

Fluoride–silicate melt immiscibility and its role in REE ore formation: Evidence from the Strange Lake rare metal deposit, Québec-Labrador, Canada

Olga Vasyukova^{*}, Anthony E. Williams-Jones

Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, Quebec H3A 0E8, Canada

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Abstract

Pegmatites and adjacent subsolvus granites (two alkali feldspars) of the Mid-Proterozoic Strange Lake pluton (Québec-Labrador, Canada) host potentially economic concentrations of high field strength elements (HFSE), including the rare earth elements (REE), zirconium and niobium. Previous studies have proposed that these concentrations were the result of a combination of extreme fractionation of a peralkaline granitic magma and later hydrothermal remobilization. However, the recent discovery of melt inclusions which, after heating to 900 or 950 °C, quench to immiscible fluoride and silicate glasses, suggests an additional mechanism of HFSE concentration.

Crystallized melt inclusions are common in quartz phenocrysts of the early hypersolvus and transsolvus granite. After heating, four types of inclusions were discerned. Type 1 inclusions quench to a single silicate glass containing a high concentration of Zr, Nb and Ti. Quenching of Type 2 inclusions produces a Zr, Nb, Ti-rich silicate glass containing a globule of calcium-rich fluoride glass with a high concentration of the REE. The third inclusion type is similar to Type 2, except that the calcium-rich fluoride glass contains a globule of REE-fluoride glass (up to 50 wt.% total REE). Type 4 inclusions contain calcium-fluoride glass with multiple silicate globules.

We propose that during or soon after emplacement, the early granitic magma exsolved a calcium fluoride melt into which rare earth elements (REE) partitioned preferentially. The conjugate silicate melt was consequently depleted in Ca and the REE, and enriched in Zr, Nb and Ti. Crystallization of the fluoride melt occurred late in the crystallization history of the silicate magma allowing it to accumulate in the volatile-rich residual magma that formed the pegmatites. This played a major role in the extreme enrichment of the pegmatites in Ca, F and REE. Crystallization of the pegmatites proceeded inwards from an outer zone in which feldspars, quartz, arfvedsonite and zirconosilicate minerals dominate to a core where the immiscible fluoride liquid collected and crystallized fluorite and REE minerals. Fluid exsolved from the silicate melt reacted with the products of both the silicate and fluoride melts, remobilizing most of the HFSE including the REE. This study reports a rare example of silicate–fluoride melt immiscibility and the first in which such immiscibility played a role in concentrating the REE to potentially economic levels.

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1. INTRODUCTION

Liquid immiscibility, which involves the coexistence of two or more liquids, often with contrasting compositions,

is a common phenomenon in alkaline igneous systems. The concept of immiscible magmas was first proposed by Rosenbush (1887) to explain the juxtaposition of rocks with contrasting compositions, e.g., rhyolite and basalt. However, it fell in disfavor in the 1920s when experiments of Greig (1927a,b) showed that, although liquid immiscibility is important in simple binary systems, the conditions at

^{*} Corresponding author. Tel.: +1 5142973770.

E-mail address: olga.vasyukova@mcgill.ca (O. Vasyukova).

which immiscibility can occur are reduced into insignificance by the addition of small amounts of a third component (e.g., alkalis or alumina). It was not until the 1970s that the discovery of melt inclusions in lunar rocks containing two compositionally different glass phases (Roedder and Weiblen, 1970) and syenitic ocelli in lamprophyre dykes and sills in the Monteregian province, Québec (Philpotts, 1970) caused researchers to re-consider liquid immiscibility in igneous petrogenesis. Since then, large numbers of field-based and experimental studies have established that liquid immiscibility is an important mechanism for producing compositional diversity in igneous rocks (Philpotts, 1970; Roedder and Weiblen, 1970; Ferguson and Currie, 1971; Lapin, 1974; Rankin and Lebas, 1974; Philpotts, 1978; Roedder, 1978; Eby, 1979; Freestone and Hamilton, 1980; Treiman and Essene, 1985; Davidson and Kamenetsky, 2001; Veksler, 2004; Peretyazhko et al., 2007; Thomas and Davidson, 2008; Kamenetsky and Kamenetsky, 2010). Two main types of liquid immiscibility have been widely recognized, namely silicate–silicate immiscibility involving feldspathic and gabbroic alkaline magmas (Philpotts, 1970; Roedder and Weiblen, 1970; Philpotts, 1971; Roedder and Weiblen, 1978; Eby, 1979; Charlier et al., 2013; Kamenetsky et al., 2013) and silicate–carbonate immiscibility (Ferguson and Currie, 1971; Lapin, 1974; Rankin and Lebas, 1974; Freestone and Hamilton, 1980; Treiman and Essene, 1985; Panina and Motorina, 2008; Mitchell, 2009; Kamenetsky and Kamenetsky, 2010; Sharygin et al., 2012). In addition to these two main types of immiscibility, silicate magmas have also been shown to exsolve sulfide liquids (long accepted as a means of forming Cu–Ni–PGE ore deposits), phosphate liquids (Panina and Motorina, 2008), and chloride liquids (Webster, 2004; Panina and Motorina, 2008).

Silicate–fluoride immiscibility, which is the focus of this paper, has rarely been observed in nature. The first published report of this phenomenon was that of Klemme (2004) who described the occurrence of fluoride glass in veinlets and as thin films along grain boundaries, including triple junctions, in mantle xenoliths trapped in Tertiary alkali basalts in East Otago, New Zealand. He also reported observing a fluoride glass bleb within a large silicate glass pocket (see Fig. 2a in Klemme, 2004). Peretyazhko et al. (2007) subsequently described sub-micrometric intergrowths of ‘fluoritic’ and ‘K-feldspathic’ phases in ongonites from the Eastern Transbaikalian region, Russia, which they interpreted as having crystallized from a micro-emulsion of immiscible calcium fluoride and aluminosilicate melts. They also observed melt inclusions, which on quenching (after being heated to 900–950 °C) yielded a silicate glass containing immiscible ‘fluoritic’ and ‘sellaitic’ (MgF₂) phases (Peretyazhko and Savina, 2010).

Experimental evidence of silicate–fluoride immiscibility has been provided for dry systems at 960–1200 °C and atmospheric pressure and for H₂O-bearing systems at 700–800 °C and 100 MPa (Veksler et al., 2005; Dolejs and Baker, 2007a; Alferyeva et al., 2011). These studies showed that silicate–fluoride immiscibility can occur at geologically relevant conditions. Moreover, and significantly for our study, the paper of Veksler et al. (2005) provided data showing that the REE partition preferentially into the fluoride melt.

Here we present data on melt inclusions from the Strange Lake peralkaline granite pluton, Québec–Labrador, Canada, which show that the silicate magma saturated with a fluorine-bearing liquid relatively early in the evolution of the system, and that it successively exsolved calcium-fluoride and REE-fluoride melt phases. Based on these data and observations of the most evolved rocks in the pluton (the pegmatites), we propose a model in which silicate–fluoride melt immiscibility resulted in the emplacement of heterogeneously mixed silicate and fluoride magmas, forming pegmatite sheets that crystallized a world-class REE–Zr–Nb deposit.

2. GEOLOGICAL SETTING

The Mesoproterozoic Strange Lake pluton (1240 ± 2 Ma; Miller, 1996) is a peralkaline granite intrusion that was emplaced along the contact between an Elsonian (1400–1500 Ma) quartz monzonite massif and paragneisses of Hudsonian age (1800–2000 Ma), and is surrounded by a fluorite-cemented ring breccia (Fig. 1). Locally (B-Zone and Main Zone), the pluton contains potentially exploitable concentrations of the REE and other high field strength elements (an indicated mineral resource has been identified in the B-Zone comprising 278 Mt of ore grading, 0.94 wt.% total rare earth oxides (38% heavy rare earth oxides), 1.92 wt.% ZrO₂ and 0.18 wt.% Nb₂O₅; www.questrareminerals.com). The rare metal mineralization is developed in and around pegmatites in the most altered subsolvus granite, and includes a large number of minerals, notably allanite-(Ce), armstrongite, bastnäsite-(Ce), elpidite, fluorcerite-(Ce), gadolinite-(Y), gagarinite-(Y), gittinsite, kainosite-(Y), monazite-(Ce), pyrochlore, titanite and zircon.

Three main granite types have been distinguished based on feldspar mineralogy. The earliest and least evolved is a hypersolvus granite containing perthite as the only alkali feldspar (Nassif, 1993). This granite occupies the central to southeastern part of the pluton. Volumetrically, the most important intrusive phase is a subsolvus granite containing discrete primary microcline and albite crystals, which comprises the outer part of the intrusion. The third granite type, transitional between hypersolvus and subsolvus granite, is transsolvus granite, containing perthite as a phenocryst phase and primary albite and microcline in the matrix. This granite surrounds the hypersolvus granite. In addition to feldspar and quartz, the three granite types also contain arfvedsonite as a major rock-forming mineral. Minerals with high concentrations of high field strength elements are common and increase in abundance from hypersolvus to subsolvus granite.

Pegmatites are observed in each of the three granite types but are much more common in the subsolvus granite, and contain the greatest abundance of high field strength element-rich minerals of any rock unit in the pluton. In two localities (the north-west and central parts of the pluton), the pegmatites form sets of relatively flat-lying sheets ranging up to 20 m in thickness, and are or have been the focus of exploration for the REE, Zr and Nb. These pegmatites may be either zoned or unzoned and, where zoned, are characterized by a marginal facies of quartz, K-feldspar, arfvedsonite and zirconosilicate and titanosilicate minerals, and a core dominated by fluorite, quartz and REE minerals.

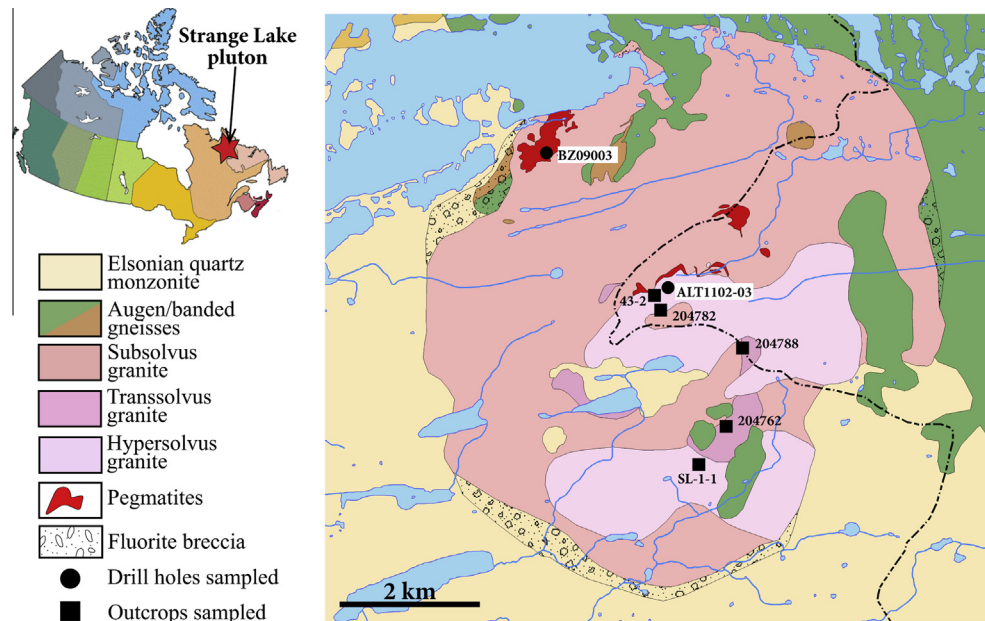


Fig. 1. Geological map of the Strange Lake pluton showing the distribution of the principal rock types, the locations of the pegmatite-rich areas containing potentially economic concentrations of the REE (B-Zone and Main Zone), and the locations of the samples used in this study. The initial letters of the drill holes from which core samples were selected for this study, BZ and ALT, refer to the B-Zone (the deposit slated for exploitation), and the Alterra zone, which is adjacent to the Main Zone.

Hydrothermal alteration is most conspicuous in the pegmatites, where arfvedsonite has been extensively altered to aegirine, and sodic zirconosilicate and titanosilicate minerals have been altered to gittinsite ($\text{CaZrSi}_2\text{O}_7$) and titanite, respectively, plus quartz. Hematization of iron-bearing minerals is widespread (and locally intense) in these rocks. The subsolvus granite is also strongly altered, especially in the vicinity of pegmatites, and exhibits the same mineral-

ogical changes as the pegmatites. By contrast, the hypersolvus and transsolvus granites are much less altered, and pegmatites in these facies of the intrusion are relatively fresh.

Hypersolvus and transsolvus granite types were selected for melt inclusion study as they were less affected by hydrothermal alteration, and were therefore most likely to preserve melt inclusions. This study is based on five

Table 1
Brief descriptions of the samples selected for the melt inclusion study.

