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Alteration, HFSE mineralisation and hydrocarbon formation in peralkaline igneous systems: Insights from the Strange Lake Pluton, Canada

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Abstract

Two characteristics of peralkaline igneous rocks that are poorly understood are the extreme enrichment in HFSE, notably Zr, Nb, Y and REE, and the occurrence of fluid inclusions dominated by methane and higher hydrocarbons. Although much of the HFSE enrichment can be explained by magmatic processes, the common intense alteration of the parts of the peralkaline intrusions most enriched in these elements suggests that hydrothermal processes also play an important role in HFSE enrichment. Likewise, although the origin of the higher order hydrocarbons that occur as inclusions in these rocks is still debated, there is strong evidence that at least in some cases their formation involved hydrothermal processes. The issues of HFSE enrichment and hydrocarbon formation in peralkaline intrusions are examined using data from the Strange Lake pluton, a small, middle-Proterozoic intrusion of peralkaline granite in northeast Canada. This pluton contains some of the highest concentrations of Zr, REE and Y ever reported in an igneous body, and is characterised by abundant hydrocarbon-dominated fluid inclusions in rocks that have been hydrothermally altered, including those that form a potential HFSE ore zone. We show that HFSE at Strange Lake were partly concentrated to near exploitable levels as a result of their transport in a high salinity magmatic aqueous liquid, and that this fluid coexisted immiscibly with a carbonic phase which reacted with hydrogen and iron oxides generated during the associated hydrothermal alteration to produce hydrocarbons via a Fischer–Tropsch synthesis. As a result, hydrocarbons and HFSE mineralization are intimately associated. We then go on to show that hydrothermal alteration, HFSE mineralisation and hydrocarbons are also spatially associated in other peralkaline complexes, and present a model to explain this association, which we believe may be applicable to any peralkaline intrusion where HFSE enrichment was accompanied by calcium metasomatism, hematisation and hydrothermal fluorite. We also suggest that, even where these criteria are not satisfied, hydrothermally enriched HFSE and hydrocarbons will be intimately associated simply because they are products of the same initial magmatic fluid. Finally, we speculate that the association of HFSE and hydrocarbons may in some cases actually be genetic, if, as seems possible, unmixing or effervescence of a reduced carbonic fluid from the original magmatic fluid caused changes in temperature, pH, fO_2 or the activity of volatile ligands sufficient to induce the deposition of HFSE minerals.

Keywords: Peralkaline rocks; Hydrothermal alteration; Abiogenic hydrocarbons; Fischer–Tropsch; HFSE mineralization; Strange Lake

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1. Introduction

Although peralkaline intrusive magmatism is only responsible for a small proportion of the total volume of igneous rocks in the Earth's crust, a relatively large proportion of the petrological literature has been devoted to its study. Two important reasons for this interest are an unusual enrichment in the high-field strength elements (HFSE) Zr, Nb, Y and REE (e.g., Salvi and Williams-Jones, 2005), and the reduced nature of the gases contained as fluid inclusions in these rocks (e.g., Potter and Konnerup-Madsen, 2003; Nivin et al., 2005).

Much of the HFSE enrichment in peralkaline intrusions can be accounted for by magmatic processes (e.g., Kogarko, 1990; Kovalenko et al., 1995; Schmitt et al., 2002; Kogarko, 2005). However, many peralkaline igneous complexes display evidence of hydrothermal alteration, particularly in those parts of the complexes that are most enriched in the HFSE, e.g., the zones of Zr, U and REE mineralisation in the Ilímaussaq nepheline syenite complex, Greenland (Sørensen, 1992), and the zones of Zr–Nb–Y–REE mineralisation in the Thor Lake granite-syenite and Strange Lake granite complexes in Canada (Trueman et al., 1988; Salvi and Williams-Jones, 1990). Moreover, there is direct evidence for the hydrothermal precipitation of the HFSE from the presence of HFSE-bearing minerals in miarolitic cavities (e.g., the Evisa complex, Corsica; Bonin, 1988), and as trapped solids or daughter minerals in fluid inclusions, e.g., bastnäsite (Strange Lake complex; Salvi and Williams-Jones, 1990) and zircon (Tamazeght complex, Morocco; Salvi et al., 2000). It is therefore reasonable to propose that HFSE enrichment in peralkaline intrusions may be the result of a combination of magmatic and hydrothermal processes.

The reduced gases take the form of methane, heavier alkanes, aromatic hydrocarbons and hydrogen, and represent a peculiar feature of peralkaline intrusions that has been reported from a number of sites, for instance, the Lovozero and Khibiny complexes in the Kola Peninsula, Russia (e.g., Ikorski, 1981; Nivin et al., 1995; Potter et al., 1998; Potter et al., 2004; Nivin et al., 2005; Beeskow et al., 2005), the Ilímaussaq complex, Greenland (e.g., Petersilie and Sørensen, 1970; Konnerup-Madsen et al., 1981; Markl et al., 2001; Krumrei and Markl, 2005; Markl, 2005), the Strange Lake complex, Canada (Salvi and Williams-Jones, 1992), and the Tamazeght complex, Morocco (unpublished data). Inclusions containing these gases generally formed as a result of late- or post-magmatic fluid entrapment. Moreover, they are commonly associated spatially with HFSE mineralisation. For example, at Strange Lake, the hydrocarbon-bearing inclusions are found in pegmatites and associated granite that were either strongly depleted or strongly enriched in HFSE as a result of their alteration by hydrothermal fluids.

In addition to the reduced gases, carbon monoxide, carbon dioxide and nitrogen are also present with the hydrocarbons at Strange Lake and some of the other complexes. Although there is a general consensus that the hydrocarbons are abiogenic, there is no agreement on how they formed. An early explanation for their occurrence had been that they were components of a C–O–H fluid, which exsolved from the magma, and evolved by cooling along a relatively reduced rock-buffered redox path (e.g., Gerlach, 1980). However, Salvi and Williams-Jones (1997a) showed for the Strange Lake complex that the observed distribution of hydrocarbons, i.e., the proportions of the various alkanes, cannot be accounted for by a simple magmatic model, but is readily explained by a Fischer–Tropsch synthesis driven partly by the products of the early subsolvus alteration of arfvedsonite to aegirine. A similar process was subsequently proposed for hydrocarbon formation in alkaline rocks from the Lovozero and Khibiny massifs and the Ilímaussaq intrusion (Potter et al., 1998; Potter and Konnerup-Madsen, 2003; Potter et al., 2004; Nivin et al., 2005), although recently a magmatic model involving polymerisation of hydrocarbons has also been proposed for these bodies (Markl et al., 2001; Beeskow et al., 2005). Despite the fact that the origin of hydrocarbons in peralkaline rocks is still a matter of some debate, it seems clear that these gases form abiogenically, either directly by magmatic processes or indirectly during subsolidus hydrothermal alteration. It is also clear that the HFSE mineralisation shares a common genetic link with the hydrocarbons inasmuch as both involved magmatic processes, both appear in some cases to have required the intervention of subsolidus processes involving magmatic hydrothermal fluids and both are spatially associated.

In this paper, we review the research that has been carried out on various features of the Strange Lake complex, and use this information to reconstruct the postmagmatic history of the pluton, highlighting the intimate links between hydrothermal alteration, HFSE mineralisation and hydrocarbon formation. We then go on to compare this history with that of other intrusions, and use it to distil a model of hydrothermal mineralisation and hydrocarbon generation broadly applicable to peralkaline igneous systems.

