A computational study of the immobilisation of arsenic in groundwater

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Arsenic is a highly toxic and carcinogenic contaminant of groundwater sources used widely for drinking and irrigation, raising massive human health problems.

Immobilisation of arsenic in the groundwater can occur through surface adsorption to minerals in the soil and we have therefore used atomistic simulation techniques to calculate the strength of binding of the As(V) species H_3AsO_4 to the major surfaces of three iron (hydr)oxides: hematite Fe_2O_3, goethite FeOOH and $Fe(OH)_2$, and to investigate the structures of the surface/adsorbate systems, where we have considered the formation of both inner and outer sphere complexes at the mineral surfaces. Experiment suggests that inner sphere complexes of the arsenate species at the surfaces are formed [1], which is borne out by our calculations. We find that surface hydroxy groups exchange spontaneously with the arsenate adsorbate to form a chemical bond directly between the adsorbate and the iron ions in the goethite and hematite surfaces, rather than a weakly interacting physisorbed species at the hydroxylated surfaces.

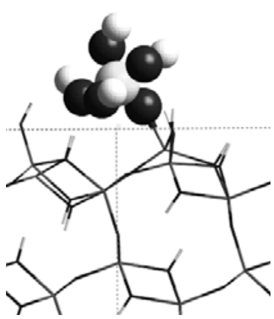

Figure 1: Formation of an inner sphere arsenate complex at the hydroxylated goethite {100} surface.

[1] Arai, Elzinga & Sparks (2001) *J. Colloid Interface Sci.* **235**, 80.

Equation of state of geological fluids

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Equation of state (EOS) is a mathematical function of temperature, pressure, volume and composition of materials such as fluids and minerals. An EOS can be used to derive various thermodynamic properties such as phases (immiscibility, boiling, solubility and phase equilibrium), volumetric properties (volume, density, isochor, compressibility, bulk modulus) , thermal properties (enthalpy, heat capacity,) and chemical properties (chemical potential, fugacity).

Since 1873, van der Waals published his famous EOS, which won him Nobel Prize, more than 3000 EOS have been published. However, most of the EOS are developed for chemical engineering, and thus are limited to pressures of a few hundred atms.

Geochemistry is a science which studies the chemical states and processes in the various spheres in the earth., requiring such quantitative and predictive models as EOS to carry out various studies. However, the temperature-pressure range of the Earth is very large, the EOS in the past are far from sufficient to meet the needs.

Geological fluids are the liquids or gases mainly composed of such components as H_2O, CO_2, CH_4, N_2, H_2S, SO_2, H_2, O_2, Ar, HCl, C_2H_6 and various aqueous ions. They played important roles in various geochemical processes.

The molecules of various fluid components differs significantly in their mass, charge, shape and affinity. Such differences exists not only among different molecules but on the same molecule sometimes. For example, NaCl becomes separated ions in water at relatively low temperature, but it turns to Na-Cl molecule with strong dipole moment when temperature increase above 600K, and it may become spheric molecule when temperature increase above 3000K. Such diversity of fluid molecules diversify various equations of state.

Over last more than ten years, we developed equations of state and thermodynamic models for various fluids. These EOS and models not only reproduces more than sixty thousand experimental points from more than one hundred laboratories, but also they extrapolate well beyond experimental range, making the appliabple value of the data increasing substantially. These models not only are proved by the late experiments of many laboratories around the world and are programmed in quite a few geochemical application softwares., but also they are widely cited in various studies including fluid inclusions, methane clathrate, fluid-rock interactions, CO_2 sequestrations and laboratory apllications.