Alkaline Granite-Syenite Deposits

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INTRODUCTION

Although alkaline intrusive magmatism is responsible for only a small proportion of the total volume of igneous rocks in the Earth's crust, a comparatively large proportion of the petrological literature has been devoted to its study. One of the reasons for this interest is undoubtedly the unusual enrichment in the high field-strength elements (HFSE) Zr, Nb, U, Y, and the rare earth elements (REE) (cf. Sørensen, 1974; Bonin, 1982; Bowden, 1985; Fitton and Upton, 1987; Wooley, 1987; Pollard, 1995) and the importance of such elements as tracers of igneous processes (e.g., Floyd and Winchester, 1975). Recently, the elevated contents of HFSE in alkaline intrusives have also attracted considerable interest from the mining industry as a result of technological developments, which have created a variety of new uses for these elements (e.g., Spooner et al., 1991; Sinclair et al., 1992). For example, the low absorption cross section for neutrons of Zr makes it an ideal cladding material for radioactive fuel elements, and its superconducting properties are now being used to produce Zr-Nb superconductor magnets. Among the new uses for Nb are the production of super alloys with the creep strength needed to operate in the hot section of aircraft gas turbine engines, and the development of superconducting Nb-Ti alloys for MRI magnets. The principal use of Y is to provide the red colour in television tubes. However, it is now also finding an important application in the automotive industry, replacing lead in anti-corrosion paints. Finally, REE, which have special properties of luminescence, magnetism and electronics, are finding applications as coloured phosphors in cathode ray tubes, X-ray sources, components of magnetic and magnetostrictive materials, hydrogen storage materials, and as auto-emission catalysts.

Many alkaline igneous complexes display extensive evidence of hydrothermal alteration, and commonly such alteration is strongest in those parts of the complexes that are most enriched in the HFSE. For example, Florovskaya and Melkov (1962) reported that the REE-apatite deposits in the nepheline syenites of the Khibina Massif, Russia, occur in heavily fenitized rocks. Fenitization is also spatially associated with Zr, U and REE mineralization in the Ilímaussaq nepheline syenite complex, Greenland (Sørensen, 1992). At Thor Lake (granite-syenite) and Strange Lake (granite), Canada, Zr-Nb-Y-REE mineralization is associated with intense albitization and Ca metasomatism, respectively (Trueman et al., 1988; Salvi and Williams-Jones 1996). Whether this association of mineralization with alteration implies an important genetic link between HFSE enrichment and hydrothermal activity or whether it is largely coincidental, i.e., HFSE enrichment was primarily the product of crystal fractionation, is still a matter of considerable debate.

In this chapter, we start by describing a number of classic alkaline plutons known to contain high concentrations of HFSE, and summarize our current understanding of the origin and evolution of alkaline magmatic systems. This is followed by descriptions of selected HFSE deposits that are well known because of their economic potential or because they have been the subject of detailed academic research. We then review the factors that lead to the formation of alkaline magmas that are rich in HFSE and discuss how the subsequent evolution of these magmas might concentrate these metals to exploitable levels. The possible role of hydrothermal processes in the mineralization is considered next by summarizing what is known (or can be inferred) about the nature of the fluids associated with HFSE deposits and the capacity of such fluids to dissolve and thus transport HFSE. Finally, we use the information presented in earlier sections of the chapter to evaluate models that have been proposed to explain the formation of HFSE deposits.

NATURE, ORIGIN AND EVOLUTION OF PERALKALINE PLUTONS

There is a large volume of literature devoted to the petrology, geochemistry and mineralogy of alkaline igneous rocks and related carbonatites, including several monographs (e.g., Sørensen, 1974; Borodin, 1974; Le Bas, 1977; Bonin, 1982, 1986; Fitton and Upton, 1987; Leelanadnam, 1989; Stumpfl et al., 1994; Comin-Chiaramonti and Gomes, 1996; Woolley, 1987; Kogarko et al., 1995; Mitchell, 1996; Gwalani and Lytwyn, 2000, 2001) and review papers (e.g., Bowden, 1970; Currie, 1976; Collins et al., 1982; Anderson, 1983; Bauer et al., 1983; Bowden, 1985; Sørensen, 1986; Whalen et al., 1987; Eby, 1990, 1992; Woolley and Ross, 1990; Larsen and Rex, 1992; Bonin, 1996; Sørensen, 1997; Barbarin, 1999). The term "alkaline" encompasses a large variety of igneous rocks, but the most widely accepted definition restricts its usage to rocks containing feldspathoids and/or alkali pyroxenes and amphiboles (Gittins, 1979; Sørensen, 1986). Thus, alkaline rocks may vary widely in composition, e.g., from ultramafic to felsic, and may include carbonatites, lamprophyres, kimberlites and other related rock types. Alkaline rocks have been further classified as peralkaline if they have an agpaitic index (i.e., whole rock atomic [Na+K]/Al) greater than unity. Sørensen (1986) pointed out that, based on this classification, all silica-saturated and silica-oversaturated alkaline rocks are peralkaline. Silica-undersaturated, feldspathoid-bearing peralkaline rocks have been further classified as agpaitic if, instead of simple Zr and Ti minerals such as zircon and ilmenite, they contain complex Zr and Ti minerals like eudialyte and mosandrite (cf. Table 1 for mineral formulae) (Le Maitre, 1989; Sørensen, 1997). The term agpaite was first used to describe a group of feldspathoid-bearing igneous rocks in the Ilímaussaq Complex, Greenland, having an agpaitic index ≥1.2 (Ussing, 1912). An important feature of peralkaline rocks, and the focus of this chapter, is that they are commonly characterized by extreme enrich-

Table 1. Mineral formulae for unusual minerals mentioned in the text

Mineral Name	Formula
aenigmatite	$Na_2Fe^{2+}_5TiSi_6O_{20}$
allanite s.l.	$(REE,Ca)_2(Al,Fe^{2+},Fe^{3+})_3(SiO_4)_3(OH)$
arfvedsonite	$Na_3Fe^{2+}_4Fe^{3+}Si_3O_{22}(OH)_2$
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.	$REECO_3F$
britholite	$(REE,Ca,Y)_5(SiO_4,PO_4)(OH,F)$
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)	$NaCaY(F,Cl)_6$
gaidonnayite	$Na_2ZrSi_3O_9\cdot 2(H_2O)$
gittinsite	$CaZrSi_2O_7$
hainite	$Na_4Ca_8(Ti,Zr,Mn)_3Si_8O_{28}F_8$
katophorite	$Na(Ca,Na)Fe^{2+}_4(Al,Fe^{3+})Si_7AlO_{22}(OH)_2$
kainosite-(Y)	$Ca_2(Y,Ce)_2Si_4O_{12}(CO_3).H_2O$
lavenite	$(Na,Ca)_2(Mn,Fe)(Zr,Ti)Si_2O_7(O,OH,F)_2$
loparite-(Ce)	$(Ce,Na,Ca)_2(Ti,Nb)_2O_6$
milarite-(Y)	$K(Ca,Y)Be_2Si_{12}O_{30}$
monazite s.l.	$REEPO_4$
mosandrite	$(Na,Ca,Ce)_3Ti(SiO_4)_2F$
murmanite	$Na_3(Ti,Nb)_4(Si_2O_7)_2O_4\cdot 4(H_2O)$
narsarsukite	$Na_2(Ti,Fe^{3+})Si_4O_{10}(O,F)$
naujakasite	$Na_6FeAl_4Si_8O_{26}(Ce,Na,Ca)_2(Ti,Nb)_2O_6$
normandite	$NaCa(Mn,Fe)(Ti,Nb,Zr)Si_2O_7OF$
phenakite	Be_2SiO_4
pyrochlore s.l.	$(Ca,Na)_2(Nb,Ta)_2O_6(O,OH,F)$
rinkite	$(Na,Ca,Ce)_3Ti(SiO_4)_2F$
rosenbuschite	$(Ca,Na)_3(Zr,Ti)Si_2O_8F$
serandite	$Na(Mn,Ca)_2Si_3O_8(OH)$
steenstrupine	$Na_{14}Ce_6Mn^{2+}Mn^{3+}Fe^{2+}_2(Zr,Th)(OH)_2(PO_4)_7(Si_6O_{18})_2\cdot 3H_2O$
thorite	$ThSiO_4$
thorianite	$(Th,U)O_2$
titanite	$CaTiSiO_5$
ussingite	$Na_2AlSi_3O_8(OH)$
vlasovite	$Na_2ZrSi_4O_{11}$
vuonnemite	$Na_{11}Nb_2TiSi_4O_{12}(PO_4)_2O_5F_2$
willemite	Zn_2SiO_4
zircon	$ZrSiO_4$
zirconolite	$CaZrTi_2O_7$

s.l. = sensu lato; i.e., includes all possible variants in which one of the REE may dominate

ment in alkali metals, high-field strength elements (e.g., Zr, Ti, Y, Nb, and REE) and halogens (F and Cl), and have low contents of compatible elements.

Despite the wealth of literature published on the topic, the origin of alkaline magmatism is still much debated (e.g., Sørensen, 1986; Eby, 1990; Kramm and Kogarko, 1994; Stevenson et al., 1997; Schmitt et al., 2000; Bailey et al., 2001). Although most authors agree that alkaline melts are products of low degrees of partial melting in a deep, undepleted mantle, an unresolved problem is the common association of silica-undersaturated and silica-oversaturated units in the same alkaline complex (e.g., Bonin and Giret, 1984; Wallace et al., 1990; Brotzu et al., 1997; Harris et al., 1999). This notwithstanding, there is consensus that although silica-undersaturated alkaline rocks and peralkaline granites and syenites may have a common source, they have a different genesis.

Isotopic studies indicate that silica-undersaturated rocks originate from differentiation of primitive mantle magmas under relatively dry and low fO_2 conditions (e.g., Halama et al., 2003; Marks et al., 2003; Halama et al., 2004). Generally, these rocks exhibit little or no sign of crustal contamination. In contrast, silica-oversaturated, peralkaline intrusions are considered by many workers to be derived from crustal contamination of mantle-derived, silica-undersaturated alkaline magmas (e.g., Goodenough et al., 2000; Marks et al., 2003).

Another poorly understood topic is the role of volatiles in the formation of highly evolved peralkaline rocks. However, it is recognized that these rocks originate from very dry and reduced melts that can evolve to extremely high Cl and F contents before exsolving an aqueous fluid phase (e.g., Kogarko, 1974; Markl et al., 2001). This permits extreme fractionation to low temperatures (down to ~400°C; e.g., Scalliet and Macdonald, 2001). Some authors have suggested that volatiles (predominantly H_2O, plus Cl, F and CO_2) can enhance fractional crystallization and permit the melt to evolve to agpaitic compositions (e.g., Kogarko, 1974; Kogarko and Romanchev, 1982). Markl et al. (2001) have shown, using the example of the Ilímaussaq syenites, that interplay between silica activity and oxygen fugacity also governs the evolution of H_2O activity via solid-solid and solid-liquid equilibria. The evolution to extremely fractionated, Na-rich compositions requires a parental magma with initially low H_2O and silica activities, and low oxygen fugacity (evident from methane-rich fluid inclusions in early-crystallizing phases). With evolution, there is an increase in H_2O activity (indicated by the presence of aqueous fluid inclusions in late-crystallizing phases), related to the rise in fO_2 needed for the formation of the agpaitic rocks (see also Marks et al., 2004). This evolution takes place at progressively lower temperatures, with the last phases crystallizing at temperatures <450°C (Markl et al., 2001; see above).

On the basis of preliminary fluid inclusion data (evidence of low salinity), Markl et al. (2001) concluded that the magma only saturates with an aqueous fluid after Na has been almost entirely consumed by crystallization of the most evolved agpaitic phases. However, more recent analyses by G. Markl (pers. comm., 2004) indicate that some of the late-magmatic fluids at Ilímaussaq have elevated salinities, which may indicate exsolution of a high-salinity fluid phase (Konnerup-Madsen, 2001; G. Markl pers. comm., 2004). A similar conclusion, based on dominant populations containing ~ 20 to 25 equivalent wt. % NaCl, was reached by Salvi and Williams-Jones (1992) and Salvi et al. (2000) for the Strange Lake granite and Tamazeght alkaline complex, respectively; Salvi and Williams-Jones (1992) also reported the presence of a second population of primary fluid inclusions with considerably lower salinity (~8 wt. %). An alternative explanation for the exsolution of a high-salinity fluid is dessication of a low-salinity magmatic fluid (Markl and Bucher, 1998; Markl et al, 1998). Regardless of whether or not these orthomagmatic fluids are of high or low salinity, they play an important role in the subsequent evolution of peralkaline igneous systems. They generally cause autometasomatism, such as transformation of arfvedsonite to aegirine (Figure 1) (e.g., Salvi and Williams-Jones, 1990; Boily and Williams-Jones 1994; Finch et al.,

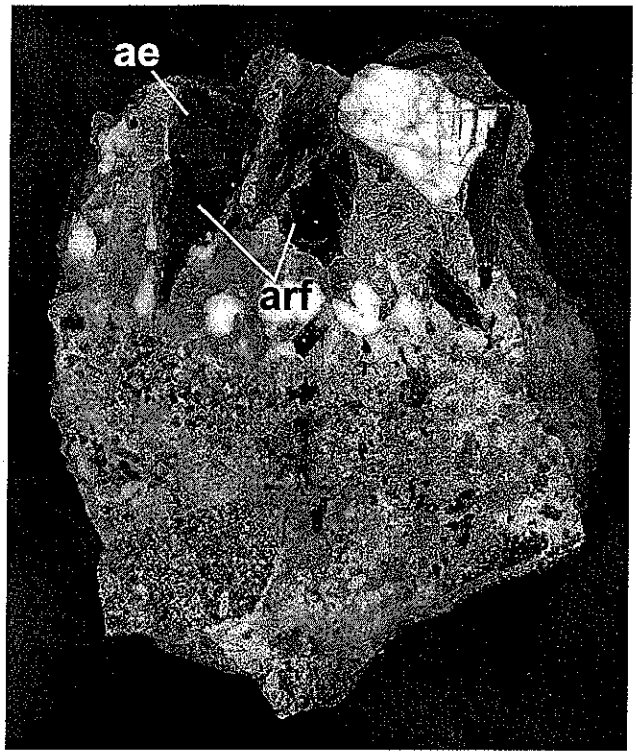

Figure 1. *Slabbed hand sample from the Strange Lake complex showing pegmatitic crystals of arfvedsonite (arf) that have been partially replaced by aegirine (ae). Sample measures ~ 15 by 20 cm.*

2001; Chakhmouradian and Mitchell, 2002; Coulson, 2003; Marks and Markl, 2003) and commonly are responsible for intense fenitization of the country rock (e.g., Kresten, 1988; Morogan, 1989). More importantly, from the perspective of this chapter, there is increasing evidence that they play an important role in the concentration of HFSE such as Zr, Y, Nb, and REE (e.g., Salvi and Williams-Jones, 1990; Salvi et al., 2000; Williams-Jones et al., 2000; Coulson, 2003; Marks et al., 2003).

In the subsections that follow we discuss the nature, origin and evolution of peralkaline plutons further by referring to specific complexes. These examples have been chosen to show a range of magma compositions and evolutionary histories. However, they also represent some of the most important examples of peralkaline plutons hosting economic or subeconomic deposits of HFSE.

