

Constraining sulfur incorporation in calcite using controlled growth experiments

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Element uptake in biogenic CaCO₃ skeletons such as those made by foraminifera and corals has been shown to provide useful information for reconstructing the marine inorganic carbon system. Examples of such carbonate parameter proxies are B/Ca, Sr/Ca, and U/Ca measured on foraminiferal shells. The sulfur over calcium ratio (S/Ca) in foraminiferal shells was proposed more recently as a new and independent proxy representing seawater [CO₃²⁻]. As sulfate (SO₄²⁻) is the dominant sulfur ion incorporated into the shell, it is assumed to substitute for CO₃²⁻ and thus resulting in increased S/Ca values with a decreasing seawater saturation state (i.e. increasing SO₄²⁻/CO₃²⁻). This assumption has been validated through foraminiferal controlled growth experiments, but field studies showed controversial results suggesting that a potential impact of [CO₃²⁻] on sulfur incorporation may be overwritten by one or more other parameters. Incomplete understanding of the inorganic processes involved, however, hampers the application of foraminiferal sulfur concentrations for reconstructing the carbon system. Hence, we here investigate S/Ca values in inorganically precipitated CaCO₃. Calcite was grown using the seeded overgrowth method in solutions of CaCl₂ - Na₂CO₃ - Na₂SO₄ - B(OH)₃ - MgCl₂, under eleven different set carbon chemistry conditions. These conditions involved four series of experiments by respectively changing 1) [DIC], 2) [DIC] and [Ca], 3) pH and [Ca], 4) [Ca] only. The calcite growth experiments confirm the effect of the carbon system on sulfur incorporation. The sulfur, boron, and magnesium concentrations of the growth solutions were kept constant during all series, thus allowing us to evaluate responses of boron and magnesium incorporation to various different carbon system parameters along with changes in S/Ca values. The results will be used to improve our understanding of controls on element incorporations in calcite in relevance for their application as CO₂-proxies and investigate the potential of multi-element approaches for reconstructing marine inorganic carbon chemistry.