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## Chemical and isotopic fractionation of boron in synthetic calcite and aragonite

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About 20 years ago the boron isotopic composition of marine carbonates has been proposed as a proxy of ancient seawater pH. Since that time, a large body of studies used boron isotopes in carbonates to reconstruct seawater paleo-pH and atmospheric paleo- CO<sub>2</sub> concentration. To date however, no systematic investigation of the physicochemical parameters that control boron incorporation in calcite and aragonite (pH, temperature, precipitation rate, etc.) has been performed. To fill this gap, we have performed precipitation kinetic experiments of calcite and aragonite at 5 and 25°C for the overall pH range 7.4<pH<9.5. In order to precisely characterize the B species incorporated in the synthetic precipitates, we performed <sup>11</sup>B MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) analyses, combined with B isotope measurements on them. The obtained results indicate that B partition coefficient, *D<sub>b</sub>*, between CaCO<sub>3</sub> and the fluid, appears to be very small ( $DB \leq 10^{-4}$  and  $\leq 10^{-5}$  for aragonite and calcite, respectively) and to exhibit a strong dependence on the solution pH and the calcium carbonate precipitation rate. They also show that, although  $\delta^{11}\text{B}$  rises with pH for all crystal types, calcite displays a smaller fractionation with respect to the precipitation solution and a much lesser sensitivity to solution pH than expected. NMR spectra show almost exclusively tetrahedral boron in aragonite but highly variable proportions of trigonal and tetrahedral boron in calcite. We suggest that both borate ion and boric acid are incorporated in calcite and that B is present in both crystalline and non-crystalline sites whereas in aragonite the borate ion is the dominant species, representing over 90% of the total boron. These results overall suggest that aragonite-based calibrations should be favoured in future paleo-pH reconstructions. Calcite-based calibrations require a rigorous characterization via NMR spectroscopy of boron speciation and site occupancy in the crystals.