Proposal for a SCOR Working Group: **Organic Ligands – A Key Control on Trace Metal Biogeochemistry in the Ocean**

Abstract

The trace metals iron (Fe), copper (Cu), nickel (Ni), cobalt (Co), cadmium (Cd) and zinc (Zn) are essential micronutrients to marine phytoplankton, controlling primary productivity in up to half of the open ocean, from tropical to polar regions. Consequently, these metals exert a major influence on the global carbon cycle and play a key role in regulating global climate. However, the availability of these metals to the biota is governed by speciation, whereby trace metals are bound by organic ligands that may reduce or enhance metal bioavailability, depending on the metal and the resulting metal-ligand complex. Organic ligands are defined as molecules that can bind to, and form a stable complex with, trace metals in the aquatic dissolved (typically <0.2 µm) phase. Electrochemical techniques have shown that trace metals in seawater are overwhelming bound (up to 99.999%) by organic ligands, and that these ligands are ubiquitous in the ocean. More recently, organic geochemical techniques have shown that at least some Fe-binding ligands are produced by the biota. Over the past three decades, major advances in analytical techniques have led to a consensus on accuracy and precision for total dissolved trace metal analyses and dramatically improved our knowledge on the global and regional distributions of trace metals. In contrast, our understanding of trace metal-binding ligands and their pivotal biogeochemical functions remains at a comparatively early stage. ***To date, we know little about the composition, source and provenance of metal-binding ligands, which is hindering further advances in the field of trace metal biogeochemistry*.**

The proposed working group would focus on advancing our understanding of trace metal-binding organic ligands in the oceans by bringing together expertise ranging from aquatic organic geochemistry to trace metal electrochemistry. Over a 4-year period the working group will (1) Summarize published results from electrochemical and organic geochemistry techniques to identify future collaborative research directions towards targeting specific approaches to determine the structure and source of metal-binding ligands; (2) Expand upon the ligand intercalibration programme, initiated by GEOTRACES, to evaluate key analytical issues with currently employed methodologies and determine how best to link ongoing efforts in trace metal and organic geochemistry to assess natural metal-binding ligands; (3) Identify how to best incorporate published and future data into biogeochemical models; (4) Employ a suite of proposed workshops and working group meetings as a forum to debate the nature of sampling strategies and experimental approaches to be employed in laboratory and field efforts that are needed to determine the composition and structure of these ligands; (5) Provide summarized recommendations at the proposed symposium for future research approaches into ligand biogeochemistry, especially with respect to complementing the ongoing decade-long GEOTRACES field efforts (*i.e.*, regional surveys and process studies) and the need for rapid incorporation of this research into biogeochemical models; (6) Establish a webpage for this SCOR working group, to promote a forum for discussion of ideas and results, soliciting input from the trace metal biogeochemistry, aquatic organic geochemistry and modelling communities, and provide a platform to propose special sessions on trace metal-binding ligands at international meetings such as Ocean Sciences, AGU and/or EGU.

Rationale

Improving our understanding of the role of metal-binding ligands in oceanic biogeochemistry is extremely important, as these ligands control the bioavailability of trace metals, and, thus, influence pivotal global elemental cycles, such as carbon and nitrogen. To a large extent, we simply do not adequately understand the role or chemical structure of metal-binding ligands in the oceans. Thus, we cannot model them with sufficient confidence to predict how they, and consequently trace metal cycles, will respond to projected global alteration of continental aridity (dust supply), ocean acidification, and oceanic oxygen minimum zones due to a changing climate.

