

# Fluoride-silicate melt immiscibility and the formation of the pegmatite-hosted Strange Lake REE deposit, Quebec-Labrador



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## Extended Abstract

Although fluoride-silicate liquid immiscibility has been demonstrated experimentally (Veksler et al., 2005, 2012), its occurrence in nature has only been reported twice, once from a mantle xenolith (Klemme, 2004; Peretyazhko et al., 2007). Herein we provide evidence that this process was essential in concentrating rare earth elements (REE) to potentially economic levels at Strange Lake, Québec-Labrador.

The Strange Lake pluton (1240 ± 2 Ma; Miller et al., 1997) is a peralkaline granite intrusion, some six kilometres in diameter, which was emplaced along the contact between an Elsonian (1.5-1.4 Ga) quartz monzonite massif and Hudsonian (2.0-1.8 Ga) banded gneisses, and is surrounded by a fluorite-cemented ring breccia (Fig. 1). Regionally, it belongs to the Nain Plutonic suite. Locally, the pluton contains potentially exploitable concentrations of the REE and other high field strength elements (HFSE). An ore-body referred to as the B-Zone has been defined recently by Quest Rare Minerals Ltd., with an indicated reserve of 278 Mt of ore, grading 0.94 wt.% REE<sub>2</sub>O<sub>3</sub> (38% heavy rare earth oxides), 1.92 wt.% ZrO<sub>2</sub> and 0.18 wt.% Nb<sub>2</sub>O<sub>5</sub>. This includes a higher grade zone containing 20 million tons of ore grading 1.44 wt.% REE<sub>2</sub>O<sub>3</sub> (50% heavy rare earth oxides), 2.59 wt.% ZrO<sub>2</sub>, and 0.18 wt.% Nb<sub>2</sub>O<sub>5</sub> (Gowans et al., 2014). Another potential orebody, referred to as the Main Ore Zone, with an indicated reserve of 30 Mt of ore grading 1.96 wt.% REE<sub>2</sub>O<sub>3</sub>, 3.25 wt.% ZrO<sub>2</sub>, and 0.56 wt.% Nb<sub>2</sub>O<sub>5</sub>, was delineated in the early 1980s by the Iron Ore Company of Canada.

Igneous activity commenced with the emplacement of a hypersolvus granite distinguished by a single alkali feldspar that was later transformed to perthite. This was followed by the emplacement of transsolvus and subsolvus granite types (Salvi and Williams-Jones, 1990; Nassif, 1993; Boily and Williams-Jones, 1994). The subsolvus granite, which is strongly altered, is characterised by the occurrence of two alkali feldspars and the transsolvus granite by perthite and separate albite and orthoclase. The other major rock forming minerals are arfvedsonite and quartz. Arfvedsonite occurs interstitially

to the other two minerals in the hypersolvus granite and was clearly the last major silicate phase to crystallize. By contrast, in the subsolvus granite, arfvedsonite occurs as phenocrysts and crystallized early. Alteration is evident mainly in the replacement of arfvedsonite by aegirine and also by hematization of the latter mineral. The last rocks to be intruded were pegmatites. They occur near the roof of the intrusion, mainly in highly altered subsolvus granite, although they are also observed in the other granite types. The pegmatites form gently dipping sheets from a few tens of centimetres to 20 metres in thickness and much less common sub-vertical dikes. Typically the pegmatites are zoned in respect to their major mineralogy. The outer parts of pegmatites are composed mainly of alkali feldspars and arfvedsonite (generally altered to aegirine and also hematite) and the cores of fluorite and quartz. The rare metal mineralisation, including the Main- and B-Zone orebodies, is developed in and around pegmatite sheets in the altered subsolvus granite. The REE are concentrated in the pegmatite cores, almost exclusively as secondary minerals, whereas the high field strength elements (HFSE), notably Zr, are concentrated in the outer parts of the pegmatites (Fig. 2); Zr is mainly in secondary minerals, notably the calcium zirconosilicate, gittinsite, which is typically accompanied by hematite and quartz. Elevated concentrations of REE (mainly the light REE) and HFSE are also observed in the immediately adjacent granite. The ore mineralogy is complex and includes minerals, such as allanite-(Ce), armstrongite, bastnäsite-(Ce), elpidite, fluocerite-(Ce), gadolinite-(Y), gagarinite-(Y), gittinsite, kainosite-(Y), monazite-(Ce), narsarsukite, pyrochlore, titanite and zircon.

