

Barium isotopes in the planktic foraminifer: a novel tracer of surface seawater isotopic signatures

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Barium isotopic ratios in marine environments are utilized as tracers for mixing processes of water masses and in reconstructing paleo-productivity [1]. The interest in this tracer has increased as our understanding of its chemical behavior, particularly in marine carbonates, has improved. Elevated Ba/Ca ratios observed in several non-spinose planktic foraminifera (*G. menardii*, *N. dutertrei*) are believed to be the result of calcification occurring in the microenvironment of marine organic aggregates, such as marine snow [2]. A comprehensive understanding of this geochemical anomaly may be achieved by examining its barium isotopic composition. In this study, following the standard cleaning protocol for foraminiferal shells, we analyzed the Ba/Ca ratios and $\delta^{138}\text{Ba}$ _NIST 3104a values of co-occurring spinose (*G. sacculifer*) and non-spinose (*G. menardii*, *G. tumida*) planktic foraminiferal shells from two core-top sediments (GH-2 and K4) in the South China Sea. The findings revealed that Ba/Ca ratios ranged from 2 to 5 $\mu\text{mol/mol}$ in spinose species and from 24 to 45 $\mu\text{mol/mol}$ in non-spinose species, consistent with LA-ICP-MS results from sediment traps in the northern Gulf of Mexico [2]. Notably, we have, for the first time, reported $\delta^{138}\text{Ba}$ values in planktic foraminiferal shells, discovering that non-spinose species (*G. menardii*, *G. tumida*) with elevated Ba/Ca ratios exhibited a narrow $\delta^{138}\text{Ba}$ range of -0.02 to 0.03‰ (n=9), whereas co-occurring spinose species (*G. sacculifer*) displayed significantly higher $\delta^{138}\text{Ba}$ values, suggesting different mechanisms of Ba incorporation. Our findings support the hypothesis that non-spinose species calcify within marine snow aggregate microenvironments enriched in barium released from biogenic particulates, while co-occurring surface water-dwelling spinose species (*G. sacculifer*) may reflect surface seawater conditions. We propose that $\delta^{138}\text{Ba}$ in planktic foraminifera serves as a novel proxy, offering valuable insights into the habitats of these species and enhancing their application in paleoceanographic research.

[1] Barium stable isotopes in the global ocean: Tracer of Ba inputs and utilization, Hsieh & Henderson (2017), *Earth Planet Sc Lett*, 269–278.

[2] Ba/Ca ratios in the non-spinose planktic foraminifer *Neoglobobulimina dutertrei*: Evidence for an organic aggregate microhabitat, Fehrenbacher, et al., (2018). *Geochim. Cosmochim. Acta*, 361–372.