Surface and electronic structure effects on interfacial charge transfer at iron oxide nanoparticle surfaces

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Transition metal oxides and oxyhydroxides form important reactive nanomaterials in certain terrestrial environments. There is considerable interest in defining and understanding nanoparticle reactivity with respect to (bio)geochemical processes, but the task is challenging due to the complex interplay of structural and chemical properties in nanoscale solids. Iron oxide and oxyhydroxide nanoparticles are of particular importance, participating in redox cycles driven by (bio)geochemical processes including inorganic precipitation, (photo)reduction and microbial metabolism. The reductive dissolution of such nanoparticles is an important link between biological and mineral geochemistry. For example, dissimilatory iron reducing bacteria use fine grain iron oxyhydroxide nanoparticles as terminal electron acceptors during anaerobic carbon respiration. Interfacial electron transfer is a key step in such reductive transformations, and is highly sensitive to the interaction between the electron donor and the surface and electronic structure of the substrate.

Soft x-ray spectroscopy can reveal the electronic structure of semiconductor minerals [1] and nanoparticles [2] and is anticipated to be a versatile method for predicting the thermodynamic basis of charge transfer at nanoparticle surfaces. Nanoscale iron oxide and oxyhydroxide nanoparticles exhibit modified electronic structure [2] that would alter the ability of surface adsorbed electron donors to drive reductive dissolution. However, aqueous chemistry studies that attempt to validate these predictions are difficult to interpret on the basis of the x-ray spectroscopy data alone.

We discuss ways to distinguish (i) the thermodynamic and kinetic controls on iron oxide nanoparticle reduction and (ii) the electronic and structural causes of modified reactivity. Optical and infrared spectroscopy do not detect differences in the binding of bidentate organic ligands to iron oxide bulk and nanoparticle surfaces, suggesting a minor effect of modified surface structure. However, deviations from the anticipated the pH-dependence of photoreactivity [3] suggests there may be considerable heterogeneity in nanoparticle redox behavior.

References

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Phosphoric acid fractionation factors for aragonite between 25 and 72°C with implications on aragonite-calcite oxygen isotope fractionation

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We determined the intramolecular kinetic oxygen isotope fractionation between CO_2 and $CO_3^{2^-}$ during reaction of phosphoric acid with aragonite and calcite between 25 and 72°C. We analyzed clear single aragonite crystals from Bilina (Czech Republic), Leogang (Austria), and Agrigento (Italy), a fine-grained coralliform aggregate from the Styrian Erzberg (Austria), and for comparison calcite NBS-19. The aragonites show a wide range of total oxygen isotope values from 17.5 to 39.5‰ (VSMOW). Our result for NBS-19 (28.76‰ VSMOW) is within 0.12‰ of the recommended value.

The oxygen isotope fractionation between acid-liberated CO_2 and aragonite at 25°C expressed as a 1000ln α value is consistent for our samples with 11.14 ±0.20‰ (n=4). Our new value is significantly larger than the commonly applied values of 10.34 or 10.20 (Sharma and Clayton, 1965) and our new value for calcite NBS-19 (10.08‰), but is similar to those of synthesized aragonite reported by Kim and O'Neil (1997). At temperatures between 25 and 72°C, the phosphoric acid fractionation (PAF) of aragonite can be expressed as:

$$1000 \ln \alpha^{\text{PAF}}_{\text{aragonite}} = 5.32^{*}(1000/\text{T}[\text{K}]) + 5.07$$

Our results imply that the published equilibrium ¹⁸O/¹⁶O fractionation factors between aragonite and water (e.g. Kim *et al.* 2006) need to be revised. Considering our new acid fractionation factors, oxygen isotope fractionation between aragonite and calcite is very small (<0.2‰) as suggested by recent theoretical calculations (Schäuble *et al.* 2006).

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