

THE ORIGIN OF RARE MINERALS IN THE KIPAWA SYENITE COMPLEX, WESTERN QUEBEC*

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ABSTRACT

The Kipawa Syenite Complex, a concordant, folded sheet of mildly peralkaline kataphorite–aegirine syenite less than 200 m thick, can be traced for more than 50 km in the Grenville Province of western Quebec. Several lenses of biotite–aegirine nepheline syenite up to 200 long by 30 m thick occur within the complex. Along its lower margin, a region 1300 m long by 5 m thick consists of diopside and magnesian richterite-rich schist with large amounts of eudialyte, agrellite and other rare minerals. This skarn-like lens is fringed on its upper side by alkali granite. The Kipawa Syenite Complex lies entirely within granitic gneiss derived from an Archean protolith and emplaced at 1247 ± 47 Ma (Guo & Dickin 1994). The complex, emplaced about 1240 Ma ago, consists mainly of deformed alkaline igneous rocks (plutonic, volcanic, or both) as shown by its geochemical signature. Marble-bearing sedimentary rocks were thrust-imblicated with the complex during northwest-directed tectonic transport at amphibolite-facies (690°C, 9.5 kilobars) metamorphic conditions. Mechanical mixing during this process, followed by alkali metasomatism and local anatectic melting, produced skarn-like rocks (contents of CaO and MgO of 12 and 10 wt.%) containing the rare minerals. U–Pb dating of zircon from the rare mineral occurrence shows that rare mineral formation occurred at 994 ± 2 Ma. Alkalis, Zr, REE, Be and other elements were redistributed on scales ranging from meters to kilometers by a combination of fluid flow and anatectic melting in the presence of F-rich brines.

Keywords: alkali syenite, metasomatism, metamorphism, amphibolite facies, magma mixing, Kipawa complex, Quebec.

SOMMAIRE

Le complexe syénitique à kataphorite + aegyrine de Kipawa, situé dans la partie occidentale du Québec, dans la province du Grenville, se présente en feuillet concordant plissé, d'une épaisseur de moins de 200 m, traçable pour plus de 50 km. Le massif comporte plusieurs lentilles de syénite néphélinique à biotite + aegyrine atteignant 200 m de longueur et 30 m d'épaisseur. Sur 1300 m de longueur et 5 m d'épaisseur le long du contact inférieur, la roche est un schiste à diopside + magnésiorichterite avec une forte proportion de minéraux rares, par exemple eudialyte et agrellite. Le contact supérieur de cette lentille, qui ressemble à un skarn, longe un granite alcalin. Le complexe se trouve entièrement encaissé par un gneiss granitique dérivé d'un protolithe archéen et mis en place il y a 1247 ± 47 million d'années (Guo et Dickin 1994). Il comporte des roches ignées hyperalcalines d'origine plutonique ou volcanique, ou les deux, selon les caractères géochimiques. Toutes ces roches ont été fortement déformées lors du charriage tectonique de ce socle vers le nord-ouest à des conditions typiques du faciès amphibolite (690°C, 9,5 kilobars). Un mélange mécanique pendant ce processus, suivi d'une métasomatose alcaline et d'anatexie locale, sont responsables de la formation de ces roches, qui rappellent des skarns (teneurs en CaO et MgO de 12 et 10% poids) contenant les minéraux exotiques. Une datation U–Pb sur zircon montre que la formation des minéraux exotiques a eu lieu à 994 ± 2 Ma. Les alcalins, le Zr, les terres rares, le Be et autres éléments ont été redistribués sur une échelle métrique ou kilométrique suite à un flux de fluide et à une fusion anatectique en présence de saumures riches en fluor.

(Traduit par la Rédaction)

Mots-clés: syénite alcaline, métasomatose, métamorphisme, faciès amphibolite, mélange magmatique, complexe de Kipawa, Québec.

INTRODUCTION

Large amounts of eudialyte, agrellite and numerous other rare minerals have been collected for more than thirty years from a site on the Kipawa River in western

Quebec (Hicks 1959, Berry *et al.* 1972, Aarden & Gittins 1974, Gittins *et al.* 1976, Plant & Roberts 1979, Ansell *et al.* 1980, Roberts & Bonardi 1983). Reconnaissance mapping (Lyll 1959, Rive 1973, Tremblay-Clark & Kish 1978) showed that this site lies on the fringe of a folded, sheet-like body of syenite (the Kipawa Syenite Complex). Since eudialyte commonly occurs in peralkaline syenite (Sørensen 1974),

* Geological Survey of Canada contribution number 57638.

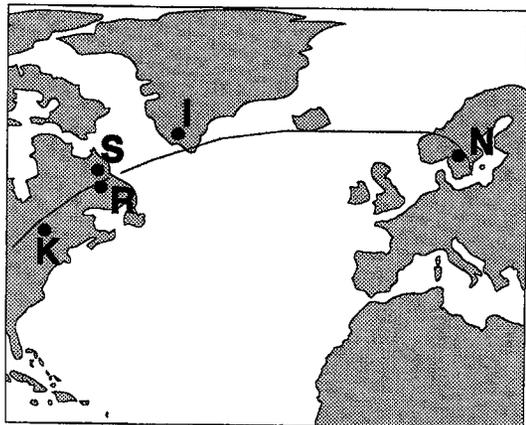


FIG. 1. Location of the Kipawa Syenite Complex relative to the Grenville Front and to other Proterozoic peralkaline complexes. K: Kipawa Syenite Complex, R: Red Wine Complex (Curtis and Currie 1983), S: Strange Lake Complex (Currie 1985), I: Ilfmaussaq (Ferguson 1970), N: Norra Karr (Adamson 1944). The Kipawa, Red Wine and Norra Karr complexes are all metamorphosed at the amphibolite grade.

discussions of the Kipawa Syenite Complex have generally assumed an igneous origin for both the complex and the rare minerals (Tremblay-Clark & Kish 1978, Sinclair *et al.* 1992, Allan 1992), a plausible view since several igneous peralkaline undersaturated complexes of Precambrian age occur along the Grenville Front (Fig. 1). However, the present mineralogy of the Kipawa Syenite Complex resulted from high-grade metamorphism (Gittins *et al.* 1976, Currie & Gittins 1993) without obvious igneous relics, and the geochemistry of some eudialyte-rich rocks strongly suggests a metasomatic origin (Currie & van Breemen 1994). This contribution summarizes present knowledge bearing on the origin of the Kipawa Syenite Complex and of the rare minerals it contains.

GEOLOGICAL SETTING

The Kipawa Syenite Complex lies on the northern fringe of the Grenville Province of the Canadian Shield, in a region consisting of northwesterly transported allochthons derived from the Grenville Province and parautochthonous fault-slices derived from structurally underlying Archean rocks of the Superior Province (Easton 1992, Guo & Dickin 1994). Boundaries between allochthons and parautochthonous rocks are not known in detail (compare Kellett *et al.* 1994), but extrapolation from the compilation of Easton (1992) and reconnaissance work by A. Davidson (pers. comm., 1993) suggest that the Kipawa Syenite Complex lies in the structurally lowest part of

the Tomiko Terrane of Easton (1992), which is characterized by middle Proterozoic (~1600–1700 Ma) metasedimentary rocks and plutonism at about 1250 Ma. Most rocks in the vicinity of the Kipawa Syenite Complex exhibit evidence of high strain followed by prolonged annealing at high temperature, to produce a coarse granoblastic fabric. Dips of gneissosity and foliation are commonly gentle, and kilometer-scale open folds of the gneissosity can be readily mapped. However, small-scale observations in areas of good outcrop demonstrate at least three stages of isoclinal folding and ductile faulting formed during low-angle, northwest-directed tectonic transport (Currie & Gittins 1993).

GEOLOGY OF THE KIPAWA SYENITE COMPLEX AND ENCLOSING ROCKS

The Kipawa Syenite Complex (Fig. 2) lies within a well-defined sequence comprising basal granitoid gneiss (Kikwissi gneiss), structurally overlain by a thin unit of metasedimentary rocks (including feldspathic quartzite, amphibolite, thin marble, and peraluminous migmatitic gneiss), a thick unit of biotite–magnetite granitic gneiss (Red Pine Chute gneiss, Villedieu pluton of Guo & Dickin 1994), and an upper unit of quartzite [possibly equivalent to the Mattawa Quartzite of Easton (1992)]. The syenite is entirely contained within the Red Pine Chute gneiss, forming a layer near the base of this unit that can be traced around a major syncline–anticline pair.

The Kikwissi gneiss comprises distinctive grey, massive to weakly foliated, biotite-dominant granitoid gneiss characterized by poikilitic oval clots of biotite up to 5 cm across, riddled with tiny inclusions of plagioclase and epidote. The rock exhibits minor migmatization, with feldspar-rich leucosomes 3–7 cm wide rimmed by a narrow, biotite-rich margin. At distances of more than two kilometers from the Kipawa Syenite Complex, the gneiss is trondhjemitic, grey green and almost massive. Closer to the syenite, the gneiss becomes strongly layered, with abundant K-feldspar, pink coloration, and occasional hornblende porphyroblasts. On its southwestern side, the gneiss is separated from the overlying metasedimentary sequence by a 10-m-wide zone of mylonite, but subconcordant dikes of Kikwissi gneiss cut the metasedimentary rocks north of Lac Sairs. Guo & Dickin (1994) reported a Sm–Nd model age of 2.70–2.77 Ga for the Kikwissi gneiss, and interpreted it to be derived from an Archean Superior Province protolith that was remobilized in late Proterozoic time.

The metasedimentary sequence structurally overlying the gneiss comprises a heterogeneous assemblage dominated by biotite schist and gneiss. Several layers of coarse-grained marble, up to 5 m thick, contain large crystals of tremolite (up to 30 by 4 by 4 cm) lying in foliation planes and accompanied by granular pale

