

THE EFFECT OF BORON ON THE GRANITE SOLIDUS

LESLEY B. CHORLTON* AND ROBERT F. MARTIN

Department of Geological Sciences, McGill University, 3450 University Street,
Montreal, Que. H3A 2A7

ABSTRACT

The addition of boron to a water-saturated granitic system lowers the solidus at 1 kbar by 125°C; the liquidus seems similarly affected. This drastic reduction reflects the incorporation of tetrahedrally coordinated boron (B^{iv}) in the place of aluminum in the liquid and the influence of this substitution on the thermal stability of the feldspars. The ratio of B^{iv} to Bⁱⁱⁱ in the melt increases with increasing pressure and alkalinity and with decreasing temperature. Reedmergnerite-bearing peralkaline pegmatites in alkaline complexes could have crystallized from melts at temperatures below 600°C.

SOMMAIRE

L'addition de bore à un système granitique saturé d'eau en abaisse le point de fusion de 125°C à 1 kbar et semble également affecter le liquidus. Cet effet résulte de la substitution du bore à l'aluminium dans les sites tétraédriques du liquide et de l'influence qu'exerce cette substitution sur le champ de stabilité thermique des feldspaths. Le rapport de B^{iv} à Bⁱⁱⁱ augmente avec la pression et l'alcalinité du milieu, et varie inversement avec la température. Les pegmatites hyperalkalines à reedmergnerite des complexes alcalins ont pu cristalliser à partir de liquides résiduels au-dessous de 600°C.

INTRODUCTION

Many experimental studies of the 'system' granite-water have been undertaken since the pioneering efforts of Goranson (1932); Tuttle & Bowen (1958) and Luth *et al.* (1964) determined solidus temperatures and phase relationships in the quaternary haplogranite system $KAlSi_3O_8-NaAlSi_3O_8-SiO_2-H_2O$ as a function of total pressure; Wyllie & Tuttle (1959, 1960, 1961, 1964) extended the applicability of these fundamental studies to natural situations by adding a number of components to the lime-free granite system. Whereas NH_3 , SO_3 and P_2O_5 produced negligible effects on the minimum melting tem-

perature of granite, CO_2 and HCl led to an increase in solidus temperature, presumably because of a reduction in the activity of water in the melt and coexisting vapor phase. Addition of HF and Li_2O led to a decrease in the solidus temperature by partitioning strongly into the melt and modifying it structurally. Boron is one minor component excluded from their preliminary survey, but of local importance in nature, especially in pegmatitic environments. This paper provides some insights into the efficiency of this constituent as a flux in granitic bulk compositions.

EXPERIMENTAL TECHNIQUE

The synthetic starting materials chosen for this study are glasses prepared by the method of coprecipitating gels (Luth & Ingamells 1965), and used in a previous study of the system $KAlSi_3O_8-NaAlSi_3O_8-SiO_2-H_2O$ (Luth *et al.* 1964). These glasses were ground, dried in a vacuum oven for four to eight hours, then stored in a desiccator until required. Boron was introduced as analytical-grade crystalline H_3BO_3 , non-hygroscopic and stable at room temperature. The B_2O_3 content of each run was calculated from the amount of H_3BO_3 added. Total water content, generally between 10 and 20 wt. %, was calculated to include the water added in the form of H_3BO_3 . Solids and distilled water were loaded into 2mm Au tubing 10 to 15mm long, and welded shut. Experiments were run at $P(H_2O) = 1$ kbar in externally heated 2.5cm O.D. stellite cold-seal pressure vessels; temperatures fluctuated ± 5 or $6^\circ C$ during the 5- to 11-day isothermal experiments.

Other experiments were run at atmospheric pressure on a tourmaline-bearing granitic segregation from a pegmatite in the Boulder batholith, Montana (Knopf 1957). This granite (1697A in Knopf's collection) consists of quartz, microcline (Or₈₈), lom albite and 20 vol. % dark green tourmaline; the rock contains 72.68 wt. % SiO_2 , 14.63% Al_2O_3 , 1.74% B_2O_3 , 0.56% CaO , 2.49% Na_2O and 4.36% K_2O (E. B. Knopf, priv. comm.; full analysis in Chorlton

*Present address: Department of Geology, Memorial University of Newfoundland, St. John's, Nfld. A1C 5S7.

