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Short Title:

THE EFFECT OF BORON ON GRANITE

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THE EFFECT OF BORON ON PHASE RELATIONS IN THE GRANITE-WATER SYSTEM

by

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ABSTRA CT

The fluxing action of $B_2 O_3$, its high vapour pressure in the presence of steam, and the capacity of boron to substitute for aluminum in some aluminosilicates led to an investigation of its effect on the phase relations in the granite system.

 B_2O_3 is found to depress the granite minimum by up to $120^{\circ}C$ with the addition of up to 10 per cent B_2O_3 at $P(H_2O) = 1$ kilobar. The presence of boron in the hydrous system Oalso leads to an apparent potash enrichment of the high sanidine solid solutions coexisting with vapour, or vapour and melt. This effect may be linked to the entry of boron into the crystal O structure or may be purely a solvation effect.

The feldspars produced hydrothermally in boronbearing charges were anomalous in that their <u>b</u> and <u>c</u> cell dimensions are reduced with respect to those of normal feldspars with the same alkali contents. These anomalies are consistent with the substitution of B for Al in T₁O sites.

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RÉSUMÉ

Les investigations de l'effet du bore sur les relations de phases dans les systèmes granitiques sont inspirées des diminutions des points de fusion dues au bore, sa haute pression de vapeur en présence d'eau aux températures élévées, et sa capacité de remplacer l'aluminium dans la structure des feldspaths. Les relations de phases dans le système haplogranitique ont eté etudiées sous une pression d'eau d'un kilobar.

On trouve que la presence de B_2O_3 fait baisser la température du point de fusion minimum des granites de $60^{\circ}C$ avec l'addition de $2\% B_2O_3$, et de $120^{\circ}C$ avec l'addition de 10%. Le B_2O_3 dans la phase vapeur enrichit les feldspaths alcalins en potassium, dû soit a l'incorporation du bore dans la structure, soit a un effet de 'solvation'.

La substitution de l'aluminium par le bore occasionme une reduction des dimensions de la maille des feldspaths. Avec des concentrations limitées de bore la reduction est un peu plus importante en <u>c</u> qu'en <u>b</u>; elle est minimum en <u>a</u>. La valeur de ces reductions est en accord avec la substitution "balancée" de l'aluminium et bore dans La position T_10 .

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Previous Work:

Goranson (1932) pioneered studies of the melting behaviour of granitic rocks in the presence of water under low confining pressures. More recently, studies were made of the effects of temperature, pressure, and bulk composition in the water-saturated part of the system $NaA1Si_3O_8-KA1Si_3O_8-SiO_2-H_2O$ at $P(H_2O)$ up to 10 kilobars (Tuttle and Bowen, 1958; Luth, Jahns, and Tuttle, 1964). The melting behaviour of natural ranites was found to conform to the behaviour of the eudoternary haplogranite system $NaA1Si_3O_8-KA1Si_3O_8-SiO_2$, an adequate model system for a study of the behaviour of natural granites.

The addition of the component anorthite, $CaAl_2Si_2O_8$; raises the minimum melting temperature, of the water-rich granite system and also appreciably restricts the stability field of alkali feldspar (James and Hamilton, 1960). The system NaAlSi_3O_8-KAlSi_3O_8-CaAl_2Si_2O_8-SiO_2 has been designated as a model system for the investigation of phase relations in granodioritic rocks (Piwinskii and Wyllie, 1968; 1970).

The effects of water undersaturation on the melting behaviour of granites and granodiorites was investigated by Whitney (1972) and Robertson and Wyllie (1971). The influences of the second volatiles CO_2 , HF, NH₃, SO_3 , P_2O_5 , HCl, and Li₂O were also explored (Tuttle and Wyllie, 1957; Wyllie and Tuttle, 1959; 1960; 1961; 1964; Wyllie, 1959). Whereas NH_3 , SO₃, and P₂O₅ showed negligible effect on the minimum melting temperature of granite, CO₂ and HCl increased the melting temperature, neither being very soluble in the silicate melt. HCl probably reacts chemically with the feldspars, combining with the alkalis and transferring them to the vapour phase, thus enlarging the primary field of quartz. HF and Li₂O lowered the minimum melting temperature by partitioning strongly into the silicate melt, i.e., by acting as fluxes.

These investigations prompted the present study of the influence of boron on the melting behaviour in the haplogramite system, since the fluxing properties of alkali borates are also well known. In addition, the similarity in valence of boron and aluminum, and the slightly smaller ionic radius of boron, suggests the possibility of boron substitution for aluminum in aluminosilicates and in the network of the corresponding melts. As well as determining the effect of boron on the beginning-of-melting of granitic compositions, it was hoped that criteria could be found by which the action of boron during the magmatic stages of granite evolution could be detected from the subsolidus assemblages.

Morey (1951) studied the system $Na_20-B_20_3-S_{10}_2$ at atmospheric pressure, with the specific intention of clarifying relations along the binary join $B_20_3-Si0_2$, still unknown after studies of the system Ca0- $B_20_3-Si0_2$ in which the

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 $B_2 O_3$ -SiO₂ binary was seriously complicated by the formation of immiscible liquids (Morey and Ingerson, 1937). Unfortunately, he was not successful, as he was unable to devitrify highly viscous glasses of borosilicate composition once they had been Later investigators failed to agree on the phase prepared. relations of this binary system until Rockett and Foster (1965) re-examined the system, making considerable effort to avoid the experimental difficulties encountered by the previous authors, i.e. those of: 1)volatilization of B_2O_3 at high temperatures; 2) rapid hydration of $B_2^0_3$ -rich melts; and 3) the very high viscosities of borosilicate melts. Experimentation on boron-bearing systems related to the haplogranite system has been minimal, apart from these investigations, and determination of the effect of k_20 , or of water under pressure in those systems already studied, has not been attempted. In order to avoid complications, B_2O_3 contents of no greater than 10 per cent were used in the present experiments; such a limit is well in excess of boron contents that could be reasonably expected in a magmatic environment, even under the most extreme magmatic čonditions.

Distribution of boron in the crust, with special reference to magmatic and related rocks:

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The earth's crust contains, on the average, less than 10 ppm B_2^{0} (3 ppm B), and igneous rocks, about 1 to 30 ppm (Goldschmidt, 1954). Based on previously published data,

A.P. Vinogradov (1956) proposed average values of 10 to 15 ppm B, with no clear enrichment in basic, intermediate or acidic rocks. In an updated compilation Vinogradov, (1962) proposes averages of 1 ppm, 5 ppm, 15 ppm, and 15 ppm for ultramafic, mafic, intermediate, and acidic rocks, respectively, and thus a relative enrichment in intermediate and felsic rock types. Wide variations of boron concentration would be expected within each category, corresponding to variations in mineralogy and degree of post-magmatic alteration (Barsukov, 1961: Lititsyn and Khitrov, 1962). Getling and Savinova (1958) noted that boron content was remarkably constant (20-30 ppm) in genetically related pre-skarn gabbros, granodiorites, and diorites, extrusive mafic porphyrites, and post-skarn spessartite lamprophyres in the Turinsk copper district of the Ural Mountains, Most of the boron in these rocks was fixed in plagioclase (phenocrysts and in groundmass). V. D. Otroschenko (1967), in his analyses of boron and cesium in volcanic rocks of western Tien-Shan, found boron enrichment in intermediate lavas (28 ppm B) and tuffs (18 ppm B) relative to silicic and mafic volcanic rocks. Boron concentration was also higher in products of submarine eruptions than in products of subaerial eruptions, and much higher in quiescently extruded material than in explosively erupted material¹. Most of the boron was contained in the plagioclases, with slightly lower concentrations

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1. Siliceous melts are more likely to erupt explosively than more mafic melts. This should be considered as a factor in evaluating the causes of boron enrichment in intermediate tuffs relative to siliceous tuffs. in the amphiboles. Boron minerals, such as dumortierite and tourmaline, were found only in altered volcanic rocks. Lititsyn and Khitrov (1962) have concluded their determinations of the boron content of comagmatic rocks of the Middle Urals (diorites, syenites, diabases, lamprophyres, porphyrites and tuffs), and associated metamorphic rocks, that the boron content of igneous rocks is dependent on their modal content of plagioclase, hornblende, and Al-rich pyroxene, all of which tend to concentrate boron.

Before these studies, boron was believed to accu. mulate in the end products of magmatic differentiation. Getling and Savinova (1960) contend that the behaviour of boron during the magmatic cycle depends largely on the boron content of the primary magma. If the original boron content is very low, all of the boron, or most of it, will isomorphously enter the silicate lattices of minerals such as plagioclase and hornblende, thereby impoverishing the melt of boron. If the original boron content is high, the boron that does not enter the silicate structures will concentrate in the residual melt, and may eventually contribute to the formation of tourmaline granite, pegmatite, or boron-rich veins. For example, the axinite-epidote-tourmaline-veins in the Lambertville, Va. diabase, described by Tomlinson (1945), may be the product of crystallization of a boron-enriched magma (in a closed system) that coexisted with crystalline phases saturated in boron. Stavrov and Khitrov (1960), in their studies of boron concentrations

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among various phases of granitoid complexes and associated pegmatites, noted that boron-rich (tourmaline-bearing) pegmatites were associated only with parent rocks having relatively high boron contents. Alternatively, if concentrations are high enough and chemical conditions are favourable, boronbearing metasomatizing fluids may be produced; these fluids may also induce metasomatism, e.g., the potash metasomatism of gneisses, as described by Gore (1967) in north-western Wisconsin. Barsukov (1961) concluded from analyses for boron in granitoids, both related and unrelated to borate mineralization, that hypogene borate deposits, e.g. kotoite or ludwigite-bearing assemblages associated with skarns, are generally associated with granitic rocks containing 8 to 15 times the average boron content for granitic rocks.

The case of boron saturation in the original magma is illustrated by the well-known tourmaline-bearing granites of ⁷Cornwall. Brammel (1923) and Exley and Stone (1964) have noted the general increase in tourmaline content, often accompanied by topaz and occasionally fluorite, in the younger intrusive units. Textural relations, as well as the reciprocal variation in the abumdances of biotite and tourmaline, suggest that brown tourmaline (schorl) has replaced biotite during magmatic crystallization. Post-joint, acicular bluegreen alkali tourmaline has replaced feldspars and biotite, and has also nucleated on tourmaline and biotite selvages (Wells, 1946). It is significant that boron was present during

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the later stages of magmatic crystallization, and was later active as a constituent of hydrothermal solutions, or was released from boron-saturated primary silicate phases by fluid faction and subsequently redistributed. 7

That volcanic activity is indirectly responsible for our most viable commercial borate deposits (Gale, 1964; Watanabe, 1967) is testimony to the fact that magmatic rocks may often be oversaturated in boron. Polyborates of K, Na, and Ca, such as borax, colemanite, and ulexite (Gale, 1964, p.4-6) are precipitated in arid climates from saline waters derived from thermal springs, e.g., at the Kramer, Borax Lake and Searles Lake deposits, California (Gale, 1964; Watanabe, High temperature hypogene borate deposits exploited 1967). elsewhere are formed in magnesian skarns close to the contacts of granitoid intrusive rocks. Orthoboric acid, sassolite, is obtained directly from fumaroles in Tuscany, and from the Showa-Shinza and Azuma volcanoes, Japan (Watanabe, 1967) and larderellite, $NH_4B_5O_6(OH)_4$, occurs in Larderello, Italy (Nies and Campbell, 1964, p.117). It has been shown that boron can be extracted from tourmaline and boriferous serpentine using high pressure steam (Clarke, 1924), supporting the hypothesis that aqueous vapour escaping from an erupting magma could leach boron from the crystallized or crystallizing magma, or from boron-rich country rock.

Although the elements K and F, as well as Cs, have been petrogenetically linked to boron (Tilley, 1951;

Barsukov, 1961; Stavrov and Khitrov, 1962), it has been shown experimentally that the most stable forms of boron in hightemperature fluids containing these elements are as the relatively simple tetraborate or metaborate ions (Barsukov and Yegorov, 1961; Stavrov and Khitrov, 1962). Meschi, Chupka, and Berkowitz (1960) verify that the most stable borate species in the system $H_20 = B_20_3$ at temperatures of 7^{8} > 0 - 1,17 * °C is the metaborate ion, HBO₂. Temperature and pH of post-magmatic solutions jointly influence the form of boron complex in solution, chemical interaction with preexisting minerals, and the variety of boron minerals precipitated under given conditions. According to Barsukov (1961), it is in the form of the metaborate ion that boron, in weakly alkaline solutions during the high temperature stages of pneumatolytic activity, reacts with aluminosilicates to form tourmaline (or other boron-bearing silicate minerals, such as axinite, $(Ca, Mn, Fe^{2*})_{3}Al_{2}BO_{3}(Si_{4}O_{12})OH$, if conditions are unsuitable for the formation of tourmaline¹) or leaves the system in solution to be deposited as orthoborate salts, i.e. salts whose structures contain isolated BO_3^{3-} groups, stable at high temperatures, and small metallic cations, such as A1³⁺, Fe³⁺, and Mg²⁺, rather than the complex polyborate salts of Ca, Na, and K, typical of low temperature deposition or replacement. Subsequently, decomposition of complexes containing strongly acid ions, such as Cl and F, lowers the alkalinity of the hydrothermal solutions to neutral or weakly acid, giving

1. Tourmaline is unstable in acid and strongly alkaline solutions (Smith, 1949; Frondel and Collette, 1957)

rise to the 'acid leaching' stage during which boron is 'commonly released from the granitoid host, perhaps through the recrystallization of minerals containing boron, magmatically trapped' in solid solution. Neutral to weakly acid conditions favour $H_2B0_3^-$ groupings, which will probably be dissociated to $B0_3^{3-}$ as acidity increases. At the lower temperatures prevailing in later stages of hydrothermal activity these $B0_3^{3-}$ ions may associate to form triangular $B_20_5^{4-}$ groups resulting in the precipitation of diborate salts (e.g. szaibelyite). If the diborate ion-bearing solutions interact with carbonate rocks, or otherwise increase their alkalinity, $B0_3^{3-}$ ions may be hydrolyzed to form tetrahedral $B0_3(0H)^{4-}$ ions that may result in the formation of datolite or danburite.