Previous studies of the Strange Lake pluton have attributed the rare metal mineralization to a combination of magmatic differentiation and hydrothermal remobilization (Salvi and Williams-Jones, 1990; Boily and Williams-Jones, 1994; Salvi and Williams-Jones, 1996; Gysi and Williams-Jones, 2013). According to this interpretation, the hypersolvus granite is the product of extreme fractional crystallization of a parent syenitic magma. This caused an unusual enrichment in fluorine and

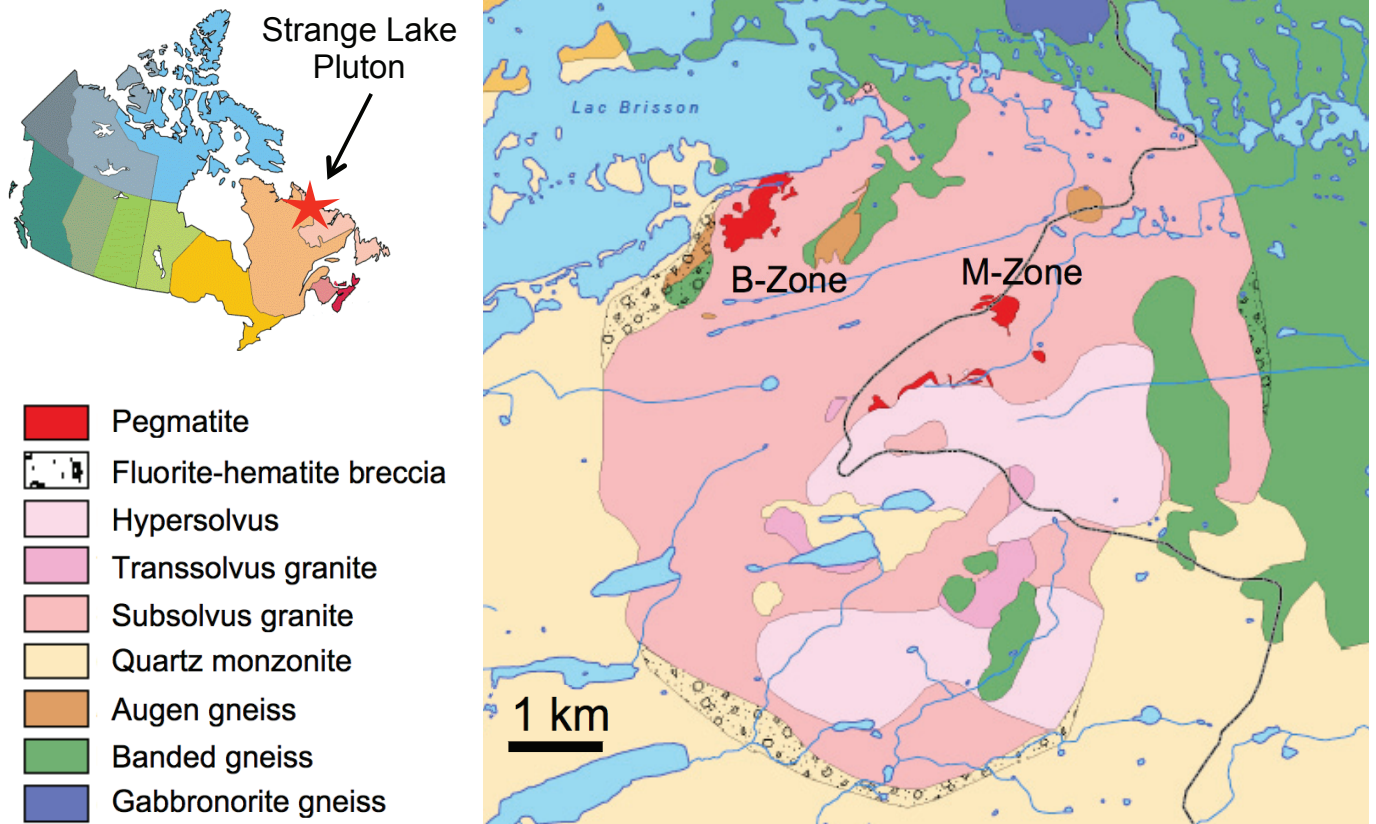


Fig. 1. Geological map of the Strange Lake Pluton showing the distribution of the principal rock types and the locations of the two pegmatite-rich zones with potential for economic REE exploitation.