1973). The 1 atm isothermal experiments lasted from 4 days (experiments above 1000°C) to 22 days (experiments at $743 \pm 5^\circ\text{C}$, the lowest temperature in this series). These run durations are not sufficiently long for equilibrium to have been attained.

RESULTS OF HYDROTHERMAL EXPERIMENTS

These experiments were designed to evaluate the effect of boron on the temperature at which granite begins to melt. This was achieved by holding a series of up to four synthetic bulk compositions isothermally and estimating the proportion of melt produced; one composition was boron-free, and a maximum of 10 wt. % B_2O_3 was added. Details of bulk composition, temperature, duration and run products are presented in Table 1 for selected experiments; full details on all experiments are provided by Chorlton (1973).

The data points in the region of the solidus allow a boundary to be drawn, separating the field of crystals + vapor from that of the vapor-saturated, partially melted assemblage (Fig. 1). The minimum melting temperature at $P(\text{H}_2\text{O}) = 1$ kbar for boron-free compositions is close to 720°C , as determined by Tuttle & Bowen (1958) and confirmed in this study. The compositions used have predicted solidus temperatures be-

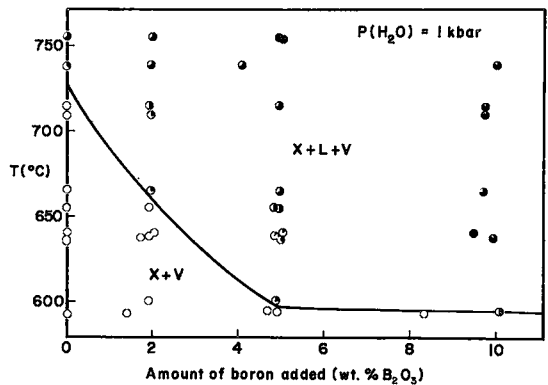


FIG. 1. Trace of the minimum melting temperature in the system $\text{KAlSi}_3\text{O}_8\text{--NaAlSi}_3\text{O}_8\text{--SiO}_2\text{--H}_2\text{O} + \text{B}_2\text{O}_3$ at 1 kbar, as a function of the amount of boron added to the system. The data pertain to bulk compositions near the quartz-feldspar field boundary in the boron-free system. These compositions vary in Ab:Or ratio from 0.167 to 1 on a weight basis. Empty circles indicate subsolidus run products; the proportion of black in a data point is indicative of the proportion of glass (quenched melt) in the run products.

TABLE 1. RESULTS OF SELECTED HYDROTHERMAL EXPERIMENTS ON HAPLOGRANITIC MIXTURES + B_2O_3 AT $P(\text{H}_2\text{O}) = 1$ KBAR

COMPOSITION Ab Or Q*	B_2O_3 ADDED*	TEMP (°C)	DURATION (DAYS)	RUN PRODUCTS†
10 50 40	4.91 8.35	593±5	7	Q+San+V+b Q+San+V+b
30 30 40	4.70 10.11	595±15	13	Q+San+V+b Q+San+35%gl+V+b
30 40 30	1.75 5.00	637±2	9	Q+San+Ab(tr)+V Q+San+Ab(tr)+30%gl+V
10 50 40	9.5	640±5	7	gl+V
30 30 40	1.94 4.96	655±5	8	Q+San+Ab(tr)+V Q+San+Ab(tr)+50%gl+V
20 30 50	0 1.97 4.98 9.73	665±5	11	Q+San+V Q+San+25%gl+V Q+San+60%gl+V Q+70%gl+V+b
10 40 50	0 1.98 9.74	709±5	9	Q+San+V Q+San+25%gl+V Q(tr)+98%gl+V+b
20 40 40	0 1.93 4.97 9.76	715±5	7	Q+San+V Q+San+50%gl+V Q+San+70%gl+V Q+90%gl+V+b
20 50 30	0 1.97	738±6	5	Q+San+30%gl+V Q+San+60%gl+V

* Values are given in weight %.

