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# A BOND-VALENCE APPROACH TO THE STRUCTURE, CHEMISTRY AND PARAGENESIS OF HYDROXY-HYDRATED OXYSALT MINERALS.
## III. PARAGENESIS OF BORATE MINERALS

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## ABSTRACT

A connection is established between the crystal structures of borate minerals and the conditions (pH, log[$H_2O$]) at which they are stable, using the approach developed by Schindler & Hawthorne (2001a, b). Structural units in borate minerals may be formally related by two types of chemical reactions, one of which consumes H and the other that consumes ($H_2O$). Combining these equations with the law of mass action, an expression for pH can be formulated that allows arrangement of the structural units in pH–log[$H_2O$] space and calculation of the slopes of the associated phase-boundaries. The result is a pH–log[$H_2O$] activity–activity diagram with the correct topology and a relative scale along each of the axes. Structural units from minerals of similar paragenesis occur in contiguous fields of this activity–activity diagram. The general classes of polymerization of borate groups in the structural units change systematically across this activity–activity diagram. With increasing activity of ($H_2O$), structural units trend from frameworks → sheets → chains → clusters → isolated polyhedra. The proportion of tetrahedrally coordinated B ($^{[4]}B \times 100 / \{^{[3]}B + ^{[4]}B\}$) in the structural units increases with increasing pH across the activity–activity diagram; this relation combines with the valence-matching principle to indicate that interstitial species of higher acidity (*e.g.*, Ca, Mg) form minerals at higher pH than interstitial species of lower acidity (*e.g.*, Na, K). The average basicity of borate clusters in aqueous solution is a linear function of the pH of that solution at the maximum concentrations of each of the clusters (Hawthorne *et al.* 1996). The proportion of $^{[4]}B$ and the average basicity of all clusters in aqueous borate solutions are smooth functions of the pH of the solution; moreover, the average basicity of the clusters (dissolved species) is a linear function of the proportion of $^{[4]}B$ in solution.

*Keywords*: borate mineral, structural unit, pH, activity–activity diagram, paragenesis.

## SOMMAIRE

Nous avons établi un lien entre la structure cristalline des minéraux boratés et les conditions (pH, log[$H_2O$]) de leur champ de stabilité en appliquant la démarche de Schindler et Hawthorne (2001a, b). Nous relions les unités structurales des minéraux boratés entre elles en écrivant deux sortes de réaction chimique, une qui consomme H et l'autre qui consomme ($H_2O$). En combinant des équations avec la loi de l'action des masses, il est possible de formuler une expression en termes de pH; celle-ci permet de disposer les unités structurales dans un diagramme pH–log[$H_2O$] et de calculer la pente des interfaces entre domaines de stabilité. Il en résulte un diagramme pH–log[$H_2O$] de type "activité–activité" ayant une échelle relative le long de chaque axe, dans lequel la topologie des domaines est correcte. Les unités structurales des minéraux de paragenèse semblable occupent des domaines contigus dans cette representation. Les classes générales de polymérisation des groupes de borate dans les unités structurales changent systématiquement en traversant le diagramme activité–activité. A mesure qu'augmente l'activité de ($H_2O$), les unités structurales définissent la séquence suivante: trames → feuillets → chaînes → groupements → polyèdres isolés. La proportion de bore tétracoordonné ($^{[4]}B \times 100 / \{^{[3]}B + ^{[4]}B\}$) dans l'unité structurale augmente avec le pH en traversant le diagramme; cette relation découle du principe de la correspondance des valences et montre que les espèces interstitielles ayant une acidité plus élevée (par exemple, Ca, Mg) forment des minéraux à un pH plus élevé que les espèces interstitielles d'acidité plus faible (par exemple, Na, K). La basicité moyenne des agencements de borate en solution aqueuse serait une fonction linéaire du pH de cette solution aux concentrations maximales de chaque agencement (Hawthorne *et al.* 1996). La proportion de $^{[4]}B$ et la basicité moyenne de tous les agencement dans les solutions aqueuses boratées sont des fonctions continues du pH de la solution; de plus, la basicité moyenne des agencements (espèces dissoutes) est une fonction linéaire de la proportion de $^{[4]}B$ en solution.

(Traduit par la Rédaction)

*Mots-clés*: minéral boraté, unité structurale, pH, diagramme activité–activité, paragenèse.

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## INTRODUCTION

Borate minerals occur in a wide variety of geological environments, ranging from volcanic fumeroles to salt deposits to granulites. Smith & Medrano (1996) reviewed the occurrence of hydroxy-hydrated borate minerals in saline deposits, and London *et al.* (1996), Dingwell *et al.* (1996) and Grew (1996) described the occurrence of borates and borosilicates in plutonic and high-grade metamorphic rocks. Except for a few fluorides, minerals containing B are O compounds in which B occurs in triangular ($B\phi_3$) and tetrahedral ($B\phi_4$) coordination [$\phi$ is an unspecified ligand, either O or (OH)]. Hawthorne *et al.* (1996) reviewed the crystal chemistry of B-bearing minerals, and divided borate minerals into two major groups: (a) borates with only ($B\phi_3$) and ($B\phi_4$) polyhedra as oxyanions, and (b) mixed oxyanion borates in which ($B\phi_3$) and ($B\phi_4$) polyhedra occur with ($SiO_4$), ($SO_4$), ($PO_4$), ($BeO_4$), ($CO_3$) and ($AsO_4$) groups. Grice *et al.* (1999) presented a detailed structural hierarchy of borate minerals of group (a), and this forms a basis for the ideas developed here.

## BORATE STRUCTURAL UNITS AND POLYMERIZATION

Hawthorne (1983) proposed that structures may be ordered or classified according to the polymerization of cation coordination-polyhedra with higher bond-valences. Schindler & Hawthorne (2001a) used a *binary structure representation* (Hawthorne 1994, 1997) to divide a mineral structure into a (usually anionic) *structural unit* with polyhedra of higher bond-valence and a (usually cationic) *interstitial complex* with polyhedra of lower bond-valence. In the structure of most borate minerals, the B–$\phi$ bonds are of much higher bond-valence ($\geq$0.70) than the remaining cation–$\phi$ bonds. Thus the composition and dimension of a structural unit in a borate mineral (with no other oxyanion) are defined by the polymerization of ($B\phi_3$) and ($B\phi_4$) polyhedra. Hawthorne *et al.* (1996) hierarchically organized the borate minerals according to the following modes of polymerization of their structural units: (1) unconnected polyhedra, (2) finite clusters, (3) infinite chains, (4) infinite sheets, (5) infinite frameworks. Detailed information on the polymerization of borate polyhedra in a structural unit can be formulated as an algebraic descriptor of a cluster (Burns *et al.* 1995). This cluster is the fundamental building block of borate polyhedra, which is repeated, commonly polymerized, to form the structural unit. The descriptor contains information on the number of borate polyhedra in the cluster, the number of ($B\phi_3$) triangles, the number of ($B\phi_4$) tetrahedra, the presence of rings of polyhedra in the cluster, the connectivity of rings within the cluster, and also denotes clusters with a common ion (Burns *et al.* 1995, Hawthorne *et al.* 1996). Table 1 lists the structural units in borate minerals that contain only ($B\phi_3$) and ($B\phi_4$) polyhedra as oxyanions, one or more examples of the corresponding borate minerals, the average basicity, the fraction of tetrahedrally coordinated boron, the mode of polymerization of the structural unit, and the geological environments in which they occur.

## AQUEOUS BORATE SYSTEMS

Hydroxy-hydrated borate minerals form primarily by evaporation of saline lakes or during diagenesis of the resulting lacustrine sediments. Hanshaw (1963) and Christ *et al.* (1967) used paragenetic relations and thermodynamic data for several Na, Na–Ca and Ca–Mg borate minerals to construct their phase relations on a $\log [Na]^6[H]^2 / [Ca]^4 - \log H_2O - 1/T$ diagram. Christ *et al.* (1967) calculated the topology of activity–activity diagrams for $\log [Na^+] / [H^+]$ and $\log [Ca^{2+}] / [H^+]^2$, respectively, *versus* $\log (H_2O)$. Smith & Medrano (1996) reviewed these phase relations and indicated that the chemical composition and occurrence of saline borate minerals depend on the composition, temperature and pH of the primary parent solutions from which they crystallize and the secondary solutions with which they interact during weathering and diagenesis. This is in contrast with the occurrence of borate minerals in high-temperature systems where pH is not a significant variable and the activities (concentrations) of the various constituents replace pH in importance.

## LEWIS BASICITY AND AVERAGE BASICITY

Hawthorne (1985, 1986, 1990) showed that a structural unit has a specific Lewis basicity that is a measure of the characteristic valence of the bonds formed by this (in many cases very large) oxyanion. Hawthorne *et al.* (1996) showed that the Lewis basicity of heteropolyhedral complexes in aqueous solution correlates very strongly with the pH of the solution at maximum concentration of the specific complex; this relation can be viewed as an extension of the *valence-matching principle* (Brown 1981, Hawthorne 1994, 1997) to aqueous solutions, and suggests a direct relation between the Lewis basicity of a structural unit of a mineral and the pH of the aqueous solution from which it crystallized. Here, we investigate this putative relation further.

Hawthorne (1985) described a method to calculate the Lewis basicity of a structural unit. However, there are some problems with this calculation: (a) initially, one has to specify (*i.e.*, guess) a mean coordination number for O in the structural unit, whereas a particular structural unit can show a range of mean coordination numbers for O atoms, the specific value correlating with the details of the constituent interstitial complex; (b) the method leads to a specific Lewis basicity for a given structural unit, whereas minerals are stable over a *range* of pH. Schindler & Hawthorne (2001a, b) developed a better method for calculating the *range* of Lewis basic-

TABLE 1. STRUCTURAL UNITS IN BORATE MINERALS WITH EXAMPLES, THEIR AVERAGE BASICITY (AB), THEIR AVERAGE ANION-VALENCE (AAV), THE PERCENTAGE OF TETRAHEDRALLY COORDINATED BORON ($^{[4]}B$), THEIR STRUCTURE MODE AND OCCURRENCE

