

Melting subducted carbonated pelites, magma hybridization in the mantle and carbonatites – The Italian ultrapotassics

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While the straightforward relation between subduction of volatiles and arc magmatism is undisputed, the melt forming process(es) themselves are largely discussed. Prevailing theories and scenarios for subduction zone magmas have and will see significant shifts of support, leading to a geo-complexity in which a few out of a large number of possible subduction related transfer processes need to be combined individually for each subduction zone.

One of the most extreme cases of subduction related magmas are the Intra-Appenine and Roman ultrapotassic kamafugites (associated with carbonatites), which constitute worldwide endmembers in terms of K_2O/Na_2O , K_2O content and CO_2 degassing. Group II kimberlites and many lamproites are geochemically similar, but occur on stable cratons.

Fluid-absent melting of carbonated pelites at ≥ 3 GPa yields ultrapotassic phonolites (64-66 wt% SiO_2 , K_2O/Na_2O up to 9), which may coexist with CaMg-carbonatites. With respect to hydrous pelite, CO_2 stabilizes residual jadeite₈₀, lowers SiO_2 and increases K/Na in the melt. Such phonolites are equilibrated with fertile, with cpx-bearing refractory mantle, and with wherlite. At 3.5 GPa, $X_{CO_2} > 0.5$, hybridization with refractory mantle produces highly subsilicic kamafugites, conserving K/Na ratios, and with $X_{Mg} > 0.7$ as characteristic of primitive melts. CO_2 reduces the olivine saturation volume and shifts the ol-cpx-opx cotectic to lower SiO_2 . Most of the variation of the Italian ultrapotassics (and of many lamproites and group II kimberlites) is covered by the range of hybrid melts obtained at 1280-1380°C, which have 38-55 wt% SiO_2 , 12-27 wt% MgO , and $CaO/Al_2O_3 = 0.9-1.4$. This suggests that most eruptive centers of the Italian ultrapotassics are fed by their own local source of variable but distinct composition. The carbonatites probably exsolve from the primitive melt upon magma rise, which also causes 5-15 % olivine fractionation.

In central Italy, plate convergence almost ceased and the slab is tearing off, which is well distinct from stable cratons below ancient orogens, but in both cases, slab sediments were introduced into the mantle and once temperatures become high enough, fluid-absent slab sediment melts interact with mantle of variable composition leading to primitive ultrapotassic CO_2 -rich magmas.

Site-selective time resolved laser fluorescence spectroscopy on Ca^{2+} -bearing mineral phases doped with Cm^{3+}

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Assessing the geochemical long-term safety of a nuclear waste repository requires a molecular level understanding of radionuclide behavior in the geosphere. In particular, the interaction of radionuclides with mineral phases (adsorption, solid solution formation) strongly affects their mobility and sequestration[1]. The actual mode of interaction is a major controlling factor of this retardation capability. Recent results on the interaction of Eu^{3+} and Cm^{3+} with calcite show the formation of solid solutions by exchange of Eu^{3+}/Cm^{3+} for Ca^{2+} [2]. Thus the question arose if this mechanism is generally applicable for Ca^{2+} -bearing mineral phases. In order to shed light on this question, aragonite and gypsum homogeneously doped with Cm^{3+} were synthesized in a mixed-flow-reactor.

TRLFS results clearly show that Cm^{3+} exhibits completely opposed sorption behavior on both investigated Ca^{2+} mineral phases. In the aragonite system formation of solid solutions by substitution for Ca^{2+} is the only observed form of interaction, which is evident by the corresponding emission spectrum and fluorescence lifetime. However, in the gypsum system no incorporation occurs, but only one inner-sphere sorption species can be found. Consequently, the exchange mechanism observed for calcite and aragonite is not generally applicable to other Ca^{2+} -bearing mineral phases. Apparently other parameters such as the binding strength of the anion have to be taken into consideration. These different modes of interaction will, however, have a considerable impact on their retardation capabilities.

[1] N.M. Edelstein *et al.* (2006) *Coord. Chem. Rev.* **250**, 948-973. [2] M. Schmidt *et al.* (2008) *Angew. Chem. Int. Ed.* **47**, 5846-5850