

## EXTREME DIFFERENTIATION OF PERALKALINE RHYOLITE, TERCEIRA, AZORES: A MODERN ANALOGUE OF STRANGE LAKE, LABRADOR?

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### ABSTRACT

We compare compositional data from a suite of Recent glassy lavas, melt inclusions, and comagmatic syenitic xenoliths from Pico Alto volcano, on Terceira Island, Azores, with the compositions of fresh and hydrothermally altered facies of the Strange Lake rare-metal granite (Quebec–Labrador). Trace-element modeling shows that magmatic enrichment in a pantelleritic magma at Pico Alto can generate *HFSE* abundances like those observed in early intrusive stages at Strange Lake. Compositional changes accompanying complete crystallization and separation of orthomagmatic fluid from pantellerite magma at Pico Alto mirror the enriched component in *HFSE*-mineralized granite at Strange Lake. We conclude that *HFSE* ores can be generated by processes of magmatic enrichment followed by separation of a *HFSE*-charged orthomagmatic fluid upon final solidification of the silicate melt, and redeposition of these elements in the roof zone of the pluton.

**Keywords:** peralkaline, granite, rhyolite, pantellerite, rare-earth elements, high-field-strength elements, orthomagmatic fluid, magmatic enrichment, Strange Lake, Quebec–Labrador, Terceira, Azores.

### SOMMAIRE

Nous comparons ici les données chimiques pour une suite de coulées vitreuses, d'inclusions vitreuses et de xénolithes syénitiques comagmatiques d'âge récent, provenant du volcan Pico Alto, sur l'île de Terceira, dans les Açores, avec la composition d'échantillons frais et altérés du granite de Strange Lake (Québec–Labrador), enrichi en métaux rares. Un modèle pétrogénétique fondé sur les teneurs en éléments traces montre qu'un enrichissement magmatique du liquide pantelleritique à Pico Alto peut expliquer les teneurs en éléments à rapport élevé de valence à rayon ionique qui caractérisent le stade intrusif précoce à Strange Lake. Les changements en composition qui accompagnent la cristallisation complète et la séparation d'une phase fluide orthomagmatique d'un magma pantelleritique à Pico Alto ressemblent de façon frappante aux changements qui caractérisent le faciès minéralisé à Strange Lake. A notre avis, les zones minéralisées en métaux rares résulteraient d'un enrichissement au stade magmatique, suivi de la séparation d'une phase fluide orthomagmatique à teneur élevée de ces éléments suite à la solidification finale du magma silicaté, avec redéposition dans les zones apicales du pluton.

**Mots-clés:** hyperalkalin, granite, rhyolite, pantellerite, terres rares, éléments à rapport élevé de valence à rayon, fluide orthomagmatique, enrichissement magmatique, Strange Lake, Québec–Labrador, Terceira, Açores.

### INTRODUCTION

Intrusive bodies of peralkaline granite may show sufficient enrichments in Zr, Nb, U, Th, Be, Y, Hf, Sn and the rare-earth elements (*REE*) to become ore deposits of these elements. As an example, the Strange Lake pluton, a Middle Proterozoic intrusion of peralkaline granite on the Quebec–Labrador border, shows an unusual level of enrichment of the high field-strength elements (*HFSE*). Reserves in the ore zone are

estimated to be 52 million tonnes at 2.93% ZrO<sub>2</sub>, 0.54% *REE* oxides, 0.38% Nb<sub>2</sub>O<sub>5</sub>, 0.31% Y<sub>2</sub>O<sub>3</sub>, and 0.09% BeO (Sinclair *et al.* 1992). Extreme levels of enrichment of the *HFSE* were attained by protracted fractional crystallization of a less evolved magma, followed by the liberation of a reduced, saline orthomagmatic fluid capable of transporting and further concentrating these elements. In this contribution, we document patterns both of magmatic enrichment and of hydrothermal remobilization of the *HFSE* in the relatively well-understood, active Pico Alto peralkaline center on Terceira Island, Azores, and draw parallels between processes at work there and those that led to mineralization at Strange Lake.