| Structural unit | Examples | Formula | AB [*vu*] | AAV [*vu*] | $^{[4]}B$ [%] | Structure mode | Occurrence * | Ref. |
|---|---|---|---|---|---|---|---|---|
| $[BO_4]^{5-}$ | sinhalite | $Mg\ Al\ [BO_4]$ | 1.25 | 0.63 | 100 | Isolated polyhedron | MT | (1) |
| $[BO_3]^{3-}$ | ludwigite | $(Mg,Fe^{2+})_2\ Fe^{3+}\ O_2\ [BO_3]$ | 1.00 | 0.50 | 0 | Isolated polyhedron | CM | (2) |
| " | nordenskiöldine | $Ca\ Sn\ [BO_3]_2$ | " | " | " | " | " | (3) |
| $[B_2O_5]^{4-}$ | suanite | $Mg_2\ [B_2O_5]$ | 0.80 | 0.40 | 0 | Dimer | CM | (4) |
| " | kurchatovite | $Ca\ (Mg,Mn,Fe)\ [B_2O_5]$ | " | " | " | " | " | (5) |
| $[B_6O_{14}]^{10-}$ | johachidolite | $Ca\ Al\ [B_3O_7]$ | 0.71 | 0.36 | 100 | Sheet | CM | (6) |
| $[B_2O_4(OH)]^{3-}$ | szaibelyite | $Mg_2\ (OH)\ [B_2O_4(OH)]$ | 0.64 | 0.33 | 0 | Dimer | CM, HY, EP | (7) |
| " | sussexite | $Mn_2\ (OH)\ [B_2O_4\ (OH)]$ | " | " | " | " | " | (8) |
| $[B_2O_4]^{2-}$ | calciborite | $Ca\ [B_2O_4]$ | 0.50 | 0.25 | 50 | Chain | CM | (9) |
| $[B_4O_7(OH)_2]^{4-}$ | fedorovskite | $Ca_2\ Mg_2\ (OH)_4\ [B_4O_7(OH)_2]$ | 0.49 | 0.25 | 50 | Cluster | CM | (10) |
| " | roweite | $Ca_2\ Mg_2\ (OH)_4\ [B_4O_7(OH)_2]$ | " | " | " | " | " | (11) |
| $[B_3O_4(OH)_4]^{3-}$ | solongoite | $Ca_2\ [B_3O_4(OH)_4]\ Cl$ | 0.48 | 0.25 | 66 | Trimer | CM | (12) |
| $[B_2O_2(OH)_4]^{2-}$ | vimsite | $Ca\ [B_2O_2(OH)_4]$ | 0.47 | 0.25 | 100 | Chain | CM | (13) |
| $[B_3O_3(OH)_6]^{3-}$ | nifontovite | $Ca_3\ [B_3O_3(OH)_6]_2\ (H_2O)_2$ | 0.47 | 0.25 | 100 | Trimer | CM | (14) |
| $[B_2O(OH)_6]^{2-}$ | pentahydroborite | $Ca\ [B_2O(OH)_6]\ (H_2O)_2$ | 0.46 | 0.25 | 100 | Dimer | EP | (15) |
| " | pinnoite | $Mg\ [B_2O(OH)_6]$ | " | " | " | " | " | (16) |
| $[B(OH)_4]^{-}$ | teepleite | $Na_2\ [B(OH)_4]\ Cl$ | 0.45 | 0.25 | 100 | Isolated polyhedron | CM, EP | (17) |
| " | bandylite | $Cu\ [B(OH)_4]\ Cl$ | " | " | " | " | " | (18) |
| " | frolovite | $Ca\ [B(OH)_4]_2$ | " | " | " | " | " | (19) |
| " | hexahydroborite | $Ca\ [B(OH)_4]_2\ (H_2O)_2$ | " | " | " | " | " | (20) |
| $[B_{10}O_{19}]^{8-}$ | priceite | $Ca_4\ [B_{10}O_{19}]\ (H_2O)_7$ | 0.42 | 0.21 | | | EP, MT, PG | (21) |
| $[B_4O_4(OH)_7]^{3-}$ | hydrochlorborite | $Ca_2\ [B_4O_4(OH)_7]\ Cl\ (H_2O)_7$ | 0.40 | 0.20 | 75 | Cluster | EP | (22) |
| $[B_7O_{13}]^{5-}$ | boracite-group | $M_3\ [B_7O_{13}]\ Cl,\ M = Mg,\ Fe^{2+},\ Mn^{2+}$ | 0.38 | 0.19 | 85–100 | Framework | EP, DG | (23) |
| $[B_3O_3(OH)_5]^{2-}$ | inyoite | $Ca\ [B_3O_3(OH)_5]\ (H_2O)_4$ | 0.38 | 0.18 | 66 | Trimer | EP, DG | (24) |
| " | inderite | $Mg\ [B_3O_3(OH)_5]\ (H_2O)_5$ | " | " | " | " | " | (25) |
| " | kurnakovite | | " | " | " | " | " | (26) |
| " | meyerhofferite | $Ca\ [B_3O_3(OH)_5]\ (H_2O)$ | " | " | " | " | " | (27) |
| " | inderborite | $Ca\ Mg\ [B_3O_3(OH)_5]_2\ (H_2O)_6$ | " | " | " | " | " | (28) |
| $[B_6O_{10}(OH)_2]^{4-}$ | fabianite | $Ca_2\ [B_6O_{10}(OH)_2]$ | 0.37 | 0.18 | 66 | Sheet | EP, DG | (29) |
| $[B_3O_4(OH)_3]^{2-}$ | colemanite | $Ca\ [B_3O_4(OH)_3]\ (H_2O)$ | 0.37 | 0.18 | 66 | Chain | EP, DG | (30) |
| " | hydroboracite | $Ca\ Mg\ [B_6O_8(OH)_6]\ (H_2O)_3$ | " | " | " | " | " | (31) |
| $[B_5O_6(OH)_6]^{3-}$ | ulexite | $Na\ Ca\ [B_5O_6(OH)_6]\ (H_2O)_5$ | 0.35 | 0.17 | 60 | Cluster | EP | (32) |
| " | brianroulstonite | $Ca_3\ [B_5O_6(OH)_6]\ (OH)\ Cl_2\ (H_2O)_8$ | " | " | " | Sheet | " | (33) |
| $[B_5O_7(OH)_4]^{3-}$ | probertite | $Na\ Ca\ [B_5O_6(OH)_6]\ (H_2O)_3$ | 0.35 | 0.17 | 60 | Chain | DG | (34) |
| $[B_5O_8(OH)_2]^{3-}$ | tuzlaite | $Na\ Ca\ [B_5O_8(OH)_2]\ (H_2O)_3$ | 0.34 | 0.17 | 60 | Sheet | EP, DG | (35) |
| $[B_5O_9]^{3-}$ | hilgardite-group | $Ca\ [B_5O_9]\ Cl\ (H_2O)$ | 0.33 | 0.17 | 60 | Framework | EP, DG | (36) |
| $[B_{11}O_{15}(OH)_9]^{6-}$ | preobrazhenskite | $Mg_3\ [B_{11}O_{15}(OH)_9]$ | 0.33 | 0.15 | 63 | Sheet | EP | (37) |
| $[B_9O_{13}(OH)_6]^{5-}$ | penobsquisite | $Ca_2\ Fe^{2+}\ [B_9O_{13}(OH)_6]\ Cl\ (H_2O)_4$ | 0.33 | ? | 50 | Framework | EP | (38) |
| $[B_{26}O_{34}(OH)_{24}]^{14-}$ | pringleite | $Ca_9\ [B_{26}O_{34}(OH)_{24}]\ Cl_4\ (H_2O)_{13}$ | 0.32 | 0.15 | 54 | Framework | EP | (39) |
| " | ruitenbergite | " | " | " | " | " | " | |
| $[B_4O_5(OH)_4]^{2-}$ | borax | $Na_2\ [B_4O_5(OH)_4]\ (H_2O)_8$ | 0.31 | 0.14 | 50 | Cluster | EP, DG | (40) |
| " | tincalconite | $Na_2\ [B_4O_5(OH)_4]\ (H_2O)_3$ | " | " | " | " | " | (41) |
| " | hungchaoite | $Mg\ [B_4O_5(OH)_4]\ (H_2O)_7$ | " | " | " | " | " | (42) |
| $[B_6O_8(OH)_5]^{3-}$ | kaliborite | $K\ H\ Mg_2\ [B_6O_8(OH)_5]_2\ (H_2O)_4$ | 0.31 | 0.14 | 50 | Chain | EP, DG | (43) |
| $[B_4O_6(OH)_2]^{2-}$ | kernite | $Na_2\ [B_4O_6(OH)_2]\ (H_2O)_3$ | 0.30 | 0.14 | 50 | Chain | EP, DG | (44) |
| $[B_4O_7]^{2-}$ | diomignite | $Li_2\ [B_4O_7]$ | 0.28 | 0.14 | 50 | Framework | PG | (45) |
| $[B_5O_7(OH)_3]^{2-}$ | ezcurrite | $Na_2\ [B_5O_7(OH)_3]\ (H_2O)_2$ | 0.26 | 0.12 | 40 | Chain | EP, DG | (46) |
| $[B_5O_8(OH)]^{2-}$ | biringuccite | $Na_2\ [B_5O_8(OH)\}\ (H_2O)_1$ | 0.24 | 0.12 | 40 | Sheet | EP, FA | (47) |
| " | nasinite | $Na_2\ [B_5O_8(OH)]\ (H_2O)_2$ | " | " | " | " | " | (48) |
| $[B_6O_6(OH)_8]^{2-}$ | ameghinite | $Na_2\ [B_6O_6(OH)_8]$ | 0.26 | 0.10 | 33 | Cluster | EP | (49) |
| $[B_6O_7(OH)_6]^{2-}$ | mcallisterite | $Mg\ [B_6O_7(OH)_6]\ (H_2O)_{4.5}$ | 0.25 | 0.10 | 50 | Cluster | EP | (50) |
| " | admontite | $Mg\ [B_6O_7(OH)_6]\ (H_2O)_{3.5}$ | " | " | " | " | " | (51) |
| " | aksaite | $Mg\ [B_6O_7(OH)_6]\ (H_2O)_2$ | " | " | " | " | " | (52) |
| " | rivadavite | $Na_{1.5}\ Mg_{0.25}\ [B_6O_7(OH)_6]\ (H_2O)_{2.5}$ | " | " | " | " | " | (53) |
| $[B_6O_8(OH)_4]^{2-}$ | aristarainite | $Na_2\ Mg\ [B_6O_8(OH)_4]_2(H_2O)_4$ | 0.23 | 0.10 | 50 | Chain | EP | (54) |

TABLE 1. Continued

| Structural unit | Examples | Formula | AB [*vu*] | AAV [*vu*] | $^{[4]}B$ [%] | Structure mode | Occurrence * | Ref. |
|---|---|---|---|---|---|---|---|---|
| $[B_6O_9(OH)_2]^{2-}$ | nobleite | $Ca\ [B_6O_9(OH)_2]\ (H_2O)_3$ | 0.22 | 0.10 | 50 | Sheet | DG | (55) |
| " | tunellite | $Sr\ [B_6O_9(OH)_2]\ (H_2O)_3$ | " | " | " | " | " | (56) |
| $[B_5O_8(OH)]^{2-}$ | gowerite | $Ca\ [B_5O_8(OH)]\ [B(OH)_3]\ (H_2O)_3$ | 0.25 | 0.12 | 500 | Sheet & | EP | (57) |
| x $[B(OH)_3]$ | veatchite-group | $Sr\ [B_5O_8(OH)]\ [B(OH)_3]\ (H_2O)_3$ | 0.14 | 0.00 | " | Isolated polyhedron | " | (58) |
| $[B_{14}O_{20}(OH)_6]^{4-}$ | ginorite | $Ca_2\ [B_{14}O_{20}(OH)_6]\ (H_2O)_5$ | 0.20 | 0.09 | 42 | Sheet | EP | – |
| " | strontioginorite | $SrCa\ [B_{14}O_{20}(OH)_6](H_2O)_5$ | " | " | " | " | " | (59) |
| $[B_8O_{11}(OH)_4]^{2-}$ | strontioborite | $Sr\ [B_8O_{11}(OH)_4]$ | 0.19 | 0.08 | 37.5 | Sheet | EP | (60) |
| $[B_5O_6(OH)_4]^{1-}$ | sborgite | $Na\ [B_5O_6(OH)_4]\ (H_2O)_3$ | 0.18 | 0.06 | 20 | Cluster | FA | (61) |
| $[B_5O_7(OH)_2]^{-}$ | larderellite | $NH_4\ [B_5O_7(OH)_2]\ (H_2O)$ | 0.16 | 0.06 | 20 | Chain | FA | (62) |
| $[B_{15}O_{20}(OH)_8]^{3-}$ | ammonioborite | $(NH_4)_3\ [B_{15}O_{20}(OH)_8]\ (H_2O)_4$ | 0.16 | 0.06 | 20 | Cluster | FA | (63) |
| $[B(OH)_3]$ | sassolite | $[B(OH)_3]$ ** | 0.14 | 0.00 | 0 | Isolated polyhedron | FA, EP | (64) |

* CM = contact-metasomatic, EP = evaporation, DG = diagenesis, HY = hydrothermal, MT = metamorphic, PG = pegmatites, FA = fumarolic activities.
** Average basicity determined by linear regression (Fig. 7).

