Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.15448

High-precision zirconium isotope analysis of Pacific seawater reveals large mass-dependent fractionations in the ocean

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Zirconium (Zr) stable isotope variations recently emerged as potential tracers of magmatic processes and, as a result, their behavior in high-temperature environments have been the focus of extensive characterization [1, 2]. In contrast, few studies have focused on Zr behavior and isotopic fractionation in low temperature or aqueous environments [3, 4]. Here, we describe a new analytical routine for highly precise and accurate determination of stable Zr isotope compositions of water samples, using a combination of double-spike and iron co-precipitation methods [5]. A series of experiments, designed to determine the influence of key parameters on the measured seawater Zr isotopic composition, were conducted on natural and synthetic water samples. Our results show that the spike-to-sample ratio, matrix composition, and HFSE concentration have negligible effects on measured seawater Zr isotopic compositions and that our Fe co-precipitationmethod yields accurate and precise Zr isotope data. We apply this method to seawater samples collected from a water column profile in the Pacific Ocean off the coast of California, with depths ranging from 5 to 711 m. We find that the natural seawater displays marked variations in $\delta^{94/90}Zr_{\ Zr\ NIST}$ values with depth, ranging from ~ +0.650 ‰ near the surface, to +1.530 ‰ near the profile bottom, with an analytical uncertainty of ± ~0.045 ‰ (2 SE). The $\delta^{94/90}Zr$ of seawater is therefore much higher than the $\delta^{94/90}Zr$ of the Earth's mantle and average continental crust. Furthermore, the seawater $\delta^{94/90}Zr$ value exhibits systematic variations with respect to water depth and salinity, suggesting that Zr isotopic compositions may be sensitive to seawater chemical properties and source.

[1]Ibañez-Mejia & Tissot (2021) Elements **17**, 379-382. [2] Aarons et al. (2021) Elements **17**, 413-418. [3] Klaver et al. (2021) GCA **310**, 221-239. [4] Tian et al. (2021) EPSL **572**, 117086. [5] Arendt et al. (2015) GGR **9**, 293-303.