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## PICO ALTO VOLCANO

TABLE 1. COMPOSITIONS OF ROCKS AND MELT INCLUSIONS FROM PICO ALTO AND STRANGE LAKE

Sample	Pico Alto							Strange Lake					
	P16	90-182	int	int	inc9	inc10	S4	S10	Ac	Chl	hyp*	fsub*	asub*
SiO <sub>2</sub>	66.78	65.86	65.50	66.80	66.38	69.00	64.58	64.83	50.37	21.83	70.50	70.27	71.00
TiO <sub>2</sub>	0.53	0.35	n.d.	n.d.	0.27	0.73	0.63	0.43	1.49	0.01	0.30	0.21	0.32
Al <sub>2</sub> O <sub>3</sub>	10.55	12.12	5.14	5.00	14.60	5.53	16.45	14.78	0.22	0.42	11.55	11.54	8.67
Fe <sub>2</sub> O <sub>3</sub>	2.57	3.27	n.d.	n.d.	n.d.	n.d.	5.15	6.07	29.97	59.52	2.63	2.05	4.15
FeO	5.80	4.32	13.29	11.78	5.35	11.32	n.d.	n.d.	n.d.	n.d.	2.77	2.87	1.47
MnO	0.34	0.33	0.68	0.66	0.22	0.48	0.21	0.26	0.99	1.94	0.11	0.10	0.14
MgO	0.08	0.20	n.d.	n.d.	0.13	0.33	0.27	0.09	0.42	0.40	0.02	0.01	0.23
CaO	0.51	0.69	n.d.	n.d.	0.42	0.43	0.94	0.34	1.46	0.23	0.64	0.77	1.56
Na <sub>2</sub> O	7.30	6.62	10.73	10.46	9.08	4.91	7.05	7.27	12.49	0.31	5.08	4.49	3.96
K <sub>2</sub> O	4.45	4.72	4.27	4.21	5.16	4.64	4.93	5.17	0.01	0.24	4.81	5.70	3.88
P <sub>2</sub> O <sub>5</sub>	0.04	0.03	n.d.	n.d.	n.d.	n.d.	0.10	0.06	n.d.	n.d.	0.02	0.02	0.02
LOI	0.00	0.87	n.d.	n.d.	n.d.	n.d.	0.16	0.50	n.d.	n.d.	0.48	0.41	0.84
Total	98.95	99.58	99.64	98.92	101.63	97.41	100.47	99.80	97.46	84.92	98.91	98.73	96.24
Ba	201	143	n.d.	n.d.	66	n.d.	745	166	n.d.	n.d.	n.d.	n.d.	n.d.
Nb	304	234	720	830	n.d.	n.d.	142	286	120	<100	356	327	926
Zr	1742	1257	3600	3210	2077	n.d.	734	1607	7990	10100	3456	3214	13115
Y	152	115	190	240	254	n.d.	58	37	n.d.	n.d.	445	705	1373
Sr	2	7	n.d.	n.d.	47	n.d.	31	2	n.d.	n.d.	35	30	79
Rb	187	142	n.d.	n.d.	n.d.	n.d.	89	183	n.d.	n.d.	600	1067	995
Th	29	22	n.d.	n.d.	n.d.	n.d.	15	30	n.d.	n.d.	82	63	252
U	19	16	n.d.	n.d.	n.d.	n.d.	<1	4	n.d.	n.d.	10	6	36
La	163.0	123.1	n.d.	n.d.	157.9	n.d.	75.7	122.5	n.d.	n.d.	414.6	736.0	831.2
Ce	296.7	240.3	n.d.	n.d.	409.8	n.d.	147.3	217.9	n.d.	n.d.	749.5	1278.0	1511.1
Pr	33.6	27.5	n.d.	n.d.	n.d.	n.d.	16.9	23.5	n.d.	n.d.	n.d.	n.d.	n.d.
Nd	120.9	99.9	n.d.	n.d.	163.3	n.d.	60.2	77.3	n.d.	n.d.	310.5	515.6	652.9
Sm	22.7	20.0	n.d.	n.d.	35.5	n.d.	11.5	12.7	n.d.	n.d.	72.8	118.5	174.4
Eu	2.8	2.6	n.d.	n.d.	7.3	n.d.	2.3	1.1	n.d.	n.d.	3.7	5.8	9.4
Gd	21.0	19.2	n.d.	n.d.	30.4	n.d.	10.3	9.2	n.d.	n.d.	64.7	95.8	207.3
Tb	3.2	2.9	n.d.	n.d.	n.d.	n.d.	1.5	1.2	n.d.	n.d.	10.5	14.9	57.7
Dy	21.5	19.4	n.d.	n.d.	34.2	n.d.	10.5	7.6	n.d.	n.d.	49.2	92.4	166.0
Ho	4.1	3.6	n.d.	n.d.	n.d.	n.d.	2.0	1.4	n.d.	n.d.	n.d.	n.d.	n.d.
Er	12.1	10.5	n.d.	n.d.	26.2	n.d.	6.1	4.4	n.d.	n.d.	n.d.	n.d.	n.d.
Tm	1.7	1.5	n.d.	n.d.	n.d.	n.d.	0.9	0.8	n.d.	n.d.	6.0	6.7	23.9
Yb	10.5	9.4	n.d.	n.d.	31.3	n.d.	5.4	6.2	n.d.	n.d.	47.2	52.6	183.9
Lu	1.6	1.3	n.d.	n.d.	n.d.	n.d.	0.8	1.0	n.d.	n.d.	4.5	6.8	23.0
Hf	23.4	21.0	n.d.	n.d.	n.d.	n.d.	9.9	16.1	n.d.	n.d.	80	113	429
Ta	15.5	11.5	n.d.	n.d.	n.d.	n.d.	9.0	14.9	n.d.	n.d.	18	26	25
F	n.d.	n.d.	n.d.	n.d.	2410	2830	n.d.	n.d.	n.d.	<100	n.d.	n.d.	n.d.
Cl	n.d.	n.d.	n.d.	n.d.	4680	11900	n.d.	n.d.	n.d.	15050	n.d.	n.d.	n.d.

