RiM Volume 33

BORON: Mineralogy, Petrology and Geochemistry

E.S. Grew & L.M. Anovitz, *Editors*

Copyright 1996

Revisions and Additions to the Second Printing, Copyright 2002

Note: The Second Printing (2002) contained numerous corrections and additions to the original (1996) text. Unfortunately, changes to several chapters were inadvertently misplaced and thus were not included in this printing. They are detailed below: new words or symbols are underlined, where useful. The first number is the page number, the symbol ¶ *n* indicates a correction in the *n*th paragraph, counting the initial partial paragraph as *n* = 1; * or 'last' indicates the line number, where needed.

* * *

Chapter 1: *Mineralogy, Petrology and Geochemistry of Boron: An Introduction*

L. M. Anovitz & E. S. Grew

7, Behierite Add series with schiavinatoite (p. 28) to column headed *Mineral group*.

16, Ludwigite Add references: Alexandrov and Troneva (2000), Appel and Brigatti (1999), Marincea (1999, 2000)

17, Magnesiohulsite No hyphen. Add reference: Rudnev (1996)

26, Vistepite Add "cf. bustamite" to column headed *Mineral group*

26, Uvite . The correct locality is East Hampton, CT (Connecticut, USA)

Addendum at Second Printing: New Minerals Since 1996

28 Note at bottom of table. Line 2: The correct formulae are:

IMA No. 2001-051 – $Ca_{16}(Mg,Li,\square)_2[B_{13}O_{17}(OH)_{12}]_4Cl_6\cdot 28H_2O$;
IMA No. 2001-059 – $(Na,\square,Ca)_{11}Ca_4(Si,S,B)_{14}B_2O_{40}F_2\cdot 4H_2O$ (reyerite group)

Two new borates have been discovered: an Al-dominant end member of the hulsite group and a silico-borate with an end-member formula Mg_2BO_3F and intermediate silicatian compositions such as $Mg_2(BO_3)_{0.8}(SiO_4)_{0.2}(F,OH)_{0.8}$, both from a granosyenite contact in the Verkhoyansk Region, eastern Siberia, Russia (Schreyer et al., 2002).

Schreyer W, Pertsev NN, Armbruster T, Bernhardt H-J, Medenbach O (2002) Two potentially new borate minerals in a kotoite-bearing marble from Eastern Siberia. 18th Gen Meeting Intl Mineral Assoc, Mineralogy for the New Millennium, Programme with Abstracts, p 205

