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BORON SUBSTITUTION IN SYNTHETIC MICAS AND CLAYS[1]

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ABSTRACT

Under hydrothermal conditions it was possible to synthesize phlogopite, muscovite and saponites which contained appreciable amounts of boron in tetrahedral sites. Synthetic phlogopite, formula $Mg_3(BSi_3)O_{10}(OH)_2 \cdot K^+$, had a very small cell ($a=5.310$ Å, $b=9.150$ Å, $c=10.234$ Å, $\beta=100°8'$), and its cell dimensions varied considerably with conditions of formation. With synthetic saponites prepared from gels in the presence of boron (with no alumina in the system), only mixed-layer clay minerals were obtained, due apparently to the limited substitution of boron in tetrahedral sites. Fully expandable saponites were obtained from glasses of the same composition. The presence of boron in the tetrahedral layer of the saponites was confirmed by infrared spectroscopy. The ease and extent of B^{3+} substitution in these clays makes the hypothesis that B^{3+} retention in sediments is due to incorporation in micas and clays appear to be very likely.

INTRODUCTION

The geochemistry of boron was extensively studied by Goldschmidt and Peters (1932) as well as Landegren (1945), and they have shown that the amount of boron involved in the sedimentary cycle is substantially higher than in igneous rocks.

The study of the distribution of boron in soils and sediments is important from two viewpoints. First, together with other trace elements, the distribution of boron may be used for the reconstruction of ancient environments as has been shown by Landegren (1945), Degens *et al.* (1957), Keith and Degens (1959). Second, the role of the boron content in soils is of considerable importance in determining the vegetation.

In soils and sediments the minor part of boron appears in the water soluble form (mobile boron). The major part, however, is in the water insoluble form (immobile boron) and in certain cases cannot be extracted even with warm concentrated hydrochloric acid. Goldschmidt and Peters (1932) expressed the opinion that the immobile part of boron is mostly bound in the boron-silicate tourmaline, which is very resistant to chemical and mechanical weathering. The relatively high amount of boron in certain feldspars can be related to the existence of boron silicates with structures similar to feldspars, *e.g.* reedmergnerite $Na[BSi_3O_8]$ and danburite $Ca[B_2Si_2O_8]$, as indicated by Harder (1959, 1961a), although as yet no experimental work on the mutual solubility of these phases has been reported. The same author has studied extensively the distribu-

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tion of boron in sediments and has come to the conclusion that most of the boron contained in the fine fractions could be connected with the clays either adsorbed on, or substituted in, the structure. Furthermore, on the basis of solubility experiments, Harder (1959) has suggested that the majority of boron in the fine fractions is possibly bound in micas or silicates which are specially enriched in boron. In the majority of cases dioctahedral micas and glauconite contain substantially higher amounts of boron than trioctahedral micas.

A similar opinion was expressed by Goldberg and Arrhenius (1958), who discussed the possibility of the formation of clay minerals in sea water from ionic solutions, in which process boron could be accepted in the structure of micas and clays.

However, due to the relatively small amount of boron in clay sediments (average values amount to 100 g B/ton), it is almost impossible to obtain definite proof whether boron is only strongly adsorbed on the surface or actually present in the structure of the micas and clay minerals. With such a small amount of a small ion having a high charge, it is hardly to be expected that the solubility experiments could provide a definitive answer. The present work was carried out to determine whether or not appreciable amounts of boron could actually be incorporated in various layer lattice silicates in regular lattice sites.

EXPERIMENTAL PROCEDURES

Synthetic micas or clays were prepared from mixtures prepared as gels or glasses containing the appropriate constitutents. As a source of silica, "Ludox" silica sol was used. Solutions of magnesium or aluminum nitrate and $Na_2B_4O_7$ were evaporated to dryness with the required amount of silica sol and then fired to about 500° C. In some cases sodium or potassium hydroxide was added to obtain the composition required. As the source of boron for the preparation of micas, solutions of B_2O_3 were used. One part of each gel was melted in a platinum crucible (usually between 1350–1400° C.). Several of the glasses were analyzed for boron by emission spectrography and the amounts of boron found were similar to the calculated amounts. The syntheses were carried out in small sealed platinum tubes with a *small* amount of water, using the usual test tube or "cold seal" vessels (Tuttle, 1949; Roy and Osborn, 1952). Recent techniques used in this laboratory have been described in some detail by Koizumi and Roy (1959).

