# Mineralogical-geochemical evolution and the formation of REE fluorocarbonates in a silicic rapakivi granite system; the Rödö complex, Central Sweden

(4 figs)

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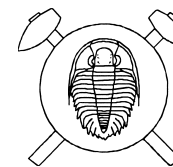
The Rödö rapakivi complex in east-central Sweden consists of a small (20 km^2) miarolitic, high-level granite pluton and associated dykes. The granite is coarse porphyritic and carries plagioclase-mantled K-feldspar ovoids (<3 cm) and drop quartz (<1 cm), typical of rapakivi granites. Abundant granite-porphyry enclaves in sizes ranging from a few dm to several hundred m are present in the granite, interpreted to represent disrupted pieces of a chilled margin. Thin aplitic dykes are also common, often associated with dark schlieren structures and relatively large vugs (up to ~ 15 cm). These dykes typically thin out and disappear in the granite and are interpreted as residual, filter-pressed melts of the granite, while the often arc-like schlieren structures represent zones of active fluid flow.

Both the granite and the country rocks are cut by three main categories of dyke rocks spatially associated with the pluton: i) dolerites, ii) intermediate, partly trachytic dykes, and iii) quartz-feldspar porphyries (QFPs). This contribution will concentrate on the QFPs, which are genetically related with the Rödö granite. The QFPs occur in three textural varieties considering the size of the phenocrysts within a fine-grained groundmass: (i) coarse porphyritic (phenocrysts of the same size as in the granite), (ii) medium-grained (<1 cm) phenocrysts of K-feldspar and quartz (the most frequent variety), and (iii) phenocrysts usually not bigger than a few mm. All three types show more or less abundant intermingling with basic magmas and carry mafic-hybrid enclaves.
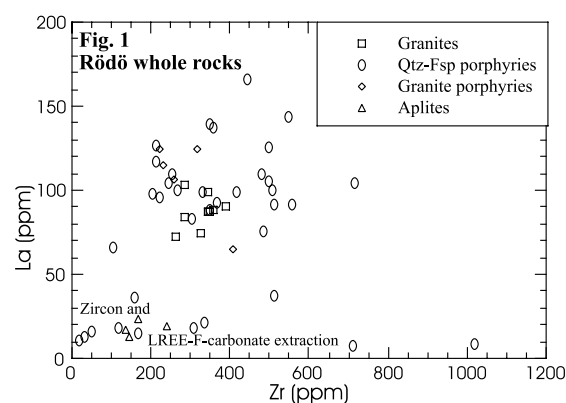
Geochemically, the Rödö granites classify as A-type (A/CNK close to 1.0), with high contents of LIL and HFS elements, though lower than those of average rapakivi granites from Finland. Ratios of Fe/Mg, K/Na and Ga/Al are typically high, while the abundances of Al, Mg, Ca, Sr, and P are characteristically low. The granite-porphyry enclaves and the coarse porphyritic dykes are essentially identical in composition to the granite. Part of the medium-grained porphyries is also similar to the granites, while others are significantly higher in LILE and HFSE. The QFPs trend distinctly into the peraluminous field. No rocks are peralkaline.

Two minor groups of highly evolved QFP dykes occur. The first group has very high contents of certain LIL and HFS elements: Rb (up to 2080 ppm), Cs (17), Nb (659), Ga (79), Y (193), Zr (1020), Pb (55), U (75), Th (240), and HREE (Yb 21). The second group differs from the first group by depletion in Zr (down to 18 ppm), Y (6), and HREE (Yb 1.1). Both groups are depleted in LREE (La 8), Ba (39), K_2O (4.24 %), and Eu (0.2 or lower) (Fig. 1). Na_2O is also enriched (high Na/K ratios), particularly so in the aplite veins (up to 5.1 %), which are also enriched in Li (up to 226 ppm). Fluorine is highest in the aplites and in less evolved parts of the Rödö suite (up to 3800 ppm), and goes down to 104 ppm in the most evolved dyke rocks. FeO*/(FeO*+MgO) values are generally high (>0.85), but drops to ~ 0.7 in some of the most evolved dykes. P_2O_5 is consistently below 0.05, usually ranging from 0.02 to 0.03 %.

The Rödö granites, granite-porphyry enclaves, dark schlieren, and most of the QFPs are enriched in the LREE over the HREE, with $(La/Yb)_{CN}$ ratios between 12 and 39, while the most evolved QFPs and the aplites display flat patterns, with $(La/Yb)_{CN}$ ratios of 0.4–6. The Eu anomalies are distinctly negative for all rocks [$(Sm/Eu)_{CN}$ = 5–10 for the granites], with the evolved rocks showing values as low as 27.

