THE EFFECT OF BORON ON THE GRANITE SOLIDUS

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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\textsuperscript{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\textsuperscript{IV} to Al\textsuperscript{III} 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.

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 KAlSiO\textsubscript{4}-NaAlSi\textsubscript{4}O\textsubscript{8}-SiO\textsubscript{2}-H\textsubscript{2}O (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 B\textsubscript{2}O\textsubscript{3}, non-hygroscopic and stable at room temperature. The B\textsubscript{2}O\textsubscript{3} content of each run was calculated from the amount of H\textsubscript{3}BO\textsubscript{3} added. Total water content, generally between 10 and 20 wt. %, was calculated to include the water added in the form of H\textsubscript{3}BO\textsubscript{3}. Solids and distilled water were loaded into 2mm Au tubing 10 to 15mm long, and welded shut. Experiments were run at P(H\textsubscript{2}O) = 1 kbar in externally heated 2.5cm O.D. stellite cold-seal pressure vessels; temperatures fluctuated ±5 or 6°C during the 5- to 11-day isothermal experiments.

Other experiments were run at atmospheric pressure on a tourmaline-bearing granitic segregate from a pegmatite in the Boulder batholith, Montana (Knopf 1957). This granite (1697A in Knopf's collection) consists of quartz, microcline (Or\textsubscript{90}), Iom albite and 20 vol. % dark green tourmaline; the rock contains 72.68 wt. % SiO\textsubscript{2}, 14.63% Al\textsubscript{2}O\textsubscript{3}, 1.74% B\textsubscript{2}O\textsubscript{3}, 0.56% CaO, 2.49% Na\textsubscript{2}O and 4.36% K\textsubscript{2}O (E. B. Knopf, priv. comm.; full analysis in Chorlton...
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1973). The 1 atm isothermal experiments lasted from 4 days (experiments above 1000°C) to 22 days (experiments at 743 ± 5°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. % B₂O₃ 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(H₂O) = 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 between 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. % B₂O₃ 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% B₂O₃) 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% B₂O₃, 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% B₂O₃ (Fig. 1) suggest that the liquidus is also drastically depressed upon addition of boron to the system KAlSi₃O₈–NaAlSi₂O₆–SiO₂–H₂O + B₂O₃ 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 glass in a data point is indicative of the proportion of glass (quenched melt) in the run products.

Although Maitrallet (1976) failed in his efforts to synthesize tourmaline in a granite + water + H₂BO₃ mixture held at P(H₂O) = 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\textsuperscript{3+}) 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 radiation, at room temperature; indexed 2\theta values corrected against a quartz internal standard were used as input for the Appleman & 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\text{Å}, between KAlSi\textsubscript{3}O\textsubscript{8} and (KBSi\textsubscript{3}O\textsubscript{8})\textsubscript{0.1}(KAlSi\textsubscript{3}O\textsubscript{8})\textsubscript{0.9} (Martin 1971); this is approximately the equivalent of 2.7 mol % Or. B\textsuperscript{3+}-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\textsubscript{3}O\textsubscript{8} and NaAlSi\textsubscript{3}O\textsubscript{8}. The trend of increasing \(a\), leading to calculated compositions from Or\textsubscript{78} at 715°C to Or\textsubscript{56} 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\textsuperscript{3+}-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\textsubscript{100}Na\textsubscript{8} feldspars containing 0, 5.5, 9.7 and 18.1 mol % KBSi\textsubscript{3}O\textsubscript{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\textsuperscript{3+}, and increasingly so at progressively lower temperatures.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{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\textsubscript{2}O\textsubscript{3}, respectively. Four sodium-free synthetic K-feldspars, represented by a diamond symbol, contain 0, 5.5, 9.7 and 18.1 mol % KBSi\textsubscript{3}O\textsubscript{8}. HS and LM refer to high sanidine and low microcline, respectively.}
\end{figure}

The \(b-c\) plot cannot be used to determine the extent of B\textsuperscript{3+}-for-Al substitution. However, a feldspar synthesized at 506°C from a mixture containing 10.19% B\textsubscript{2}O\textsubscript{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\textsubscript{3}O\textsubscript{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\textsuperscript{3+}, although extent of solid solution toward reedmergnerite, NaBSi\textsubscript{3}O\textsubscript{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\textsuperscript{3+}.