Historically, the primary technique for characterizing metal-binding ligands in seawater has been competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV), which provides ligand concentrations and conditional stability constants for the ambient metal-ligand complexes. This technique, however, does not provide meaningful information on the structural characteristics required for identification of these ligands. In the past few years, analytical advances in organic geochemistry using liquid chromatography-electrospray ionization-mass spectrometry (LC-ESI-MS) methods, coupled with nuclear magnetic resonance (NMR), have led to novel research focused on determining the link between the binding strength of ligands measured in natural seawater and their structural identity. As CLE-ACSV provides ligand concentrations, but not structural characteristics, while LC-ESI-MS/NMR provides structural characteristics but no quantitative information on ligands, it is essential to combine these approaches in order to drive progress toward determining sources and composition of metal-binding ligands in the ocean. Each of these techniques alone constitute a powerful, though insufficient, approach to determining metal speciation- ***combining these approaches would constitute a significant step towards assessing metal-binding ligands in the ocean, and lead to new research directions for metal speciation similar to that achieved with 'The Biogeochemistry of Fe' (SCOR WG 109) for dissolved Fe analysis.***

It is timely to focus on the issue of trace-metal binding ligands now, as a SCOR-sponsored international programme, GEOTRACES, was launched in late 2009 with the goal of determining the distributions of trace metals in the global ocean. Trace metal speciation, at least for Fe, has been identified as a core measurement on the GEOTRACES section cruises. The GEOTRACES ocean section cruises commenced in 2010, generating a considerable body of metal speciation data for Fe, Cu, Co and Zn by CLE-ACSV from depth profiles on each cruise. Although the use of CLE-ACSV measurements on the GEOTRACES cruises will provide substantial insights into the distributions of metal-binding ligands measured and their respective binding constants, ***critically, they will not allow for characterization of the ligands themselves***, which requires the application of organic geochemistry techniques. Further, CLE-ACSV studies increasingly suggest that different types of metal-binding ligands (stronger vs. weaker, colloidal vs. truly soluble) play distinct roles in the biogeochemical cycling of trace metals like Fe and Cu, and yet the identities and sources of these ligands remain elusive.

Given the need for a multidisciplinary solution to this problem, a SCOR working group, consisting of trace metal biogeochemists, aquatic organic geochemists and modelers, is the best mechanism to focus current international scientific expertise on metal-binding ligands. Appropriate scientific expertise will be assembled from different countries and an international working group will help develop this topic in developing nations. Other organizations cannot ensure that such an activity is suitably interdisciplinary, involving scientists from a wide range of disciplines and countries, while also helping train young scientists. A webpage will be constructed to help facilitate discussion between working group members, as well as to ensure other large science programs like GEOTRACES, CLIVAR and SOLAS (and a proposed geochemical global ocean survey similar to GEOTRACES) remain involved. The results of this working group will be presented during the proposed symposium and published in a special issue of a journal or book, as well as a report to SCOR.

Background

A short background is provided here to summarize the issues that have motivated us to propose a working group on metal-binding ligands at this time.

Metal-binding ligands appear to facilitate bioavailability and uptake of the trace metals Fe and Co (Maldonado *et al.* 2005; Saito *et al.* 2005), while those binding Cu, Ni, Cd and Zn may sequester and

decrease the bioavailability of these metals (Vraspir & Butler 2009). The pioneering work of Rue & Bruland (1995) and Gledhill & van den Berg (1994) established using CLE-ACSV measurements that dissolved Fe in the ocean was 99.99% bound to organic ligands, which in turn increased the solubility of this important micronutrient. Other trace metals such as Cu, Ni, Co, Cd and Zn are also bound to varying degrees by organic ligands, although there are considerably less data available on the organic complexation of these metals in the oceans. The lack of analytical technologies sensitive enough to directly characterize these organic ligands at ambient seawater concentrations has restricted research progress in this field until very recently. Siderophores produced by iron-limited bacteria to acquire Fe have been shown previously by CLE-ACSV to have similar measured stability constants as strong Fe-binding ligands (L_1) measured in surface waters (Macrellis *et al.* 2001), and new approaches with LC-ESI-MS and NMR have now detected these siderophores directly in natural seawater (Mawji *et al.* 2008, Velasquez *et al*. 2011). Further, recent incubation studies of natural seawater have documented the production of strong Fe and Zn-binding ligands, presumably by the ambient biota, using CLE-ACSV (Buck *et al.* 2010; Lohan *et al.* 2005), as well as the production of siderophores by bacteria in seawater using LC-ESI-MS (Gledhill *et al.* 2004). This proposal aims to ***combine the strengths of both the biogeochemistry and aquatic organic geochemistry communities to take a substantial step forward in our knowledge of the source and provenance of metal binding ligands in the ocean.***

