

Stable calcium isotope fractionation in basaltic catchments (Iceland)

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Calcium (Ca) isotope studies of river water have potential to reveal information about biogeochemical processes affecting calcium, one of the most abundant elements in the Earth's crust. In this study, river water samples were taken from twenty-five different rivers draining basaltic lithology in Iceland. Previous studies in this region have shown that 1) calcium containing secondary phases are prevalent in these catchments [1] and 2) there are clear differences in weathering regime between different parts of the island [e.g. 2]. The aim of this study was to investigate whether the aforementioned factors would impact on the calcium isotopic composition of river water, and thus help develop the use of Ca isotopes as a viable tracer of catchment scale biogeochemical processes.

Calcium isotopic compositions were measured by TIMS, after chemical purification, using a ⁴³Ca-⁴⁶Ca double-spike. The measured water samples span a range of 0.22‰ in $\delta^{44/42}\text{Ca}$ (0.45‰ – 0.67 ‰), with rivers draining glaciated catchments tending to have higher $\delta^{44/42}\text{Ca}$ values than rivers unaffected by present-day glaciation. An ice-melt sample, representing precipitation inputs, and a hydrothermal sample were also measured.

The Ca isotopic composition of river water samples draining unglaciated catchments was consistent with a mixture of the basaltic rock isotopic composition ($\delta^{44/42}\text{Ca} = 0.41\%$) and precipitation, which is characterised by a seawater Ca isotopic composition ($\delta^{44/42}\text{Ca} = 0.95\%$). Mixing between rock and precipitation sources for divalent cations was corroborated by radiogenic strontium measurements.

Calcium isotopic compositions from rivers draining glaciated catchments could not be explained by mixing of known sources and it is probable that isotope fractionation processes affect the Ca isotopic compositions of these rivers. The water samples from the presently glaciated samples fitted a simple Rayleigh distillation model, consistent with isotope fractionation during the removal of Ca from the dissolved phase by the formation of secondary minerals.

This study demonstrates that in Iceland 1) differences in riverine Ca isotopic values may simply reflect differences in precipitation volume and 2) glaciation significantly affects the weathering regime, resulting in different controls on Ca isotopic compositions, as compared to unglaciated terrain.

[1] Crovisier *et al.* (1992) *Appl. Geochem.*, **Suppl. Issue No. 1**, 55-81. [2] Georg *et al.* (2007) *Earth Planet. Sci. Lett.*, **261**, 476-490.

Interaction of Fe(II) with phosphate and sulfate on iron oxide surfaces: Implications for interfacial electron transfer

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Adsorption and coprecipitation reactions on iron oxide surfaces exert considerable controls on trace element and oxoanion concentrations in soil and aquatic environments [1]. Biogeochemical cycling of iron by microorganisms, involving the reductive dissolution and oxidative precipitation of iron oxides, activates interfacial electron transfer and atom exchange (ET-AE) reactions between aqueous Fe(II) and solid Fe(III) oxide minerals, causing mineral recrystallization [2,3]. This dynamic recrystallization of iron oxide minerals causes the incorporation of divalent metal adsorbates into the mineral and the release of preincorporated divalent metal ions to solution [4,5]. However, the effect of ET-AE reactions on the behavior of structurally incompatible oxoanions is not well understood. Recent research has shown that Fe(II) does not significantly affect arsenate adsorption mechanisms, yet Fe(II) adsorption is suppressed in the presence of arsenate through competitive adsorption processes [6]. This indicates that oxoanion adsorption can affect as well as be affected by ET-AE interactions between aqueous Fe(II) and Fe(III) oxides.

Here we consider the effect of aqueous Fe(II) on phosphate and sulfate adsorption onto hematite and goethite, and the effect of phosphate and sulfate on Fe(II) adsorption. We observe that the pH dependent adsorption of Fe(II) onto hematite and goethite slightly increases in the presence of phosphate and sulfate. The effect of phosphate and sulfate on Fe(II) adsorption, probed by metal release from doped iron oxides reacted with Fe(II) and oxoanions, will also be presented. We find that sulfate and phosphate adsorption also increases with the addition of Fe(II). If the observed adsorption behavior is the result of electrostatic effects, ET-AE reactions may be promoted. However, if the behavior is due to ternary complexation then ET-AE reactions may be suppressed because such complexes may stabilize adsorbed Fe(II) or inhibit electron transfer to the surface. The effect of Fe(II) on oxoanion adsorption mechanisms, determined by ATR-FTIR spectroscopy, will also be discussed. This work will further clarify the interactions between iron oxide minerals and common aqueous species in regions with active biogeochemical iron cycling.

[1] Brown & Parks (2001) *Int Geol Rev* **43**, 963-1073. [2] Handler *et al.* (2009) *Environ Sci Technol* **43**, 1102-1107. [3] Yanina & Rosso (2008) *Science* **320**, 218-222. [4] Frierdich & Catalano (2012) *Environ Sci Technol* doi: 10.1021/es203272z. [5] Frierdich, Luo & Catalano (2011) *Geology* **39**, 1083-1086. [6] Catalano, Luo & Otemuyiwa (2011) *Environ Sci Technol* **45**, 8826-8833.