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REE distribution in the water column of the Eastern Pacific Oxygen Minimum Zone

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The concentration of Rare Earth Elements (REEs) in seawater varies with distance from margins, water depth, water mass ventilation age, and particle cycling. Cerium (Ce) is unique among REEs as it can exist as Ce(IV) in oxygenated environments, thus rendering Ce concentrations oxygen-dependent. Moreover, the observed variability in seawater Ce may partially reflect losses to redox cycling during sampling and sample processing. While speculative, REE intercalibration efforts produce deviations of up to 44% for Ce, as compared to 15% or less for all other REEs [1].

We collected seawater at eleven different depths from a station in the Eastern Equatorial Pacific, away from the coast to minimize riverine inputs. Samples were taken from above, within and below the oxygen minimum zone (OMZ) in order to capture the Ce gradient. The samples were acidified and spiked with enriched Ce, Nd and Yb following shipboard collection and filtration. There being no Ce isotope fractionation during redox cycling or scavenging between collection and analysis, the Ce concentrations as determined by isotope dilution will remain the same.

The REE from the samples were collected using Toyopearl resin after adjusting their pH to approximately 6.0, and then eluted in 1N HNO_3. In addition to the Pacific samples, this method was used on splits of two different seawater standards with distinct REE concentrations. This method reproduced the differences between the standards attesting to the reliability of the data acquired based on interlaboratory calibration.

The REE concentrations were performed by ICP-MS and isotope dilution calculations were made offline. When normalized to post-Archean Australian Shale (PAAS), the seawater samples portray an enrichment in the heavy REE (HREE) that is positively correlated with increasing depth (Fig. 1). Additionally, there is a negative Ce/Ce* that correlates negatively with the expected changes in oxygen concentrations (Fig.2), considering the OMZ exists between 200 and 1000m in this region. This is in full agreement with what has been observed in another OMZ [2] and specifically in Pacific waters.

[1] van de Flierdt et al. (2012) L&O: Methods, 10(4), 234-251.
[2] Haley et al. (2021) EPSL, 576, 117233.

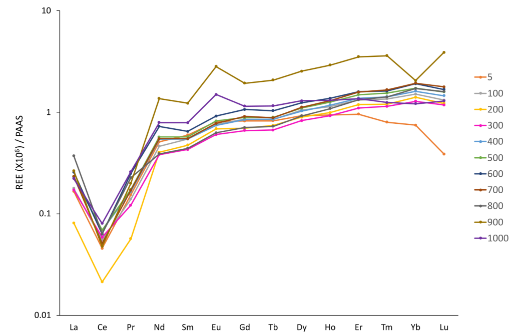

Figure 1: REE patterns of the water at the station with respective depths indicated.

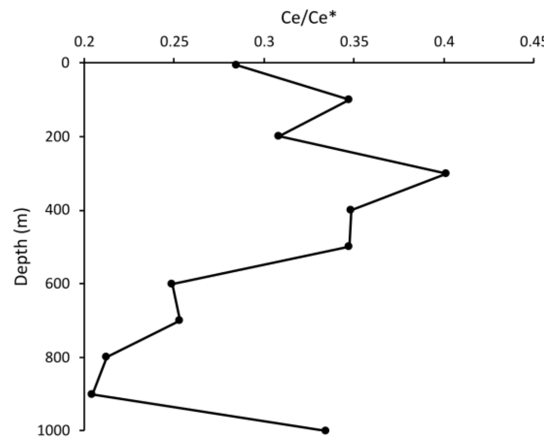

Figure 2: Ce anomaly variation with respect to depth.