Much of the boron in magmatic rocks is thought to have been introduced by the assimilation or melting of argillaceous sedimentary rocks, or by the introduction of boron-bearing solutions from these sources (Landergren, 1945; Wasserstein, 1951; Getling and Savinova, 1959; Barsukov, 1960). Although arenaceous sediments contain a limited amount of boron, usually in the form of the resistant mineral tourmaline, marine argillaceous sediments contain considerable amounts, from 50 to 1,000 ppm B, concentrated in the clay fractions (Goldschmidt and Peters, 1932; Goldschmidt, 1954: Harder, 1970) As a rule, freshwater argillites contain very little boron (Harder, 1970). Wasserstein (1951) related the higher boron content of the younger South African and Rhodesian granites, relative to that

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of the older ones, to their closer association with high-boron sedimentary host rocks; due to their shallower depth of erosion more of the outcrop exposed at the surface is located not far from contacts with sediments: the younger granite bodies are intersected by the surface at their smaller, upper diameters. His evidence is somewhat tenuous because:

- 1) The boron-bearing younger granites sampled, as well as the few older granites that contain boron, are mineralogically classified as true granites, whereas the older intrusive rocks are classified as granodiorites. It would be hard to completely discount evolutionary enrichment.
- 2) The sensitivity of his analytical technique is low, the limit of detection being .007 per cent. Most igneous rocks contain less B_2O_3 than this amount. If the boron content of the older rocks were just under the limit of detection, the enrichment of the younger rocks would be minor.
- 3) There is a greater possibility of boron removal from the older rocks by post-magmatic alteration.

However, in view of the high boron contents of marine sediments and metasediments (Yegorov, 1961) an ultimate sedimentary origin for high boron concentrations in magmas, and in solutions resulting, in mineralization cannot be discounted. Some boron-rich mineral deposits, such as magnetite iron formation, localized in skarns of the Tayezhnoye

region, U.S.S.R., probably derive their boron from rocks of sedimentary origin (Yegorov, 1961). The boron and iron content of biotite gneisses and pyroxene or hornblende schists of the Tayezhnoye area decreases with increasing granitization (formation of migmatite). Boron and iron, in the proportions found in nongranitized gneiss terrain, are introduced into the vicinity of the dolomite zones of the regional sequence as metasomatic magnetite and tourmaline. It is also possible that the borate portion of the hypoborate fluids invoked by Gore (1967) to explain the mobility of potash may have been released during the regional metamorphism from the sediments themselves. If this were so; the following sequence would be suggested: marine sediment -- schist -- granitized rock, or migmatite (process accompanied by loss of boron in an open system) --granite(?), with a low boron content relative to that of the schist or sediment.

The geochemistry of boron has been documented in less detail than that of most other minor elements. This is due to analytical difficulties related to its low atomic number, and to close association to silicon and aluminum. Promising colorimetric techniques have been recently developed (Fleet, 1967; Uppstrom, 1968). It would be advantageous to have boron included in many routine analyses, as some aspects of the geochemical behaviour of boron, and some perspective as to its relative petrologic importance, would thus be clarified.

The role of boron in melts:

To predict what part, if any, boron might play in the nucleation of solid phases from a cooling or undercooled melt, as well as to analyze its effect on the phase relations in the system under consideration, it is pertinent to consider its probable structural position in the melt under the appropriate chemical and physical conditions. Boron is capable of 1 -1 existing in tetrahedral as well as in triangular coordination with oxygen. A structural transition from triangular to tetrahedral coordination might be pictured as a shift from sp^2 hybrid bonding with oxygen to sp^3 hybridization. Since the outer, bonding electron shell of boron contains only three electrons, as does that of aluminum, the shift is facilitated by the 'donation' of an electron by a cation, e.g. K, Li, Na, or H, but this is not strictly necessary as in the case of pure B_20_3 glass (Bockris et al, 1960). If appreciable tetrahedrally coordinated boron is linked into the Al-Si network, it could easily enter the structure of the first forming feldspar in equilibrium with the melt. If, on the other hand, boron is bound loosely in the melt and either exists mainly in threefold coordination, or tends to form clusters apart from the rest of the silicate network, there is little possibility of it being incorporated into nuclei growing crystals of a tectosilicate, although it may form a crystalline phase of its own. The result of clustering to the extent that a separate network is formed would be the

separation of immiscible borate liquid. This is known to occur metastably below the liquidus in the alkali-poor part of the metastable vitreous system $Na_20 - B_20_3$ -SiO₂ (Charles, 1964), and also in glasses of the system B_2O_3 -SiO₂ (Charles and Wagstaff, 1968). Immiscible behaviour was observed at temperatures above the liquidus in the system $CaO-B_2O_3$ -SiO₂ (Morey and Ingerson, 1937), although no evidence was found for liquid immiscibility in the system $Na_2O-B_2O_3$ -SiO₂ (Morey, 1951).

Because of the similarity of compositions used in this study to those of silicate glass_systems, it is possible , to draw indirect evidence concerning the role of composition in determining the structural behaviour of boron in borosilicate glasses. To explain anomalies in the variation of physical properties such as viscosity, density and coefficient of expansion with composition it has been proposed that these glasses contain boron in both threefold and fourfold coordination (Warren, 1941; Abe, 1952). As an alkali modifier such as Li_20 or Na₂0 is added; these properties increase or decrease until a maximum or minimum is reached, usually at slightly under 20 mole per cent modifier (with respect to the sum of alkali plus borate, in moles). This suggests that for each mole alkali modifier one fifth of the boron in the glass converts from threefold to fourfold coordination. This behaviour would naturally be dependent on the thermal history of the glass. It seems probable that boron will revert to its threefold

coordination state if the glasses are held above their softening temperatures (Abe, 1951); however, one possible explanation for partial molar volume and viscosity data determined at $1,300^{\circ}$ C for <u>melts</u> in the system B_20_3 -Si0₂ at compositions with over 60 mole per cent B_20_3 is that boron may be forced into tetrahedral coordination, without the influence of an alkali modifier (Riebling, 1964).

Bray (1967) used nuclear magnetic resonance techniques to show that the proportion of tetrahedral to triply coordinated boron in borate glass increases smoothly up to 45 per cent with the addition of up to 35 per cent alkali modifier, a proportion lying above the limit set empirically by the other authors. In boron-doped CABAL glasses, belonging to the system $CaO-Al_2O_3-SiO_2$, Bray also found tetrahedral boron in cases in which, due to the relative deficiency of mono- or divalent cations, aluminum was not completely converted to tetrahedral coordination. Boron may, therefore, compete with aluminum for tetrahedral sites in glass. It is unfortunate that similar data are not available for melts.

The influence of pressure is another factor worthy of consideration, as tetrahedral coordination should result in more compact 'packing' in glassy or melt structures. Bockris and Kojenen (1960) attribute the negative coefficient of adiabatic compressibility of pure borate melt to the shift from ^{-III}B to ^{IV}B. With increase in temperature, thermal motion will resist the transfer, but the addition of Li₂O as an alkali

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modifier lessens this effect by favouring the transfer of boron to four-coordination as well. At constant temperature, the compressibility of $M_20-B_20_3$ (M refers to a monovalent cation) decreases with increasing M_20 , up 50 mole per cent M_2^0 , by inducing a more rigid network bases on tetrahedral coordination; in the case of silicate melt, the addition of M_20 increases the compressibility by causing bonds to break. Thus in a granite melt under pressure, $(M_{20}O-A1_{2}O_{3}-B_{2}O_{3}-SiO_{2})$, at least part of the boron could be expected to exist in tetrahedral coordination. An additional implication of this predicted behaviour is that the addition of $B_2 O_3$ in basic magmas might favour the nucleation . of chain silicates or tectosilicates as liquidus phases, rather than olivine. This effect, previously mentioned by Belov (1961) is consequence of the ability of boron to maintain tetrahedral linkages in alkali silicate glasses; it has been utilized in glass blowing (Nies and Campbell, 1964). This might be one of the reasons that the highest boron concentrations in primary igneous silicates occur in plagioclase, hornblende, and pyroxene.

Boron in silicates:

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As already mentioned, boron is capable of existing in both triangular and tetrahedral coordination with oxygen. For instance, it occurs in triangular coordination in common borosilicate minerals, such as tourmaline, axinite, and searlesite and in tetrahedral coordination in datolite, danburite, and kornerupine. The edge of the BO_A^{5-} tetrahedron is approximately 2.4 Å, while that of SiO_4^{4-} is 2.6 Å, and that of AlO_4^{5-} is 2.8 Å. The formal charge on a BO_4 tetrahedron is the same as on the $A1O_4$ tetrahedron, leading one to anticipate the substitution of boron for aluminum in silicate lattices. Solid solution of this nature was found to occur in the system $Ca0-A1_20_3-B_20_3-Si0_2$ in which the join $CaAl_2SiO_7(gehlenite) - CaB_2SiO_7$ becomes pseudobinary, with the solid solution of up to 60 mole per cent CaB_2SiO_7 in gehlenite (Bauer, 1962). Similarly, synthetic albite exhibits solid solution with synthetic reedmergnerite, NaBSi $_{3}0_{8}$, up to a limit of Ab $_{80}$ Rd $_{20}$ (Eugster and McIver, 1959). As synthetic boriferous micas isostructural with phlogopite and muscovite have been prepared hydrothermally, solid solution of both micas with their boron analogues can be expected (Stubican and Roy, 1962). Boriferous dioctahedral micas have subsequently been discovered (Harder, 1971; Oftedal, 1963). Minor quantities of boron have been reported in the following minera'ls: plagioclase (Barsukov, 1958; Otroschenko, 1961, 1967; Getling/and Savinova, 1958, 1959; Yegorov, 1961); hornblende (Otroschenko, 1967, 1969; Lititsyn and Khitrov, 1962); pyroxene (Lititsyn et al. 1962; Malinko, 1967); garnet (Barsukov, 1960; Litit/syn et al, 1962);

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epidote, chlorite, and sphene (Lititsyn et al, 1962); serpentine (Varlakov, 1961; Otroschenko et al, 1969; Thompson and Melson, 1970); sapphirine (Moore, 1968); sillimanite (Varley, 1965), and rare earth or metamict pegmatite minerals (Oftedal, 1963). It is interesting to note that whereas boron is commonly lost during post-magmatic alteration, it is concentrated in the alteration products epidote and chlorite (Lititsyn et al, 1962); similarly, the boron content of serpentinite is 5 to 30 times that of the parent peridotite (Otroschenko et al, 1969).

The bord analogue of anorthite is danburite, whose melting behaviour has been studied by Morey and Ingerson (1937). The boron analogues of both albite and potash feldspar have been synthesized at P(H20)=2 kilobars in the temperature range of 300°C to 550°C (Eugster and McIver, 1959). A natural boron analogue of albite, reedmergnerite, has been discovered as an authigenic mineral in shales of the Green River Formation, Utah (Milton and Axelrod, 1954; 1960). It was also discovered as a pegmatite mineral in the Turkestan-Alasian province of the U.S.S.R. (Dusmatov et al, 1967). Cell parameters of both occurrences are comparable, although the Russian reedmergnerite reportedly melts congruently at 1,000°C, whereas the Green River reedmergnerite melts incongruently at 862°C to tridymite plus The structure of the reedmergnerite from the Green River melt. Formation was determined by Appleman and Clark (1965).

Authigenic potassium feldspars containing 0.55 to 0.97 per cent B_2^{0} have been found in the Barstow Formation,

San Bernardino County, California (Sheppard and Gude, 1965), and in other similar lacustrine tuff deposits (Martin, 1971). They are derived from the devitrification of rhyolite tuffs in the presence of highly saline pore fluids. R. F. Martin (pers. com., 1970) reports that these feldspars melt congruently, unlike orthoclase which melts incongruently to leucite plus melt. The cell dimensions of these disordered potash feldspars were studied using X-ray powder techniques (Martin, 1971). This st. study revealed anomalously low b and c cell dimensions, though the a cell dimensions seem 'normal' according to the generally accepted relations between Or content, refractive indices and a cell dimension. The low <u>b</u> and <u>c</u> cell parameters were shown to be due to the substitution of boron for aluminum in the disordered structure by comparison with synthetic boronbearing sanidines, which exhibit similar anomalies, but possess more Si-A1(B) disorder. Appleman and Clark (1965) suggest that it is impossible for the sodic part of the boriferous feldspar system to possess complete disorder, a suggestion which is substantiated in part in that the powder pattern of synthetic reedmergnerite is identical to that of the natural mineral (Eugster and McIver, 1959). If this discrepancy of ordering behaviour between potassic and sodic boriferous feldspar is real, then the relationship between the boron content of transitional Na-K boriferous feldspars and their cell parameters will be seriously complicated.

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EXPERIMENTAL TECHNIQUE

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Hydrothermal Experiments:

The starting materials were glasses made by the method of coprecipitating gels (Luth and Ingamells, 1965). They were supplied as powders by W. C. Luth, and were the same as those used in a previous study of the granite system (Luth, Jahns, and Tuttle, 1964). They were ground and dried in a vacuum oven for four to eight hours, then stored in a dessicator until required. As very little starting material was available, each run had to be prepared individually. Further heating was avoided in this way to prevent alkali loss and sintering, which would tend to produce inhomogeneities in the starting materials.

Boron was introduced in the form of boric \mathbb{A}^{d} , H₃BO₃, A C A approved analytical grade, stable at room temperature and also nonhydroscopic. Boric acid was added in crystal form, because it tended to collect and adhere preferentially to the agate mortar when ground with the granitic glass, and therefore could be neither mixed nor removed with the rest of the material., , The B₂O₃ content of each run was calculated from the amount of H₃BO₃ added, and the total percentage was calculated as percentage of dry ingredients, i.e. granite mix plus weight of B₂O₃.

Distilled water was used in small quantities. The total water content was calculated as the weight of water added plus the weight of water added in the form of H_3BO_3 , and the weight per cent of water as: $\frac{wt.H20 \text{ total } (g)}{wt. \text{ capsule contents } (g)}$. Run compositions are shown in Table 1, Appendix I, in weight per cent $\stackrel{\wedge}{\rightarrow}$ oxide components, and in per cent Ab:0r:Q.

