

MICRO-ANALYSIS OF MINERALS FOR BORON BY SREF, SIMS AND EMPA: A COMPARATIVE STUDY

FRANK C. HAWTHORNE AND MARK COOPER

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

PIERO BOTTAZZI AND LUISA OTTOLINI

C.N.R. Centro di Studio per la Cristallochimica e la Cristallografia, via Abbiategrasso, 209, I-27100 Pavia, Italy

T. SCOTT ERCIT

Research Division, Canadian Museum of Nature, P.O. Box 3443, Station "D", Ottawa, Ontario K1P 6P4

EDWARD S. GREW

Department of Geological Sciences, University of Maine, Orono, Maine 04469, U.S.A.

ABSTRACT

Kornerupine, $(\square, \text{Mg}, \text{Fe})(\text{Mg}, \text{Fe}, \text{Al})_9(\text{Si}, \text{Al}, \text{B})_5(\text{O}, \text{OH}, \text{F})_{22}$, contains from 0 to 4 wt% B_2O_3 , and is an ideal material for the evaluation of accuracy and precision of different micro-methods for boron analysis. We have analyzed 32 well-characterized crystals of kornerupine for their B content by SREF (crystal-Structure REFinement), SIMS (Secondary-Ion Mass Spectrometry) and EMPA (Electron-MicroProbe Analysis). The physical phenomena underlying these three analytical methods are entirely different, and hence there should be no systematic errors *common* to all three methods; this allows evaluation of the accuracy and precision of each method. In the range 0.5–4.4 wt% B_2O_3 , the precisions of the three methods are as follows: SREF (from least-squares refinement) 1–2% relative, 0.01–0.08 wt% absolute; SIMS (from reproducibility) 1–2% relative, 0.01–0.08 wt% absolute; EMPA (from counting statistics) 5–22% relative, 0.1–0.2 wt% absolute. Comparison of SREF and SIMS results shows them to agree on average within 3% relative. Hence SREF and SIMS are accurate within the limits of their assigned precision. Comparison of SREF and EMPA results shows a slight systematic difference between the two sets of results, the EMPA values being 7% higher than the SREF (and SIMS) results.

Keywords: site-scattering refinement, secondary-ion mass spectrometry, electron-microprobe analysis, boron, kornerupine, accuracy, precision.

SOMMAIRE

La kornerupine, $(\square, \text{Mg}, \text{Fe})(\text{Mg}, \text{Fe}, \text{Al})_9(\text{Si}, \text{Al}, \text{B})_5(\text{O}, \text{OH}, \text{F})_{22}$, contient entre 0 et 4% B_2O_3 (poids), et s'avère ainsi un matériau de choix dans l'évaluation de la justesse et de la précision des diverses méthodes d'analyse de micro-échantillons pour leur teneur en bore. Nous avons examiné trente-deux cristaux de kornerupine, tous bien caractérisés, par affinement de leur structure cristalline (SREF), par spectrométrie de masse sur ions secondaires (SIMS) et par microsonde électronique (EMPA). Les phénomènes physiques exploités par ces trois méthodes analytiques sont complètement différents; il ne devrait donc pas y avoir d'erreurs systématiques communes, ce qui permet une évaluation de la justesse et de la précision des trois méthodes. Dans l'intervalle 0.5–4.4% B_2O_3 , leur précision serait comme suit: SREF (précision évaluée par affinement par moindres carrés de la dispersion associée au bore) 1–2% en termes relatifs, 0.01–0.08% (poids) en termes absolus; SIMS (précision évaluée à partir de reproductibilité) 1–2% en termes relatifs, 0.01–0.08% (poids) en termes absolus; EMPA (précision évaluée à partir des statistiques de comptage) 5–22% en termes relatifs, 0.1–0.2% (poids) en termes absolus. Une comparaison des résultats obtenus par SREF et SIMS indique une concordance à 3% près, en termes relatifs. Il semble donc que SREF et SIMS produisent des résultats justes à l'intérieur des marges d'erreurs citées pour décrire la précision ces méthodes. Une comparaison des résultats obtenus par SREF et EMPA indique un léger décalage entre les deux résultats, les teneurs indiquées par EMPA étant de 7% supérieures aux résultats obtenus par SREF (et SIMS).

(Traduit par la Rédaction)

Mots-clés: affinement de dispersion de site, spectrométrie de masse sur ions secondaires, analyse à la microsonde électronique, bore, kornerupine, justesse, précision.