2. The Strange Lake complex

The Strange Lake pluton is a Mesoproterozoic (1240±2 Ma; Miller et al., 1997; see also Pillet et al., 1989) intrusion, consisting of several facies of HFSE-enriched peralkaline granite, which outcrop over area of about 36 km^2 on the border between the provinces of Québec and Newfoundland, Canada, at latitude 56°18′N and longitude 64°07′W (Fig. 1). After its discovery in 1979, the pluton was explored for economic HFSE mineralisation and a potential ore zone delimited in the central part of the intrusion containing some 30 million tonnes grading 3.25 wt.% ZrO_2, 1.3 wt.% REE oxides, 0.66 wt.% Y_2O_3, 0.56 wt.% Nb_2O_5 and 0.12 wt.% BeO (Iron Ore Company of Canada, unpublished data; see also Zajac et al., 1984). The principal ore mineral is gittinsite, and is accompanied, locally, by abundant armstrongite, kainosite-(Y), bastnäsite s.l., gagarinite-(Y), monazite s.l., pyrochlore s.l. and gadolinite s.l. (cf. Table 1 for mineral formulae).

Table 1
Mineral formulae for unusual minerals mentioned in the text

Mineral name	Formula
Aenigmatite	$Na_2Fe_5^{2+}TiSi_6O_{20}$
Allanite s.l.	$(REE,Ca)_2(Al,Fe^{2+},Fe^{3+})_3(SiO_4)_3(OH)$
Arfvedsonite	$Na_3Fe_4^{2+}Fe^{3+}Si_8O_{22}(OH)_2$
Armstrongite	$CaZrSi_6O_{15}\cdot 2.5H_2O$
Astrophyllite	$(K,Na)_3(Fe^{2+},Mn)_7Ti_2Si_8O_{24}(O,OH)_7$
Baddeleyite	ZrO_2
Bastnäsite s.l.	$REECO_3F$
Ca-catapleiite	$CaZrSi_3O_9\cdot 2H_2O$
Dalyite	$K_2ZrSi_6O_{15}$
Elpidite	$Na_2ZrSi_6O_{15}\cdot 3H_2O$
Eudialyte	$Na_4(Ca,Ce)_2(Fe^{2+},Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$
Gadolinite s.l.	$REE_2Fe^{2+}Be_2Si_2O_{10}$
Gagarinite-(Y)	$NaCaY(F,Cl)_6$
Gittinsite	$CaZrSi_2O_7$
Kainosite-(Y)	$Ca_2(Y,Ce)_2Si_4O_{12}(CO_3)\cdot H_2O$
Lavenite	$(Na,Ca)_2(Mn,Fe)(Zr,Ti)Si_2O_7(O,OH,F)_2$
Milarite-(Y)	$K(Ca,Y)Be_3Si_{12}O_{30}$
Monazite s.l.	$REEPO_4$
Narsarsukite	$Na_2(Ti,Fe^{3+})Si_4O_{10}(O,F)$
Rinkite	$(Na,Ca,Ce)_3Ti(SiO_4)_2F$
Pyrochlore s.l.	$(Ca,Na)_2(Nb,Ta)_2O_6(O,OH,F)$
Saryarkite	$Ca(Y,Th)Al_5(SiO_4)_2(PO_4,SO_4)_2(OH)_7\cdot 6H_2O$
Thorite	$ThSiO_4$
Titanite	$CaTiSiO_5$
Vlasovite	$Na_2ZrSi_4O_{11}$

2.1. Geological setting

The intrusion is part of the Rae tectonic Province of the Canadian Shield, and is located at the contact between Archean basement and an Elsonian quartz monzonite (Fig. 1) (Currie, 1985; Pillet, 1985; Miller, 1986). The Archean host rocks comprise intercalated quartzo-feldspathic, calc-silicate, graphitic, dioritic, gabbroic and anorthositic gneisses, which were metamorphosed to upper-amphibolite facies during the Aphebian Hudsonian orogeny (Bélanger, 1984); the quartz monzonite is post-tectonic. The age of the pluton and its peralkaline character suggest that it represents

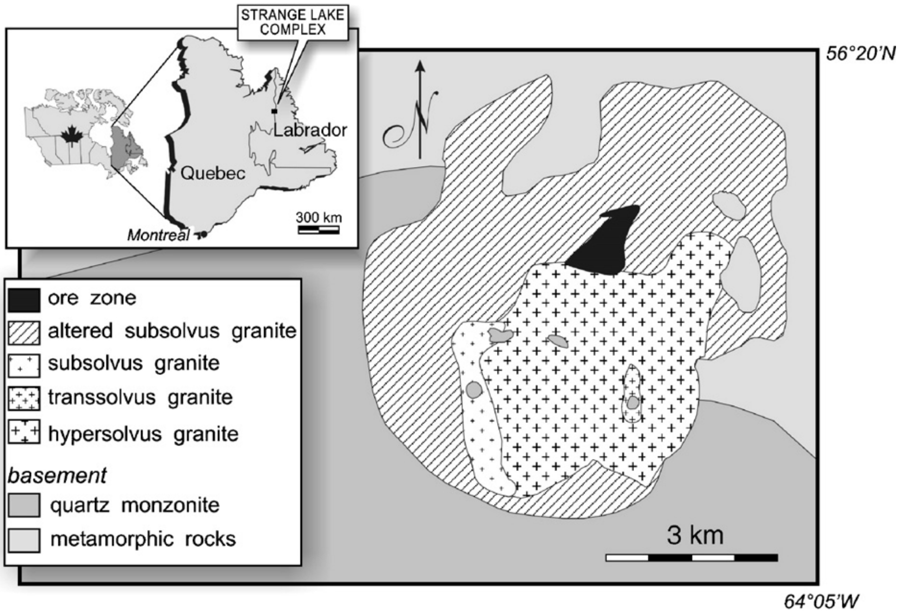


Fig. 1. Location and geological map of the Strange Lake complex. Modified after Salvi and Williams-Jones (1990, 1996).

part of the anorogenic Gardar province of southern Greenland (e.g., Currie, 1985).

Mapping of the surface geology and logging of drill core lead to the recognition of several facies of peralkaline granite, which, on the basis of their feldspar mineralogy, are classified as hypersolvus, transsolvus and more evolved subsolvus granite (Nassif and Martin, 1991); the subsolvus granite hosts the potential ore zone (Fig. 1). In addition, there are numerous pegmatites and rare aplites, which are located mainly in the subsolvus granite. These form thin (10 to 50 cm), largely planar bodies, which are generally east–west striking and have subvertical dips. An outwardly dipping ring fracture, marked by a heterogeneous breccia with a fluorite-filled matrix, surrounds the pluton. Field evidence (roof pendants, miarolitic cavities) and the low trapping pressure estimated for primary orthomagmatic fluid inclusions (Salvi and Williams-Jones, 1992) suggest that the whole intrusive system was emplaced at shallow crustal levels (<3 km).

The hypersolvus granite consists of phenocrysts of quartz and perthite, interstitial arfvedsonite, and subordinate proportions of albite, aenigmatite, astrophyllite, vlasovite, dalyite and other exotic phases (Miller, 1986). The mineralogy of the transsolvus granite is similar, except that microcline is common, and arfvedsonite occurs predominantly as fine-grained anhedra which impart a dark colour to the rock. The subsolvus granite (most of which is altered) occupies more than 60% of the complex. The unaltered variety is composed mainly of quartz, albite, microcline and arfvedsonite (arfvedsonite is present both as phenocrysts and in the groundmass). Locally, the zirconosilicate mineral, elpidite, can also be a major phase, comprising up to 20% of the mode. The principal accessory phases are hematite, fluorite, thorite, bastnäsite, monazite, pyrochlore, kainosite, allanite, milarite-(Y) and several unidentified HFSE-bearing minerals (Table 1).

