

Complexation of high-field strength elements in subduction zone aqueous fluids: *Ab initio* molecular dynamics and X-Ray absorption spectroscopy

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Magmatic rocks related to subduction zones commonly display element patterns characterized by depletion of high-field-strength elements (HFSE, i.e., Ti, Zr, Hf, Nb and Ta). The depletion is usually attributed to aqueous fluids that are involved in the processes at subduction zones. The geochemical budget of HFSE is largely controlled by accessory phases such as zircon. Therefore, knowledge is needed on the parameters controlling phase solubility or stability. Fluid composition appears to be the most important parameter because it may strongly affect complexing of HFSE in aqueous fluids. Solubility measurements have been interpreted as indicating the formation of complexes with alkali and silica dissolved in the fluid. The formation of these complexes has been suggested as an efficient mechanism to promote HFSE mobility [1,2]. However, direct evidence on the HFSE speciation in fluids at subduction zone conditions is lacking.

A combined experimental-theoretical approach coupling X-Ray absorption spectroscopy and *ab initio* molecular dynamics (Car Parinello-MD) simulations is attempted to get insight into the structural details of the HFSE complexes in aqueous solution. Experimental Zr K-edge and Hf L_{III}-edge EXAFS and XANES spectra are compared with theoretical spectra simulated with the FEFF9 code [3]. The latter are obtained as statistically averaged spectra computed for a set of selected snapshots extracted from the MD trajectory of composition systems in which the stability of different candidate complexes is tested. Presently, *ab initio* MD simulations can only be carried out over short times, stable complexes are not likely to have formed from random configurations. Therefore runs are set up with data obtained from experimental XANES and EXAFS spectra of the present study and literature. All simulation runs are carried out at T=1000 K and the pH and pressure dependencies are investigated.

Experimental spectra were measured in fluids containing Na₂Si₃O₇ (NS3), Na₂Si₃O₇+1 or 5 wt% Al₂O₃, NaOH or HCl equilibrated with zircon or hafnon in hydrothermal diamond-anvil cells at T up to 750 °C and P up to 1 GPa. XANES and EXAFS spectra were collected in-situ at high P and T at beamlines ID 24 and ID 26 (ESRF). Analysis of XANES and EXAFS at Zr-K and Hf-L₃ edge measured in NS3 ± Al₂O₃ solutions already indicated complexes with 6 oxygens in the first shell. In contrast, 7 oxygens are indicated in the NaOH solution. For HCl solutions, a spectrum simulated for a (Zr,Hf)O₄Cl₃ cluster reproduced qualitatively the features of the experimental spectra.

References:

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