1. Introduction

The meeting agenda is given in Appendix 1, and the list of participants in Appendix 2. Several guests from collaborating projects also participated. The meeting took place in parallel with the first meeting of Working Group 151 "Iron Model Intercomparison Project (FeMIP)". The two Working Groups have common interests in Fe speciation, and some overlap in membership (see Appendix 2). The day ended with a joint session between the two Working Groups to explore the potential for future collaboration.

2. Review of achievements and current status

The progress to date, organised according to the Terms of Reference, is summarised in the Table below.

Terms of reference	**Progress**
1. To document the current status, and basis in laboratory measurements, of Pitzer models of seawater and estuarine water focusing on the chemistry of ocean acidification and micronutrient trace metals (including, but not limited to, Fe, Cu, Cd, Co, Mn, and Zn). Current capabilities and limitations for oceanographic and biogeochemical calculations will be defined, and future needs established. Important gaps in knowledge, which should have high priority for new measurements, will be identified. The components to be covered will include the seawater electrolytes, the selected trace metals, and buffer solutions and key organic ligands such as those used in CLE-CSV titrations.	• Documentation in progress for artificial seawater and for full seawater. • Current status and future modelling developments have been documented in the Frontiers paper. • NERC/NSF project funded for 3 years (2017-2020). • Collaboration with national standards laboratories on TRIS buffers in artificial seawater. • Contact established with pH monitoring programmes (GOA-ON, IOC).
2. To publish the results of the first term of reference in the refereed scientific literature, and to introduce the conclusions and recommendations to the oceanographic community at a "town hall" event or special session at an international ocean sciences meeting.	• Town Hall presentation at Ocean Sciences 2016. • Paper published in Frontiers in Marine Science (Turner et al., 2016). • Handout for wide distribution at Ocean Sciences 2018.
3. To specify the functions and capability for a web-based modelling tool that will make chemical speciation calculations easily accessible for a wide range of applications in oceanography research and teaching, and thus improve understanding and spread best practice.	• Two "Survey Monkeys" completed.
4. To implement the web-based tool for chemical speciation calculations, based upon the specification developed in the third term of reference which will also be used to obtain external funding to develop the programs, documentation, and site.	

The Working Group proposal to SCOR made clear that completion of the full terms of reference would require significant research funding, and that it might be necessary to suspend work while the necessary funds were being generated, or to disband the Working Group. The first option has been used in effect, since no meeting was held during 2017, and much of the available effort was devoted to securing funding. These efforts were successful with the award of a grant from the NERC-NSF joint programme to Simon Clegg, Andrew Dickson, and Heather Benway. This project will run from late 2017 to late 2020, with objectives that are closely aligned with those of the Working Group. It supports: (i) speciation model development to be carried out at the University of East Anglia (Simon Clegg); (ii) experimental studies using Harned Cells in support of model development (Andrew Dickson); (iii) user outreach and communication with the oceanography community (Heather Benway).
A second development has been the establishment of collaboration with several national standards laboratories, who have a strong interest in developing a pH scale for seawater traceable to the SI base units.
The following groups and projects are contributing new data that will support the Working Group's activities:

- National Standards laboratory PTB (Germany)
- National Standards Laboratory NMIJ (Japan)
- National Standards Laboratory LNE (France)
- Research group of WG member Eric Achterberg (Germany)
- (Discussions are also under way on potential contributions from the University of Belgrade, Serbia)

These contributions, together with the NERC/NSF grant, demonstrate that SCOR's investment in this Working Group has leveraged extensive resources focused on the Working Group's objectives.

An active dialogue has also been established with two projects focusing on the use of indicators for seawater pH measurements: representatives of these projects attended the meeting as guests.

