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LETTER

Boron analysis by electron microprobe using MoB_4C layered synthetic crystals

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ABSTRACT

Preliminary electron microprobe studies of B distribution in minerals have been carried out using MoB_4C-layered synthetic crystals to improve analytical sensitivity for B. Use of this crystal for B analysis in geologic samples should be approached with caution if Cl is present. Any microprobe measurements of the B contents of minerals using this crystal must include analyses for Cl to assess and correct for the interference of Cl X-rays on the B*Kα* peak.

Microprobe analyses for B can be made routinely in tourmaline and other B-rich minerals, and minor B contents also can be determined in common rock-forming minerals. The approximate limit of detection is 0.3 wt% B_2O_3 for counting times of 3–5 min. Incorporation of unusually high B contents in minerals other than borosilicates has been discovered in prograde and retrograde minerals in tourmalinites from the Broken Hill district, Australia, and may reflect high B activities produced during the metamorphism of tourmaline-rich rocks.

INTRODUCTION

During the past few years, layered synthetic microstructure (LSM) crystals have been used increasingly in electron microprobe analysis and X-ray spectrometry for improved detection of elements of low atomic number (*Z*) (Wood et al., 1985; Nicolosi et al., 1986; Huang et al., 1989). Low-*Z* elements are difficult to analyze quantitatively for several reasons, including low yields and absorption of X-rays, nonuniform absorption correction procedures, interference caused by overlaps of higher order X-ray lines, peak shifts and shape alterations, and contamination (Bastin and Heijligers, 1990). LSM crystals have been developed to provide improved reflectivity and stability and suppression of high order spectra, compared with traditional single crystals and organic multilayered crystals such as lead stearate (PbSD). LSM crystals also have been shown to be less sensitive than PbSD to pronounced peak-shape alterations (Bastin and Heijligers, 1990).

LSM crystals are manufactured by depositing alternating low- and high-Z elements on a Si substrate, forming artificial crystal lattices with specific *d* values (Nicolosi et al., 1986). The alternating elements and *d* values are chosen to optimize reflectivity for the selected low-*Z* elements of interest. LSM crystals commonly used for mineralogical applications are WSi ($2d \sim 60$ Å) for analysis of F, O, N, and C, and MoB_4C ($2d = 140–165$ Å) for analysis of B and Be. Analytical characteristics of the WSi crystal have been reviewed recently by Potts and Tindle (1989). They noted that although the WSi crystal provides enhanced count rates and improved detection limits for F, first-order Fe*Lα* and second-order Mg*Lα* peak interferences with the F*Kα* peak require a correction procedure (Potts and Tindle, 1989). Analytical tests in our laboratories confirm the need to correct for these minor interferences, especially for the Fe*Lα* line, because of the common presence of significant amounts of Fe in F-bearing minerals.

ANALYTICAL PROCEDURES

We have installed an Ovonics[1] MoB_4C LSM crystal with a $2d$ value of 163 Å on the U.S. Geological Survey ARL-SEMQ electron microprobe in Reston, Virginia. This crystal was chosen to optimize the detectability of B. A MoB_4C crystal with a $2d$ value of 148 Å is installed on the JEOL JXA-8600 microprobe at JEOL research laboratories in Peabody, Massachusetts, where some of our work was conducted. These LSM crystals are used with flow-proportional detectors using P-10 gas (90% Ar, 10% methane). Analytical conditions and count data are summarized in Table 1. The B*Kα* peak, located at ~67.4 Å, is quite broad (Fig. 1), approximately 0.8 Å at full-width half-maximum (FWHM). Backgrounds thus have to be measured at ±6–10 Å on either side of the peak. Because of the low yield of B counts, accurate background

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[1] Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. government.