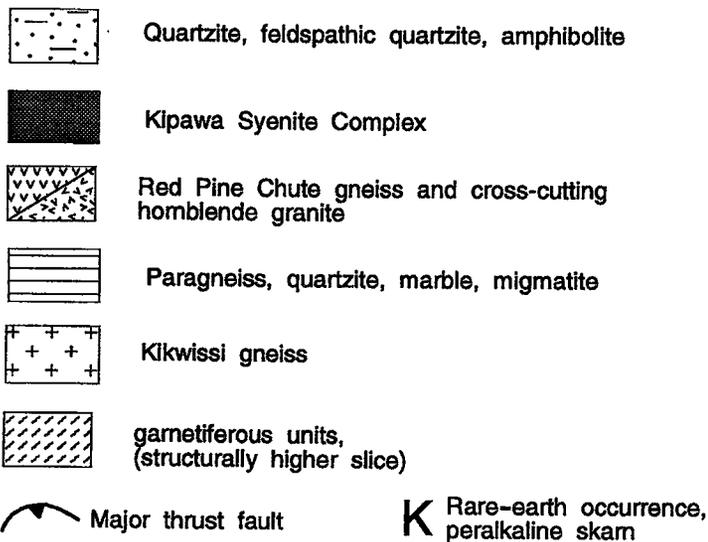
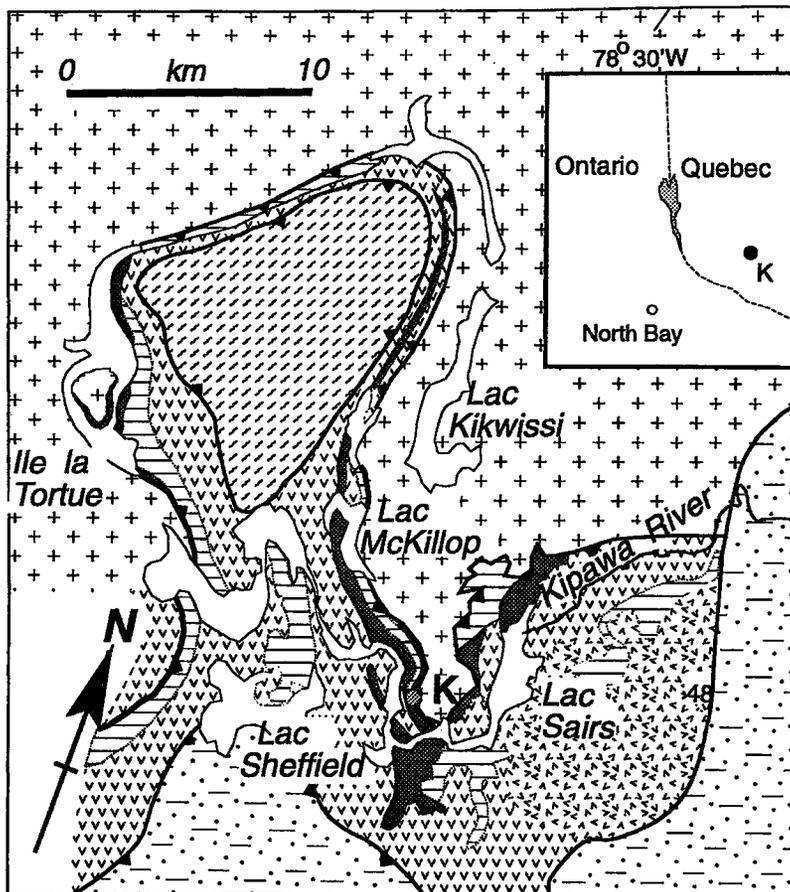


FIG. 2. Simplified geological map of the Kipawa Syenite Complex and surrounding units.

green diopside and minor phlogopite. Feldspathic quartzite, commonly rich in muscovite, is abundant, but the bulk of the unit consists of heterogeneous biotite gneiss and muscovite-bearing migmatite. The biotite gneiss ranges from garnetiferous biotite amphibolite, possibly developed from mafic flows or intrusions, to rather leucocratic, compositionally layered quartz – feldspar – biotite gneiss. All varieties are cut by abundant pink, boudined dykes of granitic pegmatite. The migmatite is a relatively leucocratic rock that grades to muscovite quartzite, and consistently contains 30–50% of pygmatically folded boudins of quartz and feldspar up to 100 by 20 cm. Both kyanite and sillimanite have been reported from this unit (Rive 1973). The contact between this migmatitic material and the Red Pine Chute gneiss seems to be entirely gradational, but is very poorly exposed.

The Red Pine Chute gneiss forms a homogeneous mass of fine- to medium-grained (1–2 mm), granoblastic biotite–magnetite granite gneiss with a strike length of more than 30 km and a width across strike of up to 2 km. The foliation is marked by thin

discontinuous foliae of fine-grained, disseminated biotite, which become thicker and more continuous toward the base and top of the unit. A characteristic feature of the gneiss is the presence of a hematitic halo around the biotite, and less commonly around magnetite, which stain the surrounding quartz grains, producing a red-spotted surface. Magnetite tends to have a platy habit, and may have been produced by an earlier oxidation of biotite. The gneiss consistently contains a small amount of muscovite (<2%), and some specimens contain pinhead-sized grains of garnet. The Red Pine Chute gneiss locally contains 15–20% by volume of pink pegmatitic layers, 1 to 5 cm thick, bounded by a biotite-rich rim a few mm thick. Guo & Dickin (1994) reported a Pb–Pb emplacement age of 1247 ± 47 Ma for the Red Pine Chute gneiss (their Villedieu pluton), and a Sm–Nd model age of 2.5 Ga; they interpreted it to be Archean material remobilized at ~ 1.25 Ga.

The Red Pine Chute gneiss contains within it the Kipawa Syenite Complex and a thin layer of altered mafic rocks. The Kipawa Syenite Complex forms a layer within the Red Pine Chute gneiss no more than

TABLE 1. COMPOSITION OF MINERALS IN THE KIPAWA SYENITE COMPLEX AND RELATED UNITS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO ₂ wt.%	42.06	49.86	34.73	50.32	51.49	54.18	52.79	34.63	53.20	35.72	42.57	37.09	37.48	38.26	36.05	34.68
TiO ₂	1.95	0.75	2.74	0.31	3.15	0.18	0.39	0.27	0.32	0.28	1.28	3.44	0.03	1.61	2.57	3.44
Al ₂ O ₃	6.09	3.15	11.22	0.18	1.42	1.75	1.27	16.59	1.09	17.10	14.16	16.32	21.65	14.46	15.15	13.76
FeO	29.98	23.83	34.39	34.93	24.96	8.61	11.91	8.40	6.93	8.66	14.92	16.19	28.47	18.16	18.03	29.58
MnO	1.05	0.73	1.03	1.06	1.30	0.81	0.19	0.34	0.22	0.35	0.11	0.08	1.48	0.30	1.10	0.74
MgO	2.02	1.07	2.73	0.92	0.38	16.49	10.49	20.98	13.29	21.64	11.13	14.44	5.52	9.04	14.38	2.91
CaO	4.83	10.81	0.06	0.43	2.58	4.72	22.57	0.19	24.65	0.20	10.47	0.02	5.04	11.01	0.01	0.02
Na ₂ O	5.70	7.77	0.07	5.60	12.41	6.89	0.22	0.18	0.22	0.19	2.10	0.23	–	3.11	0.46	0.06
K ₂ O	3.33	0.22	10.00	1.58	0.03	2.08	0.02	9.74	0.02	10.05	0.71	9.51	–	1.09	10.02	9.82
Cl	0.02	–	0.06	0.27	–	0.04	–	0.02	–	0.53	0.40	0.45	–	0.40	0.27	0.43
F	0.68	–	0.84	1.48	–	4.22	–	6.52	–	0.17	0.01	0.15	–	0.33	0.87	1.68
Cl+F+O	-0.30	-0.38	-0.71	-1.87	-2.88	-0.19	-0.09	-0.17	–	-0.22	-0.44	-0.84	–	–	–	–
Total	97.41	98.19	97.49	96.57	97.72	98.10	99.85	94.98	99.94	94.70	97.77	97.75	99.67	97.55	97.47	96.28
Si	6.862	1.932	2.859	7.954	1.962	7.924	1.971	2.607	1.982	2.607	6.191	2.726	2.948	5.822	2.712	2.827
Ti	0.239	0.022	0.169	0.037	0.090	0.020	0.011	0.015	0.009	0.015	0.140	0.190	0.002	0.184	0.146	0.211
Al	1.171	0.144	1.089	0.034	0.064	0.302	0.056	1.472	0.048	1.471	2.428	1.414	2.007	2.593	1.343	1.322
Fe ³⁺	0.441	0.542	0.000	1.805	0.750	0.000	0.000	0.292	0.000	0.288	0.924	0.000	0.094	0.674	0.000	0.000
Fe ²⁺	3.650	0.230	2.368	2.812	0.046	1.053	0.372	0.237	0.216	0.240	0.891	0.995	1.778	1.637	1.135	2.017
Mn	0.145	0.024	0.072	0.142	0.042	0.100	0.006	0.022	0.007	0.022	0.014	0.005	0.099	0.039	0.007	0.051
Mg	0.492	0.062	0.334	0.217	0.022	3.595	0.584	2.355	0.738	2.355	2.413	1.582	0.648	2.051	1.613	0.354
Ca	0.845	0.449	0.006	0.073	0.105	0.740	0.903	0.015	0.984	0.016	1.631	0.002	0.425	1.796	0.001	0.002
Na	1.803	0.584	0.012	1.716	0.917	1.954	0.016	0.026	0.016	0.016	0.592	0.033	–	0.918	0.067	0.010
K	0.693	0.011	1.050	0.319	0.002	0.388	0.001	0.935	0.001	0.936	0.132	0.891	–	0.212	0.961	1.022
Cl	0.006	–	0.009	0.072	–	0.010	–	0.003	–	0.066	0.098	0.056	–	0.104	0.035	0.060
F	0.353	–	0.217	0.740	–	1.952	–	1.552	–	0.039	0.005	0.034	–	0.160	0.207	0.432

91092 Nepheline syenite; column 1: kataphorite, column 2: aegirine, column 3: biotite. This rock also contains albite (Ab_{99.2}), potassium feldspar (Or_{98.2}) and nepheline (Ks_{92.2}). 91125 Peralkaline granite; column 4: riebeckite, column 5: aegirine. This rock also contains potassium feldspar (Or_{98.2}) and albite (Ab_{99.2}). 91118 Peralkaline eudialyte amphibolite; column 6: magnesiochloritoid (average of 9), column 7: diopside (average of 7), column 8: phlogopite (average of 6). This rock also contains abundant eudialyte, minor potassium feldspar (Or_{97.1}), albite (Ab_{99.2}), britholite, mosandrite, and hordahlite. Note the high content of F in columns 6 and 8. 91113 Marble, column 9: diopside, column 10: phlogopite. Note the similarities in composition to pyroxene and phlogopite of 91106. 91110 Garnet amphibolite; column 11: pargasite (average of 8), column 12: biotite (average of 7), column 13: garnet (average of 9). This rock also contains plagioclase (An_{13.2}). These compositions were used to calculate the P–T conditions shown in Fig. 3 (see text for discussion). 91089 Scapolite amphibolite, column 14: pargasite (average of 5), column 15: biotite (average of 7). This rock also contains major scapolite (Me_{96.4}) and plagioclase (An_{18.2}). 91091 Red Pine Chute gneiss. Column 16: biotite. This rock also contains albite (Ab_{98.2}), potassium feldspar (Or_{98.2}) and magnetite. Amphibole compositions calculated on 46 charges, then reduced to (Si + Ti + Al + Fe + Mn + Mg) ≤ 13 by oxidation of iron. Pyroxene compositions calculated on 12 charges, then reduced to (Si + Ti + Al + Fe + Mn + Mg + Ca + Na + K) ≤ 4 by oxidation of iron. Biotite compositions calculated on 22 charges, then reduced to (Si + Ti + Al + Fe + Mn + Mg) ≤ 8 by oxidation of iron. Garnet compositions calculated on 24 charges, then reduced to (Si + Ti + Al + Fe + Mn + Mg + Ca + Na + K) ≤ 8 by oxidation of iron.

200 meters thick; it can be traced almost continuously for more than 50 kilometers along strike from Lac Sairs to Ile la Tortue. The presence of a thin layer (5 to 20 meters thick) of distinctive Red Pine Chute gneiss below the syenite can be observed along the west side of Lac Sheffield and at the rare mineral site, where its presence has been verified by drill-holes (Allan 1992). The large thickness of syenite (up to 1300 m) suggested by Lyall (1959) and Tremblay-Clark & Kish (1978) resulted from one or more of the following factors (a) structural complexity, such as accordion folding between Lac Sairs and Lac Sheffield and numerous small-scale recumbent folds at the rare mineral locality, (b) low dips, making determination of thickness difficult and unreliable, and (c) inclusion of unrelated hornblende-bearing granitoid rocks around Lac Sairs.

