

Theoretical investigation of iron isotope fractionation between pyrite, hematite and siderite

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In addition to equilibrium isotopic fractionation factors experimentally derived, theoretical predictions are needed for interpreting isotopic compositions measured on natural samples because they allow exploring more easily a broader range of temperatures and compositions. In this work, equilibrium iron isotope fractionation factors for the common minerals pyrite (FeS₂), hematite (Fe₂O₃), and siderite (FeCO₃) were determined as a function of temperature, using first-principles methods based on the density functional theory [1]. The fractionation factors calculated between hematite and siderite compare well with the one estimated from experimental data while those calculated between solid and aqueous species, i.e. Fe (III)_{aq}-hematite and Fe (II)_{aq}-siderite are significantly higher than experimental values. The potential causes of this discrepancy will be discussed.

Most of the time, equilibrium isotopic fractionation factors are determined experimentally using pure phases. However, natural samples often contain impurities. This work also investigates the effect of impurities on mineral isotopic compositions, with the example of aluminous hematite. The same theoretical method was used to determine iron and oxygen isotope fractionation factors for a series of hematites containing various amounts of aluminum and hydroxyl groups [2]. Results show a linear dependence of the iron and oxygen reduced partition functions on the aluminum content. This effect is sufficiently large to be measurable and to affect the interpretation of natural isotopic compositions. On the other hand, the effect of hydroxyl incorporation in the hematite structure is found to be negligible.

[1] Blanchard *et al.* (2009) *GCA* **73**, 6565–6578.

[2] Blanchard *et al.* (2010) *GCA*, submitted.

Impact of amorphous ferric oxide reactions during the dissociation of organically complexed Fe(III)

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While chemical reactions that take place at the surface of amorphous ferric oxides (AFO) are known to be important in aquatic systems, incorporation of these reactions into kinetic models is hindered by a lack of ability to reliably quantify the reactivity of the surface and the changes in reactivity that occur over time. Long term decreases in the reactivity of iron oxides may be considered to result from changes in the molecular structure of the solid, however, over shorter time scales where substantial aggregation may occur, the mechanisms of reactivity loss are less clear. Precipitation of AFO may be described as a combination of homogeneous and heterogeneous reactions, however, despite its potentially significant role, the latter reaction is usually neglected in kinetic models of aquatic processes. Here, we investigate the role of AFO in scavenging dissolved inorganic ferric (Fe (III)) species (Fe³⁺) via the heterogeneous precipitation reaction during the net dissociation of organically complexed Fe (III) in seawater. Using sulfosalicylic acid (SSA) as a model ligand, AFO was shown to play a significant role in inducing the net dissociation of the Fe-SSA complexes with equations describing both the heterogeneous precipitation reaction and the aging of AFO being required for the kinetic model to adequately describe the experimental data. An aggregation based mechanism provided a good description of AFO aging over the short time scale of the experiments. The behaviour of AFO described here has implications for the bioavailability of iron in natural systems as a result of reactions involving AFO which are recognised to occur over time scales of minutes, including adsorption of Fe³⁺ and AFO dissolution, precipitation and ageing.