EXPERIMENTAL STUDY OF TITANIUM SPECIES IN SUBCRITICAL ACID FLUIDS

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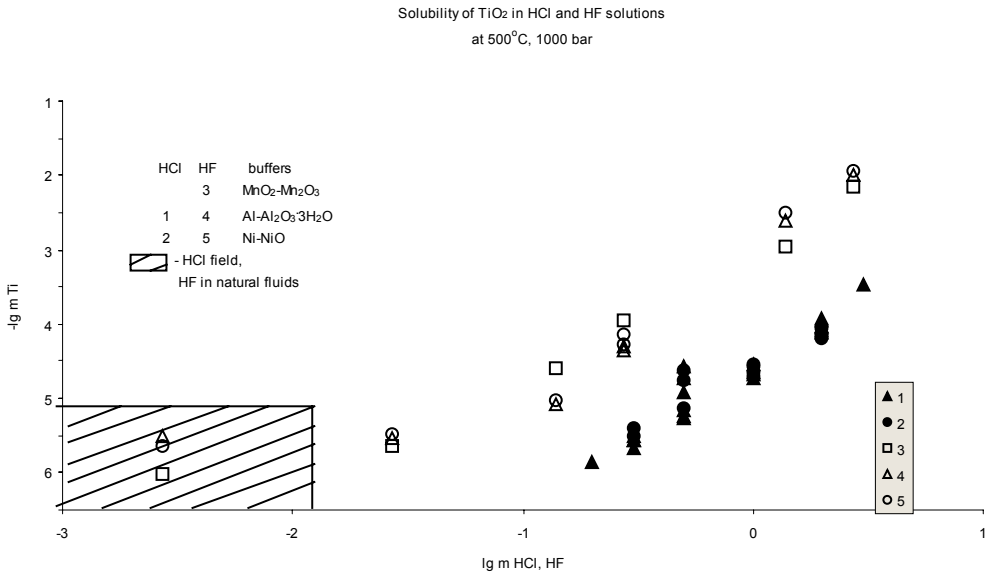
Titanium migration in postmagmatic fluids is discussed. The experimental determination of titanium speciation in supercritical fluids at various hydrogen fugacities is done. Melted pink-yellow and black TiO_2 crystals are used. The crystal color depends on oxygen potential during growth. Solubility measurement is performed by capsule technique and it is done in hydrogen chlorine and hydrogen fluorine acid solutions at 500°C, 1000 bar under hydrogen fugacity of interval from 8×10^{-12} to 10.3 bars. Equilibrium constants are calculated.

Titanium determination in experimental aqueous solutions is done by ICP technique (ICAP 9000, USA). Calibration is done using aqueous solution containing 10 microgram/l. Sensibility level is 0.1 micrograms/ml.

Rutile reversibly changes its color from pink (MnO_2-Mn_2O_3 buffer) to black one (Ni-NiO buffer and Al). The intensive black color at reduced conditions is due to oxygen vacancy arise in rutile crystal and partial titanium (+4) to (+3) reduction. Existence of titanium (+3) is known in artificial and natural titanium-bearing violet micas. Color change is connected with interaction of titanium (+3) and (+4) ions [2]. So titanium (+3) is presented in the solids. Solubility of rutile under extended reduction potential is studied. Aqueous titanium (+3) is not determined in experimental solutions.

The experimental results are in the figure. In 0.01-0.1 m hydrochloric acid rutile solubility is less than 0.01 microgram/ml at all buffers. Aqueous titanium concentration is proportional to hydrochloric or hydrofluoric acid concentrations: in 0.2-3.0 m HCl solution the aqueous titanium concentration is equal to $n\times10^{-6}$-10^{-4} m, in 0.003-2.74 m HF solution the aqueous titanium concentration is equal to $n\times10^{-6}$-10^{-2} m. The equilibrium constants of the following reactions: TiO_2 (rutile) + $2HCl^0$ = $Ti(OH)_2Cl_2$ (pK = 4.51) and TiO_2(rutile)+$2HF^0$=$Ti(OH)_2F_2$ (pK=2.99) at 500°C, 1kbar are determined.

Experimental studies of rutile solubility have been done for wide range hydrothermal conditions. They show the low values of rutile solubility (order of $n\times10^{-5}$ m) and so low titanium mobility in hydrothermal systems. On the other side the aqueous titanium concentration in natural waters of oxidation zone [4] indicates on possible existence of the other aqueous species of titanium besides chloride and fluoride complexes. Determination of them is the task of coming research.



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