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The role of magmatic and hydrothermal processes in the chemical evolution of the Strange Lake plutonic complex, Québec-Labrador

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Abstract The Strange Lake plutonic complex consists of three annular Mid-Proterozoic arfvedsonite-aegirine-bearing alkali granites emplaced in the Rae province of the Canadian Shield. The mineralogy, chemistry and structural setting of the complex are very similar to that of many peralkaline central salic complexes associated with the development of the Gardar rift in southern Greenland. The Strange Lake granites are highly fractionated (Rb/Sr = 5 to 160 and K/Rb = 27 to 120) and carry unusually high abundances of HFSE and REE-bearing exotic minerals (e.g. pyrochlore, gittinsite, elpidite, gadolinite and kainosite) which are reflected in the elevated HFSE (e.g. Zr = 307 to 16800 ppm) and REE (e.g. La = 84 to 1337 ppm) contents of the granites. HFSE and REE increase from the oldest intrusive unit, which is hypersolvus and unaltered, to the youngest, which is subsolvus and metasomatized. The unaltered granites display a restricted range of δ^{18}O values (+ 8.2 to + 9.6‰) and low δ^{18}O signatures for fresh arfvedsonite/aegirine (+ 4.8 to + 5.2‰). Anomalously high CaO (0.7 to 3.2 wt%) and MgO (0.1 to 0.6 wt%) concentrations characterize the altered subsolvus granites. These rocks also have elevated whole rock δ^{18}O values (+ 9.6 to + 11.9‰), negative $\Delta\delta^{18}O_{\text{quartz-alk.feld.}}$ (− 0.1 to − 1.6), and high δ^{18}O values of altered arfvedsonite (i.e. + 6.5 to 13.75‰) that correlates positively with whole rock δ^{18}O values. The chemical and isotopic data are consistent with a model in which the least evolved alkali granites are formed through differentiation from trachytic (syenitic) parents. Extreme HFSE and REE-enrichment may have been accomplished by differentiation through fractional crystallization and heterogenous distribution of F-rich silicic residual melts in which the REE and HFSE are transported as fluorocomplexes. The O-isotopic values are consistent with the circulation of low temperature (< 200° C) hydrothermal fluids in the youngest subsolvus intrusive unit which caused extensive Ca (Mg and Sr) metasomatism and fluorine leaching, widespread hematization, and remobilization of the HFSE and REE.

Introduction

The Strange Lake plutonic complex is a composite Mid-Proterozoic intrusion of alkali granites located in Labrador, Canada. The complex has amongst the highest contents of REE and HFSE ever reported for alkali granites giving rise to a large suite of exotic minerals some of which are unique to the complex. Locally, the HREE, Nb, Zr and Be concentrations are sufficiently high that they have been considered for economic exploitation (Miller 1985). Three intrusive units were recognized from crosscutting relations, petrographic criteria and exotic mineral contents (e.g. Miller 1986). Their origin and evolution, including the degree of HFSE and REE enrichment, were considered to be magmatic or late magmatic/early hydrothermal (Miller, 1985, 1986, 1990; Currie 1985; Birkett et al. 1992). However, recent petrographic and fluid inclusion studies by Salvi and Williams-Jones (1990, 1993a, b) identified a low temperature (< 200° C), sub-solidus Ca-metasomatic event which affected the youngest intrusive unit. This hydrothermal event caused widespread replacement of Na-HFSE and REE-bearing silicates by calcic pseudomorphs, major volume loss and remobilization of HREE and Y in the economically interesting zones.

In this paper we make use of major element, trace element and stable isotope geochemistry to investigate the petrogenesis of the complex and, in particular, the

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importance of magmatic and hydrothermal processes in the enrichment of HFSE and REE. Our data suggest that, although differentiation by alkali feldspar fractionation may have played a role in concentrating HFSE and REE, the extraordinarily high contents of these elements are best explained by a model involving a fluorine-rich primitive syenitic magma which was able to dissolve unusually high amounts of HFSE and REE as fluoro-complexes and concentrate them in late low-temperature residual silicic melts. Finally, the paper documents major and trace element variations and a $\delta^{18}O$ increases, which are attributed to extensive sub-solidus hydrothermal alteration.

Geological setting

The Strange Lake plutonic complex was emplaced in the Rae province of central Labrador, a high grade metamorphic terrane of Archean to Aphebian age (Currie 1985; Hoffman 1988). This anorogenic Mid Proterozoic complex (K-Ar age of 1163 ± 21 Ma on arfvedsonite and a whole rock Rb-Sr isochron of 1189 ± 32 Ma; Pillet et al. 1989) was intruded at the contact between Aphebian gneiss and an Elsonian monzonitic massif (Bélanger 1984; Miller 1986; Pillet 1989). The peralkalinity, mode of emplacement and age of the complex lead Currie (1985) and Pillet (1989) to suggest that it may belong to the Gardar igneous province (1320-1120 Ma; Upton and Emeleus 1987).

The complex forms a circular epizonal pluton 6 km in diameter which is surrounded by a fluorite and hematite-rich breccia (Fig. 1). Contacts with the wall rocks are extremely sharp. Crosscutting relations observed in the field and in core samples, combined with the occurrence of granite inclusions and marginal fine-grained facies, indicate that the complex comprises at least three major intrusive units of alkali granite successively emplaced as annular plutons around a central core (Miller 1985; Pillet 1989; this study, Fig. 1). Miller (1985), Pillet (1989) and Salvi (1990) identified several subtypes of alkali granites ranging from fine-grained equigranular granite to medium and coarse-grained porhyritic granite. The core of the complex is occupied by a small circular body of unaltered hypersolvus granite which was subsequctly intruded at its margins by an unaltered subsolvus granite. The latter contains abundant subrounded to amoeboid-shaped inclusions of fine-grained trans-solvus melanocratic granite (presumably a marginal facies forming the roof of the hypersolvus unit) and numerous rafts and roof pendants of the host monzonites. The youngest intrusive consists of an altered subsolvus granite which defines the external shell of the complex. Peralkaline granitic pegmatites form thin (10 to 50 cm), subvertical EW-trending dykes that were emplaced mainly into the altered subsolvus facies and are generally more intensely altered than their host. At the centre of the complex, a 6 to 20 m thick pegmatite-aplite sill comprises the bulk of the potential ore zone (Miller 1990).

The mineralogy and modal abundances of the granites and pegmatites are presented in Table 1. Alkali feldspar (albite, microcline and perthite), quartz, arfvedsonite, aegirine, aenigmatite, astrophyllite and fluorite are the principal mineral constituents of the Strange Lake granites and pegmatites. Microcline and/or arfvedsonite and/or quartz occur as phenocrysts; they can reach up to 1 cm in diameter. The complex, however, acquired its name from the unusual nature and abundance (up to 50%) of exotic REE and

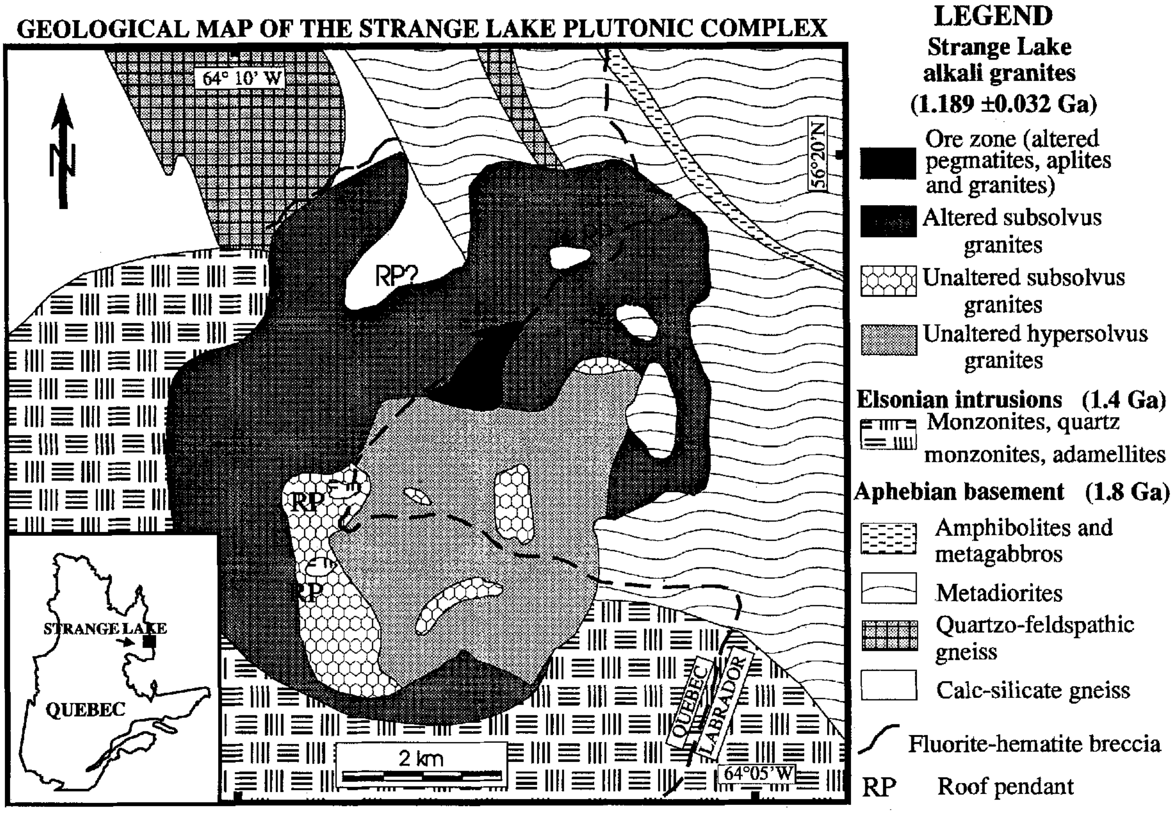


Fig. 1 Geologic map of the Strange Lake plutonic complex modified from Miller (1986) as a result of new geological data gathered by the McGill group

Table 1 Mineralogy and mode of the alkali granite units and the pegmatites and aplites forming the Strange Lake plutonic complex.