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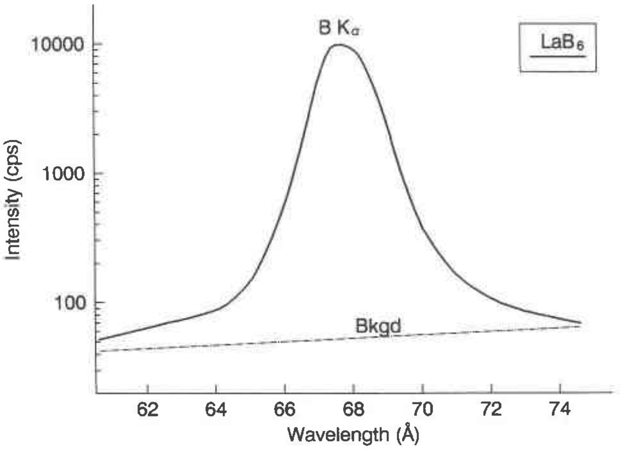

Fig. 1. $BK\alpha$ peak profile on LaB_6 (~31.8 wt% B) at 10 kV accelerating voltage and 15 nA sample current, U.S. Geological Survey microprobe, MoB_4C crystal $2d$ = 163 Å. $BK\alpha$ peak position is at ~67.4 Å. Peak counts/s = ~9800. Bkgd = approximate background count level across peak profile, based on measurements at high (78 Å) and low (58 Å) offsets.

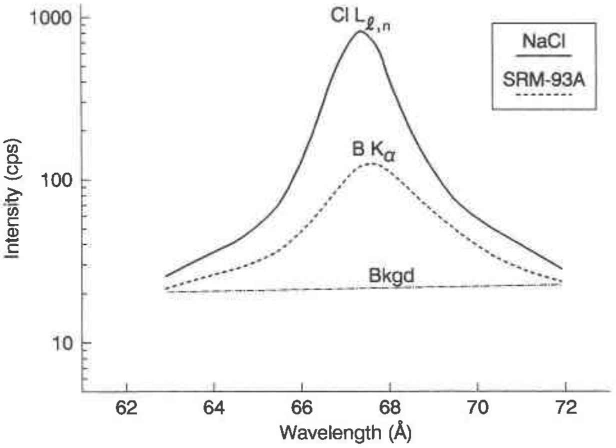

Fig. 2. $BK\alpha$ peak profile on NIST SRM-93A borosilicate glass standard (12.5 wt% B_2O_3) and profile of $ClL_{n,l}$ peaks (not resolved) on pure NaCl (60.7 wt% Cl) showing proximity of the $ClL_{n,l}$ peaks to the $BK\alpha$ peak. $BK\alpha$ peak position is at ~67.9 Å. JEOL microprobe, 15 kV accelerating voltage, ~45 nA sample current, MoB_4C crystal $2d$ = 148 Å. Bkgd = approximate background count level across peak profiles, based on measurements at high (74 Å) and low (62 Å) offsets.

corrections are especially important in order to obtain reliable measurements of B in minerals that generally have only minor B. For the data reported here, we used a background calculation that measures background counts as a function of average Z for the standards and then calculates backgrounds of the unknown by interpolation (McGee, 1985). Our tests of this background calculation method for this study show that the calculated backgrounds agree well with backgrounds measured by spectrometer offset methods. This method of background calculation shortens analysis time, thus minimizing potential erroneous measurements resulting from contamination or mobilization of elements, but it may be less accurate than actual measurements on materials (such as hydrous minerals) in which not all components are measured. For example, if the estimate of the average Z of the unknown material is in error by a value of 1 Z, the resulting estimate of B concentration could be in error by as much as 0.5 wt% B_2O_3. Our estimates of unknown average Z, however, are probably not in error by this large an amount.

Count data obtained on a variety of materials for this study (Table 1) indicate a minimum detection limit (MDL) of approximately 0.1 wt% B (~0.3 wt% B_2O_3). A National Institute of Science and Technology (NIST) standard borosilicate glass (SRM-93A) containing 12.5 wt% B_2O_3 was used as a primary standard for the analyses of tourmaline and associated minerals (Table 1; Fig. 2). No significant peak shift or variation in peak shape exists between the standard and unknowns, although we did not rigorously evaluate peak shapes. All analytical data in Table 2 were obtained with the U.S. Geological Survey microprobe using correction procedures of Bence and Albee (1968). Gem-quality uvite from Sri Lanka (Dunn, 1977) and buergerite from Mexico (Donnay et al., 1966) were analyzed repeatedly as working standards to gauge the accuracy and precision of the data (Table 2). Total error based on these data is estimated to be 5% for the major elements (including B) and 10% for the minor elements.