* * *

Chapter 3: *Experimental Studies on Borosilicates and Selected Borates*

G. Werding & W. Schreyer

119 ¶ 5 A more detailed discussion is given by Schreyer and Werding (1997)…

120	¶ 2 *6	For mere synthesis runs…
120	¶ 5 *8	… mineral melanophlogite. It is likely…
121	Fig. 1 *5	… form at least two polymorphs.
122	¶ 1 *4	… Schreyer and Werding (1997)
122	¶ 2	…$\mathrm{Rd}_{\underline{9}7}\mathrm{Ab}_{3}$ and $\mathrm{Ab}_{\underline{9}0}\mathrm{Rd}_{10}$.
122	¶ 3	…(Ufer 1996; Ufer and Schreyer 1996).
124	¶ 1 last	See also Pöter and Schreyer (1998).
124	¶ 2 *12	… by Schreyer and Werding (1997).
125	¶ 2 last	… and Schreyer (1998).
125	Fig. 4 last	ditto
126	Fig. 5 *4	ditto
126	¶ 2 *6,*15, last	ditto
127	Fig. 6 *6	… (1992). 3:1:4 represents…
128	¶ 4 *3	… $\mathrm{Si}_{2.91}\mathrm{O}_{13.\underline{9}4}$
129	¶ 4 last	… at $P \geq 20$ kbar.
130	¶ 1 *3	$P \leq 20$ kbar.
132	¶ 1 *5	… angles 2θ_…
132	¶ 1 last	… Mg. For updating see Wodara and Schreyer (2001).
132	¶ 2 last	… chemistry. See also Schreyer et al. (2002).
132	¶ 3 *2	(§3.4) are…
132	Fig. 9 last	… in the order $\mathrm{MgO:Al_2O_3:B_2O_3}$.
137	¶ 1 *5	A paper … “pseudosinhalite” was published by Daniels et al. (1997).
138	¶ 1 last	…14. For pseudosinhalite as a new mineral, see Schreyer et al. (1998).
139	¶ 5 *5,*7	*Remove “ ” from pseudosinhalite.*
141	¶ 1 *1	*delete* =
143	Fig. 20	En = enstatite
143	¶ 3 *11	… structure (Klaska and Grew, 1991).
148	¶ 4 *7	*Add* □ *before formula:* □[Fe_2 …]
149	¶ 2 last	… yet. For magnesiofoitite as a mineral, see Hawthorne et al. (1999).
153	¶ 3 *4	… Al and Li (1.5 atoms each).
153	¶ 4 *8	$\mathrm{Na}_{1-x}\mathrm{Al}_{3}\mathrm{Al}_{\underline{6}}\mathrm{B}_{3}$…
154	¶ 1 last	For updating, see Schreyer et al. (2000, 2002).
154	¶ 5 *3	Ca_{2}…$\mathrm{Si}_{3}\mathrm{O}_{2\underline{0}}$
156	¶ 1 *4	In a study at Bochum by Jung (1996), stoichiometric…

156	¶ 1 *7	… phase. Jung (1996) has…
156	¶ 2 last	See an update on boromuscovite by Jung and Schreyer (2002).
157	¶ 3 *10	… that $KBSi_3O_8$, crystallized…
157	¶ 3 *15	… was synthesized at … (Ufer and Schreyer, 1996;
157	¶ 3 *16	The phase $Na_2O{\cdot}B_2O_3{\cdot}2SiO_2$ prepared…
159	¶ 2 *4	Schreyer and Werding (1997) for the
159	¶ 3 *4	… paper, Schreyer and Werding (1997)

References corrected:

Schreyer W, Werding G (1997) High-pressure behaviour of selected boron minerals and the question of boron distribution between fluids and rocks. Lithos 41:251-266

Stachowiak A, Schreyer W (1998) Synthesis, stability and breakdown products of the hydroxyl endmember of jeremejevite in the system Al_2O_3-B_2O_3-H_2O. Eur J Mineral 10:875-888

ADDENDUM AT SECOND PRINTING (2002) *[TO PAGE 163]*

§ 3.4. Phase relations in the limiting system MgO-B_2O_3-H_2O were reported by Pöter and Schreyer (1998).

§ 3.6.1. Pöter et al. (1998) recognized that certain orthorhombic “boron-mullites“ are followed, in longer experiments at 0.1-1.0 GPa, by a monoclinic phase with properties identical to that of the new natural mineral boralsilite (Grew et al., Am. Mineral. 1998).

§ 3.6.3. Much progress has been made in synthesizing and defining the composition of “alkali-free Al-tourmaline,” which carries excess boron in the tetrahedral ring site (Wodara and Schreyer, 2001).

§ 3.7.3. After the discovery of “pseudosinhalite” as a mineral in nature replacing sinhalite (Schreyer et al., 1998), it became clear that pseudosinhalite is a structural isotype of chondrodite (Strunz and Nickel, 2000). Daniels and Schreyer (2001) pointed out, however, that there are no other synthetic boron analogues of humite-group minerals.

§ 3.9.4. Regarding the tourmaline end-member olenite, $NaAl_3Al_6[Si_6O_{18}]$-$(BO_3)_3O_3(OH)$ (Hawthorne and Henry, 1999), important new insights were obtained which may require considerable revisions in the crystal chemistry of the whole tourmaline group. Synthetic olenites may contain excess boron replacing Si up to at least 2.0 per formula unit, following mainly the substitution B+H for Si (Schreyer et al., 2000; Marler et al., 2002); thus, in contrast to the ideal formula, they show almost no hydrogen deficiency. Moreover, they may have octahedral vacancies. The excess amounts of boron seem to rise with increasing pressure and decreasing temperature. Natural olenites with similar properties are described by Ertl et al. (1997), Kalt et al. (2001), and Schreyer et al. (2002).

