

Unconventional matrices prevent novel isotopes turning traditional

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Do 'non'-traditional isotopes still deserve their prefix? It only takes a look at your preferred stable isotope systems compilation to realise that variations are largest in the biosphere and its geologic derivatives. Hence, to move the field into the next decade, and beyond the Geosciences, we need to develop tools to cater for matrices that are by any geological standard non-traditional. Here we review progress on this effort from our laboratories' past years work.

Biomedical

Metal isotopes are superb tools to trace the process and timing humans metabolize nutrients. Each human bears a distinct stable Fe isotope signature in its blood, which is identical to that in muscle tissue and that of blood plasma, suggesting that this characteristic ratio is set when Fe is received by the transferrin molecule during intestinal absorption.

Plant Physiology and human nutrition

Higher plants induce substantial fractionation of Mg, Si, Ca, Fe, and Zn isotopes. Fe isotope fractionation has been shown to differ between grasses and non-grasses, where the former are enriched in light Fe through reduction in soils, and the latter take up unfractionated complexed Fe(III). Plants induce similar fractionation as metals are being moved through their tissue.

Crude oil

First results of various types of crude oil yielded surprisingly heavy Fe isotope compositions, tracing bacterial iron oxidation/reduction processes during oil biodegradation in the reservoirs.

Weathering at the micrometer scale

The large diversity of weathering and biotic products in soils requires detection of their isotope variability at the micro-scale. We have now developed a second-generation UV-femtosecond laser ablation system, and measure novel stable isotopes in bulk soil (as fused glass beads or powder pellets), at the mineral scale in thin sections, individual phytoliths, and by ablating fluids after element separation and evaporation.

The challenge to all these cases is to (1) develop tailor-made matrix-suited methods; (2) demonstrate that the analyses are free of artefacts, requiring reference materials; (3) understand the underlying processes - the ultimate aim.

The ¹⁰Be(meteoric)/⁹Be ratio as a tracer of weathering and erosion

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We provide a systematic framework to derive weathering and erosion rates from the ratio of the meteoric cosmogenic nuclide ¹⁰Be to stable ⁹Be, suggested to serve as proxy for weathering and erosion over the late Cenozoic [1].

In a weathering zone some of the ⁹Be, present in silicate minerals, is released and partitioned between a reactive phase (adsorbed to clay and hydroxide surfaces), given the high partition coefficients at intermediate pH, and to a minor degree into the dissolved phase in pore waters. The combined mass flux of both phases is defined by the soil formation rate times a mineral dissolution rate – and is hence proportional to the chemical weathering rate. The surface of the weathering zone is continuously exposed to fallout of meteoric ¹⁰Be. This ¹⁰Be percolates into the weathering zone where it mixes with dissolved ⁹Be. Both isotopes may exchange with the adsorbed Be, given that equilibration rates of Be are fast relative to soil residence times. Hence a ¹⁰Be/⁹Be (reactive) ratio results from which the ⁹Be weathering flux can be calculated given that the delivery rate of ¹⁰Be is now often known. If the loss of ¹⁰Be into the dissolved phase is furthermore small, the ratio of ¹⁰Be (reactive) to that of the residual mineral-bound ⁹Be provides a physical erosion rate.

We have tested this approach in sediment of the Amazon and Orinoco basin, and compared it to dissolved Be isotope data [2]. The reactive Be was extracted from sediment by combined hydroxylamine and HCl leaches. In the Amazon trunk stream, the Orinoco, Apure, and La Tigra river ¹⁰Be/⁹Be (dissolved) agrees well with ¹⁰Be/⁹Be (reactive), showing that in most rivers these two phases also equilibrate. ¹⁰Be/⁹Be ratios range from 5×10^{-9} for the Brazilian shield rivers to 2×10^{-10} for the Beni river draining the Andes, corresponding to denudation rates of 0.01mm/yr for the shields and 0.5mm/yr for the Andes, compatible with denudation rates from *in situ*-produced cosmogenic ¹⁰Be [3]. 10-50% of the ⁹Be was mobilised from bedrock.

Once delivered to the ocean, this riverine Be, be it dissolved or reactive, will eventually drive ¹⁰Be/⁹Be ratios of ocean water and disclose global weathering rates.

[1] Willenbring & von Blanckenburg (2010) *Nature* **465**.

[2] Brown, E. *et al.* (1992) *Geochim Cosmochim Acta* **56**.

[3] Wittmann *et al.* (2011) *Geol Soc. Am. Bull.* **123**.