

Original Paper

New SIMS Procedures for the Characterization of a Complex Silicate Matrix, $\text{Na}_3(\text{REE,Th,Ca,U})\text{Si}_6\text{O}_{15} \cdot 2.5\text{H}_2\text{O}$ (Sazhinite), and Comparison with EMPA and SREF Results

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Received May 22, 2003; accepted October 20, 2003; published online February 23, 2004

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Abstract. Analytical methods based on secondary ion mass spectrometry were developed for the characterisation of a complex layered silicate REE-mineral, named sazhinite, for which a number of issues are still open regarding its chemistry and structure. Such procedures involved the analysis and quantification of light, volatile, alkaline, medium-Z, rare earth and actinide elements. The accuracy of the SIMS data is within the assigned precision of the concentration values assumed as reference in the calibration standards employed. REE and actinide data yield a good agreement in terms of calculated site scattering at the M site: 58.42 electrons per formula unit (epfu) vs. 60.39 epfu obtained by Single Crystal Structure-Refinement (SREF). Accuracy is estimated on the order of 5% rel. for H, Li, Be and B, and 10% rel. for F. Na analysis was crucial to solve the open questions about the structure, and excellent agreement was obtained by comparing data from SIMS (REE, Y, actinides, Na) + EMPA (SiO_2 , CaO, SO_3 and K_2O) with information derived from SREF: site scattering of the M site + Na sites = 92.56 epfu calculated from chemical data, against 91.95 epfu from SREF. Such

procedures can be easily extended to the analysis of variously complex, silicate REE-minerals.

Key words: SIMS; EMPA; SREF; REE and actinides; light and volatile elements; sazhinite.

Sazhinite is a layered REE-, volatile-rich mineral, with simple wavy layers of silicon tetrahedra $[\text{Si}_6\text{O}_{15}]^{6-}$ that are linked by REE in seven-fold coordination (capped octahedron). The silica–REE framework gives rise to channels that host alkali cations and water molecules. Studies on analogous $\text{MSi}_6\text{O}_{15}$ -based silicates ([1] and references therein) report high metal exchange properties for similar frameworks.

Sazhinite was first described as $\text{Na}_3\text{CeSi}_6\text{O}_{15} \cdot 6(\text{H}_2\text{O})$ [2] occurring in the Jubilee alkaline pegmatite at Mt. Karnasurt, Lovozer massif, Kola Peninsula (Russia). Shumyatskaya et al. (1980) [3] described its structure. Since then, it has only been reported in two additional localities: at the Poudrette quarry, Mont Saint-Hilaire, Québec, Canada [4, 5], and at the Demix-Varennes quarry, Saint-Amable sill, Varennes, Verchères Co., Québec, Canada [6].

A number of issues are still open regarding its chemistry and structure: the species and quantity of alkali cations, and coordinating water molecules within the channels; accurate quantification of REE

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and possible actinides; the presence and location of other minor additional chemical species such as fluorine and sulphur. Although the content of alkali cations and light REE can be readily measured in small sample volumes with electron-probe methods, EMP analysis of H and Li is not possible, and accurate quantification of heavy lanthanides and actinides is not straightforward due to complex interferences and background corrections. Furthermore, the presence of Na, which is weakly bonded within the channels, may give rise to diffusion processes within the matrix under the electron beam, yielding underestimation of the actual contents of this element. This effect can be even enhanced by channelling phenomenon depending, in this matrix, on the crystallographic orientation of the structure channels relative to the e-beam.

Accurate results were achieved with a proper selection of standards, correction of interferences, and study of matrix effects. The SIMS data were then compared with those derived by EMPA, and all the analytical “oddities” discussed. Moreover, in order to supply additional constraints to the chemical composition, single crystal X-ray diffraction (XRD) and structure refinement (SREF) were performed on one single crystal prior to its analysis by EMP and SIMS. Both information were then combined and used to obtain the element partitioning in each structural site.

Experimental

In this work we have studied a couple of crystals from a new occurrence of sazhinite at Aris phonolite, which is located about 25 km south of Windhoek, Namibia. The samples were collected from a quarry being mined for road and railway ballast. The phonolite is highly vesicular, fine-grained, aphyric and consists of other mineral species as alkali feldspars, nepheline and acmite, with minute accessory apatite, zircon, and monazite [7]. The vesicles in our samples range from <1 mm to over 10 cm in diameter. New mineral species have also been described in the same locality [8, 9].

In addition to sazhinite, the vesicles contain villiaumite, natrolite, aegerine, microcline, apophyllite, analcime, fluorite, hydroxyapatite, galena, sphalerite, makatite, quartz, kanemite [10] and taperssuatsiaite [8, 9].