Major elements, Ba, Nb, Zr, Y, Sr, Rb, Th, U data for whole rocks from Pico Alto (P16 and 90-182 are pantellerite, S4 and S10 are quartz syenite) by X-ray fluorescence; concentrations of the REE and Hf, Ta by INAA. All data for melt inclusions (inc) and interstitial glass (int) from Pico Alto pantellerite by electron microprobe with defocused beam, 15 kV accelerating voltage and counting times of up to 300 seconds, except for trace elements in inc9, which were done by SIMS. \* data for Strange Lake granites from Nassif (1993, Tables 1, 2); hyp is hypersolvus granite, fsub is unaltered subsolvus granite, asub is altered subsolvus granite. Data in upper part of the table in wt.%, in lower part of the table, in ppm.

Pico Alto is a recently active center of peralkaline magmatism located in the north-central sector of Terceira Island (Self 1976, Mungall & Martin 1995). The center consists of a pre-caldera, shield-like pantellerite complex of domes and flows, which is cut by a caldera-collapse structure and overlain by associated ignimbrite erupted 22,000 years ago. Post-caldera flows and domes of pantellerite vented from the caldera rim. The caldera-forming eruptions of ignimbrite carried with them xenoliths of quartz syenite that are comagmatic with the pantellerite suite (Mungall & Martin 1995). These holocrystalline xenoliths provide a view of the final stages of crystallization and early hydrothermal activity associated with slow cooling of pantelleritic magma.

The pantellerite typical of Pico Alto contains several modal percent of phenocrysts of sanidine, aegirine-augite, fayalite, ilmenite, apatite and rare pyrite, set in a glassy microlite-rich groundmass. Some flows contain amphibole and aenigmatite. Representative compositions of the lava and comagmatic syenites appear in Table 1. Fayalite phenocrysts commonly contain glass inclusions bearing small shrinkage-induced bubbles; we suggest that these inclusions represent samples of the host liquid trapped during growth of the phenocrysts.

We have analyzed the melt inclusions within fayalite phenocrysts, and intratelluric glass in partially crystallized pantellerite, using an electron microprobe. Details of the analytical procedure appear in Mungall (1993), and results appear in Table 1. Trace element data for a single melt inclusion (inc9) were obtained by Secondary Ion Mass Spectrometry (SIMS) on the ion probe at the Centre de Recherches Pétrographiques et Géochimiques (CRPG), Nancy. The proportion of Na<sub>2</sub>O reported is likely to be too low for all compositions more peralkaline than the host lava, whose aegirite index ([Na+K]/Al, cation units) is 1.6, due to loss of Na under the electron beam; similarly in less strongly peralkaline compositions, the Na<sub>2</sub>O content is likely to be overestimated, because the rate of loss of sodium during analysis was found to depend on degree of peralkalinity.

The extreme iron enrichment recorded in the melt-inclusion data resulted from evolution at a very low oxygen fugacity (Mungall & Martin 1995). Evolution of the suite at a higher fugacity of oxygen would have led to less extreme enrichment of iron and a comenditic liquid line of descent more closely resembling that at Strange Lake, but enrichment of HFSE would show only minor dependence on the oxygen fugacity. The compositions of some intratelluric glasses were found to result from disequilibrium crystallization (Mungall 1993) and have been omitted from this study. Others, which have evolved along the liquid line of descent as defined by melt inclusions within crystals, are

included.

Quartz syenite xenoliths (Fig. 1) from Pico Alto are dominantly composed of alkali feldspar ranging from fresh sanidine to turbid micropertite. Other primary phases include all the phenocrysts typical of the lavas. The framework of interlocking crystals of feldspar encloses an extensive network of miarolitic cavities that make the rock highly porous and permeable. Within the cavities are a number of unusual mineral species and textures (Fig. 2). Euhedral quartz and alkali amphibole, both with pronounced growth-zones,