TABLE 1. B count data using MoB_4C crystals on electron microprobes

Material	Voltage kV	B wt%	Current nA	Peak Å	Peak cps	Background offset (Å)	Background cps	$\frac{P - B^*}{B}$	MDL%**
LaB_6†	10	31.8	15	67.4	9800	±10	50	195	0.01
SRM-93A†	10	3.9	15	67.8	80	±8	13	5.2	0.1
SRM-93A‡	15	3.9	46	67.9	130	±6	23	4.6	0.1
SRM-93A†	15	3.9	28	67.9	65	±8	10	5.5	0.1
SRM-93A†	15	3.9	18	67.9	55	±8	8	5.8	0.1

* Ratio of background-corrected peak counts to background counts.

** MDL % = estimated minimum detection limit, in wt% B, for count times of 30 s.

† U.S. Geological Survey microprobe, MoB_4C crystal $2d$ = 163 Å.

‡ JEOL microprobe, MoB_4C crystal $2d$ = 148 Å.

TABLE 2. Analyses of tourmaline, mica, and apatite standards (U.S. Geological Survey microprobe)

Standard	Smithsonian uvite		Smithsonian buergerite		Methuen muscovite		Lemhi biotite		Apatite (6.8 wt% Cl)		Durango apatite	
no. analyses	25*	ideal†	5*	ideal‡	5	ideal	10	ideal	2	ideal	3	ideal
SiO_2 wt%	35.84 (0.35)	35.96	33.58 (0.31)	33.86	45.38	44.94	33.52	33.09	0.03		0.24	0.34
TiO_2	0.66 (0.03)	0.62	0.56 (0.08)	0.55	0.16	0.16	1.35	1.30	0.00		0.00	
B_2O_3	11.47 (0.52)	11.49	11.26 (0.26)	10.86	0.00	0.00	1.39§	0.00	12.68§		1.23§	
Al_2O_3	27.44 (0.59)	26.80	31.67 (0.44)	30.79	35.02	35.71	17.31	17.65	0.01		0.03	0.07
FeO	0.39 (0.01)	0.41	17.68 (0.15)	17.12	2.29	2.18	30.40	31.40	0.00		0.06	0.00
MnO	0.04 (0.03)	0.00	0.30 (0.07)	0.13	0.11	0.06	0.11	0.04	0.03		0.05	0.01
MgO	15.17 (0.09)	15.20	0.29 (0.14)	0.13	0.54	0.57	2.88	2.83	0.10		0.08	0.01
CaO	5.09 (0.18)	5.50	0.37 (0.05)	0.69	0.00	0.08	0.02	0.10	54.02	53.84	54.64	54.02
Na_2O	0.23 (0.02)	0.13	2.45 (0.06)	2.46	0.50	0.76	0.15	0.13	0.00		0.00	0.23
K_2O	0.01 (0.00)	0.00	0.06 (0.00)	0.07	10.30	10.87	8.74	9.04	0.00		0.00	0.01
F	1.52 (0.07)	1.49	1.91 (0.05)	1.86	0.37	0.30	0.25	0.23	0.01		3.43	3.53
Cl	0.01 (0.00)	0.00	0.01 (0.00)	0.00	0.00	0.00	1.11	1.11	6.15	6.81	0.51	0.41
P_2O_5									41.06	40.88	40.60	40.78
SUM	97.86	97.60	100.14	98.52	94.67	95.63	97.22	96.92	114.10	101.53	100.85	99.40
Sum (O ≡ F + Cl)	97.22	96.97	99.33	97.74	94.52	95.50	96.87	96.57	112.70	100.00	99.31	97.82

Note: Standard deviations (in parentheses) are in wt%.