\section*{Results of Dry Melting Experiments}

Upon heating, the microcline (Or\textsubscript{95}) in tourmaline granite 1697A reequilibrates compositionally, presumably by homogenization with nearby albite grains: Or\textsubscript{78} at 841°C and Or\textsubscript{56} at 1005°C, as revealed by \(a\) cell edges. 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 green-

ish mineral, apparently an isotropic breakdown
product of tourmaline. A diffraction peak iden-
tified 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, mi-
crocline, albite, hematite and bundles of mullite
fibres coexist with melt. The solidus tempera-

ture of tourmaline granite 1697A is evidently
about 80 to 90°C lower than 960°C, the mini-

mum melting temperature at 1 atm in the sys-

tem KAlSi3O8-NaAlSi3O8-SiO2 (Tuttle & Bowen

1958). Interestingly, none of the unsealed
charges showed significant weight loss on heat-

ing, even to temperatures above the breakdown
temperature of tourmaline. Run products were essen-
tially the same whether the capsules were sealed or left
open. This suggests that boron derived by break-
down of tourmaline partitions strongly among
coexisting liquid + crystals; very little is lost
as volatile borates. Anomalies in the cell dimen-
sions of mullite (Chorlton 1973) are tentatively
attributed to Biv-for-Al substitution.

**Discussion**

Work done on industrial borosilicate and bo-
roaluminate glasses (e.g., Warren 1941, Riebling
1964, Bray 1967) suggests that boron occurs in
the melt both triply coordinated, in BO3 groups,
and tetrahedrally coordinated, in BO4 groups.
The ratio of Biv to Biv in a melt, as determined
by proton NMR spectra, depends on temper-

ature, pressure and bulk composition. Increasing

temperature favors Biv over Biv, whereas in-
creasing pressure favors Biv due to the denser
packing of atoms in this configuration (Bockris &
Kojonen 1960). Addition of alkali atoms to
melts in the system B2O3-SiO2 can be correlated
with increasing proportion of tetrahedrally co-
ordinated boron (Bray 1967). Thus, low temper-

ature, high pressure and peralkalinity can be ex-
pected to favor the occurrence of Biv 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 tetra-
hedrally coordinated boron could be expected at
temperatures close to 500°C 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: Biv occurs in
feldspars and possibly in mullite, Biv is found
in borates deposited from the vapor phase, es-
pecially in bulk compositions containing more
than 5% B2O3. Approximately 5 mol % of the
boriferous feldspar end-member could be pre-
sent in the K-feldspars forming upon crystal-

lization of such low-temperature granitic liquids.

Although the importance of boron is well-
appreciated in low-temperature sedimentary en-
vironments, little pertinent information is avail-
able 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 Biv/
Biv ratios readily available. Tourmaline-bearing
granites are well-known, especially in Cornwall,
England. Brammall & Harwood (1925) and
Exley & Stone (1964) have noted the general in-
crease in tourmaline content, commonly accom-
panied 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 accompany-
ing feldspars contain Biv substituting for Al
would provide an interesting subject of research
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was depressed because of appreciable boron con-
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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 reedmergne-
rite (Dusmatov et al. 1967). In such peralkaline
environments, Biv may well predominate over
Biv, 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 te-
trahedrally coordinated boron. The mineral as-
semblage in these pockets could have crystallized
from a water-saturated, Biv-enriched granitic melt
at temperatures below 600°C or from the co-
existing high-pH fluids. Cell dimensions of the
aluminous feldspars suggest that Biv-for-Al sub-
stitution is more extensive in albite than in the
coeexisting 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 (NaBSiO₄ → tridymite + L at 862°C; Milton et al. 1960) and with preliminary documentation of a miscibility gap between NaAlSiO₄ and NaBSiO₄ (Eugster & McIver 1959), are directly applicable to pegmatites, especially those in which (Na + K) > Al. The influence of boron on the melting temperature of granitic compositions will likely be in addition to depressions in melting points caused by F and Li 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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