Kinetics of Fe(II)-catalyzed transformation of ferrihydrite under anaerobic dynamic flow conditions

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The reduction of iron oxides, both biotically and abiotically, is one of the most important chemical processes for cycling of iron in the environment and has a profound influence on the mobility of soil and groundwater contaminants. The ferrous ions produced during this process will be absorbed onto the surfaces of remaining Fe-hydroxides, which play an important role in controlling the subsequent transformations of host Fe-hydroxide minerals. However, the detailed mechanisms, pathways and kinetics of such Fe(II)-catalyzed transformation of Fe-hydroxides is still unclear, especially under dynamic flow micro-porous subsurface environment.

To better understand this process, an inorganic ferrous ion solution was directly injected into 100 μm I.D. capillary tubes packed with ferrihydrite coated glass spheres under anaerobic circumneutral pH conditions to study the kinetics of secondary mineral transformations from ferrihydrite in flow through micro-porous environment. Synchrotron XRD techniques were used to monitor the phase transformations over time. The reacted products were further characterized by TEM. The study showed a complete conversion from ferrihydrite into magnetite within 30 hours at 20mM ferrous ion injection without any intermediate phase being detected. When injected with 2mM ferrous ion solution, magnetite was still the only secondary mineral phase detected, although the transformation took 150 hours to complete. Instead of a constant rate, the transformation reactions at the two conditions studied both showed slow rates at the beginning, but increased rapidly thereafter following a power rate law. The transformation rates obtained in this study are faster compared to the values obtained in traditional bench reactors experiments. The overall fast transformation process indicates a topotactic structure rearrangement resulting from electron transfer between injected ferrous ion and ferrihydrite without any significant dissolution and recrystallization. The transformation process conforms to a solid state transformation mechanism.

Mineral chemistry of carp otoliths reflecting water quality change

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The chemistry of fish otoliths is derived directly from their living environment, and once deposited the elements will be fixed forever. Therefore, analysing the mineral chemistry of otoliths is useful in the chemical evaluation of waters where the fish lived [1]. Our research reveals that the mineral chemistry of otoliths is a potential proxy for monitoring water quality change. Samples of carp and lake water were collected from Baiyangdian Lake, suffering from serious intermittent pollution, and Miyun Reservoir, supplying drink water for Beijing, which is little polluted. Both of these waters are located in northern China. The minerals within otoliths from both sites were vaterites. Trace elements As, Ba, Cr, Pb, Zn in the water samples were analyzed separately on AFS and ICP-MS. The contents of the elements in the water samples from the Baiyangdian Lake are all higher than those from Miyun Reservoir. Contents of all elements but Ba in otoliths from Baiyangdian Lake are higher than those from the Reservoir. These trace elements within lapillus were also measured on LA-ICPMS. The otoliths from the Baiyangdian Lake show higher concentrations of trace elements during winter to next spring and lower in the summer and autumn. This result is due to the discharging of waste water from the local factories during the winter to next spring, and replenishment from the upriver reservoirs by the government in the summer and autumn to prevent the lake from drying up and also to attract people for sightseeing. Otoliths from the Miyun Reservoir also show interesting records with quite high levels of As, Ba, Cr, Pb and Zn before the year 2003, but levels of nearly zero afterwards. This finding is consistent with strict water quality protection instigated by the city government.

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[1] Thorrold *et al.* (1998) *Mar. Ecol. Prog. Ser.* **173**, 253-265.