* Values reported are averages of 25 (for uvite) and 5 (for buergerite) sets of previously averaged multiple (3–5) analytical points.

† NMNH no. C5212 (Dunn, 1977).

‡ USNM no. 35468 (Donnay et al., 1966).

§ Artifact of Cl interference.

Cl SPECTRAL INTERFERENCE

We have identified spectral interference of Cl with B using the MoB_4C crystal that has significant effect on B analyses of Cl-bearing minerals (Figs. 2, 3; Table 2). This interference was discovered during a study of minute chloride phases (retrograde or supergene) in the Broken Hill samples (Slack and McGee, 1990). The interference results from the overlap of the B*K*α line by the ClL_l and L_η lines (Fig. 2). Unfortunately, the interfering Cl X-rays are first-order peaks (LSM crystals filter peaks of higher order), and although of relatively minor intensity, the yield of Cl X-rays is high relative to that of B X-rays, producing a serious interference when Cl is present (Figs. 2, 3). The B*K*α wavelength is 67.6 Å (183.3 eV), whereas the ClL_l and L_η wavelengths are 67.9 Å (182.6 eV) and 67.33 Å (184.1 eV), respectively. Thus the two Cl peaks are less than 1 eV on either side of the B*K*α peak, making peak discrimination virtually impossible, considering the relative yield of the B and Cl X-rays (Figs. 2, 3). We were unable to isolate the B peak from the Cl peaks by pulse height analysis.

Preliminary evaluation of the effect of the Cl interference on B counts was made by analysis of Cl-bearing micropobe standards (Fig. 3; Table 2). In general, a given Cl content yields erroneous B_2O_3 values between one and two times the Cl content, depending on standardization procedures (Table 2). For example, analysis of a biotite standard from Lemhi County, Idaho (Lee, 1958) that has a known content of 1.1 wt% Cl yields a spurious concentration of about 1.4 wt% B_2O_3; analysis of a synthetic apatite standard with 6.8 wt% Cl produces an erroneous value of approximately 12 wt% B_2O_3. A natural apatite standard from Durango, Mexico, likewise yields spurious B_2O_3 at about twice its Cl content. Cl-bearing standards such as the Lemhi biotite, which have analytic summations <100 wt% (as a result of unanalyzed components such as H_2O and Fe_2O_3), have spurious B_2O_3 values that may reflect inappropriate calculated backgrounds and matrix corrections, in addition to the contribution from the Cl interference (Table 2). Standards known to lack detectable Cl and B, such as muscovite from Methuen, Ontario, show no spurious B_2O_3 in their analyses (Table 2). Clearly, any microprobe studies of B in minerals must include analyses for Cl, and corrections are required based on analyses of B-free, Cl-bearing standards. Caution must also be used in interpreting measured B contents when unanalyzed components or inaccurate estimates of average *Z* result in inappropriate background subtraction and, thus, erroneous calculations of "corrected" B values.

ANALYSIS FOR B IN MINERALS

The quantitative in situ determination of the B contents of geologic materials generally has required the use of ion microprobes (e.g., Jones and Smith, 1984; Grew et al., 1990). Measurement of B contents has seldom been done quantitatively by electron microprobe because of the low yield of B X-rays by crystals available previously (e.g., PbSD). The MoB_4C crystal should allow for routine microprobe analysis of B at major and minor concentrations.

