Melting equilibria of F-bearing silicic magmas: an experimental study

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Fluorine is an important volatile constituent of granitic magmas, which are often linked to economic ore deposits. Chemical interaction of fluorine with silicate melts creates significant changes in their equilibrium and transport properties (liquidus- and solidus-temperature lowering, viscosity decreases, water solubilities). However, differentiation paths, saturation limits by fluorine-bearing solid phases and immiscible liquids remain unknown. Experiments performed in cold-seal pressure vessels (500-800 ºC, 100 MPa) and quenching furnaces (800-1100 ºC, 1 atm) along sections in the albite-K-feldspar-quartz-F_2O_{-1}-H_2O system serve as a model for the investigation of the late-magmatic and hydrothermal evolution of F-bearing granitic suites.

At near-solidus conditions (600 ºC, ≤ 100 MPa), feldspathic assemblages coexist with topaz/corundum, cryolite or villiaumite (in order of increasing alkali/alumina ratio). At low f_{F2O-1}, topaz or corundum are incompatible with villiaumite and at high f_{F2O-1}, albite does not coexist with chiolite.

Fluorine interaction with silicate melts results in the formation of Na-Al-F associates and a highly-polymerized SiO_4 framework, which implies large stability of silica polymorphs and leads to fluoride-silicate liquid-liquid immiscibility at supraliquidus conditions. The miscibility gap extends from the cryolite-silica binary (> 1060ºC, 1 atm) through peralkaline albite-silica-cryolite ternary (> 930ºC, 1 atm) into subaluminous albite-silica-cryolite-topaz quaternary (> 750ºC, ≤ 100 MPa) at anhydrous conditions. The fluoride-silicate miscibility gap rapidly closes at hydrous conditions and common quartz-feldspar-bearing magmas saturate with solid cryolite and/or topaz. Increased quartz stability causes F-bearing silicate magmas to become feldspathic or even feldspathoidal by extensive quartz fractionation. Residual liquids in the haplogranite-F_2O_{-1}-H_2O and haplotrondhjemite-F_2O_{-1}-H_2O systems are SiO_2-poor (~ 53 wt. %), weakly peraluminous (A/NK ~ 1.15), F-rich (13-18 wt. %) and crystallize at 540ºC and 580ºC (at 100 MPa, 10 wt. % H_2O), respectively.

Stabilities of fluoride solids are determined by activity products of their components. Fluorite saturation severely limits the fluorine enrichment (< 0.2 wt. %) in most Ca-rich metaluminous magmas. In low-Ca melts, topaz stability is controled by interrelated effects of melt peraluminosity and its fluorine content ($Al_2O_3^{excess}$ * F_2O_{-1} ~ 9 mol. % at 720ºC, 1 kbar, H_2O-saturation). During degassing of hydrous F-bearing silicate magmas, high alkali-aluminofluoride solubilites and hydroxy-complexing in aqueous vapour suggest the formation of alkaline solute-rich fluids. These can explain contrasting natural occurrences of quenched F-rich topaz ongonites *versus* intrusive F-poor topaz-free feldspathites, which lost their volatiles into hydrothermal aureoles.

Nitrogen 15 signals of anthropogenic nutrient loading in *Anemonia sulcata* from the Adriatic Sea

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Coastal and estuarine environments near urbanized area and tourist centres along the Adriatic coast are more or less subject to pollution due to anthropogenic nitrogen inputs, which can have profound detrimental effects on coastal ecosystems. The objective of this study was to test the hypothesis that the ^{15}N content of *Anemonia sulcata* tissue collected near shore and offshore along the eastern coastal part the Central and Northern Adriatic is a reliable indicator of the anthropogenic nitrogen impact on coastal Adriatic water ecosystems. The results shown in Figure 1 indicate that $\delta^{15}N$ of *Anemonia sulcata* tissue was significantly higher at the polluted sites of Pirovac Bay, Prosika, and the Western Istrian coast than in the reference location in the unpolluted Kornati Islands. The $\delta^{15}N$ enrichment was as high as 5.93‰ and is larger that would be expected from natural variations alone. The $\delta^{13}C$ values of sewage-affected *Anemonia sulcata* also suggests enrichment with light ^{12}C isotope, most probably due to a higher degree of anthropogenic nutrition. Our results indicate that $\delta^{15}N$ of *Anemonia sulcata* tissue appears to be a promising indicator of anthropogenic N loading if caution is used in selecting reference sites.

Figure 1: $\delta^{15}N$ and $\delta^{13}C$ variations in *Anemonia sulcata* tissue (Central Adriatic: - Kornati Island, - Pirovac Bay, - Prosika, - Pri_njak; Northern Adriatic: - Western Istrian coast)