The margins of the syenite are marked by appearance of large crystals, clots and spindles of amphibole (kataphorite, Table 1), disappearance of quartz, and coarsening of grain size. The contact approximately coincides with the appearance of amphibole clots in the rock, but single crystals or polycrystalline spindles of kataphorite occur in the Red Pine Chute gneiss up to 100 meters above the syenite, although most are within 10 meters. Red amphibole-aegirine quartz syenite forms a narrow (<2 meters thick) fringe around the quartz-free rocks, except at the rare mineral locality, where quartz syenite and peralkaline granite may be up to 20 meters thick (see below). The syenite forms a coarse-grained xenomorphic, granular rock, commonly red to orange in color, with a variably developed $L>S$ fabric. The major minerals are twinned albite ($Ab_{99.8}$), fine string microcline perthite ($Or_{96.1}$ and $Ab_{99.6}$).

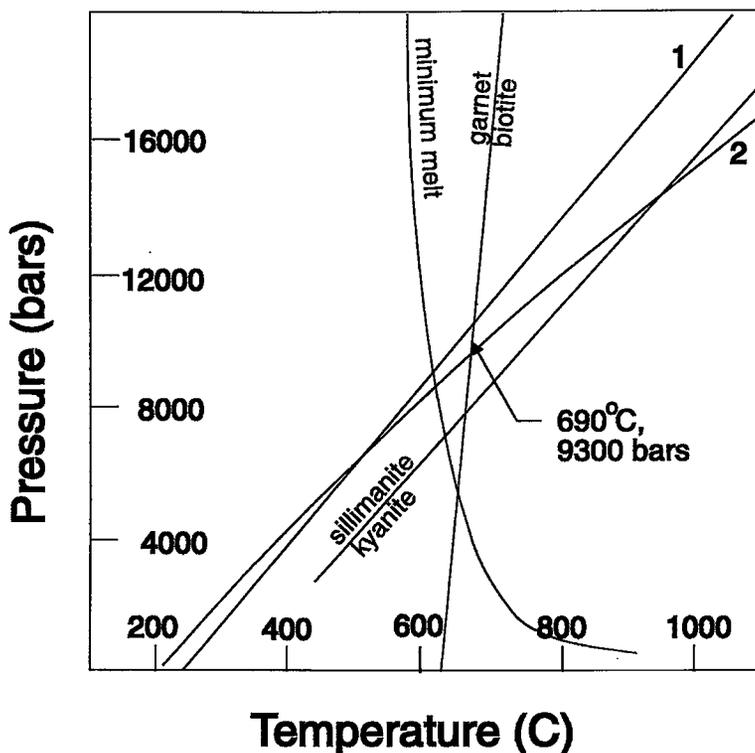


FIG. 3. Peak metamorphic conditions in the Lac Sairs region, compared to experimental data for beginning of melting of quartz + albite + potassium feldspar mixtures in the presence of excess water (labeled "minimum melt") and the equilibrium of kyanite and sillimanite. The curve labeled "garnet-biotite" gives P and T calculated from these minerals, whereas curve 1 gives data from the equilibrium 4 grossular + 2 pyrope + 12 quartz + 3 tschermakite = 3 tremolite + 12 anorthite, and curve 2, data from the equilibrium 2 grossular + pyrope + 18 quartz + 3 pargasite = 3 tremolite + 6 anorthite + 3 albite. The best estimate of equilibrium P-T, as given by the method of Mäder & Berman (1992), is 690°C and 9300 bars. Note that the beginning of melting may be at lower temperatures in the presence of F-rich fluids.

riebeckite, aegirine and minor biotite (see Table 1 for compositions). Fluorite and titanite are common accessories. Although the feldspar fabric is coarse, xenomorphic and granoblastic, the compositions of the coexisting feldspars suggest that this rock has re-equilibrated down to relatively low temperatures.

The syenite complex contains within it boudin-like masses of biotite-aegirine syenite up to 200 meters long that contain nepheline ($Ks_{23,0}$) or products of its alteration in amounts ranging from traces to more than 25%. Molybdenite and pyrite occur ubiquitously in trace amounts. The combination of coarse granoblastic texture and disintegration around sulfides creates exposures that are essentially *grus*.

Rare lenses of biotite syenite gneiss up to 3 m thick occur in the Red Pine Chute gneiss above the Kipawa Syenite Complex. These layers exhibit sharp but conformable boundaries, and resemble the surrounding gneiss, except for low quartz content, rare small crystals of amphibole and, in some cases, a distinctive orange color. Since they closely resemble their host, some layers may have been overlooked during mapping. About 25 to 30 m above the Kipawa Syenite Complex, a persistent layer of scapolitized biotite amphibolite extends for more than 20 km, although it is never more than 20 m thick. Like the Kipawa Syenite Complex, its boundaries are sharp, but completely conformable with the surrounding granitoid gneiss. The rock consists of strongly aligned amphibole (pargasite, Table 1) and scapolite crystals up to a cm long with varying amounts of interstitial, partially scapolitized plagioclase (An_{33}), biotite and titanite. There is a moderate foliation, but the rock exhibits a strong $L > S$ fabric.

The upper quartzite unit is not exposed in the immediate vicinity of the Kipawa Syenite Complex, but southwest of Lac Sheffield, it rests on the Red Pine Chute gneiss with a sharp, structurally conformable contact. The quartzite contains a variable but low tenor of microcline and muscovite (<5%), and commonly exhibits relics of cross-bedding defined by thin lenses of opaque minerals.

A coarse, almost massive, hornblende granite cuts both the Red Pine Chute gneiss and the meta-sedimentary sequence in and east of Lac Sairs. The contact is largely under water, but dikes of hornblende granite up to 5 meters wide cut both older units on the west shore of the lake.

Six boudins of gabbro and ultramafic rocks occur within the Red Pine Chute gneiss and the hornblende granite. The boudins range from 10 to 200 m in length and 5 to 50 m in width, with the enclosing gneiss wrapping around them. The rock type in the boudins varies from massive leucogabbro through ophitic-textured gabbro to coronitic melagabbro. These are the only rocks in the Kipawa region known to preserve relics of a primary igneous texture. Their form, petrography and chemistry strongly suggest derivation

from dikes of the Sudbury swarm, emplaced about 1235 Ma (Dudas et al 1994, K. Bethune, pers. comm.). A quantitative estimate of P-T conditions subsequent to emplacement was obtained from a layer of coronitic melagabbro in Lac Sairs in which the minerals biotite, amphibole and garnet coexist in apparent equilibrium. Using the method of Mäder & Berman (1992), this assemblage of minerals, whose compositions are given in Table 1, gives a P-T estimate of 690°C and 9300 bars (Fig. 3), in reasonable accord with the observation of coexisting kyanite and sillimanite, and the occurrence of partial melt (migmatite). It agrees with the conclusions of Anovitz & Essene (1990) that the Tomiko terrane underwent metamorphism at temperatures of <700°C and pressures below 9000 bars.

GEOLOGY OF THE RARE MINERAL OCCURRENCE

The geology in the vicinity of the rare mineral occurrence (Fig. 4) has been previously described by Allan (1992) and Currie & Gittins (1993), on the basis of extensive trenching and drilling by Unocal Canada to assess the rare-earth potential of this prospect. Prior to trenching, rock exposure was insufficient for a detailed description. In general, the rocks strike northwest and dip gently (10–30°) to the southwest, but mesoscale, recumbent folds are ubiquitous (Fig. 5). From the structural base upward, the apparent succession of units is (1) Kikwissi gneiss, (2) 2–10 m of Red Pine Chute gneiss, (3) 0–2 m of pink Kipawa Syenite Complex with lineated amphibole, (4) 0–5 m of marble and calc-silicate rocks, (5) 2–10 m of melanocratic amphibole schists with eudialyte and agrellite, (6) 10–50 m of peralkaline granite and quartz syenite, and (7) Red Pine Chute gneiss. Comparing this succession with that normally found around the Kipawa Syenite Complex, two differences are apparent. Firstly, the metasedimentary sequence is missing between the Kikwissi gneiss and Red Pine Chute gneiss. Secondly, “extra” layers of calc-silicate rocks, peralkaline amphibole schist and peralkaline granite occur above the syenite.

The Red Pine Chute gneiss and Kikwissi gneiss are mylonitic with well-developed quartz ribbons and S-C fabrics (Piasecki 1988), and their contact is interpreted to be a relatively late, northwest-directed thrust. The overlying syenite is little deformed. The contact between the syenite and an overlying marble and calc-silicate unit, which contacts syenite over 1100 m of the 1300 m strike length exposed by the Unocal Canada trenches, is sharp and conformable, but the marble is complexly small-folded and locally contains meter-scale blocks of diopside- and phlogopite-rich material that are rotated relative to the matrix. This contact is interpreted to be a ductile thrust. The marble is coarse-grained magnesian calcite with various amounts of tremolite, diopside, phlogopite (Table 1)

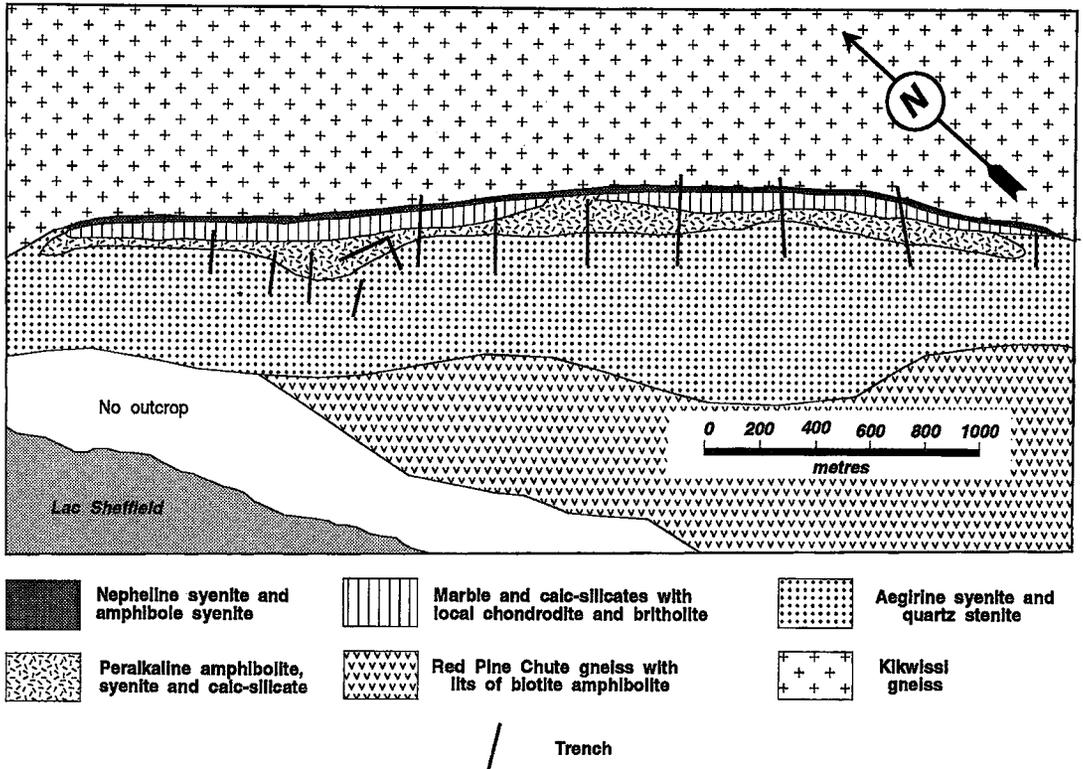


FIG. 4. Geological map of the rare mineral occurrence within the Kipawa Syenite Complex.

