Liquid immiscibility in the CaF_2-Granite system

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The recent discoveries of Ca-fluoride melt in magmatic deposits, and especially in peralkaline granite where these melts are strongly REE enriched [1], has raised questions about the presence and nature of liquid immiscibility in the CaF_2-granite system, as well as the partitioning of trace elements between these immiscible liquids. We have experimentally evaluated the liquid immiscibility field in this system using natural granite-fluorite starting materials at fast and slow cooling rates, temperatures from 500 to 1200°C and 1 atm pressure. Our experiments confirm the presence of a miscibility gap in the CaF_2-granite system over a wide range of temperatures. The compositions of the fluorosilicate (*fm*) and oxysilicate (*sm*) liquids in slow-cooling experiments show that immiscibility is encountered when the bulk F-content exceeds approximately 0.5 wt% below 900°C, and then rapidly increases with temperature to more than 5 wt% at 1200°C. These results are consistent with the natural occurences of silicate - calcium fluoride liquid immiscibility found in melt inclusions [1][2]. This indicates that calcic magmas are able to evolve to the liquid immiscibility domain by the residual enrichment of fluorine resulted from fractional crystalization. The compositions of the liquids in fast-cooling experiments show a significantly larger miscibility gap which is characterized by, compared to slow-cooling runs, similar *sm* compositions but higher Ca and F content in *fm*. This difference is caused by suppression of fluorite nucleation and is interpreted as metastable. The liquid immiscibility results in strong fractionation of trace elements, rare earth element in particular, between the two melts, especially at lower temperatures with D(La)=41 at 500°C. The fluorosilicate melt will thus effectively sequester the REE and, given its higher density and lower viscosity compared to the silicate melt, fractionate the REE from the host silicate melt, in agreement with its suggestion as a potential mineralising process [2].

[1] Peretyazhko et al. (2010) *Petrology* **18**, 514-543. [2] Vasyukova et al. (2014) *Geochim. Cosmochim. Acta*. **139**, 110-130