The capsules used in the hydrothermal experiments were cut from 2mm 0.D. gold tubing into 10 to 15mm long, and sealed at one end with an arc welder. Each capsule was first weighed, then .001 to .002 g of distilled water was added with a disposable syringe. The capsule was reweighed upright, and one to three crystals of boric acid were added and the capsule reweighed. According to proposed run composition, an appropriate amount of granitic material was calculated and added as accurately as possible, after being ground in acetone. The capsule was tapped lightly to settle the contents and the rim cleaned with a fresh pipe cleaner, then pinched shut. It was again weighed, trimmed and welded. The basal part of the capsule was held in ice and water while it was being welded to prevent vaporization. The sealed capsule was weighed and placed in a drying oven overnight. The capsule was reweighed to check for leakage.

Experiments were run in externally heated, 1" 0.D. stellite cold seal pressure vessels with water as the pressure medium. The vessels were immersed in vertically wound furnaces controlled with Pt-Pt87Rh13 Ether potentiometric controllers. The temperature of the contents of the vessel were measured with a Pt-Pt87Rh13 thermocouple inserted into a special well in the side wall, or, in from the base, of the pressure vessel, as close to the charges as possible. Stainless steel filler rods were placed inside the vessel on top of the charges to minimize the thermal gradient in the vicinity of the capsules. The difference

between the actual run temperature and the recorded temperature was probably in the order of 5 to 10° C (Boettcher et al, 1971) plus the additional error due to the noncalibration of the thermocouples. Temperatures were recorded from a Pike digital voltmeter and corrected to room temperature. They were monitored twice daily. The maximum fluctuation recorded during runs lasting 5 to 11 days was $\pm 10^{\circ}$ C, usually ± 5 to 6° C. To achieve the desired temperature it fwas occasionally necessary to raise the position of the vessel from that of maximum immersion and of minimum temperature gradient along the capsule, to several inches above that position, a region of reduced temperature but steeper thermal gradient.

All runs were performed at $P(H_20)$ 1 kilobar. The pressure was partially raised before the bomb was lowered into the furnace. Pressure was measured with Bourdon tube gauges calibrated with a standard Heise gauge. The^s bombs were quenched by removing them from the furnace and allowing them to coûl in air.

After the run, the capsules were dried and weighed to determine whether leakage had occurred. The run products were first examined under a binocular microscope, and then petrographically, using oil immersion techniques. Percentage glass was estimated visually, often by a number of independent observers. It is likely that the visually estimated values are accurate to within 10 per cent (Piwinskii and Wyllie, 1968).

Petrographic identification of the crystalline phases was verified by the Debye-Scherrer powder method (Cukor radiation). More precise measurements were made using a Guinier-Hagg powder camera (Cukor), with quartz as the internal standard. The compositions and structural states of the feldspars were estimated directly from 20 values from ZO1, 060, and ZO4 diffraction peaks using the three peak method of Wright (1968). Unambiguously indexed feldspar reflections were then used as input into a Fortran IV version of Evans, Appleman, and Handwerker's (1963) least squares unit cell refinement program. Composition and structural state were again calculated using these data.

Dry melting experiments:

A tourmaline-bearing granite (1.7 wt. per cent B_2O_3) from the Boulder Batholith, Montana (Knopf,1952) was used in dry melting experiments at atmospheric pressure. An analysis of the granite powder #1697A, is given in Table 2, Appendix II. A few charges were purposefully contaminated with a slight excess of B_2O_3 which was ground with the granite powder. Unfortunately, the borate again formed a waxy paste that adhered to the walls of the mortar so that the amount of the addition could not be determined accurately. These charges were run alongside uncontaminated charges to observe the effect of added boron.

The granite powder was pulverized in acetone. Platinum crucibles of about 20mm in length, and welded at the base, were filled with powder. They were dried overnight in a vacuum oven.

Half of the capsules were welded shut and half were left unsealed. Sealed and unsealed capsules were run concurrently in an open $Pt_{60}Rh_{40}$ -wound furnace. The charges were lowered into the furnace in a platinum crucible. The run temperatures were measured with a $Pt-Pt_{87}Rh_{13}$ thermocouple positioned inside the crucible, level with the capsules but not in contact with them. The thermocouple was attached to the Pike digital voltmeter and was internally calibrated with an ice and water bath. Runs lasted several days, after which they were quenched in air, weighed and examined optically. Run products were then examined by X-ray powder techniques.

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RESULTS

Hydrothermal experiments:

The products of the experiments on haplogranitic materials with $B_2 O_3$ and water are given in Table 3, Appendix III. Values of 2θ for the 201, 060, and 204 X-ray diffraction peaks of the feldspars are given in Table 4, Appendix III, as well as the composition of the feldspars calculated using the linear relationship between Or content and $2\theta(201)$, employed by Tuttle and Bowen (1958), Orville (1967), and Wright (1968). Alternate values for composition were derived graphically from the relationship between Or content and a cell dimension (Wright and Stewart, 1968), and from the relationship between Or content and cell volume (Orville, 1967; Luth and Querol-Suñé, 1970). Luth and Querol-Suhé (1970) propose that both <u>a</u> and cell volume, \underline{V} , give more accurate values for composition than does 20(201); however, all estimates are in approximate agreement. Table 5, Appendix III, contains refined cell parameters for the feldspars of all runs in which feldspar is abundant enough to produce a fair number of X-ray diffraction lines. For convenience in the text, truns are classified according to their $B_2^{0}_{3}$ contents as follows: Group I), runs containing no B_20_3 ; Group II), those containing 1.5-2.0 weight per cent B₂O₃; Group III), those containing 4.5-5.0 weight per cent B_2O_3 ; and Group IV), those containing 8.5-10.0 weight per cent B_2O_3 .

In all runs there was evidence of the presence of a vapour phase. Partially melted charges formed a tough rounded bead. Whitish films of devitrification spread over the surface

within several seconds after opening, probably as a result of the escape of fluid. All charges emitted a rotten eggs odour when first opened. Tiny white-coated spheres of soft vitreous material (chalcedony or opal?) were found separate from the main charge in many capsules, in runs at subsolidus as well as solidus temperatures. It was assumed that these were vapour phase condensate, possibly of a siliceous nature, because they were found in capsules containing no $B_2^{0}_{3}$, as well as in those rich in $B_2 O_3$. Colourless idiomorphic laths were occasionally observed on the surfaces of sintered or melted charges. Most of these crystals were doubly terminated prisms with monoclinic, if not orthorhombic, symmetry and are possibly feldspar. One unique occurrence displayed a peculiar platy cleavage, or parting, and was extremely soft; this was probably a form of boric acid. A few charges of Group III that contained no water beside that introduced as boric acid (3-4 per cent H_20) also showed signs of abundant vapour; 3 per cent H_20 was thus enough to saturate the melts formed. In addition, it is likely that HBO_2 constitutes part of the volatile phase.

Crystalline products

Before describing the crystalline products, it is pertinent to mention that equilibrium was probably not fully attained in many of the experiments. Most of the bulk compositions studied lie in the $KA1Si_30_8-Si0_2$ - rich portion of the pseudoternary system, in which equilibrium is achieved with

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difficulty (Tuttle and Bowen, 1958). Piwinskii (1967) has suggested that minimum run durations of 8 to 10 days are necessary to bring granite compositions to equilibrium, even under hydrothermal conditions. Longer periods may be needed to approach compositional equilibrium among subsoludus phases in the alkali feldspar system¹ (Parsons, 1969). Subsolidus in the present study might be especially_ crystallization sluggish if reaction kinetics are complicated by the presence $\mathcal{I}^{\mathcal{F}}$ of quartz. The run durations of the present study rarely exceed 10 days. Some subsolidus runs showed evidence of incomplete reaction at the end of this time span; this may also be attributed to unexplained broad temperature fluctuations which occurred during only a few runs, as well as by inadequate run durations. Although the X-ray reflections from the crystalline products were generally sharp, occasionally the (201) (060) or (204) lines were diffuse, indicative or inhomogeneity or zoning. Very diffuse lines were most noticeably observed in runs bordering on, or within, the alkali feldspars solvus² (e.g.064b, D63b, F62b, D99, F98, O89, D88, and F87), and grade in intensity from relatively strong peaks on the low 20 side (corresponding to potash rich components) to broad, weak bands on the high 2θ side.

The crystalline phases produced in these experiments are high sanidine and beta quartz (Plates 1 and 2). Weak $\overline{2}01$

1. A state characterized by constant d-spacing for $\overline{2}01$.

2. Orville (1963) has noted the tendency for alkali feldspar glasses of intermediate composition to crystallize inhomogeneously which is independent of the position of the solvus. It was presumed that the present run durations were generally long enough to preclude this tendency, except in runs with temperature bulk composition coordinates very close to the solvus. Possibly this assumption is not justified.

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reflections from albite were detected in the powder patterns of several runs: F115 at 567°C, F119 at 119°C, 081, D80, and F78 at 655° C, and possibly D96 at 755°C, all with Ab:0r:Q = 30:30:40: 089, D88 and F87 at 637° C with Ab:Or:Q = 30:40:30; and D99 and F98 at 600° ć with Ab:0r:0 = 20:40:40. Unidentified, very highly birefringent phases appear in run products from GroupsIII and IV, generally in minute quantities dispersed throughout clusters of quartz and feldspar, or in glass. The optical properties of these phases resemble those of several hydrous alkali borates (Winchell and Winchell, 1964, p.114-116), but they could not be detected by X-ray diffraction. It seems likely that these borates are precipitated from the hydrous vapour upon quenching, and that their greater abundance in runs of higher borate content, in subsolidus runs especially, results from the saturation of the melt and silicate phases with boron.

It is noteworthy that among charges of the same Ab:Or:Q ratio, held at the same temperature, the Or contents of the feldspars produced, as calculated from $2\theta(\overline{2}01)$, and from <u>a</u> and \underline{Y} if possible, increase with B_2O_3 (bulk) providing the charges have bulk compositions with non-extreme Ab:Or ratios, i.e. runs with Ab:Or:Q = 10:60:30 and 10:50:40 do <u>not</u> show this relationship, whereas runs with Ab:Or:Q = 30:40:40 show it to the greatest extent. In addition, temperature is probably an important control on this effect, as it is not observed at all in charges run at 755°C, or above.

For each feldspar, the $2\theta(060)$ is plotted against 20(204) in Figures 1 (Group I) and 2 (Group II, III, and IV). The results are superimposed on the $2\theta(201)$ -contoured, $2\theta(060)$ versus $2\theta(\overline{2}04)$ quadrilateral given by Wright (1968) for series of isostructural alkali feldspars. All feldspars plot near or to the right of the high sanidine - high albite sideline of the quadrilateral. Even among feldspars of Group I runs, several show a normalous values of $2\theta(\overline{2}01)$ with respect to values estimated graphically from Figures 1 and 2^{1} . A comparison of Figures 1 and 2 shows that whereas $2\theta(\overline{2}01)$ obs. - $2\theta(\overline{2}01)$ est. graph. is invariably negative for feldspars of Groups II, III, and IV, the same value for feldspars of Group I varies from positive to negative, the mean and average values being positive. According to the linear relation between $2\theta(\overline{2}01)$ and derived by Wright (1968), anomalously low $2\theta(\overline{2}01)$ values а correspond to a cell dimensions that are higher than those predicted from values for <u>b</u> and <u>c</u>. Refined cell parameters, plotted onto a c versus b quadrilateral contoured for values of <u>a</u> (Wright and Stewart, 1968), give anomalous values for a^2 and also fall to the right of the high sanidine - high albite sideline (Figs. 3, 4, 5, and 6; Table 6). <u>aobs. - aest.graph.</u> (Table 6) is positive for most feldspars of Groups II, III, and IV, but is less consistent in sign for feldspars of Group I, thus confirming the previous observations. Luth and Querol-Suñé (1970)

1. $2\theta(\overline{2}01)$ observed differs from the value predicted from the contours of the $2\theta(060) = 2\theta(\overline{2}04)$ quadrilateral by $\cdot 1^{\circ}$ or more (Wright, 1968).

2. <u>a</u> observed differs from the value, predicted from the contours on the <u>b</u> - <u>c</u> quadrilateral by .02 A, or more (Wright & Stewart,



Figure 2: 28(060) plotted against 28(204) for feidspars of Groups II, III, and IV, superimposed on a portion of the 28(201)contoured quadrilateral derived by Wright (1968). Open circles represent feldspars of Group II, triengles represent feldspars of Group III, and squares represent feldspars of Group IV. Solid symbols are described in Figure 1.

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Figure 4: <u>b</u> - <u>c</u> coordinates of the feldspars of Group II, plotted on a portion of the a-contoured quadrilateral of Wright and Stewart (1968) modified after Stewart and Ribbe (1969). Error bars represent \pm one standard deviation of the cell parameter.


Table 6: Refined 'a' cell parameters compared with those estimated from an 'a'-contoured,'b"d quadrilateral (Wright and Stewart, 1968, Fig. 2b).

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Number	Group	'a'observed	'a' estimated graphically	difference
[`] €059		8.55 Å	8.48 Å	.07 Å
09	o - I	8.55	8.54	
₩073	I	8.57	8.53	.04
0103	I	8.54	8.52	
022	I	8.53	8.52	0 V
076	I	8.53	5.54	
~068a	T	8.52	8.49	. 03
~067a	I	8.55	8.58	03
∻064 Ъ	I	8.43	8.47	04
089	I	8.44	~. 43	υ
~ 085	, I	8.50	8.56	06
÷081	í	8.45	8.41	. Ô4
097	I	8.44	8.44	
*D57	II	8.55	ک ۰4 6)	.09
D16	Ĩ	8.54	8.52	. •
~D102	II	8.5 4	8.50	. 0 [°] 4
-•• D14 [°]	II	٥.56	8.48	.08
D75	" ' II	8.55 "	8.54	
∻D 99	II	₹.51 گ	8.45	.06
*D66a	, II		8.49	. 03
D63b	` II	∘ ° 8.44 。	8.46 -	•

* anomalous values of'a'as defined by Wright and Stewart (1968), i.e, those with a discrepancy of greater than 0.02 A between observed and estimated values

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Table 6: continued...