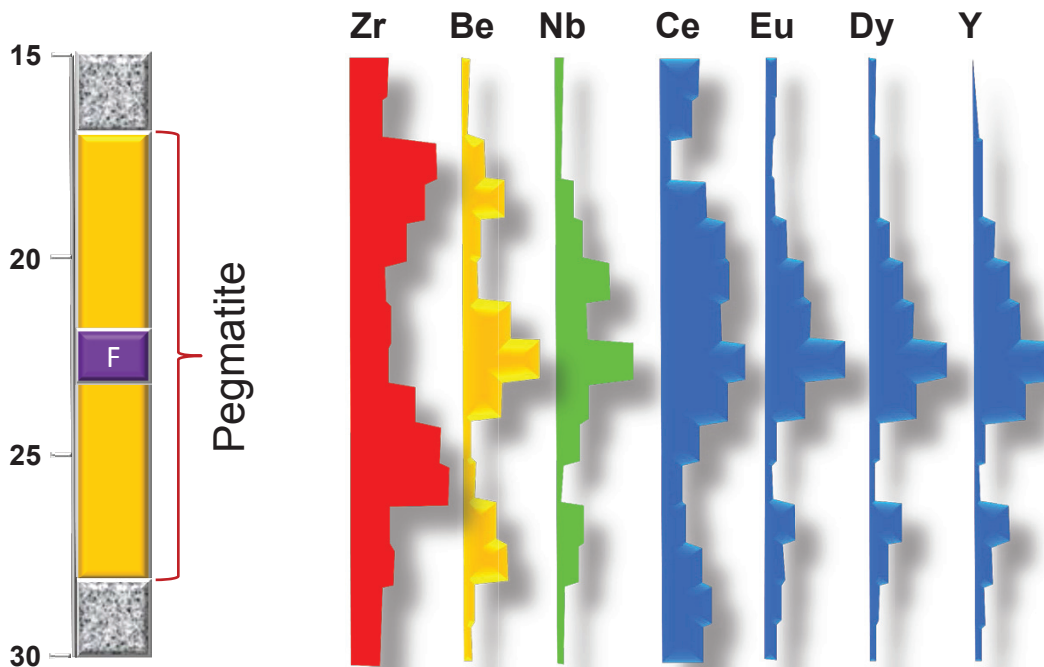


Fig. 2. A schematic drillhole through subsolvus granite and pegmatite illustrating the concentration of fluorite in the pegmatite core and the distribution of selected elements. Note that Zr is concentrated at the pegmatite margins and the heavy REE in the core. Cerium concentrations are more evenly distributed and are elevated in the adjacent granite.

other incompatible elements, including the REE and HFSE; dissolution of the REE and HFSE was facilitated by fluoride complexation. Further fractional crystallization, mainly of alkali-feldspar, lead to the formation of the transsolvus and subsolvus granites and ultimately the pegmatites. As a result there was hyper-enrichment of the REE and HFSE, particularly in the pegmatites. During this fractionation, the H<sub>2</sub>O fugacity increased progressively, as did the concentrations of the other incompatible components. As a result, the size of the alkali feldspar immiscibility field increased, and crystallization of a single alkali feldspar was succeeded by crystallization of K-feldspar and albite to form the subsolvus granite. This increase in H<sub>2</sub>O fugacity culminated in the exsolution of a hydrothermal phase, which auto-metasomatized the subsolvus granite and pegmatites, altering the primary mineralogy. Rare metals, including the REE, were mobilized locally by these fluids to form a variety of secondary minerals. In the apical parts of the pluton, further alteration ensued as a result of the infiltration of formational waters heated by the intrusion. Primary and secondary sodic minerals, including HFSE and REE phases, were replaced by low temperature secondary calcic minerals, and iron-bearing phases, notably arfvedsonite, were oxidised to hematite. This further concentrated the REE and HFSE. The recent discovery of melt inclusions in the granites has allowed us to build on the above model by identifying a potentially important new and powerful mechanism for concentrating the REE and HFSE in granitic rocks, namely silicate-fluoride liquid immiscibility (Vasyukova and Williams-Jones, 2014).

