Fe(II) exchange at titanomagnetite-water interfaces

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Spinel-type iron oxides such as magnetite are an important source of solid-state Fe (II) that can affect the transport of redox-active contaminants, such as ^{99}Tc (VII), in the subsurface. Natural magnetites present in sediments are typically highly impure with titanium, and structural Fe (III) replacement by Ti (IV) yields a proportional increase in the relative Fe (II) content in the metal sublattice to maintain bulk charge neutrality. Titanomagnetite ($Fe_{3-x}Ti_xO_4$) nanoparticles provide a high surface area pristine material for batch studies to evaluate the availability and reactivity of Fe (II) at the mineral surface. $Fe_{3-x}Ti_xO_4$ nanoparticles accept structural Ti (IV) into the octahedral metal sublattice up to $x = 0.4$; higher values up to $x = 0.6$ yield discrete amorphous Fe (II)/Ti (IV) phases on particle exteriors. In aqueous suspension, there is a net driving force for the movement of Fe (II) from the bulk $Fe_{3-x}Ti_xO_4$ structure to the nanoparticle surface with subsequent release of Fe (II) into solution to reach an equilibrium distribution between interior structural Fe (II)/Fe (III), near-surface Fe (II)/Fe (III), and aqueous Fe (II). Consumption of structural Fe (II) through both dissolution and redox reactions results in the replacement of octahedral cations with vacancies to form an Fe (II)-deficient titanomaghemitized surface. Spontaneous Fe (II) release from the solid into solution increases in extent systematically with both Ti-content and decreasing pH. The presence of Tc (VII) in solution, as an electron accepting probe molecule, also increases this driving force as Fe (II) at the surface reacts with the Tc (VII) to form of a mixed Fe (III)-Tc (IV) co-precipitate. In principle, this titanomaghemitization process is reversible and, under reducing conditions, structural reducing equivalents can be restored by an external Fe (II) source. Pre-oxidized $Fe_{3-x}Ti_xO_4$ nanoparticles were found to be systematically restorable to Tc (VII) reduction rate behavior of pristine titanomagnetites by exposure to various concentrations of aqueous Fe (II). The findings demonstrate that the reactive structural Fe (II) pool can be resupplied in these $Fe_{3-x}Ti_xO_4$ phases and suggest that the mechanism involves facile coupled electron/ion transport across the mineral-water interface.

Stable strontium (δ^{88}Sr) isotopic fractionation during hydrological cycling

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The stable strontium (δ^{88}Sr) isotope system has considerable promise for resolving source and flux variations during elemental transfer to the oceans by continental weathering. In combination with radiogenic Sr isotope ratios (^{87}Sr/^{86}Sr), δ^{88}Sr provides an additional compositional space in which the riverine source and weathering flux effects can be distinguished.

Analysis of >40 % of the global Sr flux to the oceans has revealed an average riverine δ^{88}Sr composition of 0.34 ‰ [1], similar to the mean seawater value of 0.36 ‰ [2]. Most continental rivers vary about this mean (between 0.2 ‰ and 0.5 ‰), although a broader range of values (0.1–0.9 ‰) is observed in rivers draining basaltic and carbonate terrains where fractionation processes relating to carbonate precipitation and dissolution are thought to occur [1].

The largest δ^{88}Sr offset in the modern hydrological cycle is observed in continental ice, with Langjökull glacier in west Iceland having a value of -0.24 ‰. The δ^{88}Sr composition of Parisian rainwater, 0.26 ‰, is also significantly lighter than seawater, and similar offsets have been previously reported in glacial meltwaters from Switzerland [3]. This evidence for the compositional differentiation of stable Sr isotopes between seawater and precipitation contrasts with results from other isotope systems (such as Li, Mg, Mo and Si), and implies that Sr-specific fractionation may be occurring during the evaporation-precipitation and/or freeze-thaw processes. This study explores the potential mechanisms responsible for this isotopic fractionation and the possibilities for using δ^{88}Sr as a monitor of the hydrological cycle.

[1] Pearce *et al.* (2010) *AGU*, *Fall Meet. Abstract.* **B21D-0342**. [2] Stevenson *et al.* (2010) *AGU*, *Fall Meet. Abstract.* **B21D-0343**. [3] de Souza *et al.* (2010) *GCA*, **74**, 2596–2614.