Linking structural isomerism of organic ligands to the precipitation and structure of ferrihydrite

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The extent of interference of organic ligands with the polymerization of Fe(III) has not been systematically studied as a function of structural ligand properties. Here I tested how the number and relative phenol group positions in hydroxybenzoic acids affect both ferrihydrite formation and its local (<5 Å) Fe coordination. To this end, acid Fe(III) nitrate solutions were neutralized up to pH 6.0 in the presence of increasing concentrations of 4-hydroxybenzoic acid (4HB), and the two constitutional isomers 2,4-dihydroxybenzoic acid (2,4DHB) and 3,4-dihydroxybenzoic acid (3,4DHB). The precipitates formed were dialyzed, lyophilized, and subsequently studied by means of X-ray absorption spectroscopy and synchrotron X-ray diffraction.

The solids contained up to 32 wt% organic C. Only precipitates formed in 3,4DHB solutions comprised significant Fe(II) ($Fe(II)/Fe_{tot}$ ≤6 mol%), implying the abiotic mineralization of the catechol-group bearing ligand during Fe (III) hydrolysis under oxic conditions. Ferrihydrite formation was significantly impaired by the ligands (4HB ~ 2,4DHB << 3,4DHB). Coordination numbers of edge- and corner-sharing Fe in the precipitates decreased with increasing initial ligand concentration by up to 100%. Linear combination fitting (LCF) of Fe K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra, however, revealed that these decreases were due to increasing proportions of organic Fe(III) complexes. All ligands reduced the coherently scattering domain (CSD) size of ferrihydrite as indicated by synchrotron X-ray diffraction analysis (4HB < 2,4DHB << 3,4DHB). With decreasing particle size of ferrihydrite its $Fe(O,OH)_6$ octahedra became progressively distorted as evidenced by an increasing loss of centrosymmetry of the Fe sites. Pre-edge peak analysis of the Fe K-edge XANES spectra in conjunction with LCF results implied that ferrihydrite contains 11 ± 2% tetrahedral Fe(III).

The results suggest that especially hydroquinone moieties of NOM effectively suppress Fe(III) polymerization and ferrihydrite formation. Organic chelates seem to control ferrihydrite formation mainly by kinetically modulating the availability of Fe(III) for nucleation and/or polymerization reactions. As a consequence, NOM may trigger the formation of smaller ferrihydrite nanoparticles possessing increased structural strain.

Helium rain and core erosion in gas giant planets

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Starting with a brief overview over the search for extrasolar planets, this talk will discuss the state of matter at high temperature and pressure conditions that prevail in the interiors of giant planets. We describe how data from the Galileo mission to Jupiter has been combined with *ab initio* simulations to demonstrate that there exists helium rain on this planet [1]. Furthermore we use such simulations to predict two new phases of water ice (figure) at megabar pressures and characterize the associated structural and electronic transitions [2]. Since water ice is assumed to be one of the primary components of the cores of gas giants, we analyzed its stability when it is exposed to metallic hydrogen. We show that the cores of Jupiter and Saturn have been eroded [3]. We conclude with discussing the erosion of heavier materials.

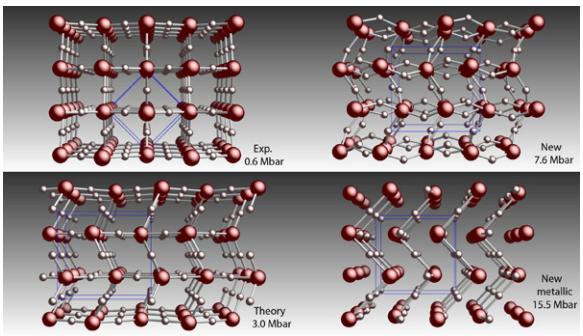

Figure 1: High pressure phases of water ice. The large and small spheres denote the oxygen hydrogen atoms, respectively.

The top left panel shows ice X, the highest pressure phase seen in experiments. On the lower left, the Pbcm phase is shown that was predicted theoretically in 1996. Recently we used *ab initio* simulations to predict the existence of the two new phases shown on the right [2]. The lower one is metallic.

[1] H. F. Wilson & B. Militzer (2010) *Phys. Rev. Lett.* **104**, 121101. [2] B. Militzer, H. F. Wilson (2010) *Phys. Rev. Lett.* **105**, 195701.[3] H. F. Wilson, B. Militzer, '*Erosion of Icy Cores in Giant Gas Planets*', http://arxiv.org/abs/1009.4722