

The Biogeochemistry of trace metal organic ligands along the GEOTRACES Alaska to Tahiti section.

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We have developed analytical techniques to detect, identify and quantify the molecular distribution of trace metal ligands (TM-Ls) in seawater and particulate matter extracts. The approach uses trace metal clean high pressure liquid chromatography to separate TM-L complexes, which are detected/quantified by ICPMS and identified by high resolution ESIMSⁿ. The approach was not ready in time to for the GEOTRACES North Atlantic or ETPZ efforts, but we did analyze samples of opportunity from the ETPZ and were able to show large changes in the distribution and concentration of siderophores and chalcophores along the cruise track (Boiteau et al., 2016; *PNAS* in revision). One advantage of our approach is its potential for coupling TM-L speciation with metagenomic sequences diagnostic for TM-L biosynthesis and uptake. We can also perform targeted TM-L tracer experiments using appropriate ligands at natural concentrations. Finally, we have found Fe, Co, Cu, Ni, and Zn ligands that have never been described before. Depending on the level of interest, we can isolate these TM-L complexes and perform full structural analyses.

Through the GEOTRACES A-T section, we hope to: 1) expand the our measurements to compare a region quite different from the ETPZ, 2) generate the first dataset of TM-L speciation at meso- and bathypelagic depths (our ETPZ samples were only underway GEOFISH surface samples), 3) use our data to work with others to perform targeted metagenomic analyses of TM-L synthesis and uptake genes, and 4) expand the suite of X-L complexes to include organic phosphorus, arsenic, halides, and nitrogen (the method works for As, and halides, but still in development for P & N).

Our proposed research is relevant to GEOTRACES science objectives to determine the global distribution and chemical speciation of select trace elements (many bio-essential TMs are complexed to organic matter), and to evaluate the sources, sinks and internal cycling of TM-Ls.