

Solubilities of arsenic oxy- and thio-compounds in calcium rich waters

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16L. Biogeochemistry of Oxyanion-Forming Trace

Elements in the Environment

The mobilisation of arsenic by thiolation is a significant driver of As solubility in sulphidic, reducing systems and alkaline environments^{1,2}. The determination of the chemistry of arsenic thioanions requires specific analytical methods to for detection. The complex chemistries of environments containing thioarsenicals create problems with regard to preservation of *in situ* arsenic speciation. Co-precipitation of arsenic with iron³ or other minerals salts has been shown to occur during the lag time between *in situ* sampling and laboratory analyses. Calcium (Ca) is a ubiquitous element in alkaline natural systems containing As. The insolubility of Ca-arsenate salts has been documented⁴ thus quantitative losses of As from *in situ* samples containing Ca is a probable mechanism.

Interactions between Ca and arsenic oxy- and thioanions were studied under anoxic, alkaline conditions. We have studied the precipitation of Ca-thioarsenate salts, and have been able to experimentally determine the K_{sp} , ΔG°_f , ΔH°_f and ΔS° , for Ca-monothioarsenate, Ca-arsenite, and Ca-arsenate. Trithioarsenite, trithioarsenate and tetrathioarsenate do not form Ca-arsenic salts or absorb to Ca carbonate ($CaCO_3$), Ca hydroxide or Ca sulphate, indicating that these species are the most soluble anionic arsenic species. Dithioarsenate is more soluble than monothioarsenate and arsenate, and arsenite is the least soluble As species. The solubilities of Ca sulphate and $CaCO_3$ are less than those of the Ca-arsenic salts, thus adsorption of arsenite and arsenate to Ca sulphate and $CaCO_3$ can be a significant mechanism of removal of As oxyanions in the environment. Increasing thiolation enhances the solubility of As anions such that no chemical interaction exists between As and Ca in the environment for tri- and tetra-thiolated species.

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Ionic force fields for electrolytes and molecular simulation of chemical potentials and aqueous solubility

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We have recently [1,2] developed the Osmotic Ensemble Monte Carlo (OEMC) method for calculating the chemical potentials and solubility of aqueous electrolytes and their mixtures by molecular simulation. OEMC is a computationally efficient algorithm that uses a type of semi grand canonical ensemble, with a fixed number of water molecules at temperature T and pressure P , and electrolyte chemical potentials specified by the inter-phase equilibrium reaction involving the ions and their crystalline solid. To calculate solubility, we use accurate chemical potential data for the solid from thermochemical tables[3]. By appropriately setting the solid's chemical potential to other values, the entire chemical potential vs concentration curve of the ions in solution can be mapped out.

Although our results show good qualitative and reasonable quantitative accuracy, improvements depend on the use of more accurate ionic force fields. In this talk, we describe calculation strategies and show results for new force-field models for Na^+ and Cl^- compatible with SPC/E water. Our new force fields demonstrate good accuracy for the combined ion pair chemical potentials, the solution density, the predicted solubility and the solid chemical potential and density. Preliminary results are shown in the figure.

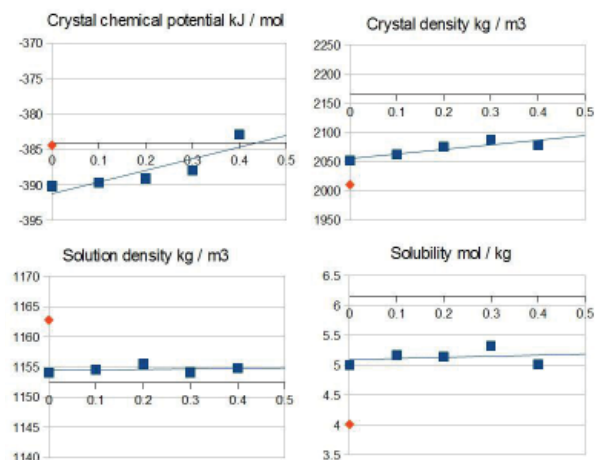


Figure: NaCl crystal and solution properties as functions of a model parameter after one iteration of the force-field adjustment strategy. Blue: our results; Orange: results using the force field of Joung and Cheatham[4]; Horizontal lines: experiment.

[1] Moučka, Lísal, Škvor, Jirsák, Nezbeda & Smith (2011) *J. Phys. Chem. B* **115**, 7849–7861.

[2] Moučka, Lísal, Smith (2012) *J. Phys. Chem. B*, submitted.

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