1. Introduction

The Working Group met at Tulane University for a full day on 21 February, and hosted a Town Hall meeting at the Ocean Sciences Meeting on 22 February. The meeting agenda is given at Appendix 1.

2. Scope of the planned review of marine speciation modelling

A draft manuscript with contributions from WG members, as identified at the first meeting, had been circulated in advance. The final version will be submitted to the Frontiers in Marine Science, Special Issue organised by WG139. The submission deadline is 31 March.

Review of the draft manuscript identified a number of points that should be addressed before submission. These are listed in short form, together with the WG members tasked with carrying out this work:

- the manuscript needs an extended introduction explaining why chemical speciation is important, most particularly in connection with global change (**David Turner**)
- define the priority levels used in the manuscript for the different environments that we describe
- this should be accompanied by 2 case studies focusing in iron (**Sylvia Sander**) and pH (**Simon Clegg**)
- an explanation of why the Pitzer approach is chosen, together with a summary for the non-specialist (**Simon Clegg**)
- the list of components should begin with a definition of the core components (seawater electrolyte and pH/weak acids) that modelling of all other components relies on (**David Turner**)
- a discussion of natural organic matter (**Stan van den Berg** & **Sylvia Sander**) including its effect on alkalinity (**David Turner**)
- a discussion of uncertainty, in particular that the required level of uncertainty will differ for different applications (**Simon Clegg** & **David Turner**)
- editing: the manuscript needs editing to stand as a coherent document rather than a collection of contributions (**David Turner** & **Maite Maldonado**)

The new and revised text sections will be completed and deposited in the Dropbox by March 11 at the latest. Members of the WG who were not part of the original writing are welcome to join the writing team by contributing text that helps to address the points listed here.

3. Planning the review of existing seawater, and seawater-related, Pitzer models

Little progress has been made since the first meeting. A number of key data gaps can be identified without significant extra work: this will be done by the end of March and then communicated widely. The document describing these gaps, and experiments needed to fill them, now exists in draft form. Responsible: **Simon Clegg**, **Andrew Dickson** & **David Turner**

4. Other activities to maximise the visibility of WG145 activities in the marine science and chemical communities

The following actions, agreed at the first meeting, have been carried out:

- A WG website has been set up, hosted at Otago University
- A Special Session on speciation modelling at the Ocean Sciences Meeting 2016 (24 February) has been organised together with WG139

- A Town Hall meeting at the Ocean Sciences Meeting 2016, held on 22 February
- Establishment of a mailing list of interested scientists.

The planned article in Frontiers in Marine Science is discussed above. Shorter news articles with be submitted as follows:

- An article presenting the WG and scope in *EOS* (**David Turner** to make contact and coordinate writing)
- An article presenting the WG and scope in *Chemistry International* (**David Turner** to make contact and coordinate writing)
- An article presenting the WG and scope in *Elements* (**Sylvia Sander** to make contact and coordinate writing)

5. External funding opportunities

The investigation of external funding opportunities did not identify any appropriate non-traditional funding sources. At the time of the meeting, two major initiatives were underway:

(i) A Visiting Professorship (10 months) for Simon Clegg at the University of Gothenburg. This is a national Swedish call covering earth and marine sciences and ecology. One Visiting Professorship will be funded. The application has been submitted, decision due in November.

(ii) A joint NERC-NSF project (PI:s Simon Clegg, Andrew Dickson, Heather Benway, Frank Millero). A Letter of Intent has been submitted in advance of a full proposal in July 2016.

Another opportunity that was identified is a Humboldt Visiting Professorship for Simon Clegg in Kiel (with Eric Achterberg). This is being pursued.

6. Review of existing speciation modelling programs

Following the first meeting, the user interface of a number of programs was reviewed, and these were presented at the meeting as follows:

Program	Reviewer () = not at meeting	Presenter
CO2SYS	David Turner	Eric Achterberg
E-AIM	Mona Wells	Mona Wells
ERSEM-CO2	(Yuri Artioli)	(not presented)
GIVAKT	(Adam Ulfsbo)	David Turner
JESS	(Darren Rowland)	(not presented)
KINETEQL	(Angel Ruacho & Randy Bundy)	Ivanka Pizeta
PHREEQE	(Darren Rowland)	David Turner
PROMCC	Ivanka Pizeta	Ivanka Pizeta
Visual MINTEQ	Sylvia Sander (Martha Gledhill)	Eric Achterberg
WHAM	Sylvia Sander	Sylvia Sander

Two programs that have been reviewed, JESS and ERSEM-CO2, currently lack user-friendly interfaces and were therefore not included in these demonstrations.