INTRODUCTION

The determination of light-element (H, Li, Be, B) contents in Earth materials is becoming of increasing importance in mineralogy and petrology. For the last 30 years, chemical analysis of minerals has been dominated by the electron microprobe, which has greatly advanced our knowledge and understanding of compositional variations in minerals at the micrometer level. Energy-dispersion spectrometry can identify the elements present, which is of particular importance in detecting (mineralogically) unusual components in minerals, and wavelength-dispersion spectrometry can provide accurate analyses. However, electron-microprobe analysis generally does not suffice to adequately characterize the chemical composition of a mineral: it cannot determine the amounts of all of the light elements, and it cannot recognize valence state. As a result, the great advances in our knowledge of mineral chemistry that have gone on over the past 30 years have tended to ignore the role of the light lithophile elements. Indeed, the "anomalous" behavior of several complex minerals (*e.g.*, staurolite: Dutrow 1991, Dutrow *et al.* 1986, Holdaway *et al.* 1986a, b, Hawthorne *et al.* 1993a, b; vesuvianite: Groat *et al.* 1992, 1994; sodic amphiboles: Hawthorne *et al.* 1993c, 1994) has been shown to be due to the incorporation of various light elements in coupled substitution with heavier ($Z > 9$) elements. Also, where light elements are known to be an important constituent of rock-forming or accessory minerals (*e.g.*, kornerupine: Grew 1988, Grew *et al.* 1987, 1990), the elucidation of the crystal-chemical details of the mechanisms of incorporation has been challenging (Moore & Bennett 1968, Moore & Araki 1979, Moore *et al.* 1989, Alaska & Grew 1991).

These few examples emphasize the importance of developing microbeam analytical methods for the light lithophile elements, so that their levels of concentration can be determined as reliably as with heavier ($Z > 9$) elements determined by electron-microprobe analysis. Ottolini *et al.* (1993) reported a new procedure for quantitative analysis of materials for Li, Be and B using SIMS (Secondary-Ion Mass Spectrometry). Here we assess the accuracy of this method for the analysis of minerals for B *via* analysis of 32 well-characterized crystals of kornerupine [$(\square, \text{Mg}, \text{Fe})(\text{Mg}, \text{Fe}, \text{Al})_9(\text{Si}, \text{Al}, \text{B})_5(\text{O}, \text{OH}, \text{F})_{22}$], with B_2O_3 contents in the range 0.5–4.0 wt%, by SIMS, SREF (Structure REFinement), and EMPA (Electron-MicroProbe Analysis).

ANALYSIS FOR LIGHT ELEMENTS BY SREF

Structure refinement (SREF) is essentially an electron-counting technique with spatial resolution; it measures the relative variation in X-ray scattering power, together with its spatial resolution within the (averaged) unit cell of the crystal. Usually, only the

relative scattering powers are determined in the experiment. However, during the refinement procedure, some of the scattering (usually that of oxygen, the most abundant component in many minerals) is assigned on an absolute basis, and this then correctly scales the rest of the scattering, such that the component scattering species can be identified. It is this *internal standardization* that is one of the strengths of this method, as every crystal carries its own standard, unlike other analytical techniques that require use of other standard materials in the quantification procedure. Hawthorne & Grice (1990) described the use of SREF for the determination of light-element contents in minerals. It should be noted that precisions (standard deviations) are always derived, as SREF involves least-squares refinement.

ANALYSIS FOR LIGHT ELEMENTS
(Li, Be, B) BY SIMS

Secondary-Ion Mass Spectrometry (SIMS) relies on the use of a focused beam of primary ions to sputter small volumes of material from a target (usually a solid sample: MacRae 1995). A fraction of the sputtered atoms, characteristic of the surface composition of the sample, are ionized; these secondary ions are the source of information in SIMS. Precision in SIMS analysis for trace elements is limited mainly by counting statistics, and by the amount of material that can be abraded during sputtering; precisions at the percent level are currently achieved for concentrations down to the ppm level. For higher levels of concentration, primary-ion beam instability, mass peak-positioning shift, charging of the sample, and the instability of the sputtering and ionization processes in the course of analysis, can greatly affect reproducibility. The nature of sputtering and ionization processes and the presence of instrumental effects do not make the conversion of ion intensities into absolute concentrations straightforward. Until now, the only successful approach to quantification has involved empirical Relative Sensitivity Factors (RSFs) (McHugh 1975) and working curves (*e.g.*, Hawthorne & Anderson 1975); accuracies of a few percent relative can be obtained. This approach relies on the availability of well-characterized standards that match as closely as possible the major-element chemistry of the unknown samples, and have well-determined trace-element concentrations.