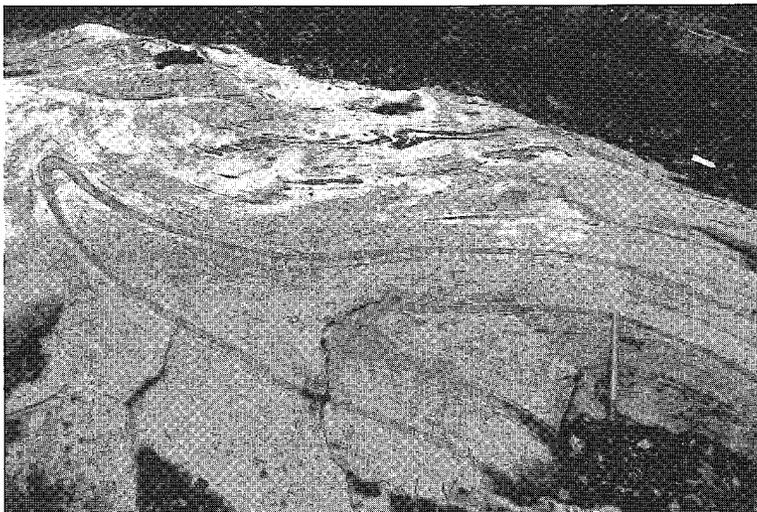


FIG. 5. Small-scale recumbent fold in alkali granite. The hammer handle is 70 cm long.

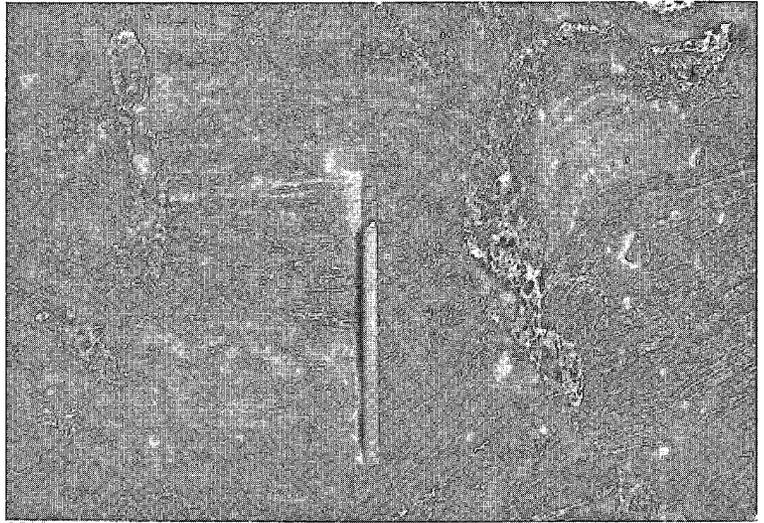


FIG. 6. Eudialyte-agrellite boudins. The right-hand boudin is folded around a small F_1 fold. The hammer handle is 70 cm long.

and graphite. There is no sharp contact between calc-silicate marble and overlying schists rich in amphibole and pyroxene. An upper fringe of the marble, 15–30 cm wide, rich in orange chondrodite + norbergite, locally contains britholite crystals up to 3 cm across, and the contact with amphibole-rich rocks is commonly marked by a glimmerite selvage up to 5 cm wide. However rotated meter-scale lenses and boudins of granular phlogopite–diopside amphibolite with abundant fluorite occur on both sides of the boundary. Some boudins contain eudialyte and other rare minerals around their margins. The rocks containing most of the rare minerals consist of thinly fissile, intricately folded amphibole-rich schists with a color index of 60–90. These rocks consist largely of steel-blue magnesiorichterite and Na-poor diopside (Table 1), with lesser amounts of phlogopite, microcline ($Or_{96,8}$), albite ($Ab_{99,6}$) and local traces of altered nepheline. Rare minerals may be disseminated, but tend to be concentrated in nebulous pegmatitic, massive patches rich in fluorite. Agrellite–eudialyte pegmatites form boudin fillings (Fig. 6) or concordant veins (Fig. 7).

The contact between the amphibolite and (structurally) overlying pink peralkaline quartz syenite and granite is gradational as a result of increasing content of feldspar, and finally of quartz. The peralkaline granite and quartz syenite consist of albite, microcline perthite and a complex assemblage of mafic minerals, with biotite in various stages of breakdown to magnetite, both veined and replaced by granular aegirine and, finally, by riebeckite (Table 1). Zircon and pyrochlore crystals up to 2 centimetres across form distinctive accessory minerals. The near-massive



FIG. 7. Concordant eudialyte-agrellite vein in peralkaline amphibolite schist. The steep cleavage parallel to the vein is axial-planar to an F_1 fold.

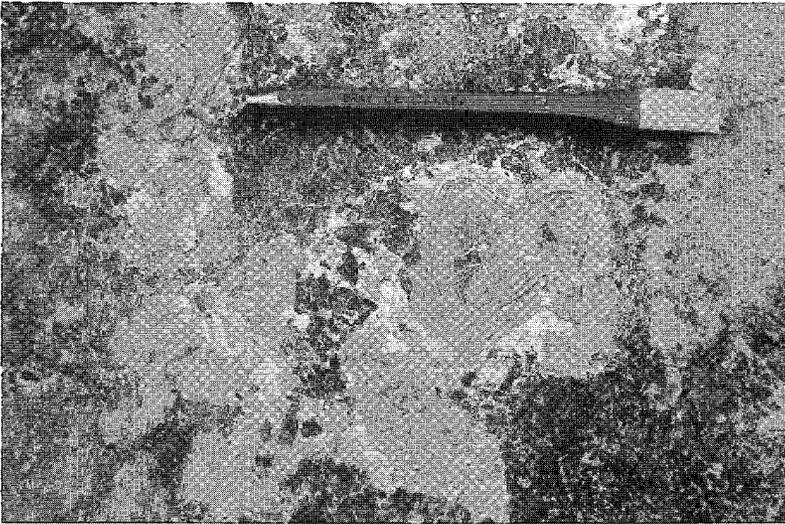


FIG. 8. Pegmatitic patch of large lilac-colored crystals of zircon in peralkaline amphibolite. Despite the spectacular zoning, these crystals are chemically homogeneous. They were chiseled directly from this outcrop for analysis, and variously abraded to produce the fractions shown in Fig. 9. Chisel is 10 cm long.

peralkaline rocks exhibit cross-cutting relations with amphibole schist (Allan 1992), but grade to Red Pine Chute gneiss, with which their original mineral assemblage was identical.

Among the more abundant unusual minerals,

britholite and chondrodite are concentrated in marble or calc-silicate masses, eudialyte, agrellite and miserite occur mainly within amphibole schist, and zircon, vlasovite and hiortdahlite occur mainly in peralkaline granite. Fluorite and mosandrite are ubiquitous, but

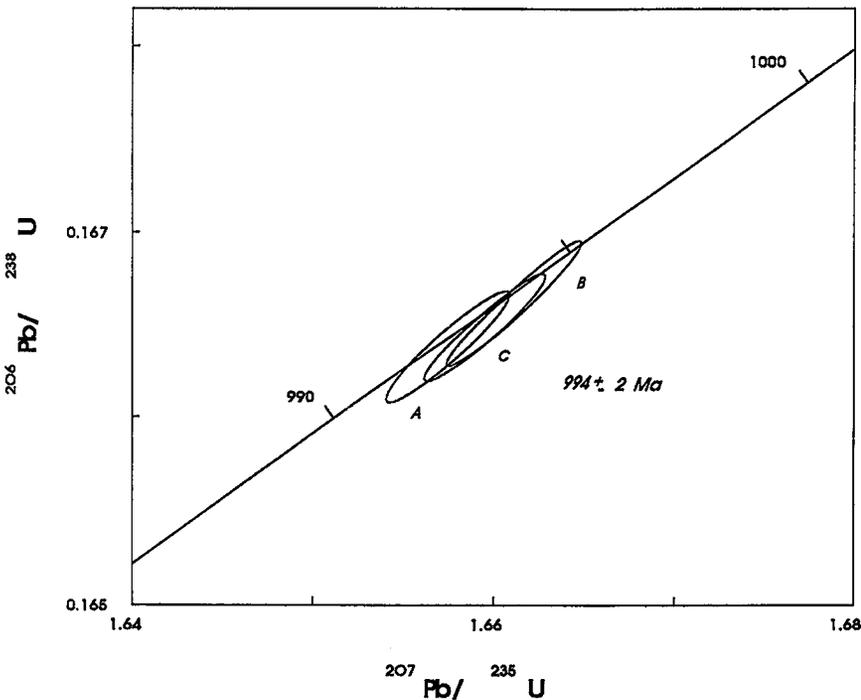


FIG. 9. Concordia diagram of the age of zircon shown in Fig. 8.

TABLE 2. U-Pb ZIRCON ISOTOPIC DATA, KIPAWA SYENITE COMPLEX, QUEBEC

1	2	3	4	5	6	7	8	9	10	11
A	70	405	79	23.549	13	21.2	0.16638 ± 0.09	1.6575 ± 0.10	0.07225 ± 0.03	993.0 ± 1.4
B	70	481	98	24.447	14	24.7	0.16662 ± 0.10	1.6612 ± 0.11	0.07231 ± 0.03	994.6 ± 1.2
C	80	412	82	10.775	29	23.2	0.16649 ± 0.09	1.6595 ± 0.10	0.07229 ± 0.03	994.2 ± 1.3

Column 1: Fraction; 2: weight in milligrams; fractions are nonmagnetic at a side slope of 1° and 1.7 Å. 3: Concentration of U (ppm). 4: Concentration of radiogenic Pb (ppm). 5: Measured $^{206}\text{Pb}/^{238}\text{U}$ ratio, corrected for spike and fractionation. 6: Concentration of common lead, corrected for spike and fractionation. 7: ^{209}Pb ; 8: $^{206}\text{Pb}/^{238}\text{U}$ corrected for blank Pb and U, common Pb; 9: $^{207}\text{Pb}/^{235}\text{U}$ corrected for blank Pb and U, common Pb; 10: $^{207}\text{Pb}/^{206}\text{Pb}$ corrected for blank Pb and U, common Pb; 11: $^{207}\text{Pb}/^{206}\text{Pb}$ model age.

sparser in quartz-bearing rocks. Large, euhedral crystals of zircon exhibit obvious zoning in specimen (Fig. 8), but proved to be remarkably homogeneous when examined by electron microprobe. Zircon from a massive pegmatitic patch in the amphibole schist gave a concordant U-Pb date of 994 ± 2 Ma (Fig. 9, Table 2). Two titanite fission-track ages from the same area gave 1008 ± 32 Ma and 1020 ± 41 Ma (G.N. Eby, pers. comm., 1991), dating closure at about 300°C.