All these granite types display some degree of heterogeneity due mainly to flow differentiation, which locally concentrated arfvedsonite and some of the denser exotic minerals, notably elpidite, in thin discontinuous layers. The hypersolvus granite facies is believed to represent the earliest intrusive phase, whereas the subsolvus granite crystallised at a late stage, as indicated by cross-cutting relationships among the different granite facies and the presence of microcline and near end-member albite in the subsolvus granite (Nassif, 1993). The pegmatites are interpreted to have formed pene-contemporaneously with fluid phase separation during crystallisation of the subsolvus granite (Nassif, 1993; Boily and Williams-Jones, 1994).

A preliminary model for the magmatic evolution of the Strange Lake pluton was proposed by Boily and Williams-Jones (1994; see also Pillet et al., 1992), which envisages an evolution similar to that of pantellerites and comendites (e.g., Mungall and Martin, 1996). The model calls for the injection of a mantle-derived, halogen-rich trachytic liquid into a crustal magma chamber. Protracted, in situ fractionation produced an extremely evolved roof zone from which batches of magma were periodically extracted and intruded to form a high-level pluton that was cryptically layered outwards from a least-evolved core of hypersolvus granite to an outer zone of more-evolved subsolvus granite. The magma was initially dry, but with continued evolution became saturated with H_2O during the later stages of subsolvus granite crystallisation and pegmatite emplacement, eventually exsolving an aqueous fluid that produced extensive alteration of these rocks, most notably the replacement of arfvedsonite by aegirine (see below) (Salvi and Williams-Jones, 1990; Boily and Williams-Jones, 1994).

2.2. Alteration and HFSE mineralisation

Two episodes of hydrothermal alteration have been recognised in the apical parts of the pluton. Early alteration is evident from the replacement of arfvedsonite by aegirine, and affected all units of the complex, particularly rocks immediately adjacent to pegmatites. This alteration is interpreted to have proceeded by reactions of the type:

$$\underset{\text{arfvedsonite}}{3Na_3Fe_5Si_8O_{22}(OH)_2}+2H_2O=\underset{\text{aegirine}}{9NaFeSi_2O_6}+\underset{\text{magnetite}}{2Fe_3O_4}+\underset{\text{quartz}}{6SiO_2}+5H_2 \quad (1)$$

and is interpreted to have been caused by high salinity orthomagmatic fluids released during crystallisation of the subsolvus granite at ≥350 °C (Salvi and Williams-Jones, 1992).

The later alteration episode is evident macroscopically by pervasive hematisation, which imparted a reddish colour to the rock and was particularly intense in subsolvus granite in the centre of the complex (Fig. 1), where the potential ore body is located. In addition to hematisation, this alteration involved extensive calcium metasomatism (Salvi and Williams-Jones, 1996). Chemically, it was characterised by an enrichment of Ca, Mg, F, Zr, Y, the heavy REE (HREE) and other HFSE, and a depletion in Na (Salvi and Williams-Jones, 1996). HFSE-bearing minerals are more abundant in rocks subjected to this later alteration than in fresh rocks or rocks subjected only to early alteration, and are mainly secondary, Ca-bearing phases. For example, gittinsite, the principal ore mineral, is exclusively secondary, occurring as bundles of feathery radiating millimetre-sized crystals, which, with quartz and hematite, pseudomorphed primary euhedral elpidite (Fig. 2) or replaced arfvedsonite and aegirine (Gagnon, 2005; Gagnon et al., 2005). More rarely, elpidite was also partially replaced by zircon. Relic elpidite is rare, except in a few drill holes where, in weakly altered rocks, it was partially replaced, in some cases by gittinsite and in others by armstrongite (Fig. 2) (Salvi and Williams-Jones, 1995). Significantly, in these weakly altered rocks, gittinsite and elpidite do not occur in mutual contact, whereas armstrongite (blue CL in Fig. 2) is commonly observed in contact with both elpidite and gittinsite. Other ore minerals, which replaced primary phases, include titanite (±fluorite±quartz±hematite) after narsarsukite and kainosite after unidentified precursors. Based on the chemical and mineralogical changes described above, fluid inclusion data discussed below, and field relationships, Salvi and Williams-Jones (1990) attributed the Ca-metasomatism to interaction of the rock with a low-temperature (150 to 200 °C) silica-undersaturated brine derived externally from the pluton. This Ca–Na exchange, which dominated the alteration, is exemplified by the reaction:

$$\underset{\text{elpidite}}{Na_2ZrSi_6O_{15}\cdot 3H_2O} + Ca^{2+} + 5H_2O = \underset{\text{gittinsite}}{CaZrSi_2O_7} + 2Na^{+} + 4H_4SiO_4^{0} \tag{2}$$

(Salvi and Williams-Jones, 1995).

Fluorite, which is a common accessory mineral in the subsolvus granite, is particularly abundant in rocks affected by the later low-temperature alteration, where it occurs principally as a secondary pore-filling phase. Other secondary fluorine-bearing minerals include the secondary HFSE phases, gagarinite, lavenite and pyrochlore.

Evidence that hydrothermal processes not only changed the HFSE mineralogy but also remobilized and concentrated these elements is provided by the occurrence of the REE mineral, bastnäsite as a daughter or trapped mineral in fluid inclusions, and textures showing that aegirine and arfvedsonite were replaced by

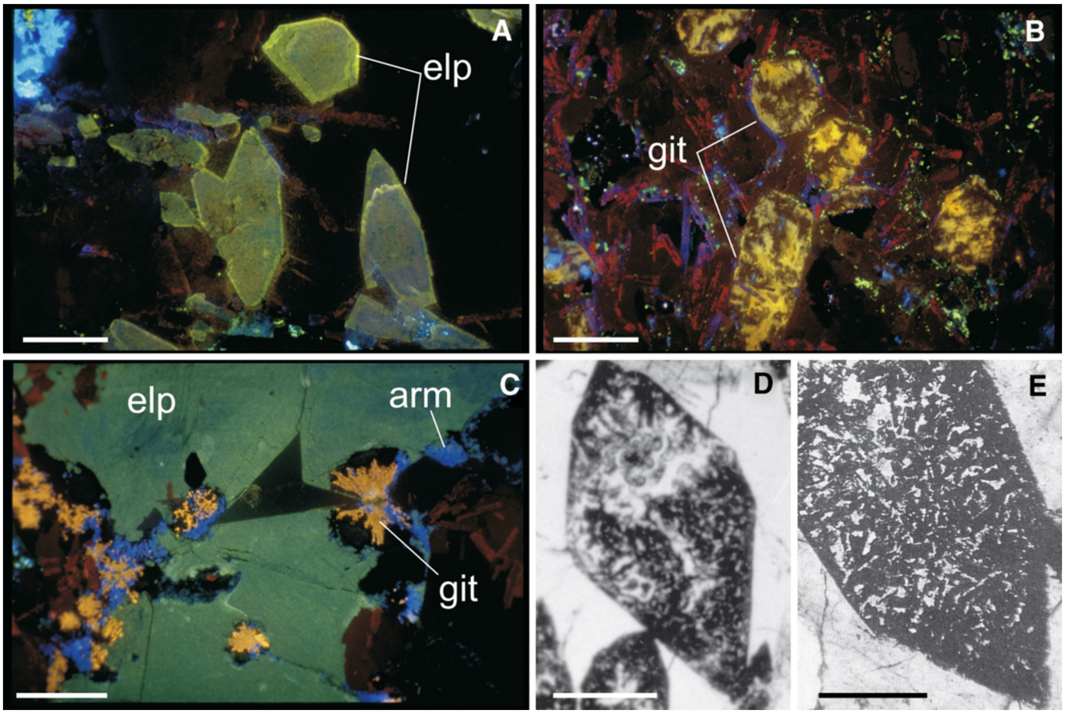


Fig. 2. (A to C) Cathodoluminescence (CL) photomicrographs illustrating the pseudomorphism of gittinsite after elpidite; (A) euhedral elpidite (elp; green CL; from unaltered subsolvus granite); (B) pseudomorphs of feathery gittinsite (git; orange CL) plus quartz after euhedral elpidite. Red laths are Fe^{III}-rich feldspar. (C) Partial replacement of elpidite by armstrongite (arm; blue CL) and gittinsite in a drill core sample that has undergone incipient Ca-metasomatic alteration. CL conditions used are: beam voltage of 10 to 15 keV, beam current of 0.5 to 1 mA and beam diameter of 5 mm. (D and E) Photomicrographs comparing similar pseudomorphs of gittinsite (+quartz) after elpidite from (D) the Strange Lake complex and (B) the Khaldzan-Buregtey massif (photo in E: modified after Kovalenko et al., 1995). Scale bars: A to D = 1 mm, E = 5 mm.