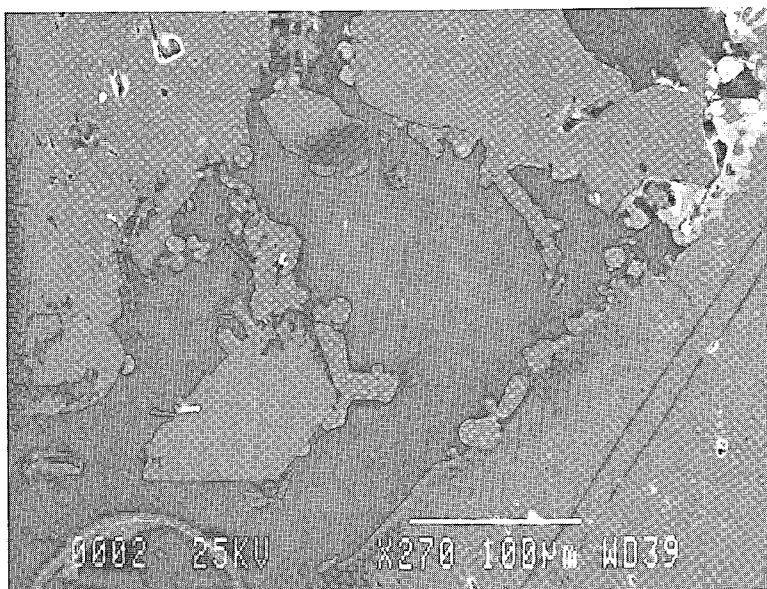


FIG. 1. Back-scattered electron image of miarolitic cavity in quartz syenite from Pico Alto. Large crystals to right and left are microperthite with albite overgrowths. Euhedral grey crystals projecting into cavity are end-member aegirine with more than 0.5 wt.% Zr. Botryoidal layered decorations on aegirine are zircon with a fibrous radial growth-habit.

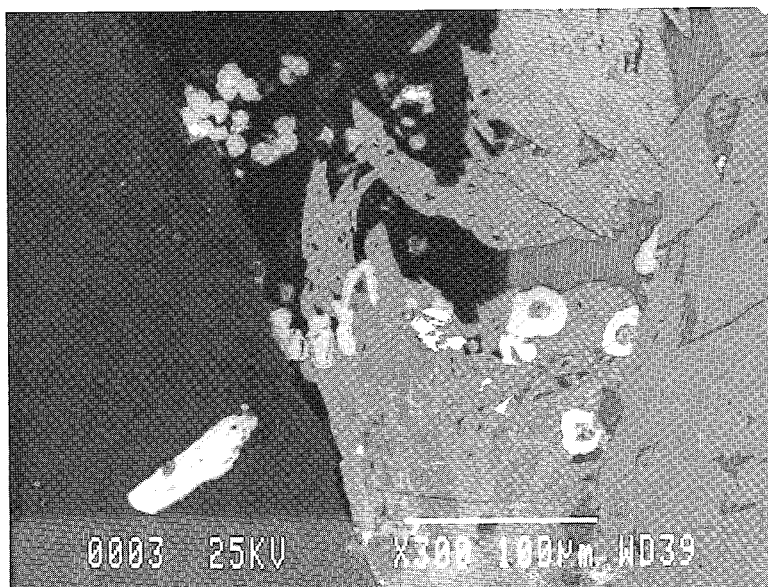


FIG. 2. Back-scattered electron image of a miarolitic cavity in quartz syenite from Pico Alto. Medium grey coxcomb in cavity is end-member delessite (Fe-bearing chlorite) containing more than 1.0 wt.% Zr. The bright streaks in the delessite are monazite. Also visible are balls of botryoidal zircon, as in Figure 1. The elongate bright crystal within microperthite at lower left is a member of the britholite-apatite series. All minerals were identified by energy-dispersion analysis.

predominate in the cavities between euhedral alkali feldspar crystals, in some cases completely filling them. Needles of nearly end-member aegirine containing more than 0.5 wt.%  $ZrO_2$  project into the cavities, and are in turn commonly decorated with botryoidal fibrous balls of zircon. An iron-rich chlorite close to end-member ferroan clinocllore, containing more than 1.0 wt.%  $ZrO_2$ , coexists with monazite and unidentified oxides of Nb and Ta. The compositions of some of these phases appear in Table 1. The unusual Zr-rich minerals, monazite, Nb oxides and botryoidal zircon all must have been deposited from a fluid phase, because the crystals project into void space. There is, therefore, clear textural and compositional evidence for large-scale mobilization of the HFSE in the orthomagmatic fluids at Pico Alto.

#### THE STRANGE LAKE PLUTON

The Strange Lake body, a small (7 km across), high-level pluton, consists of texturally variable, but mineralogically simple, peralkaline granite. It was emplaced along the contact between Middle Proterozoic quartz monzonite and Late Archean to Early Proterozoic metagabbroic, metagranitic and metasedimentary rocks. One source of textural variability concerns the order of crystallization of the

arfvedsonitic amphibole and aegirine. These minerals may be close to the liquidus in some intrusive units and close to the solidus in others. Whether a single magmatic alkali feldspar crystallized (hypersolvus case) or coexisting sodic and potassic feldspars (subsolvus case) provides an additional dimension of textural variability (Nassif & Martin 1992). These internal variations, as well as the presence of roof pendants, suggest that the depth of crystallization was on the order of 4–7 km, corresponding to water vapor pressures of approximately 1 to 2 kbar.

