The uranium-isotope proxy of oxygenation changes in the ancient oceans: Global versus local controls on $^{238}U/^{235}U$ in black shales

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Trace metals play many important roles in the biogeochemistry of the oceans and, via connections with the carbon and sulfur cycles, are intrinsically linked to global climate. The oceanic distribution of uranium (U) and its two primordial isotopes (^{238}U and ^{235}U) is significantly influenced by the concentration of dissolved oxygen. The U-isotope system has therefore emerged as a powerful tracer of global-scale oxygenation changes in the ancient oceans based on $^{238}U/^{235}U$ variations in black shale and carbonate sediments.

To date, reconstructions of oxygen-depleted palaeoenvironments assume that (*i*) U-isotope variations are exclusively controlled by U oxidation–reduction, and (*ii*) the U-isotope fractionation factor between U(IV)-bearing black shale and contemporaneous U(VI)-bearing seawater is spatially and temporally invariant, as fixed by the U-isotope systematics of a limited number of anoxic to euxinic basins in the modern ocean. However, the veracity of both assumptions remains uncertain, with profound implications for constraints on the size of the anoxic sink of U in the ancient oceans.

Here, we interrogate the U-isotopic systematics of a suite of ancient and modern black shales to expand the utility of the U-isotope system as a tracer of past ocean redox changes. As an example, a well-studied section of organic-rich black shale (Bonarelli Level) from Furlo, Marche–Umbria, Italy, deposited during 'Ocean Anoxic Event 2' (OAE 2; occurring ~94 million years ago), displays a fundamental change in the U-isotope systematics at the onset of the event, likely revealing a shift from local to global controls on the U-isotope system, in parallel with major regime shifts in the ocean–atmosphere system. Taken together, these new records provide additional insights into the exact mechanisms controlling the biogeochemical cycling of U in sedimentary systems and imply that the U-isotope systematics of ancient black shales must be scrutinized in detail in order to extract reliable constraints on oxygenation changes in the ancient oceans throughout Earth's history.