

Volatile Control of Contrasting Trace Element Distributions in Peralkaline Granitic and Volcanic Rocks

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Abstract. Anomalous enrichments of Zr (> 500 ppm), Zn (> 100 ppm), Nb (> 25 ppm), Y (> 60 ppm), Th (> 20 ppm), U (> 5 ppm), LREE (> 230 ppm) and HREE (> 35 ppm), and high Rb/Sr (> 5) characterize peralkaline granites, in contrast to their peraluminous and calc-alkaline equivalents. Within the peralkaline suite, comenditic and pantelleritic volcanics exhibit two- to five-fold increases in the concentrations of these trace elements over comagmatic granites. These cannot be explained by crystal-liquid fractionation processes, and require the evolution of a sodium-enriched fluid. Corresponding trace element increases in the granites in areas of alkali metasomatism support this argument, and reflect the partial confinement of this volatile phase within the high-level magma chambers. REE studies in particular might eventually allow an evaluation of the role of Cl^- versus F^- and CO_3 -complexing in the evolution of the volatile fluid.

Introduction

Oversaturated peralkaline igneous rocks tend to be highly silicic, enriched in alkalis and depleted in alumina, and are enriched in an incongruous assemblage of trace elements (e.g. Ni and Zn along with Rb, Nb and Zr) unlike that resulting from typical igneous enrichment trends. They are characteristic of extensional (at least locally) tectonic environments, forming high-level plutons, often with a cogenetic volcanic carapace. They may be associated with a range of other igneous rocks such as metaluminous biotite granites, alkali syenites, and alkali basalts, but no general genetic relationships have been established. Indeed, the petrogenetic interpretations of these rocks appear to be as varied as the number of occurrences. Because few of these interpretations have considered the importance of rare earth element (REE) data, we have conducted a study of REE variation in twenty-six representative samples from the peralkaline-metaluminous Topsails igneous complex of western Newfoundland (Taylor et al. 1980). These data suggest that volatiles, probably CO_2 -dominated and mantle-derived, play an important role in the genesis of oversaturated peralkaline rocks.

The Topsails Complex

General

The Topsails igneous complex, one of three large peralkaline intrusions recognized in Newfoundland, occurs along the western margin of the Dunnage Zone – a terrane dominated by Ordovician island-arc type

volcanic rocks formed during destruction of the lower Paleozoic Iapetus Ocean – and is associated with a bimodal basalt-rhyolite assemblage of Silurian-Devonian age formed after closure of Iapetus (Strong 1978; Williams 1978). The complex intrudes both the Ordovician and the Silurian-Devonian volcanic rocks (some of the latter are cogenetic with the intrusive rocks), as well as amphibolitized gabbroic and ultramafic rocks of the older Hungry Mountain complex (Thurlow, in press). In the south it intrudes gneissic and other metamorphic rocks of undetermined affinity. The Topsails igneous complex was emplaced after the main tectonic evolution of the Dunnage Zone, i.e. in a post-orogenic or anorogenic setting, taken to represent the dilational zones in an overall “megashear” environment (Strong 1980a).

There are four granitoid facies in the complex, which are divisible into a peralkaline suite and a peraluminous to metaluminous (“non-peralkaline”) suite (Taylor et al. 1980), all shallow intrusive rocks with local extrusive equivalents. The peralkaline suite consists of intimately related granite, quartz-feldspar porphyry dikes, and comenditic flows and ignimbrites. The non-peralkaline suite comprises a series of comagmatic biotite and biotite-hastingsite granites, with associated syenites and hybrid rocks, and intrudes the Hungry Mountain Complex and the Buchans Group. Small diabase dikes and mafic globules indicate contemporaneous basalt magmatism. Non-peralkaline silicic volcanic rocks occur both as roof pendants within the complex or as marginal host rocks. Large circular structures within the complex which are evident from aerial photographs and aeromagnetic maps are suggestive of ring dikes, but ground exposure is inadequate to confirm this interpretation.

