Paired B/Ca and δ^{11}B measurements on inorganic calcite: Constraints on boron incorporation and implications for boron proxies

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Boron concentrations (B/Ca) and isotopic compositions (δ^{11}B) of biogenic marine carbonates are widely applied to reconstruct past changes in ocean carbonate chemistry. Such applications typically assume that borate ion ($B(OH)_4^-$) is the principal boron species incorporated into carbonates. However, recent δ^{11}B, B/Ca and B coordination studies in both inorganic and biogenic carbonates suggest more complex B incorporation pathways, potentially involving boric acid ($B(OH)_3$) and/or intermediate deprotonated B species[1,2]. To provide insight on B incorporation into inorganic carbonates, here we present δ^{11}B measurements on inorganic calcites grown under controlled laboratory conditions for which B/Ca data were previously reported[1]. Our δ^{11}B data highlight three results: First, inorganic calcite δ^{11}B decreases when either solution [DIC] or solution [Ca^{2+}] is increased. Second, the sensitivity of inorganic calcite δ^{11}B to pH decreases with increasing solution [B]. Third, the B isotope fractionation between inorganic calcite and $B(OH)_4^-$ decreases systematically with increasing precipitation rate (R). These results suggest that kinetic effects govern B incorporation into inorganic calcite, as previously suggested[1]. While published B/Ca studies argued for preferential $B(OH)_3$ incorporation at higher R[1], which should cause higher δ^{11}B at higher R, our data instead show lower δ^{11}B (relative to $B(OH)_4^-$) at higher R. This may imply that either the B species incorporated at higher R more dominantly reflects $B(OH)_4^-$, or kinetic isotope effects occur that favor incorporation of lighter isotopes at higher R. We will present insights on these B/Ca and δ^{11}B observations gained from surface reaction kinetic modeling of boron incorporation. Implications of these inorganic calcite experiments for aqueous boron proxies will also be discussed.

[1]Uchikawa, J. *et al*., GCA v. 150 (2015)
[2]Balan, E. *et al*., GCA v. 193 (2016)