The role of organic metal-binding ligands in the uptake and cycling of trace metals

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Trace metals such as iron are essential for many fundamental cellular processes, yet several aspects of its biogeochemical cycling remain poorly understood. This is in large part because dissolved iron speciation is dominated by complexation to an unknown pool of organic metal-binding ligands, which control its reactivity, bioavailability, and residence time. Basin-scale organic iron-binding ligand distributions produced using voltammetric techniques in the GEOTRACES program have shed unprecedented insight on the distributions and sources and sinks of these ligands, yet their identity remains largely unknown. Recent advancements in mass spectrometry-based analytical approaches in the last decade have enabled the identification of discrete iron-binding ligands in seawater called siderophores, which are microbially-produced compounds with high binding affinities for iron. Emerging patterns in siderophore distributions show coherence with traditional voltemmetric techniques. In the North Pacific subtropical and subpolar gyre, the highest concentrations and diversity of siderophores are found in regions with elevated nitrate relative to dissolved iron, a proxy for iron limiting conditions, and suggest that these compounds likely influence iron uptake. Siderophores are also present below the euphotic zone, suggesting a portion of the strong ligands observed by voltammetric tecniques in GEOTRACES datasets may be comprised of siderophores. In many samples siderophores comprise only 1% of the total ligand pool determined by voltammetric techniques, yet play a disproportionately significant role in the complexation and uptake of dissolved iron, perhaps facilitating the competition among organisms for this essential micronutrient. Elucidation of organic iron-binding ligand pool in seawater using mass spectrometry based techniques combined with voltammetric apporaches are revealing the sources and relative importance of distinct organic ligands in the cycling of dissolved iron in the ocean.