Structure Refinement (SREF)

Most of sazhinite crystals found in these vesicles are altered to secondary products. Some others consist of a polycrystalline aggregate. After careful inspection under polarised light, we selected one single crystal of sazhinite suitable for X-ray diffraction (crystal 1). Complete collection of diffraction data was done using a Bruker-AXS SMART-Apex single crystal diffractometer. Details of data collection and structure refinement strategies will be described elsewhere.

Electron Microprobe Analysis (EMPA)

The crystal 1, used for X-ray diffraction, and another (hereafter called crystal 2) were embedded in one epoxy mount. Analyses were done using a Cameca SX100 electron microprobe at the B. Pascal University (Clermont-Ferrand, France). Natural and synthetic compounds were used as standards. Analysing crystals and standards were: TAP for Na, Si (albite) and F (apatite); PET for K (orthoclase), Ca (wollastonite), Th (ThO₂), S (baryte); LIF for LREE, and PET for Y. Synthetic Ca–Al–silicate glasses REE1, REE2, and REE3 [11] were the standards selected for La, Ce, Pr, Nd and Y calibration. Data were corrected using Cameca built-in $\varphi(\rho-Z)$ spinoff. Comparison with standard ZAF procedures yielded basically identical results.

Strong beam damage occurred in sazhinite for high probe-currents even when using defocused beam. For this reason we chose two sets of analytical conditions for each analysis: a first counting time of 10 s for Na and Si at 15 kV and 2.0 nA, then 15 kV and 30 nA for the other elements, with counting times of 10 s (K, Ca, Th, S, La, Ce), 20 s (Pr, Nd, Y) and 60 s (F). In all cases, the electron probe was defocused to 5 μ m.

REE analysis with the electron microprobe is impeded by line interference for REEs above Ce. $L\beta$ lines were used for Pr and Nd because their $L\alpha$ lines interfere with La and Ce $L\beta$ lines, respectively. In addition, preliminary observations and qualitative X-ray maps were performed using a Jeol JSM-5910LV SEM fitted with a PGT EDS microanalysis system.

Investigation of the Na loss with the microprobe showed that the very “mild” conditions used for this element are barely sufficient to insure accurate analysis of this element. The highest Na counts were obtained using 15 kV, 2 nA, and 10- μ m defocused beam, but the small size of the crystals and their numerous cleavages led us to choose a 2-nA and 5- μ m defocused beam for most analyses. No beam damage was visible for those analytical conditions. Other elements were checked to be immobile under the high beam current (30 nA) -required for achieving proper detection limits- even if extensive beam damage was apparent.

Secondary Ion Mass Spectrometry (SIMS)

A Cameca IMS 4f ion microprobe installed at CNR-IGG (Pavia) was used in this study. After structure refinement (SREF) of single-crystal X-ray diffraction data on crystal 1 and EMP analysis in both crystals 1 and 2, the mount was gold coated (~ 400 Å thickness) in order to minimise charge pile up during analysis.

Measurements of Na, K, Sc, Ti, V, Cr, Rb, Sr, Y, Zr, Nb, Cs, Ba, REE, actinides (U, Th) were done with a $^{16}\text{O}^-$ primary beam, accelerated at 12.5 kV, with 1 nA current intensity. The focused beam diameter was <5 μ m. The width of the energy slit was 50 eV, and the voltage offset applied to the sample accelerating voltage (+4500 V) was -100 V under the 25- μ m image field, the 400- μ m contrast diaphragm and the 1800- μ m field aperture.

The crystals were analysed by cycling through the series of masses in automatic peak-jumping mode. Peaks were magnetically centred by calibration carried out on NIST SRM 610 glass. During sputtering (300 s) the magnet was cycled repeatedly through the masses in order to minimise hysteresis effects, and the analysis was done over the next 5 cycles. The SIMS methods employed here for trace-element analysis were similar to those previously developed for silicates [12]. The main differences in the mass acquisition list concern the following: (i) the additional detection of Na at 23 mass number (u) and Pr at mass 141; (ii) shorter counting times per cycle for LREE (i.e., 2, 2, 4 s for La, Ce and Pr, respectively), and MREE (4 and 12 s for Nd and Sm, respectively); longer counting times for all HREE (10 s for Dy, Er and Yb, each). Y was added as $^{89}\text{Y}^+$, Ba