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	Number	froun	1a1	observed	'a' ° øra	estimated phically	difference
-	D88	TI	4	0.501 Veu 0. 8.44 A		8.46 Å	
	D80	u II		्रह् 8.44 ⁰		8.46	, i i i i i i i i i i i i i i i i i i i
	D96	II		8.47	_ît'	8.50	03
	∻ F 5 3 ^	- III ÷		8.55		×.51 °	.04
•	~F17	ŢĪĪ		8.54	(1	8.48	• .06
and a second	F101	111		8°55 🔋 💈		8.54	
	F74.	`III		8.55	_	8.55	
	≁F98 ́.	, III [©]	U	8.49		5.46	· · 03
	。 F64a	° III		8.52	ر ، ب <u>ل</u> ے	8.53	·
	*F62b	III		8.52		8.55 🖙	 03
	F87	III	, <i>1</i> 2	8.49		8.48	
	*F83	رم III		8.51	•	۲.57	 06
-	-F78	III		8.53	~	8.46	. 07
		111		8.57	3	8.50	.07
	[¢] F104	111		8.55	¢ 1 _	8.42	.13
	₹F 119 、	III		8.48	5. 2 [°]	8.43	.05
2	[≉] ∕, ≁T55 y	IV	•	8.58	i ES	8.50	.08
	<u>"</u> Т7,	IV		8.53 ·		8.50	. 03
- -	**T 2 1	IV		8.57 ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	¢	8.52	. 05*
U	*T77 -	IV .		8.56		8.52	.04
	T123	IV		8.52	ſ	8.52	(

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* anomalous values of 'a' as defined by Wright and Stewart (1968), i.e, those with a discrepancy of greater than 0.02 A between observed and estimated values.

found that the <u>b</u> - <u>c</u> coordinates of a series of synthetic alkali feldspars, prepared by the hydrothermal crystallization of dessicated peraluminous persilicic gels similarly fell to the right of the high sanidine - high albite sideline, apparently of higher structural state than the limiting high sanidinehigh albite series of Orville (1967). This behaviour resulted from <u>b</u> cell edges that were larger than those of **compositionally** equivalent disordered feldspars studied by other authors (e.g., Orville, 1967), together with slightly larger <u>c</u> cell edges and 'normal' <u>a</u> dimensions; therefore, when their <u>b</u> and <u>c</u> parameters are plotted on the <u>a</u>-contoured <u>b</u> - <u>c</u> quadrilateral of Wright and Stewart (1968), predicted values of <u>a</u> are higher than those observed i.e., <u>aobs.</u> - <u>a</u>est. graph. is negative, in marked contrast to the behaviour of feldspars from the boronbearing runs of this study.

In an attempt to isolate the possible effects of boron substitution from the effects resulting from varying alkali content, a <u>c</u> versus <u>b</u> diagram was prepared for Group III feldspars within the compositional limits $0r_{50} - 0r_{90}$ (Fig. 7). The resulting plot exhibits a linear trend which diverges slightly in a counterclockwise fashion from the high sanidine - high albite sideline of Wright and Stewart (1968), indicating reduction in both <u>b</u> and <u>c</u> cell parameters. This trend resembles the oblique trend found by Martin (1971) for disordered boriferous potash feldspars, but due to the lack of supporting data on boron and alkali content determined by chemical analyses in the present case the resemblance may be fortuitous. Although plots of cell

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Percent Of

Figure B: Cell volume, V, plotted against percent Or, estimated from a (Wright abd Stewart, 1968). Open Fircles represent feldspars from Group I, crosses represent feldspars from roup IF, triangles represent feldspars from Group III, and squares represent feldspars from Group IV. bolid symbols represent stoichiometric feldspars on the join KALSi3O8-KBSi3O8, prepared hydrothermally at P(H2O) = 1 kilobar by Martin (1971). Percent boron and member is indicated on the right of each symbol.

volume versus composition, as estimated from a reveals no significant difference between feldspars of boron-bearing and non boron-bearing runs, two Group III feldspars, T104 and F78, do plot on the low volume side of the general trend (Fig. 8), exhibiting a volume reduction similar in magnitude to the volume reduction shown by the synthetic feldspars containing 5.5 per cent $\text{KBSi}_{2}0_8$, prepared by Martin (1971). This feature can most easily be explained by a proportionally greater reduction in \underline{b} and \underline{c} than in the <u>a</u> cell edge, which is <u>linearly</u> related to the Or content in normal feldspars, (a relationship assumed in Figure 8 for reasons explained in the discussion later). The <u>a</u> of these feldspars may or may not differ significantly from the a cell dimensions of feldspars of equivalent alkali contents. Unfortunately, the refined cell parameters of F75, have unacceptably large standard errors; however, the <u>b</u> - <u>c</u> coordinates of T104 on Figures 5 and 8 show it to have low <u>b</u> and <u>c</u> cell edges with respect to <u>a</u>, which is anomalously high (Fig. 5). Other feldspars with anomalously high \underline{a} cell edges do not seem to show a similar reduction in volume, even though their \underline{b} and \underline{c} parameters plot below the high sanidine high albite sideline. Much of the volume decreases may be lessened by a readjustment of the axial angle β , and perhaps the other axial angles.

The magnitude and quality of the relationship between boron content and the departure from normalcy of the feldspars of the present study may be obscured for several reasons: the

maximum range of boron content among the feldspars, as well as the maximum absolute value, both unknown, are intuitively relatively low; moreover, an apparent correlation would be .more reliable if equilibrium had been ensured.

Melting behaviour:

Crystals from supersolidus runs are distributed throughout clear colourless glasses, whose indices of refraction vary within the narrow limits of 1.475-1.452. The values correspond to the values which can be expected for a broad range of the NaAlSi₃0₈-KAlSi₃0₈-Si0₂ compositional field (Schairer and Bowen, 1955: 1956). It was felt that the melts formed just above the solidus of Groups III and IV runs might be borate-rich. However, as the refractive indices of silica glass and orthoborate glass are almost identical, being 1.588 and 1.58, respectively, (Morey and Merwin, 1936), and as the refractive indices in both alkali borate and alkali silicate systems increase with increasing alkalis, it would be very difficult to distinguish optically between borate-rich and alkali-rich glasses. Runs that, at 600°C or lower, contained clear glass patches separate from clusters of crystals, or crystals and glass, were discarded because it was concluded that some of the fused starting material had not reacted.

The experiments were not arranged in the manner most suitable for bracketing the beginning-of-melting temperatures of each of the 36 compositions. Each run set (contents of one

hydrothermal vessel held at a specific temperature) was composed of four capsules containing granitic material with the same Ab:Or:Q ratio, but with B_2O_3 contents ranging from 10 per cent (Group IV) to 0 per cent (Group I). The Group I charge in each set was used as a control, since relations in the pure system are known. The solidus temperatures for Groups I, II, III, and IV, runs differ considerably, so that more information regarding the minimum melting behaviour would have been obtained if the experiments had been augmented by additional run sets, each containing charges of the same group, but with different granite compositions. Unfortunately, problems adjusting the Ether controlling devices made the achievement of the lower temperatures required to bracket the solidus temperatures of Groups III, and IV difficult.

The melts expected just above the solidus temperatures for bulk compositions used in this study, having Ab:Or ratios (weight) from 1.0 to 0.167, will lie in the thermal trough which separates the primary phase fields of guartz and feldspar in the isobaric Ab-Or-Q-H₂O phase diagram (Tuttle and Bowen, 1958). The maximum temperature difference along this cotectic between the point of intersection with the quartz-orthoclase binary to the ternary minimum is approximately 40° C (taken from the data of Tuttle and Bowen, 1958). The difference in temperature between the solidus of the most orthoclase-rich bulk composition and that of the most albite-rich bulk composition used in this study would be 20° or less in the pure system. On the assumption that

this is also the case for the compositions of Groups II, III, and IV, generalized beginning-of-melting temperatures ranges were estimated from the results (Table 3). Thus, the approximate range of the solidus temperatures in Group I compositions would be 720-740°C, and that of Group II compositions would be 660-680°C. The solidus range for runs of Group III should be approximately 610-640°C -- grain mounts of F122 showed evidence of a partial melt in some grains, while some of the material appeared incompletely reacted, probably due in part to the large temperature iluge tuation. The solidus range for runs of Group IV is harder to define as most compositions in this group were run only above their solidus temperatures, except those with Ab:Or:Q = 30:30:40 (one at 30:40:30) which are totally crystalline at temperatures up to $567-5^{\circ}C$, but partially melted (35-40 per cent glass) at $595-15^{\circ}C$ (T123). From the amount of glass produced at this temperature, it seems likely that $595-15^{\circ}C$ is close to the solidus for this particular composition, and is at the lower end of the range of solidus temperatures. Minimum melting temperatures (beginning-of-melting temperatures for compositions projecting onto the central portion of the Ab-Or-Q compositional field, expected to be at the lower limit of solidus temperatures for each group) are plotted against per cent B_2O_3 bulk in Figure 9. The resulting curve flattens as the bulk composition reaches 10 per cent $B_2 O_3$, suggesting that melts of the compositions produced in these experiments approach saturation in $B_2 O_3$ in runs of Groups III and IV. This is in accordance with the increasing appearance of borates in Groups III and IV runs.

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Figure 9: Minimum melting temperatures for haplogramites at P(fluid) = 1 kilobar plotted against B_2O_3 content in the presence of excess water.

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Dry melting experiments:

The results of heating tourmaline granite, #1697A, in an open furnace, are listed in Table 7, Appendix IV. Compositions of alkali feldspars from several runs, estimated using the linear relationship between $2\theta(\overline{2}01)$ and 0r content (Wright, 1968), are also given in Table 7. The original granitic powder consists of dark green tourmaline (20-25 per cent), quartz, microcline ($0r_{05}$, Spencer U equivalent), and The feldspars, particularly the albite, minor low **al**bite. are occluded with sericite or another fine-grained green mineral. On heating, the microcline reequilibrates compositionally, as shown by a decrease in Or content from $0r_{75}^{1}$ at 841° C to $0r_{64}$ at 1,005°C (Fig. 10), and partially disorders to Spencer B equivalent (Fig. 11). This structural state then persists metastably to higher temperatures until feldspar disappears as a supersolidus phase. The albite undergoes a less regular compositional change, becoming more potash-rich at higher run temperatures. In the lowest temperature experiments, hematite appears as a coating on the surface of an unidentified high relief green mineral, apparently nonpleochroic and nonbirefrigent, which may represent a stage in the breakdown of tourmaline. A peak corresponding to the (122) reflection of tourmaline is observed in the X-raypowder pattern of the products of runs held at temperatures of up to $877^{\circ}C$ (#49); however, no unaltered tourmaline is observed optically in runs held at temperatures

1. The microcline from this run produces two $\overline{201}$ reflections, one corresponding to $0r_{75}$ and the other to $0r_{90}$. It is probable that the feldspar had incompletely equilibrated and is inhomogeneous, or zoned with a potash-rich core, or that the feldspar is beginning, on the outside, to break down at temperatures approaching the solidus.

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Figure 10:28(060) plotted against $28(\overline{2}04)$ for potash feldspars obtained from dry melting experiments on tourmaline granite #1697A, superimposed on the $28(\overline{2}01)$ -contoured quadrilateral derived by Wright (1968). Superscripts indicate corresponding $28(\overline{2}01)$ value and subscripts indicate run number.



Figure 11: Composition of potesh-rich feldspars versus run temperature for dry melting experiments on tourmaline gramits #1697A.

above 841° C. The beginning-of-melting marks the first appearance of an unknown acicular mineral of relatively high relief (with respect to the glass in which it is usually embedded) and weak blue-green pleochroism. It occurs in fibrous bundles, invariably accompanied by hexagonal plates of hematite, and often by feldspar or quartz, (Plate 3). This phase may be the wellformed equivalent of the unknown green mineral mentioned above, and therefore may represent a final product of the breakdown of tourmaline. Nevertheless, an X-ray reflection of 16.45-16.50° $2\theta(CuK\alpha_1)$ is uniquely diagnostic of the presence of the acicular phase, and is observed only in coincidence with the occurrence of fibrous bundles and melt. X-ray powder data for this mineral, extracted from the diffraction patters of runs C15 and 014 $(1,100^{\circ}C)$, are given in Table 5, Appendix V. This mineral is probably a form of mullite, close in composition and structure to that studied by Durović (1962), with $A1_20_3$: Si 0_2 = 1.7:1.

Melting begins in the temperature interval $858^{\circ}-877^{\circ}C$. A very small amount of glass appears after 10 days at the latter temperature. Quartz, microcline, albite, hematite, and mullite(?) coexist with melt, with both feldspars disappearing between $1,005^{\circ}$ and $1,095^{\circ}C$. It must again be mentioned that the products from these experiments cannot be interpreted as representing equilibrium, as reactions are more sluggish than under hydrothermal conditions (e.g. Schairer, 1950), and only an approach to equilibrium can be cited. The production of melt, the disordering of Al and Si in the feldspars and their compositional readjustment are time

dependent processes that are sluggish even in hydrothermal experiments (Piwinskii and Martin, 1970).

It is interesting to note that none of the unsealed charges showed weight loss on heating, even at temperatures above the breakdown temperature of tourmaline. Run products were essentially the same whether the capsules were sealed or left open.

DISCUSSION

Effect on feldspar structure:

From a study of the cell dimensions of feldspars produced in the experiments on haplogranitic compositions, it has been shown that the presence of boron may cause preferential reduction of the b and c cell parameters, occasionally accompanied by a noticeable decrease in unit cell volume. In normal alkali feldspars all cell dimensions, a, b and c, as well as volume, \underline{V} , decrease with increasing substitution of Na for K; however, a and V are much more sensitive indicators of K/(Na+K) than are <u>b</u> and <u>c</u>, especially so in the Or-rich portion of the system (Wright and Stewart, 1968, Fig.1). Martin (1971) noted a greater reduction of <u>b</u> and <u>c</u> relative to a in disordered authigenic potash feldspars, and found that the Or content of these feldspars as determined from a was close to that determined from chemical analyses. (It was for this reason that it was assumed in this study that a could be used to estimate per cent Or.¹). He also found that the reduction in <u>a</u> between pure KA1Si $_{3}0_{8}$ and K(A1,B)Si $_{3}0_{8}$ with 5.5 per cent of the boron end member (structurally slightly more disordered than the natural feldspars) was only .02 per cent, a value within the standard error of the refinements. As chemical analyses of the feldspars from the present study are unavailable, it is impossible to determine directly whether or not <u>a</u> is reduced with respect to normal feldspars of equivalent alkali content. It may be argued that if a were reduced by boron substitution

1. In reference to the assumptions made in Figures 7 and 8 previous section.

at a rate equivalent to that of <u>b</u> and <u>c</u>, a plot of <u>b</u> - <u>c</u> coordinates on the <u>a</u>-contoured, <u>c</u> versus <u>b</u> plot of Wright and Stewart (1968) would indicate non-anomalous to anomalously low values for <u>a</u> rather than the anomalously high values observed.¹ Thus it is tentatively concluded that <u>a</u> is reduced to a lesser extent than <u>b</u> and <u>c</u>, and that it can still be used as an indicator of Or content at low concentrations of boron, though with less accuracy.

