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Quantification of H, B and F in Kornerupine: Accuracy of SIMS and SREF (X-Ray Single-Crystal Structure-Refinement) Data

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Abstract. We use a multiple-analytical approach based on secondary-ion mass-spectrometry (SIMS), X-ray single-crystal structure refinement (SREF) and electron-probe micro-analysis (EPMA) to derive the complete crystal-chemical formula of a B-rich kornerupine-group mineral, prismatine, from Hrarigahy, Madagascar: $(Ca_{0.01}Li_{0.02}Mg_{0.20}Fe^{2+}_{0.10})$ $(Mg_{3.57}Fe^{2+}_{0.06}Al_{5.37})$ $(Si_{3.84}B_{0.91}Al_{0.26})O_{21}$ $(OH_{1.08}F_{0.07})$. SIMS matrix effects related to crystal structure were investigated by analyzing two grains with a known crystallographic orientation relative to the ion beam.

Boron orders at the *T3* site. The refined site-scattering for *T3*, 6.33 eps (electrons per site) agrees well with the mean bond-length for this site (1.512 Å), which indicates nearly complete occupancy by B (85% rel.). B_2O_3 ($\sim$ 4 wt%), derived by SREF, agrees with the SIMS data within analytical uncertainty using Si as the inner reference for the matrix. The occupancy of the *X* site obtained by combining the SIMS and EPMA data (5.30 eps; electrons per site) agrees with the refined site-scattering value (5.75 eps). Trace quantities of Li and Ca are ordered at this site. SIMS data for H_2O is in accord with the stoichiometric value, indicating complete occupancy at *O10* by OH. Fluorine ($\sim$ 0.17 wt%) orders at *O10*: it corresponds to $\sim$ 0.07 atoms per formula unit (apfu) vs. 0.15 apfu (atoms per formula unit) by SREF, indicating a slight overestimation of F with SREF, as previously observed in fluoborite.

Our data show that SIMS chemical matrix effects are well-calibrated, and emphasize the usefulness of independent micro-analytical techniques in testing the mutual accuracy and consistency of experimental data.

Key words: SIMS; SREF; crystallographic orientation; light elements; kornerupine.

SIMS is a key technique for *in-situ* micro-analysis of elements and isotopes. The light lithophile elements (H, Li, Be, B) show high ion yields, low detection limits (in the ppb – ppm wt range), and interferences (if any) can generally be discriminated at low mass-resolving power. The principal drawbacks are matrix effects that introduce difficulties in quantitatively relating ion yield in sample and standard. Such effects are more prominent for major and minor constituents than for trace elements. The empirical approach to quantification has been hampered primarily by the absence of suitable standards that chemically match the composition of each sample. For silicates, the bulk composition of a sample can affect the sensitivity for a given element by a factor of up to $\sim$ 2–3 [1]. With the use of energy filtering (75–125 eV secondary ions) for SIMS analysis of Li, Be and B, Ottolini et al. [2] showed that matrix effects are reduced. This reduction is very significant for Li, from a factor of 2 to ±20–25% rel. in the silicates investigated. Matrix effects are somewhat less for B and Be. Nevertheless, for all these elements, the reproducibility of SIMS analysis is improved relative to that obtained for low-energy ions.

The determination of H by SIMS, done using low-energy ions, suffers from two major problems: a) a high intercept of the calibration graph; b) severe matrix effects (factor > 3), which make it essential to calibrate hydrogen signals on standard samples of similar chemical composition to the unknown. Matrix effects constitute a major drawback, as homogeneous

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reference materials for hydrogen are scarce, and the use of standards of composition appropriate to all samples is not generally practical for complex matrixes, such as, staurolite, amphibole or mica. A marked reduction of both problems occurs when the secondary beam is "energy filtered" [3, 4]. Recently, we analysed H in hellandite and britholite, complex REE(U, Th)-rich silicates [5], monitoring H^+/Ca^+ medium-to-high-energy secondary ions. The relative-to-Ca ion yield for H, IY(H/Ca), derived in some silicate reference samples (Ca was chosen as the inner reference element) was used to quantify H in hellandite and britholite, for which no matrix-matched standard is available. In order to get a rough estimation of the accuracy of the procedure, such IY(H/Ca) was then compared with the IY(H/Ca) obtained in some apatites (Ca-rich phosphates) whose chemical composition is considerably different from that of our "unknowns". The *residual* matrix effects among Ca-bearing silicates and apatites (no Si) were on the order of $\sim 40\%$ rel. This is additional indirect proof of the validity of this approach.

