MARCHEMSPEC

Chemical Speciation Modelling in Seawater to Meet 21st Century Needs

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Lead authors:

David R. Turner,
Dept. of Chemistry and Molecular Biology,
University of Gothenburg,
Gothenburg, SE-412 96,
Sweden
phone: +46 31 7869054
email: davidt@chem.gu.se

Simon L. Clegg,
School of Environmental Sciences,
University of East Anglia,
Norwich NR4 7TJ, UK
phone: +44 (0)1603 593185
email: s.clegg@uea.ac.uk

1   Summary

Trace elements are important in the world's oceans and near-shore environments as nutrients, tracers, and contaminants. The dissolution of anthropogenic CO_2, a component in the oceanic carbon cycle, is a cause of ocean acidification. Despite the importance of chemical speciation in these marine biogeochemical processes and their consequences for global change, the available models and other calculation tools – often based upon the Pitzer equations – are relatively fragmented and are usually restricted to particular chemical compositions and ranges of temperature and pressure. The models are often neither user-friendly nor freely available, and the community lacks a comprehensive evaluation that relates the capabilities of speciation models to current needs in chemical oceanography (e.g., programmes such as GEOTRACES). To address these problems we will review and document the current status, uncertainties, and basis in laboratory measurements of Pitzer models of seawater and complexation of trace metals (including micronutrients such as Fe, Cu, and Zn). We will define their current capabilities and limitations for oceanographic and biogeochemical calculations, and establish requirements for the future. We will consult widely and develop a specification for a set of speciation models and associated documentation that will be interactive and web-based. Making use of our previous very successful work in this area (and with external funding) we will create the website and associated tools. This requires a coordinated international effort, particularly to ensure that the modelling tools meet the needs of a wide range of potential users in both research and capacity building. A SCOR Working Group is the ideal mechanism for this development.

2   Background and Rationale

2.1   Speciation models and data

Chemical speciation is defined as the distribution of a chemical element between different molecular and ionic forms in seawater. It determines the reactivity and bioavailability of the elements in seawater, and is key to our understanding of biogeochemical and acidification processes in the ocean. It is necessary to model speciation in order to predict how the rate and extent of chemical reactions in the global ocean will be affected by increasing temperature and decreasing pH.

The form in which a trace element or other component of seawater is present, and its tendency to react, depends on its *activity* (Clegg and Whitfield, 1991). This is the product of its concentration (usually molality) and an activity coefficient (γ) which is a complex function of temperature, pressure, and salinity (or, more generally, solution composition). Many of the important reactions in seawater involve acid-base equilibria, which introduces pH as a further variable. Changing pH is also at the heart of the process and effects of CO_2 uptake by the oceans, and of the speciation of dissolved inorganic carbonate. The definitions of pH and the use of buffers to calibrate pH instruments, and the relationship of measured pH to that calculated using thermodynamic models of seawater, are complex and not always appreciated.

It is desirable to be able to calculate pH, and the activities and speciation of all seawater components, within a unified framework that, (i) includes the major and trace elements in seawater and its mixtures with freshwaters,

(ii) encompasses the buffers that are used to calibrate pH and other instruments, and (iii) can be extended to include other saline environments such as brines and pore waters. Progress has been made towards this goal, mainly in the 1980s and 1990s, and today the principal chemical speciation model of seawater is that of Millero and co-workers at the University of Miami (Waters and Millero, 2013, and references therein; see also Clegg and Whitfield, 1995). The model uses the equations of Pitzer (1991) to calculate activity coefficients, and is applicable primarily to major ion seawater (from 0 to 50 ^{o}C, and 0 to >40 salinity) containing the species H^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cl^{-}, Br^{-}, OH^{-}, HCO_3^{-}, $B(OH)_4^{-}$, HSO_4^{-}, SO_4^{2-}, CO_3^{2-}, CO_2, $B(OH)_3$, and H_2O.

The measurements that are used to build models of mixtures such as seawater include: solvent and solute activities, apparent molar enthalpies and heat capacities (yielding the variation of the model parameters with temperature), apparent molar volumes (yielding the variation of the parameters with pressure), and other data. Complexation of trace metals by a number of ligands, both inorganic and organic, has been measured in artificial seawaters or simplified analogues (e.g., $NaCl_{(aq)}$), but usually over restricted ranges of concentration, at a single temperature (often 20 or 25 ^{o}C), and only at atmospheric pressure. The results often depend on the methods used to make the measurements.

The numbers of new studies yielding the activity, thermal, and volumetric data and stability constants needed to develop our quantitative understanding of speciation in the oceans have been in decline for many years, even as the need to model the biogeochemistry and especially the carbonate chemistry of the oceans has become greater. The numbers of skilled experimenters and modellers have also fallen. Furthermore, there is no comprehensive evaluation that relates the capabilities of speciation models, and the measurements upon which they are based, to current and future needs in chemical oceanography as exemplified in current programmes such as GEOTRACES. **Objective 1** of this working group is therefore to document the current status, and basis in laboratory measurements, of Pitzer models of seawater and estuarine water and the complexation of key trace metals including Fe, Cu, Mn, Cd, Mn, and Zn. We will define current capabilities and limitations for oceanographic and biogeochemical calculations, and establish what is needed (in both laboratory measurements and modelling) to meet future requirements. The associated **Objective 2** is to provide a database of Pitzer model parameters and equilibrium constants for seawater (and their variation with temperature and pressure), including trace metal complexation, which can be used by skilled practitioners. The uncertainties, and the effects on calculated properties such as pH, will be evaluated.