STRUCTURE OF THE KIPAWA SYENITE COMPLEX

The Kipawa Syenite Complex outcrops on both limbs of an open, gently doubly-plunging syncline-anticline pair that can be readily seen on large-scale geological maps (Fig. 2). Small-scale studies at the rare mineral occurrence show that these folds represent at least a third period of folding superimposed on earlier deformation. The oldest recognizable folds (F_1) form recumbent, sheath-like structures with amplitudes up to 5 meters, whose axes trend 125–145° and plunge gently to the southeast, with local reversals to northwest plunges. The apparent vergence of these folds reverses across the axial plane of F_3 folds. Agrellite-eudialyte pegmatites (Fig. 6) occur in (folded) cleavage axial planar to F_1 folds. Axes of F_2 folds trend about 210°. The folds are recumbent, north-verging and asymmetrical, with long upright limbs and short overturned limbs. Many F_1 and F_2 folds with amplitudes from 1 to 10 meters can be mapped in trenches on the rare mineral occurrence, suggesting that the simple cross-sections shown by Allan (1992) do not give a realistic representation of the structure of the occurrence.

F_3 structures form the kilometer-scale open folds noted above. Smaller folds related to these structures appear in the vicinity of the rare mineral occurrence as mesoscale chevron-style folds with wavelengths of a few cm to a few hundred meters, which produce a zig-zag pattern of the syenite across the major antiformal nose east of Lac Sheffield. A pervasive mineral and stretching lineation associated with F_3 folding plunges 5–20° toward 125 to 140°. This plunge locally reverses to northwest, notably around the klippe in the core of the major syncline. Brittle or semibrittle shatter zones up to a meter thick cut F_3 structures.

The structural history and style of the Kipawa region are compatible with prolonged southeast-over-north-west thrusting under ductile conditions. On this model, F_1 folds have been completely rotated into the transport direction, whereas the asymmetry of F_2 folds indicates the transport direction. F_3 folds are assumed to result from lateral constriction of an advancing mass due to passage over irregularities or prominences in the substrate. Late brittle deformation indicates the persistence of high stresses after cooling.

GEOCHEMISTRY

Approximately 1-kg samples were collected from surface outcrops; we took care to avoid obvious veins and alteration. Samples were slabbed, obvious weathered material cobbled off, and after cleaning with distilled water and acetone, samples were reduced to powder in a jaw crusher followed by a rotary pulverizer with ceramic plates, and grinding in a ceramic mortar.

Concentrations of major elements were determined mainly by X-ray-fluorescence analysis of fused disks in the Geological Survey laboratories. The concentration of Fe^{2+} was determined by titration, and that of F and Cl, by ion chromatography. Replicate analyses of USGS standard samples indicate a precision of $\pm 2\%$ for major elements, except H_2O , CO_2 , F and Cl, for which a precision of $\pm 5\%$ is estimated. Concentrations of Be, Co, Cr, Ni, Rb, Sc, V, Cu, Zn and Ga were determined by X-ray fluorescence on pressed powder pellets, with an estimated precision of 5%. Concentrations of Ba, Nb, Zr, the rare-earth elements (REE), Y, Hf, Ta and Th were determined by inductively coupled plasma – mass spectrometry (ICP-MS) in the laboratories of Memorial University of Newfoundland after Na_2O_2 sintering, with an estimated precision of $\pm 2\%$. Representative results are displayed in Table 3. Complete results are available on request from the senior author and from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1S 0S2.

All compositions of the Kipawa Syenite Complex are mildly to moderately peralkaline [(Na + Al)/K of 1.01 to 1.59], with the degree of peralkalinity increasing in the order nepheline syenite, syenite, quartz syenite and peralkaline granite. The present

TABLE 3. SELECTED MAJOR- AND TRACE-ELEMENT DATA FOR THE KIPAWA SYENITE COMPLEX

	1	2	3	4	5	6	7	8	9	10
SiO ₂	57.47	64.12	70.51	52.20	73.60	67.01	71.37	2.61	16.53	44.30
TiO ₂	0.31	0.37	0.42	0.27	0.36	0.56	0.27	0.03	0.04	3.16
Al ₂ O ₃	19.38	15.57	10.92	6.00	13.63	13.89	15.43	0.30	1.10	17.74
Fe ₂ O ₃	2.09	3.10	5.18	3.85	1.71	3.35	0.44	0.19	0.21	3.89
FeO	3.79	1.82	0.76	2.21	1.03	2.46	1.07	0.62	0.78	10.18
MnO	0.16	0.11	0.09	0.26	0.03	0.13	0.02	0.04	0.06	0.18
MgO	0.45	0.34	0.24	10.17	0.46	0.59	0.62	20.38	20.37	5.61
CaO	1.77	1.32	0.43	14.53	1.27	1.27	2.31	30.20	22.71	8.27
Na ₂ O	9.10	7.50	6.18	4.55	4.07	4.53	6.03	0.03	0.20	3.90
K ₂ O	4.36	4.85	3.64	1.88	3.14	3.23	1.12	0.09	0.83	1.14
H ₂ O	0.70	0.35	0.46	0.85	0.66	0.47	0.53	0.41	0.00	1.49
CO ₂	0.10	0.08	0.03	0.16	0.10	0.29	0.10	45.27	34.72	0.10
P ₂ O ₅	0.11	0.11	0.12	0.34	0.04	0.07	0.07	0.02	0.01	0.47
F	0.28	0.34	0.11	2.31	0.07	0.07	0.06	0.03	3.46	0.08
Cl	0.04	0.02	0.01	0.04	0.02	0.03	0.02	0.03	0.03	0.09
F+Cl=O	-0.13	-0.16	-0.05	-0.99	-0.03	-0.04	-0.03	-0.02	-1.46	-0.05
Total	99.98	99.84	99.05	98.63	100.16	99.53	99.43	100.23	99.59	100.55
Be	7.2	10.4	18.5	67.0	4.5	2.4	3.6	4.3	3.5	1.2
Zr	35	37	34	26	19	23	19	0	4	21
Ga	949	592	6140	1336	239	273	167	6.7	11	146
Hf	19.17	15.54	161	46.29	5.75	6.39	4.09	0.16	0.39	3.06
Nb	41	26	12	105	16	17	12	1.64	11	17
Ta	1.59	0.89	0.59	7.1	0.50	0.66	0.58	0.03	0.27	0.77
Sr	300	76	76	247	293	78	616	106	202	814
Rb	140	210	274	301	109	85	26	10	178	21
Th	6.89	15.98	8.41	47.20	10.06	5.09	5.56	0.10	0.14	1.37
Ba	1859	491	207	253	604	720	313	10.6	547	573
Y	109	106	37	567	27	33	23	14	129	18
La	99.66	103.5	37.41	457.0	56.77	39.79	28.63	14.60	114.3	18.89
Ce	215.0	227.1	69.62	898.1	102.7	90.47	65.51	24.93	204.0	43.19
Pr	25.77	21.51	9.31	100.9	12.48	10.65	6.55	2.38	20.49	5.76
Nd	98.75	102.2	26.82	391.9	45.09	42.26	24.42	7.08	67.97	25.22
Sm	20.52	20.07	5.18	79.61	7.81	8.02	4.75	1.28	11.93	5.04
Eu	4.38	2.39	0.54	9.45	1.17	1.59	0.92	0.25	1.47	1.89
Gd	18.67	17.49	4.47	75.70	6.03	6.73	3.92	1.00	11.47	4.58
Tb	3.15	2.59	0.78	12.93	0.84	0.99	0.63	0.18	2.02	0.61
Dy	22.33	18.41	5.44	90.42	5.10	6.27	4.14	1.22	16.35	3.66
Ho	4.58	3.85	1.29	18.91	0.97	1.27	0.88	0.24	3.90	0.70
Er	13.95	11.99	4.87	57.12	2.85	3.76	2.61	0.80	14.00	2.04
Tm	2.06	1.82	0.98	8.58	0.42	0.57	0.40	0.14	2.29	0.27
Yb	13.93	13.37	9.43	57.11	2.83	3.97	2.53	0.76	14.68	1.66
Lu	2.00	1.87	1.89	8.54	0.41	0.56	0.34	0.07	1.86	0.24
Sc	4.2	3.4	2.2	6.3	3.3	4.4	2.3	0.5	0.5	12.0

Compositions expressed in wt. % (major elements, expressed as oxides, with F and Cl) and ppm (trace elements). 1. Nepheline syenite (average of 2). 2. Syenite (average of 4). 3. Peralkaline granite (average of 3). 4. Peralkaline skarn (average of 4). 5. Red Pine Chute gneiss (average of 3). 6. Kikwissi gneiss (average of 4). 7. Tromdljemeite (average of 3). 8. Marble. 9. Chondroite marble. 10. Mafic boudin (hornblende-garnet amphibolite). Columns 1, 2 and 3: Kipawa Syenite Complex; 4: skarn; 5, 6 and 7: host gneisses; 8 and 9: marble; 10: dyke.

mineralogy and geometry of the complex are the result of deformation and metamorphism, and the chemistry of igneous precursors, if any, is not necessarily preserved. However, the chemistry of the Kipawa Syenite Complex resembles that of felsic igneous peralkaline rocks (*cf. Civetta et al. 1984, Harris et al. 1986, Macdonald et al. 1987*), and the compositional variations in terms of the major elements can be explained by crystal fractionation and minor assimilation from a slightly peralkaline undersaturated syenitic parent magma. Least-squares fitting (Stormer & Nicholls 1978), using the bulk composition (Table 3) and compositions of analyzed minerals (Table 1) in the nepheline syenite, shows that the major-element composition of the nepheline-free syenite can be produced by removing alkali feldspar, nepheline, amphibole and aegirine from the nepheline

TABLE 4. LEAST-SQUARES FRACTIONATION CALCULATIONS FOR THE KIPAWA SYENITE COMPLEX AND RELATED ROCKS

	1	2	3	4	5	6	7	8
SiO ₂ wt. %	58.08	64.68	64.68	71.98	71.97	53.36	4.79	53.35
TiO ₂	0.31	0.37	0.44	0.43	0.51	0.28	0.06	0.25
Al ₂ O ₃	19.59	15.71	15.72	11.15	11.14	6.13	0.55	6.26
FeO(t)	5.73	4.65	4.65	5.53	5.51	5.79	1.45	5.72
MnO	0.16	0.11	0.07	0.09	0.10	0.27	0.07	0.22
MgO	0.45	0.34	0.33	0.24	0.23	10.40	37.39	10.14
CaO	1.79	1.33	1.32	0.44	0.44	14.85	55.41	15.07
Na ₂ O	9.20	7.57	7.56	6.31	6.30	4.65	0.06	4.53
K ₂ O	4.41	4.89	4.88	3.72	3.71	1.92	0.17	2.08
F	0.28	0.34	0.33	0.11	0.09	2.36	0.06	2.37
Sum of squares of residuals			0.0071		0.0078			0.1814

1. Average nepheline syenite (recalculated to 100%)
2. Average syenite (recalculated to 100%)

3. Composition obtained by removing from composition 1 crystals with a total weight of 62.52 weight % of the starting material and consisting of albite 52.16, potassium feldspar 20.06, nepheline 8.91, kataphorite 11.61, aegirine 6.20, biotite 0.59, fluorite 0.47 weight %, all with the compositions given in Table 1 for nepheline syenite. (Fluorite is assumed to have the composition CaO 51.33, F 48.67 weight %).