Finally, a single working curve for F/Si in silicates was obtained using the same instrumental set-up [6]. The deviation of the measured points from the linear working curve was typically $< \pm 20\%$ rel. for F concentrations higher than ~ 0.1 wt%, i.e., those measurable by the electron microprobe (further details can be found in [6]).

For all these elements, the direct advantage of energy filtering has been a reduction of the number of standards required for quantitative analysis of light elements in silicates.

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; this accurately scales the rest of the scattering, and the component scattering species can be identified. This internal standardization represents one of the strengths of the method, as each mineral has its own inner standard: SREF can be used in an absolute way and does not need any external calibration [7].

Kornerupine is an orthorhombic silicate mineral with space-group symmetry C*mcm*. Its structure contains nine cation-sites (tetrahedrally coordinated: *T1*, *T2*, *T3*; octahedrally coordinated: *M1*, *M2*, *M3*, *M4*, *M5*; [8]-coordinated: *X*). Complex chemical substitutions involve Al for Si at *T1* and *T2*, Al and B for Si at *T3*; Mg for Al at *M3*, *M4* and *M5*, Fe^{2+} for Mg at *M1* and *M2*, and Fe^{3+} for Al at *M4*, and variable occupancy of Mg, Fe and Na, at *X*. Anion sites show chemical substitution only at the *O10* site, involving F and OH [8–12]. The sample studied here is the B-rich member of the kornerupine group, prismatine. It belongs to a set of samples that were mounted with known crystallographic orientation relative to the electron and ion beam [13].

We have evaluated the accuracy of the SIMS measurements of H, B, (Li) and F through the constraints derived from SREF. The present results show that a high level of accuracy has been achieved in SIMS quantification of these elements in complex silicate minerals. At the same time, they point out the key role of mutually-independent techniques in cross-checking the consistency and accuracy of experimental data.

Experimental

Kornerupine sample HS-112233 is from Hrarigahy, Madagascar. Two crystals of kornerupine were selected, and data collection, orientation and mounting followed the procedures described in [13].

Table 1. Refined cell parameters and data-collection parameters

Crystal	1
Identification code[a]	gcr
Crystal size (mm)	$0.8 \times 0.2 \times 0.5$
Crystal system	Orthorhombic
Space group	*Cmcm*
Unit-cell dimensions a(Å)	15.934(3)[b]
b(Å)	13.739(3)[b]
c(Å)	6.699(1)[b]
Volume (Å^3)	1466.5(5)[b]
θ range for data collection (°)	2.56 to 30.04
Index ranges	$-23 < h < 23$
	$-20 < k < 20$
	$-1 < l < 10$
Reflections collected/unique	4549/1198
R_{merging} [$R_{(\text{int})}$](%)[c]	3.46
Restraints/parameters	0/130
Goodness-of-fit on F^2	1.194
Final R[d] [$I > 2\sigma(I)$] = R1	2.19
wR^2(%)[e] [$I > 2\sigma(I)$]	5.90
$R_{(\text{all data})}$[d] = R1	2.28
wR^2(%)[e] (all data)	5.94

[a] Sequence number in CSCC database, [b] in brackets 1σ error on the last digit, [c] $R_{\text{merging}} = \Sigma|F^2(i) - F^2(h)|/\Sigma F^2(i)$, where $F^2(i)$ is the i^{th} reflection intensity and $F^2(h)$ is the mean intensity of symmetry related h, k, and l, [d] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, where F_o is the observed structure factor and F_c is the calculated structure factor, [e] wR^2 stands for weighted R factor.

Korn 1 has its *b* axis perpendicular to the analysis surface, and korn 2 has its *a* axis perpendicular to the analysis surface.

Weighted full-matrix least-squares refinement of diffraction data of crystal korn 1 was done using SHELX97 [14]. Scattering factors were taken from the International Tables for Crystallography: neutral vs. ionized scattering-factors were used for the O sites [7] and fully ionized scattering factors for the *O10* site (O^- vs. F^-) and for the cation sites, except for B. After refining anisotropic atom-displacement parameters, a very weak maximum at 0.859(1) Å from the *O10* site was present in difference-Fourier maps; this H site was included in the model with fixed coordinates and occupancy, and a variable isotropic-displacement parameter. Table 1 reports the crystal information and refinement results. Atom coordinates and isotropic displacement parameters can be obtained from the authors on request.