Sample	Granite type	Texture	Description	Types of inclusions observed
43-2	Hypersolvus	Equigranular medium-grained	Perthite (0.3–2 mm, 30 vol.%), quartz (0.2–2 mm, 40 vol.%), arfvedsonite (0.3–1 mm, 20 vol.%), fluorite, $\text{Na}(\pm\text{K})$ zirconosilicates	Silicate melt, fluoride melt, silicate–fluoride melt inclusions
SL-1-1	Hypersolvus	Equigranular coarse-grained	Perthite (0.5–6 mm, 40 vol.%), quartz (0.5–6 mm 40 vol.%), arfvedsonite (0.4–3 mm, 10 vol.%), fluorite, $\text{Na}(\pm\text{K})$ zirconosilicates	Silicate melt inclusions
204782	Hypersolvus	Equigranular medium-grained	Perthite (0.4–6 mm, 40 vol.%), quartz (poikilitic; 40 vol.%), arfvedsonite (0.4–3 mm, 10 vol.%, 50 vol.% of it is aegirized), fluorite (0.5–2 mm, 1–2 vol.%), elpidite, zircon	Silicate melt, fluoride melt, silicate–fluoride melt inclusions
204762	Transsolvus	Porphyritic	Phenocrysts of arfvedsonite (1–5 mm, 20 vol.%, unaltered), quartz (1–5 mm, 10 vol.%), gagarinite surrounded by fluorite (1–2 mm, 3 vol.%), perthite (1–2 mm, 2 vol.%). Groundmass: arfvedsonite, quartz, microcline, albite, elpidite, narsarsukite	Silicate melt, fluoride melt, silicate–fluoride melt inclusions
204788	Transsolvus	Porphyritic	Phenocrysts of quartz (1–5 mm, 15 vol.%), arfvedsonite (1–7 mm, 10–15 vol.%, 15–20 vol.% of it is aegirized) and perthite (1–2 mm, 5 vol.%). There are several large poikilitic narsarsukite crystals (5–20 mm). Groundmass: fluorite, arfvedsonite, quartz, perthite, microcline, albite, elpidite, thorite and interstitial aggregates of Ca- and REE-fluorides (fluorite + gagarinite + bastnäsite)	Silicate melt, fluoride melt, silicate–fluoride melt inclusions

samples, two of transsolvus granite and three of hypersolvus granite (Fig. 1). Brief descriptions of these samples are presented in Table 1. We also made use of results of bulk chemical analyses provided by Quest Rare Minerals Ltd. of core from three drill holes (Fig. 1). Two of them (ALT11002 and ALT11003) are located close to the Main Zone, a pegmatite-rich field with potentially economic grades of REE mineralization. The third drill hole is within a pegmatite-rich field (B-Zone) being considered for rare metal (REE, Nb and Zr) exploitation.

3. METHODS

The initial screening for melt inclusions was performed using polished thin sections. After detailed petrographic examination, five samples were selected for melt inclusion study. These samples were then crushed and quartz phenocrysts were removed from the matrix. The quartz phenocrysts were examined for melt inclusions and the nature of the latter carefully documented using a petrographic microscope. Quartz phenocrysts were placed in ceramic crucibles and heated to temperatures of 900 or 950 °C for 48 or 24 h, respectively; heating to lower temperature failed to completely homogenize the inclusions. After heating, the phenocrysts were quenched in air to room temperature.

The quenched melt inclusions were exposed by polishing, and studied using a Hitachi S-3000 N VP Scanning Electron Microscope equipped with solid state BSE and EDS detectors for imaging and semi-quantitative analyses, respectively. This revealed the presence of both silicate and fluoride glass. Selected inclusions were analyzed quantitatively using a JEOL JXA-8900L electron microprobe equipped with five WDS spectrometers and a PulseTor Maxim EDS detector. To avoid volatilization of Na under the electron beam and to optimize analytical conditions for each type of glass, preliminary tests were performed on melt inclusions of the four inclusion types (see below). Based on the results of these tests, wavelength-dispersive spectrometric (WDS) analyses were conducted at 15 kV, with a 6.5 nA beam current and a beam diameter of 5 µm for the fluoride glasses and 15 µm for the silicate glass. The instrumental uncertainty ($\pm$ wt.%) estimated from the count statistical error is given for the silicate and fluoride glasses in Tables 2 and 3. The standards employed, the counting time and the detection limits are reported in Appendix C.

4. RESULTS

4.1. Petrographic characterization of melt inclusions

4.1.1. Unheated melt inclusions

Prior to being heated, the melt inclusions are commonly spherical to ovoid, vary in diameter from <5 to ~100 µm and contain multiple crystalline phases, and in some cases a vapor bubble. Four types of crystallized or devitrified inclusions were recognized in hypersolvus and transsolvus granites. Type 1 inclusions, the most common type (~90% of all inclusions), contain silicate minerals, e.g., K-feldspar, albite, elpidite and arfvedsonite, plus or minus vapor (Fig. 2a). In rare cases (sample SL-1-1 and 204762),

villiumite is also observed, and occupies up to 20% of inclusions by volume. Type 2 inclusions (2–3% of the melt inclusion population) contain a fluorite crystal in addition to silicate minerals and in some cases a vapor bubble (Fig. 2b). Type 3 inclusions are similar to Type 2 inclusions (they are also present in similar proportions), except that they contain a REE-mineral with a composition close to that of gagarinite, which is in close spatial association with fluorite (Fig. 2c). The fluorite/gagarinite volume ratio varies considerably and, in the extreme, only gagarinite is present. Finally, Type 4 inclusions, which comprise about 5% of the melt inclusion population, consist largely of spherical fluorite, to or within which a REE-rich mineral and/or fluid are attached or included, respectively (Fig. 2d). All minerals in unheated melt inclusions show textural evidence of *in situ* crystallization, and in some cases it is possible to discern the crystallization sequence. For example, in Fig. 2c, it is evident that quartz and albite crystallized first, followed by elpidite, and then fluorite and gagarinite; the early minerals protrude into the fluorite, which is partly spherical.

Most of the melt inclusions are isolated and randomly distributed. In rare cases, they are distributed along growth zones in the quartz and are clearly primary in origin; this includes examples of each of the types described above, although not necessarily in the same growth zone. Some melt inclusions occur along healed fractures (examples of all inclusion types were observed along these fractures), and in some cases they appear to represent melt redistributed from larger inclusions.

4.1.2. Heated/quenched melt inclusions

Despite being heated to 900–950 °C, some Type 1 melt inclusions did not homogenize completely. After quenching, these inclusions generally contain a silicate glass, a fluid bubble and multiple zircon crystals (Fig. 3a). Before being heated, the zirconium phase in these inclusions was an alkali zirconosilicate, such as elpidite or vlasovite, but invariably not zircon. We therefore interpret the zircon in the quenched Type 1 inclusions to be a product of a reaction in which the zirconosilicates decomposed to form melt plus zircon. Some Type 1 inclusions also contain single crystals of K-feldspar and/or albite after being quenched. Most quenched Type 1 inclusions, however, only contain silicate glass and a vapor bubble.

After quenching, Type 2 inclusions generally contain a globule of transparent fluoride glass within silicate glass and in some cases a vapor bubble (Fig. 3b). The silicate/fluoride glass volume ratio, however, varies considerably among inclusions and some Type 2 inclusions consist entirely of fluoride glass. Type 3 inclusions generally have rims of silicate glass and transparent fluoride glass around an opaque globule of a second fluoride glass phase and a vapor bubble (Fig. 3c and d). As is the case for Type 2 inclusions, the volume proportions of the melt phases vary considerably among Type 3 inclusions. In some Type 3 inclusions, only the second fluoride glass phase and silicate glass can be observed (Fig. 3e). Type 4 inclusions consist of transparent fluoride glass containing droplets of silicate glass (Fig. 3f).

Table 2

Composition of silicate glass in melt inclusions (wt.%).

Inclusion number	Name	Inclusion type	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ (total)	CaO	Na ₂ O	K ₂ O	ZrO ₂	Nb ₂ O ₅	F	Cl	Total
1	204762d900-2_1	Type 1	71.67	0.38	7.70	6.46	bdl	2.66	6.72	0.59	0.29	0.71	0.04	97.29
2	204762d900-2_2		74.77	0.37	7.44	5.08	bdl	4.07	4.10	2.04	0.28	bdl	0.12	98.43
3	204762d900-2_3		74.56	0.35	7.85	4.19	bdl	4.03	3.94	1.48	0.32	bdl	0.20	96.94
4	204782d900_7		72.07	0.70	5.54	4.87	0.17	4.76	4.02	3.79	0.49	0.32	0.32	97.05
5	SL-1_6_18		74.45	0.47	8.54	4.27	0.10	4.66	2.63	1.20	bdl	0.31	0.14	96.85
6	204788d900_10		73.70	0.51	7.45	5.36	0.15	5.48	3.66	1.74	0.45	1.13	0.16	99.79
7	204788d900_13		73.54	0.31	8.88	4.06	bdl	5.78	2.14	1.64	bdl	0.53	0.13	97.14
8	204762e950-1pr_15-1		73.57	0.29	7.88	4.92	bdl	6.03	0.66	1.18	bdl	0.65	bdl	95.20
9	204762e950-1pr_16-2		76.95	0.34	9.93	2.76	0.09	5.49	0.61	1.14	0.36	bdl	0.10	97.94
10	204762e950-1pr_18		74.61	0.49	6.95	5.11	0.11	4.06	4.06	1.06	0.33	0.92	0.05	97.73
11	204762e950-1pr_19		75.61	0.40	5.98	3.85	bdl	1.95	5.71	1.90	0.26	0.52	0.05	96.26
12	204762e950-2_24-1		73.21	0.47	6.20	7.31	0.26	4.18	3.84	1.92	0.34	0.60	0.10	98.43
13	204762e950-2_26		74.51	0.37	5.05	3.11	0.22	3.26	4.28	3.09	0.42	1.70	0.10	96.12
14	204762d900-3_4		70.49	0.51	7.78	7.07	bdl	6.03	2.53	1.12	0.27	0.77	0.20	96.84
15	204762d900-3_6avof2		70.39	0.61	6.24	6.67	bdl	4.71	3.85	1.86	0.43	0.93	0.07	95.82
16	SL-1_1_1		72.91	0.20	10.43	3.99	bdl	4.03	4.98	bdl	bdl	0.54	0.12	97.27
17	SL-1_1_2		73.17	bdl	10.69	4.73	bdl	5.86	3.97	0.34	bdl	0.99	0.14	99.97
18	SL-1_1_4		74.87	0.97	6.78	0.41	bdl	2.98	6.75	1.69	0.85	1.23	0.17	96.71
19	SL-1_1_4-1		73.93	bdl	5.61	1.66	0.29	5.56	3.68	0.68	bdl	0.62	0.05	92.18
20	SL-1_1_5		73.76	0.21	7.41	7.83	0.09	4.57	4.14	bdl	bdl	0.76	0.13	99.07
21	SL-1_1_7		73.89	0.27	7.67	7.42	0.11	4.55	3.33	0.31	bdl	0.91	0.11	98.68
22	SL-1_3_8avof2		70.74	0.27	9.44	6.48	bdl	5.85	4.14	0.85	bdl	1.43	0.05	99.37
23	SL-1_5_13		70.03	0.19	12.45	4.22	bdl	6.81	3.53	0.57	bdl	1.59	0.05	99.51
24	SL-1_6_20		73.73	1.14	5.91	2.97	bdl	3.56	4.89	1.76	0.83	0.72	0.23	95.76
25	204788d900_12		73.58	0.35	6.90	4.27	bdl	4.08	3.17	1.95	0.29	bdl	0.04	94.90
26	SL-1_1_6		69.61	1.38	3.91	2.41	0.22	4.88	2.87	2.02	0.56	0.88	0.35	89.09
27	SL-1_2_8avof2		69.68	1.91	3.73	3.17	0.24	5.57	2.89	4.64	1.37	0.94	0.20	94.31
28	SL-1_3_10		69.96	0.83	6.09	2.90	0.08	5.97	3.17	3.84	0.76	1.49	0.07	95.13
29	SL-1_5_12		72.79	0.70	4.87	1.72	0.09	4.46	2.87	0.92	0.57	bdl	0.08	89.31
30	204762a900-1avof2		69.90	0.48	9.71	4.05	0.07	5.47	4.47	0.84	na	1.78	0.11	96.11
31	204788a900-1avof2		69.00	0.48	6.29	6.55	0.10	5.47	4.71	3.68	na	1.06	0.19	97.03
32	204788b900-3		70.04	0.25	11.87	2.87	0.10	4.71	6.74	bdl	na	1.26	0.10	97.50
33	204762a900-4		71.49	0.76	9.20	4.84	0.10	4.87	4.71	0.06	na	1.17	0.07	96.75
34	204762b900-1		72.73	0.34	8.63	4.43	0.07	3.79	4.01	0.72	na	0.46	bdl	95.00
35	204782b900-1-2avof4		70.39	0.66	6.37	7.58	0.08	4.83	4.88	1.64	na	0.38	0.10	96.72
36	204782b900-4		77.20	bdl	10.48	bdl	bdl	3.52	5.79	bdl	na	0.88	0.04	97.58
37	204782b900-3		76.92	0.17	9.95	0.79	bdl	3.70	5.84	bdl	na	1.33	0.07	98.22
38	204762_d900-3_5-2		78.02	bdl	10.05	0.58	bdl	2.36	6.20	bdl	bdl	0.35	bdl	92.81
39	204762e950-1pr_16-1		76.03	0.22	11.42	1.48	bdl	5.32	2.67	0.39	bdl	0.25	0.09	97.99
40	204788d900_11		76.78	bdl	10.88	0.62	bdl	2.44	6.11	bdl	bdl	0.30	bdl	96.84
41*	204788a800-1	Type 2	70.15	0.39	6.63	3.13	0.22	5.18	3.61	1.65	na	1.67	0.31	92.15
42*	204762a900-2avof2		71.19	0.45	10.43	3.31	0.86	5.93	3.40	0.98	na	1.35	0.09	97.41
43* #	204762a900		61.48	1.30	1.85	9.80	0.64	2.50	1.78	3.49	na	1.04	0.44	83.76
44*	204788b900-4	Type 3	68.85	0.27	8.11	1.95	0.13	2.66	7.61	1.34	na	1.96	0.04	92.09
45*	204782d900_8avof3		67.12	0.47	5.99	5.06	0.34	4.75	3.78	2.92	0.41	2.53	0.11	93.49
46* #	43-2_23F_F1 with Si blebs	Type 4	64.08	0.00	6.86	7.65	3.28	9.17	3.67	2.60	bdl	2.19	0.49	100.00
Instrumental error (±wt.%)			0.48	0.08	0.17	0.31	0.05	0.26	0.25	0.46	0.18	0.78	0.05	

na, not analyzed.

bdl, below the detection limit.

* Inclusions in which both silicate and fluoride glass were analyzed.

Semi-quantitative EDS analyses.

4.2. Composition of melt inclusion phases

The composition of the glasses is given in [Tables 2 and 3](#). The SiO₂ content of the silicate glass of Type 1 inclusions

ranges from 69 to ~78.02 wt.%, the Al₂O₃ content from 3.73 to 12.45 wt.%, the Fe₂O₃ (total) content from 0.41 to 7.83 wt.%, the Na₂O content from 1.95 to 6.81 wt.% and the K₂O content from 0.61 to 6.75 wt.%. As might be

Table 3
Composition of fluoride glass in melt inclusions (wt.%).

