

Fingerprinting subtle redox fluctuations using vanadium isotopes

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Ocean deoxygenation can severely impact the chemical cycling (e.g. carbon and nutrient elements) and biological evolution of the ocean-atmosphere system. The chemical/biological response to marine deoxygenation may occur at different parts on the marine redox ladder, thus, it is pivotal to refine redox proxies for local and/or global conditions to better constrain ocean deoxygenation on Earth's surficial evolution. Vanadium (V) isotope values have the potential to distinguish different local redox conditions — euxinic condition, anoxic-suboxic condition (suppression of bioturbation; typically oxidized compounds, e.g. nitrate and Mn/Fe oxides, are reduced) and dysoxic-oxic conditions (biological activities impacted by oxygen depletion). Importantly, V isotopes may be able to constrain the chemically ambiguous anoxic-dysoxic fluctuation. However, more detailed modern sedimentary research is required to be better constrain the potential early diagenetic processes.

We present downcore authigenic sedimentary V isotope ($^{51/50}\text{V}_{\text{auth}}$) profiles at six sites with varying oxygen contents ($[\text{O}_2]$) and organic carbon fluxes along the California-Mexico oxygen minimum zone. This work systematically explores impacts from local redox condition, organics flux and early diagenesis over $^{51/50}\text{V}_{\text{auth}}$ records. Along with the varying bottom water $[\text{O}_2]$, the downcore pore fluid trace metal profiles at individual sites document a range of values indicating different biogeochemical processes likely related to $[\text{O}_2]$. The pore fluids at the oxic-to-dysoxic sites (bottom water $[\text{O}_2] > 20\mu\text{M}$), show the dissolution of Mn oxides and/or Fe oxides occurring at deeper depth in the sediments with limited oxygen penetration. While under suboxic (bottom water $[\text{O}_2]$: $0\sim 20\mu\text{M}$) and more reducing conditions, there is no accumulation of Mn oxides in sediments and pore fluids document the dissolution of Fe oxides thus in the ferruginous zone. In contrast to the varying redox structures in pore fluids, there are relatively homogeneous downcore $^{51/50}\text{V}_{\text{auth}}$ profiles with limited variations ($< 0.11\%$, our long-term lab precision). The stable V isotope profiles suggest limited alteration of the $^{51/50}\text{V}_{\text{auth}}$ signatures from early diagenesis under both oxic and oxygen-deficient conditions and likely fingerprint the initial depositional conditions. The good correlation of $^{51/50}\text{V}_{\text{auth}}$ values with the bottom water redox conditions rather than other depositional factors also proposes V isotopes robustly record local redox fluctuations.