Microchim Acta 155, 229–233 (2006)
DOI 10.1007/s00604-006-0548-3

Microchimica Acta
Printed in Austria

Original Paper

Strategies for Quantification of Light Elements in Minerals by SIMS: H, B and F

Luisa Ottolini[1,*], **Fernando Cámara**[1], and **Frank C. Hawthorne**[2]

[1] CNR – Istituto di Geoscienze e Georisorse (IGG), Sezione di Pavia, Via Ferrata 1, I-27100 Pavia, Italy
[2] Department of Geological Sciences, University of Manitoba, Winnipeg, MB R3T 2N2, Canada

Received May 26, 2005; accepted November 7, 2005;

Abstract. Using a large set of silicate crystals, characterized by Structure REFinement (SREF), Electron Probe Micro-Analysis (EPMA) and Secondary Ion Mass Spectrometry (SIMS), and mounted with known crystallographic orientation [1], we propose a new SIMS quantification for H, B and F (from ppm level to several wt.%), using $^{27}Al^+$ and $^{44}Ca^+$, in turn, as the reference isotope for the matrix, and propose suitable calibration standards to obtain accurate results. The final SIMS data are then compared to those obtained using Si as the reference element, with those available from EMPA (B and F), and with the crystallographic constraints derived from SREF investigation. The results of this study can be extended to the measurement of light elements in complex silicate or non-silicate samples.

Key words: SIMS; calibration procedures; crystallographic orientation; light and volatile elements; silicates.

One of the major limitations in applying SIMS to the analysis of light elements in silicate minerals is the presence of ‘‘matrix effects’’ that affect sputtering-ionization phenomena. The existence of such matrix effects has introduced major difficulties in quantification: secondary-ion intensities are generally nonlinearly related to elemental concentrations, and depend (to various extent) on the concentration of other element(s) in the matrix. This effect is more significant for major and minor constituents than for trace elements. So far, the only way to circumvent matrix effects is the empirical approach based on relative sensitivity factors and working curves. This approach relies on the availability of well-characterized standards which match as closely as possible the major-element chemistry of the ‘‘unknowns’’ and have accurately known concentrations of the elements to be characterized. In this way, matrix effects are not eliminated, but calibrated. In SIMS work, Si is generally chosen as the reference element for silicates. By means of the relative-to-Si ion yield of the element (El), defined as $IY(El/Si) = [I^+(El)/I^+(Si)]/[C(El)/C(Si)]$ (where I^+ represents the ion signal and C the atomic concentration) and derived from a calibration standard, it is possible to convert the ion-intensity ratio $I^+(El)/I^+(Si)$ from the unknown sample to the relative-to-Si concentration of the element (El) in the sample. It turns out that several matrix effects must be considered: those affecting the ionization of the isotope of the element of interest (for instance, $^7Li^+$ for Li, or $^{11}B^+$ for B) and those affecting Si, generally monitored as $^{30}Si^+$.

Here, we present the results of SIMS quantification of H, B and F, choosing Ca and/or Al, as the reference for the matrix. These data will be compared with those obtained using Si as the SIMS reference element in the same sample set, and published in [1].

---

[*] Author for correspondence. E-mail: ottolini@crystal.unipv.it

Table 1a. EMPA data (wt%) for the major/minor constituents (SiO_2, Al_2O_3, CaO, B_2O_3 and F) of the minerals in study. See [1] for more details

	Reference EMPA (wt%)						
Sample	SiO_2	Al_2O_3	CaO	H_2O*	B_2O_3	B_2O_3*	F
Phc-1	54.49						
Phc-2	54.05						
Knp-5	31.87	39.67		1.26	5.30	4.02	
Knp-6	31.94	39.71		1.27	5.70	4.03	
Dnb-7	48.55		23.09		32.30	28.25	
Dnb-8	48.75		23.05		34.90	28.33	
Axi-9	42.33	17.10	20.25	1.62	7.70	6.13	
Axi-10	42.10	17.80	20.32	1.63	7.90	6.14	
Spo-13	64.46	27.68					
Spo-14	64.38	27.74					
Sch-15	34.13	33.94		3.38	10.60	10.29	0.36
Sch-16	34.07	33.90		3.39	9.80	10.26	0.32
Drv-17	34.74	22.33	2.59	3.39	10.70	10.23	0.29
Drv-18	34.86	22.54	2.58	3.38	10.30	10.25	0.33
Elb-19	36.75	35.74		3.19	10.80	10.75	1.08
Elb-20	36.72	35.61		3.19	10.60	10.73	1.07
Mu-22a	51.34	25.71		4.45	1.00		
Mu-22b	51.34	25.71		4.45	1.00		

* Calculated by stoichiometry.