Mode (vol. %)				
Mineral	Hypersolvus Unaltered	Subsolvus Unaltered	Subsolvus Altered	Pegmatites/ Aplites
Quartz	20(15–25)	25(20–35)	25(20–35)	15–25
K-Feldspar	2(0–5)	40(35–45)	35(30–45)	20–40
Albite	2(1–5)	7(5–10)	5(0–10)	5–10
Perthite	60(45–70)	Tr.	Tr.	0–10
Aegirine	2(0–5)	5(0–10)	2(0–15)*	10–20
Arfvedsonite	10(5–15)	15(5–20)	15(0–20)*	10–20
Aenigmatite	Tr.	Tr.	N	N
Astrophyllite	Tr.	Tr.	N	N
Fluorite	0–1	0–2	0–10	5–20
Hematite	N	Tr.	0–10	5–20
REE and HFSE-bearing minerals	0–5	5–10	10–20	10–50

* Aegirine and arfvedsonite are often intergrown. Source: Pillet (1989), Miller (1990), Salvi (1990) and this study. *Tr* = trace, N = none

HFSE-bearing minerals of which elpidite ($Na_2ZrSi_6O_{15}H_2O$), gittinsite ($CaZrSi_2O_7$), pyrochlore ($(Na, Ca, LREE)_2(Nb, Ta)_2O_6(OH, F)$), gadolinite ($Y_2Fe^{+2}Be_2Si_2O_{10}$ + HREE), kainosite ($Ca_2(Ce, Y, HREE)_2Si_4O_{12}(CO_3))H_2O$, gagarinite ($Na(Y, Ca, Na, REE)_2F_6$), bastnäsite ($(LREE)CO_3F$) and thorite ($ThSiO_4$) are amongst the most common (Miller 1985; Birkett et al. 1992). The abundance of exotic HFSE and REE-bearing minerals increases from the hypersolvus granite to the late pegmatite-aplite dykes and sills. The alteration of the subsolvus granite is conspicuous and is largely reflected by: (1) the presence of scattered patches of hematite enclosing a variety of REE, HFSE and Ca-bearing minerals, (2) the replacement of arfvedsonite by hematite ± aegirine ± quartz, (3) the pseudomorphism of sodic exotic phases by calcic equivalents + quartz, and (4) the appearance of secondary blue-purple fluorite.

Whole rock isotopic, major and trace element geochemistry of the Strange Lake plutonic complex

Analytical procedures

Each sample collected from outcrops represents 2 to 5 kg of granite rock or 3 to 8 kg of pegmatite-aplite dyke material. Also analyzed were crushed samples of split core forming 1 to 5 m of a homogeneous granite section or the entire thickness of pegmatite dykes (5 to 15 kg). We believe the analytical results to be reliable due to the medium to coarse-grained size of the minerals in the pegmatites and aplites (< 2 mm to 3 cm, but mostly in the range of 5 mm to 1 cm; Miller 1985) and the large quantities of material processed. The major elements were analyzed by X-ray fluorescence following the standard procedures established by Norrish and Hutton (1969). The trace elements Zr, Nb, Y, Rb, Sr, Ba and Zn were also determined by XRF according to the method of Schroeder et al. (1980). However, due to the unusually high Zr, Nb, Y and Zn abundances of all granitic samples, we slightly modified the standard procedures. (1) After preliminary determinations of Zr, Y, Nb and total REE concentrations by XRF and INAA, we included these values in order to recalculate the total absorption coefficients (μ values) for the all trace elements analyzed by XRF. (2) We carefully selected the standard samples to establish calibration curves from which we extrapolated several Zr, Nb and Y values. Miller (1985) used special "spiked" standards for determining the Zr, Nb and Y abundances of the Strange Lake granites and pegmatites. We re-analyzed several of his samples and found that our Zr, Nb and Y values agreed to within 10% of his. Moreover, for the entire granitic and pegmatite suites, we observe an excellent linear correlation between Zr(XRF) and Hf(INAA), two elements analyzed by different methods but with identical behaviour in granitic systems.

Fe^{+2}/Fe^{+3} were determined by wet chemistry. Concentrations of the rare earth elements (REE) and Ta, Hf, Th, U, Cs and Sc were measured by INAA using a method which is fully described by Boily et al. (1989). Extractions for oxygen isotopic analyses were performed using the standard BrF_5 reaction technique described by Clayton and Mayeda (1963), followed by conversion of O_2 to CO_2 by reaction with hot graphite. Mass spectrometric analyses were carried out at the Université de Montréal on a Nuclide 6-60-RMS triple collector mass spectrometer. Values were corrected for instrumental errors using the method of Craig (1957) and Deines (1970). All oxygen isotope compositions are reported in δ notation relative to Standard Mean Ocean Water (SMOW; Baertschi 1976). Analytical precision is ± 0.3‰ for whole rock determinations and ± 0.1‰ for silicate mineral separates.

Results

In Table 2, we present representative major and trace element analyses of each granitic intrusive unit accompanied by their respective averages. Concentrations for selected samples of melanocratic inclusions, pegmatite-aplite dykes, and aphyric dykes are also provided. The complete set of analytical data can be obtained on request from the authors. Oxygen isotope analyses of whole rocks and mineral separates are reported in Table 3.

The granitic intrusives forming the Strange Lake complex have chemical compositions that are similar in many respects to those of other highly evolved peralkaline granites. Their agpaitic indices (molar $Na_2O + K_2O/Al_2O_3$) are commonly > 1 (0.86 to 1.35) and they exhibit extremely low K/Rb (25 to 120) and MgO, Ba, Sr, Sc and TiO_2 contents. They also show elevated Rb/Sr (5 to 160), strong negative Eu anomalies and high concentrations of fluorine ($F = 0.1$ to 1.2 wt%), iron ($FeO_t = 2.8$ to 6.5 wt%) and total alkalis ($Na_2 + K_2O = 7.8$ to 9.6 wt%). The Strange Lake alkali granites are exceptional for their enrichment in HFSE, REE and Zn and wide ranges of values for these elements (e.g. Zr = 307 to 16800 ppm, Nb = 26 to 1791, Y = 76 to 3600, Hf = 33 to 569, La = 84 to 1337, Yb = 25 to 346, Zn = 83 to 1158, Th = 12 to 727 ppm). Whole rock samples display a wide spread of $\delta^{18}O$ values (e.g. + 8.2 to 11.9‰; Table 2 and Fig. 2f).

The unaltered subsolvus and hypersolvus granites have very similar major element contents (Table 2). Their whole rock $\delta^{18}O$ values are also comparable (Table 3) and there is considerable overlap in their trace element abundances. However, the subsolvus granites are slightly more enriched in HFSE and REE (Fig. 2a–c). Various plots using the major elements reveal a lack of correlation (Fig. 2g) or considerable scatter (Fig. 2h). However, the unaltered granites exhibit positive linear correlations between all pairs of incompatible elements, notably amongst the HFSE (Hf, Zr, Ta, Nb, Th, Y), REE, Zn and Rb (Fig. 2a–c). Moreover, Al_2O_3 and Sc contents decrease systematically with K/Rb (Fig. 2d), whereas the HFSE (e.g. Y, Fig. 2e) and REE display a negative correlation with K/Rb. Σ REE, Σ HFSE and CaO show weak positive correlations with F and Sr.

With the exception of silica, the altered subsolvus granites have significantly different compositions from their unaltered equivalents. A major difference from the unaltered rocks is their strong and anomalous enrichment in CaO (0.7 to 3.2 wt%), MgO (0.1 to 0.6 wt%; Fig. 2h) and Sr (23 to 132 ppm.). On average, they have lower Al_2O_3, Na_2O, K_2O, F and lower and relatively constant K/Rb and Sc, slightly higher TiO_2 and total FeO, and significantly higher $\delta^{18}O$ and Fe_2O_3/FeO (Tables 2, 3; Figs. 2, 3). The altered granites show poor correlations amongst the incompatible elements (Fig. 2a–c) as well as with the major elements. HFSE and REE abundances of the altered granites are considerably higher than those of the unaltered granites, but show no obvious correlation with the degree of alteration (e.g. extent of hematization and abundance of secondary blue fluorite). This enrichment is also reflected in the REE chondrite-normalized profiles of the altered and unaltered granites, despite a wide range of values and overlapping patterns (Fig. 4).