Ilímaussaq Complex

One of the best known and most studied alkaline complexes in the world is the 1.13 Ga Ilímaussaq complex (Figure 2) of the Gardar Igneous Province, South Greenland (see Sørensen, 2001, for a recent review). The latter, which has been interpreted to be a failed rift, contains nine other major alkaline complexes (e.g., Upton and Emeleus, 1987; Macdonald and Upton, 1993), all of which are considered to be products of mantle melting (e.g., Larsen and Sørensen, 1987; Upton et al., 2003). Most Gardar complexes evolved along silica-undersaturated (syenites, foyaites, and peralkaline to agpaitic nepheline syenites) or silica-oversaturated trends (augite syenites to peralkaline granites). However, the Ilímaussaq pluton, which was one of the last Gardar complexes to form, is an exception, as both trends are represented, i.e., it contains agpaitic nepheline syenites and peralkaline granites. Emplacement of this pluton and formation of the various alkaline suites are believed to have taken place in three distinct pulses from a deep seated magma chamber that was probably located at the crust-mantle boundary, and which was fed by a single, mantle-derived nephelinitic basaltic magma (cf. Larsen and Sørensen, 1987; Stevenson al., 1997; Markl et al., 2001; Sørensen, 2001). Successively more-fractionated batches of magma upwelled to high crustal levels, where they evolved further by low-pressure fractionation. The first batch caused the intrusion of silica-undersaturated augite syenite. This was followed by injection of quartz syenite and alkali granite sheets into the upper parts of the augite syenite, the high silica content being the result of crustal contamination (e.g., Larsen and Sørensen, 1987; Marks et al., 2003), whereas the earlier augite syenite shows only local signs of contamination with upper crustal rocks (Marks and Markl, 2001). Continued fractionation in the deep magma chamber produced a phonolitic magma, which was the last batch injected into the crystallizing complex, and where continued fractionation lead to the formation of the layered agpaitic suite (Figure 3). Markl et al. (2001) proposed that early magma batches lined the conduit, which helped to prevent later crustal contamination, thereby explaining the agpaitic character of the most evolved melt. The agpaitic suite formed in a closed system by in situ fractionation, giving rise to pulaskite, foyaite, sodalite foyaite and naujaite roof cumulates, and floor cumulates represented by spectacularly layered kakortokites (Figure 4) and lujavrites (Larsen and Sørensen, 1987; see also Sørensen, 1986) (cf. Table 2 for definitions of unusual rock types). The pulaskites represent the earliest phase and the lujavrites the latest and most evolved phase of this agpaitic series. The crystallization history of Ilímaussaq ended with the intrusion of numerous pegmatites, formation of hydrothermal veins rich in Zr and REE minerals (e.g., steenstrupine, pyrochlore, e.g., Sørensen, 2001) and Be-bearing phases such as chkalovite, and tugtupite, (cf. Markl, 2001), and some fenitization of the country rock.

Khibina-Lovozero Massif

The Khibina (also spelled Khibini or Khibiny) and Lovozero complexes are among the largest peralkaline igneous bodies in the world (they outcrop over a combined area of about 2000 km^2) and are the source of more exotic minerals than any other site in Russia (e.g., Khomyakov, 1995; Semenov, 1997). They form two horseshoe-shaped ring complexes, which are only a few kilometres apart and separated from each other by Lake Umbozero (Figure 5). Because of their close proximity and similar age, they have been considered

Table 2. Unusual alkaline igneous rock types mentioned in the text.

Mineral Name	Formula
ijolite	consists mainly of nepheline (50 to 70%) and aegirine
kakortokite	layered eudyalite-bearing nepheline syenite
khibinites	coarse-grained nepheline syenites
lujavrite	melanocratic nepheline syenite
malignite	nepheline-syenite rich in aegirine and orthoclase
naujaite	sodalite-rich nepheline syenite
nordmarkite	quartz-bearing alkali-syenite
pulaskite	nepheline-bearing alkali feldspar syenite
rischorrite	K-rich nepheline syenite
shonkinite	coarse-grained melanocratic syenite, with little nepheline
urtite	leucocratic ijolite very rich in nepheline (>80%)

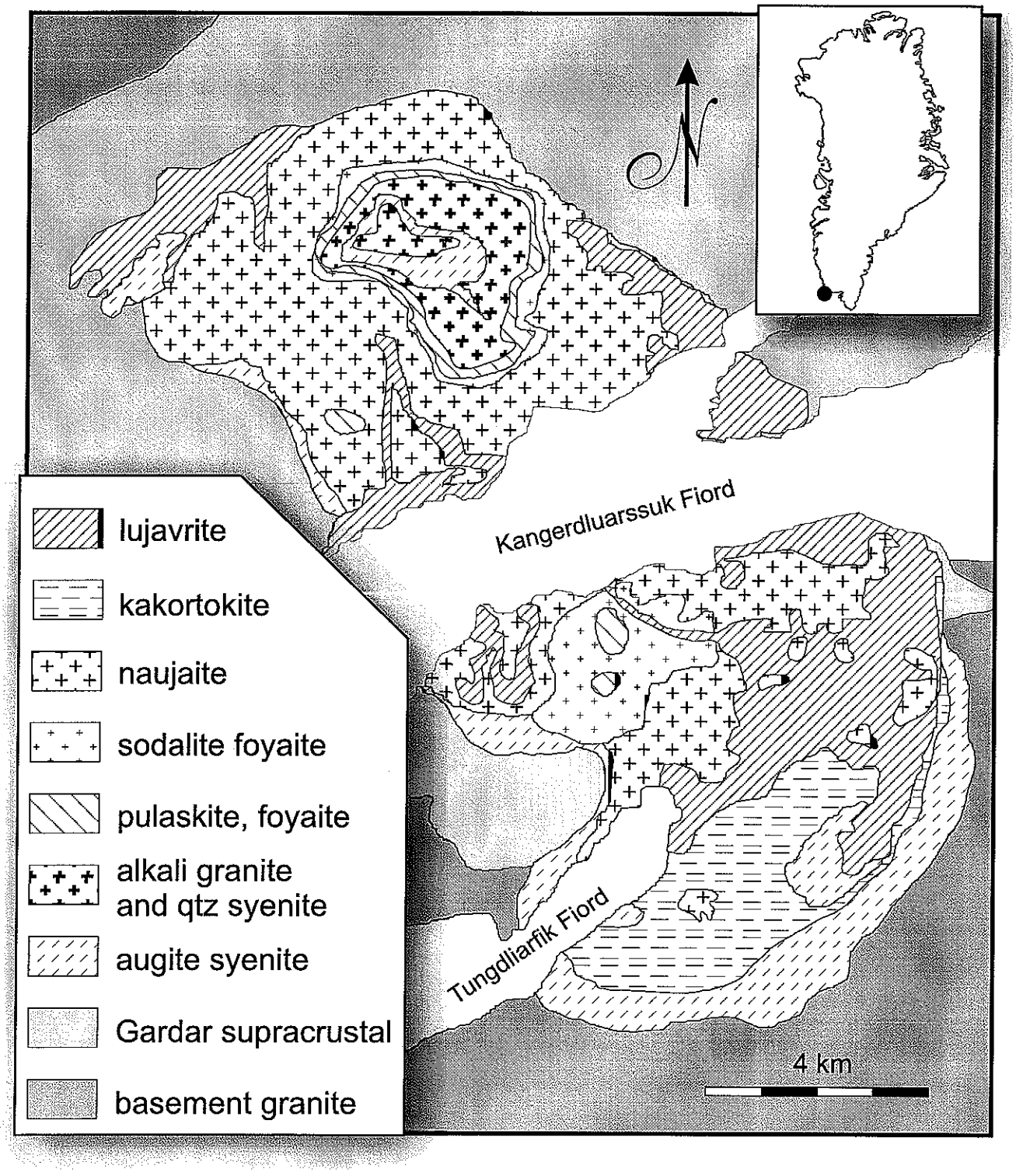

Figure 2. *Geological Map and location of the Ilimaussaq peralkaline complex. Modified after Sørensen (2001).*

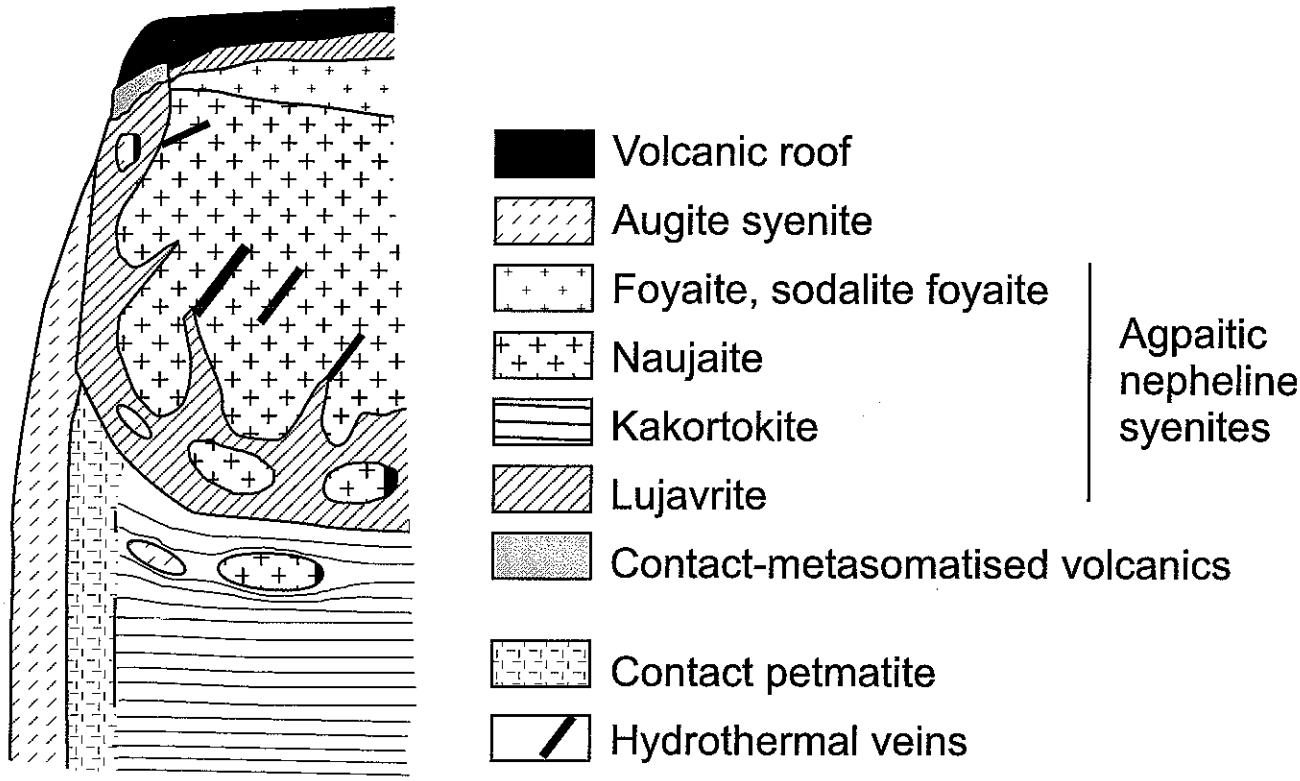

Figure 3. *Sketch of an idealized vertical section through most stratigraphic units in the Ilímaussaq peralkaline complex. Modified after Sørensen (2001). The section represents about 1500 m vertically.*

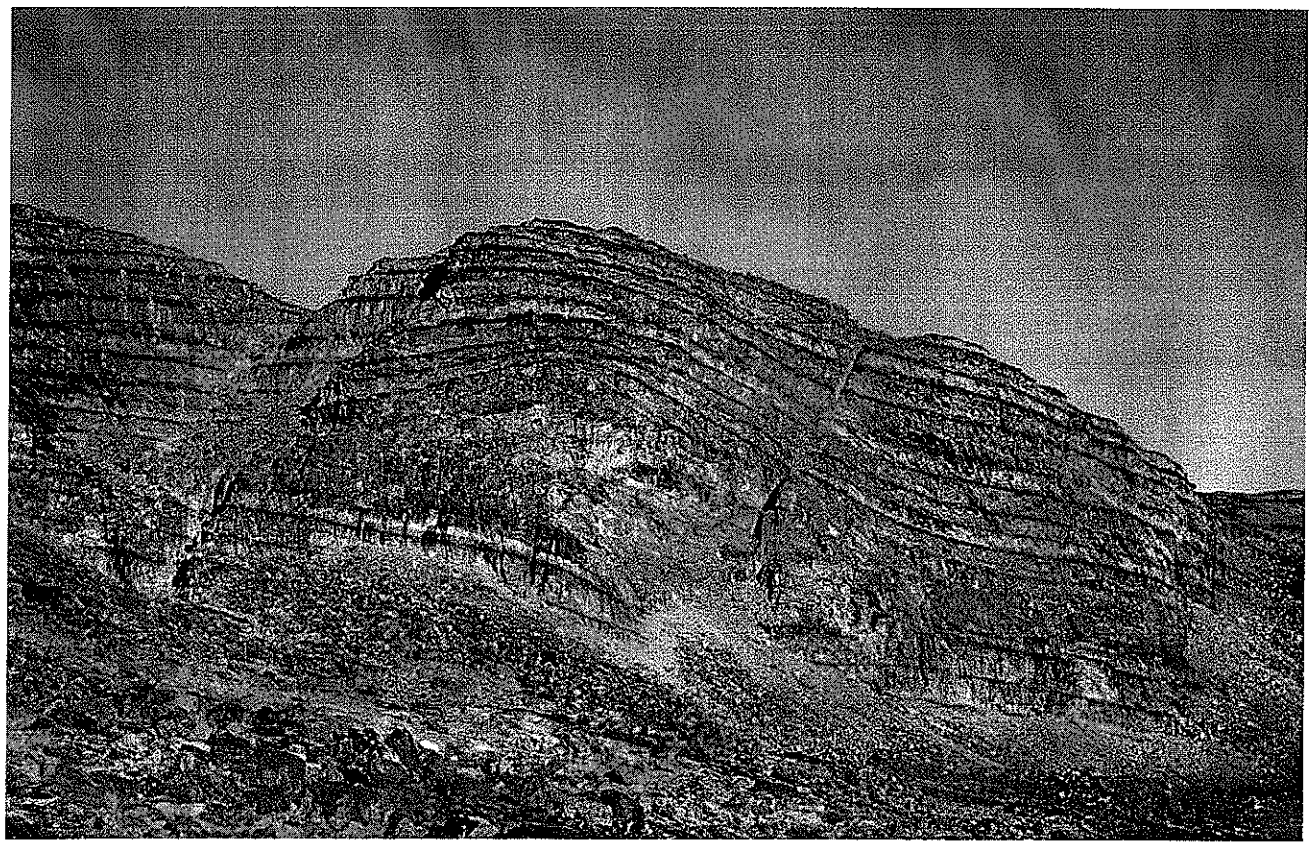

Figure 4. *Rhythmic layering in kakortokite in the Ilímaussaq complex (cliff is about 150 m high). Photo courtesy of G. Markl.*

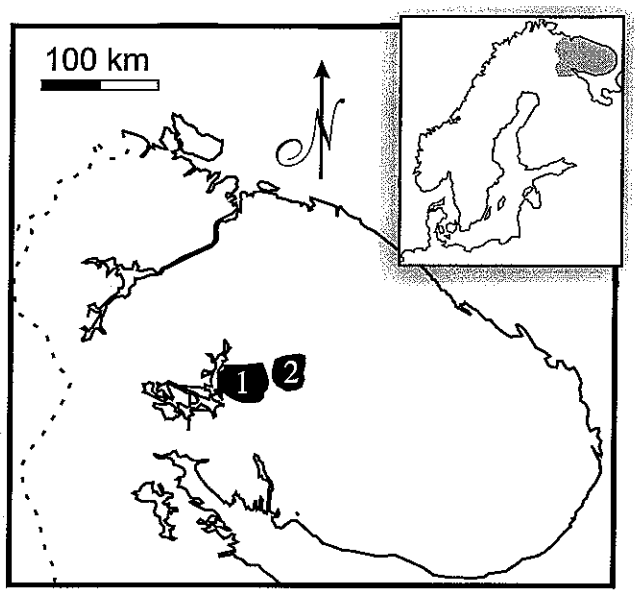

Figure 5. *Location of the Khibina (1) and Lovozero (2) intrusions. Modified after Potter et al. (2004).*

by some researchers as a single intrusion, however, geophysical data indicate that they have separate roots (e.g., Jébrak and Sustrac, 1985; Kramm and Kogarko, 1994; Arzamastesev et al., 2000). The complexes were emplaced into an Archean granite-gneiss basement and are part of the Kola alkaline igneous province of eastern Scandinavia. Igneous activity in the province took place during two major episodes. The first, during the Proterozoic (1900-1600 Ma; cf. Kogarko, 1987), was marked by the emplacement of alkaline gabbroic rocks. This was followed by a Palaeozoic episode, during which some 25 ultramafic/peralkaline alkaline complexes were emplaced over a relatively short time span from 380 to 360 Ma (Kogarko, 1987; Kramm et al., 1993). The Khibina and Lovozero complexes are the largest of these Palaeozoic centres, and also the most evolved, consisting mostly of agpaitic rocks and to a lesser extent of ultramafic alkaline rocks and carbonatites. Tectonically, they are related to the NE-SW-trending Kontozero Graben, which extends through Sweden and Norway.