Inclusion number	Name	Inclusion type	Type of glass	Na	F	Ca	Y	La	Si	Ce	Nd	Nb	Total
38*	204788a900-1	Type 2	Ca-fluoride	2.08	46.96	37.70	4.68	1.36	0.02	3.73	1.99	na	98.52
40*	204762a900-1			0.84	51.00	39.92	4.54	1.19	0.14	2.92	1.71	na	102.25
44	204762a900-2			0.75	47.10	40.81	3.99	1.29	0.38	2.61	1.53	na	98.46
45	204762b900-3			1.01	45.82	40.27	3.76	1.39	0.08	3.33	1.83	na	97.48
46	204762b900-1			0.82	49.08	38.90	4.84	1.34	0.12	3.65	2.19	na	100.94
47	204762e950_1pr_14F_Si-FI incl			0.18	45.51	44.92	2.43	0.49	0.47	1.25	0.94	bdl	96.20
48	204762e950_2_17F_Si-FI incl			0.69	46.13	42.01	3.95	0.78	0.06	1.61	1.30	bdl	96.52
49	204762e950_2_20F_Si-FI incl	Type 3	REE-fluoride	0.36	51.91	41.65	3.22	0.87	0.66	1.95	1.56	bdl	102.22
50	204762d900-2_1F_Si-FI incl			0.41	45.97	42.49	3.85	0.80	0.13	2.14	1.41	bdl	97.21
41*	204788b900-4			2.97	37.51	11.65	2.54	12.13	0.32	23.97	8.15	na	99.24
42*	204782d900_6F_Si-FI incl			2.60	42.29	14.52	1.84	10.52	0.21	18.16	6.75	bdl	96.89
51	204782b900-2			2.91	38.14	13.36	2.74	11.98	0.20	23.66	7.80	na	100.80
52	204788b900-2			3.21	38.39	12.83	2.75	12.32	0.15	24.22	8.15	na	102.01
53	204782b900-1			2.00	37.89	10.34	2.65	14.47	0.20	25.08	8.65	na	101.28
54	204788d900_10F_FI with Si blebs	Type 4	Ca-fluoride	0.47	49.24	40.96	4.01	1.00	0.16	2.33	1.75	bdl	99.90
55	204782d900_8F_FI with Si blebs_avof2			0.77	49.07	46.17	2.36	0.14	0.05	0.53	0.54	bdl	99.62
56	43-2_23F_FI with Si blebs			1.23	46.87	41.69	3.07	0.90	0.04	2.32	1.50	bdl	97.62
57	204788d900_13F_FI			2.02	53.10	39.00	2.91	1.06	0.19	2.34	1.58	bdl	102.20
58	43-2_24F_FI			0.12	49.98	50.29	0.18	0.00	0.13	bdl	bdl	bdl	100.76
59	43-2_26F_FI			0.22	47.58	48.92	0.20	0.06	0.09	bdl	bdl	bdl	97.18
60	43-2_22F_FI			0.15	48.41	50.27	0.20	0.10	0.16	bdl	bdl	bdl	99.40
61	43-2_25F_FI			0.30	50.09	49.12	0.52	0.31	0.10	0.40	0.32	bdl	101.16
66	204782d900_7F_FI			1.32	54.88	42.08	1.30	0.32	0.13	0.94	0.87	bdl	101.82
67	204762e950_2_19F_FI			0.33	50.41	40.91	4.13	0.82	0.17	2.32	1.51	bdl	100.59
68	204782d900_9F_FI			0.16	46.15	41.61	4.32	1.03	0.85	2.30	1.73	bdl	98.15
69	204762b900-2			0.68	55.20	36.21	5.44	1.57	1.85	3.78	2.07	na	106.80
	Instrumental error ($\pm$ wt.%)			0.19	3.51	0.79	0.61	0.36	0.08	0.49	0.47		

* Inclusions in which both silicate and fluoride glass were analyzed; na, not analyzed; bdl, below the detection limit.

expected from the peralkaline nature of the magma, the CaO content is extremely low, from 0.07 to 0.29 wt.%. Also, as might be expected, the concentrations of the high field strength elements range up to very high values. The ZrO_2 content reaches 4.64 wt.%, the TiO_2 content 1.91 wt.% and the Nb_2O_5 content 1.37 wt.%. The content of fluorine, a highly incompatible volatile element, is also very high, up to 1.78 wt.%; the Cl content ranges up to 0.35 wt.%.

Compositionally, the silicate glass of Types 2 and 3 inclusions is very similar to that of Type 1 inclusions, except that the CaO and F contents are somewhat higher (Table 2 and Fig. 4). Although the latter may represent a real difference, it is also possible, particularly for the Type 3 inclusions, that it is an artifact related to the relatively small volume of silicate glass and its close proximity to fluoride glass. The silicate globules in Type 4 inclusions were too small for electron microprobe WDS analyses, but semi-quantitative EDS analyses suggest that they are compositionally similar to the silicate glass of Type 1 inclusions (Table 2).

Evaluation of the compositional data for the silicate melt in inclusion Types 1–4 reveals systematic variations in the concentration of elements as a function of the aluminum saturation index of the melt (ASI; $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O})$ in moles). There is a strong negative correlation of the high field strength element oxides, i.e., ZrO_2 , TiO_2

and Nb_2O_5 with the ASI index (Fig. 4a–c). The volatiles, F and Cl, also correlate negatively with the ASI index, although the correlation is less pronounced for F than it is for Cl (Fig. 4d and e). Despite the extremely low CaO concentration of the silicate melt inclusions (≤ 0.29 wt.%), CaO also displays a strong negative correlation with ASI (Fig. 4f). Finally, like the other elements, Fe (total Fe_2O_3) shows a negative, albeit weak, correlation with the ASI index (Fig. 4g).

The transparent fluoride glass in Type 2 inclusions consists mainly of fluorine (37.51–55.2 wt.%) and calcium (35.35–50.29 wt.%) but contains appreciable concentrations of the REE, i.e., Ce (0.4–5.2 wt.%), Y (0.18–5.44 wt.%), Nd (0.32–2.64 wt.%), and La (0.06–2 wt.%). It also contains significant Na (0.12–2.19 wt.%) and Si (0.02–1.85 wt.%); the concentrations of the high field strength elements, Zr and Nb are below the detection limit (Table 3). It can thus be classified as a calcium-fluoride glass.

As mentioned above, transparent fluoride glass is also found in Type 3 inclusions. Unfortunately, it is not present in sufficient volume for quantitative analysis. Semi-quantitative EDS analyses reveal, however, that it is compositionally similar to the Ca-fluoride glass in Type 2 inclusions, i.e., it is composed mainly of Ca and F but also has significant concentrations of the REE. Fluoride glass in Type 4 inclusions is indistinguishable in composition from

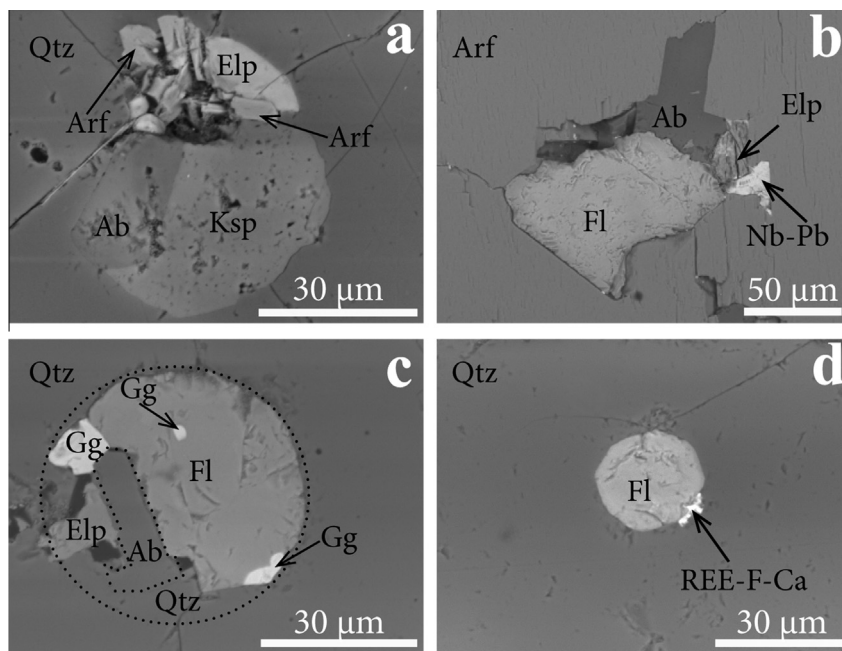


Fig. 2. Backscattered electron (BSE) images of melt inclusions before heating. (a) Type 1 inclusion; note the spherical shape of the inclusion, (b) irregular Type 2 inclusion, (c) Type 3 inclusion; note the spherical boundary of the fluoride phase against its host and the irregular contact with the crystallized silicate phase, (d) Type 4 inclusion. The inclusions are hosted by quartz except for (b), which is hosted by arfvedsonite. Qtz, quartz, Alb, albite, Arf, arfvedsonite, Ksp, K-feldspar, Fl, fluorite, Elp, elpidite, Gg, gagarinite.

fluoride glass in Type 2 inclusions, i.e., the La/Ce and Ca:REE molar ratios are the same (Fig. 5).

The opaque fluoride glass in Type 3 inclusions contains 37.51–42.29 wt.% F, 10.34–14.52 wt.% Ca and 40.09–53.64 wt.% total REE (18.16–25.08 wt.% Ce, 10.52–14.47 wt.% La, 6.75–8.65 wt.% Nd and 1.84–2.65 wt.% Y (Table 3). This glass is distinguished compositionally from the calcium fluoride glass by its high REE and low Ca content, and is referred to hereafter as REE-fluoride glass. Both fluoride glasses, however, have the same La/Ce molar ratios (Fig. 5c). Finally, the total REE and F contents of the fluoride phase in melt inclusion Types 2–4 increase with decreasing Ca content (Fig. 5a and b).

5. DISCUSSION

As mentioned earlier, we interpret the textural relationships in our Types 2–4 melt inclusions to reflect the coexistence of immiscible silicate and fluoride melts. We cannot ignore the possibility, however, that the fluorite in these inclusions (unheated) represents fluorite that crystallized directly from the silicate magma, particularly as fluorite is known from nature and experiments to crystallize under magmatic conditions (Marshall et al., 1998; Scaillet and Macdonald, 2004; Gabitov et al., 2005; Lukkari and Holtz, 2007). Nonetheless, we consider this possibility very unlikely for several reasons. One of these reasons is that magmatic fluorite is either euhedral or anhedral (interstitial) but as far as we can discern not ovoid or spherical (Marshall et al., 1998; Sallet et al., 2000; Badanina et al., 2006; Huang et al., 2007). By contrast, the fluoride melt inclusions (unheated) observed by us are commonly either

spherical, if not co-entrapped with a silicate melt (e.g., Fig. 2d) or the fluoride phase forms part of an ovoid or sphere of which the other part is composed of silicate minerals (Fig. 2c). In the case of the melt inclusion shown in Fig. 2c, the silicate phases (albite and quartz) protrude into the fluorite, showing clearly that the latter was liquid at the time of crystallization of the silicate phases. The fluoride phase is only anhedral if trapped in arfvedsonite (Fig. 2b; the inclusions studied by us were all in quartz). It could be argued that the fluoride phase represents fluorite that became rounded during our heating experiments, i.e., fluorite that did not dissolve completely in the silicate phase. If, however, this were the case, we would not observe vapor trapped in the Ca-fluoride phase, nor would we observe a REE-fluoride phase within the Ca-fluoride phase (Fig. 3b and c).

5.1. Melt phase separation and entrapment

The observations and arguments presented above provide compelling reasons to believe that the melt inclusion textures record the coexistence of immiscible silicate and fluoride melts. Moreover, from the observation that the phase ratios vary considerably, it is reasonable to conclude that the separate melts existed prior to entrapment. This is also consistent with the occurrence of silicate-only, Type 1 inclusions, some fluoride-only Type 2 inclusions and Type 4 inclusions that contain tiny droplets of silicate glass in the fluoride glass (post-entrapment exsolution). It thus follows that the melt phases in most Types 2 and 3 inclusions were entrapped heterogeneously. It also follows that the REE-rich fluoride phase within Type 3 melt inclusions represents

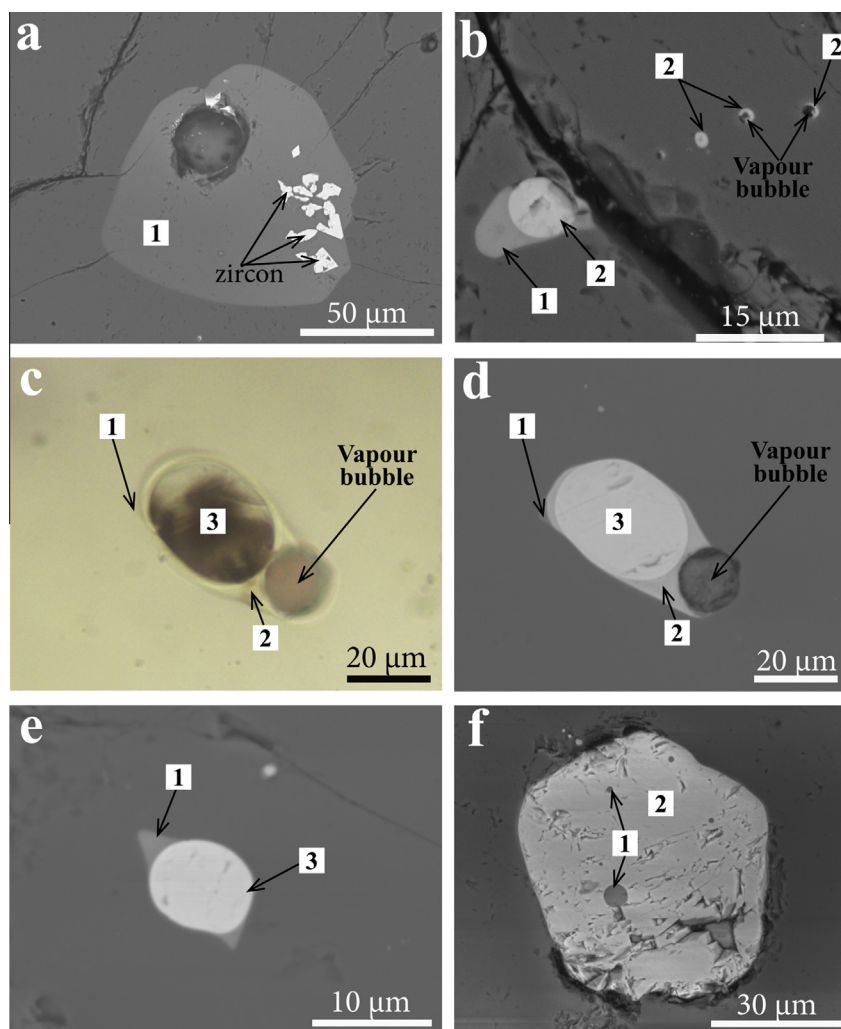


Fig. 3. Images of melt inclusions after being heated to 900 or 950 °C. (a) A BSE image of a Type 1 inclusion containing silicate melt, zircon crystals and a fluid bubble. (b) A BSE image of Type 2 inclusions along a healed fracture; they contain silicate glass (1) and Ca-fluoride glass (2); some of the smaller ones only contain fluoride glass (with or without a vapor bubble). (c) An optical image of a Type 3 inclusion with silicate melt (1), Ca-fluoride melt (2) and REE-fluoride melt (3). (d) A BSE image of the Type 3 melt inclusion shown in (c). The dark circle on the right end of the inclusion in (c) and (d) is a cavity, which we interpret to have been a vapor bubble. (e) A BSE image of a Type 3 inclusion with silicate melt (1) and REE-fluoride melt (3) but without observable Ca-fluoride melt. (f) A BSE image of a Type 4 inclusion containing silicate melt globules (1) in fluoride melt (2).

a second fluoride liquid that separated from a calcium-rich fluoride liquid, also largely prior to entrapment.