as $^{137}\text{Ba}^+$ and the actinides as $^{232}\text{Th}^+$ and $^{238}\text{U}^+$ secondary ions (overall counting times over 5 cycles: 25 s for Y and Ba each, 50 s for Th and U, each). Ion intensities were thus detected at masses 23 (Na), 30 (Si, assumed as the inner reference element for the matrix), 39 (K), 45 (Sc), 47 (Ti), 51 (V), 52 (Cr), 85 (Rb), 88 (Sr), 89 (Y), 90 (Zr), 93 (Nb), 133 (Cs), 137 (Ba), 139 (La), 140 (Ce), 141 (Pr), 146 (Nd), 149 (Sm), 163 (Dy), 167 (Er) and 174 (Yb). Eu and Gd ion signals were obtained by deconvolution of the secondary-ion mass spectrum at mass numbers 151, 154, 156, 158, 162 by taking into account the interferences from BaO (on Eu), CeO and NdO on Gd (and Dy), respectively. Treatment of such oxide interferences on Gd and Eu, as well as those on $^{167}\text{Er}^+$ ($^{151}\text{Eu}^{16}\text{O}^+$) and $^{174}\text{Yb}^+$ ($^{158}\text{Gd}^{16}\text{O}^+$), is similar to that described in [13]. Furthermore, Sc concentration was obtained after correction of interferences due to $^{29}\text{Si}^{16}\text{O}^+$ at mass number 45 u.

Analytical sessions for H, F, and other light elements were carried out on the two crystals (1 and 2) on separate days from those of other elements, to permit the crystals to be degassed at the vacuum of $\sim 1.33 \times 10^{-7}$ Pa with the proper H-reference sample in the dual specimen holder inlet chamber. The primary O^- current intensity was 1 nA. Analyses were performed after 10-min bombardment at the same sites previously investigated in terms of trace elements. In order to avoid any topographic effects due to the pre-existing craters, the crystals were polished smoothly before analysis and gold coated again. The fingerprint of previous spots allowed for light-element investigation at the same sites. Even if the sample homogeneity is unknown in depth, we believe that this approach is reasonably accurate to match analytical data for H, Li, Be, B, F with those derived for the other heavier elements at the sites selected in the two crystals. Counting times were: 20 s for H^+ , 10 s for $^7\text{Li}^+$ and Be each, 15 s for $^{11}\text{B}^+$, 20 s for $^{19}\text{F}^+$ and 15 s for $^{30}\text{Si}^+$.

Standards with uniform, high REE- and actinide concentrations, and major-element composition similar to that of our samples in study are not available. We considered the similarity of silica content between standard(s) and our crystals as the best choice in the standardisation procedure. On the basis of our previous experience, Si in silicates changes its ionisation as a function of the silica content itself ([14] and reference therein). Moreover, high-silica silicates show higher ion yields (IY) for REE than those in low-silica samples. This result was obtained in comparing IY(REE/Si) for ultramafic/mafic rock samples with those derived from acidic ones, all the samples being analysed as fused glass beads [15].

In the present study, we made the hypothesis that major matrix effects are related to the silica content: as standards we used NIST SRM 610 and a basalt reference sample represented by the BB glass [16]. The ion yields used in the quantification of all the elements represent the best fit between those derived from NIST-610 ($\text{SiO}_2 = 72.276$ wt%) and BB ($\text{SiO}_2 = 49.83$ wt%).

Ceran [17], Pyrex, and a danalite sample were chosen for the quantification of Li, B and Be, respectively [17]. Tremolite [18] was used for H, whereas britholite Los [16] was selected for F. In the latter case, due to the very different silica content between britholite Los and the samples in study, we made proper corrections to the IY(F/Si).

Results and Discussion

SREF

As it is well known, SREF can allow precise determination of the scattering power at each site (s.s., expressed in terms of electrons per site) as well as a

precise description of the coordination geometries and thus of the bonding features. Structure refinement allowed us to identify four tetrahedral sites occupied by Si (T-sites), one capped octahedron (M-site) that hosts REE, Ca, Th and U, and three interchannel sites occupied by Na and K (Na-sites) and coordinated with water molecules (O12, O13, and O14 sites) in three structural sites within the channels (Fig. 1). In terms of refined site scattering we obtained 31.56 ± 10 electrons per formula unit (epfu) at the interchannel Na-sites and 60.39 ± 11 epfu at the M-site. One of the Na-sites (Na3) and one of the water molecule sites (O14) are only half occupied due to geometrical constraints. Hence, the stoichiometry of sazhinite is $\text{Na}_3(\text{REE}, \text{Th}, \text{Ca}, \text{U})\text{Si}_6\text{O}_{15} \cdot 2.5(\text{H}_2\text{O})$.

