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Uranium isotope fractionation in the Paleoproterozoic ocean: A multi-core study of the Rove and Virginia Formations, Superior Province, North America

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The uranium isotope system is commonly used for reconstructing Phanerozoic and Proterozoic global ocean redox conditions. In non-euxinic settings, sedimentary $\delta^{238}U$ (Equation 1) is closer to coeval seawater ($\delta^{238}U_{sw}$) whereas reduction and burial of isotopically heavy U in euxinic settings produces black shales with significantly higher $\delta^{238}U$ than $\delta^{238}U_{sw}$. Areas where U reduction occurs are limited in the modern ocean, thus, modern $\delta^{238}U_{sw}$ (–0.4‰) is not significantly lower than continental input (–0.3‰). In widely anoxic oceans, global $\delta^{238}U_{sw}$ should be lower. Recently, Proterozoic application of this proxy has been questioned because other geochemical data suggest largely anoxic deep oceans, but $\delta^{238}U$ in some Proterozoic carbonates approach continental inputs, suggesting different and/or muted U isotope fractionation mechanism(s) compared to the present.

To better understand U isotope behavior in the Paleoproterozoic oceans, we present U isotope data from black shales of the ~1.83 Ga Rove/Virginia formations from four locations in the Animikie Basin. The shales have a wide range of $\delta^{238}U$ (–0.45‰ to +0.43‰). Generally, $\delta^{238}U$ correlates positively with local redox indicators (e.g., Fe speciation, U, V, Mo, Re, organic carbon). Euxinic samples record the highest $\delta^{238}U$ (0.08 ± 0.14‰), whereas ferruginous (–0.06 ± 0.10‰) and non-anoxic samples have lower $\delta^{238}U$ (–0.24 ± 0.15‰) (Figure 1), consistent with modern U isotope systematics. We estimate that $\delta^{238}U_{sw}$ was between –0.8‰ and –0.4‰ using the above average $\delta^{238}U$ values and sediment–seawater offsets of 0.6–0.8‰ and <0.4‰ in locally euxinic and ferruginous environments, respectively, as observed in modern settings. In one core interval, higher $\delta^{238}U$ (0.28 ± 0.14‰) may have been produced by dynamic redox conditions, a phenomenon also observed in Recent organic-rich sediments. A seawater–sediment isotope offset in these environments closer to the theoretical maximum of 1.2‰ gives a $\delta^{238}U_{sw}$ estimate from the dynamic Rove interval that aligns with the low end of the aforementioned range of $\delta^{238}U_{sw}$. We conclude that at least some U isotope fractionation mechanisms observed today occurred in the Paleoproterozoic oceans and that global ocean redox models using U isotopes should consider large fractionations in dynamic redox environments.

Equation 1

$$\delta^{238}U\ (‰) = \left(\frac{^{238}U/^{235}U_{sample}}{^{238}U/^{235}U_{CRM145}} - 1 \right) \times 1000$$

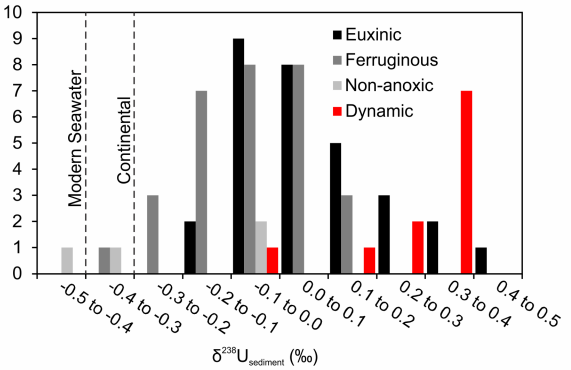

Figure 1. Distribution of uranium isotope compositions in sediments ($\delta^{238}U_{sediment}$) of the Rove and Virginia formations deposited under various redox conditions (defined by Fe speciation). A 'dynamic' interval spanning 30 cm in one core contains samples of non-anoxic, ferruginous, and euxinic deposition, and typically records higher $\delta^{238}U_{sediment}$ than other intervals.