2.2 Applications in research and capacity building

The use of computer programs to carry out chemical speciation and other complex calculations for aqueous solutions and natural waters has traditionally involved obtaining the program from the authors, understanding input and output facilities intended only for the authors' use, and learning to use the program with few instructions. These obstacles have hampered the use of state-of-the-art models and the spread of best practice in modelling.

The world-wide-web is the ideal means of making modelling tools universally available for interactive use – with a variety of user interfaces suitable for the problems being solved and the skills of the user –   and for

providing the supporting information and tutorials needed by both researchers and students. For example the ecological modelling package ERSEM (European Regional Seas Ecosystem Model) has just been released as a freely available download to the marine science community (see http://www.shelfseasmodelling.org/) One of us (SLC) has over 15 years' experience providing chemical speciation and gas/liquid/solid equilibrium models that can be used *interactively* on the web (the Extended Aerosol Inorganics Model (*E-AIM*: http://www.aim.env.uea.ac.uk/aim/aim.php, see Wexler and Clegg, 2002). Usage statistics for *E-AIM* demonstrate the benefits for research and capacity building that universal availability and ease of use can bring: in 2013 more than 32,000 individually entered calculations were carried out by users around the world (38% from the Americas, 35% from Europe, and 24% from Asia).

We believe that a similar website, for chemical oceanography applications related to the carbonate system and to trace metal speciation, could bring even greater benefits. **Objective 3** is to develop a written specification for such a website, based upon consultation within the group and with other programmes. This will, for example, define the range of chemical systems and types of problems to which the speciation models will be applied (hence the design of the user interfaces and supporting "help" information), and requirements for capacity building (tutorials and demonstrations). Other modes of use will also be considered (e.g., calls from users' own program code; generation of lookup tables for use in large scale models). **Objective 4** is to create the fully-functioning website.

2.3   Why a SCOR working group?

The work that we propose cannot be driven solely by the modellers who are experts in their field. An in-depth understanding of the requirements of different potential user groups is essential. This will enable us to define the key equilibria and chemical species to be included, and give direction to the review of currently available data (on which current models are based). It will also enable us to specify the requirements for web-based modelling tools and associated training and teaching elements. SCOR, with its broad coverage and links to other international programmes, provides the ideal basis for developing a consensus across the global chemical oceanography community. The outputs of this Working Group will both stimulate new measurements of physico-chemical properties to better understand chemical speciation, and advance our ability to model speciation and its role in oceanographic and biogeochemical processes. The work that we propose, including its strongly international element, is rarely fundable by standard research grants from national research agencies. That is why we are approaching SCOR.

3   Terms of Reference

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, Mn, Cd, 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.

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.

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 in modelling.

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.

4   Work Plan

There are several parallel strands to the activities of the WG. The timetable is given below, after further details of the objectives.

In the review and database constituting **Objectives 1 and 2**, the range of physicochemical conditions to be covered will be those relevant to estuarine and oceanic waters: temperature -2°C to 40°C; salinity 0 to concentrated brines (but with a strong focus on salinity 35); pressure 1 to 1000 atmospheres. The matrix of Pitzer model parameters for a major ion seawater of the composition noted in section 2.1, even excluding Sr^{2+} and boric acid, is considerable: 40 sets of cation-anion interactions, and potentially 250 ternary or "mixture" parameters. Although some can be neglected where all the interacting species are at very low concentration, the large numbers of interactions and the fact that they can vary with both temperature and pressure in the oceans emphasises the need to: (1) assess the completeness of any model and its basis in measured thermodynamic properties, (2) carry out an uncertainty analysis for the calculated quantities, and (3) establish what further measurements are required to completely characterise the behaviour of the seawater/estuarine water for its major and minor components, and trace metals, for the ranges of conditions encountered at sites around the world.

Our survey will relate the modelling and data needs to current developments in marine biogeochemistry, including the consequences of climate change and other anthropogenic forcing functions. This assessment will result in a state-of-the-art, self-consistent, database. It will also identify knowledge gaps that limit our ability to complement current research programmes such as GEOTRACES, IMBER and SOLAS with relevant calculations of chemical speciation.

To attain **Objective 3** we will first review current calculation tools and programs, including their availability and use by oceanographers. These programs include Pitzer seawater and brine models, and those for specific problems such as *CO2SYS* for the inorganic carbonate system. We will define the scope of solution chemistry and speciation modelling to be implemented, the types of problems to which the speciation models will be

applied (hence the design of the user interfaces and supporting "help" information), and requirements for capacity building (tutorials and demonstrations). We will develop the specification for the website and speciation tools, matched to the capabilities, needs, and levels of expertise of users. Consultation between members of the WG, and with other programmes, will feed into this.

