

The osmium isotope record of seawater: 20 years of research

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Secular variations in the $^{187}\text{Os}/^{188}\text{Os}$ of seawater were discovered twenty years ago [1]. Since then, significant progress has been made towards reconstructing $^{187}\text{Os}/^{188}\text{Os}$ variations throughout the Cenozoic, and select time intervals in the Mesozoic and Palaeozoic.

Osmium is an ultra-trace element in seawater with a residence time of less than 50,000 years, and possibly as short as a few thousand years. While initially thought to be well mixed throughout the oceans, high-precision data – including in the modern ocean – have indicated spatial variations of the order of a few percent. The residence time of osmium makes the isotope system not only ideally suited for tracing processes on time scales of glacial-interglacial variations, but also for investigating longer, tectonically driven changes on the Earth's surface.

Osmium is enriched in marine sediments that have been deposited under reducing, and - to a lesser extent – oxic, conditions. In such sediments, variations in its isotope composition - recorded as $^{187}\text{Os}/^{188}\text{Os}$ - have left a rich archive that reflects changes on the Earth's surface. The affiliation of osmium with sedimentary organic matter makes the marine $^{187}\text{Os}/^{188}\text{Os}$ record a sensitive indicator of cycling of old sedimentary organic matter. The lack of a buffering mechanism similar to the formation and weathering of marine carbonates in the $^{87}\text{Sr}/^{86}\text{Sr}$ record of seawater leads to variations that span most of the range in isotope variations between geochemical endmembers.

Here we focus on the most highly resolved events in the Cenozoic and Mesozoic that are reviewed in detail in the soon to be published chapter 8 in the *Geologic Time Scale 2012* [2]. These events fall into two categories: transient excursions to more radiogenic values that are thought to be caused primarily by hyperthermal events (e.g. PETM), and transient excursions to less radiogenic values that are caused by extraterrestrial impacts (e.g. KTB, late Eocene impacts), large volcanic eruptions (e.g., CAMP, Deccan, and Yemeni-Ethiopian flood basalts), or erosion of osmium-rich, unradiogenic lithologies at convergent plate margins (e.g. erosion of the Papuan ophiolite in the late Eocene).

Widespread anoxia may lead to rapid removal of osmium from the water column, thereby generating conditions for the predominance of local fluxes to seawater in an isotopically non-homogenous water column (e.g. Ocean Anoxic Events in the Mesozoic). In addition, the isolation and reconnection of ocean basins to the global circulation may leave an isotope fingerprint if inputs to such basins deviate from the globally averaged input of osmium to seawater (e.g. Arctic Ocean).

[1] Pegram et al. (1992) *EPSL* **113**, 569-576.

[2] Peucker-Ehrenbrink and Ravizza (2012) *Geologic Time Scale 2012, Chapter 8: Osmium isotope stratigraphy* (Gradstein et al., Eds.), doi: 10.1016/B978-0-444-59425-9.00008-1.

Does the naturally elevated sulfur content of *Ulva lactuca* play a role in the uptake and speciation of arsenic?

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Algae are ubiquitous in surface waters and are known to influence the chemodynamics of the priority toxic metalloid, arsenic (As), in polluted marine environments. Marine algae initially transform As(V) to As(III), after which As(III) is methylated and then converted to a diverse set of organoarsenic compounds by mechanisms that remain unclear.[1] Recently it has become evident that the common marine green alga *Ulva lactuca* contains elevated levels of sulfur (S) and has the capacity to generate toxic concentrations of H₂S in the presence of excess nitrates. In light of the fact that As is chalcophilic, it is important to understand the interaction between As, S, and nitrates in *Ulva lactuca* because the algae may serve as an As reservoir and pose an emerging threat to coastal environments where nitrate inputs are increasing.

In the present study, using synchrotron-based X-ray absorption spectroscopy and X-ray microfluorescence mapping, we investigated the bioavailability and chemical speciation of As in *Ulva lactuca* sampled from contaminated coastal waters in order to understand As cycling in the marine environment. We also conducted batch culture experiments with *Ulva lactuca* to explore the role of thiolation in As biotransformation and toxicity.

Using X-ray microfluorescence mapping, we observed trends in the distribution of S along the thallus of *Ulva lactuca*. We are investigating whether the As distribution and concentration may be correlated with areas of elevated S content along the thallus. Using synchrotron-based X-ray absorption spectroscopy, we characterized the complexation of As with S moieties in environmental samples collected from industrially-polluted sites.

Our research aims to determine the potential risks As may pose to both aquatic ecosystem and human health as it is transformed into various chemical forms and moves from algae up trophic levels, potentially to fish and humans.

[1] Edmonds, JS and Francesconi, KA (1977) *Nature* **265**, 436.