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.


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)\(_{12}\)]\(_4\)Cl\(_6\); 28H\(_2\)O;
IMA No. 2001-059 – (Na,\(\square\),Ca)\(_{11}\)Ca\(_4\)(Si,S,B)\(_{14}\)B\(_2\)O\(_{40}\)F\(_2\)·4H\(_2\)O (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\(_2\)BO\(_3\)F 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).


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)…
For mere synthesis runs…

… mineral melanophlogite. It is likely…

… form at least two polymorphs.

… Schreyer and Werding (1997)

…Rd97Ab3 and Ab90Rd10.


See also Pöter and Schreyer (1998).

… by Schreyer and Werding (1997).


ditto
ditto
ditto


… Si2.91O13.94

… at P \geq 20 kbar.

P \leq 20 kbar.

… angles 20…

… Mg. For updating see Wodara and Schreyer (2001).

… chemistry. See also Schreyer et al. (2002).

… in the order MgO:Al2O3:B2O3.

A paper … “pseudosinhalite” was published by Daniels et al. (1997).

…14. For pseudosinhalite as a new mineral, see Schreyer et al. (1998).

Remove “” from pseudosinhalite.

delete =

En = enstatite

… structure (Klaska and Grew, 1991).

Add \square before formula: \square[Fe2 … ]

… yet. For magnesiofoitite as a mineral, see Hawthorne et al. (1999).

… Al and Li (1.5 atoms each).

Na1.4Al3Al6B3…

For updating, see Schreyer et al. (2000, 2002).

Ca2…Si3O20

In a study at Bochum by Jung (1996), stoichiometric…
... phase. Jung (1996) has...

See an update on boromuscovite by Jung and Schreyer (2002).

... that KBSi$_3$O$_8$, crystallized...

... was synthesized at ... (Ufer and Schreyer, 1996; Schreyer and Werding (1997) for the

... 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


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

§ 3.4. Phase relations in the limiting system MgO-B$_2$O$_3$-H$_2$O 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$_3$Al$_6$[Si$_3$O$_{18}$]-(BO$_3$)$_3$O$_2$(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).
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: Ca₄B₄(BO₄)(SiO₄)₃(OH)₃·H₂O(?)
Table 1, Hulsite correct formula: \((\text{Fe}^{3+},\text{Mg})_2(\text{Fe}^{3+},\text{Fe}^{2+},\text{Sn}^{4+})\text{BO}_5\)
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, $\Box$, in mineral formulae has with rare exception been replaced by “G”.

388 Table 1, bottom  Vistepite  Triclinic  $\text{SnMn}_4\text{B}_2\text{Si}_4\text{O}_{16}(\text{OH})_2$

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

392 ¶ 3 *4  … dumortierite: 1.03 wt % $\text{Sb}_2\text{O}_3$ and 3.58 wt % As as $\text{As}_2\text{O}_3$ or 0.22 As pfu (Voloshin et al., 1987; Groat et al., 2001)

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

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

459 ¶ 1 *1  Vistepite, $\text{SnMn}_4\text{B}_2\text{Si}_4\text{O}_{16}(\text{OH})_2$, 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**


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
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
(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
fluorite layer in leucocratic orthogneiss at Nedvidice, Svrata 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
prograde metamorphism of sedimentary rocks in the Swiss Central Alps. Am Mineral 81:1223-1236
Mineral 84:1451-1455
MgO-Al2O3-SiO2-B2O3-H2O and Na2O-MgO-Al2O3-SiO2-B2O3-H2O-HCl in hydrothermal solutions
and siliceous melts. Can Mineral 37:1025-1040
MgO-Al2O3-SiO2-B2O3-H2O-HCl and the distribution of Na between tourmaline and fluid at 300 to
Zacek V, Petrov A, Hyrsl J (1998) Chemistry and origin of povondraite-bearing rocks from Alto Chapare,

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

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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 $^{11}\text{B}/^{10}\text{B}$ 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
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$_2$O (Williams et al., 2001a) and silicate melt (rhyolitic and basaltic)-H$_2$O (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$_2$O 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**