Owing to their high efficiency of ionization as positive ions, Li, Be and B are ideal constituents to be analyzed by SIMS. In SIMS analysis, the secondary ions have an energy distribution with its peak at low energies of emission (0–10 eV) and a high-energy tail extending many hundreds of eV. In general, analysis tends to be done at low energies, where the ion yields are most intense. However, in this energy range, the matrix can have a significant effect on ion yield, and the relationship between ion intensity and concentra-

tion can be nonlinear (Steele *et al.* 1981, Shimizu 1986). Analysis using medium- to high-energy ions is known as CEF (Conventional Energy Filtering), and is generally used to eliminate molecular interferences (Shimizu *et al.* 1978, Zinner & Crozaz 1986). However, it is also useful for reducing the matrix influence on ionization of several elements, including the rare-earth elements (Crozaz & Zinner 1986). These results suggest CEF as a potential method for greatly improving quantification in the analysis for light elements by SIMS. Until now, one of the major obstacles in applying SIMS to *in situ* investigation of light elements has been the lack of well-characterized standards of composition appropriate for all samples to be analyzed. In the absence of suitable standards, quantification relies on the possibility of calibration with silicate standards of arbitrary major-element composition, in which the influence of the matrix upon secondary-ion yields is reduced to an acceptable level. Operating their instrument in the energy range 75–125 eV, Ottolini *et al.* (1993) have shown that matrix effects are reduced and reproducibility is improved with respect to analysis for Li, Be and B using low-energy ions. In the case of Be, there is evidence for a possible reduction of matrix effects, whereas in the case of boron, matrix effects are minor at any ion energy in the silicate samples investigated. On the other hand, strong matrix effects have been reported for boron in quartz, glass and feldspars (Kovalenko *et al.* 1988), with boron-ion yield varying by a factor of seven.

The calibration curves obtained by CEF for Li/Si, Be/Si and B/Si hold over extended ranges of concentration from ppm to weight percent for light elements in matrices with silica contents ranging from 20 to 80% SiO₂. Figure 1 shows the relevant calibration-curve for B; there is a perfectly linear relationship between the measured values of ¹¹B/³⁰Si (corrected for isotopic abundance) and the analytical values for B/Si in the standard materials. Ottolini *et al.* (1993) estimated both precision and accuracy as less than 20% relative at the ppm level and less than 10% relative for B values in the range of tens of ppm to wt%. However, these estimates are derived from Figure 1, which is also the calibration curve. Ideally, a separate set of measurements should be used to estimate accuracy. The validity of the method has been checked on another set of samples; briefly, the relative sensitivity factor for boron was used to recalculate the concentrations (ppm wt) of B in samples considered as unknown. Boron values were found to be within 13% of the nominal reference values for a lead-crystal glass and a phosphate glass, and within 1.8% for a synthetic glass (about 65% by weight SiO₂). Among the available rock standards, only a few values for boron are convenient for comparison with SIMS results, even at concentrations of tens to hundreds of ppm. It is the lack of suitable reference-data that makes the accuracy of the

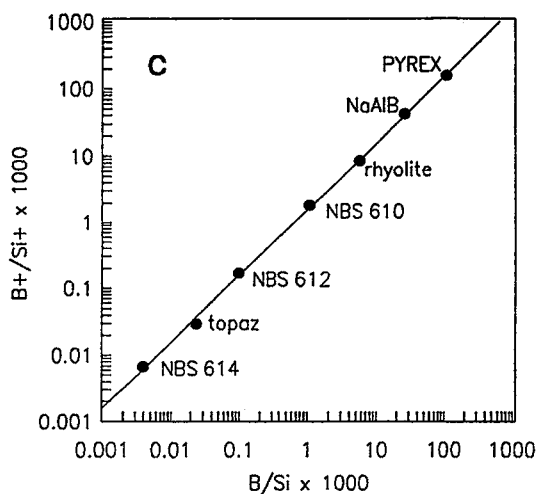


FIG. 1. The calibration curve for B in standard materials, showing the ion intensity for ¹¹B⁺ relative to ³⁰Si⁺ (corrected for natural abundances) versus nominal concentration normalized to Si concentration (by weight); after Ottolini *et al.* (1993), who gave full details of the standard materials used.

CEF method, as applied to boron, difficult to assess. Through the set of kornerupine crystals, the aim of the present work is to test the accuracy of the SIMS measurements obtained by CEF.

