

CONTRIBUTIONS TO THE MINERALOGY
OF NORWAY

No. 29. Vesuvianite as a Host Mineral for Boron

BY

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Abstract. Vesuvianites from contact deposits in the Oslo Region are found to contain B_2O_3 in concentrations ranging from about 0.05% to more than 2%. The great variations in the B-contents are believed to be in support of the present view that the boron found in these deposits originates mainly from the sediments, not from the magmas. Some vesuvianites from localities outside the Oslo Region are practically B-free. All examined vesuvianites which contain B_2O_3 notably in excess of 0.5% are optically positive, the others negative.

Chemical analyses made three quarters of a century ago and quoted in the comprehensive mineralogical texts show that vesuvianite may contain considerable quantities of boron. The figures given for vesuvianites from Vilui in Siberia ("viluite") and from Arendal ("colophonite") are about 3% and 2% B_2O_3 respectively. On the other hand these vesuvianites appear to be practically the only ones in which boron contents have been recorded so far. WEIBULL (1896) found 0.1% B_2O_3 in *one* other vesuvianite (Cziklowa). GOLDSCHMIDT (1911, p. 432) quotes after WIDMAN: "Bor soll im Vesuvian von Hamrefjeld fehlen." Spectrochemical analyses have shown that boron is a minor constituent of many other vesuvianites and that the concentrations vary over a wide range. The present paper deals mainly with vesuvianites from deposits within the contact aureoles of the Oslo Region. The mineralogy of these deposits is well known through the work of V.M. GOLDSCHMIDT (1911).

The spectrograms were taken with a Hilger "Large" quartz spectrograph with a rotating stepped sector in front of the slit. The carbon electrodes (Ringsdorff RW-I) were highly purified and did not

contain detectable traces of boron. The cathode carbons containing the samples for evaporation were of a standardized size and shape. Preliminary spectrograms were taken using pure vesuvianite samples. A number of these showed very strong B-lines, far too strong for intensity readings, and the samples in question were subsequently subjected to quantitative spectrochemical analysis. All samples for quantitative treatment were mixed with much larger quantities of apatite. Depending on the varying B-concentrations the ratio apatite to vesuvianite was made equal to 4 or 9 or 24. Also in the standard mixtures the base substance was apatite; known percentages of boron were added as tourmaline. Thus all spectrograms contain P-lines of nearly constant intensities and very convenient as internal intensity standards. The resulting working curves for the two sensitive boron lines are well represented by straight lines of equal slopes and give fairly consistent B-determinations. The method was tested by means of the vesuvianites from Vilui and Arendal. The results were about 3% and 1.5% B_2O_3 respectively, in satisfactory agreement with the old analyses. Thus the accuracy of the method appears to be satisfactory. The spectrograms of pure vesuvianites were evaluated by means of an approximate working curve obtained by comparing spectrograms of a few samples with and without apatite admixture. These determinations are somewhat less accurate. They apply to the lowest B-contents recorded. B_2O_3 -contents not recorded or recorded as traces are in general lower than 0.01%. — The results are shown in the table.

Discussion. It is seen that all examined vesuvianite specimens from contact deposits in the Oslo Region contain appreciable quantities of boron. In most cases the boron present in the deposit appears to be nearly quantitatively concentrated in the vesuvianite. The chemically very similar associated garnet (grossularite) contains at most quite insignificant traces of boron. In a few cases the boron mineral axinite occurs together with the vesuvianite (e.g. Årvoll valley). This, however, by no means implies that the vesuvianite is particularly rich in boron. As pointed out by GOLDSCHMIDT (1911) the axinite is found mainly in druses, deposited on earlier crystals of vesuvianite etc. Thus there is no question of an equilibrium distribution of boron between vesuvianite and axinite; such a distribution would apparently require a maximum content of B_2O_3 in the vesuvianite (perhaps