The Khibina complex measures about 30 x 40 km across, and consists of a variety of nepheline syenites arranged in eight concentric circles with inwardly decreasing ages (Kramm and Kogarko, 1994) (Figure 6). The oldest units are nepheline syenites sensu stricto, and are followed inwards by khibinites (Table 2), which make up most of the western parts of the complex. Further inwards, there is

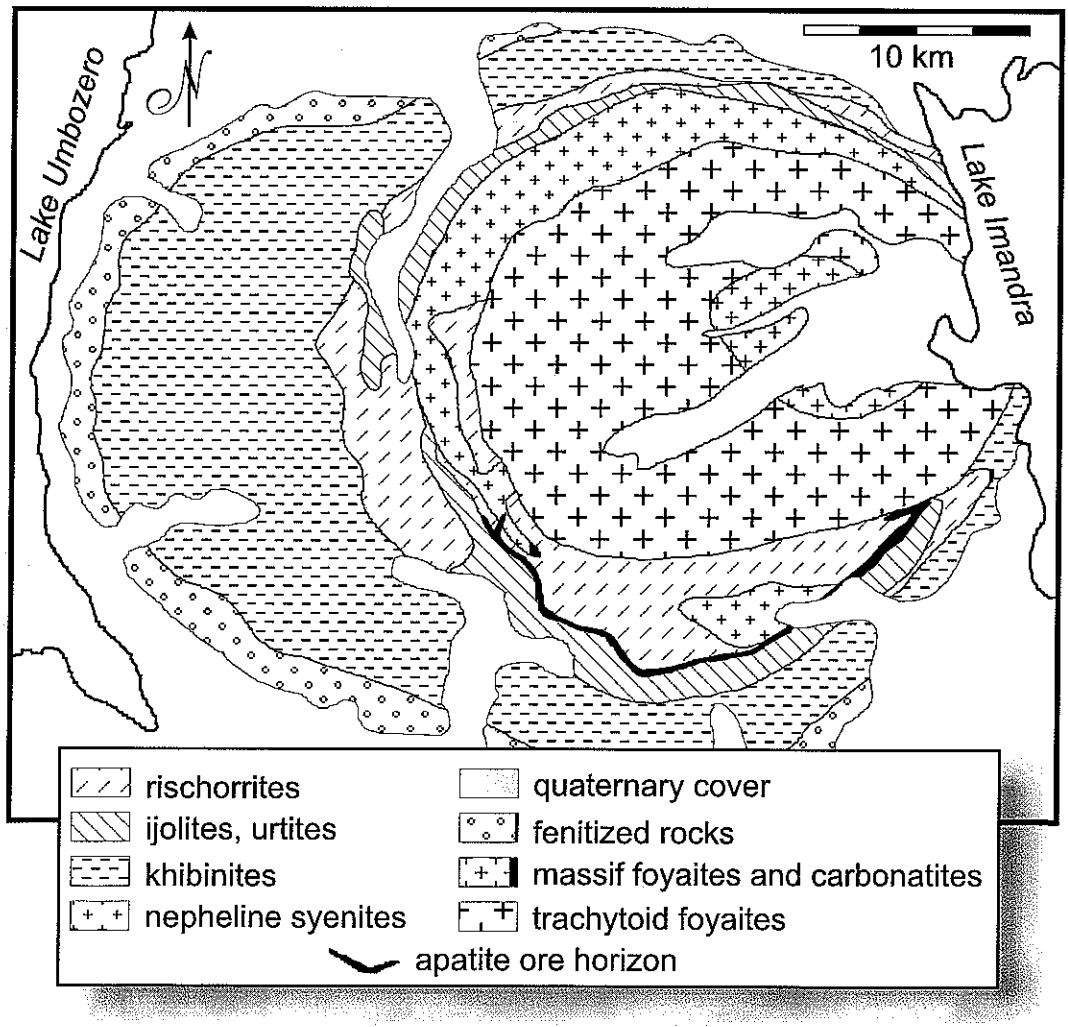

Figure 6. *Geological map of the Khibina complex. Modified after Pekov and Pavlov (1995).*

a complexly stratified urtite/ijolite zone, followed, in the southern part of the complex, by rischorrite. Apatite ores forming the large Rasvumchorr, Yukspor, Kukisvumchorr and Koashva deposits occur at the contact between these last two zones, and are associated with extensive alteration of the host rocks (Florovskaya and Melkov, 1962). The centre of the complex is composed almost entirely of foid syenite, which locally contains carbonatite xenoliths. However, a recent geophysical survey and drilling has led to the discovery of a pulaskite body within the foyaite (Korobeinikov and Pavlov, 1990), which is believed to be closely related genetically to it (Korobeinikov et al., 2000). Pegmatites and dikes of alkaline gabbro and lamprophyric rocks represent the final stages of igneous activity, and occur throughout the complex. Alkaline volcanic rocks (trachytes, phonolites) are exposed in the eastern part of the complex. Around the western edge of the complex, the country rock is fenitized to varying degrees and the pegmatites are locally aegirinized.

The geology of Lovozero is somewhat simpler than that of Khibina (Figure 7). Three main intrusive phases have been recognized (Kramm and Kogarko, 1994). The first phase involved intrusion of nepheline- and nosean-syenites. This was followed by emplacement of a thick, stratified, sill-like body consisting of layered sequences of lujavrites, urtites and foyaites. The last of these phases, which was volumetrically the most important, is represented by layered eudialyte-lujavrites (some of which contain up to 80

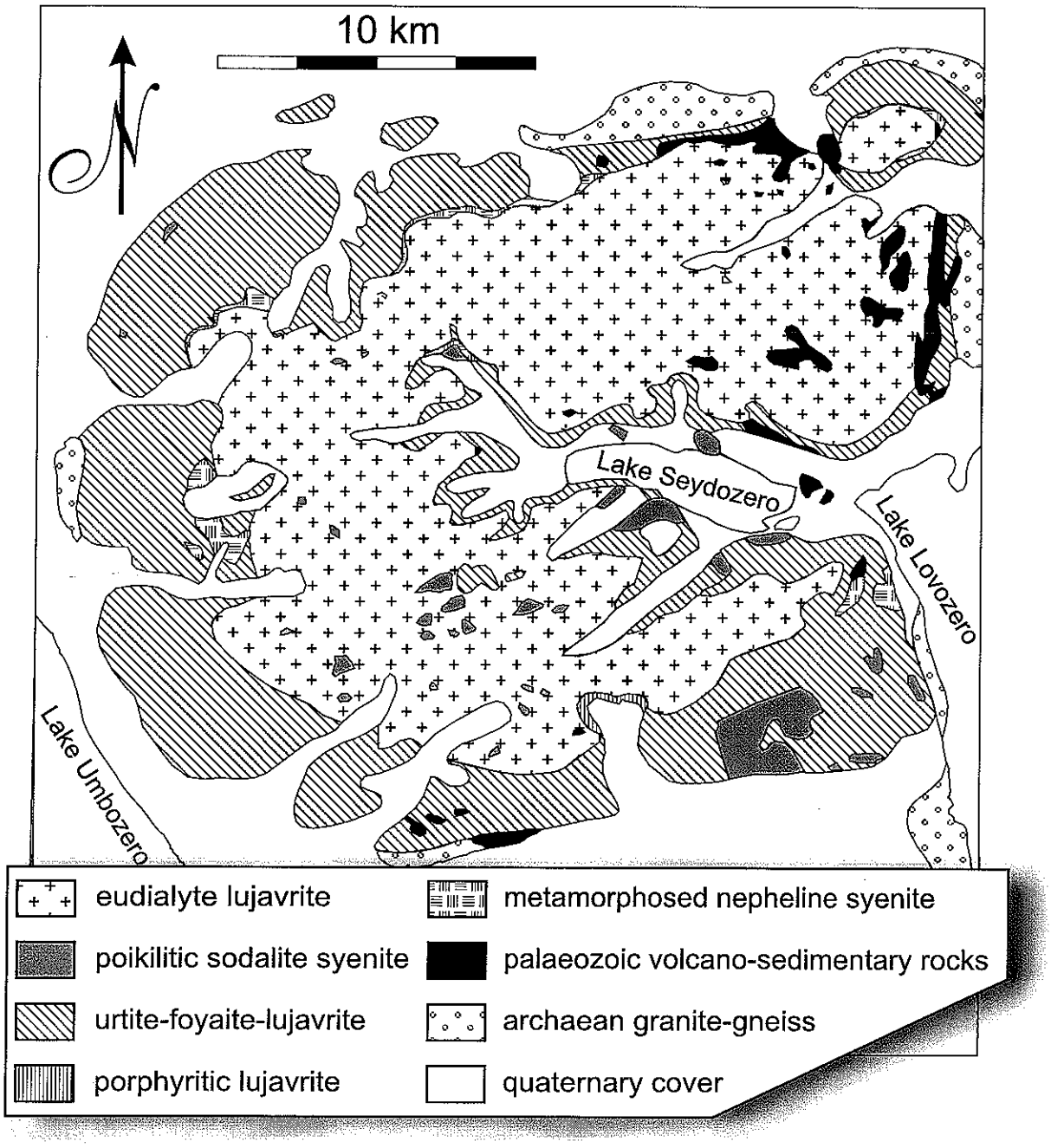

Figure 7. *Geological map of the Lovozero complex. Modified after Britvin et al. (1995) and Potter et al. (2004).*

vol. % eudialyte; Kogarko, 1987) in the core of the complex. Igneous activity culminated with the intrusion of highly differentiated pegmatitic veins and dikes of porphyritic murmanite-bearing lujavrite, considered to be a fourth intrusive phase by Gerasimovsky (1969). An important difference between Lovozero and Khibina is the presence of ussingite veins at Lovozero (these veins also contain vuonnemite, serandite, and steenstrupine; de Graaf, 2003). Similar veins have also been described from the Ilímaussaq complex (Sørensen, 1962).

The similar ages and consistently low initial Sr isotopic ratios suggest that all the Palaeozoic alkaline complexes of the Kola Province were co-magmatic and, unlike the alkali granite in Ilímaussaq, crustal contamination processes did not play a role in the genesis of even the most evolved of these complexes, e.g., Khibina and Lovozero (Kogarko, 1987; cf. also Sørensen, 1997). All of these complexes are interpreted to have formed by dynamic-flow fractional crystallization of nephelinitic-type magmas at upper mantle pressures (Kramm and Kogarko, 1994).

Strange Lake Complex

The Strange Lake intrusive is a small, Mesoproterozoic pluton (1240 ± 2 Ma; Miller et al., 1997), consisting of several HFSE-enriched peralkaline granites, which outcrop over an area of about 36 km^2 on the border between the provinces of Quebec and Newfoundland and Labrador (Figure 8). The first published map of the pluton was by Currie (1985), who recognised its peralkaline character, and reported the first determination of its age, 1.24 Ga, from K-Ar geochronology. He suggested, on the basis of this age and its peralkaline character, that the pluton might represent an extension of the Gardar peralkaline province of Greenland into Canada. Miller (1986; see also 1996) subsequently divided the pluton into exotic-rich, exotic, and exotic-poor facies of granite, from the distribution of HFSE (exotic) minerals, and further subdivided the exotic-poor facies, which makes up the bulk of the complex, into inclusion-absent and inclusion-bearing facies (the inclusions are of melanocratic granite varieties). Nassif and Martin (1991) reclassified these facies into hypersolvus and subsolvus (60 % of the pluton), based on the occurrence of two or one alkali feldspars, respectively, and also identified a unit of transsolvus granite transitional between the two facies. The exotic and exotic-rich granites of Miller (1986) were shown to represent less- and more-altered varieties of subsolvus granite, respectively (Salvi and Williams-Jones, 1990). All these granite types display some degree of heterogeneity, due mainly to flow differentiation near the site of emplacement, which locally concentrated arfvedsonite and some of the denser exotic minerals, notably elpidite (which locally can comprise up to 15 to 20 % of the mode), in thin, discontinuous layers (Figure 9A). In addition, numerous pegmatites, which almost invariably display extensive alteration of arfvedsonite to aegirine, and rare aplites are located mainly in the subsolvus granite (Figure 9B). An outwardly dipping ring fracture, marked by a heterogeneous breccia with a fluorite-filled matrix, surrounds the pluton. The hypersolvus granite

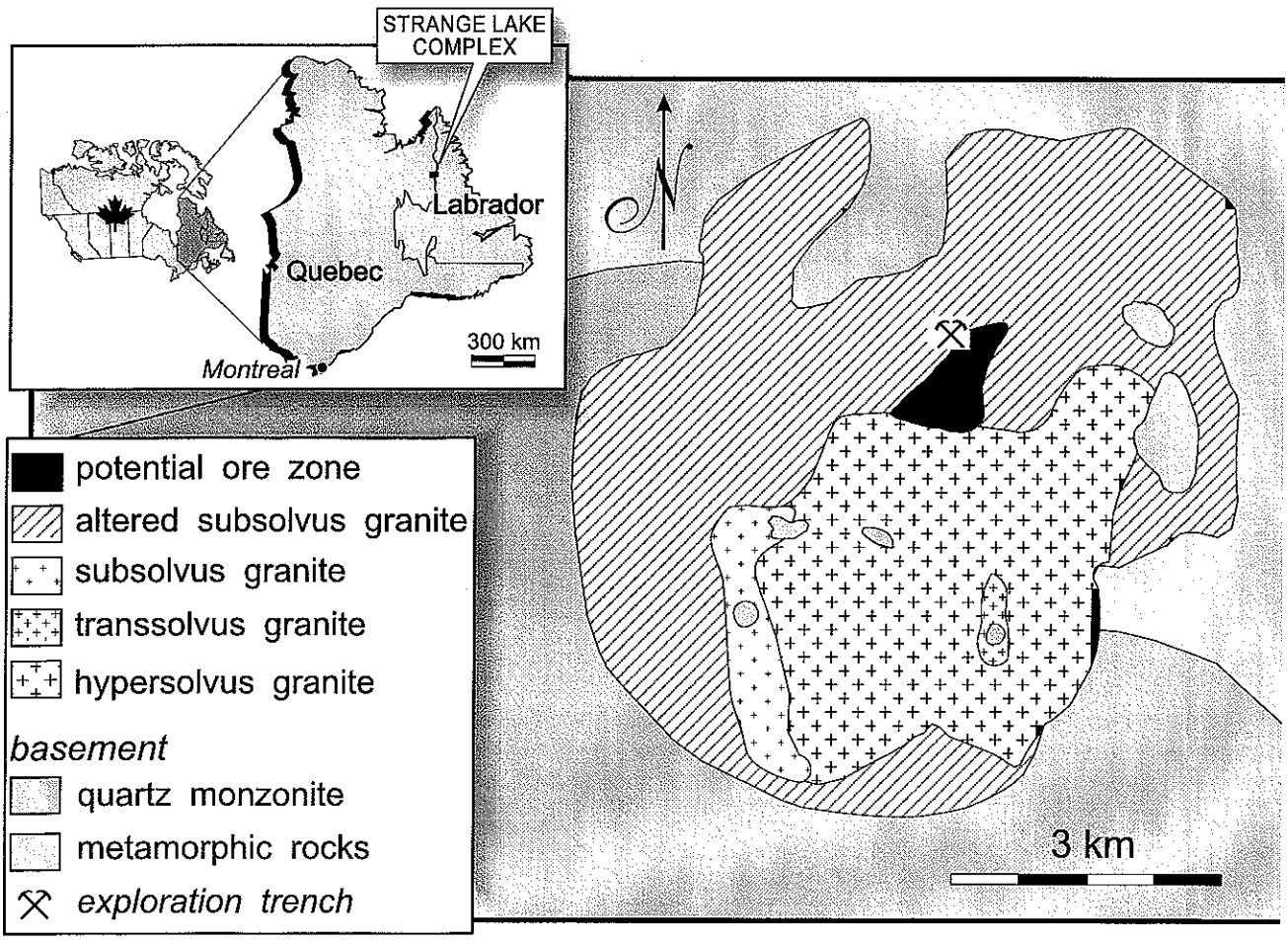

Figure 8. *Location and geological map of the Strange Lake complex. Modified after Salvi and Williams-Jones (1996).*