Bell and Blenkinsop (in press) have provided whole-rock Rb/Sr isochrons of 419 ± 5 Ma for the peralkaline granite and 386 ± 9 Ma for the peraluminous-metaluminous (“alkali”) granite. Recent work (Taylor and Strong, in prep.) has provided Rb/Sr whole-rock isochrons of 388 ± 9 Ma for the peraluminous granite and 416 ± 11 Ma for the peralkaline granite, confirming the dates of Bell and Blenkinsop. A U/Pb date on zircon from the Topsails syenite gives an age of 418 ± 1 Ma.

Rare Earth Data

Taylor et al. (1980) presented geochemical data for 52 samples from the Topsails complex, demonstrating a strong enrichment in the peralkaline suite of lithophile elements such as Zr, Rb, Nb, along with Zn and Ni. Twenty-seven of these samples, representing each of the main rock types, were analysed for rare earth elements by the thin film X-ray fluorescence method of Fryer (1977). These data, with an estimated precision and accuracy of $\pm 10\%$, are presented in Table 1, and illustrated in Figs. 1–3.

The non-peralkaline syenites (Fig. 1a) form a tight grouping with more or less straight line negative slopes, except for a slight positive Eu anomaly for sample number 31, and slightly negative Eu anomalies for the other three samples. These can

Table 1. Rare earth concentrations (ppm) in representative rocks of the Topsails Complex

Syenite					Hastingsite-biotite granite						
	22	27	31	36		25	29	295	297		
La	24.3	23.2	16.1	24.1	La	28.4	51.0	30.4	21.9		
Ce	61.8	56.4	38.8	58.0	Ce	64.3	105	53.8	51.3		
Pr	8.2	7.5	5.6	7.6	Pr	7.8	11.9	8.5	6.4		
Nd	34.3	30.6	23.3	31.5	Nd	28.7	41.9	31.6	23.6		
Sm	8.1	7.4	6.1	7.6	Sm	6.4	8.0	6.9	5.6		
Eu	2.0	2.1	2.2	2.0	Eu	0.89	0.82	0.62	0.56		
Gd	7.8	7.0	6.4	7.4	Gd	5.8	6.59	6.4	5.5		
Dy	8.2	7.5	8.9	7.7	Dy	6.5	6.7	6.9	6.0		
Er	4.8	4.1	3.5	4.0	Er	4.0	4.1	4.4	3.7		
Yb	4.4	4.0	3.5	3.5	Yb	4.0	4.0	4.8	4.12		
Biotite-granite					Peralkaline granite						
	230A	276	315A	315B		50	195	196	200	282	284
La	30.7	19.3	31.7	26.5	La	50.5	50.4	54.5	58.5	35.6	28.6
Ce	61.0	42.7	68.2	61.1	Ce	113.6	113.1	122.8	149.5	84.1	73.5
Pr	8.3	5.5	8.4	6.5	Pr	14.2	14.0	17.6	20.2	10.9	11.1
Nd	29.1	20.5	27.6	22.7	Nd	56.2	56.7	70.9	81.3	40.6	42.3
Sm	7.2	4.6	6.0	4.7	Sm	11.9	13.0	18.5	27.6	7.7	8.8
Eu	0.04	0.60	0.27	0.36	Eu	2.1	1.8	2.4	3.3	0.76	0.87
Gd	6.0	4.6	5.5	4.36	Gd	10.2	11.0	18.2	32.9	7.5	8.8
Dy	4.3	4.8	6.4	5.2	Dy	10.2	9.2	16.6	44.3	7.3	8.4
Er	2.6	3.2	4.2	3.7	Er	5.6	5.6	9.6	26.0	4.8	3.9
Yb	2.9	3.3	4.5	4.1	Yb	5.7	6.3	10.0	21.5	4.7	3.9
QTZ-FSP porph.					Comendite						
	208	322			202	303					
La	30.7	53.3			La	27.3	101				
Ce	76.3	126			Ce	58.7	188				
Pr	10.6	17			Pr	10.6	32.8				
Nd	41.2	67.3			Nd	45.5	124				
Sm	9.7	13.8			Sm	12.0	29.8				
Eu	1.1	2.3			Eu	0.6	2.5				
Gd	10.1	13.8			Gd	14.1	30.5				
Dy	9.9	12.2			Dy	15.1	29.0				
Er	5.8	7.2			Er	8.9	17.7				
Yb	5.9	6.9			Yb	8.6	16.3				

be readily interpreted as representing one melt with slight variation in the proportion of plagioclase phenocrysts, which accords well with their petrography and their decreasing CaO and increasing SiO₂ and total REE content from samples 31 to 22.

