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Phosphate-Bound Zinc Storage in Marine Phytoplankton

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Background: Zinc is an essential micronutrient for marine phytoplankton, functioning as a cofactor in enzymes that catalyze key biogeochemical processes. Recent synchrotron X-ray fluorescence microscopy studies of phytoplankton samples have shown strong correlations between Zn and phosphorus in phytoplankton cells, suggesting the presence of a Zn-phosphate cellular storage mechanism. Here, we used X-ray absorption spectroscopy (XAS) to investigate the molecular speciation of Zn in marine phytoplankton to elucidate intracellular Zn storage.

Materials and Methods: Cultures of the cyanobacterium *Prochlorococcus marinus* and the diatom *Thalassiosira pseudonana* were grown in artificial seawater with replete trace metal concentrations buffered using EDTA. Cells were harvested during late exponential phase and zinc speciation was examined using (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. Spectral data were compared with Zn standards representing phosphate, cysteine, histidine, and citrate coordination environments. Linear combination fitting and quantitative EXAFS modeling were used to determine the molecular Zn coordination.

Results and Discussion: XAS analyses revealed that Zn in marine phytoplankton is predominantly associated with phosphate rather than proteins. The XANES spectra from both organisms closely match Zn–phosphate standards, indicating that phosphate groups dominate the Zn coordination environment. The EXAFS results showed that Zn in *Prochlorococcus* is almost entirely present as Zn–phosphate complexes, and *Thalassiosira* contains approximately 80% Zn–phosphate and 20% Zn–cysteine. The local coordination environments derived from EXAFS indicate Zn is bound to oxygen atoms in mixed tetrahedral and octahedral configurations consistent with $Zn–O_4$ and $Zn–O_6$ binding to phosphate ligands. These results suggest that phytoplankton store excess Zn primarily in the form of Zn-polyphosphate, creating an intracellular reservoir that buffers cells against low environmental Zn. This storage helps explain why Zn limitation is rarely observed despite extremely low oceanic Zn concentrations and highlights a new pathway by which Zn cycling is coupled to phosphorus regeneration dynamics.