Oxyanion control on boron incorporation into inorganic calcite.

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Precise understanding of the fluid-$CaCO_3$ B partitioning mechanism is crucial for using $\delta^{11}B$ and B/Ca of marine biogenic $CaCO_3$ as a reliable proxy for ocean pH and CO_2 chemistry. Yet, it is a challenging task as there are numerous factors influencing B incorporation. For example, salinity has been shown to influence the extent of B incorporation (B/Ca). Because the salinity effect has been recognized both in planktic foraminifers and in inorganic calcite grown in synthetic seawater [1~3], it calls for a common non-biological mechanism. It has been previously argued that the effect is rooted in charge compensation by Na^+ via coupled $CO_3^{2-}/B(OH)_4^-$ and Ca^{2+}/Na^+ substitution in $CaCO_3$ [4]. However, given much higher abundance of Na^+ over B in natural and synthetic seawater to begin with, it is questionable if Na^+ variations via salinity changes can induce notable changes in B/Ca. Also, we previously found that PO_4^{3-} enhances B incorporation into inorganic calcite [3]. This leads us to hypothesize that the presence of certain oxyanions may enhance B incorporation, and therefore the salinity effect on B/Ca may be driven by SO_4^{2-}, which is the most abundant oxyanion in seawater.

Indeed, in our new set of laboratory experiments, we observed enhanced B incorporation into inorganic calcite when Na_2SO_4 is added to growth solutions. In contrast, addition of the same mole-equivalence of Na^+ from NaCl caused negligible changes in B/Ca. The effect was also evident when, instead of Na_2SO_4, K_2SO_4 was used as the SO_4^{2-} source. These lines of evidence make a strong case that the effect is in fact driven by SO_4^{2-}. Furthermore, we are currently conducting additional experiments to address whether oxyanions other than SO_4^{2-} would likewise cause an increase in B/Ca. Preliminary results from these experiments will also be featured in this presentation.

[1] Allen et al. (2012) EPSL, 351-352, 270-280. [2] Henehan et al. (2015) G-Cubed, GC005514. [3] Uchikawa et al. (2017) GCA, 218, 291-307. [4] Balan et al. (2016) GCA, 193, 119-131.