

Microstructures and geochemistry in the subcontinental lithospheric mantle of NE Spain

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Mantle xenoliths in alkaline basaltic rocks of Neogene-Quaternary age from NE Spain are mainly anhydrous spinel lherzolites and harzburgites. New samples from different volcanoes indicate that lherzolites are more abundant than harzburgites and that they show frequent porphyroclastic and equigranular microstructures, along with protogranular varieties. Since deformation could enhance basaltic melt percolation favouring refertilization of harzburgites, the relationships between microstructures and chemistry of lherzolites are evaluated using major and trace element compositions of whole rocks and minerals.

Lherzolites show very fertile to more refractory compositions grading to harzburgites. The most fertile lherzolites are porphyroclastic, while the least fertile ones show protogranular microstructures. Based on their variable REE patterns, three main types of lherzolite clinopyroxene are distinguished: (1) highly LREE depleted ($La/Yb_N < 0.1$), (2) slightly LREE depleted ($La/Yb_N = 0.6-0.9$) and (3) LREE enriched ($La/Yb_N = 10.5-29$). These patterns are not related to any specific microstructure, although the most LREE enriched clinopyroxenes are from porphyroclastic lherzolites. Clinopyroxene from harzburgites is always enriched in LREE and MREE ($La/Yb_N = 5.6-23$, $Nd/Yb_N = 5.2-18$).

These data indicate that there is no clear relationship between deformation and lherzolite compositions. Some lherzolites could have been formed by percolation of relatively depleted basaltic melts through harzburgites, but both peridotites were affected by a subsequent alkaline metasomatic component. The most depleted lherzolites would have escaped both refertilization process and the later alkaline metasomatism.

Quantum-mechanical calculations on uranium (co)adsorption and reduction on iron and aluminum (oxyhydr)oxides

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Minerals have been shown to promote redox reactions; *i.e.* nanoparticulate hematite catalyzes the reduction of U(VI) by Fe(II), which is otherwise kinetically inhibited in the absence of the mineral.¹ These surface-mediated redox processes are not well-understood though. The proximity effect may explain this phenomenon: a semiconducting mineral can act as a medium for electrons to be transported from one adsorbate to another one, both being spatially separated by a few Å.² To investigate the influence of semiconducting properties of iron minerals', coadsorption and reduction processes on these are compared to insulating aluminum isostructures. Aluminum (oxyhydr)oxides isostructures can be structural analogs for iron (oxyhydr)oxides while their different electronic properties enable observations of whether electron transfer is more prevalent in semiconducting than in insulating minerals.

The coadsorption of a uranyl complex and a reductant (*e.g.*, Fe(II) or H₂S) onto iron and aluminum (oxyhydr)oxide clusters was studied using quantum mechanical density functional theory (DFT) calculations. These simulations allow for visualization of electron density of states (DOS) and molecular orbitals (MOs) that are involved in electron transfer. Analyses of DOS and MOs for the (co)adsorption of uranyl on a goethite cluster (α -FeOOH, *Pnma*) show Fe *d*-orbitals overlap with U *f*-orbitals. Visualization of the MOs shows the participation of the iron atoms in the coadsorption of uranyl provide a continuous pathway where electrons from the reductant can be transferred through the goethite to the uranyl complex. Conversely, with the aluminum isostructure diasporite (α -AlOOH, *Pnma*), Al *p*-orbitals and U *f*-orbitals do not overlap, consistent with diasporite's insulating behavior.

Hirshfeld, Bader, and Mulliken analyses provide static charge and spin distributions; U(VI) atoms were shown to acquire spin density (<0.1 au) upon (co)adsorption to iron substrates. To better understand the influence of mineral substrates, the electron transfer rate is being quantified using Marcus Theory, showing if pronounced differences in the rate exist for semiconducting and insulating minerals.

[1] Liger *et al* (1999) *GCA* **63**, 2939-2955. [2] Becker *et al* (2001) *GCA* **65**, 2641-2649.