ANALYSIS FOR BORON BY EMPA

For years, the analysis for boron by EMPA was prevented by the lack of analyzing crystals with suitably large *d*-values. This shortcoming was initially overcome by the development of organic synthetic multilayer crystals such as lead stearate (STE). These have been displaced by inorganic layered synthetic multilayer crystals such as W/Si crystals (LDE) and Mo/B₄C (OVH, *e.g.*, McGee *et al.* 1991, Raudsepp 1995). The new multilayer crystals have several advantages over STE, including much greater peak-intensities (2 to 15 times) and a lower sensitivity to peak-shape variation; on the other hand, they have significantly poorer resolution than STE, and peak overlap is a potentially greater problem (Bastin & Heijligers 1991).

Despite considerable recent attention, analysis for boron by EMPA is still not a routine procedure. Bastin & Heijligers (1986) showed that BK α peaks are multi-component, have variable height:area ratios (34% range for a variety of compounds) and peak locations, and have an orientation dependence ascribable to polarization. High degrees of absorption of BK α X-rays by samples is a problem that is compounded by inaccurate mass-absorption coefficients and (historically) inadequate data-reduction methods. Absorption

effects can be minimized by working at low voltages (e.g., 5 kV), but this tends to result in large corrections for atomic number (Z) in the ZAF factor. Despite some successful attempts to compensate for many of the above problems, the precision of an analysis for boron remains low: Bastin & Heijligers (1991) reported a root-mean-square error of 6 to 7% for the determination of boron by EMPA. The importance of a good internally consistent set of mass-absorption coefficients, of a modern data-reduction routine (such as the $\phi[\rho Z]$ -related approach), and of a good match (composition, symmetry and orientation) between standards and sample, cannot be overemphasized.

EXPERIMENTAL METHODS

As part of a general study on the crystal chemistry of kornerupine (Cooper *et al.*, work in progress), we have assembled a suite of 32 samples from 20 localities, including 14 samples analyzed by Grew *et al.* (1990, 1991 and references therein). This suite spans most of the compositional range reported for kornerupine: 0.64–4.04 wt% B_2O_3 , 0.04–12.08% FeO, 37.75–47.24% Al_2O_3 , and 0.02–0.84 wt% F. In addition to the measurements reported here, the crystals used for these measurements were analyzed for Li and Be by SIMS. Approximately half of the samples were analyzed for H_2O content and Fe^{3+}/Fe^{2+} ratio, and the role of H in the structure was examined by polarized infrared spectroscopy. The detailed results of this work will be reported elsewhere.

SREF

Crystals were ground to spheres approximately 0.2 mm in diameter in an air-driven grinder, and cell dimensions and X-ray intensity data were measured on a Nicolet R3m automated four-circle diffractometer according to the procedure of Hawthorne & Groat (1985). Absorption corrections were done with the psican method, modeling the crystal shape as a triaxial ellipsoid; azimuthal R values are of the order of 1%. Subsequent to the crystallographic work, the crystals used were mounted (in random orientations), polished, coated with carbon (for EMPA) and gold (for SIMS), and analyzed by electron microprobe (at least 10 points per crystal) and ion microprobe.

Crystal structures were refined to R indices of $\sim 2\%$ using the program system SHELXTL Plus PC. Full details of the experimental and refinement procedures will be given elsewhere (Cooper *et al.*, in prep.). However, some comment is required, as we are demanding a lot from the diffraction results to determine approximately 0.5% of the total scattering with a relative accuracy and precision of 1–2% relative. The effective scattering at each site with variable occupancy was determined by *unconstrained* refinement of the scattering at that site. This is an important point to

make, as the use of compositional constraints has been a common feature of site-occupancy refinement in the past 20 years. However, the true role of such constraints is merely to obscure the fact that there might be systematic error present in the diffraction data, error that adversely affects site-occupancy refinement. If one wants accurate results from the structure-refinement process, one cannot tolerate significant systematic error in the diffraction data. Consequently, it is preferable to refine the effective scattering at each (variably occupied) site in the structure in an unconstrained way. If there is no significant systematic error in the diffraction data *and* in the electron- (and ion-) microprobe data *for the same crystal*, the results from the two processes should be compatible, *with no need for any constrained refinement*. Any disagreement between the two sets of data indicates systematic error; the source of this error must be identified, and the data recollected.