While most of the focus has been on Fe to date, very little is known about the composition and sources of other essential trace metal-binding ligands. Metal-binding ligands are typically present everywhere in the water column for the bioactive elements, suggesting that they are either highly recalcitrant, and/or a result of passive biological production *in-situ* (*e.g.*, remineralization). In the case of Fe, the bioremineralization of sinking particles contributes iron-binding ligands (Boyd *et al.* 2010), humic substances can bind Fe and may be the source of some Fe-binding ligands in the deep ocean (Laglera & van den Berg 2009), while zooplankton grazing on phytoplankton (Sato *et al.* 2007) and viral cell lysis (Poorvien *et al.* 2011) also release Fe-binding ligands. In surface waters, saccharides, which are an abundant component of the reactive dissolved organic matter (DOM) pool produced by phytoplankton (Benner 2011) have recently been shown to complex dissolved Fe and enhance Fe bioavailability to some phytoplankton (Hassler *et al.* 2011). In addition, hydrothermal input of organic ligands for both Fe and Cu to the deep ocean may be much larger than previously thought (Sander *et al.* 2007, Bennet *et al.* 2008, Sander & Koschinsky 2011), and has only just been incorporated into models for Fe cycling (Tagliabue *et al.* 2010). An over-arching question from these observations is: ***What is the relationship between the source and function of metal-binding ligands?***

The ubiquitous presence of metal-binding ligands, with similar ligand concentrations typically measured by CLE-ACSV for Fe, Cu and Zn, would seem to indicate that at least some of these ligands are not metal-specific (Hirose 2007). This is crucial as recent evidence suggests that Fe availability depends on Cu availability (Peers *et al.* 2005), with the bioavailability of both metals governed by organic complexation; similar synergistic behavior between other trace metals (*e.g.*, Co, Cd, Zn) may also be important. Further, these metal-binding ligands are all a component of the oceanic pool of DOM, which itself is largely uncharacterized other than the operationally defined refractory, recalcitrant and labile components. The working group will ***use compiled field speciation data to assess potential interplays between metal-binding ligands for the suite of bioactive metals and determine which DOM pools would be most appropriate to target for additional insights.***

Members of the working group in this proposal have recently set up a wiki on trace metal speciation data https://portal.ifm-geomar.de/web/tmsis/wiki/ to encourage community discussion of speciation techniques and of approaches to submitting speciation data for a database. Currently, in the absence of structural characterization of ligands, conditional stability constants (determined by measuring the binding capacity of these ligands using CLE-ACSV) provide the only means to distinguish between different ambient metal-ligand complexes in the ocean. The distinction between strong L_1 and weaker

L_2 ligands remains an operational definition that varies between analysts, and is dependent on the method employed and the analytical window applied. Compiling published speciation data for the elements from different analysts will provide a broader perspective for the ligand class divisions and highlight discrepancies between chosen definitions. We additionally propose to enhance the intercalibration efforts pioneered by GEOTRACES with attention toward the other organically bound trace metals (Cu, Co, Ni, Cd, Zn). The compilation of published speciation data combined with continuing intercalibration work for these methods will enable us to better ***characterize measured metal-binding ligand classes in terms of measured conditional stability constants and determine how to best standardize these ligand class definitions for future work.*** The interdisciplinary nature of this working group, including organic geochemists alongside analytical chemists and biogeochemists, will advance our understanding of the limits and potential applications of both CLE-ACSV and LC-ESI-MS/NMR techniques to this problem. Assessing the available data from this perspective will allow insight into ligand sources and functions, as well as an additional framework for incorporating metal-binding ligands into models.

Modelling trace metal distributions is a formidable task at present. A good example is provided by recent attempts to model the Fe cycle, where models were restricted to broad assumptions because of poor knowledge about the speciation of Fe (see review by Boyd & Ellwood 2010). Even less is known about the speciation of other trace metals in the oceans, and these are typically left out of models despite their importance to phytoplankton growth and global elemental cycles. Thus, a primary goal of the proposed working group is to ***assess how to better incorporate metal-binding ligands into biogeochemical models***. Modellers require knowledge not only on the distribution of metal-binding ligands, but also on the speed of reactions between trace metals and these ligands. The database, workshops and interactive webpage will best facilitate evaluation of this issue, the results of which will be presented at the proposed dedicated symposium.