References: (1) Fang & Newnham (1965), (2) Bonazzi & Menchetti (1989), (3) Effenberger & Zemann (1986), (4) Guo *et al.* (1995), (5) Yakubovich *et al.* (1976), (6) Moore & Araki (1972), (7) Takéuchi & Kudoh (1975), (8) Epprecht (1959), (9) Egorov-Tismenko *et al.* (1980), (10) Malinko *et al.* (1976), (11) Moore & Araki (1974), (12) Yamnova *et al.* (1977), (13) Shashkin *et al.* (1968), (14) Simonov *et al.* (1978), (15) Kazanskaya *et al.* (1977), (16) Krogh-Moe (1967), (17) Effenberger (1982), (18) Li & Burns (2000), (19) Simonov *et al.* (1976a), (20) Simonov *et al.* (1976b), (21) Anovitz & Grew (1996), (22) Brown & Clark (1978), (23) Schindler & Hawthorne (1998), (24) Clark *et al.* (1964), (25) Corazza (1976), (26) Corazza (1974), (27) Burns & Hawthorne (1993b), (28) Burns & Hawthorne (1994c), (29) Konnert *et al.* (1970a), (30) Burns & Hawthorne (1993a), (31) Sabelli & Stoppiani (1978), (32) Ghose *et al.* (1978), (33) Grice *et al.* (1997), (34) Menchetti *et al.* (1982), (35) Bermanec *et al.* (1994), (36) Burns & Hawthorne (1994d), (37) Burns & Hawthorne (1994b), (38) Grice *et al.* (1996), (39) Grice *et al.* (1994), (40) Levy & Lisensky (1978), (41) Powell *et al.* (1991), (42) Wan & Ghose (1977), (43) Burns & Hawthorne (1994e), (44) Cooper *et al.* (1973), (45) Krogh-Moe (1962), (46) Cannillo *et al.* (1973), (47) Corazza *et al.* (1974), (48) Corazza *et al.* (1975), (49) Dal Negro *et al.* (1975), (50) Dal Negro *et al.* (1969), (51) Walenta (1979), (52) Dal Negro *et al.* (1971), (53) Dal Negro *et al.* (1973), (54) Ghose & Wan (1977), (55) Clark *et al.* (1964), (56) Burns & Hawthorne (1994a), (57) Konnert *et al.* (1972), (58) Clark & Christ (1971), (59) Konnert *et al.* (1970b), (60) Brovkin *et al.* (1975), (61) Merlino & Sartori (1972), (62) Merlino & Sartori (1969), (63) Merlino & Sartori (1971), (64) Zachariasen (1954).

ity of a structural unit using a new parameter, the *average basicity* of the structural unit. This is defined as *the average bond-valence sum per O atom contributed by the interstitial species and other structural units* (Schindler & Hawthorne 2001a, b). This is a very easy quantity to calculate: it is the modified charge of the structural unit divided by the number of oxygen atoms in the structural unit, where the modified charge is the formal charge of the structural unit as modified by transfer of charge involved in the hydrogen bonds emanating from the structural unit. The average bond-valence is a measure of the bond valence required for stability of the structural unit, and it seems reasonable to propose that it should correlate with the pH of the solution from which the mineral crystallizes. Moreover, the average basicity of a structural unit correlates with the mean coordination number of O atoms of the structural unit (Fig. 1). The fact that the data spread over a narrow band rather than define a curvilinear correlation indicates that small changes in pH of the ambient solution are moderated by small adjustments in the coordination of the O atoms of the structural unit, and thus the structural unit (*i.e.*, the mineral) is stable over a *range* of pH values of the ambient solution. Thus when developing the relation between structural units and the pH of the ambient environment, we will use the *average basicity* of the structural unit as the parameter that relates to the pH of the environment.

## DEVELOPMENT OF A pH–LOG$[H_2O]$ ACTIVITY–ACTIVITY DIAGRAM FOR STRUCTURAL UNITS IN BORATE MINERALS

We wish to relate the occurrence of borate minerals to such chemical parameters as pH through the Lewis basicities and acidities of their structural units and interstitial cations. Thus we need to develop a connection between some parameter of the structural unit or interstitial complex and the relative positions of structural units on activity–activity diagrams. We will use the average basicity of the structural unit for this purpose, as this has proven to be a robust parameter to characterize the structural units of borate minerals (Schindler & Hawthorne 2001a, b). Hawthorne *et al.* (1996) showed that there is a direct correlation between the Lewis basicity of borate clusters (complexes) in solution and the pH of the aqueous solution at the maximum concentration of the complex. Figure 2 shows that this correlation also extends to the average basicity of the clusters, and supports our use of average basicity as a relative measure of pH. Thus we can arrange the structural units occurring in borate minerals (Hawthorne *et al.* 1996, Grice *et al.* 1999) in terms of relative average basicity and $(H_2O)$ content.

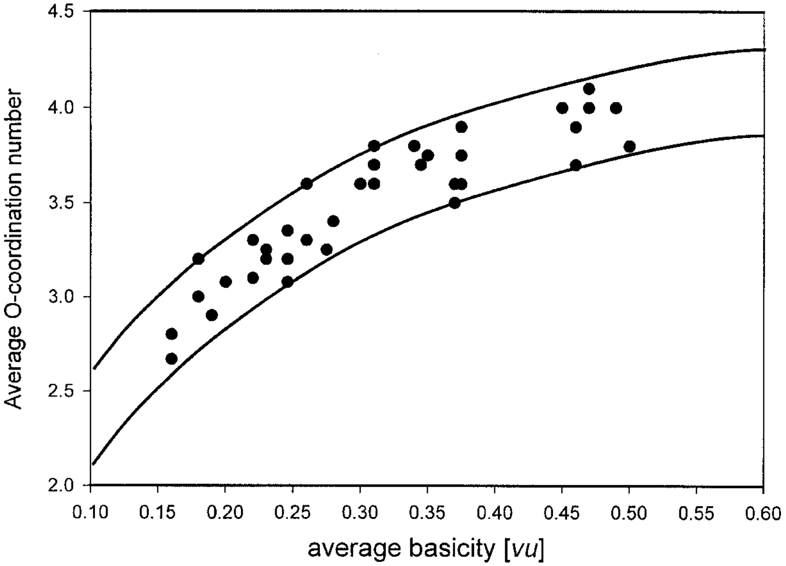

FIG. 1. Variation in average basicity of structural units in borate minerals as a function of the average coordination number of O atoms in the corresponding structural units (after Schindler & Hawthorne 2001a).

*Chemical reactions between structural units*

Let us now consider what type of reactions there can be between structural units on such a type of activity–activity diagram. There are two types of reactions to consider (Fig. 3): (1) Constant activity of ($H_2O$), variable pH; (2) constant pH, variable activity of ($H_2O$). We may write these reactions as follows:

$$[B_k\,O_{n-x}\,(OH)_{m+x}]^{(a-x)-} \leftrightarrow [B_k\,O_n\,(OH)_m]^{a-} + xH^+ \qquad [1]$$

$$[B_k\,O_{n-y}\,(OH)_{m+2y}]^{a-} \leftrightarrow [B_k\,O_n\,(OH)_m]^{a-} + y(H_2O) \qquad [2]$$

Forward reaction [1] produces free $H^+$. Thus an increase in pH of the system would reduce the activity of [$H^+$], forcing the reaction to the right to increase the activity of [$H^+$] until equilibrium is re-established. Thus an increase in pH of the system favors forward reaction [1]. Forward reaction [2] produces ($H_2O$). Therefore, decreasing the activity of [$H_2O$] in the system favors forward reaction [2] until equilibrium is re-established. Simultaneous variation in both $H^+$ and $H_2O$ may be represented by linear combinations of reactions [1] and [2], with both positive and negative values of $x$ and $y$. Now let us examine the changes in average basicity of the constituent structural units in these reactions.

*Reaction [1]*: the average basicity of the structural unit $[B_kO_n(OH)_m]^{a-}$ is

$$(a + hm) / (m + n) \qquad (1)$$

where $a$ is the number of formal negative charges on the structural unit, $m$ is the number of (OH) groups in the structural unit, $h$ is the strength of the hydrogen bonds emanating from the structural unit, and $n$ is the number of O atoms [exclusive of (OH)] in the structural unit. The average basicity of the structural unit $[B_k\,O_{n-x}\,(OH)_{m+x}]^{(a-x)-}$ is

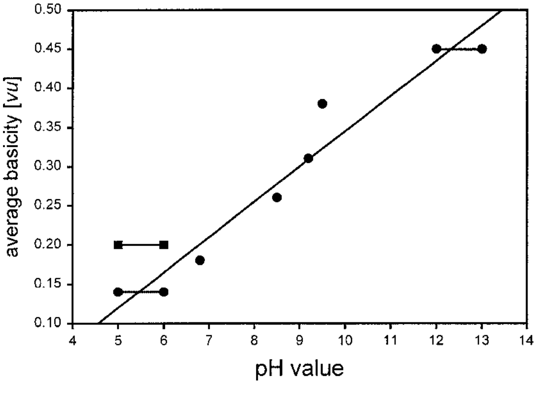

FIG. 2. The variation in average basicity as a function pH at maximum concentration for the borate clusters in aqueous solution described by Ingri (1963) and Christ *et al.* (1967).

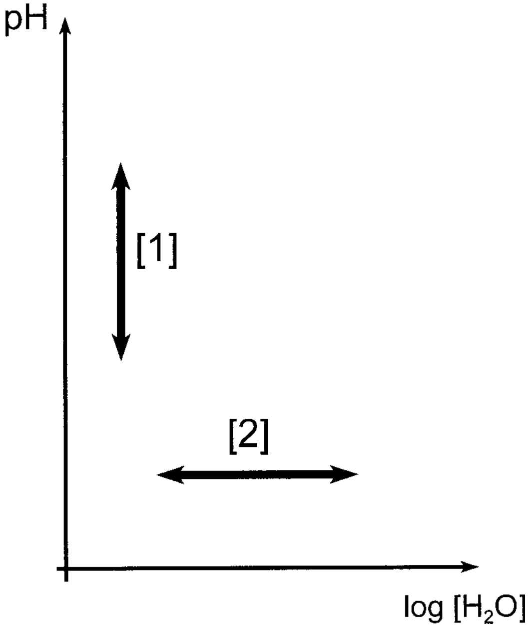

FIG. 3. The directions of reactions [1] and [2] on a pH–log[$H_2O$] diagram.

$$(a - x + h\,\{m + x\}) \,/\, (m + n) \qquad (2)$$

where $x$ is the amount of $H^+$ produced by the forward reaction. For the forward reaction, we may write the change in the average basicity of the structural units, $\Delta$, as follows:

$$\Delta = [(a + hm) \,/\, (m + n)] - [(a - x + hm + hx) \,/\, (m + n\,)] \qquad (3)$$

We may rearrange this expression to give

$$\Delta = [(a + hm) - (a - x + hm + hx)] \,/\, (m + n) \qquad (4)$$

from which we get the following:

$$\Delta = x\,(1 - h) \,/\, (m + n) \qquad (5)$$

As $m \geq 0$, $n \geq 0$, $x > 0$ and $(1 - h) > 0$, relation (5) must be positive, and hence forward reaction [1] must always produce an increase in the average basicity of the structural unit.

*Reaction [2]*: the average basicity of the structural unit $[B_k\,O_{n-y}\,(OH)_{m+2y}]^{a-}$ is

$$(a + h\,\{m + 2y\}) \,/\, (m + n + y) \qquad (6)$$

where $y$ is the amount of ($H_2O$) produced by the forward reaction. We may write the change in the average basicity of the structural units, $\Delta$, as follows:

$$\Delta = (a + hm) \,/\, (m + n) - (a + hm + 2hy) \,/\, (m + n + y) \qquad (7)$$

We may rearrange this expression to give

$$\Delta = [(a + hm)\,(m + n + y) - (a + hm + 2hy)\,(m + n)] \,/\, [(m + n)\,(m + n + y)] \qquad (8)$$

from which we get the following:

$$\Delta = y\,[a - h\,(2n + m)] \,/\, [(m + n)\,(m + n + y)] \qquad (9)$$

For the structural unit $[B_kO_n(OH)_m]^{a-}$, we may write $a = 2n + m - 3k$; substituting for $a$ in equation (9) gives

$$\Delta = y\,[(1 - h)\,(2n + m) - 3k] \,/\, [(m + n)\,(m + n + y)] \qquad (10)$$

As $m \geq 0$, $n \geq 0$, $y > 0$, $k > 0$ and $(1 - h) > 0$, for $\Delta$ to be zero

$$(1 - h)\,(2n + m) - 3k = 0 \qquad (11)$$

This is a very curious relation; it indicates that, in forward reaction [2], which produces ($H_2O$) and does not affect [$H^+$], if there is no change in average basicity, the strength of the O–H bond in the structural unit is equal to the ratio of the cation charge to anion charge in the structural unit. If $3k \,/\, (2n + m)$ is greater than $(1 - h)$, the average basicity decreases; if $3k \,/\, (2n + m)$ is less than $(1 - h)$, the average basicity increases. Examining numerical solutions to equation (10) for physically reasonable values of $h$ (*i.e.*, $h = 0.20 \pm 0.15$ *vu*), $n$, $m$ and $k$, we see that such changes in average basicity tend to be quite small, particularly compared to reaction [1]. Thus reaction [2], on average, represents reactions parallel to the log [$H_2O$] axis of the activity–activity diagram, but small deviations from constant average basicity (pH) can occur.