The hastingsite-biotite granites (Fig. 1b) are slightly enriched, with a wider range, in LREE relative to the syenites, but the HREE all cluster around the same chondrite-normalized ratio of 20. They also show significant negative Eu anomalies, indicating that plagioclase fractionation could account for the derivation of these granites from the syenites, although no direct field evidence is available to support such an interpretation. The slight concavity of these patterns could reflect removal of the intermediate REE by apatite and/or amphibole.

The biotite granites (Fig. 1c) show REE patterns somewhat similar to those of the hastingsite-biotite granites, except for a slightly greater downward spread of the HREE, and larger Eu anomalies. The former may result from crystallization of amphibole and the observed accessory minerals apatite and zircon and the latter from further feldspar fractionation.

Figure 2 shows the chondrite-normalized REE patterns for the Topsails peralkaline granites. They are characterized by negative slopes with relatively consistent patterns for the light rare earths (LREE), with chondrite normalized La_n ratios between

90 and 200. All have negative Eu anomalies with Eu/Eu* between 0.15 and 0.30, similar to those of the non-peralkaline granites. With the heavy rare earths (HREE), however, there is a systematic change from Yb_n of 19 for sample number 284 to 105 for sample number 200. This variation accompanies a progressive alteration of the granites, reflected in increasing albitization and concentration of riebeckite needles in quartz and feldspar (illustrated in Fig. 3 of Taylor et al. 1980), culminating in sample number 200 with abundant calcite, zircon, riebeckite, and fluorite.

The systematic change resulting from metasomatism within the granites (Fig. 2b) can also be seen in a peralkaline sequence from these granites through their quartz-feldspar porphyry margins and dikes to the comenditic ignimbrites (Fig. 3). We attribute this change to increasing volatile activity in the upper levels and volcanic equivalents of the granites. The most highly enriched comendite, sample number 203, is characterized by the metasomatic oikocrysts of aegirine and riebeckitic arfvedsonite illustrated by Taylor et al. (1980) in their Fig. 2.

In summary, it can be seen from Figs. 1–3 that the REE patterns of the non-peralkaline suite can be readily explained by a differentiation series from the syenites through hastingsite-biotite granites to biotite-granites, caused by fractionation of feldspar and amphibole with minor accessory minerals. The per-