4. Average peralkaline granite (recalculated to 100%)

5. Composition obtained by removing from composition 4 crystals with a total weight of 36.77 weight % of the starting material and consisting of albite 56.48, potassium feldspar 28.36, aegirine 12.32, biotite 1.78, and fluorite 1.06, all with the compositions given in Table 1 for nepheline syenite. An amount of quartz (assumed to have composition SiO₂ 100 %) equal to 9.61 weight % of the starting material is added, together with an amount of kataphorite 0.59 weight % of the starting material. (Note that according to these calculations, the Kipawa Syenite Complex should consist (in weight %) of 60.21 nepheline syenite, 13.27 syenite, and 26.53 peralkaline granite.)

6. Average peralkaline skarn (recalculated to 100 %)

7. Average marble (recalculated to 100 %)

8. Mix of 54.80 weight % average peralkaline granite (column 4), 26.76 average marble, 8.53 quartz, 7.59 aegirine (SiO₂ 53.85, FeO 30.28, MnO 1.98, Na₂O 13.89) and 2.31 F.

syenite (Table 4). The calculated proportions of the removed material are similar to those of observed nepheline syenite lenses. Peralkaline granite compositions can be produced from the syenite by removing alkali feldspar, aegirine, biotite and fluorite and adding small amounts of quartz and amphibole (Table 4). Addition of amphibole could be explained by minor cumulation, but addition of quartz suggests assimilation of wallrocks or, possibly, metasomatism.

The high FeO(total) content (3.27–7.03%) content of the Kipawa Syenite Complex is suggestive of strongly peralkaline (pantelleritic) compositions and inconsistent with the slightly to moderately peralkaline values observed (*cf. Civetta et al. 1984, Macdonald et al. 1987, Harris et al. 1986*). The complex may have lost alkalis owing to alkali metasomatism of the Red Pine Chute and Kikwissi gneiss, as evidenced by the local occurrence of peralkaline compositions within these generally peraluminous units. Such metasomatism could have taken place during original emplacement (finitization), or subsequent deformation. The contents of Sr and especially Ba are markedly high for peralkaline rocks, which commonly contain <50 ppm of both elements, but contents decrease systematically and markedly from nepheline syenite to syenite to peralkaline granite, suggesting that high contents of Sr and Ba were an original feature. There is also a correlation between the concentration of Zr and

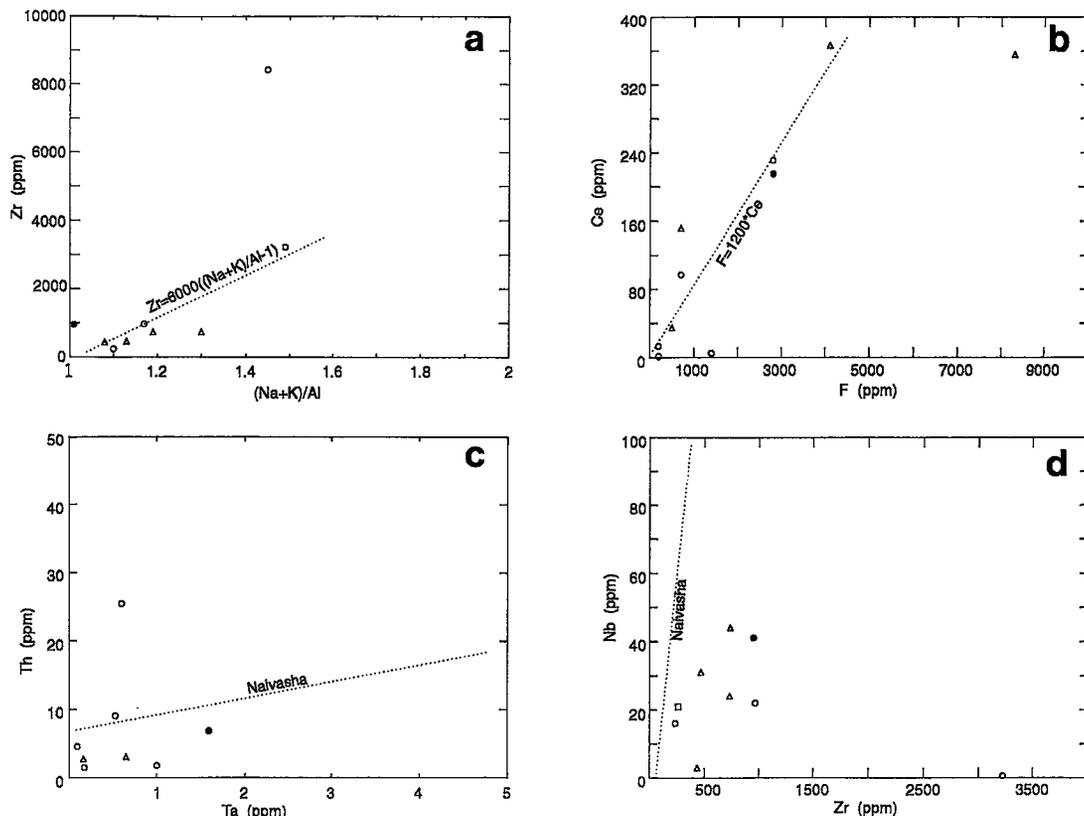


FIG. 10. Correlation of (a) $(\text{Na}+\text{K})/\text{Al}$ with Zr, (b) F with Ce, (c) Ta with Th, and (d) Zr with Nb in the Kipawa Syenite complex. The lines marked "Naivasha" in (c) and (d) show the trends found by Macdonald *et al.* (1987) for peralkaline rhyolite at Naivasha.

$(\text{Na} + \text{K})/\text{Al}$ and between that of the rare-earth elements and F (Fig. 10), which may be relict from magmatic processes. Although the range of composition within the Kipawa Syenite Complex can be generally explained by fractionation, a number of chemical features suggest that other processes have occurred. Geochemical ratios that are commonly preserved in igneous peralkaline suites, such as Nb/Zr , Ta/Th (Fig. 10) and La_n/Lu_n (0.055–9.78) show great variability. Normalized *REE* abundances not only vary in absolute amount but also in shape of the pattern (Fig. 11). Most of the strongly peralkaline granites are depleted in light *REE* (*LREE*) by a factor of 10–100, a feature not observed in igneous suites, where the most differentiated rocks are relatively *LREE*-enriched. These same rocks are enriched in Zr and Hf by a factor of 10 (Fig. 12), too much to be accounted for by fractionation required to produce the bulk compositions.

The marble and peralkaline amphibolite schist that contain most of the rare minerals differ greatly from the Kipawa Syenite Complex. The marble seems to be

essentially identical to metasedimentary marble in the region, with addition of F and minor Fe (Table 3). Some apatitic syenite complexes contain a late mafic-mineral-rich phase very rich in Zr and other incompatible elements (lujavrite, kakortokite: Ferguson 1970, Sørensen 1974), but such rocks are low in Ca and Mg, almost devoid of Sr and Ba, and contain sodic, very iron-rich, mafic minerals. The eudialyte-rich mafic rocks at Kipawa exhibit high concentrations of Ca and Mg as well as Ca/Mg values similar to those typical of metasedimentary marble, Ba and Sr contents similar to or higher than in the marble, $\text{Fe}/(\text{Fe}+\text{Mg})$ less than 0.2, and Mg-rich mafic minerals some of which are almost devoid of Na (*e.g.*, diopside, Table 1). Although the $(\text{Na}+\text{K})/\text{Al}$ values are high (1.18–1.92), these values are due more to low Al contents than high alkali contents. The rare-earth-element patterns and extended normalized element plots resemble the syenite in relative abundance and strong relative Nb, Sr and Ti depletion (Figs. 11, 12). These relations suggest that the skarn-like rocks might be due to physical mixing or assimilation involving peralkaline granite

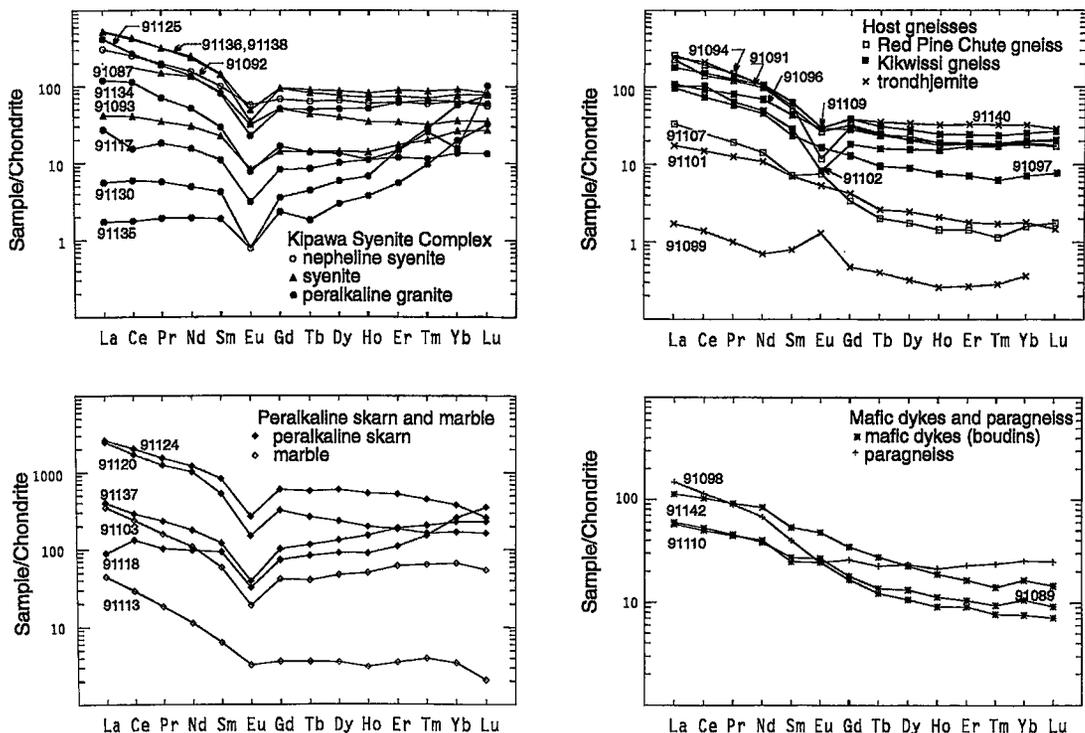


FIG. 11. Normalized rare-earth-element patterns for the Kipawa Syenite Complex and related units. Abundances are chondrite-normalized, with normalization factors from Sun & McDonough (1989). Sample numbers and descriptions are listed in Appendix 1.

and marble. Attempts to model this process by least-squares calculation (Table 4) showed that a reasonable fit could be obtained for major elements (sum of squares of residuals 0.69), by assuming mixing of 26.76 wt.% average marble with 54.80 wt.% average peralkaline granite (compositions from Table 3), and adding 8.53% SiO_2 (quartz), 7.59% $\text{NaFeSi}_2\text{O}_6$ (aegirine) and 2.31% F. (The CO_2 originally in the marble is assumed to be lost during this process.) The addition of silica and aegirine shows the necessity for fenitization-like metasomatism, as well as physical mixing. Metasomatism also is required to explain trace-element abundances, particularly of Be, Nb, F and the REE, which cannot be explained by mixing.