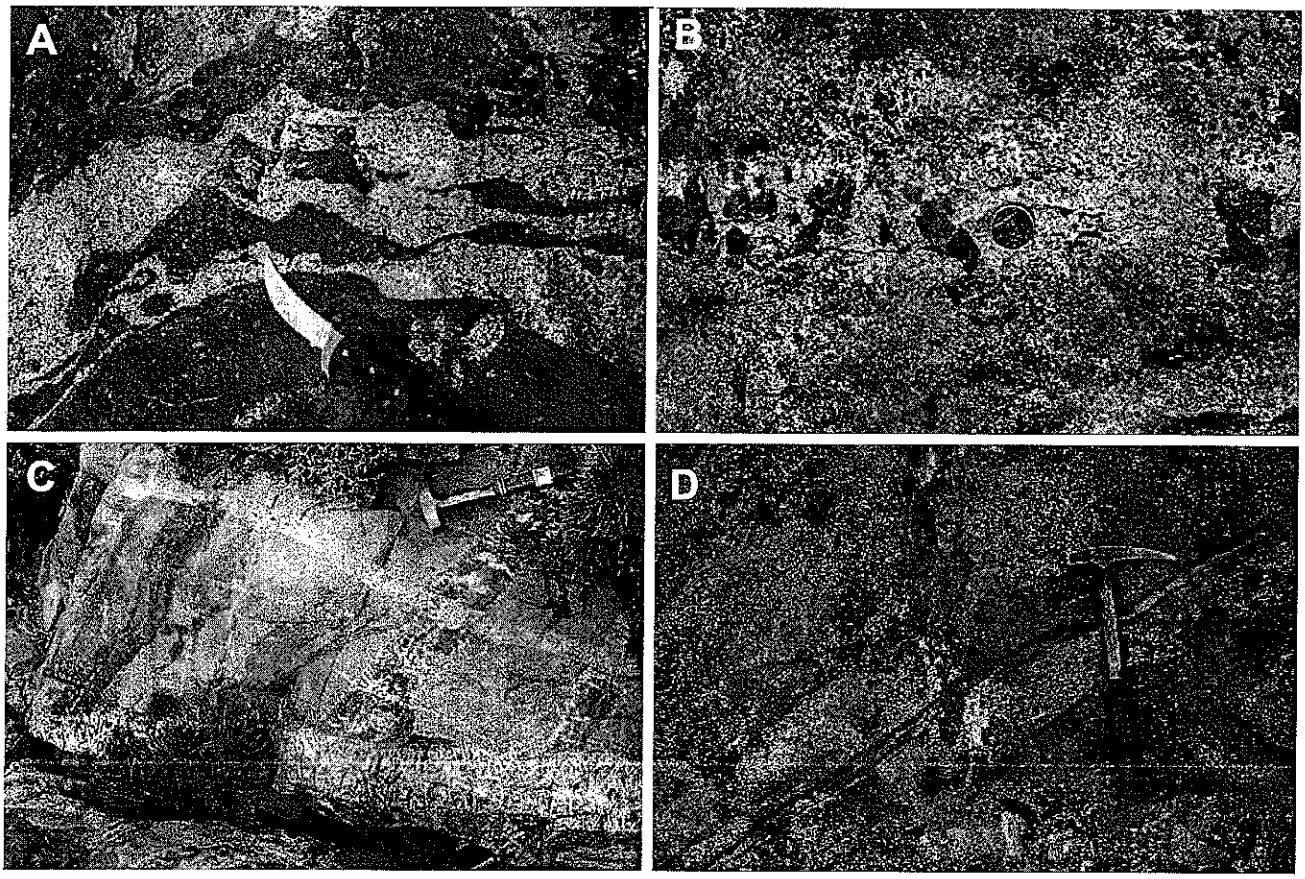

Figure 9. *A) Photograph of an outcrop showing apparently immiscible layers of a melanocratic granitic phase in subsolvus granite at Strange Lake. The dark colour of the rock is due mainly to the presence of fine-grained arfvedsonite. B) Small pegmatitic vein in subsolvus granite of the Strange Lake complex. C) Several generations of pegmatites in the Tamazeght complex, showing cross-cutting relationships. D) Analcime-albite-aegirine vein cross-cutting dark naujaite at Ilimaussaq (photo courtesy of G. Markl).*

facies is believed to represent the earliest intrusive phase, whereas the subsolvus granite crystallized at a late stage, as indicated by cross-cutting relationships among granite types, and by the presence of microcline and near-end-member albite in the subsolvus granite (Nassif, 1993). The pegmatites are interpreted to have formed penecontemporaneously with fluid phase separation during crystallization of the subsolvus granite (Nassif 1993; Boily and Williams-Jones, 1994).

A preliminary model for the 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 crystallization and pegmatite emplacement, eventually exsolving an aqueous fluid that produced extensive alteration of these rocks, most notably the replacement of arfvedsonite by aegirine (Salvi and Williams-Jones, 1990; Boily and Williams-Jones 1994).

Tamazeght Complex

The Tamazeght alkaline complex, Morocco is ~30 x 17 km at surface (Figure 10), and was emplaced in Jurassic limestones during an episode of Eocene rifting (44 ± 4 Ma; Tisserant et al., 1976). Rocks of the complex range from felsic to ultramafic in composition, and are both volcanic and plutonic, the latter comprising ultrabasite (Bouabdli and Liotard, 1992), shonkinite, monzogabbro, malignite, syenite, carbonatite and numerous HFSE-rich pegmatites (Figure 9C) (Aghchmi, 1984; Mourtada et al., 1997). The most important rock type volumetrically is syenite, which includes both miaskitic and agpaitic variants; the latter, which host a large number of rare minerals, resemble in some respects the more evolved parts of the Ilimaussaq complex in Greenland (cf. Sørensen, 1997; Robles et al., 2001).

Kchit (1990) described the Tamazeght complex as being composed of juxtaposed, cross-cutting, pipe-shaped bodies, which he interpreted to have been injected at the intersections of faults produced by SW-NE sinistral shearing during post-Cretaceous Atlas folding (Laville and Harmand, 1982). He also interpreted the primary magma to be a mantle-derived nephelinite that differentiated prior to emplacement, giving rise to separate jacupirangite-melteigite-ijolite and plagisyenite-malignite-syenite successions; Bouabdli et al. (1988) had previously proposed that this magma was monchiquitic in composition. On the basis of structural features and

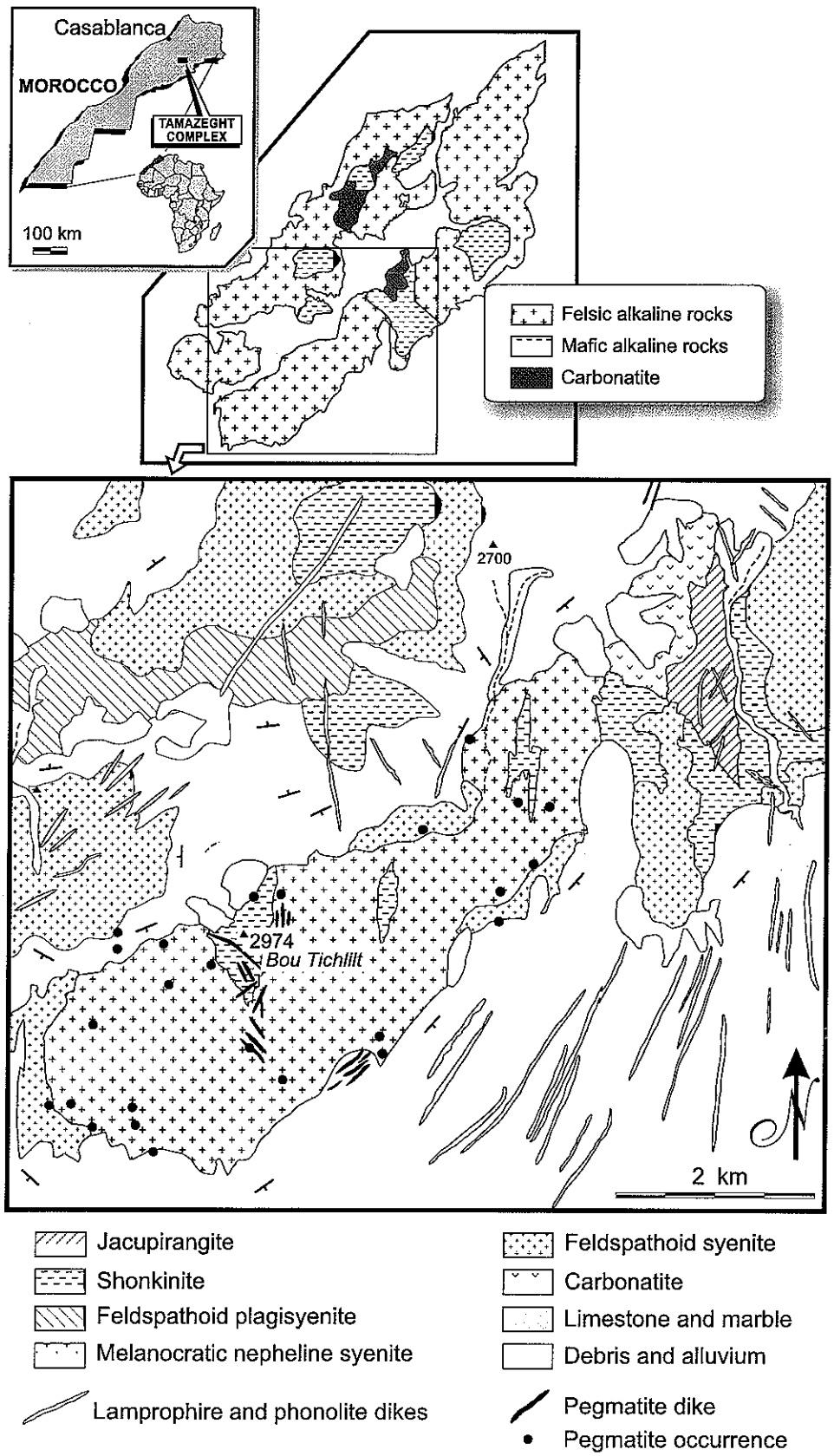

Figure 10. *Location and geological map of the Tamazeght complex. Shown in detail is the southern part of the complex where the HFSE contents are highest. Modified after Salvi et al. (2000).*

cross-cutting relations, Kchit (1990) concluded that the earliest intrusion was an alkaline ultrabasite, followed by shonkinite and foïd monzogabbro, plagiosyenite, malignite, foïd syenite, and monzonite (this last unit occurs locally at the north-east end of the complex). Subvolcanic stocks (carbonatite, carbonatite dikes, phonolite, trachyte) cross-cut all plutonic units.

CHARACTERISTICS OF Zr-Y-Nb-REE MINERALIZATION

Alkaline igneous rocks arguably contain the highest concentrations of Zr and other HFSE of any igneous rock type, and intrusions of such rocks commonly host exploitable resources of these elements. Examples of peralkaline plutons that host economic or subeconomic deposits of HFSE include those described above, i.e., Ilímaussaq, Greenland (Zr and U in eudialyte and pitchblende; Sørensen, 1974, 1992; 2001), the Khibina Complex, Russia (REE-bearing apatite; Kogarko, 1990), the Lovozero Complex, Russia (Zr, REE and Nb in eudialyte; Vlasov et al., 1966; Kogarko, 1990), and the Strange Lake granite, Quebec-Labrador, (Zr, Y, REE, Nb in gittinsite, pyrochlore and kainosite-Y; Miller, 1986, 1990; Zajac, 1992). Other important examples are the Khaldzan-Buregtey Massif, Mongolia, which contains large resources of Zr, Nb, and REE as zircon, zirconosilicates, pyrochlore and REE fluorocarbonates (Kovalenko et al., 1995; Kempe et al., 1999), the Pilanesberg Complex, South Africa, which contains Zr, REE and Nb in eudialyte (Olivo and Williams-Jones, 1999), the Kipawa peralkaline complex in Quebec, also a potential source of eudialyte (Allan, 1992; Currie and van Breemen, 1996), the Blatchford lake granite-syenite complex, North West Territories, which is the site of the subeconomic, polymineralic, Thor Lake Zr-Y-REE-Nb-Be deposit (Trueman et al., 1988; Taylor and Pollard, 1996), the Gallinas quartz syenite in New Mexico, USA, which host REE mineralization mainly in the form of bastnäsite (Schreiner, 1993), and the Amis complex (Brandberg Massif) in Namibia, which hosts significant Zr, Nb and REE mineralization (Schmitt et al., 2000).

Ilímaussaq Complex

The Ilímaussaq complex was discovered in 1806, and since then has attracted attention from explorationists worldwide. The Danish State took over exploration for radioactive elements between 1955 and 1982, and conducted a short drilling campaign in 1962. Rare metals present in elevated concentrations in the complex include U, Th, Nb, Ta, Zr, Y, REE, Li, and Be (e.g., Sørensen, 1992; 2001; Secher, 2002).

