

## Oxygen isotope modification through assimilatory sulfur cycling

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Isotope modification of oxygen isotopes in sulphate in natural environments is widely understood to be dominated by microbially mediated exchange with water during dissimilatory sulphate reduction, and possible abiotic exchange with water at high temperatures and pressures in hydrothermal systems. Here we show a separate mechanism that can also modify the oxygen isotope composition of sulphate ( $\delta^{18}\text{O}_{\text{SO}_4}$ ) in natural environments, through *assimilatory sulphur cycling*. We define this as the assimilation of sulphur into proteins and biomolecules during cellular growth and its return to the extracellular sulphur pool during cellular turnover. Oxygen isotopes in sulphate are replaced during this cycling and thus this process might be an important, and as yet unconstrained factor in understanding the variability of the  $\delta^{18}\text{O}_{\text{SO}_4}$  in natural environments. The cyanobacterium *Synechococcus* sp. PCC7002 and the diatom *Phaeodactylum tricoratum* were grown separately in pure culture and the sulphate in the media was monitored for changes in oxygen isotopes relative to a sterile control flask. The media used contained 3mM sulphate and water with  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  of 40‰. The  $\delta^{18}\text{O}_{\text{SO}_4}$  increased significantly over the period of cell growth (3 weeks). Replicate experiments in media with sulphate concentrations of 30mM (similar to marine environments) show smaller but analytically resolvable changes in the  $\delta^{18}\text{O}_{\text{SO}_4}$  over the period of cell growth. Our results suggest that the  $\delta^{18}\text{O}_{\text{SO}_4}$  of marine sulphate could be significantly modified by assimilatory sulphur cycling in regions of high biological productivity, and may be a novel proxy for constraining total carbon turnover in an ecosystem.

## Tungsten isotopic anomalies in Archean komatiites

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Late or heterogeneous accretion, early mantle differentiation, and/or core-mantle interaction are processes that could have created subtle  $^{182}\text{W}$  isotopic heterogeneities within Earth's mantle (where  $^{182}\text{Hf} \rightarrow ^{182}\text{W} + \beta$ ;  $t_{1/2} = 9$  Myr). To facilitate the search for such effects, we have developed a new ultra-high precision measurement protocol using a *Triton* thermal ionization mass spectrometer, allowing us to resolve  $^{182}\text{W}$  anomalies at a  $\pm 6$  ppm level. Here, we present ultra-high precision W isotopic compositions and W abundances of Archean komatiites from Komati, Weltevreden, Belingwe, Kostomuksha and Vetreny.

Within each komatiite sequence, W abundances are generally correlated with proxies for lava differentiation. In some samples, however, W clearly shows open system behaviour, indicated by large enrichments that are accompanied by enrichments in U and Re. This is likely due to post-eruption alteration and highlights the care that must be taken when examining W isotopes in altered rocks. Of greatest note, Kostomuksha samples exhibit  $^{182}\text{W}$  excesses relative to the modern upper mantle, ranging from +12 to +35 ppm. A plot of  $\epsilon^{182}\text{W}$  vs.  $1/\text{W}$  defines a binary mixing line that extrapolates to an ambient terrestrial composition ( $\mu^{182}\text{W} = 0$ ), as would be expected due to the variable open-system behaviour of W identified in some samples.

The positive  $^{182}\text{W}$  anomaly in the mantle source of the Kostomuksha komatiites is inconsistent with incorporation of a core component, as was initially suggested to explain the  $^{186}, ^{187}\text{Os}$  enrichments that are also present in the system. Our results, therefore, indicate that the Kostomuksha source included a primordial component characterized by high Hf/W, Re/Os and Pt/Os. The short half-life of  $^{182}\text{Hf}$  requires that this reservoir was created within the first  $\sim 50$  Ma of the Solar System. We speculate that this reservoir represents a product of metal-silicate partitioning at the base of a deep magma ocean and is consistent with reduced metal-silicate D values observed at high P/T for Pt and Re. This component would have contributed highly radiogenic  $^{182}\text{W}$ ,  $^{187}\text{Os}$  and  $^{186}\text{Os}$ , but its low elemental abundances would have been largely eliminated by mixing with mantle re-enriched in moderately and highly siderophile elements via late accretion. The generation of these komatiites at 2.8 Ga attests to the long-lived nature of the reservoir, and highlights the evident sluggish mixing of the mantle, even during the Hadean.