Martin (1971) demonstrated that a reduction of cell edges in disordered potash feldspars reflected the substitution of B for Al in the feldspar framework, and that synthetic sanidines of the system KBSi₂0₈- KA1Si₃0₈ show volume reductions directly proportional to the amount of boron end member in solid solution. Since these feldspars appear to be fully disordered, one might consider the simplest case, where boron enters equally into each tetrahedral position occupied by aluminum i.e., randomly distributed among the four tetrahedral sites, T_1^0 , T_1^m , T_2^0 , and T_2^m . Due to the smaller size of boron, this scheme of substitution would probably result in a roughly equivalent decrease in all cell dimensions, the number of tetrahedral sites per Å being approximately the same in all crystallographic directions: <u>a</u> contains .47 T/A b contains .46 T/A, and \underline{c} contains .43 T/A. Any inequality in the rate of reduction should then be toward greater decrease in a and b than in \underline{c} , which is contrary to the observations for the feldspars

1. Since da/d(0r) is greater than db/d(0r) or dc/d(0r) in normal feldspars, then a estimated from the a-contoured, <u>b-c</u> quadrilateral from the reduced <u>b</u> and <u>c</u> cell parameters would be greater than the observed value if da/d(B) = db/d(B) = dc/d(B).

from this study (Table 9) and for those prepared by Martin (Table 10), and also for the relations between the cell dimensions of reedmergnerite and those of low albite. In going from low albite to reedmergnerite the per cent reduction in <u>a</u>, <u>b</u>, and <u>c</u> are 4.14, 3.32_{a} and 4.96 per cent, respectively, whereas the \underline{a} , \underline{b} , and \underline{c} parameters of Martin's disordered potash feldspars are reduced by .15, .31, and .45 per cent, respectively, in going from boron-free sanidine to sanidine containing 18 per cent KBSi308 (data from Martin, 1971). Both the reedmergnerite low albite system and the boriferous sanidine system show the reduction of \underline{b} and \underline{c} in approximately the same ratio, although in the first case a comparison is made between pure ond members; with potash feldspars, the comparisons are made among the feldspars of a continuous series along the $\text{KBSi}_{2}0_8$ -KAlSi $_20_8$ join, with a limiting composition of 18 per cent $\text{KBSi}_3^{0}_8$. Thus, in the consideration of the behaviour of boron the fundamental difference between the two systems is that in the feldspars of this study and of Martin's study aluminum is present in greater molecular concentrations than is boron, whereas reedmergnerite contains no aluminum.

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The problem of determining how boron fits into the alkali feldspar structure bears directly on the validity of <u>a</u> as an estimator of K/(k+Na) in the potassic feldspars. The question can be simplistically approached as proposed by Stewart and Ribbe (1969) in their account of the variations of cell

Charge number	<u>a</u>	b	<u>c</u>	<u>v</u>
T104	8.5462 X .0026	13.0053 .0039	R 7.1570 R .0016	714.63 8 ³ 0.28
) 067a	8.5469 .0021	13.0244 .0034	7.1779	718:37 0.27
. 0103	5417	13.0213 .0016	7.1702 .0010	716.32 0.17
09 -	8.5498 .0017	13.0283 .0025	7.1686 .0014	717.27 0.18
Transition to T104 from:	A b	%	Å <u>c</u> %	- A ³ V %
067a	-0.0191' <u>+</u> .0073	-0.147 / - +.056	-0.0209 -0.291 $\pm .0036 \pm .050$	-3.74 -0.521 +0.55 +.077
.01 03 **	-0.0160 <u>+</u> .0055	-0.123 +.042	$\begin{array}{r} -0.0132 \\ \pm .0026 \\ \pm .036 \end{array}$	-1.69 -0.236 $\pm .45 \pm .063$
09*	-0.0230 <u>+</u> .0064	-0.176 - <u>+</u> .049	$\begin{array}{c} -0.0116 \\ \pm .0030 \\ \end{array} \begin{array}{c} -0.162 \\ \pm .042 \end{array}$	-2.64 = -2.64 $\pm .46 = -0.368$ $\pm .064$

Table 9: Comparison of cell dimensions of T104 with feldspars

from this study with similar values of \underline{a}^*

* Standard error is reported below each value

** The <u>a</u> cell dimensions of these feldspars do not coincide exactly with that of T104, within the margins of error quoted. Therefore they should not be directly compared, only as approximations of the nature of shrinkage.

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Table 10: Comparison of cell dimensions of feldspars along the join KBSi308 - KA1Si308*

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Percent KBSi ₃ 08	a	<u>b</u>	- <u>c</u>	<u>v</u>	<u>a</u> (percent)	<u>b</u> (percent)	(percent)	$\underline{V}(percent)$
0.00	8.6034 ±.0010	13.0234 <u>+</u> .0018	7.1812 <u>+</u> .0007	723.14 ±.09				ð
5.51	8.6017	13.0112 .0015	7.1711	721.34 0.11	.0017 ±.0019	.0122(0.094) $\pm .0028(0.022)$.'0101(0.141) ±.0014(0.020)	1.80(0.249) ±.20(0.028)
9.68	8.6002	12.9979 .0011	7.1634	719.68 0.08	.0032(0.037) .0016(0.019)	.0255(0.196) .0024(0.018)	.0178(0.248) .0013(0.018)	3.46(0.478) .17(0.023)
18.10	8.5908	12.9827 .0013	7.1486 .0011	716.55 0.14	.0126(0.146)	.0407(0.312) .0026(0.020)	.0326(0.454) .0018(0.025)	6.59(0.911) .23(0.032)
	*	*	\$	١		*		•

* (a

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* Data taken from Martin (1971). Standard error is reported below each value.

parameters <u>a</u>, <u>b</u>, and <u>c</u> with degree of structural disorder. Disordered feldspars are considered to have completely random distribution of one aluminum and three silicon atoms among the four potentially non-equivalent tetrahedral sites in each formula With increasing order, aluminum concentrates first in unit. the mirror-related T_1 sites $(T_1 0 \text{ and } T_1 m)$ in a monoclinic phase, and then tends to concentrate in the T₁0 site, at which point the structure converts from monoclinic to triclinic symmetry (Brown, 1962). Both steps overlap to a certain extent. Therefore, "the Al occupancy of all T sites in a disordered structure will ideally be .25, but the Al occupancy of the T_20 , \P_2m , and T_1m tends to 0 as that of the T_10 site approaches 1.0 in the ordered In following a path in the a direction of the feldspar structure. framework, either two T_10 's, one T_20 , and one T_2m , or two T_1m 's, one T_2^0 , and one T_2^m will be encountered; in following a path along the <u>b</u> direction one T_1^0 , one T_1^m , two T_2^0 's, and two T_2^m 's will be encountered; and finally, in following a path in the \underline{c} direction one T_10 , one T_1m , and either one T_20 or one T_{2m} will be encountered. Significant differences in axial dimensions will be caused by varying the lengths of the T-O bonds of the tetrahedral ions occupying these sites, and will be the direct result of varying the long-range Al/Si distribution among these sites (Stewart and Ribbe, 1969), or of substituting a different tetrahedral ion, such as boron, with a B-O bond length shorter than either A1-0 or Si-0, into the structure. By arguments analogous to those of Stewart and Ribbe (1969), the sole manner

in which boron can substitute for aluminum in the framework and cause a greater reduction in <u>c</u> than in <u>b</u> is to enter only T_1 This is known to be the case in the reedmergnerite sites. structure, in which boron occupies T_1O sites (Appleman and As synthetic reedmergnerite shows the same Clark, 1965). powder pattern as natural, ordered reedmergnerite (Eugster and McIver, 1959), it may be impossible for boron to enter sites other than T_1O in soda-rich feldspars. This seems reasonable for potash feldspars as well, in view of the similar electron orbital configurations of boron and aluminum, and the slightly greater electronegativity of boron. Thus, in a structure disordered with respect to trivalent tetrahedral sites, the limit of B-for-Al substitution would be reached when B/(A1+B). .25 if substitution is restricted to T_1^0 , or .50 if substitution is restricted to T₁ sites. Simple substitution of boron into the T_10 site or into both T_1 sites, would lead to a reduction in a that is intermediate in magnitude between that of \underline{b} and \underline{c} (ratio of T_1/T_2 sites is $\frac{1}{2}$ along \underline{a} , $\frac{1}{3}$ along \underline{b} , and $\frac{2}{3}$ along \underline{c}). On the other hand, if the substitution of B for Al in the T_10 site is coupled with a transfer of Al from T_1m to adjacent T_10 sites in exchange for Si, the length of <u>a</u>, a direct function of the lengths of bonds that have large components in the a direction, will be decreased by only an amount equivalent to the total replacement of Al by Si in both T₁ sites, because the sum of B-0 and Al-0 bond lengths equal twice the Si-0 bond length.¹ This type of 'compensated' substitution may predominate

1. The average B-0 distance in reedmergnerite is 1.465 Å, whereas the average Si-0 and A1-0 bond lengths in albite are 1.613 and 1.744 Å (Appleman and Clark, 1965). (A1-0) + (B-0) = 3.209, and 2X (Si-0) = 3.226 Å.

at-low concentrations of boron. At higher concentrations, in a structure with equal numbers of trivalent ions in T_1 and T_2 sites, boron substitution would become uncompensated for size, especially when the boron occupancy of T_1 sites reaches .25, and probably somewhat below this level. As a result, the <u>a</u> cell edge would decrease at a higher rate than with more limited boron substitution. Boron may begin to substitute in T_2 sites at these concentrations, or alternatively aluminum may leave T_2 sites in exchange for silicon, thereby increasing c and \Rightarrow decreasing <u>b</u>. For perfect substitution of the latter type, the unit cell may appear monoclinic at B=.50. It is noteworthy that most of the decrease in a between the pure potash feldspars and that containing 18 per cent boron end member, synthesized by Martin (1971), occurs in going from 9.8 per cent boron end member to the 18.1 per cent boron end member (Table 10), in agreement with the former suggestion.

As a consequence of the substitution of boron into T_10 sites, the unit cell of these feldspars would become triclinic, as the mirror plane would be violated. With this prediction in mind, the cell parameters of feldspars that had shown large standard errors when refined as monoclinic cells were re-refined assuming triclinic cells. The second set of refined cell parameters fell within the standard errors of the previous refinements, and improvement was noted only for D96, F62b, D80, and to a lesser extent for 081. α and δ fell within 5' of 90° in

1. Compare cell parameters of F78 from Table 5 - not very reliable because of high standard errors.

all cases (Table 5, Appendix III). Cell parameters of F78 showed higher standard errors when re-refined in this way, although it appears from the volume reduction (Fig.8) that the feldspars from this run contain considerable boron. The apparent retention of monoclinic character in F78 could be explained by the decrease in Al occupancy of T_2 sites, mentioned above. This would mean that the <u>a</u> cell dimension is somewhat reduced with respect to that of a feldspar with similar alkali content, i.e., the Or content would be higher than that indicated from the <u>a</u> cell edge, and consequently the volume reduction would be increased as compared to pure binary feldspar with the same alkali content.

Regardless of the validity of any of the arguments posed to explain how boron fits into the feldspar structure, such substitution is suggested by the anomalous cell parameters, and also by the tendency of runs containing $B_2 \theta_3$ to yield feldspars enriched in potash over those of borate-free runs held at the same temperature, although this may have alternative explanations.

Effect on partitioning of alkalis:

Orville (1963), in his investigations of alkali exchange between feldspars and aqueous chloride-bearing vapours, found that the distribution of alkalis between fluid phases and coexisting feldspars is strongly temperature dependent, but almost independent of the physical state of the fluid, i.e, the partition of K and Na between crystals and water-saturated melt resembles that between crystals and dilute aqueous chloride

solution with the same dependence on temperature (illustrated in Figs. 11 and 12 of Orville, 1963). At lower temperatures, the hydrothermal fluid is persodic, with a corresponding depletion of Na in the feldspars. Iiyama (1965) suggested that the anion of the aqueous solution has some effect on the partitioning of alkalis in hydrous systems, showing that the essence of Orville's normalized alkalı distribution curves was maintained tor solutions of C1⁻, I⁻, SO_4^{-2} , and CO_3^{-3} -bearing Na and K salts, but that the curves were shifted according to the valence of the anions and the degree of dissociation of the Na and K salts in solution. The valence factor seems to predominate in his experiments, the divalent anions tending to shift the equilibria toward higher Na content of the fluid phase and a corresponding enrichment of k in the feldspar phase (see Fig.2). According to Bachinski (1972), Na enrichment in the fluid phase . (aqueous) is due to the higher 'solvation energy' of Na relative to K, and it follows that the equilibrium will be shifted by any factor that effects the solvating characteristics of the fluid medium, such as temperature and the anion species in solution.

In the present experiments, the potash enrichment in feldspars from charges containing $B_2^{0}_{3}$ over those from boratefree charges with the same granitic constituents run at the same temperature and pressure, suggests that the effect of a volatile borate in the presence of steam is equivalent to that of a

divalent anion in solution (perhaps implying that the volatile, borate species is HBO_3^{-2} under these conditions). Another factor to be considered here is the entry of boron into the feldspar structure, which will in turn affect the stability of the crystal, and therefore the equilibrium composition of coexisting phases. It is difficult to evaluate the relative importance of these two factors. However, a shift of the solvus curve in the direction corresponding to the shift of the alkali distribution curve towards potash enrichment in the crystals is indicated by subsolvus runs 081, D80, and F78 at 055°C; therefore, it is probable that crystal chemical principles may exert some influence on the alkali distributions involving feldspars.

