

Reconstitution of the isotopic composition of boron in seawater over geological times

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The reconstruction of seawater paleo-pH based on the boron isotopic composition ($\delta^{11}\text{B}$) of fossil carbonate shells requires the knowledge of the $\delta^{11}\text{B}_{\text{sw}}$ of the seawater in which the calcifying organisms lived. Boron has a long residence time in the ocean (14 Ma) and its $\delta^{11}\text{B}_{\text{sw}}$ has changed throughout the Phanerozoic, resulting from changes in the source (continental weathering) and sink (adsorption onto ocean floor sediments and oceanic crust alteration) fluxes (1). Here we provide direct determinations of the $\delta^{11}\text{B}_{\text{sw}}$ variations from the historical collection of primary halites (2), that allowed the reconstruction of the ocean paleochemistry over the Phanerozoic. Because B is almost absent in the halite matrix and is enriched in brine inclusions, bulk halite analysis yields an average $\delta^{11}\text{B}$ value of the brine inclusions within the sample. This has been validated by the analysis of modern halite samples having the actual seawater $\delta^{11}\text{B}_{\text{sw}}$ value (39.6 ‰), as shown by the pioneering work of (3). Our results (assessed through the measurements of ten aliquots of each salt sample) reveal a relative homogeneity of the $\delta^{11}\text{B}$ for each halite sample but large variations in the $\delta^{11}\text{B}$ through the geologic time: the $\delta^{11}\text{B}$ value was 39.2 ± 3.8 ‰ for the Plio-Pleistocene, 17.1 ± 2.1 ‰ for the Permian, 33.1 ± 1.9 ‰ for the Devonian, 11.2 ± 6.8 ‰ for the Cambrian and 28.1 ± 2.1 ‰ for the Late Proterozoic. Using a numerical model, we propose a set of explanations for the $\delta^{11}\text{B}_{\text{sw}}$ evolution during the Phanerozoic.

(1) Lemarchand et al., 2002, *Chem. Geol* 190, 123-140,

(2) Horita et al., 2002. *GCA* 66, 3733-3756

(3) Paris et al., 2010, *Geology* 38, 1035-1038