

## **Growth rate controlled barium partitioning in calcite and aragonite**

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The barium (Ba) content and the Ba/Ca molar ratios in biogenic and abiotic carbonates have been widely used from the scientific community as a geochemical proxy especially in marine and early diagenetic settings. The Ba content of carbonate minerals has been earlier associated to changes in oceanic circulation that may have been caused by upwelling, changes in weathering regimes and river-runoff as well as melt water discharge. The physicochemical controls of Ba ion incorporation in the two most abundant  $\text{CaCO}_3$  polymorphs found in Earth's surface environments, i.e. calcite and aragonite, have adequately been studied only for calcite. These earlier studies (i.e. [1]) suggest that at increasing growth rate, Ba partitioning in calcite is increasing as well. In contrast, to date the effect of growth rate on the partitioning of Ba in aragonite remains questionable, despite the fact that this mineral phase is the predominant carbonate-forming polymorph in shallow marine environments. To shed light on the mechanisms controlling Ba ion uptake in carbonates in this study we performed steady-state Ba co-precipitation experiments with calcite and aragonite at 25°C. The obtained results for the partitioning of Ba in calcite are in good agreement with those reported earlier by [1], whereas those for aragonite indicate a reduction of Ba partitioning at elevated aragonite growth rates, with the partitioning coefficient value between solid and fluid to be approaching the unity. This finding is in good agreement with the formation of a solid solution in the aragonite-witherite system, owing to the isostructural crystallography of the two mineral phases. Moreover, our data set provides new insights that are required for reconstructing the evolution of the Ba content of pristine marine versus diagenetically altered carbonate minerals commonly occurring in marine subsurface settings, as the thermodynamically less stable aragonite will transform to calcite enriched in Ba, whilst affecting the pore water inventory of aqueous Ba in the surface-near sediments.

[1] Tesoriero and Pankow, 1996, GCA