Experimental

Most of the samples for this study come from the Harvard University mineral collection and include phenacite, kornerupine, danburite, axinite, spodumene, schorl, dravite, elbaite and phengite. Three of the samples (dravite, schorl, elbaite) have been characterised by several authors [2, 3]. The phengitic muscovite was extracted from eclogite mica schists from Oropa Sanctuary, Western Alps, Italy. Each crystal was studied by SIMS in two orientations, which, depending on the crystal structure of each sample, allowed us to investigate the effect of crystallographic orientation on ion yield. EPMA methods are described in [1]. A selection of electron probe data (SiO_2, Al_2O_3, CaO, B_2O_3 and F (wt%)) was reported in Table 1a, together with the H_2O and B_2O_3 (wt%) values as derived by stoichiometry for the minerals in study. Secondary-ion signals of the following isotopes were monitored at the electron multiplier: H^+, $^{11}B^+$, $^{19}F^+$, $^{27}Al^+$, ($^{30}Si^+$) and $^{44}Ca^+$ in each analytical run. Acquisition times were 40 s (H), 20 s (B, Al, each), 60 s (F), 30 s (Si) and 40 s (Ca) over 10 cycles, under $^{16}O^-$ primary-beam bombardment ($I_p = 1$–1.5 nA) and energy-filtered secondary ions (75–125 eV emission kinetic energies). Details of the experimental set-up can be found in [1].

Results

H(Ca)

Some samples [danburite (crystals 7 and 8), axinite (crystals 9 and 10)], and our calibration standard NIST SRM 610, contain Ca in sufficient quantity for it to be used as a reference element in the quantification procedures. Those samples were used to investigate Ca/Si ionization. IY(Ca/Si) is as follows: 3.22(2) in crystal 7; 3.19(1) in 8; 3.10(1) in 9, and 3.05(1) in crystal 10. The IY is close to that derived from NIST 610 [IY(Ca/Si) = 3.47(32), average of all analytical sessions over a one-year span], and to the value of 3.26 from Hinton (1990) on the same glass [4]. In Table 1b, we report the H_2O values obtained using IY(H/Ca) as derived from IY(H/Si) for each sample and normalized to the IY(Ca/Si) value derived in the same matrix. The H_2O value in danburite 8 is comparable (or close) to our present detection limits for H in silicates, and therefore the data uncertainty is rather high.

H(Al)

Cordierite Great Bear (32.99 wt% Al_2O_3) [5] was used as the primary standard for spodumene and phengite; tourmaline standards L4e and L1v [6] were used for elbaite, schorl and dravite, respectively. Crystallographic orientation effects were negligible for all samples except phengite 22a and 22b, for which we obtained ~30% difference in H_2O concentrations (see Table 1b) with different sample orientation. The higher H_2O value pertains to the sample with the *c* crystallographic axis perpendicular to the analysis surface. As when quantifying relative to H/Si, the agreement with reference values is within the analytical uncertainty for all samples except dravite and phengite.

B(Ca)

Little has been reported about the relative-to-Ca ionization of B in silicates. In the present study, we used as a reference standard axinite 'A' (19.54 wt% CaO) that was previously investigated by EPMA and SIMS [6]; the B content was derived by stoichiometry. The IY(B/Ca) in axinite is 0.157, much lower than typical IY(B/Si) values for silicates (~0.53 for Pyrex glass), which is a result of the high ionization efficiency of Ca as a secondary positive ion. The value of IY(B/Ca) derived from axinite 'A' was used to quantify B in axinite crystals 9 and 10, and danburite crystals 7 and 8. As a comparison, in NIST 610 (B = 354.9 ppm wt; CaO = 11.827 wt%) [7], IY(B/Ca) is somewhat higher (0.163).