Our initial electron microprobe analyses of metamorphic minerals in tourmalinites from the Broken Hill district, New South Wales, Australia, show unusually high B concentrations (Slack and McGee, 1990). In addition to its presence in tourmaline, B was detected in prograde sillimanite, muscovite, biotite, and albite, and in retrograde muscovite, biotite, margarite, chlorite, staurolite, and chloritoid (Fig. 4). Cl is generally below detection in these minerals, so the measured B contents are not the result of Cl interference. B appears to be concentrated mainly in chlorite and the micas. Our reconnaissance work suggests that the retrograde biotite may contain as much

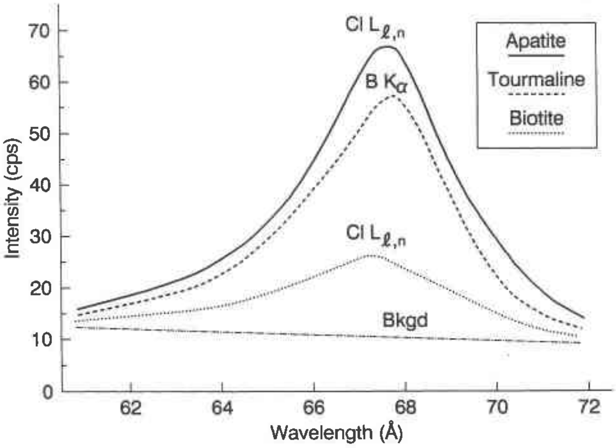

Fig. 3. Peak profiles for Cl-free tourmaline standard, B-free synthetic apatite (6.8 wt% Cl), and B-free Lemhi biotite standard (1.1 wt% Cl) (Table 2). Bkgd = approximate background count level across peak profiles, based on measurements at high (76 Å) and low (60 Å) offsets. U.S. Geological Survey microprobe, 15 kV accelerating voltage, ~18 nA sample current, MoB_4C crystal $2d = 163$ Å.

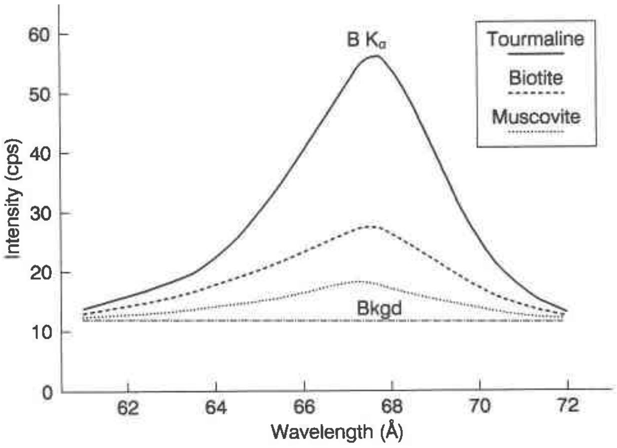

Fig. 4. B$K\alpha$ peak profile for tourmaline, biotite, and muscovite in tourmaline-rich rocks from Broken Hill, Australia. Bkgd = approximate background count level across peak profiles, based on measurements at high (76 Å) and low (60 Å) offsets. U.S. Geological Survey microprobe, 15 kV accelerating voltage, ~18 nA sample current, MoB_4C crystal $2d = 163$ Å.

as 1–2 wt% B_2O_3, acquired from the breakdown of local tourmaline (Slack and Robinson, 1990).

The B contents of tourmaline were measured reliably by electron microprobe using relatively short counting times (60 s); peak and background count rates indicate an approximate MDL of 0.4–0.5 wt% B_2O_3. Longer counting times are necessary for the analysis of minerals that have low B concentrations, however. Using 3–5 min counting times, MDLs in the range 0.2–0.3 wt% B_2O_3 (i.e., ~800–900 ppm B) are obtained. No significant variation in B count rates exists during these longer counting times, indicating that mobilization or beam contamination effects are not a problem for B measurements. However, the low B count rate produces measured B contents with a high sensitivity to variations in background measurements caused by either instrumental drift or inaccurate background calculation schemes. Our preliminary work suggests that such inaccuracies in background measurements can yield as much as 0.5 wt% spurious B_2O_3. This is a particularly serious problem for microprobe analyses of hydrous minerals that cannot be easily evaluated for stoichiometry and for which analytical accuracy is difficult to assess. We are continuing work on the analysis of low concentrations of B in these minerals and plan to evaluate our data with ion microprobe studies.

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