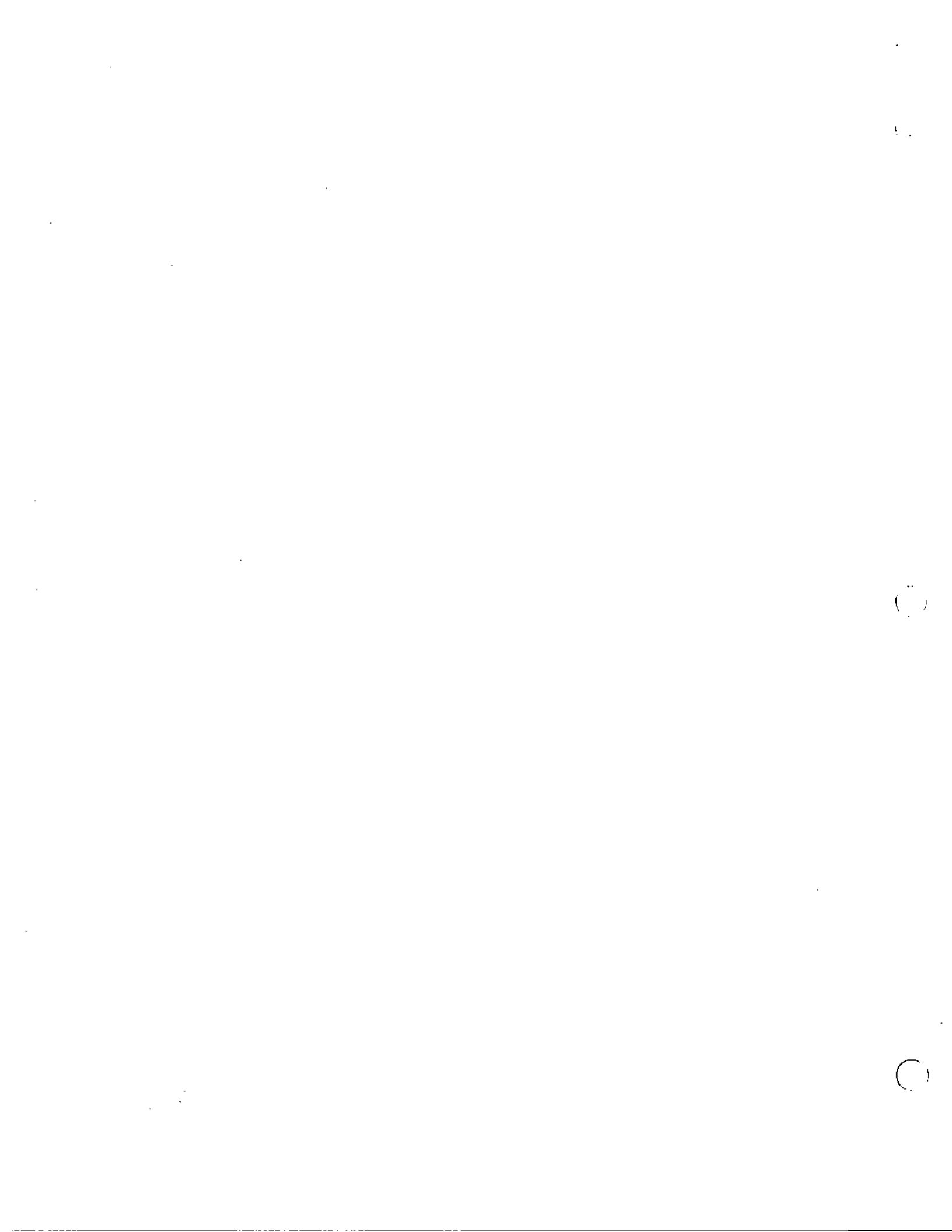


Boron

5

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5-A. Crystal Chemistry

Boron is one of the less abundant elements, the average amount of boron in the earth's crust being estimated as less than 10 parts per million. However, large quantities of boron are concentrated in deposits of hydrated borate minerals; these deposits occur in closed basins and under arid conditions. Deposits are found in the United States (Mojave Desert), Turkey, U.S.S.R. (Inder district), Tibet, Italy, Germany, Argentina, Bolivia, Canada, China, India, Iran, New Zealand, New Guinea, and Syria. The minerals of chief commercial importance are borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and kernite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$. Large quantities of these minerals are mined at the Kramer deposit, Boron, California, and borax is extracted, also in large amounts, from the brine at Searles Lake, California. A discussion of the geochemistry of the paragenetic relations in the system $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$, particularly for deposits in the western United States, was given by CHRIST *et al.* (1966).

With the exception of the minerals ferrucite, NaBF_4 , and avogadrite $(\text{K}, \text{Cs})\text{BF}_4$ (both of which contain $[\text{BF}_4]^{1-}$ tetrahedra), boron always occurs in chemical combination with oxygen, i. e., as a borate. Boron, which has an oxidation number (valence) of +3, never acts as a cation; for example, salts of the type $\text{B}_2(\text{SO}_4)_3$, or $\text{B}(\text{NO}_3)_3$, are not known. Instead, a boron atom will combine with three oxygen atoms to form a plane triangular group, BO_3 , or with four oxygen atoms to form a regular tetrahedron, BO_4 . These groups of threefold and fourfold coordination can result in isolated ions such as $[\text{BO}_3]^{3-}$, or $[\text{B}(\text{OH})_4]^{1-}$, or the $\text{B}(\text{OH})_3$ molecule contained in sassolite. In most crystals, however, the triangular or tetrahedral groups polymerize to form polyanions of varying degree of complexity. The crystal chemistry of the borates is similar to that of the silicates, with the additional complication that boron can occur in either triangular or tetrahedral coordination, or in both types of coordination in the same polynuclear anion. Borate minerals may contain silicate, phosphate, arsenate, or carbonate groups; these are, specifically, the borosilicates, the borophosphates, the boroarsenates, or the borocarbonates. Of these, the borosilicates constitute the largest group, by far. In crystals, values of the B—O bond length for triangularly coordinated boron cluster around 1.37 Å; for tetrahedrally coordinated boron the values cluster around 1.47 Å. Boron does not substitute for cations in crystals in the way that Fe^{2+} and Mg^{2+} substitute for one another in some silicates, for example; instead boron always enters a crystal in a boron-oxygen group. For this reason, it is meaningless to assign an ionic radius to boron.

Crystal Structures

Boron and oxygen combine to form a wide variety of anions in crystals. In addition to the mononuclear anions $[\text{BO}_3]^{3-}$ and $[\text{BO}_4]^{5-}$, and their protonated or partially protonated equivalents, there exists an extensive series of polynuclear anions formed by corner-sharing of triangular or tetrahedral B—O groups. In the subsequent discussion, examples of all the well-established mineral borate structures

Table 5-A-1. Borate minerals

Mineral names	Structural formula	Reference
<i>With planar triangular B(O, OH)₃ groups</i>		
Kotoite	Mg ^[6] ₃ [BO ₃] ₂ rh	SADANAGE, SR 1947-8, 425
Nordenskiöldine	Ca ^[6] Sn ^[6] [BO ₃] ₂ trig	ZACHARIASEN, SB 1928-32, 403
Ludwigite	(Mg, Fe'') ^[6] ₂ Fe'' ^[6] O ₂ [BO ₃] ₂ rh	TAKÉUCHI <i>et al.</i> , SR 1950, 350; TAKÉUCHI, SR 1955, 422; DA SILVA <i>et al.</i> (1955)
Warwickite	(Mg, Fe'') ^[6] ₃ Ti ^[6] O ₂ [BO ₃] ₂ rh	TAKÉUCHI <i>et al.</i> , SR 1950, 350
Sassolite	B(OH) ₃ m	ZACHARIASEN, SR 1954, 394
Fluoborite	Mg ^[6] ₃ (OH, F) ₃ [BO ₃] ₂ h	TAKÉUCHI, SR 1950, 349
Hambergite	Be ^[6] ₃ (OH, F) ₃ [BO ₃] ₂ rh	ZACHARIASEN <i>et al.</i> (1963)
Suanite (monoclinic Mg ₂ B ₂ O ₆)	Mg ^[6] ₂ [B ^[6] ₂ O ₆] m	TAKÉUCHI, SR 1952, 332
Szaibelyite (= Ascharite)	Mg ^[6] ₃ (OH, F) ₃ (OH)[B ₂ O ₄ (OH)] rh	P'ENG <i>et al.</i> (1963)
<i>With tetrahedral B(O, OH)₄ groups</i>		
Sinhalite	Mg ^[6] Al ^[6] [BO ₄] ₂ rh	CLARINGBULL and HEY, SR 1952, 334
Behierite	(Ta, Nb) ^[6] [BO ₄] ₂ t	MROSE and ROSE (1961)
Cahnite	Ca ^[6] ₃ [AsO ₄][B(OH) ₄] ₂ t	PREWITT and BUERGER (1961)
Bandyllite	Cu ^[6] ₃ (OH, F) ₃ Cl[B(OH) ₄] ₂ t	COLLIN, SR 1950, 346
Teepleite	Na ^[6] ₃ (OH, F) ₃ Cl[B(OH) ₄] ₂ t	FORNASERI, SR 1949, 263
Pinnoite	Mg ^[6] ₃ (OH, F) ₃ [B ₂ O(OH) ₆] ₂ t	PATON and MACDONALD, SR 1957, 428
Synthetic-cubic metaboric acid	∞[B ^[6] O(OH)] k	ZACHARIASEN (1963)
Danburite	∞Ca ^[6] ₂ [BSiO ₄] ₂ rh	JOHANNSON, SR 1959, 467
Reedmergnerite	∞Na ^[6] [BSi ₃ O ₈] trkl	APPLEMAN and CLARK (1965)
Datolite	∞Ca ^[6] ₂ (OH, F) ₂ [BSiO ₄ (OH)] m	ITO and MORI, SR 1953, 554; PAVLOV and BELOV, SR 1959, 470

are given, but no attempt is made to list all minerals of a given structural type. For this purpose, one may consult TENNYSON (1963), who has followed the scheme proposed by CHRIST (1960) in presenting a detailed treatment of the systematic classification of both synthetic and natural borates based on crystal-chemical grounds, using data published through 1962.

In Table 5-A-1 are listed examples of all mineral borate structures that have been well-determined by X-ray diffraction methods. In addition, results are given for synthetic cubic metaboric acid, γ -HBO₃, (ZACHARIASEN, 1963), a substance shown to exist as the mineral metaborite (LOBANOVA and AVROVA, 1964). Also listed is the synthetic compound CaB₃O₅(OH) (CLARK *et al.*, 1962), apparently a dimorph of fabianite (KÜHN *et al.*, 1962). Fabianite undoubtedly has the same B—O structure as

Table 5-A-1 (Continued)

Mineral names	Structural formula	Reference
<i>With both triangular B(O, OH)₃ and tetrahedral B(O, OH)₄ groups</i>		
Meyerbofferite	$\text{Ca}^{(\text{H}_4\text{O}, 3\text{OH} + \text{OH}, 2\text{O} + \text{O})}[\text{B}_2^{(4)}\text{B}^{(3)}\text{O}_3(\text{OH})_5] \cdot \text{H}_2\text{O}$ trkl	CHRIST and CLARK (1960); CLARK <i>et al.</i> (1964)
Inderite	$\text{Mg}^{(\text{H}_4\text{O}, 2\text{OH})}[\text{B}_2^{(4)}\text{B}^{(3)}\text{O}_3(\text{OH})_2] \cdot 5\text{H}_2\text{O}$ m	RUMANOVA and ASHIROV (1964a)
Colemanite	$\text{Ca}^{(\text{H}_4\text{O}, 3\text{OH} + \text{OH}, \text{O} + 2\text{O})}[\text{B}_2^{(4)}\text{B}^{(3)}\text{O}_4(\text{OH})_2] \cdot \text{H}_2\text{O}$ m	CHRIST <i>et al.</i> (1958); CLARK <i>et al.</i> (1964)
Hydroboracite	$\text{Mg}^{(\text{H}_4\text{O}, 2\text{OH})}\text{Ca}^{(2\text{OH} + 2\text{OH}, 4\text{O})}[\text{B}_2^{(4)}\text{B}^{(3)}\text{O}_4(\text{OH})_2]_2 \cdot 3\text{H}_2\text{O}$ m	RUMANOVA and ASHIROV (1964b)
Synthetic	$\text{Ca}^{(3\text{OH} + \text{OH}, 3\text{O})}[\text{B}_2^{(4)}\text{B}^{(3)}\text{O}_5(\text{OH})]$	CLARK <i>et al.</i> (1962)
Tunellite	$\text{Sr}^{(2\text{H}_4\text{O} + 2\text{H}_4\text{O}, 4\text{O} + 2\text{O})}[\text{B}_2^{(4)}\text{B}_2^{(3)}\text{O}_9(\text{OH})_2] \cdot 4\text{H}_2\text{O}$ m	CLARK (1964)
Borax	$\text{Na}_2^{(2\text{H}_4\text{O})}[\text{B}_2^{(4)}\text{B}_2^{(3)}\text{O}_6(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ m	MORIMOTO, SR 1956, 376
Kernite	$\text{Na}_2^{(2\text{H}_4\text{O})}[\text{B}_2^{(4)}\text{B}_2^{(3)}\text{O}_6(\text{OH})_2] \cdot 3\text{H}_2\text{O}$ m	GEISE (1966)
Ulexite	$\text{Na}_2^{(\text{H}_4\text{O}, 2\text{OH})}\text{Ca}^{(2\text{H}_4\text{O}, 3\text{OH}, 3\text{O})}[\text{B}_2^{(4)}\text{B}_2^{(3)}\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$ trkl	CLARK and APPLEMAN (1964)
Probertite	$\text{Na}_2^{(2\text{H}_4\text{O} + \text{H}_4\text{O}, \text{OH}, \text{O})}\text{Ca}^{(\text{H}_4\text{O}, \text{OH} + 2\text{OH}, 4\text{O} + \text{O})}[\text{B}_2^{(4)}\text{B}_2^{(3)}\text{O}_7(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ m	RUMANOVA <i>et al.</i> (1966)

the synthetic. Other structures determined for synthetic compounds are not given if they have no mineral counterparts. The interesting minerals tourmaline, axinite, and boracite are not treated because the structures reported for these must be considered to be only approximate ones.

A number of the structures listed in Table 5-A-1 are illustrated in Fig. 5-A-1 to 5-A-8. The minerals in Table 5-A-1, beginning with kotoite and extending through fluoroborate, all contain isolated planar triangular $[\text{BO}_3]^{3-}$ groups. In these structures (excepting $\text{B}(\text{OH})_3$), stable arrangements are attained by the packing of the oxygens of the $[\text{BO}_3]^{3-}$ groups, and any other anions present, around the cations. The structure of ludwigite is shown in Fig. 5-A-1; warwickite has a related structure. The structure of fluoroborate is illustrated in Fig. 5-A-2. In kotoite there is distorted hexagonal close-packing of oxygens, with the borons in trigonal positions, and the magnesium ions in octahedral positions. Nordenskiöldine has the dolomite structure. Sassolite consists of plane hexagonal sheets of $\text{B}(\text{OH})_3$ groups linked by hydrogen bonds. In hambergite, $[\text{BeO}_3(\text{OH})]^{5-}$ tetrahedra link at corners to form a three-dimensional structure, with BO_3 triangles sharing corners of two adjacent tetrahedra.

In suanite, the first example of a polynuclear anion cited here, two BO_3^{3-} triangles share a corner oxygen to form the dimer $[\text{B}_2\text{O}_5]^{4-}$, shown in the suanite structure in Fig. 5-A-3; szaibelyite contains this dimer with one proton added to form the $[\text{B}_2\text{O}_4(\text{OH})]^{2-}$ group.