In the refinement procedure, anisotropic displacement factors were refined for all positions, the scattering at all sites with variable occupancy was refined without constraints, and all variable parameters were refined simultaneously in the final stages of refinement. Convergence was considered to be attained when all shift/error values were less than 0.01. Boron was located in the kornerupine structure by site-scattering refinement. Previous work (Moore & Bennett 1968, Moore & Araki 1979, Finger & Hazen 1981, Moore *et al.* 1989, Klaska & Grew 1991) showed that B occupies the $T(3)$ tetrahedron, together with Si and Al. The scattering power of B ($Z = 5$) is significantly different from Si ($Z = 14$) and Al ($Z = 13$), and hence the B content of the tetrahedral sites can be determined by site-scattering refinement. In addition, the radii of the three species are significantly different, *and* the microprobe analyses provide constraints on the total content of Si. This information was sufficient to enable us to assign B, Si and Al occupancies of the three tetrahedral sites, and hence the small difference in scattering between Si and Al was accounted for in the refinement of the B populations.

SIMS

Analyses were done on a CAMECA IMS-4F ion-microprobe at CNR-CSCC, Pavia, with a beam of O^- ions focused to a spot of 15–20 μm diameter, a primary accelerating voltage of ~ 12.5 kV and a primary current intensity of 10 nA. Positive secondary ions were nominally accelerated through 4.5 kV, and secondary ions at masses 11 and 30 were collected under an ion-imaged field 25 μm in diameter. Medium- to high-energy ions were selected by offsetting the sample accelerating voltage with constant electrostatic-analyzer voltages, and width and position of the energy slit. The energy-slit position was initially set by closing the window to ~ 2 eV and physically moving it to

obtain maximum intensity for $^{30}\text{Si}^+$ ions; the energy window was then symmetrically opened to 50 eV. For the B measurements, we used a voltage offset of -125 V relative to the voltage at which the intensity drops to 10% of its maximum value; thus we analyze secondary ions with emission energies of $\sim 100 \pm 25$ eV. Secondary ions were counted by an electron multiplier in the pulse-counting mode, and count times were 20 s for ^{30}Si and 100 s for ^{11}B over 10 cycles. Ottolini *et al.* (1993) have shown that $^{10}\text{BH}^+$ interferences are negligible in these silicate samples. Further experimental details are given in Ottolini *et al.* (1993).

Relative sensitivity factors were calculated on well-characterized synthetic glasses, and checked daily on a natural rhyolite (Macusani). On each sample holder, the first sample analyzed was re-analyzed again after the last one; the results for B agree to within $\pm 1\%$ relative. One sample (K9) was analyzed twice after each day's calibration as an internal reference; reproducibility of the analysis for B was $\pm 2\%$ relative. The reproducibility of SIMS analyses is 1–2%, and is limited mainly by the instability of the sputtering-ionization process and by instrumental drifts; any uncertainty related only to counting statistics for the kornerupine crystals would be 1–2 orders of magnitude lower. The analysis of a few samples also was repeated, and results were confirmed. Figure 1 shows the calibration curve used to convert the B/Si counts to B content relative to Si (after correction for natural isotopic abundance). The value for Si obtained from the electron-microprobe analysis was then used to obtain the B content.

EMPA

A JEOL 733 electron microprobe with Tracor Northern 5500 and 5600 automation was used for electron-microprobe analysis of the same crystals for boron (wavelength dispersion). Operating conditions were 5 kV, 100 nA beam current, 20 μm beam diameter, 50 s count time. Danburite was used as the standard ($\text{BK}\alpha$), and lead stearate was used as the analyzing crystal. All samples were examined for chemical heterogeneities by back-scattered electron imaging and for surface imperfection by secondary-electron imaging. A measurement was considered as observed only if it is significant at the 4σ (meas.) level. Wavelength-dispersion scans were done on the standards and one sample (K18) in order to (1) modify pulse-height analyzer settings so as to minimize line overlaps, (2) monitor peak shifts, (3) determine how much peak heights had to be modified to represent true peak intensities (*i.e.*, peak areas). The $\text{BK}\alpha$ peak for kornerupine was shifted +0.20 nm from the same peak for danburite, and the $\text{BK}\alpha$ peak for kornerupine had a peak-area:peak-height ratio 9% higher than in danburite. Reduction of the corrected data was done with a conventional ZAF routine in the Tracor Northern

TASK series of programs.

In order to assess the homogeneity of B, three points per grain were selected for analysis where possible. Only one sample, K31, showed a significant and reproducible variation in B (minimum 0.60, maximum 1.73 wt% B_2O_3).

