Gives a

persistent green color to the flame when heated with potassium bisulphate and fluorite.

The samples of hulsite first submitted for chemical investigation were apparently homogeneous. They were, however, strongly magnetic, and though it was suspected that they consisted of a mixture of a non-magnetic borate with magnetite, various tests that were made failed to show the presence of the latter mineral. The very finest powder suspended in water was completely attracted by a magnet and numerous chemical tests failed to lead to a separation of the magnetite from the borate. After the analytical work on these samples had been finished, some specimens of hulsite, collected in pre-



Fig. 1. Hulsite (opaque mineral) intergrown with vesuvianite and calcite. Magnified 12 diameters.

vious years, were found, which when tested were non-magnetic. These specimens showed that the earlier ones contained admixed magnetite, and a careful examination of all of the samples on hand showed the very frequent presence of magnetite in varying amounts included in the hulsite. Analyses of the non-magnetic and magnetite free hulsite serve to establish its formula, and on the basis of these analyses the data obtained on the first samples become intelligible, the samples analyzed being about $1/5$ magnetite. While there were a number of specimens of hulsite which were not magnetic and therefore free from magnetite, several of them had become more or less altered to a limonitic substance. Only half a gram of pure material, unaltered and non-magnetic, could be obtained. This was divided into three portions of about $1/6$ gram each for the following analyses, the size of the grains being $<60> 100$ mesh:

Analyses of Hulsite.

	1	2	3	Average.
FeO	33.27	-----	-----	33.27
MgO	-----	10.17	-----	10.17
Fe ₂ O ₃	-----	-----	-----	17.83
Total iron as Fe ₂ O ₃ ..	54.40	54.20	-----	-----
H ₂ O	-----	-----	1.24	1.81 (calc.)
B ₂ O ₃	-----	-----	-----	27.42 (calc.)
Insol.	-----	10.00	-----	10.00
				100.00

Ratio Av. Anal.

FeO	482	}	7.00	7
MgO	254			
Fe ₂ O ₃	108	1.05	1	
H ₂ O	101	.98	1	
B ₂ O ₃	392	3.83	4	

The formula for hulsite then becomes 7(Fe,Mg)O.Fe₂O₃.H₂O.4B₂O₃.

The values given for B₂O₃ and water are calculated from the figures obtained from the magnetite-hulsite mixture as given beyond. The direct water determination, 1.24 per cent, is of no exact value on account of the small quantity of water weighed, being in this case only 2.3^{ms}, so that more reliance is placed on the figures obtained from the hulsite-magnetite mixture, from which the value 1.81 per cent is calculated. As above stated, the determinations on this sample were made on powder of <60> 100 mesh. Considerably more material of the magnetite-hulsite mixture was available for chemical analysis and the following results were obtained, about 1/4 gram substance being used for a determination:

Analyses of Magnetite-Hulsite.

	1	2	3	4	5	Average.
FeO	34.48	34.35	-----	-----	-----	34.44
MgO	8.60	8.83	8.36	8.12	-----	8.48
Fe ₂ O ₃	-----	-----	-----	-----	-----	27.64
Total iron as Fe ₂ O ₃ ..	66.24	67.08	65.70	65.42	65.32	-----
H ₂ O	1.63	1.68	-----	-----	-----	1.66
B ₂ O ₃	25.27	-----	-----	-----	-----	25.27
Insol.	2.25	1.97	2.24	2.48	-----	2.24
						99.73

The total iron determinations given were all made volumetrically, as the gravimetric determinations gave very varied

results, due to the retention of boric acid. It seems as if the presence of so much iron had a very great tendency to retain some of the boric acid, for the lowest gravimetric determinations of iron were several per cent higher than the volumetric ones, even though the solutions of iron chloride were repeatedly evaporated with methyl alcohol. The ferrous iron was determined by a modification of Pratt's method, which has been shown (Hillebrand) to give reliable values.* The water was determined by heating the mineral (size $<20> 60$ mesh) in a glass tube and weighing the water directly in a portion of that tube (Penfield's method). The boric acid was determined by fusing the mineral with sodium carbonate, leaching with water, refusing the residue, acidifying the solution with nitric acid, distilling with methyl alcohol, collecting in ammonia, and finally weighing boric acid as calcium borate.

The ratios obtained from the average analysis are shown below, the proportion of magnetite present being obtained as presently to be described.