5.2. Controls on melt composition

The data presented earlier show that the composition of the silicate melt inclusions (Type 1) and the silicate phase in the other melt inclusion types (Types 2–4) varies greatly (see [Tables 2 and 3](#)). The most likely reason for this variation is that the inclusions represent trapping of melt at different times, and therefore record the temporal evolution of the magma. Silicate melts comprise network formers, i.e., SiO_4 and AlO_4 (or Fe^{3+}O_4) tetrahedra, and network modifiers, which are usually monovalent and divalent cations, i.e., alkalis, alkaline earths, and Fe^{2+} ([Mysen, 1983](#)). Fractional crystallization decreases the proportion of network

formers and increases the proportion of network modifiers, thereby facilitating the capacity of magmas to concentrate incompatible elements like the HFSE and F ([Lithout, 1984](#); [Scaillet and Macdonald, 2004](#)). Accordingly, fractional crystallization should produce negative correlations of ZrO_2 , TiO_2 , Nb_2O_5 and F with the aluminum saturation index. This is precisely what is observed for the silicate phase of the melt inclusions, and provides strong evidence that the silicate melt in Strange Lake evolved by fractional crystallization ([Fig. 4](#)).

5.3. Comparison of melt inclusion and bulk rock compositions

In the preceding section, we concluded from the negative correlation of ZrO_2 , TiO_2 , Nb_2O_5 and F with the AS index that the composition of the silicate phase in the melt

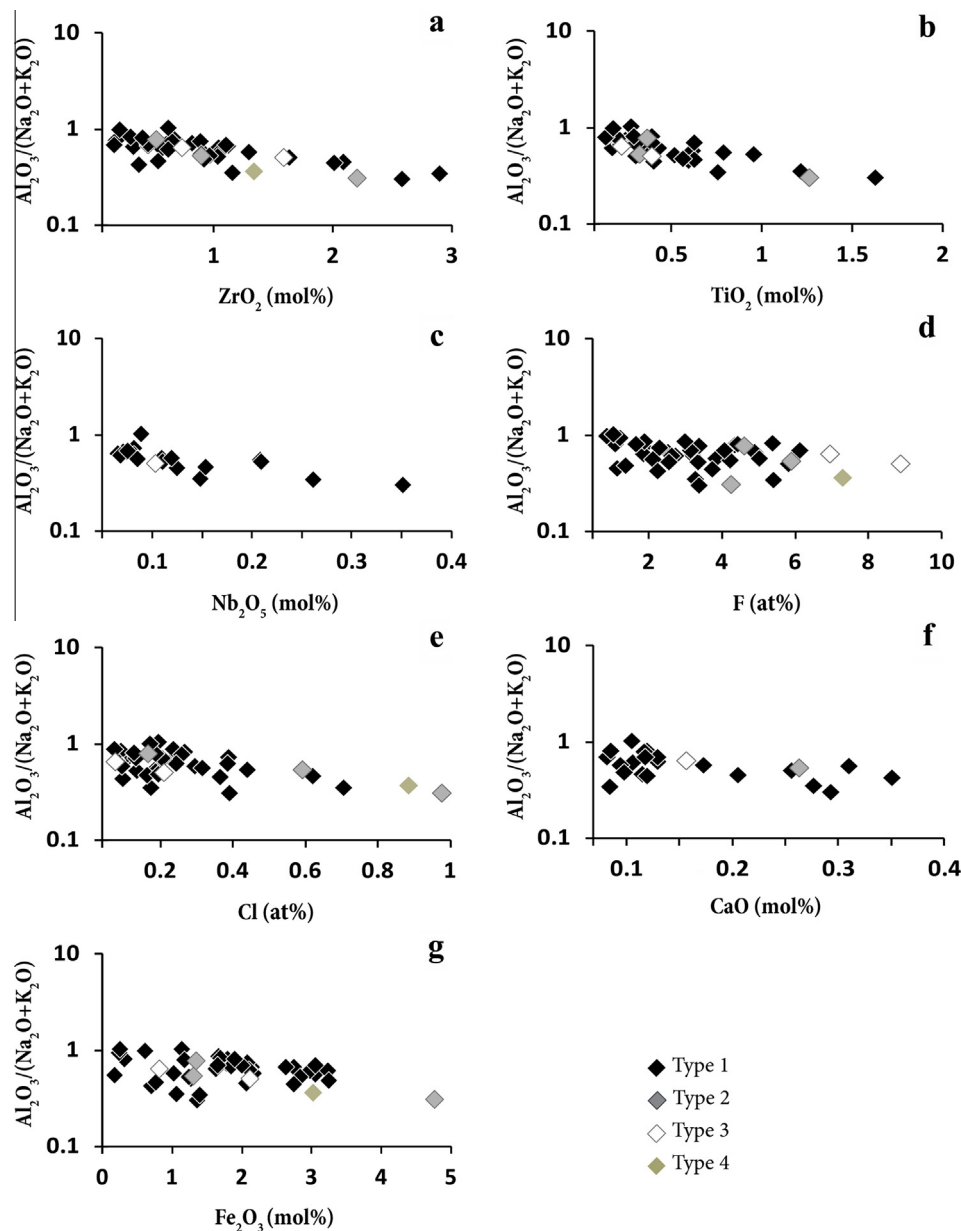


Fig. 4. Binary diagrams showing molar masses (%) of selected elements/oxides in the silicate glass of Types 1–4 melt inclusions versus the AS index ($\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O})$).

inclusions records a history of fractional crystallization of the Strange Lake magmas. The same conclusion was reached by Boily and Williams-Jones (1994), who proposed, from an analysis of bulk rock chemical data, that the Strange Lake magma evolved by fractional crystallization of alkali feldspar (the only mineral able to remove aluminum).

Superficially, and in apparent contrast to the silicate phase in the melt inclusions, the bulk concentrations of ZrO_2 , TiO_2 , Nb_2O_5 and F in the Strange Lake granites appear to be independent of the aluminum saturation index (Fig. 6a–d). If, however, the most altered samples are omitted, a negative trend is evident for these elements; pegmatite

and subsolvus granite lost most of their sodium to the fluid, thereby precluding reliable interpretation of their evolution using the AS index. Nonetheless, given the higher concentration of ZrO_2 , TiO_2 , Nb_2O_5 and F in the altered rocks, we can predict that the subsolvus granite and pegmatite are more evolved than the hypersolvus granite, as demonstrated previously by Boily and Williams-Jones (1994).

For most elements, the silicate melt inclusion compositions overlap the bulk rock compositions for hypersolvus and subsolvus granite on plots of element or oxide concentration versus the AS index (Fig. 6a–d and f). In the case of Fe_2O_3 , however, the overlap is only partial, with some subsolvus granite samples having higher Fe_2O_3 concentrations.

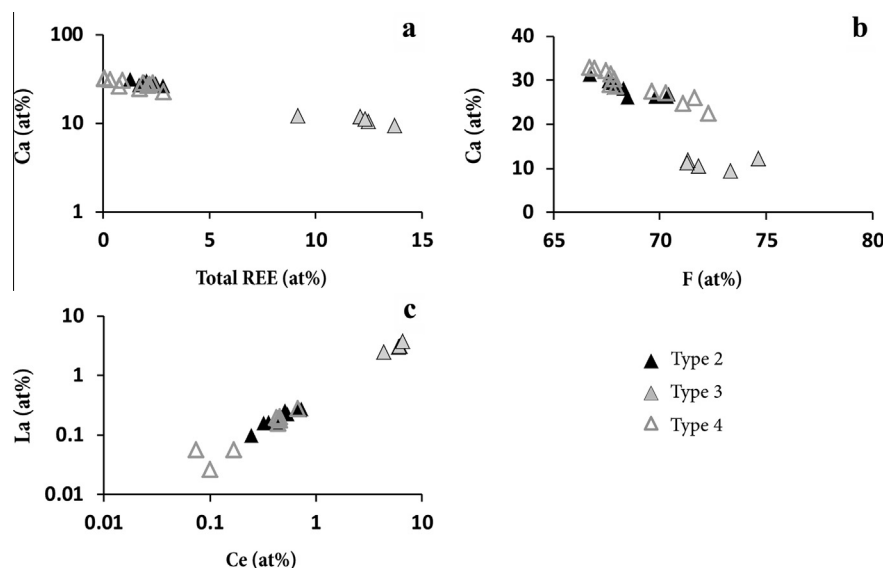


Fig. 5. Binary diagrams showing molar masses (%) of Ca, F, La, and Ce in the fluoride glass(es) in Types 2–4 melt inclusions. (a) Ca versus TREE (b), Ca versus F and (c) La versus Ce.

This may be due to sampling of arfvedsonite-rich pockets produced by flow segregation (Salvi and Williams-Jones, 1996), suggesting that iron-rich subsolvus granite samples are probably not representative of the magma composition.

An element for which there is no overlap between melt inclusion and bulk rock composition is calcium (Fig. 6e). The concentration of CaO reaches a maximum of 0.29 wt.% in the silicate melt inclusions. By contrast, its concentration ranges up to 2.49 wt.% in the hypersolvus granite and up to 2.71 wt.% in the subsolvus granite; in the pegmatites, CaO concentrations may be >10 wt.% (Appendices A and B). Furthermore, whereas CaO concentration in the melt inclusions correlates negatively with the AS index (Fig. 4f), in the granites, no such correlation is evident (Fig. 6e). This indicates clearly that the calcium concentration in the granites did not evolve by simple fractional crystallization, as the other elements, and that its source was not the silicate magma as represented by the silicate phase in the melt inclusions analyzed in this study.

5.4. The source of calcium in the Strange Lake granites

The anomalous enrichment of Ca in the Strange Lake granites, and particularly in the subsolvus granites and pegmatites was noted previously by Salvi and Williams-Jones (1990, 1996), who provided petrographic evidence for the replacement of sodic minerals by calcic minerals and fluid inclusion evidence for the circulation of a low temperature calcium-rich brine in the pluton. Based on these observations, they proposed that calcium was added to the granites from the gneisses that partly host the pluton, and that alkalis were removed (Salvi and Williams-Jones, 1996). Indeed, consistent with this hypothesis, the CaO concentration of the granites correlates negatively with the concentration of alkalis (Fig. 7). However, the calcium concentration of the granite most enriched in alkalis, i.e., the least altered (hypersolvus) granite, is, on average, nearly an order of

magnitude higher than that of the silicate melt inclusions (Fig. 7). This indicates that either additional calcium was introduced into the granitic magmas by some other process or that the silicate melt composition, at least in respect to calcium, is not representative of the granitic melt composition.

In principle, exsolution of a calcium fluoride melt from the silicate melt and its subsequent mechanical mixing with the latter could explain the higher concentration of calcium in the granites compared to the silicate melt inclusions. Provided that there was no loss or gain of Ca or F, this mechanical mixing of fluoride and silicate melts would be evident from a distribution of the compositions of the bulk rocks along a line joining the compositions of the silicate and fluoride melt on a plot of Ca versus F. As can be seen from Fig. 8, however, all bulk rock compositions lie below the ‘mixing’ line, although they trend roughly parallel to this line. The trend is best developed for the hypersolvus granites (Fig. 8b) but the pegmatite trend (Fig. 8d) extends closest to the fluoride end member, albeit with greater scatter of the data than for the other trends. The considerable scatter of the data for the subsolvus granites and particularly the pegmatites is readily explained by the observation that they underwent much greater degrees of calcium metasomatism than the hypersolvus granite; this would have scattered the data in respect to Ca. Thus, if the trends in the bulk rock data represent mixing, then either there was a loss of F, an addition of Ca independent of Ca metasomatism (even the least altered hypersolvus granites plot below the mixing line) or, as has already mentioned, the silicate melt composition is not representative of the granitic melt composition.