In the same manner as a thermal gradient may be invoked as a driving force for alkali exchange in two-feldspar rocks (Orville, 1963), it is possible to invoke gradients in boron content of volatile phases as a driving force for the alkali metasomatism reported in Cornwall and Devon granites, known to have experienced sporadic influxes of boron-rich vapour. Textural evidence for the replacement of plagioclase and the constituents of aplite by potash feldspar megacrysts and perthite has been cited by Exley and Stone (1964). In the same rocks, Brammel (1923) described the replacement of the albite lamellae in perthite by tourmaline, and of biotite by secondary tourmaline (accompanied by the release of K), suggesting that many simultaneous reactions, with the aid of thermal gradients and a volatile phase could contribute to the compositional gradients necessary for the autometasomatic processes invoked

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by Exley and Stone (1964). For example, influxes of boriferous pneumatolytic fluids would tend to induce reactions that increase the potash content of the Teldspar, though reduction of the concentrations of volatile borates by the crystallization of borosilicate minerals, such as tourmaline, would probably induce the reverse effect. Influxes of boron-bearing vapour along shear zones in the Neillsville area may be responsible for the development of microcline in the vicinity of these zones, as suggested by Gore (1968), although it seems improbable that a hydrated borate ion is the transporting agent for the potash required, as she has tentatively proposed.

In addition, the solidification of granitic magmas that are relatively rich in boron may produce alkali feldspars that are unusually high in potash, coexisting in a two-feldspar granite with a soda-rich plagioclase, and with a volatile phase enriched in Na. In this context, an investigation of the effect of $B_2 0_3$ on phase relations in the 'granodiorite' system might be fruitful.

Effect on melting behaviour:

A comparison of Figure 9 of this studyl with Figure 4 of Wyllie and Tuttle (1961) indicates that the introduction of B_2O_3 has an effect on the minimum melting temperature of the water-saturated granite system similar to that of HF. The figures are not directly comparable, since the experiments of Wyllie and Tuttle were performed at $P(H_2O)= 2750$ bars; also, the values on the abscissa of Figure 4 are in weight per cent

HF in solution, but since the HF-bearing capsules are prepared with a 1:1 ratio of silicate to solution, values comparable to those of the present experiments (per cent B20, recorded as weight per cent of dry ingredients) can be obtained by multiplying the values on the abscissa by $\frac{100}{100 + \% HF \text{ solution}}$. The granite minimum is depressed by 60° C with the addition of 2 per cent B_2O_3 and $100^{\circ}C$ with the addition of 5 per cent B_2O_3 at $P(H_2O)=$ 1 kilobar, whereas the addition of 5 per cent HF depresses the minimum by approximately 70° C at P(H₂O)= 2750 bars. A melting point depression of the magnitude caused by 2 per cent $B_2 0_3$ would be equivalent to that caused by an increase in $P(H_20)$ of 2 kilobars (from the data of Tuttle and Bowen, 1958), corresponding to, an increase in depth in the earth's crust of about 7 km (from the relation given by Verhoogen et al, 1970, Chapter 9). It is therefore evident, as in the case of HF, that B_2O_3 partitions more strongly in the melt than in the solid or volatile phases.

The beginning-of-melting temperature for tourmaline granite, #1697A, is about 80 to 90° lower than the accepted value ($960^{\circ}C$) for normal granitic rocks at 1 atmosphere, cited by Piwinskii and Wyllie (1968). However, because the first melt was derived from the breakdown of tourmaline to a mullitelike phase and hematite plus melt, and not from the breakdown of quartz and feldspar, a close comparison between #1697A and a haplogranite model is not strictly valid; the sample is compositionally similar to the Westerly granite used by

Tuttle and Bowen (1958), but is slightly poorer in alkalis.¹ It is possible that the first melt be prevented from reacting with the other phases because of the high viscosity of the dry boraluminosilicate melt and/or that the melt is metastable with respect to components of the other phases. Feldspar appears to be breaking down at 898° C, and a drastic increase in the amount of melt at 941° C indicates that the feldspar has partially melted at this temperature. There is, therefore, some depression of the solidus with the addition of B_20_3 , but the magnitude of the effect cannot be evaluated from experiments on this rock alone.

3.

Melting in this rock could not occur before the breakdown of tourmaline releases boron to the system. In addition, its seems possible that the mullite-like phase could incorporate some of the boron, preventing its participation in melting phenomena. The occurrence of solid solution between mullite and sillimanite has been discussed by several authors (e.g. Agrell and Smith, 1960; Hariya, Dollase, and Kennedy, 1969). The following observations suggest that borate, too, could be involved in solid solution in the system:

- 1. An artificial boraluminate, $2B_2O_3$. $10A1_2O_3$, crystallographically similar to sillimanite and mullite has been described (Baumann and Moore, 1942).
- 2. Sillimanite containing .30 per cent B_2O_3 has been reported from Madhya Pradesh, India (Varley, 1965). B_2O_3 is rarely included in chemical analyses, so that it is not known whether such borate concentrations are common.

3. Christophe-Michel-Levy (1950) has reported that a sillimanite-like phase can be synthesized from its components at $450-500^{\circ}$ C at P(H₂0)= 500 bars in the presence of 20 per cent Na₂B₄0₇.10H₂0. It seems

likely that some boron is incorporated in the structure. The X-ray reflections and cell parameters from the aluminosilicate produced in these experiments correspond superficially to those of 1.71:1 mullite and synthetic mullités characterized by Agrell and Smith (1900). In plots of unit cell volume, \underline{V} , versus cell edge, \underline{c} , they fall between the ranges of natural iron- and titanium-bearing mullites and natural sillimanites, whereas in plots of the axial ratios $\underline{a}/\underline{b}$ versus $\underline{b}/\underline{c}$ they fall far outside the fields of all of the aluminosilicates studied. This posgs-a complex crystallographic problem outside the scope of the present study. Perhaps a detailed study of these phases would indicate that the occurrence of boron in aluminosilicates is one of the many factors influencing aluminosilicate stability in metamorphic rocks, particularly in metapelites of marine origin.

Possible effects of pressure and composition on the behaviour of boron:

The review of the structural state of boron in borosilicate melts and glasses, presented in the introduction, revealed that boron tended to adopt four-coordination with oxygen with increasing pressure, and alkali, or alkaline earth, concentration. If this behaviour is retained in melts that are more complex chemically, then the role of boron in phase equilibria in magmatic

rocks will be altered with changes in pressure. For instance, in a dry magmatic environment, at depth, boron may partition into the tetrahedral sites of aluminosilicates, or into minerals containing essential boron in four-coordination, to a degree which increases with pressure, and possibly alkali content. This may be in part responsible for the marked absence of tourmaline in peralkaline silicic rocks mentioned by Bowden (1970).

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SUMMARY AND SUGGESTIONS FOR FURTHER WORK

It has been shown in the experimental section of this study that the presence of boron in the granite system has the following effects:

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1. The beginning-of-melting temperatures of watersaturated granite compositions are lowered by intervals ranging from 60° C with the addition of 2 per cent B_2O_3 to 120° C with the addition of 10 per cent B_2O_3 to the system at $P(H_2O)=1$ kilobar.

2. B-for-Al substitution causes reductions of the cell dimensions of feldspars. At low concentrations of boron, the cell edge, <u>c</u>, is reduced to a greater \mathcal{A} extent than is <u>b</u>, whereas the <u>a</u> cell dimension undergoes minimal? reduction. Essentially, this is consistent with the preferential occupancy of B and Al of the T₁0 sites in a generally disorded structure.

3. The presence of boron in the system influences the composition of the alkali feldspar phases, favouring potash enrichment over feldspars produced under the same conditions of temperature and pressure, from the same granific constituents, in the absence of boron.

As this investigation of the granite- $B_2O_3 - H_2O$ system is only preliminary, it is recommended that liquidus, and solidus temperatures be determined in more detail, with both albite-rich and orthoclase-rich compositions.¹ The effect $\sigma_{F''}B_2O_3$ on the position of the cotectic between the primary phase fields of quartz and feldspar, and the minimum melt in the haplogramite composition diagram should also be studied. A more detailed study of alkali partitition among the feldspar and vapour phases in both the haplogramite and alkali feldspar systems in the presence of boron is also needed, paying particular attention to the compositions of fluids. Similarly, the effect of B_2O_3 on the ternary feldspar and granodiorite system should be investigated, as should the effect of varying pressures.

In view of the influence of boron on the compositions of the alkali feldspars and the possibility that its presence may be detected in the feldspar structure by anomalies in cell dimensions, which may, or may not, accompany changes in equilibrium alkali concentrations, it is suggested that known occurrences of boron-rich granites and their hosts be examined for evidence of boron active y as it has affected feldspar stability. Because B_2O_3 also depresses the minimum melting temperatures of granitic bulk compositions, and will probably, affect the normative compositions of the melts produced, the role of boron in the partial melting of metasediments, especially those of marine origin, resulting in the production of migmatite, or palingenic granites, should be considered.

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Plate 1: Grain mount of beta quartz (inverted) in glass of low refractive index.x480 Plane polarized light.

Plate 3: Grain mount of tourmaline granite, #1697A,-run at I095°C, 9 days. Note the development of the acicular,mullité-like phase in radiating clusters embedded in glass (R.I = appr. 1.510). x120 Plane polarized light.

Grain mount of penetration twins in sanidine.

Plate 2:

 $\mathcal{L}_{\mathcal{O}}$

x450 X-nicols.

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١	APPENDIX	I		
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Table 1: Chemical comositions of haplogramitic starting materials, calculated

	in weight	per cent.	•	· ·	A	
Run No.,	⁸ 2 ⁰ 3	A1203	Si02	Na ₂ 0	K ₂ 0 .	H20
059	0.00	12.93	75.73	1.18	10.1,5	12.8
D57	`1.92 [*]	12.68	74,26	1.16	9.95	13.2
F53	4.89	12.30	72.02	1.12	9.65	14.0
T55	9.96	11.64	68.18	1.06	9.14	20.7
0 60 ,	0.00	12, 93	, 75.73	1.18	10,15	10.7
D5 B	1 ,95	12.68	74.25	1.16	9,95	9 ,51
F54	4.12 '	12.40	72.71	1.13	9,73	15,8
156	9 . 79 '	11.66	68,32	1.06	9.16	20.0
022	0.00	9,27	82.78	1.18	6.77	38.60
D14	1.98	9,109	81.14	1.16	6.43	30, 9
T21 /	° 9 . 74 [°] '	8.36	74.72	1.06	6.11	- 27.4
F15	4,92	68 .81	78.71	1.12	6.44	14.9
T6 ,	9,40	8.40	75.00	1.07	-6-13	16.52
0690	0,00	9,27	82.78	1.18	6 .77	11.54
D67b	1.96	9.09	81.16	1.16	6.64	11.57
F66b	' 4 .95	8, 81	78.68	1.12	6.44	12.8
165b	10.98	8.25	73.68	1.05	6.03	20.82
09	U. 00 · .	11,10	79.26	1.18	8.46	22.73
D 1 6	1.41	10.94	78.13	1.16	8.34	10.89
F17 .	4.91	10.55	75.37	1.12	8.04	17.48
, T 7	8.35	10,17	72.64	1.08	7.75	26.53
0103 ·	0.00	11.10	79.26	1.18	ົ 8.46	16. 56
D1 02	2°•05	10,87	77.64	1,16	8,29	14,61
F101 '	5.03	10,54	75.27	1.12	8.03	20.42
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APPENDIX I

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Table 1: continued

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Run No.	8203	A1203	Si02	Na20	K20	H ₂ D
036	0.00	13.04	76,13	2.36	。 8.46	17.15
D35	₽ 1,96	12.78	74.64	2.31	8.29	7.70
D30	1,96	12.78	74.64	2.31	8.29	25 . 97 ⁵²⁴
F 29	5,21	12.36	72.17	2.24	8.02	24.85
T28	9,88	11.75	68.61	2.13	7.62	19.48
076	0.00	13.04	76,13	2.36	8. 46	13 . 58
D75	1,97	12.78	74.63	2.31	8.29	11 . 82
F74	4.07	12.51	73.03	2.26	<mark>,</mark> 8 . 12	16.59
067a	0,00	11.21	79.66	2.36	6.77	10,39
D65a	ı.84	11.00	78.19	2.32	6.65	,27.94
F63a	4.89	10.66	75.75	2.24	-6.44 ⁴	16.77
, Т61в	9,86	10,10	71.80	2.13	6.10	18,14
068a	0.00	11.21	79.66	2.36	6.77	17,50
D66a	1.93	10.99	78,10	2.31	6.64	12.73
F64a	4.97	10.65	₽ 75.70	2.24	6.43 -	10.30
T62a	9.76	10.12	71.89	2.13	6 . 11 ·	18.40
دد D 99	1.96	10,99	8,10	2.31	6.64	9.20
F98	4.87	10.67	75.83	2.25 .	6.44	26.77
024	0.00 /	9:138	83.18	2.36	5.08	38.77
¢: D19	2.02	29.,19	81.50	** 2.31	4.98	35.16
T23 '	11.97	8,26	73.22	2.08	4.47	29.86
0 50 ,	0.00	9.38	83,18	2.36	5.08	13.31
F49	4.97	8 .91	79.05	2.24	4,83	14.53
064b	û .0 0	9.38	. 83,18	2.36	5.08	16.40
D63b	1.97	9,19	81,53	2.31	4.98	13.98,
F62b	4. 98	8,91	19.04	2.24	4.83	, 16.25

