Growth and aggregation of ZnS nanoparticles during coprecipitation with aquatic humic substances

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Nanoparticulate metal sulfides such as ZnS are important for the speciation of pollutant metals in sediments, wastewater effluent, and other sulfidic environments. The aim of this work was to investigate how the composition of dissolved natural organic matter (NOM) influences colloidal stability as these nanoparticles precipitate in natural waters. In our previous work, we showed that for low molecular weight organics, surface association by thiol groups was important for stabilizing ZnS nanoparticles in water [1]. Humic substances, however, are complex macromolecules that can interact with surfaces through long-range interactions (e.g. electrosteric effects) that will influence overall nanoparticle stability. In this study, we compared NOM fractions that were isolated from several surface waters and represented a range of characteristics (molecular weight, type of carbon, sulfur content, etc.). Dynamic light scattering was employed to monitor the size of ZnS nanoparticles as they precipitated and aggregated over hours to days in solution containing dissolved NOM isolates. Overall, growth rates were slower as NOM concentration increased (from 1 to 10 mg-C/L) and faster as ionic strength increased (up to 0.1 M). For the same NOM concentration and ionic strength, particle growth rates varied for the different types of NOM isolates. Rates appeared to correlate with the molecular weight of the NOM (R^2 =0.7), weakly correlate with aromatic C content (R^2 = 0.45), and poorly correlate with reduced-S content (R^2 =0.01). We performed additional experiments with small angle X-ray scattering to elucidate the size and structure of ZnS aggregates that coprecipitated with humic and fulvic acids. Overall our results highlight the important molecular components of NOM that may be responsible for surface association with ZnS nanoparticles, and ultimately, colloidal stability and mobility

[1] Lau & Hsu-Kim (2008) *Environmental Science & Technology* **42**, 7236–7241.

The presence of molecular water in addition to structural hydroxyl in nominally anhydrous minerals from UHP metamorphic rocks

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Commonly the concentrations of structural hydroxyl in nominally anhydrous minerals (NAMs) have been determined by the FTIR method for UHP eclogites and mantle-derived xenoliths. The results have been used as a proxy for the concentration of water in the NAMs for the purpose of estimating water concentration in the mantle. However, significant amounts of the molecular water are also present in the NAMs as indicated by the occurrence of fluid microinclusions in NAMs. This is detected by the qualitative TEM observations and the quantitative FTIR and TC/EA-MS analyses of such NAMs as garnet, omphacite, rutile and quartz from UHP metamorphic eclogite and jadeite quartzite in the Dabie-Sulu orogenic belt, China.

While the TEM observations show different sizes of fluid microinclusions in the NAMs, the FTIR and TC/EA-MS analyses via stepwise heating gave water concentrations in the forms of total water, molecular water and structural hydroxyl, respectively. For UHP eclogite at Bixiling in the Dabie orogen, the results yield molecular water concentrations of 550 to 1755 ppm in omphacite and 240 to 710 ppm in garnet, and structural hydroxyl concentrations of 1240 to 2810 ppm H_2O in omphacite and 280 to 745 ppm H_2O in garnet. The TC/EA-MS online analysis also enables determination of mineral hydrogen isotope composition in addition to water concentration. The results are that the molecuar water has δD values of −112 to −92‰ for omphacite and −98 to −94‰ for garnet; the structural hydroxyl has δD values of −91 to −85‰ for omphacite and −87 to −72‰ for garnet. Stepwise-heating TC/EA-MS analyses indicate that the molecular water are depleted in D relative to structural hydroxyl and has higher mobility than the structural hydroxyl in the NAMs. The low δD values are consistent with incorporation of continental deglacial meltwater into eclogite protolith by high-T hydrothermal alteration. The meltwater H isotope signature was preserved in the UHP minerals during the deep subduction of continental crust, with only limited activity of fluid within the UHP slab. Nevertheless, the fluid became active during exhumation due to a decrease in water solubility with pressure decrease. Therefore, exsolution of both structural hydroxyl and molecular water from the NAMs is the important source for retrograde fluid.