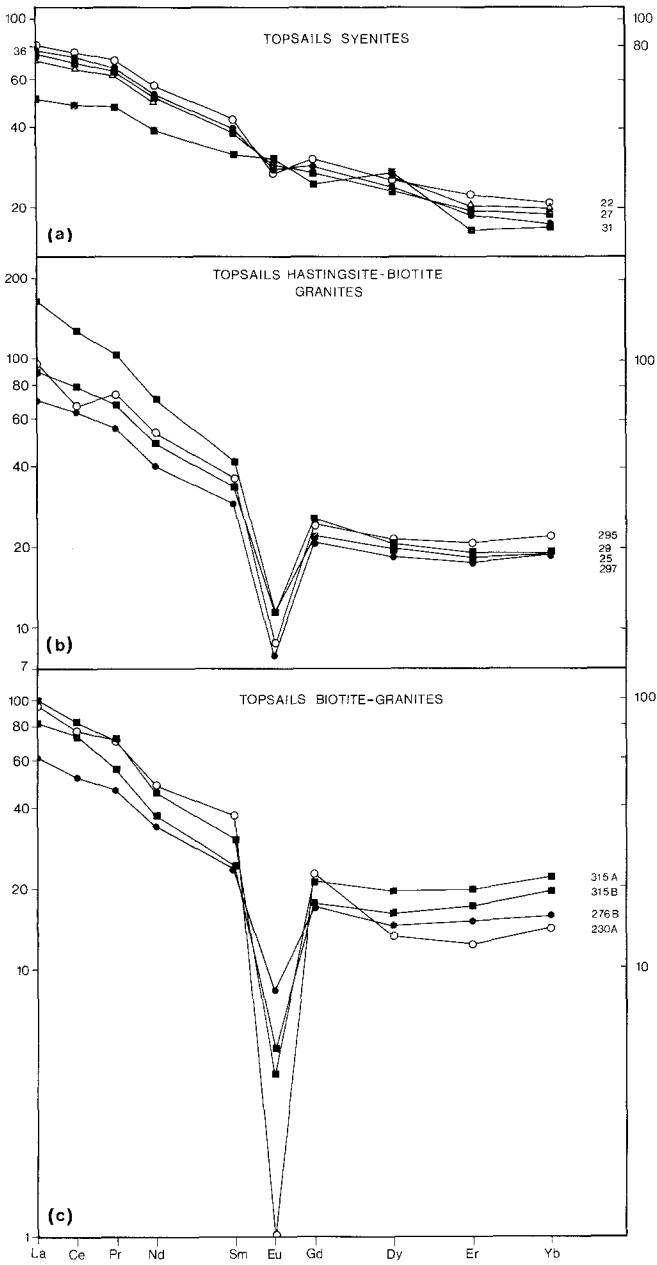


Fig. 1a-c. Chondrite-normalized rare earth patterns from the non-peralkaline intrusive rocks of the Topsails Complex

alkaline REE patterns do not accord with this explanation, and are interpreted as resulting from the action of volatiles on both the granitic melts before solidification and metasomatically after solidification. The similar enrichment of REE and other trace elements in the peralkaline volcanic rocks requires a similar explanation.

Discussion

REE data for peralkaline suites are generally scarce, so it remains to be seen whether or not these observations on the Topsails complex are generally applicable. One example for comparison is the Nordmarkite-Ekerite (alkali syenite-peralkaline granite) suite of the Oslo Paleorift, for which the REE data of Neumann et al. (1977) are shown in Fig. 4.

Both the syenites and the granites of the Oslo region are significantly more enriched in total REE than those of the Top-

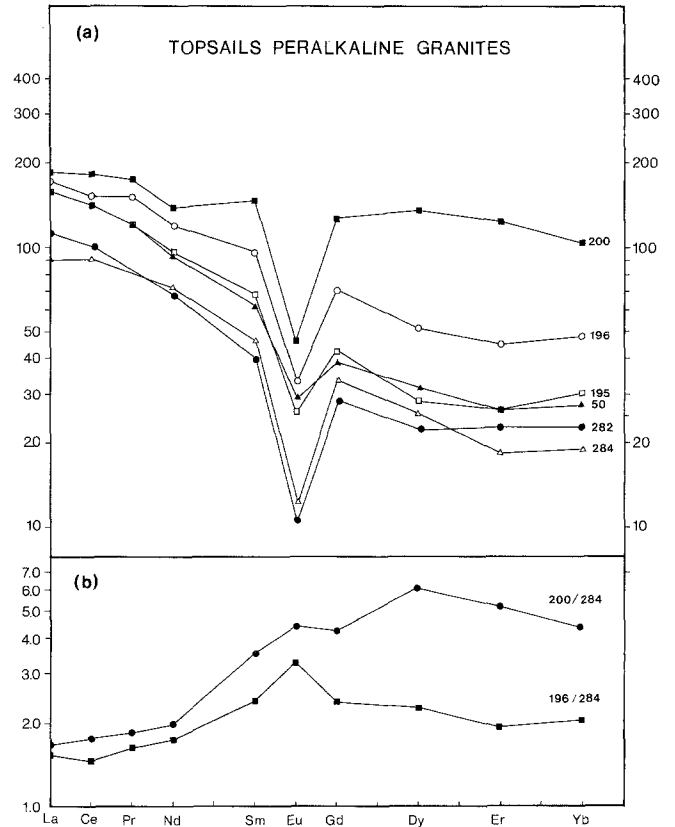


Fig. 2a, b. Chondrite-normalized REE patterns of the peralkaline granites of the Topsails Complex. Note that the sequence of increasing enrichment of HREE (sample 284 to 200) is characterized by increasing carbonate and sodium metasomatism