We have been unable to identify a process that could have added calcium to the magma other than those of calcium metasomatism and mechanical mixing with an immiscible fluoride melt, and therefore consider that the departure of the bulk rock data from the mixing line defined by the melt inclusions was not due to an addition

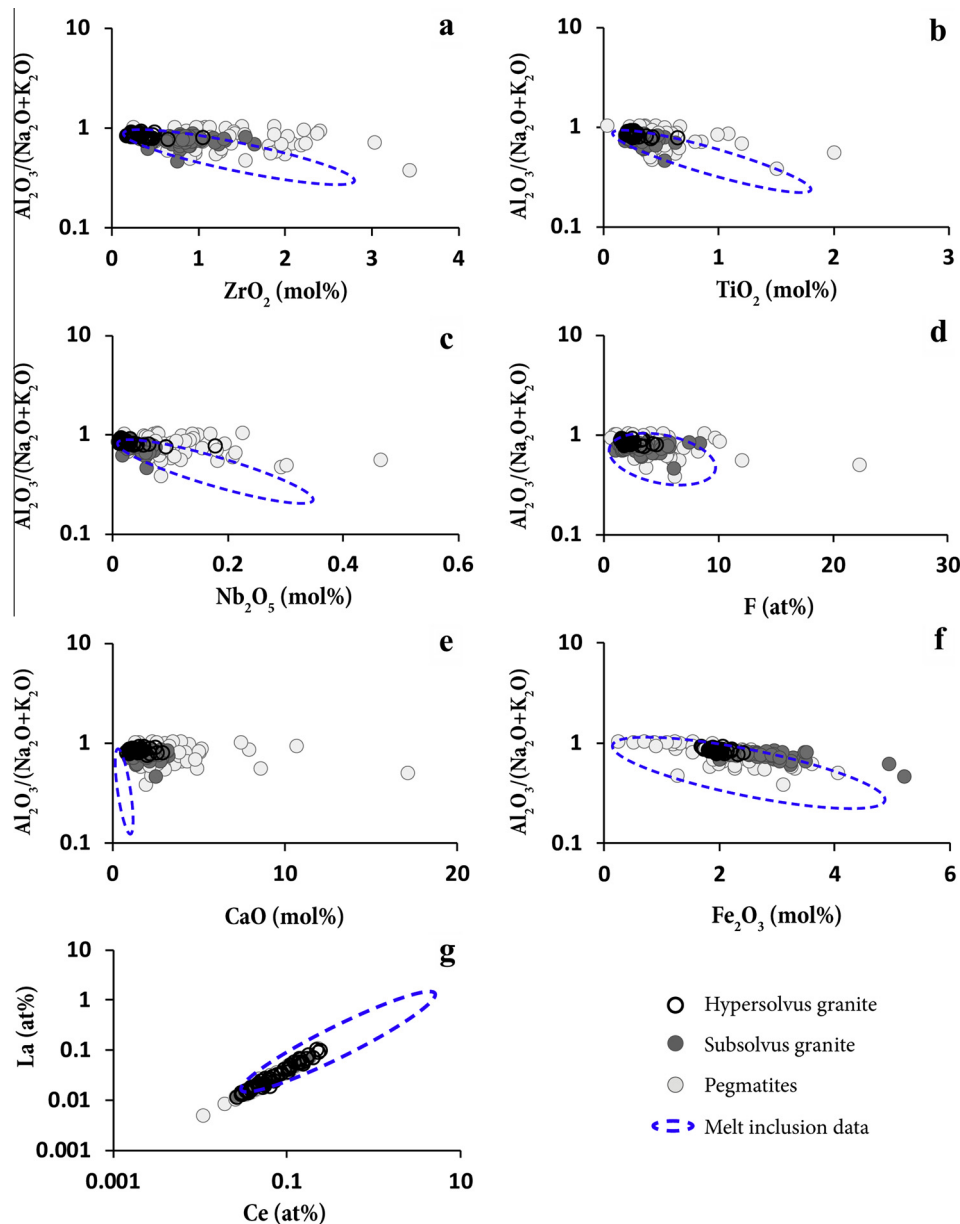


Fig. 6. Binary diagrams showing the molar masses (%) of selected elements/oxides in bulk rocks of the different granitic phases of the Strange Lake pluton versus the AS index (a–f). For comparison, the corresponding fields for the silicate phase of melt inclusions from Fig. 4 are also shown. Diagram (g) compares the molar masses of La and Ce (%) in the bulk rocks with those of the melt inclusions. The bulk rock chemical data were supplied by Quest Rare Minerals Ltd.

of calcium. By contrast, a loss of fluorine due to exsolution of a volatile phase and preferential partitioning of fluorine into this phase is a plausible explanation, given the observation that villiaumite (NaF) is present in some melt inclusions and the development of a fluorite-cemented ring breccia around the pluton (Fig. 1).

In summary, although appreciable calcium was introduced metasomatically, as proposed previously by Salvi and Williams-Jones (1996), it is also clear that much of the calcium in the Strange Lake granites was added from a fluoride melt that mixed mechanically with the silicate magma. It is also clear that this addition of fluoride melt

increased with the evolution of the magmas and reached its maximum in the pegmatites that host the REE deposit.

5.5. The timing and conditions of silicate–fluoride and fluoride–fluoride liquid immiscibility

The occurrence of primary silicate, fluoride and mixed silicate–fluoride melt inclusions with variable phase ratios in hypersolvus granite indicates that a fluoride liquid exsolved relatively early in the evolution of the Strange Lake magma, and that during crystallization of early quartz phenocrysts the melt was already unmixed. Early

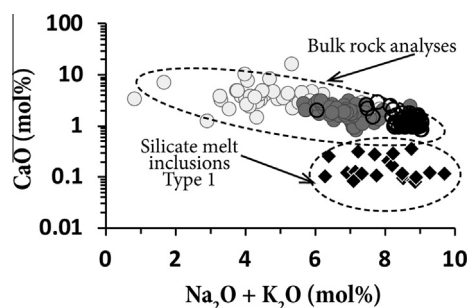


Fig. 7. A binary diagram showing the molar mass (%) of CaO in bulk rocks and melt inclusions versus the molar mass of $\text{Na}_2\text{O} + \text{K}_2\text{O}$. The significance of the different circles is described in the legend for Figs. 4 and 6. The bulk rock chemical data were supplied by Quest Rare Minerals Ltd.

separation of the two melts is also consistent with the extremely low Ca content of early crystallized phenocrystic phases (Boily and Williams-Jones, 1994).

Apparently, silicate–fluoride immiscibility occurred when the fluorine content of the melt reached ~ 4 mol%, which corresponds to the lowest F content of the silicate phase in a Type 2 inclusion (Fig. 4f). It should be cautioned, however, that the elevated F content of the Type 2 inclusions, as mentioned earlier, may be an artifact of analysis.

The exsolved fluoride melt evolved compositionally through enrichment in REE and F and depletion in Ca. When the total REE and F contents reached 8–12 and 71–72 mol%, respectively (Fig. 5), exsolution of a REE-rich fluoride phase occurred. As noted earlier, the Type 3 inclusions record this exsolution, and trapped silicate, Ca-fluoride and REE-fluoride melts heterogeneously (evident from the highly variable phase proportions).

It is difficult to determine when each of the phase separation events occurred, but it seems likely, from the primary nature of some inclusions in quartz phenocrysts containing two melt phases, that silicate–fluoride immiscibility occurred during or shortly after magma emplacement. This may suggest that the pressure drop associated with magma emplacement was a trigger for silicate–fluoride un-mixing in the same way that decreasing pressure leads to un-mixing of simple binary fluids, e.g., CO_2 – H_2O , or the exsolution of volatiles from magmas.

Separation of a REE-fluoride melt from the Ca-fluoride melt clearly occurred later than silicate–Ca-fluoride melt separation, but still early in the crystallization history of the granites; gagarinite phenocrysts (as in sample 204762, see Table 1) most likely crystallized from REE-fluoride melt, suggesting that this phase had separated by the time that the transsolvus granite started to crystallize. Indeed, arfvedsonite phenocrysts in sample 204762 contain crystallized Types 2 and 3 inclusions, indicating that separation of a REE-fluoride melt from a Ca-fluoride melt had occurred prior to their crystallization.

Unfortunately, the results of our experiments provide limited information on the probable temperature of fluoride melt exsolution. However, insight is provided by the experimental studies of Gramenitskii and Shchekina (2005), Veksler et al. (2005, 2012), Dolejs and Baker (2007a,b) and Alferyeva et al. (2011). In dry peralkaline (Ca-free) granite systems, silicate–fluoride liquid immiscibility only occurs at temperatures above 970°C (Dolejs and Baker, 2007a). By contrast, in hydrous granitic systems, the field of immiscibility may extend down to 800°C (Alferyeva et al., 2011) and even to 650°C (Veksler et al., 2012), provided that the systems are Li-bearing; the presence of Li permits the field of fluoride liquid to exist at relatively

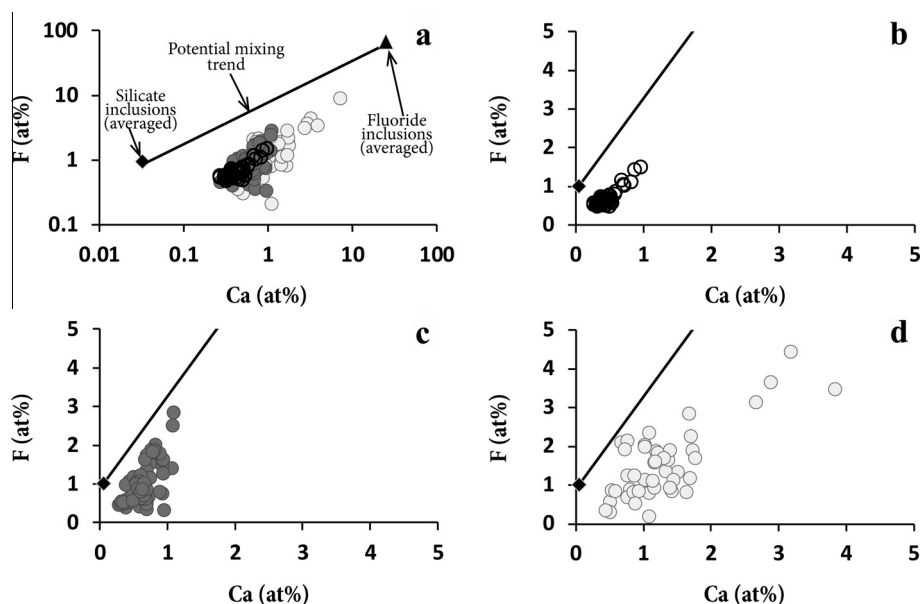


Fig. 8. Plots of Ca versus F (atomic %) for melt inclusions and bulk rocks. (a) All rock types, (b) hypersolvus granite, (c) subsolvus granite, (d) pegmatite. The black line and diamond in b–d show the average composition of the silicate melt inclusions and the mixing trend between silicate and fluoride melt inclusions illustrated in (a). The significance of the other symbols is explained in the legend in Fig. 6.

Table 4
Ionic potential of selected elements.

Element	Nominal charge (valency)	Ionic radii	Ionic potential
K	1	0.133	8
Na	1	0.095	11
Ca	2	0.099	20
Y	3	0.136	22
La	3	0.106	28
Ce ³⁺	3	0.103	29
Nd	3	0.1	30
Fe ²⁺	2	0.064	31
Fe ³⁺	3	0.064	43
Zr	4	0.079	47
Ti	4	0.068	51
Al	3	0.05	59
Nb	5	0.07	60

low fluorine concentration and lowers the liquidus temperature by suppressing crystallization of F-rich minerals such as cryolite and topaz (Gramenitskii and Shchekina, 2005; Veksler et al., 2012). Although we did not measure the concentration of Li in our melt inclusions, it is known from studies of the arfvedsonite composition (Hawthorne et al., 2001) that the Strange Lake magmas were enriched in Li. In the presence of REE, the field of immiscibility may extend to even lower temperature. It is thus reasonable to conclude that, although the fluoride melt at Strange Lake

exsolved early and probably at high temperature, it may have remained stable to relatively low temperature, perhaps as low as 650 °C. Eventually, perhaps due to crystallization of fluorite, the fluoride melt became sufficiently enriched in the REE (and F) to exsolve a separate REE-fluoride melt.

5.6. Metal partitioning between immiscible fluoride and silicate melts

The separation of silicate and fluoride melts acted as an extremely efficient fractionation mechanism for the economically significant trace elements at Strange Lake, with the REE partitioning preferentially into the fluoride melts and Zr, Ti and Nb into the silicate melt. Similar partitioning has also been demonstrated experimentally, and shown to be determined largely by the ionic potential (Z/r , where Z is the nominal charge and r is atomic radius; Veksler, 2004). According to these studies, ions with Z/r values of ~ 20 – 30 partition preferentially into the fluoride melt, whereas ions with smaller or larger Z/r tend to prefer the silicate melt. Our data point to the same behavior. Thus, Ca, Y, La, Ce and Nd, which have Z/r values between 20 and 30 (Table 4), partitioned strongly into the fluoride melt; concentrations of the REE reached 12.86 wt.% in the Ca-fluoride melt (Table 3). By contrast, Al, Ti, Fe, Zr and Nb, which have Z/r values from 31 to 60 (Table 4), remained in the silicate melt.