The minerals in Table 5-A-1 beginning with sinhalite and extending through teepelite contain isolated tetrahedral $[\text{BO}_4]^{5-}$ or $[\text{B}(\text{OH})_4]^{1-}$ groups. Sinhalite has the olivine structure, while behierite has the zircon structure. Cabrite contains isolated $[\text{AsO}_4]^{3-}$ tetrahedra and $[\text{B}(\text{OH})_4]^{1-}$ tetrahedra. The structure of reepelite is shown in Fig. 5-A-4; the structure of bandylite is related to that of teepelite. Cubic meta-boric acid has a three-dimensional structure in which BO_4 tetrahedra share all four

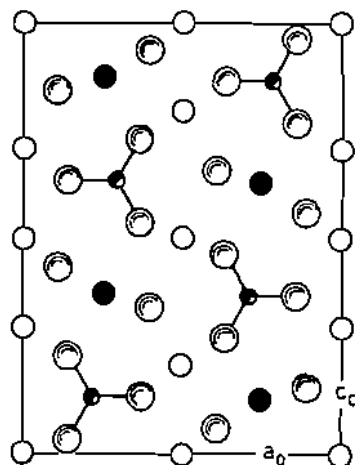


Fig. 5-A-1

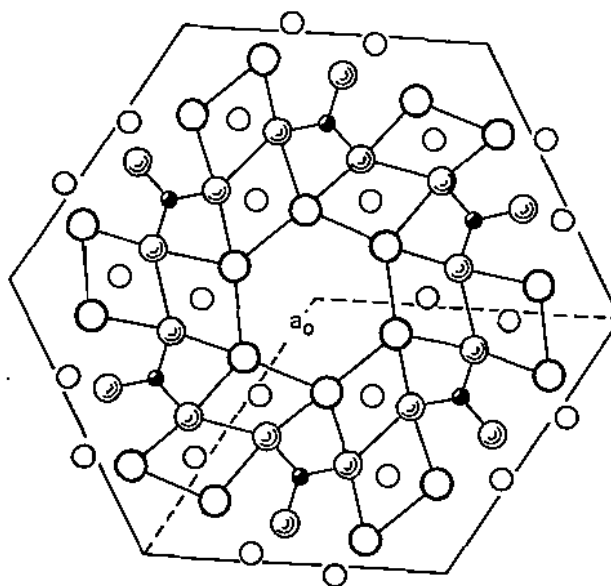


Fig. 5-A-2

Fig. 5-A-1. Structure of ludwigite, $(\text{Mg}, \text{Fe}'')_2\text{Fe}'''\text{O}_2[\text{BO}_3]$, projected on (010). ● B; ● Fe'''; ○ Fe'', Mg; ⊙ oxygen

Fig. 5-A-2. Structure of fluorborite, $\text{Mg}_3(\text{F}, \text{OH})_3[\text{BO}_3]$, projected on (001). ● B; ○ Mg; ⊙ F, OH

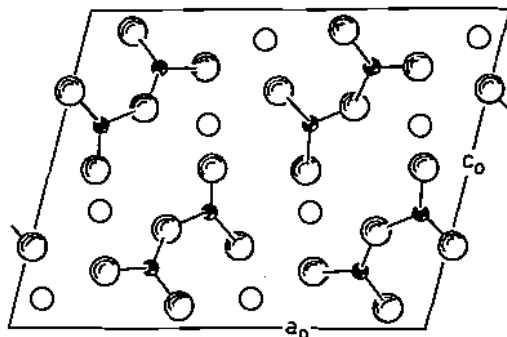


Fig. 5-A-3

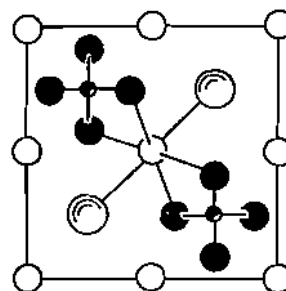


Fig. 5-A-4

Fig. 5-A-3. Structure of suanite, $\text{Mg}_2[\text{B}_2\text{O}_5]$, projected on (010). ● B; ○ Mg; ⊙ oxygen

Fig. 5-A-4. Structure of teepleite, $\text{Na}_2\text{Cl}[\text{B}(\text{OH})_4]$, projected on (001). ● B; ● OH; ○ Na; ⊙ Cl

corners; hydrogen bonds cross-link some of the oxygens. Pinnoite contains the dimer $[\text{B}_2\text{O}(\text{OH})_6]^{2-}$, consisting of two tetrahedra sharing a common corner oxygen.

Danburite and reedmergnerite are horosilicates in which silicate tetrahedra and borate tetrahedra share corners in various ways to build up framework structures. Danburite is built of Si_2O_7 and B_2O_7 groups sharing corners with one another to form a three-dimensional framework. Reedmergnerite has the low-albite structure.

Datolite contains infinite sheets of composition $[\text{BSiO}_4(\text{OH})]_n^{2n-}$. In forming a sheet, SiO_4 tetrahedra and $\text{BO}_3(\text{OH})$ tetrahedra link at corners so that each SiO_4 shares three corners and has one unshared corner, and each $\text{BO}_3(\text{OH})$ shares three corners, with the unshared (OH) at the fourth corner. The structure of datolite has

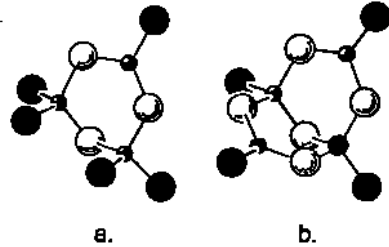


Fig. 5-A-5

Fig. 5-A-5. (a) The $[B_3O_3(OH)_3]^{2-}$ group found in meyerhofferite; (b) the $[B_4O_5(OH)_4]^{2-}$ group found in borax. ● B; ● OH; ⊙ oxygen

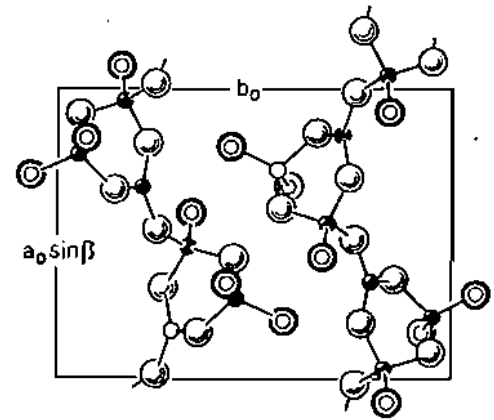


Fig. 5-A-6

Fig. 5-A-6. Boron-oxygen chains of colemanite, $Ca[B_2O_4(OH)_2] \cdot H_2O$, projected on (001) . ● B; ⊙ OH; ⊙ oxygen

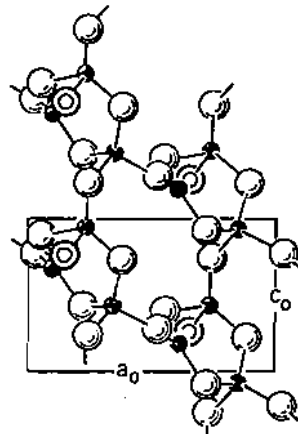


Fig. 5-A-7

Fig. 5-A-7. Boron-oxygen sheets in $Ca[B_3O_5(OH)]$ projected on (010) . ● B; ⊙ OH; ⊙ oxygen

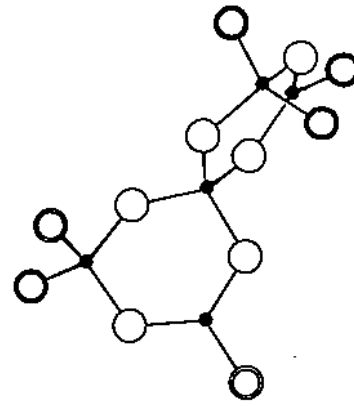


Fig. 5-A-8

Fig. 5-A-8. The $[B_5O_6(OH)_6]^{2-}$ group found in ulexite. ● B; ⊙ OH; ⊙ oxygen

provided the key to an understanding both of other hydrated borosilicate structures (CHRIST, 1959), and of the substitution of non-essential boron in silicate minerals (CHRIST, 1965).

The structures listed in Table 5-A-1 as containing both triangular and tetrahedral borate groups are all based on ring structures; the polyanion rings involved are shown in Figs. 5-A-5 and 5-A-8. The meyerhofferite and inderite structures contain the $[B_2^{[4]}B^{[3]}O_3(OH)_6]^{2-}$ polyanion shown in Fig. 5-A-5a. In colemanite, these isolated polyanions polymerize by splitting out water to form infinite chains of composition $[B_2^{[4]}B^{[3]}O_4(OH)_3]_n^{2n-}$ of the kind shown in Fig. 5-A-6. In $CaB_3O_5(OH)$, cross-linking of colemanite-type chains by further polymerization results in sheets of composition $[B_2^{[4]}B^{[3]}O_5(OH)]_n^{2n-}$, as shown in Fig. 5-A-7. Borax contains rings of the type shown in Fig. 5-A-5b. Kernite contains infinite chains of compo-

sition $[\text{B}_2^{[4]}\text{B}_2^{[3]}\text{O}_6(\text{OH})_2]_n^{2n-}$. Ulexite contains isolated polyanions of composition $[\text{B}_3^{[4]}\text{B}_2^{[3]}\text{O}_6(\text{OH})_6]^{3-}$ of the kind shown in Fig. 5-A-8. In probertite, these polyanions polymerize with splitting out of water to form infinite chains of composition $[\text{B}_3^{[4]}\text{B}_2^{[3]}\text{O}_7(\text{OH})_4]_n^{3n-}$. The polyanion on which the structure of tunellite is based is related to those described, but differs from these in that one oxygen of the polyanion is linked to three borons, rather than the usual two borons.

The crystal chemistry of this group of fully-hydrated borates is well understood, and a set of rules governing the nature of these complex polyanions (CHRIST, 1960) has been very fruitful in permitting correct prediction of new polyanions (CHRIST *et al.*, 1966; CLARK, 1964).

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5-B. Stable Isotopes in Nature

Natural boron is composed of two stable isotopes, ^{10}B and ^{11}B with the following average abundance: 18.98% ^{10}B and 81.02% ^{11}B (BAINBRIDGE and NIER, 1950). The isotope ^{10}B reacts with slow neutrons to produce He and Li. Boron isotopes can be produced during nucleosynthesis in the solar or star systems through reaction of ^{16}O with high-energy protons. The isotope geochemistry of boron has been reviewed by INGRAM (1946) and RANKAMA (1954). INGRAM (1946) reported the ratio $^{11}\text{B}/^{10}\text{B}$ to be 4.31 on the basis of BF_3 gas analysis. Most of these studies suffer from experimental difficulties (memory effects of BF_3 etc.).

Because of the relatively great mass difference between the two boron isotopes and the volatility of some boron compounds, natural isotopic fractionation is to be expected. It is argued that ^{11}B migrates more rapidly into the crust than ^{10}B and that the mantle thus has a lower $^{11}\text{B}/^{10}\text{B}$ ratio than the crust (SHERGINA *et al.*, 1968).

^{11}B enrichment has been found in boric acid vapors ($^{11}\text{B}/^{10}\text{B} = 4.41$), boron deposits and in kimberlite (CHEREPANOW, 1967). The latter author suggests degassing of the mantle as a cause for enrichment of the more volatile ^{11}B isotope. SHERGINA and KAMINSKAYA (1963) show that fractionation of boron isotopes occurs up to 2.5% in nature. Fractionation during the formation of hydrothermal ore deposits might be partly of thermal origin and partly due to exchange in wall-rock alterations. The ore body is enriched in ^{11}B . The boron-isotopes may be used in geochemical prospecting.

Sea water is enriched in ^{11}B by approximately 5 percent with respect to continental and volcanic inputs (SCHWARCZ *et al.*, 1969). These authors have proved that this

Table 5-B-1. Boron isotope ratios in natural materials

Sample	$^{11}\text{B}/^{10}\text{B}$	Reference
Terrestrial rocks and minerals	3.952 — 4.080	SCHWARCZ <i>et al.</i> (1969)
Basalt, granite, gabbro	4.04 — 4.09	SHIMA (1963)
Slate	4.108 \pm 0.02	SHIMA (1963)
Hambergite	4.026 \pm 0.008	FINLEY <i>et al.</i> (1962)
Colemanite, U.S.A. and Turkey	3.995 \pm 0.08	FINLEY <i>et al.</i> (1962)
Borax (Searles Lake)	4.040 \pm 0.01	McMULLEN <i>et al.</i> (1961)
Tincal (California)	4.07 \pm 0.012	McMULLEN <i>et al.</i> (1961)
Borax (California)	4.24 \pm 0.06	SHIMA (1963)
Sea water, Pacific Ocean	4.071 — 4.02	SHIMA (1963)
Sea water	4.208 — 4.240	SCHWARCZ <i>et al.</i> (1969)
Iron meteorite (Toluca)	3.85	SHIMA (1963)
Cbondrites (3) and achondrite (1) (Richardton, Ehole, Achilles, Pasamonte)	3.96 — 3.89 \pm 0.02	SHIMA (1963)

is due to an isotope effect during absorption of boron by clay minerals (see Sub-section 5-K-V).

The ratio of boron isotopes $^{11}\text{B}/^{10}\text{B}$ in terrestrial samples (Table 5-B-1) varies between 4.24 and 3.92. Unfortunately there is not much agreement between the data from different laboratories to allow further conclusions.

The isotopic ratios of B in lunar and terrestrial samples agree within 1% (EUGSTER, 1971). The isotopic abundance of boron in meteorites is of interest in connection with the nuclear synthesis of the light elements. Some values for meteorites are reported by SHIMA (1963).

5-C. Abundances in Meteorites, Tektites and Lunar Materials

I. Meteorites

The data on B in meteorites were recently summarized by QUIJANO-RICO and WÄNKE (1969). The values in Table 5-C-1 indicate that the results for stone meteorites given by HARDER (1959) and the mineral analyses by MASON and GRAHAM (1970) are generally higher than the values reported by SHIMA (1962) and QUIJANO-RICO and WÄNKE (1969). Carbonaceous chondrites are usually higher in readily volatile elements. The values for iron meteorites given by QUIJANO-RICO and WÄNKE (1969) are considerably lower than the values of SHIMA (1962). It may be that the analysed sample was not homogeneous, or that dissolving by H_2SO_4 was incomplete, or that some meteorites were contaminated by terrestrial soils. Nevertheless all meteoritic values show that boron in meteorites is a lithophilic and not a siderophilic element.

II. Tektites

Data on boron content in tektites are given by PREUSS (1935), HARDER (1961), MILLS (1968) and others. These values run from 6 to 53 ppm B. The average value of boron in tektites may be 23 ppm B. The boron contents in the moldavites (HARDER) and indochinites (MILLS) are not uniform and vary from sample to sample. The boron content of tektites is much higher than that of meteorites and slightly higher than that of lunar samples. They are comparable with the boron content of terrestrial sediments. The observed high but not uniform boron content of tektites may be expected if terrestrial shales or soils were fused.

III. Lunar Materials and Cosmic Abundance

Determination of boron abundances in some Apollo and Lunar samples is reported by EUGSTER (1971). The different analyses vary between 2.6 and 20.9 ppm B. The mean value of all boron data on lunar materials is 3.7 ppm B. Lunar abundances of B are in good agreement with those in terrestrial basalts. Boron abundances in meteorites, tektites and the cosmos show that the abundance of boron is abnormally low for its atomic weight. GREVESSE (1968) reports a solar B abundance of < 14.5 (relative to $Si = 10^8$ atoms), which is considerably lower than the abundance of about $100 B/10^8 Si$ atoms based on meteorite data. In the stellar and solar atmospheres the presence of boron is still not definitely established. Probably boron is used up by nuclear reactions (see GOLES in this handbook, Vol. I, p. 119).

Table 5-C-1. *Abundance in meteorites and tektites*

	Analytical method	Number of analyses	Range ppm B	Average ppm B	Reference
<i>Meteorites</i>					
Bronzite chondrites (CH)	W/C	35	0.12—5.95	0.8	QUIJANO-RICO and WÄNKE (1969)
Hypersthene chondrites (CL)	W/C	10	0.14—1.70	0.74	QUIJANO-RICO and WÄNKE (1969)
Carbonaceous chondrites	W/C	3	5.60—9.65	7.2	QUIJANO-RICO and WÄNKE (1969)
Carbonaceous chondrites (Cc1)	W/C	4	5.1 —7.1	5.7	MILLS (1965)
Achondrites	W/C	4	0.34—1.08	0.8	QUIJANO-RICO and WÄNKE (1969)
Stones (3 CH chondrites, 2 achondrites)	W/C	5	0.3 —1.3	0.6	SHIMA (1962)
Stones	S	10	1.4 —5.6	4.1	HARDER (1961)
Stones, feldspar	S	4	2 —3		MASON and GRAHAM (1970)
Stones, olivine	S	4	0.5 —3		MASON and GRAHAM (1970)
Iron meteorite (O)	C	1		0.45	SHIMA (1962)
Iron meteorites (O)	C	2	0.02—0.03	0.025	QUIJANO-RICO and WÄNKE (1969)
Troilite	S	1		0.5	HARDER (1961)
<i>Tektites</i>					
Indochinites	C	12	6—53	29	MILLS (1969)
Australites, bediasites etc.	C	10	12—25	19	MILLS (1969)
Moldavites	C	3	17—20	19	MILLS (1969)
Moldavites	S	4	10—35	20	HARDER (1961)

5-D. Abundance in Rock-Forming Minerals, Boron-Minerals

I. Rock-Forming Minerals

a) Silicates

The boron content of most minerals and rocks varies over a wide range. If the amount of boron available during the crystallization of major minerals is too low to allow the formation of independent boron minerals such as tourmaline, boron will replace major elements in their minerals. Data on the B content of rock-forming minerals are not very numerous; GOLDSCHMIDT and PETERS (1932), BERTOLANI (1949), HARDER (1959a) and OFTEDAHL (1964) have published some values. The boron content of rock-forming minerals is given in Tables 5-D-1 and 5-D-2. The wide range of variation makes it impossible to give meaningful average values. The most important rock-forming minerals containing trace amounts of boron are micas (HARDER, 1958) and serpentines (SAHAMA, 1945). Neso-, soro-, cyclo- and tectosilicates usually contain several ppm B or the concentrations are lower than the detection limit of 0.0X ppm; however higher boron-values are sometimes found, for instance

Table 5-D-1. *Boron content of silicates.* (According to HARDER, 1959a, except pegmatite minerals: OFTEDAHL, 1964, and pyroxenes: MOXHAM, 1965). (Analytical method: S)

Type	Number of samples	Abundant concentrations in ppm	Maximum values (in ppm B) of minerals with high boron concentrations
Nesosilicates	60	0.0X—X	gadolinite 8,000 special garnets 1,000
Sorosilicates	30	0.0X—X	vesuvianite 8,000 milinophane 1,500
Cyclosilicates	20	0.0X—X	cordierite 150
Inosilicates	20	X	wollastonite 100 pyroxenes 59
Phyllosilicates ^a	300	X—X00 especially mica, serpentine and montmorillonite	
Tectosilicates	60	0.0X—X	sodalite 100 scapolite 100 sericitized plagioclases 2,000

^a See Fig. 5-D-1.