Table 2. EMPA, SIMS data (wt%) and mineral formulae (atoms per formula unit) for the crystals studied. Refined site-scattering factors (s.s.$_{obs}$) and assigned site population (s.s.$_{calc}$) in electrons per site are also reported

Mineral mount name orientation§	Korn. 1 A	Korn. 2 B
SiO_2	31.87	31.94
B_2O_3*	4.32	4.37
Al_2O_3	39.67	39.71
FeO	1.56	1.60
MgO	21.11	21.09
Li_2O*	0.03	0.03
CaO	0.11	0.10
F*	0.16	0.18
H_2O*	1.34	1.35
TOTAL	100.17	100.37
O=F	0.07	0.07
TOTAL	100.11	100.29
Si	3.84	3.84
B	0.90	0.91
Al	0.27	0.26
Σ T	5.00	5.00
Al	5.36	5.37
Mg	3.58	3.58
Fe^{2+}	0.06	0.06
Σ Oct.	9.00	9.00
Mg	0.21	0.20
Fe^{2+}	0.10	0.10
Li	0.02	0.02
Ca	0.01	0.01
Σ X	0.34	0.33
F	0.06	0.07
OH	1.08	1.08
(OH + F)	1.14	1.15
Σ Cations	14.34	14.33
s.s. T_{calc}	12.33	12.32
s.s. T_{obs}		12.41
s.s. Oct_{calc}	12.68	12.69
s.s. Oct_{obs}		12.70
s.s. X_{calc}	5.45	5.30
s.s. X_{obs}		5.75
s.s. $Total_{calc}$	30.46	30.32
s.s. $Total_{obs}$		30.86
Δ s.s. Total		−0.54
s.s. $(OH, F)_{calc}$	8.06	8.07
s.s. $(OH, F)_{obs}$		8.15

§ Orientation- A: *b* axis perpendicular to the analysis surface; B: *a* axis perpendicular to the analysis surface;

* By ion microprobe.

Electron-probe micro-analysis was done at the University of Manitoba and the Geological Survey of Canada (Ottawa) on a fully automated CAMECA SX50 operating in wavelength-dispersion mode: excitation voltage 15 kV; specimen current 20 nA; peak-count time 20 s; background-count time 10 s. The standards were the following (in parentheses, the crystals for X-ray dispersion is mentioned): P: VP_2O_7 (PET); Si: almandine (PET); Al: kyanite (TAP); Ti: titanite (LiF); Fe: olivine (LiF); Mn: spessartine (LiF); Zn: gahnite (LiF); Mg: forsterite (TAP); Ca: diopside (PET); Sr: celestite (PET); Na: albite (TAP); K: orthoclase (PET); F: fluororiebeckite (TAP). Each grain was analyzed at a minimum of 25 points to check for compositional zoning and to obtain good counting statistics; no compositional zoning was observed. Data were reduced using the method of Pouchou and Pichoir [15, 16]. Chemical analyses are given in Table 2.

SIMS measurements were done with a Cameca IMS 4f ion microprobe at CNR-CSCC (Pavia). We used a 12.5-kV accelerated $^{16}O^-$ primary-ion beam with a current intensity of 1–1.5 nA, and monitored (75–125 eV) secondary ions of the following isotopes: H^+, $^7Li^+$, $^{11}B^+$, $^{19}F^+$, and $^{30}Si^+$. The beam diameter was less than 5 µm ø and the ion beam impinged the sample at 60° to the sample surface. The SiO_2 values (as wt%), used as inner reference for SIMS quantification, were derived by EPMA. The final results for Li and B are the average of all data (typically four or five points for each crystal) collected on the different runs over a one-year span, whereas those for H and F were recorded in two analytical sessions. The ion yield used for F and B quantification were obtained by averaging the yields from topaz Mountain and mica 1B, Pyrex glass and axinite A (6.06 wt% B_2O_3), respectively. The standard Ceran was used for Li, and cordierite Great Bear was used for H. Further details can be found in [13].

Results and Discussion

SREF data

The *T3* tetrahedron is the more regular of the three tetrahedra in the structure. The refined site-scattering (6.33 eps) and the mean bond-length (1.512 Å) for the *T3* site are in agreement with B ordering at this site. All these features indicate nearly full occupancy of *T3* by B (ca. 85%).

