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The Marine Carbonate System: Ionic Interactions and Biogeochemical Processes

Adam Ulfsbo

Institutionen för kemi och molekylärbiologi
Naturvetenskapliga fakulteten

Akademisk avhandling för filosofie doktorsexamen i Naturvetenskap, inriktning kemi som med tillstånd från Naturvetenskapliga fakulteten kommer att offentligt försvaras fredagen den 28 maj kl. 10:00 i KB, Institutionen för kemi och molekylärbiologi, Kemigården 4, Göteborgs universitet, Göteborg.

Fakultetsopponent: Professor Dieter A. Wolf-Gladrow, Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Bremerhaven, Tyskland.

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Abstract

The absorption of atmospheric carbon dioxide (CO_2) by seawater and subsequent equilibrium reactions within this ionic medium give rise to a complex chemical system often referred to as the marine carbonate system. This system is influenced by physical and biogeochemical processes in the ocean. The marine carbonate system is a major component of the global carbon cycle and is, by virtue of its interaction with atmospheric CO_2, of fundamental importance to the Earth's climate. Accurate knowledge of the properties of the marine carbonate system is a prerequisite for understanding the chemical forcing and consequences of key biogeochemical processes such as biological production, organic matter respiration, or uptake of anthropogenic carbon. The assessment of the marine carbonate system builds on precise measurements by state-of-the-art analytical methods as well as an understanding of the underlying fundamental chemistry in terms of ionic interactions and equilibrium thermodynamics. This thesis focuses on different aspects of the marine carbonate system with emphasis on biogeochemical processes and thermodynamic modelling of the seawater ionic medium. A quantitative understanding of the equilibrium solution chemistry of seawater ultimately relies on accurate estimations of activity coefficients of all the various components that make up the solution. Activity coefficients of the carbonate system in sodium chloride solution of varying ionic strength were estimated by Monte Carlo simulations at different temperatures, as well as activity coefficients of chloride and sulfate salts of a simplified seawater electrolyte, suggesting that a complete Monte Carlo description of seawater activity coefficients may be achievable using the hard sphere approach with a very limited number of fitted parameters. Chemical speciation modelling showed that the measured excess alkalinity of Baltic seawater is consistent with an organic alkalinity derived from humic substances of terrestrial origin. In deep waters of the Baltic Sea, oxygen and sulfate was found to be the major electron acceptors to the remineralization of organic matter under different redox conditions. It was further suggested that this organic matter predominantly had a terrestrial origin. The subsurface waters of the central Arctic Ocean were found to be a sink of anthropogenic CO_2, attributed to uptake by source waters of Atlantic origin. The sea-ice covered central Arctic Ocean was also shown to harbor low, but significant biological productivity. Late summer net community production was estimated using multiple approaches based on both discrete and underway measurements and results showed large spatial variability between the deep basins with extremes at the marginal ice zone.

Keywords: Marine | seawater | carbonate system | CO_2 | Arctic Ocean | Baltic Sea | organic alkalinity | Pitzer | Monte Carlo | activity coefficients | biogeochemical processes

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