sails Complex, but they do show similar relative trends. For example, the syenites (nordmarkites) numbers 113, 126 176 and 158 (Fig. 4a, b) have concave-up patterns, with slightly negative Eu anomalies in the first two and complementary positive Eu anomalies in the latter two. As with the Topsails Complex, these patterns could reflect slight variation in feldspar proportions, with some control of the intermediate REE by apatite fractionation. The peralkaline syenite number 537 shows an enrichment over the alkali syenite (Fig. 4b) in total REE, with the intermediate REE preferentially enriched except for a significant negative Eu anomaly. These features are most readily explained by fractionation of feldspar, with some apatite and/or amphibole/pyroxene accumulation.

The peralkaline granites (ekerites) of the Oslo suite (Fig. 4c, d) all have LREE abundances in the syenite range, but they are significantly enriched in HREE and all have negative Eu anomalies. The Eu anomalies could be explicable by feldspar fractionation, but the HREE enrichment requires a process other than crystal-liquid equilibria. By analogy with the Topsails suite, for which there is also petrographic evidence, we suggest that this results from volatile activity. In support of this interpretation, we note that Neumann et al. (1977, p. 318) found it "impossible to reproduce the observed change in REE patterns by simulated fractionation with the data available", that the ekerites (peralkaline granites) "have abundant miarolitic cavities containing a number of rare earth minerals", and that "it is therefore also possible that the REE patterns of the ekerites have been affected by gaseous transfer".

Given that volatile or supercritical fluids appear to be important in the genesis of peralkaline rocks, it is most important to try and establish both the nature and the source of these

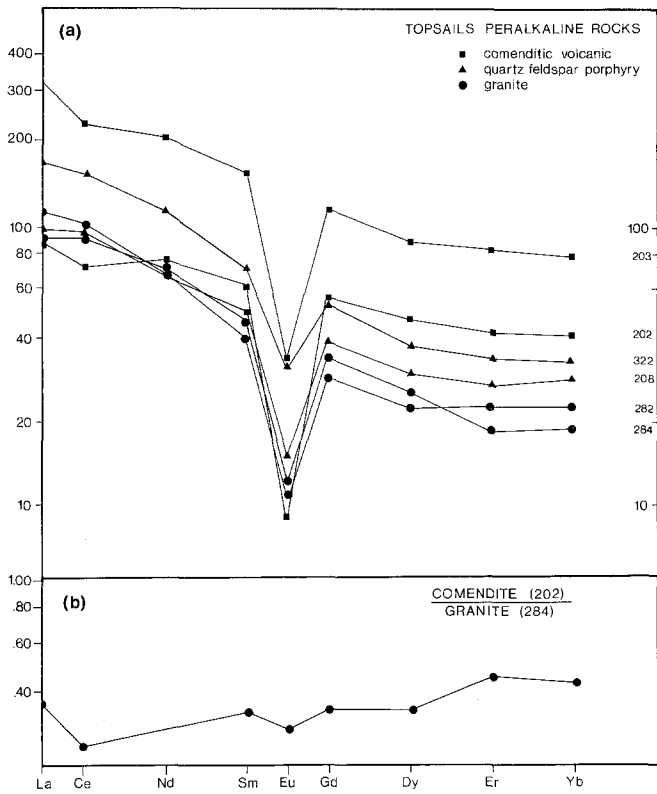


Fig. 3a, b. Chondrite-normalized patterns of Topsails peralkaline rocks showing increasing REE concentration from granites through quartz-feldspar porphyry to comenditic volcanics (cf. Fig. 2)

fluids. Although different sulfur species, methane, nitrogen and other compounds might be considered, the halides and carbonates are the only ones for which there is significant natural evidence in continental magmatism (e.g. Bailey 1978, 1980; Bailey and MacDonald 1975). Because of the differing behavior of REE with respect to these compounds, it may eventually be possible to use them as indicators of the chemical complexes active in the Topsails and other peralkaline suites. Although there are not conclusive experimental data available for a sufficiently wide range of conditions, there are some which suggest possible interpretations.