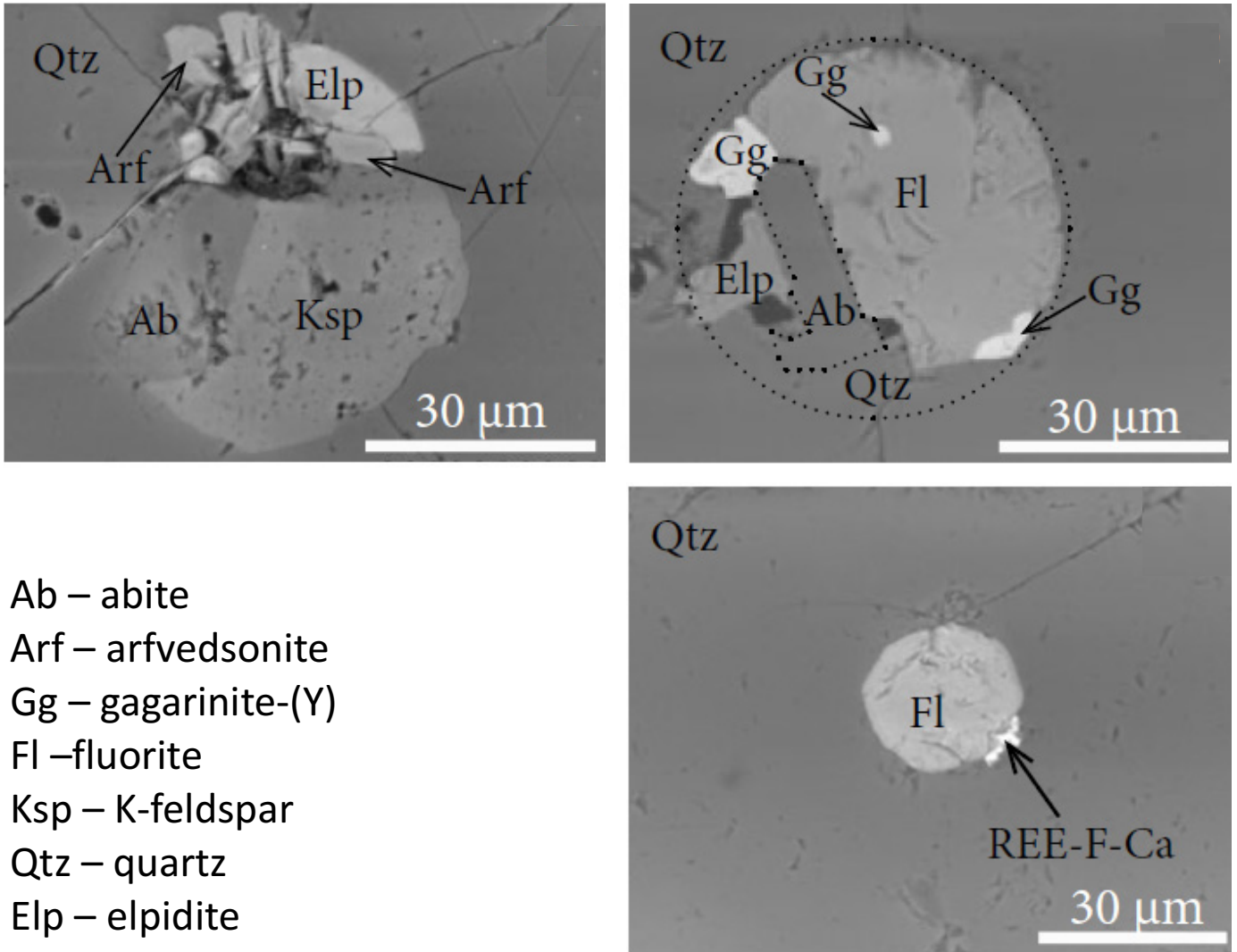
Melt inclusions represented by micron-scale spherical accumulations of minerals (post-entrapment crystallization) are common in the early granites (hypersolvus and transolvus, with respect to alkali feldspar); the later granites (subsolvus) and pegmatites have been strongly altered and evidence of inclusions destroyed (Fig. 3). The melt inclusions were overlooked in earlier studies because of their small size and post-entrapment crystallization. After being heated to 900 or 950°C, a significant proportion of the melt inclusions quench to immiscible fluoride and silicate glasses (Fig. 4). The relative proportions of fluoride and silicate glass, however, vary enormously. Some of the inclusions are composed only of silicate glass, others only of fluoride glass and still others of variable proportions of silicate and fluoride glass, suggesting heterogeneous entrapment of silicate and fluoride melt. Where the proportions of the two glasses are appreciable, the silicate glass forms an annulus in the outer part of the inclusion and the fluoride glass forms the core. The silicate glass contains several weight percent Zr and the fluoride glass >10 wt.% REE. In some cases, there are two fluoride glasses, an outer glass with predominantly Ca containing 10-15 wt.% REE, and an inner glass containing up to 50 wt.% REE (Fig. 4).