The [8]-coordinated *X* site has a refined site-scattering that indicates 1/3 occupancy of this site. Moore and Araki [17] postulated that partial occupancy of *X* by Mg (or Fe^{2+} [18]) is coupled with depletion of hydrogen bonded to oxygen (OH bond) at the *O10* site. As we localized the centroid of the hydrogen atom in our difference-Fourier synthesis, we analyzed the geometry of the hydrogen environment. Previous work on a set of kornerupines [12] has shown that there are two possible positions for hydrogen in the kornerupine structure, i.e., *H1* and *H2*. In the present

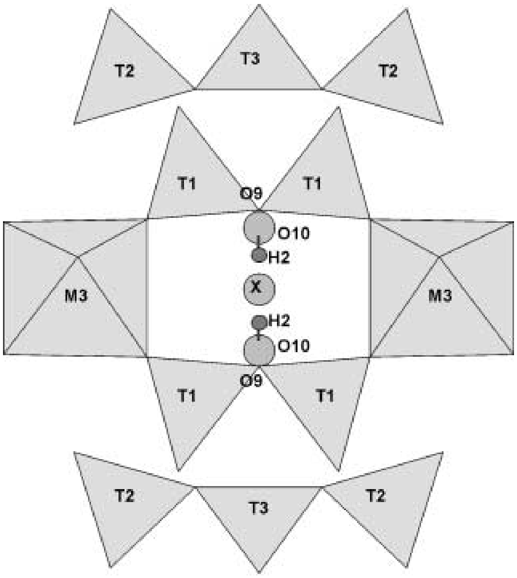

Fig. 1. Projection of the kornerupine structure down the [001] direction. The local environment of the *X* site and the bonding between *O10* and *H2* sites is shown. As *H2* is very close to *X*, the simultaneous presence of hydrogen and Mg (Fe^{2+}) in the *X* cavity is not possible (see text for discussion)

case, we found hydrogen only at the *H2* site. The *O10-H2* bond (OH bond) points toward the center of the *X* site (Fig. 1), and therefore a hydrogen bond is possible between hydrogen and oxygen at the *O9* site, which links pairs of *T1* tetrahedra (*O10-H2...O9* = 2.778 Å; *H2-O9* = 2.320 Å). When the *X* site is empty, there are two hydrogen atoms in the *X* cavity. However, occupancy of the center of the *X* cavity is not compatible with the hydrogen position that we have refined (*X-H2* = 1.217 Å) and therefore there must be an alternation along the *c*-axis of *X* sites occupied by a cation (Mg, Fe^{2+}) and *X* sites occupied by two symmetrically related hydrogen atoms at the *H2* sites. Considering that the refinement yields a cation occupancy of 1/3 at the *X* site, the maximum possible amount of hydrogen in this crystal is 1.33 atoms per formula unit (apfu), unless F is also present at the *O10* site. Refinement of the scattering power at the *O10* site results in a F occupancy of 0.15 apfu (Table 2). A more detailed discussion of the OH-F substitution is given in [12].

SIMS Data

The effect of crystallographic orientation on light-element ionization is slight: maximum $\leq 7\%$ rel. for F; $\leq 3\%$ rel. for Li and B, and negligible for H; these differences are mostly within the uncertainty of the analysis ($\pm 3\sigma$). The average SIMS B concentration is slightly higher, for both crystal orientations, than that derived by SREF (~ 4 wt% B_2O_3). Nevertheless, the present data coincides with SREF data within the uncertainty of the analysis over a one-year span. They are also within the uncertainty of our working curve for B in low-Fe silicates (accuracy = $\leq \pm 10\%$ rel.) [2]. An accuracy of $\sim 3\%$ rel. was obtained in a set of kornerupines [19] using Pyrex glass as the primary standard. For the present low-Fe kornerupine, Pyrex glass is confirmed as the best calibration standard. Recalculation of B content from the ion yield [IY(B/Si)] derived only with Pyrex glass would have given 4.08 and 4.12 wt% B_2O_3 for korn1 and 2, respectively.

The partial occupancy of *X* site obtained by combining SIMS and EMPA data (5.30 eps) agrees well with the refined site-scattering value (5.75 eps) when considering the trace quantities of Li and Ca to be ordered at this site (Table 2). SIMS data for H_2O agree with the stoichiometric value within analytical error of $\sim \pm 10$–15% rel. [3], indicating nearly full occupancy of *O10* by OH. Fluorine is rather low (~ 0.16, 0.18 F wt% for the two crystals) and orders at *O10*: it corresponds to 0.06–0.07 apfu, respectively, vs. 0.15 apfu obtained by SREF, indicating slight overestimation of F with SREF, as previously observed for fluoborite [20].

Finally, the (OH + F) = 1.15 apfu found by SIMS is higher than the expected stoichiometric value (OH + F) = 1, which is compatible with the analytical uncertainty of SIMS work.

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