The specimens obtained were investigated by means of x-ray diffraction technique and infrared spectroscopy. Infrared spectra were recorded with a Perkin-Elmer model 21 instrument using the KBr technique and 2 mg of specimen in 300 mg of KBr.

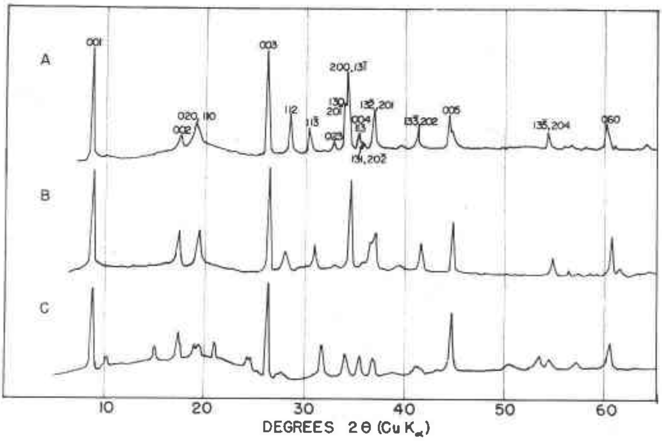

FIG. 1. *X*-ray diffraction patterns of
A) synthetic phlogopite, composition K $Mg_3(AlSi_3)O_{10}(OH)_2$.
B) synthetic phlogopite, composition K $Mg_3(BSi_3)O_{10}(OH)_2$ obtained from glass.
C) synthetic phlogopite, same composition as B, obtained from gel.

RESULTS

The results of experiments on materials of phlogopite composition are given in Fig. 1, where three diffraction patterns are shown. Figure 1A shows the diffraction pattern of synthetic phlogopite of the composition $KMg_3(AlSi_3)O_{10}(OH)_2$ and Figs. 1B and C of synthetic phlogopite of the composition $KMg_3(BSi_3)O_{10}(OH)_2$ obtained from glass (B) and gel (C). The conditions of synthesis in this case were: 710° C., 14,000 psi for 10 days. In the entire range of the stability field of phlogopite, boron-phlogopite is easily formed, without the presence of aluminum ions.[1] The diffraction pattern of the boron-phlogopite (Fig. 1C) obtained from gels always showed some extra lines as compared with the boron-phlogopite obtained from glass. It seems that we are dealing here with a mixture of at least two phases, one of which is B-phlogopite.

The expected decrease in cell dimensions was found, but in addition it was noted that the cell dimensions are influenced by the temperature and pressure of formation. The contraction of the cell of boron-phlogopite due to pressure (at 710° C.) is illustrated in Fig. 2, where d spacings for (005) and (060) planes are shown as a function of pressure of the run. At approximately 60,000 psi, the lowest values of d spacings were reached. From these values computed *b* and *c* parameters for boron-phlogopite are 9.150 Å and 10.234 Å, respectively,[2] compared with

[1] Similar results have been reported in concurrent work by H. P. Eugster and T. L. Wright (1960), "Synthetic Hydrous Boron Mica," *U. S. Geol. Survey Prof. Paper* **400-B,** 441–442.

[2] The values obtained for *a* and *β* were 5.310 Å and 100°8′, respectively.

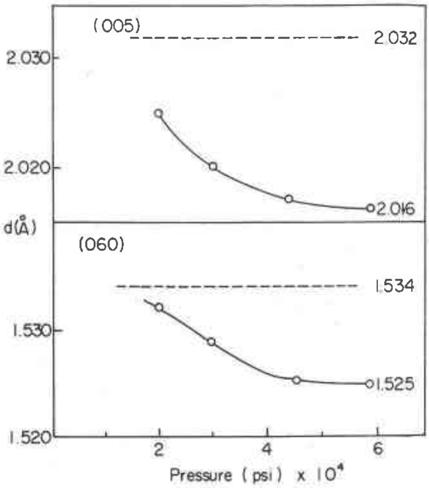

FIG. 2. The variation of d spacings with pressure for a synthetic phlogopite of the composition K $Mg_3(BSi_3)O_{10}(OH)_2$ prepared at 710° C. Broken lines are d spacings for synthetic phlogopite K $Mg_3(AlSi_3)O_{10}(OH)_2$.