According to Mineyev (1963), some REE complexes such as NaYF_4 and $\text{Na}_5\text{Ce}_3\text{F}_{14}$ have been experimentally demonstrated to be stable under hydrothermal and supercritical conditions. From his study of an albite-riebeckite apogranite massif in Kazakhstan, he claimed that the "yttrium earths" (Gd-Lu) are concentrated by some geochemical processes because of the greater mobility of their complexes, and that the relative stability of the complexes is directly related to the acidity of the solutions. According to Mineyev the sequence of abundance $\text{Ce} \gg \text{Nd} > \text{La} > \text{Gd}$ gives a good estimate of the relative basicity of the solutions, and that a zonation or paragenetic sequence such as $\text{Yb} \rightarrow \text{Dy} \rightarrow \text{Ce}$ reflects deposition from increasingly basic solutions. Higher fluorine and alkali contents and degree of albitization accompanying early phases also attest to their deposition from more acid solutions under which their complexes were not stable. A direct linear correlation between F and the HREE (Gd-Lu) and an inverse linear correlation between F and the LREE suggests that the HREE were transported by fluoride complexes. The concentration of F and HREE in the apical

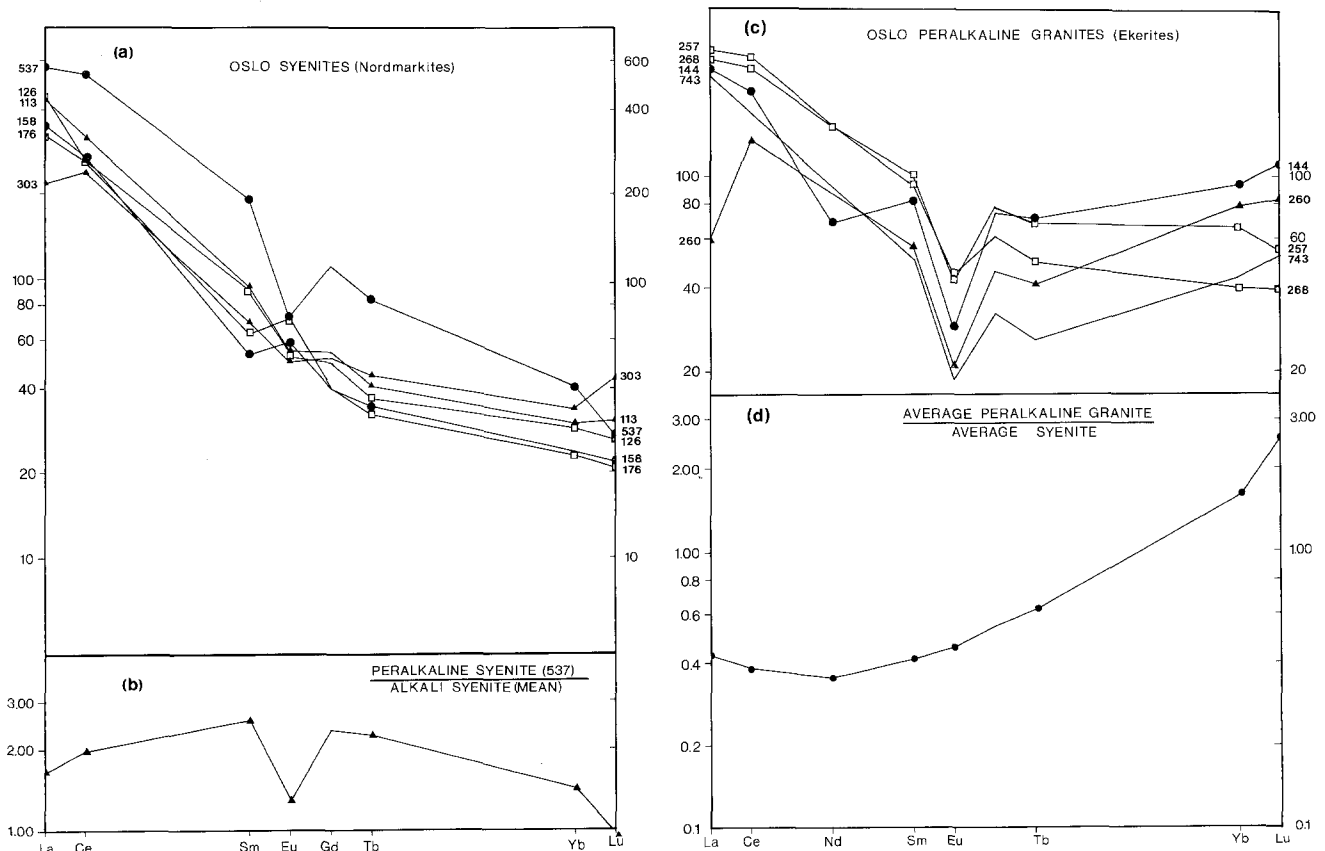


Fig. 4a-d. Chondrite-normalized REE patterns of peralkaline syenites (nordmarkites) and granites (ekerites) from the Oslo Rift, Norway. Data from Neumann et al. (1977). Note the strong relative enrichment of HREE in the peralkaline granite, similar to that of the Topsails Complex (Fig. 2). Fig. 4(d) shows the ratio of average peralkaline granite (numbers- 144, 257, 260, 268 and 143) to average syenite (numbers 113, 126, 158, 303, and 176)

albitized parts of plutons suggest that the transporting fluid was very mobile, presumably volatile.

Although little data are available, it has been demonstrated both empirically (Kerrick and Fryer 1979; Taylor and Fryer 1980; McLennan and Taylor 1979; Kosterin 1959) and experimentally (Flynn and Burnham 1977) that the light and intermediate REE are concentrated by Cl^- -bearing fluids whereas the heavy REE are concentrated by F^- - or CO_3^{2-} -bearing fluids. This confirmed the conclusions of Balashov and Krigman (1975), who also showed that the stability constants of REE-chloride complexes are lower by several orders of magnitude than those of fluorides, phosphates and carbonates of the alkalis, the latter thus