At present, GEOTRACES is primarily focused on accumulating field data for core parameters, including speciation, and does not have the resources to support the necessary synthesis activities proposed here. Therefore, to ensure that GEOTRACES maximally benefits from undertaken fieldwork, it is important that this SCOR working group is established as soon as possible and liaises appropriately with the GEOTRACES Scientific Steering Committee (SSC). Several members of the GEOTRACES SSC are included as members or corresponding members of this proposed working group. The synthesis activities proposed for this working group will both better help in interpretation of data on trace metals and ligands generated on the GEOTRACES cruises, as well as inform sampling and analytical strategies for future efforts. We anticipate that the combined interactions of the proposed working group will culminate in proposals targeting GEOTRACES process studies specifically designed to study ligand dynamics, ideally at an established reference site that may be used as a natural laboratory.

Statement of Work/Terms of Reference

1. To inform the Ocean Sciences community of this WG and related objectives via a widely distributed publication in EOS or analogous journal.
2. To summarize published results on all aspects of metal-binding ligands in the oceans (*e.g.*, distributions, chemical structure, sources, sinks, stability constants), and to contribute to the organic ligand database for use in biogeochemical models and for those working in the field (including results from ongoing GEOTRACES, SOLAS and CLIVAR efforts). The summary will be included in a review paper published after year 2, as well as in the database on the proposed website.
3. To expand upon the ligand intercalibration programme, initiated by GEOTRACES, to evaluate key analytical issues with currently employed methodologies and determine how to best link ongoing efforts in trace metal and organic geochemistry to assess natural metal-binding ligand.

In a recent intercalibration the preservation of samples for Fe and Cu-organic speciation by freezing at -20°C as been found suitable and will enable to make samples taken during GEOTRACES cruises available to interested scientists. A large intercalibration will thus be possible in the future without additional joint cruises or sampling exercises, but could be performed with samples from several 'normal stations' of a GEOTRACES leg. Results from intercalibration efforts will be presented in a manual available via download from the proposed WG website.

4. To identify how best to incorporate published and future data into biogeochemical models.
5. To debate the nature of sampling strategies and experimental approaches employed in laboratory and field efforts from different communities in workshops and meeting discussions to foster cross-fertilization of ideas across groups, capitalize on joint expertise between specialties and ultimately enhance our understanding of the links between the provenance, fate, distribution, and chemistry and biological functions of these organic metal-binding ligands in the oceans.
6. To recommend future approaches to ligand biogeochemistry in a designated symposium, including ongoing GEOTRACES field efforts (i.e., regional surveys and process studies), integration of CLE-ACSV and organic geochemistry techniques, and the need for rapid incorporation of this research in biogeochemical models. Such future recommendations will also be included in the aforementioned downloadable manual. It will also include a series of recommended downloadable digital products on multiple platforms for interpreting ACSV data.
7. To establish a webpage for this SCOR working group, to promote a forum for discussion of ideas and results in form of a blog, soliciting input from the trace metal biogeochemistry, organic geochemistry and modeling communities and provide a platform to propose special sessions on trace metal-binding ligands at international meetings such as Ocean Sciences, AGU and/or EGU.
8. To produce conclusions resulting from the outcome of the above objectives in the form of a Website, a journal special issue or book, and a report to SCOR.

Capacity Building

The recommendations and intercalibration results will be a helpful tool for emerging scientists and newcomers to the field. The WG will additionally foster the exchange of interested scientists from developing countries to spend some time in the laboratories of working group members. Financial support will be sought from bilateral funding agencies (COST, ISAT, BMBF, NSF etc.) to support this exchange. This WG will post a manual for appropriate methodological approaches to ligand studies that interested parties may download directly from our webpage. Furthermore, the blog on the proposed WG webpage will enable newly interested scientists to openly discuss any theoretical or practical questions they may have with the WG members and the wider community. The blog will be password secured via membership.

