

Influence of nanoscale iron oxyhydroxide growth on metal sorption / desorption mechanisms

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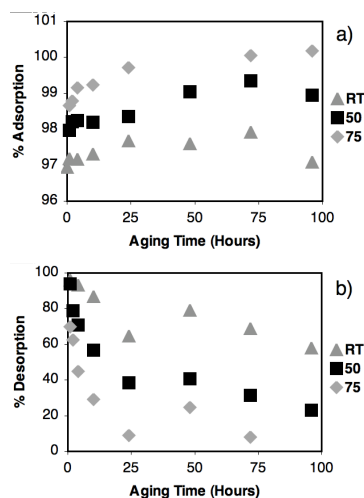
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Iron oxyhydroxide nanomaterials play important roles in the mobility of aqueous metal species through sorption and desorption processes. The growth of such nanophases leads to changes in their structure and reactivity and may additionally modify the mechanisms by which metal ions are adsorbed and retained. In this study, macroscopic and microscopic techniques were used to elucidate the sorption, desorption and incorporation mechanism of metals onto and within nanoscale iron oxyhydroxides during their aging and growth.

The retention of Zn(II) and Cu(II) to iron oxyhydroxide nanoparticles aged at 25 – 75°C for 0 – 96 hours was demonstrated through macroscopic uptake and desorption experiments. While uptake of Zn(II) (Fig. a) and Cu(II) (data not shown) was rapid and complete within an hour, desorption was found to be partially irreversible (Fig. b) and showed a clear relationship with both nanoparticle aging time and temperature. Less Zn was desorbed from material aged at either higher temperature or for longer time periods, indicating stronger adsorption or the role of physical incorporation mechanisms in these cases. X-ray absorption spectroscopy (XAS) of selected sorption and desorption samples supports the hypothesis that the retained metals are present as structurally incorporated sorption complexes. This is evident by the higher metal-Fe coordination observed in samples from which the readily desorbed material has been removed.

Used together such techniques provide information about how these and possibly other metals are 1) complexed on the surface of iron oxyhydroxides or 2) are incorporated into the iron oxyhydroxide structure. These findings have implications for the long-term removal of hazardous metals from the aqueous phase and the development of possible remediation strategies targeting contaminated environments.



Paleosols in Cappadocia – Archives of ecosystem changes in the Late Neogene

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In Cappadocia, Central Turkey, paleosol-sequences are interlayered with 13 plateau-forming dacitic to rhyolitic ignimbrites and fallout tephra layers of Miocene/Pliocene age (11-3 Ma, Schumacher *et al.* 2001). The stratigraphic interval is of special interest as the Late Miocene phase of extreme aridity (the “Messinian crisis”) is included. While this is represented in the marine record of the Mediterranean Sea by widespread salt deposits (5.5 – 4.8 Ma) it is indicated in the terrestrial sediment section of Cappadocia by an interval of Aridisols that contains calcretes, gypsum pseudomycelia and palygorskite. These paleosols also conserve the last major vegetational change from C3- to C4- dominated ecosystems, from woodland to grassland. This last major global ecosystem change is archived within the $\delta^{13}\text{C}$ isotope shift from -10 to ± 0 ‰ in the pedogenic calcretes in Kenya, Pakistan, the badlands of North America, and China and started between 8 and 5 Ma with differences in timing, duration and amount of shifting (Cerling *et al.* 1993, Cerling 1999, Ding and Yang 2000, Quade and Cerling 1995). For the Mediterranean region the possibility of such a shift was excluded (Quade *et al.* 1994). However, due to the exposed position of Cappadocia, Central Anatolia, at altitudes above 1000m, mediterranean climate dominated this area neither today nor in the Late Miocene. Cappadocia is part of the cold dry mid-latitude climate zone. The necessary temporal constraints are provided by K/Ar dating of the volcanoclastic sediments (ignimbrites and fall-out tephra layers) as well as the biostratigraphy of vertebrate fossils embedded in lahars and paleosols.

The aim of the project is to investigate (a) the change in vegetation from C3 to C4 dominated ecosystems by analyzing the stable isotope geochemistry in pedogenic carbonates as well as (b) paleoclimate changes in the Late Neogene by analyzing mineralogy and chemistry of paleosols in Cappadocia, Central Turkey.

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