To get some quantitative control on the magmatic evolution of the silicic Rödö system, least square major-element modelling was undertaken. Because the Rödö granite represents the least evolved member of the system and apparently lacks cumulus geochemical signatures, it was chosen as parental magma composition. Phenocryst phases observed in the dykes are mainly K-feldspar (Kfs), quartz (Qtz), and plagioclase (Plag). In addition, amphibole (Amph) or clinopyroxene and Fe-Ti oxides (Mt+ilm, Ox) were assumed to have joined the fractionating mineral assemblage. Mineral compositions either were taken directly from the Rödö rocks or, if lacking, from lit-


Fig. 1
Rödö whole rocks

Legend:
□ Granites
○ Qtz-Fsp porphyries
◇ Granite porphyries
△ Aplites

(Axes: La (ppm) vs. Zr (ppm); labels "Zircon and" and "LREE-F-carbonate extraction")

erature compilations used for rapakivi modelling else-where.

Different combinations of starting granite and mineral compositions result in relatively homogeneous results. For the aplites, modelling suggest more than 90 % crystallization of 27 % quartz, 31 % plagioclase, 34 % K-feldspar, 4 % amphibole and 1 % oxide. For the most evolved QFP composition, calculations suggest 85–95 % crystallization of 27–31 % Qtz, 29–31 % Plag, 29–36 % Kfs, 2–6 % Amph, and 1–2 % Ox, while some other slightly less evolved dykes give results of 50–90 % crystallization of 25–35 % Qtz, 20–27 % Plag, 33–43 % Kfs, 4–8 % Amph, and 1–2 % Ox.

These models were tested by Rayleigh-type crystalfractionation calculations for trace elements utilizing literature values of mineral/melt partition coefficients and the formerly mentioned major-element models additionally considering trace amounts of zircon. The results are in reasonable agreement for the HREE, LILE, and most of the HFSE, but completely inconsistent for the LREE implying the presence of additional phases and/or operation of more complex processes in the system. In particular, a phase capable to extract the LREE from the system is needed.

Search for potential LREE-concentrating minerals revealed no monazite, and allanite (or an allanite-like phase) was detected only in one sample of a strongly evolved QFP. Instead, abundant grains of a reddish brown phase, often associated with fluorite, were encountered and defined as Ca-REE-fluorocarbonate minerals by electron microprobe (Fig. 2). These minerals crystallized interstitially or in small, rounded microscopic 'vugs'. They mostly occur as masses of fine-grained needles usually intergrown with other minerals such as fluorite and Fe-bearing species. The intimate intergrowths and small grain size of the needles complicated the analytical work. The associated fluorite is completely devoid of REE, and no fluocerite or cerianite have been observed so far. No textural evidence suggests that the fluorocarbonates are alteration products of monazite and/or xenotime.
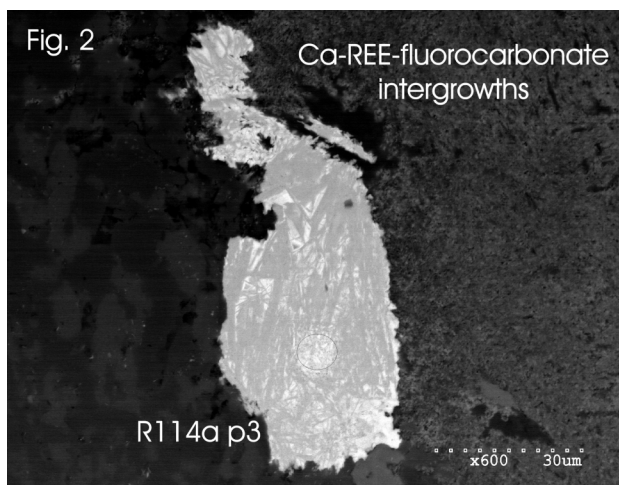
The composition of the fluorocarbonates reflects the composition and evolutionary level of their host rock. Thus, $(La/Sm)_{CN}$ and $(La/Y)_{CN}$ ratios decrease concomitantly in rocks and minerals with increasing fractionation (Fig. 3). The Y content increases with rock evolution up to ~14.5 wt% $Y_2(CO_3)_3$ in the fluorocarbonate from the most evolved QFP, while being <1 wt% in those from the least evolved QFP. The fluorocarbonate species varies in