Relative to the altered granites, the chemistry of the pegmatites and aplites is characterized by anomalously high CaO, MgO and TiO_2, low Al_2O_3, SiO_2 and Na_2O concentrations and slightly higher $\delta^{18}O$ values. These rocks also have extraordinarily high HREE, Y, Ta, Nb, Th and U contents that reach up to 20 times those of the altered subsolvus granites (Fig. 2a–c). Furthermore, they differ significantly from the altered subsolvus granites in having chondrite-normalized profiles that show even greater HREE enrichment relative to the LREE (Fig. 4).

Table 2 Selected major and trace element compositions of the principal rock types forming the Strange Lake plutonic complex: the hypersolvus and subsolvus alkali granites, granitic melanocratic inclusions, pegmatite-aplite dykes and aphyric granitic dykes, (—— not determined,* total iron as Fe_2O_3, A.I. agpaitic index, *L.O.I.* loss on ignition). Averages for the hypersolvus and subsolvus granites and for the pegmatites-aplites are also provided. n.d. = not detected.

Altered subsolvus alkali granites	25-C-1	LB13-8	LB54-44	SL183-1	SL5D-36
Major elements					
SiO_2 (wt %)	70.69	70.40	70.85	70.41	70.61
TiO_2	0.48	0.31	0.36	0.41	0.43
Al_2O_3	9.00	8.27	8.58	8.40	7.99
Fe_2O_3	4.27	5.77	4.50	2.88	4.80
FeO	1.45	0.32	1.06	1.02	0.63
MnO	0.20	0.11	0.15	0.14	0.15
MgO	0.16	0.48	0.18	0.10	0.25
CaO	1.40	1.39	2.27	1.16	2.72
Na_2O	3.98	3.46	4.06	3.98	3.76
K_2O	3.79	4.64	3.85	4.17	3.73
ZrO_2	1.61	2.12	1.76	2.38	2.46
Y_2O_3	0.36	0.42	0.32	0.91	0.29
Nb_2O_5	0.25	0.30	0.22	0.55	0.16
P_2O_5	0.02	0.02	0.02	0.02	0.02
F	0.61	0.18	0.51	0.24	0.59
A.I.	1.18	1.30	1.26	1.32	1.28
L.O.I.	0.79	0.63	0.60	1.88	0.72
Total	99.06	98.82	99.29	98.65	99.31
Trace elements					
Ba (ppm)	161	67	n.d.	50	13
Rb	791	1128	968	1232	963
Sr	39	83	132	80	108
Ta	52	65	62	126	49
Hf	352	506	427	534	569
Th	198	373	183	727	131
U	32	65	40	108	36
Zn	987	613	1002	1103	91
Sc	—	—	—	—	—
La	1003	781	972	686	655
Ce	1913	1418	1687	1453	114
Nd	774	619	693	619	501
Sm	167	182	182	286	130
Eu	11.1	9.7	8.2	16	6
Tb	30	38	29.2	79	20
Dy	205	249	195.3	530	153
Tm	19	28	204.5	53	21
Yb	161	199	156.6	346	189
Lu	20	26	21	42	26
Cs	—	—	—	—	—

Unaltered subsolvus alkali granites	38-A-1	57-A-2	57-D-1	58-C-4	SL204D-19
Major elements					
SiO_2 (wt %)	71.40	70.28	70.04	70.62	70.13
TiO_2	0.20	0.16	0.31	0.23	0.30
Al_2O_3	10.44	11.26	11.84	12.01	8.71
Fe_2O_3	2.65	2.85	1.51	1.98	4.50
FeO	2.73	2.16	3.20	2.81	1.53
MnO	0.11	0.13	0.11	0.14	0.15
MgO	0.01	0.01	0.01	0.01	0.25
CaO	1.40	0.79	0.71	0.55	0.15
Na_2O	4.99	4.65	5.23	5.13	6.28
K_2O	3.76	5.20	4.71	4.98	3.64
ZrO_2	0.81	1.25	1.64	0.30	1.46
Y_2O_3	0.20	0.26	0.16	0.13	0.28

Table 2 (continued)

Unaltered subsolvus alkali granites

	38-A-1	57-A-2	57-D-1	58-C-4	SL204D-19
Nb_2O_5	0.11	0.18	0.16	0.06	0.18
P_2O_5	0.01	0.02	0.02	0.02	0.02
F	0.69	0.76	0.67	0.68	1.0
A.I.	1.21	1.18	1.58	1.18	1.64
L.O.I.	0.43	0.50	0.41	0.49	1.51
Total	99.94	100.46	99.73	100.14	100.09
Trace elements					
Ba (ppm)	n.d.	26	86	60	n.d.
Rb	965	1086	521	481	746
Sr	53	26	18	12	37
Ta	19	—	33	13	—
Hf	134	192	91	61	—
Th	75	66	51	37	—
U	11	20	20	5	—
Zn	728	687	502	394	890
Sc	0.30	0.76	1.20	1.52	—
La	1113	473	395	311	—
Ce	1884	987	672	534	—
Nd	771	356	260	239	—
Sm	172	98	65	59.2	—
Eu	7.9	6.2	3.6	3.1	—
Tb	18	171	12	11	—
Dy	102	111	83	50	—
Tm	7	9	6	5	—
Yb	49	64	56	38	—
Lu	6	8	8	5	—
Cs	—	0.7	5.8	—	—

Unaltered hypersolvus alkali granites

	SL13D-12	49-A-1	48-A-8	LB10D-33	LB9D-13
Major elements					
SiO_2 (wt %)	69.55	72.08	69.99	70.18	70.68
TiO_2	0.32	0.31	0.23	0.28	0.30
Al_2O_3	11.81	10.90	10.71	12.44	12.22
Fe_2O_3	4.48	3.01	3.35	2.05	1.50
FeO	0.26	2.44	4.31	2.40	3.92
MnO	0.11	0.08	0.13	0.10	0.10
MgO	0.01	0.01	0.01	0.01	0.01
CaO	0.52	0.32	0.37	0.85	0.80
Na_2O	5.33	4.97	5.27	5.66	5.57
K_2O	4.34	4.70	4.56	4.92	4.75
ZrO_2	0.65	0.30	0.19	0.26	0.54
Y_2O_3	0.15	0.14	0.05	0.07	0.12
Nb_2O_5	0.12	0.13	0.08	0.04	0.09
P_2O_5	0.01	0.02	0.01	0.02	0.02
F	—	0.49	0.51	0.69	0.69
A.I.	1.28	1.22	1.27	1.18	1.17
L.O.I.	0.62	0.50	0.30	0.42	0.45
Total	98.28	100.40	100.04	100.39	101.76
Trace elements					
Ba (ppm)	44	36	13	95	100
Rb	604	622	489	378	514
Sr	27	8	13	21	44
Ta	—	17	12	—	—
Hf	—	43	33	—	—
Th	—	104	45	—	—
U	—	9	6	—	—
Zn	731	196	291	261	371
Sc	—	0.57	1.29	—	—
La	—	199	107	—	—
Ce	—	355	224		—

Table 2 (continued)

Unaltered hypersolvus alkali granites

	SL13D-12	49-A-1	48-A-8	LB10D-33	LB9D-13
Trace elements					
Nd	—	142	105	—	—
Sm	—	32	28.3	—	—
Eu	—	2.0	1.76	—	—
Tb	—	8	4.8	—	—
Dy	—	64	31	—	—
Tm	—	8	2.6	—	—
Yb	—	62	25	—	—
Lu	—	8	3.7	—	—
Cs	—	2.8	1.5	—	—

	Melanocratic incl.	Dyke rock	Pegmatites/aplites		
	47-A-1A	57-A-3	25-A-2	LB13D-43	MB-TR-1
Major elements					
SiO_2 (wt %)	68.66	69.90	70.24	65.39	65.17
TiO_2	0.13	0.31	0.27	1.23	0.79
Al_2O_3	12.68	12.50	8.97	5.64	8.76
Fe_2O_3	5.24*	5.13	3.79	6.42	3.24
FeO	—	0.05	3.29	0.65	0.84
MnO	0.09	0.05	0.16	0.11	0.25
MgO	0.01	0.01	0.35	0.70	0.63
CaO	0.76	0.44	1.68	4.31	3.58
Na_2O	4.87	8.71	4.65	2.95	3.22
K_2O	5.71	2.42	2.42	3.27	4.13
ZrO_2	0.64	0.14	1.36	2.61	3.01
Y_2O_3	0.20	0.16	0.17	1.21	1.56
Nb_2O_5	0.01	0.17	0.17	0.49	1.24
P_2O_5	0.02	0.02	0.01	0.01	0.02
F	—	—	—	1.11	0.90
A.I.	1.12	1.16	1.24	1.49	1.11
L.O.I.	0.50	0.53	0.86	1.97	1.94
Total	99.02	99.96	97.52	96.10	97.34
Trace elements					
Ba (ppm)	28	4	8	105	91
Rb	773	22	276	845	1137
Sr	21	7	28	109	180
Ta	—	—	36	127	238
Hf	—		278	631	487
Th	—	—	83	689	931
U	—	—	16	100	102
Zn	512	349	529	534	1652
Sc	—	—	1.9	0.60	0.30
La	—	—	1007	1264	736
Ce	—	—	2271	2872	1304
Nd	—	—	911	1245	617
Sm	—	—	142	200	260
Eu	—	—	6.3	20.4	17.6
Tb	—	—	36	102	114
Dy	—		112	637	741
Tm	—	—	n.d.	677	97
Yb	—	—	55	591	660
Lu	—	—	6.4	70	85
Cs	—	—	1.3	—	1.58