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Table 1: continued

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Run No.	⁸ 2 ⁰ 3	A1203	SiO ₂	Na ₂ O	K20	H ₂ O
т61ь	۵ 73	8 47	75 da	2 1 3	A 50	, 22 67
0.95	0.00	13 16	76 53	3 2,13	4.JJ	10.76
085	للروپر م	10.00	70.00	3,35		10.70
D84	1.96	12.90	75.03	3,48	6.64	19,53
F82 /	4.80	12.52	′7 2. 83	3.38	6.44	20.23
F83	4.77	_{.0} 12.53	72.86	, 3,38	6.44	3.59
089	0.00	13.16	76.53	3.55	,6 . 7 7 '	6.38
D88	1.75	12.93	75.19	3.49	6.65	20.51
F87	5.00	12.50	72.70	3.37	6.43	22.44
T 1 04	10, 19	10.17	7 1. 88	3.18	4.56	24.18
F112	7.39	10.49	7 4. 14	3.28	4.70	45,33
T113	9. 86	10.21	72.16	3.20	4.58	11.20
F115	7.20	10.51	74.29	3.29	4.72	36.53
F117	6.94	10,54	74.50	3.30	4.72	10.96
T11 8	9.71	10.22	72.29	3.20	4.58	2 5.86
F119	4.97	10.76	76.07	° 3,37	4.82	15.29
T12 0	9.35	10.26	72.57	. 3.21 *	4.60	12.46
F122	4.70	10.79	76.29	3.38	4.84	9.64
T123	10.11	10.18	7 1, 96	3.19	4.56	17.67
D 80	1.94	11.10	78.49	3.48	A,98	12.94
F78	4.90	10.77	76.14	3.38	4.83	13.40
F79	4.85	10.77	76.17	3,38	4.83	3.62
097	0.00	. 11.32	80.05	3,55	5.08	21.42
D 9 6	1,99	11.09	78.46	3. 48	4.98	11.13 .
F94	5.02	10-75	°76.03	3.37	4.82	11.08
F95	4.97	10.76	76.07	3.37	4.83	3.71

APPENDIX I

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	Run No.	B ₂ O ₃	A1203	Si0 ₂	Na ₂ 0/	K20	H2U	
	F32	4.73	9.0B	79.63	3.21	3.38	20.30	Ň
	T31	9.34	8,60	75.77	3. 06	3.22	24.15	-
	052	0.00	9.49	83,58	3.38	3.55	12.40	1
	F5 1	4.89	9.02	79.48	3.21	3.38	16.98 🔨	
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APPENDIX II

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/	• Weight p	er cent
·Si0 ₂ .	72.6	18
A1 ₃ ⁰ 3		3
$\operatorname{Fe}_{2}^{0}_{3}$	1.8	37
Fe0	·	4
MgD	6	0
Ca0	• 5	6
Na ₂ 0	. 2.4	.9
κ ₂ 0	• 4•3	6
H ₂ 0-	• • 5	1
H ₂ 0+	·· · · · · · · · · · · · · · · · · · ·	5
Ti0 ₂	• • • • • • • • • • • •	4
P205 .	.0	8
Mn0	. 0	1
co ₂	.0	0
F	.0	7
′ C1 [™]	.0	1
·B ₂ 0 ₃	1.7	4 _
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1. analysis by Elaín Munsen, U.S.G.S.

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APPENDIX IIT

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Table 3:	Results constitue	of hydroth ents of P()	ermal ex ₁ H ₂ 0)= 1 H	periments kilobar.	on haplogranit	cic
ِءُ Run No.	АЪ:Оr:Q (Wt. %)	Tempera- ture (°C)	Time 🗠 (days)	B2 ⁰ 3 (Wt. %)	Run Products*	% glass
059	10:60:30	638 <u>±</u> 4	6	0.00	Q+San+v	0
D 5 7		**	**	1.92	$Q+San+v_0$	0
F 5 3	**	**	11	4.89	Q+San+gl+v	15+
T 5 5	t 1 «	f 1	۲. ۲1	9.96	Q+San+g1+v (Q < San) ↓	85、
060	***	809 <u>±</u> 2	6	0.0	San+g1+v	70-75
D 5 8	11	11 ⁴⁴ 1	r TT	1.95	San+g1+v	85
F 5 4	TT	"	tt ,	4.12 [San+gl+v	90_
T56 -	* ** *		18	9.79	gl+v+b	· 98+
09	10:50:40	. 593 <u>+</u> 5	7	0.00	Q+San+v .	0
D16	. 11	tt	tt .	1.41	Q+San+v	0
F17	11	Ħ	TT	4.91	Q+San+v+b	0
Т [′] 7	**	** `	73	8.35	Q+San+v+b	0
0103	**	640±5	9	0.00	Q+San+v	0
D102	**	7 7	**	2.05	Q+Sen+v+b	0
F101	. 11	**	**	5.03	Q+San+gl+v	15-20
073	10:`50:50	798 <u>+</u> 3	7.	0.00	Q+San+g1+v	80
D72	ri ^{(*}	, H	· 11	1 - 2	$(\underline{v} > \operatorname{San})/$ \underline{v}	80
F71	م ۱۱ ۲	r 11	11,	4-5	Q+San+g1+v ($Q > San$)	95

'Q= quartz; San= Sanidine; Ab= albite: gl= glass; v= vapour; b= borate precipitate in noticable quantities.

Table 3: continued...

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. A	Run No.	Ab:Or:Q (Wt. %)	Tempera- ture (°C)	Time (days)	B203 (Wt. %)	Run Products [*] .	% glass
r	T70	10: 50: 40	640 <u>+</u> 5	7	9-10	gl+v	100
	· 022	10:40:50	709 <u>-</u> 5	7 9	0.00	Q+San+v	0,
	D14	17	17	"	1.98	Q+San+g1+v	25+
Ċ.)	T 2 1	. 11	11	**	9.74	Q(tr)+g1+v+b	9 8
	F15	11	791 <u>+</u> 5	7	4.92	Q+g1+v	80
	Т6	**	11	**	9.40	Q+g1+v+b	98 .
	065b	, ft	800 <u>±</u> 6	10	0.00	Q+g1+v	75
	D ó7b	11	T	11	• 1.96	Q+San+g1+v (Q ≯ San)	85 " 🔊
	F66b	**	**	, 11	4.95	Q+g1+v+b	90
	Т65Ь	**	1. II.	**	10.98	, gl+v •	100
r N	0	20:50:30	7 3 * <u>+</u> 6	5	0.00	Q+San+g1+v (Q < San)	30
ر م	D75	* 1 **	**	**	1.97	Q+San+g1+v	60
-	F 7 4	11	**	11	4.07	Q+San+g1+v ($Q < San$)	7 5
1	Т77	11	11	11	10	Q+San+g1+v	95+
	030	**	825 <u>+</u> 7	· 6 ·	0.00	(Q < San) San+gl+v	90 5
ÿ	D35	**	11	**	1.96	gl+v+b	99 +
· · *	D99	20:40:4p	600 <u>±</u> 1	10	1.96	Q+San+v	0
	595 ·	**	. 11	11	4.87	Q+San+gl+v	⁻ 2 5
	060a)	*1	715 <u>±</u> 5	7	0.00	Q+San+v	0
	D66a	**	*1	11	1.93	′ Q+San+g1+v	- 50
;	Fó4a	**	11	11	4.97	Q+San+g1+v	65-70
	Т62а	11	11	*1	9.76	Q+g1+v	90
	ja r		-		· · · · · · · · · · · · · · · · · · ·	~	-

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Table 3: continued...

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Run No.	Ab:0r:Q (Wt. %)	Tempera- ture (^O C)	Time (days)	B ₂ O ₃ (wt. ³ %)	Run Products 9	glass
067a	20:40:40	797 + 2	7	0.00	Q+San+g1+v (Q= San)	65
D65a	11	**	**	1.85	Q+San(tr)+gl+v	85
F63a	11 -	**	",	4.89	Q+San+gl+v (Q San)	•90
T61a	11	n	**	9.36	g1+v+Q(tr)	99
064b	20:30:50	665 <u>+</u> 5	11	0.0	Q+San+v	0
D63b	**	TI	* TT	1.97	Q+San+g1+v	20-25
Fó2b	"	n -	"	4.98	Q-San-gl-v (Q> San)	55-60
Tʻ 61b	**	` tT	"	9.73	Q+g1+v	70
050	20:30:50	800 <u>+</u> 5	10	0.0	Q+gl+v	65
· Г49	11	77	11	4.97	Q +g1+v	, 85
024	**	825 <u>+</u> 5	5	0.00 🐜	Q+gl+v	80-85
D19	n	ŤŤ	11	2.02	Q+g1+v	90-95
T 2 3	tt c	** 、	**	11.97	gl+v+b	99 - ·
052	30:20:50	800 <u>+</u> 6'` [°]	1 10	0.0	Q+gl+v	70
· F 51	**	11	11	4.89	Q+gl+v	80+ ,
F 32	/· 11	825 ± 7	6	4.73	Q(tr)+gl+v	95+
T31	0 11) (11	9.34	gl+v+b	99 +
059	30:40:30	637 <u>+</u> 2	9	0.00	Q+San+Ab(tr)+v	0
$D \succ \succ$	"	12	ุ่าา	1.75	Q+San+Ab(tr)	0
, F ≒7	**	TT	**	5.00	Q+San+Ab(tr)+gl	+v30
085 🖘	n	777 <u>+</u> 3	6	0.00	′ S an+Q +gl+v √Q<< San)	90 [°]
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•	Run No.	Ab:0r:Q (Wt. %)	Temper- ature (°C)	Time (days)	B203 (Wt.%)	Run products	% glass
ł	D84	30:40:30	77-7 <u>+</u> 3,	, 6	1.96	San+gl+v	90
	F82	ft	77	**	4 - 77	San+g1+v	90
	т83	ŤŤ	**	**	4	San+Q(tr)+gl+v	85+
0	T104	30:30:40	506±5	۴ 7	10.19	Q+San+v+b	0
	F112	17	530±4	5	7.39	Q+San+v (incomplete reaction)	0
	T113	۲t	11	5	9.86	Q+San+v (incomplete reaction)	0
	F115	11	558 <u>+</u> 4	11	7.20	Q+San+v+b	, 0
	F117	**	• • •	TT	6.94	Q+San+v+b	0
	T11 8 [.]	11	TT	fr	9.71	Q+San+v+b	o
	F119	17	567 <u>+</u> 5	13	4.97	Q+San+v+b	0
	Т120	17	**	**	9.35	Q+San+v+b	0
\ \.	F122	TT 2	595 <u>+</u> 1 <u>5</u>	**	4.70	Q+San+v+b (partially unreacted)	0
-	T 1 2 3	· · · ·	t t	11	10.11	Q+San+g1+v+b	35-40
	051	**	655±5	. 8	0.00 .	► Q+San+Ab(?)+v	0
	D80	11 ·	71	11	1.94	Q+San+Ab(tr)+v	ວົ
	F78	. **	11	11 - 1	4.96	$Q_{+}San_{+}Ab(tr)_{+}gl$	+50+
	F79		**	11	4.85	+v Q+San+g1	50 +
	097	rt 🔍	755±5	7	0.00	Q+San+g1+v	60
	D96	11	ţţ	**	1.99	Q+San+gl+v (Q:San= 5:1)	70
		-				, / ⁻	

Table 3: continued...

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Run No.	Ab:0r:0 (Wt. %)	Tempera- ture (°C)	Time 、(days)	B ₂ O ₃ (Wt.%)	Run products	% glass
F95	30:30:40	755 <u>+</u> 5	7	4•97	Q+g1+v+San(tr)	95
T '94	. 11	**	18	5.02	Q+g1+v	95
+		41	ţ			
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APPENDIX III

∖ Run No.	20 (201)	values (060)	(°) <u>*</u> (204)	0 <u>r</u> content (201)	(%), <u>a</u>	from: <u>V</u>
059	21.06	41.57	50.91	89	87	85 .
D57	21.06	41.60	50.93	89	86.5	84
F 5 3	21.03	41.59	50.91	92	92	90
T 5 5	21.00	41.59	50.89	94	92.5	91-92
060	20.96	41. 55	50.88	9 8		
D58	20.99	41.59	50.86	94		
F 5 4	20.95	41.56	50.89	99		
09	21.09	41-55	40.97	86	85	84-85
D16	21.09	41.55	50.97	86	84.5	82-83
f 17	21.12	41.60	50.96	83	81	79-80
Τ7	21.12	41.58	50.92	83	81	80
0103	21.11	41.58	50.90	84	84	81-82
D102	21.11	41.58	50.96	84	84	81
'F101	21.09	41.55	50.91	86	86	8.5
073	21.03	41.58	50.87	91	91	90
D7 2	21.04	41.56	50.88	·91		
F71	21.01		k,	93 L	- 4°	-
022	21.13	41.58.	50.91	.82	81	r 81
D14	21.04	41.58	50.93	91	89	88
T21~	21.04	41.56	50.93	91	89 É	88
D67b	21.02 '	41.57	, 50.86	9/2		

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Table 4: 20 (CuK α_1) for (201), (060), and (204) of feldspars, with Or content estimated from 20 (201), <u>a</u>, and <u>V</u>.

* all 20 values \pm .010

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ble 4: continued...

	Table 4:	continue	d	43 1			*	
	Run No.	2 0 (701)	values (060)	(ð) (7 04)	0r (cant (201)	ent (%),	from: ` <u>V</u>	
	076	21.13	41.54	50.87	82	.83	82 .	
	D75	<u>21.06</u>	41.58	50.89	89	86	86	
	F74	21.06	41.55	50.88	89	86	86 ~ `	8
	T77	21,05.	41.58	50.91	, 90	86.5	88	
•	D99 **	21.22 (21.85)	41.63	50.97	75 (15)	74	· 74	
	F98 ***	21.24 (21.89)	41.62	50.96	72' (13)	72	70	
	068a)	21.16	41.62	50.90	80	78	77-78	
	D66a	21.16	41.58	50.90	80	78.5	7 8 [′]	
	F6 4a	21.11	.41.58	50.88	84	° 81 «	82	
	067a ·	21.10	41.56	50.85	85	85	87.	
	D65a	21.10		ۍ د	85	¢		un
*	F63a	21.08	r	L	· 5 87	,		1
	064b [°]	21.34	41.61	5 0. 95	63	<i>,</i> 61	61	
	D63b	21.30	41.60	50.95	67	62.5	61 °	
	F62b	2D.14	41.55	50.89	81	, 79	. 81	ų
-	0×9 **	21.34 (21.84)	41.64	50.97	62 (15)	61	, 1 60	
	D88**	21.32 (21.80)	41.64	59.96	66 (23)	62.5	64	
	F87 **	21,22 (21.05)	41.60	50.94	75 (34)	72	71	
	085	21.19	41.56	50.89	77	4" - 75	77	
	D84	21.16			79	- 1	,	

 \approx all'20 values - .01⁰ \approx 2 feldspars are produced in these runs, values of 20(201) for Ab are listed in brackets.