being more effective agents of concentration. Kosterin (1959) and Langmuir (1978) have demonstrated that carbonate complexes of the HREE and uranyl ions are stable under relatively alkaline and oxidizing conditions. This would allow for the transport of the HREE and U and their concentration in late stage fluids such as those responsible for metasomatism in the Topsails Complex. There the presence of magmatic and metasomatic carbonates appear to support such a suggestion, although the presence of fluorite might also reflect fluoride complexing. With regard to the latter case, however, we have REE data from other peralkaline granites of Newfoundland such as Traytown and St. Lawrence which are extremely enriched in fluorine (the latter containing veins of economic importance), which show no significant effect on separating the HREE from the LREE. This may mean that fluoride complexes are unimportant in such plutons, or that pH and other variables were unsuitable for the stability of such complexes.

The source of the fluids is difficult to establish, but we do note that in two suites which show good evidence for peralkalinity arising through sodium-metasomatism, viz. the Topsails and the Evisa complex of Corsica (Bonin et al. 1978), and for which isotopic data are available, the more peralkaline suites exhibit the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios (0.7029 and 0.7034 respectively) implying that the Na-rich fluids were mantle-derived. Furthermore, we note that there is increasing evidence for and acceptance of the importance of mantle CO_2 , the degassing of which could have profound effects ranging from chemical transport (Green, 1979) and control of phase relations (Wyllie and Huang 1975), to transport of heat for the production of thermal domes (Schuiling and Krueen 1979). We support Bailey (1978, 1980) in suggesting that it is more than coincidence that peralkaline suites are common in areas of thermal doming, rifting, and even carbonatite magmatism. We would go further and suggest that the Ni, and possibly the Zn, Sn and other elements concentrated in these suites originated in the mantle and was transported by outgassing CO_2 . Evaluation of these suggestions requires detailed studies, especially of fluid inclusions and stable isotopes, along with more systematic experimental studies like that of Flynn and Burnham on volatile transport of REE and other elements.

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