Stabilization of iron oxide nanoparticles by the adsorption of sulfate, phosphate and arsenate

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Iron oxides are well known for their adsorption capacity of anions such as sulfate, phosphate, silicate, carbonate, and arsenate. It is easy to verify that ferrihydrite with adsorbed anions transforms to the more stable iron oxides (goethite, hematite) much more slowly than pure ferrihydrite. The difference in the transformation rate has been ascribed to the surface "poisoning", where the anions located at the surface may hinder the dissolution-precipitation processes. In other words, the cause of the slower rates is considered to be purely kinetic. Here we show that the adsorption of the anions significantly stabilizes the hydrous ferric oxide (HFO) also in a thermodynamic sense.

We have synthesized a set of schwertmannite samples (a poorly crystalline iron hydroxysulfate) and a series of ferrihydrite samples with adsorbed arsenate and phosphate. The enthalpies of solution of these samples in 5 N HCl were then measured by acid-solution calorimetry. The dissolution enthalpies are markedly different for the pure ferrihydrite and for the HFO samples with adsorbed anions. The dissolution enthalpies (ΔH_{diss}) of pure ferrihydrite vary between -510 and -570 J/g (depending on the crystallinity of ferrihydrite). On the other hand, the ΔH_{diss} for HFO with adsorbed arsenate, phosphate, or sulfate are significantly less exothermic, indicating stabilization of the iron oxide nanoparticles by the adsorption of the anions. The ΔH_{diss} values for the HFO with adsorbed anions vary between -370 and -270 J/g. Currently, we are calculating the formation enthalpies of the HFO with adsorbed anions in order to assess its stability with respect to the crystalline iron oxides and the crystalline iron oxysalts (sulfates, arsenates, phosphates).

Alternate method for Sulfate $\delta^{17}O$ measurements

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Sulfate in the environment from natural or anthropogenic sources are often determined using isotopic analysis. Usually isotopic ratios of sulfur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) of the sulfate samples are measured to obtain this information. Other isotopic ratios ($\delta^{33}S$, $\delta^{36}S$ and $\delta^{17}O$) are generally not measured due to low abundances and are assumed to fractionate mass-dependently ($\delta^{33}S = 0.515 * \delta^{34}S$[1], $\delta^{36}S = 1.91 * \delta^{34}S$[1], $\delta^{17}O = 0.5164 * \delta^{18}O$[2]). Recent studies have found some sulfate samples do not conform to the mass-dependant rule for oxygen and, from these results, further details in the oxidation pathways of sulfate could be obtained.

Current published methods for $\delta^{17}O$ measurements required thermal decomposition of sulfate samples to SO_2 and O_2 and analyzing both gases separately (SO_2 for $\delta^{34}S$ and O_2 for $\delta^{18}O$ and $\delta^{17}O$) using isotope ratio mass spectrometry (IRMS). An alternate method to obtain these values is proposed that concurrently uses SO_2 gas only. Assumptions made about sulfate samples are a) oxygen is uniformly distributed in the sample and b) sulfur fractionates mass-dependently. The method requires isotopic measurements of $^{64}SO_2$, $^{65}SO_2$ and $^{66}SO_2$ and application of mass fraction equations to determine the δ values for the sulfate sample which, in turn, provides a value for the oxygen anomaly ($\Delta\delta^{17}O = \delta^{17}O_{mea} - 0.52\ \delta^{18}O$).

Measurements made to date have been completed with standards of known $\delta^{34}S$ and $\delta^{18}O$ to test the method. Preliminary results have found the ratio of $\delta^{17}O/\delta^{18}O$ to vary between 0.6 and 0.4. Refinement of the method to reduce the ratio variaton is currently in progress.

[1] Farquhar & Wing (2003) *Earth and Planetary Science Letters*, **213**, 1-13. [2] Santrock *et al.* (1985) *Anal. Chem.* **57**, 1444-1448.