Frank Millero presented the new Excel-based version of the MIAMI model program, and explained that it is planned to make this program freely available at an appropriate website. It currently calculated speciation of a large number of elements at given salinity and temperature, specifying also sulphide and phosphate concentrations. It is planned to extend the program to include the effect of pressure on equilibria.

The ensuing discussion on program features that contribute to user-friendliness identified graphical output as playing an important role. It was, however, recognised that the best form for input and output will depend on the user's application. This led to the identification of four levels of usage:

- Black box: a fixed program configuration calculates the equilibrium speciation based on inputs of salinity, temperature, composition etc.
- Additions to database: for example a user wishing to add additional metal binding ligands, or to alter the composition of the seawater from its normal stoichiometry.
- Large scale: processing large amounts of data, e.g. from major cruise programmes.
- Professional: calling the model from other applications, potentially also making code changes as well as alterations to the chemical database.

In addition to these different types of usage, the scientists using the model can be expected to have varying levels of expertise which implies the need for well-designed and tailored "help" information and example calculations on the website.

7. Obtaining feedback from the marine science community

The first stage in this process was the Town Hall meeting held on 22 February. The introductory presentation is reproduced in Appendix 2.

The Town Hall was attended by 70 participants including WG members; the participants' email addresses were collected in order to extend the WG's mailing list. The meeting was strongly supportive of the WG's aims. When asked which usage category/categories they belonged to, a show of hands gave the following approximate percentages: Black box 75%; Additions to database 60%; Large scale 50%; Professional 10%.

The inputs from the audience identified three themes of broad interest:

- Speciation calculations in nearshore and estuarine waters where the composition departs from diluted seawater, most particularly in respect of the CO_2 system.
- The thermodynamics of redox reactions.
- Incorporation of speciation calculations into kinetic models.

Additional themes suggested were:

- Organic vs. inorganic complexation of trace metals.
- Palaeooceanographic applications (e.g. exploring changing Mg/Ca ratios).
- Reversible vs. irreversible scavenging.
- Sulphides in oxic waters.

The following comments were made concerning the user interface:

- Additions and changes of options should be able to be made through the user interface where possible (as opposed to within the code, for ease of use).
- Documentation, training materials and examples are essential, both for the non-expert user and to make the programs available for university courses
- Flexibility in input/output formats is important (e.g., Excel as well as text files, in addition to web-based)
- For the large scale applications, outputs should be ODV-compatible.
- Provide information on the uncertainties in the calculated results.
- The program(s) should be available in downloadable form for use out of contact with the internet (cruises).

This first survey will be followed up by a Survey Monkey with the assistance of Ed Urban at SCOR.

8. Plan for the next meeting

The next meeting will be held in conjunction with the 2017 EGU meeting (Vienna, 23-28 April): a WG meeting is best held before the EGU meeting starts. A key aim for that meeting is to assess what can realistically be achieved by the WG given the resources available following the outcome of the proposals submitted.

Appendix 1: Meeting programme

Participants

David Turner (chair)
Simon Clegg (vice-chair)
Sylvia Sander (vice-chair)
Eric Achterberg
Heather Benway
Arthur Chen
Andrew Dickson
Vanessa Hatje
Maite Maldonado (via Skype)
Frank Millero
Ivanka Pizeta
Alessandro Tagliabue
Rodrigo Torres
Stan van den Berg
Christoph Völker
Mona Wells
Ed Urban (SCOR)

Programme

9:00 Review minutes of the first meeting

9:15 Review the draft paper describing the proposed model scope and priorities
Updates are accumulating in the Dropbox: an edited revision for review at the meeting will be posted on Monday 15 February. We will need to discuss how we justify the priorities that have been proposed.

10:30 Coffee

11:00 Review publication plans
Frontiers Special Issue, popular science / news items

11:30 Review of funding opportunities and initiatives under way

12:00 Demonstration of the good/desirable user-friendly features of the program that have been reviewed (see table below for details: max 15 minutes per program including discussion). Here we are focusing on the **user interface**.

13:00 Lunch

14:00 Demonstration of the good/desirable user-friendly features of the program that have been reviewed (continued).

15:00 Presentation by Frank Millero of his new program

15:30 First synthesis of good/desirable features

16:00 Coffee

16:30 Review of Town Hall presentation (22 February)

17:00 Review of progress against the Terms of Reference

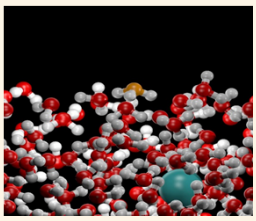
17:30 Plans for future meetings

18:00 (latest) Close of meeting

MARCHEMSPEC, MARine CHEMical SPECiation

SCOR Working Group 145

Chair: David Turner (Gothenburg, Sweden)
Vice-chairs: Simon Clegg (Norwich, UK); Sylvia Sander (Dunedin, New Zealand)



Chemical speciation – a cornerstone of marine chemistry

An element's chemical reactivity and biological availability depend on its chemical speciation.