§ 3.9.5. Details on the synthesis of pure end-member boromuscovite and its properties were reported by Schreyer and Jung (1997) and Jung and Schreyer (2002). Boron fractionation between muscovite and tourmaline was discussed by Schreyer (2000).

MORE RECENT REFERENCES

Daniels P, Krosse S, Werding G, Schreyer,W (1997) “Pseudosinhalite“, a new hydrous MgAl- borate: synthesis, phase characterization, crystal structure, and PT-stability. Contrib Mineral Petrol 128: 261-271

Daniels P, Schreyer W (2001) Comments on: Strunz and Nickel: “Pseudosinhalite is a structural isotype of chondrodite“ Am Mineral 86: 583-584

Ertl A, Pertlik F, Bernhardt H-J (1997) Investigations on olenite with excess boron from the Koralpe, Styria. Österreichische Akad Wissenschaften, Math-Naturwiss Klasse, Abt I, Anzeiger 134:3-10

Hawthorne FC, Henry DJ (1999) Classification of the minerals of the tourmaline group. Eur J Mineral 11: 201-215

Hawthorne FC, Selway JB, Kato A, Matsubara S, Shimizu M, Grice JD, Vaifak J (1999) Magnesiofoitite, _$(Mg_2Al)Al_6(Si_6O_{18})(BO_3)_3(OH)_4$, a new alkali-deficient tourmaline. Can Mineral 37:1439-1443

Jung I (1996) Experimentelle Studien über borhaltige Glimmer im System K_2O-MgO-Al_2O_3-SiO_2-B_2O_3-H_2O. Unpublished Diplom Arbeit, Ruhr-Universität Bochum 101 p

Jung I, Schreyer W (2002) Synthesis, properties and stability of end-member boromuscovite, $KAl_2[BSi_3O_{10}](OH)_2$. Contrib Mineral Petrol 143:684-693; 144:507

Kalt A, Schreyer W, Ludwig T, Prowatke S, Bernhardt H-J, Ertl A (2001) Complete solid solution between magnesian schorl and lithian excess-boron olenite in a pegmatite from the Koralpe (eastern Alps, Austria) Eur J Mineral 13:1191-1205

Marler B, Borowski M, Wodara U, Schreyer W (2002) Synthetic tourmaline (olenite) with excess boron replacing silicon in the tetrahedral site: II. Structure analysis. Eur J Mineral 14:763-771

Pöter B, Schreyer W (1998) Synthesis experiments in the system MgO-B_2O_3-H_2O and the resulting phase relations. Abstr Suppl 1 Terra Nova 10:50

Pöter, B, Werding G, Schreyer W, Bernhardt H-J (1998) Synthesis and properties of the new borosilicate mineral boralsilite. Berichte Deutschen Mineral Gesell, Beiheft z Eur J Mineral 10,1:220

Schreyer W. (2000) Is the partitioning of boron between tourmaline and muscovite dependent on the crystallization conditions? J Czech Geol Soc 45:13-20

Schreyer W, Jung I (1997) Boromuscovite, $KAl_2[AlSi_3O_{10}](OH)_2$: A high-pressure mineral. Abstr Suppl 1 Terra Nova 9:32-33

Schreyer W, Pertsev NN, Medenbach O, Burchard M, Dettmar D (1998) Pseudosinhalite: discovery of the hydrous MgAl-borate as a new mineral in the Tayozhnoye, Siberia, skarn deposit. Contrib Mineral Petrol 133:382-388