Fig. 3

Rödö quartz-feldspar porphyries
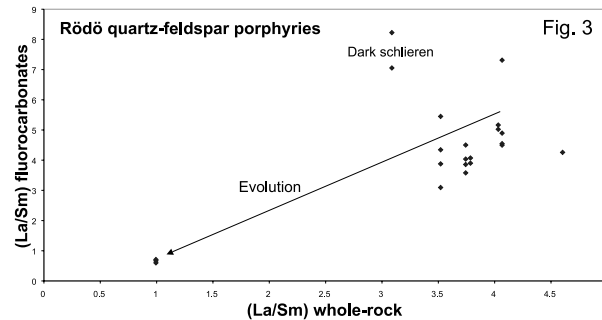
a way, which is not apparently systematic. For example, in the dark schlieren and in one of the more evolved QFPs, the $CaCO_3$ content of the fluorocarbonates is lowest (4–10 wt%), identifying them as parisite-(Ce) $(CaLn_2(CO_3)_3F_2)$ or compositions intermediate between parisite and bastnäsite-(Ce) $(LnCO_3F)$. In both the primitive and the most evolved QFPs, synchysite $(CaLn(CO_3)_2F)$ containing 20–32 wt% $CaCO_3$ formed. In the former synchysite-(Ce) and in the latter synchysite-(Y). Compositions intermediate between parisite and synchysite were measured in the more primitive QFPs, presumably reflecting the presence of röntgenite-(Ce) $(Ca_2Ln_3(CO_3)_5F_3)$. On the other hand, BSE-imaging often shows an intricate pattern of intergrowths indicating that the analyses in instances may represent mixtures between different F-carbonate phases (Fig. 4). Mixed analyses of synchysite and bastnäsite may account for röntgenite and intermediate parisite-bastnäsite compositions. The Th

Fig. 2 — Ca-REE-fluorocarbonate intergrowths. R114a p3. x600 30µm

Fig. 4 — Rödö Ca-REE-F-carbonates
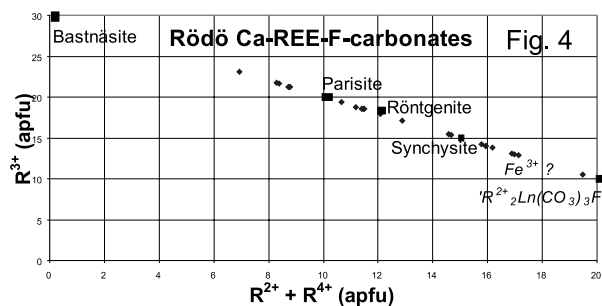
content usually is low, but reaches 4.0 wt% $Th(CO_3)_2$ in fluorocarbonate from the most evolved QFPs. A diagnostic feature of the fluorocarbonates from Rödö is their generally high Fe content, sometimes approaching 10–15 wt% $FeCO_3$. When plotting atomic proportions of $R^{2+} + R^{4+}$ vs. R^{3+}, where Fe is treated as Fe^{2+}, the analytical data closely follows a stoichiometric line from parisite to synchysite. Some analyses plot at compositions more

R^{2+}-rich than synchysite, towards a mineral of the theoretical composition $R^{2+}_2Ln(CO_3)_3F$. This could, however, be due to the presence of Fe^{3+}. Additionally, some analyses plot at more R^{3+}-rich compositions than parisite and are interpreted as mixed analyses between bastnäsite and more R^{2+}-rich phases. One sample contains abundant small 'vugs' filled with REE-poor Fe-carbonate $(Fe,Ca)CO_3$.

The extended fractionation of dominantly feldspars and quartz, up to more than 90% crystallization for the most evolved QFPs and aplites, explains the strong enrichment in certain incompatible LIL and HFS elements noted formerly. Columbite or altered columbite-type minerals have been documented in these most evolved QFPs. The drop in Zr, Hf, and (Y+HREE) in certain evolved rock members indicate removal of zircon, while in other parts the strong increase also in these elements suggests that zircon did not fractionate. The Qtz-feldspar phenocryst assemblage in the QFPs, the strong depletion in K, Ca, Ba, Sr, and Eu, and the pure albitic nature of the plagioclase in both of the most evolved QFP-groups are in concert with the fractionation assemblage considered in the calculations.

The Rödö magmas were originally rich in CO_2 and F. Fractionation in the primary magma system is suggested to have occurred in a chamber at some depth below the present erosion level. The granite and geochemically indistinguishable QFPs represent early intrusions separated from this chamber before the onset of major differentiation. Because the retention of volatiles in granite magmas, and especially CO_2, is strongly pressure-dependent, a $CO_2(-H_2O)$-dominated fluid phase exsolved from these early magmas and caused the precipitation of carbonates (calcite and siderite), quartz, Fe-chlorite, minor rutile (?), and zircon. Associated fluid flow leached especially the feldspars in the granite, causing formation of the arc-like dark schlieren structures. At this stage, however, most of the F was retained in the melt, as F is strongly partitioned into the melt phase over the fluid phase, which is corroborated by the high F contents in the late, filter-pressed aplite dykes.

The more primitive, F- and CO_2-rich QFPs are enriched in LREEs, similar or more than the granites, and precipitated La-Ce-rich, Y-poor fluorocarbonates as late interstitial phases, whereas in more evolved dykes, the fluorocarbonates are enriched in (MREE+HREE). The most strongly evolved QFPs lack such phases. Thus, it appears as most of the LREE formed complexes with CO_2 and F and were removed early from the crystallizing magmas, leaving behind more evolved residual melts depleted in LREE and volatiles but enriched in HREE and other incompatible elements. Particularly the CO_2-rich nature of the Rödö magmas may have prevented crystallization of common granite REE accessory minerals such as monazite and xenotime.