gittinsite (+ quartz+hematite). In the case of aegirine, this replacement proceeded according to the reaction:

$$\underset{\text{aegirine}}{2NaFeSi_2O_6}+Ca^{2+}+Zr^{4+}+2H_2O=\underset{\text{gittinsite}}{CaZrSi_2O_7}+2SiO_2+Fe_2O_3+2Na^{+}+4H^{+} \tag{3}$$

(Gagnon, 2005) or, assuming that the stable form of Zr in the fluid is the hydroxy-fluoro complex (see below and Salvi et al., 2001):

$$2NaFeSi_2O_6 + Ca^{2+} + Zr(OH)_2F_2^0 = CaZrSi_2O_7 + 2SiO_2 + Fe_2O_3 + 2Na^{+} + 2HF^{0}. \tag{4}$$

This confirms estimates, based on whole-rock data from the ore zone, that up to 0.5 wt.% Zr were added to the rock during the late alteration event (Salvi and Williams-Jones, 1996).

2.3. Fluid inclusions

Detailed investigations of fluid inclusions in the Strange Lake rocks have permitted the physical and chemical properties of the fluids responsible for both the high-temperature alteration (Salvi and Williams-Jones, 1992, 1997a,b) and the low-temperature, calcic alteration (Salvi and Williams-Jones, 1990) to be characterized. A brief summary of the results of these investigations is provided below.

Subsolvus granites and pegmatites in the ore zone contain small (<10 μm across) primary fluid inclusions that help define the boundaries of the pseudomorphs of gittinsite+quartz after elpidite and titanite+quartz after narsarsukite, i.e., the fluids were trapped during formation of the ore minerals. These inclusions are hosted in quartz, contain a liquid and a vapour phase, and less commonly one or two solid phases; bastnäsite and hematite were identified by EDS-SEM in opened inclusions. Microthermometric data for these inclusions are summarised in Table 2 and show that they trapped a moderately saline, Ca-rich fluid at a temperature between 150 and 200 °C.

Primary fluid inclusions were found also in rocks that only had undergone the high-temperature alteration and occur mainly in pegmatites along growth zones in late quartz. Inclusions with identical phase ratios and microthermometric behaviour also occur in numerous trails within quartz grains in subsolvus granite. These inclusions trapped immiscible aqueous and carbonic fluids at about 350 °C. The aqueous fluid had high salinity and sodium was the only cation detected (Table 2). The carbonic fluid composition was dominated by methane, however, under ultra-violet light illumination, the methane-dominated carbonic vapour bubble in several of these inclusions was seen to be surrounded by an orange or green fluorescing ring (Salvi and Williams-Jones, 1992). These samples were subsequently analysed by on-line gas chromatography (cf. Salvi and Williams-Jones, 1997b, 2003) and shown to contain up to ~10 mol% saturated and unsaturated aliphatic hydrocarbons (up to C_6), and as much as 35 mol% hydrogen, in addition to minor nitrogen and CO_2 (Salvi and Williams-Jones, 1997a). A suite of quartz samples from pegmatites that had been exposed to the Ca-metasomatising fluid was also analysed. They contain fluid inclusions with a similar hydrocarbon composition, but a much higher proportion of CO_2 (Salvi and Williams-Jones, 1997a) (Fig. 3).

Table 2
Summary of fluid-inclusion microthermometric data for the Strange Lake Complex

Phase change	Data range	Data peak
Low-temperature alteration		
Th	90 to 225 °C	130 °C
Th daughter min.	130 to 150 °C	145 °C
Te	−70 to −15 °C	−48 °C
Tm ice	−24 to −8 °C	−19 °C
Salinity[a]	12 to 25	16
Principal cations	Na, Ca, K	
Principal anion	Cl	
Trapping T[b]	150 to 200 °C	
High-temperature alteration[c]		
Th	300 to 360 °C	340 °C
Te	−26 to −20 °C	−22 °C
Tm ice	−22 to −20 °C	−21 °C
Tm hydrohalite	−22 to 5 °C	−20 °C
Salinity[a]	23 to 27	24
Principal cations	Na	
Principal anion	Cl	
Trapping T[b]	340 °C	

Th=homogenization T, Te=eutectic T, Tm=final melting T.

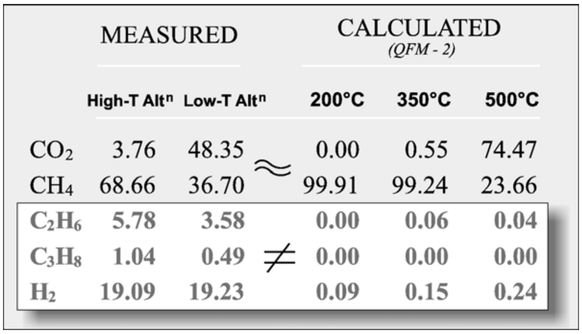
[a] Salinity expressed in equivalent wt.% NaCl.

[b] Pressure corrected.

[c] For the gas composition, cf. Fig. 4 and Salvi and Williams-Jones (1997a).

2.4. Carbonic fluid evolution and hydrocarbon genesis

In order to determine the origin of the hydrocarbons present in the high-temperature fluid inclusions at Strange Lake, Salvi and Williams-Jones (1997a) carried out thermodynamic calculations in the C–O–H system designed to estimate the equilibrium composition of an evolving orthomagmatic carbon-bearing fluid. The calculations showed that the composition of the bulk carbonic fluid in the Strange Lake samples could not



	MEASURED			CALCULATED (QFM - 2)		
	High-T Altⁿ	Low-T Altⁿ		200°C	350°C	500°C
CO_2	3.76	48.35	≈	0.00	0.55	74.47
CH_4	68.66	36.70		99.91	99.24	23.66
C_2H_6	5.78	3.58		0.00	0.06	0.04
C_3H_8	1.04	0.49	≠	0.00	0.00	0.00
H_2	19.09	19.23		0.09	0.15	0.24

Fig. 3. Average hydrocarbon composition of fluid inclusions from pegmatites that have undergone high and low temperature alteration. The right-hand-side columns show species proportions in the system C–O–H at 200, 350 and 500 °C obtained from equilibrium thermodynamic calculations (cf. Salvi and Williams-Jones, 1997a).

represent the equilibrium gas composition at the conditions of entrapment; the calculated abundances of H_2, C_2H_6 and C_3H_8 are at least 1, 2 and 3 orders of magnitude lower than measured, respectively (Fig. 3). Moreover, increasing fO_2 to QFM or decreasing it to 5 log units below QFM, and/or increasing the temperature to 500 °C, did not improve the fit to the measured composition.

