

Zirconium isotopic fractionation in the ocean and its application as tracer of seawater composition

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Reconstructing past seawater compositions becomes more challenging with increasing time. Trace elements and their isotopes can inform us about changes in ocean circulation and biogeochemical cycling[1]. Stable isotopes of zirconium (Zr) may be a useful proxy for tracing water mass movement and biological productivity without a significant influence from fluctuations in physical or chemical weathering rates or sediments

source provenance[2, 3]. We present the stable Zr isotope compositions of 13 detrital sediment samples from the nearshore Pacific Ocean, and 21 oceanic sediments, including abyssal clays, carbonates, and Fe-Mn nodules from the Pacific, Atlantic and Indian Oceans. Detrital sediments display a narrow range in $\delta^{94/90}\text{Zr}_{\text{Zr NIST}}$ from -0.001 to +0.035‰, indicating the uniform Zr isotopic composition of terrigenous source material. On the contrary, the authigenic oceanic sediments display marked variations in $\delta^{94/90}\text{Zr}_{\text{Zr NIST}}$ ranging from $\delta^{94/90}\text{Zr}_{\text{Zr NIST}} = -0.432$ to + 0.535‰. The Fe-Mn crusts have the highest Zr isotopic compositions of all oceanic sediments. The sediments from the Pacific Ocean have the highest Zr isotopic composition of oceanic sediments measured here, which may indicate the accumulation and enrichment of heavy Zr isotopes over time in seawater with increasing age. The Zr isotopic compositions observed in the oceanic sediments could possibly be inherited from the seawater composition and these fractionations may occur during scavenging onto sinking particulates. If these isotope effects are driven by scavenging of dissolved Zr onto sinking particulates, stable Zr isotopes may be useful in tracking variations in productivity and/or large-scale shifts in seawater composition.

[1] Frank (2002), *Reviews of geophysics* 40(1),1-1-1-38.

[2] Huang et al. (2024), *Geochimica et Cosmochimica Acta* 365, 202-214.

[3] Tian et al. (2021), *Earth and Planetary Science Letters* 572, 117086.