



The fate of alkalinity during seawater freezing: insights from a thermodynamic model of concentrated solutions (FREZCHEM)

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In springtime, the polar marine boundary layer exhibits drastic ozone depletion events (ODEs), associated with elevated bromine oxide (BrO) mixing ratios. The current interpretation of this peculiar chemistry is believed to require the existence of acid and bromide-enriched surfaces to heterogeneously promote and sustain ODEs. Sander et al. (ACP, 6, 4653 – 4658, 2006) have suggested that calcium carbonate (CaCO_3) precipitation in any seawater-derived medium could potentially decrease its alkalinity, making it easier for atmospheric acids such as HNO_3 and H_2SO_4 to acidify it. We performed simulations using the state-of-the-art FREZCHEM model, capable of handling the thermodynamics of concentrated electrolyte solutions, to investigate this issue in more details. When carbonate precipitation is artificially removed from the simulation, the alkalinity of the brine increases monotonously with decreasing temperature, like all ionic species, due to the volume reduction of the brine and the exclusion of ions from the ice lattice. Including the possibility for carbonate salts to precipitate drives major change in the alkalinity/temperature relationship. The precipitation of either calcite (CaCO_3) or ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) prevents a significant increase in the alkalinity of the solution during freezing. However, ikaite precipitation leads to much less alkalinity depletion than calcite precipitation. Given that ikaite has been identified in Antarctic brines, our simulations are relevant to explore the potential impact of brine acidification on the halogen activation phenomenon, which is likely to be much less pronounced than anticipated by the conceptual study of Sander et al. (2006).