It could be argued that the hydrocarbons formed at an early magmatic stage (e.g., via polymerization, cf. Kenney et al., 2002) and that the present composition of the fluid inclusions reflects re-equilibration of the gases at lower temperature. However, since fO_2 is not buffered in the inclusions and the high-temperature fO_2 conditions represent states of extreme oxidation at low temperature (e.g., Holloway, 1984), we can assume that the dominant fluid at room temperature would be CO_2. In view of the fact that the Strange Lake pluton is intruded into upper amphibolite to granulite facies gneisses that are locally graphitic, we also considered the possibility that the hydrocarbons were produced by reaction of the aqueous orthomagmatic fluid with graphite. However, the fit of the calculated equilibrium gas composition at 350 °C to the measured composition is even worse than that discussed above. It must therefore be concluded that the gas species in the carbonic inclusions are not, and never were, in equilibrium.

An alternative abiogenic explanation for the presence of the higher hydrocarbons species in the Strange Lake fluid inclusions is that they were produced by the disequilibrium reactions:

$$nCO + (2n+1)H_2 = C_nH_{2n+2} + nH_2O \qquad (5)$$

$$nCO_2 + (3n+1)H_2 = C_nH_{2n+2} + 2nH_2O \qquad (6)$$

These reactions are the basis for the Fischer–Tropsch (F–T) synthesis, a well-known industrial process used to convert coal to petroleum (e.g., Anderson, 1984). The overall reaction consists of a series of steps, including breaking of the C–O bond and replacing it by a C–C or C–H bond. In the case of reaction (6), CO_2 is first transformed to CO, which is then hydrogenated to form hydrocarbons (Weatherbee and Bartholomew, 1984). The process of breaking the C–O bond is catalysed by a group VIII metal in its native form or as an oxide (e.g., Anderson, 1984) and could occur naturally in the presence of wustite or magnetite (e.g., Madon and Taylor, 1981; Röper, 1983). The length of the carbon chain in F–T synthesis is dictated by the probability of the addition to the chain of a carbon or hydrogen atom. As a result, complex mixtures are produced, but the lighter, shorter chain hydrocarbons are always favoured (e.g., Anderson et al., 1976; Satterfield and Huff, 1982). Chain growth probability is a function of reaction temperature, pressure and the ratio of H_2 to C species; higher temperature and higher H_2/CO favour the formation of shorter chains, and higher pressure produces low olefin/paraffin ratios (unsaturated/saturated aliphatics). Within a given product, the molecular ratios of hydrocarbons with successive carbon numbers are ~constant ($C_{n+1}/C_n = C_{n+2}/C_{n+1}$), resulting in the Schulz–Flory distribution of hydrocarbons (they decrease linearly on a plot of log X_i vs. C_n). Since the purpose of the industrial application of the Fischer–Tropsch synthesis is to produce oil, i.e., relatively long-chain unsaturated and cyclic compounds, most syntheses are conducted at temperatures <400 °C and pressures below 100 bar. However, Anderson (1984) has shown that significant yields of hydrocarbons up to at least C_6 are obtained at temperatures as high as 600 °C.

The ratios of the mole fractions of pairs of progressively heavier hydrocarbons in altered pegmatites at Strange Lake are, on average, $C_2/C_1 = 0.084$, $C_3/C_2 = 0.180$, $C_4/C_3 = 0.340$ and $C_5/C_4 = 0.339$. With increasing carbon number, these ratios level off to a constant value of approximately 0.34 and thus conform with the Schulz–Flory distribution rule; the low ethane/methane ratio is explained by the fact that some methane was present at equilibrium. Moreover, the limiting ratio of 0.34 is consistent with the finding that synthetic product mixtures dominated by light hydrocarbons have C_{n+1}/C_n values below ~0.6 (e.g., Szatmari, 1989).

The question that next needs to be addressed is whether CO_2, CO and H_2 were potentially present in sufficient concentrations to produce the measured concentrations of the heavier hydrocarbons. The total content of heavier hydrocarbons in inclusions in the altered pegmatites ranges from ~5 to ~10 mol% of the volatile content of the inclusions (excluding H_2O). Assuming equilibrium in the system C–O–H, Salvi and Williams-Jones (1997a) demonstrated, using the calculations referred to earlier, that the amounts of CO_2, CO and CH_4 are more than sufficient to produce the measured hydrocarbons at temperatures between 500 °C and 600 °C and at fO_2 2 to 3 log units below QFM. However, at all the above conditions, the proportion of H_2 in equilibrium with these gases would be <1 mol%. By contrast, the inclusions in the altered pegmatites contain 20 mol% H_2 and a minimum additional 30 mol% H_2 would have been consumed in producing the ethane and heavier hydrocarbons. It therefore follows that an independent source of H_2 would have been necessary to account for the measured hydrogen content. One such source of H_2 is believed to be the alteration of arfvedsonite to aegirine (cf. reaction 1), which, as discussed earlier, occurred as a result of the exsolution of orthomagmatic fluids during pegmatite emplacement. This reaction, as is readily evident, produces 5 mol of H_2 for every 3 mol of arfvedsonite altered. Furthermore, the magnetite produced in reaction (1) could have acted as the catalyst for reactions (5) and (6).

Thus, in summary, we propose that the hydrocarbons analysed in pegmatite quartz from Strange Lake were formed from an orthomagmatic fluid, which, when it separated from the magma was composed mainly of a mixture of CO, CO_2 and CH_4, and was in equilibrium with the rock at 500 °C to 600 °C and fO_2 between 2 and 3 log units below QFM. According to this model, the CO and CO_2 in the fluid reacted with H_2 derived from the oxidation of arfvedsonite to aegirine, and as a result of magnetite-catalysed Fischer–Tropsch synthesis,

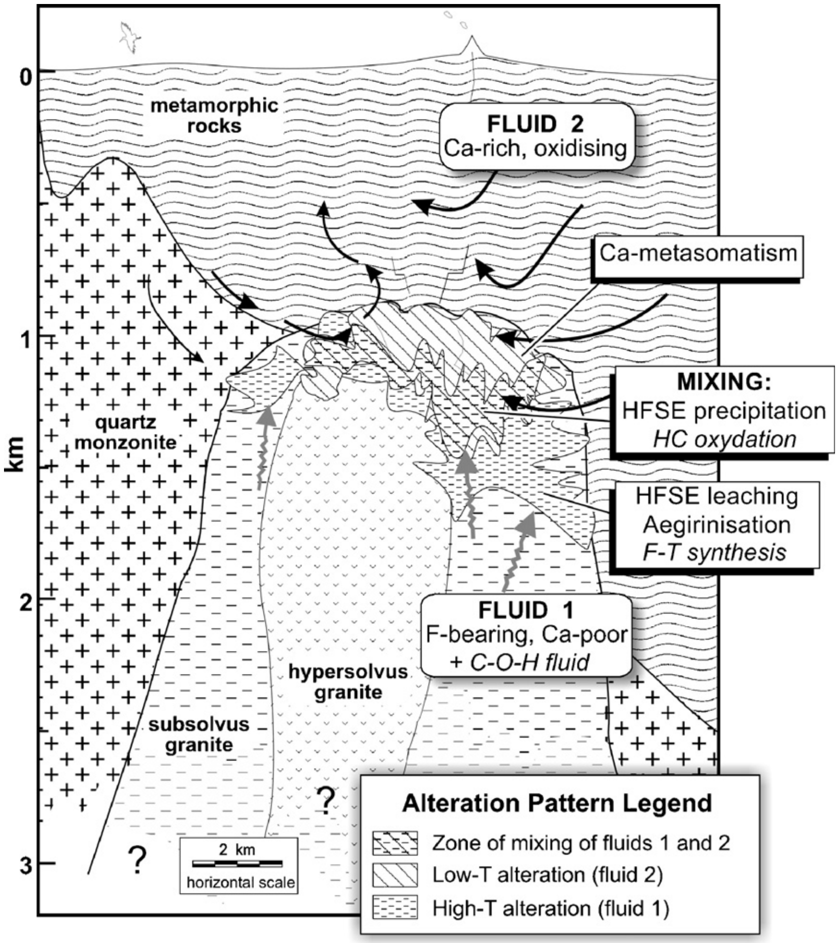


Fig. 4. Schematic cross-section through the Strange Lake pluton depicting the main events envisaged during subsolidus hydrothermal alteration (see text). HC = hydrocarbons, F–T = Fischer–Tropsch.

produced the hydrocarbons presently preserved in the Strange Lake fluid inclusions. Once formed and trapped, these species remained in a continual state of disequilibrium for the same kinetic reasons that necessitate the use of catalysts in the commercial production of light alkanes from crude oil.