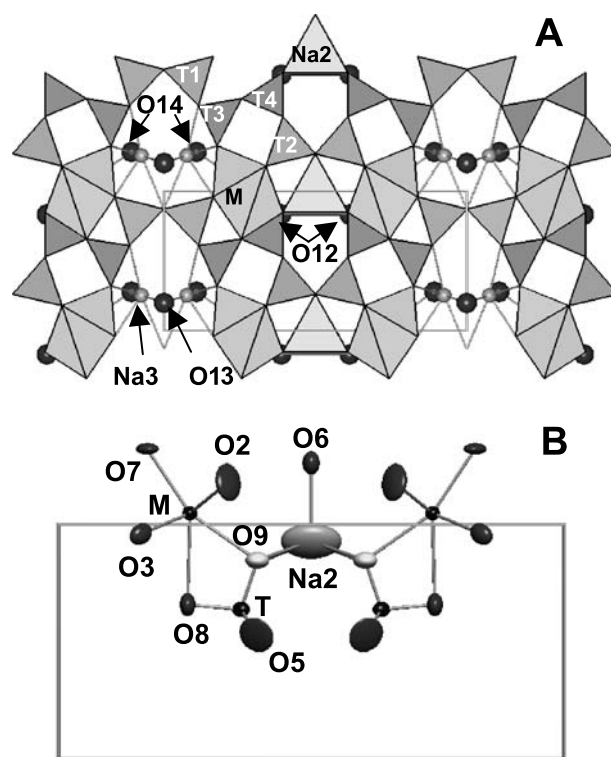


Fig. 1. The sazhinite structure projected onto (100) plane: (A) Location of crystallographic sites are shown. Sites with 4-fold coordination (T1, T2, T3, T4) host Si. REE, Th, U, Y, Zr, Ca (and trace quantities of Ti, Sc, Nb) enter the 7-fold coordinated M site. Na and K are present at the channels at 5-fold and 6-fold coordinated Na1, Na2 and Na3 sites. The Na1 site is located under the M in this projection. H_2O molecules are located at the O12, O13, and O14 sites within the channels, coordinating Na atoms. (B) Detail of the coordination environment of the O9 site. High charge substitutions at the M and T4 sites can be locally charge balanced by $\text{O} = -1\text{F}_1$ substitution at the O9 site

EMPA

Averages of analyses performed in the two crystals are reported in Table 1. Overall analytical uncertainty for each chemical specie are also reported. Significant S contents were observed by EMPA, and they show a negative correlation with Si abundance. In fact, the T4-site exhibits a mean bond length (1.604 Å) which is smaller than the predicted value from the sum of the ionic radii of Si + O ($^{[IV]}Si^{4+} = 0.25$ Å and $^{[III]}O^{2-} =$

1.36 Å [19]) in agreement with up to 10% sulphur ($^{[IV]}S^{6+} = 0.12$ Å) hosted at this site. Local charge balance is obtained by O₁F substitution at O9 site, which coordinates the T4, M and Na2 sites and compensates for the excess charge from Th at the M site and S at the T4 site (Fig. 1B). Therefore, analyses were normalised on the basis of Si + S = 6 atoms per formula unit (apfu). The analytical results testify a significant chemical heterogeneity in a single grain, La, Ce and Th being the species that vary mostly.

