Garnet-spinel subsolidus re-equilibration and K-metasomatism in Cape Verde lithospheric mantle

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Mantle xenoliths from two lower Tertiary necks of Sal Island were studied in order to highlight the evolution of the Cape Verde (CV) lithospheric mantle. Xenoliths are constituted by anhydrous spinel-bearing lherzolites, harzburgites and minor wehrlites, with widespread metasomatic textures. Protogranular-clinopyroxenes (cpx1) are endiopside, characterized by CaO (16.4-18.1 wt%) and Cr_2O_3 (1.1-1.8 wt%) contents respectively lower and higher than those expected for primary clinopyroxenes (cpx) in spinel-bearing lherzolites. They show remarkable homogeneous, strong convex-upward REE patterns, with a maximum around Sm (Sm_N=8.3–12.8) and a minimum for both heavy (Yb_N=2.4–4.8) and light REE (La_N=3.6–5.3). HREE concentration is significantly lower than that of abyssal peridotite at comparable modal cpx contents. Metasomatic cpx show trace element concentrations much higher than cpx1 (La_N=5.7–64.1) with remarkable Zr and Ti negative anomalies. As for cpx1, large orthopyroxene (opx) grains are considerably richer in CaO (0.76-1.73 wt%) and Cr_2O_3 (0.48-1.07 wt%) with respect to opx of fertile spinel-bearing lherzolites. They show fractionated chondrite-normalized incompatible element patterns systematically depleted in LREE, with Zr and Ti positive anomalies. Major and trace element features of cpx1 and opx suggest a process of partial melting in anhydrous garnet peridotite. Trace element patterns of cpx1 were in fact successfully modelled by about 5-6% incongruent partial dynamic melting, leaving 4-5% and 13-14% of residual garnet and cpx respectively. The model reproduces the distinctive convex-upward REE patterns, but the calculated residual cpx is too low in HREE. Thus, a subsolidus re-equilibration in the spinel stability field is invoked. Partitioning the garnet REE contents between spinel and cpx, the HREE contents of cpx increase and the appropriate REE humped pattern is reproduced. Subsequently CV xenoliths experienced a metasomatic enrichment responsible for the secondary mineral assemblage and glass. High silica glasses are similar in composition to mantle glasses worldwide, but for an extremely high K_2O contents (5.58–8.78 wt%): they are among the K-richest glasses found so far in both oceanic and continental settings. Mass balance calculations and trace element contents of secondary cpx and glasses are reproduced considering a reaction between the primary paragenesis and a K-rich alkali silicate metasomatic melt, close in composition to a K-lamprophyre. Lavas with potassic character are rare in oceanic environment and totally absent, to the best of our knowledge, in Cape Verde Archipelago, thus the nature and provenance of the metasomatic melts responsible for Cape Verde glasses are quite puzzling.

Radionuclides immobilization by cement and cement phases studied by EXAFS

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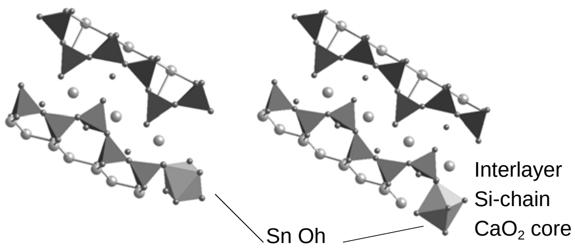
Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of radioactive wastes in underground repositories. Cement is used to condition the waste materials, as well as for the construction of the repositories and is constituted of a complex mixture of mainly calcium silicate hydrates (CSH phases), portlandite and calcium aluminates. The near-field of a cementitious repository acts as chemical barrier for radionuclides, retarding migration of waste ions into the far-field.

However, the mechanistic aspects of radionuclides uptake by cement and cement phases remain poorly understood. Our current studies are hence focused on probing the local chemical environment of the immobilized radionuclides by EXAFS (Extended X-ray Absorption Fine Structures) (1-3). Some detailed examples will be given. The $CaSn(OH)_6$ precipitation versus Sn(IV) direct bonding to cement will be evidenced and some structural models will be proposed for Sn(IV) immobilization by CSH (cf. Fig. 1). The U(VI)/cement system will also be examined and the identification of the solubility limiting phase as well as U(VI) inner sphere complexes formation will be examined.

Figure 1: Structural models proposed according to the EXAFS results for Sn(IV) immobilization by CSH.



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