2.5. Genetic model for the Strange Lake complex

The formation of methane-and higher-hydrocarbon-dominated fluid inclusions in the Strange Lake pluton, alteration of arfvedsonite to aegirine, and the enrichment of Zr, Y and REE in the most altered rocks, were intimately related. The primary magmatic enrichment of HFSE, as demonstrated by the correlation of HFSE content with parameters reflecting magma evolution, was substantial. However, as discussed above, the HFSE were enriched primarily by post-magmatic hydrothermal processes. Similarly, although the carbonic fluid was likely of magmatic origin, calculations discussed above suggest that the observed hydrocarbon species, except for methane, did not escape from the magma or form spontaneously on cooling. Rather, they formed as a result of reactions driven by the products of early hydrothermal alteration.

The hydrothermal history of the pluton (Fig. 4) commenced with exsolution from the magma of a high salinity aqueous liquid and an immiscible, CO_2-dominated C–O–H–N fluid, at temperatures above 350 °C and a pressure of ~700 bar, respectively. The aqueous fluid affected all units in the pluton, and altered primary arfvedsonite to an assemblage of aegirine and magnetite in a reaction, which also produced hydrogen. The hydrogen, in turn, reacted with the CO_2 of the C–O–H–N fluid in a magnetite-catalysed Fischer–Tropsch synthesis to form appreciable quantities of methane, ethane and aliphatic hydrocarbons as heavy as hexane.

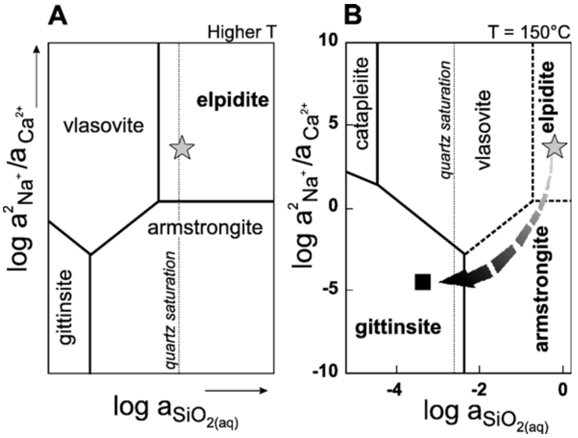


Fig. 5. Log a^2Na^+/aCa^{2+} vs. log $aSiO_{2(aq)}$ diagrams depicting the stability fields of zirconosilicate minerals involved in the elpidite alteration at Strange Lake (cf. Fig. 2). Also shown are the hypothetical compositions of the unaltered elpidite-bearing granite (star) and meteoric fluid (square), the quartz saturation boundary and the possible compositional path of the fluid during alteration. The diagram in (A) depicts high temperature (near-magmatic) equilibrium of elpidite with quartz, as observed in unaltered granite. Diagram (B) represents mineral equilibria in the meteoric fluid (150 °C). Mineral stability boundaries at 150 °C (B) are from Aja et al. (1997). The dashed lines indicate unstable areas of the diagram with respect to quartz saturation. Because of the lack of high temperature data, the diagram in (A) is dimensionless; the limit of quartz saturation is based on field observations.

In addition to altering arfvedsonite, the orthomagmatic brine also leached Zr, Y and REE from primary minerals. These highly charged metals were kept in solution as fluoride complexes at mildly acidic conditions (pH above 4.7, i.e., high enough to prevent the reaction of K-feldspar to muscovite at ~350 °C). Penecontemporaneously with release of the orthomagmatic fluid, a low-temperature, oxidising, ground-water-dominated convective system, initiated by heat from the pluton, developed in the apical region of the intrusion. This later fluid was enriched in Ca from interaction with the host gneisses, but was undersaturated with respect to quartz (Fig. 5). Upon reacting with the granites, it added Ca and Mg to the rock and removed Na, causing the transformation of sodic HFSE-bearing minerals, notably elpidite, but also aegirine and arfvedsonite, to calcic equivalents, primarily gittinsite and, to a lesser extent, armstrongite. This alteration, because of the much smaller molar volume of gittinsite relative to elpidite, was accompanied by significant porosity creation (cf. Fig. 2). Near the base of the alteration zone, the increased porosity enhanced leaching of Zr and Y by greatly improving access of the rising orthomagmatic fluid to sites containing minerals rich in these elements, which explains the depletion of Zr and Y immediately below the main gittinsite plus quartz alteration zone (Salvi and Williams-Jones, 1996). At higher levels, however, there was extensive mixing of the orthomagmatic fluid with the Ca-rich, meteoric fluid, which caused precipitation of Zr, Y and REE minerals, as a result of decreased ligand concentration due to saturation of the fluid with fluorite and/or an increase of pH. This mixing also promoted partial oxidation of the carbonic fluid, as indicated by the higher CO_2/CH_4 ratio of fluid inclusions in Ca-metasomatised rocks, extensive hematisation and increased silica activity to quartz saturation, thereby filling pores and sealing the rock to further fluid circulation.

3. Application to other alkaline systems

The fact that magmatic processes play an essential role in the formation of HFSE deposits is readily apparent from studies of melt inclusions, which show that concentrations of HFSE in peralkaline magmas are orders of magnitude higher than in other magma types. For example, Kovalenko et al. (1995) reported Zr, Nb and REE concentrations as high as 2.7, 0.6 and 0.3 wt.%, respectively, in melt inclusions from the Khadlzan-Buregtey peralkaline granitoid, and Schmitt et al. (2002) reported similar concentrations in melt inclusions from peralkaline granites of the Amis complex, i.e., 2 wt.% Zr, 0.3 wt.% Nb and 0.2 wt.% REE. The important role of magmatic processes is also evident from the extreme enrichment of Nb and REE (6 wt.% REE oxides and 1 wt.% Nb) as primary minerals in lujavrites of the Ilímaussaq complex, which Markl (2001) attributed to liquid immiscibility. On the other hand, it would appear that other processes must have played an important role in producing the concentrations required to form exploitable deposits in some peralkaline complexes. At Strange Lake, for example, the average Zr content in unaltered granite is ~3000 ppm, and the Y and REE contents ~500 ppm, whereas the corresponding deposit grades are 3.25 wt.% ZrO_2, 0.66 wt.% Y_2O and 1.3 wt.% REE oxides, representing an apparent enrichment factor of 7 to 22. Similarly, the quartz-syenite associated with the Gallinas Mountains REE deposits contains ~650 ppm REE, whereas the deposit grade is 1.5 to 2.5 wt.% REE, i.e., the enrichment factor is ~25 (cf. Williams-Jones et al., 2000). Finally, unaltered granite and syenite at Thor Lake have average Zr, REE and Nb contents of around 400 ppm, 300 ppm and 150 ppm, respectively, whereas the corresponding grades in the deposit are 3.5 wt.% Zr, 1.7 wt.% REE and 0.4 wt.% Nb (Trueman et al., 1988), indicating that the enrichment factor was between approximately 25 and 85.