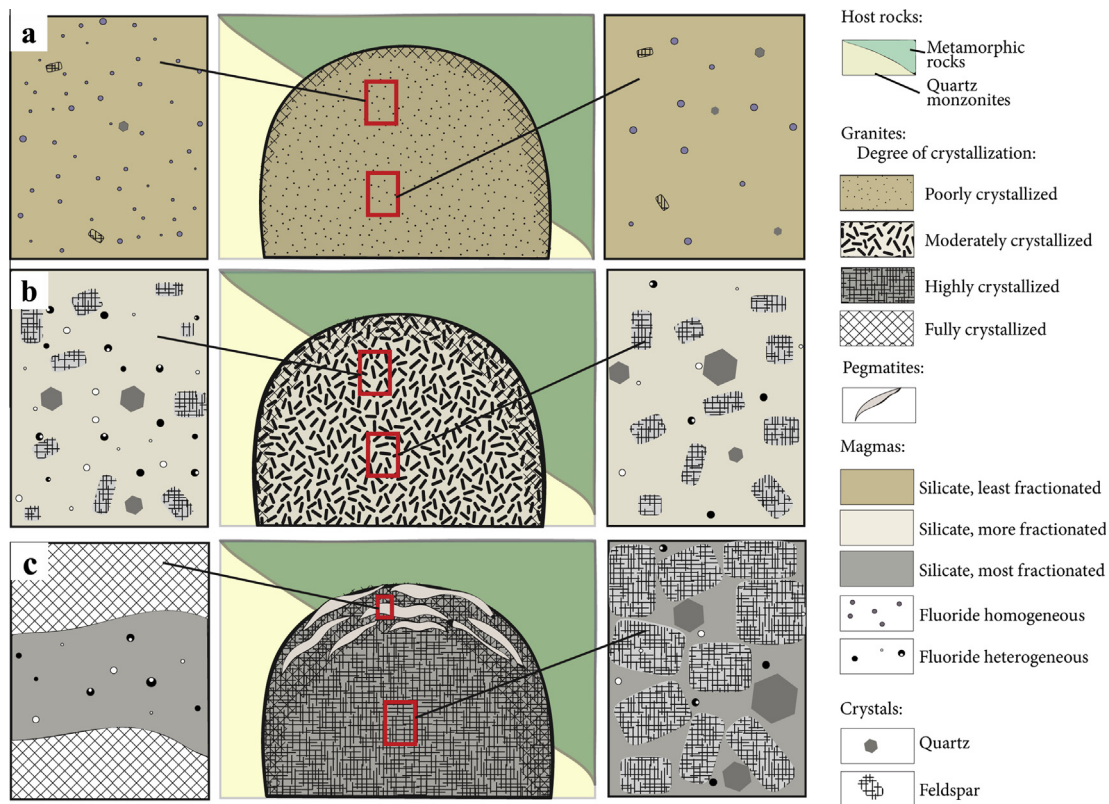


Fig. 9. Sketch showing the possible evolution of the Strange Lake magmatic system. (a) The early onset of silicate–fluoride immiscibility, (b) later Ca-fluoride–REE-fluoride immiscibility, (c) emplacement of the pegmatites. Refer to the main text for further details.

5.7. Liquid immiscibility and the emplacement of the Strange Lake pluton

As previously mentioned, silicate–fluoride immiscibility likely occurred relatively early and probably was coincident with magma emplacement. We envisage that after unmixing, the magma was an emulsion, in which surface tension forces held calcium fluoride melt droplets suspended in the silicate melt (Fig. 9a).

During further evolution, the silicate liquid crystallized quartz, feldspar and arfvedsonite, enriching the residual liquid in titanium, zirconium and niobium and increasing the proportion of fluoride melt, which remained largely liquid. The latter evolved by exsolving REE-fluoride droplets (Fig. 9b). Whether this occurred because of cooling of the fluoride liquid and/or partial crystallization of fluorite, however, is unclear. Rapid crystallization within the cupola led to formation of a carapace, which fractured subhorizontally owing to contraction, thereby providing spaces, in which the residual volatile-rich silicate melt and accumulated fluoride melt could intermingle and form pegmatite sheets (Fig. 9c).

Although the relative proportions of the silicate and fluoride melts cannot be known with any accuracy, a rough estimate is provided by comparing the average REE content of the different granite types analyzed in the drill cores considered in this study with the average REE content of the Type 2 melt inclusions (Table 5). Based on this comparison, the fluoride melt formed 2.7 wt.% of the hypersolvus

granite, 6 wt.% of the subsolvus granite and 12.1 wt.% of the pegmatites. These figures, however, ignore the contribution of the REE fluoride melt, which exsolved from the Ca-fluoride melt, and thus probably somewhat overestimate the actual proportion of fluoride melt.

5.8. Crystallization of the Strange Lake REE pegmatites

Crystallization of the pegmatite sheets started with quenching of the silicate liquid against the relatively cold granite of the carapace to form aplitic zones (Fig. 10a). Slower crystallization of the remaining melt ensued, and coarse-grained pegmatite formed due to the combination of a lower rate of cooling and a build-up of volatiles that lowered the melt viscosity.

The residual silicate melt and the suspended droplets of fluoride-melt were squeezed into the cores of the sheets where they crystallized to form fluorite and REE-mineral-(gagarinite)-rich pegmatite (Fig. 10b). Whether the fluoride melts started to crystallize prior to their emplacement in the pegmatite cores is unclear, although the absence of fluorite in the outer parts of the pegmatites suggests that this was not the case. At some time prior to final crystallization of a pegmatite, the magma saturated with an aqueous fluid that created overpressures and fractured the partly crystallized pegmatite and adjacent aplite and granite (Fig. 10c and d). Based on the composition of the silicate melt inclusions, this fluid was enriched in chlorine, fluorine and alkalis (Table 2). The fluid was chemically aggressive and decomposed the primary HFSE and REE minerals, remobilizing most of the HFSE and REE (Gysi and Williams-Jones, 2013). Through continued interaction with the crystallized parts of the pegmatite and perhaps with external fluids, the HFSE and REE were reprecipitated in response to the decrease in temperature and increase in pH that resulted from these interactions.

According to the above model, HFS elements like Zr would have concentrated preferentially with crystallization of the silicate melt in the outer parts of the pegmatites and the REE would have concentrated in their cores, together with the crystallized fluoride melts. This is precisely what is observed in many of the pegmatites. They are commonly zoned with Zr-enriched outer parts and fluorite and REE-rich cores (Fig. 11).

Table 5

Estimate of the proportion of fluoride melt relative to silicate melt involved in the formation of hypersolvus/subsolvus granites and pegmatites.

Units	REE wt.%	Weight% fluoride melt
Hypersolvus granites	0.25 ¹	2.7
Subsolvus granites	0.55 ¹	6.0
Pegmatite	1.12 ¹	12.1
Fluoride melt	9.25 ²	

¹ Average content of La + Ce + Nd + Y in core from drill holes ALT 1102 and ALT 1103 (Appendix B).

² Average content of Type 2 inclusions (Table 3).

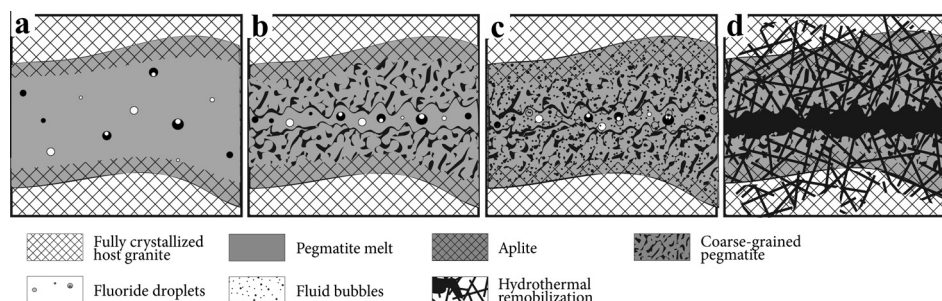


Fig. 10. Sketch showing the possible evolution of the Strange Lake pegmatites. (a) Formation of aplite, (b) formation of coarsely crystalline border pegmatite, (c) crystallization of the fluoride melts in the pegmatite core and exsolution of a hydrothermal fluid, (d) fluid overpressure-induced fracturing of the pegmatites and remobilization of REE/HFSE into fractures and dissolution-related porosity. Refer to the main text for further detail.

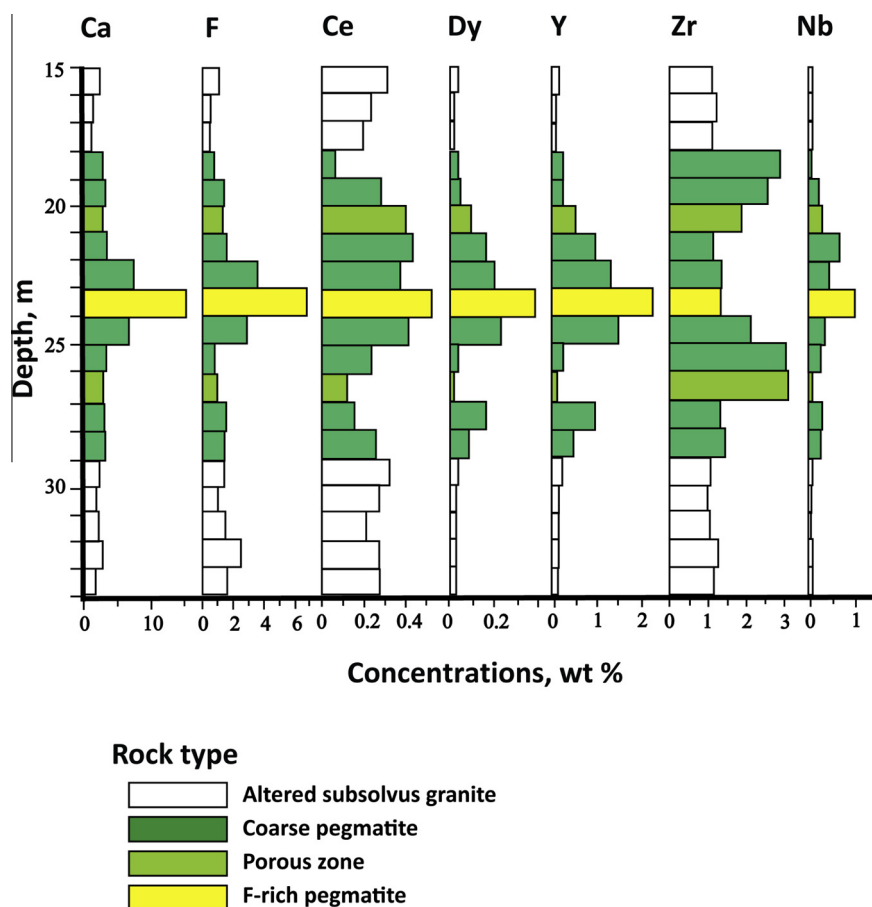


Fig. 11. The distribution of selected elements in a typical pegmatite and adjacent granite from the potential ore zone (drill hole BZ09003). The REE, Nb, Ca and F are concentrated in the core of the pegmatite, whereas Zr is concentrated in its outer parts. After Brosseau-Liard (2012).

5.9. The genesis of a world class REE deposit at Strange Lake

Multiple processes acted in concert to provide the enrichment needed to make Strange Lake a world class rare metal deposit, namely fractional crystallization, which concentrated the incompatible high field strength elements, e.g., Zr and Nb, in the residual silicate magmas, liquid immiscibility that partitioned the REE preferentially into the fluoride melts and Zr and Nb into the silicate melt, and post-magmatic hydrothermal processes that remobilized Zr, Nb and REE. With progressive fractional crystallization, the proportion of fluoride droplets gradually increased in the residual magmas and scavenged REE, and the most evolved silicate melt and its suspension of fluoride droplets eventually intruded fractures within the crystallized carapace, forming pegmatite and associated aplite sheets. There Zr concentrated with the early crystallizing silicate minerals in the outer parts of the pegmatites, and Nb and REE with the late crystallizing silicate and fluoride melts, respectively, in their cores. Redistribution of the REE, Zr and Nb and their further concentration ensued with the exsolution of an aggressive aqueous fluid, which decomposed primary REE and HFSE minerals in the pegmatites and adjacent granites and reprecipitated

them as secondary minerals at relatively low temperature, culminating in the formation of a deposit that is now the target of economic exploitation.

6. CONCLUSIONS

This study has documented a rare example of natural fluoride–silicate melt immiscibility and the first example in which exsolution of a fluoride melt has provided a new means of metal concentration. Analogous to the sulfide liquids that are responsible for the formation of magmatic Ni-Cu-PGE deposits, this liquid not only preferentially partitioned the REE from its conjugate silicate liquid but continued to scavenge REE from the residual silicate melts eventually concentrating the REE to potentially economic levels in the pegmatite cores. Immiscibility of the type described here probably will continue to be a rarely observed phenomenon. Further examples will most likely be found in lithium-rich systems, as the presence of lithium serves to reduce the concentration of fluorine required to produce an immiscible fluoride melt. In such systems, as at Strange Lake, the Ca-fluoride melt will likely evolve by exsolving a REE-fluoride melt, potentially further enriching the REE, and the conjugate silicate melt will concentrate HFSE like Zr and Nb.

Appendix A

Bulk rock compositions in wt.%; B-Zone, drill hole BZ09003 (wt.%). The data were provided by Quest Rare Minerals Ltd.

