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Marine paleoproductivity linked to ocean circulation and phosphorus cycling in the North Pacific: Insights from Ba concentrations and Ba isotopes in Fe-Mn crusts

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Reconstructing marine biological productivity and its connection to ocean circulation and climate change throughout geologic history is crucial for understanding Earth's climate system. Concentrations and isotopic signatures of barium (Ba) are sensitive to changes in ocean circulation and biogeochemical cycles[1]. It is highly enriched in Fe-Mn crusts, whose chemical compositions and mineralogy vary during periods of high productivity. As such, Ba in Fe-Mn crusts could provide information on productivity and seawater chemistry in the past.

Here, we present Ba isotopic compositions from surface scrapping samples of modern Fe-Mn crusts and ambient seawater from the North Pacific Ocean, and time-series concentrations of bioactive elements and Ba/Mn ratios from a Fe-Mn crust sample (CXD31). Our preliminary results show that the mean $\delta^{138/134}$Ba value for surface crusts in the North Pacific is 0.04 ± 0.08‰ (2SE, n=11), similar to values of biogenic barite. Barium concentrations in the surface layers and the profile of Fe-Mn crust show a positive relationship with productivity. Both pieces of evidence suggest that particulate Ba likely plays a dominant role in the Ba incorporation process, and that Ba content in Fe-Mn crusts could serve as a proxy for biological productivity. Concentrations of Ba, Cu, Ni and Zn and ratios of Ba/Mn of CXD31 show a steady declining trend from Miocene to present. During the same period, CXD31 transverses areas of high productivity to low productivity as it moves northwestward. The Ba/Mn ratios and P concentrations peak during high-productivity intervals (~22.5 Ma and ~2.7 Ma). The coincidence of these variations implies that surface productivity has an important impact on trace metal and Ba concentrations within Fe-Mn crusts. We propose that enhanced productivity and P accumulation were driven partly by the cessation of North Pacific Deep Water and the intensification of oxygen-rich Antarctic Bottom Water. Additionally, strengthened Antarctic Intermediate Water and increased aeolian dust input likely further enhanced productivity during high-productivity periods. Our study illustrates a strong coupling of marine paleoproductivity, the biogeochemical cycles of Ba and P, and water mass circulation.

[1] Hsieh & Henderson (2017), *EPSL*, 473:269-278.