RESULTS

The B contents (in atoms per formula unit) derived from SREF were converted into wt% B_2O_3 using the program FORMULA (Ercit & Hawthorne, in prep.); the resulting values are given in Table 1. The standard deviations of the determinations from SREF are derived from the refinement procedure; these were propagated through the calculation of the B_2O_3 contents, and are 1–2% relative.

TABLE 1. B_2O_3 CONTENTS (wt%) OF KORNERUPINE CRYSTALS BY SIMS, SREF AND EMPA

	SIMS	SREF	EMPA
K(1)	1.98	1.84	2.15
K(2)	2.52	2.41	2.68
K(3)	3.84	3.69	3.80
K(4)	2.35	2.28	2.80
K(5)	3.62	3.50	3.72
K(6)	3.15	3.32	3.99
K(7)	3.66	3.56	3.57
K(8)	2.45	2.48	2.33
K(9)	3.98	3.96	4.38
K(10)	3.06	3.21	3.52
K(11)	3.86	3.86	3.55
K(12)	1.35	1.47	1.63
K(13)	4.36	4.04	4.01
K(14)	3.38	3.44	3.41
K(15)	3.15	3.23	3.38
K(16)	3.81	3.82	3.50
K(17)	3.37	3.49	3.97
K(18)	3.43	3.51	3.69
K(19)	4.05	3.92	4.14
K(20)	3.98	3.94	4.50
K(21)	1.70	1.79	1.69
K(22)	2.05	1.99	1.97
K(23)	3.51	3.49	3.61
K(24)	3.70	3.75	3.98
K(25)	3.73	3.88	4.05
K(26)	2.28	2.36	2.25
K(27)	3.50	3.51	3.19
K(28)	3.54	3.52	3.48
K(29)	2.88	2.99	3.33
K(30)	0.44	0.64	0.59
K(31)	1.54	1.53	1.28
K(32)	3.76	3.79	4.34

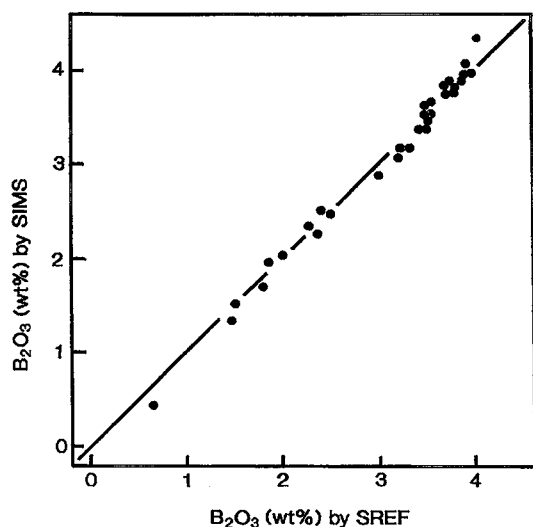


FIG. 2. Comparison of B_2O_3 (wt%) contents in 32 crystals of kornerupine, determined by SIMS and SREF; the diagonal line is drawn with a slope of unity and is not a least-squares line.

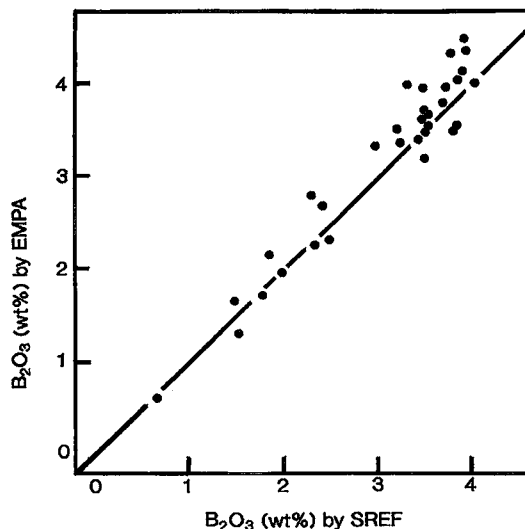


FIG. 3. Comparison of B_2O_3 (wt%) contents in 32 crystals of kornerupine, determined by EMPA and SREF; the diagonal line is drawn with a slope of unity.

The B_2O_3 contents of the 32 kornerupine crystals, as determined by SIMS, is given in Table 1, and a graphical comparison of the SIMS and SREF values is given in Figure 2. Day-to-day reproducibility was $\pm 2\%$ relative.

