

## MORNING SESSION

*The material presented during the morning can be found at the end of this report, so these notes summarise the discussion only.*

### 1. Review Terms of Reference (David)

- The ToR describe our commitment to SCOR, based on the Working Group proposal. Progress towards fulfilment is reviewed in #10 below.

### 2. WG Timeline (Simon)

- Discussion points have been moved to the relevant detail sections.

### 3. Pitzer model overview (David)

- Questions: can the model include precipitation reactions and sea-ice systems? David and Simon explained that these are potential extensions to be considered in the future (the solver used is readily applicable to precipitation reactions), and the output from the current model can readily be used to assess the saturation state of specific solid phases. It was pointed out that calculations of the model below 5°C are hampered by lack of data: they can be done, but accuracy is reduced relative to temperatures closer to 25°C.
- The lack of adequate data on the interactions of TRIS and TRISH<sup>+</sup> with the components of artificial seawater provided the starting point for new measurements discussed in sections 4 and 5.
- Wei-Jun took up the problem of modelling very low salinity waters, in particular the transition between total scale pH measurements in saline waters and NBS scale measurements in fresh waters. The total pH measurements do not extrapolate to the measured NBS pH in freshwaters. The discussion concluded that this is because the NBS scale, unlike the total pH scale, is not concentration-based (rather, it is a measure of H<sup>+</sup> activity), indicating an incompatibility between pH measurements in saline and fresh waters. This would be a good topic for discussion in the upcoming IAPSO Study Group (#10 below).

### 4. Solubility Experiments (Pablo)

- Analysing and modelling the results of the extensive measurements of solubilities in the TRIS/NaCl system have proved problematic: inclusion of the unusual TRIS-TRIS-Na interaction provoked discussion. This is the result of a data fitting exercise and does not provide any evidence of a physical interaction: this would require other methods such as spectroscopy, but is not needed for our purposes.
- Andrew asked about TRIS-Na complexation as an alternative approach. Simon replied that the TRIS-Na interaction is relatively weak and best treated with Pitzer coefficients, while Ca and Mg interactions are much stronger (with negative coefficients), which are generally indicative of complexation. Indeed, complexation of Mg<sup>2+</sup> by TRIS has been measured in the past.

- David reported that Flo Gregson at Bristol University has recently measured the osmotic coefficient of TRIS in water at a range of concentrations well into supersaturation. In the range 1 – 10 mol/kg, these data are well fitted with interaction coefficients for TRIS-TRIS and TRIS-TRIS-TRIS. Preliminary results from the inclusion of these coefficients in our data analysis indicates a much improved quality of fit at TRIS concentrations up to 6 mol/kg, but large residuals at higher concentration. If confirmed, these data would indicate that TRIS self-interactions at higher concentrations are not readily explained by the current Pitzer formulation. However, this problem encountered at high concentrations is not relevant to modelling of TRIS buffers in artificial seawater. Furthermore, the Bristol measurements have large uncertainties, and not consistent with a small set of isopiestic measurements of the osmotic coefficient.
- Arthur asked whether TRIS would interact with organic acids in coastal systems. Almost certainly, but here we are only aiming to model TRIS in organic-free artificial seawater.

#### **5. Collaboration with National Metrology Institutes. (Simon)**

- Daniela described the JPI intercomparison that was noted on the second LNE slide. This was for pH, and she spoke of 3 "nodes": primary standard; calibration laboratories; and end users making observations. At the "calibration" level the solutions were measured by IFREMER, IOW and NIVA. LNE calculated the uncertainty budget for pH measured potentiometrically. NIVA encountered technical problems. Data are still being processed.
- Frank discussed a traceability chain for pH(T), and referred to the work on low salinity buffers with IOW.
- Regina reported that purified m-cresol (99.95% purity) has been bottled, but not yet priced. NIST are carrying out experiments in which the ratio of TRIS to TRISH<sup>+</sup> is varied giving pH values in the range 7.3 to 8.2. The temperature range is 5 - 45°C.

