

River denudational transport to the sea using the oceans $^{10}\text{Be}(\text{meteoric})/^{9}\text{Be}$ ratio

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The ratio of the meteoric cosmogenic nuclide ^{10}Be ($T_{1/2} = 1.39$ My) to the stable isotope ^9Be is a proxy of terrigenous input into the oceans. The system combines a tracer of roughly constant flux to the Earth surface (over time scales characteristic of weathering) with one that depends on its release rate from rock by weathering. Using a mass balance model we previously quantified how the $^{10}\text{Be}(\text{meteoric})/^{9}\text{Be}$ traces weathering and erosion from the soil to the river scale [1].

Here we take this tracer further by exploring this isotope ratio when river dissolved and sedimentary material is discharged into the ocean, where meteoric ^{10}Be is added by direct precipitation into the oceans. Using river Be data we first find that the fraction of mobile ^9Be (meaning unlocked from silicate minerals that is now either dissolved or adsorbed onto sedimentary particles) in rivers is globally 20%. We next find that a measured ocean dissolved $^{10}\text{Be}/^9\text{Be}$ ratio of about 1×10^{-7} [2] is satisfied by the mass balance if only 10% of the mobile river Be is eventually dissolved into the oceans by boundary exchange. This number is obtained using the sum of global solid and dissolved river fluxes [3], an average crustal ^9Be concentration of 2.5ppm, and an atmospheric ^{10}Be flux of 1×10^6 atoms g^{-1}cm^2 .

There is good agreement between modeled and measured ocean $^{10}\text{Be}/^9\text{Be}$ ratios when we perform this mass balance for each ocean basin. Only the southern Atlantic deviates from the predicted value, which can be explained by the dominant external deep and bottom water inputs that affect the measured ratio.

We show that the fraction of mobile ^9Be does not change significantly over a large range of global denudation rates. Therefore, the $^{10}\text{Be}/^9\text{Be}$ ratio can serve as a tracer that, unlike radiogenic and stable isotope ratios, truly quantifies past denudation rate and hence terrigenous input into the oceans at a temporal resolution exceeding the residence time of Be in the oceans (ca. 600 years).

[1] von Blanckenburg *et al.* (2012) *EPSL* **351-352**. [2] Kusakabe *et al.* (1990), *Geochemical Journal* **24** [3] Milliman and Farnsworth (2011) Cambridge University Press

Quantification and speciation study of the marine solid-phase iron pool

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Iron chemistry is tightly linked to marine primary productivity, particularly in High Nutrient Low Chlorophyll (HNLC) regions of the world's oceans, where Fe is commonly the limiting nutrient. Only about one third of the total iron present in the upper 200m of the open ocean water column is present in the smallest 'soluble' size fraction; the remainder is bound to colloidal ligands or incorporated into particles and biology greater than the $0.02\mu\text{m}$ -1000kDa size cut-off. From analyses of a global dataset, colloidal Fe (cFe) behaviour is found to vary between different ocean basins and there is evidence for a seasonal cycle in cFe concentration, associated with depletion during the summer growth season. Controls on distribution and concentration of this (quantitatively more important) larger Fe size class are linked to distance from shore, ambient ligand concentration, and colloid stability and inorganic solubility.

Despite the importance of size-fractionated Fe study, complementary chemical and mineralogical information is required to more fully understand the role of solid phase Fe in the marine system. We have developed a novel Fe L-edge x-ray technique that incorporates both high-resolution (12nm resolution) scanning transmission X-ray microscopy and *in-situ* L₃-edge XANES spectroscopy. Local chemical information derived from the XANES spectra reflect variations in Fe valence state, ligand type and coordination, and the degree of distortion within Fe polyhedra. For use in mineralogical identification of sub-micron sized particles, we present a 2D graphic plot based on variations in the spectral parameters of standard Fe-rich phases. Despite some limitations associated with particle thickness and spectral saturation, this plot has been successfully applied in speciation studies of particles collected from both marine and fluvial systems. A case study is presented highlighting significant chemical differences identified in marine particles (20-700nm in diameter) sampled from the euphotic zone of the different frontal zones of the Southern Ocean. The implications of these differences are discussed in terms of particle solubility and biological availability.