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EDITORIAL
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Editorial: Organic Ligands—A Key Control on Trace Metal Biogeochemistry in the Ocean

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Editorial on the Research Topic

Organic Ligands—A Key Control on Trace Metal Biogeochemistry in the Ocean

This Research Topic results from the activities of Scientific Committee on Oceanic Research Working Group (SCOR WG) 139: Organic Ligands—A Key Control on Trace Metal Biogeochemistry in the Ocean. Organic ligands govern the bioavailability of trace metals that are essential micronutrients to marine phytoplankton and exert a major influence on the global carbon cycle. The aim of SCOR WG 139 has been to improve understanding of metal-binding ligands in the oceans, and their pivotal biogeochemical functions in the oceans, through an interdisciplinary collaboration of trace metal biogeochemists, organic geochemists and biogeochemical modelers.

Three central goals of this WG were to:

1. Promote improvements in quality, accessibility, and development of analytical methodologies for characterizing metal-binding ligands in seawater.
2. Characterize which components of the dissolved organic matter pool make a significant contribution to the biogeochemistry of trace metals in the oceans.
3. Identify the role of ligands in microbial ecology and marine biogeochemical cycles.

Several papers in this Research Topic emphasize improvements in methodology for characterizing metal-binding organic ligands in seawater. Best practices for comparing competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-AdCSV) results are provided in a GEOTRACES field data intercomparison (Buck et al.). The assessment of side reaction coefficients of a model siderophore by voltammetry (Schijf and Burns) and of the complexes formed between model ligands and iron and copper using voltammetry and Fourier transform-ion cyclotron resonance-mass spectrometry (FT-ICR-MS) (Waska et al.) illustrate the heterogeneity of metal-ligand complexes. Waska et al. also underscore the strength of combining CLE-AdCSV and mass spectrometry tools to characterize metal-binding ligands. In a Perspective, Wichard details the applicability of metal isotope coded profiling in ultra high performance liquid chromatography-electrospray ionization-mass spectrometry (UHPLC-ESI-MS) to identify metal-binding organic ligands and decipher their ecosystem function. A crucial step in mass spectrometry ligand identification is the separation of metal-binding ligands from the seawater matrix. In their paper, Nixon and Ross document an 81% average recovery of a model copper ligand on an immobilized metal-ion affinity chromatography (IMAC) column.

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Rapidly advancing mass spectrometry tools coupled with CLE-AdCSV has led to new insights into metal and ligand cycling in the ocean. Using a combination of CLE-AdCSV, LC-ESI-MS and chemical assays, Velasquez et al. show siderophore production during particle remineralization, representing a novel source of strong iron-binding ligands to subsurface waters. Bundy et al. also report iron-binding ligand sources in particle remineralization experiments, and variable photochemical losses. The production of strong iron-binding ligands during remineralization (Bundy et al.; Velasquez et al.) has important implications for iron resupply to the surface ocean, providing a mechanism for stabilizing subsurface iron. Fecal pellets from salps were found to be a source of iron-binding humic-like substances and a vector for iron transport to the deep Southern Ocean, suggesting a tendency for iron export over recycling where salps are abundant (Cabanes et al.).

Two papers in this Research Topic highlight exciting new links between viruses, iron and ligands in the ocean. Iron limitation was found by Slagter et al. to reduce viral infection of marine phytoplankton and the extent of iron cycling through the viral shunt. Bonnain et al. build on established literature in non-marine model systems to propose that viruses themselves are iron-binding organic ligands in the oceans and that iron in virus tails may serve as a Trojan horse for viral infection of bacteria.

An emerging paradigm regarding iron-binding ligands in seawater is the combined contribution of siderophores, humic-like substances and exopolysaccharides to the ligand pool. Hassler et al. use these ligand groups to propose regional distinctions in iron speciation and identify knowledge gaps. In a data report, Caprara et al. note that nearly 70% of the existing open ocean iron speciation data originate from the Atlantic, creating an inherent bias in evaluating global distribution patterns.

Compared to iron, the organic complexation of other bioactive metals is less understood. The application of LC-ESI-MS to South Pacific surface waters identified a diverse suite of copper- and nickel-binding organic ligands (Boiteau et al.). A copper radiotracer method introduced by Semeniuk et al. and applied with CLE-AdCSV showed rapid cycling of copper by natural phytoplankton communities in the North Pacific. Voltammetric measurements of copper-binding ligands, humic substances and thiols in a salt marsh estuary suggest that ammonia-oxidizing archaea also grow on organically complexed copper (Whitby et al.).

CLE-AdCSV studies of metal-binding organic ligand distributions continue to inform understanding of the role these ligands play in ocean biogeochemistry. In this Research Topic, stabilization of dissolved iron inputs was attributed to strong iron-binding organic ligands in the Yellow Sea (Su et al.), in a buoyant hydrothermal plume from a shallow island arc system (Kleint et al.) and across the redox boundary of the Black Sea (Gerringa et al.). In the first CLE-AdCSV study of zinc speciation in the Indian Ocean, Kim et al. report a predominant river influence in this region.

Changing ocean chemistry is expected to influence the speciation, bioavailability, and biogeochemical cycling of trace metals in seawater. Avendaño et al. use a combination of CLE-AdCSV and speciation modeling to evaluate how declining seawater pH levels alters the complexation of iron and copper by natural organic ligands in shelf seas. This Research Topic also introduces a new SCOR working group, SCOR WG 145, aimed at developing a quality controlled and widely accessible model of trace metal speciation across ocean chemistry conditions (Turner et al.).

This Research Topic emphasizes vast methodological improvements made in quantifying and identifying metal-binding ligands in seawater, and advancements in our understanding of how organic ligands govern trace metal speciation and how they are cycled through marine biological processes. Altogether, these studies point to the diverse range of metal-binding organic ligands present in the ocean and highlight the crucial role they play in supporting primary productivity by maintaining essential bioactive trace metals in the upper water column.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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