#### **6. Best practices paper on chemical speciation modelling (David)**

- There was general support for the revised paper outline, with the preferred journal still being *Frontiers in Marine Science* and their Best Practice topic. Eric noted that the publication charge for this topic has been reduced. SCOR funds only one publication charge per Working Group, so since this would be our second paper we need to look elsewhere for funds.
- The paper should include illustrate the argument with real-life examples. Estuarine systems, where CO2SYS can struggle, would be a good starting point. It was emphasised that such concrete examples in the paper, with step by step instructions for repeating the calculations, are essential.
- A key advantage that should be illustrated is the ability to model the CO<sub>2</sub> system and trace metal speciation in an integrated fashion. Regular CO2SYS users – those who work almost exclusively with seawater of standard

composition - are expected to be one of the harder groups to convince of the merits of our approach.

- The discussion of uncertainties should be placed in context of user needs – what levels of uncertainty are acceptable for specific applications.
- The potential for using the software as a management tool / decision support tool when interpreting environmental monitoring data should be highlighted (e.g., pH used as an indicator variable of "good environmental status").
- Stoichiometric and thermodynamic approaches and not necessarily mutually exclusive; e.g. stoichiometric constants may need to be incorporated where data are scarce, and the thermodynamic approach can be used to adjust measured stoichiometric constants for changes in the composition of the ionic medium, i.e., to that of the natural water of interest. The demonstration programs we have placed on the web are an example of this
- Documentation of all the constants and coefficients used in the model is essential in order that speciation calculations can be repeated, and that complementary calculations can be made using exactly the same model.

#### **7. Software tools and codes (Simon)**

- Andrew asked whether it would be possible to include uncertainties in the input composition in the overall uncertainty budget. Simon agreed that this is important to include, and will be added to the model
- Andrew also asked whether the concentrations of  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  could be used as composition inputs for inorganic carbon. Simon replied that this would be possible if needed. It was noted that this option is to be included in CO2SYS.
- The presenters should collect comments and suggestions from the “software testers” at the SCOR booth.

#### **8. IAPWS/SCOR/IAPSO Joint Committee on Seawater (Andrew)**

- The new IAPSO Study Group may contribute to our compilation of knowledge gaps and research needs

#### **9. NICA-Donnan modelling of marine OM (Martha)**

- David asked about interactions with Ca and Mg – initial measurements suggest that these are too weak to measure
- Peter asked about the preconcentration method – the column used takes up primarily hydrophobic material, about 40% of the total DOC. Discussion of the possibility of also targeting hydrophilic material.
- There was some discussion to dispel the misapprehension that this type of model could be applied to TRIS thermodynamic behaviour.

#### **10. Progress on ToR (David)**

- No specific discussion: actions arising are documented in #11 below.



## AFTERNOON SESSION

### 11. Completing the ToR

A realistic timescale for fulfilling the remaining elements of ToR is the time period of the NERC/NSF project, which provides the major framework and funding source for this work. Following extension, the project is now planned to run until February 2022. Although our SCOR money has all been used, we see that continuation of our status as a SCOR Working Group until early 2022 would be a win-win arrangement:

- SCOR would benefit from the 2022 software release being clearly labelled as a SCOR product
- The SCOR association would enhance the status of the software release, substantially improving the prospects for adoption by the marine science community

The case will need to be out to SCOR in our annual report, which will be due in April/May. The SCOR meeting is in October, after which we will get a response to our proposal. Important points that should be made in addition to the win-win argument:

- We have attracted external funding central to our ToR (NERC/NSF project)
- We have attracted collaboration from partners who provide substantial additional support from their own resources (NMIs, GEOMAR)
- We have been very productive, and are on course to fulfil our ToR within the coming 2 years
- We should state what additional achievements, over and above the current ToR, there will be if we are granted an extension. Example: the improvements to the models made using the data provided by our NMI and GEOMAR partners.
- We have established effective collaboration with JCS; we have a strong presence in a recently approved IAPSO Study Group on seawater pH measurements; we have been invited to participate in a planned GESAMP Working Group on the effects of climate change on contaminants in seawater
- Collaboration within the WG and our partners has generated a community of marine speciation scientists who are keen to continue collaboration in the longer term
- The unusually long WG lifetime that we are proposing is in large part due to the time taken to generate the necessary external funding in the form of the NERC/NSF grant, and to accommodate the timetables of our partners. The need for external funding, and the risk that it would result in delays to the WG work, was highlighted in the WG proposal.