Table 4: continued ...

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₩ Run No.	(201) ²⁰	values (060)	(⁰) <u>*</u> (204)	0 <u>r</u> coñt (201)	ent (%), <u>a</u>	from: <u>V</u>
F83	21.15	41.57	50.89	80	77	80 ° '
.F82	21.18			78		ক
T104	21.09	41.63	50.98	86	′85 [≆]	⁷⁹ , 79
[°] F115 [†] ·	26	41.66	51.07	70	້ 70 [°]	69-70
, F19 ≁ ↔	21.23 (21.88)	41.66	• 51.00	74 (13)		• · · · ·
T123	21.145	_41.57	_ر 50.91 _،	. 81	79 ·	79
097	21.32	41.62	50.96	65	62	62 ,
D96 ** ●	21.22 (21.65)	41.60	50.92	72 (34)	68.5	69
F95	21.06	41.57	50.94	89	91 \	89
, , , , , , , , , , , , , , , , , , ,	v		۶.	· · · · · · · · · · · · · · · · · · ·	. /	· · · · ·
, -∻ all 2	A values	010			~	*

all 20 values - .01°
2 feldspars are produced in these runs, values of 20(201)
for Ab are listed in brackets. * 1 .

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Table 5: Cell parameters of feldspars produced in hydrothermal experiments. *

		۰. ۲.	, v	ì	
NO.	<u>a</u>	<u> </u>	<u>c</u>	. ₿ «	<u></u>
059	8.5540 Å	13.0141 Å	7.1686 \$	`116 ⁰ 1. 51	717.11 Å ³
	±.0022	±.0037	±.0018	±.50	±.26
D57	8.5507	13.0108	7.1653	`115 ⁰ 59.91	716.48
	.0014	.0027	.0012	. ⁸⁶	.17
F53	8.5746	13_0211	7.1684	116 ⁰ 1.87	719.16
	.0014	_0021	.0011	.88	.16
T55	8.5794	13.0184	7.1685	115 ⁰ 56.47	719.98
	.0074	.0056	.0027	4.09	.62
09	8.5498	13.0283	7.1686	116 ⁰ 4.20	717.27
	.0017	.0025	.0014	• 96	.18
D16	8.5446 .0010	13.0298 .0013	7.1640 .0007	116 ⁰ 3.33	716.54 .10
F17.	8.5359	13.0178	7.1631	116 ⁰ 1.45	715.25
	.0009	.0010	.0006	.47	.16
77	8,5329 .0016	13.0208 .0021	7.1657 .0011	116 ⁰ 1.45	715.43 .16
0103	8.5417	13.0213	7,1702	116 ⁰ 4.56	716.32
	.0014	.0016	.0010	1.14	.17
D 1 02	8.5419	13.0222	7,1655	116 ⁰ 2.75	716.11
	.0011	.0016		.54	.11
F101	8.5499 .0013	13.0277 .0018	7.1689	116 ⁰ 2.44 .84	717.45 .15
073	8.5729	13.0195	7.1732	116 ⁰ , 1.92	719 .41
	.0027	.0027	.0012	1.47	.26
022	8,5315	13.0212	7.1700	11,6 [°] 2.75	715.62
	.0015	.0019	.0010	.86	.15
D 1 4	8.5652	13.0237	7.1673	1 15⁰59. 10	718.69
	.0023	.0019	.0011	1 . 25	.21
T21	8.5665	13.0262	7.1669	116 ⁰ 1.32	718.68
	.0012	.0015	.0007	.65	.12

*Standard error reported below each value.

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APPENDIX III

Table 5: continued

		_	L		' 2	1/	
	NO.	<u>a</u>	<u></u>	<u> </u>	<u>B</u>	<u> </u>	G
	07 6	8.5355 Å ±.0023	13.0237 Å ±.0030	7.1740 Å ±.0016	116 ^b 3.03 ±1.33	7.16.47 ±.23	Å
	D 7 5	8,5521 ,0015	13.0228 .0022	7 .1717 .0010	115 ⁰ 58 <u>.</u> 05 0.90	718,09 ,16	
	F74	8.5532° .0021	13.0244 [*] • .0028 [*]	7.1743 .0012	, 116 ⁰ 0.46 1.05	718.28 .20	
	t77 ₀	8,5616 ,0029	13 .022 0 .0028	7.1709 .0012	115 ⁰ 56.97 1.48	718.87 .26	A
~	D 99	8.5060 .0095	13.0089 .0052	7.1624	115 ⁰ 56.30 / 4.03	712.71 - .78	
	F98	6.4881 [/] .0034	13.0122 .0018	7.1633 .0009	115 ⁰ 59.90 1.35	711.12 27	
	068a	8.5179 0026	13.0114 .0029	7.1723	116 ⁰ 1.54 1.38	714.36 .25	
	D66a	8.5216 .0011	13.0156	7.1687 .0009	115 ⁰ 59.87 0.66	714.65 .13	
	F64a %	8,5308 ,0031	13.0216 0035	7.1726 .0019	116 ⁰ 2.20 2.12	715.91 .34	
•	067a	8.5469 .0021	13.0244 .0034	7.1779 .0020	115 ⁰ 57.90 1.48	718.37 .27	
•	064b	8.4344 .0066	13.0147 .0031	7.1636 .0022	116 ⁰ 4.49	706.32 .56	
	D6 3 b	8.4444 .0046	13.0068 .0025	7.1623 .0013	116 ⁰ 5.64 2.15	706.48	<i>(</i>
	089 	8.4367 .0057	13.0030 .0026	7.1610 .0016	116 ⁰ 3.56 2.42	705.71 .46	
	088.	.8.4442 .0034	13.0125 .0037	7,1630 .0014	115 ⁰ 58.36 1.97	°707.58 .30	
	F87	8.4877 .0043	13.0154 .0022	7.1658 .0014	115 ⁰ 58.93 , 1.84	7 11. 61 .34	

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APPENDIX III

Table 5	: continued			¢	
)	h		,	
ND.	<u>8</u>	<u> </u>	/ <u>c</u>	, B `	<u>v</u>
0.85	8.5032 .0025	13.0259 .0027	7.1755 0013	√ ↓ 116 ⁰ 1.62 1.12	714.17
F83	8,5121	- 13.0283	7.1754	116 ⁰ 0.20	715.19
	.0035	.0033	.0017	1.94	.34
F78	8.5325	13.0097	7.1669	116 ⁰ ,9.54	713.57
	.0104	.0087	.0046	5.47	.81
097	8.4439	13.0033	7.1660	11 6 ⁰ 3.99	706.'79
	.0064	.0029	.0021	- 2.77	.51
F 95	8.5719	13.0205	7.1672	115 ⁰ 58.40	719.15
	9018	.0024	.0015	1.40	.21
T1 04	8,5462 .0026 >	13.0053 .0039	7.1570	116 ⁰ 3.32 1.41	714.63 .28
F119	8.4826 .0102	13.0052	7.1595 .0030	115 ⁰ 58 .3 1 4.15	710.06
T123	8.5210	13.0210	7.1715	•116⁰ 3.07	714.85
	.0023	.0019	.0009	1.50	.23
FG2b*	8.5210	°13.0316	7 .1720	116 ⁰ 5.42	715.24
	.0024	.0022	,0009	1.38	.26
081++	8.45 34	12,9987	7.1637	115 ⁰ 58.62	707.64
	.0067	.0041	.0022	3.71	.69
D81***	8.4705	13.0107	7.1613	115, ⁰ 57.55	709.60
^***	.0067	.0030	.0014	2.89 *	.56
[`] D96 *** ≭ ∕	8.4742	13.0151	7.1686	116 ⁰ 6.88	709.93
	.0048	.0036	.0016	2.42	.45

* $\propto = 89^{\circ} 58.73 + 1.54'; = 89^{\circ}55.00 + 1.37'$ ** $\propto = 89^{\circ}58.82' + 1.97'; = 90^{\circ} 5.46' + 2.31'$ *** $\approx = 89^{\circ}55.95' + 1.97'; = 90^{\circ} 2.99' + 3.12'$ **** $\propto = 89^{\circ}57.91' + 2.57'; = 89^{\circ} 52.82' + 2.35'$

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APPENDIX IV

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Table 7: Products of dry melting experiments at atmospheric pressure using tourmaline granite #1697A

Run	No.	Material	Tempera- ture ¢ ^o C)	Time (days)	Products**	Or content of feldspars (from (201))
#169	97A s	tarting mat	terial		T+Kfp+Q +Ab(minor)	0r95 0r1
cì.	44	#169 7A	743 <u>+</u> 5	22	T(20%)+Kfp(45% +Q(30%)+Hem+ Fm alt.)
C.	4 6	#1697A- B ₂ 0 ₃	743±5	22	T(20%)+Kfp(30% Q(40%)+Fm alt.)+ +Hem.
C2 02 C1	20 21 19	#1697A "	821 <u>+</u> 7 "	. 9 11 11	T(20%)+Kfp(30% Q(45%)+Fm alt.)+ +op
C2 02	2 2 2 3	#1697A	841 <u>+</u> 5	8	T(20%)+Q+Kfp+ Fm alt. (5%)	0r90 0r75
C2 C2	24 25	$#1697A - B_2O_3$	841 <u>+</u> 5	\$	T(25%)+Q(34%)+ Kfp(30%)+M?	-
C2 02	26 27	#1697A	858±3	10	T(breaking dow Q+Kfp+Hem+Fm a	n)+ 1t.
02	28	#1697A- B ₂ O ₃	858 <u>+</u> 3	10 "	T+Q = Kfp+Ab(t +Fm alt.+Hem	r)
C2	19	#1697 A	877±4	14	Q(20%)+Kfp(zon +Fm alt.+Hem+M +gl.	ed,30%)0r69 ? 0r14
Cg	50 /	#1697 A -	877 <u>+</u> 4	14	Q(15%)+Kfp(zon +M?+Hem+g1.	ed 55%)
Cg	31 、、	#1697 A	883 <u>+</u> 4	7	Q+Kfp+Fm alt./I +Hem+gl	M? .
СЗ	30	#1697 A	883±4	12	Q+Kfp+Fm alt./N +Hem+gl	M?

* T = tourmaline; Q = quartz; Kfp = microcline; Hem = haematite; Fm alt = unknown ferromognesian alteration product; M? = mullite-like phase; op = opaques.

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Table 7: continued...

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Rı	un No.	Material	Tempera- ture (°C)	Time (days)	Products*	Or content of feldspars (from (201))
	032	#1697 A	883 <u>+</u> 4	· 7	Q+Kfp+Hem+ M?+gl	
	C33 、	#1697 A	, 883 <u>+</u> 4	12	Q+Kfp+Hem+ Fm alt.+M?(tr)	•
	C34	$#1697A - B_2O_3$	883 <u>+</u> 4	12	Q+Kfp+Fm alt. +Hem+gl	· · .
0	035	n	r. 11	12	Q+Kfp+Fm alt.+ Hem+gl	
	C16,17	#1697 A	898 <u>+</u> 5	. 8	.Q+Kfp+Hem+M?-g1 { · ·	0r68 0r 8
\mathcal{O}	018	#1697 A	89,8 <u>+</u> 5	., ×	Q+Kfp+Hem+M?+g1	` e ,
	C37	#1697A	898 <u>+</u> 5	11	Q+Kfp+Hem+M?-g1	
c	036	#1697 A	898 <u>+</u> 5	11	Q+Kfp+Hem+Fm al M?+gl	t./
	038	#1697 A -	898 <u>+</u> 5	11 .	Q+Kfp+M?/Fm alt Hem+gl(feldspar going).	•+
	C39	#1697 A -	898 <u>+</u> 5	11	Q+Kfp+M?/Fm alt Hem+gl(feldspar going)	•- •, •
	C3,4	#1697A	915 <u>+</u> 6	7	Q+Kfp+M?+Hem+gl	
	01,2	#1697A	915 <u>+</u> 6	7	Q+Kfp+M?+Hem+gl	
	C45	#1697 A	941 <u>+</u> 5	` ^{'8}	Q(30))+Kfp(40%) g1(10%)+Hem+M?	• 0r67 0r19
	C47	#1697A	941 <u>+</u> 5	8	Q(30%)+Kfp+gl(3 +Hem+M?	0%)
	C6,8	#1697A	1005 <u>+</u> 4	4	Q+Kfp(tr)+M?+He	m+gl
	07	#1697 A	1005 <u>+</u> 4	4	Q+Kfp+M?+gl	

Run No.	Material	Tempera- ture (^o C)	Time (days)	Products (201)
C41	#1697A	1095±5	14	Q+M?+Hem+g1 (over 50%)
C42	#1697A- B ₂ 0 ₃	1095 <u>+</u> 5	14	Q+M?+Hem+g1
C13, 19	5 [*] #1697À	1100±8	r ⁹ .	Q(25%)+g1(60%)+ M?+Hem
014	#1697A	1100 <u>+</u> 8	9	Q+M?+Hem+g1
C40	#1697A a	1095 <u>+</u> 4 nd 941 <u>+</u> 5	14 8	∂ +M?+Hem+g1(50%)
C43	#1697 A , th	(1095 ± 4) en 743\pm5	14 ° 4	Q+M2+Hem+g1(60%)

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	#014	#C15	1.71:1 mullite (Durović, 1962)
Index		$2\theta (CuK\alpha_1)$	······································
110	16.46	16.50	16.45
120	25.95		26.01
210	26.27?	26.28	26.29 -
121	40.81		40.88
211	41.11	41.0 5 [°]	41.07
Cell Dimensions*		~	
<u>a</u>	7.5052 Å ±.0033	7.5617 Å	7.549 Å
<u>b</u>	7.7151 ±.0018	7.6214	7.681
<u>c</u>	2.8873 () ±.0006	2.8664	2.884
⊻́ ▼	03 167.185 A ±.049	166.34 A	167.22 A
Axial ratios		د <mark>ب</mark> ر بر بر بر	1
<u>a/b</u>	•973	.992	.983
<u>c/b</u>	. 3742	• 3787	. 37 5 5

Table 8; X-ray data for the acicular mullite-like unknown

* Standard errors are reported below each value when possible.

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