Table 1. Averages of EMPA data in the different contrast areas shown in Fig. 2

Zone	Crystal 1		Crystal 2		
	1	2	3	4	5
SiO ₂	53.99 ± 1.43	52.05 ± 1.39	53.11 ± 1.41	54.82 ± 1.45	52.95 ± 1.40
La ₂ O ₃	10.98 ± 0.24	10.10 ± 0.23	9.27 ± 0.21	12.48 ± 0.26	9.07 ± 0.21
Ce ₂ O ₃	9.27 ± 0.22	8.39 ± 0.20	11.16 ± 0.25	11.21 ± 0.25	9.97 ± 0.23
ThO ₂	3.60 ± 0.19	8.35 ± 0.27	5.50 ± 0.22	0.76 ± 0.12	3.69 ± 0.20
Y ₂ O ₃	0.19 ± 0.04	0.05 ± 0.03	0.07 ± 0.03	0.00 ± 0.00	0.84 ± 0.08
Pr ₂ O ₃	0.30 ± 0.07	0.41 ± 0.07	0.43 ± 0.07	0.39 ± 0.07	0.43 ± 0.07
Nd ₂ O ₃	0.43 ± 0.12	0.29 ± 0.12	0.64 ± 0.12	0.05 ± 0.06	0.88 ± 0.12
CaO	0.65 ± 0.03	0.33 ± 0.02	0.14 ± 0.02	0.37 ± 0.02	0.26 ± 0.02
K ₂ O	0.16 ± 0.02	0.20 ± 0.02	0.25 ± 0.02	0.11 ± 0.02	0.30 ± 0.02
Na ₂ O	6.59 ± 0.28	7.99 ± 0.31	10.98 ± 0.36	11.69 ± 0.37	10.70 ± 0.35
Na ₂ O ^a	13.95	13.55	13.60	14.07	13.47
F	0.19 ± 0.02	0.33 ± 0.03	0.15 ± 0.02	0.12 ± 0.02	0.13 ± 0.02
H ₂ O ^a	6.81	6.63	6.85	6.67	6.62
SO ₃	0.70 ± 0.06	1.35 ± 0.08		0.39 ± 0.05	0.02 ± 0.04
TOTAL	100.54	100.66	101.20	101.00	98.61
O=F	0.08	0.14	0.05	0.06	0.05
TOTAL	100.46	100.52	101.15	100.94	98.56
Si	5.942	5.886	5.967	6.000	5.998
S	0.058	0.114	0.033	0.000	0.002
Σ T	6.000	6.000	6.000	6.000	6.000
Na ^a	2.978	2.971	2.964	2.986	2.957
K	0.022	0.029	0.036	0.015	0.043
Σ Na-sites	3.000	3.000	3.000	3.000	3.000
Na	1.407	1.753	2.393	2.483	2.363
Ca	0.077	0.040	0.016	0.044	0.031
La	0.446	0.421	0.384	0.504	0.379
Ce	0.374	0.347	0.459	0.449	0.413
Pr	0.012	0.017	0.018	0.016	0.018
Nd	0.017	0.011	0.026	0.002	0.036
Th	0.090	0.215	0.141	0.019	0.095
Y	0.011	0.003	0.004	0.000	0.051
Σ M-site	1.027	1.054	1.048	1.032	1.023
F	0.068	0.118	0.053	0.039	0.046
OH	5.000	5.000	5.000	5.000	5.000
Na ss _(calc) ^a	33.17	33.23	33.29	33.12	33.34
Na ss _(calc) ^b	16.50	20.14	24.14	27.89	27.12
M ss _(calc) ^b	58.93	66.08	64.27	58.34	59.95

^a Calculated by stoichiometry on the basis of SREF results.

^b ss_(calc): site scattering calculated from chemical formulae in electrons per formula unit.

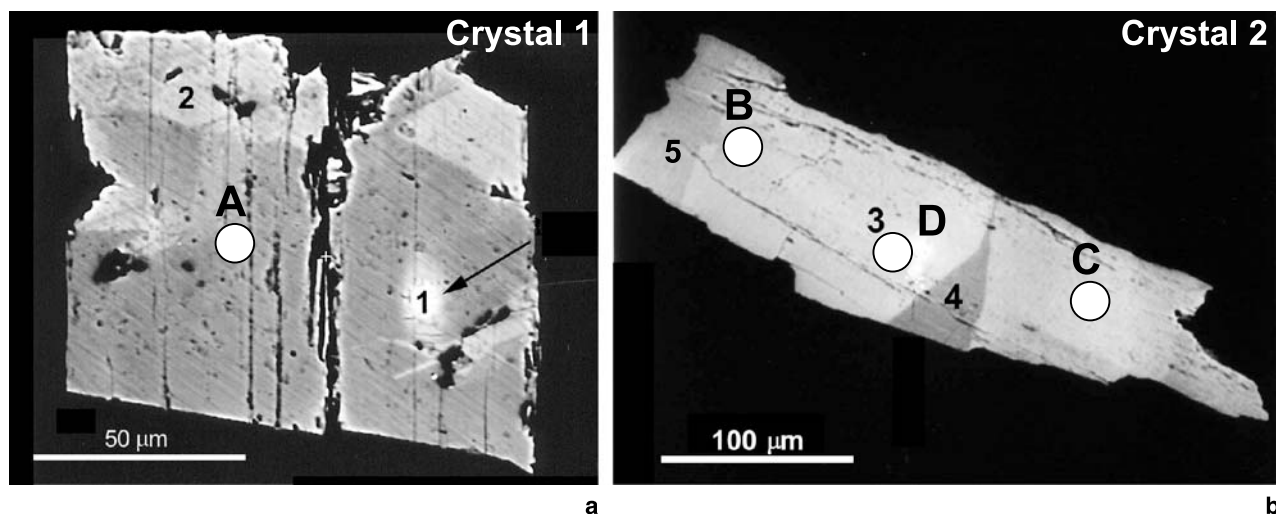


Fig. 2. Back scattered electron images of crystal 1 (a) and 2 (b) showing the different contrast zones analysed by EMP (1–5) and SIMS (A–D) analyses

Crystal 1 is La-dominant (i.e., $\text{La} > \text{Ce} > \text{Th}$), whereas crystal 2 is Ce-dominant ($\text{Ce} > \text{La} > \text{Th}$). In both crystals Th changes dramatically from zone to zone. Figure 2 reports back-scattered electron (BSE) images of the two studied crystals. Different contrast in those images corresponds to the chemical variations in REE and Th. The agreement between EMPA and SREF is limited by the missing elements, mainly medium-, heavy-REE and U, the only heavy elements investigated being La, Ce, Pr, Nd and Th.