The work remaining to fulfil our ToR commitments to SCOR can be organized under four headings (see # 10 in the morning material):

- a) Extend the model to trace metals (the GEOTRACES core metals) and key organic ligands.

Inorganic complexation of trace metals is included in the Pierrot & Millero model, but the data sources and coefficient values should be confirmed as has

been done for the TRIS/artificial seawater and seawater electrolyte systems as described in #3 of the morning material. The key (CLE/CSV) ligands are more challenging since earlier searches by David and Peter have noted that the thermodynamic data are sparse and /or scattered. Martha's project (morning material #9) will provide some information on complexation by natural organic matter. Peter also noted that WG139 has assembled a good deal of data on trace metal complexation by marine organic matter.

**Lead responsibility: David and Peter**

b) Document major knowledge gaps

Much of this has already been done, but not documented in a complete form. The organic ligands discussed above will probably contribute. Paper(s) describing the software, and the uncertainty treatment, may provide routes to publication.

**Lead responsibility: Simon**

c) Complete the Best Practice paper

The outline in the morning material #6, together with the discussion earlier in this report, give the guidelines for this work. The work will be carried out by two groups:

Writing Group: David, Simon, Matthew, Andrew and Eric

Internal review group: Peter, Wei-Jun, Arthur, Regina and Maite

**Lead responsibility: David**

d) General release of the software in early 2022

This will not be in any way a final version, but will provide much of the planned capabilities. We discussed options for a high-profile launch of the software. One obvious option is the next OSM (February 2022), but this will be in Honolulu. Difficult for us with no remaining SCOR funding; it is also generally a less attractive location due to cost and long travel times. We therefore concluded that Webinars would provide a better option. Here we need to target two communities: operational oceanographers and research oceanographers. Operational oceanographers can be targeted by contributing to the GOOS Webinar series. For research oceanographers we can use our existing contact fora (SCOR, OCB, GEOTRACES etc.). Heather has access to software for Webinar generation. Peter raised the question of raising awareness outside Europe and North America. Unfortunately our South American members were unable to come to San Diego. David suggested that we talk to Elena Masferrer Dodas at the GEOTRACES IPO who organized excellent advance publicity for the launch of the first GEOTRACES data product as an OSM Town Hall.

**Lead responsibility (software): Simon**

**Lead responsibility (Webinar and PR): Heather**

We also discussed upcoming meetings where it would be good to have a presence:

- High-CO<sub>2</sub> World Meeting Sept 7-10 (Lima) – abstracts due in March. Andrew and Matthew may attend. This meeting clashes with the next JCS meeting in Turin: Simon will probably go to the Turin meeting
- GOA-ON meetings just before the High CO<sub>2</sub> World Meeting (also in Lima). Andrew may attend
- ICOS meeting, Utrecht, September. Matthew may attend if not going to Lima
- CERF meeting in Fall 2021, Richmond, VA. Regina will attend.

## 12. Plans and timelines for ongoing activities

- The NERC/NSF project.
  - Finish the core science (uncertainties)
  - Coding for the 2022 software release
  - Paper on uncertainties
  - Contribute to writing up existing data from NMIJ and GEOMAR (Pablo)
  - Following Ellen's resignation, work on the Harned cells at SIO has progressed very slowly, although some testing is being done to resolve the difficulties recently encountered (and likely attributable to the Cl<sup>-</sup> electrode). There are ongoing discussions as to how we should proceed.
  - There are no solid plan to address the bisulphate constant, which is however important. Simon noted that the uncertainty can make a difference of 0.01 in calculated pH.
- National Metrology Institutes
  - The intercalibration of Harned cell measurements needs to be completed
  - NMIJ have already contributed their planned Harned cell measurements
  - LNE cannot provide new measurements without external funding
  - PTB: in other conversations Frank said they still haven't got to the bottom of the offsets they are encountering in measured emfs, which are just outside the acceptable range. This will probably delay the WG 145 experiments, due to a backlog of other work, but PTB are committed to contributing the planned WG145 work
  - NIST have Harned cells ready, with electrodes working well. Highest priority is the measurements under way (see #6 above), which must be finished by June. After that there is scope for additional Harned cell work in support of WG145.
- GEOMAR
  - Pablo: priority is to write up the solubility data together with David and Simon. Additional work (e.g. TRIS-Mg and TRIS-Ca interactions) would need new money
  - Martha: more testing of Ca and Mg interactions; will have data to look at organic contributions to total alkalinity but this is not a priority. Work will focus on variability in the preconcentration and characterization of pre-concentrated DOM; improving methods for