The directions of the reactions [1] and [2] relative to the axes of an activity–activity diagram involving pH and log [$H_2O$] are shown in Figure 3.

### *Calculation of the topology of a pH–log [$H_2O$] diagram of borate structural units*

We have arranged the structural units in borate minerals in terms of their relative variations in average basicity (proportional to pH) and ($H_2O$) content [proportional to the activity of ($H_2O$)]. Next, we write equilibrium equations between structural units of similar average basicity and ($H_2O$) content (*i.e.*, those "species" that will be adjacent on such an activity–activity diagram). From the law of mass action, we may then write the following relation:

$$pH = k \log[H_2O] + \log K \qquad (12)$$

We do not know log $K$, and hence our calculated values are only given on a relative basis. However, the slope of the boundary between stability fields is given by $k$, which we do know, and hence we can construct an activity–activity diagram with the correct topology.

*Example*: Consider the structural units $[(B_2 O (OH)_6]^{2-}$ and $[(B_4 O_4 (OH)_7]^{3-}$. The average basicities are $(2 + h \times 6) / (1 + 6) = 3.2 / 7$ (setting $h = 0.2$ *vu*) = 0.46 *vu* and $(3 + h \times 7) / (4 + 7) = 4.2 / 11 = 0.38$ *vu*, respectively, and we can write the equilibrium between them as follows:

$$2\ [(B_2 O (OH)_6]^{2-} + H^+ \leftrightarrow$$
$$[(B_4 O_4 (OH)_7]^{3-} + 3\ H_2O \qquad (13)$$

Both structural units are solids and have, by definition, activities of one. Formulating the law of mass action, we get

$$K = [H_2O]^3 / [H^+] \qquad (14)$$

Writing this in logarithmic form and substituting pH for $-\log [H^+]$

$$pH = -3\log [H_2O] + \log K \qquad (15)$$

and the boundary between these two phases has a slope of –3.

Thus, given the relative placement of structural units in pH–log$[H_2O]$ space, together with the slopes of the phase boundaries between adjacent structural units, we produce the activity–activity diagram shown in Figure 4. In this diagram, one unit on the pH axis is equal to five units on the log $(H_2O)$ axis. Moreover, the stability field of a structural unit can represent minerals with different interstitial cations or different numbers of $(H_2O)$ groups, *e.g.*, borax, $Na_2 [B_4 O_5 (OH)_4] (H_2O)_8$, and tincalconite, $Na_2 [B_4 O_5 (OH)_4] (H_2O)_3$.

## CORRELATION OF PARAGENESIS AND pH–LOG$[H_2O]$

Different borate-mineral parageneses in pH–log$[H_2O]$ space are indicated in Figure 4b, where we have divided the occurrence of borate minerals into three major groups: (1) high-temperature borates from metamorphic rocks, pegmatites and skarns (shown in red; (2) borates formed by evaporation, diagenesis or low-temperature hydrothermal activity (shown in yellow), and (3) borates formed by fumarolic activity (shown in green). Stability fields with stripes indicate structural units that occur in minerals from more than one of these environments. It is immediately apparent from Figure 4b that structural units from minerals of the similar paragenesis occur in contiguous fields of the diagram. Of course, this has been proposed before, but the relation of Figure 5b takes us a step further in *quantitatively* establishing such a relation.

## CORRELATION OF POLYMERIZATION OF THE STRUCTURAL UNIT AND pH–LOG$[H_2O]$

Figure 5a shows the activity–activity diagram with the average basicities of the corresponding structural units shown in their stability fields, and Figure 5b shows the general classes of polymerization of borate groups (Hawthorne *et al*. 1996, Grice *et al*. 1999) in the constituent structural units: isolated polyhedra or polyhedron clusters (shown in yellow), chains of borate polyhedra (shown in green), sheets of borate polyhedra (shown in red), and frameworks of borate polyhedra (shown in purple). With increasing activity of $[H_2O]$, there is the following trend: frameworks to sheets to chains to clusters and isolated polyhedron structures. Exceptions to this trend are the $[B_{26} O_{34} (OH)_{24}]^{14-}$ structural unit in pringleite and ruitenbergite (Table 1) and the $[B_5 O_6 (OH)_6]^{-3}$ structural unit in brianroulstonite. Here, the structural units are zeolite-like frameworks and a sheet that occur at higher log $[H_2O]$ values than other borate framework or sheet structural units. This issue will be addressed elsewhere. At lower pH, the frameworks are missing from this sequence, *i.e.*, at average basicities of less than 0.33 *vu*. It is notable that framework borate structures do not contain hydrogen as a constituent of their structural unit. This is in accord with the general discussion of Hawthorne (1992) that emphasizes the major role of hydrogen [as (OH) and $(H_2O)$] in controlling the type of polymerization (and generating the large diversity) of structural units in minerals. Note that 0.33 *vu* is about the common maximum strength of a hydrogen bond in minerals (there are a few exceptions, such as those minerals containing symmetrical hydrogen-bonds), suggesting that the details of the interaction of the structure with its nascent aqueous solution are what dictate the occurrence of frameworks, as distinct from other polymerizations, in borate minerals. This is worthy of further examination, and will be examined elsewhere.

## THE OCCURRENCE OF $^{[3]}$B AND $^{[4]}$B IN LOW-TEMPERATURE BORATE MINERALS

Ingri (1963) and Christ *et al*. (1967) showed that $\{B (OH)_3\}^0$ and $\{B (OH)_4\}^-$ are stable in aqueous solution at low and high pH, respectively. This being the case, one can conjecture that there is a relation between the ratio of [3]-coordinated B to [4]-coordinated B and the average basicity of a structural unit. This relation is examined for the structural units of Table 1 in Figure 6a. The percentage of $^{[4]}$B in the higher hydrated structural units increases with increasing pH. This is not necessarily the case for less hydrated structural units at low pH, where the percentage of $^{[4]}B$ can change with decreasing activity of $[H_2O]$ (for example, from 33% in $[B_6O_6(OH)_8]^{2-}$ to 50% in $[B_6O_7(OH)_6]^{2-}$).

The average basicity of a structural unit is affected by the type of polymerization of the borate polyhedra, and the coordination of the constituent B cations. The average bond-valence of a $^{[4]}B–\phi$ bond is 0.75 *vu*, whereas a $^{[3]}B–O$ bond has an average bond-valence of 1.0 vu. In the first case, the O atom requires an additional 1.25 *vu* to satisfy its bond-valence requirements,

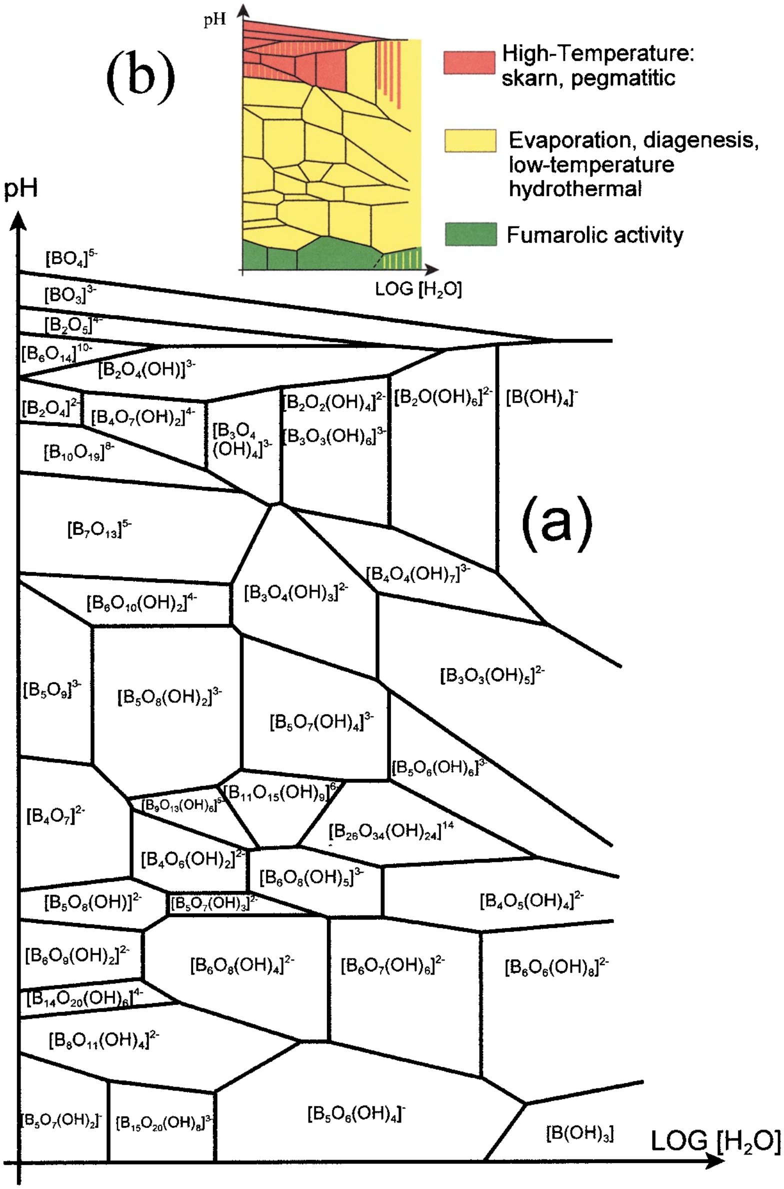

FIG. 4. (a) The topology of the pH–log$[H_2O]$ activity–activity diagram for all the structural units in borate minerals without other oxyanions. The sizes of the stability fields are somewhat arbitrary, but their general arrangement and the slopes of the phase boundaries should be correct. One unit on the pH axis is equal to five units on the log $(H_2O)$ axis. (b) General geological occurrence of the corresponding minerals. Stability fields with stripes represent structural units that occur in minerals of different geological environments.

whereas in the second case, the O atom requires only 1.0 *vu* to satisfy its bond-valence requirements. Thus the coordination of the constituent B cations will be an important control on the average basicity of the structural unit: for structural units of similar polymerization, those with a higher proportion of $^{[4]}$B will always have a higher average basicity. This is shown in Figure 6b for structural units in minerals formed during evaporation and diagenesis.

## INTERSTITIAL COMPLEXES IN THE ACTIVITY–ACTIVITY DIAGRAM

Figure 7a shows the occurrence of interstitial complexes in the activity–activity diagram, and Figure 7b shows the geological environment of the corresponding borate minerals; these figures are discussed more extensively below.

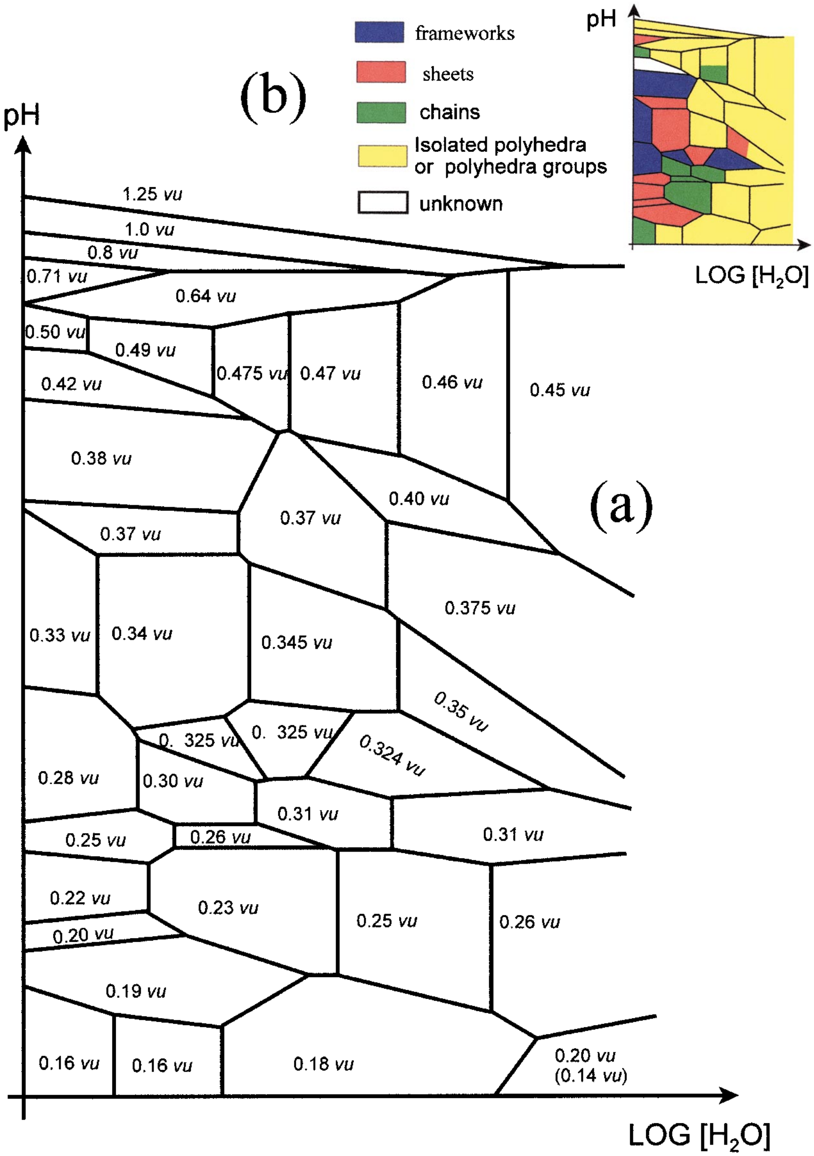

FIG. 5. (a) Activity–activity diagram with the average basicity of the structural units marked in their stability fields. (b) The mode of polymerization of the structural units superimposed on the activity–activity diagram.