SIMS

Close agreement (1.3% rel.) was shown for $\text{IY}(\text{Na}/\text{Si})$ $[(\text{Na}^+/\text{Si}^+/\text{Na}(\text{at})/\text{Si}(\text{at}))]$ between NIST-610 and BB glass standards. On the whole, the discrepancy between the ion yields was typically $\leq 5\%$ for all the elements (exceptions: $\sim 10\%$ for Ce and Er, 14% for Yb, $\sim 12\%$ for Pr, $\sim 20\%$ for Sc and 8% for Zr). These differences are within the uncertainty of the concentration data assumed here as the reference values (mostly within 1–2 standard deviations) for each element analysed in both standards. Thus, the accuracy of the SIMS data is on the order of the assigned precision of the concentration values assumed as reference in the standards. SIMS analyses of REE and actinides in crystal 1 yield a good agreement in terms of calculated site scattering at the M site (58.42 epfu vs. 60.39 epfu obtained by SREF).

Concentration is rather low, at the level of few tens of ppm (by wt) for Li and B and at ppm level for Be. A water content by $\sim 2 \text{ wt}\% \text{ H}_2\text{O}$, well less than originally expected by stoichiometric considerations from

SREF data (ca. 6.8 wt%), was found in both crystals. Fluorine concentration is significant and on the order of few thousands of ppm. Accuracy for light elements is estimated on the order of 5% rel. for H, Li, Be and B, and 10% rel. for F. Element concentration obtained by SIMS are reported in Table 2.

The discussion about the agreement between EMPA and SIMS for heavy elements will be confined to La, Ce, Pr, Nd, and Th for the actinides. While for La, Ce and Th there is a close agreement (Fig. 3A), for Pr and Nd the differences are significant. Such a discrepancy is much higher than the overall uncertainty on the concentrations of Pr and Nd in the SIMS standards adopted as well as than the reproducibility errors in the SIMS analysis of REE (typically, on the order of few percent rel. or better). Concerning the Pr and Nd measurements at the electron micro-probe, their concentrations are close to the detection limits ($\text{DL} = 0.21$ and $0.36 \text{ wt}\%$ for Pr and Nd, respectively), so the error is high. The absolute errors on EMP analysis depend on the peak/background ratios for both standards and unknowns. The detection limits are high for Pr and Nd because of the interferences with La and Ce which increases the background. It is critical with sazhinite since La and Ce are more abundant than in the synthetic glasses used as standards. If we now consider the full errors, then the EMP and SIMS data should be nearly within the error range.

Worse results are obtained for light elements, especially for Na by EMPA. In spite of the particular analytical conditions chosen for the EMP analyses, Na content was always lower than that predicted by

Table 2. SIMS data at the different locations shown in Fig. 2(a,b). Concentration data are reported as ppm (wt) and ox. (wt%)

Point Zone	Crystal n.1		Crystal n.2						
	A	A	B	B	C	C	D	D	
	1	1	3	3	3	3	3	3	
	ppm	ox. (wt%)	ppm	ox. (wt%)	ppm	ox. (wt%)	ppm	ox. (wt%)	
La	86833	10.18	65696	7.70	68159	7.99	85507	10.03	La ₂ O ₃
Ce	74127	8.68	107679	12.61	102175	11.97	90623	10.61	Ce ₂ O ₃
Pr	4826	0.565	7316	0.856	7212	0.844	5290	0.619	Pr ₂ O ₃
Nd	9256	1.080	13906	1.622	12734	1.485	10113	1.180	Nd ₂ O ₃
Sm	659	0.076	878	0.102	849	0.098	511	0.059	Sm ₂ O ₃
Eu	104	0.012	117	0.014	114	0.013	66	0.008	Eu ₂ O ₃
Gd	364	0.042	419	0.048	342	0.039	100	0.011	Gd ₂ O ₃
Dy	385	0.044	131	0.015	144	0.016	48	0.005	Dy ₂ O ₃
Er	234	0.027	46	0.005	54	0.006	20	0.002	Er ₂ O ₃
Yb	217	0.025	33	0.004	45	0.005	17	0.002	Yb ₂ O ₃
Th	31905	3.631	36185	4.117	34669	3.945	40541	4.613	ThO ₂
U	1945	0.221	1000	0.113	1100	0.125	269	0.031	UO ₂
Na		13.6		15.4		15.7		15.8	Na ₂ O
K	5074	0.611	4615	0.556	4362	0.525	4370	0.526	K ₂ O
Li	82.3	0.018	12.7	0.0027	26.7	0.0058	27.2	0.0059	Li ₂ O
Be	0.5		0.2		0.8		2.2		
B	136.6	0.044	43.5	0.014	46.6	0.015	90.1	0.029	B ₂ O ₃
H		1.79		1.91		1.97		1.68	H ₂ O
F	4110	0.411	1200	0.120	1900	0.190	3270	0.327	F
Sc	2.8		0		0.8		3.5		
Ti	22	0.004	26.7	0.004	8	0.001	14	0.002	TiO ₂
V	6.8		7.5		6.4		8.0		
Cr	0.6		0.5		0.5		0.5		
Rb	42		23		21		34		
Sr	1269	0.150	183	0.022	247	0.029	1696	0.201	SrO
Y	1963	0.249	485	0.062	574	0.073	162	0.021	Y ₂ O ₃
Zr	1360	0.184	210	0.028	266	0.036	39	0.005	ZrO ₂
Nb	189	0.027	134	0.019	16	0.002	117	0.017	Nb ₂ O ₅
Cs	45		34		32		28		
Ba	64	0.007	21	0.002	22	0.002	58	0.006	BaO