Vesuvianite

	B ₂ O ₃ , %	2V	Optic sign
<i>Oslo Region</i>			
"Essexite" contact.			
Viksbergene, Hadeland	0.1	≤ 20°	÷
Nordmarkite contact.			
Dalstjern, Hakadal	0.04	0	÷
Årvoll valley, axinite locality	0.05	0	÷
Årvoll valley, west side.			
Crystal 1.	0.4		
Crystal, 2, core	0.6		
— outer zone	0.5	~ 0	÷
Ekerite contact.			
Hamrefjell, Eiker.			
Crystal 1.	0.75		
Crystal 2, core	0.25	0	÷
— outer zone	0.6	≤ 20	+
Granite contact.			
Sata, Konnerudkollen	0.1	0	÷
Myrseter, north of Drammen.			
Crystal 1.	1.4		
Crystal 2, core	2.5	0	+
— outer zone	0.6	> 50	—?
<i>Arendal</i> . Iron ore deposit.			
"Colophonite", dark	1.4	0	+
— brown	1.0	0	+
<i>Graslien</i> , Froland	tr.?	0	÷
<i>Kristiansand</i> . Large crystal	—	0	÷
<i>Sauland</i> , Telemark. Cyprine	—	0	÷
<i>Straumshei</i> , Setesdal. Cyprine	tr.?	0	÷

Vesuvianite samples from Banat and Vesuvius contain about 0.1% B₂O₃. Garnets associated with the vesuvianites from the Årvoll valley, from Hamrefjell, from Sata and from Arendal are all extremely poor in boron. The traces sometimes observed (lower than about 0.01%) may be partly or wholly due to contamination of the samples with small quantities of vesuvianite.

3% or more). The formation of axinite at a later stage, after completion of the vesuvianite-formation, would not require large quantities of boron in the environment since the total quantity of axinite in a

deposit is usually very small. Similar considerations also apply to the association vesuvianite — tourmaline, which has been observed in a few contact deposits. But tourmaline is on the whole a rare mineral in the Oslo Region. Thus it can hardly be doubted that vesuvianite is the main carrier of boron in the Oslo contact deposits.

As to the origin of the boron found in deposits due to igneous activity, the earlier view was that it was an original constituent of the magma, like fluorine and other pneumatolytic agents. The present view is based on the fact that igneous rocks are in general very poor in B while most of the B in the crust is found concentrated in argillaceous sediments of marine origin and in rocks derived from them by diagenesis and metamorphism (GOLDSCHMIDT and PETERS, 1932). Contact metamorphism and metasomatism may be expected to mobilise the boron of such rocks and make it available for concentration in suitable contact minerals like vesuvianite. Observations by GOLDSCHMIDT and PETERS (1932) and by LANDERGREN (1945) are in support of such an interpretation, *i.e.* that most of the boron found in contact minerals derives from the sediments and not from the magma. Also the above data seem to be in support of this interpretation. The boron concentrations along the contacts of the nordmarkite and the granite evidently vary strongly and irregularly. If the boron had been supplied by the rather homogeneous magmas one would hardly expect such pronounced irregularities. On the other hand the boron contents of the sediments (Cambro-Silurian mostly) are highly dependent on the character of the rock (shale, limestone, sandstone), which will naturally exhibit local variations along the contacts.

Among the examined vesuvianite localities *Myrseter* is of particular interest. This locality was discovered after the publication of GOLDSCHMIDT's monograph (1911), and as far as the writer knows it has not been mentioned in the literature. Part of the material which is kept in the Mineralogisk-Geologisk Museum in Oslo was purchased in 1911, and the locality appears to have been visited by V. M. GOLDSCHMIDT in 1911 and by W. C. BRØGGER and J. SCHEDELIG in 1913. The crystals form druses in a nearly white hornfels. Garnet crystals have not been discovered so far. The vesuvianite crystals are most beautifully developed and are up to at least 2 cm in size. The colour is light greenish yellow, the greenish tint usually decreasing towards the central part. As to the crystal habit the bipyramid $\{111\}$ predomi-

nates and is moderately truncated by {001}. Also {101} is usually developed. The prism zone {110}, {100} is very short. In addition a steep bipyramid {hhl} and a ditetragonal bipyramid are sometimes observed. This makes the crystals resemble square buttons in shape.