The B_2O_3 contents obtained by EMPA are given in Table 1, and a graphical comparison with the SREF values is given in Figure 3. The relative precision of analysis as estimated from counting statistics ranges from 5% [crystal K(9)] to 22% [crystal K(30), in which the B value is close to the limit of detection]; in terms of absolute amounts, the corresponding values of the precision are 0.22 and 0.13 wt%, respectively.

DISCUSSION

The three methods used here for the analysis of kornerupine for B content are physically independent; SREF involves X-ray scattering, SIMS involves ion ablation and mass spectrometry, and EMPA involves the fluorescence of X rays by electrons. Hence there should be no *systematic* error common to these methods. This gives us an opportunity to evaluate the accuracy of the methods; agreement of two independent sets of measurements within their combined level of precision indicates the accuracy of each within the assigned level of precision.

SIMS

SIMS shows a reproducibility of 2% relative, simi-

lar to the SREF estimated standard deviations of 1–2% relative. Comparison of the SIMS and SREF results (Fig. 2) shows them to agree on average within 3% relative, their combined level of precision. Hence both SIMS and SREF are accurate within their assigned levels of precision.

The ion microprobe is seldom used to measure concentrations of major elements because the accuracy is limited by matrix effects. Where matrix-matched standards are not available, matrix effects must be taken into account to evaluate the reliability of results. Shimizu (1986) investigated the ionization of major elements in simple silicate systems and found simple linear relationships between the intensity of high-energy ions and composition (both relative to Si). He found concentrations of Ca and Al in Fe-free silicate minerals to be accurate to within 4.5%. For high-energy ions, the presence of Fe introduces a nonlinear behavior in the ionization of other major elements (Shimizu *et al.* 1978), resulting, for instance, in a variation of the relative-to-Si ion yield of Ca in Ca-rich clinopyroxene by a factor of ~ 1.5 . Moreover, the effect of Fe is different from one mineral group to another, even in Ca-rich and Ca-poor pyroxenes. Only after careful calibration of the effect of Fe on the ionization of the other major elements (and of Fe itself) was an accuracy of 5% achieved for a range of augite compositions (Shimizu & Le Roex 1986).

Another effect that can reduce the reliability of SIMS measurements is the instability of the ion currents observed for some elements. This is the case

for Na, which can migrate under primary-beam bombardment (Havette 1985), limiting the precision of the calibration factors for Na (and other alkali elements) to 10% instead of 5% as for other elements. Drifts in the ion signal for F (collected as high-energy positive ions) also are commonly observed; in the kornerupine crystals examined here, we measured F and observed variations up to 20% in the F^+ signal during the time required for one analysis. This fact obviously limits the precision of the measurement to a level corresponding to the amount of the variation itself; SIMS data for F agrees within $\pm 20\%$ (relative) with EMPA determinations (above a F content of 0.25 wt%).

Following this argument, and considering that the concentrations of B were determined here using standards of different composition (30–80% SiO_2 , and very low or zero Fe), the excellent agreement of SIMS with SREF data (3% average discrepancy) might seem surprising. The reasons are as follows: (1) there are no significant interferences with either of the B isotopes; (2) B ionizes very efficiently; (3) there is negligible instrumental background; (4) sputtering and ionization quickly stabilize (within a few minutes) and are constant (within $\sim 1\%$ relative) for the duration of analysis; (5) matrix effects on B/Si ionization are small. Points (1) to (4) are well established, and can be easily checked before (and during) any analytical session. It is more difficult to assess the importance of matrix effects for all silicate matrices. Ottolini *et al.* (1993) estimated that they are less than $\pm 10\%$ on the basis of the available standards, but a comprehensive assessment requires a much larger set of control samples. However, for dramatic changes in the matrix composition (as for the phosphate and lead glasses of Ottolini *et al.* 1993), the B values are correct within 13%. As the B/Si ion yield differs by only 13% between silicates and the two "exotic" matrices cited above, one would expect a much smaller variation within silicates. The results of this work strongly suggest that accuracy for B determination in silicates, measured by standards of various compositions, is significantly better than previously estimated.

We considered the possibility of bias for our kornerupine results due to differences in composition within the sample set. In particular, we considered Fe because it is known to affect the ionization of other major elements (Shimizu *et al.* 1978, Havette & Slodzian 1980) and because Fe is the element with the largest relative variation in kornerupine: from 0.04 to 12.08 wt% as FeO. If the relative difference between SIMS and SREF results for B is plotted against FeO content, a weak inverse correlation is observed ($r^2 = 0.34$). We can conclude that within the kornerupine group, any effect of Fe on the ionization of B relative to that of Si is within the reproducibility of the measurement.