† Symbols used to describe the run products: Q (quartz), San (sanidine), V (vapor phase), b (unidentified borates that crystallize from the vapor phase), tr (trace), Ab (albite), gl (glass).

tween 720 and 740°C , depending on the ratio Ab/Or (in the range of 0.167 to 1 on a weight basis). The addition of 5 wt. % B_2O_3 to the granitic bulk compositions lowers the melting temperature drastically to approximately 595°C , a drop of 125°C . Additional boron does not lead to further reduction (a horizontal solidus is drawn in Figure 1 on the basis of the data point at 8.3% B_2O_3) but does lead to the appearance of specks of unidentified birefringent borates in tiny white vitreous spheres that are interpreted as quenched vapor phase. These findings suggest that saturation in tetrahedrally coordinated boron has been achieved with 5% B_2O_3 , and that additional boron partitions more strongly into the vapor phase, where it occurs in part as B^{III} , coordinated to three oxygen atoms. The differences in proportion of melt produced in bulk compositions containing 5 and 10% B_2O_3 (Fig. 1) suggest that the liquidus is also drastically depressed upon addition of boron to the system $\text{KAlSi}_3\text{O}_8\text{--NaAlSi}_3\text{O}_8\text{--SiO}_2\text{--H}_2\text{O}$.

Although Maitrallet (1976) failed in his efforts to synthesize tourmaline in a granite + water + H_3BO_3 mixture held at $P(\text{H}_2\text{O}) = 2$ kbar, he did confirm that at 625°C , the rock was partially melted; without boron in the system, the minimum melting temperature is 680°C (Tuttle & Bowen 1958). Maitrallet found an even greater degree of melting when he added 2.5 wt. % NaF to the mixture, suggesting that the influence of

fluorine and boron on melting phenomena is additive.

As there is ample evidence that tetrahedrally coordinated boron (B^{IV}) can replace aluminum in feldspars (e.g., Eugster & McIver 1959, Barsukov 1961, Sheppard & Gude 1965, Martin 1971), some indication of B-for-Al substitution was sought in the unit-cell dimensions of the K-rich feldspars in the run products. Cell parameters were determined on products of subsolidus experiments, so that boron would be partitioned only between crystals and vapor phase. X-ray diffraction patterns of powders were obtained with a Guinier-Hägg camera, $CuK\alpha_1$ radiation, at room temperature; indexed 2θ values corrected against a quartz internal standard were used as input for the Appelman & Evans (1973) cell-refinement program.

A plot of the cell edges b vs c is commonly used to obtain information on composition and degree of Si-Al order of feldspars. The resulting quadrilateral can be contoured for composition with the a cell edge; a should increase with decreasing proportion of Na in the K-feldspar. However, a is found to contract slightly, by 0.013\AA , between $KAlSi_3O_8$ and $(KBSi_3O_8)_{18.1}$ ($KAlSi_3O_8$)_{81.9} (Martin 1971); this is approximately the equivalent of 2.7 mol % Or. B^{IV} -for-Al substitution leads to greater reduction in b and c cell edges, and should thus be reflected in anomalous trends in the b - c plot.

Compositions calculated from the a cell edge as if the feldspars were boron-free suggest that the sanidines become increasingly K-rich with decreasing temperature of synthesis, as fully expected in view of the widening solvus between $KAlSi_3O_8$ and $NaAlSi_3O_8$. The trend of increasing a , leading to calculated compositions from Or₇₀ at 715°C to Or₈₄ at 506°C, should therefore lead to displacements toward the high sanidine-low microcline sideline (Fig. 2), reflecting larger b and c values. Instead, both b and c contract, defining a trend away from this sideline; shrinkage in b and c is expected as a result of B^{IV} -for-Al substitution due to the small size of the boron atom. The trend in Figure 2 is analogous to that defined by four synthetic monoclinic $K_{100}Na_0$ feldspars containing 0, 5.5, 9.7 and 18.1 mol % $KBSi_3O_8$ (Martin 1971). As the value of N_{Or} quoted in Figure 2 for the feldspars synthesized from the granitic mixtures are slightly low because the feldspars are boron-bearing, the anomaly in location of points in the b - c plot even exceeds that suggested by the apparent N_{Or} contents. These results suggest that the K-rich feldspars do incorporate B^{IV} , and increasingly so at progressively lower temperatures.