stoichiometry from SREF data (Fig. 3B). In sazhinite, Na is located in channels of the structure and bonded to water molecules. Partial volatilisation of water under the electron beam probably aggravates the usual mobility of Na. In particular, Na by EMPA is much lower for crystal 1 (52% lower), in clear disagreement with SREF results. We make the hypothesis that besides the e-beam damage, crystal 1 has been embedded in a preferential crystallographic orientation, i.e., with one set of channels parallel to the electron beam during the analysis. This is supported by the very distinct traces of cleavage on Fig. 2a, indicating that the beam was nearly parallel to the corrugated silicate layers for crystal 1, contrary to crystal 2. The overall result is thus an enhanced Na migration promoted by the beam by channelling effects. SIMS is in better agreement with SREF results. Interestingly, Na content by SIMS in crystal 2 is higher by ~10% rel. than that in crystal 1. The SIMS results on both crystals were confirmed by analytical tests carried out

on different days, showing that such a discrepancy is real and higher than the uncertainty derived from Na calibration. Unfortunately, for crystal 2 we do not have any constraint from SREF. An hypothesis is that its Na content is higher than that in crystal 1. More likely, crystal 2 is in a different crystallographic orientation, i.e., its corrugated silicate layers are more or less parallel to the mount surface. If it is the case, it is very probable that we are in the presence of SIMS matrix effects related to the crystal structure, similar to those affecting H/Si ionisation in micas [20].

Table 3 reports the final formula obtained with data from SIMS (REE, Y, actinides, Na, light and volatile elements) + EMPA (SiO₂, CaO, SO₃ and K₂O), and comparison with information derived from SREF, carried out in crystal 1. The agreement on the chemistry of the Na sites and of the M site in terms of electrons per formula unit is within a 3.2% and 0.7% rel., respectively. This excellent agreement allow us to give an answer to the open questions on this complex

