Analysis of geochemical "twins" Al/Ga and Si/Ge in rock-forming silicate minerals in granitoides using LA-ICP-MS

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The aim of this study is to determine ratios of Al/Ga and Si/Ge in natural silicate minerals from different types of granitoids from Bohemian massif and compare these ratios with elemental ratios commonly used in geochemistry like K/Rb, Nb/Ta and Zr/Hf. All these ratios represent (i) different source lithology (metasedimentary or metaigneous rocks, subduced slab, metasomatised lover crust) of granitic melts, (ii) evolution via fractional crystallisation, mixing, reaction with fluid atc., (iii) ability of particular crystal lattice of rock-forming minerals to preferentially accommodate Ga or Ge.

The presented results was obtained using three different methods – pneumatic nebulization with inductively coupled plasma mass spectrometry (PN-ICP-MS), laser ablation with ICP-MS (LA-ICP-MS) and electron probe microanalysis (EPMA). PN-ICP-MS was used for determination of whole content of the rock samples after fusion with $LiBO_2$. LA-ICP-MS and EPMA was used for local microanalysis of individual grains of silicate minerals.

The first results show that of Al/Ga-ratio in analyzed rock is relatively stable (Al/100Ga ~5-15), whereas Si/100Ge-ratio during fractionation increased: in the Třebíč pluton from about 80 in amphibole-biotite durbachites to 250-300 in late biotite durbachites, in orthogneisses from about 230 in biotite otrhogneisses to about 380 in some of two-mica facies, in the Melechov pluton from about 150 in the Lipnice facies do about 400 in the Melechov facies. In the Podlesí granite system, the Ge- and Ga-contents are influenced by greisenisation: namely the Ga is during hydrothermal processes mobile and its content remarkably decreases (Al/Ga-ratio increase).

Laser-ablation analyses of individual silicate minerals from the Cínovec borehole showed, that Ga is preferentially concentrated namely in mica (zinnwaldite and protolithionite), and more in albite than in associated K-feldspar. Ge is namely concentrated in mica. Contents of both Ga and Ge in quartz are lower than their detection limits.

Production of superoxide and hydrogen peroxide on photolysis of natural organic matter

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Irradiation of Suwannee River fulvic acid (SRFA) at pH 8.1 with simulated sunlight resulted in production of nanomolar concentrations of superoxide and hydrogen peroxide. Analysis of the results obtained confirmed that SRFA contains a redox-active chromophore which reduced oxygen to yield superoxide upon photoexcitation. Hydrogen peroxide was generated exclusively via uncatalysed disproportionation of superoxide produced in this way.

Superoxide decayed through both uncatalysed disproportionation and an oxidative pathway that did not result in hydrogen peroxide production, whereas hydrogen peroxide did not undergo further reaction to any discernible extent over the one-hour duration of irradiation. Singlet oxygen did not contribute substantially to production of superoxide or hydrogen peroxide, but was found to play a critical role in controlling the mechanism and associated rate of superoxide decay in the irradiated solution.

A kinetic model based on these observations is presented which provides an excellent description of the experimental results and is also consistent with observations from a wide range of other studies investigating various aspects of SRFA redox chemistry and photochemistry.