Foraminiferal Na/Ca suggests decreased seawater Ca concentration and reduced hydrothermal activity since mid-Miocene

XIAOLI ZHOU[1], WEIMIN SI[1], JONATHAN EREZ[2], AND YAIR ROSENTHAL[1]

[1] Institute of Marine and Coastal Sciences, Rutgers University, New Brunswick, NJ, USA
[2] Institute of Earth Sciences, the Hebrew University, Jerusalem, Israel

On multi-million-year timescale, seawater (sw) [Ca] and [Mg] are coupled through Mg-Ca exchange during basalt-seawater reaction in mid-ocean ridges (MOR) and also tied to ocean alkalinity through silicate weathering[1]. Here we reconstructed $[Ca]_{sw}$ in the late Neogene using foraminiferal Na/Ca values, and tested mechanisms that explain the covariation of $[Ca]_{sw}$ and $[Mg]_{sw}$.

Given the different residence time of Na (100 Myr) and Ca (1 Myr) in the ocean, secular variations in Na/Ca indicate changes in $[Ca]_{sw}$ rather than $[Na]_{sw}$. In cultured planktonic foraminiferal shells, Na/Ca values increase with those in ambient solutions[2], thus can possibly reflect $[Ca]_{sw}$ history on multi-million-year timescale.

Our Na/Ca records of planktonic foraminifera *G. sacculifer* and benthic foraminifera *C. wuellerstorfi* generally increase from 15 Ma to present, suggesting a decrease in $[Ca]_{sw}$. Fluid inclusion data imply an increase of $[Mg]_{sw}$ during the same time interval[3]. This coupled change in $[Ca]_{sw}$ and $[Mg]_{sw}$ could result from the variation in either silicate weathering or Mg-Ca exchange at hydrothermal vents. To test these two hypotheses, we reconstructed the alkalinity flux from weathering using carbonate mass accumulation rates (MARc) of the past 15 Myr from over 20 pelagic sites.

The MARc in the global ocean decreased from 15 Ma to present, suggesting that alkalinity input from continental weathering has not increased, thus unlikely to drive $[Ca]_{sw}$ down and $[Mg]_{sw}$ up. This additional constraint from MARc suggests that the changes in seawater $[Ca]_{sw}$ and $[Mg]_{sw}$ are likely due to a reduction in the Mg-Ca exchange at MOR since mid-Miocene.

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