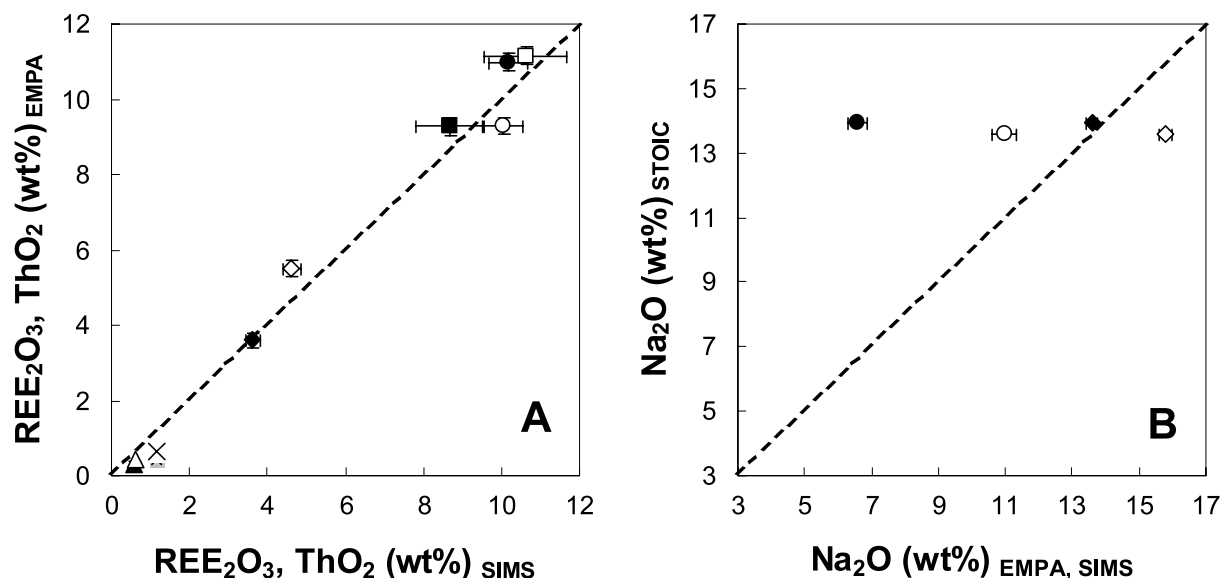


Fig. 3. Agreement between: (A) EMPA and SIMS data for REE and Th (dots: La_2O_3 ; squares: Ce_2O_3 ; diamonds: ThO_2 ; triangles: Pr_2O_3 ; crosses: Nd_2O_3); (B) stoichiometric Na_2O content (as obtained from single crystal X-ray diffraction), SIMS (diamonds) and EMPA (dots). In both figures, filled and open symbols indicate crystal 1 and 2, respectively

Table 3. Formula on the basis of $(\text{Si} + \text{S}) = 6$ atoms per formula unit, obtained with SIMS analyses (Table 2) and EMPA (Table 1, SiO_2 , CaO , SO_3 , K_2O) for crystal 1, the only one (of the two) investigated by SREF

Si	5.942	Ca	0.077
S	0.058	La	0.417
Σ T sites	6.000	Ce	0.353
		Pr	0.023
B	0.008	Nd	0.043
		Sm	0.003
Sr	0.010	Eu	0.000
Li	0.008	Gd	0.002
Na	2.928	Dy	0.002
K	0.020	Er	0.001
Ba	0.000	Yb	0.001
Σ Na sites	2.966	Zr	0.010
		Th	0.092
Na ss _(calc) ^a	32.59	U	0.005
M ss _(calc) ^a	59.97	Y	0.015
Na ss _(obs) ^b	31.56	Σ M	1.044
M ss _(obs) ^b	60.39		
Δ Na ss (% rel)	3.2	F	0.144
Δ M ss (% rel)	0.7	OH	1.326

^a ss_(calc): site scattering calculated from chemical formulae in electrons per formula unit.

^b ss_(obs): site scattering obtained by SREF.

silicate: there are three alkaline sites within the channels Na1, Na2 and Na3, which host Na and minor quantities of K, Li, Rb, Cs, Sr, and Ba; the capped octahedron hosts light-to-heavy REE, being LREE the most abundant, as well as significant although never dominant quantities of Th, and minor quantities of U,

Y, Nb, Zr, Ti, V, and Sc; four tetrahedral sites host Si, while minor quantities of S (and trace quantities of B and Be) may be hosted at the T4 site, and local charge balance may be achieved by O_{-1}F substitution at the O9 site; there are three different crystallographic positions occupied by H_2O within the channels. Water contents found by SIMS analyses are on the order of 1:4 when compared to stoichiometric values. This is compatible with the lost of ~ 2 water molecules under extreme vacuum conditions in the ion probe sample chamber (1.33×10^{-7} Pa). We cannot discern which water molecule is degassed. However, it is highly probable that those are the ones at the O12 and O14 sites. The O13 site presents short distances with Na3 than the other water molecules. This implies a stronger interaction and thus the water molecule at O13 would have more difficulty to leave the structure. In terms of unit formula, the lost of water molecules at O12 and O14 implies the lost of ~ 2 water molecules.

The nice agreement between EMPA and SREF for the M site (Table 1) must be interpreted as circumstantial, since in the comparison with SIMS data it seems that EMPA overestimates some LREE and Th, and underestimates Pr and Nd, whereas U and HREE are dropped in the EMP analysis due to their low concentrations.

Finally, the complete characterisation of the chemistry of this silicate reveals that its structure is able to

host significant quantities of actinides (U, Th) at the M site. Such properties would make this material a feasible candidate for radioactive waste sieving.

Acknowledgements. We thank R. Gastoni and M. Palenzona, M. Veschambre and J.-L. Devidal for sample preparation and instrument maintenance. The Italian CNR is acknowledged for financing the ion microprobe at IGG (Pavia). D. Shannon and L.A.J. Garvie kindly provided the samples and isolated sazhinite crystals, respectively. "This work was supported in part by the European Community's Human Potential Programme under contract HPRN-CT-2002-002 "Euromelt", and in part, by the Italian CNR".

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