(continued on next page)

Table 2 (continued)

	Pegmatites-/aplites		Subsolvus Altered (n = 28)	Subsolvus Unaltered (n = 10)	Hypersolvus Unaltered (n = 15)	Pegmatites-aplites (n = 7)
	MB-TR-4A	37-E-3				
Major elements						
SiO_2 (wt %)	61.97	63.17	70.80	70.48	70.92	64.75
TiO_2	0.82	3.67	0.35	0.24	0.30	1.74
Al_2O_3	4.77	5.72	8.86	11.40	11.44	5.72
Fe_2O_3	5.40	1.53*	4.15	2.90	2.59	4.18
FeO	0.29	—	1.43	2.20	2.68	0.37
MnO	0.22	0.02	0.14	0.11	0.11	0.16
MgO	1.00	0.68	0.27	0.04	0.02	0.80
CaO	8.68	12.49	1.50	0.67	0.61	6.03
Na_2O	1.98	0.72	3.82	4.96	5.03	1.92
K_2O	3.42	4.23	4.01	4.71	4.73	3.57
ZrO_2	2.42	0.77	2.01	0.85	0.50	2.46
Y_2O_3	2.47	0.23	0.38	0.21	0.12	1.57
Nb_2O_5	0.87	0.17	0.29	0.13	0.01	0.96
P_2O_5	0.02	0.01	0.03	0.02	0.02	0.05
F	> 1.0	—	0.44	0.67	0.51	0.63
A.I.	—	—	1.20	1.16	1.17	1.23
L.O.I.	2.10	2.87	0.71	0.63	0.46	2.18
Total	97.30	96.28	98.48	99.59	99.68	95.01
Trace elements						
Ba (ppm)	136	352	38	32	57	162
Rb	1036	1004	964	746	509	960
Sr	781	784	67	28	27	329
Ta	166	—	56	24	16	305
Hf	366	—	410	162	49	429
Th	1446	—	239	86	68	2014
U	—	—	40	17	8	136
Zn	1589	160	966	562	460	992
Sc	0.20	—	0.32	0.82	0.67	0.27
La	1237	—	794	514	130	1165
Ce	1896	—	1472	1050	248	3510
Nd	719	—	618	398	106	850
Sm	—	—	164	94	27	246
Eu	27	—	9	5	1.8	25
Tb	188	—	32	17	6	182
Dy	1195	—	191	109	47	1085
Tm	147	—	22	8	5	127
Yb	879	—	169	61	42	843
Lu	108	—	21	8	6	27
Cs	4.6	—	1.7	2.6	2.2	2.9

Oxygen isotope chemistry of mineral separates

Oxygen isotopic analyses were carried out on quartz, alkali feldspar and arfvedsonite/aegirine mineral separates (Table 3). The results show that there was strong isotopic disequilibrium between all mineral pairs, except between quartz and arfvedsonite in the unaltered granites. The fractionation factor between these two minerals ($\Delta\delta^{18}O_{\text{quartz-arfv}}$) ranges between + 3.0 and + 3.8‰ and corresponds to temperatures of 550° to 650° C according to the geothermometer of Bottinga and Javoy (1975). The $\delta^{18}O$ composition of the alkali feldspar is systematically higher by 0.1 to 1.6‰ than that of the coexisting quartz, which is the reverse of what is expected from equilibrium fractionation between these minerals (Clayton et al. 1972). This may indicate re-equilibrium of the alkali feldspar with low temperature hydrothermal fluids (Wenner and Taylor 1976; Taylor 1978). Unaltered arfvedsonite and bottle-green aegirine yield low $\delta^{18}O$ values (+ 4.8 to 5.2‰) relative to most amphiboles and clinopyroxenes of contental peralkaline granites ($\delta^{18}O$ = + 6.8 to + 8.2‰; Sheppard 1986). These low numbers are similar to those of arfvedsonite in vlasovite and dalyite-bearing granite inclusions in oceanic comendites (e.g. Ascension, $\delta^{18}O_{\text{arfv}}$ = + 4.66 to + 4.91‰; Sheppard and Harris 1985).

Within the unaltered granites, the pristine (black) arfvedsonite (samples MBTR-3 and 48-A-1) and that intergrown with bottle green aegirine (sample 46-B-3) display low $\delta^{18}O$ values (+ 4.8 to + 6.1‰). However, in the altered subsolvus granites, the whole rock $\delta^{18}O$ enrichment appears to have been controlled by the

Table 3 Whole rock and mineral $\delta^{18}O$ values of selected samples of the Strange Lake plutonic complex

$\delta^{18}O_{SMOW}$ Sample #	W.R.	Quartz	Alk.-felds.	Arfved.	$\Delta\delta^{18}O_{Qtz\text{-}felds.}$	$\Delta\delta^{18}O_{Qtz\text{-}Arfv}$
Unaltered hypersolvus and subsolvus granites						
38-A-1	+ 8.2					
46-E-1	+ 8.9					
46-B-3*	+ 8.5	+ 8.6	+ 8.9	+ 4.8	− 0.3	+ 3.8
48-A-1	+ 9.4	+ 8.5	+ 9.6	+ 5.2	− 1.1	+ 3.3
57-A-2	+ 9.2					
57-D-1	+ 9.1					
MBTR-3	+ 9.6	+ 9.1	+ 9.4	+ 6.1	− 0.3	+ 3.0
Altered subsolvus granites						
25-C-1	+ 11.5	+ 10.1	+ 11.0	+ 11.9	− 0.9	− 1.8
25-E-1	+ 11.1		+ 10.3	+ 11.3		
27-A-4*	+ 10.0		+ 9.9	+ 4.8		
27-B-1	+ 11.9	+ 8.6	+ 9.6	+ 13.1	− 1.6	− 5.2
46-G-3*	+ 10.5	+ 9.7	+ 10.6	+ 6.5	− 0.9	+ 3.2
LB13D-8	+ 10.6					
LB13D-43	+ 11.6					
LB15D-16	+ 10.3					
LB54D-44	+ 10.8					
SL5D-36	+ 10.8					
SL16D-2	+ 11.3					
SL183-1	+ 11.9					
Pegmatites and aplites						
MBTR-1	+ 11.4					
MBTR-2A	+ 11.3					
MBTR-4A	+ 11.8	+ 9.3	+ 9.1	—	− 0.1	—
37-E-6	+ 13.7					
Aphyric dykes						
44-C-1	+ 6.8					
25-A-2	+ 8.5					
Melanocratic fine-grained granitic inclusions						
38-A-5	+ 8.3					
57-E-2	+ 8.4					
TTR-28	+ 9.0					

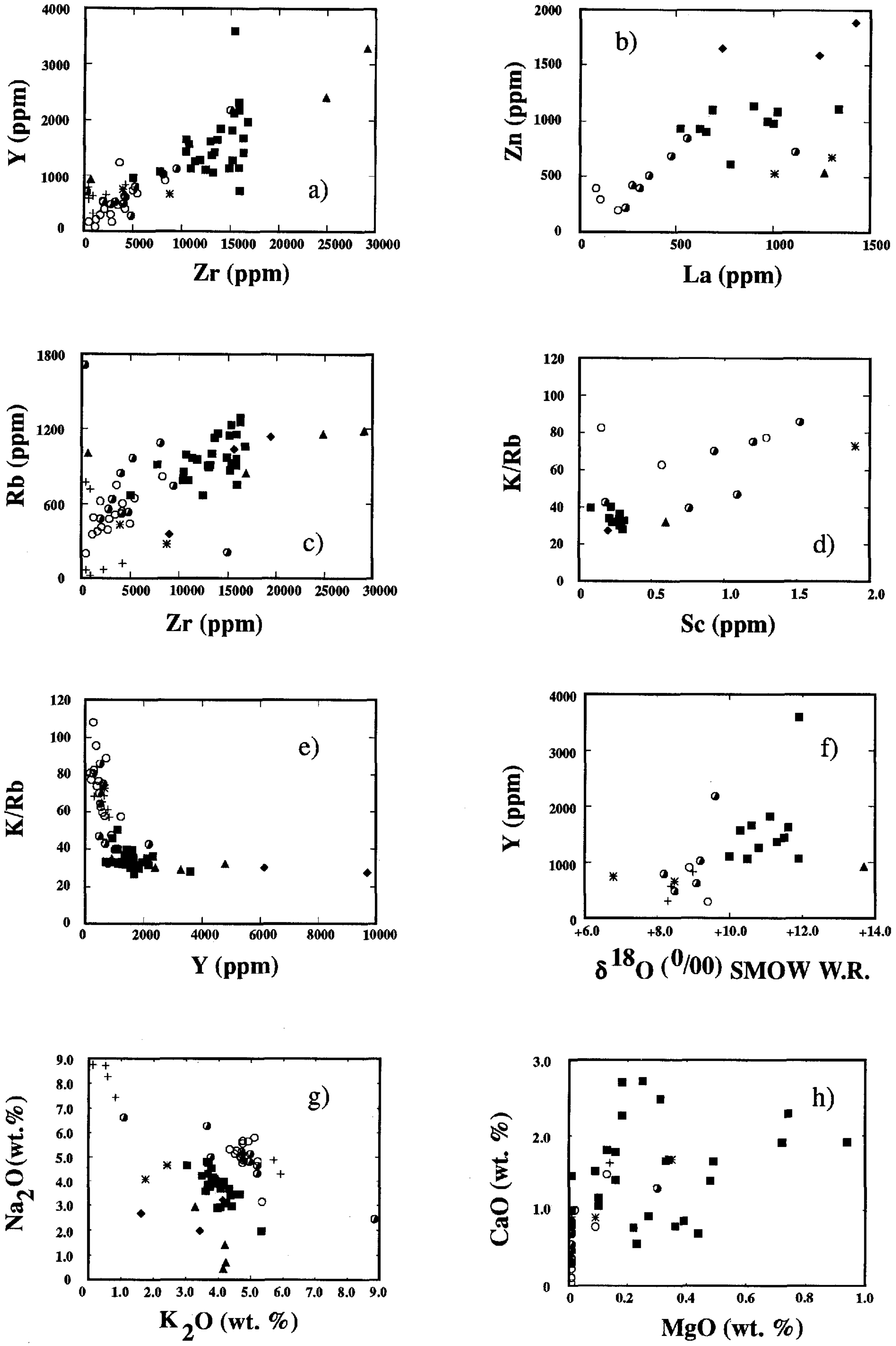
* Aegirine and arfvedsonite are often intergrown