3. Summary of work on pH buffers

3.1 Database and work at NMIJ, Japan (Igor Maksimov)

David Turner explained that all raw data from the laboratories contributing new measurements are being assembled in a relational database (Microsoft Access) that will be available to all the contributing groups. At present the database includes measurements by NMIJ (Japan) on two systems: HCl/TRISHCl and NaCl/HCl/TRISHCl. Literature data is available for the first of these systems at 25°C only: plots of ln γ_{HCl} at this temperature show excellent agreement between the new data and the literature data from the 1970's and 1980's.

3.2 Low salinity TRIS buffer measurements at PTB, Germany (Frank Bastkowski)

In advance of their work in direct support of the Working Group, PTB have recently completed Harned cell measurements of TRIS-artificial seawater buffers at low salinities (<20) in the temperature range 5-40°C. Measurements were also made at salinities of 20 and 35 for comparison with work from Andrew Dickson's laboratory that covered the salinity range 20-40. The observed calculated pH differences in these comparisons was at most 0.002, which indicates good agreement between the two laboratories.

3.3 Solubility measurements at GEOMAR, Germany (Pablo Lodeiro)

Initial measurements have been made on the solubility of TRIS in different NaCl concentrations up to 5 molal at temperatures of 25, 30 and 35°C: the temperature range will be extended later. The experimental system uses 8 bottles in a water bath. Some work is required to improve the internal consistency of the measurements to the target value of 1%. The major contribution to the uncertainty is the difference between duplicate bottles. A practical problem encountered is the tendency of the magnetic stirrer to become stuck in bottles containing large amounts of crystals.

3.4. Next steps

The laboratories carrying out Harned Cell measurements will participate in an intercomparison study during the spring of 2018, to ensure consistency of the data sets that will later be used to develop the speciation model of Tris buffers. These laboratories (Scripps Institution of Oceanography, NMIJ, PTB, and LNE) will be joined, for the intercomparison, by Regina Easley and Jason Waters of the National Institute of Standards and Technology (NIST, USA).

The solubility measurements being made at GEOMAR, which provide information about activity coefficients in saturated solutions, will be continued once the minor experimental problems have been resolved.

4. Related projects

4.1. Development of Spectrophotometric pH Measurement Capabilities in Estuaries (Bob Byrne, USA)

The project aims to extend spectrophotometric measurements of pH to estuarine waters, and involves calibration of several indicators in order to cover a wide pH range. These will be based on the established characterisation of meta-cresol purple and make use of the overlap between different indicators' pH ranges. All data will be archived so that advantage can be taken of new data on meta-cresol purple.

4.2. Establishing the traceability of pH measurements for long-term carbon system monitoring from coastal waters to open ocean, Regina Easley, Jason Waters and Wei-Jun Cai USA)

The project has a large batch (250g) of purified m-cresol purple that will be calibrated against TRIS buffers over the salinity range 5-45, temperature range 5-50°C, and pH range 7.1 to 8.8. They are investigating the use of NMR for an independent determination of the indicator pK, and have access to an isothermal titration calorimeter, which they may try to use to constrain the temperature dependence of pK.

5. Communication with the user community

The pause in activities while funding was secured also resulted in minimal communication activity since there was little new information to present: it was for this reason that the decision was taken not to apply for a Town Hall at the 2018 Ocean Sciences meeting. The WG now plans for a Town Hall at the 2020 Ocean Sciences meeting, and has also developed plans for communication activities leading up to that meeting:

- Articles in newsletters distributed by relevant organisations (SCOR, OCB, GEOTRACES, SOLAS, …)
- A paper setting out the specification for the planned software package, A potential publication channel is the theme "Best Practices in Ocean Observing" in Frontiers in Marine Science. The following timeline was agreed:
    - Text describing the background, and also the user needs based on the Survey Monkeys and the Working Group (David Turner and Heather Benway, 31 March)
    - Text setting out the software specifications (Simon Clegg and Matthew Humphreys, 30 April)
    - Internal review of the combined text (Vanessa Hatje, Sylvia Sander, Peter Croot, Maite Maldonado, Arthur Chen, Wei-Jun Cai, 30 June)
    - Revision following internal review and manuscript submission (David Turner, Heather Benway, Simon Clegg, Matthew Humphreys, 30 August)
- A Webinar based on the submitted manuscript, with organisations such as GOOS as a target audience

- A name and/or acronym for the software would be a great plus factor. Ideas are welcome, ideally before the manuscript submission.