### *General occurrence of interstitial cations*

Intermediate-size (0.53–0.83 Å) divalent and trivalent interstitial cations such as Al, $Fe^{2+}$, $Fe^{3+}$ and $Mn^{2+}$ occur exclusively in high-temperature borate minerals. Interstitial complexes with Ca occur mainly with structural units of higher average basicity, and interstitial complexes with Na occur with structural units of lower average basicity (Schindler & Hawthorne 2001b). Mg occurs either with structural units of lower average basicities and higher hydration or with structural units of higher average basicity and lower hydration. The occurrence of Mg can be generally described by a line from the upper left corner to the lower right corner of Figure 7a. Interstitial cations such as Sr and $(NH_4)^+$ occur only with structural units of lower average basicity and lower hydration. The corresponding minerals are products of evaporation-diagenesis and of fumarolic activity, respectively. However, the dominant interstitial cations are Na, Ca and Mg.

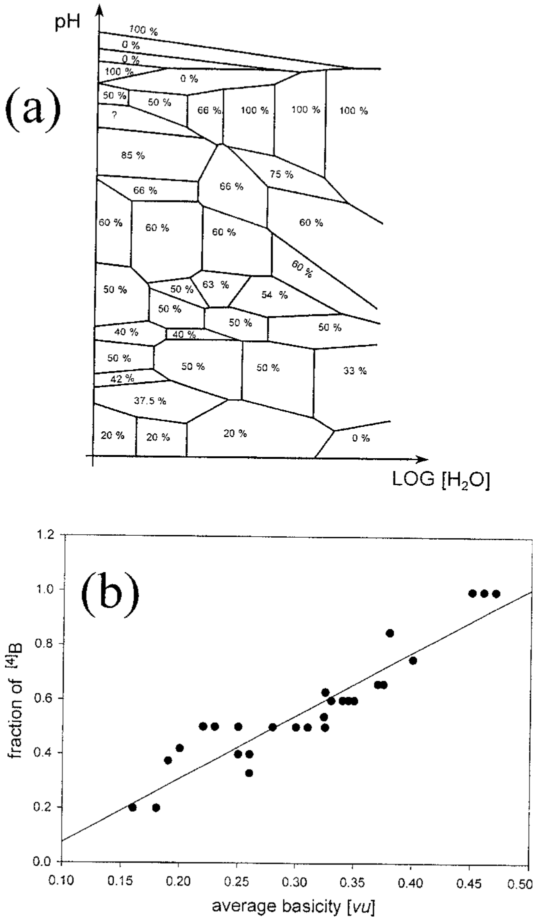

FIG. 6. (a) Activity–activity diagram with the fraction of tetrahedrally coordinated B in the structural units marked in the appropriate fields of stability. (b) Correlation between the average basicity and the fraction of tetrahedrally coordinated B ($^{[4]}B$) in structural units of minerals formed during evaporation and diagenesis.

### *General occurrence of transformer ($H_2O$) groups and $Cl^-$ anions*

Transformer ($H_2O$) groups occur only in interstitial complexes of minerals formed during evaporation and diagenesis, and only then with structural units of average basicity less than or equal to 0.40 *vu* (Figs. 5a, 7a) . The structural unit with the highest average basicity (0.40 *vu*) occurs in hydroboracite, $Ca (H_2O)_2 Cl [B_4 O_4 (OH)_7]$, in which transformer ($H_2O$) groups occur with Ca and $Cl^-$ in the interstitial complex. With decreasing average basicity of the structural unit, transformer ($H_2O$) groups occur dominantly with Mg and Ca, and rarely with Na, in the corresponding interstitial complexes.

Almost all $Cl^-$-bearing borate minerals in the activity–activity diagram are formed during evaporation and diagenesis of sediments. The only exception is solongoite, $Ca_2 Cl [B_3 O_4 (OH)_4]$ which occurs in skarns (Anovitz & Grew 1996). Chlorine occurs in borates in five different interstitial complexes with Ca, twice with $Fe^{2+}$, and once in complexes with Cu, Na, Mg and Mn. All these interstitial complexes occur with structural units of average basicities between 0.324 *vu* ($[B_{26} O_{34} (OH)_{24}]$ in pringleite) and 0.475 *vu* ($[B_3 O_4 (OH)_4]^{3-}$ in solongoite).

### *Interstitial complexes and the corresponding Lewis basicities of the structural units*

Above, we showed that forward reaction [1] proceeds with a change in pH, and that the forward reaction also produces a change in the average basicity of the constituent structural units. Thus the average basicity is correlated with pH of the ambient environment. The average basicity is correlated with the average coordination-number of O in the structural unit (Fig. 1), and from the range in coordination number of O, we can calculate the range in Lewis basicity of the structural unit. From the Lewis basicity, we can make some correlations and predictions concerning the details of the interstitial complex. Moreover, from the above chain of connections, we can semiquantitatively correlate the Lewis basicity of the structural unit with the pH of formation of the mineral. This connection is made somewhat more directly in Figure 8, which correlates the activity–activity diagram for borate minerals with the range of Lewis basicity expressed as a function of average basicity (Schindler & Hawthorne 2001a, b). The maximum (0.45 *vu*) and minimum (0.16 *vu*) values of the average basicity to the right of the figure match the corresponding stability-fields of the structural units in the activity–activity diagram. It is apparent that an increase in pH correlates with the Lewis basicity of the structural units that are stable. Thus, we see, for the first time, the direct influence of the nascent solution on the chemical composition of crystallizing minerals, and understand the mechanism whereby such influence is exercised.

Structural units formed at higher pH have, on average, higher ranges in Lewis basicity than those formed at lower values of pH (Schindler & Hawthorne 2001b). This accounts for the absence of medium and large monovalent cations in interstitial complexes with structural units formed at high pH: it is caused by the corresponding range in Lewis basicity of each structural unit rather than by the lower activities of monovalent cations under these conditions.

### *Composition of interstitial complexes as an indicator of pH*

We can now use the compositions of interstitial complexes as indicators of pH during crystallization of minerals. On the basis of the general trends in the activity–activity diagram, we can make the following observation: interstitial complexes with exclusively Ca (or Na) and Cl indicate a higher range in pH than interstitial complexes with exclusively Ca (or Na) and no Cl.

## OCCURRENCE OF INTERSTITIAL CATIONS WITH SPECIFIC STRUCTURAL UNITS

Erd *et al.* (1959) synthesized gowerite, $Ca [B_5 O_8 (OH)] [B (OH)_3] (H_2O)_3$, at 35°C and pH 5. Gowerite and ginorite, $Ca_3 [B_{14} O_{20} (OH)_6] (H_2O)_5$, can form during surface weathering of priceite, $Ca_4 [B_{10} O_{19}] (H_2O)_7$, and colemanite, $Ca [B_3 O_4 (OH)_3] (H_2O)$ (see below). Thus, minerals with more highly polymerized structural units, such as $[B_5 O_8 (OH)]$ (0.25 *vu*) and $[B_{14} O_{20} (OH)_6]^{4-}$ (0.20 *vu*), crystallize from surface or near-surface aqueous solutions, and their occurrence is not restricted to diagenetic reactions. Figure 7a shows that more highly hydrated structural units with similar average basicities (0.20–0.25 *vu*) occur exclusively with Na and Mg. At a given pH and independent of the $[H_2O]$ activity, the type of interstitial cation available thus determines the occurrence of a structural unit in a mineral.

On the basis of the distribution of cations in the activity–activity diagram (Fig. 7a), we can make the following conclusions:

1) The average basicity of a structural unit in Na-, Ca- and Mg-bearing borate minerals depends primarily on the value of pH.

2) Exceptions may occur at low pH and extremely high activities of one or all cations ([Na] + [Ca] + [Mg]), or at high pH and low activities of all cation species (low log $[M^+] / [H^+]$ and log $[M^{2+}] / [H^+]^2$ ratios). Thus sassolite, $[B (OH)_3]$, may occur at relatively high values of pH if there is complete deficiency of interstitial cations in solution.

3) The occurrence of a specific structural unit depends on the ratios of the activities of the interstitial cations in solution.

## WEATHERING OF BORATE MINERALS

We may write two different types of chemical reactions for weathering processes of minerals with divalent cations:

$$M^{2+}{}_b [B_k O_n (OH)_m]^{2b-} + 2xH^+ \leftrightarrow M^{2+}{}_{b-x} [B_k O_{n-x} (OH)_{m+x}]^{2(b-x)-} + xM^{2+} \quad [3]$$

$$M^{2+}{}_b [B_k O_n (OH)_m]^{2b-} + y(H_2O) \leftrightarrow M^{2+}{}_b [B_k O_{n-y} (OH)_{m+2y}]^{2b-} \quad [4]$$

In equations [3] and [4], the stability of a structural unit depends on the $[M^{2+}] / [H]^2$ ratio and the activity of $(H_2O)$, respectively. During weathering processes, the interstitial $M^{2+}$ cation can be removed from the host, and the ratio $[M^{2+}] / [H]^2$ decreases. As noted earlier, minerals with structural units of low average basicity can occur at high pH but low activities (or complete deficiency) of interstitial cations. In these cases, the average basicity should be used as an indicator of the $[M^{2+}] / [H]^2$ value of the parent solution.

### *An example*

McAllister (1958) examined the weathering of priceite (structural unit: $[B_{10} O_{19}]^{8-}$, average basicity = 0.42 *vu*) and colemanite (structural unit: $[B_3 O_4 (OH)_3]^{2-}$, average basicity = 0.37 *vu*) in veins in olivine basalt and "basaltic sandstone" in the Furnace Creek district, Death Valley, California. These veins are exposed to carbonate-saturated rainwater, which reacts with colemanite and priceite to form inyoite ($[B_3 O_3 (OH)_5]^{2-}$, 0.38 *vu*), meyerhofferite ($[B_3 O_3 (OH)_5]^{2-}$, 0.38 *vu*), hydroboracite ($[B_6 O_8 (OH)_6]^{4-}$, 0.37 *vu*), ulexite ($[B_5 O_6 (OH)_6]^{3-}$, 0.35 *vu*), gowerite ($[B_5 O_8 (OH)] [B (OH)_3]^{2-}$, 0.25 *vu*), ginorite ($[B_{14} O_{20} (OH)_6]^{2-}$, 0.20 *vu*) and sassolite ($[B (OH)_3]^0$, 0.20 *vu*) (McAllister 1958, Erd *et al*. 1959). In Figure 7a, this weathering process is shown by arrows from the reactants to the products. Both primary Ca-borates are characterized by structural units of low hydration and high average basicity. These minerals are not in equilibrium with rainwater, and therefore they dissolve. There are only low contents of Na, Mg and Cl in the host rock, and only Ca borates and sassolite can form during the weathering process. Following the direction of the arrows in Figure 7a, the more highly hydrated structural units in inyoite and meyerhofferite are products of increasing $[H_2O]$ activity. The formation of minerals with structural units of lower average basicity clearly indicates a decreasing $[M^{2+}]$ / $[H^+]^2$ value (low pH of the solution and removal of Ca), *e.g.*, formation of ulexite (0.35 *vu*), ginorite (0.20 *vu*), gowerite (0.25 *vu*), and sassolite (0.20 *vu*).