Depth (m)	Lithology	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ (total)	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Zr	Nb	F	Y	TRE	LRE	Total
5.00	Subsolvus granites	70.81	8.48	5.02	0.18	0.52	1.82	3.22	3.88	0.32	0.05	1.26	0.13	0.58	0.19	0.89	0.61	97.15
7.00		70.57	8.08	5.56	0.18	0.42	1.73	3.28	3.95	0.25	0.04	1.29	0.13	0.72	0.16	0.71	0.48	96.91
9.00		71.21	8.14	6.85	0.15	0.08	1.57	3.57	3.79	0.25	0.02	1.23	0.10	0.56	0.17	0.80	0.55	98.32
11.00		68.83	8.35	7.04	0.28	0.85	2.26	3.62	3.61	0.33	0.03	0.89	0.13	0.71	0.23	1.02	0.69	97.95
12.00		69.71	8.45	8.25	0.20	0.21	1.52	4.08	3.42	0.31	0.02	1.04	0.08	0.55	0.18	0.79	0.53	98.63
13.00		69.45	8.05	8.27	0.17	0.08	1.51	3.73	3.42	0.27	0.02	0.92	0.09	0.74	0.20	0.90	0.61	97.63
14.00		70.77	8.13	7.37	0.18	0.04	1.73	3.74	3.58	0.43	0.02	1.07	0.08	0.55	0.18	0.71	0.46	98.41
15.00		72.13	8.53	4.84	0.17	0.14	2.44	3.72	3.31	0.43	0.06	1.10	0.14	1.13	0.19	0.95	0.68	99.08
16.00		69.34	8.24	6.57	0.13	0.06	1.54	4.31	3.70	0.21	0.06	1.23	0.12	0.55	0.12	0.67	0.50	96.73
17.00		69.99	8.29	5.91	0.14	0.31	1.22	4.32	3.42	0.25	0.07	1.10	0.11	0.51	0.11	0.58	0.42	96.22
18.00	Pegmatites	67.77	5.02	6.84	0.53	0.16	2.80	2.57	2.82	1.39	0.03	2.87	0.10	0.77	0.25	0.55	0.15	94.21
19.00		68.89	5.17	5.70	0.47	0.38	3.33	2.12	2.21	1.29	0.15	2.53	0.29	1.39	0.26	1.01	0.59	94.94
20.00		73.04	4.36	5.90	0.10	0.15	2.88	2.88	0.37	1.20	0.14	1.88	0.41	1.37	0.56	1.66	0.84	96.34
21.00		73.71	3.43	5.07	0.09	0.20	3.47	2.80	0.47	0.64	0.12	1.14	0.87	1.62	0.99	2.37	0.96	96.00
22.00		58.79	4.20	6.45	0.32	1.77	7.45	4.28	0.33	0.51	0.05	1.35	0.48	3.55	1.33	2.75	0.88	92.29
23.00		37.27	4.36	10.31	0.74	2.99	15.28	4.77	0.72	0.51	0.18	1.30	1.27	6.74	2.27	4.49	1.31	90.94
24.00		58.03	5.46	6.14	0.39	2.12	6.69	1.16	3.98	0.71	0.09	2.10	0.50	2.89	1.50	3.04	0.94	93.32
25.00		68.72	4.91	8.05	0.29	0.31	3.43	1.61	3.86	0.94	0.04	2.99	0.38	0.79	0.29	0.92	0.47	97.25
26.00		74.83	6.26	3.07	0.16	0.06	2.91	0.89	5.09	0.67	0.01	3.34	0.10	0.99	0.15	0.49	0.25	98.87
27.00		68.79	4.88	8.71	0.25	0.16	3.02	3.50	1.92	0.79	0.01	1.31	0.43	1.57	0.99	1.85	0.44	97.18
28.00		68.14	6.57	6.70	0.44	0.32	3.24	3.20	3.24	0.43	0.02	1.43	0.35	1.45	0.49	1.26	0.56	96.78
29.00	Subsolvus granites	69.53	7.83	6.42	0.18	0.09	2.39	2.85	4.57	0.38	0.06	1.06	0.13	1.43	0.25	1.01	0.65	97.92
30.00		70.21	8.37	5.61	0.26	0.26	1.89	3.41	4.42	0.27	0.01	0.97	0.11	1.02	0.17	0.80	0.55	97.62
31.00		68.52	8.14	6.66	0.22	0.09	2.24	3.64	4.19	0.33	0.01	1.03	0.08	1.55	0.17	0.71	0.46	97.40
32.00		69.79	8.22	5.59	0.07	0.05	2.81	3.18	4.23	0.30	0.08	1.27	0.11	2.52	0.18	0.84	0.58	99.06
34.00		69.31	8.17	5.38	0.08	0.05	1.92	3.96	3.85	0.30	0.03	1.15	0.10	1.64	0.16	0.81	0.58	96.74
36.00		70.05	8.17	7.14	0.06	0.02	0.97	4.19	3.94	0.30	0.05	1.14	0.10	0.85	0.20	0.98	0.69	97.95
38.00		71.01	8.45	5.17	0.04	0.02	2.81	3.42	4.00	0.29	0.05	1.16	0.10	2.23	0.17	0.77	0.52	99.51
40.00		70.41	8.35	6.52	0.05	0.03	1.27	3.82	4.00	0.25	0.05	1.40	0.10	1.04	0.18	0.79	0.54	98.08
42.00		70.51	8.51	5.42	0.05	0.03	2.00	3.51	4.02	0.29	0.05	1.09	0.10	1.59	0.16	0.71	0.48	97.87
44.00		69.96	8.48	5.48	0.06	0.03	2.05	3.38	4.10	0.29	0.03	1.19	0.12	1.65	0.15	0.83	0.61	97.65
46.00		70.17	8.44	6.30	0.06	0.03	1.77	3.69	3.87	0.32	0.05	1.07	0.10	1.54	0.16	0.72	0.49	98.12
48.00		70.40	8.21	6.50	0.07	0.03	1.71	4.04	4.11	0.30	0.05	1.07	0.11	1.45	0.14	0.72	0.51	98.75
50.00		69.83	8.08	6.50	0.12	0.03	2.01	3.42	4.28	0.25	0.04	1.03	0.12	1.61	0.15	0.74	0.52	98.05
52.00		69.92	8.19	6.95	0.16	0.12	1.55	4.16	3.76	0.31	0.06	0.85	0.11	1.07	0.14	0.91	0.70	98.11
54.00		70.23	8.38	6.81	0.16	0.13	1.37	4.12	3.76	0.25	0.04	1.15	0.11	0.93	0.17	0.86	0.61	98.30
56.00		69.89	8.55	7.07	0.20	0.20	1.57	4.21	3.71	0.33	0.01	1.05	0.10	0.93	0.14	0.69	0.48	98.51
58.00		71.45	8.71	6.46	0.20	0.15	1.54	4.11	3.87	0.35	0.03	1.14	0.08	0.96	0.14	0.71	0.50	99.76
60.00		70.17	8.54	6.72	0.20	0.28	1.38	3.75	3.71	0.29	0.06	1.16	0.08	0.89	0.13	0.72	0.52	97.94
62.00		71.35	8.29	6.38	0.16	0.17	1.43	3.84	3.89	0.33	0.06	1.15	0.10	0.79	0.12	0.70	0.53	98.63
64.00		71.04	8.34	6.07	0.16	0.17	1.69	4.00	3.70	0.34	0.09	1.21	0.10	0.71	0.15	0.71	0.48	98.33
66.00		70.58	8.18	6.46	0.15	0.08	1.68	4.05	3.66	0.35	0.08	1.11	0.17	0.63	0.17	0.75	0.49	97.92
68.00		70.28	8.03	6.92	0.14	0.21	1.54	3.57	4.23	0.26	0.09	1.10	0.16	0.70	0.21	0.92	0.62	98.14
70.00		70.69	7.21	5.91	0.13	0.51	1.74	2.11	4.82	0.55	0.03	2.09	0.12	0.76	0.23	0.84	0.50	97.51
72.00		70.41	7.58	7.35	0.12	0.12	1.66	3.50	4.35	0.40	0.07	1.63	0.10	0.90	0.19	0.76	0.49	98.95

Appendix B

Bulk composition in wt.% of hypersolvus granites from the Alterra area, drill holes ALT11002 and ALT11 003. The data were provided by Quest Rare Minerals Ltd.

Depth (m)	Lithology	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ (total)	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Zr	Nb ₂ O ₅	F	Y	TRE	LRE ¹	Total
4.92	Hypersolvus granite	70.32	11.30	4.87	0.11	0.09	0.99	4.83	4.65	0.29	0.04	0.46	0.07	0.47	0.06	0.21	0.16	98.75
6.92		69.89	11.33	5.30	0.13	0.11	1.18	4.83	4.64	0.27	0.01	0.39	0.07	0.46	0.06	0.22	0.16	98.88
8.92		70.21	11.35	4.49	0.09	0.07	1.00	4.64	4.59	0.31	0.02	0.43	0.06	0.48	0.06	0.21	0.16	98.01
10.92		69.60	11.53	4.35	0.09	0.05	0.92	4.89	4.43	0.32	0.02	0.38	0.05	0.46	0.06	0.23	0.18	97.38
12.27		70.15	11.88	4.58	0.09	0.06	1.14	4.42	5.88	0.27	0.02	0.32	0.05	0.48	0.05	0.17	0.13	99.55
14.27		69.12	11.31	4.43	0.09	0.06	1.31	3.89	6.50	0.24	0.02	0.23	0.04	0.57	0.04	0.16	0.12	98.02
17.10		69.42	11.57	4.46	0.09	0.05	1.33	4.36	5.96	0.25	0.02	0.26	0.04	0.67	0.05	0.14	0.10	98.67
18.10		69.60	11.54	4.59	0.10	0.06	1.39	4.84	5.27	0.26	0.01	0.26	0.04	0.52	0.04	0.16	0.12	98.68
19.65		69.78	11.38	4.50	0.12	0.12	1.38	4.83	4.42	0.25	0.02	0.44	0.05	0.53	0.05	0.19	0.14	98.05
24.00		71.26	10.85	4.97	0.16	0.15	1.31	6.51	0.96	0.31	0.03	0.67	0.12	0.44	0.14	0.31	0.21	98.19
38.14		68.91	9.77	4.92	0.23	0.06	2.49	5.84	2.32	0.37	0.04	0.55	0.17	1.33	0.15	0.40	0.27	97.54
44.25		69.29	10.62	5.06	0.12	0.06	0.99	4.20	5.45	0.26	0.02	0.32	0.10	0.47	0.10	0.33	0.24	97.39
48.25		69.49	11.24	4.56	0.09	0.06	0.84	4.67	4.81	0.26	0.02	0.38	0.06	0.47	0.05	0.19	0.14	97.17
50.25		70.65	11.45	4.62	0.08	0.06	0.83	4.74	4.80	0.25	0.03	0.34	0.05	0.43	0.04	0.18	0.13	98.56
52.25		69.72	11.45	4.66	0.09	0.04	0.86	4.80	4.71	0.26	0.01	0.41	0.06	0.49	0.04	0.18	0.13	97.79
54.25		70.36	11.43	4.75	0.11	0.04	0.87	4.93	4.53	0.30	0.02	0.46	0.06	0.46	0.04	0.19	0.15	98.55
55.58		70.38	10.85	4.90	0.13	0.05	0.91	4.92	4.19	0.28	0.02	0.64	0.07	0.51	0.09	0.24	0.17	98.18
56.30		73.14	7.20	5.69	0.23	0.06	1.75	4.41	2.02	0.50	0.06	0.52	0.38	1.02	0.27	0.62	0.41	97.87
57.45		69.54	10.82	5.79	0.17	0.05	0.85	6.14	3.13	0.32	0.03	0.60	0.11	0.52	0.13	0.38	0.27	98.58
58.45		69.85	10.84	5.24	0.14	0.05	0.84	5.07	4.38	0.32	0.03	0.53	0.09	0.47	0.10	0.31	0.22	98.26
59.45		69.90	11.57	4.83	0.11	0.05	1.11	5.16	4.44	0.36	0.02	0.49	0.09	0.61	0.07	0.21	0.15	99.01
60.45		69.25	11.45	4.65	0.09	0.05	1.03	5.21	4.96	0.28	0.01	0.45	0.06	0.53	0.06	0.21	0.15	98.28
62.45		69.47	11.70	4.53	0.08	0.04	1.14	5.23	5.07	0.26	0.01	0.31	0.05	0.59	0.04	0.16	0.12	98.67
64.45		70.20	12.01	4.51	0.09	0.05	1.11	5.21	5.04	0.26	0.02	0.31	0.05	0.59	0.04	0.16	0.12	99.64
66.45		70.24	11.82	4.58	0.09	0.04	1.18	5.34	4.91	0.27	0.01	0.31	0.05	0.57	0.04	0.16	0.12	99.58
68.45		69.18	11.63	4.82	0.10	0.05	1.55	5.07	5.01	0.32	0.02	0.48	0.06	0.78	0.06	0.26	0.20	99.39
70.45		70.17	11.51	4.82	0.10	0.05	1.02	5.06	4.62	0.30	0.02	0.40	0.05	0.55	0.04	0.19	0.15	98.92
72.45		69.57	12.17	4.08	0.08	0.04	1.52	4.87	4.73	0.29	0.03	0.47	0.06	0.72	0.06	0.24	0.18	98.92
74.45		69.94	11.42	4.24	0.05	0.05	1.85	4.67	4.73	0.25	0.02	0.35	0.05	0.94	0.04	0.17	0.13	98.77
76.00		69.30	11.55	4.14	0.04	0.04	2.13	4.55	4.77	0.25	0.01	0.31	0.05	0.99	0.05	0.16	0.12	98.34
27.53		70.51	11.46	5.21	0.10	0.04	0.96	4.50	5.85	0.25	0.01	0.31	0.05	0.58	0.09	0.25	0.19	100.17
29.53		70.69	10.75	4.81	0.11	0.04	0.81	4.74	4.51	0.26	0.01	0.55	0.07	0.46	0.08	0.28	0.20	98.18
31.53		70.15	10.78	4.83	0.11	0.04	0.79	4.76	4.51	0.27	0.02	0.53	0.07	0.47	0.08	0.26	0.19	97.67
33.53		70.85	9.97	5.00	0.14	0.03	0.84	6.06	2.42	0.30	0.02	0.64	0.14	0.51	0.15	0.50	0.35	97.57
38.30		70.64	9.10	4.74	0.20	0.06	1.87	5.74	2.03	0.78	0.06	0.90	0.72	0.92	0.39	0.79	0.47	98.94
38.67		70.56	10.10	4.77	0.17	0.06	1.27	6.76	1.41	0.51	0.02	0.64	0.21	0.67	0.15	0.42	0.27	97.72
40.25		70.36	10.87	4.87	0.13	0.07	0.87	5.44	4.01	0.33	0.01	0.59	0.09	0.49	0.09	0.25	0.17	98.47
42.25		70.38	11.07	4.70	0.11	0.06	0.83	5.01	4.69	0.29	0.02	0.46	0.10	0.47	0.06	0.23	0.16	98.49
44.25		70.14	11.48	4.81	0.12	0.06	0.83	4.89	4.65	0.30	0.01	0.48	0.09	0.48	0.07	0.21	0.14	98.60
46.25		70.76	11.11	4.77	0.12	0.06	0.82	4.79	4.85	0.29	0.02	0.47	0.08	0.48	0.08	0.23	0.16	98.94
47.50		71.20	11.36	4.90	0.12	0.05	0.97	5.01	4.46	0.30	0.01	0.48	0.09	0.55	0.10	0.24	0.15	99.83
49.23		69.35	9.43	4.67	0.16	0.05	2.23	6.10	1.46	0.45	0.02	1.46	0.26	1.25	0.15	0.41	0.28	97.45
53.62		70.13	11.28	4.77	0.13	0.04	0.97	5.12	4.60	0.30	0.01	0.57	0.09	0.61	0.08	0.27	0.19	98.97
55.62		69.91	11.31	4.71	0.11	0.03	0.82	5.26	4.35	0.28	0.02	0.44	0.08	0.52	0.07	0.21	0.15	98.11