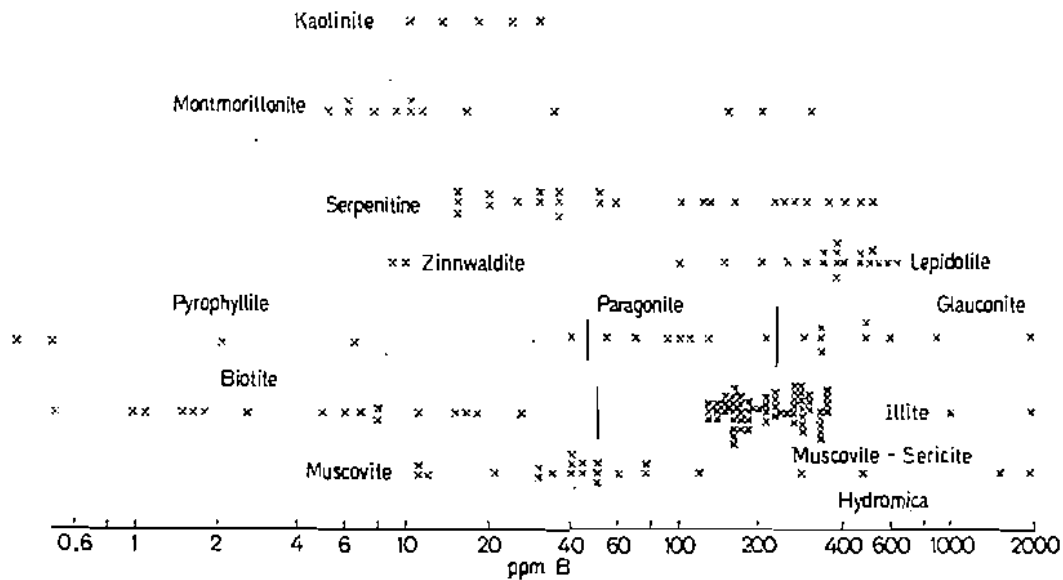


Fig. 5-D-1. Histogram showing the distribution of boron values of phyllosilicates. References: HARDER (1959a), BARSUKOV and KURILCHIKOVA (1957), FAUST *et al.* (1965), STAVROV and KHITROV (1960), MOXHAM (1965)

in pyroxenes (MOXHAM, 1965). MALINKO (1967) showed a close correlation between boron and aluminum contents in pyroxenes. The analyses presented in Table 5-D-1 demonstrate clearly that phyllosilicates contain more boron than the other silicates. Muscovite, paragonite, sericite, illite, montmorillonite (TOURTELOY *et al.*, 1961) and serpentine (FAUST *et al.*, 1956) in particular can have very high values of boron (see Fig. 5-D-1). Pegmatitic muscovites and lepidolites contain up to 1,000 ppm B. According to STAVROV and KHITROV (1962) there exists a geochemical relationship between cesium and boron in pegmatites and granitic rocks. On the other hand the level of B contents in minerals depends on the boron concentration of the melt or solution from which the minerals have been formed. It is assumed that the boron concentration increases during magmatic differentiation processes. Micas from pegmatites do not contain boron in excess. REYNOLDS (1965) studied muscovites from tourmaline-bearing pegmatites and found that the boron concentrations (range 39 to 115 ppm B) are relatively low. The majority of dioctahedral micas contain substantially higher amounts of boron than trioctahedral micas. The charge and size of the boron atom makes it probable that it replaces aluminum or silicon in the tetrahedral positions (HARDER, 1959b; LEBEDEV, 1960). Infrared studies by STUBICAN and ROY (1962) on synthetic boron-containing micas confirm this hypothesis. It is probable that boron replaces silicon in the other silicate minerals in the tetrahedral positions. MOXHAM (1964) assumes that boron occupies octahedrally-coordinated positions in biotites and amphiboles. Serpentine have low or high values (FAUST *et al.*, 1956) depending on their origin. Minerals from pegmatite deposits in general do not contain high boron contents; exceptions are some very special minerals of pegmatites. Boron is highly concentrated — up to several thousand ppm — in minerals containing beryllium (HARDER, 1959a) or rare earth elements (including thorium,

or both (OFTEDAHL, 1964), and in metamict pegmatite minerals (OFTEDAHL, 1964). The substitution of B for Be and P is to be expected from a crystallochemical point of view. The inhomogeneous distribution of boron in many metamict minerals indicates a relation between the alteration process and the boron accumulation. Most feldspars contain several ppm boron. It may be that an intergrowth with reedmergnerite, NaBSi_3O_8 , which is isostructural with low albite, can explain the boron content of feldspars (APPLEMAN and CLARK, 1965). BARSUKOV (1958) concludes that the boron content in plagioclases increase with increasing anorthite content. Higher boron contents in many plagioclases can, however, be explained by sericitization of the feldspars (HARDER, 1959a).

b) Oxides, Carbonates, Phosphates etc.

The boron content of quartz ranges from 0.0 to 25 ppm B (HARDER, 1959a). However in most magmatic rocks the boron content of quartz is very low: 0.X to 1 ppm B. During the pegmatite stage an enrichment of boron in quartz is possible. According to STAVROV *et al.* (1960) boron occurs in gas-liquid inclusions in quartz, but an incorporation of boron in the quartz lattice may also be possible. The amount of boron is controlled by the cations which compensate the charge, if a replacement of silicon in the SiO_4 tetrahedron takes place. A co-precipitation of boron together with sulfate minerals may be possible (see Subsection 5-K-VII). It seems that recrystallized sulfate minerals are poor in boron. Apatites and also phosphorites have a variable boron content (Table 5-D-2). Boron may be used as an indicator of the genesis of phosphorites as it is always present in marine phosphorites and is frequently absent from continental phosphorites (especially the non-argillaceous varieties) (ZANIN *et al.*, 1971).

Table 5-D-2. Boron abundances in common oxides, carbonates, phosphates, etc. (According to HARDER, 1959a, except data on braunite by WASSERSTEIN, 1943, on quartz by STAVROV *et al.*, 1960, and on magnesite by BRANDENSTEIN and SCHROLL, 1960). (Analytical method: S)

Mineral group	Number of samples	Range in ppm	Abundant values in ppm
Quartz	35	0.0 — 25	0.X
Agate, opal	25	0.0 — 90	X
Hematite, goethite	40	0.0 — 300	0.X
Manganite etc.	5	0.X — 100	X
Carbonates	10	0.0 — 0.X	0.X
Magnesite	76	<1 — 100	X
Apatite, phosphorites	10	<0.0 — 25	0.X

II. Boron Minerals

Boron is present in igneous and metamorphic rocks as a trace element in rock-forming minerals or in the form of boron silicates. Minerals containing boron as a major component are listed in Table 5-D-3. In the structure of silicates, boron forms

Table 5-D-3. *Boron minerals*

<i>Fluorides</i>	
Ferruccite	NaBF ₃
Avogadrite	(K, Cs)BF ₃
<i>Hydroxide</i>	
Sassolite	B(OH) ₃
<i>Borates</i>	
Jeremejewite	AlBO ₃
Eichwaldite	Al ₄ B ₂ O ₁₅ (OH) ₃
Kotoite	Mg ₃ [BO ₃] ₂
Jimboite	Mn ₃ [BO ₃] ₂
Nordenskiölddine	CaSn[BO ₃] ₂
Warwickite	(Mg, Fe) ₃ Ti[O BO ₃] ₂
Pinakiolite	(Mg, Mn ²⁺) ₂ Mn ²⁺ [O ₂ BO ₃]
Hulsite	(Fe ²⁺ , Mg, Fe ³⁺ , Sn ⁴⁺) ₃ [O ₂ BO ₃]
Ludwigite	(Mg, Fe ²⁺) ₂ Fe ³⁺ [O ₂ BO ₃]
Vonsenite	(Fe ²⁺ , Mg) ₂ Fe ³⁺ [O ₂ BO ₃]
Orthopinakiolite	(Mg, Mn ²⁺) ₂ Mn ²⁺ [O ₂ BO ₃]
Gaudefroyite	3 · CaMn ²⁺ [O BO ₃] · Ca[CO ₃]
Nocerite	Mg ₃ [BO ₃]F ₃
Fluoborite	Mg ₃ [BO ₃](F, OH) ₃
Berberite	Bc ₂ [BO ₃](OH, F) · H ₂ O
Wightmanite	Mg ₉ [BO ₃] ₂ (OH) ₁₂ · 25H ₂ O
Johachidolite	Ca ₃ Na ₂ Al ₄ H ₄ [BO ₃] ₆ (F, OH) ₆
Sakhaite	Ca ₁₂ Mg ₁ [CO ₃] ₄ [BO ₃] ₇ (Cl)(OH) ₂ · H ₂ O
Seamanite	Mn ₃ [PO ₄][BO ₃] · 3H ₂ O
Sulfoborite	Mg ₃ [SO ₄][BO ₃](OH) ₂ · 4H ₂ O
Sinhalite	MgAl[BO ₄]
Behierite	(Ta, Nb)[BO ₄]
Bandyllite	Cu B(OH) ₄ (Cl)
Teepleite	Na ₂ B(OH) ₄ (Cl)
Cahnite	Ca ₂ [AsO ₄]B(OH) ₄
Suanite	Mg ₂ [B ₂ O ₅]
Ascharite (szaibelyite)	Mg ₂ [B ₂ O ₅] · H ₂ O
Sussexite	Mn ₂ [B ₂ O ₅] · H ₂ O
Magnesiumsussexite	(Mg, Mn) ₂ [B ₂ O ₅] · H ₂ O
Roweite	CaMn[B ₂ O ₅] · H ₂ O
Sibirskite	Ca ₂ [B ₂ O ₅] · H ₂ O
Carborborite	Ca ₂ Mg[CO ₃][B ₂ O ₅] · 10H ₂ O
Wiserite	Mn ₄ (OH, Cl) ₄ [B ₂ O ₅]
Lueneburgite	Mg ₃ [PO ₄] ₂ B ₂ O(OH) ₄ · 6H ₂ O
Kurnakovite	Mg[B ₃ O ₃](OH) ₅ · 5H ₂ O (tricl.)
Inderite	Mg[B ₃ O ₃](OH) ₅ · 5H ₂ O (monocl.)
Inderborite	MgCa[B ₃ O ₃] ₂ (OH) ₁₀ · 6H ₂ O
Meyerhofferite	Ca[B ₃ O ₃](OH) ₅ · H ₂ O
Inyoite	Ca[B ₃ O ₃](OH) ₅ · 4H ₂ O
Ameghinite	Na ₂ [B ₃ O ₃] ₂ (OH) ₈
Tinkalkonite	Na ₂ [B ₄ O ₅](OH) ₄ · 3H ₂ O
Borax	Na ₂ [B ₄ O ₅](OH) ₄ · 8H ₂ O
Halurgite	Mg ₂ [B ₄ O ₅] ₂ (OH) ₈ · H ₂ O
Hungchaoite	Mg[B ₄ O ₅](OH) ₄ · 7H ₂ O

Table 5-D-3 (continued)

Ezcurrite	$\text{Na}_2[\text{B}_5\text{O}_6](\text{OH})_5 \cdot \text{H}_2\text{O}$	(tricl.)
Nasinitc	$\text{Na}_2[\text{B}_4\text{O}_6](\text{OH})_5 \cdot \text{H}_2\text{O}$	(monocl.)
Proberite	$\text{NaCa}[\text{B}_5\text{O}_6](\text{OH})_6 \cdot 2\text{H}_2\text{O}$	
Ulexite	$\text{NaCa}[\text{B}_5\text{O}_6](\text{OH})_6 \cdot 5\text{H}_2\text{O}$	
Pandermite	$\text{Ca}_2[\text{B}_5\text{O}_6](\text{OH})_7$	
Tertschite	$\text{Ca}_2[\text{B}_5\text{O}_6](\text{OH})_7 \cdot 6.5\text{H}_2\text{O}$	
Priceite	$5\text{CaO} \cdot 6\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ (?)	
Larderellite	$\text{NH}_4[\text{B}_5\text{O}_6](\text{OH})_4$	
Ammonioborite	$\text{NH}_4[\text{B}_5\text{O}_6](\text{OH})_4 \cdot 2/3\text{H}_2\text{O}$	
Sborgite	$\text{Na}[\text{B}_5\text{O}_6](\text{OH})_4 \cdot 3\text{H}_2\text{O}$	
Ginorite	$\text{Ca}_2[\text{B}_4\text{O}_6](\text{OH})_4[\text{B}_5\text{O}_6]_2(\text{OH})_8 \cdot 2\text{H}_2\text{O}$	
Volkovite	$(\text{Sr}, \text{Ca})[\text{B}_5\text{O}_6](\text{OH})_4[\text{B}_5\text{O}_6]_2(\text{OH})_8 \cdot 2\text{H}_2\text{O}$	
Kaliborite	$\text{KMg}_2\text{H}[\text{B}_5\text{O}_6](\text{OH})_5 \cdot 4\text{H}_2\text{O}$	
Pinnoite	$\text{MgB}_2\text{O}(\text{OH})_6$	
Frolovite	$\text{CaB}_2\text{O}(\text{OH})_6 \cdot \text{H}_2\text{O}$ (?)	
Calciborite	$\text{Ca}[\text{B}_2\text{O}_4]$ (?)	
Kurgantaitc	$(\text{Sr}, \text{Ca})_2[\text{B}_4\text{O}_6] \cdot \text{H}_2\text{O}$	
Veatchite	$\text{Sr}[\text{B}_3\text{O}_4]_2(\text{OH})_4$	
p-Veatchite	$(\text{Sr}, \text{Ca})[\text{B}_3\text{O}_4]_2(\text{OH})_4$	
Volkovskite	$\text{Ca}[\text{B}_3\text{O}_4]_2(\text{OH})_4 \cdot \text{H}_2\text{O}$	
Aksaitc	$\text{Mg}[\text{B}_3\text{O}_4]_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}$	
Gowcrite	$\text{Ca}[\text{B}_3\text{O}_4]_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}$	
Rivadarite	$\text{Na}_6\text{Mg}[\text{B}_3\text{O}_4]_6(\text{OH})_{16} \cdot 14\text{H}_2\text{O}$	
Colemanite	$\text{Ca}[\text{B}_3\text{O}_4](\text{OH})_3 \cdot \text{H}_2\text{O}$	
Hydroboracite	$\text{MgCa}[\text{B}_3\text{O}_4]_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$	
Kernite	$\text{Na}_2[\text{B}_4\text{O}_6](\text{OH})_2 \cdot 3\text{H}_2\text{O}$	
Biringuccite	$\text{Na}_2[\text{B}_5\text{O}_7](\text{OH})_3 \cdot 1/2\text{H}_2\text{O}$ (?)	
Preobratschenskite	$\text{Mg}_3[\text{B}_5\text{O}_7]_2(\text{OH})_8 \cdot 1/2\text{H}_2\text{O}$ (?)	
Braitschite	$7(\text{Ca}, \text{Na})\text{O} \cdot \text{Se}_2\text{O}_3 \cdot 11\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$	
Teruggite	$\text{Ca}_4\text{Mg}[\text{AsO}_4][\text{B}_6\text{O}_{10}]_2 \cdot 18\text{H}_2\text{O}$	
Vimsite	$\text{Ca}[\text{B}_2\text{O}_4](\text{OH})_1$	
Uralborite	$\text{Ca}[\text{B}_2\text{O}_4] \cdot 2\text{H}_2\text{O}$ (?)	
Nifontovite	$\text{Ca}[\text{B}_2\text{O}_4] \cdot 2.3\text{H}_2\text{O}$ (?)	
Pentahydroborite	$\text{Ca}[\text{B}_2\text{O}_4] \cdot 5\text{H}_2\text{O}$ (?)	
Fabianite	$\text{Ca}[\text{B}_3\text{O}_6](\text{OH})$	
Hilgardite	$\text{Ca}_2[\text{B}_5\text{O}_8](\text{OH})_2(\text{Cl})$	(monocl.)
Parahilgardite	$\text{Ca}_2[\text{B}_5\text{O}_8](\text{OH})_2(\text{Cl})$	(tricl.)
Strontiohilgardite	$\text{SrCa}[\text{B}_5\text{O}_8](\text{OH})_2(\text{Cl})$	(tricl.)
Tyretskite	$\text{Ca}_2[\text{B}_5\text{O}_8](\text{OH})_3$	
Heidornite	$\text{Ca}_3\text{Na}_2[\text{SO}_4]_2[\text{B}_5\text{O}_8](\text{OH})_2(\text{Cl})$	
Nobleite	$\text{Ca}[\text{B}_5\text{O}_8](\text{OH})_2 \cdot 3\text{H}_2\text{O}$	
Tunellite	$\text{Sr}[\text{B}_5\text{O}_8](\text{OH})_2 \cdot 3\text{H}_2\text{O}$	
Mcallisterite	$\text{Mg}[\text{B}_6\text{O}_9](\text{OH})_2 \cdot 6 \frac{1}{2}\text{H}_2\text{O}$	
Korschinskiite	$\text{Ca}_2[\text{B}_4\text{O}_6](\text{OH})_4$	
Hamburgite	$\text{Be}_2[\text{BO}_3](\text{OH})$	
Rhodizite	$\text{KNaLi}_4\text{Al}_4[\text{Be}_3\text{B}_{10}\text{O}_{27}]$	
Low boracite (stassfurtite)	$\alpha\text{-Mg}_3[\text{B}_7\text{O}_{13}](\text{Cl})$	
Boracite	$\beta\text{-Mg}_3[\text{B}_7\text{O}_{13}](\text{Cl})$	
Ironboracite	$(\text{Mg}, \text{Fe})_3[\text{B}_7\text{O}_{13}](\text{Cl})$	
α -ericaite	$\alpha\text{-(Fe, Mg, Mn)}_3[\text{B}_7\text{O}_{13}](\text{Cl})$	(rhomb.)
β -ericaite	$\beta\text{-(Fe, Mg, Mn)}_3[\text{B}_7\text{O}_{13}](\text{Cl})$	(cubic)
Chambersite	$\text{Mn}_3[\text{Cl} \text{B}_7\text{O}_{13}]$	
Metaborite	$\gamma\text{-HBO}_2$	

