Meeting 1, 25 February 2012
Salt Lake Room, Shilo Inn,
Salt Lake City, UT, USA

SCOR WG 139, General Information

Full Members:
Sylvia Sander (Chair 1st in 4-year term)
Kristen Buck (Chair 2nd in 4-year term)
Maeve Lohan (Chair 3rd in 4-year term)
Ron Benner
Katsumi Hirose
Ivanka Pizeta
Martha Gledhill
Alessandro Tagliabue
Rujun Yang
Kathy Barbeau

Participation not limited to members; to join our email list, please contact Sylvia Sander (sylvias@chemistry.otago.ac.nz)

Associate Members:
Stan van den Berg
James Moffett
Philip Boyd
Mak Saito
Rick Keil
Torsten Dittmar
Micha Rijkenberg
Jay Cullen
Christel Hassler
Ken Bruland
Peter Croot
François Morel
Barbara Sulzenberger

Action Items at end of document.

In attendance: Ron Benner (USCarolina), Mak Saito (WHOI), Rick Keil (UWashington), Christel Hassler (UTech Sydney), Jay Cullen (UVictoria), Jim Moffett (USCalifornia), Phil Boyd (NIWA), Stan van den Berg (ULiverpool), Micha Rijkenberg (NIOZ), Katsumi Hirose (MRI, Japan), Ed Urban (SCOR), Ivanka Pizeta (IRB, Croatia), Thorsten Dittmar (Max Planck), Maeve Lohan (UPlymouth), Sylvia Sander (UOtago), Kristen Buck (BIOS), Martha Gledhill (NOCS; via Skype)

First Meeting Agenda

8.00 am	Breakfast
8.30 am	Welcome and introduction of the SCOR WG 139 – proposed Terms of Reference (TOR) and planned outputs
8.50 am	Short (2min) self introduction of all members with specific focus on their specific expertise field of organic metal binding ligands (oral, no slides please).
9.30 am	Summary on recent progresses in methodology, approaches and models (Sylvia), discussion, additions
10.00 am	Coffee break
10.30 am	Intercalibration approaches past and future (Kristen)
11.15 am	Additional funding sources, where are we at with database (Maeve)
12.00 pm	Lunch
1.00 pm	Groups to discuss specific goals and appoint people to specific tasks.
3.00 pm	Break: cookies and drinks
3.30pm	Feedback from group discussions, continue discussion, possibly regroup
4.30 pm	Report on outcomes of group discussions to all participants and agree on tasks and timelines following this meeting.
	Discuss and agree on deliverables of WG as well as determine second meeting time and place
The end	Finish, stroll to bar

Terms of Reference (summarized from original proposal; *amendments from meeting in italics*)

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, and to contribute to the organic ligand database for use in biogeochemical models and for those working in the field. 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 ligands. 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 ligand 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. *This will 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 the 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.
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.

These Terms of Reference for SCOR WG 139 were accepted as amended.

Overarching, Long-Term Goals

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

Discussion Groups Identified

1. Ligand Database
2. Intercalibration and Methodology, ACSV
3. Other Methodology for Ligand Characterization

1. Ligand Database

Database uses include providing parameters for biogeochemical modelers and facilitating the evaluation of trends in ligand parameters between ocean basins and biogeochemical provinces.

Ligand parameters and related information requested by modelers:

- K, [L], chemical structure, bioavailability, biological function within cell, sources and sinks of L, kinetics of formation and decay, impact on residence time of M
- What is the difference in these parameters between L1 and L2

Some of this information is available now; access would be facilitated by the proposed database. However, need to connect distinct approaches (see box figure from SS) for more complete answers.

Reviewed example of previous database, Trace Metal Speciation in Seawater (TMSIS) Wiki, portal.geomar.de/web/tmsis/wiki

It was suggested that someone be hired to initiate the proposed database and assist in data acquisition from participants.

It was noted that NSF and other funding agencies are increasingly pushing incorporation of data into accessible databases, and several large databases in existence for this (e.g., BCO-DMO in US, BODC in UK). Our database should be made compatible with these larger databases, and ideally be linked.

It was agreed that our database should start with one or two locations with overlapping organic and metal speciation data to identify which parameters to include and which should be linked to separately. Time-series stations were identified as a good starting point, specifically BATS in the North Atlantic and Line P in the North Pacific.

2. Intercalibration and Methodology, ACSV

Intercalibration has been conducted for Cu speciation by ACSV and ASV (Bruland et al. 2000; Buck et al. under review) and for Fe speciation by ACSV (Buck et al. under review). For both Fe and Cu speciation, similar methods within the same analytical window compared well, although more participants are desired. Freezing speciation samples appears to be a suitable storage technique for Fe and Cu speciation samples from the open ocean. The analytical window applied strongly influences Cu speciation and may impact Fe speciation measurements as well, although this remains uncertain. There was a distinct difference in the Fe speciation results from deep (1000 m, 3000 m) samples between SA and TAC methodologies that may reflect an interference of humics in the TAC measurements, or an analytical window effect. The nature of this difference, however, remains unresolved and requires a more thorough assessment of deep waters in future intercomparison exercises.