We also considered the possibility of quantifying B(Ca) in dravite crystal 17, that has a much lower Ca content (CaO ~2.6 wt%) than NIST 610, by using as a standard for B, the reference elbaite from Madagascar [8] which has a Ca concentration comparable to

Table 1b. Hydrogen, boron, and fluorine SIMS data for the samples studied. The values in brackets represent (1σ) standard deviations

Sample	Phc-1	Phc-2	Knp-5	Knp-6	Dnb-7	Dnb-8	Axi-9	Axi-10	Spo-13	Spo-14	Sch-15	Sch-16	Drv-17	Drv-18	Elb-19	Elb-20	Mu-22a	Mu-22b
SIMS data																		
H_2O wt% (Si)	0.017	0.019	1.34	1.35	0.016	0.011‡	1.57	1.55	b.d.l.	b.d.l.	3.41	3.51	2.81	2.77	3.16	3.20	4.90	3.73
(1σ)	(0.001)	(0.002)	(0.14)	(0.09)	(0.003)		(0.05)	(0.03)			(0.13)	(0.09)	(0.02)	(0.04)	(0.04)	(0.07)	(0.22)	(0.22)
H_2O wt% (Al)			1.32	1.32			1.50	1.58	b.d.l.	b.d.l.	3.36	3.46	2.64	2.61	3.27	3.31	5.03	3.75
(1σ)			(0.12)	(0.07)			(0.05)	(0.08)			(0.12)	(0.05)	(0.03)	(0.06)	(0.01)	(0.05)	(0.18)	(0.17)
H_2O wt% (Ca)					0.025	0.020	1.57	1.55										
(1σ)					(0.003)	(0.0014)	(0.08)	(0.02)										
B_2O_3 wt% (Si)			4.32	4.37	28.39	28.79	6.22	6.11			10.24	10.25	10.13	10.21	10.45	10.53	0.008	0.008
(1σ)			(0.01)	(0.05)	(1.16)	(0.92)	(0.06)	(0.08)			(0.08)	(0.08)	(0.08)	(0.04)	(0.09)	(0.08)	(0.0009)	(0.0009)
B_2O_3 wt% (Al)			4.14	4.22			6.33	6.30			10.40	10.43	10.00	10.00	11.02	11.05	0.009	0.008
(1σ)			(0.10)	(0.10)			(0.08)	(0.08)			(0.20)	(0.20)	(0.10)	(0.20)	(0.20)	(0.20)	(0.001)	(0.001)
B_2O_3 wt% (Ca)					30.44	31.08	6.23	6.24					9.92	9.93				
(1σ)					(0.94)	(0.99)	(0.13)	(0.07)					(0.04)	(0.13)				
F wt% (Si)			0.163	0.175			0.007	0.005			0.328	0.304	0.310	0.296	1.07	1.05	0.106	0.104
(1σ)			(0.02)	(0.03)			(0.002)	(0.001)			(0.051)	(0.033)	(0.040)	(0.041)	(0.05)	(0.05)	(0.009)	(0.006)
F wt% (Al)			0.168	0.179							0.333	0.303	0.302	0.287	1.13	1.08	0.109	0.104
(1σ)			(0.01)	(0.02)							(0.020)	(0.022)	(0.010)	(0.020)	(0.01)	(0.04)	(0.005)	(0.010)
Δ(%) H																		
SIMS-ref/ref. (Si)			6.0	6.0			−3.0	−5.0			1.0	4.0	−17.0	−18.0	−1.0	0.3	10.0	−16.0
SIMS-ref/ref. (Al)			4.0	4.0			−7.0	−3.0			0.0	2.0	−22.0	−23.0	2.5	3.8	13.0	−16.0
SIMS-ref/ref. (Ca)							−3.0	−5.0										
Δ(%) B																		
SIMS-ref/ref. (Si)			7.5	8.4	0.0	2.0	1.5	−0.5			−0.5	−0.1	−1.0	−0.4	−2.8	−1.9		
SIMS-ref/ref. (Al)			3.0	4.7			3.3	2.6			1.0	2.0	−2.2	−2.4	2.0	3.0		
SIMS-ref/ref. (Ca)					8.0	9.7	1.6	1.6					−3.0	−3.1				
Δ(%) F																		
SIMS-ref/ref. (Si)											−9.0	−5.0	7.0	−10.3	−0.8	−1.6		
SIMS-ref/ref. (Al)											−7.0	−5.0	4.0	−13.0	4.0	1.0		

Note: (Si) and, in turn (Al) and (Ca), are the reference element for the matrix used in the quantification procedures; Δ(%) represents the relative difference between the SIMS data and the concentration assumed as the reference; b.d.l. Below detection limits; ref. value of H_2O in dravite 17 and 18, calculated by the relationship $OH = 4 - F_{EMPA}$, gives high Li stoichiometric value, which is clearly overestimated (see [1]).