The earliest phase to be emplaced was a hypersolvus arfvedsonite granite; later units consist of transolvus and subsolvus granite facies. Miarolitic cavities are developed both in the granites and in sheet-like bodies of associated pegmatite and aplite (Miller 1996) near the ore zone. The original pore-space has largely been filled by a variety of hydrothermal minerals including quartz, albite, fluorite, and zirconosilicates. Some secondary pore space formed as a result of late-stage dissolution of quartz at low temperatures (Salvi 1995). There is controversy about just what is primary and what is hydrothermal among the zirconosilicates, and the issue is clouded by complex pseudomorphic reactions that obliterate the primary assemblages (Birkett *et al.* 1992, Salvi 1995).

It is evident that the hydrothermal chapter of the

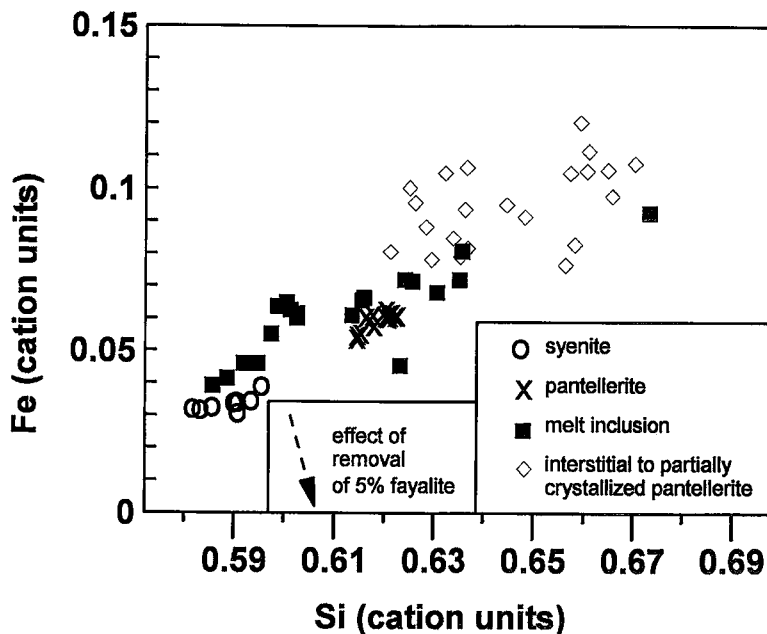


FIG. 3. Compositions of pantellerite, syenite, melt inclusions and intratelluric glass from partially crystallized pantellerite; Fe versus Si (cation units, dry). Syenite, melt inclusions, intratelluric glass and lavas together define a liquid line of descent for the pantellerite suite of Pico Alto. An olivine-control line indicates the effect of removal of 5% fayalite from a composition starting on the liquid line of descent. Host-mineral crystallization has evidently not affected the compositions of the melt inclusions.

mineralization has been very important at Strange Lake. The presence of zirconosilicates as daughter minerals and of methane and higher hydrocarbons in primary and pseudosecondary fluid inclusions (Salvi & Williams-Jones 1990, 1992) has led to the hypothesis that the ore zone at Strange Lake is the result of mixing of a reduced orthomagmatic fluid containing abundant *HFSE* with a second, Ca-rich and more oxygenated fluid derived from the country rocks (Salvi 1995). Mixing of the two fluids is considered to have caused precipitation of fluorite, by removing a primary ligand for dissolved *HFSE* (e.g., Wood 1990, Salvi 1995), thereby leading to precipitation of Ca-zirconosilicates.

#### PETROGENETIC MODELS

The compositions of glassy melt inclusions, and of whole-lava samples, from Pico Alto are plotted in Figure 3. The whole lavas and the melt inclusions define a clear trend. If, as we have assumed (Mungall 1993), the melt inclusions represent aliquots of host liquid trapped within growing phenocrysts of fayalite, then the trend of their compositions can be inferred to represent the liquid line of descent of the pantellerite suite. We first address the possibility that the melt inclusions do not represent the host liquid, either because of the possible presence of a diffusive

boundary-layer surrounding the phenocryst during growth (*cf.* Wang & Merino 1993) or because of post-entrapment crystallization of the host mineral. Since fayalite is a very minor constituent of the crystallizing assemblage of the pantellerite suite, either possible problem should be evident in the form of dispersion of the data along fractional-crystallization-induced control lines passing through the composition of the host fayalite. The effects of 5% fayalite crystallization appear in the inset in Figure 3; there is evidently little such dispersion, and we therefore dismiss these effects as insignificant.

