Kinetics of Ba partition and Ba isotope fractionation during its incorporation in aragonite

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The mechanisms controlling the incorporation and the stable isotope composition of trace elements in carbonate minerals are of great importance for the geoscientific community as they can provide insights on the environmental conditions prevailing at the time of mineral growth. In this study we examine the effect of growth rate on the incorporation of Ba in aragonite together with the associated Ba isotope fractionation between forming aragonite and the reactive fluid. The obtained results show that at aragonite growth rates as low as 10^{-9} (mol/m^2/s) a Ba partitioning coefficient, D_{Ba}, of 0.22, which increases towards unity as mineral growth rate approaches a value of $10^{-7.8}$. The determined D_{Ba} values come in contrast to previous experimental works on aragonite nucleation (Dietzel et al., 2004; Gaetani and Cohen, 2006). They are, however, in excellent agreement with the theoretical free energy correlation model by Wang and Xu (2001) that considers the effect of ionic radii size. Although aragonite and witherite ($BaCO_3$) are both precipitating in the orthorhombic crystal system, the large difference of more than 25% in Ca and Ba ionic radii controls the incorporation of the latter in the aragonite structure.

The isotopic fractionation of Ba between aragonite and fluid exhibits a growth rate dependence. At the lowest growth rate, the heavier Ba isotopes are preferentially incorporated in the solid phase. The measured fractionation, expressed as the difference between the isotopic composition of the solid and the fluid, is +0.25‰ in $\Delta^{137/134}$Ba. The $\Delta^{137/134}$Ba values exhibits a linear decrease at increasing aragonite growth rate up to a value of 10^{-8} (mol/m^2/s). At higher rates, no significant fractionation has been observed. This is the first time that the enrichment of the heavy isotopomer of an alkaline earth metal in the carbonate solid phase has been measured. The observed enrichment of the heavier Ba isotopomers in the solid phase is likely controlled by the difference of Ba-O bond length in the solid and the aqueous phase, with Ba in aragonite exhibiting shorter distances to the neighbour oxygen atoms. The results have great significance for interpretation of Ba in natural aragonites, such as corals, as they can provide insights into biomineralization processes.