Controls on the HFSE mineralogy of alkaline rocks: Peralkalinity vs. volatiles

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Alkaline igneous rocks are potential sources of rare elements. Enrichment of e.g. Zr and REE in such rocks is closely related to the mineralogy of the rocks, and understanding the factors controlling the stable mineral assemblage is nessesary to understand their economic potential.

In most alkaline igneous rocks, Ti and Zr are hosted in the common minerals titanite, ilmenite, zircon and baddeleyite. In highly peralkaline rocks, ranging from perovskite-bearing nephelinite, through agpaitic nepheline syenite to elpidite granite, these minerals are not stable. In classical agpaitic nepheline syenites (e.g. in the Ilímaussaq complex), eudialyte group minerals are the main host phases for Zr, but in other examples Na-Ca-Zr-Ti-F disilicate minerals my be of equal or higher importance, and in some rocks, Zr is contained mainly in clinopyroxene and amphibole. Several percent of ZrO_2 can be accomodated in aegirine at high peralkalinity and relatively low oxygen fugacity by the $Fe^{3+}{}_{-2}ZrFe^{2+}$ substitution.

There is no one-to-one correlation betweeen mineralogy and whole-rock (Na+K)/Al: Trapped liquids in mildly peralkaline White Foyaite in the Pilanesberg complex (South Africa) crystallized an increasingly agpaitic sequence of titanium minerals, whereas Zr remained hosted by aegirine. In contrast, the related Green Foyaite, which is only marginally more peralkaline, has eudialyte as an early crystallizing, rock-forming mineral.

Chemographic modelling of mineral-melt equilibria provides some insight in the factors that control the mineralogy of agpaitic nepheline syenites. Increasing peralkalinity is a major cause of agpaitic crystallization, but volatile fugacities may control which HFSE mineral assemblages are stable in an agpaitc rock. The contrast beteween the Pilanesberg White and Freen Foyaite is due to distinctly higher water activity in the former. In nepheline syenite pegmatites in the Oslo Rift, changes in water (promoting catapleiite) or fluorine (stabilizing hiortdahlite or wöhlerite) may be equally important for stabilization of agpaitic mineral assemblages as increase in peralkalinity.