Meetings, Workshops and Symposia

It is proposed that the first formal meeting of this working group take place before the Ocean Sciences Meeting in Salt Lake City, Utah (Feb. 19-24, 2012). Preliminary communications leading up to this meeting will take place during the preceding year and will lead to identification of additional Associate Members, fine-tuning of the Terms of Reference, and creation of an Agenda. During the meeting, the WG will set up intercalibration efforts and start work on the format for the database and webpage, which will also act as a forum for information exchange and details of new meetings. Other funding sources for the intercalibration efforts, the workshop and final publication will be determined.

Approximately one year after the first meeting a second meeting and an international workshop on trace metal-binding ligands in seawater will be held. This will allow a nominal one-year period over which to structure the workshop agenda, issue announcements and invitations, secure needed funds, and make other necessary preparations. To keep costs at a minimum this would be in combination with

the AGU Meeting in San Francisco, USA (Dec. 2012) The workshop will provide the opportunity for all Full and Corresponding members of the working group to discuss all points of the terms of references. Groups will be formed and tasks assigned to work on projects and prepare material to be presented at the special symposia and in the special issue or separate book.

Full members of the working group will meet again in year 3 to determine the progress made by different groups and discuss necessary actions to successfully present at a dedicated symposium in year 4 during the Ocean Science meeting in 2015. That conference would also set the date for the fourth and final meeting during which the working group will be rounding off the results and outcomes and finalize the publications. Separate funding will be sought from EU-GEOTRACES, COST Action, and other sources for the working group third meeting. Place and exact time for this meeting are to be determined but could again be in combination with the Aquatic Sciences Meeting 2014.

Working Group Membership

The final working group membership is proposed to consist of 10 specialists, which along with the Associate members includes several who serve on the GEOTRACES Scientific Steering Committee (*):

Name	**Affiliation**	**Specialty within the field of trace metal speciation in seawater**
Kristen Buck (Chair 2nd third of 4 year term, vice-chair remaining time)	Bermuda Institute of Ocean Sciences, Bermuda	Trace metal biogeochemist; Organic complexation, expert in CLE-ACSV, bioavailability of trace metals
Maeve Lohan* (Chair 3rd third of 4 year term, vice-chair remaining time)	University of Plymouth, United Kingdom	Trace metal/analytical biogeochemist; organic complexation, expert in CLE-ACSV, flow injection analysis
Sylvia Sander (Chair 1st third of 4 year term, vice-chair remaining time)	University of Otago, New Zealand	Analytical chemist; organic metal speciation by electrochemical methods, LC-ESI-MSMS, hydrothermal systems. Assoc. member of SCOR WG 135
Ronald Benner	University of South Carolina, USA	Aquatic organic geochemist; origin and reactivity of DOM
Katsumi Hirose	Meteorological Research Institute, Japan	Aquatic organic geochemist & trace metal biogeochemist; metal-organic matter interactions
Kathy Barbeau	Scripps Institution of Oceanography, USA	Trace metal biogeochemist; bioavailability and reactivity of different metal species, photochemistry
Ivanka Pizeta	Rudjer Boskovic Institute, Croatia	Pseudovoltammetric determination of trace metal speciation,TM speciation in sediments, solid electrodes.
Martha Gledhill	National Oceanography Centre, Southampton, United Kingdom	Trace metal/organic geochemist; mass spectrometric determination of ligands in seawater, LC-ESI-MS.
Alessandro Tagliabue	France CSIR, Southern Ocean Carbon & Climate Observatory, Cape Town, South Africa	Modeler; models of ocean biogeochemistry
Rujun Yang	College of Chemistry, Ocean University of China, China	Analytical chemist; organic complexation, metal complexation by humics

Associate Members

Stan van den Berg (UK), James Moffett (USA), Phil Boyd* (NZ), François Morel (USA), Barbara Sulzenberger (CH), Ken Bruland* (USA), Mak Saito (USA), Micha Rijkenberg (NL), Peter Croot (UK), Rick Keil (USA), Thorsten Dittmar (Germany), Jay Cullen (Canada), Christel Hassler (Australia)

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