

Comparing the surface-promoted hydrolysis of phosphate mono- and diesters on goethite

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Phosphorus is an essential nutrient for both plants and microorganisms. However, in order for it to cross cell membranes, it must be in the form of orthophosphate or in some cases as small organophosphates. The majority of organic phosphates input into the biosphere are in the diester form, via pesticides, plasticizers, and hydraulic fluids. However, the P found in most soils is dominated by monoesters. Hydrolysis of phosphate esters in biological systems is important since it is a step that is required to make these large phosphate esters more bioavailable. While the hydrolysis of these phosphate esters is thermodynamically favourable, the reaction in water or a strong electrolyte solution is a slow process.

Phosphorus is a unique essential nutrient in its ability to strongly sorb to environmental particles. Therefore, reactions at the surfaces of these particles can control the fate and transport of phosphorus in the biosphere. Minerals, such as goethite, have been shown to increase the rate of hydrolysis of organophosphates by acting as a catalyst. In this study we have investigated the abiotic hydrolysis of a phosphate monoester and diester, p-nitrophenyl phosphate (pNPP) and Bis-[p-nitrophenyl] phosphate (BNPP), respectively. To determine the mechanisms and rate of the hydrolysis of pNPP and BNPP adsorbed on goethite surfaces we have used a combination of spectroscopic methods. The concentration of phosphate remaining in solution was determined by UV-vis spectroscopy, while the surface reactions were examined using infrared spectroscopy via the ATR sampling technique.

Spectroscopic results for the pNPP-goethite system show quick and complete adsorption of the ligand, followed by the subsequent hydrolysis, with the release of nitrophenol (NP) into solution. After 30 hours nearly 100% of the pNPP was hydrolyzed to NP and orthophosphate. Alternately, in the BNPP-goethite system, the ligand adsorbs much more slowly and to a lesser extent than the pNPP. Between pH 4 and 6, the maximum hydrolysis observed over 48 hours is less than 25%. Our results suggest that differences in surface affinity and surface-promoted hydrolysis between mono- and diesters are important factors to consider in order to explain differences in the overall biogeochemical behaviour of these two classes of phosphorus compounds.

Water in the mantle, melting, and the evolution of Earth's atmosphere

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Water and carbon are the most important volatiles in Earth's interior, but they strongly differ in their behaviour. While carbon is mostly sequestered in accessory phases such as carbonates and elemental carbon, water mostly resides as OH point defects in the nominally anhydrous minerals of the mantle. In this presentation, I review (1) the observational constraints on water abundance in the mantle (2) the effect of water on mantle melting and the associated changes in electrical conductivity and (3) the coupling between the water abundance in Earth's mantle and the redox evolution of the atmosphere.

Water may be essential for inducing melting in the seismic low velocity zone of the upper mantle as well as above the 410 km discontinuity. Both effects are ultimately related to depth-dependent changes in the capability of mantle minerals to dissolve water as point defects. Major experimental advances in recent years have shown that both the solubility of water in olivine at the base of the upper mantle as well as the solubility of water in pyroxenes in the uppermost mantle are much higher than previously thought. Moreover, new *in situ* measurements show that water has a much stronger effect in enhancing the electrical conductivity of basaltic melts than anticipated and this effect increases with pressure. A consequence of these observations is that very likely, small fractions of hydrous melt can explain the electrical conductivity in the seismic low velocity zone of the upper mantle.

It has long been recognized that Earth's atmosphere became much more oxidized in the 'great oxidation event' 2.3 billion years ago. This event may be due to a change in oxidation state of volcanic gases or to photosynthesis by cyanobacteria. Changes in the oxidation state of volcanic gases 2.3 billion years ago have often been dismissed on the ground that there is no evidence for a corresponding change in mantle redox state at this time interval. However, the relevant gas equilibria between sulfur and nitrogen species do not only depend on oxygen fugacity, but also on water. I show that degassing of water from the mantle – at constant oxygen fugacity – may well induce the changes in the oxidation state of sulfur and nitrogen in volcanic gases required to oxidize the atmosphere.