Simple fractional crystallization can account for the range of bulk compositions documented in the melt inclusions and whole-rock samples of lava. A least-squares mixing model of fractional crystallization of the suite (Mungall & Martin 1995) indicated that the most silicic melt inclusion could be produced from the least silicic one by 74% perfect fractional crystallization of ilmenite, fayalite, sodic hedenbergite and sanidine.

Magmatic enrichment *via* fractional crystallization has been shown to have produced greater than 30-fold enrichments in *HFSE* in the basalt–pantellerite suite of Pico Alto (Mungall & Martin 1995). Here we explore the potential of similar processes to generate the types of enrichment observed at Strange Lake, through the

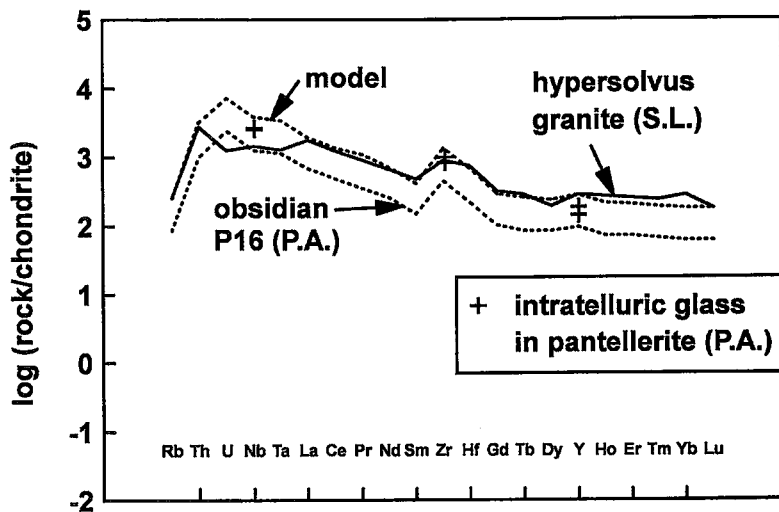


FIG. 4. Trace-element abundances in pantellerite from Pico Alto, hypersolvus granite from Strange Lake, and model composition resulting from 70% crystallization of the pantellerite, normalized to C1 chondrite [chondritic abundances in this and subsequent figures from Sun & McDonough (1989)]. Also shown are Nb, Zr and Y concentrations measured in intratelluric glass in pantellerite from Pico Alto. The model profile and that of the intratelluric glass match early intrusive rocks from Strange Lake, except for U, Nb and Ta, indicating that the primary enrichment of *HFSE* at Strange Lake could have been achieved simply by fractional crystallization of a pantelleritic magma.

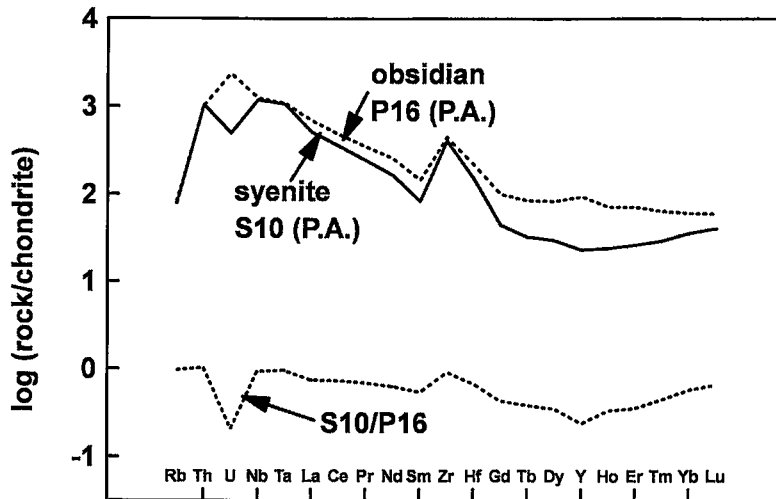


FIG. 5. Trace-element abundances in pantellerite and quartz syenite from Pico Alto. Abundances of elements inferred to be immobile upon crystallization are identical in the two rocks. Pronounced depletions of U, Y and REE are attributed to their mobilization in orthomagmatic fluids. The bottom curve shows the relative difference between the two profiles.

use of simple models of trace-element enrichment expected by fractionation of the observed assemblage of phenocrysts and the partition coefficients of Mungall & Martin (1995). Figure 4 is a spidergram showing the concentrations of lithophile elements in a single sample of obsidian from Pico Alto. Also shown is the average composition of the early-formed, unaltered hypersolvus granite at Strange Lake. The curve labeled "model" shows the composition produced by 70% fractional crystallization of the magma represented by obsidian sample P16 from Terceira. Although they disagree in some details, especially U concentrations, the model and the Strange Lake compositions are remarkably close. Indeed all three patterns in the diagram are essentially parallel, reflecting the effects of fractional crystallization on a suite of essentially incompatible elements in magmas with very similar compositions of the parental magma. In addition, we have shown the concentrations of Nb, Y and Zr in glass interstitial to pantellerite after approximately 50% fractional crystallization of the pantelleritic liquid, as determined by electron-microprobe analysis (data from Table 1; see also Mungall 1993). These data show that the actual intratelluric liquid present in the Pico Alto pantelleritic magma was already as HFSE enriched as the magma that was first intruded at Strange Lake. Thus, simply separating the phenocrysts from the melt in the erupted lavas at Pico Alto would be sufficient to

generate a residual liquid very closely resembling the hypersolvus granite at Strange Lake.