Schreyer W, Wodara U, Marler B, van Aken PA, Seifert F, Robert J-L (2000) Synthetic tourmaline (olenite) with excess boron replacing silicon in the tetrahedral site: I. Synthesis conditions, chemical and spectroscopic evidence. Eur J Mineral 12:529-541

Schreyer W, Hughes J, Bernhardt H-J, Kalt A, Prowatke S, Ertl A. (2002) Reexamination of olenite from the type locality: detection of boron in tetrahedral coordination. Eur J Mineral 14:935-942

Strunz H, Nickel E (2000) Pseudosinhalite is a structural isotype of chondrodite. Am Mineral 85: 1828-1829

Ufer M (1996) Synthese und Stabilität von Reedmergnerit im System Na_2O-B_2O_3-SiO_2-H_2O. Unpublished Diploma Thesis, Ruhr-Universität Bochum, 81 p

Ufer M, Schreyer W (1996) Synthese und Hochdruckstabilität des ‘Bor-Albits’ Reedmergnerit. Berichte Deutschen Mineral Gesell, Beiheft z Eur J Mineral 8,1:292

Wodara U, Schreyer W (2001) X-site vacant Al-tourmaline: A new synthetic end-member. Eur J Mineral 13:521-532

* * *

Chapter 5: *Thermodynamics of Boron Minerals: Summary of Structural, Volumetric and Thermochemical Data*

L. M. Anovitz & B. S. Hemingway

184 ¶ 1 *5 The symbol for vacancy, □, in mineral formula should replace “G”

227 Table 1, Holtite ditto

230 Table 1, Prismatine ditto

223 Table 1, Bakerite correct formula: $Ca_4B_4(BO_4)(SiO_4)_3(OH)_3\cdot H_2O$(?)

227 Table 1, Hulsite correct formula: $(Fe^{2+},Mg)_2(Fe^{3+},Fe^{2+},Sn^{4+})BO_5$

Chapter 9: *Borosilicates (exclusive of tourmaline) and Boron in Rock-forming Minerals in Metamorphic Environments*

E. S. Grew

Throughout in text, tables and references, the symbol for vacancy, □, in mineral formulae has with rare exception been replaced by "G".

388 Table 1, bottom Vistepite Triclinic $SnMn_4B_2Si_4O_{16}(OH)_2$

390 Table2, *2 Add to boralsilite: Dispersion r>v, weak; twinning

392 ¶ 3 *4 … dumortierite: 1.03 wt % Sb_2O_3 and 3.58 wt % As as As_2O_3 or 0.22 As pfu (Voloshin et al., 1987; Groat et al., 2001)

402 Table 6, *9 Add boralsilite to *Major associated minerals* at Almgjotheii, Norway

443 Table 13, last entry Moose River, NY: add Tur to *Associated minerals*

459 ¶ 1 *1 Vistepite, $SnMn_4B_2Si_4O_{16}(OH)_2$, forms…

* * *

Chapter 10: *Metamorphic Tourmaline and its Petrologic Applications*

Darrell J. Henry & Barbara Dutrow

ADDENDUM AT SECOND PRINTING [*TO PAGE 558*]

NEW REFERENCES FOR METAMORPHIC TOURMALINE AND TOURMALINE CRYSTAL STRUCTURE

Bloodaxe ES, Hughes JM, Dyar MD, Grew ES, Guidotti CV (1999) Linking structure and chemistry in the schorl-dravite series. Am Mineral 84:922-928

Brocker M, Franz L (2000) The contact aureole on Tinos (Cyclades, Greece): tourmaline-biotite geothermometry and Rb-Sr geochronology. Mineral Petrol 70:257-283

Dutrow B, Henry DJ (2000) Complexly zoned fibrous tourmaline: A record of evolving magmatic and hydrothermal fluids. Can Mineral 38:131-143

Dutrow BL, Foster CT, Henry DJ (1999) Tourmaline-rich pseudomorphs in sillimanite zone metapelites: Demarcation of an infiltration front. Am Mineral 84:794-805

Dyar MD, Guidotti CV, Core DP, Wearn KM, Wise MA, Francis CA, Johnson K, Brady JB, Robertson JD, Cross LR (1999) Stable isotope and crystal chemistry of tourmaline across pegmatite-country rocks boundaries at Black Mountain and Mount Mica, southwestern Maine, USA. Eur J Mineral 11:281-294

Hawthorne FJ, Henry DJ (1999) Classification of the minerals of the tourmaline group. Eur J Mineral 11:201-216.

