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Si-F complexing in aqueous fluids: experimental study and implications for transport of immobile elements

David Dolejš

Charles University, Institute of Petrology and Structural Geology, 128 43 Praha 2, Czech Republic
(david.dolejs@natur.cuni.cz)

Intepretation of fluid-mineral interaction mechanisms and hydrothermal fluxes requires knowledge of predominant solubility and speciation reactions and their thermodynamic properties. Fluorine represents a hard electron donor, capable of complexing and transporting high-field strength elements, which are traditionally considered to be immobile. Reactions responsible for element mobility have general form $MO_x + y$ HF (aq) + $x - y$ H_2O = $M(OH)_{2x-y}F_y$ (aq), and their extent and transport efficiency relies on hydrogen fluoride activity. In natural fluids, a[HF] is controlled by various fluorination equilibria including neutralization of silicates with consequent formation of silicohydroxyfluoride complexes. Quartz solubility in HF-H_2O fluids was experimentally determined at 400-800 ^{o}C and 100-200 MPa using rapid-quench cold-seal pressure vessels and the mineral weight-loss method. Quartz solubility significantly increases in the presence of hydrogen fluoride: at 400 ^{o}C and 100 MPa, dissolved SiO_2 ranges from 0.18 wt. % in pure H_2O to 12.2 wt. % at 8.3 wt. % F in the fluid, whereas at 800 ^{o}C and 200 MPa it rises from 1.51 wt. % in pure H_2O to 15.3 wt. % at 8.0 wt. % F in the fluid. The isobaric solubilities of quartz appear to be temperature-independent, i.e., effects of temperature vs. fluid density on the solubility are counteracting. The experimental data are described by the density model: log $m[SiO_2] = a + b\log\rho + c\log m[F] + dT$, where a = -1.049 mol kg^{-1}, b = 0.816 mol cm^{-3}, c = 0.802 and $d = 1.256 \cdot 10^{-3}$ mol kg^{-1} K^{-1}. Solubility isotherms have similar $d(\log m[SiO_2])/d(\log m[F])$ slopes over the entire range of conditions indicating that $Si(OH)_2F_2$ is the major aqueous species. Several factors promote breakdown of silicohydroxyfluoride complexes and precipitation of silica solute: (i) decreasing temperature and pressure, i.e., fluid ascent and cooling and/or (ii) neutralization and increase in the alkali/H ratio of fluids during alteration reactions or removal of hydrogen halides by fluid boiling. Thermodynamic analysis of mineral equilibria in the system SiO_2-Al_2O_3-FeO-MgO-CaO-Na_2O-K_2O-H_2O-F_2O_{-1} indicates that cryolite, topaz, fluorite and sellaite represent fluoride buffers with decreasing chemical potential of F_2O_{-1} or a[HF], in a sequence from peralkaline to peraluminous silicic, intermediate to progressively Ca-rich mafic and, finally, ultramafic environments. Corresponding a[HF] decrease from $10^{0.2}$ to 10^{-1} and from $10^{-1.6}$ to $10^{-3.0}$ mol kg^{-1} at 800 and 400 ^{o}C, respectively, and 100 MPa. These results imply that: (i) silicohydroxyfluoride and aluminumhydroxyfluoride complexes transport Si and Al in quantities appreciably greater than SiO_2 (aq) and aluminate species in peraluminous granite and greisen environments only, and (ii) significant transport (10-100 ppm) of high-field strength (e.g., Ti, Zr) and rare earth elements in aqueous fluids is predicted when formation constants of metal-fluoride complexes exceed 10^{1-2} under hydrothermal conditions. This study concludes that in fluorine-bearing environments the transport of Si and Al remains little affected, but HFSE and REE are largely mobile.