

## U.S. GEOTRACES South Pacific Expedition (GP17)

### Statement of Interest

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### *Objectives:*

- 1) To characterize the dissolved iron-binding organic ligands across the GP17 transect using a combination of approaches.
- 2) To determine the concentrations and binding strengths of iron-binding ligands, and the speciation of ambient dissolved iron.
- 3) Molecularly identify specific organic compounds binding iron, allowing insight into the sources, sinks, and bioavailability of iron complexes.

### *Proposed work:*

We are interested in proposing to measure the concentrations and characteristics of dissolved iron-binding organic ligands from full water column stations of the U.S. GEOTRACES section GP17. We intend to employ competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-AdCSV) to determine total iron-binding ligand concentrations (L) and their conditional stability constants (K), and calculate the speciation of dissolved iron, including the concentration of Fe'. We will also employ cutting edge liquid chromatography inductively coupled plasma mass spectrometry with high-resolution electrospray ionization mass spectrometry (LC-ICP/ESI-MS) to characterize the concentrations and molecular structures of specific iron-binding ligands. Although our primary goal will be to characterize the iron-binding ligands, we will also get information from the LC-ICP/ESI-MS on organic ligands from other elements of interest (e.g., Co, Ni, Cu, Zn, Mn, Th, As), and of the isotopic composition (e.g.,  $^{56}\text{Fe}/^{54}\text{Fe}$ ) of specific compounds, shedding light on isotopic fractionation associated with organic ligand complexation.

### *Justification:*

Iron is a key trace element identified by the GEOTRACES Science Plan, and iron-binding ligands play a critical role in governing iron cycling in the oceans. In particular, the incorporation of iron-binding ligand concentrations and binding characteristics has proven essential for modeling iron in ocean biogeochemical models, and these data are uniquely provided by CLE-AdCSV measurements. This approach has been extensively intercalibrated in the GEOTRACES program to allow for continued development of a global picture of iron-binding ligand distributions.

In addition to providing key information on the distributions and characteristics of the entire iron-binding organic ligand pool, we will also improve our understanding of the specific organic compounds contributing to the ligand pool by employing LC-ICP/ESI-MS in conjunction with CLE-AdCSV analyses. The MS-based analyses will provide us with novel insights into the sources of specific iron-binding ligands, such as siderophores, and will allow us to quantify the contribution of specific compounds to the total ligand pool.

### *Expected outcomes and support of GEOTRACES mission:*

Our expected outcomes are measurements of the concentrations of total iron-binding ligands along the transect, as well as information on the concentrations and identities of specific compounds contributing to the ligand pool. Our total ligand concentration and binding strength data will be used to further our understanding of how ligands impact iron biogeochemistry through modeling efforts, while our data on specific compounds will be used to begin to understand the mechanisms behind ligand sources and sinks. The measurements of both of these parameters contribute to the GEOTRACES mission of understanding the key impacts of sources, sinks and internal cycling of trace elements in the ocean.