Henry DJ, Dutrow BL (2001) Compositional zoning and element partitioning in nickeloan tourmaline from a metamorphosed karstbauxite from Samos, Greece. Am Mineral 86:1130-1142

Henry DJ, Kirkland BL, Kirkland DW (1999) Sector-zoned tourmaline from the cap rock of a salt dome. Eur J Mineral 11:263-280

Hughes JM, Ertl A, Dyar MD, Grew ES, Shearer CK, Yates MG, Guidotti CV (2000) Tetrahedrally coordinated boron in a tourmaline: boron-rich olenite from Stoffhutte, Koralpe, Austria. Can Mineral 38:861-869

Hughes KA, Hughes JM, Dyar MD (2001) Chemical and structural evidence for $^{[4]}$B – $^{[4]}$Si substitution in natural tourmaline. Eur J Mineral: 13:743-748.

Jiang S (1998) Stable and radiogenic isotope studies of tourmaline: Overview. J Czech Geol Soc 43:75-90

Jiang S, Palmer MR, Peng Q, Yang J (1997) Chemical and stable isotope compositions of Proterozoic metamorphosed evaporites and associated tourmalines from the Houxianyu borate deposit, eastern Liaoning, China. Chem Geol 135:189-211

Jiang SY, Han F, Shen J, Palmer MR (1999) Chemical and Rb-Sr, Sm-Nd isotopic systematics of tourmaline from the Dachang Sn-polymetallic ore deposit, Guangxi Province, P.R. China. Chem Geol 157:49-67

Kawakami T (2001) Tourmaline breakdown in the migmatite zone of the Ryoke metamorphic belt, Japan. J Met Geol 19:61-75

Kawakami T (2001) Boron depletion controlled by the breakdown of tourmaline in the migmatite zone of the Aoyama area, Ryoke Metamorphic Belt, southwestern Japan. Can Mineral 39:1529-1546

Losos Z, Selway JB (1998) Tourmaline of dravite-uvite series graphitic rocks of the Velke Vrbno Group (Silesicum, Czech Republic). J Czech Geol Soc 43:45-52

Michailidis K, Kassoli-Fournaraki A, Dietrich RV (1996) Origin of zoned tourmalines in graphite-rich metasedimentary rocks from Macedonia, northern Greece. Eur J Mineral 8:393-404

Novák M (1998) Blue dravite as an indicator of fluid composition during subsolidus replacement processes in Li-poor granitic pegmatites in the Moldanubicum, Czech Republic. J Czech Geol Soc 43:24-30

Novák M, Selway JB, Houzar, S. (1998) Potassium-bearing, fluorine-rich tourmaline from metamorphosed fluorite layer in leucocratic orthogneiss at Nedvidice, Svratka Unit, western Moravia. J Czech Geol Soc 43:37-44

Pieczka A (2000) Modeling of some structural parameters of tourmalines on the basis of their chemical composition: 1. The ordered structural model. Eur J Mineral 12:589-596

Povondra P, Vrána S (1996) Tourmaline and associated minerals in alkali-feldspar orthogneiss near Hluboke nad Vltavou, southern Bohemia. J Czech Geol Soc 41:191-200

Sperlich R, Giere R, Frey M (1996) Evolution of compositional polarity and zoning in tourmaline during prograde metamorphism of sedimentary rocks in the Swiss Central Alps. Am Mineral 81:1223-1236

