

Wave length.	Intensity.	Wave length.	Intensity.	Wave length.	Intensity.	Wave length.	Intensity.
5744.1	1	5790.0	1	5838.7	8	5893.3	2
51.7	6	94.4	4	42.5	3	5900.5	8
54.7	1	98.3	2	46.1	2	03.7	3
58.4	1	5801.6	1	52.9	1	27.3	2
60.6	7	04.0	3	55.7	1	28.2	2
65.2	4	11.0	1	66.5	6	34.2	3
71.3	2	15.3	2	68.8	1	57.7	3
76.3	3	19.5	7	74.7	4	83.2	6
80.5	1	20.7	3	76.3	2	86.0	3
82.3	10Cu	34.9	4	77.8	3	97.7	3
87.7	6						

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

**OCCURRENCE OF BORIC ACID IN VESUVIANITE.**

BY EDGAR T. WHERRY AND WM. H. CHAPIN.

Received August 21, 1908.

The observation of Jannasch<sup>1</sup> that the Wili vesuvianites contained boric acid and the discovery of it in specimens of the same mineral from Fritz Island, Pa., by Mr. Daniel L. Wallace, of this laboratory, led Dr. Edgar F. Smith to suggest to us that we enter upon a careful examination of specimens of the mineral from nearly all of the principal known localities of the world, the material having been procured by him years before for the purpose of carrying out a similar study. In this connection, however, we must also acknowledge the kindness of Mr. W. T. Schaller and other members of the United States Geological Survey to whom we are indebted for additional material upon which was tried the methods of determining boric acid which appear in the paper following this one.

As far as possible selected crystals were used for analysis and in every case, when boric acid was found, a thin section of the crystal under analysis was made and any inclusions shown by it were most carefully examined. The presence of tourmaline or other objectional minerals was not established in any of them, so there can be no doubt that the observed boric acid was actually a part of the vesuvianite itself.

*Discussion of Results.*—From the following table it is evident that boric acid, although not an essential constituent of vesuvianite, is present in this mineral much more frequently than is ordinarily supposed.<sup>2</sup> Its source, however, is evident enough. Vesuvianite is commonly produced by contact metamorphism—the effect of an intrusion of igneous rock upon the surrounding sedimentaries. Intrusive magmas, as is well known, often carry boric acid, which is given off during their solidification and, carried

<sup>1</sup> *Neues Jahrb. Min. Geol.*, 1, 269.<sup>2</sup> Compare Klein, *Sitzb. Akad. Wiss.*, Berlin, 1904, p. 653.

by heated waters into the adjoining shales or limestones, there enters into the formation of new minerals.

## RESULTS ON VESUVIANITES.

No.	Locality.	Previous determination.	Results.		Average.
			Chapin.	Wherry.	
1.	Wili, Siberia.....	Jannasch	2.81	4.12	4.07
		Rammelsberg	2.54	4.14	4.14
		Id, calc	2.66	....	....
2.	Fritz's Island, Penna.....	Wallace	3.56	2.03	2.04
3.	Arendal, Norway.....	Nordenskiöld	1.96	....	....
4.	Morelos, Mexico.....	....	1.89	1.92	....
		....	1.96	1.97	1.94
5.	Brooks Mt., Alaska.....	Schaller	present	0.89	0.88
6.	Litchfield, Maine.....	....	0.63	0.63	0.63
7.	Monzoni, Tyrol.....	Lindström	trace	0.56	0.52
		Weibull	trace	....	0.53
8.	Helena, Montana.....	....	0.21	0.21	0.21
9.	Ala, Piedmont, Italy.....	....	0.18	0.18	0.19
		....	0.21	....	....
10.	Jacobsberg, Sweden.....	....	0.10	0.11	....
		....	....	0.11	0.11
11.	Cziklowa, Hungary.....	Weibull	0.10	....	....
12.	Magnet Cove, Arkansas...	....	0.07	0.09	0.08
13.	Warwick, New York.....	....	trace	trace	trace
14.	Canzocoli, Lower Austria .	....	trace	trace	trace
15.	Woodstock, Maine.....	....	trace	trace	trace
16.	Kedabek, Russia.....	Weibull	trace	....	....
17.	Wakefield, Canada.....	....	0.00	0.00	0.00
18.	Kiura Bunga, Japan.....	....	0.00	0.00	0.00
19.	Monte Somma, Vesuvius..	....	0.00	0.00	0.00
20.	Zermatt, Switzerland....	....	0.00	0.00	0.00
21.	Haslau (Eger), Bohemia...	....	0.00	0.00	0.00
22.	Tellemarken, Norway ....	....	0.00	0.00	0.00
23.	Hamrefjeld (Eker), Norway	Stenberg	none	....	....
24.	Tenneberget, Norway.....	Weibull	none	....	....
25.	Vaticha, Sweden.....	Sjögren	none	....	....

## NOTES ON THE TABLE.

## A. References.

- Jannasch, *Neues Jahrb. Min. Geol.*, 1, 269, 1884; *Z. anal. Chem.*, 2, 40, 1896; Rammelsberg, *Z. geol. Ges.*, 38, 507, 1886.
- Mr. D. L. Wallace, Univ. of Penna., private communication.
- Nordenskiöld (and Widman), *Geol. Fören. Förhand.*, 12, 20, 1890.
- Mr. W. T. Schaller, U. S. Geol. Survey, private communication.
- Lindström, *Geol. Fören. Förhand.*, 10, 191, 1888; Weibull, *Z. Kryst. Min.*, 25, 1, 1896.
16. Weibull, *Loc. cit.*
- Stenberg (and Widman), *Geol. Fören. Förhand.*, 12, 20, 1890.
- Weibull, *Loc. cit.*
- Sjögren, *Geol. Fören. Förhand.*, 17, 268, 1895.