## AQUEOUS SPECIES IN CONCENTRATED BORATE SOLUTIONS

The pioneering work of Ingri and coworkers (summarized by Ingri 1963) showed that the following bo-

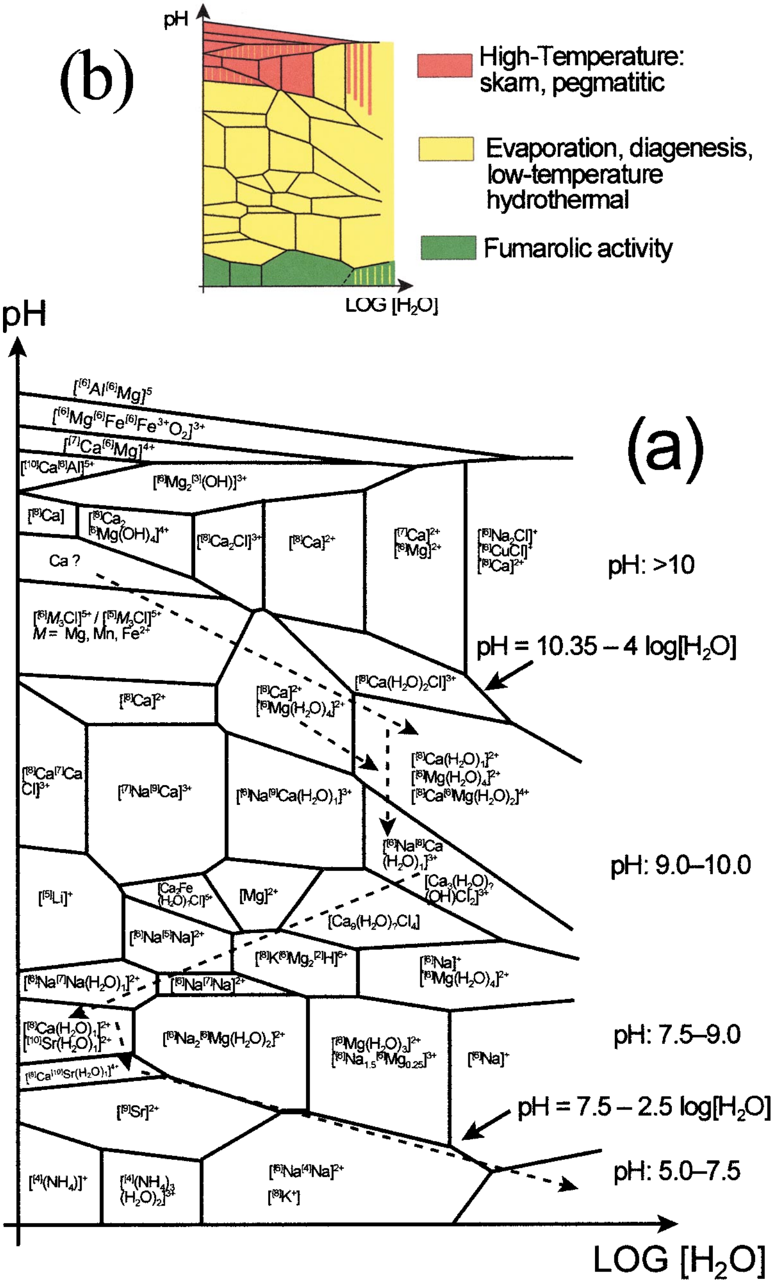

FIG. 7. Activity–activity diagram with the composition of the corresponding interstitial complexes. On the right side are indicated the approximately ranges in pH of the parent solutions. The arrows indicate the formation of different structural units during the weathering process of priceite and colemanite at Furnace Creek, Death Valley (see text).

rate species occur in highly concentrated aqueous borate solutions: $[B(OH)_3]^0$, $[B_5O_6(OH)_4]^-$, $[B_3O_3(OH)_4]^-$, $[B_3O_3(OH)_5]^{2-}$, $[B_4O_5(OH)_4]^{2-}$ and $[B(OH)_4]^-$ (Fig. 8a). Raman spectroscopy (Maya 1976, Janda & Heller 1979a) and $^{11}$B–NMR spectroscopy (Janda & Heller 1979b, Salentine 1983, Müller *et al.* 1993) have confirmed the occurrence and pH ranges for all these aqueous species except $[B_3O_3(OH)_5]^{2-}$.

### *Tetrahedrally coordinated B in aqueous solution*

Ingri (1963) showed in detail the distribution and concentration of aqueous borate species over the pH range 4–14 (Fig. 9a). At low pH, the stable aqueous species is $[B(OH)_3]^0$, and the constituent B is [3]-coordinated. At high pH, the stable aqueous phase is $[B(OH)_4]^{1-}$, and the constituent B is [4]-coordinated. Thus the variation in coordination number shows a crude correlation with ambient pH. At pH values close to neutrality, more complex aqueous borate species are present (Fig. 9a). These species occur as structural units in minerals, and the topological and geometrical details of their structures are well known. Thus we may calculate the percentage of tetrahedrally coordinated B, $^{[4]}$B, in each species; this value decreases from 100% in $[B(OH)_4]$ to 66% in $[B_3O_3(OH)_5]^{2-}$ to 50% in $[B_4O_5(OH)_4]^{2-}$ to 33% in $[B_3O_3(OH)_4]^-$ to 20% in $[B_5O_6(OH)_4]^-$ to 0% in $[B(OH)_3]$. From Figure 9a, we may also calculate the percentage of each species at a specific pH. Combining these two sets of results, we derive the fraction of tetrahedrally coordinated B for each integer pH value between 4 and 14 (Fig. 9b). Below pH 7 and above pH 11, the curve smoothly approaches the limiting values of 0 and 1, respectively. Where pH is in the range 7–11, the proportion of tetrahedrally coordinated B varies rapidly as a function of pH. This type of curve can be described by the general equation $f(x) = a + b / [1 + (e^{(x-c)/d})^n]$, where $a = 0.037(16)$, $b = 1.04(2)$, $c = 9.96(14)$, $d = 0.48(7)$ and $n = 0.30(7)$.

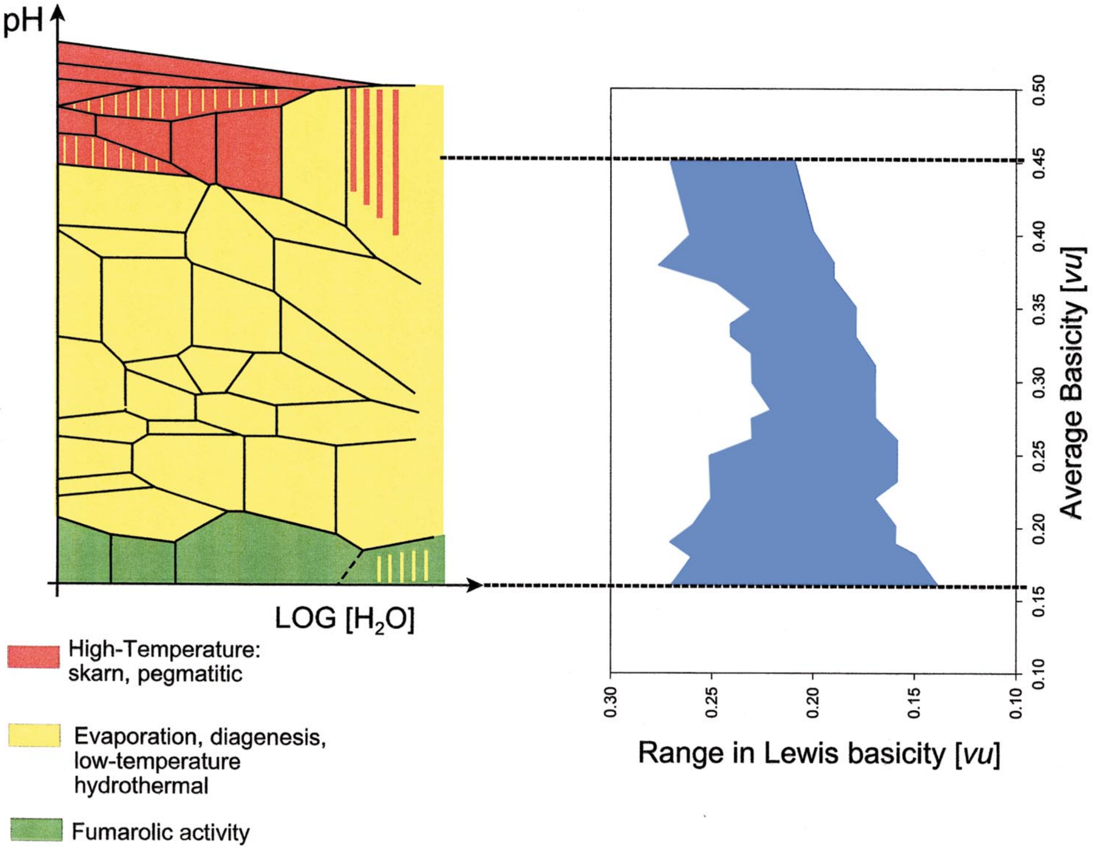

FIG. 8. The correlation between the activity–activity diagram for borate minerals with their general occurrence and with the variation in range of Lewis basicity as a function of average basicity. The average-basicity scale on the right correlates with the average basicity of the structural units represented on the activity–activity diagram.

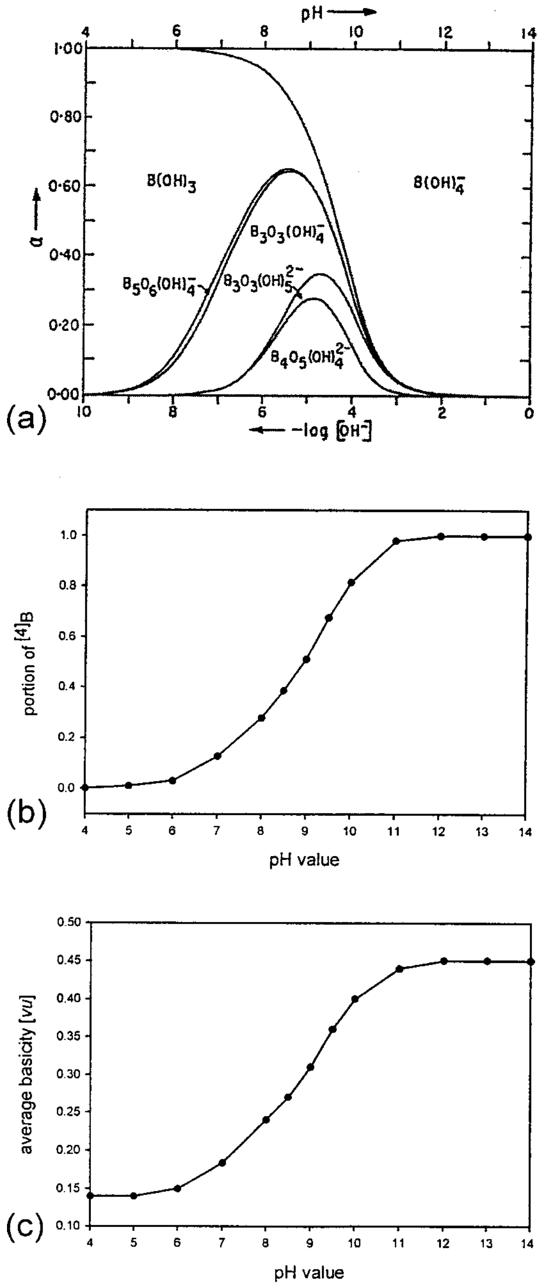

FIG. 9. (a) Distribution and occurrence of the aqueous species in solution, after Ingri (1963). At a given value of pH, the vertical distance between successive curves gives the fraction _ of the ion present; (b) the fraction of tetrahedrally coordinated boron ($^{[4]}$B) in the aqueous species at a specific value of pH, (c) the average basicity of the aqueous species at a specific value of pH.