metal-pH titrations; and applying this knowledge to test environments (e.g. the Amazon estuaries)

- The IAPSO Study Group led by Andrew will meet in conjunction with the next IAPSO conference in Korea, July 2021, following the preliminary meeting in San Diego this week.
- The Joint Committee on Seawater will continue to focus on SI-traceability of seawater pH measurements. Here Daniela took up the question of the use of Pitzer equations vs. the Bates-Guggenheim hypothesis to define chloride activity coefficients needed to obtain pH from measured acidity functions of pH buffers. A discussion is ongoing, but it may be possible to determine in which ionic strength range the two approaches provide closely similar values. A difficulty, however, is that it is unlikely that there are Pitzer parameters for solutions of the substances used, even for common pH buffers.

### 13. New initiatives

- Sylvia reported on a proposed GESAMP Working Group on effect of climate change on contaminants in marine system, to include Ocean Acidification and knock-on effects on speciation and solubility, including radionuclides. The proposal has been well received and is expected to be approved at the upcoming GESAMP annual meeting in Monaco in September. The proposal will be highlighted in a side event at the GESAMP meeting. WG145 is welcome to participate in the side event and in the new WG if approved. David, Peter and Eric expressed interest. Sylvia will pass on further information to the SCOR WG.

### 14. Future collaborations

- Most of those present expressed in remaining in contact even after we lose SCOR affiliation. Since we have no funding for this, we will focus on virtual meetings and opportunistic in person contacts at conferences. Future JPI calls may provide a mechanism within Europe, and there may be opportunities for joint funding of software development and applications.
- Options for virtual meetings:
  - SCOR GoToMeeting licence, which we can continue to use while we have SCOR affiliation
  - Zoom is free for meetings of up to 40 minutes. The University of Gothenburg has a licence for Zoom, which should provide better options. David will look into this.
  - WHOI has a licence for Webex. Heather will look into this.
  - The NERC/NSF project will continue biweekly telephone meetings.
  - We should convene virtual meetings of the whole group or subgroups as necessary with relevant subgroups addressing specific issues
- Simon will continue to maintain the SCOR WG website [marchemspec.org](http://marchemspec.org). It would be good if this could be used to provide updates to the group at regular intervals (e.g. quarterly).
- We have number of different Dropboxes: David will look at rationalizing this.



## WORKING GROUP 145: MARCHEMSPEC Report from Meeting #4, 16 February 2020, San Diego, USA

- David will put together a summary of this meeting based on his notes and those of Heather and Simon
- This report will go first to the meeting participants with an invitation to suggest corrections, and to indicate interest in future collaboration
- The report will then go to the remaining WG members, and to guests at previous meetings, for information and with an opportunity to indicate interest in future collaboration.

### **PARTICIPANTS**

#### **WG members**

David Turner  
Simon Clegg  
Sylvia Sander (via video link)  
Heather Benway  
Arthur Chen  
Andrew Dickson  
Eric Achterberg  
Martha Gledhill  
Peter Croot (not whole meeting)  
Regina Easley  
Frank Bastkowski  
Daniela Stoica (via video link)

#### **Guests**

Matthew Humphreys (NIOZ/UEA)  
Wei-Jun Cai (U Delaware, not whole meeting)  
Pablo Lodeiro (GEOMAR)  
Kechen Zhu (GEOMAR)

#### **SCOR**

Ed Urban (parts of meeting)  
Patricia Miloslavich (parts of meeting)