Table 5-D-3 (continued)

<i>Silicates</i>	
Elbaite ^a	$\text{Na}(\text{Li}, \text{Al})_3\text{Al}_6(\text{OH})_{1+3}[\text{BO}_3]_3[\text{Si}_6\text{O}_{18}]$
Dravite ^a	$\text{NaMg}_3\text{Al}_6(\text{OH})_{1+3}[\text{BO}_3]_3[\text{Si}_6\text{O}_{18}]$
Schoerl ^a	$\text{NaFe}^{2+}_3\text{Al}_6(\text{OH})_{1+3}[\text{BO}_3]_3[\text{Si}_6\text{O}_{18}]$
Uvite ^a	$\text{CaMg}_3(\text{Al}_5\text{Mg})(\text{OH})_{1+3}[\text{BO}_3]_3[\text{Si}_6\text{O}_{18}]$
Bucrgerite ^a	$\text{NaFe}^{2+}_3\text{Al}_6(\text{F})\text{O}_3[\text{BO}_3]_3[\text{Si}_6\text{O}_{18}]$
Tianshanite ^a	$\text{Na}_2\text{BaMnTi}[\text{BO}_2]_2[\text{Si}_6\text{O}_{18}]$
Axinitic	$\text{Ca}_2(\text{Fe}, \text{Mn})\text{Al}_2(\text{OH})[\text{BO}_3][\text{Si}_4\text{O}_{12}]$
Datolite	$\text{CaB}(\text{OH})[\text{SiO}_4]$
Bakerite	$\text{CaB}(\text{OH})[(\text{BH}, \text{Si})\text{O}_4]$
Homilite	$\text{Ca}_2\text{Fe}^{2+}\text{B}_2[\text{O} \text{SiO}_4]_2$
Calcioadolinite	$\text{CaYFe}^{2+}(\text{B}, \text{Be})_2[\text{O} \text{SiO}_4]_2$
Stillwellite	$\text{CeB}[\text{O} \text{SiO}_4]$
Cappelenite	$(\text{Ba}, \text{Ca}, \text{Ce}, \text{Na})(\text{Y}, \text{Ce}, \text{La})_2[\text{B}_2\text{O}_5 \text{SiO}_4]$
Kornepupine	$\text{Mg}_4\text{Al}_6(\text{O}, \text{OH})_2[\text{BO}_4][\text{SiO}_4]_4$
Painite	$5\text{Al}_2\text{O}_3 \cdot \text{Ca}_2[(\text{Si}, \text{BH})\text{O}_4]$
Dumortierite	$(\text{Al}, \text{Fe})_7[\text{O}_3 \text{BO}_3][\text{SiO}_4]_3$
Serendihite	$(\text{Ca}, \text{Mg})_6(\text{AlO})_6[\text{BO}_3][\text{SiO}_4]_3$
Grandidierite	$(\text{Mg}, \text{Fe})\text{Al}_3[\text{O} \text{BO}_4][\text{SiO}_4]$
Howlite	$\text{Ca}_2[\text{BOOH}]_5[\text{SiO}_4]$
Harkerite	$\text{Ca}_{18}\text{Mg}_{10}\text{Al}_7(\text{Cl})_2(\text{OH})_6[\text{BO}_3]_{15}[\text{CO}_3]_{12}[\text{SiO}_4]_{12} \cdot 3\text{H}_2\text{O}$
Garrels site	$\text{Na}, \text{Ba}_3(\text{OH})_4\text{Si}_2\text{B}_7\text{O}_{18}$
Melanocerite	$\text{Na}_4\text{Ca}_{16}(\text{Y}, \text{La})_2(\text{Zr}, \text{Ce})_6(\text{F})_{12}[\text{BO}_3]_3[\text{SiO}_4]_{12}$
Karyocerite	$\text{Na}_4\text{Ca}_{16}(\text{Y}, \text{Th}, \text{La})_2(\text{Zr}, \text{Ce})_6(\text{F})_{12}[\text{BO}_3]_3[\text{SiO}_4]_{12}$
Hyalotekite	$(\text{Pb}, \text{Ca}, \text{Ba})_4\text{B}[\text{Si}_5\text{O}_{17}](\text{F}, \text{OH})$
Searlesite	$\text{Na}_2\text{B}_2(\text{OH})_4[\text{Si}_3\text{O}_{10}]$
Reedmergerite	$\text{Na}[\text{BSi}_3\text{O}_8]$
Danburite	$\text{Ca}[\text{B}_2\text{Si}_2\text{O}_8]$
Hellandite	$\text{Ca}_3(\text{Y}, \text{Yb} \dots)_4\text{B}_4[\text{O} \text{OH}]_2[\text{Si}_2\text{O}_7]_3$
Spencite	$(\text{Y}, \text{Ca}, \text{La}, \text{Fe})_6[\text{Si}, \text{B}, \text{Al}]_6(\text{O}, \text{OH}, \text{F})_{13}$

^a Tourmaline group.

$[\text{BO}_4]^{5-}$ tetrahedra, and $[\text{BO}_3]^{3-}$ groups or boron replaces silica in the $[\text{SiO}_4]^{4-}$ tetrahedra. Minerals of the tourmaline group with 9 to 11.5% B_2O_3 are the most important of the boron minerals. In granites, tourmaline has been formed generally at the end of the main stage of crystallization. Axinite and datolite occur mainly in mafic rocks. All other minerals are comparatively rare, however, and are of little geochemical importance.

5-E. Abundances in Common Igneous Rock Types

GOLDSCHMIDT and PETERS (1932) made the first fundamental contribution to the knowledge of the geochemistry of boron. However the analytical precision at that time was only half an order of magnitude. The boron content of different rock types seems to be extremely variable. Nevertheless unaltered rocks generally have a relatively small range of boron contents. Because boron is a mobile element, postmagmatic processes can produce high secondary accumulations however.

Serpentine in mafic rocks and sericite in salic rocks are important boron hosts in altered magmatic rocks. Independent boron minerals are rare. Glass is an important boron carrier in volcanic rocks.

I. Ultramafic Rocks

The boron contents of ultramafic rocks vary widely (see Table 5-E-1). Extremely high values occur in kimberlite (factor of enrichment up to 100) and low values of several ppm are found in the common ultramafic rocks, if they are not serpentinized.

Table 5-E-1. *Boron in ultramafic rocks* (Analytical method: S)

Rock	Locality	Number of ana- lyses	Abundance (ppm B)		Reference
			range	average	
Dunites, peridotites	Siberia (U.S.S.R.)	300		1—10	VARLAKOV and ZITUSZHGOVA (1964)
Serpentinites	Siberia (U.S.S.R.)	150	40—130		VARLAKOV and ZITUSZHGOVA (1964)
Ultramafic rocks	Siberia (U.S.S.R.)			1	VINOGRADOV (1954)
Ultramafic rocks	S. Lapland (Finland)	1		31	SAHAMA (1950)
Peridotite	Sweden	1	100		LUNDEGÅRDH (1947)
Peridotites	Tianshan (U.S.S.R.)	8		64	ORTROSHCHENKO <i>et al.</i> (1969)
Ultramafic rock	Germany	1		10	HAHN-WEINHEIMER (1960)
Paleopicrite	Germany	8	36—365	210	HAHN-WEINHEIMER (1960)
Paleopicrite	Siberia (U.S.S.R.)		7— 60		CHEREPANOW (1967)
Kimberlite	Siberia (U.S.S.R.)	260	9—590	120	CHEREPANOW (1967)
Kimberlite (compilation)				150	HARRIS and MIDDLE- MOST (1968)

Tentative average for ultramafic rocks (without serpentinization): 5 ppm B.

High concentrations of B related to serpentinisation have been reported by SAHAMA (1945) and FAUST *et al.* (1956). Boron can be irregularly distributed in rock massives and even in a single sample. Factors of enrichment up to 1,000 as compared with the parent mafic rocks have been observed in areas of serpentinization. In some areas of Siberia a very high concentration of boron (150—390 ppm) in mafic rocks is related

Table 5-E-2. *Boron in mafic plutonic and volcanic rocks.* (Analytical method: S)

Rock	Locality	Number of analyses	Abundance (ppm B)		Reference
			range	average	
Gabbro	Germany	7	3—20	6	HARDER (1959a)
Gabbro (composite of 11)	Germany			6	HARDER (1959a)
Gabbro	Lapland (Finland)			9	SAHAMA (1945)
Gabbro	Norway		0.3—1.7		LANDMARK (1944)
Gabbro	Sweden			<5	LUNDEGÅRDH (1947)
Gabbro		2	5—10		SHIMA (1963)
Gabbro	Urals (U.S.S.R.)	4	30—30	30	GETLING <i>et al.</i> (1958)
Gabbro	Urals (U.S.S.R.)	4	0—30		DUNAEV (1959)
		2	7—13		STAVROV (1960)
Gabbro	Tienshan (U.S.S.R.)	29		20	OTROSHCHENKO <i>et al.</i> (1969)
Gabbro	Tienshan (U.S.S.R.)	6		700	OTROSHCHENKO <i>et al.</i> (1969)
Norite	Tienshan (U.S.S.R.)	11		22	OTROSHCHENKO <i>et al.</i> (1969)
Basalt	Hawaii	1		3.2	SHIMA (1963)
Basalt	Pacific Ocean	1		4.2	SHIMA (1963)
Basalt	New Zealand	1		7.5	ELLIS (1964)
Basalt and "Diabase"	Germany and world	20	2.2—26	5	HARDER (1959a)
Basalt (composite of 9)	Deccan (India)			6	HARDER (1959a)
Basalt, andesite-basalt	Tien Shan (U.S.S.R.)	25	3—6	4.3	OTROSHCHENKO <i>et al.</i> (1969)
"Diabase"	Tien Shan (U.S.S.R.)	7		22	OTROSHCHENKO <i>et al.</i> (1969)
Mafic lava	Tien Shan (U.S.S.R.)	41	6—8	7	OTROSHCHENKO <i>et al.</i> (1969)
Basalt (Geochem. Standard JB-1)	Kita-Matsuura (Japan)	1		10	IKEDA in ANDO <i>et al.</i> (1971)

to serpentinization or tourmalinization which seems to be connected with later emplacement of granitoids (OTROSHCHENKO *et al.*, 1969). Dunites are usually poorer in boron than peridotites. CHEREPANOW (1967) assumes degassing of the mantle as the cause of the anomalously high concentration of boron in kimberlites.

II. Gabbroic and Basaltic Rocks

Boron data for mafic rocks (Table 5-E-2) have also a large range of variation. In general mafic rocks have similar but slightly higher B contents than ultramafic rocks. If we exclude the serpentinized samples, the range of B contents in mafic rocks decreases. No regional variation of boron abundances in basaltic rocks from all over the world could be observed. 5 ppm B may be an average for basaltic rocks. The mean value for mafic plutonic rocks is probably slightly higher (8 ppm).

III. Alkalic Rocks

Boron data is only available on a few typical rocks which are listed in Table 5-E-3. Boron is homogeneously distributed in different mineral fractions from a Nor-

Table 5-E-3. Boron in alkalic plutonic and volcanic rocks (Analytical method: S)

Rock	Locality	Number of analyses	Abundance (ppm B)		Reference
			range	average	
Syenite	Dresden (D.D.R.)	1		20	HARDER (1959a)
Syenite	U.S.S.R.	2	9—16	13	STAVROV and KHRITOV (1966)
Syenite	Urals (U.S.S.R.)	4	53—2,000		LISITSYN and KHRITOV (1962)
Syenite	Turkestan	26	<10—180	60	DUSMATOV (1972)
Syenite	Lapland (Finland)	1		9	SAHAMA (1945)
Syenite	Urals (U.S.S.R.)	2	30—90	60	DUNAEV (1959)
Nepheline syenite	World	2	8—34	21	HARDER (1959a)
Nepheline syenite (composite of 22)	World			8.5	HARDER (1959a)
Nepheline syenite (composite of 19)	Kola (U.S.S.R.)	19	5—38		GERASIMOVSKII <i>et al.</i> (1956)
Nepheline syenite	Chibina Tundra (U.S.S.R.)	1		3	VOLADCHENKO and MELENTIEV (1941)
Trachyte	Germany	2	3—10	6.5	HARDER (1959)
Trachyte	Italy		16—240		TADDEUCCI (1964)
Phonolite (2 composites of 24)	Germany, Czechoslovakia			5	HARDER (1959)

wegian nepheline syenite (HARDER, 1959). The number of analyses is too small to compute a mean and to observe systematic differences in boron between plutonic and volcanic rock types.

IV. Diorites, Andesites

Boron seems to be slightly more abundant in intermediate than in mafic rocks and slightly less abundant than in the granitic rocks. The range of variation in boron contents is not very large, and boron is more or less homogeneously distributed in intermediate rocks (see Table 5-E-4). Mineral fractions from a German diorite locality have small differences in boron: mafic minerals, 6 ppm B; plagioclase, 10 to 15 ppm B (HARDER, 1959a). The minerals of a diorite from Central Tien-Shan contain: quartz, 11 ppm; plagioclase, 23 ppm; biotite, 13 ppm; amphibole, 13 ppm B (YEZHKOV and LEVCHENKO, 1972). OTROSHCHENKO (1967) reports for the mineral fractions of andesites: plagioclase, 20 ppm B; orthoclase, 7 ppm B; biotite, 8 ppm B; amphibole, 11 ppm B; ground mass, 9 ppm B. A systematic difference in boron between diorites and andesites can be observed, the latter having a higher average boron concentration.

Table 5-E-4. Boron in intermediate plutonic and volcanic rocks. (Analytical method: S)

Rock	Locality	Number of analyses	Abundance (ppm B)		Reference
			range	average	
Diorite	Europe	9	6—20	14	HARDER (1959a)
Diorite	Sweden	1		20	LUNDEGÅRDH (1947)
Diorite	Scotland		30—60		NOCKOLDS and MITCHELL (1948)
Diorite porphyry	Urals (U.S.S.R.)	12	<10—300		GETLING <i>et al.</i> (1958)
Andesite	Italy	5	3—30		TADDEUCCI (1964)
Andesite (2 composites of 20)	Greece			24	HARDER (1959)
Intermediate volcanite	Norway			4.8	LANDMARK (1944)
Andesite	Siberia	86	7—88	20	SUXHOROKOV (1964)
Andesite tuff	Siberia	49	7—132	40	SUXHOROKOV (1964)
Andesite	New Zealand	1		22	ELLIS (1964)
Porphyrite	Urals (U.S.S.R.)	10	20—60	35	GETLING and SAVINOVA (1959)
Andesite tuff	Urals (U.S.S.R.)	3	340—2,100		LISITSYN and KHITROV (1962)
Intermediate volcanite	Siberia (U.S.S.R.)	105	1—60	28	OTROSHCHENKO (1969)

V. Granitic Rocks and Related Effusives

The boron content of granitic rocks varies over a wide range (see Fig. 5-E-1 and Table 5-E-5). The minimum content seems to be about 0.3 ppm B; the maximum content may be 300 ppm B in normal granitic rocks, but can be much higher in tourmaline granites. Boron has been strongly enriched in some pegmatites (up to 30% tourmaline; STOICOVICI *et al.*, 1957) and granite greisen. Boron-rich greisen granites are characterized by the occurrence of tourmaline (see Table 5-E-5). On the

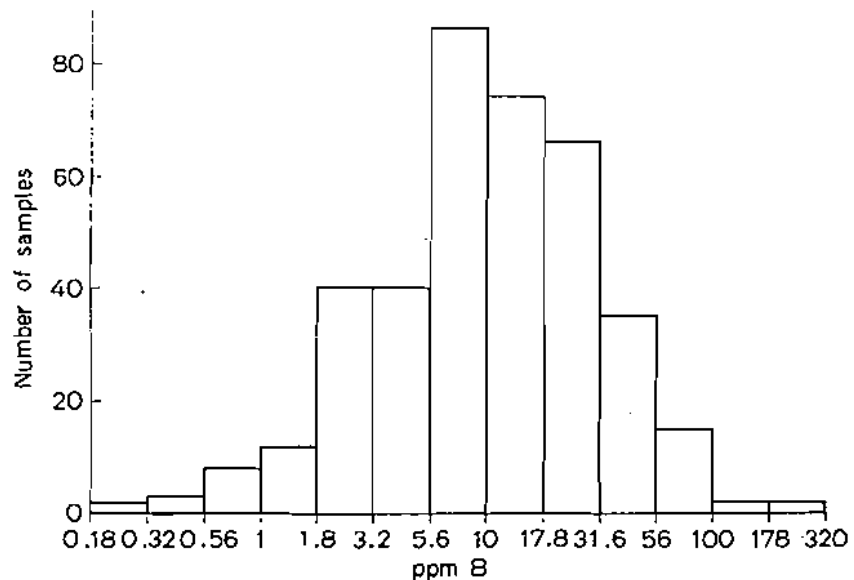


Fig. 5-E-1. Frequency distribution of boron in granitic rocks. Based on data of Japanese granites by OKADA (1956; 140 samples) and KURODA (1955; 137 samples), Russian granites by KOSALS and MAZUROV (1968; 59 samples), STAVROV and KHIRROV (1960; 29 samples), and HARDER (1959a; 50 analyses mostly from Germany and 9 from different localities and authors)

other hand, topaz, beryll, mica and quartz-bearing greisen may contain very small boron concentrations. HARDER (1959a) reports the distribution of boron in the mineral fractions of granitic rocks (Table 5-E-6). These data demonstrate that the trace boron content of the rock-forming minerals is more important for the total boron of the rock than the tourmaline content. The main carrier of boron is sericite intergrown with plagioclase. Sericite has been formed after consolidation of the magmatic melt when boron was relatively abundant in the vapor phase or solutions. The variation of boron content in sericite is one of the reasons for the appreciable scattering of boron values of granitic rocks. Granitic rocks from the roof of plutonic intrusions (Harz and Oberpfälzer Wald, Germany) and granitic proportions of migmatites generally have higher concentrations of boron. The boron contents of granitic rocks can differ with age and area (WASSERSTEIN, 1951; OKADA, 1955). Granitoids that are genetically related to borate deposits contain 8 to 15 times as much boron as those without deposits (BARSUKOV, 1961). Paleozoic, Mesozoic and Tertiary granitic rocks from Japan show similar boron values (KURODA, 1955, see Table 5-E-5). Boron values of granodiorites scatter in the same range as those of