Tagg SL, Cho H, Dyar MD, Grew ES (1999) Tetrahedral boron in naturally-occurring tourmaline. Am Mineral 84:1451-1455

von Goerne G, Franz, G. (2000) Synthesis of Ca-tourmaline in the system $CaO-MgO-Al_2O_3-SiO_2-B_2O_3-H_2O-HCl$. Mineral Petrol 69:161-182

von Goerne G, Franz G, Robert J–L (1999) Upper thermal stability of tourmaline + quartz in the system $MgO-Al_2O_3-SiO_2-B_2O_3-H_2O$ and $Na_2O-MgO-Al_2O_3-SiO_2-B_2O_3-H_2O-HCl$ in hydrothermal solutions and siliceous melts. Can Mineral 37:1025-1040

von Goerne G, Franz G, Heinrich W (2001) Synthesis of tourmaline solid solutions in the system $Na_2O-MgO-Al_2O_3-SiO_2-B_2O_3-H_2O-HCl$ and the distribution of Na between tourmaline and fluid at 300 to 700°C and 200 MPa. Contrib Mineral Petrol 141:160-173

Zacek V, Petrov A, Hyrsl J (1998) Chemistry and origin of povondraite-bearing rocks from Alto Chapare, Cochabamba, Bolivia. J Czech Geol Soc 43:59-67

COMPREHENSIVE TOURMALINE BIBLIOGRAPHY

<http://geol.lsu.edu/henry/Research/tourmaline/bibliography/TurBibliography.htm>

This series of references related to tourmaline is meant to be a relatively comprehensive list that can be used by anyone interested in the subject. However, there are likely to be many more references of which I am currently unaware. I would welcome input from the users of the list either in terms of any additional references or corrections to the list. Any inquiries can be e-mailed to Darrell Henry at <dhenry@geol.lsu.edu>

The references are broadly broken into a series of general topics. There is a link to the appropriate webpage in each of these topics in the left-hand column. Many of the references could go into several categories. In most cases tourmaline is the main topic of the article, but in other cases information on tourmaline may play a very minor role in the article.

~~~~~~

Chapter 16: *Analysis of Geological Materials for Boron by Secondary Ion Mass Spectrometry*

Richard L. Hervig

Page 789 should be:
~~~~~~

Chapter 16

ANALYSES OF GEOLOGICAL MATERIALS FOR BORON BY SECONDARY ION MASS SPECTROMETRY

Richard L. Hervig

Center for Solid State Science and
Department of Geology
Arizona State University
Tempe, Arizona 85287 USA

INTRODUCTION

The purpose of this chapter is to describe the usefulness of the secondary ion mass spectrometer (SIMS, or ion microprobe) in quantitative determination of boron in minerals and glasses. SIMS has broad analytical uses in the earth sciences, and its use for the analysis of boron represents one of its earliest applications (e.g., Blanchard et al., 1972; Hinthorne and Ribbe, 1974; Steele et al., 1980; Jones and Smith, 1984). Below, we present a short description of the instrumentation, discuss some properties of boron secondary ions, and show how SIMS can generate quantitative microanalyses for B from several wt.% down to sub-ppm abundances. Being a mass spectrometric technique, SIMS allows the analyst an opportunity to obtain precise $^{11}B/^{10}B$ measurements on selected phases in polished thin sections. SIMS can also provide qualitative images of the microdistribution of boron in complex mineral assemblages.

ANALYTICAL TECHNIQUES

Instrumentation

Most SIMS analyses for B have come from three types of instruments. The ARL ion microprobe mass analyzer (IMMA), the AEI (Banner and Stimpson, 1975), and the Cameca 3f-6f series (Lepareur, 1980). Because very few AEI and ARL machines are still operative, I will describe only the design of the Cameca. Another commercially available SIMS is constructed by ANUTECH (known as the SHRIMP; Clement et al., 1977). The SHRIMP is best known for its application to microanalyses of zircon for dating purposes (e.g., Froude et al., 1983). These analyses are possible because of the very large radius magnet (~1 m) in the SHRIMP (compared to ~10x smaller in the Cameca 3f-6f instruments). The SHRIMP has also been successfully applied to S isotope work (Eldridge et al., 1989; McKibben and Eldridge, 1989) and can also be used for micro- and isotopic analyses for boron. Cameca also manufactures a SIMS with a magnet having a size similar to the SHRIMP. This model (the 1270) has only been commissioned in one lab as of 1995, and so will not be discussed, but experience with the 3f-6f series should be broadly applicable to this instrument, except that significant improvements in transmission of ions through the mass spectrometer at high mass resolving power is expected.