degree of hematization of the arfvedsonite as suggested by the excellent positive correlation obtained in Fig. 5. Sample 27-A-4, consisting of bottle green aegirine intergrown with arfvedsonite, has the lowest $\delta^{18}O$ value (+ 4.8‰), whereas sample 46-G-3, showing aegirine intergrown with arfvedsonite but also incipient hematization, is slightly more enriched in ^{18}O ($\delta^{18}O$ = + 6.5‰). Samples 25-C-1, 25-E-1 and 27-B-1, which are completely hematized, display the highest $\delta^{18}O$ values (+ 11.3 to + 13.1‰). The similarity of the $\delta^{18}O$ values of alkali feldspar and quartz in unaltered and altered rocks indicates that these minerals did not contribute to the higher $\delta^{18}O$ values of the latter.

The magmatic evolution of the Strange Lake plutonic complex

According to the Al_2O_3 (wt %) vs FeO_t(wt %) diagram used by Macdonald (1974) to classify peralkaline volcanics (Fig. 6), the unaltered Strange Lake peralkaline granites (subsolvus and hypersolvus) are related to comendites (high Al_2O_3, low FeO_t), whereas the altered subsolvus granites have a pantelleritic affinity (low Al_2O_3 and slightly higher FeO_t). Positive linear correlations between the HFSE and REE, systematic enrichments in HFSE, Zn and REE and depletions in Sc, Cr, Sr and Eu of pantellerites relative to comendites are also common characteristics shared by the Strange Lake granites peralkaline volcanics (Upton et al. 1971; Gibson 1972; Villari 1974; Upton 1974; Harris 1982; Macdonald 1987). Although there is no evidence of associated volcanism at Strange Lake, it is possible that the complex represents the shallow root of a comendite-pantellerite volcanic edifice.

Proposed mechanisms of HFSE and REE enrichment for comendite-pantellerite systems fall into two categories: (1) crystal fractionation controlled by the separation of alkali feldspar and (2) complexing of REE and HFSE with F and/or Cl and subsequent transport in melts or aqueous fluids (Villari 1974; Ferrara and Treuil 1974; Bailey and Macdonald 1975; Hildreth 1981; Leat et al. 1984; Macdonald 1987).


a)
Y (ppm)
Zr (ppm)
0
1000
2000
3000
4000
0
5000
10000
15000
20000
25000
30000
b)
Zn (ppm)
La (ppm)
0
500
1000
1500
2000
0
500
1000
1500
c)
Rb (ppm)
Zr (ppm)
0
600
1200
1800
0
5000
10000
15000
20000
25000
30000
d)
K/Rb
Sc (ppm)
0
20
40
60
80
100
120
0
0.5
1.0
1.5
2.0
e)
K/Rb
Y (ppm)
0
20
40
60
80
100
120
0
2000
4000
6000
8000
10000
f)
Y (ppm)
$\delta^{18}O$ ($^0/00$) SMOW W.R.
0
1000
2000
3000
4000
+6.0
+8.0
+10.0
+12.0
+14.0
g)
Na_2O (wt. %)
K_2O (wt. %)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
h)
CaO (wt. %)
MgO (wt. %)
0
1.0
2.0
3.0
0
0.2
0.4
0.6
0.8
1.0

Crystal fractionation of alkali feldspar

The unaltered hypersolvus and subsolvus granites display a trend of decreasing K/Rb values with Al_2O_3 which is accompanied by uniform increases in HFSE, REE, Zn, Th and U concentrations. At Strange lake, alkali feldspar is a phenocryst phase accompanied by arfvedsonite and quartz (Pillet 1989; Salvi and Williams-Jones 1990; Nassif 1993). The fractionation of this mineral assemblage can be roughly evaluated using a least squares mixing approach. For the hypersolvus granites, the best fit for the model is obtained by the removal of 19 wt% of alkali feldspar, having a composition close to the alkali feldspar thermal minimum, and of 2 wt% of arfvedsonite (totalling 21% solidification of the parental granite). This reproduces the observed trend of Al_2O_3, K_2O and Na_2O depletion and slight CaO enrichment within the hypersolvus granites (Table 4). However, modelling the HFSE, REE, Zn and Rb variations, using the equation established for Rayleigh fractionation (see Wood and Fraser 1976) and assuming a minimum bulk distribution coefficient (K_O) equal to zero, would require the crystallization of 65 to 80% of a parental granitic liquid to explain the observed concentrations of these elements. Since some of the Rb, Zr and Y would enter the structure of feldspars and amphibole, the realistic requirement for the degree of crystallization is much higher. Similar conclusions are obtained from modelling the internal chemical variations within the unaltered subsolvus granites.

Nearly 22% of the parent liquid would have to crystallize in order to match the composition of the average altered subsolvus granite (daughter) with that of the average unaltered subsolvus granite (parent), through separation of alkali feldspar (19 wt%) and minor arfvedsonite (3 wt%). However, the model does not predict the strong and unusual increases in CaO and MgO. Alkali feldspar fractionation also fails to explain the lack of variation in K/Rb values and Al_2O_3 abundances (Fig. 3), and the three to five-fold increases in HFSE and REE concentrations within the altered subsolvus granites. In conclusion, it appears that the separation of alkali feldspar and arfvedsonite from a peralkaline silicic parent, while accounting for part of the observed HFSE and REE variations within the unaltered units, is incapable of producing sufficient ernrichment of these elements.

The role of fluorine in the REE and HFSE enrichment of the Strange Lake granites

Each granitic unit at Strange Lake also carries high fluorine contents (i.e. 0.44 to 0.67 wt%; Table 2). In the unaltered granites, the total concentrations of REE, HFSE and F are positively correlated, but this correlation breaks down for the altered granites and pegmatites. However, the late magmatic and sub-solidus evolution of the granites provide strong clues as to the mobility of fluorine indicating that the present F concentrations reflect only a fraction of what was originally dissolved in the melts. These are as follows: (1) Fluorine was partitioned into a hydrothermal fluid at a deuteric stage to form the fluorite and hematite-rich matrix of the breccia surrounding the granite. The matrix supports clasts of host rocks and alkali granites and contains as much as 4.5 wt% fluorine and 9.2 wt% FeO_t (Miller 1985). (2) Fluorine also entered an aqueous hydrothermal fluid and/or a silicate melt fraction during the formation of the pegmatite and aplite sills and dykes. The latter contain from 1.0 to 3.8 wt% fluorine (Miller 1985, and this study). (3) Finally, the sub-solidus alteration of the late subsolvus granite may have been characterized by substantial leaching of fluorine.

High fluorine contents dissolved in peralkaline felsic melts cause the distortion of the aluminosilicate structure, depolarize the melt, lower the solidus and produce a large range of sites of various size and coordination (Manning 1981; Collins et al. 1982; and Manning and Pichavant 1985). This allows the highly charged cations (e.g. the REE and HFSE) to form stable compounds with fluorine and the excess alkalis (e.g. Na_3TaF_8, Na_2NbF_7, Na_2UF_6, $KCeF_4$, $NaZrF_7$, $NaZnF_3$; Collins et al. 1982). Thus, the net effect of excess alkalis and high fluorine content is to produce homogeneous REE and HFSE enrichments in silicic melts by forming highly soluble and mobile alkali-fluorocomplexes with these elements.