The main rare-metal deposits are in the Kangerluarsuk area, where potentially exploitable Zr, Y, REE, and Nb are present in eudialyte-rich layers of the kakortokite suite (Figure 11A). These form part of a repetitive cycle of fractionation comprising a basal arfvedsonite-rich layer, an intermediate eudialyte-rich layer, and an upper layer rich in microcline (Sørensen, 2001). Twenty-nine separate eudialyte-rich layers have been identified, containing up to 6 wt. % ZrO_2, 0.2 wt. % Y, 3 wt. % REE and 0.2 wt. % Nb_2O_5. The average grade is 3 wt. % ZrO_2, 0.1 wt. % Y_2O_3, 1.5 wt. % REE_2O_3 and 0.1 wt. % Nb_2O_5, and the total resource comprises approximately 2 million tons of rock (Secher, 2002; cf. also Sørensen, 1992). In addition to being an important cumulate phase, considerable eudialyte is also present as an interstitial phase in the overlying lujavrites

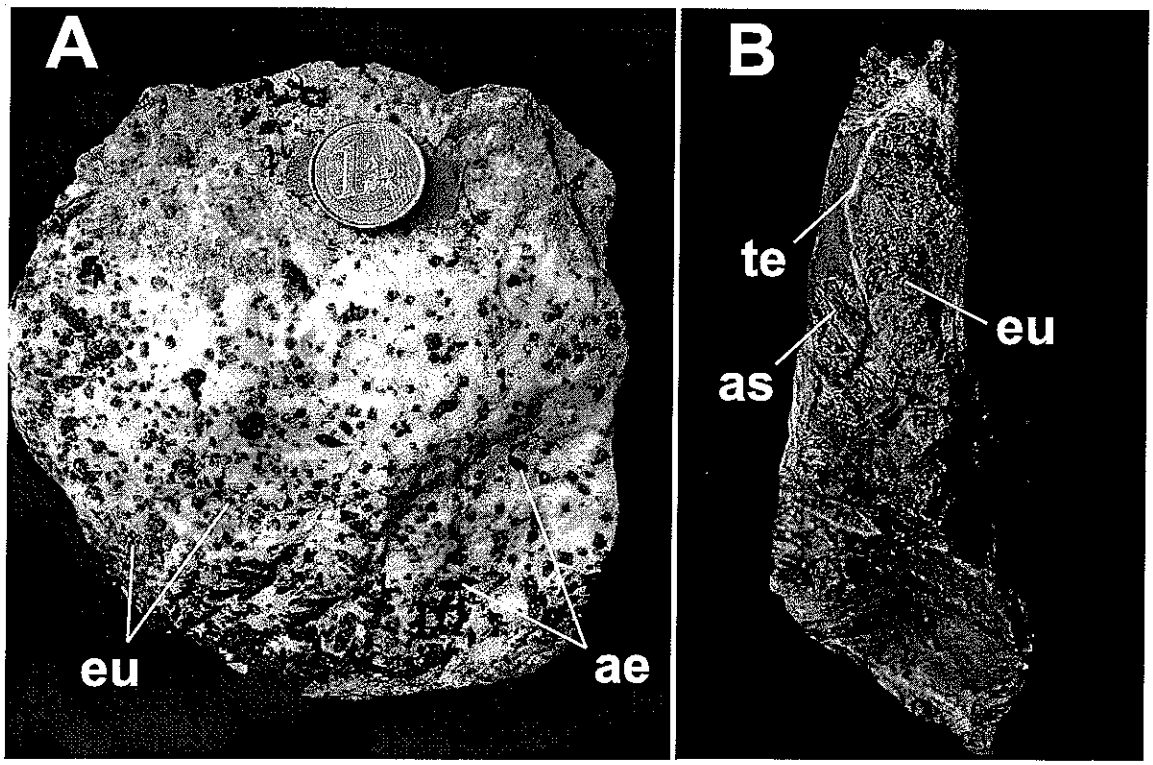

Figure 11. *A) Eudialyte-aegirine albitite from the kakortokite layered series of the Ilímaussaq Complex (eu: eudialyte; ae: aegirine). B) Euhedral crystals of eudialyte undergoing rim replacement by terskite (te). Aegirine-astrophyllite (as)-eudialyte pegmatite from the Schkatulka UO_2 mines, Alluaiv Mountains, Lovozero, exploited for loparite and steenstrupine. The scale is the same in the two photos. Samples courtesy of F. Fontan.*

and in the naujakasite lujavrites, which are interpreted to be the most evolved rocks in the complex (Sørensen, 2001), although it is possible that they represent an altered variety (G. Markl, pers. comm., 2004). In the latter, steenstrupine replaces eudialyte as the principal HFSE mineral. Cumulatively, these lujavrites contain a resource of about 54 million tons grading 1.1 wt. % ZrO_2, 0.09 wt. % Y_2O_3, 0.56 wt. % REE oxides and 0.11 wt. % Nb_2O_5 (Steenfelt, 1991).

The other important area for rare-metal mineralization in the Ilímaussaq complex is at Kvanefjeld, which hosts appreciable U-Nb mineralization in the form of pitchblende, pyrochlore and epistolite, and also contains significant reserves of Zr, Be, Li, Y, and REE (Sørensen, 1992). These deposits are clearly hydrothermal in origin, occurring either as veins in the lujavrites or, in the case of steenstrupine (REE, Zr and Th), as fenites developed in the roof zone and in xenoliths. Fluid inclusion and phase equilibrium studies conducted on some of the chkalovite- and tugtupite-bearing veins (Be) (Figure 9D) suggest that this hydrothermal mineralization involved orthomagmatic fluids that had evolved to relatively high pH as a result of metasomatic reactions involving nepheline (Konnerup-Madsen and Rose-Hansen, 1982; Markl, 2001; Markl and Baumgartner, 2002).

Khibina-Lovozero Massif

The nepheline syenite-hosted apatite deposits of the Khibina complex represent one of the largest resources of phosphate in the world, comprising 2.7 billion tons averaging 17.5 % P_2O_5. Recently, they have produced 20 million tons of apatite annually (Semenov, 1997). The richest deposits occur in a 200 m-thick lens with a strike length of 3 km, sandwiched between the urtite/ijolite and rischorrite zones (see above). The ore consists of massive apatite, comprising ~60 wt. % of the rock (up to 90 wt. % locally; Kogarko, 1990), accompanied by diopside, titanite, K-feldspar, titanomagnetite, and nepheline, and minor aenigmatite, lepidomelane, and katophorite. Adjacent to the rischorrite (hanging-wall), apatite is enriched in Ti, Nb and Y, whereas at the foot-wall (urtite/ijolite) it contains elevated concentrations of Sr (Semenov, 1997). The apatite is interpreted to have crystallized from a magma, based on microthermometric studies of crystallized melt inclusions in apatite and nepheline, which homogenized between 700 and 1000°C (Kogarko, 1990; Kogarko et al., 1995). Proposed models for the formation of the deposits involve crystal fractionation and convective accumulation (cf. Kogarko et al., 1995, and references therein). Nevertheless, the origin of this quite unique lithology is not entirely clear and, on the basis of textural relationships, some authors have suggested that the deposits may be partly or wholly metasomatic (e.g., Florovskaya and Melkov, 1962).

At Lovozero, the principal commodities are Zr, Nb, REE, Y, Sr, Ba, and P, which occur as eudialyte, loparite, and apatite. Loparite has been mined on and off for more than 50 years (Pekov, 2000) and is found in lujavrites of the second intrusive phase (see above). Approximately 30 000 tons of loparite concentrate (95 % pure; 40 wt. % TiO_2, 34 wt. % REE_2O_3, 8 wt. % Nb_2O_5, and 0.7 wt. % Ta_2O_5) are produced annually (Semenov, 1997). Eudialyte occurs in the succeeding eudialyte lujavrite, where locally it forms almost monomineralic layers, and is an important source of Zr Hf, Y, Nb, and Ta in the complex (Kogarko, 1990). Based on homogenization temperatures of crystallized melt inclusions on the order of 850°C, and experimental data on the solubility of zirconium in peralkaline melts, Kogarko (1990) attributes the concentration of eudialyte to a combination of melt saturation with respect to this mineral and gravitational segregation.

In addition to the deposits discussed above, HFSE minerals are also concentrated in veins of pegmatitic and/or hydrothermal origin at both Khibina and Lovozero (Semenov, 1997). These minerals include eudialyte, narsarsukite, catapleiite, gaidonnayite, and many other rare phases which together with aegirine, astrophyllite, and sodalite, commonly replace earlier minerals (Figure 11B) (see also Pekov and Pavlov, 1995).

Strange Lake Complex

Potentially exploitable rare-metal mineralization is concentrated at the centre of the Strange Lake pluton. The complex was discovered by the Iron Ore Company of Canada while exploring for uranium mineralization in 1979, and followed a report of a Pb and F anomaly in waters and sediments of Strange Lake, some 30 km northeast of the pluton, by the Canada-Newfoundland Uranium Reconnaissance Program (Geological Survey of Canada, 1979). The actual discovery was made by re-tracing the path of a glacially transported boulder train (cf. Zajac et al., 1984). However, instead of finding important concentrations of uranium, the exploration led to delineation of a subeconomic deposit with reserves comprising approximately 30 million tons grading 3.25 wt. % ZrO_2, 0.66 wt. % Y_2O_3, 0.12 wt. % BeO, 0.56 wt. % Nb_2O_5 and 1.3 wt. % REE oxides (Zajac et al., 1984; Currie, 1985; Miller, 1986). The mineralization consists of a large number of unusual minerals, of which the most important is gittinsite. Other locally important minerals include pyrochlore, bastnäsite, monazite, kainosite-(Y), elpidite, thorite, gadolinite, and titanite (cf. Table 1 for mineral formulae). This mineralization is hosted by subsolvus granites and pegmatites that were strongly affected by Ca-metasomatism and hematization. Fluorine is also common at Strange Lake, in particular in the altered rocks, where it occurs principally as pore-filling fluorite but also in a variety of other HFSE minerals (e.g., gagarinite, lavenite, and pyrochlore). The main Zr ore mineral is the calcic zirconosilicate gittinsite, which occurs almost exclusively with quartz in pseudomorphs after the primary sodic zirconosilicate, elpidite (Figure 12A to C). Locally, elpidite is also partially replaced by zircon, which forms clusters of radiating crystals (Figure 12D). Other secondary ore minerals include titanite (± fluorite ± quartz ± hematite), which forms pseudomorphs after narsarsukite, and kainosite, which replaces "dickgerenite" (a new, still-unnamed Ca-Y silicate; cf. Salvi and Williams-Jones, 1990). The quartz accompanying these secondary minerals commonly contains small (<10 μm across), primary fluid inclusions that, in the case of the pseudomorphs of gittinsite + quartz after elpidite, and titanite + quartz after narsarsukite, help define the boundaries of the precursor minerals. These inclusions contain liquid and vapour, and, less commonly, one or two birefringent solid phases. Bastnäsite and hematite have been tentatively identified as daughter minerals (Figure 13). Quartz outside the pseudomorphs hosts larger inclusions (up to 70 μm in diameter), which, based on similarities in morphology, phase ratios and micro-thermometric data, are interpreted to have trapped the same fluid as the clearly primary inclusions. Microthermometric data for these inclusions are summarized in Table 3; they are moderately saline, Ca-rich, and were trapped at temperatures between 150 and 200°C.

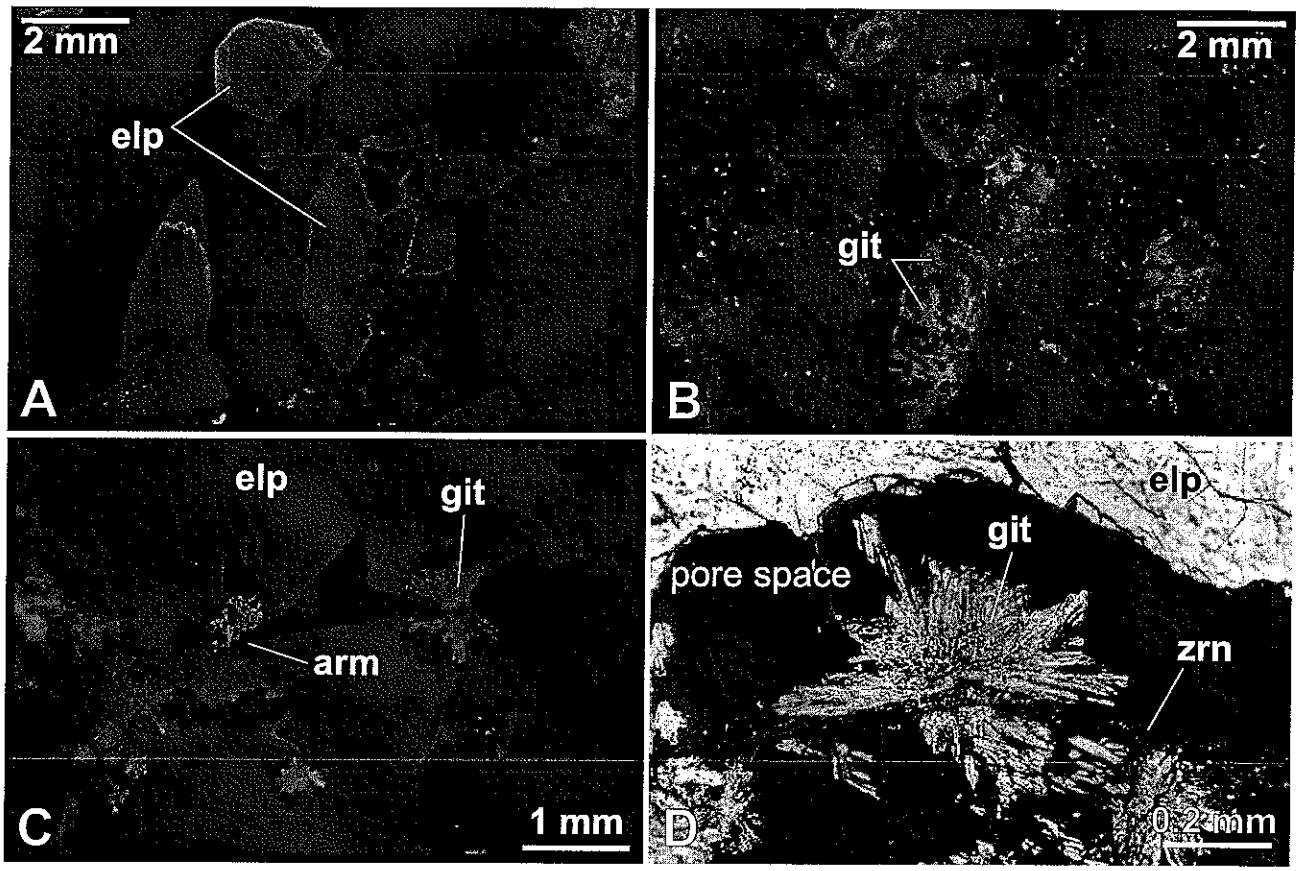

Figure 12. *Photomicrographs of zirconosilicates from the Strange Lake complex: A) Euhedral crystals of elpidite (elp); B) pseudomorphs of feathery gittinsite crystals (git) plus quartz after euhedral elpidite; laths are Fe^{III}-rich feldspar; C) partial replacement of elpidite (elp) by armstrongite (arm) and gittinsite rosettes; D) radiating gittinsite crystals attached to a string of secondary zircon (zrn), growing adjacent to a partially altered elpidite crystal (Modified after Salvi and Williams-Jones, 1995). Photos A, B and C are cathodoluminescence images, obtained with a beam voltage of 10 to 15 keV; beam current of 0.5 to 1 mA; beam diameter of 5 mm. Photo D is taken under plain polarized light.*

Tamazeght Complex

Because the Tamazeght complex outcrops at an elevation of about 3000 m and is very inaccessible, it is not considered a potential HFSE ore deposit. Despite this, the complex has been the subject of economic feasibility studies on at least two occasions. Metals of interest include REE as fluorocarbonate minerals in the carbonatites, and Zr ± Nb ± REE in agpaitic nepheline syenites, especially in the southern part of the complex (Figure 10) where there are large bodies of evolved syenites (including nepheline-rich varieties) and numerous pegmatites. The nepheline syenites and pegmatites in this sector are the most enriched in Zr of any of the units in the complex (0.1 to 0.5 wt. % ZrO_2), and are mineralogically similar to the Zr-enriched bodies of the Ilímaussaq complex. They are host to more than fifty mineral species (Khadem-Allah, 1993), including several alkali and alkali-earth zirconosilicates (e.g., eudialyte, Ca-catapleiite, lavenite, rinkite; Table 1). Both syenites and pegmatites commonly show evidence of hydrothermal alteration, similar to that observed in the rare-metal-rich peralkaline complexes at Strange Lake and Thor Lake. Whole-rock Ca and F contents are unusually high (Khadem-Allah, 1993), a feature that is reflected by the extensive pseudomorphism of primary phases by Ca- and F-rich minerals (Khadem-Allah et al., 1998).

As is the case for the Strange Lake deposit, primary HFSE-bearing phases, in particular Zr minerals, show evidence of complex phase transformations. In syenite units of intermediate composition, the rims of primary zircon crystals are commonly replaced by rosenbuschite, or by Ti-bearing lavenite-normandite plus Mn-bearing phases, which are accompanied by fluorite. In the more evolved nepheline syenites and pegmatites, rinkite is partially or completely pseudomorphed by zircon (± fluorite, calcite, and natrolite) (Figure 14B). Primary eudialyte is pseudomorphed to varying degrees by Ca-rich catapleiite plus Fe and Mn hydroxides (Figure 14A). In these pseudomorphs, Ca-catapleiite has a radiating, fibrous habit that is reminiscent of the texture displayed by gittinsite that has pseudomorphed elpidite in the Strange Lake complex. Significantly, this gittinsite contains structural Mn. The same rocks contain euhedral eudialyte crystals that have undergone incipient alteration. This is illustrated in Figure 15, which shows microcrystals of zircon and fluorite replacing the rims of partially dissolved eudialyte. These textures are remarkably similar to those observed in deep drill core sections at Strange Lake, where elpidite has been altered partially at the rims, leaving strings of microscopic zircon and radiating gittinsite crystals (Figure 12D). Other alteration minerals include Mg- and F-rich phlogopite, plus, locally, muscovite, natrolite, and cancrinite.