## B. Qualitative tests.

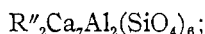
The limit of sensibility of the flame test, performed by mixing the powdered

mineral with potassium bisulphate and calcium fluoride, and introducing into the non-luminous Bunsen burner flame on a clean platinum wire, was found to be 0.2 per cent.; the specimen from Helena, Montana, gave a distinct green flash, while that from Ala. failed to show the slightest effect.

The turmeric paper test, carried out by drying in a desiccator at ordinary temperatures, as recommended by Low<sup>1</sup> proved to be more sensitive. A small drop of the sodium borate solution obtained in the course of the second method hereinafter described just before the final titration, was used to make the tests, for if the boric acid is low, the iron salts in the original solution have an interfering action. Specimen No. 12, containing only 0.08 per cent., produced a distinct coloration; Nos. 13 and 14, however, which required in the titration less than one full drop of alkali (0.04 per cent.) yielded no stronger color than a blank test with the same reagents and paper.

It would seem quite probable, then, that the reason for the variation of boric acid content is simply the presence of an excess or deficiency of this substance in the respective igneous masses. But we still have to consider what peculiarity is shown by the vesuvianite molecule in order that the boric acid should enter it instead of the associated garnet, epidote or scapolite.

The wide variation shown in published analyses of vesuvianite makes it difficult to assign it any definite formula, but a fairly satisfactory expression has been recently proposed by Clarke:<sup>2</sup>



in which  $R''$  may be  $H_2$ ,  $K_2$ ,  $Na_2$ ,  $Mg$ ,  $Ca$ ,  $Fe''$ ,  $Mn''$ , and especially  $AlOH$  and  $AlF$ ; and  $Al$  may be replaced by  $Fe'''$ ,  $Mn'''$  (or  $B'''$ ).

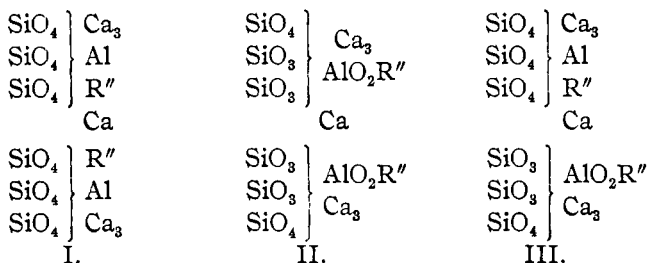
The mutual replaceability of the various bivalent elements and groups is generally recognized and it does not seem capable of throwing any light on the constitution. But with the trivalent elements, it is a different matter. Of these  $Mn'''$  probably always acts as an acid and  $Fe'''$  always as a base, while  $Al'''$ , as is well known, can occur in either relation. In the published analyses of vesuvianite where ferrous oxide has been separately determined, the amount of ferric oxide never exceeds 5 per cent. It seems incredible that this could be wholly due to a scarcity of iron during the formation of the mineral. It is more probable that only a limited amount of aluminium exists in the molecule in the basic condition, so as to be replaceable by ferric iron; but that most of it is, on the contrary, acting as part of the acid residue (anion). Herein, then, vesuvianite differs from garnet and epidote, for in these, all of the aluminium is replaceable by ferric iron, and thus must exist in the basic state.

Boron is normally an acid-forming element, and shows but little tendency to act as a base. Boric oxide, therefore, enters the vesuvianite instead of the garnet simply because in the former a part of the sesquioxide is present in the acid condition.

<sup>1</sup> THIS JOURNAL, 28, 807 (1906).

<sup>2</sup> U. S. Geological Survey, Bull. 262, 1905, p. 74.

The structural formula suggested by Clarke shows all the aluminium as basic, as shown in formula I. If, on the other hand, it were all to be regarded as acid, this would become formula II. But if the considerations discussed above are valid, then a combination of the two, as shown in formula III, most nearly represents our present knowledge of the constitution of the mineral.



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**DETERMINATION OF BORIC ACID IN INSOLUBLE SILICATES.**

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Two methods were employed in the estimation of the boric acid, for the investigation described in the previous paper. The first method is really a volumetric procedure and was in this particular study the method applied by Edgar T. Wherry, while the second method, which is a distillation process, was used by William H. Chapin. The comparison of their final results is represented in the table.

**Volumetric Method (Wherry).**

In entering upon a description of the volumetric process it may be stated at once that in the determination of boric acid in silicates, when distillation is not resorted to, the great difficulty encountered is the separation of the desired constituents from the alumina. If the mineral is fused with alkali carbonate, and extracted with water, boric acid will remain in the residue. If, on the other hand, the fusion is taken up with acid, and ammonium hydroxide added, boron will be carried down with the sesquioxides, even after repeating several times. Precipitation of these oxides by treatment with ammonium chloride, with ammoniacal zinc oxide and with carbon dioxide were tried in this laboratory by Sargent,<sup>1</sup> without success. Morse and Burton<sup>2</sup> had obtained the boric acid by extracting a sodium hydroxide fusion with alcohol, finally weighing as barium metaborate, but this method did not meet with a favorable reception. Neutralization with potassium

<sup>1</sup> THIS JOURNAL, 21, 858 (1899).<sup>2</sup> *Am. Chem. J.*, 10, 154 (1888).