Table 5-E-5. *Boron in granitic rocks* (Analytical method: S)

Rock type	Locality	Number of analyses	Range ppm B	Average ppm B	Reference
<i>Granite</i>					
Granite	Brocken, Harz (Germany)	3	11—18	13	HARDER (1959)
Granite (roof area)	Brocken, Harz (Germany)	7	11—60		HARDER (1959)
Granite	Schierke, Harz (Germany)	1		48	HARDER (1959)
Granite	Oberpfälzer Wald (Germany)	2	12—20	16	HARDER (unpublished)
Granite (roof area)	Oberpfälzer Wald (Germany)	6	7—9	8	HARDER (unpublished)
Granite	Saxonia, Thuringia Vosges (Europe)	12	4—85		HARDER (1959)
Granite	Alps etc. (Europe)	7	0.7—7	3	HARDER (1959)
Granite (composite of 14)	Odenwald, Bayer. Wald, Fichtelgebirge, Schwarzwald, Saxonia, Vosges, Silesia (Europe)			14	HARDER (1959)
Granite	France, Yugoslavia, Portugal, Norway	18	2.5—40		HARDER (1959)
Granite	Lapland (Finland)	2	1—3	2	SAHAMA (1945)
Rapakivi granite (composite)	Finland			6	SAHAMA (1945)
Granite	Sweden	2	3—50		LANDERGREN (1945)
Granite	West Scotland	3	1—8		NOCKOLDS and MITGHEL (1948)
Granite	South Africa	40	<20—150	15	WASSERSTEIN (1951)
Granite	Cape (South Africa)	34	20—240		KOLBE (1966)
Granite	Bitu-Dzhida, Siberia (U.S.S.R.)	22		39	KOSALS and MAZUROV (1968)
Leuco granite	Bitu-Dzhida, Siberia (U.S.S.R.)	14		30	KOSALS and MAZUROV (1968)
Aplite granite	Bitu-Dzhida, Siberia (U.S.S.R.)	23		22	KOSALS and MAZUROV (1968)
Tourmalinized granite	Turkestan (U.S.S.R.)	16	430—2,000	900	DUSMATOV <i>et al.</i> (1972)
Granite	Turkestan (U.S.S.R.)	27	<10—245	80	DUSMATOV <i>et al.</i> (1972)
Granite, gneisse (tourmaline-free)	Shamakorskii Massif (U.S.S.R.)	8	0.3—7	1.4	LYAKHOVICH (1965)

Table 5-E-5 (continued)

Rock type	Locality	Number of analyses	Range ppm B	Average ppm B	Reference
Granite (composite)	Siberia (U.S.S.R.)			40	RUB (1964)
Granite	U.S.S.R.	20	0—19	8	STAVROV and KHITROV (1960)
Granite	Hida Mountain (Japan)	135	0—32	7	OKADA (1956)
Granite	Kitakami Mt. (Japan)	15	7—160	34	OKADA (1956)
Granite	Palaeozoic, Japan	26	0—31	11	KURODA (1955)
Granite	Mesozoic, Japan	21	0—25 (>300)	8 (22)	KURODA (1955)
Granite	Tertiary, Japan	7	0—31	15	KURDDA (1955)
Hybride granite	Japan	56	3—250	32	KURODA (1955)
Gneiss granite	Japan	13	3—62	32	KURODA (1955)
Granite	Canada		40—300		BOYLE (1959)
Granite (G-1 standard)	Rhode Island (U.S.A.)			1.2 1.5 1.7	HARDER (1959) SHIMA (1962) FLANAGAN (1973)
<i>Greisens etc.</i>					
Mica-topas greisen	Europe	6	4—10		HARDER (1959a)
Lithium greisen	Cornwall (England)	1		150	HARDER (1959a)
Tin greisen	Siberia (U.S.S.R.)	30	1—470	200	LYAKHOVICH (1965)
Tin greisen	Siberia (U.S.S.R.)		up to 6,000		RUB (1964)
Greisen (composite of 24)				1,300	HARDER (1959a)
Tourmaline greisen			up to 5% B ₂ O ₃		HARDER (1959a)
Pegmatite granite	Canada		200—2,000		BOYLE (1959)
<i>Granodiorite</i>					
Granodiorite		7	7—87	9	HARDER (1959)
Granodiorite	Monte Capanne, Elba (Italy)	20	5—280	50	TONANI (1957)

Table 5-E-5 (continued)

Rock type	Locality	Number of analyses	Range ppm B	Average ppm B	Reference
Granodiorite	Giglio (Italy)	20	10—200	25	TONANI (1957)
Aplite	Giglio (Italy)	8	500—2,500	550	TONANI (1957)
Granodiorite	Canada	2	20—40	30	BOYLE (1959)
Granodiorite, partly gneis	Shamakorskii Massif, Siberia (U.S.S.R.)	5	0.3—15	3	LYAKHOVICH (1965)
Granodiorite	Urals (U.S.S.R.)	3	12—25	17	DUNAEV (1959)
Granodiorite	U.S.S.R.	15	6—95	20	STAVROV and KHITROV (1960)
Granodiorite (standard JG-1)	Sori, Gumma-Ken (Japan)	1	5 and 7	6	CHAMP and IKEDA in ANDO <i>et al.</i> (1971)

Tentative averages: Granite 12 ppm B, granodiorite 15 ppm B.

Table 5-E-6. Boron in mineral fractions of granitic rocks from Brocken, Harz Mountains (Germany). a: Granite, poor in tourmaline (17 ppm B). b: Granite, rich in tourmaline (46 ppm B) (Analytical method: S)

Mineral	Mineral-content in %	ppm B in mineral	% of B as fraction of total rock boron in a given mineral	
			a	b
Plagioclase	14	100	63	37
Potassium feldspar	52	15	35	21
Biotite + chlorite	5	2	0.5	0.3
Quartz	29	1	1.3	0.8
Tourmaline	a 0.00006 b 0.05	10% B ₂ O ₃	0.1	41

granites. Plagioclase (perhaps intergrown with sericite) contains about 80% of the total boron of granodiorites. Numerous high boron values from rocks from Elba (Italy) are reported by TONANI (1957). A tentative mean value of granodiorites (15 ppm B) is slightly higher than that of granites (12 ppm B). Loss of boron during metamorphism could explain the low content of granites from the Alps and from Scandinavia; however, this is in contradiction to the observation that granitic gneisses of Japan are higher in boron than non-metamorphic granites (OKADA, 1956; KURODA, 1955).

Salic volcanic rocks and volcanic glasses (Table 5-E-7) are higher in boron than granitic rock types (HARDER, 1959a). The most important boron host proved to be volcanic glass (TADEUCCI, 1964), and the following boron contents in rock fractions

Table 5-E-7. Boron content in salic volcanic rocks. (Analytical method: S)

Rock type	Locality	Number of analyses	Range		Average ppm B	Reference
			ppm B	ppm B		
Rhyolite	Europe	20	1—650			HARDER (1959a)
Liparite (2 composites of 20)	Sardinia Hungary				23	HARDER (1959a)
Rhyolite etc.	Siberia (U.S.S.R.)	87	6—165	24		SUKHORUKOV <i>et al.</i> (1964)
Silicic tuff	Siberia (U.S.S.R.)	45	5—120	26		SUKHORUKOV <i>et al.</i> (1964)
Rhyolite dacite	New Zealand	2	11—20	~16		ELLIS (1963)
Obsidian	New Zealand	2	25—50	~38		ELLIS (1963)
Obsidian	Europe	10	5—155			HARDER (1959a)
Obsidian (composite of 8)	Iceland, U.S.A., Lipari (Italy)				73	HARDER (1959a)
Volcanics	Colli Albani (Italy)	18	37—292	77		TADDEUCCI (1964)
Pozzolan	Colli Albani (Italy)	10	<10—134			TADDEUCCI (1964)
Pozzolan	Cimino Apparato di Vico (Italy)	35	<10—1,500			TADDEUCCI (1964)
Lava and tuffs	Cimino Apparato di Vico (Italy)	70	<10—950			TADDEUCCI (1964)
Obsidian	Lipari, Vesuvius etc. (Italy)	5	<10—200			TADDEUCCI (1964)
Silicic lava	Siberia (U.S.S.R.)	155	7.5—36	16		OTROSHCHENKO <i>et al.</i> (1969)

Tentative average: Salic volcanic rocks 30 ppm B.

from Monte Cimino, Italy, were reported: glass, 420 ppm B; plagioclase, 29 ppm B; sanidine, 10 ppm B; biotite, 33 ppm B; pyroxene, 46 ppm B. Lavas and tuffs from salic volcanic activity have similar boron contents but often tuffs are slightly higher in boron. A relationship between mercury and boron in various igneous rock types has been mentioned by BULKIN (1965).

VI. Terrestrial Boron Distribution

The geochemistry of boron is characterized by an abnormally large range of variation in common rocks (more than three orders of magnitude). This is due to the volatility of boron and makes the computation of representative means for mantle and crust extremely difficult. The boron content in the mantle can be estimated using

a model of ordinary chondrites (about 1 ppm B) or of carbonaceous chondrites (about 7 ppm B) (see Table 5-C-1). The latter figure is close to a tentative mean for ultramafic rocks, but for volatile elements the selection of the model is difficult. The anomalously high concentrations of boron in kimberlite may be an indicator for degassing of the mantle (see Subsection 5-E-I).

The boron content of the oceanic crust (about a quarter of the mass of the total crust) may be similar to the mean value of basaltic rocks of 5 ppm B (see Subsection 5-E-II). The average boron abundance in the upper continental crust has been calculated in Table 5-E-8 as being 13 ppm B. The lower crust is mainly composed of metamorphic rocks. Gneisses and schists generally have lower boron contents than their magmatic or sedimentary equivalents of comparable chemical composition (see Sections E and M). 10 ppm B may be a probable boron value for the continental crust, and the boron content in the crust is about one order of magnitude above that of the mantle. However, only 5% of the total terrestrial boron probably occurs in the crust.

Table 5-E-8. *Boron abundance of magmatic rocks in the upper continental crust*

	Abundance of rock type (in percent)	Boron abundance in rock class ppm	Boron fraction relative to rock abundance
Granite etc.	44	12	5.3
Granodiorite etc.	42	15	6.3
Gabbro etc.	13	8	1.04
Abundance in magmatic rocks:			13 ppm

5-F. Behavior in Magmatogenic Processes

Boron is an element accumulated in the late stages of magmatic crystallization. The primary boron content of magmatic melts is generally not high enough to form independent boron minerals. Solutions and vapors connected with magmatism will sometimes produce independent boron minerals. A moderate degree of enrichment in residual fractions would be expected from the small ionic dimensions of boron (GOLDSCHMIDT, 1954).

Boron in volcanic gases has been investigated in several areas (WHITE and WARING, 1963). Boron in fumarolic vapor ranges from 0 to 730 mg H_3BO_3/H_2O . The highest value was found in New Zealand. In Japan, values range from 0 to 36 ppm. The ratio H_3BO_3/HCl generally varies from 0.001 to 0.05. In Lardarello, Italy, H_3BO_3 has a concentration of 0.47% in the "active" gases. Boron in volcanic gases can be present as BF_3 (boiling point: $-101^\circ C$), BCl_3 (boiling point: $+12.5^\circ C$), B_4H_{10} (boiling point: $+17.6^\circ C$), B_2H_6 (boiling point: $-92.5^\circ C$), or B_2O_3 (melting point: $294^\circ C$). All these volatile compounds form boric acid with water. The behavior of boron under natural conditions is characterized by its change from covalent (BO_3^{3-}) to ionic (B^{3+}) bonding (LEBEDEV, 1960). In processes of pneumatolytic mobilization boron is related to elements like fluorine, lithium, tin and germanium.

5-G. Behavior during Weathering and Alteration of Rocks

Boron silicates (for instance tourmaline) are relatively stable during weathering; borate-minerals become soluble. During weathering, rockforming silicates containing boron, such as alkali-feldspars and micas, are decomposed and boron goes into solution with the other elements. The distance of boron mobilization in a weathering profile depends on the country rock and the weathering conditions. The behavior of boron during weathering in a humid climate was investigated by HARDER (1959 b) in a profile of weathered granite of the Harz mountains, in which the major minerals and the illite are almost preserved during weathering. The general tendency of boron to be concentrated in residual materials together with illite leads to an enrichment of boron in the soils of these profiles (150 ppm B). HARDER (1959 b) has also published boron data from several bauxite samples (10 samples: 0—79 ppm B, mean value 50), and data from one laterite profile on granite in India (4 to 53 ppm B in different horizons). Bauxite which developed on magmatic or sedimentary rocks has lost or mostly accumulated boron relative to the primary rocks. Boron is expected to be fixed by the high adsorption on freshly precipitated ferric and aluminum hydroxides. Trends in the abundance of boron with depth are too variable and only limited data are available to make generalizations.

5-H. Processes Controlling Boron Concentrations in Natural Waters; Adsorption Processes

I. Processes in Natural Waters

During chemical weathering of rocks boron goes into solution. It is present in water as the $B(OH)_4^-$ ion, undissociated boric acid $B(OH)_3$, and as $NaB(OH)_4$ (sea water). The dissociation constant of this aqueous complex is low:

$$\frac{[Na][B(OH)_4]^-}{[NaB(OH)_4]} = 1.36 \times 10^{-2} \text{ (SILLÉN and MARTELL, 1964).}$$

Undissociated boric acid is important in the buffering of sea water. The structure of boron as being 3- or 4-fold coordinated in aqueous solutions can be investigated by infrared absorption. VALYASHKO and VLASOVA (1966) report that the increase of alkalinity and of cation concentration causes a gradual increase of the 4-coordinated boron in solution. The increase of concentration leads to the polymerization of complexes.

The concentration of boron in water is primarily controlled by adsorption or incorporation in illite minerals.

II. Adsorption Processes and Incorporation in Clay Minerals

Boron in sediments can be present both in detrital and authigenic clay minerals.

a) Boron in Detrital Clay Minerals

The occurrence of boron in marine sediments was assumed by LANDERGRÉN (1945) to be due to adsorption of borate ions on clay mineral surfaces, being directly proportional to the boron concentration in solution. GOLDBERG and ARRHENIUS (1958) and HARDER (1958) have proved that only a minor fraction of the boron (less than 10%) can be removed with distilled water. The major part of the boron is incorporated in the clay minerals.

By treating various clays with boron-containing solutions, it was shown that illite and other micas are particularly capable of taking up boron in a non-exchangeable form (HARDER, 1961b; FLEET, 1965; LERMAN, 1966; COUCH and GRIM, 1968; JASMUND and LINDNER, 1972; BROCKAMP, 1971 and 1973). The amount of boron taken up depends on: (1) concentration of boron in solution; (2) salinity; (3) duration and temperature of the treatment; (4) crystallinity and surface of the clay mineral.

PARKS and WHITE (1952) reported that kaolinite and bentonite in the H-saturated form do not fix boron, but when bentonite is saturated with bases, fixation of varying amounts of boron is possible. Recent investigations of BROCKAMP (1973) demonstrate that the boron uptake seems to be partly controlled by magnesium. If magnesium — in solution or on the surface of the clay minerals — is present, boron uptake is much

higher. Boron, probably as magnesium borate, is fixed to the clay mineral and cannot be washed off easily with water.

The uptake of boron may have occurred in two steps, first a rapid adsorption, probably in the form of magnesium borate on the surface of the clay mineral, followed by a slow boron incorporation in the tetrahedral sites of the mica structure. It may proceed during deep burial diagenesis (PERRY, 1972).

b) Boron in Authigenic Clay Minerals

Authigenic clay minerals forming in sea water can also incorporate boron.

Experiments of the present author have demonstrated that amorphous silica-Al-hydroxides accumulate potassium. On aging these hydroxides at low temperatures it was possible to synthesize montmorillonite and mixed-layer illite (HARDER, 1969) within several months. It is to be assumed that the synthesized illite and montmorillonite will incorporate boron in the lattice in relation to the boron concentration of the solution. BROCKAMP (1971) has found 1,600 ppm B in synthetic montmorillonite from a solution containing 5 ppm B (seawater concentration). A mica (glauconite) newly formed in sea water contains the same amount of boron. The larger portion of the micas is certainly of detrital origin—reworked material from magmatic, metamorphic or sedimentary rocks. The amount of the newly-formed illite can be computed from the dissolved aluminum content in river waters; 0.4 ppm Al can form 3 ppm illite by precipitation at the discharge into the sea. Additional illite (or rarely glauconite) can be formed from the colloidal Al and Fe oxides in river waters. At an annual stream discharge of 3.5×10^{13} t, the total illite formation in the sea from continental waters is approximately 10^8 t illite per year. These micas, by incorporating about 1,000 ppm B, will contain 10^8 t B. They have extracted about 0.006 ppm B from river and sea water.

5-I. Abundance in Natural Waters and in the Atmosphere

I. Continental Surface Waters

Boron contents in waters are listed in Table 5-I-1. Boron in river waters is derived from rain water (cyclic salt or volcanic exhalations), normal or hydrothermal weathering of magmatic, metamorphic or sedimentary rocks, formation waters of sedimentary strata, and occasionally hydrothermal solutions.