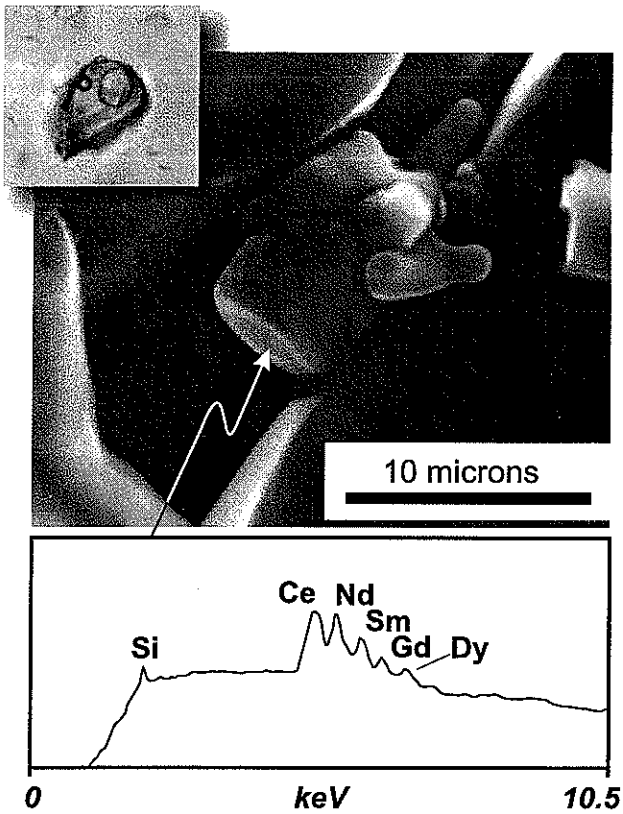

Figure 13. *Opened fluid inclusion from the Strange Lake complex showing a daughter mineral identified as probable bastnäsite (arrow) (similar inclusion in the inset, plane polarized light, ~25 μm across). Modified after Salvi and Williams-Jones (1990).*

Nepheline crystals in the altered rocks contain fluid inclusions that are interpreted to have formed during replacement of eudialyte and other HFSE minerals (Salvi et al., 2000). These inclusions homogenize at moderate temperatures (~300°C), and comprise a Ca-bearing brine containing ~25 equivalent wt. % NaCl (Table 4). In addition, most inclusions contain several solids, which, based on consistency of phase volume ratios, are interpreted to have precipitated within the inclusions after trapping. SEM examination of opened inclusions revealed the presence of several HFSE-bearing daughter minerals, tentatively identified as parisite, zircon, and Nb-bearing rutile (Figure 16).

Khaldzan-Buregtey Massif

The Khaldzan-Buregtey Massif is a multiphase peralkaline granitoid located in western Mongolia that hosts two large Zr-Nb-Ta-REE deposits, which are currently being explored for possible exploitation, and several smaller deposits. The larger of the two, the Khaldsan-Buregtey deposit contains 4 x 10^6 tons of ZrO_2, 6 x 10^5 tons of Nb_2O_5, 3.5 x 10^3 tons of Ta_2O_5, 1 x 10^6 tons of REE, and 1 x 10^5 tons of Y_2O_3, whereas the smaller Tsakhir deposit contains 8 x 10^5 tons of ZrO_2 (Kempe et al., 1999). Accurate estimates of grade are not available. However, Kovalenko et al. (1995) report figures for Zr, Nb and REE of 2 wt. %, 0.4 wt. % and 0.3 wt. %, respectively. The massif measures some 30 km in length and 8 km in width, and consists largely of barren nordmarkite and peralkaline granite (dated at 423 Ma; Kempe et al., 1999), which are intruded by numerous dikes of weakly mineralised peralkaline granite pegmatite, lesser numbers of pantellerite dikes, and dikes of alkaline diabase. The rare-metal mineralization of the Khaldzan-Buregtey deposit is located in the southern part of the massif, and is contained in two, relatively late peralkaline granite stocks (dated at 396 Ma; Kempe et al., 1999), the earlier of which intrudes nordmarkite, and is in turn intruded by the later stock. The earlier stock is a medium-grained peralkaline granite and has highly sheared contacts, whereas the later stock is a fine-grained miarolitic peralkaline granite and

Table 3. Summary of fluid-inclusion microthermometric data for the Strange Lake Complex

Phase Change	Range	Peak
Low-temperature alteration		
Th	90 to 225°C	120 to 140°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[1]	12 to 25	16
principal cations:	Na > Ca ≈ K	
principal anion:	Cl	
trapping T[2]:	150 to 200°C	
High-temperature alteration[3]		
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[1]	23 to 27	24
principal cations:	Na	
principal anion:	Cl	
trapping T[2]:	340°C	

Th=homogenization T; Te= eutectic T; Tm=final melting T.
[1] salinity expressed in equivalent wt% NaCl.
[2] pressure corrected
[3] For the cabonic gas composition see Salvi and Williams-Jones (1997)

Table 4. Summary of fluid-inclusion microthermometric data for the Tamazeght Complex

Phase Change	Range	Peak
Th	180 to 330°C	250°C
Te	-45 to -20°C	-40°C
Tm ice	-23 to -20°C	-20°C
Tm hydrated salt	-15 to 30°C	-15 to 0°C
salinity[1]	-	24 to 27
principal cations:	Na, Ca, Mn, Fe, K	
principal anion:	Cl	
trapping T[2]:	300°C	

Th=homogenization T; Te= eutectic T; Tm=final melting T.
[1] salinity expressed in equivalent wt% NaCl.
[2] pressure corrected

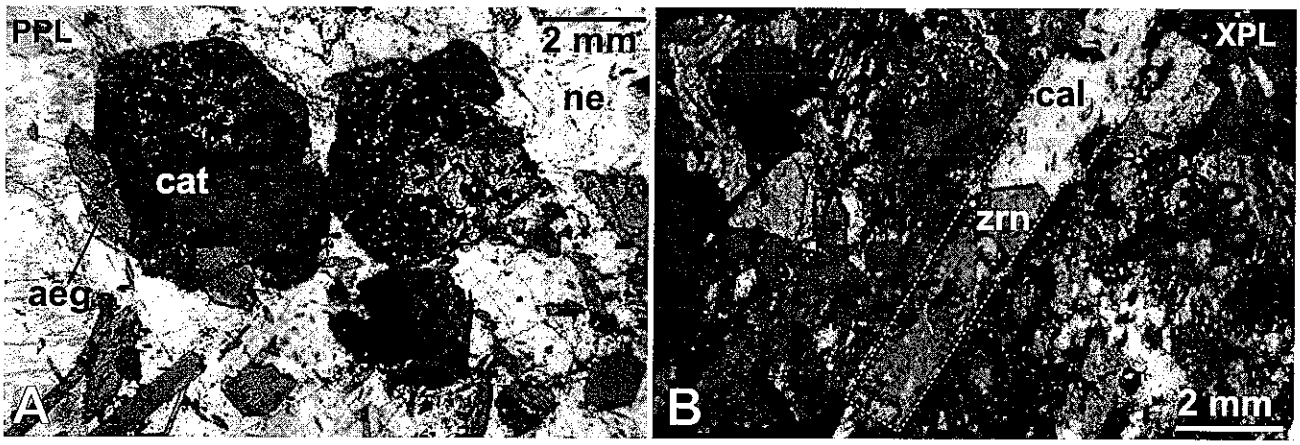

Figure 14. *Photomicrographs of zirconosilicates from the Tamazeght complex: A) pseudomorphs of Ca-catapleiite (cat) plus Mn and Fe hydroxides after euhedral eudialyte (plane polarized light); B) pseudomorphs of zircon (zrn) plus calcite (cal) after a rinkite subhedral crystal (dashed outline). These zircons are Th- and Y-rich. Note that the crystallographic c-axis of the zircon labeled in the photograph is perpendicular to the long axis of the pseudomorph (crossed polars). Other minerals are aegirine (aeg) and nepheline (ne). Modified after Salvi et al. (2000).*

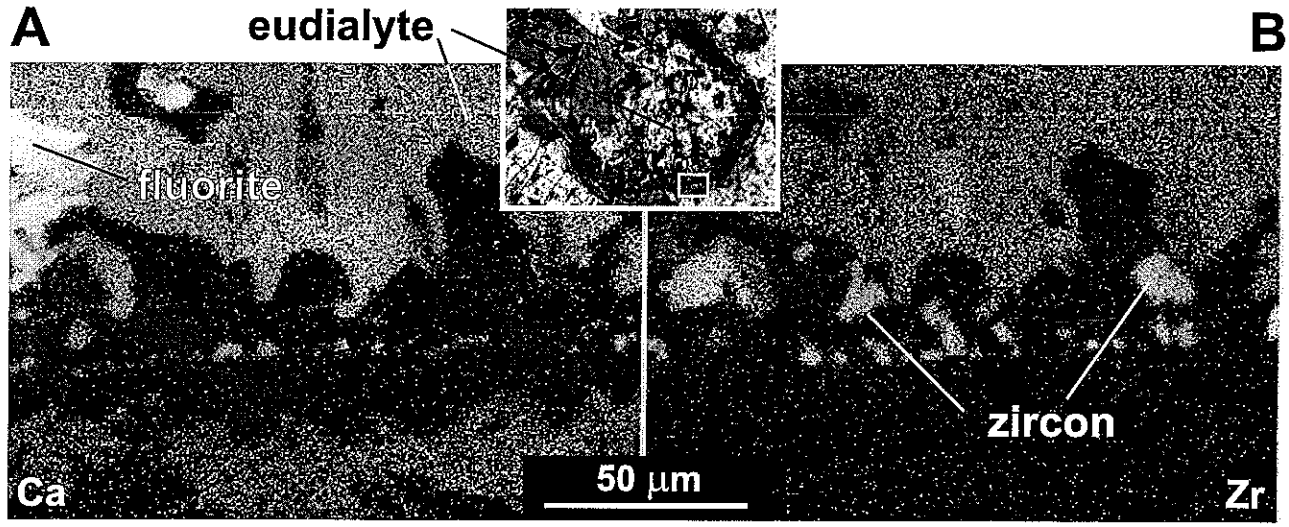

Figure 15. *A euhedral eudialyte crystal (shown in the inset in plane polarized light, 2 mm across) from a nepheline aegirine syenite of the Tamazeght complex, undergoing rim alteration. The white rectangle in the inset outlines the location of the electron microprobe WDS X-ray maps for Ca (A) and Zr (B). In these images, the concentration of white dots is proportional to element abundance. Note the embayed rim of eudialyte, and formation of secondary zircon and fluorite in the alteration. Modified after Salvi et al. (2000).*

has sharp contacts (Kovalenko et al., 1995). Kempe et al. (1999) described these two bodies as being sheared, calcite-bearing and strongly altered (see also Andreev et al., 1994; Andreev and Ripp, 1996). The Tsakhir deposit is located in the northern part of the massif and comprises "vein-like zones of metasomatic alteration" (Kempe et al., 1999). Mineralization in the Khaldzan-Buregtey deposit consists mainly of zircon-quartz pseudomorphs after aegirine and arfvedsonite, quartz-gittinsite pseudomorphs after elpidite, plus elpidite, pyrochlore, rare earth fluorocarbonates, and monazite, which are disseminated together with fluorite (these minerals locally comprise up to 25 vol. % of the rock) in porphyritic quartz-K-feldspar-albite-arfvedsonite-aegirine granite (Kovalenko et al., 1995; Kempe et al, 1999). In many respects the mineralization is similar to that described above for the Strange Lake deposit. The Tsakhir deposit consists of zircon and pyrochlore-bearing calcite-epidote-quartz rock, and is clearly entirely metasomatic. Both deposits were affected by fluorine-rich fluids, approximately 70 Ma after emplacement of the rare-metal granite stocks.

Pilanesberg Complex

The Pilanesberg Complex in South Africa is the world's second-largest alkaline igneous body (after the giant Khibina-Lovozero massif). It consists of pyroclastic and lava-flow sequences, as well as inwardly dipping ring-dikes, concentrically disposed around a core of red nepheline syenite (Lurie, 1986). Moving outwards from the core, these arcuate units comprise green nepheline syenite, foyaite, tinguaite, and red syenite (cf. Olivo and Williams-Jones, 1999, for a map). Although potentially exploitable rare-metal deposits have not been identified, rocks of the Pilanesberg Complex are

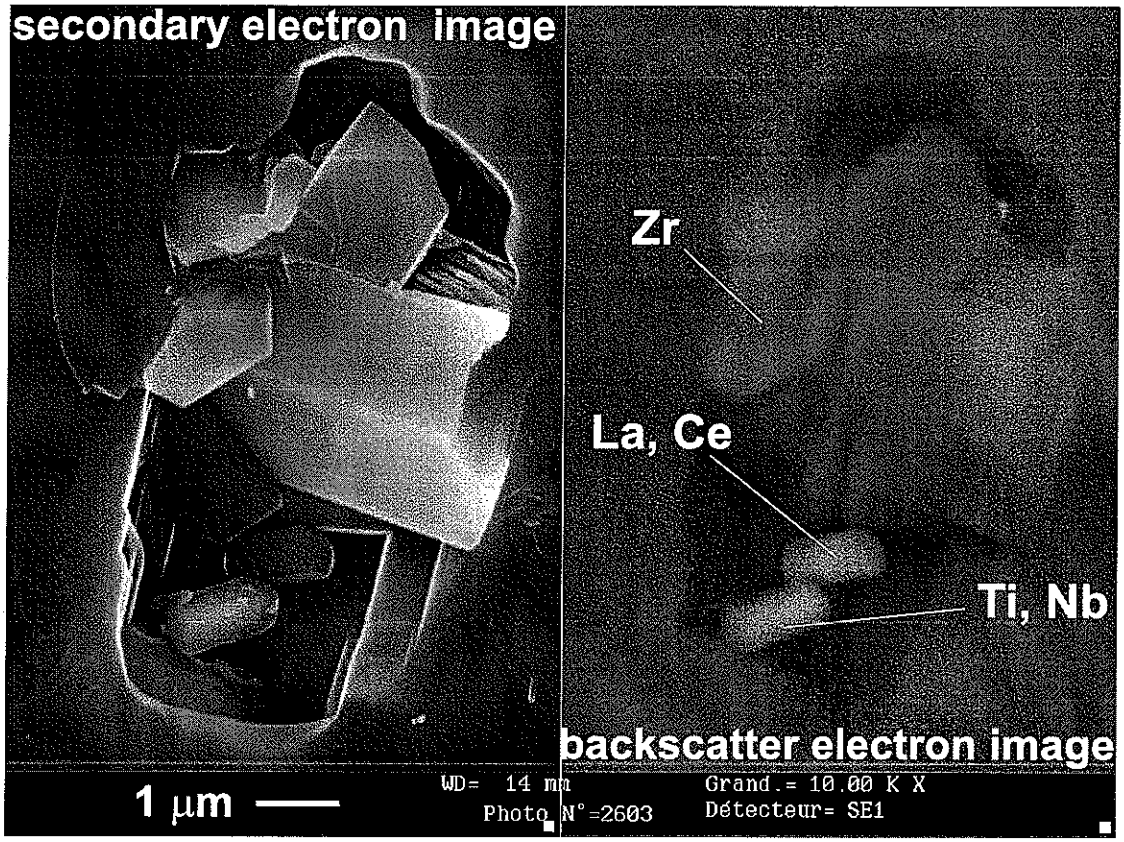

Figure 16. *SEM secondary and backscatter electron image pairs of a particularly solid-rich opened inclusion (Tamazeght). HFSE daughter or trapped crystals include zircon (Zr), parisite (La, Ce), and an unidentified Ti-Nb silicate. Modified after Salvi et al. (2000).*

enriched in Zr, Hf, REE, Nb, Ta, Sr, Th, U, and F (Lurie, 1986). The highest concentrations of these elements are in the green nepheline syenite, which locally contains up to 20 vol. % eudialyte, corresponding to a concentration of up to 2 wt. % Zr and 0.65 wt. % REE (Olivo and Williams-Jones, 1999). In these rocks, eudialyte forms large poikilitic crystals (cm size) that include most other minerals of the rock, and fills-in embayments in hydrothermally corroded aegirine, feldspar, nepheline, zircon and alkali-Zr-silicates. Eudialyte also fills fractures and occurs along cleavages in feldspar. Subsequent alteration locally converted eudialyte to britholite and fergusonite-(Y). These textures indicate that the principal HFSE-bearing minerals formed partly at a post-magmatic, hydrothermal stage in the evolution of the complex.