57.62		71.00	10.55	4.44	0.11	0.03	0.95	4.98	4.17	0.26	0.01	0.44	0.15	0.65	0.08	0.25	0.18	98.07
58.96		70.74	11.81	4.54	0.09	0.04	0.98	5.07	5.22	0.26	0.01	0.37	0.06	0.53	0.05	0.16	0.12	99.93
60.00		71.08	11.35	4.52	0.09	0.04	1.32	4.87	5.08	0.27	0.01	0.33	0.11	0.71	0.08	0.24	0.17	100.11
61.55		70.88	11.78	4.57	0.09	0.04	0.89	4.52	5.88	0.26	0.01	0.31	0.06	0.46	0.05	0.19	0.14	99.98
63.55		70.65	11.78	4.25	0.07	0.04	1.22	4.98	4.94	0.28	0.02	0.29	0.05	0.57	0.05	0.18	0.13	99.37
65.55		70.89	11.65	4.50	0.07	0.04	1.28	5.14	5.03	0.25	0.02	0.31	0.05	0.58	0.04	0.14	0.10	99.99
67.55		69.70	11.51	4.40	0.10	0.04	1.22	4.95	4.81	0.25	0.01	0.32	0.05	0.58	0.04	0.16	0.12	98.13
69.55		70.21	11.66	4.58	0.09	0.04	1.32	5.00	4.80	0.26	0.01	0.35	0.06	0.63	0.05	0.17	0.13	99.21
71.55		70.63	11.66	4.75	0.11	0.05	0.84	5.20	4.70	0.28	0.01	0.40	0.05	0.49	0.05	0.19	0.15	99.41
73.55		70.10	11.34	4.91	0.12	0.06	0.80	5.17	4.75	0.30	0.01	0.52	0.07	0.50	0.06	0.21	0.16	98.91
75.55		70.64	11.23	4.93	0.12	0.04	0.71	5.37	4.71	0.32	0.02	0.54	0.09	0.52	0.06	0.25	0.19	99.54
77.55		70.77	11.41	4.83	0.11	0.06	0.85	5.27	4.82	0.29	0.01	0.46	0.07	0.50	0.07	0.21	0.15	99.73
79.55		70.80	11.41	4.81	0.11	0.05	0.71	5.31	4.77	0.29	0.01	0.43	0.06	0.49	0.05	0.21	0.16	99.52
11.48	Pegmatites	70.60	9.70	3.11	0.10	0.07	2.03	2.54	5.13	0.59	0.03	2.03	0.22	0.78	0.27	0.39	0.22	97.59
16.27		70.23	11.47	4.67	0.11	0.06	1.32	4.37	5.85	0.26	0.01	0.31	0.04	0.52	0.04	0.16	0.12	99.42
16.79		71.80	8.35	3.77	0.07	0.05	3.07	1.65	5.50	0.65	0.06	1.21	0.29	1.67	0.08	0.40	0.32	98.63
19.03		68.61	7.78	2.85	0.24	0.22	3.70	1.18	5.52	0.51	0.05	3.00	0.23	1.14	0.31	0.49	0.26	95.83
21.00		78.34	6.93	1.22	0.03	0.08	1.29	0.80	4.96	0.80	0.04	1.48	0.28	0.27	0.29	0.46	0.23	97.26
22.00		69.45	6.52	3.60	0.07	0.20	3.24	0.72	4.63	0.53	0.15	2.51	0.88	1.14	0.96	1.53	0.83	96.12
23.00		69.41	6.39	4.27	0.08	0.22	2.60	0.96	4.37	0.60	0.08	1.70	0.56	0.66	0.74	1.07	0.56	93.70
24.82		73.92	6.75	3.19	0.12	0.33	2.57	0.73	5.09	0.36	0.05	1.40	0.48	0.99	0.51	0.71	0.39	97.18
25.88		72.67	8.62	2.95	0.08	0.18	1.92	1.00	6.04	0.43	0.10	2.05	0.31	0.61	0.41	0.62	0.35	97.99
26.88		83.11	4.71	2.13	0.06	0.09	1.13	0.41	3.60	0.28	0.06	1.01	0.32	0.32	0.26	0.47	0.31	97.96
27.65		74.84	6.48	2.58	0.11	0.16	2.13	1.13	4.07	0.42	0.08	1.54	0.67	0.72	0.49	0.87	0.53	96.29
28.26		87.67	1.41	0.65	0.04	0.23	3.23	0.07	1.14	0.04	0.01	0.37	0.08	1.61	1.35	1.04	0.26	98.93
28.89		68.22	2.62	1.66	0.33	0.73	6.18	0.47	1.61	0.36	0.03	1.31	0.55	2.48	2.62	2.34	0.67	91.50
29.68		68.63	4.66	4.96	0.20	0.63	4.18	1.81	2.46	0.66	0.09	1.53	0.77	1.58	1.92	2.20	0.94	96.27
30.70		55.48	5.41	3.50	0.80	1.46	8.50	0.72	4.22	0.47	0.03	1.82	0.53	2.63	3.36	2.63	0.84	91.56
30.90		66.51	4.99	4.29	0.29	0.87	4.17	1.70	2.56	0.72	0.09	1.87	0.51	1.38	2.09	2.29	0.98	94.33
31.80		74.19	4.50	4.57	0.20	0.87	2.31	2.34	2.15	0.52	0.11	1.69	0.31	0.74	0.67	0.86	0.42	96.02
32.77		69.77	8.54	2.10	0.18	0.56	2.68	1.00	6.74	0.31	0.13	3.20	0.24	0.18	0.37	0.73	0.46	96.72
33.28		71.20	6.33	5.79	0.32	0.57	2.20	3.93	2.26	0.68	0.03	2.83	0.30	0.46	0.16	0.33	0.19	97.39
34.10		64.36	5.17	6.50	0.46	2.10	3.91	1.79	3.86	0.99	0.02	4.02	0.26	0.68	0.36	0.39	0.13	94.86
35.00		70.75	5.43	4.55	0.45	0.88	3.51	1.24	4.22	0.61	0.17	1.34	0.35	0.73	0.37	0.99	0.67	95.58
35.88		68.28	4.86	4.30	0.26	0.27	2.45	2.37	4.03	0.49	0.23	1.67	0.39	1.68	0.58	1.12	0.69	92.96
36.74		63.47	4.33	7.23	0.30	0.14	1.58	4.58	3.38	1.75	0.03	4.55	0.32	1.70	0.34	0.44	0.18	94.12
37.40		65.79	6.62	6.65	0.27	0.07	1.87	5.86	2.17	0.74	0.03	2.72	0.33	1.81	0.21	0.37	0.20	95.51
38.58		66.53	6.24	5.93	0.38	0.64	3.54	3.95	2.59	0.59	0.06	2.42	0.49	0.96	0.27	0.58	0.36	95.18
56.60		64.30	6.10	7.72	0.37	0.19	2.46	4.13	3.79	0.62	0.04	1.59	0.71	1.66	0.81	1.13	0.59	95.63
7.59		69.92	5.75	4.90	0.17	0.27	4.17	1.18	4.51	0.43	0.25	2.76	0.29	1.01	0.42	1.18	0.86	97.21
34.02		80.28	2.72	3.19	0.08	0.06	1.97	2.55	1.37	0.53	0.04	2.21	1.22	1.11	0.15	0.61	0.47	98.08
34.79		66.26	7.57	7.55	0.21	0.04	1.31	5.69	3.13	0.42	0.05	2.50	0.23	0.74	0.16	0.39	0.24	96.26
37.45		71.01	6.86	4.85	0.18	0.05	2.21	4.80	2.84	0.55	0.06	1.75	0.33	1.10	0.41	0.76	0.42	97.75
39.21		64.38	5.07	5.43	0.19	0.24	4.12	3.79	2.56	2.39	0.01	2.49	1.86	1.87	0.49	1.01	0.66	95.90
39.60		68.39	8.61	4.81	0.18	0.09	1.44	4.89	3.73	0.44	0.03	1.85	0.71	0.74	0.17	0.52	0.36	96.59

(continued on next page)

Appendix B (continued)

Depth (m)	Lithology	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ (total)	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Zr	Nb ₂ O ₅	F	Y	TRE	LRE ¹	Total
48.52		74.62	5.55	3.83	0.06	0.16	3.39	2.86	1.93	0.23	0.18	1.40	0.23	1.56	0.19	0.85	0.66	97.04
49.88		67.34	6.12	4.69	0.09	0.13	4.12	2.90	3.75	0.59	0.07	2.75	0.28	2.40	0.28	0.64	0.40	96.15
58.61		68.56	6.88	5.45	0.19	0.06	1.79	5.02	2.89	0.46	0.04	0.87	0.83	1.66	0.54	0.79	0.44	96.04
61.30		67.80	6.66	5.50	0.11	0.24	2.65	2.85	3.88	0.28	0.10	0.67	0.62	1.98	0.75	0.97	0.53	95.06
38.96	Subsolvus granite	69.58	6.85	7.62	0.23	0.05	1.09	5.21	2.37	0.40	0.05	1.05	0.22	0.92	0.24	0.73	0.52	96.62
39.46		68.74	8.69	5.61	0.15	0.08	1.98	5.28	2.37	0.33	0.03	1.02	0.20	1.36	0.24	0.79	0.57	96.86
41.00		73.43	6.97	4.79	0.13	0.05	1.15	3.92	3.26	0.35	0.03	0.94	0.19	0.80	0.20	0.58	0.41	96.79
42.00		69.68	8.15	5.31	0.17	0.08	2.71	2.67	5.82	0.53	0.05	0.67	0.23	1.23	0.09	0.52	0.42	97.89
43.00		68.74	9.39	4.97	0.17	0.12	1.69	3.87	5.10	0.30	0.03	0.93	0.13	0.70	0.14	0.42	0.30	96.70
1.03		71.85	7.00	6.15	0.18	0.26	2.35	3.17	3.22	0.63	0.03	1.60	0.22	0.67	0.16	0.36	0.23	97.85
3.00		72.20	7.41	6.86	0.21	0.49	1.43	3.88	3.14	0.44	0.02	1.14	0.24	0.43	0.16	0.47	0.33	98.50
5.00		70.98	6.90	7.00	0.22	0.24	1.48	3.36	3.32	0.54	0.05	1.38	0.29	0.36	0.14	0.43	0.31	96.68
7.00		71.88	6.47	6.81	0.19	0.14	1.74	2.98	3.42	0.55	0.04	1.75	0.23	0.31	0.14	0.36	0.24	97.02
7.98		69.57	6.32	6.85	0.25	0.32	2.36	3.25	3.34	0.72	0.03	2.18	0.27	0.29	0.11	0.32	0.21	96.19
9.00		70.24	6.89	7.47	0.23	0.11	1.73	3.85	3.20	0.52	0.02	1.63	0.20	0.43	0.10	0.49	0.37	97.10
10.00		72.47	9.46	6.89	0.19	0.08	1.00	4.73	3.78	0.35	0.01	0.79	0.14	0.37	0.13	0.48	0.36	100.85
11.21		70.44	8.14	7.34	0.20	0.12	1.63	4.60	2.84	0.38	0.01	1.33	0.11	0.55	0.12	0.51	0.39	98.32
13.21		70.84	8.91	6.93	0.15	0.07	1.01	4.66	3.22	0.31	0.01	0.59	0.08	0.50	0.09	0.51	0.41	97.88
15.21		69.34	10.94	4.86	0.12	0.21	1.13	4.03	5.66	0.25	0.01	0.35	0.08	0.48	0.11	0.23	0.16	97.81
16.70		72.89	8.02	7.32	0.17	0.30	1.04	4.13	3.75	0.32	0.01	0.62	0.09	0.55	0.12	0.63	0.50	99.95
18.00		70.93	8.69	6.70	0.14	0.23	0.87	4.10	3.82	0.29	0.01	0.54	0.08	0.44	0.10	0.56	0.45	97.52
19.70		71.94	8.53	6.77	0.14	0.10	0.70	4.38	3.30	0.24	0.02	0.42	0.07	0.41	0.09	0.49	0.39	97.59
21.70		73.36	7.99	7.95	0.17	0.32	0.81	4.47	3.33	0.29	0.01	0.63	0.08	0.46	0.09	0.51	0.41	100.46
23.70		70.93	7.66	8.17	0.18	0.29	0.81	4.07	3.66	0.31	0.01	0.59	0.08	0.49	0.10	0.55	0.44	97.90
25.05		70.68	11.81	4.88	0.10	0.06	0.90	5.80	3.87	0.22	0.01	0.23	0.04	0.48	0.06	0.21	0.16	99.33
26.28		67.15	7.38	11.56	0.22	0.11	1.14	4.93	3.29	0.39	0.01	0.54	0.06	0.88	0.10	0.79	0.66	98.56
34.26		71.18	9.16	4.99	0.17	0.04	1.24	6.71	0.47	0.46	0.07	1.04	0.27	0.66	0.23	0.64	0.43	97.33
34.99		68.49	7.68	7.87	0.21	0.05	2.35	5.46	2.27	0.46	0.04	1.24	0.20	1.29	0.22	0.68	0.48	98.51
36.00		67.29	7.32	8.34	0.22	0.07	2.32	4.85	2.70	0.53	0.05	1.06	0.25	1.39	0.29	0.90	0.64	97.58
50.63		68.63	8.15	7.36	0.20	0.08	1.78	5.46	3.01	0.54	0.04	1.22	0.23	1.20	0.18	0.64	0.46	98.73
51.63		64.07	6.25	12.44	0.28	0.10	2.06	6.02	3.08	0.63	0.03	1.02	0.23	1.73	0.24	0.93	0.69	99.12

¹ LREE is the total of La, Ce and Nd.

Appendix C

Electron microprobe standards, counting times and detection limits used in this study.

Element	Standard	Counting time (s)	Detection limits (ppm)	
			Silicate melt	Fluoride melt
Si	Diopside	20	661	299
Ti	TiO ₂	20	1136	–
Al	Orthoclase	20	496	–
Fe	Fe ₂ O ₃	20	748	–
Ca	Diopside	20	560	500
Na	Albite	20	531	463
K	Orthoclase	20	491	–
F	CaF ₂	20	2771	3537
Cl	Vanadinite	20	298	–
Zr	Zircon	20	2013	–
Nb	Na ₂ Nb ₂ O ₆	20	1363	841
Y	MAC-Y	20	–	1632
La	MAC-La	20	–	1934
Ce	MAC-Ce	20	–	1745
Nd	MAC-Nd	20	–	3260

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APPENDIX

See Appendices A, B and C.

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