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Pliocene weathering at the Peruvian Margin tracked by iron speciation: new insights provided by a consolidated technique

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Iron speciation analysis has been widely applied to rocks and sediments to determine the redox conditions of the depositional environment. This technique consists of extracting Fe from different iron mineral phases. After the extractions, the total Fe (Fe_T) is divided into two pools: The highly reactive (Fe_{HR}) and the poorly reactive (Fe_{PR}) pool. Based on modern environments, Fe_{HR}/Fe_T ratios <0.22 have been ascribed to sediments deposited under oxic conditions whereas ratios >0.38 have been interpreted as accumulation of Fe under ferruginous (anoxic and Fe-rich) or euxinic (anoxic and sulfidic) conditions. The amount of Fe incorporated into sulfide (Fe_{py}) is used to distinguish between the last two scenarios as Fe_{py}/Fe_{HR} ratios > 0.80 are understood to represent euxinia. Another commonly used tool to determine redox conditions in the water column is enrichment in trace metals, particularly U and Mo. In short, sediments are enriched in U in anoxic environments and in Mo in euxinic environments.

Seeking to better understand the relationship between these proxies, we performed Fe speciation and trace metal analysis of ODP Site 680A (expedition 112) comprising. Pliocene to Pleistocene sequences from the Peruvian oxygen minimum zone (OMZ). Our results demonstrate that during the Pleistocene the OMZ operated similarly to today (*i.e.*, it was anoxic). However, for the Pliocene, the samples show consistently high Fe_{HR}/Fe_T values and low contents of Mo, U, and pyrite, which does not reflect anoxic conditions. At that time, this depositional site was shallower and sedimentation rates were higher than during the Pleistocene. The OMZ likely shifted into the basin and the studied site remained oxygenated. We attribute the enrichment of Fe_{HR} to stronger chemical weathering coupled with high sediment delivery during the Pliocene warm period leading to enhanced transport of iron(oxyhydr)oxides to the Peruvian Margin. This hypothesis is corroborated by a shift in the RW[1] weathering index during the Pliocene.

[1] Cho, T., & Ohta, T. (2022). A robust chemical weathering index for sediments containing authigenic and biogenic materials. Palaeogeography, Palaeoclimatology, Palaeoecology 608, 111288.