Acid-base and copper binding properties of three organic matter fractions isolated from a soil solution

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Vast amounts of knowledge about the proton- and metal-binding properties of dissolved organic matter (DOM) in natural waters have been obtained in studies on isolated humic and fulvic (hydrophobic) acids. Although macromolecular hydrophilic acids normally make up about one-third of DOM, their proton- and metal-binding properties are poorly known. Here we investigated the acid-base and Cu-binding properties of the hydrophobic (fulvic) acid fraction and two hydrophilic fractions isolated from a soil solution. Proton titrations revealed a higher total charge for the hydrophilic acid fractions than for the hydrophobic acid fraction. The titration curves were poorly predicted by both Stockholm Humic Model (SHM) using generic parameter values, but could be modelled accurately after optimisation of the proton-binding parameters ($\text{pH} \leq 9$). Cu-binding isotherms for the three fractions were determined at pH values of 4, 6 and 9. With the optimised proton-binding parameters, the SHM model predictions for Cu binding improved. Iron(III) and aluminium competed strongly with Cu for binding sites at both pH 4 and pH 6. The SHM model predicted this competition reasonably well. Overall, the Cu-binding behavior of the two hydrophilic acid fractions was very similar to that of the hydrophobic acid fraction, despite the differences observed in proton-binding characteristics. These results show that for modelling purposes, it is essential to include the hydrophilic acid fraction in the pool of ‘active’ humic substances.

High field strength element mobility in metamorphic fluids

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High field strength elements are important geochemical indicators in many geological settings. Mineral phases, which are known to incorporate the high field strength elements are rutile, ilmenite, Fe-Ti spinels, and other Ti-rich phases such as pyroxenes or amphiboles. A number of recent studies investigated the partitioning of HFSE between accessory phases and silicate melts [1-4]. Whilst the behaviour of Zr, Hf, Nb, Ta in magmatic systems seems to be relatively well understood, there is still a fundamental lack of experimental data in fluid-saturated systems [5].

To partially address these matters, we have performed new experiments to investigate the behaviour of the high field strength elements (Ti, Nb, Ta, Zr, Hf, and W) in high-pressure high-temperature fluids. The experiments provide quantitative constraints on accessory mineral solubility and the partitioning of trace elements between accessory phases and supercritical fluids at elevated pressures and temperatures. Experimental results will be presented from runs, which were performed at pressure between 0.5 and 1.5 GPa in a gas pressure apparatus and in a piston-cylinder apparatus. The experimental run products were analysed with ICPMS techniques and confirm very high accessory phase solubility in saline fluids. New partition coefficients between accessory phases and saline fluids will be presented and implications on the budget of the high field strength elements in subduction zone rocks will be discussed.

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