### *Average basicity of aqueous borate species*

Every structural unit or aqueous species is also characterized by its average basicity (Table 1). However, in trying to examine the relation between average basicity and pH, the following question arises: What is the average basicity of the neutral [B (OH)$_3$] species? Following the definition given above, the average basicity of [B (OH)$_3$] is [0 + (3 × 0.2)] / 3 = 0.20 *vu*. The problem with this calculation is that the resulting value is higher than that of [B$_5$ O$_6$ (OH)$_4$]$^-$ (0.18 *vu*) (Table 1).

We may approach this issue from a different direction by considering the stable species in Figure 9. Hawthorne *et al.* (1996) showed that there is a well-defined linear correlation between the Lewis basicity of the aqueous species and the pH at their maximum concentrations in solution; a similar correlation exists for the average basicity. If we plot the average basicity of each aqueous species against the proportion of tetrahedrally coordinated B [omitting B (OH)$_3$], a linear correlation results (Fig. 10). Extrapolating this curve to $^{[4]}$B = 0 gives a value for the average basicity of [B (OH)$_3$]: 0.14 *vu*. Sassolite, [B (OH)$_3$], consists of planar layers of [B(OH)$_3$] triangles that are linked in the plane by hydrogen bonds and are linked out of the plane by van der Waals forces. Each O atom is coordinated by one $^{[3]}$B, one H atom, and receives one hydrogen bond from an adjacent [B (OH)$_3$] group: $\Sigma = 1.0 + y + (1 - y) = 2.0$ *vu*, where $y$ is the bond valence of the O–H bond. In sassolite, satisfaction of the valence-matching principle is unrelated to the bond valence of the hydrogen bond ($1 - y$ *vu* above), and hence $y$ can ostensibly take any value. This is not the case in most structures: $y$ usually has to take a specific value to satisfy the anion bond-valence requirements. According to Brown (1981), the most common value for $y$ is 0.80 *vu*, and this value is also in accord with our experience. As there is no bond-valence constraint on $y$ in sassolite, it appears that our "average value" of 0.80 *vu* is inappropriate in this particular case. Hence we will use the value of 0.14 *vu* for the Lewis basicity (*i.e.*, $1 - y$) in sassolite. This value allows us to examine the overall mean value of the average basicities as a function of pH between pH 4 and 14. This relation (Fig. 9c), $f(x) = a + b / (1 + e^{(x-c)/d})^n$, where $a$ = 0.126(7), $b$ = 0.325(7), $c$ = 9.7(2), $d$ = 0.58(10) and $n$ = 0.37(12), is very similar to the relation between tetrahedrally coordinated B and pH value (Fig. 9b). The minimum and maximum average basicities of borate species in aqueous solution are thus 0.14 and 0.45 *vu*, respectively. The maximum average basicity (0.45 *vu)* observed in aqueous solution is in accord with the observation that average basicities greater than 0.45 *vu* occur mainly in minerals formed at higher temperature (Fig. 4b).

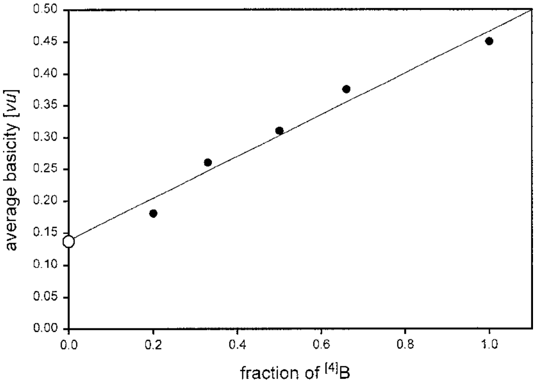

FIG. 10. Correlation between the fraction of tetrahedrally coordinated B in the aqueous species ($^{[4]}$B) and their average basicity (after Hawthorne *et al.* 1996). The calculated average basicity of [B(OH)$_3$] (0 $^{[4]}$B) was determined *via* linear regression, and its value is marked with a white large circle.

### *Assignment of pH values in the activity–activity diagram*

We know from Figure 5 that pH is the primary control on the average basicity of the structural unit in borate minerals. Furthermore, we know the occurrence and average basicity of the aqueous species in solution as a function of pH. Hence we may now assign pH ranges to different regions of the activity–activity diagram (Fig. 7a). These ranges are approximate, and the occurrence of each structural unit depends also on the activity ratios of the interstitial cations. The pH ranges assigned are supported by thermodynamic data for the aqueous species (Distanov & Kopeykin 1990, Li *et al.* 2000) and by mineral synthesis (*e.g.*, gowerite, Erd *et al.* 1959). Two equations based on the thermodynamic data are shown in Figure 7a.

## SUMMARY

(1) The average basicity of borate clusters in aqueous solution is a linear function of the pH of that solution at maximum concentration of the borate cluster.

(2) We may formally relate different structural units in borate minerals using two chemical reactions, one that produces H and the other that produces ($H_2O$).

(3) Combining the above two equations with the law of mass action, we may write an expression for pH that allows us to arrange structural units in pH–log[$H_2O$] space and to calculate the slopes of the associated phase-boundaries. The result is a pH–log[$H_2O$] activity–activity diagram with the correct topology and a relative scale along each of the axes.

(4) Structural units from minerals of similar paragenesis occur in contiguous fields of the pH–log[$H_2O$] activity–activity diagram.

(5) The general classes of polymerization of borate groups in the structural units change systematically across the pH–log[$H_2O$] activity–activity diagram: with increasing activity of ($H_2O$), structural units trend from frameworks → sheets → chains → clusters → isolated polyhedra.

(6) The proportion of $^{[4]}$B in the structural units increases with increasing pH across the pH–log[$H_2O$] activity–activity diagram.

(7) The positive correlation of basicity of the structural unit and pH combines with the valence-matching principle to indicate that interstitial species of higher acidity (*e.g.*, Ca, Mg) form minerals at higher pH than interstitial species of lower acidity (*e.g.*, Na, K).

(8) The proportion of $^{[4]}$B and the average basicity of all species in aqueous borate solutions are smooth functions of the pH of the solution.

(9) In aqueous borate solutions, the average basicity of the dissolved species is a linear function of the proportion of $^{[4]}$B.

(10) For the first time, we see the direct influence of the pH of the nascent solution on the chemical composition of crystallizing minerals, and understand the mechanism whereby such influence is exercised.

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## REFERENCES

ANOVITZ, L.M. & GREW, E.S. (1996): Mineralogy, petrology and geochemistry of boron: an introduction. *Rev. Mineral.* **33**, 1-40.

BERMANEC, V., ARMBRUSTER, T., TIBLJAS, D., STURMAN, D. & KNIEWALD, G. (1994): Tuzlaite, NaCa[$B_5O_8(OH)_2$]•3$H_2O$, a new mineral with a pentaborate sheet structure from the Tuzla salt mine, Bosnia and Hercegovina. *Am. Mineral.* **79**, 562-569.

BONAZZI, P. & MENCHETTI, S. (1989): Contribution to the crystal chemistry of the minerals of the ludwigite–vonsenite series. *Neues Jahrb. Mineral., Monatsh.*, 69-83.

BROVKIN, A.A., ZAYAKINA, N.V. & BROVKINA, V.S. (1975): Crystal structure of strontioborite Sr[$B_8O_{11}(OH)_4$]. *Sov. Phys. Crystallogr.* **20**, 563-566.

BROWN, G.E. & CLARK, J.R. (1978): Crystal structure of hydrochloroborite $Ca_2[B_2O_3(OH)_4$•$OB(OH)_3]Cl$•7$H_2O$, a seasonal evaporite mineral. *Am. Mineral.* **63**, 814-823.

BROWN, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II (M. O'Keeffe and A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).

BURNS, P.C. & HAWTHORNE, F.C. (1993a): Hydrogen bonding in colemanite: an X-ray and structure-energy study. *Can. Mineral.* **31**, 297-304.

________ & ________ (1993b): Hydrogen bonding in meyerhofferite: an X-ray and structure energy study. *Can. Mineral.* **31**, 305-312.

________ & ________ (1994a): Hydrogen bonding in tunellite. *Can. Mineral.* **32**, 895-902.

________ & ________ (1994b): Structure and hydrogen bonding in preobrazhenskite, a complex heteropolyhedral borate. *Can. Mineral.* **32**, 387-396.

________ & ________ (1994c): Structure and hydrogen bonding in inderborite, a heteropolyhedral sheet structure. *Can. Mineral.* **32**, 533-539.

________ & ________ (1994d): Refinement of the structure of hilgardite-1A. *Acta Crystallogr.* **C50**, 653-655.

________ & ________ (1994e): Kaliborite: an example of a crystallographically symmetrical hydrogen bond. *Can. Mineral.* **32**, 885-894.

________, GRICE, J.D. & HAWTHORNE, F.C. (1995): Borate minerals. I. Polyhedral clusters and fundamental building blocks. *Can. Mineral.* **33**, 1131-1151.

CANNILLO, E., DAL NEGRO, A. & UNGARETTI, L. (1973): The crystal structure of ezcurrite. *Am. Mineral.* **58**, 110-115.

CHRIST, C.L., TRUESDELL, A.H. & ERD, R.C. (1967): Borate mineral assemblages in the system $Na_2O$–$CaO$–$MgO$–$B_2O_3$–$H_2O$. *Geochim. Cosmochim. Acta* **31**, 313-337.

CLARK, J.R., APPLEMAN, D.E. & CHRIST, C.L. (1964): Crystal chemistry and structure refinement of five hydrated calcium borates. *J. Inorg. Nucl. Chem.* **26**, 73-95.

________ & CHRIST, C.L. (1971): Veatchite: crystal structure and correlations with p-veatchite. *Am. Mineral.* **56**, 1934-1954.

COOPER, W.F., LARSEN, F.K., GIESE, R.F. & COPPENS, P. (1973): Electron population analysis of accurate diffraction data. V. Structure and one-center charge refinement of the light-atom mineral kernite, $Na_2B_4O_6(OH)_2 \cdot 3H_2O$. *Am. Mineral.* **58**, 21-31.

CORAZZA, E. (1974): The crystal structure of kurnakovite: a refinement. *Acta Crystallogr.* **B30**, 2194-2199.

________ (1976): Inderite: crystal structure refinement and relationship with kurnakovite. *Acta Crystallogr.* **B32**, 1329-1333.

________, MENCHETTI, S. & SABELLI, C. (1974): The crystal structure of biringuccite, $Na_4[B_{10}O_{16}(OH)_2] \cdot 2H_2O$. *Am. Mineral.* **59**, 1005-1015.

________, ________ & ________ (1975): The crystal structure of nasinite, $Na_2[B_5O_8(OH)] \cdot 2H_2O$. *Acta Crystallogr.* **B31**, 2405-2410.

DAL NEGRO, A., MARTIN POZAS, J.M. & UNGARETTI, L. (1975): The crystal structure of ameghinite. *Am. Mineral.* **60**, 879-883.

________, SABELLI, C. & UNGARETTI, L. (1969): The crystal structure of mcallisterite, $Mg_2[B_6O_7(OH)_6]_2 \cdot 9H_2O$. *Accad. Nazionale dei Lincei, Rend. Classe. Sci. Fis. Mat. Nat.* **XLVII**, 353-364.

________, UNGARETTI, L. & SABELLI, C. (1973): The crystal structure of rivadavite. *Naturwiss.* **60**, 350.

________, ________ & ________ (1971): The crystal structure of aksaite. *Am. Mineral.* **56**, 1553-1566.

DINGWELL, D.B., PICHAVANT, M. & HOLTZ, F. (1996): Experimental studies of boron in granitic melts. *In* Boron: Mineralogy, Petrology and Geochemistry (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 331-385.

DISTANOV, E. & KOPEYKIN, G.A. (1990): Calculation of the thermodynamic properties of borates from solubility data. *Dokl. Acad. Sci. USSR* **312**, 250-253.

EFFENBERGER, H. (1982): Verfeinerung der Kristallstruktur von synthetischem Teepleit. *Acta Crystallogr.* **B38**, 82-85.

________ & ZEMANN, J. (1986): The detailed crystal structure of nordenskiöldine, $CaSn(BO_3)_2$. *Neues Jahrb. Mineral., Monatsh.*, 111-114.

