

New boron adsorption experiments to constrain past changes in $\delta^{11}\text{B}$ of seawater

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The boron isotopic composition ($\delta^{11}\text{B}$) of foraminiferal calcite is a powerful tool for the reconstruction of ancient ocean pH and atmospheric CO_2 concentrations. A prerequisite for this proxy is the $\delta^{11}\text{B}$ value of bulk seawater, which is poorly known for the geologic past and hence adds considerable uncertainty. One promising avenue to constrain seawater $\delta^{11}\text{B}$ is the modelling of mass fluxes within the marine boron cycle, such as dissolved riverine input or adsorption onto clastic sediments, and their respective changes through time [1]. However, modelling attempts are hampered by a lack of experimentally-grounded parameters. Sorption onto phyllosilicates (clays) in particular is known to prefer the lighter ^{10}B isotope [2], but to what degree this fractionation and its dependence on properties like pH differs between various clay minerals is currently unknown. To remedy this, we carried out sorption experiments on kaolinite, smectite and illite, which together comprise a majority of suspended sediment export to the ocean. Fixed amounts of pretreated clay were equilibrated with solutions of known composition and their effect on dissolved boron was measured by MC-ICPMS. Our results confirm that clays adsorb boron over a large range of pH but that clay types differ significantly in the magnitude and associated isotopic fractionation of boron adsorption. This demonstrates that the mineralogy of suspended sediments is an important but overlooked control on the $\delta^{11}\text{B}$ of aqueous systems. The gradual Cenozoic shift of clastic sedimentation towards an assemblage dominated by illite [3] may, therefore, have been a significant contributor to past changes in seawater $\delta^{11}\text{B}$ that needs to be considered in geochemical models.

[1] Lemarchand, Gaillardet, Lewin & Allège (2002), *Chemical Geology* 190, 123-140.

[2] Palmer, Spivack & Edmond (1987), *Geochimica et Cosmochimica Acta* 51, 2319-2323.

[3] Cermenó, Falkowski, Romero, Schaller & Vallina (2015), *Proceedings of the National Academy of Sciences of the United States of America* 112, 4239-4244.