

ART. XXVI.—*On the Chemical Composition of Howlite, with a note on the Gooch method for the determination of boracic acid*; by S. L. PENFIELD and E. S. SPERRY.

THIS interesting mineral was first identified as a new species by Prof. Henry How,† of Windsor, Nova Scotia, who named it silicoborocalcite, assigning to it the composition $2\text{CaO} \cdot \text{SiO}_2 + 2(\text{CaO}_2 \cdot \text{BO}_3 \cdot \text{HO}) + \text{BO}_3 \cdot 3\text{HO}$, written in the old system and in the form suggested by Prof. How. He described it as occurring in dense, chalk-like nodules in the gypsum beds at Brookfield, near Windsor, N. S. In later papers‡ he mentions its occurring in four distinct localities near Windsor, the nodules being sometimes as large as a man's head and composed of minute scaly and silky crystals. The name howlite was substituted for silicoborocalcite by Prof. J. D. Dana and used by him in the fifth edition of his System of Mineralogy.

The specimen which we have examined was collected in the gypsum quarries at Windsor, N. S., by Mr. Charles G. Rupert, of Minneapolis, Minn., who generously presented it to the mineralogical department for investigation. It consisted of an egg-shaped nodule about one and one-half inches in its greatest diameter, embedded in massive gypsum. The nodule was composed of intergrown microscopic needles which under the

* This Journal, III, vol. ii, 1871, 402.

† Phil. Mag., IV, xxxv, p. 32.

‡ Phil. Mag., IV, xxxvii, 270 and xxxix, 278.

microscope were resolved into flattened prismatic forms, having somewhat the shape of thin stilbite crystals, the largest 0.23×0.27 mm., usually broken at the extremities but occasionally terminated by two dome faces. In polarized light they showed parallel extinction, brilliant polarization colors, red and yellow of the first order, according to the thickness of the crystal, the longer axis being the axis of least elasticity. In convergent light an obtuse bisectrix was very indistinctly seen, the plane of the optic axes being at right angles to the longer axis of the crystal. The crystallization is therefore probably orthorhombic. Owing to the slight solubility of the mineral in water its specific gravity was taken in alcohol and found to be 2.59 referred to water. A sample was taken for analysis by breaking into the nodule and carefully freeing from adhering gypsum by hand picking, but it was impossible to obtain the borate perfectly pure, a little SO_3 being found on analysis which undoubtedly resulted from adhering gypsum. The results of analysis of the air-dry powder are as follows:

	I.	II.	Mean.
SiO_2	14.65	14.74	14.70
B_2O_3	42.68	42.70	42.69
CaO	28.22	28.19	28.20
Na_2O55	.47	.51
K_2O12	.12
H_2O	12.01	11.94	11.97
SO_3	1.93	2.10	2.01
			<hr/> 100.20

Below the results are given after deducting 4.32 per cent of gypsum corresponding to 2.01 per cent of SO_3 , and calculating to 100.00 per cent together with the analysis of How and the theoretical percentages derived from our ratio.

	Ratio.		How.	Calculated for H ₅ Ca ₂ B ₅ SiO ₁₄ .
SiO ₂ -----15.33	.255	2.00	15.25	15.31
B ₂ O ₃ -----44.52	.636	5.00	[44.22]	44.65
CaO-----27.94	.498	} 5.07 3.99	28.65	28.56
Na ₂ O----.53	.008			
K ₂ O----.13	.001			
H ₂ O-----11.55	.641	5.04	11.84	11.48
<hr/> 100.00			<hr/> 100.00	<hr/> 100.00

The ratio of $\text{SiO}_2 : \text{B}_2\text{O}_3 : \text{CaO} : \text{H}_2\text{O} = 2 : 5 : 4 : 5$ very closely, with a small part of the CaO replaced by Na_2O and K_2O . This is exactly the ratio obtained by Prof. How, but the analysis is of importance as proving the identity of this curious boro-silicate as a distinct species, the original analysis having been made on dense chalk-like varieties and the most important con-

