Uranium "stable" isotope fractionation in nature: A potential paleo redox- and bio-tracer?

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We investigated variations of the $^{238}U/^{235}U$ isotope ratio in natural samples with MC-ICP-MS. A mixed ^{236}U-^{233}U isotopic tracer (double spike) was added prior to chemical separation of U from the sample matrix to correct for isotope fractionation during sample purification and instrumental mass bias [1, 2]. The uranium isotope ratios were measured relative to the international U standard U950a and are reported as $\delta^{238}U$.

The total range observed from the isotopically lightest to the heaviest sample was 1.3‰, exceeding by far the analytical precision of our method (≈ 0.06‰ for $\delta^{238}U$, 2SD). The lightest U isotope compositions were observed for two Banded Iron Formations (Lake Superior and Central India) which have $\delta^{238}U$ of -0.71‰ and -0.88‰, respectively. The heaviest $\delta^{238}U$ were observed for two Unit II sediments from the Black Sea (+0.25 and +0.44‰, respectively). The U isotope composition of seawater ($\delta^{238}U$ = -0.41‰) is only slightly fractionated relative to the major U source and sinks of U from the oceans (continental crust and suboxic margin sediments, $\delta^{238}U \approx$ -0.15‰ to -0.40‰).

However, we observed significant isotope fractionation during (1) incorporation of U into manganese crusts and (2) U removal into black shales. In the first case we hypothesize that adsorption leads to an enrichment of light U isotopes ($\delta^{238}U \approx$ -0.52‰ to -0.62‰), as is the case for Mo and Tl isotopes [3, 4]. In the second case reduction of soluble U^{VI} to insoluble U^{IV} might result in the observed heavy U isotope compositions of black shales compared to seawater. U burial in black shales also results in a correlation of U isotopes with U concentrations and TOC values. The latter might suggest that microbial reduction is involved in fractionating U-isotopes [2].

The range and direction of our observed U isotope variations agree with theoretical considerations [5] which predict U equilibrium isotope fractionation between the species U^{IV} and U^{VI}. Our results indicate that U isotopes may be a promising tracer for paleo-redox-conditions and microbial reduction.

References

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What the evolution of soil profiles tell us about weathering rates

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A soil chronosequence developed along coastal California exhibited, with increasing time (65 to 226 kyrs), progressively deeper and more intensively weathered depth profiles. Weathering reactions involve the relative rapid, non-stoichiometric release of Na, Ca and Sr from plagioclase and the slower release of K, Rb and Ba from K-feldspar

The spatial geometry of the weathering profiles, describing the relationship between plagioclase and K-feldspar concentrations and depth, evolves with time at Santa Cruz and is interpreted in terms of weathering mechanisms and rates. Profile linearity over the intermediate range in residual feldspar concentrations is approximated by the relationship

$$R = \left(\frac{1}{b_s}\right) \cdot \frac{\omega}{S_v}$$

where R, the weathering rate, b_s is he weathering gradient or slope, S_v the volumetric surface area and ω, the velocity at which the weathering front moves downward through the regolith. The non-linear regions of the mineral profiles, at low and high residual concentrations are described, using a spread sheet-base profile calculator, by relating R to exponential functions describing mineral surface/volume ratios and to the approach to thermodynamic saturation. A faster plagioclase weathering velocity, ω, compared to K-feldspar, reflects greater thermodynamic solubility (500x). Fluid fluxes, based on weathering profiles agree closely with independent estimates using Cl mass balances (q_h = 0.07 to 0.17 m yr^{-1}).

Under saturation-controlled and transported- limited weathering, the rate becomes defined as,

$$R = \left[\frac{q_s}{b_s}\right] \cdot \left[\frac{m_{sat}}{M_{total}}\right] \cdot S_v$$

an expression containing no explicit kinetic term but defined by measurable terms, i. e., the ratio of fluid flux to mineral gradients in the profile and the ratio of feldspar solubility m_{sat} to the protolith mass M_{total}. The above approaches yield plagioclase weathering rates at Santa Cruz of R = 0.5 to 1.4 x 10^{-15} moles m^{-2} s^{-1} that agree closely to those reported for other weathering environments of comparable climate and age.