The comparison of SIMS with SREF data for B confirms that matrix effects between and within silicate

mineral groups are quite small and that B can be determined accurately by SIMS in any silicate mineral. The results of this study indicate that SIMS analysis for B can be done with an accuracy of better than 5% relative. Moreover, owing to its high sensitivity for B, SIMS can easily cover the complete range of B from a major constituent to trace levels (less than ~ 25 ppb: Ottolini *et al.* 1993), provided that problems associated with contamination (Shaw *et al.* 1988) are avoided.

EMPA

Comparison of SREF and EMPA results (Fig. 3) shows a slight systematic difference between the two sets of results, the EMPA values being on average 7% higher than the SREF (and SIMS) results. This is of the same order as the assigned analytical precision (5–22% relative), and is within the range of expectations given by Bastin & Heijligers (1991) for the determination of B concentration by EMPA. However, there is no doubt that the deviation in Figure 3 is systematic. Improved precision could be achieved by longer count-times or by use of LDE or OVH crystals (not currently available to us), but Figure 3 indicates that this would not necessarily result in improved accuracy. Danburite, $CaB_2Si_2O_8$, has [4]-coordinated B, similar to kornerupine, and should have far lower potential for polarization effects than minerals with [3]-coordinated B; however, we cannot rule out a small effect attributed to polarization due to the (fixed) orientation of the standard.

Comparison with previous data

Grew *et al.* (1990, 1991 and references therein) reported wet-chemical data for B in seven of the samples analyzed here, and SIMS data for B on 14 of the samples analyzed here. Samples K(8) and K(12) are heterogeneous and, hence, not directly comparable with the present results. Omitting these two samples from consideration, we get extremely good agreement between the present set of results and previous data. Figure 4a shows the correspondence between the SREF data of the present study with the values reported by Grew *et al.* (1990, 1991) from wet-chemical analysis. The data accord with the 1:1 line very closely, and linear regression gives the relationship $B_2O_3(\text{wet}) = 1.026 B_2O_3(\text{SREF}) - 0.024$ [$r^2 = 0.943$; 7 samples]. Similarly, there is good agreement between the two sets of SIMS results (Fig. 4b, in which the earlier SIMS data are referred to as IMMA (Ion-Microprobe Mass Analyzer) data. Again, there is close correspondence with the 1:1 line, and linear regression gives $B_2O_3(\text{SIMS}) = 0.988 B_2O_3(\text{IMMA}) + 0.067$ [$r^2 = 0.946$; 12 samples].

This agreement with previous wet-chemical results provides an important link between the results of these instrumental methods and those of classical chemical

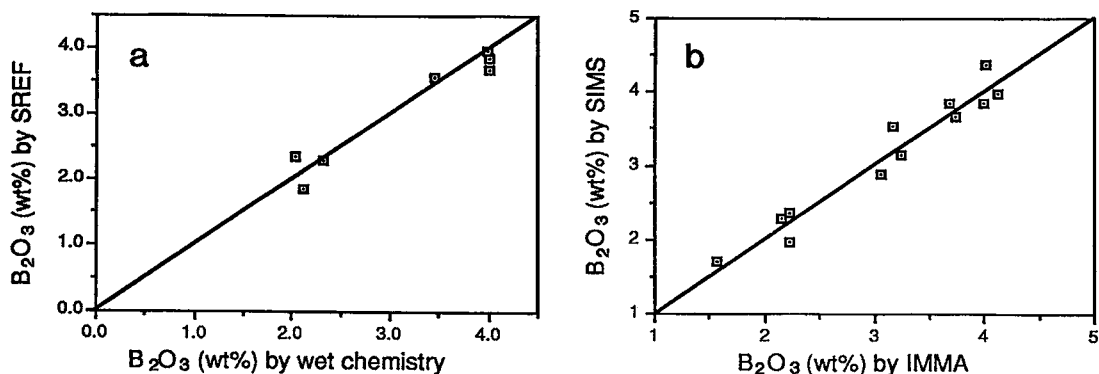


FIG. 4. Comparison of B₂O₃ (wt%) contents of kornepupine from this work with the results of Grew *et al.* (1990, 1991); (a) SREF versus wet chemistry (7 samples); (b) SIMS versus IMMA (12 samples).

analysis. This is further proof of our assertion that there is no significant systematic error in the SREF or SIMS results given here.

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