The normalized REE patterns and extended trace-element patterns for the Red Pine Chute and Kikwissi gneiss show a strong resemblance to the syenite patterns (Figs. 11, 12), with only the trondhjemite departing markedly. Since trondhjemite predominates at distances greater than 2 km from the Kipawa Syenite Complex, the data suggest that alkali and trace element contents of granitic gneiss near the complex either have been affected by emplacement of the complex, or were derived from similar sources.

THE ORIGIN OF RARE MINERALS IN THE KIPAWA SYENITE COMPLEX

The geochemical signature of the Kipawa Syenite Complex suggests that it was originally an igneous body, although the trace-element content, and probably the alkali content, have been substantially modified by post-igneous processes. The age of emplacement has not been dated directly, but it postdates the 1247 Ma age of emplacement of the host Red Pine Chute gneiss, and predates the 1235 Ma age of the Sudbury dyke that cuts hornblende granite, which in turn cuts the Kipawa Syenite Complex. The age of emplacement is, therefore, constrained between about 1235 and 1245 Ma, in the same range as other peralkaline syenites along the Grenville Front [Red Wine, 1337 Ma: Gandhi *et al.* (1988), Flowers River, 1271 Ma: Hill (1981), Strange Lake, 1244 Ma: Lumbers *et al.* (1991), Gardar Province, 1160–1300 Ma: Blaxland *et al.* (1978)]. Mildly peralkaline syenitic (trachytic) compositions can result from fractional crystallization of more mafic compositions (for example, Mahood 1981), but the volume of such differentiates is small compared to more mafic compositions, and such differentiates

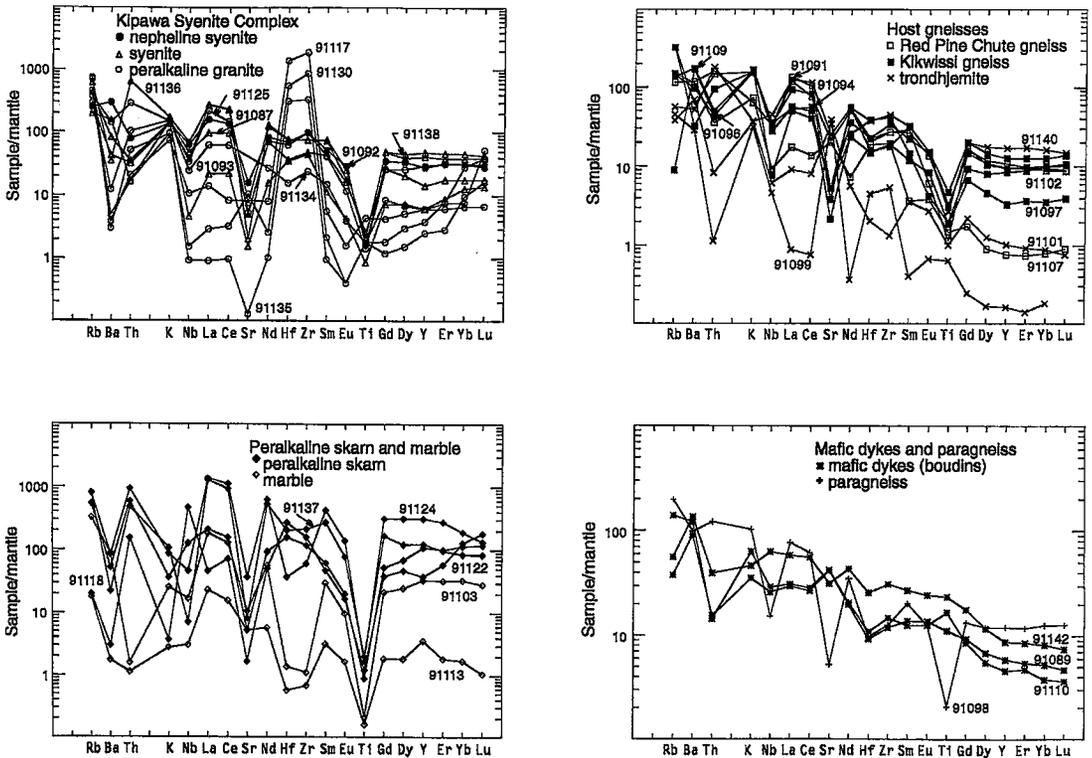


FIG. 12. Element-abundance patterns for the Kipawa Syenite Complex and related units, normalized to primitive mantle abundances. Normalization factors are from Sun & McDonough (1989).

exhibit strong depletion of Eu (due to feldspar fractionation) and strong *LREE* enrichment (due to extreme fractionation). None of these phenomena are observed in the Kipawa Syenite Complex, which apparently lacks a mafic phase, has low $(La/Lu)_n$ (0.055–9.78), and moderate Eu/Eu^* (0.055–0.127). Peralkaline felsic compositions can be obtained directly by partial melting of metasomatized mantle protoliths (Eby 1990) particularly those rich in F and Cl (Manning 1981, Davies & Macdonald 1987). Both nepheline-bearing and quartz-bearing rocks commonly occur in such suites [for example Blatchford Lake (Sinclair *et al.* 1992), Red Wine (Curtis & Currie 1981), Gardar (Ferguson 1970)], a well-known petrological conundrum (Currie 1989), and an association with mildly alkaline basaltic dykes may also occur (Gardar: Ferguson 1970). Rock types associated with tensional tectonics (regional dyke-swarm, peralkaline rocks) but showing geochemical characteristics suggestive of orogenic origin (Nb, Sr and Ti depletion) suggest late to post-orogenic emplacement. Because of the deformation and remobilization of the Kipawa Syenite Complex, more detailed statements on its origin are not presently possible. It cannot be stated with certainty whether the complex represents

deformed plutonic rocks, volcanic rocks, or both together. Virtually no relics of igneous minerals have been found. Despite a similar degree of metamorphism, such evidence is abundant in the peralkaline Red Wine igneous complex (Curtis & Currie 1981). If concentrations of rare minerals formed in the Kipawa Syenite Complex during original crystallization, they have not survived subsequent deformation and metamorphism. A fenitization aureole may have been present, as suggested by local peralkaline compositions in the enclosing gneiss, but this phenomenon may also be due to later deformation and metasomatism.

The rare minerals presently observed associated with the Kipawa Syenite Complex developed in alkali metasomatized skarn, as shown by the chemical composition of the host rocks and the persistence of Na-poor diopside, Mg-rich amphibole and phlogopite. Consideration of the regional lithostratigraphic succession and structure suggests that the host marble and calc-silicate unit originally lay structurally below the syenite complex and separated from it by a septum of the Red Pine Chute gneiss, but has been juxtaposed with the syenite by northwest-directed thrusting associated with amphibolite-grade metamorphism. The presence of numerous rotated and deformed calc-

silicate blocks, and complex flow structure within the marble, suggest that it marks a ductile thrust surface along which significant mechanical mixing has occurred. Precise dating shows that the latest phase of this process occurred 994 Ma ago. Deformation and metamorphism induced mobilization of alkalis, halogens, the REE, Zr, Nb, Be and other elements, followed by their fixation in the calc-silicates. The process resembled fenitization (Currie & Ferguson 1971), and since alkali and halogen-rich brines scavenge Zr and REE from the surroundings (Watson 1979), much of the transport could have been due to subsolidus circulation of fluids on fault planes. Although such processes are incompletely understood, depletion of LREE in the peralkaline granites could be ascribed to greater stability of alkali-HREE fluorides (Christiansen *et al.* 1983). However, evidence of anatectic melting is ubiquitous in the Kipawa region, and many of the rare minerals occur in undeformed pegmatitic patches that surely formed directly from a magmatic fluid. Peralkaline granites have been observed to intrude their surroundings on a small scale, a relation requiring late to post-tectonic melting. Development of the rare mineral locality, therefore, was a complex process involving a combination of metasomatism and anatectic melting, which redistributed alkalis and trace elements on scales ranging from a few meters to several kilometers.

The present knowledge regarding origin of the rare minerals associated with the Kipawa Syenite Complex may be summarized as follows. A peralkaline complex was originally emplaced about 1240 Ma, either as a pluton, as volcanic rocks, or as a combination of both. Emplacement probably accompanied development of the Sudbury dyke swarm, and postdated more extensive orogenic magmatism. Any concentrations of rare minerals associated with emplacement have not survived later deformation and metamorphism. At about 995 Ma, ductile northwest-directed thrusting under amphibolite-facies metamorphic conditions juxtaposed a marble and calc-silicate unit with the syenite along a surface of movement marked by mechanical mixing on a meter scale. This juxtaposition was followed by metasomatic reactions and anatectic melting in the presence of F-rich brines. These processes produced not only the spectacular rare minerals, but redistributed alkalis and trace elements on scales varying from a few meters to several kilometers.

ACKNOWLEDGEMENTS

We acknowledge the generous cooperation and assistance of J.F. Allan of J.F. Allan Mineral Consultants, without whose help this study would not have been possible. Unocal Canada allowed us to examine the drill core from the Kipawa rare-earth prospect. We also acknowledge John Gittins, who

introduced us to the complexities of Kipawa geology and has remained interested throughout. Tony Davidson, Simon Hanmer and Kathy Bethune of the Geological Survey of Canada provided invaluable unpublished information and advice. Anlin Guo of McMaster University kindly provided further unpublished data on his age-dating results. Naturally none of these workers necessarily endorses the views laid out here. We are also grateful to the critical readers, John Gittins and Nelson Eby, whose constructive comments led to substantial improvement of the manuscript, and to Robert F. Martin, who patiently corrected errors and infelicities of expression. The defects that remain are entirely our own.