$b=9.20$ Å and $c=10.314$ Å for aluminum-phlogopite (1M). The same effect of pressure on the unit cell of synthetic muscovite was demonstrated by Crowley and Roy (1960). The possible explanation for the variable cell parameters of boron-phlogopite with pressure and temperature could be potassium-boron ordering (c parameter) and boron-silicon ordering (b parameter).

Starting with gel or glass of boron-muscovite $KAl_2(BSi_3)O_{10}(OH)_2$ composition, single-phase synthetic muscovite was prepared at 500° C. and 30,000 psi in seven days. Boron-muscovite synthesized from glass was usually much better crystallized than muscovite prepared from gel. The above mentioned results show very clearly that BO_4 groups can, under appropriate conditions, replace completely AlO_4 groups in the tetrahedral layer of the mica structure, since it is highly unlikely that any B^{3+} will enter the octahedral layer in appreciable amounts.

In further experiments the synthesis of boron saponites with the formula $Mg_3(B_xSi_{4-x})O_{10}(OH)_2Na_x^+$ was attempted, with no aluminum ions present in the system. Successful synthesis of the expandable saponites under determined conditions would clearly indicate substitution of boron in the tetrahedral layer. Starting materials for the synthesis were gels and glasses which contained amounts of boron consistent with $x=0.33$ or 0.66. The syntheses were carried out at 350° C., 17,000 psi, for 15 days.

In Fig. 3 the results of three runs can be observed. Figure 3A shows

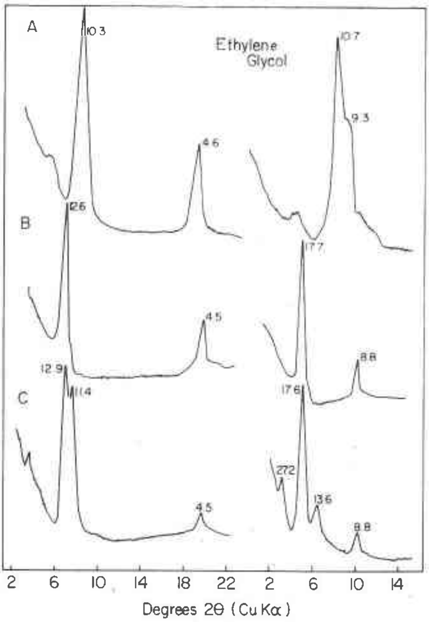

Fig. 3. *X*-ray diffraction patterns of

A) a synthetic mixed-layer clay mineral obtained from gel of the composition 3 $MgO \cdot 0.33B_2O_3 \cdot 3.44\ SiO_2 \cdot 0.33Na_2O$.

B) a synthetic fully expandable saponite obtained from glass of the same composition as A.

C) a regular mixed-layer clay mineral obtained from glass of the composition 3 $MgO \cdot 0.17B_2O_3 \cdot 3.66SiO_2 \cdot 0.17Na_2O$.

the *x*-ray diffraction patterns of a mixed-layer clay mineral which was obtained from gel where the amount of boron was $x = 0.66$. The (001) diffraction peak of this specimen was at 10.3 Å, and after treatment with ethylene glycol two diffraction peaks at 10.7 and 9.3 Å were observed. The obtained mixed-layer clay mineral contained no more than 20% of expandable layers (see Weaver, 1956). However, with the same amount of boron in the starting glass, a fully expandable saponite was formed (Fig. 3B). With the glass where the amount of boron was $x = 0.33$, a regular mixed-layer clay mineral with approximately 70% of expandable layers was obtained (Fig. 3C). The formation of the mixed-layer clay minerals (Figs. 3A and 3C) is apparently caused by the fact that not all boron present in gel or glass was accepted by the clay mineral lattice.[1] Better results obtained with glasses than with gels *may* be attributed to the fact that B^{3+} is undoubtedly already in four-fold coordination with