In addition to the melt inclusions, there are rare examples of larger fluorine- and REE-rich inclusions in the hypersolvus granite, including one ~5 cm in diameter that contains ~25 wt.% REE (Fig. 5). This latter inclusion consists of a rim composed mainly of chevkinite-(Ce) and zircon in a fluorite

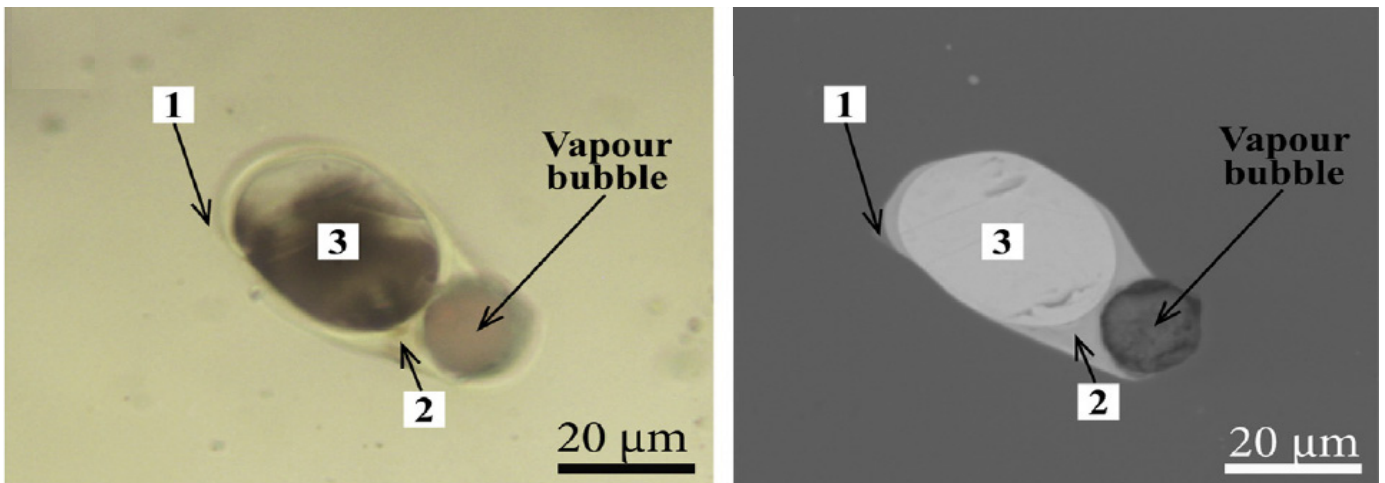
matrix, an intermediate zone of gagarinite-(Y), bastnäsite-(Ce) and fluorite and a core of fluorbritholite-(Ce) and fluorite. Alkali feldspar, and arfvedsonite are concentrated in the outer parts of the globule.

We propose a model (Fig. 6) in which extreme fractional crystallization caused the early hypersolvus magma to saturate with and exsolve an immiscible Ca-fluoride melt (Vasyukova and Williams-Jones, 2014). Consistent with recent experimental data (Veksler et al., 2005, 2012), the REE partitioned preferentially into this melt, leaving behind a silicate melt in which HFSE (e.g., Zr and Nb) were further enriched. With progressive fractional crystallization and evolution of the silicate melt, the proportion of immiscible fluoride melt grew, reaching 6 wt.% in the subsolvus granite magma and 12 wt.% in the pegmatite magma. Although the fluoride magma was probably denser than the silicate magma, the low viscosity of the latter and strong convection ensured that it remained in the residues of silicate magma that formed the pegmatites in the apical parts of the intrusion. Crystallization of the pegmatites proceeded with alkali feldspar, arfvedsonite, quartz and zirconosilicate minerals in the outer parts of the sheets pushing the fluoride melt and volatiles into the core, where finally the fluoride melt crystallized fluorite and a variety of REE minerals. The quartz likely crystallized from the volatile phase. The timing of exsolution of the second, REE-rich fluoride melt phase is unclear but its exsolution likely occurred after the bulk of the fluoride melt in the pegmatites. A very small proportion of the fluoride melt remained trapped in the earlier granites documented by the 5 cm diameter fluoride melt inclusion. Based on observations of this inclusion, primary chevkinite-(Ce) crystallized in the fluoride melt along its boundary with the silicate melt taking Ti from the latter and the REE from the fluoride melt; the accompanying zircon took its components from the silicate melt. Within the body of the fluoride melt, fluorbritholite-(Ce) and gagarinite-(Y) were the main REE phases to crystallize. During or after crystallization of fluoride melt, the crystallized or partly crystallized pegmatite core 'stewed in its own juices' altering the primary magmatic mineralogy and releasing REE, particularly light REE into the immediately adjacent granite (Gysi and Williams-Jones, 2013).

