

Algal mats of the North Pole: How sea ice melt can cause anoxic spots on the Arctic deep-sea floor

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The centric diatom *Melosira arctica* forms kelp-like accumulations under the Arctic sea ice, in the form of meter-long filaments, anchoring in troughs and depressions under ice floes. These mat-forming algae are extremely sensitive to warming and melting of the ice, leading to their rapid sedimentation. The research icebreaker POLARSTERN visited the ice-covered eastern-central basins between 82° to 89°N and 30° to 130°E in summer 2012 in the framework of the expedition ICEARC. By September, the Arctic sea ice had declined to a record minimum of 3.6 million square kilometers. Consequently, we observed the massive sedimentation of sub-ice algal biomass of up to 150 g C per m² (median: 9 g C per m²) to the deep-sea floor of the Arctic basins. Patches of algal mats of 1-50 cm in diameter covered up to 10% of the seafloor at 3300-4500m water depth. *in situ* and *ex situ* microprofiling of diffusive oxygen fluxes into sediments covered by algal aggregates showed elevated rates of 5-6 O₂ mmol m⁻² d⁻¹, compared to <0.4 mmol m⁻² d⁻¹ in the surrounding sediments. Apparently only sediment bacteria, and large mobile megafauna were able to profit of the ice-algae deposition event. In cores covered by *Melosira* strands, oxygen penetration in the sediment was reduced to a few mm as compared to the surrounding sediment, where oxygen penetrated >50 cm deep. From the *in situ* oxygen profiles we conclude that the sinking *Melosira* strands had contributed >85% of total carbon flux to the deep-sea floor in 2012, but that such massive algal falls were previously rare. Our observations support the hypothesis that the thinning ice cover enhances under-ice productivity and export. If this phenomenon repeats seasonally, substantial changes in the biogeochemistry and biodiversity of the ice-covered Arctic basins are expected.



Figure 1: Sea cucumbers feeding on freshly deposited algal mats at 4500 m water depth

Aqueous Li⁺ speciation and ancient climate monitoring

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Lithium is recognized as a valuable trace metal in the area of ancient climate monitoring. This arises from the isotopic composition of Li in seawater being strongly influenced by continental weathering, one of the major sources of Li in seawater, and the incorporation of aqueous Li⁺ into calcium carbonate shells. By systematically analyzing the isotopic composition of Lithium in ancient calcium carbonate it is possible to reconstruct a record of Li isotope fractionation (IF) in seawater over the past 68 Ma. Due to the close association of Li IF with ancient weathering, this record is able to provide critical information concerning the ancient earth climate.

Previous studies base their paleo-reconstructions on the close correspondence between modern values of Li isotope ratios in calcium carbonates and seawater. Implicit is the assumption that Li IF is not sensitive to environmental conditions such as Temperature and pH. This assumption is not supported from a molecular structure point of view; there is little information concerning the identity and molecular structure of aqueous Li⁺ species and it is not clear to what extent ligand coordination effects may play in the incorporation of Li⁺ into calcium carbonate.

We have carried out a theoretical (Density Functional theory) study of aqueous Li⁺ speciation including effects of ligand coordination, temperature and solution pH. We have calculated the isotope exchange equilibrium constant associated with the Li Acid/Base equilibrium and can constrain it to positive values. The consequences of this species dependent IF are then studied using a model for Li-Carbonate coordination. We define an effective IF to model temperature and pH induced changes in Li IF in Li-Carbonates. We predict that under normal oceanic conditions Li IF is not sensitive to pH but may be significantly influenced by temperature.

Based on our results we revisit the basic assumption that Li IF is not sensitive to environmental conditions such as Temperature and pH. Namely, our observation of significant species dependent Li IF strongly suggests that the mechanism through which Li is incorporated into calcium carbonate is not sensitive to the Li speciation.