Thor Lake Deposits

The Thor Lake rare-metal deposits (Be, Y, REE, Nb, Ta, Zr, and Ga), Northwest Territories, Canada, were discovered in 1983 and subjected to extensive exploration, including underground development for bulk sampling and a study for potential mining feasibility (Trueman et al., 1988). The deposits were found to be subeconomic and were consequently not brought into production. The HFSE mineralization is hosted by rocks that form part of the Aphebian Blatchford Lake igneous complex, mainly in the Thor Lake syenite, although some mineralization is also present in the co-magmatic peralkaline Grace Lake granite. U-Pb radiometric analyses of zircon and monazite yielded ages for the latter of 2176.2 ± 1.3 (Bowring et al., 1984) and 2175 ± 7 Ma (Sinclair et al., 1994), respectively. Two main deposits have been delineated by drilling, the Lake deposit, which is located wholly in the Thor Lake syenite and the T deposit, which straddles the boundary between the Thor Lake syenite and the Grace Lake granite (cf. Trueman et al., 1988, for a map). The T deposit is the smaller of the two (1. 6 million tons) but contains the bulk of the Be mineralization (0.85 wt. % BeO) and also contains subordinate amounts of Nb (0.35 wt. %), REE (0.17 wt. %) and Y (0.13 wt. %) (Trueman et al., 1988; Taylor and Pollard, 1996). The Lake deposit contains 64 million tons of ore grading 3.5 wt. % Zr, 1.7 wt. % REE, 0.4 wt. % Nb and 0.03 wt. % Ta (Trueman et al., 1988).

Both deposits are described as being enveloped in contiguous wall zones consisting essentially of K-feldspar and albite with accessory quartz, fluorite and Fe-oxides (Trueman et al., 1988). The core of the Lake deposit is a complex mixture of essentially unaltered syenite, altered syenite, and zones of coarse shards, crystals, and crystal fragments set in a fine-grained matrix of amphibole, biotite, albite, and magnetite. Alteration, which clearly also affected the wall zone, consists of K-feldspathization, that was overprinted by albitization. The principal ore minerals are: zircon, columbite-tantalite, uraninite, and uranothorite. The central part of the T deposit is significantly different from the Lake deposit, and has been subdivided into three zones (lower Intermediate zone, upper intermediate zone, and quartz core) based on the nature and style of alteration. Field relationships indicate that the wall zone of both the Lake and T deposits formed first. In the T deposit this was followed successively by formation of the lower intermediate zone, the upper intermediate zone, and the quartz core. The lower intermediate zone varies from a fine-grained, highly altered rock containing the

assemblage quartz-magnetite-chlorite adjacent to the wall zone, to a central part that contains recognizable fragments of syenite and granite in a quartz-K-feldspar-albite-chlorite matrix. Important economic mineralization (Nb, Y, and subordinate Be) is hosted by the lower intermediate zone, largely in the form of columbite, xenotime, and phenakite. The upper intermediate zone consists of a crudely banded quartz-polylithionite-albite subunit containing appreciable phenakite and minor bastnäsite and fluorite, and a subunit consisting of anastomosing veins of quartz and REE fluorocarbonate minerals (bastnäsite, parasite, synchysite and roentgenite) that surround quartz centres, which gives it a breccia-like appearance. Textural relations indicate that REE fluorocarbonates were among the earliest ore minerals to form in the upper intermediate zone but are nevertheless secondary; pseudomorphs of REE fluorocarbonate minerals after earlier minerals are common. By contrast, phenakite was relatively late and, with fluorite, replaced earlier minerals including the REE fluorocarbonates. The upper intermediate zone is host to the bulk of the Be and REE mineralization in the T deposit, the Be being concentrated mainly in the banded quartz-polylithionite-albite subunit and the REE in the quartz-REE fluorocarbonate subunit. Locally, grades in the latter are extremely high; e.g., a small potential orebody containing 60 000 tons grading 8 wt. % REE (Sinclair et al., 1992). The core of the deposit is a zone consisting of almost mono-mineralic quartz containing abundant vugs filled by REE-bearing minerals, sulphides and fluorite.

On the basis of fluid inclusion and stable isotope data for the T deposit, alteration and associated HFSE mineralization of the Thor Lake syenite and adjacent Grace Lake granite are interpreted to have resulted from interaction of these bodies with a boiling H_2O-NaCl-CO_2 brine of orthomagmatic origin (Taylor and Pollard, 1996). However, as Ar-Ar dating of polylithionite yielded hydrothermal ages that are somewhat younger than those of the host intrusives (an average of three determinations indicate an age of 2109 ± 47 Ma; Taylor and Pollard 1996), the latter are not interpreted to be the source of the fluids. Instead, the fluids are considered to have been released by an unexposed intrusive phase at depth, possibly an agpaitic nepheline syenite, which was intersected during drilling of the Lake deposit.

Gallinas Mountains

Fluorite-bastnäsite mineralization was discovered in the Gallinas Mountains, New Mexico, in 1942, and exploited for REE in several small mines until 1956 (Schreiner, 1993). The REE mineralization occurs either in breccia pipes (up to 100 m wide) hosted by an alkaline Tertiary quartz syenite laccolith or in narrower breccias localized along faults in Permian sandstones that host the laccolith (cf. Williams-Jones et al., 2000, for a map). In the former, the clasts consist dominantly of heavily fenitized quartz syenite and in the latter of weakly altered (minor fluorite and pyrite) sandstone. The cement in both cases is fluorite, which contains subordinate bastnäsite, quartz and minor parasite and barite. Average grades in the different mines varied between 1.5 and 2.5 wt. % REE. Unfortunately, production figures are incomplete and not available for some of the mines, but it would appear that less than 20,000 tons of ore were treated. Petrographic and fluid inclusion studies indicate that mineralization commenced with the deposition of quartz at a temperature of ~400°C from a sulphate-rich fluid with a salinity of ~15 equivalent wt. % NaCl, interpreted to have been of orthomagmatic origin (Williams-Jones et al., 2000). Fluorite and bastnäsite deposition occurred at slightly lower temperatures and coincided with the introduction of separate CO_2-bearing sulphate-poor brines into the system from the surrounding sandstones. As discussed later, these data are consistent with a model for mineralization in which REE and fluorine-bearing magmatic fluids deposited bastnäsite and fluorite and later parisite as a result of mixing with Ca- and CO_2-bearing meteoric or formational fluids. The Gallinas Mountains mineralization is also discussed by Samson and Wood (this volume).

Amis Complex

The Amis Complex, Namibia, is a peralkaline granitic intrusion hosting significant concentrations of Zr, Nb and REE, and forms a satellite to the Brandberg Massif, one of 20 subvolcanic anorogenic granites emplaced during the Early Cretaceous break-up of western Gondwana (see Schmitt et al., 2002). HFSE minerals occur in two facies, an arfvedsonite-bearing subsolvus granite with associated pegmatites, and aegirine-albite aplite, which occurs mainly as segregations along the borders of the pegmatites. The main HFSE minerals in the arfvedsonite-bearing rocks are pyrochlore, dalyite, monazite and bastnäsite, and, except for pyrochlore, are interstitial to the main rock-forming phases; bastnäsite also occurs with fluorite in microscopic veinlets. In addition to these HFSE minerals, the aegirine aplites also contain zircon, gadolinite, wulfenite, and thorite, and have the highest concentrations of HFSE (up to 1.7 wt. % Zr, 0.20 wt. % Nb, 0.13 wt. % Ce and 0.22 wt. % Y; Schmitt et al., 2000). Hydrothermal alteration was widespread and takes the form of pervasive replacement of arfvedsonite by hematite and quartz. Alteration within the aplites is said to be restricted to replacement of basaltic xenoliths by albite, mica and sodic amphibole (Schmitt et al., 2002). However, the mention of intergrowths of aegirine with arfvedsonite suggests that aegirine may be an alteration phase rather than a primary constituent of the aplite (cf. Salvi and Williams-Jones, 1990, 1997).

CONROLS ON HFSE MINERALIZATION

As has already been discussed, there is a large body of literature devoted to the origin and evolution of alkaline igneous complexes. Despite this, the genesis of the associated HFSE mineralization is poorly understood and there is still considerable debate on as basic an issue as whether this mineralization is magmatic, hydrothermal or a combination of the two. In some cases, such as the Kangerluarsuk area of the Ilímaussaq Complex and in the Lovozero complex, where eudialyte-rich layers form part of a cumulate sequence, the magmatic nature of the Zr, Y, REE, and Nb mineralization is beyond doubt (cf. Sørensen, 2001). Similarly, there can be little doubt that the breccia-hosted REE mineralization in the Gallinas Mountains deposits, which occurs both within syenite and in the adjacent sandstones, is hydrothermal (Williams-Jones et al., 2000), although even in this case magmatic processes were probably important in initial REE concentration. There is also strong evidence, from the secondary nature of the HFSE mineralization and its intimate association with intense alteration, that the Thor Lake deposits are also dominantly hydrothermal (Taylor and Pollard, 1996), and a similar case can be made for skarn-hosted Y mineralization in the Kipawa peralkaline complex (Allan, 1992; Currie and van Breemen, 1996). In other cases, however, the relative importance of magmatic and hydrothermal processes is open to debate. For example, at Strange Lake, there are elevated concentrations of HFSE in the form of primary magmatic minerals like elpidite, which led Birkett et al. (1991), Richardson and Birkett (1995), and Miller (1996) to conclude that the mineralization is entirely magmatic. However, the most strongly mineralized zones are characterized by intense hematization and silicification, and in these zones

the HFSE mineralization is entirely secondary (Salvi and Williams-Jones, 1990, 1996). Moreover, whole-rock geochemical data indicate that the alteration involved significant enrichment of Ca, F and HFSE, and bastnäsite is present as a daughter mineral in fluid inclusions. Salvi and Williams-Jones (1990, 1996) therefore concluded that hydrothermal processes played a major role in the formation of the main zone of Zr-Nb-Y-REE mineralization at Strange Lake (cf. Boily and Williams-Jones, 1994). The situation is similar for the peralkaline, granite-hosted Khadlzan deposit (Mongolia), where Kovalenko et al. (1995) attributed Zr, Nb, REE and Y enrichment entirely to magmatic fractionation, on the basis of trace element and isotopic data for melt inclusions. As in the case of Strange Lake, studies by Andreev et al. (1994) and Andreev and Ripp (1996) of the Khadlzan deposit emphasized the fact that the potentially economic mineralization is restricted to zones that are intensely altered, and Kempe et al. (1999) have shown that much of this mineralization is in the form of secondary minerals, some of which pseudomorphed primary HFSE silicates. Understandably, these latter studies concluded that both magmatic and hydrothermal processes are likely to have contributed to the formation of this and other similar deposits in the Mongolian Altai.

From the above discussion it seems clear that, in all cases, there is initial enrichment of HFSE by magmatic processes, that in some cases the resulting HFSE concentrations are entirely the result of magmatic processes, and that in other cases hydrothermal processes have played the dominant role in producing the concentrations required to form exploitable deposits. Thus, in the case of the hydrothermal Gallinas Mountains REE deposits, the total REE concentration in the quartz-syenite, which is believed to have been the source for the mineralizing fluids, is ~650 ppm, whereas the deposit grade is 1.5 to 2.5 wt. % REE, i.e., there was a ~25 times hydrothermal enrichment. Similarly, 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 hydrothermal-enrichment factor was between approximately 25 and 85. At Strange Lake, 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 hydrothermal-enrichment factor of 7 to 22.

Magmatic Enrichment

The importance of magmatic processes in producing the extreme enrichment of HFSE required to form economic deposits of these elements is readily apparent from studies of melt inclusions. These studies show that the concentrations of HFSE in peralkaline magmas are orders of magnitude higher than in other types of magma, and that, in some cases, they may reach percentage levels. For instance, 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 analyzed from the Khadlzan-Buregtey peralkaline granitoid, and Schmitt et al. (2002) reported similar concentrations of these metals 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 high concentrations of the HFSE commonly encountered in peralkaline rocks are likely the result of a combination of several factors. Firstly, peralkaline magmas are derived from metasomatically enriched lithospheric mantle (Upton et al., 2003; Halama et al., 2004), i.e., mantle that is richer in HFSE than, for example, mantle that produces MORB or subduction-related magmas. Secondly, peralkaline magmas have high concentrations of alkalies and fluorine, which are well known to increase the solubility of HFSE, at least in metaluminous melts, by promoting the formation of polymeric alkali-silicate complexes and/or alkali-fluoride complexes (e.g., Watson, 1979; Collins et al., 1982; Collerson, 1982; Keppler, 1993; Linnen, 1998). Thirdly, the elevated agpaicity of peralkaline melts results in them having a much higher proportion of non-bridging oxygens than metaluminous or peraluminous melts, which permits correspondingly higher proportions of the high valence HFSE to be accommodated in the melt structure (e.g., Scarfe, 1977; Peiffert et al., 1996). This is well illustrated by experimental studies, which show that the solubility of zircon in metaluminous and peraluminous melts is <100 ppm Zr (e.g., Watson, 1979; Hanchar and Watson, 2003; see also review in Linnen and Cuney, this volume), whereas in peralkaline melts its solubility is > 1 wt. % Zr (Kogarko, 1990; Marr et al., 1998). Fourthly, the HFSE are highly incompatible elements, i.e., they do not partition into early-crystallizing minerals, and consequently are enriched in the residual magma. Finally, the HFSE are commonly concentrated in relatively dense phases, which readily form gravity-settled cumulates in these low-viscosity melts (cf. Johannes and Holtz, 1996), such as was the case at Ilímaussaq and Lovozero, where Zr crystallized from the most evolved magmas to form nearly mono-mineralic layers of cumulate eudialyte.

Hydrothermal Concentration

The evidence presented earlier that hydrothermal processes play an important and, in some cases, even 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, evidence for hydrothermal HFSE mobility is also available for other environments. For example, the REE are commonly enriched during greisenization of peraluminous granitic rocks (e.g., Alderton et al., 1980; Poitrasson et al., 1995, 1998; Hecht and Cuney, 2000), in some hydrothermal deposits such as the Olympic Dam-type deposits (cf. Samson and Wood, this volume), and during chloritic alteration associated with the formation of massive sulphide deposits (e.g., MacLean, 1988; Shandl and Gordon, 1991). There are fewer examples of mobility of the other HFSE. However, Rubin et al. (1989) showed that Zr (up to 3.8 wt. % as zircon) in the Sierra Blanca limestone-hosted fluorite replacement bodies, Texas, was mobilized hydrothermally from peraluminous granites, and Moine et al. (1998) were able to relate the high concentrations of Th in the sapphire-bearing fluorphlogopite skarns of southeastern Madagascar to nearby peraluminous intrusions. There is also direct evidence for the hydrothermal transport of the HFSE from their occurrence as daughter minerals in fluid inclusions, e.g., bastnäsite (Kwak and Abeysinghe, 1987; Heinritzi et al., 1989; Salvi and Williams-Jones, 1990), baddeleyite (ZrO_2) (Philippot and Selverstone, 1991; Belkin, 1992), weloganite ($Sr_5Zr_2(CO_3)_9{\cdot}4H_2O$) (Vard and Williams-Jones, 1993), and zircon (Salvi et al., 2000).

The importance of hydrothermal processes in the formation of HFSE deposits 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 elements, and partly to the fact that these melts are

also highly enriched in halogens like Cl and F (e.g., Kovalenko et al., 1995; Markl et al., 2001). This ensures that the hydrothermal fluids most likely to be responsible for HFSE transport are in contact with a highly enriched HFSE source and also with high concentrations of ligands that might form stable aqueous HFSE species. Unfortunately there is only limited information on the behaviour of the HFSE in aqueous solutions at hydrothermal conditions and most of this information is for the REE.