In Figure 5, we present abundances of the lithophile elements in a glassy pantellerite lava (P16) and a holocrystalline syenite xenolith (S10), both from Terceira. Comparison of the abundances of Rb, Ba, Th, Nb, Ta and Zr indicates that these two comagmatic rocks had evolved to essentially identical degrees of HFSE enrichment. On this basis, the trace-element patterns of both the obsidian and the crystalline xenolith would be expected to be identical. However, U, Y, Hf and REE are depleted in the fully crystalline syenite (S10) relative to the glassy lava (P16), indicating that these elements were mobile during the final stages of crystallization (*cf.* Baker & Henage 1977, Weaver *et al.* 1990).

In Figure 6, we compare the trace-element abundances found in hydrothermally altered subsolvus granite associated with the ore zone at Strange Lake with those typical of the unaltered subsolvus granite. There is considerably more scatter in the data for the altered subsolvus granite than is evident for the unaltered equivalent, or in any sample from the Terceira suite. We attribute this variability to the sequestering of the "trace" elements into rare-element minerals in these coarse-grained rocks, leading to inevitable statistical noise in compositions of hand specimens collected in the field. However, there is a clear pattern of enrichment of U, Y, Hf and REE in the altered granite;

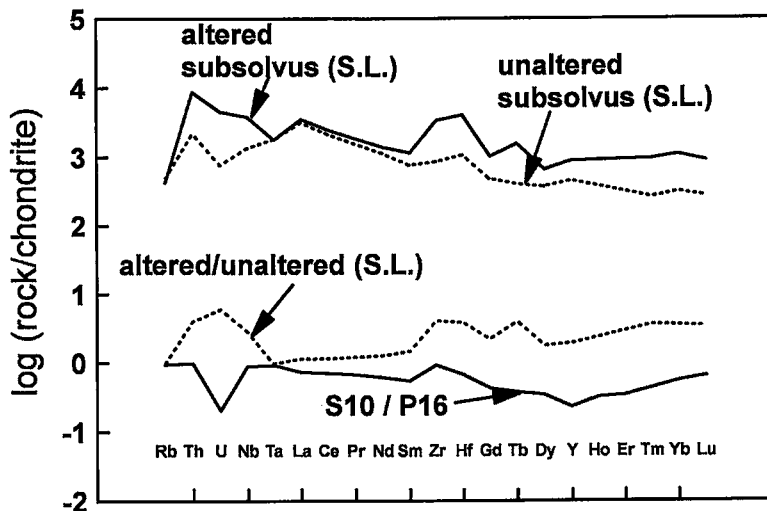


FIG. 6. Comparison of trace-element abundances in altered *versus* unaltered subsolvus granite from Strange Lake. The dashed line at the bottom shows the relative difference between the two, indicating very-large-scale enrichment of U, REE, Y, and Hf, mirroring the pattern of depletion of these elements in the syenites of Pico Alto. The additional enrichment in Th, Nb and Zr may reflect enhanced mobility of these elements in the fluids that separated from the extremely evolved Strange Lake magma.

Th, Nb, and Zr also are enriched. At the bottom of Figure 6, the relative depletions of trace elements inferred to have resulted from complete crystallization of the Pico Alto lava are contrasted with the pattern of enrichment of the same elements in the transition from unaltered to altered subsolvus granite at Strange Lake. With the exception of Zr, the patterns are complementary. In general, where elements are depleted by crystallization of pantellerite at Pico Alto, they are enriched by the alteration process at Strange Lake. The anomalous behavior of Zr probably results from increased mobility of Zr in the more strongly evolved and presumably more complex magmatic-hydrothermal system at Strange Lake.