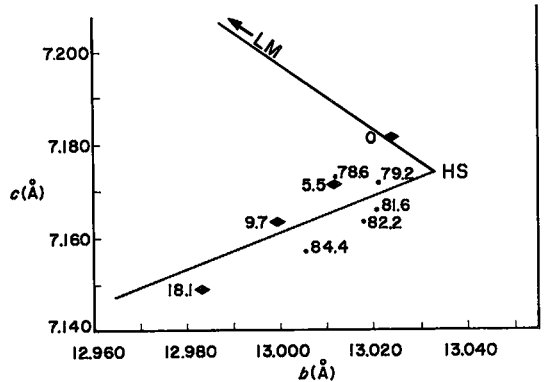


FIG. 2. Anomalous b - c coordinates of K-rich feldspars synthesized from boron-bearing haplogranitic compositions; apparent mol % Or is shown next to each dot. The sanidine containing 78.6% Or was synthesized at 715°C from a boron-free mixture; its position in the b - c plot is as expected for its composition, calculated from the a cell edge. Sanidines containing 79.2, 81.6, 82.2 and 84.4% Or were synthesized at 595, 593, 593 and 506°C, respectively, from mixes that had 10.1, 8.4, 4.9 and 10.2% (wt.) B_2O_3 , respectively. Four sodium-free synthetic K-feldspars, represented by a diamond symbol, contain 0, 5.5, 9.7 and 18.1 mol % $KBSi_3O_8$. HS and LM refer to high sanidine and low microcline, respectively.

The b - c plot cannot be used to determine the extent of B^{IV} -for-Al substitution. However, a feldspar synthesized at 506°C from a mixture containing 10.19% B_2O_3 differs from its expected location in a b - c plot contoured for a (Stewart 1975) by roughly the same extent as the separation between compositions 0 and 5.5% $KBSi_3O_8$ (Fig. 2). We tentatively conclude that the K-rich feldspar contains approximately this proportion of the boriferous end-member. The coexisting sodic feldspar, not studied by X-ray diffraction, presumably also contains B^{IV} , although extent of solid solution toward reedmergnerite, $NaBSi_3O_8$, may be limited by a miscibility gap (Eugster & McIver 1959). The specks of borates deposited from the fluid phase presumably contain boron primarily as B^{III} .

RESULTS OF DRY MELTING EXPERIMENTS

Upon heating, the microcline (Or₈₅) in tourmaline granite 1697A re-equilibrates compositionally, presumably by homogenization with nearby albite grains: Or₇₅ at 841°C and Or₆₄ at 1005°C, as revealed by a cell edge. Microcline also attempts to re-equilibrate structurally, by disordering the intermediate microcline, a metastable state that persists until K-feldspar is

completely melted. In experiments at the lowest temperatures, hematite appears as a coating on the surface of an unidentified high-relief greenish mineral, apparently an isotropic breakdown product of tourmaline. A diffraction peak identified as the (122) reflection of tourmaline is present in run products up to 877°C. Melting begins in the interval 858 to 877°C; quartz, microcline, albite, hematite and bundles of mullite fibres coexist with melt. The solidus temperature of tourmaline granite 1697A is evidently about 80 to 90°C lower than 960°C, the minimum melting temperature at 1 atm in the system $KAlSi_3O_8-NaAlSi_3O_8-SiO_2$ (Tuttle & Bowen 1958). Interestingly, none of the unsealed charges showed significant weight loss on heating, even to temperatures above the breakdown of tourmaline. Run products were essentially the same whether the capsules were sealed or left open. This suggests that boron derived by breakdown of tourmaline partitions strongly among coexisting liquid + crystals; very little is lost as volatile borates. Anomalies in the cell dimensions of mullite (Chorlton 1973) are tentatively attributed to B^{IV} -for-Al substitution.

DISCUSSION

Work done on industrial borosilicate and boraluminate glasses (e.g., Warren 1941, Riebling 1964, Bray 1967) suggests that boron occurs in the melt both triply coordinated, in BO_3 groups, and tetrahedrally coordinated, in BO_4 groups. The ratio of B^{III} to B^{IV} in a melt, as determined by proton NMR spectra, depends on temperature, pressure and bulk composition. Increasing temperature favors B^{III} over B^{IV} , whereas increasing pressure favors B^{IV} due to the denser packing of atoms in this configuration (Bockris & Kojonen 1960). Addition of alkali atoms to melts in the system $B_2O_3-SiO_2$ can be correlated with increasing proportion of tetrahedrally coordinated boron (Bray 1967). Thus, low temperature, high pressure and peralkalinity can be expected to favor the occurrence of B^{IV} in natural environments.