The same homogeneous behaviour cannot be predicted if the REE and HFSE are partitioned into a separate Cl or F-rich aqueous phase. Experimental and theoretical studies have shown that, at various ranges of magmatic temperatures, (500°–1000° C): (1) transport by fluoride species is unimportant, and (2) REE, Nb and Y partition into a Cl-rich aqueous fluids, while Ta, Zr and probably Hf are not

◄

Fig. 2a–b Binary trace element plots illustrating the compositional variations of the granitic intrusive units, pegmatites-aplite and dyke rocks of the Strange Lake plutonic complex. **a** Y (ppm) vs Zr (ppm), **b** Zr (ppm) vs Nb (ppm), **c** La (ppm) vs Zn (ppm), **d** Sc (ppm) vs K/Rb, **e** Y (ppm) vs K/Rb, **f** $\delta^{18}O_{smow}$ w.r. vs Y (ppm), **g** K_2O (wt %) vs Na_2O (wt %), **h** MgO (wt %) vs CaO (wt %). Note the unusually high concentrations of HFSE and REE, and their systematic enrichment from the oldest hypersolvus granites to the youngest altered subsolvus granites and pegmatites-aplites. Note also the good to excellent linear correlations within the unaltered granites and poor correlation within the altered subsolvus granites. Alkali granites: *open circles* unaltered hypersolvus, *half-filled circles* unaltered subsolvus, *filled squares* altered subsolvus. *Plus signs* melanocratic inclusions, *stars* aphyric dykes, *diamonds* pegmatites-aplites in ore zone, *triangles* pegmatites-aplites in granites.

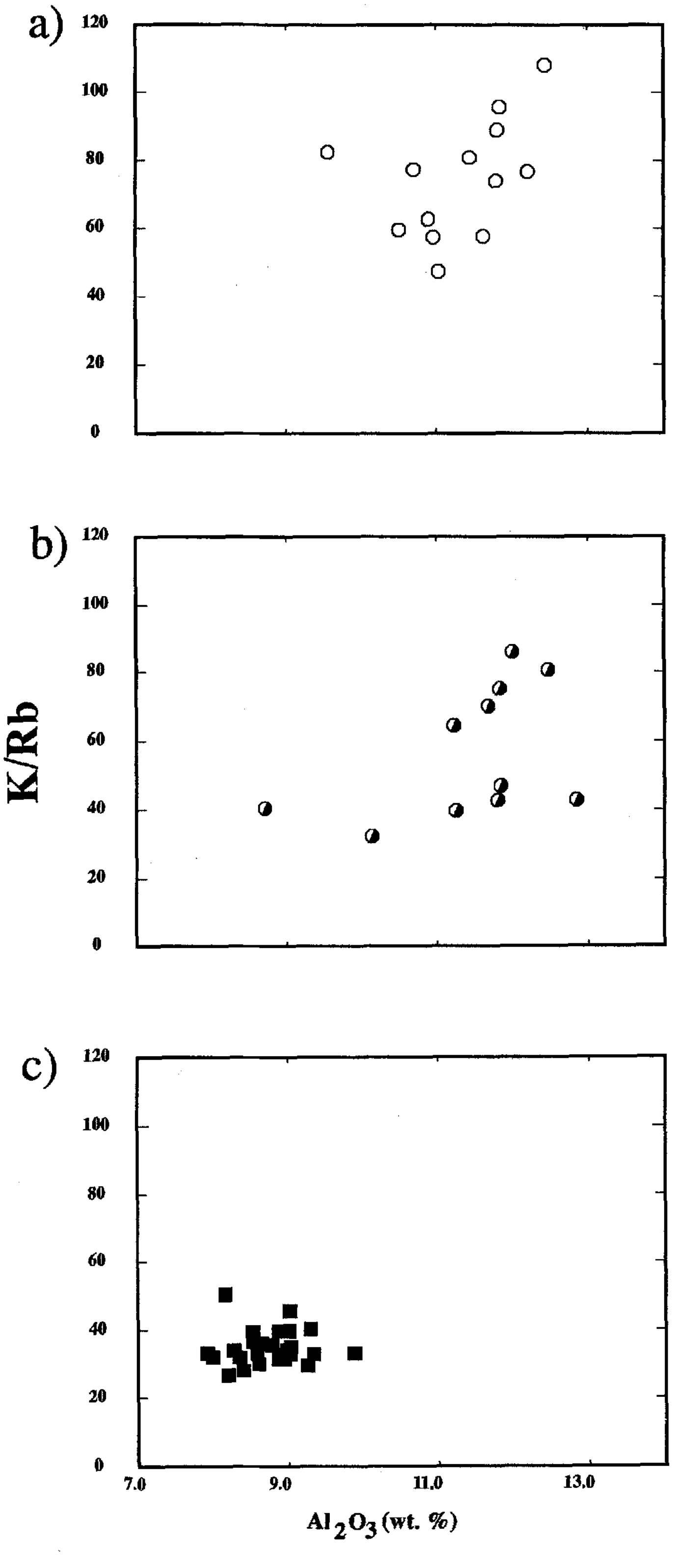


Fig. 3a–c Al_2O_3 (wt%) vs K/Rb plots showing the positive correlation expressed by the unaltered hypersolvus and subsolvus granites. This contrasts with the lack of correlation given by the altered subsolvus granites. Symbols as in Fig. 2

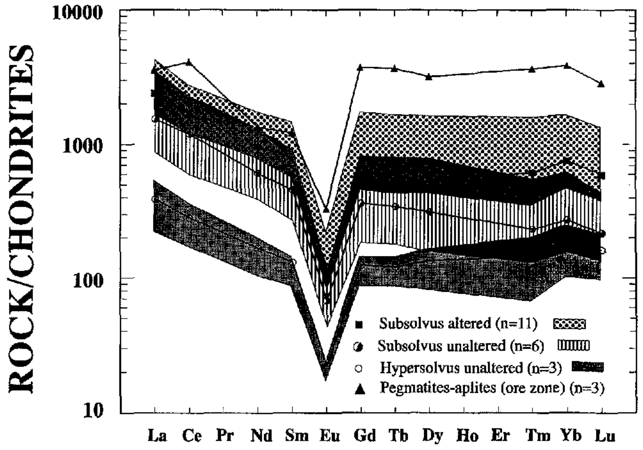


Fig. 4 Average chondrite normalized REE patterns for the granitic intrusives and pegmatite and aplite samples from the ore zone. Observe the moderate HREE enrichment in the altered subsolvus granites and extreme HREE enrichment characteristic of the ore zone

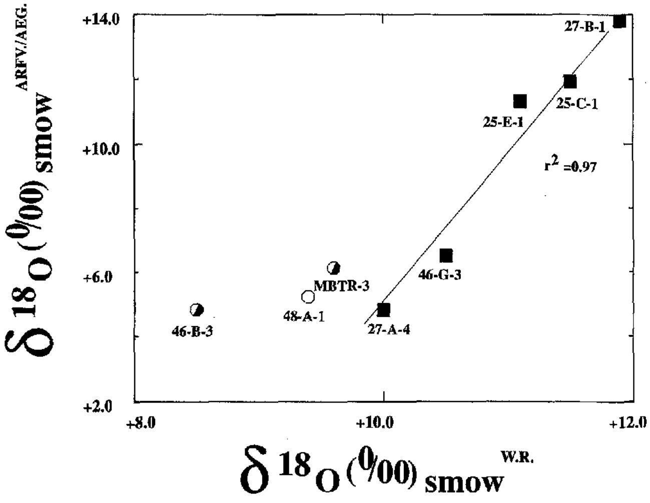


Fig. 5 A plot of $\delta^{18}O_{smow}$ w.r. vs $\delta^{18}O_{smow}$ arfv./aeg.. The excellent linear correlation (r^2 = 0.97) within the altered subsolvus suggests that the degree of hematization of the amphiboles and pyroxenes is largely responsible for the increase in whole rock $\delta^{18}O$ values. Symbols as in Figure 2

significantly transported in aqueous vapour, either as chloride or fluoride species (Krauskpof 1964; Flynn and Burnham 1978; Webster et al. 1989; Wood 1990a, b). Consequently, if the separation of an aqueous phase and subsequent partitioning of the HFSE and REE during the evolution of silicic peralkaline systems is the principal mechanism of rare metal enrichment, we should observe a strong decoupling between several elements (e.g. Zr over Nb), which we do not. We thereby propose that extreme fractionation of an unusually F-rich granitic magma produced low-temperature, highly depolymerized and extremely

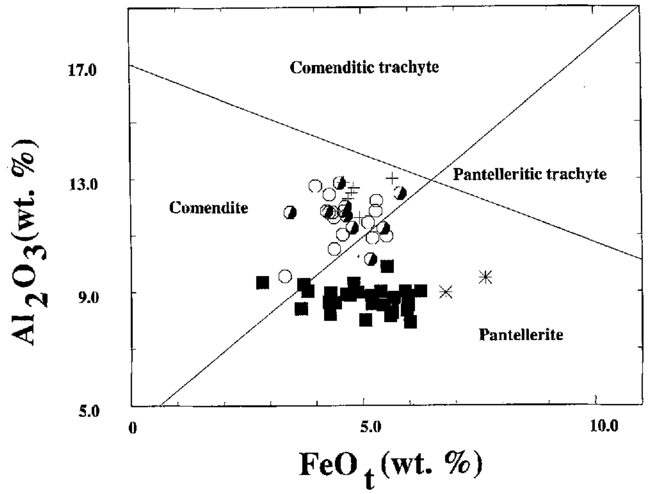


Fig. 6 FeO_t (wt %) vs Al_2O_3 (wt %) classification plot used for quartz normative peralkaline volcanic rocks, from Macdonald (1974). The Strange Lake unaltered hypersolvus and subsolvus alkali granites are located in the field of comendites, whereas most of the altered subsolvus granites fall in the field of pantellerites. Symbols as in Figure 2

mobile HFSE, REE, F and alkali-rich residual melts. The heterogenous redistribution of these melts, prior to the separation of pegmatite/aplite melts and a free aqueous phase, in nearly consolidated granitic units may have generated the observed range of HFSE and REE-enrichments.