General description of analysis conditions

In the Cameca design (see Fig. 1), a beam of primary ions at an impact energy of ~3-20 keV is focused to a spot and directed at a sample. Each incoming ion leads to multiple collisions with the atoms in the near-surface environment (known as a collision cascade), and from 1 to ~12 atoms are ejected, or sputtered, from the top few monolayers of the

799 Fig. 7, add Image diameter = 60 microns.

ADDENDUM AT SECOND PRINTING (2002) [*TO PAGE 803*]

Since 1996, SIMS analyses for boron isotopes have expanded significantly: see Chaussidon et al. (1997) for a detailed description of the technique. They included a method for removing adsorbed boron (contamination). It can also be removed by soaking the bulk material or thin section in a solution of mannitol (Hingston, 1964). Compared to washing clay minerals (for example) in deionized water, soaking them in mannitol decreased the $\delta^{11}B$ value determined by SIMS by >10‰ (Williams, 2000; Williams and Hervig, 2002). This is the easiest way to remove adsorbed boron from samples prior to SIMS analysis, and mannitol can also be used to inhibit evaporative loss of boron from solutions (Xiao et al., 1997). SIMS analyses have recently been used to characterize the boron isotopic composition of many diverse samples such as Precambrian tourmalines, to estimate the $\delta^{11}B$ of ancient sea water (Chaussidon and Appel, 1997), trapped melt inclusions containing only ~1 ppm B (Rose et al., 2001), kerogen in drill cores from hydrocarbon-rich sedimentary basins (Williams et al., 2001c), subduction zone materials (Peacock and Hervig, 1999), tourmalines associated with ore deposits (Smith and Yardley, 1996), and chondrules in meteorites (Hoppe et al., 2001). The last study suggested a variation in $\delta^{11}B$ about one-half as large as determined earlier by Chaussidon and Robert (1995). Interpretation of these measured values (by SIMS or bulk techniques) requires knowledge of fractionation factors among minerals, melts, and fluids. The most recent measurements of these factors (mostly obtained through SIMS analyses on small volumes of experimental run products) are shown in Figure 8. These data include studies of illite-H_2O (Williams et al., 2001a) and silicate melt (rhyolitic and basaltic)-H_2O (Hervig et al., 2002). Measured fractionation factors are large, even at 1100°C. Hervig et al. (2002) suggested that this is a result of a change in coordination from trigonal (preferring ^{11}B) in hydrous fluids to tetrahedral (preferring ^{10}B) in silicate melts, micas, and clay minerals. Note that the coordination of boron in silicate melts is concentration-dependent (Yun and Bray, 1978); B likely enters into trigonal sites at concentrations >~1%. The curve in Figure 8 is different (larger isotopic fractionation) than earlier determinations of coordination-dependent boron isotopic fractionation of non-silicates (see Palmer and Swihart, this volume). The fractionation measured on silicates has been applied to problems in diagenesis, contact metamorphism, and petroleum recovery (Williams et al., 2001b,d).