Among the most important equilibria in seawater:

- **those controlling pH and the speciation of the carbonate system**
- **those controlling the speciation of trace metals (micronutrients and/or toxins)**

Important applications include understanding the chemical responses to global change, not least in vulnerable environments such as coral reefs and polar waters

Why is understanding chemical speciation a challenge?

- The concentrations of many key chemical species (e.g. $CO_2(aq)$, HCO_3^-, CO_3^{2-}, Cu^{2+}…) cannot be measured directly.
- We therefore require a "model" comprising chemical equations (most commonly Pitzer equations) that calculate activities from temperature, pressure and solution composition
- These models are based on a wide variety of experimental data from simpler solutions, and can be used to calculate speciation in all natural waters (subject to the availability of the necessary data)
- Developing accurate models of this type therefore has many potential applications and benefits. This is the subject of SCOR Working Group 145

SCOR Working Group 145

MARCHEMSPEC goals

- To document the current status of Pitzer models of seawater, and to identify key gaps in knowledge
- To specify the functions and capability of a user-friendly web-based modelling tool for chemical speciation calculations
- To implement the web-based modelling tool
- To present our work to the wider marine science community

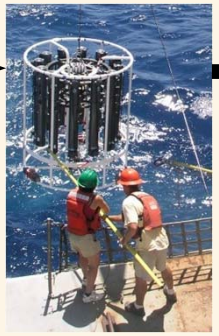
  (.. and receive feedback)

SCOR Working Group 145

Role of Chemical Speciation Models

1. Calibrate

2. Measure



3. Interpret & Predict

Chemical Speciation Modelling

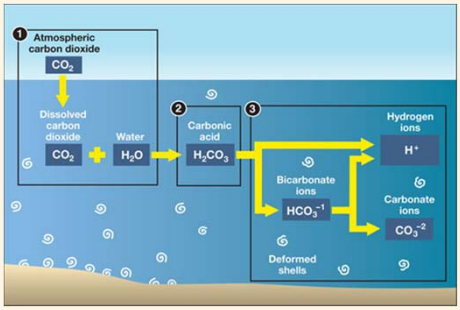
The "models" can be as simple as empirical equations such as CO2Calc ("*user-friendly seawater-carbon calculator*"), or as complex as a Pitzer ion interaction model in which concentrations of all species can be varied individually (deviations from seawater composition).

SCOR Working Group 145

Which Chemical Species?

The minor, but very important, species which are involved in equilibria and whose behaviour is complex.

- **pH** (carbonate, sulphate, borate, fluoride species)
- **Carbonate system**: CO_2 uptake, pH, carbonate mineral solubility (H^+, CO_2, HCO_3^-, CO_3^{2-}).
- **Nutrients and trace metals** (complexation and availability, mainly Fe, Cu, Cd, Co, Mn, Zn).



These properties and equilibria vary as functions of:

- **Salinity**,
- **Temperature**,
- **Pressure**, and
- **Composition** (for environments differing from seawater stoichiometry)

Speciation Equilibria – Bicarbonate Example

$$K^*_{HCO_3} = [H^+] \cdot [CO_3^{2-}] / [HCO_3^-]$$

Empirical Eqns as f(*T, S, P*), e.g. CO2Calc.

$$K^*_{HCO_3} = K_{HCO_3} \cdot \gamma HCO_3^- / (\gamma H^+ \cdot \gamma CO_3^{2-})$$

K_{HCO_3} is f(*T, P*) only.

The "γ" are activity coefficients (they are f(*T*, *P*, *x*)).

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Purpose of the Speciation Model

$$\gamma HCO_3^- , \gamma H^+, \gamma CO_3^{2-}, \gamma CO_2, \gamma HSO_4^-, \gamma SO_4^{2-}...$$

The job of the chemical speciation (Pitzer) model is to calculate γ for all species of interest for any *T*, *P*, and solution composition, inc. variations from seawater stoichiometry, and hence determine chemical equilibrium and speciation in the solution.

These include: H^+, HCO_3^-, CO_3^{2-}, CO_2, HSO_4^-, SO_4^{2-}, $B(OH)_4^-$, $B(OH)_3$, F^-, HF.

Sounds like a lot of work, so why bother....