#### RELATION TO RARE-METAL DEPOSITS

The high halogen contents observed in the glass inclusions in the fayalite phenocrysts (Table 1) are probably complemented by high H<sub>2</sub>O contents. Several investigators have reported or inferred water contents on the order of 4.0 wt.% in peralkaline felsic magmas at other localities (Wolff & Storey 1983, Kovalenko *et al.* 1988, Lowenstern & Mahood 1991, Webster *et al.* 1993). If the Strange Lake granite was derived from a pantelleritic parental magma with a similar composition by an extended process of fractional crystallization, then the residua might carry as much as 8.0% H<sub>2</sub>O along with a minimum of 1.5% halogens,

giving great potential for generation of orthomagmatic fluids. The nature of the melt-water solvus in strongly peralkaline systems is not well understood (*e.g.*, McMillan 1994), and it is not possible to predict water concentrations at saturation in these magmas without experiments. However, the solubility of volatiles in strongly peralkaline magma is certainly very high, and, furthermore, these melts are expected to release large quantities of a peralkaline fluid phase near the solidus of the silicate melt. It may even be possible, in strongly peralkaline systems, for a second critical end point to be passed at pressures that obtain in the upper crust (*e.g.*, McMillan 1994). Supercritical fluids so generated would be expected to be able to carry extraordinary loads of solute, and would depart from the rock to leave a void space behind them.

The unusual assemblage of fluid-deposited minerals in the miarolitic cavities in the plutonic equivalents of the pantellerite at Pico Alto provides direct evidence for the action of HFSE-charged orthomagmatic fluids, the existence of which has been inferred by numerous investigators in the past (*e.g.*, Weaver *et al.* 1990, Salvi 1995). We suggest that in the last stages of crystallization, a saline aqueous fluid was released, containing major quantities of U, Hf, Y and REE (*cf.* Bailey & Ragnarsdottir 1994, Collins & Ragnarsdottir 1994, Poitrasson *et al.* 1995), and possibly also containing very large quantities of dissolved silicate minerals. Such fluids, represented by fluid inclusions

containing REE phases as daughter minerals, have been documented in Strange Lake rocks (Salvi & Williams-Jones 1990, 1992). A large flux of mineralizing fluid from subjacent crystallizing pantellerite might have passed through the roof zone of the intrusion at Strange Lake. The observed high primary porosity and inferred permeability of the early-crystallized subsolvus granite would allow local focussing of fluid flow. Decreases in temperature and mixing with an externally derived, subalkaline and more oxygenated fluid phase in the roof zone (Salvi 1995) can be expected to destabilize the dissolved HFSE and promote their precipitation in the pore space.

In this discussion, we have avoided modeling the major-element compositions during the fractionation process, because it is an underdetermined problem that does not need to be solved in the context of this study. All of the trace elements with which we have concerned ourselves are essentially incompatible; see, for example, the compilation of partition coefficients in Mungall & Martin (1995). Mungall (1993) measured mineral-glass partition coefficients for Zr in amphibole, aenigmatite, clinopyroxene, apatite, fayalite, ilmenite and sanidine in pantellerite of, respectively, 0.10, <0.05, 0.25, <0.08, <0.03, <0.08, and <0.04. Since in any reasonable model sanidine is the main crystallizing phase, the first-order parameter is the amount of crystallization, whereas the exact nature of the crystallizing assemblage is of secondary importance. In the course of the modeling, we confirmed the validity of this assumption by modeling fractionation processes with widely varying solid assemblages, and found minimal differences in the outcome. This approach also allows us to compare the Pico Alto pantellerite complex directly with the Strange Lake granite without concern for the minor differences evident in major-element composition between the two suites.

There are a few other occurrences in the world of HFSE ore deposits associated with extensive magmatic enrichment processes. In particular, the Thor Lake rare-metal deposit strongly resembles Strange Lake (Sinclair *et al.* 1992, Pinckston & Smith 1995), and shows similar evidence for the importance of late-stage alteration in the final steps of concentration of ore metals. Perhaps in contrast to this model of combined magmatic and hydrothermal processes, the Brockman rare-metal deposit in northwest Australia (Taylor *et al.* 1995) appears to represent an erupted equivalent of the magmatically enriched residual melt found at Pico Alto, and inferred to be the melt parental to the orthomagmatic fluids at Strange Lake. In this case, the ore grade is distinctly lower than that at Strange Lake, suggesting again that magmatic concentration of ore metals is an important stage in the development of extractable reserves of the HFSE.

## CONCLUSIONS

We have documented the occurrence of uniquely peralkaline, volatile- and HFSE-rich glasses that represent a liquid line of descent during a protracted process of fractional crystallization of pantellerite. The extreme enrichment recorded for the HFSE supports the results of simple models, which suggest that magmatic enrichment of these components is sufficient to account for the abundances of the HFSE in unaltered granitic rocks at rare-metal deposits such as the Strange Lake intrusion. Observed depletions of U, Y, and REE in crystalline equivalents of the glassy lavas at Pico Alto mirror observed enrichments of these elements in mineralized granitic rocks at Strange Lake. We infer that HFSE ore deposits can be generated by protracted fractional crystallization followed by release of an orthomagmatic fluid charged with U, Y and REE. If the flow of this fluid is channeled into a spatially restricted zone where it can be mixed with externally derived fluids, its uniquely high capacity for HFSE transport will be lost, resulting in ore deposition.

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