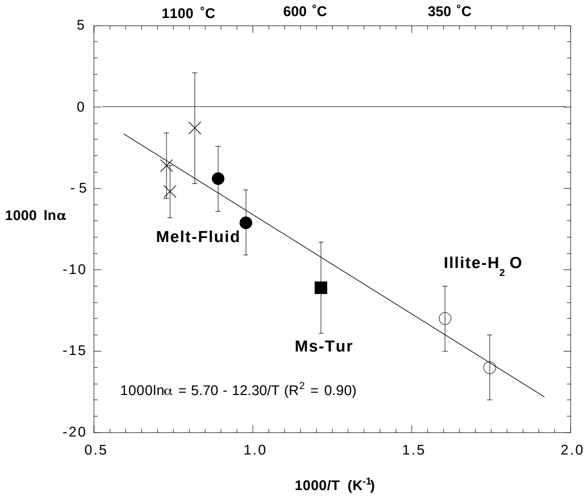
Figure 8 (next page). Reciprocal temperature vs. natural logarithm of the B isotopic fractionation factor between phases with B in tetrahedral coordination

basaltic melt ×
rhyolitic melt ●
muscovite ■
illite ○

and phases with B in trigonal coordination

H_2O fluid or tourmaline.

Results are from experiments except for the natural muscovite-tourmaline pair from a metamorphic rock with well-constrained peak metamorphic temperature. Line is least-squares regression. Error bars: 2σ. Redrawn from Hervig et al. (2002).



ADDENDUM REFERENCES

Chaussidon M, Appel PWU (1997) Boron isotopic composition of tourmalines from the 3.8 Ga-old Isua supracrustals, West Greenland: implications on the δ^{11}B value of early Archean seawater. Chem Geol 136:171-180

Chaussidon M, Robert F, Mangin D, Hanon P, Rose E (1997) Analytical procedures for the measurement of boron isotope compositions by ion microprobe in meteorites and mantle rocks. Geostandard Newslett 21:7-17

Hervig RL, Moore GM, Williams LB, Peacock SM, Holloway JR, Roggensack K (2002) Isotopic and elemental partitioning of boron between hydrous fluid and silicate melt. Am Mineral 87:769-774

Hingston FJ (1964) Reactions between boron and clays. Australian J Soil Res 2:83-95

Hoppe P, Goswami JN, Krähenbühl U, Marti K (2001) Boron in chondrules. Meteoritics Planet Sci 36:1331-1344

Peacock SM, Hervig RL (1999) Boron isotopic composition of subduction-zone metamorphic rocks. Chem Geol 160:281-290

Rose EF, Shimizu N, Layne GD, Grove TL (2001) Melt production beneath Mt. Shasta from boron data in primitive melt inclusions. Science 293:281-283

Smith MP, Yardley BWD (1996) The boron isotopic composition of tourmaline as a guide to fluid processes in the southwestern England orefield: An ion microprobe study. Geochim Cosmochim Acta 60:1415-1427

Williams LB. (2000) Boron isotope geochemistry during burial diagenesis. PhD dissertation, p 168, Dept Geology & Geophysics, University of Calgary, Calgary, Canada

Williams LB, Hervig RL (2002) Exploring intra-crystalline boron isotope variations in mixed-layered illite/smectite. Am Mineral (2002) 87 (in press)

Williams LB, Hervig RL, Holloway JR, Hutcheon I (2001a) Boron isotope geochemistry during diagenesis, Part I. Experimental determination of fractionation during illitization of smectite. Geochim Cosmochim Acta 65:1769-1782

Williams LB, Hervig RL, Hutcheon I (2001b) Boron isotope geochemistry during diagenesis, Part 2. Applications to organic-rich sediments. Geochim Cosmochim Acta 65:1783-1794

Williams LB, Hervig RL, Wieser ME, Hutcheon I (2001c) The influence of organic matter on the boron isotope geochemistry of the Gulf Coast Sedimentary Basin, USA. Chem Geol 174:445-461

Williams LB, Wieser ME, Fennell J, Hutcheon , Hervig RL (2001d) Application of boron isotopes to understanding fluid/rock interactions in a hydrothermally stimulated oil-reservoir in the Alberta Basin, Canada. Geofluids 1:229-240

Xiao YK, Vocke RD, Swihart GH, Xiao Y (1997) Boron volatilization and its isotope fractionation during evaporation of boron solution. Analyt Chem 69:5203-5207