

Seawater pH at the advent of metazoan calcification

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The boron isotopic composition ($\delta^{11}\text{B}$) of bulk limestones provides a potentially powerful tool for reconstructing seawater pH deep into the geologic past (Kasemann et al., 2005; Paris et al., 2010; Ohnemueller et al., 2014). Here, we present $\delta^{11}\text{B}$ of 35 calcitic limestones derived from a ca. 9 m.y. interval of the terminal Proterozoic Nama Group of southern Namibia. These units immediately precede the so-called Cambrian Radiation—the greatest diversification of metazoans in Earth history marked by the near-simultaneous advent of calcification across most animal phyla.

The Nama Group represents one of the best preserved (average $[\text{Sr}] = 1805$ ppm; $\text{Mn}/\text{Sr} < 2$; $\delta^{18}\text{O} > -10\text{‰}$) and most continuous terminal Proterozoic limestone sequences known in the world. The carbonate units investigated here were deposited between ca. 552 and 543 Ma in a semi-divided foreland basin of the Kalahari Craton (Grotzinger and Miller, 2008). Depositional environments were shore-associated and ranged from upper shoreline/tidal flats to below-wave-base lower shoreface, and comprise calcisiltites, calcarenites, heterolithic interbeds, grainstones, and microbialites (Saylor et al., 1998; Grotzinger and Miller, 2008).

The $\delta^{11}\text{B}$ of the 35 sampled Nama Group carbonates were obtained via MC-ICP-MS. Samples were screened for contamination of the $\delta^{11}\text{B}$ signal by clays (using $[\text{Al}]$ as a proxy for clay content) (Paris et al., 2010) and by open-system meteoric diagenesis ($\delta^{11}\text{B}$ - $\delta^{18}\text{O}$ correlation). The $\delta^{11}\text{B}$ values of the limestones ranged from 0.5 to 10.8‰ (avg. = 5.3‰, which is consistent with the previously observed increasing trend in carbonate $\delta^{11}\text{B}$ (Paris et al., 2010) from the -6.2 to 2.7‰ values reported for Neoproterozoic cap carbonate dolostones (Kasemann et al., 2005) to the ca. 25‰ value reported for most modern marine carbonates. B/Ca ratios for the sampled limestones ranged from 3.4 to 24.0 ppm (avg. = 11.0).

Assuming a seawater temperature of 25° C, a salinity of 35, a depth of 10 m, a seawater $\delta^{11}\text{B}$ of 25‰ (based upon 380 Ma halites; Paris et al., 2010), and a boron isotope fractionation factor of 1.0272 (Klochko et al., 2006), the measured $\delta^{11}\text{B}$ of the Nama Group carbonates suggests that seawater pH ranged from ca. 7.6 to 8.6 (avg. = 8.2) over the 9 My interval of Neoproterozoic time. Furthermore, seawater pH exhibited consistent oscillations of 0.6 to 1.0 units over relatively short timescales (200 ky to 1 my) between 552 to 545 Ma.

Notably, seawater pH stabilized between 545 and 543 Ma—the 2 my interval immediately preceding the Cambrian Radiation of animal life. These results raise the possibility that it was the relative stabilization of seawater pH within carbonate shelf environments that fostered the polyphyletic advent of calcification within the animal kingdom during this remarkable period of Earth history.