3.1. *The role of hydrothermal alteration in HFSE mineralisation*

Hydrothermal alteration, e.g., the replacement of arfvedsonite by aegirine, as mentioned in the introduction to this paper, is a common feature of many peralkaline intrusions (e.g., Sørensen, 1974; Bonin, 1988; Sørensen, 1997; Potter et al., 1998; Potter et al., 2004). Moreover, as is the case at Strange Lake, hydrothermal alteration is commonly associated with HFSE enrichment to potential ore-forming levels. For example, many of the Nigerian peralkaline granites contain Nb–U mineralisation where they have undergone sodic metasomatism (Kinnaird, 1985). The main mineralised zone of the Thor lake Zr–Nb–Y–REE deposit, Canada, was intensely albitised (Trueman et al., 1988; Taylor and Pollard, 1996). The Zr–Nb–Ta–REE deposits in the Khaldzan-Buregtey massif, western Mongolia, are associated with intense hematisation and Ca-metasomatism (Kempe et al., 1999), and the same is true of zones of Y enrichment in the Kipawa peralkaline complex (e.g., Allan, 1992; Currie and van Breemen, 1996) and the peralkaline units hosting the highest concentrations of HFSE in the Tamazeght complex, Morocco (Khadem-Allah et al., 1998; Salvi et al., 2000). As a last example, we note that, although they are generally interpreted to have formed mainly by magmatic processes (e.g., Kogarko, 1990), the REE deposits in the Khibiny complex are associated with numerous hydrothermal veins and pegmatites (e.g., Nivin et al., 2005 and references therein), and it has been suggested that they may be at least partly metasomatic (e.g., Florovskaya and Melkov, 1962; see also recent discussion on REE mobility in Samson and Wood, 2005; Salvi and Williams-Jones, 2005).

Accepting that there is at least a spatial association between hydrothermal alteration and HFSE mineralization, the question that next arises is whether this association is also genetic, i.e., did the nature of the alteration play a role in the HFSE mineralization. In the case of the Ca-metasomatism, which has been reported for several of the examples mentioned above and for Strange Lake, the answer to this question is most assuredly “yes”. For example, in the Khaldzan-Buregtey deposits in western Mongolia, the potential ores are characterised by secondary Ca-bearing HFSE pseudomorphs after primary Na-bearing HFSE minerals, similar to those described above for the Strange Lake deposit, e.g., quartz-gittinsite pseudomorphs after elpidite (Kovalenko et al., 1995; Kempe et al., 1999) (Fig. 2). Gittinsite also forms pseudomorphs (after an unknown phase) in the peralkaline granites of Paharito, New Mexico (A.N. Mariano, pers. comm., 1990), and after vlasovite in the Kipawa peralkaline complex, Quebec (Gittins et al., 1973; Ansell et al., 1980). Further examples of the alteration of primary HFSE minerals by Ca-bearing fluids are provided by the Tamazeght complex where rinkite is partially or completely pseudomorphed by zircon (±fluorite, calcite and natrolite) and primary eudialyte is pseudomorphed by Ca-rich catapleiite plus Fe and Mn hydroxides or replaced along its rims by zircon and fluorite. The examples presented above demonstrate at the very least that the Ca-metasomatising fluids have directly affected the HFSE mineralogy in a significant number of peralkaline intrusive complexes.

3.2. Behaviour of HFSE in hydrothermal fluids

The evidence that hydrothermal processes may play a dominant role in the formation of some HFSE deposits is perhaps surprising given the fact that these elements have long been considered essentially inert or immobile in hydrothermal systems, and are widely used as tracers of geological processes (e.g., Finlow-Bates and Stumpfl, 1981; MacLean and Kranidiotis, 1987; Lipin and McKay, 1989). However, although there is only limited information on the behaviour of the HFSE in aqueous solutions at hydrothermal conditions, the few studies available show that certain ligands have strong affinity for these metals. Theoretical studies by Wood (1990) and Haas et al. (1995) indicated that the REE form their most stable complexes with F^-, although they also form strong complexes with CO_3^{2-} and SO_4^{2-} (these are all hard anionic species consistent with the prediction of Pearson, 1963, that hard cations attract hard anions), and somewhat weaker complexes with Cl^-; experimental studies are restricted to those for REE complexation with Cl^- (Gammons et al., 1996, 2002; Migdisov and Williams-Jones, 2002) and sulphate (Migdisov et al., 2006). It thus follows that the REE are substantially more mobile than previously suspected. For further information on REE speciation, the reader is referred to the reviews of Wood (2003) and Samson and Wood (2005). There is considerably less information on the solubility and speciation of other HFS elements in aqueous fluids. We will only consider one of these elements here, namely Zr, because of its reputation as being the least mobile of the commonly occurring HFSE and the fact that it is typically present in higher concentrations in peralkaline complexes than other HFSE. To our knowledge, there have been only four experimental studies reporting quantitative data on the behaviour of Zr at high temperature. Korzhinskaya and Ivanov (1988) measured the solubility of zircon in H_2O–HCl solutions; Mottet (1991) measured the solubility of baddeleyite in chloride, sulphate and mixed sulphate-chloride solutions; Aja et al. (1995) reported formation constants for hydroxy and fluoride species, based on the solubility of zirconosilicate minerals and weloganite; and Salvi et al. (2001) measured the solubility of baddeleyite in HF-bearing and HF-free solutions. These studies indicate that the solubility of Zr is generally very low but can be appreciable at high fluoride activities due to the formation of very strong zirconium fluoride complexes. Zirconium solubility also can be enhanced by the formation of carbonate, sulphate, hydroxy-chloride and hydroxide species, although far less is known about the stability of these species than those involving fluorine (cf. Wood, 2005 for a review).

3.3. Hydrothermal transport and deposition of HFSE

From the preceding discussion, it is clear that the HFSE can be mobilised by hydrothermal fluids containing high concentrations of hard anionic species, notably F^- but also CO_3^{2-} and SO_4^{2-}, and possibly even Cl^-. All these species are reported to be in high concentrations in aqueous fluids exsolving from peralkaline magmas or associated carbonatites (e.g., Williams-Jones et al., 2000; Williams-Jones and Palmer, 2002), an observation that can be attributed partly to the fact that peralkaline magmas only become saturated with aqueous fluids very late in their crystallization history, i.e., when the residual melts are highly enriched in these species, and partly to the fact that these species are highly soluble in peralkaline melts (e.g., Kovalenko et al., 1995; Markl et al., 2001). As the HFSE considered in this paper are incompatible in the principal silicate minerals crystallizing from peralkaline magmas, they too concentrate in the residuals melts, thereby assuring interaction of aqueous fluids capable of dissolving high concentrations of HFSE with a highly enriched HFSE source, a situation that strongly favours the hydrothermal transport of HFSE. Whether such transport actually occurs to any extent is still a matter of some debate. However, it is significant that most deposits of HFSE minerals are accompanied by appreciable quantities of minerals in which one or more of the above ligands (F^-, SO_4^{2-}, CO_3^{2-}) is an important component. For example, fluorite is an important gangue mineral in many HFSE deposits and in some, e.g., the Gallinas Mountains REE deposit, is the dominant gangue mineral (Williams-Jones et al., 2000). Similarly, barite is important in the REE subeconomic mineralization in syenites of the Ambatofinandrahana complex, Madagascar (in prep.) and in the hydrothermal Kizilcaören REE deposit in Turkey (Gültekin et al., 2003), and calcite is common at Tamazeght. Barite and calcite (and other carbonates) are also present in the ore zones of the Gallinas Mountains and Strange Lake complexes, respectively, although not in important amounts (Williams-Jones et al., 2000, unpublished data). It is also significant that in many cases the ore minerals also contain these species in their structures. For example, the principal REE ore mineral is commonly the fluorocarbonate, bastnäsite, and fluorine and sulphate and carbonate are essential constituents of HFSE minerals like gagarinite-(Y), saryarkite and kainosite, respectively.