6. Priorities for future work

While there is currently a strong focus on TRIS buffers, which necessarily include an optimised model for artificial seawater, other components and systems need to be treated. The Frontiers paper presented a wide range of components and systems, which in total are far more than can be addressed in the scope of the three-year funded project. The two broad areas that were given high priority in the Survey Monkey were:

- Trace metals, including bioavailability and metal-organic interactions. The trace metals listed in the terms of reference, which are also GEOTRACES core trace metals, are the first priority
- Coastal and estuarine waters, low salinities. A particular problem area here is pH measurement: there needs to be a seamless transition between freshwater pH calibrated with NIST buffers and pH_T in saline waters. There is also a potential problem with the accepted values of the carbonate constants at zero ionic strength: overdetermination of the CO_2 system in very low salinity waters casts doubt on the correctness of these constants.

It is also of great importance that the first version of the software package is available by the end of the funded project.

7. Joint meeting with Working Group 151

Working Group 151 is keen to improve representation of iron speciation in its models. In addition to iron-organic interactions, two areas were identified as being of specific interest:

- Speciation at low temperatures (<5°C): it was pointed out that much of the oceans lie in this temperature range, which is however more challenging for the laboratory measurements that provide the input data for the development of speciation models
- Oxidation kinetics of Fe(II): here the equilibrium speciation of Fe(II) can be important since the oxidation rates are species-dependent.

8. Next meeting

Following the pause in activities and the award of the NERC-NSF grant, the Working Group will propose to SCOR that the Group remain active until the end of 2020 when the funded project will end, and will apply for funding for one final meeting at the 2020 Ocean Sciences meeting. This meeting will be supplemented by virtual meetings of the whole Working Group and/or subgroups.

Appendix 1: Agenda

SCOR WG145 meeting, Portland, 11 February 2018

9:00 Introduction, overview of progress to date (David Turner)

9:20 NERC/NSF project (Simon Clegg, Andrew Dickson, Heather Benway)

9:50 Measurements at PTB, Germany (David Turner)

10:10 Measurements at GEOMAR (Eric Achterberg, Pablo Lodeiro)

10:30 Coffee break

11:00 Project at NIST/University of Delaware (Regina Easley, Jason Waters, Wei-Jun Cai)

11:20 Project at the University of South Florida (Bob Byrne)

11:40 Development of the WG145 database – results from the Japanese standards laboratory NMIJ (David Turner)

12:00 Discussion on the pH and buffer work

12:30 Lunch

13:30 Survey Monkey results: review of draft report

14:15 Discussion on future plans

15:00 Coffee break, together with WG151

15:30 Joint meeting with Working Group 151

17:00 End of meeting

Appendix 2: list of participants

Working Group members

David Turner (chair, Sweden)
Simon Clegg (vice-chair, UK)
Sylvia Sander (vice-chair, Monaco, via Skype)
Eric Achterberg (Germany)
Heather Benway (USA)
Arthur Chen (Taiwan)
Peter Croot (Ireland, also member of WG151)
Andrew Dickson (USA)
Regina Easley (USA)
Vanessa Hatje (Brazil)
Maite Maldonado (Canada, also member of WG151)
Alessandro Tagliabue (UK, also member of WG151)
Christoph Völker (Germany, also member of WG151)

Guests

Bob Byrne (USA)
Wei-Jun Cai (USA)
Nora Douglas (USA)
Matthew Humphreys (UK)
Pablo Lodeiro (Germany, via Skype)
Jason Waters (USA)