A Devonian example of why an integrated geochemical approach is needed to infer global ocean redox

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The Mo and U isotope ratios of black shales are used to infer the isotopic composition of ancient seawater and thus constrain global ocean redox conditions. However, an incomplete understanding of local depositional processes may result in misinterpretation of global redox using a single isotope system. We report a strong inverse correlation (R^2 = 0.7) between U isotopes ($\delta^{238}U$ = –0.3‰ to +0.5‰ relative to CRM145 = 0‰) and Mo isotopes ($\delta^{98}Mo$ = +0.5‰ to +2.0‰ relative to NIST SRM 3134 = 0.25‰) in Mo-, U-, and V-rich black shales of the Devonian Kettle Point Formation (Ontario, Canada). A stratigraphic trend towards lower $\delta^{98}Mo$ and higher $\delta^{238}U$ upsection implies conflicting interpretations of globally expanded ocean anoxia/euxinia ($\delta^{98}Mo$) and oxia ($\delta^{238}U$). However, recent studies on modern anoxic basins suggest the inverse isotope correlation can be explained by local depositional controls without invoking significant global redox variation. The highest $\delta^{98}Mo$ and lowest $\delta^{238}U$ likely reflect more efficient Mo and U removal from more sulfidic bottom waters and sediment pore-waters, and thus come closest to capturing global seawater values. Less efficient Mo and U removal associated with less sulfidic conditions (possibly associated with higher sea-level) would cause greater seawater-sediment isotope fractionation, resulting in lower $\delta^{98}Mo$ and higher $\delta^{238}U$. In addition, the highest Mo (and V) enrichments occur in samples with low $\delta^{98}Mo$ (0.5-1.0‰), suggesting these samples record delivery of Mo- and V-bearing Fe-Mn oxides to anoxic sediments. Compilation of new and existing coupled Mo-U isotope data for black shales reveals no overall correlation between the two isotope systems. An integrated elemental and multi-isotope approach (e.g., Mo, U, Tl) is recommended to better constrain local depositional effects on black shale isotope systematics on a case-by-case basis, which will help facilitate more robust interpretations of global ocean redox conditions.