Surface complexation and proton promoted dissolution in aqueous apatite systems

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Apatites ($Ca_5(PO_4)_3(F,Cl,OH)$) are the most abundant phosphorus-bearing minerals in nature. They are very important in agriculture as phosphorus containing fertilisers, as well as in medicine as main constituents of mammalian bones and teeth enamel.

Surface layers of hydroxyapatite have been suggested to have a composition that is different from the bulk [1,2]. This change is caused by a creation of vacancies on Ca and OH sites and the protonation of phosphate groups. The range of composition may be expressed as $Ca_{(10-x)}(HPO_4)_x(PO_4)_{(6-x)}(OH)_{(2-x)}$. It thus seems important to characterize these surface layers in order to be able to interpret not only surface complexation reactions but also different types of dissolution processes.

The surface chemistry, in terms of surface complexation models, of apatite minerals is very much unexplored, and the dissolution mechanism is still debated. The objectives with our apatite studies are to characterize possible surface phase transformations and to clarify surface acid/base properties, ion exchange and readsorption reactions involving phosphate, calcium and fluoride.

The strategy in modelling surface complexation and dissolution of apatite is to yield information provided by different macroscopic techniques: i) potentimetric pH measurements; ii) dissolution characteristics with respect to soluble fractions of calcium, phosphate and fluoride; iii) readsorption studies of phosphate, fluoride and calcium, as well as iv) surface charge measurements. Furthermore, this information is combined with surface spectroscopic characterizations using FTIR, XPS and NMR methods. The presentation will highlight similarities and differences found in the hydroxyl- and fluorapatite systems.

[1] Brown & Martin (1999) *J. Phys. Chem.* **103**, 1671-1675.
[2] Ishikawa *et.al* .(1989) *Langmuir* **5**, 144-147.

Nitrogen isotope fractionation during the oxidation of substituted anilines at manganese oxides

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Many important soil and water contaminants such as pesticides, antibacterial agents, or dyes contain aromatic amino functional groups. In the environment such compounds are susceptible to oxidation of the amino group by manganese oxides (MnOOH, MnO_2), one of the most important naturally occurring oxidizing agents. Previous studies of the reaction kinetics of substituted anilines and structurally related compounds with manganese oxides have shown that the rate-determining step of the degradation involves multiple elementary reaction steps, that is transport to reactive surface sites, formation of precursor complexes between the contaminant and the mineral surface, and the subsequent electron transfer. To obtain a diagnostic tool for the identification of this degradation pathway and to elucidate the mechanism of aromatic N atom oxidation at manganese oxide surfaces in greater detail, we investigated the ^{15}N-kinetic isotope effects associated with this reaction by compound-specific nitrogen isotope analysis.

In laboratory batch model systems we studied the N-isotope fractionation of substituted anilines during their oxidation by MnO_2-surfaces and the evolution of ^{15}N signatures of selected reaction products. The disappearance of the anilines was characterized by fast initial oxidation followed by slower transformation. Substituted azobenzenes were identified as reaction products. Only the initial fast oxidation step showed a moderate ^{15}N depletion owing to a preferential oxidation of ^{15}N isotopologues. In contrast, δ^{15}N trends of azobenzenes, were associated with a more substantial enrichment of ^{15}N isotopologues. We hypothesize that the small inverse kinetic isotope effect during the oxidation of substituted anilines (apparent ^{15}N-KIE of 0.997) is characteristic for the surface-catalyzed oxidation of aromatic nitrogen atoms because an oxidation at the aromatic ring, i.e. in enzymatic reactions, results in substantially more inverse ^{15}N isotope effects. The preferential formation of light 14N azobenzene isotopologues confirm that azobenzene is not formed directly from aniline oxidation products but requires an additional intermediate (eg., hydrazobenzene), which reacts to azobenzene with a normal kinetic isotope effect.