‡ Close to our SIMS detection limits for H_2O.

dravite. The result was low by $\sim$10% rel., significantly higher than the SIMS analytical uncertainty for B in dravite ($\sim$1% as 1σ%). The major difference in chemical composition between dravite and elbaite from Madagascar is the higher (Fe + Mn, Mg) content of the former ($\sim$14 FeO and $\sim$8 wt% MgO) versus 0.1 FeO, $\sim$4 wt% MnO and negligible Mg in the latter. Another difference lies in the Al content: $\sim$22 wt% Al_2O_3 in dravite (see Table 1a) and 38 wt% Al_2O_3 in elbaite from Madagascar. For lower values of FeO (and MgO), differences in IY(B/Ca) are smaller. This is confirmed for axinite 'A' (FeO = 7.86; MnO = 4; MgO = 0.51; Al_2O_3 = 17.31 wt%) and elbaite from Madagascar for which the IY(B/Ca) (=0.154) is similar to that for axinite 'A' (=0.157). Thus, B in dravite was quantified by applying an empirical correction to IY(B/Ca), the effect of which is to reduce the ion yield when (Fe + Mn) is higher in the matrix, as in [9].

The agreement between B by SIMS and that calculated by stoichiometry is within the analytical error (3σ) for danburite 7 and axinites 9 and 10 (Table 1b). In the latter case, the discrepancy between B by SIMS and EPMA is significant: $\sim$25% relative for the two crystals. There is no significant difference as a function of crystallographic orientation of the samples.

B(Al)

We used axinite 'A' as the primary standard for B in axinites 9 and 10. The IY(B/Al) value is 0.227(3), which coincides with 1/2 IY(B/Si) within 3σ analytical uncertainty. The ion yield derived from tourmaline L4e, belonging to our regression line for tourmaline [9], was used for kornerupine (5 and 6) and elbaite (19 and 20); schorl L1v (14.45 wt% FeO; 0.26 wt% MnO) [6] was used for schorl (15 and 16) and dravite (17 and 18). There is a slight decrease in IY(B/Al) in this compositional range relative to that for low-(Fe + Mn) tourmaline [9]. The B/Al ionization in all samples does not seem to be affected by crystallographic orientation (Table 1b).

F(Al)

Fluorine was quantified using Al as the reference element for the matrix. We used the average IY(F/Al) of topaz [10] and mica 1B [1], which was $\sim$1/2 IY(F/Si). The agreement with EPMA is $\leq$8% for schorl, with a variation of SIMS data between the two crystals (15 and 16) of $\sim$10% relative, which is comparable to the analytical uncertainty at 2σ level. Dravite crystal 17 has an average F content from SIMS analysis higher than that of crystal 18 (0.302 wt% vs. 0.287 wt% F) in accord with that obtained when quantifying relative to Si, but on the whole the concentrations are comparable at 1σ standard deviation. The difference between EPMA and SIMS results is $\leq$15% relative, which is on the order of EPMA analytical error at this level of concentration for F.

Discussion

A decrease in the relative-to-Al ion yield of H, B and F with increasing (Fe + Mn) content in the matrix occurred throughout the sample set, independent of crystal structure; conversely, high Al (Si) concentrations are associated with higher light-element ion-yields. This confirms results previously obtained for tourmaline [9] and other silicates ([11] and references therein) with variable Fe (+Mn) content of the matrix. Changes in IY(El/Al) are similar to those for IY(El/Si) and the amount of variation is, on average, comparable.