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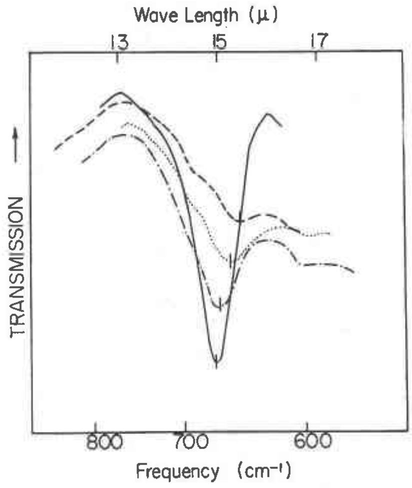
[1] The stability fields of mixed-layer clay minerals obtained from gels of the composition 3 $MgO \cdot (4-x)SiO_2 \cdot x/2Na_2O$ were determined by T. Iiyama and R. Roy (in press).

Si in the glass and may therefore—possibly metastably—prevent a higher content B-saponite to be formed.

Direct evidence of the substitution of boron in the tetrahedral layer of the structure was obtained by infrared spectroscopy. Figure 4 shows the absorption spectra in the frequency region 600–800 cm^{-1} of the synthetic specimens of the boron saponite composition obtained from glass. It was previously shown by Stubican and Roy (1961) that the absorption band in this region is strongly influenced by the presence of trivalent ions in tetrahedral sites. In general, this band moves in the direction of lower frequencies and decreases in intensity with increasing amount of trivalent ions. This is due to the increase in the average (Si, Al)—0 or in this case average (Si, B)—O distance. It is evident from Fig. 4 that the increasing amount of boron in tetrahedral sites strongly influences the frequency and the intensity of this band.



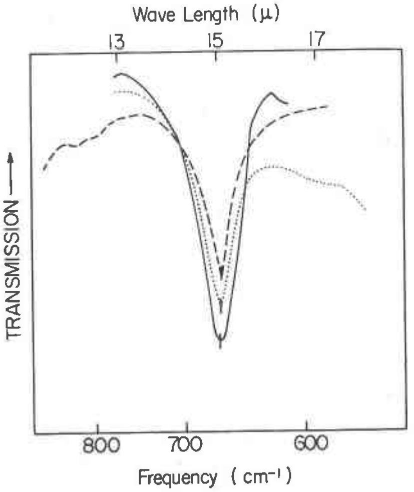


FIG. 4 (left) Infrared spectra in the region 600–800 cm^{-1} of synthetic clays obtained from glasses of the composition $3\ MgO \cdot x/2B_2O_3 \cdot (4-x)SiO_2 \cdot x/2Na_2O$ where $x=0.17$ (dashed-dotted line), $x=0.33$ (dotted line), $x=0.66$ (dashed line). Full line is the same band for talc.

FIG. 5 (right) Infrared spectra in the region 600–800 cm^{-1} of synthetic clays obtained from gels of the composition $3MgO \cdot x/2B_2O_3 \cdot (4-x)SiO_2 \cdot x/2Na_2O$, where $x=0.33$ (dotted line), $x=0.66$ (dashed line). Full line is the same band for talc.

With the specimens obtained from gels (Fig. 5), the same absorption band changes only slightly in frequency and intensity, which indicates that the major part of boron was not in tetrahedral sites. This is in agreement with the conclusions obtained from *x*-ray diffraction data.

DISCUSSION

It is known that boron can be found in tetrahedral coordination with respect to oxygen in several boro-silicates (*e.g.* danburite, datolite, etc.). Comeforo *et al.* (1953) have obtained boron-fluroine-phlogopite from high temperature melts, where most certainly boron should be incorporated in tetrahedral sites of the silica layer. Our results with synthetic micas and clays show clearly that the BO_4 groups can be substituted in the silica layer at much lower temperatures. Where this substitution is permissible, moreover, the extent of the substitution with micas under ideally favorable conditions can be the same as with aluminum. If we compare the results for micas and saponites, particularly those for phlogopite and saponites prepared from gels, it can be concluded that boron is more easily accepted in the mica lattice. These results are in agreement with the fact that the boron content of natural micas and illites is always several times higher than the content of boron in montmorillonites or chlorites (see Harder, 1961b). There is no straightforward explanation for such a behavior, but it is not impossible that potassium ions could have some influence on the stabilization of boron with fourfold coordination during the formation of micas.

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