* Bull. 305, U. S. Geol. Survey. p. 138. Both of the two new borates here described dissolve readily in hydrofluoric acid, so that no difficulty was had in rapidly making the ferrous iron determinations. The powder was always coarser than 100 mesh and for the paigeite coarser than 60 mesh, so that very little, if any, oxidation of the ferrous iron resulted from the grinding. That such oxidation occurs, sometimes to a large extent, has recently been shown by Manzelius (Sveriges Geol. Undersökning, Yearbook I, 1907, No. 8. See Chem. Abstracts, 1907, 2361, for an abstract of the article). For the paigeite samples the oxidation caused by grinding is considerable, the value for ferrous iron falling from 44.48 per cent (on $<20> 60$ mesh) to 39 per cent on the finely ground material. The direct determination of total water was similarly made on coarse material, so that the amount of hygroscopic water in the sample was a minimum. What increase in the water (given off at 110°) is caused by grinding these borates is not known, but the following results made on ludwigite from Hungary (a mineral of analogous composition) show that a very considerable amount of water is taken on by the mineral during grinding. Direct duplicate determinations of water at 110° on powder of $<10> 20$ mesh gave:

(1) 0.09 per cent. (2) 0.12 per cent.

On same powder finely ground:

(1) 0.50 per cent. (2) 0.52 per cent.

Therefore a total water determination on a mineral such as these borates must, to be of any value, be made on coarse material such as was used for hulsite and paigeite. It is therefore believed that the water content given for these minerals is an essential part of their composition and is not to be taken as hygroscopic or accessory water. However, the question is still an undecided one as to just what rôle the water plays and it may be that future work will show that the water content of these two minerals is extraneous and does not actually belong to the minerals themselves. See a paper soon to be published by Dr. Hillebrand for a discussion of the effect of grinding on the water content, as well as on the oxidation of ferrous iron. To Dr. Hillebrand the writer is under obligation for calling his attention to these points, which served to explain the very varying results first obtained on paigeite for ferrous iron. Data showing the oxidation of ferrous iron for these borates as well as for other minerals will be given in a later paper.

Ratios	Hulsite	Magnetite	Hulsite	Magnetite				
FeO 479	} =	86 + 87	} =	7·02				
MgO 212					392	87	4·56	1·01
Fe ₂ O ₃ 173					212		2·46	
H ₂ O 092					86	+ 87	1·00	+ 1·01
B ₂ O ₃ 361					92		1·07	
	361		4·19					

The proportion of magnetite present is calculated as follows: The analysis of the magnetite-free hulsite shows that the ratio of Fe₂O₃:RO is 1:7. Therefore from the ratios of Fe₂O₃ and RO in the average analysis of the magnetite-hulsite mixture there must be deducted such an amount (x) of both Fe₂O₃ and RO (in the proportion 1:1 to form magnetite) that the resulting ratio shall be 1:7. $\frac{\text{Fe}_2\text{O}_3}{\text{RO}} = \frac{173}{691}$ in the mixture of mag-

netite and hulsite. Then $\frac{173-x}{691-x} = \frac{1}{7}$; solving, $x=87$. Subtracting 87 from both 173 Fe₂O₃ and 691 RO, the resulting ratio becomes 86:604 or 1:7. This mixture of minerals then becomes one part of hulsite (7RO.Fe₂O₃.H₂O.4B₂O₃) with one of magnetite (FeO.Fe₂O₃). That all the magnesia belongs to the hulsite is shown by the analysis of the magnetite-free mineral, which gives as the ratio of FeO:MgO = 453:249, while that in the above analysis is 453:244, or practically the same. The composition of the sample analyzed is then found by calculation to be as follows, the formula for hulsite being taken as 9FeO.5MgO.2Fe₂O₃.2H₂O.8B₂O₃.

(Insoluble)	Vesuvianite	2·24
	Hulsite	77·40
	Magnetite	20·36
		100·00

The density of this mixture is 4·438. Taking the density of vesuvianite as 3·40 and that of magnetite as 5·17, the density of hulsite is found by calculation to be 4·28.