Ca, Mg, Sr and $\delta^{18}O$ enrichments: limitations of the magmatic model

A magmatic model is, however, inadequate to explain features as such as the O isotopic variations, widespread hematization and Ca, Sr and Mg enrichments of the altered subsolvus granites. In the case of MgO and CaO, it could be argued that, since the internal evolution of pantellerite and comendite magmas is partly controlled by the fractionation of alkali feldspar, Ca will act as an incompatible element and become enriched in the residual magma. Indeed, a study of Ca partitioning between alkali feldspar phenocrysts and coexisting silicic peralkaline melt by Noble et al. (1972) showed the preference of calcium for the melt. However, in order to reach the average CaO content of the altered subsolvus granites (i.e. 1.5 wt%) from an initial concentration of 0.5 wt% (the average content of the unaltered granites) nearly 60% crystallization of alkali feldspar is required while the concentrations of the other major elements are obtained after 25% crystallization (Fig. 7). The highest CaO content recorded by the altered subsolvus unit obviously cannot be simulated, as it would require 95% feldspar crystallization. Moreover, in the subsolvus granites, the crystallized plagioclase is almost pure albite (An_{01-05}) and the arfvedsonite and aegirine contain virtually no Ca and Mg. As these minerals crystallized late in the mineral paragenesis of the Strange Lake granites, often simultaneously with the HFSE and REE-bearing exotic phases

Table 4 Mass balance calculations using the Wright and Doherty (1970) algorithm for estimating the degree of alkali feldspar fractionation experienced by the hypersolvus granites. LB-10-33, representing the least evolved granite of this suite with high Al_2O_3 and moderate HFSE and REE concentrations, serves as a parental granite, whilst 46-E-1 having low Al_2O_3 and high HFSE and REE contents is an appropriate daughter. The low degree of feldspar fractionation (19%) conflicts with the large degree required to model the HFSE variations (65–80%)

	LB-10-33 (parent)	Albite	K-Felds.	Arfveds.	46-E-1 (daughter)
SiO_2 (wt%)	70.25	68.52	64.85	50.12	71.83
TiO_2	0.28	0.00	0.00	1.86	0.21
Al_2O_3	12.46	19.48	17.45	2.79	11.28
FeO	4.25	0.00	0.00	29.79	4.58
MnO	0.10	0.00	0.00	0.00	0.12
Mgo	0.01	0.00	0.00	1.61	0.09
CaO	0.85	0.00	0.00	3.86	0.79
Na_2O	5.67	11.85	0.43	7.66	5.10
K_2O	4.93	0.15	16.28	1.28	4.77
P_2O_5	0.20	0.00	0.00	0.00	0.20
Solution % cumulate					
	LB-10-33	1.00			
	Albite	− 0.121	57.88		
	Microcline	−0.068	32.47		
	Arfvedsonite	−0.020	9.65		
	46-E-1	0.79			
R^2: 0.068					
	LB-10-33	46-E-1	% crystallization (Rayleigh)		
Rb (ppm)	378	819	65		
Y	284	906	70		
Zr	1912	9511	80		
Nb	127	479	75		

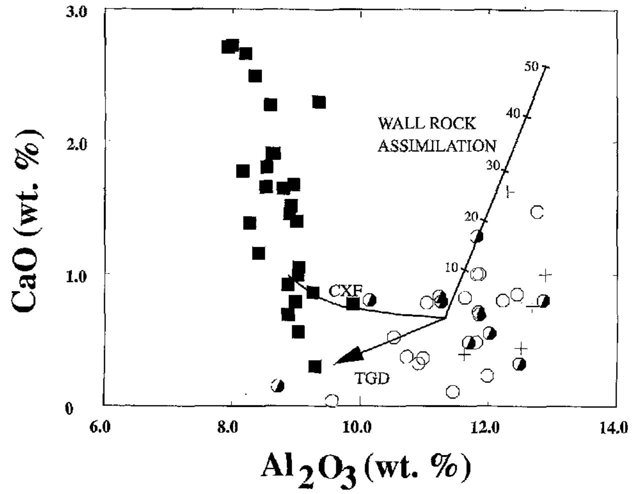


Fig. 7 Al_2O_3 (wt %) vs CaO (wt %) plot showing the unusual calcium enrichment of the altered subsolvus granites which no magmatic process can explain. Less than 25% crystallization of alkali feldspar (CXF) will account for the Al_2O_3 variations between altered and unaltered granites, but this model predicts considerably lower CaO concentrations even if the latter is considered perfectly incompatible. Thermogravitational (TGD) diffusion commonly generates depletions in CaO and Al_2O_3 in the most HREE and HFSE-enriched silicic rocks whilst bulk wall-rock assimilation will drive the granitic magmas toward lower Al_2O_3 concentrations (see text). The wall rock assimilant is represented by a composite chemical average of Aphebian metamorphic rocks surrounding the Strange Lake complex. *Tick marks* represent the degree (in wt %) of wall-rock assimilation. Symbols as in figure 2

(Pillet 1989; Nassif 1993), they would obviously have incorporated Ca and Mg in their structures if they had equilibrated with a melt enriched in the latter elements. Other magmatic processes also appear inadequate. For example, thermogravitational diffusion invariably produces a depletion in Ca and Mg in the most REE and HFSE-rich liquids, instead of the observed increases (Mahood 1981 and Hildreth 1981). Moreover, from 20 to 30% bulk assimilation of wall rocks (a chemical composite of gneisses and schists hosting the complex) during the consolidation of the outer subsolvus granite would be necessary to augment Ca and Mg to their observed values. However, such a high rate of assimilation would also have produced depletions in Al_2O_3, K_2O and SiO_2 and $\delta^{18}O$ compositions that are not observed (Table 2 and Fig. 7). We must conclude that the CaO, MgO (and Sr) enrichment characterizing the altered subsolvus granite cannot be of magmatic origin but most likely stemmed from metasomatic processes.

The sub-solidus evolution of the Strange Lake plutonic complex

A metasomatic origin for the Ca enrichment of the ore zone pegmatites and aplites has already been demonstrated by Salvi and Williams-Jones (1990), confirming the preliminary investigations of Curie (1985) carried on the altered subsolvus granites. Petrographic observations recently completed by Salvi and Williams-Jones (1993b) have shown that elpidite, a Na-zirconosilicate of magmatic origin, was replaced by armstrongite and gittinsite (two Ca-zirconosilicates), the latter replacement being accompanied by major volume loss. Their studies of fluid inclusions in pseudomorphs of elipdite and other HFSE minerals indicated that Ca metasomatism was caused by low-temperature saline hydrothermal fluids which, they argued, acquired high $CaCl_2$ by circulating in the gneisses hosting the complex.

At Strange Lake, the negative $\Delta\delta^{18}O_{\text{quartz-alk. feldspar}}$ (Table 2) provides conclusive evidence of the circulation of low temperature fluids within the altered subsolvus granites and the ore zone pegmatites. Such unusual isotopic signatures can only occur by partial or total subsolidus re-equilibration of the feldspars with low temperature meteoric and groundwater fluids ($< 300°$ C) with no substantial isotopic exchange with quartz (Wenner and Taylor 1976; Shieh 1983; Kyser 1983). The fluid entrapment temperatures provided by Salvi and Williams-Jones (1990) (e.g. 135°–195° C) can be used in conjunction with the temperature $-\ \delta^{18}O_{\text{alkali feldspar}}$ diagram of Wenner and Taylor (1976) to estimate the bulk isotopic composition of the low temperature hydrothermal fluids. If it is assumed that the range in alkali feldspar $\delta^{18}O$ values (e.g. $+9.4$ to $+11.0‰$) represents a state of equilibrium between fluid and mineral under a closed system and at low water/rock ratio, e.g. ≈ 1 (Wenner and Taylor 1976), then the $\delta^{18}O$ fluid compositions should range between -1 $+3‰$. At higher water/rock ratios, e.g. $\gg 1$, slightly lower values (e.g. 0 to $-5‰$) are indicated. These $\delta^{18}O$ compositions are clearly outside the range of magmatic values and may reflect mixing of depleted (meteoric/groundwaters) and enriched (magmatic/metamorphic) waters or evolved meteoric fluids that had exchanged with the host monzonites and gneisses.