The model proposed for the Strange Lake deposit and more recently for the Gallinas Mountains REE deposit, as discussed above, envisages that the HFSE were transported by magmatic hydrothermal fluids as fluoride complexes, and that the HFSE minerals were deposited as a result of the interaction of these fluids with Ca-rich groundwaters. The resulting mixing lead to the deposition of fluorite, which because of its low solubility, buffered fluoride activity to very low levels, thereby destabilizing the HFSE complexes and saturating the fluid with HFSE minerals. This model is attractive because it explains why fluorite is an important gangue mineral in many of these deposits and why commonly there is an association with Ca-metasomatism. A similar model could be proposed involving HFSE transportation as sulphate or carbonate complexes, with deposition of a sparingly soluble sulphate (e.g., barite or anhydrite) or carbonate gangue mineral (e.g., calcite) (cf. examples cited above) serving to buffer ligand activity to low levels, and thereby induce HFSE mineral saturation. Alternatively, as the available data show that the stability of HFSE complexes increases sharply with increasing temperature, models could be proposed involving processes that will induce a rapid drop in temperature, e.g., boiling, or effervescence of a carbonic fluid (these processes will also increase pH and fO_2 and lower the activity of volatile ligands like sulphate and carbonate by releasing SO_2 and CO_2, all of which could promote complex destabilization and HFSE mineral deposition). Given the association of reduced carbonic fluids with HFSE mineralization at Strange Lake and many other peralkaline complexes (see below), and evidence for the unmixing of these fluids from potential aqueous ore fluids (Salvi and Williams-Jones, 1992), carbonic fluid effervescence is a potential HFSE ore-forming mechanism that deserves further scrutiny. Finally, it should be noted that, although Cl^- form weaker complexes with HFSE than the other ligands discussed above, appreciable concentrations of these elements could be transported in this form because of the very high concentrations of chloride ions in the fluids (e.g., 4 molal at Strange Lake; Salvi and Williams-Jones, 1992), and thus the mechanisms invoked for the formation of other orthomagmatic deposits in which chloride complexation is important, e.g., porphyries and lode tin deposits, should also be considered.

3.4. The hydrocarbon–HFSE association

In addition to being present in the Strange Lake complex, hydrocarbon-bearing fluid inclusions have been reported in alkaline rocks from the Khibiny and Lovozero complexes (see reviews by Potter and Konnerup-Madsen, 2003; Nivin et al., 2005 and references therein), where they mostly form secondary trails in primary magmatic minerals. Similar fluid inclusions also have been described from nepheline syenites and hydrothermal veins of the Ilímaussaq complex (e.g., Petersilie and Sørensen, 1970; Konnerup-Madsen and Rose-Hansen, 1982, 1984; Krumrei and Markl, 2005) and from nepheline syenites in the Tamazeght complex (unpublished data). Furthermore, in many of these complexes, there is a close spatial association between the hydrocarbons and the HFSE mineralization. For example, in the Tamazeght complex, reduced gas-bearing inclusions are only known to occur in nepheline syenites that host abundant late pegmatites and have very high HFSE concentrations. Similarly, in the Khibiny complex, they are largely restricted to albitized nepheline syenites, pegmatites and hydrothermal veins of the Central Arch, which host the bulk HFSE-bearing apatite ore (cf. Nivin et al., 2005).

The fluid inclusions in the Khibiny, Lovozero and Ilímaussaq complexes have similar hydrocarbon compositions to those found at Strange Lake and, like the latter, are dominated by methane and contain appreciable proportions of H_2. Moreover, as at Strange Lake, the proportions of alkanes in the inclusions are consistent with a Schulz–Flory distribution (cf. Potter and Konnerup-Madsen, 2003), which lead Potter et al. (1998, 2004) and Potter and Konnerup-Madsen (2003) to also invoke a Fischer–Tropsch synthesis to explain the formation of the hydrocarbons (this hypothesis was first proposed by Salvi and Williams-Jones, 1997a,b). Production of H_2 and the catalyst needed for the synthesis (magnetite), as at Strange Lake, was attributed to wall rock alteration reactions. Recently, however, the Fischer–Tropsch model was rejected for the Ilímaussaq intrusion by Markl et al. (2001) and Krumrei and Markl (2005) in favour of a high-temperature magmatic origin for the hydrocarbons on the basis of petrographic and fluid inclusion data, and because of the absence of CO_2 (see also Markl, 2005). They argued that the hydrocarbons formed at mantle conditions by polymerization (cf. Kenney et al., 2002; Beeskow et al., 2005). A high-temperature magmatic model has also been recently proposed to explain the formation of the hydrocarbons in the Khibiny massif based on new data and the paucity of CO_2 (Beeskow et al., 2005), although in another study also published this year Nivin et al. (2005) presented new isotopic data which they claim supports the Fischer–Tropsch hypothesis. An evaluation of this debate is clearly beyond the scope of this paper, but irrespective of which of the two competing hypotheses is ultimately shown to be correct, it does not change the essential conclusion that there is a close spatial association between reduced carbonic species and HFSE mineralization in peralkaline complexes and potentially an important genetic association.

A model that may explain some of the examples of the association of hydrocarbons and HFSE mentioned above is the relatively low-temperature exsolution from a peralkaline magma of a reduced, C–O–H (± N) fluid dominated by CO_2 and a Ca-poor, F-bearing high salinity aqueous liquid in which HFSE are dissolved as fluoride complexes. Upon interaction with the crystallized peralkaline rock, the aqueous liquid induces alteration of primary minerals, notably arfvedsonite, to secondary minerals such as aegirine, and leaches HFSE from primary minerals. By-products of these reactions include hydrogen and Fe-oxides, which catalyse a Fischer–Tropsch synthesis of hydrocarbons from the magmatic CO_2. Subsequent interaction of the aqueous liquid with a Ca-bearing meteoric fluid rapidly saturates the system in fluorite, causing precipitation of this mineral and a corresponding reduction in the activity of the fluoride ion, which destabilises the HFSE-fluoride complexes, leading to the deposition of HFSE-bearing minerals. Pre-existing HFSE minerals are replaced by calcium-bearing equivalents and there is extensive hematisation. Both the mixed aqueous fluid and the hydrocarbon fluid continue to be intimately associated during ore formation and, as the groundwater is oxidising, the hydrocarbon fluid may evolve through the conversion of some of its hydrocarbon content to CO_2, as appears to have been the case at Strange Lake. This model, in addition to explaining most of the features of the Strange Lake deposit, is potentially applicable to any peralkaline intrusion where HFSE and hydrocarbons are associated and where HFSE enrichment was accompanied by calcium metasomatism, hematisation and hydrothermal fluorite. We note that, although this model cannot explain all associations of hydrocarbons and HFSE, it does contain an essential element that is broadly applicable, namely that hydrothermally enriched HFSE and hydrocarbons are intimately associated because they are the product of the same initial magmatic fluid. Finally, we speculate that the association of HFSE and hydrocarbons may in some cases even be genetic, if, as suggested above, effervescence of a reduced carbonic fluid from the hydrothermal liquid caused changes in temperature, pH, fO_2 or the activity of volatile ligands sufficient to induce the deposition of HFSE minerals.

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