The ferrous iron and magnesia are doubtless not present in any definite ratio, but vary reciprocally, so that hulsite may be considered as a mixture of a ferrous with a magnesian borate. The ratio of 9FeO:5MgO just given is therefore only an approximate one. Ferrous iron and magnesia are doubtless isomorphous in hulsite as well as in paigeite, and similarly in the related borate ludwigite.* Any discussion as to the structural formula of hulsite would be very premature, as our knowledge of such minerals is very scanty. The formula

* An analysis of ludwigite from Montana shows this particularly well, this mineral containing very little ferrous iron while that from Hungary contains about 15 per cent.

$7\text{RO}\cdot\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}\cdot 4\text{B}_2\text{O}_3$, does not lead to any simple constitutional formula.

Paigeite.

The specimens of paigeite from Brooks Mt. show a coal-black lustrous mineral of a laminated appearance. No distinct crystals were seen, but the entire mass has a crystalline appearance and in thin sections is seen to be composed of innumerable hair-like needles, often forming radiating groups. The characteristic appearance of paigeite is shown in the photomicrograph (fig. 2). The mineral apparently possesses an imperfect

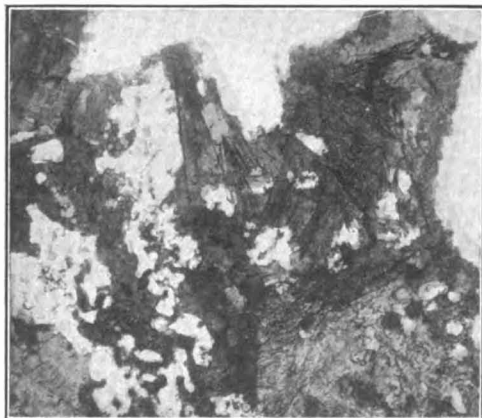


Fig. 2. Paigeite fibers embedded in tourmaline. Colorless mineral is fluorite. Magnified 60 diameters.

cleavage, is soft, hardness about 3, with a density of 4.71. The color is coal-black, streak the same, and the luster very shining. It is readily soluble in HCl and HF and in its pyrognostic properties resembles hulsite.

Analyses of paigeite from Brooks Mt. gave the following results:

	Analyses of Paigeite.				Av. Anal.
	1	2	3	4	
FeO	43.91	44.30	45.82	43.87	44.48
MgO	1.70	1.22	1.39	----	1.44
Fe ₂ O ₃	----	----	----	----	16.72
Total iron as Fe ₂ O ₃	66.26	65.95	66.22	----	----
H ₂ O	2.03	----	----	----	2.03
B ₂ O ₃	20.89	----	----	----	20.89
Insol	14.25	14.46	14.35	----	14.35
					99.91

		Ratios
FeO618	} 6.00
MgO036	
Fe ₂ O ₃105	.97
H ₂ O113	1.04
B ₂ O ₃298	2.74

These ratios lead to the formula $6(\text{Fe}, \text{Mg})\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} \cdot 3\text{B}_2\text{O}_3$.

The methods of procedure were similar to those described for hulsite. The reason for the single high value for ferrous iron (45.82 per cent) is not known, but as the other three values agree well, the average of all four is taken rather than to give preference to the single higher value, which may be due to error in the manipulation. (See footnote on page 328 for reference to the ferrous iron and water determinations.) The value here given for FeO includes that of the vesuvianite present, but it is probably so small that it may be neglected. While this mineral has not yet been analyzed, the ferrous iron in the 14 per cent vesuvianite present is doubtless less than .3 per cent. The effect of the arsenopyrite was probably *nil*, as the mineral particles were so large that the arsenopyrite remained undissolved in the hydrofluoric acid solution. Of the insoluble material about 1.20 per cent was arsenopyrite, the remainder being vesuvianite. The boric acid determination is probably too low.

The density of the sample analyzed was determined as 4.544. By calculation the density of pure paigeite is found to be 4.71, the sample analyzed consisting of the minerals in the proportion shown below:

Vesuvianite,	density	3.40 = 13.75
Arsenopyrite	"	6.0 = 1.20
Paigeite	"	4.71 = 85.05
		100.00

While these two minerals are very similar in composition, there is sufficient difference between them to preclude their being referred to the same species. The mode of occurrence, the hulsite in stout crystals, the paigeite in long hair-like needles, and the general appearance of these two minerals render it very easy to distinguish them on sight. The only borates known of analogous composition to these new minerals are ludwigite, pinakiolite and warwickite, of which only the first is similar in composition, this being $4(\text{Fe}, \text{Mg})\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$.