The positive linear correlation between $\delta^{18}O$ values of altered arfvedsonite and whole rock $\delta^{18}O$ compositions within the altered subsolvus granites also indicates low temperature alteration, and apparently contradicts Bonin's (1986) assertion that the destabilization of arfvedsonite into aegirine + quartz + hematite + H_2O takes place at near solidus temperatures (600°–625° C), when the amphibole reacts with a late magmatic F-depleted oxidizing fluid. The fractionation factors between quartz, amphibole, aegirine, hematite (the product of arfvedsonite destabilization) are too low, at these temperatures (e.g. $\Delta\delta^{18}O_{\text{mineral}} - \delta^{18}O_{\text{water}} < +2$), for equilibrium reaction with orthomagmatic fluids ($< +10‰$; Taylor 1978) to have been able to generate the observed trend of $\delta^{18}O$ enrichment in the altered arfvedsonite ($+4.8$ to $+13.1‰$). It is, however, difficult to conceive how the latter could also occur through interaction with a low

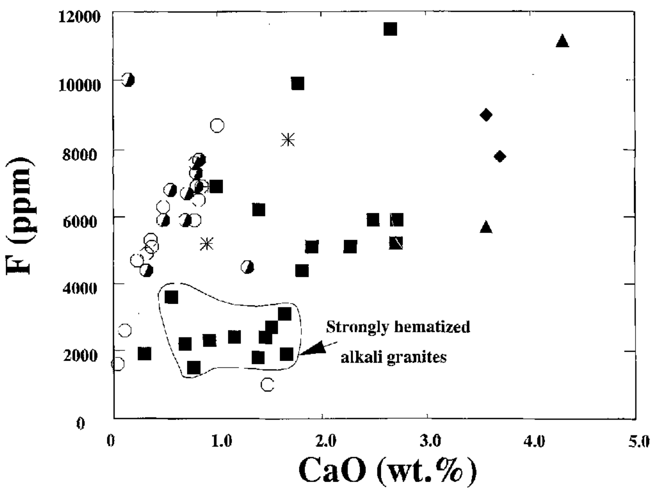


Fig. 8 Plot of CaO (wt%) vs F (ppm) showing the excellent correlation observed in the unaltered granites which probably indicate control by fluorite. The data from the altered subsolvus granite exhibit considerable scatter which we attribute in a large part to the circulation of low temperature sub-solidus oxidizing fluids which leached fluorine from the granites. The strongly hematized samples carry the lowest F concentrations. Symbols as in figure 2

$\delta^{18}O$ fluid (e.g. $< +5‰$). Only quartz becomes substantially enriched in ^{18}O relative to water at low temperature ($\delta^{18}O_{\text{quartz-water}} = +10$ to $+15$ from 250° to 150°C; Clayton et al. 1972; Kawabe 1978), whilst hematite-water fractionation factors ($\Delta\delta^{18}O_{\text{hematite-water}} = < -2$) and those extrapolated with the Na-pyroxene-water pair ($\Delta\delta^{18}\ O_{\text{Na.px-water}} \approx +3$) are much too low at these temperatures (Matthews et al. 1983; Yapp 1991). Perhaps, μm-sized clay or mica flakes are interspersed with aegirine, hematite and quartz. Fractionation factors between micas/clays and water being very large at temperature below 200°C ($> 10‰$; Kyser 1987, chapter 1), elevated $\delta^{18}O$ values could then be obtained even if the arfvedsonites reacted with low ^{18}O waters.

In their model, Salvi and Williams-Jones (1990) suggested that an oxidizing, low salinity Ca-poor groundwater may have leached fluorine and rare metals (notably Y and REE) from the granites surrounding the ore zone and deposited them when these fluids mixed with external fluids rich in Ca. Mobilization of REE and Y within the ore pegmatites is also supported by the presence of secondary fluid inclusions trapped in quartz veins and Ca-pseudomorphs which contain HFSE and REE-bearing daughter minerals (e.g. bastnäsite, gagarinite and pyrochlore).

Evidence for the circulation of oxidizing fluids in the altered subsolidus granites is given by scattered patches of hematite, hematization of arfvedsonite and the distribution of fine grained hematite dust in the alkali feldspars. The loss of fluorine in the strongly hematized granites and the absence of a correlation between CaO and F (Fig. 8) further testify to subsolidus high mobility of fluorine. Nontheless, our investigations have yet to demonstrate substantial HFSE and REE leaching, but the excellent correlations displayed by the unaltered granites as opposed to the lack of correlation between the HFSE and REE in the altered subsolvus granites, could at least indicate that some remobilization took place within the latter.

A preliminary model for the evolution of the Strange Lake plutonic complex

We propose that F-rich, mantle-derived, trachytic (syenitic) magmas established chemically zoned magma chambers in the upper crust. Extensive crystal fractionation produced HFSE, REE and F-rich comendite and/or pantellerite roof zones that were periodically tapped and injected at higher crustal levels ($\approx$ 1–3 km) to form successive annular alkali granite intrusives. Injection of the hypersolvus core occurred principally in the Elsonian quartz monzonites. Rapid crystallization and chilling at the roof zone and on the side-walls generated the melanocratic fine-grained facies. While the intrusive core was consolidating, it underwent cauldron subsidence and/or roof collapse, giving way to a new batch of slightly more differentiated (hence more HFSE, REE, Zn and F-rich) subsolvus granitic magma which was then emplaced by stoping and foundering of roof slabs. The altered enriched subsolvus granite was later emplaced in a similar fashion to form the external shell of the complex.

We suggest that the alkali granites acquired pantelleritic or comenditic compositions depending on the time that elapsed before the extraction of the uppermost part of the magma chamber. A prolonged residence time created pantelleritic residual liquids by allowing extreme fractionation, principally by alkali feldspar separation, to occur (hence the extreme depletion in K/Rb and Al_2O_3), while promoting enrichment in HFSE and REE by volatile complexing with F in the melt. Shorter residence times would have allowed for less differentiation thereby forming less HFSE and REE-enriched comenditic liquids. The most evolved stages of magmatic differentiation occurred during the emplacement of each intrusive and were controlled by the heterogeneous migration of REE and HFSE-alkali-fluorocomplexes in residual melts accompanied by minor alkali feldspar and arfvedsonite fractionation.

At a late (deuteric?) stage, a hydrothermal fluid carrying substantial amounts of fluorine and iron forcefully escaped from the late subsolvus granite creating a fluorite and hematite-rich breccia surrounding the complex. The segregation of a F-rich aqueous phase (probably enriched in HREE, Nb, Y-fluoro-complexes) was accompanied by an extremely REE and HFSE-rich, highly fractionated felsic melt which was intruded in fractures as sub-vertical pegmatite-aplite dykes and sills in the cupola, while the roof of the altered granite cooled and contracted. The presence of a F-rich aqueous phase may have caused substantial fractionation and decoupling of rare metals (e.g. HREE/HFSE and Nb/Zr), thereby explaining the unusual HREE-rich patterns of the pegmatites and aplites (Figs. 2, 4).

At present we propose two preliminary models to account for the complex sub-solidus history of the Strange Lake complex. One possibility is that the escape of orthomagmatic F-rich aqueous fluid and heat loss during the consolidation of a low solidus (500°–600° C) subsolvus granite may have initiated a low-temperature hydrothermal system within the granite and in the surrounding wall rocks which involved fluids of several origins and compositions (e.g. groundwater, meteoric and magmatic). The interaction of low temperature ($< 200°$ C) Ca-rich fluid with the granites and pegmatites produced extensive Ca-metasomatism and the replacement of sodic minerals by calcic equivalents. A low temperature Ca-poor oxidizing fluid may also have been responsible for destabilization of arfvedsonite, disequilibrium between $\delta^{18}O$ of quartz and alkali-feldspar, loss of fluorine and rare-metal remobilization within the altered subsolvus granites.

Alternatively, the metasomatism and hydrothermal alteration of the subsolvus granite may be related to the burial of the granites under their own volcanic ejecta (now eroded) or the intrusion of late granitoids at depth which may have raised the local geothermal gradient and initiated the circulation of low temperature connate and/or meteoric waters in the upper part of the subsolvus granite. This process has been invoked to explain the reverse quartz-feldspar $\delta^{18}O$ fractionation and alkali feldspar hematization in Mid-Proterozoic brick-red granites and granophyres (e.g. Muskox granophyres and St. François Mountain granites; Wenner and Taylor 1976; Taylor 1978).

Conclusions

This paper provides a new assessment of the role of magmatic and sub-solidus processes in the generation of HFSE and REE-enriched peralkaline granites. It stresses the strong similarities in the chemical evolution of the Strange Lake alkali granites to that of pantellerites and comendites. While extreme differentiation from mafic-intermediate (trachytic-syenitic) precursors by alkali feldspar fractionation may have played a substantial role in the HFSE and REE-enrichment of the granites, extremely high concentrations of these elements are more reasonably explained by the formation of fluoro-complexes in low-temperature residual silicic melts and their heterogeneous distribution in the late magmatic evolution of the Strange Lake complex. This process may have been enhanced by the unusually high fluorine contents initially dissolved in the granitic magmas. The sub-solidus evolution of the plutons involved the circulation of low temperature fluids in the granites and pegmatites which caused widespread Ca-metasomatism, hematization, loss of fluorine and enrichment in $\delta^{18}O$ values. The possibility that these fluids may have remobilized the REE and HFSE within the altered subsolvus granite emphasizes the importance of addressing the role of hydrothermal processes in the formation of granite-hosted HFSE and REE deposits.

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