The boron content of river water varies but is mostly very low. An average can be estimated to be 0.01 ppm. Higher contents are due to local special conditions such as leaching of boron deposits and contributions from hot-spring water (California

Table 5-I-1. *Boron in natural waters*

	Number of ana- lyses	Range in ppm	Reference
Rain		0.01	Tentative estimate by HUTCHINSON (1957) in: TUREKIAN (1969)
Rain, snow		0.02—0.085	HASLER (1944) in: GMELIN (1954)
Streams U.S.S.R.		0.013—0.01	KONOVALOV (1959) in: TUREKIAN (1969)
Streams U.S.A., Norway		0.0116	DURUM in: LIVINGSTONE (1963)
Streams, Japan	20	median 0.27	MUTO (1956)
Streams, California (U.S.A.)	95	0.02—5 median 0.5	SCOFIELD <i>et al.</i> (1931) in: GMELIN (1954)
Formation waters	54	0.2—1.89 median 0.6	GMELIN (1954)
Oil field waters	133	0.6—2,150 median 81	GMELIN (1954)
Lakes (fresh water)	about 10	0.2—3	GMELIN (1954)
Salt lakes	about 100	0.5—1,000	GMELIN (1954)
Hydrothermal waters	about 200	0.5—1,000	GMELIN (1954)
Rivers, volcanic areas		100	GMELIN (1954)
Lakes, volcanic areas	about 100	3,000	GMELIN (1954), FEIGELSON (1939), LIVINGSTONE (1963)
Borax lakes		9,000	GMELIN (1954)
Sea water (35‰ salinity)		4.45	GREENHALGH <i>et al.</i> (1955) in: TUREKIAN (1969)

and Japan). If the surface run-off is 35×10^{15} liters/year (LIVINGSTONE, 1963; TUREKIAN: this handbook, Vol. I, p. 312), the annual boron contribution to the sea from rivers is approximately 3.5×10^6 tons.

River waters are more than 400 times lower in boron than sea water, but the boron: chlorine ratio in river water (0.0013) is about four times higher than in sea water (0.000228). This is due to the influence of the leaching process during weathering. The dissolution of boron and chlorine during weathering is not related.

Lake waters have very variable boron contents, increasing from normal fresh water lakes to continental salt lakes to boron salt lakes. MUN and ZHAIMINA (1962) and other authors (references in GMELIN, 1954) investigated the distribution of boron in recent salt- and fresh-water lake sediments. The highest concentrations of boron in salt water lakes are found in soda lakes and the lowest in lakes rich in calcium chloride and magnesia. There is a direct correlation between the accumulation of boron and magnesium (KOZIN, 1966). The bottom sediments of fresh-water lakes contain from 5 to 100 times as much boron as their pore solutions. There is another correlation in the mud between water soluble boron and organic matter.

II. Subsurface Waters

Boron in formation water originates partly from sea water trapped as pore solutions which have reacted with sedimentary minerals during diagenesis and low grade metamorphism. Formation waters have characteristic ratios of boron to chloride which distinguish them from each other and from Recent sea water (GULJAEVA, 1948; KOZIN, 1966)

The B/Cl ratio ranges from 0.00015 to 0.0499. Boron in ground waters depends on their salinity and the boron content of related country rocks (OBORIN and ZALKIND, 1964). BUDZINSKIY (1965) has studied in detail boron in carbonate waters and their associated volcanic, sedimentary and metamorphic rocks. According to BUDZINSKIY (1965) boron partly originates from deep zones of the earth crust.

Appreciable boron is present in saline ground water. The highest concentrations of boron occur in soda-solutions and the lowest in Ca, Mg and Cl rich solutions (MUN and ZHAIMINA, 1962). There is a direct correlation between the accumulation of boron and magnesium. Boron is enriched in oil field water (TAGEEVA, 1942, and GULJAEVA, 1940, in: GMELIN, 1954). This boron is ultimately derived from organic substances. ALIYEV *et al.* (1966) observe in nature a correlation between the degree of oil formation and concentration of boron and iodine etc. in oil-field water. It has been proved that most boron contained in oil is present in resinous oil components (GULYAYEVA *et al.*, 1966). It has been assumed that some boron concentrations in oil fields are genetically related to volcanic activity (TAMRYAZIN, 1957; ALBOV, 1957).

III. Hydrothermal Waters

Boron often occurs in high concentrations in hot springs and fumarole condensates. It is likely that its occurrence in these products has a causal relation to magmatic activity. High temperature volcanic gases and solutions are comparatively rich in boron: 4 to 36 ppm B in water (MIZUTANI, 1962). On the other hand some hot springs in volcanic areas and fumarole products contain only very little boron, as

in Iceland. Most boron in hot springs is derived from the country rocks and not from emanations of the magma. ELLIS and SEWELL (1963) have proved this by experiments in some detail on the hot springs of New Zealand. LEONOWA (1968) obtained similar results for the source of boron in hot springs of the Kurile Islands. Most boron in volcanic rocks occurs in the glass fraction, from which it is readily extracted by hot water. Spring waters which contain volcanic or metamorphic water have a B/Cl ratio between 0.02 and 0.4 (WHITE and WARING, 1963). This B/Cl ratio is much higher than that of sea water (0.00023).

IV. Sea Water

Boron in sea water is controlled by supply from river water, by volcanic activity by reaction with clay minerals (adsorption and incorporation in illite) (see Section 5-H and Subsection 5-K-V), and by biological activity (see Section 5-L). In all oceans the boron content is 4.45 ppm B. In general the boron/chlorine ratio of sea water and brackish water is almost constant: 0.00023. All oceans vary only very slightly in their boron content. If brackish water has slightly higher B/Cl ratios this can be explained by the higher B/Cl ratio in river waters.

V. Atmosphere

The concentration of boron in the atmosphere (0.17 ng B/l) is very low and sea water may not be the source of boron in the atmosphere (NISHIMURA and TANAKA, 1972).

5-K. Abundance in Common Sediments and Sedimentary Rock Types

The fundamental investigations of boron in marine sediments have been published by GOLDSCHMIDT and PETERS (1932) and LANDERGREN (1945). Due to the mobility of boric acid in water, steam and volcanic emanations, ocean water and especially marine sediments have accumulated boron.

Mean data on B in common sedimentary rocks are listed in Table 5-K-1. This table contains boron values of the most important types of sediments as determined in recent studies. A wide range of variation within each group of sediment types makes it difficult to compute reliable average values. The clays and shales have higher boron contents than sandstones and limestones; ironstones, especially glauconitic rocks, can be very rich in boron.

Table 5-K-1. *Mean boron contents of common sedimentary rock types*

Sediment type	Number of analyses, approx.	Range ppm B	Average ppm B
Clay and shale	2,000	25—800	130
Saline clay	20	230—2,500	
Sandstone and sand	50	5—70	30
Graywacke	20	18—37	35
Siliceous sediment, radiolarite, chert etc.	20	5—100	
Limestone	200	2—95	20
Dolomite	30	10—400	60 (?)
Ironstone	50	20—200	
Manganese nodules	60	70—600	290
Glauconite rock	10	350—2,000	

I. Limestones and Dolomites

Limestones have striking differences in boron content. The lowest concentration was found in some fresh-water limestone (travertines) and in very pure chalk. Marly limestones and dolomites are higher in boron. An average for carbonate rocks of 27 ppm B has been computed from published data (HASLER, 1942; HEIDE and THIELE, 1958; HARDER, 1959b; WEBER, 1964; see Table 5-K-2). In all calcareous skeletons or shells, boron could be detected (see Section 5-L). Only a few values are available from calcareous fresh water deposits (26 ppm B) and marine oozes (20—300 ppm B; see Table 5-K-8).

There are no characteristic differences between the boron levels of lacustrine and marine limestones. Most dolomites are higher in boron than limestones (WEBER,

Table 5-K-2. *Boron in limestones and dolomites.* (Analytical method: S)

Type, age	Locality	Number of analyses	Range ppm B	Average ppm B	Reference
Limestone	Germany, Switzerland	29	2—95	27	HARDER (1959b)
Limestone, Muschelkalk	Germany		3—43	15	HEIDE and THIELE (1958)
Limestone, Cretaceous (composite of 16)	Germany			35	HARDER (1959b)
Limestone, Jurassic (composite of 45)	Germany			20	HARDER (1959b)
Limestone, Devonian (composite of 32)	Germany			25	HARDER (1959b)
Limestone	Switzerland		2—(240)	13	HASLER (1942)
Limestone, Pennsylvanian	U.S.A.	90	1—200	18	OSTROM (1957)
Limestone	Scotland			10	MITCHELL (1944)
Limestone	U.S.S.R.		10—75		BULCIN (1965)
Limestone, travertine	U.S.S.R.		25—50		KRESTOW (1966)
Dolomite	Germany	7	12—70	30	HARDER (1959b)
"Primary" dolostone	U.S.A. etc.	93 ^a		68.1	WEBER (1964)
"Secondary" dolostone	U.S.A. etc.	30 ^a		66.8	WEBER (1964)
Argillaceous dolostone	U.S.A. etc.			337	WEBER (1964)
"Primary" dolomite	U.S.A. etc.	9		148	WEBER (1964)
"Secondary" dolomite	U.S.A. etc.	3		133	WEBER (1964)

^a Only 52% of the samples contain measurable concentrations.

1964). The boron content of calcareous rocks is apparently mainly incorporated in their clay content. The clay proportion depends on various properties of the environment of deposition. Studies on the acid-insoluble residues of limestones and dolomites (HARDER, 1959b; REYNOLDS, 1965) proved the boron content of clay in limestones to be considerably lower (150—300 ppm B) than that of dolomites (300—530 ppm B). The highest contents have been detected in insoluble residues of dolomites of Upper Permian age (1,000 ppm B). Therefore the assumption is that the salinity of sea water was substantially higher during the formation of most dolomite than during the formation of limestone. The boron content of insoluble residues can thus indicate the salinity of the depositional environment of carbonate rocks.

II. Sand, Sandstone and Siliceous Sediment

The boron content of sands and sandstones varies widely. Low values are found in pure and almost mono-mineralic quartz sands (several ppm B), and in such sands

Table 5-K-3. *Boron in sedimentary illites. (Analytical method: S)*

Geological formation	Locality	Abundance (ppm B)		Reference
		range	average	
<i>Limestones</i>				
Mesozoic	Switzerland and Germany	210—300	300	HARDER (1959b)
Carboniferous	Britain	180—228	210	WALKER (1964)
Post Precambrian	U.S.A.		459 ± 10 ^a	REYNOLDS (1965)
Precambrian	U.S.A.	240—750 ^a	422 ± 24 ^a	REYNOLDS (1965)
<i>Dolomites</i>				
Cretaceous, Muschelkalk	Germany		300	HARDER (1959b)
Permian (Saline)	Germany		700	HARDER (1959b)
<i>Clays, shales</i>				
Recent, marine	Ocean	> 150		HARDER (1959b)
Cretaceous, marine brackish freshwater	New Mexico,	300—480 ^a	390 ^a	FREDERICKSON and REYNOLDS (1960)
	Canada	170—230 ^a	200 ^a	
		100—130 ^a	120 ^a	
Lower Triassic	Vosges (France)	120—360	120	MOSSER <i>et al.</i> (1972)
Precambrian	U.S.A.	250—450 ^a		REYNOLDS (1965)
<i>Clays of saline deposits</i>				
Permian	Germany	up to 3,000	1,000	HARDER (1959b)

^a These boron data are based on the assumption that pure illite contains 10.0% K₂O (REYNOLDS, 1965).

most boron can be attributed to tourmaline. Quartz itself contains only about 1 ppm B or even less. Higher boron contents in sands and sandstones often cannot be explained by higher tourmaline but by mica (HARDER, 1959b) or occasionally by a volcanic glass fraction (ISHIZUKA *et al.*, 1970). Coarse mica of several sandstones contains 75 ppm B, whereas plagioclase intergrown with sericite can contain up to about 100 ppm B (HARDER, 1959b). Especially high boron in sandstones with higher proportions of clay can be attributed to the latter. MOSSER *et al.* (1972) report analyses of more than 100 illite samples from "Buntsandstein" sampled in France, with a range of 120 to 360 ppm B. Here boron indicates the salinity of the environment of deposition. The lower boron content (18 ppm) of a coarser greywacke (Tanner system, Harz Mountains, Germany) than that of a finer type (37 ppm) can be explained by a lower clay content.

Table 5-K-4. *Boron in Sand, Sandstone and Greywacke.* (Analytical method: S)

Rock type	Locality	Number of analyses	Range ppm B	Average ppm B	Reference
Sandstone	Germany	10	3.5—73		HARDER (1959b)
Sandstone, Cretaceous (composite of 11)	Germany			25	HARDER (1959b)
Sandstone, Cretaceous	U.S.S.R.		22—33		GULJAEVA <i>et al.</i> (1966)
Sandstone etc., conglomerate	U.S.S.R.		10—400		BULKIN (1965)
Sandstone, arkose, Buntsandstein (composite of 23)	Germany			40	HARDER (1959b)
Sandstone, greywacke Carboniferous (composite of 11)	Germany			35	HARDER (1959b)
Greywacke, Carboniferous, Devonian (composite of 17)	Germany			35	HARDER (1959b)
Greywacke, fine grained	Harz (Germany)	1		37	HARDER (1959b)
Greywacke, coarse grained	Harz (Germany)	1		18	HARDER (1959b)
Greywacke	New Zealand	1		35	ELLIS and MAHON (1964)
Molasse sandstone	Switzerland	1		10	HASLER (1942)
Sand, marine, Recent	U.S.S.R.	2	29—107		GULYAYEVA (1948)
Sand, Recent	Volga (U.S.S.R.)	1		6.5	GULYAYEVA (1948)
Sand, Recent (volcanogenic)	U.S.S.R.	2	60—120		KRESTOW (1966)

Boron in siliceous sediments is substantially higher than in pure sands. Recent radiolarians and siliceous muds from the oceans contain 50 to 200 ppm B. Radiolarite and chert have boron contents in the same range. Boron in these sediments may be related to the primary boron content of Recent siliceous organisms (up to 0.1% B) (GOLDSCHMIDT and PETERS, 1932). The boron content of siliceous sinters is related primarily to the boron concentration in the original solution from which they are deposited (ICHIKUNI, 1968).

III. Sedimentary Ironstones

The boron contents of marine and lacustrine sedimentary ironstones vary greatly (GOLDSCHMIDT and PETERS, 1932) as related to the mineral composition.

Table 5-K-5. *Boron in marine clays and shales of different geologic age.* (Analytical method: S)

Age	Locality	Number of ana- lyses	Range ppm B	Average ppm B	Reference
Recent	Oceans		37—300	140	Table 5-K-8
Quaternary	Germany			240	PORRENGA (1963)
Tertiary	Germany			130	ERNST (1963)
Mesozoic	Germany	17	90—300	150	HARDER (1959b)
Mesozoic (composite of 10)	Japan	10		50	HARDER (1959b)
Jurassic	North America	20	20—245	153	SHAW and BUGRY (1966)
Triassic (saline)	North America	17	1—275	95	SHAW and BUGRY (1966)
Paleozoic (composite of 14)	Japan			50	HARDER (1959b)
Paleozoic (composite of 36)	Europe			95	HARDER (1959b)
Paleozoic	Norway		60—360		SPJELDNAES (1962)
Mississippian	U.S.A.	20	76—345	172	SHAW and BUGRY (1966)
Devonian (marine?)	U.S.A.	20	30—125	76	SHAW and BUGRY (1966)
Devonian	U.S.A.	17	94—384	278	SHAW and BUGRY (1966)
Pennsylvanian	North America	15		115	KEITH and DEGENS (1959)
Pennsylvanian	North America	17	40—300	130	OSTROM (1957)
Carboniferous	Germany	81	94—189	141	ERNST <i>et al.</i> (1958)
Devonian	Germany	4	38—63	51	ERNST <i>et al.</i> (1958)
Silurian (un- known salinity)	U.S.A.	17	175—390	300	SHAW and BUGRY (1966)
Cambro-Ordovician	U.S.A.	20	6—286	141	SHAW and BUGRY (1966)
Ordovician	Estonia (U.S.S.R.)	1		185	ERNST <i>et al.</i> (1958)
Silurian	Sweden	4	40—90	55	LANDERGREN (1945)
Ordovician	Sweden	18	20—180	75	LANDERGREN (1945)
Cambrian	Sweden	359	65—140	100	LANDERGREN (1945)
Cambrian	Sweden	321		115	LANDERGREN (1945)
Cambrian	Wales	22	23—70	46	WALKER and PRICE (1963)
Precambrian	Norway		60—200		SPJELDNAES (1962)
Precambrian	Germany	3	50—90		HARDER (1959b)
Precambrian	U.S.A.	~6	70—200		REYNOLDS (1965)
Proterozoic	North America	20	51—125	65	SHAW and BUGRY (1966)

Iron ores formed in fresh water are essentially lower in boron than those of marine origin. Fine-grained iron oxides or hydroxides precipitated in a marine environment can contain as much as 300 ppm B (HARDER, 1959 b and 1961 a). Chamositic rocks are close in boron contents, whereas glauconitic rocks can be very rich in boron (Sub-section 5-K-IV). In iron oxide, hydroxide, and iron silicate minerals (except glauconite), boron is probably adsorbed at the surface. This weak type of fixation is responsible for the decrease in boron content after even superficial weathering. The effects of diagenesis and metamorphism are obviously more pronounced, as exemplified in the following iron silicate ores: Liassic chamosite contains 60 ppm, whereas Ordovician iron ores from Thuringia, Germany, has only about 15 ppm, and a specimen of a completely recrystallized rock, a garnet-thuringite schist from Vivero, Lugo Province (Spain), has only 3.5 ppm. Considerably lower values were also found in various ancient hematite ores, according to the degree of recrystallization. The effect of weathering was observed in various specimens of Liassic ores. Completely fresh material from the mines had 60 ppm of boron, decreasing to 46 ppm in almost unweathered outcrops, and in the weathered chamosite ores, now found as goethite, there was only 5 to 20 ppm left. Thus, weathering substantially diminished the boron content of these iron ores. The lowering of the boron content during weathering and diagenesis is due to the inability of oxides or the iron silicates (except glauconite) to incorporate boron into the crystal structure. Continental weathering products (bauxites, laterites etc.) formed by disintegration are low in boron.