The data presented in this paper confirm that in granitic bulk compositions in which (Al + B) exceeds (Na + K) only slightly, more tetrahedrally coordinated boron could be expected at temperatures close to 500° than above 700°C, as suggested by the trend of feldspars in Figure 2. The various run product further confirm the presence of the two coordination states of boron in granitic bulk compositions: B^{IV} occurs in feldspars and possibly in mullite, B^{III} is found in borates deposited from the vapor phase, es-

pecially in bulk compositions containing more than 5% B_2O_3 . Approximately 5 mol % of the boriferous feldspar end-member could be present in the K-feldspars forming upon crystallization of such low-temperature granitic liquids.

Although the importance of boron is well-appreciated in low-temperature sedimentary environments, little pertinent information is available on the distribution of boron among the minerals of granites and pegmatites. Boron is unfortunately not among the commonly sought constituents of rocks and minerals, nor are B^{III}/B^{IV} ratios readily available. Tourmaline-bearing granites are well-known, especially in Cornwall, England. Brammall & Harwood (1925) and Exley & Stone (1964) have noted the general increase in tourmaline content, commonly accompanied by topaz and, occasionally, fluorite, from the earliest to the latest intrusive units. Textural relationships suggest that two generations of tourmaline, one possibly magmatic and the other post-magmatic, may characterize many rocks in this association. Whether or not the accompanying feldspars contain B^{IV} substituting for Al would provide an interesting subject of research and a possible test of the likelihood that some of these granites formed from liquids whose solidus was depressed because of appreciable boron concentrations. If a tourmaline granite contains only B^{III} , enrichment in boron may have occurred entirely via a fluid phase, after the primary crystallization of the feldspars and thus clearly at the postmagmatic stage. Late development of tourmaline may also result from the release of B^{IV} from structures of primary silicates during episodes of rock-water interaction.

At least one pegmatitic complex is known in which boron enrichment seems to have occurred at the end stages of magmatic crystallization. Pockets in the Dara-Pioz alkaline pegmatite, Alai range, Tadzhik SSR, contain quartz, albite, perthitic microcline, aegirine and reedmergnerite (Dusmatov *et al.* 1967). In such peralkaline environments, B^{IV} may well predominate over B^{III} ; for example, tourmaline is not expected in peralkaline pegmatites, presumably because it is invariably a peraluminous phase, *i.e.*, $(Na + K) < Al$. All silicate minerals in the pegmatitic pockets, including aegirine and the aluminous feldspars, contain appreciable quantities of tetrahedrally coordinated boron. The mineral assemblage in these pockets could have crystallized from a water-saturated, B^{IV} -enriched granitic melt at temperatures below 600°C or from the coexisting high-pH fluids. Cell dimensions of the aluminous feldspars suggest that B^{IV} -for-Al substitution is more extensive in albite than in the coexisting microcline (R. F. Martin & V. D. Dus-

matov, unpubl. data). Other examples similar to the Dara-Pioz pegmatite may have been overlooked, as the reedmergnerite there looks very much like an ordinary feldspar.

This investigation was planned to explore empirically the effect of adding boron to granitic bulk compositions. Because this component has a tendency to occur in two types of coordination polyhedra, general statements concerning the distribution of boron among solids, liquid and vapor are difficult to make at this stage. However, our observations on depression of melting temperatures, coupled with the relatively low temperature of the incongruent melting of reedmergnerite ($\text{NaBSi}_3\text{O}_8 \rightarrow \text{tridymite} + \text{L}$ at 862°C , 1 atm: Milton *et al.* 1960) and with preliminary documentation of a miscibility gap between $\text{NaAlSi}_3\text{O}_8$ and NaBSi_3O_8 (Eugster & McIver 1959), are directly applicable to pegmatites, especially those in which $(\text{Na} + \text{K}) > \text{Al}$. The influence of boron on the melting temperature of granitic compositions will likely be in addition to depressions in melting points caused by H_2O and by elements like fluorine and lithium (Wyllie & Tuttle 1961, 1964), which modify the structure of the silicate melt in completely different ways than does a network-forming cation like boron.

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