The use of Ca for light-element calibration in silicates is uncommon in SIMS work. Our investigations on the quantification of Rare Earth Elements (REE) and other heavy elements in complex matrixes indicated lower variability in IY(REE/Ca) than IY(REE/Si) with varying chemical composition of the matrix (see for instance [12]). In the present study, matrix effects on B/Ca ionization are limited. The maximum difference between IY(B/Ca) from NIST 610, axinite 'A', elbaite from Madagascar and dravite (assuming for the latter the stoichiometric value for B) is $\sim$18% relative.

This study shows that the most significant SIMS matrix effects for light elements are related to different chemical composition of the matrix, and crystallographic orientation of the sample (except in mica) plays a minor role. SIMS matrix effects related to crystallographic orientation are within 10% relative for all samples analyzed. The only structure for which there is a significant influence of crystallographic orientation ($\sim$30% relative) on H^+/Al^+ (and H^+/Si^+) intensity ratios, is phengite. These results suggest strong orientation effects and need to be followed by an examination of several mica samples of differing composition to see if the orientation effect is reproducible. Nevertheless, if we average both SIMS determinations of H_2O (relative to two crystallographic orientations), we obtain an experimental value for H_2O which agrees with stoichiometry within 1.4% relative using Al as the inner reference element for the matrix.

Conclusions

H, B and F were quantified by SIMS in a suite of minerals [1] using, in turn, Al and Ca (instead of the more used Si) as the reference element for the matrix. The accurate results obtained indicate that these two elements may be used in the quantification procedure. Moreover, on the basis of our experience and on literature data [4], it seems that $\mathrm{IY(El/Si)}$ is sensitive to changes which occur with time and with differing ion-bombardment conditions. Variations in ion yield are also dependent on changes in beam density and focusing across the sample during analysis. Using Al or Ca instead of Si, the ion yields for light elements in silicates seem to be more stable with time and less sensitive to instrumental conditions.

The light elements that can be profitably analysed by SIMS includes volatiles such as C, Cl and N, and low-Z elements such as Li and Be (see Ottolini et al., 2002 and reference therein). C and N analysis as secondary positive ions in silicates requires high-mass resolution. Cl^+ is generally investigated by SIMS using both ($^{35}Cl^+$, $^{37}Cl^+$) isotope signals [13].

The extension of the SIMS quantification in minerals and natural glasses in Earth Sciences will benefit from the development and adoption of carefully certified trace-level, homogeneous samples for various matrix chemical compositions. Artificial glasses seem to be very promising in the quantitative analysis of light elements such as Li and B (see, for instance [14]). Ion-implanted samples could be, in principle, usefully adopted for the standardization of light and volatile elements. So far, however, their use is rather scarce in the Earth Sciences. At CNR-IGG (Pavia) we are currently testing several natural and artificial glasses as calibration materials for a wide range of silicate matrixes.

References

[1] Ottolini L, Cámara F, Hawthorne F C, Stirling J (2002) Amer Mineral 87: 1477

[2] Dyar M D, Taylor M E, Lutz T M, Francis C A, Guidotti C V, Weise M (1998) Amer Mineral 83: 848

[3] Cámara F, Ottolini L, Hawthorne F C (2002) Amer Mineral 87: 1437

[4] Hinton R W (1990) Chem Geol 83: 11

[5] Vry J K, Brown P E, Valley J W (1990) Amer Mineral 75: 71

[6] Andreozzi G B, Ottolini L, Lucchesi S, Graziani G, Russo U (2000) Amer Mineral 85: 698

[7] Pearce N J G, Perkins W T, Westgate J A, Gorton M P, Jackson S E, Neal C R, Chenery S P (1997) Geostand Newslett 21: 115

[8] Aurisicchio C, Demartin F, Ottolini L, Pezzotta F (1999) Eur J Mineral 11: 237

[9] Ottolini L, Hawthorne F C (1999) Eur J Mineral 11: 679

[10] Barton M D, Haselton H T Jr, Hemingway B S, Kleppa O J, Robie R A (1982) Amer Mineral 67: 350

[11] Ottolini L, Hawthorne F C (2001) J Anal Atom Spectrom 16: 1266

[12] Ottolini L, Oberti R (2000) Anal Chem 72: 3731

[13] Scambelluri M, Müntener O, Ottolini L, Pettke T T, Vannucci R (2004) Earth Planet Sci Lett 222: 217

[14] Le Fevre B, Ottolini L (2005) Microchim Acta 155: 189