IV. Argillaceous Sediments (General Observations)

Clays contain more boron than sand or carbonate. The boron concentration in argillaceous sediments depends on various parameters: mineral composition, boron content of detrital minerals, salinity, temperature of deposition, rate of deposition (for equilibration) and diagenesis.

Boron is not uniformly distributed among the various grain size fractions of clays in clastic deposits. It has been shown in many papers that boron concentration varies inversely with grain size in the clay fraction of modern and ancient sediments. In many sediments there are two pronounced maxima. The highest values occur in the $< 2 \mu$ or $< 0.6 \mu$ fraction. Several investigators have shown that the major control of boron is by grain size. The boron concentration in the medium size fraction often is only a third of that in the finest fraction. A potential second maximum in the boron to grain size distribution curve (Fig. 5-K-1) in the coarser fraction (about 20μ) is partly due to the presence of tourmaline. The existence should also be mentioned of argillaceous sediments with no minimum in the boron distribution curve in the 2 to 20μ fractions.

Which minerals are the host of the major boron concentration? As the tourmaline content decreases with decreasing grain size, boron increases distinctly. As demonstrated in Table 5-D-2, phyllosilicates can be relatively high in boron, especially muscovite. Fine grained sericitic micas in feldspars are extremely rich in boron; values of 2,000 ppm or almost 1% B_2O_3 are not uncommon.

In samples of sediments from the same depositional environment, the specimens rich in illite have a higher boron content. A further indication that the mica structure is capable of incorporating larger proportions of boron, is the high boron content

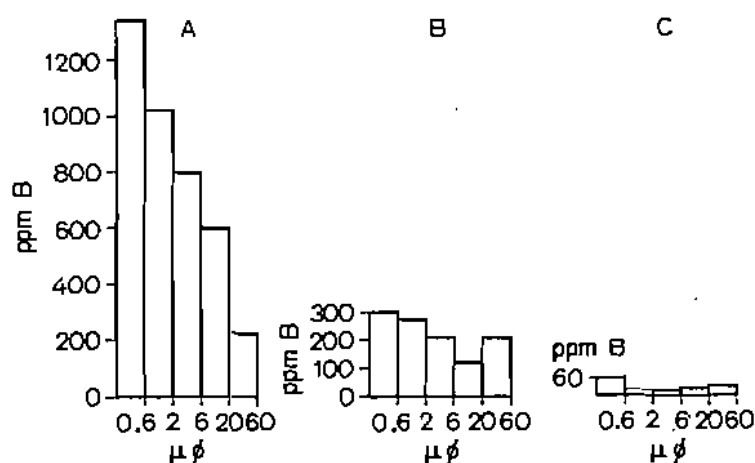


Fig. 5-K-1 A—C. Boron content in grain size fractions of: A saline shale, Reyershausen, near Göttingen (Germany); B marine shale, Rhät, Göttingen (Germany); C fresh-water varved clay, Frykerud, Värmland (Sweden)

of glauconite. Chamosite with its kaolinite-type structure only contains up to 60 ppm B. The assumption that illites are the boron hosts in fine grained sediments comes from solubility experiments in cold and hot water as well as HCl and HF.

The importance of illite as a boron carrier (HARDER, 1958) has been confirmed by FREDERICKSON and REYNOLDS (1960) and EUGSTER and WRIGHT (1960). The latter authors have synthesized a hydrous boron mica. The boron content of montmorillonite is in most cases lower than that of illite, but apparently montmorillonite and mixed-layer minerals can contain appreciable boron (TOURTELOT *et al.*, 1961). These authors found bentonite of the marine Pierre Shale containing up to 200 ppm B. According to SCHWERTMANN (1962), montmorillonite in soil also has high boron contents. These montmorillonites can be formed from illites.

In illites of saline clays and shales a boron content of several thousand ppm can be expected, whereas in normal marine clays it is a few hundred ppm; lacustrine sediments generally contain much less boron. The boron content of illites (200—2,000 ppm B) depends more or less on the salinity of the environment of deposition (HARDER, 1959b) (see Tables 5-K-3, 5-K-6). Because of the incorporation of boron into illite, boron and potassium of clays can be correlated (WALKER, 1963).

V. Boron as a Paleosalinity Indicator

Soon after the fundamental publication of GOLDSCHMIDT and PETERS (1932), an attempt was made to use the boron content of a sediment as an indicator of the marine or lacustrine character of the deposit. The main trend of the relation between salinity and boron concentration has been observed in many sequences of sediments: lacustrine clays often contain less than 80 ppm B; marine argillaceous sediments about 100 ppm B (or slightly more) and saline clays 1,000 ppm B or more. Details including values with overlapping ranges of marine and fresh-water samples are given in Table 5-K-6. FREDERICKSON and REYNOLDS (1960) observed a correlation

Table 5-K-6. Boron in marine and fresh-water shales. (Analytical method: S)

Shale	ppm B		
	marine	brackish	fresh-water
<i>Carboniferous, Westphalia (Germany)</i>			
BRADACS and ERNST (1956)			
ERNST <i>et al.</i> (1958)	100—200	45—100	15—45
ERNST and WERNER (1964)	110	80—110	80
PORRENGA (1963)	150		50
<i>Carboniferous, Great Britain</i>			
FREDERICKSON and REYNOLDS (1960)	300		150
CURTIS (1964), SPEARS (1965)	50—120 (average: 85)		
NICHOLLS and LORING (1962)		50—75 (average: 60)	
EAGER (1962)			12—141 (average: 76)
<i>Carboniferous, Pennsylvania (U.S.A.)</i>			
Degens <i>et al.</i> (1957)	>80		<60
KEITH and DEGENS (1959)	115		44
<i>Cretaceous (U.S.A.)</i>			
TOURTELOT (1964)	40—220 (average: 130)	60—160 (average: 110)	30—160 (average: 85)

between boron of water and that of Recent sediments of the Gulf Coast. PORRENGA (1963) reports a good correlation between the occurrence of salinity-specific diatoms and boron content in clay: clays with fresh-water diatoms contain 25 ppm B; with brackish diatoms, 130 ppm B; and with marine diatoms, 140—220 ppm B. In consolidated shales a relationship between boron content and salinity has also been observed (BRINKMANN and DEGENS, 1956; BRADACS and ERNST, 1956; ERNST *et al.*, 1958; DEGENS *et al.*, 1957; see Table 5-K-6).

In order to decide from the boron content whether the environment of deposition was marine or lacustrine, it is necessary to know all the parameters mentioned above, especially the mineral composition (HARDER, 1963). For reasonable results, one should compare only strata with similar mineral composition, grain size and diagenetic history; KREJCI-GRAF (1963) made a similar recommendation. Data from many investigators show that total boron strongly correlates with the proportion of clay. SHIMP *et al.* (1969) and POTTER (1963) have stated that "because marine muds are commonly finer grained than fresh-water ones, they are generally richer in boron". The increase of B in sediments with increased distance from a delta is often related to the increase of total clay content (Dewis *et al.*, 1972).

The boron content of the illite fraction is a better facies indicator than that of the bulk sample (WALKER and PRICE, 1963), but there is no simple relationship between illite, its potassium content and salinity and dissolved boron content of natural waters. WALKER and PRICE (1963) found in a detailed study an antipathetic relationship between boron and potassium contents of sedimentary illite. Sometimes the organic compounds influence the boron content of clays. EAGER (1962), CURTIS (1964) and SPEARS (1965) have observed an inverse relationship between boron and organic carbon. Illites from carbonate rocks are useful materials for paleosalinity studies (HARDER, 1959b; REYNOLD, 1965). The data suggest that the boron concentration in sea water has been fairly constant at least since Cambrian time (see Table 5-K-3). Thus anomalous cases are not rare and the boron-paleosalinity relationship is not universally regarded as valid (SPEARS, 1965; LERMAN, 1966). The most important boron deposits are found in nonmarine sedimentary beds associated with volcanic activity.

An important factor that particularly affects the boron content of lacustrine sediments is the pre-depositional history of the clay. Most clays are recycled material and this influence can be observed in investigations of Quaternary lacustrine sediments from different sources. Table 5-K-7 gives the probable sources of the material, based on analyses of pebbles. The more that Mesozoic rocks were eroded from the bedrock by Pleistocene glaciers, the higher were the boron contents of the resulting tillite. Extreme values were observed in a Pleistocene clay from the Northeim (Germany) area. These fresh-water clays were derived from the Upper Buntsandstein and are rich in boron. The time available for the equilibration of Quaternary sediments in most cases has been too short; short-time variation of paleosalinity during sedimentation of evaporite sediments (of Middle Triassic age) has no effect on the boron concentration (HELING, 1967). Primary boron content of reworked material could often account for higher boron contents than those expected (WALKER, 1963:

Table 5-K-7. *Boron in Pleistocene fresh-water clays from Sweden and Germany* (HARDER, 1959b).
(Analytical method: S)

Rock type	Locality	Source of material	ppm B
Varved clay	Frykeryd, Värmland (Sweden)		26
Boulder clay	Stoltera, Warnemünde (Germany)	Tertiary etc.	35
Glacial clay	Papendorf, Mecklenburg (Germany)		65
Glacial clay	Siebethhaus, Jever (Germany)		45
Interglacial clay	Kerr Brick Works, Northeim (Germany)	Triassic and Jurassic marine red marl	105
Interglacial clay	Bilshausen, Northeim (Germany)	Triassic marine sand- stone	120 190 220

Table 5-K-8. *Boron in Recent marine, brackish and fresh-water sediments (of normal salinity, if not indicated) (Analytical method: S)*

Sediment type	Number of analyses	Range ppm B	Average ppm B	Reference
Clay, Pacific	384	37—198	130	LANDERGREN (1964)
Clay, Pacific	31	120—370	260	GOLOBERG and ARRHENIUS (1958)
Clay, Pacific	3	131—174	136	POTTER (1964)
Clay, continental shelves, Pacific	27	73—183	108	POTTER (1964)
Clay, Pacific	2	160—190		MURATA and ERD (1964)
Radiolarian mud, Pacific	1		150	HARDER (1959)
Silty clay, Pacific	1		70	MURATA and ERD (1964)
Carbonate ooze, Pacific	4	96—320	185	GOLDBERG and ARRHENIUS (1958)
Carbonate ooze (> 25% CaCO ₃), Pacific	15	20—100	75	MURATA and ERD (1964)
Siliceous and carbonate ooze, Pacific	2	100—210	160	MURATA and ERD (1964)
Clay, Arctic			115	MCDUGALL and HARRIS (1969)
Clay, Atlantic	38	44—183	130	LANDERGREN (1964)
Clay, Atlantic		65—350		ERICSON <i>et al.</i> (1961)
Clay, Atlantic	14	76—174	126	POTTER (1964)
Clay, Atlantic	12	100—190	135	HARDER (1959b)
Carbonate ooze, Atlantic		18— 60	30	THOMPSON (1972)
Carbonate ooze, Atlantic	4	50— 80	60	HARDER (1959b)
Clay, Indian Ocean	46	44—183	115	LANDERGREN (1964)
Clay, Mediterranean	36	96—225	143	LANDERGREN (1964)
Carbonate, Adriatic Sea	3	135—174	147	SHIMP (1969)
Clay, tidal shoals, North Sea	2	50— 70		ERNST (1962)
Clay, North Sea	4	38—124	85	SHIMP <i>et al.</i> (1969)
Clay, Skagerrak-Kattegat (salinity 33.5‰)			115	LANDERGREN and CARVAJAL (1968)
Clay, Gullmarsfjorden, Alsbäck (salinity 18‰)			100	LANDERGREN and CARVAJAL (1968)
Clay, southern Baltic Sea (salinity 16‰)			105	LANDERGREN and CARVAJAL (1968)
Estuary sediment, Angermanälven River, Sweden (salinity 6.0‰)			52	LANDERGREN and CARVAJAL (1968)

Table 5-K-8 (continued)

Sediment type	Number of analyses	Range ppm B	Average ppm B	Reference
Euxenic sediment, Baltic Sea fjord (salinity 5.5‰)			62	LANDERGREN and CARVAJAL (1968)
Clay muds, fresh-water	43	12—159	62	SHIMP <i>et al.</i> (1969) POTYER (1964)
Clay suspension, rivers, Urals	5	50—300		OBORIN and ZALKIND (1964)
Carbonate, fresh-water, Lake of Neuenburg, Switzerland			26	HARDER (1959)
River sediment, Canadian Arctic	80		49	DEWIS <i>et al.</i> (1972)
River and delta sediment, Canadian Arctic	133	2—125	74	DEWIS <i>et al.</i> (1972)

British Purbeck beds; RIEDEL, 1966: Tertiary clays, Lower Rhine, Germany). Little or no boron has been taken up by some terrestrial clay minerals as they enter the marine environment in the polar region (MACDOUGALL and HARRIS, 1969).

Another point that must be considered in discussing the boron content is the rate of deposition (HARDER, 1959 b). The average content of the Atlantic Ocean sediments (Table 5-K-8) is 130 ppm, and the highest value for all ocean sediments is 370 ppm (GOLDBERG and ARRHENIUS, 1958). A great number of modern marine and fresh-water muds was analysed by SHIMP *et al.* (1969) (see Table 5-K-8). According to their results modern marine muds (from shallow continental shelves) contain about 30—45 ppm more B than fresh-water muds. Deep-sea clays have slightly higher boron contents than clays from the shelves. The above values demonstrate the range of boron contents of sediments at the same salinity and about the same temperature.

Diagenesis (HARDER, 1961 a) and transformation of 1 Md into 2 M mica modifications (REYNOLDS, 1965) lower the boron content of illites (see Section 5-M). Illites which contain more than 25% of the 2 M polymorph are not suitable for paleosalinity studies. Inasmuch as many factors affect the boron content of sediments, it is not a very suitable indicator element. If the various parameters can be controlled it can be of use in studies of paleosalinity.

VI. Marine Evaporites

Boron in oceanic evaporites is mainly accumulated in clay (see Table 5-K-9), in anhydrite and in potassium-magnesium salts. Halite rocks are low in boron except those interlayered with clay or anhydrite (HARDER, 1959 b; BRAITTSCH, 1961). Besides sulfates and micas, boron occurs in its own minerals: boracite, stassfurtite, szaibelyite (ascharite), pinnoite, sulfoborite, strontiohilgardite, lueneburgite, probertite, priceite, ulexite, howlite, colemanite, danburite and tourmaline. Na-Ca borates and Mg borates are connected with the anhydrite layers and Mg borate with the potassium-

Table 5-K-9. Boron in marine salt deposits. (Analytical method: S)

Age	Number of analyses	Range ppm B	Average ppm B	Reference
<i>Permian saline clays from Northern Germany</i>				
Stassfurt series		300—700		HARDER (1959b)
Leine series	30	1,000—2,200	1,500	HARDER (1959b)
Aller series (composite)		230—500		HARDER (1959b)
<i>Permian anhydrite from Northern Germany and U.S.A.</i>				
Werra series	26	1—70	25	HARDER (1959b)
Stassfurt series	11	100—500	200	HARDER (1959b)
Leine series	16	24—90	55	HARDER (1959b)
Aller series	4	3—80	40	HARDER (1959b)
Average:			70	
Anhydrite, Permian, Oklahoma (U.S.A.)	150	39—90	72	HAM <i>et al.</i> (1961)
Gypsum, Permian, Oklahoma (U.S.A.)			13	HAM <i>et al.</i> (1961)
Recent sulfate precipitates		40—90		HAM <i>et al.</i> (1961)
Halite, Cambrian to Quaternary		0.3—0.7		MOORE (1971)
<i>Permian halite from Northern Germany</i>				
Werra series	4	0.X	15	HARDER in BRAITSCH (1962)
Stassfurt series	50	0—70		
Leine series	4	0.X—3		
<i>Permian potassium magnesium salts from West Germany and U.S.S.R.</i>				
Werra series	3	0.X		HARDER (1959b)
Stassfurt series	20	0.2—60		HARDER (1959b)
Stassfurt series	100	100—2,000	400	KOKORSCH in BRAITSCH (1962)
Potassium magnesium salts, Solikamsk (U.S.S.R.)			80	DIAROV (1966)
Potassium magnesium salt, (U.S.S.R.)	26	0.2—2.2%	6,000	DIAROV (1966)

magnesium layers (HAM *et al.*, 1961; BRAITSCH, 1962; KÜHN, 1968). It is assumed that the boron concentrations are related to the seas from which the evaporites were precipitated. The mechanism of boron precipitation during evaporation is not well-known. D'ANS and BEHRENDT (1957) published data on the solubility of boracite.

Primary formation of boracite is possible during the stage of potassium-magnesium salt precipitation. If boracite crystals occur in anhydrite, they cannot be of primary origin. A co-precipitation of boron together with sulfate may be possible (HARDER, 1959; HAM *et al.*, 1961). A fraction of the boron in anhydrite is assumed to substitute SO_4 in the lattice (HAM *et al.*, 1961). Boron has been strongly enriched in the final state of evaporation (in some Russian deposits) and in the middle stage of the Stassfurt basin. Boron-rich saline waters partly form the Stassfurt nodules and the high boron content of saline clays and anhydrites. The boron content of Zechstein deposits in Germany may be lower but is not higher than that expected from evaporation of normal sea water. Progressive evaporation can form borate deposits containing up to 2.2% B. DIAROV (1967) has investigated the boron distribution in these potassium salts deposits, and the data indicate that the boron concentration is independent of the K and Mg content.

