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Ocean redox conditions in a less-oxygenated Ordovician world: Perspectives from uranium isotope compositions of the Katian organic-rich mudrocks in southern Ontario, Canada

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Understanding ocean redox conditions before the Late Ordovician mass extinction (LOME) event is important to test the hypothesis of expanded anoxia as a driver for extinction. Katian organic-rich mudrocks (ORM) of the Collingwood Member (CW) and overlying Rouge River Member (RR) were deposited in the Appalachian Basin and Michigan Basin (MB). Here, we present redox-sensitive trace metals (RSTM) and uranium isotope compositions ($\delta^{238}U$, relative to CRM145) to constrain local and global ocean redox conditions.

Both the CW and RR contain ORMs with pronounced enrichments of Mo relative to U, suggesting operation of an Fe-Mn particulate shuttle. Most CW samples from basinal environment were primarily deposited from anoxic bottom waters (Mo/U enrichment factor ratios greater than the modern seawater Mo/U ratio [Mo/U_{SW}]), with the most U- and Mo-enriched samples possibly representing euxinic conditions. By contrast, the CW near the Algonquin Arch (AA) was deposited from O_2-bearing bottom waters (0.1-1 of Mo/U_{SW}). Predominantly oxic-suboxic with sporadic anoxic conditions are inferred for the RR.

Uranium isotope data was obtained for samples with appreciable authigenic U enrichments. The CW exhibits modest variation in $\delta^{238}U_{auth}$ (−0.64‰ to −0.23‰; average = −0.44‰) whereas the RR has a narrow range of $\delta^{238}U_{auth}$ (−0.37‰ to −0.11‰; average = −0.25‰). The CW from the anoxic MB localities has a higher average $\delta^{238}U_{auth}$ (−0.40‰) compared to suboxic settings near the AA (−0.59‰), whereas the RR exhibits little spatial variations in $\delta^{238}U_{auth}$. Strong positive correlations between $\delta^{238}U_{auth}$ and RSTM enrichments are observed for the CW, indicating that redox gradients, rather than the particulate Fe-Mn shuttle, controlled the magnitude of local U isotope offsets between the water column and sediments. Therefore, the lowest $\delta^{238}U_{auth}$ (−0.64‰) is regarded as the highest possible $\delta^{238}U$ of coeval seawater. A minimum of 2% global euxinic seafloor area is estimated from a U isotope mass balance model. No correlations between $\delta^{238}U_{auth}$ and RSTM enrichments are observed for RR and hence coeval seawater $\delta^{238}U$ is difficult to deduce. Although the estimated global extent of ocean euxinia during CW deposition is similar to the second pulse of LOME, the Katian ocean anoxia/euxinia did not trigger a LOME-type of extinction.