Polyelectrolyte injection increases mobility of nanoscale zero-valent iron in carbonate sand

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The limited mobility of nanoscale zero-valent iron (nZVI) remains one major obstacle to widespread utilization of this agent for *in situ* groundwater remediation [1]. The nZVI mobility is strongly affected by aquifer heterogeneities, which include mineralogical variations [2]. In our previous study we showed that the presence of carbonates in porous aquifers significantly reduces the nZVI mobility [3]. New strategies are therefore required to improve the nZVI mobility in such porous media. This might be achieved by increasing the repulsion between nZVI and the porous media, which can be provided by the injection of anionic polyelectrolytes in the subsurface. We tested this hypothesis by studying the effects of various co-injected polyelectrolytes (natural organic matter, humic acid, carboxymethyl cellulose, and lignin sulfonate) on the mobility of polyacrylic acid coated nZVI in two model porous media; quartz and carbonate sand.

The results demonstrated that co-injection of the chosen polyelectrolytes at concentrations of 50 mg L^{-1} does not influence the nZVI mobility in quartz sand. This can be explained by the highly negative surface charge of quartz (-40 mV), which prohibited any surface interactions with the negatively charged polyelectrolytes. Contrarily, in less negatively charged carbonate sand (-10 mV) the co-injection resulted in an increased nZVI mobility. We related this to polyelectrolyte adsorption onto the carbonate surface. Lignin sulfonate was selected to further investigate the effect of increasing polyelectrolyte concentrations (10, 25, 50, 250, and 500 mg L^{-1}) on the nZVI mobility in carbonate sand. At concentrations above 10 mg L^{-1} an increase in nZVI mobility was observed. Furthermore, the nZVI transport distance was almost doubled when the particles were co-injected with 500 mg L^{-1} lignin sulfonate.

Overall, the results indicated that polyelectrolyte adsorption onto the carbonate sand reduces the nZVI deposition onto aquifer grains and consequently promote its mobility, an effect which is more pronounced with higher concentrations of co-injected polyelectrolyte.

[1] O'Carroll *et al*.. (2013) Adv. Water Resour. 51, 104-122. [2] Kim *et al*.. (2012) J. Colloid Interface Sci. 370, 1-10. [3] Laumann *et al*.. (2013), accepted, Environ. Pollut.

Metal-silicate partitioning of the HSE at high pressures and temperatures in S-bearing systems

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The highly siderophile elements (HSE - Os, Ir, Ru, Rh, Pt, Pd, Re, Au) are unique geochemical tracers of Earth's accretion and differentiation history. From high pressure-high temperature experimental work it is known, that the HSE were effectively scavenged from the Earth's mantle during core formation, leaving the mantle strongly depleted in HSE. After core formation was complete, a "late-veneer" of highly oxidized, chondritic material then delivered a small amount of HSE back to the mantle [1]. However, the observed HSE abundances of the primitive upper mantle cannot be reproduced by any known meteorite group, questioning how the HSE abundances were established. A possible clue to this problem could lie in the effect of S on metal-silicate partitioning of the HSE: As S is known to strongly influence the partitioning behaviour of chalcophile trace elements such as Mo or Ni, it may also have played an important role for the behaviour of the HSE, especially during the late stages of accretion and core formation.

In order investigate if sulfur has an effect on the behaviour of the HSE during core formation, we studied the metal-silicate partitioning of Pt, Pd and Ru in S-bearing systems under high pressure-high temperature conditions. A molten peridotite was equilibrated with a S-bearing Fe-HSE-alloy at pressures from 6 to 18 GPa and temperatures between 2200 °C and 2400 °C in a multianvil apparatus. Sulfur concentration in the alloy varied between 5-15 wt. %. Quenched metal and silicate were analyzed by electron microprobe (major elements) while trace element concentrations were determined using LA-ICP-MS.

Results indicate that Pd and Ru, the two most chalcophile HSE, become significantly less siderophile with increasing S-content of the metal. In contrast, Pt being less chalcophile shows only a small effect. These results indicate that, besides pressure and temperature, composition also has a significant effect on the partitioning behaviour of HSE. The presence of sulfur may induce HSE fractionation during core formation and might be responsible for observed HSE abundances in the Earth's mantle.

[1] Mann U, Frost D. J., Rubie D. C., Becker H. and Audétat A. (2012) *GCA* 85, 593-316.

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