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-}, and somewhat weaker complexes with Cl^- (see also Samson and Wood, this volume). This would suggest that the REE are transported mainly as fluoride complexes in hydrothermal fluids derived from peralkaline magmas, a conclusion that is supported by the fact that the principal REE ore mineral is commonly a REE fluorocarbonate, bastnäsite, and that fluorite is an important gangue mineral in many HFSE deposits, e.g., Gallinas Mountains, Strange Lake, Khadazan-Buregtey, and Thor Lake. However, F partitions preferentially into the melt (cf. Fig. 4.18 in Johannes and Holtz, 1996), and thus F concentrations may be low in the aqueous phase, unless aqueous phase separation is extremely late. This raises the question of whether or not F concentrations are likely to be sufficient for fluoride species to be the main form of REE in solution. In contrast to fluorine, chlorine is partitioned strongly into the aqueous phase, and has been reported to be in concentrations represented by salinities in excess of 20 equivalent wt. % NaCl in some HFSE deposits (Salvi and Williams-Jones, 1992; Taylor and Pollard, 1996; Williams-Jones et al., 2000). Moreover, recent experimental data (Gammons et al. 1996, 2002; Migdisov and Williams-Jones, 2002) suggest that REE chloride complexes are significantly more stable than predicted by the earlier theoretical studies. It is thus possible that chloride complexation may play a more important role in REE transport than was previously suspected. Finally it should be noted that sulphate is reported to be present in appreciable concentrations in fluid inclusions at the Galinas Mountains REE deposit (Williams-Jones et al., 2000) and the fluids at Thor Lake were CO_2-bearing. The possibility therefore cannot be excluded that sulphate and carbonate ligands may play an important role in REE transport in some systems. For further information on REE speciation the reader is referred to the reviews of Samson and Wood, this volume, and Wood, 2003)

There is considerably less information on the solubility and speciation of other HFS elements in aqueous fluids than there is for REE. For example, 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) reported data for the solubility of baddeleyite in HF-bearing and HF-free solutions. The summary conclusion that can be drawn from these studies is 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 is also enhanced by the formation of carbonate, sulphate, hydroxyl-chloride and hydroxide species although far less so than through complexation with fluoride (cf. Wood, this volume, for a review). There is even less information on the solubility and speciation of Nb. Indeed there have been only two experimental studies (Aleksandov, 1967; Zhou and Tokuda, 2000) at elevated temperature and neither yielded thermodynamic information that could be used to extract thermodynamic data. However, based on data at ambient temperature, Nb is predicted to form strong complexes with fluoride and, at high pH, may have elevated solubility due to the formation of hydrolyzed anionic species (Wood, this volume). As in the case of Zr, carbonate complexation may also enhance Nb solubility (cf. Wood, this volume, for a review).

Thus, although it is clear that hydrothermal fluids can play an important role in the enrichment of HFSE in peralkaline igneous systems, until more information is available on the behaviour of HFSE at high temperatures, the extent to which this enrichment is possible and the conditions under which it can occur are still a matter of considerable conjecture.

MODELS FOR THE FORMATION OF PERALKALINE PLUTON-RELATED Zr-Y-Nb-REE DEPOSITS

The information that has been presented in this chapter indicates quite clearly that most HFSE deposits originate from a combination of magmatic and hydrothermal processes, although in some cases, one or the other class of processes may be dominant. Most researchers agree that alkaline melts are products of low degrees of partial melting under relatively dry (low fH_2O) and low fO_2 conditions in deep, undepleted mantle. Consequently, the primary melts are enriched in incompatible elements, such as the HFSE, compared to melts forming in other environments. Moreover, they can evolve to extremely high halogen (Cl and F) and alkali metal (Na and K) contents before exsolving an aqueous fluid phase. This lowers the solidus substantially and permits fractionation to continue to unusually low temperatures (e.g., down to ~400°C; Scalliet and Macdonald, 2001). In addition, the high concentrations of alkalis and fluorine increase the solubility of HFSE by promoting the formation of polymeric alkali-silicate complexes and/or alkali-fluoride complexes and by increasing the proportion of non-bridging oxygens. As a result, the residual magmas are extremely differentiated, and saturation with Zr, Y, Nb, and REE minerals is suppressed until crystallization of the most evolved melt phases.

The first essential requirement for the formation of an economic HFSE deposit is thus extreme fractionation of a peralkaline magma and the resulting magmatic enrichment of HFSE to levels comparable to those reported above from analyses of melt inclusions, i.e. >1 wt. % Zr and >0.1 wt. % each of Nb, Y and REE. In some cases, e.g., the Kangerluarsuk area of the Ilímaussaq complex and in the Lovozero complex, further fractionation involving saturation and crystal settling of HFSE minerals may be sufficient to produce an economic deposit. In other cases, however, particularly where aqueous phase separation precedes saturation of HFSE minerals, hydrothermal processes may play an important or defining role in the formation of an HFSE deposit.

The high concentrations of halogens in highly evolved peralkaline magmas are predicted to lead to high concentrations of chlorine in the exsolving fluid as chlorine partitions strongly into the aqueous phase even in peralkaline melts (supported by fluid inclusion studies; cf. also Webster and deVivo, 2002). However, the extent to which F concentrates in the fluid is unclear because of its stronger affinity to for the melt phase over the aqueous phase. In addition, this behaviour depends on several other parameters such

as the silica content of the melt (e.g., Johannes and Holtz, 1996). Nonetheless, there is clear evidence from some deposits, e.g., Gallinas Mountains (fluorite-cemented breccias), that appreciable concentrations of fluorine must have been present in the aqueous phase. In view of this and the preceding discussion of HFSE complexation, it seems reasonable to conclude that the HFSE are dissolved in hydrothermal fluids mainly as fluoride or chloride complexes. However, as noted earlier we do not exclude a role for carbonate and sulphate HFSE complexation.

An interesting feature of the Strange Lake, Tamazeght, and Khaldzan-Buregtey HFSE desposits is extensive evidence of Ca metasomatism and the replacement of primary Na-bearing HFSE minerals by secondary, Ca-bearing HFSE minerals; the latter are the only form of HFSE mineral in the potential ore zone at Strange Lake (cf. Salvi and Williams-Jones, 1996). Also interesting is the fact that fluid inclusions defining boundaries of gittinsite and other secondary HFSE pseudomorphs at Strange Lake contain a moderately saline, Ca-rich meteoric fluid (Figure 17). The same is true for fluid inclusions in nepheline crystals adjacent to secondary HFSE minerals in the Tamazeght deposit. By contrast, inclusions in unaltered granite at Strange Lake contain a Ca-free orthomagmatic brine. Textural and fluid inclusion evidence also indicates that formation of the Gallinas Mountains deposit involved mixing of a magma-derived, essentially Ca-free fluid and a somewhat cooler, Ca-bearing fluid (Williams-Jones et al., 2000). Finally, as mentioned above, fluorite is the main gangue mineral in the Gallinas Mountains deposits and is a common gangue mineral at Strange Lake, Tamazeght, and Khaldzan-Buregtey.

A model that reconciles the above observations is exsolution from the peralkaline magma of a Ca-poor fluid in which HFSE are dissolved as fluoride complexes, and subsequent interaction of this fluid with a Ca-bearing fluid of meteoric origin. As fluorite is extremely insoluble, this interaction would rapidly saturate the fluid in fluorite, causing precipitation of this mineral and a corresponding reduction in the activity of fluoride ion. The reduction in fluoride ion activity would in turn destabilize the HFSE-fluoride complexes, eventually leading to the deposition of HFSE-bearing minerals (Figure 18). Instead of a Ca-bearing fluid, the same effect would also be produced by interaction of the magmatic aqueous fluid with a Ca-bearing rock, such as limestone, and this may explain some of the Zr-Nb-Y-REE mineralization of the Tamazeght complex, which is hosted by marble.

If, however, hydrothermal HFSE transport is the result of chloride rather than fluoride complexation, then the controls of mineralization are likely to be quite different. Possible controls suggested by the behaviour of chloride complexes of other metals are precipitation of HFSE minerals due to a pH increase, a reduction in fO_2 and a decrease in temperature, all of which commonly accompany fluid-rock interaction. Likewise, controls of mineralization may be different in environments where carbonate (e.g., Thor Lake and Khaldzan-Buregtey) or sulphate (e.g., Gallinas Mountains) may have been important ligands. For further discussion of possible factors controlling HFSE mineral deposition and more specifically REE mineral deposition the reader is referred to theoretical studies by Burt (1989) and Williams-Jones and Wood (1992).

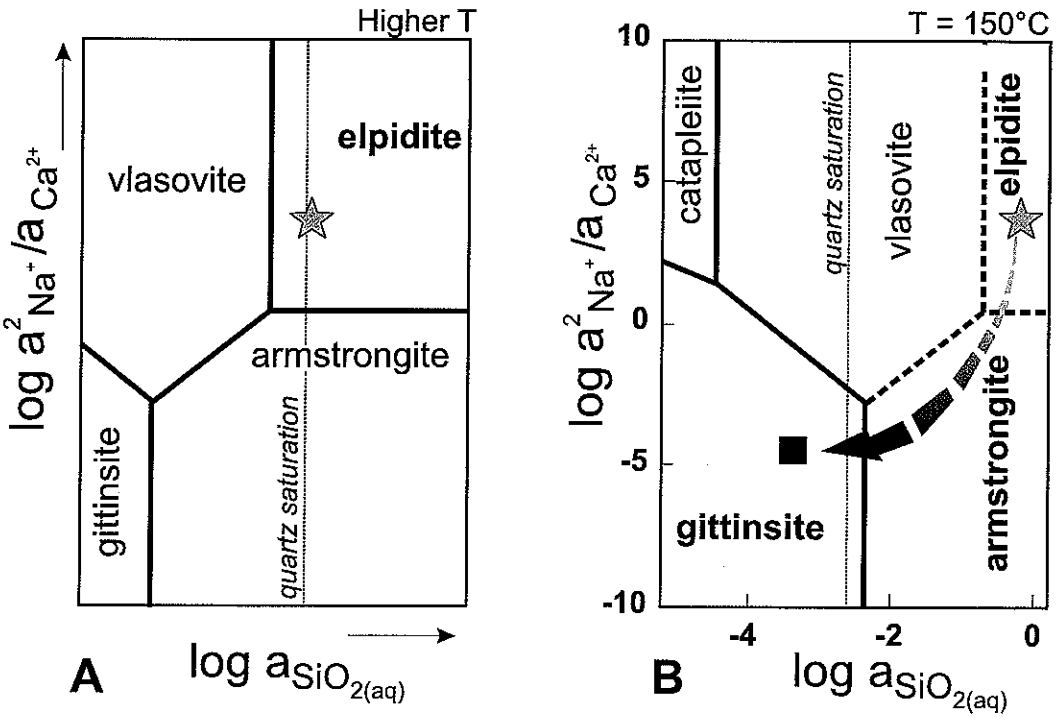

Figure 17. Log a^2Na^+/aCa^{2+} vs. log $aSiO_{2(aq)}$ *diagrams depicting the stability fields of zirconosilicate minerals involved in the alteration of elpidite at Strange Lake (cf. Figure 10A to C). Also shown are the hypothetical compositions of the unaltered elpidite-bearing granite (star) and meteoric fluid (square), the quartz saturation boundary in the fluid, and a possible path of metasomatic transformation of the rock 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 boundary locations 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, and the position of quartz saturation is based on field observations.*

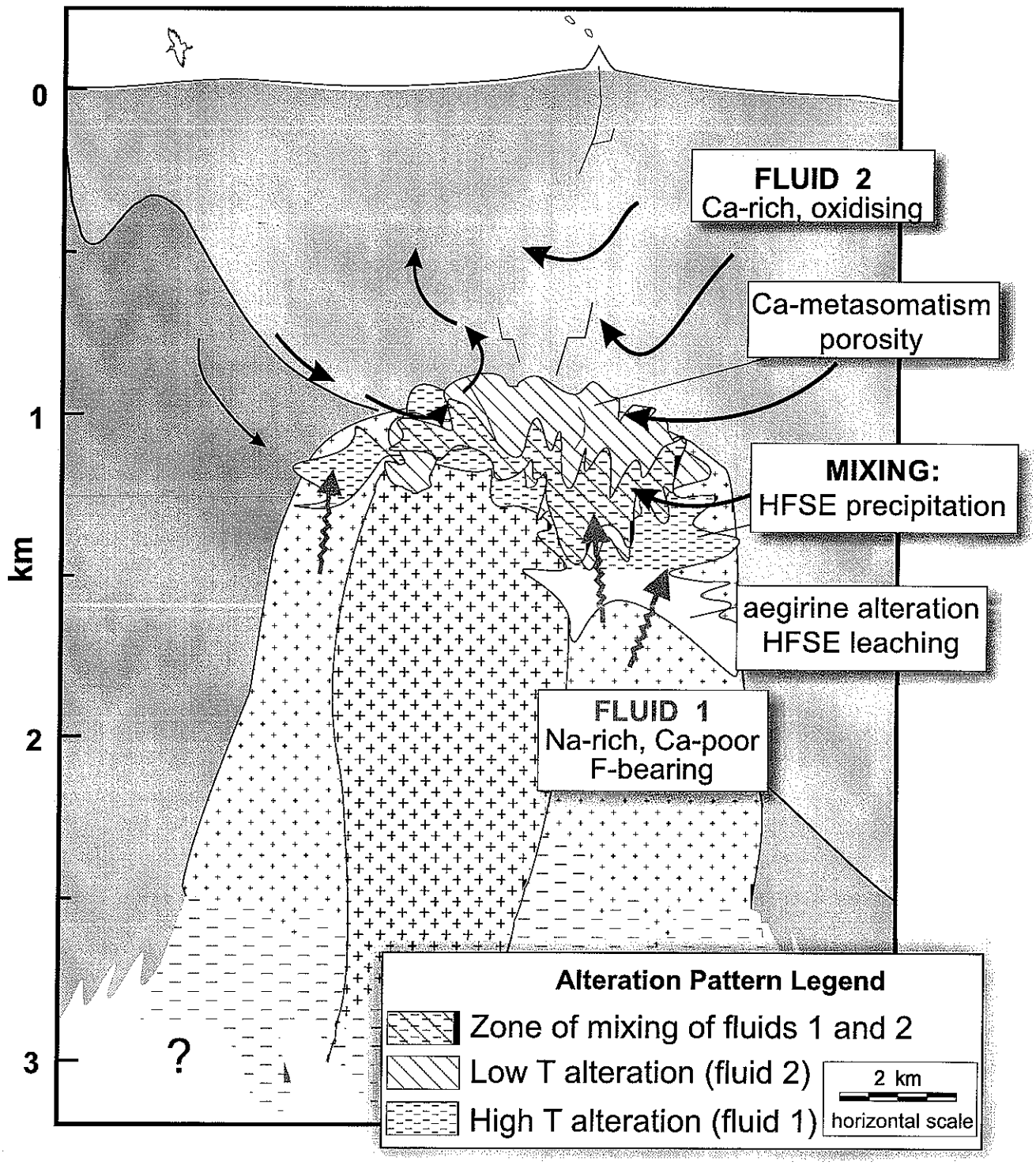

Figure 18. *Schematic cross-section through the Strange Lake pluton depicting the evolution of sub-solidus hydrothermal alteration. Modified from Salvi and Williams-Jones (1996). A Ca-poor, F-rich orthomagmatic fluid caused alteration of arfvedsonite and leached HFSE from the granite or incorporated these elements from the magma. At the same time, heat from the pluton triggered meteoric fluid convection. This fluid acquired Ca from the country rock, caused Ca metasomatism and created porosity in the apical parts of the pluton (cf. Figs. 12 and 17). Interaction of the two fluids caused precipitation of fluorite and, because of the consequent buffering of a_{F^-} to low values, precipitation of HFSE minerals.*

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