In summary, although fractional crystallization and hydrothermal mobilization are clearly important processes in the formation of economic and potentially economic REE deposits from peralkaline magmas, the evidence presented in this contribution shows clearly that fluoride-silicate liquid immiscibility is an additional process that needs to be considered when evaluating the genesis of REE deposits in alkaline silicate igneous rocks. Indeed, it is possible that, as is the case for sulphide-silicate liquid immiscibility in concentrating Ni, Cu and the PGE in mafic and ultramafic igneous rocks, fluoride-silicate liquid immiscibility may be the dominant process in forming REE deposits in some alkaline silicate rocks and not just in granites but also in silica-undersaturated rocks such as nepheline syenites.



**Fig. 3.** Backscattered electron images of near-spherical crystallized melt inclusions before heating. The inclusions are hosted in quartz in hypersolvus granite.



**Fig. 4.** Transmitted light (left) and backscattered electron (right) images of a melt inclusion with 1) silicate glass containing ~3 wt.% Zr, 2) calcium fluoride glass containing ~10 wt.% REE, 3) REE fluoride glass containing 47 wt.% REE, and a vapour bubble after being heated to 900°C and quenched.

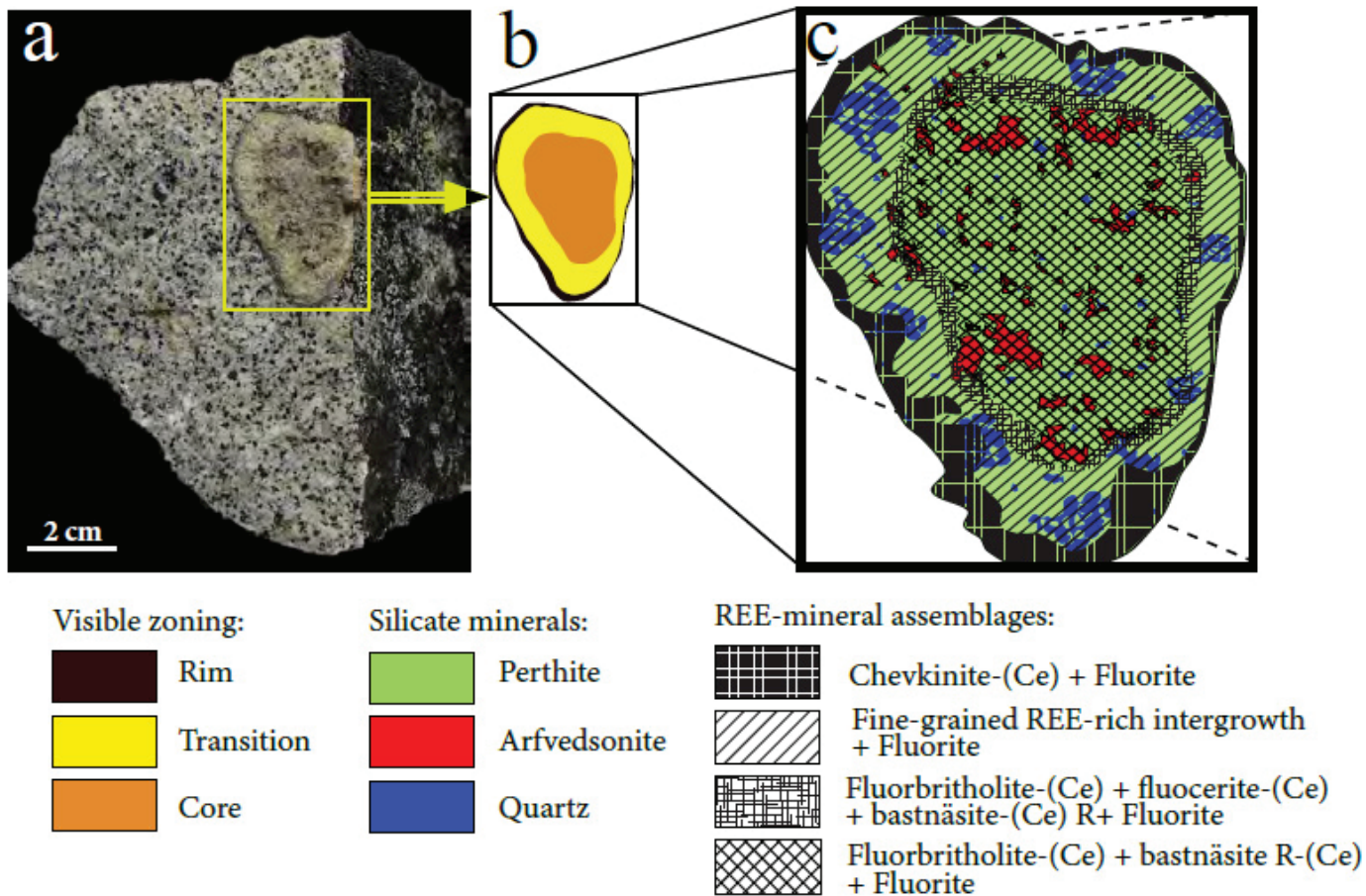


Fig. 5. An immiscible fluoride inclusion in hypersolvus granite. a) Photograph showing the inclusion in the host granite. b) Sketch identifying macroscopic zoning in the inclusion. c) Sketch showing the distribution of silicate minerals and REE mineral assemblages in the inclusion.

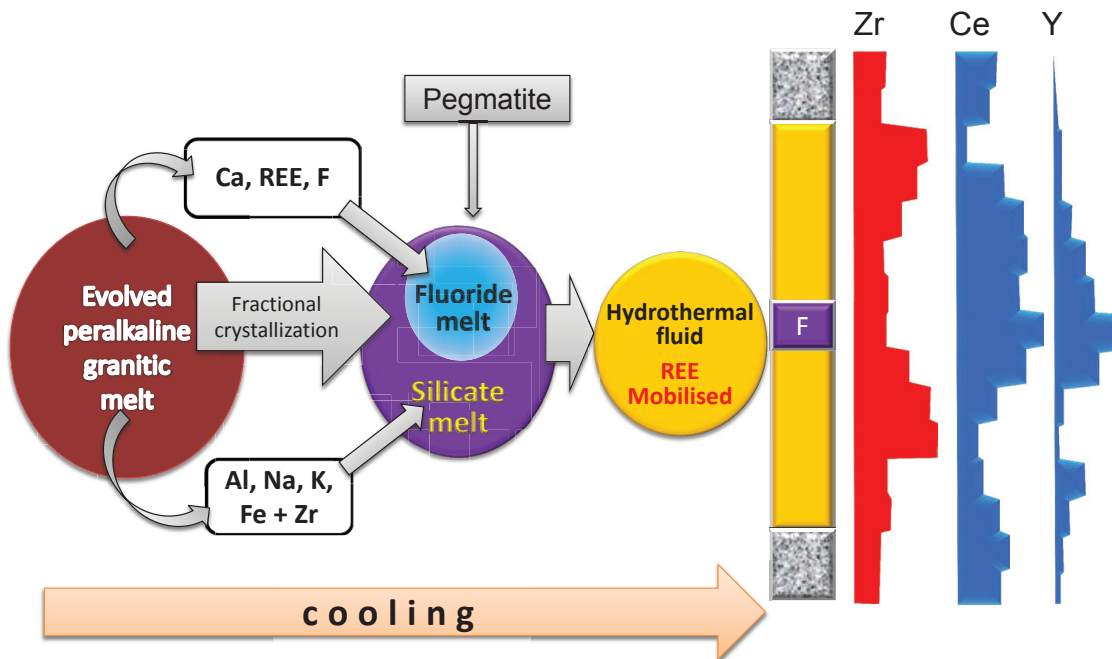


Fig. 6. A schematic model for the evolution of the Strange Lake Pluton and the concentration of the REE.

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