**[238]U/[235]U IN MARINE CARBONATES AS A TRACER OF PRECAMBRIAN PALEOREDOX CONDITIONS.**

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**Introduction:**

The timing and magnitude of the oxygenation of Earth's ocean is still a matter of intense debate. Previous work suggested that the uranium isotope variations recorded in ancient marine sediments, such as shales and carbonates, could provide valuable insights into paleoredox conditions [*e.g.*, 1-11]. In this work, we study U concentration and isotopic composition of a large number of Precambrian carbonates to place constraints on long-term variations in oceanic redox conditions.

**Background:**

Uranium is a redox-sensitive element that occurs in two main oxidation states in natural waters: $U^{4+}$ and $U^{6+}$. In the oxic modern ocean, highly soluble $U^{6+}$ exists as a uranyl carbonate complexes [12-14]. In anoxic settings $U^{6+}$ is reduced to $U^{4+}$, which has low solubility. Precipitation of U under anoxic/euxinic conditions preferentially enriches the sediments in $^{238}U$ (relative to $^{235}U$), resulting in lower $\delta^{238}U$ values in the residual aqueous $U^{6+}$ form [3,4]. An increase in the extent of oceanic anoxia will thus shift seawater composition towards lower U concentrations and lighter U isotope composition. Furthermore, since the residence time of U in the modern ocean ($\tau$~400 kyr) is much longer than the global ocean mixing time (~1-2 kyr), U in seawater is well-mixed and homogeneous vertically and laterally, both in concentration and isotopic composition [5]. It is thus expected that the U isotopic composition of seawater records the global redox conditions.

Quantitative paleoredox reconstructions rely on the capacity of a given paleoredox proxy to capture the global oceanic conditions. This assumption was proven to be valid in the modern ocean for U isotopes [5] and the seawater $\delta^{238}U$ value reflects the mass balance between riverine inputs and U removal into several sinks with different fractionation factors. The anoxic/euxinic reservoir has the largest fractionation factor compared to other sinks by a factor of three, and consequently the $\delta^{238}U$ of seawater is largely influenced by the size of the anoxic/euxinic sink: *i.e.*, extent of global oceanic anoxia. As such, estimate of the $\delta^{238}U$ value of seawater through time will provide constraints on the redox state of the global ocean.

Though black shales were used early on, to track the $\delta^{238}U$ value of past seawater, marine carbonate is likely to be a more reliable proxy since the fractionation factor associated with the carbonate sink is small [7,15], and varies much less than the one associated with the anoxic/euxinic sink. The wide spatial and temporal distribution of carbonates should make it possible to build a continuous and global record of the redox evolution of Earth's surface envirionments.

**Methods:**

In order to reconstruct the long-term redox evolution of the ocean, a large suite of marine carbonates (n>200) are currently being processed for U isotopic analysis (*i.e.*, step-leaching, column chemistry, and high-precision measurement on MC-ICPMS) [see details in 5]. The samples were carefully selected so as to satisfy three crucial criteria: (1) the samples must be marine sediments deposited in the open ocean in order for the U isotopes to record the global seawater signature, (2) the samples must have experienced limited secondary alteration in order to minimize elemental and/or isotopic resetting of the U systematics, (3) the entire sample set must span most of Earth's history, with a high time resolution. We identified the least altered and best-preserved samples based on a combination of petrography and an array of geochemical tracers that reveal the extent of post-depositional resetting of geochemical signatures (Mg/Ca, Sr/Mn, $\delta^{18}O$ and $\delta^{13}C$ values) [16,17].

A simple step-leaching approach was developed and we added the amount of 1N HCL to digest only 1% of the samples in order to remove the easily mobilized U, which is more likely to have secondary origin. This can help us access the original $\delta^{238}U$ signal recorded by the carbonates and minimize artifacts from secondary processes. The remaining bulk carbonates were digested using 1N HCL and insoluble residues were removed via centrifugation.

**Results:**

Using the two-step leaching protocol, we measured the U concentration and isotope composition of 68 carbonate samples ranging in age from 0.68 Ga to 2.85

Ga. The data obtained so far is presented together with a compilation of literature data in Figure 1.

U concentrations are unvariably low throughout the Archean and most of the Proterozoic. The sample with high [U] at 1.5 Ga is likely an outlier. An increase in [U] seems to start as early as 0.81 Ga, consistent with the rise of atmospheric oxygen level during the Neoproterozoic Oxygenation Event (NOE) as inferred from other paleoredox proxies [18]. No clear secular trend is visible in the $\delta^{238}U$ values of marine carbonates. While several sample sets record the extensive anoxic conditions with coherently low $\delta^{238}U$ values at ~2.42 Ga as well as at ~1.05 Ga, U isotopic composition is quite variable and, taken at face value, the $\delta^{238}U$ values of many Archean samples would suggest that the Archean oceans were not more extensively anoxic than the Phanerozoic oceans. This is clearly in disagreement with studies focused on other proxies or the U concentrations reported here and in previous studies for Precambrian carbonates and shales. One possible explanation is that in the Archean, U residence time in the oceans was much shorter than what it is today and the U isotopic composition of carbonates was stronger influenced by proximal sources and quantitative uptake in extensively anoxic oceans. In contrast, larger range of U isotope fractionations along with larger [U] recorded by carbonates deposited starting with the NOE might reflect longer seawater U residence time and non-quantitative uptake once extensively developed oxic environments emerged. Our results provide an important baseline for seawater U isotopic composition throughout Earth's history. Further work should be focussed to fill in the remaining gaps in our secular U isotope record of carbonates.

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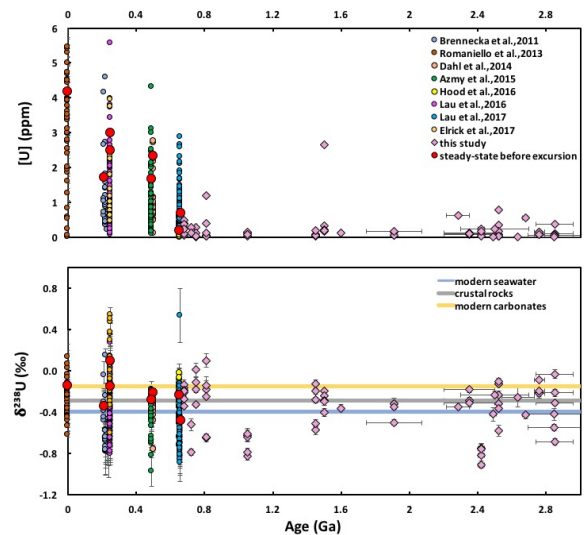


***Figure 1****: U concentration and isotopic composition as a function of age of the carbonates.*