It is well known that vesuvianite crystals usually exhibit a pronounced zoning which is highly conspicuous between crossed nicols. Sometimes outer zones can even be peeled off. Most vesuvianites are optically negative with a very low birefringence. Parts of the crystals, usually the core, are strictly uniaxial with more or less normal interference colours. But the outer zones generally show strong optical anomalies: highly abnormal interference colours and 2 optic axes, $2V$ varying over a wide range. While the core appears to be in general homogeneous the outer zones are not. They usually consist of a series of very narrow zones with varying optical properties. If the crystal is on the whole optically negative some of these zones may be more weakly negative or even positive. See *e.g.* the descriptions by GOLDSCHMIDT (1911, pp. 436). P. CHR. SÆBØ has kindly made optical studies of most of the material for the present investigation. His main results are included in the table. A few optical data given in the table have been taken from other papers (BUGGE 1940, BARTH 1963, NEUMANN and SVINNDAL 1955, NEUMANN 1955). The boron-rich viluite has been known to be optically positive for a long time. The relations between the chemical composition and optical properties of vesuvianite have been discussed in several old papers. WEIBULL (1896) assumed that boron-carrying vesuvianites would in general be optically positive, but analyses sufficient to corroborate this were not available. The above data seem to be in substantial support of this view. As pointed out above only the samples which are optically uniaxial or nearly so may be considered as homogeneous. They all conform to the rule that vesuvianites containing less than about 0.5% B_2O_3 are optically negative while those containing 1% or more are optically positive. As to the zoned optically anomalous samples it can not be ascertained that the observed optical properties correspond exactly with the spectrochemical analysis. The analysis samples may be mixtures of several zones of varying composition, while the optical examination may have been carried out on powder particles representing specific narrow zones. Nevertheless the results agree well with the above rule. The outer zone of crystal 2 from Hamrefjell indicates that the transi-

tion negative-positive occurs at a B_2O_3 -concentration of just a little more than 0.5%. It must be pointed out that the transition negative-positive in vesuvianite implies very small changes in the refractive indices only, since the birefringence is in general extremely low. Therefore very minor changes in the chemical composition may be expected to influence this property notably. Now the quantities of the major constituents Mg, Fe, Al, etc. are known to vary somewhat in vesuvianite, and it seems probable that these variations would be reflected in the optical properties. But it appears that the variations in the boron-content are the main reason for the observed optical variations. The relative variations in the B-content are extreme, from zero to about 1%, and it may perhaps be expected that a notable content of a "foreign" element like boron will influence certain properties of the crystal appreciably.

Other minor constituents in vesuvianite are Cr and Ni. In the Oslo Region vesuvianites they are found in concentrations of the order of 0.1%. In crystal 2 from Myrseter Cr varies from about 0.5% in the core to about 0.1% near the surface.

According to BUGGE (1940) vesuvianite seems to be a rare mineral in the skarn deposits of the Arendal district. He found it in one locality (Nødebros). Apart from this vesuvianite, B-rich minerals are not common in the deposits, but the occasional occurrence of tourmaline and datolite shows that boron has been concentrated in a few localities.

In the calcite and skarn rocks near Kristiansand no boron minerals are known to occur (BARTH 1925). This is in accordance with the fact that no boron was found in vesuvianite from these deposits.

In the two cyprine localities no boron minerals have been found (NEUMANN and SVINNDAL 1955, NEUMANN 1955).

It is probably of little use to discuss the possible B-sites in the vesuvianite structure at present. The highest observed B-contents would correspond to about 4 B per unit cell, or one B per formula unit: tentative substitution of 1 B for 1 Al in the vesuvianite formula



gives a B_2O_3 -content of 2.4%. This formula is based on the structure determination by WARREN and MODELL (1931). Considering the ionic radii and charges it seems most natural to assume that B substitutes for Si in some of the tetrahedral positions, even if this substitution has

not been shown to occur in borosilicates. However, as pointed out by BARTH (1963), the vesuvianite structure seems to permit rather extensive mutual substitutions of Mg, Fe, Al and also substitution of Al for Si. This indicates a certain flexibility of the structure, and possibly also a substitution of the small B-ion for Al might be imagined. The vesuvianite structure contains large open spaces, 2 in each unit cell, but it is difficult to see how the small B-ions might be accommodated in these.

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