Kinetic and step-specific effects on boron incorporation into calcite during growth

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Reconstructions of ancient ocean pH are critical for evaluating past changes in the atmospheric CO_2 concentration and thus to obtain insights into the evolution of Earth's climate. These reconstructions are currently based on analysis of the boron composition of marine carbonates such as foraminifera or corals, e.g. [1,2]. The correlations observed between B concentrations and $\delta^{11}B$ in carbonates and the pH of the precipitating fluid in inorganic experiments [3,4] suggest that $\delta^{11}B$ and, possibly, the boron composition of carbonates, reflect changes in the pH of the solution from which they precipitated.

Nevertheless, there are still several aspects on the use of boron isotopes for the reconstruction of past seawater pH that require further investigation. In particular, questions related to the mechanism of boron coprecipitation with carbonates remain essentially unexplored. Although the increase in B incorporation with increasing pH can be explained largely by the change in boron speciation, it cannot be ruled out that other factors, such as kinetic effects associated with changes in growth rate [3], may also play a role.

As has been shown for many other elements, boron incorporation mechanisms cannot be simply studied by means of macroscopic measurements; molecular-scale studies are essential to obtain truly representative information of the surface processes taking place during B coprecipitation with calcite. In this study, boron incorporation during calcite growth was investigated using Atomic Force Microscopy (AFM), as a function of pH, supersaturation and boron concentration. Our results indicate that, together with pH, changes in the saturation degree of the precipitating solution and, as a consequence, in the calcification rate are a key factor to consider when using boron in marine carbonates as a paleo-pH proxy, as these factors could influence the extent of boron incorporation and, maybe, its isotopic signature. As well, this study shows that the calcite crystallographic form in which boron is incorporated may be also a critical factor controlling the amount of boron incorporated and that a change in the site preference of boron for its incorporation into calcite could occur depending on the species which is incorporated and, consequently, on the pH of the precipitating solution. Finally, our nanoscale observations give indirect evidence of the incorporation of boron in non-lattice sites.

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Nucleation and crystal growth in confined nanopores

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Storage of carbon dioxide in deep geological formations has emerged as an important option in managing anthropogenic CO_2 [1]. One concern of this storage method is the unknown long-term stability of injected CO_2. Moreover, it will be necessary to seal injection reservoirs to prevent release of gases and fluids. The precipitation of metal carbonate bearing minerals in pore spaces is one possible path for both sealing off reservoirs and securely binding injected CO_2. In general, crystallization from solution occurs at solid-liquid interfaces. The detailed structure of the solid surface plays a critical role in liquid-solid phase transformations [2]. Nucleation and crystallization of these metal carbonates are greatly influenced by the surface shape, roughness, chemical species present, and nanoscopic confinement of the native metal oxides. Current understanding of the thermodynamics and kinetics of nucleation and growth is primilarly based upon analyses of homogenous systems near equilibrium; distinctly different from the supersaturated systems with complex interface structures that would be found at real reservoir sites.

Our aim is to bridge this gap, gaining a better understanding of how the subsurface environment influences the earliest stages of mineralization of sequestered CO_2 at nanoscale dimensions. We will examine the rates of metal carbonate nucleation and growth as a function of material surface structure and chemistry. Thin films of silica containing nanometer sized pores of different shapes and dimensions will be screened for preferential crystal nucleation and growth. In-situ transmission electron microscopy utilizing a fluid cell designed with temperature and electrochemical control will be employed to monitor and drive surface-directed crystal growth in real time.

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