

Barium isotopic evidence for reduced marine productivity during Eocene hyperthermals

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Marine biological production plays a significant role in carbon sequestration from atmosphere and surface- to deep-ocean. With ongoing global warming, understanding marine productivity during past transient warming events, as paleo-analogues of future climate changes, has gained considerable attention. The early Eocene, which records several short-term warming events known as hyperthermals (50-200 kyrs), offers this crucial opportunity. However, a detailed understanding of the responses of marine productivity to these events has not yet been achieved, largely due to inconsistencies among various paleoproductivity proxies (e.g., barite accumulation rate, planktonic foraminifera test size, and foraminiferal accumulation rate)[1,2].

We adopted here the non-conventional, recently developed proxy - the seawater barium stable isotope ratio ($\delta^{138}\text{Ba}$)[3,4]. The $\delta^{138}\text{Ba}$ of seawater is based on isotopic fractionation between seawater and barite (BaSO_4), which precipitates during organic matter decomposition. During barite precipitation, isotopically light Ba is preferentially incorporated into barite particulates from ambient seawater, with a constant fractionation factor[3]. Therefore, the rise in barite $\delta^{138}\text{Ba}$ indicates an increase in seawater $\delta^{138}\text{Ba}$, resulting from a high barite precipitation rate (i.e., high productivity) and vice versa[3]. The $\delta^{138}\text{Ba}$ of bulk sediments without a significant contribution of detrital materials is likely controlled by that of barite in the sediments[3], which is expected to reflect variations in seawater $\delta^{138}\text{Ba}$. Reconstructing the paleoseawater $\delta^{138}\text{Ba}$ record can indeed allow to unravel the main changes in marine productivity in Earth's history.

We selected sediments from the Ocean Drilling Program (ODP) Holes 762C and 738C[4] in the Indian Ocean that provide reliable stratigraphic constraints of early Eocene hyperthermals. Analyses were performed through thermal ionization mass spectrometry (TIMS)[4,5]. Our results show systematic decreases in $\delta^{138}\text{Ba}$ during multiple hyperthermals, including the Paleocene-Eocene Thermal Maximum (PETM). By integrating $\delta^{138}\text{Ba}$ record, ocean Ba isotopic mass-balance simulations and

other paleoproductivity evidence from microfossils, our findings suggest a reduction in marine productivity during hyperthermals.

[1] Carter et al. (2020) *Minerals* 10, 1-24. [2] Griffith et al. (2021) *Paleoceanogr. Paleoclimtol.* 36, e2020PA004053. [3] Bridgestock et al. (2019) *Earth Planet. Sci. Lett.* 510, 53-63. [4] Miyazaki et al. (2023) *Geochem. J.* 57, GJ2301. [5] Miyazaki et al. (2014) *J. Anal. At. Spectrom.* 29, 483-490.