EGOROV-TISMENKO, Y.K., SIMONOV, M.A. & BELOV, N.V. (1980): Crystal structures of calciborite $Ca_2[BO_3BO]_2$ and synthetic calcium boraluminate $2CaAl[BO_3] = Ca_2[AlO_3BO]_2$. *Sov. Phys. Dokl.* **25**, 226-227.

EPPRECHT, W.T. (1959): Über Wiserit, Sussexit und ein weiteres Mineral aus den Manganerzen vom Gonzen (bei Sargans). *Schweiz. Mineral. Petrogr. Mitt.* **39**, 85–104.

ERD, R.C., MCALLISTER, J.F. & ALMOND, H. (1959): Gowerite, a new hydrous calcium borate from the Death valley region, California. *Am. Mineral.* **44**, 911-919.

FANG, J.H. & NEWNHAM, R.E. (1965): The crystal structure of sinhalite. *Mineral. Mag.* **35**, 196-199.

GHOSE, S. & WAN, CH'ENG (1977): Aristarainite: $Na_2Mg[B_6O_8(OH)_4]_2 \cdot 4H_2O$: a sheet structure with chains of hexaborate polyanions. *Am. Mineral.* **62**, 979-989.

________, ________ & CLARK, J.R. (1978): Ulexite, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$: structure refinement, polyanion configuration, hydrogen bonding, and fiber optics. *Am. Mineral.* **63**, 160-171.

Grew, E.S. (1996): Borosilicates (exclusive of tourmaline) and boron in rock-forming minerals in metamorphic environments. *In* Boron: Mineralogy, Petrology and Geochemistry (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 387-502.

Grice, J.D., Burns, P.C. & Hawthorne, F.C. (1994): Determination of the megastructures of the borate polymorphs pringleite and ruitenbergite. *Can. Mineral.* **32**, 1-14.

________, ________ & ________ (1999): Borate minerals. II. A hierarchy of structures based upon the borate fundamental building block. *Can. Mineral.* **37**, 731-762.

________, Gault, R.A. & van Velthuizen, J. (1996): Penobsquisite: a new borate mineral with a complex framework structure. *Can. Mineral.* **34**, 657-665.

________, ________ & ________ (1997): Brianroulstonite: a new borate mineral with a sheet structure. *Can. Mineral.* **35**, 751-758.

Guo, Guo-Cong, Cheng, Wen-Den, Chen, Jin-Tong, Zhuang, Hong-Hui, Huang, Jin-Shun & Zhang, Qian-Er (1995): Monoclinic $Mg_2B_2O_5$. *Acta Crystallogr.* **C51**, 2469-2471.

Hanshaw, B.B. (1963): Preliminary relations in the system in the system $Na_2B_4O_7$–$Ca_2B_6O_{11}$–$H_2O$. *In* Geological Survey Research 1963. *U.S. Geol. Prof., Pap.* **475-B**, 24-27.

Hawthorne, F.C. (1983): Graphical enumeration of polyhedral clusters. *Acta Crystallogr.* **A39**, 724-736.

________ (1985): Towards a structural classification of minerals: the $^{vi}M^{iv}T_2Ø_n$ minerals. *Am. Mineral.* **70**, 455-473.

________ (1986): Structural hierarchy in $^{VI}M_x{}^{III}T_y\phi_z$ minerals. *Can. Mineral.* **24**, 625-642.

________ (1990): Structural hierarchy in $M^{[6]}T^{[4]}Ø_n$ minerals. *Z. Kristallogr.* **192**, 1-52.

________ (1992): The role of OH and $H_2O$ in oxide and oxysalt crystals. *Z. Kristallogr.* **201**, 183-206.

________ (1994): Structural aspects of oxide and oxysalt crystals. *Acta Crystallogr.* **B50**, 481-510.

________ (1997): Structural aspects of oxide and oxysalt minerals. *In* Modular Aspects of Minerals (S. Merlino, ed.). *Eur. Mineral. Union, Notes in Mineralogy* **1**, 373-429.

________, Burns, P.C. & Grice, J.D. (1996): The crystal chemistry of boron. *In* Boron: Mineralogy, Petrology and Geochemistry (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 41-115.

Ingri, N. (1963): Equilibrium studies of polyanions containing $B^{III}$, $Si^{IV}$, $Ge^{IV}$ and $V^{V}$. *Svensk Kem. Tidskr.* **75**, 3-34.

Janda, R. & Heller, G. (1979a): Ramanspektroskopische Untersuchungen an festen und in Wasser gelösten Polyboraten. *Z. Naturforsch.* **34b**, 585-590.

________ & ________ (1979b): B–NMR-spektroskopische Untersuchungen an wäßrigen Polyboratlösungen. *Z. Naturforsch.* **34b**, 1078-1083.

Kazanskaya, E.V., Chemodina, T.N., Egorov-Tismenko, Yu.K., Simonov, M.A. & Belov, N.V. (1977): Refined crystal structure of pentahydroborite $Ca[B_2O(OH)_6]•2H_2O$. *Sov. Phys. Crystallogr.* **22**, 35-36.

Konnert, J.A., Clark, J.R. & Christ, C.L. (1970a): Crystal structure of fabianite, $CaB_3O_5(OH)$, and a comparison with the structure of its synthetic dimorph. *Z. Kristallogr.* **132,** 241-254.

________, ________ & ________ (1970b): Crystal structure of strontioginorite, $(Sr,Ca)_2B_{14}O_{20}(OH)_6•5H_2O$. *Am. Mineral.* **55**, 1911-1931.

________, ________ & ________ (1972): Gowerite, $CaB_5O_8(OH)•B(OH)_3•3H_2O$: crystal structure and comparison with related borates. *Am. Mineral.* **57**, 381-396.

Krogh-Moe, J. (1962): The crystal structure of lithium diborate, $Li_2O•2B_2O_3$. *Acta Crystallogr.* **15**, 190-193.

________ (1967): A note on the structure of pinnoite. *Acta Crystallogr.* **23**, 500-501.

Levy, A.H. & Lisensky, G.C. (1978): Crystal structures of sodium sulfate decahydrate (Glauber's salt) and sodium tetraborate decahydrate (borax). Redetermination by neutron diffraction. *Acta Crystallogr.* **B34**, 3502-3510.

Li, J. , Li, B. & Gao, S. (2000): Calculation of thermodynamic properties of hydrated borates by group contribution method. *Phys. Chem. Minerals* **27**, 342-346.

Li, Yaping & Burns, P.C. (2000): Refinement of the structure of bandylite. *Can. Mineral.* **38**, 713-715.

London, D., Morgan, G.B., VI & Wolf, M.B. (1996): Boron in granitic rocks and their contact aureoles. *In* Boron: Mineralogy, Petrology and Geochemistry (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 299-330.

Malinko, S.V., Shashkin, D.P.& Yurkina, K.V. (1976): Fedorovskite, a new boron mineral, and the isomorphous series roweite–fedorovskite. *Zap. Vses. Mineral. Obshchest.* **105**, 71-85 (in Russ.).

Maya, L. (1976): Identification of polyborate and fluoropolyborate ions in solution by Raman spectroscopy. *Inorg. Chem.* **15**, 2179-2184.

McAllister, J.F. (1958): Borate minerals from weathering of late Tertiary borates in the Furnace Creek District, Death Valley, California. *Geol. Soc. Am., Bull.* **69**, 1695 (abstr.).

Menchetti, S., Sabelli, C. & Trosti-Ferroni, R. (1982): Probertite $CaNa[B_5O_7(OH)_4]•3H_2O$: a refinement. *Acta Crystallogr*. **B38**, 3072-3075.

Merlino, S. & Sartori, F. (1969): The crystal structure of larderellite, $NH_4B_5O_7(OH)_2•H_2O$. *Acta Crystallogr*. **B25**, 2264-2270.

________ & ________ (1971): Ammonioborite: new borate polyion and its structure. *Science* **171**, 377-379.

________ & ________ (1972): The crystal structure of sborgite, $NaB_5O_6(OH)_4•3H_2O$. *Acta Crystallogr*. **B28**, 3559-3567.

Moore, P.B. & Araki, T. (1972): Johachidolite, $CaAl[B_3O_7]$, a borate with very dense atomic structure. *Nature Phys. Sci*. **240**, 63-65.

________ & ________ (1974): Roweite, $Ca_2Mn^{2+}{}_2(OH)[B_4O_7(OH)_2]$: its atomic arrangement. *Am. Mineral.* **59**, 60-65.

Müller, D., Grimmer, A.-R., Timper, U., Heller, G. & Shakaibaie-Moghadam, M. (1993): $^{11}$B-MAS–NMR-Untersuchungen zur Anionenestruktur von Boraten. *Z. anorg. allg. Chem*. **619**, 1262-1268.

Powell, D.R., Gaines, D.F., Zerella, P.J. & Smith, R.A. (1991): Refinement of the structure of tincalconite. *Acta Crystallogr*. **C47**, 2279-2282.

Sabelli, C. & Stoppiani, A. (1978): Refinement of the structure of hydroboracite. *Can. Mineral.* **16**, 75-80.

Salentine, C.G. (1983): High-field $^{11}$B NMR of alkali borates. Aqueous polyborate equilibria. *Inorg. Chem*. **22**, 3920-3924.

Schindler, M. & Hawthorne, F.C. (1998): The crystal structure of trembathite $(Mg_{1.55}Fe_{1.43}Mn_{0.02})B_7O_{13}Cl$, a mineral of the boracite group: an example of the insertion of a cluster into a three-dimensional net. *Can. Mineral*. **36**, 1195-1201.

________ & ________ (2001a): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. I. Theory. *Can. Mineral.* **39**,

________ & ________ (2001b): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. II. Crystal structure and chemical composition of borate minerals. *Can. Mineral.* **39**,

Shashkin, D.P., Simonov, M.A. & Belov, N.V. (1968): Crystalline structure of the recently discovered natural borate vimsite $Ca[B_2O_2(OH)_4]$. *Sov. Phys. Dokl*. **13**, 974-977.

Simonov, M.A., Egorov-Tismenko, Yu.K., Kazanskaya, E.V., Belokoneva, E.I. & Belov, N.V. (1978): Hydrogen bonds in the crystal structure of nifontovite $Ca_2[B_5O_3(OH)_6]_2•2H_2O$. *Sov. Phys. Dokl*. **23**, 159-161.

________, Kazanskaya, E.V., Egorov-Tismenko, Yu.K., Zhelezin, E.P. & Belov, N.V. (1976a): Refinement of the crystal structure of frolovite $Ca[B(OH)_4]_2$. *Sov. Phys. Dokl*. **21**, 471-473.

________, Yamanova, N.A., Kazanskaya, E.V., Egorov-Tismenko, Yu.K. & Belov, N.V. (1976b): Crystal structure of a new natural calcium borate, hexahydroborite $CaB_2O_4•6H_2O \equiv Ca[B(OH)]_2•2H_2O$. *Sov. Phys. Dokl*. **21**, 314-316.

Smith, G.I. & Medrano, M.D. (1996): Continental borate deposits of Cenozoic age. *In* Boron: Mineralogy, Petrology and Geochemistry (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 263-298.

Takéuchi, Y. & Kudoh, Y. (1975): Szaibelyite, $Mg_2(OH)[B_2O_4(OH)]$: crystal structure, pseudosymmetry, and polymorphism. *Am. Mineral.* **60**, 273-279.

Walenta, K. (1979): Admontite, a new borate mineral from the gypsum deposit Schildmauer near Admont in Styria (Austria). *Tschermaks Mineral. Petrogr. Mitt*. **26**, 69-77.

Wan, Ch'eng & Ghose, S. (1977): Hungchaoite, $Mg(H_2O)_5B_4O_5(OH)_4•2H_2O$: a hydrogen-bonded molecular complex. *Am. Mineral*. **62**, 1135-1143.

Yakubovich, O.V., Yamnova, N.A., Shchedrin, B.M., Simonov, M.A. & Belov, N.V. (1976): The crystal structure of magnesium kurchatovite, $CaMg[B_2O_5]$. *Sov. Phys. Dokl.* **21**, 294-296.

Yamanova, N.A., Simonov, M.A. & Belov, N.V. (1977): Refined crystal structure of solongoite $Ca_2[B_3O_4(OH)_4]Cl$. *Sov. Phys. Crystallogr.* **22**, 356-359.

Zachariasen, W.H. (1954): The precise structure of orthoboric acid. *Acta Crystallogr.* **7**, 305-310.

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