REFERENCES

- AARDEN, H.M. & GITTINS, J. (1974): Hjordahlite from Kipawa River, Villedieu Township, Temiskaming County, Québec, Canada. *Can. Mineral.* **12**, 241-247.
- ADAMSON, O.J. (1944): The petrology of the Norra Kärr district; an occurrence of alkaline rocks in southern Sweden. *Geol. Fören. Stockholm Förh.* **66**, 113-255.
- ALLAN, J.F. (1992): Geology and mineralisation of the Kipawa yttrium-zirconium property, Quebec. *Explor. Mining Geol.* **1**, 283-293.
- ANOVITZ, L.M. & ESSENE, E.J. (1990): Thermobarometry and pressure-temperature paths in the Grenville Province of Ontario. *J. Petrol.* **31**, 197-241.
- ANSELL, H.G., ROBERTS, A.C. & PLANT, A.G. (1980): Gittinsite, a new calcium zirconium silicate from the Kipawa agpaite syenite complex, Quebec. *Can. Mineral.* **18**, 201-203.
- BERRY, L.G., LIN, H.-C. & DAVIS, G.C. (1972): A new occurrence of miserite from the Kipawa Lake area, Quebec. *Can. Mineral.* **11**, 569 (abstr.).
- BLAXLAND, A.B., VAN BREEMEN, O., EMELEUS, C.H. & ANDERSON, J.G. (1978): Age and origin of the major syenite centers in the Gardar Province of south Greenland: Rb-Sr studies. *Geol. Soc. Am., Bull.* **89**, 231-244.
- CHRISTIANSEN, E.H., BURT, D.M., SHERIDAN, M.F. & WILSON, R.T. (1983): The petrogenesis of topaz rhyolites from the western United States. *Contrib. Mineral. Petrol.* **83**, 16-30.
- CIVETTA, L., CORNETTE, Y., CRISCH, G., GILLOT, P.Y., ORSI, G. & REQUEJO, C.S. (1984): Geology, geochronology and chemical evolution of the island of Pantelleria. *Geol. Mag.* **121**, 541-562.
- CURRIE, K.L. (1976): The alkaline rocks of Canada. *Geol. Surv. Can., Bull.* **239**.
- _____ (1985): An unusual peralkaline granite near Lac Brisson, Quebec-Labrador. *Geol. Surv. Can., Pap.* **85-1A**, 73-80.

- _____ (1989): New ideas on an old problem – the peralkaline rocks. In *Alkaline Rocks* (C. Leelanandam, ed.). *Geol. Soc. India, Mem.* **15**, 117-136.
- _____ & FERGUSON, J. (1971): A study of potash fenitisation around the alkaline complex carbonatite complex at Callander Bay, Ontario. *Can. J. Earth Sci.* **8**, 498-517.
- _____ & GITTINS, J. (1993): Preliminary report on peralkaline silica-undersaturated rocks in the Kipawa syenite gneiss complex, western Quebec. *Geol. Surv. Can., Pap.* **93-1E**, 197-205.
- _____ & VAN BREEMEN, O. (1994): Tectonics and age of the Kipawa syenite complex, western Quebec. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **19**, A25.
- CURTIS, L.W. & CURRIE, K.L. (1981): Geology and petrology of the Red Wine alkaline complex, central Labrador. *Geol. Surv. Can., Bull.* **294**.
- DAVIES, G.R. & MACDONALD, R. (1987): Crustal influences in the petrogenesis of the Naivasha basalt-comendite complex: combined trace element and Sr-Nd-Pb isotope constraints. *J. Petrol.* **28**, 1009-1031.
- DUDAS, F.Ö., DAVIDSON, A. & BETHUNE, K.M. (1994): Age of the Sudbury diabase dykes and their metamorphism in the Grenville Province, Ontario. *Geol. Surv. Can., Current Research 1994-F*, 97-106.
- EASTON, R.M. (1992): The Grenville Province and the Proterozoic history of central and southern Ontario. *Ont. Geol. Surv., Spec. Vol.* **4(2)**, 715-904.
- EBY, G.N. (1990): The A-type granitoids: a review of their occurrence and chemical characteristics and speculations on their petrogenesis. *Lithos* **26**, 115-134.
- FERGUSON, J. (1970): The differentiation of apgaitic magmas; the Ilimaussaq intrusion, south Greenland. *Can. Mineral.* **10**, 335-349.
- GANDHI, S.S., KROGH, T.E. & CORFU, F. (1988): U-Pb zircon and titanite dates on two granitic intrusions of the Makkovik orogen and a peralkaline granite of the Red Wine intrusive complex. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **13**, A42-A43.
- GITTINS, J., BROWN, M.G. & STURMAN, D. (1976): Agrellite, a new rock-forming mineral in regionally metamorphosed apgaitic alkaline rocks. *Can. Mineral.* **14**, 120-126.
- GUO, ANLIN & DICKIN, A.P. (1994): Determination of the southern limit of Archean crust in the Grenville Province of western Quebec by Nd model age mapping. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **19**, A44.
- HARRIS, N.B.W., MARZOUKI, F.M.H. & ALI, S. (1986): The Jebel Sayid complex, Arabian Shield: geochemical constraints on the origin of peralkaline and related granites. *J. Geol. Soc. London* **143**, 287-296.
- HICKS, W.D. (1959): Eudialyte and euclite in Canada. *Can. Mineral.* **6**, 297-298.
- HILL, J.D. (1981): Geology of the Flowers River area, Labrador. *Newfoundland Mineral Devel. Div., Rep.* **81-6**.
- KELLETT, R.L., BARNES, A.E. & RIVE, M. (1994): The deep structure of the Grenville Front; a new perspective from western Quebec. *Can. J. Earth Sci.* **31**, 282-292.
- LUMBERS, S.B., WU, TSAI-WEY, HEAMAN, L.H. & MACRAE, N.D. (1991): Petrology and age of the A-type Mulock granite batholith, northern Grenville Province, Ontario. *Precamb. Res.* **53**, 199-231.
- LYALL, H.B. (1959): Preliminary report on the McLachlan-Booth area, Temiscamingue Electoral District. *Quebec Dep. Mines, Geol. Surv., Branch Prelim. Rep.* **391**.
- MACDONALD, R., DAVIES, G.R., BLISS, C.M., LEAT, P.T., BAILEY, D.K. & SMITH, R.L. (1987): Geochemistry of high-silica peralkaline rhyolites, Naivasha, Kenya Rift Valley. *J. Petrol.* **28**, 979-1008.
- MÄDER, U.K. & BERMAN, R.G. (1992): Amphibole thermobarometry: a thermodynamic approach. *Geol. Surv. Can., Pap.* **92-1E**, 393-400.
- MAHOOD, G. (1981): A summary of the geology and petrology of the Sierra La Primavera, Jalisco, Mexico. *J. Geophys. Res.* **86**, 10137-10152.
- MANNING, D.A.C. (1981): The effect of fluorine on liquidus phase relationships in the system Qz-Ab-Or with excess water at 1 kb. *Contrib. Mineral. Petrol.* **76**, 206-215.
- PIASECKI, M.A.J. (1988): Strain-induced mineral growth in ductile shear zones and a preliminary study of ductile shearing in western Newfoundland. *Can. J. Earth Sci.* **25**, 2118-2129.
- PLANT, A.G. & ROBERTS, A.C. (1979): New data on unnamed CaZr₂SiO₇ from Kipawa, Quebec. *Geol. Surv. Can., Pap.* **79-1A**, 391-392.
- RIVE, M. (1973): Géologie de la région des lacs Ogascanane et Sairs, Comté de Témiscamingue. *Ministère des Richesses Naturelles du Québec, Service de l'Exploration géologique, Rapport Préliminaire* **606**.
- ROBERTS, A.C. & BONARDI, M. (1983): Potassian gaidonnayite from the Kipawa apgaitic syenite complex, Quebec. *Geol. Surv. Can., Pap.* **83-1A**, 480-482.
- SINCLAIR, W.D., JAMBOR, J.L. & BIRKETT, T.C. (1992): Rare earths and the potential for rare earth deposits in Canada. *Explor. Mining Geol.* **1**, 265-281.

SØRENSEN, H. (1974): *The Alkaline Rocks*. J. Wiley & Sons, London, U.K.

STORMER, J.C. & NICHOLLS, J. (1978): XLFRAC: a program for the interactive testing of magmatic differentiation models. *Computers Geosci.* **4**, 143-159.

SUN, SHEN-SU & McDONOUGH, W.F. (1989): Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In *Magmatism in the Ocean Basins* (A.D. Saunders & M.J. Norry, eds.). *Geol. Soc., Spec. Publ.* **42**, 313-345.

TREMBLAY-CLARK, P. & KISH, L. (1978): Le district radioactif de Kipawa. *Ministère des Richesses Naturelles du Québec, Direction Générale des Mines, Rapport Préliminaire DPV-579*.

WATSON, E.B. (1979): Zircon saturation in felsic liquids; experimental results and applications to trace element geochemistry. *Contrib. Mineral. Petrol.* **70**, 407-419.

Received September 13, 1994, revised manuscript accepted June 7, 1995.

APPENDIX I. DESCRIPTION AND LOCATION OF CHEMICALLY ANALYZED SPECIMENS*

91087 (31L/16, 691800,5183260)	Biotite-amphibole syenite, Lac Sheffield
91089 (31L/15, 689850,5184000)	Scapolitized biotite amphibolite, Lac Sheffield
91091 (31L/15, 681950,5192450)	Red Pine Chute gneiss, Lac Sheffield
91092 (31L/15, 683400,5191530)	Biotite-nepheline syenite, Lac McKillop
91093 (31L/15, 683440,5191120)	Amphibole syenite, Lac McKillop
91094 (31L/15, 684050,5190600)	Red Pine Chute gneiss, Lac McKillop
91096 (31L/16, 692850,5192050)	Kikwissit gneiss, (granite phase), Lac Sairs
91097 (31L/16, 692850,5192050)	Kikwissit gneiss, (granite phase), Lac Sairs
91098 (31L/16, 691650,5191850)	Muscovite granite gneiss, Lac Sairs
91099 (31L/16, 690000,5191300)	Kikwissit gneiss (trondhjemite phase), Lac Sairs
91101 (31L/15, 688500,5190300)	Kikwissit gneiss (trondhjemite phase), Lac Sairs
91102 (31L/16, 691300,5186250)	Kikwissit gneiss, (granite phase), Lac Sairs
91103 (31L/16, 691300,5186250)	Chondrodite marble, Lac Sheffield
91107 (31L/16, 695200,5187300)	Red Pine Chute gneiss, Lac Sairs
91109 (31L/16, 695300,5186800)	Biotite gneiss, quartzite schlieren, Lac Sairs
91110 (31L/16, 695300,5186500)	Coronitic garnet amphibolite, Lac Sairs
91113 (31L/16, 695700,5186200)	Coarse diopside-phylogopite marble, Lac Sairs
91117 (31L/16, 690100,5186850)	Coarse amphibole quartz syenite, Lac Sheffield
91118 (31L/16, 690100,5186850)	Eudialyte-bearing pyroxene skarn, Lac Sheffield
91122 (31L/16, 690160,5186750)	Eudialyte-bearing amphibolite schist, Lac Sheffield
91124 (31L/15, 690050,5186950)	Eudialyte-fluorite pegmatite patch in amphibolite schist, Lac Sheffield
91125 (31L/15, 689950,5187050)	Aegirine-riebeckite quartz syenite, Lac Sheffield
91130 (31L/16, 690290,5186590)	Aegirine granite, Lac Sheffield
91134 (31L/16, 690390,5186490)	Aegirine-riebeckite quartz syenite, Lac Sheffield
91135 (31L/16, 690390,5186490)	Aegirine granite, Lac Sheffield
91136 (31L/16, 690390,5186490)	Aegirine-riebeckite syenite, Lac Sheffield
91137 (31L/16, 690490,5186590)	Eudialyte-bearing amphibole schist, Lac Sheffield
91138 (31L/16, 690490,5186590)	Amphibole syenite, Lac Sheffield
91140 (31L/15, 689190,5186400)	Kikwissit gneiss, (trondhjemite phase), Lac Sheffield
91142 (31L/15, 689190,5186400)	Altered gabbro, Lac Sheffield

* Specimen locations given by NTS block and grid reference.