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Benefits of a Comprehensive Speciation Model (1)

Integrate, within a single self consistent model, the calculation of:

(1) Speciation in buffers used for calibration (pH)

(2) pH (on its different scales, hence interconversion)

(3) Carbonate equilibria and $CaCO_3$ saturation,

(4) Trace metal complexation and availability

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Benefits of a Comprehensive Speciation Model (2)

Apply across many environments:

1. Ocean Water Column

2. Estuaries & Shelf Seas

3. Sea Ice Environments

4. Pore Waters

- Wide variations of ***T***, ***S***, and ***P***.
- Deviations from seawater composition.
- Very challenging to quantitatively understand the chemistry of individual ions and molecules.

The Pitzer Model (1)

There are two ion-interaction “Pitzer” models:

The Models

1. “Miami” model of Frank Millero and co-workers (developed since 1993, most comprehensive).
2. Clegg and Whitfield model (1995, created to calculated NH_3 speciation in estuaries and seas).

How are they constructed?

- The models contain interaction parameters that must be fitted to data for aqueous solutions containing the solutes of interest.
- Both are based upon large array of activity and thermal data for single electrolyte solutions and mixtures at different temperatures; and use model parameters drawn from other studies (often for salt solubilities in brines).

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The Pitzer Model (2)

Why are such models not already in widespread use?

Scientific reasons

- Activity coefficients are expressed sums of interactions between all pairs and triplets of ions and uncharged solutes in the solution.
  So data for a very large number of solutions are needed to determine values of binary and ternary parameters expressing these interactions.
- It can be hard to relate uncertainties in these original data to uncertainties in model-calculated speciation.
- More measurements and validation are needed for a comprehensive coverage of marine conditions, and buffers used for instrument calibration.

Practical reasons

- Complex computer codes are rarely either easy to use, properly documented, or widely distributed.

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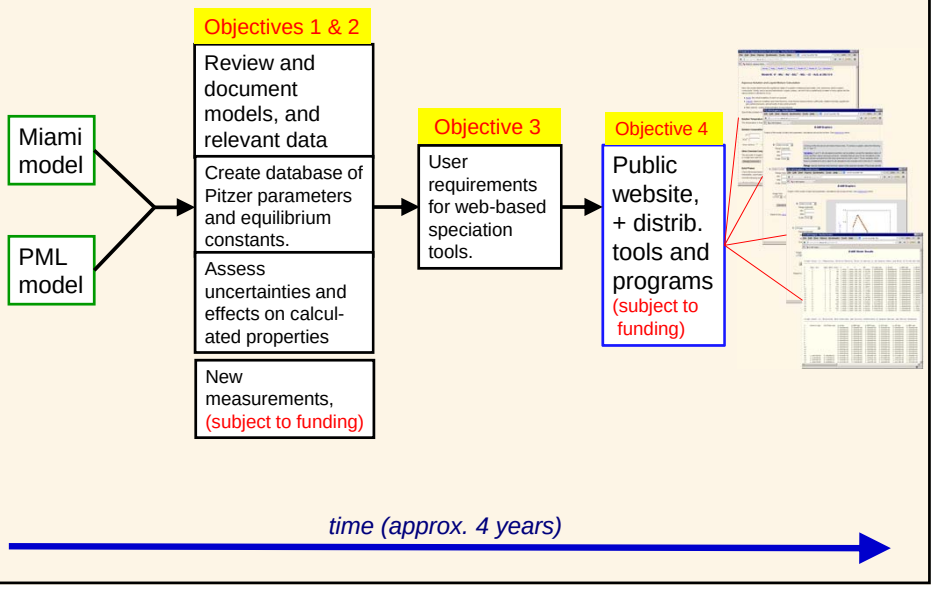
This Working Group



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Why Now?

(1) Need: ocean acidification isn't going away. It's effects are diverse and complex, and will be felt in many marine environments. An accurate, self-consistent, model that can be applied from oceanographic measurements (arctic, tropics, open ocean, estuaries) through to prediction of the effects will be invaluable.

(2) Expertise: there are relatively few people both experienced in the use of the model and with a deep knowledge of the thermodynamic literature and data. Most of these are either late in their careers of retired.

Why do **YOU** need speciation modelling?

What type of marine environment?

What scientific problem?

What chemical species?

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What kind of speciation modelling program do you want?

1. Black box (simple input – output)
   In: [DCu], T, S, P, pH
   Out: Cu-speciation
2. Make changes to database
   e.g., add ligand parameters
3. Import large datafiles and (re)calculate
   e.g.calc TM speciation for large datasets
4. The Pro: make changes to the code

What are features you want or don't want?

1. Black box (simple input – output)

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What are features you want or don't want?

2. Make changes to database
   e.g., add ligand parameters

What are features you want or don't want?

3. Import large datafiles and (re)calculate
   e.g. calc TM speciation for large datasets

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What are features you want or don't want?

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