stituent, B_2O_3 , being determined by difference. The air-dry powder of the mineral lost water slowly at $100^\circ C.$ but soon came to a constant weight at $150^\circ C.$ losing 0.83 per cent, the mineral suffering no further loss by heating to 360° . The loss of 0.83 per cent corresponds closely to 0.90 per cent, the amount of water contained in the 4.32 per cent of gypsum which the analyzed portion contained. Thus the loss of water at $150^\circ C.$ as well as the SO_3 determination and the occurrence of the nodule in massive gypsum suggest that there was a slight impurity of gypsum in the material which was analyzed. The fact that the mineral does not part with its water at $360^\circ C.$ indicates that the hydrogen is very firmly united in the molecule, probably as hydroxyl. The mineral is therefore a very acid silico-borate and its formula may be written $H_2Ca_2B_3SiO_{14}$, differing essentially from the more common silico-borates of calcium, datolite and danburite, in containing much less silica and more boracic acid, causing the mineral to be classified more naturally with the borates than with the silicates.

On igniting the mineral in a closed tube water is given off which reacts strongly for boracic acid with tumeric paper; the water in the above analysis was therefore obtained by ignition and absorption in a chloride of calcium tube. The boracic acid was determined by the admirable method suggested by Prof. F. A. Gooch.* The other constituents were determined by the usual methods.

2. *Note on the Gooch method for the determination of boracic acid.*

Before commencing the above analysis we carefully reviewed the method described by Prof. Gooch,† making a number of determinations of B_2O_3 in borax in order to become fully acquainted with the method. The distilling apparatus described by him proved very satisfactory. The boracic acid in our experiments was set free by nitric acid, distilled over with methyl alcohol and evaporated with a weighed quantity of ignited calcium oxide. Without the use of very large platinum crucibles the evaporation of the boric ether with slaked lime is attended with some difficulty. The calcium borate together with the excess of lime form as a thick crystalline precipitate at the bottom of the crucible and if the methyl alcohol boils during the evaporation some of the precipitate will be carried mechanically out of the crucible; then too the very strong ignition of the CaO necessary to bring it to a constant weight is not so readily accomplished if the crucibles are very large. The following method was found to give very good satisfaction and can be used by any one having an ordinary sized platinum crucible and preferably a platinum dish.

* Am. Chem. Journal, ix, p. 23.

† Loc. cit.

The lime after being ignited to a constant weight and slaked is transferred to a large platinum dish and warmed with water till it becomes of a milky consistency; it is not necessary to remove all the lime from the crucible, the latter being put away and used later on. Strong ammonia is poured into the receiving flask of the distilling apparatus described by Gooch, and after conducting the distillation as directed the contents of the receiver are poured into the platinum dish containing the slaked lime, water being freely used in rinsing out the receiver. The dish is then placed on a triangle over the water bath or otherwise gently heated till the volatile products, methyl alcohol and ammonia, are driven off, which by boiling might cause mechanical loss. When these are removed the contents of the dish can be evaporated to dryness. The dried calcium borate and the excess of lime are now transferred to the crucible in which the lime was weighed, this being easily accomplished by moistening the contents of the dish with water and shoving the bulk of the precipitate into the crucible with a spatula, by rinsing with a little water and by using a rubber on the end of a glass rod all but a very little of the borate and lime can be transferred to the crucible; that which sticks too firmly to the dish can be dissolved in one or two drops of dilute nitric acid which is brought in contact with all parts of the dish with the rubber; the solution is then transferred and rinsed into the crucible. The transfer and washing can readily be made by using not over 30 cc. of water which can be contained in an ordinary student's crucible. The evaporation from this point goes on very simply, the borate drying out nicely on the water-bath. By placing the platinum crucible in a large porcelain one and gradually raising the heat to strong ignition the borate may be further dried out without any danger of snapping. The residue is finally ignited over the blast lamp till a constant weight is obtained.

In slaking the lime we have found it convenient not to add the water directly to the ignited lime, causing danger from excessive heating and mechanical loss, but to place the open crucible on a watch glass containing water and covered with a bell jar: in this way the lime soon slakes and in case of special hurry hot water may be placed in the watch-glass from time to time so that the atmosphere under the bell jar will be thoroughly saturated; in this way the lime will become so thoroughly slaked in one or two hours that there will be no danger of excessive heating on further addition of water.

The following results were obtained using in all cases about one gram of crystallized borax and one gram of lime: B_2O_3 in borax 36.55, 36.42, 36.58, 36.64, calculated 36.64 per cent.

Mineralogical Laboratory,
Sheffield Scientific School, April 14, 1887.