

Force field for oxoanions in solid state and aqueous solutions

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A delicate balance between ion hydration and crystallization plays a crucial role in natural processes leading to dissolution and precipitation of minerals, and forms the basis of many technological applications, such as nuclear waste separation and storage. Our primary interest is to investigate salt crystallization from mixed electrolyte solutions in porous rocks, but the results also pertain to the rational design of complexation agents used in selective crystallization of homologous series of oxoanions.

A reliable description of molecular and ionic interactions is needed to understand atomic-scale mechanisms underlying the thermodynamics and dynamics of electrolyte solutions. Our goal is to develop a consistent force field for the study of oxoanions including CO_3^{2-} , NO_3^- , and those of general formula XO_4^{2-} ($\text{X}=\text{S}, \text{Se}, \text{Cr}, \text{Mo}, \text{W}$). While several force fields exist for the description of simple alkali metal and halide ion series [1], and isolated models for selected oxoanions have been published [2], a consistent force field for oxoanions suitable for comparative studies is missing.

The choice of an appropriate potential model form is dictated by intended applications, balancing accuracy and computational efficiency. Since adsorption and salt precipitation happen over large time and length scales, the simplicity of the model is of high importance. While most of the concerned ions are highly polarizable, their mineral environment is consistently polar, justifying the use of effective pair potentials. We therefore consider pair potentials represented by a combination of point charges and Lennard-Jones interactions compatible with the SPC/E model of water [3].

The force field is optimized against experimental data including hydration free energy at infinite dilution [4], chemical potential at finite concentration obtained from Kirkwood-Buff equations [5], lattice constant and lattice energy for selected crystals, and diffusion coefficient [4]. The potential parameters (at least 5 for each oxoion) were determined using global optimization based on the coupling parameter technique [6].

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Dynamic precipitate formation during Fe(II) oxidation in aerated phosphate-containing water

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The oxidation of Fe(II) at biogeochemical redox interfaces results in the formation of nanoparticulate Fe(III)-precipitates that act either as immobilizing sorbents or colloidal carriers for contaminants and nutrients. In previous work on Fe(I) oxidation products in neutral aqueous suspensions [1, 2], we concluded that nanoparticulate amorphous Fe(III)-phosphate is the first precipitate that forms during Fe(II) oxidation in the presence of phosphate (P), with a molar P/Fe ratio of the solid of ~ 0.55 (in absence of Ca). At initial dissolved P/Fe ratios less than ~ 0.55 , the formation of Fe(III)-phosphate is followed by the precipitation of amorphous to poorly crystalline Fe(III)-(hydr)oxides (depending on silicate/Fe ratio). These conclusions, however, were based on the study of precipitates collected after complete Fe oxidation and precipitation (no time-resolution) and covering a limited number of P/Fe ratios.

In ongoing work, we explore the dynamics of precipitate formation during Fe(II) oxidation in aerated phosphate-containing solutions (bicarbonate-buffered to pH 7.0) time-resolved and over a larger number of initial P/Fe ratios. We monitor the decrease in filterable ($<0.2 \mu\text{m}$) element concentrations during Fe(II) oxidation and characterize precipitates collected during and after complete Fe(II) oxidation by a suite of complementary techniques, including X-ray absorption spectroscopy and transmission electron microscopy. To monitor precipitate evolution in-situ, additional experiments are performed using time-resolved UV-Vis spectroscopy.

The results from time-resolved experiments confirm the initial formation of an amorphous Fe(III)-phosphate with a P/Fe ratio of ~ 0.55 (at the time when dissolved P is depleted). However, our results also suggest that in systems with initial dissolved P/Fe ratios substantially below 0.55, initially formed Fe(III)-phosphate transforms or dissolves during ongoing Fe(II) oxidation in P-depleted solution, resulting in the formation of Fe(III)-(hydr)oxides with higher degree of Fe(III) polymerization to which P is sorbed. From our current results, we conclude that at initial dissolved P/Fe ratios less than ~ 0.17 , initially formed Fe(III)-phosphate is absent in the final product of Fe(II) oxidation at near-neutral pH. These results demonstrate that Fe(III) precipitation during Fe(II) oxidation in aqueous solutions is a highly dynamic process that may involve formation of transient precipitates that are absent in the fresh precipitate after complete Fe(II) oxidation. In future work, we plan to further investigate Fe(III) precipitation dynamics during Fe(II) oxidation and the aging of fresh precipitates, also with respect to implications for the solubility and mobility of co-transformed trace elements.

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