VII. Average Abundance in Sedimentary Rocks

Argillaceous sediments (clays, shales) are by far the most abundant sedimentary rocks and are the important boron carriers. A mean value of 100 ppm B for clays and shales has been computed by HARDER, mainly on the basis of 700 analyses reported by LANDERGREN (1950) and about 150 additional samples (HARDER, 1959b). In recent years a tendency of additional data to a slightly higher mean can be observed. SHAW and BUGRY (1966) report 160 ppm B for 171 samples and different authors obtained 135 ppm B for 150 shales. Boron values of Recent deep-sea clays plot in the same range, but are often slightly higher than those of consolidated argillites. From these results a mean value of about 120 ppm B can be assumed for clays and shales except those of Precambrian age.

Limestones contain on average 20 ppm B, quartz-sandstones 30 ppm B and greywackes 35 ppm B. The proportion of shale to greywacke is rather uncertain. The abundance of the sedimentary rocks has been compiled by WEDEPOHL in Chapter 8 of Volume I of this handbook. If alternatively 77% or 55% argillaceous sediments (mean value 120 ppm B) is considered, then the average sediment contains 100 or 80 ppm B. Slightly less than 100 ppm B is probably the mean value for sediments.

This value is nearly ten times higher than the average of magmatic rocks. Boron is unbalanced between average weathered magmatic rocks and average sediment (plus sea water). The relative accumulation of boron in the marine environment is probably a consequence of the mobility of boron compounds in geothermal vapors and volcanic emanations.

5-L. Biogeochemistry

Boron can be detected in nearly all organisms and it is physiologically important in plants. Appreciably large amounts of boron occur in blossoms, fruits and roots of certain plants such as maize (10 ppm B in the dry substance), grape (10 to 100 ppm B), and saffron (up to 0.5% B) (GMELIN, 1954).

Boron has been reported as stimulating plant growth (in rice, potato, tomato, cotton, wine, tobacco, etc.) and to prevent certain plant diseases (sterility of pollen and seed organs, etc). Small quantities of borax are therefore included in some mineral fertilizers, although large doses of boron are toxic. Boron is stored in the illite and montmorillonite fraction of soils (HARDER, 1959a; SCHWERTMANN, 1962). As a result of plant decomposition, boron passes into clays, humus and peats.

The boron content of plants has been used in biochemical prospecting of boron deposits (SCHWYRJAWEA, 1957). Boron is also concentrated in ashes of woods and coals (GOLDSCHMIDT and PETERS, 1932) and in seaweed. ZUBOVIC *et al.* (1961, 1964, 1966, 1967) analysed more than 1,100 coal ashes from Eocene, Cretaceous, Jurassic and (mostly) Pennsylvanian ages from different places of the United States. The boron values of the ash of coal samples vary between 12,000 and 20 ppm B with a mean value of 1,400 ppm B. The boron content from one sample to another varies over a very wide range, but no significant differences in boron content were found by comparing the mean values of different coal types, coals of different age and different area. Australian coals (BROWN *et al.*, 1964) range from 10 to 300 ppm B (on an air-dried coal basis). Boron contents in the coal ashes from Tertiary age of Germany vary between 12,000 and 50 ppm, with a mean value of 800 ppm B (OEHLSCHEGEL, 1964; HARDER, 1959); coals from Central and East Germany have similar values (LEUTWEIN *et al.*, 1956). During coalification of peat some boron has been lost.

Marine calcareous algae and some corals contain up to 300 ppm B in their structure (GOLDSCHMIDT and PETERS, 1932; BERENSTEJN, 1953). The results of NICHOLLS (1959) and VINOGRADOV (1959) support the view that boron is concentrated by marine plankton. The former author reports that 11 samples range from 50 to 760 ppm B with a mean value of 240 ppm B. YAMAMOTO *et al.* (1973) have spectrophotometrically analyzed 11 samples of marine phytoplankton containing 18 to 104 ppm B in dry matter, 16 samples of limnetic plankton ranging from 6 to 3,200 ppm B, and 34 samples of marine zooplankton containing 33 ppm B as an average. Still higher contents occur in siliceous sponges. After recrystallization, the boron contents have been partly lost. Most of the boron taken up by living organic matter is not removed from the oceanic reservoir by sedimentation after the death of the organisms. It will be recycled into the hydrosphere (see Section 5-O-2).

In higher animals boron is always present but the amount tends to be low (0.5 ppm B) (BOWEN, 1966). Boron does not seem to be essential for animals. For additional information see BREWER (1950), GMELIN (1954), SCHARRER (1955), STILES (1961) and BOWEN (1966).

5-M. Abundance in Common Metamorphic Rock Types

During diagenetic and metamorphic processes the primordial boron content of most sediments and several magmatic rocks decreases. Higher than primary boron concentrations occur in serpentinites and contact zones of magmatic rocks.

I. Contact Metamorphism

Metamorphic sedimentary rocks from contacts with granite and basalt have been investigated by HARDER (1961a). The altered granitic rocks of the border zone are higher in boron than granite from the inner core of the pluton. Boron is concentrated in sericite intergrown with plagioclase or in serpentine minerals. Sediments from the contact zone often have lost boron. Locally higher boron concentrations occur, sometimes in the form of boron minerals (see Fig. 5-M-1). The heterogeneous distribution in contact rocks (hornfels) can be explained by local boron mobilization of sedimentary rather than magmatic origin.

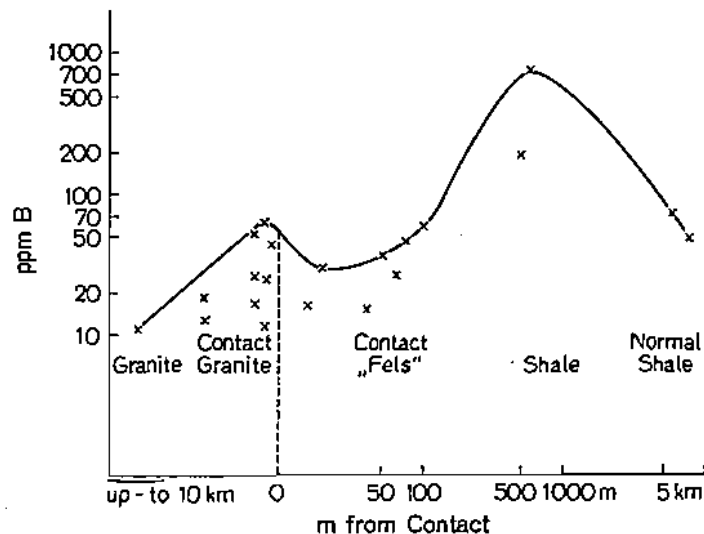


Fig. 5-M-1. Distribution of boron at a granite meta-shale contact, Harz Mountains, Germany (HARDER, 1961a)

Boron metasomatism of dolomite rocks has been discussed in detail by WATANABE (1939, 1958), WATANABE *et al.* (1963), BARSUKOV (1958, 1960, 1961), ALEKSANDROV *et al.* (1968), MARAKUSHEV (1958), EGOROV (1960), and SHABYNIN (references in PERZEV, 1970). Many boron-containing minerals occur in the skarn paragenesis with magnetite and manganese ore (ludwigite, suanite, kotoite, sinhalite, datolite, jimboite etc.). If boron does not form independent minerals during the skarn deposition, it is dispersed among various skarn minerals. Garnets from skarns contain up to 400 ppm

B (LISITSYN and KHITROV, 1962) and wollastonite up to 200 ppm B. Magnesium silicate and borate contents in skarns can be inversely related (EGOROV, 1960). Vesuvianite (idocrase), the latest skarn mineral, is a major host of boron (MUESSING, 1959).

II. Regional Metamorphism

There is only a limited number of reliable boron analyses of regional metamorphic rocks available as listed in Table 5-M-1.

Table 5-M-1. *Boron in metamorphic rocks.* (Analytical method: S)

Rock type	Locality	Number of analyses	Range ppm B	Average ppm B	Reference
Schist	Germany	20	35—155	80	HARDER (1959b)
Mica schist	Alps, Urals etc.	30	40—2,000	100	HARDER (1961a) DUNAIEV (1959)
Paragonite schist	Alps, Yugoslavia	10	70—2,000		HARDER (1961a)
Andalusite cordierite schist	U.S.S.R.	4	110—170		STAVROV (1960)
Chlorite schist			10—40		DUNAIEV (1959) HARDER (1961a)
Glaukophane schist	Switzerland	10	3—30		HARDER (1961a)
Biotite amphibolite schist		10	3—30		HARDER (1961a)
Talc chlorite schist	Münchberg Mass, Bavaria (Germany)	3	0—11		HAHN-WEINHEIMER (1960)
Sericite graphite schist	Münchberg Mass, Bavaria (Germany)	4	68—1,000		HAHN-WEINHEIMER (1960)
Orthogneiss	Germany	6	0.5—3.5		HARDER (1961a)
Paragneiss	Germany	4	8—50		HARDER (1961a)
Granite gneiss	U.S.S.R.	2		4	STAVROV and KHITROV (1960)
Gneiss	Norway	8	1—14	5	LANDMARK (1944)
Gneiss and schist	Yakutia (U.S.S.R.)	17	30—80	55	YEGOROV (1961)
Granitized rock	Yakutia (U.S.S.R.)	18	<20—20		YEGOROV (1961)
Charnockite	Africa, Sweden	5	<1—7		HARDER (1961a)
Serpentinite	Urals	2	13—80		DUNAIEV (1959)

5-N. Behavior in Metamorphic Reactions

When boron-containing minerals participate in metamorphic reactions, boron is gradually released. The loss of boron depends on the composition and temperature of the gas phase taking part in the metamorphic reactions and on the host minerals. During metamorphic processes boron in tourmaline is stable. If no stable boron mineral or a stable boron host mineral (like mica or serpentine) is available, the loss of boron during diagenesis and metamorphism is very large. For example marine sedimentary ironstones contain as recent hydroxide silicate precipitates 300 ppm B (see Subsection 5-K-III); Liassic chamositic ores contain 60 ppm B, Ordovician ores 15 ppm B, and garnet-thuringite schists contain 3.5 ppm B only. Shales show a small loss of boron during diagenesis and low grade metamorphism (HARDER, 1961). In an investigation of boron in mica during metamorphism, REYNOLDS (1965b) could prove that some boron is lost during the transformation of the 1 Md into the 2 M polymorph. Boron released from illite is trapped locally as dravite (tourmaline). Relatively little boron is lost at lower grades of metamorphism (greenschist facies). Data of REYNOLDS (1965b) indicate that during metamorphism of carbonate rocks no significant decrease of boron has occurred, but boron as a trace element in mica and serpentine can easily be released during higher grade regional metamorphic processes under conditions that accompany the destruction of white mica. The low boron content of some granitic gneisses (see Table 5-M-1 and Subsection 5-E-V) can be explained in the same way. Some tourmaline is possibly formed at this stage of metamorphism. Partial melting of metamorphic rocks is connected with a mobilization of boron leaving only tourmaline and other stable boron minerals in restites.

5-O. Relation to Other Elements, Economic Importance

I. Relation of Boron to Other Elements

Boron is an element widely distributed in low concentration in rockforming minerals. It replaces silicon and beryllium to some extent. Boron as a typical element of residual magmas is sometimes correlated with such elements as lithium, beryllium, tin, fluorine and chlorine in rock derived from late stages of magmatic processes. Boron and germanium have a distinct tendency to combine with organic matter.

II. Balance and Cycle of Boron

The bulk of boron is present in marine sediments and in sea water. Data of LANDERGREEN (1945), HARDER (1959 b), REYNOLDS (1965), SHAW and BUGRY (1966) etc. suggest that the boron concentration in marine sediments from a steady state ocean has been fairly constant with time. A certain loss of boron from older sediments must be attributed to diagenesis (HARDER, 1961 a).

Illite in sediments is a large sink of boron in the rock cycle. Boron mobilized during metamorphism cycles back to sea water. At elevated temperatures boron is discharged directly from a magma into the atmosphere, but at lower temperatures hydrothermal solutions feed it directly into surface waters. This cycle keeps the boron concentration in sea water in a steady state system.

Another feature characteristic of its cycle is the transfer of boron from rocks and waters into organisms and back. The amount of boron incorporated in organic matter is larger than the quantity taken up by illite from water. During the decay of the concentrating organisms, boron is liberated and ultimately finds its way back to the hydrosphere. Thus the cycle of boron is connected with the surface waters.

Fig. 5-O-1 is a diagram of the boron cycle in the upper earth's crust, hydrosphere and atmosphere.

III. Economic Importance

Since Egyptian or Roman times boron has been used probably as a flux in ceramic and metallurgical processes. "Būrāh" (Persian word for borax) was imported during the Middle Ages from Tibet to Europe. Considerable advances in the industrial chemistry of boron has been made in the last few decades. Elemental boron, organic and inorganic boron compounds are the object of intensive research. Fused borax readily dissolves many metallic oxides to produce beads of characteristic colours (borax beads). Borax finds considerable use as a flux in soldering and as a glaze for pottery and enamels. It prevents devitrification of some optical and hard glasses with high melting points. Boron is used for reactor materials (neutron absorber) and as light metal in aeroplanes and rockets. Boron alloys are applied in iron foundries as the addition of 10 to 30 ppm B increases the hardness of steel as much as far larger quantities of other agents (Nirosta contains 1% B). Metal borides as Ni_3B , Co_3B , Fe_3B

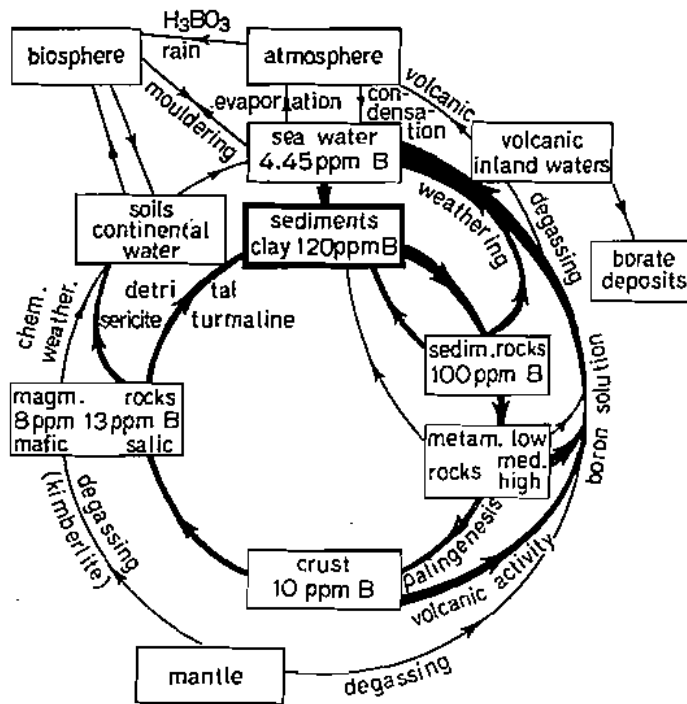


Fig. 5-O-1. The cycle of boron according to data published by LANDERGREN (1945), HARDER (1960, 1961a), and GREGOR (1965)

and other refractory borides are resistant to heat, corrosion and abrasion. Zirconium boride has been tested for use in jets and rocket nozzles. The use of boron as a deoxidizer in the metallurgy of copper is also important. Boron is a hard element and forms hard compounds such as BN with a diamond structure, boron carbide (B_4C), and boron silicide (B_4Si). They are nearly as hard or harder (boron carbide) than diamond and are used as abrasives etc. B_4Si and BN are stable under high temperature oxidizing conditions. Perborates serve as materials for washing and as disinfectants. Because of its mild antiseptic and detergent properties it may be an ingredient of soaps, cosmetics and disinfectants. Some insecticides contain borax. Methyl borate has been tested as a citrus fungicide. Agricultural use for borax has been mentioned in Section 5-L. The element is used for the production of plastics. Organic boron compounds are being developed for use as dehydrating agents, catalysts and fire retardants. Some organic boron compounds such as borane or boron-hydrogen polymers and alkyl boranes have also been used for high energy jet and rocket fuels. Some oil companies are marketing a gasoline for high compression engines that contains a boron compound as an anti-knock agent. For additional references, see KOHN *et al.* (1960) and MATKOVICH (1972).

IV. Boron Mineral Deposits of Commercial Value

Of more than hundred known boron minerals, only a few are used commercially: borax (from saline lakes) and kernite (from Tertiary bedded deposits at Kramer Borate district, California), colemanite, ulexite and priceite (from Turkey), boracire (from Permian salt deposits in Germany), and sassolite (boric acid from volcanic steam vents

in Larderello, Toscana, Italy, and Kertsch, USSR, Inder Area, eastern Urals). Currently boron-rich ground water or skarn-boro-silicates are an economic source of boron. Recent thermal springs have deposited borate minerals in the High Andes in Argentina, Bolivia, Chile and Peru (MUESSING, 1959 and 1961) (Additional references: SCHALLER, 1930; MEIXNER, 1952; SMITH, 1968). The most important boron deposits are found as terrestrial salt deposits in non-marine sedimentary beds. These borate evaporites are genetically connected with geologically young volcanic rocks in the neighborhood of the deposits. In the Kramer borate district (California) are the world's largest known reserves of boron minerals. They supply today more than 90% of the boron used in the world. The Kramer sodium borate deposit consists of particular sedimentary borax and kernite (BARNARD and KISTLER, 1966; BOWSER and DICKSON, 1966; MORGAN and ERD, 1969; VER PLANCK, 1957).

The world production is about 1 million tons of borax per year.

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