The group agreed that there were some "best practices" for ACSV approaches that are currently known but not necessarily published and should be made available for review and further input. The group also identified several aspects to ACSV measurements that could be assessed by multiple groups on individual samples to assess insight on the different methods employed.

Three basic intercalibration exercises were proposed from the WG discussion:

1. Independent interpretation of simulated metal speciation data as an assessment of variability in interpretation of the same titration data across analysts and techniques;
2. Lab-based intercomparison of metal speciation results from a homogenized UVSW sample amended with a natural DOM extract and/or SRFA reference material;
3. Field-based SAFe-style intercomparison for ACSV techniques for Fe, Cu, Co, Zn, Ni (as possible with range of interested analysts)

Thorsten Dittmar volunteered a DOM extract his group has collected from deep water near Hawaii; this will need to be tested by ACSV first to ensure no inherent problems with approach. It was noted that the Suwanee River Humic or Fulvic Acid reference materials have recently been employed as standards in ACSV methods for humic substances, and this may be a useful standard for comparisons.

It was agreed that voltammetric analysts present would attempt some intercomparison exercises within their own methods on samples currently in their labs. Examples included assessing the effect of pH (i.e., using usual buffer vs. buffers for ambient sample pH) and purging (vs. not purging).

It was agreed that trace metal clean uv-oxidized seawater would be more useful for the lab-based intercomparison than artificial seawater. The Bruland lab was proposed as a possible source for such seawater.

A field-based intercomparison will require separate funding and broad participation. Funding options will be explored over the next 12-15 months, with an aim at a cruise in late 2014/early 2015. In the meantime, Sylvia Sander offered to investigate the possibility of collecting seawater on the upcoming NZ GEOTRACES Process Study cruise in 2012, freezing samples at -20º C and distributing to interested analysts.

3. <u>Other Methodology for Ligand Characterization</u>

Within organic geochemistry, two general approaches to ligand characterization were identified:

1. Examination of individual molecules isolated from seawater matrix for structure
2. Examination of bulk material by functional group or other structural character

Different techniques are applied to these two approaches, with suites of possible methodologies.

Other direct approaches may include pseudo-polarography and cyclic voltammetry. Indirect approaches include photochemistry, manipulation experiments and process studies to identify availability of metal complexes with ligands characterized.

It was noted that filtering (size-fractionation) is a crucial component between approaches, and we need a clear assessment of the operational definitions between methodological groups.

ACTION ITEMS (ANTICIPATED TIMELINE IN PARENTHESES)

Ron Benner

- (Aug 2012) Identify target year and season for BATS data compilation, with P. Boyd
- (Aug 2012) Collate DOM data and references from targeted BATS studies

Phil Boyd

- (Apr 2012) Summary page of candidates for metal-binding ligands with references
- (Aug 2012) Identify target year and season for BATS data compilation, with R. Benner
- (Aug 2012) Identify possible 'omics data resources for BATS and Line P, with J. Moffett
- (Aug 2012) Write Job Description for database coordinator position
- (Feb 2013) Investigate options to coordinate our database/ database format with BODC

Kristen Buck

- (Apr 2012) Pass BATS database website information to R. Benner and P. Boyd
- (Apr 2012) Investigate UVSW options with K. Bruland

Jay Cullen

- (Apr 2012) Summary page of metal-biology relationships, substitutions and antagonisms
- (Aug 2012) Identify target year and season for Line P data compilation, with R. Keil

Thorsten Dittmar

- (Sep 2012) Summary page(s) with references on organic geochemistry techniques employed for ligands, target DOM classes for ligands, and related terminology

Rick Keil

- (Aug 2012) Identify target year and season for Line P data compilation, with J. Cullen
- (Aug 2012) Collate DOM data and references from targeted Line P studies

Maeve Lohan

- (Apr 2012) Summary page of SAFe metal profiles with references
- (Apr 2012) Pass list of operational definitions and size fractionation terminology with references to R. Benner, R. Kiel and T. Dittmar
- (Aug 2012) Collate metals data and references from BATS studies

Jim Moffett

- (Apr 2012) Summary page of current best practices for ACSV measurements
- (Aug 2012) Identify possible 'omics data resources for BATS and Line P, with P. Boyd

Ivanka Pizeta

- (Apr 2012) Provide simulated titration data for interested parties to interpret, with S. Sander

Mak Saito

- (Apr 2012) Summary page of ACSV and ACSV interpretation approaches in use, with references and people/labs currently active

Sylvia Sander

- (Apr 2012) Provide simulated titration data for interested parties to interpret, with I. Pizeta
- (Sep 2012) Summary page(s) with references on electrochemistry techniques employed for ligands, information provided by these techniques

Ed Urban

- (Feb 2013) Identify funding sources for database coordinator