

## Diffusive fractionation of Nb and Ta in rutile

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The fractionation of the HFS elements Nb and Ta, referred to as geochemical twins because of their similarities in ionic radii, ionic charge and compatibilities, has long been debated. Various equilibrium fractionation processes were suggested to explain the sub-chondritic Nb/Ta ratio of the accessible silicate Earth and the spread of Nb/Ta observed among the major terrestrial reservoirs. Differences in equilibrium partition coefficients in partial melting processes are, however, too small to explain the natural spread in Nb/Ta ratios.

A key mineral controlling the geochemical behaviour of the two elements is rutile. Despite of it being an accessory mineral, it is acting as the major host of Nb and Ta in subducted oceanic crust and in lower crustal granulites. We consider kinetic fractionation during diffusion in rutile as an important process to fractionate the two elements, which although chemically similar, differ by a factor of two in their atomic masses. We thus employed an experimental setup to determine diffusivities of Nb and Ta in rutile. It consists of thin film diffusion couples prepared by PLD [1], which are annealed in gas mixing furnaces between 900 and 1200°C at  $fO_2$  either close to the NiNiO-buffer or at atmospheric oxygen pressure. The TiO<sub>2</sub> thin films were enriched with 1-3 wt% Nb, Ta and/or Sm. The annealed samples, as well as reference samples characterising the starting material, were analysed by RBS and by SIMS in the depth profiling mode.

Our experiments demonstrate unequivocally that (1) Nb diffuses faster than Ta by a factor of 5 to 10 (!), (2) diffusion of Nb, Ta, and Sm is strongly sensitive to the  $fO_2$ , in which Nb and Ta become faster and Sm slower with increasing  $fO_2$ , and (3) Nb and Ta diffusivities in rutile are ~3 orders of magnitude higher than previously published values for Hf and Zr [2].

The significantly higher mobility of Nb compared to Ta in rutile may have direct consequences for their liquid-rock fractionation during partial melting. The Nb/Ta systematics of partial melts and restites will be influenced by kinetic factors, and will not be solely governed by equilibrium partitioning in scenarios such as partial melting of subducting oceanic crust.

[1] Dohmen *et al.* (2002) *Eur. J. Min.* **14**, 1155-1168.

[2] Cherniak, Manchester & Watson (2007) *Earth Planet. Sci. Lett.* **261**, 267-279.

## Halogens in silicic magmas, from the upper mantle to the crust

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Halogens are minor constituents in silicate magmas which, however, exhibit important interactions with the silicate melt structure thus affecting equilibrium and transport properties, and partitioning behavior. We have experimentally determined phase equilibria in F- and Cl-bearing K<sub>2</sub>O-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts at 500-1600°C and up to 3 GPa. Solubilities of fluorine and chlorine in silicate magmas strongly depend on the melt composition. Fluorine solubility increases from 1.7 wt.% in the peraluminous granites through a sharp maximum of 32 wt.% at molar Al/(Na+K)~1 and it drops to 4.2 wt.% in the peralkaline systems. In addition, small temperature changes result in large changes of fluorine solubility in melts buffered by topaz or cryolite. By contrast, the solubility of chlorine increases with the concentration of network modifiers and by progressive substitution of aluminum in the silicate network. Changing alumina saturation index from unity (subaluminous) to 0.6 or 1.2 have comparable effects and it leads to a solubility increase by a factor of 1.5 to 3. The chlorine solubility appears to be independent of temperature but it substantially increases with pressure, by 0.44 to 0.62 wt.% Cl/GPa. The absence of temperature dependence implies that the dissolution of NaCl into the silicate network is entropic and it is compatible with NaCl being completely associated and passively incorporated as a molecular species in the melt structure. The positive pressure dependence of solubility requires a negative volume change upon dissolution, that is, local contraction of the tetrahedral silicate network. The presence of CO<sub>2</sub> lowers the chlorine solubility comparably on equimolar basis which is an expected result of competition for sites or free volume in the silicate melt structure. Our experimental results demonstrate that fluorine and chlorine exhibit opposite solubility trends and distinct pressure and temperature dependencies. Subaluminous melts become enriched in fluorine but depleted in chlorine. The chlorine solubility strongly decreases with decreasing pressure and in CO<sub>2</sub>-bearing magmas. These two factors increase chloride activity, hence promote halide saturation during magma ascent or in the presence of additional volatiles. The partitioning coefficient of chlorine,  $D^{fl/melt}$ , and the fluid salinity are predicted to increase towards low-pressure subaluminous systems.