In the final phase, for **Objective 4**, we will create a fully-functioning chemical speciation site for oceanographers. Experience with the *E-AIM* aerosol chemistry website, developed partly with external funding, shows that this will require specialist expertise in web implementation that is not available within the WG. We will therefore seek the additional resources necessary for this work, and work on the speciation models, during second year of the WG. In this phase the WG members will act as a test and advisory panel, and help ensure that the supporting information (help texts and training material) is sufficient and correct. Success (or otherwise) in the funding effort constitutes a decision point in the timetable, which is shown below.

Month 1: 1st full WG Meeting.

- This will focus on planning. Issues include: the seawater components and trace elements, and ranges of physicochemical conditions, to be covered (based upon user needs); the allocation of tasks; compilation of a list of external contacts for consultation (in other programmes); and plans for securing additional funding for the web development.

Months 2 - 11

- Objectives 1 & 2: Collection and review of relevant physico-chemical information for the seawater electrolyte; analyses of current Pitzer parameter databases for data sources and coverage of agreed systems and environmental conditions; uncertainty analysis.
- Objective 3: User representatives defining requirements for the web-based speciation tools in research and capacity building (including external consultations); drafting of a proposal for funding to develop the web-based speciation tools and site.

Month 12: WG Sub-group Meetings

- There will be two sub-group meetings: the first will discuss progress on the Pitzer parameter database, and the second will agree the basic specification of the web-based modelling tools sufficient for a draft proposal.

Months 13 - 23

- Objectives 1 and 2: Collect and review all relevant information for trace components, and for pressure effects. Individuals will work on their sections of the draft paper and database. Assembly and completion of the draft paper, delivery to internal reviewers.
- Objective 3: Further consultations with working group members and participants in other programmes to define requirements for the user interface(s) of the web-based calculation tools and for associated teaching (capacity building) materials.

- Objective 4: Submission of proposal(s) to support the development of the web-based tools.

Month 24: 2nd full WG Meeting

- We will review the draft manuscripts of the chemical speciation review paper, and the Pitzer model database, in preparation for submission to a journal. This is also a **decision point** for the development of the web-based modelling tools: we will report on the results of efforts to secure funding, and future prospects. If we have been successful, the project will continue as indicated below. Otherwise, we will either request a postponement (to allow further time to obtain support), or end the WG with the publication of the review paper, Pitzer parameter database, and report defining the needs for web-based tools for speciation calculations. Thus, even if additional funds are not obtained, the WG will (i) produce products valuable for scientists in this field; (ii) establish needs and give direction to future research; (iii) document the tasks needed to complete a Web-based tool.

Months 25 - 47

- Objective 4: Development of the web-based modelling tools and supporting programs and website information, with internal testing and review by WG members and other individuals towards the end of this period.

Month 48: 3rd and final full WG Meeting.

- Members will report on their experiences testing the web-based modelling tools, from both research and capacity-building perspectives. We will agree any necessary revisions, and changes will be made within 2 months of this meeting. The website will then be made public.

We will, where possible, organise WG meetings to coincide with relevant conferences so that the normal SCOR funding for three meetings can be stretched to four, and will explore the possibility of co-sponsorship by IAPSO and IUPAC.

5   Deliverables

1) A review paper, to be published in an international chemistry journal. This will include a statement of current speciation modelling capabilities, a survey of the available physico-chemical data for the major and minor chemical components (particularly related to chemical speciation and equilibria), and the identification of gaps and needs for future models and measurements. (Objective 1)

2) Accompanying the paper, a database listing the currently available Pitzer model parameters and equilibrium constants for seawater and trace components, their variations with temperature and pressure, and their origins in laboratory measurements (how they were obtained, uncertainties, and the references). (Objective 2)

3) Presentation of the results and conclusions of the review paper, for discussion and to stimulate new work, at a talk or special session on chemical speciation at an international ocean sciences meeting. (Objectives 1 and 2)

4) A report defining (a) the scope and specification of speciation modelling tools needed by chemical oceanographers for research and teaching (capacity building); (b) how these tools should be implemented on a website to meet the needs of different potential user groups. (Objective 3)

5) A public website, with associated programs and documentation, meeting the specification set out in (4). (Objective 4)

6) Presentation of the website and its capabilities at a "town hall" meeting at an international ocean sciences conference. (Objective 4)

6   Capacity Building

There is an urgent need for capacity building in chemical speciation modelling. For example, many national and international research programmes are focused on Ocean Acidification (OA). Chemical speciation modelling is essential to an understanding of the development and consequences of OA, yet access to state of the art chemical speciation modelling tools is effectively restricted to a small (and ageing) group of marine scientists who are active researchers in the area. This WG will address the need for capacity building – training, and providing practical tools – at several levels.

Our vision is that state of the art chemical speciation modelling should be easily available to all marine researchers and students, not just the select few who have active research projects in the area. This will be achieved by the development of a web-based modelling tool that builds on a published, consistent and quality-controlled Pitzer database. The active involvement of representatives of key user communities in the WG will ensure that the structure and function of the web tool is appropriate for both research and teaching. In the case of teaching, we already have experience in providing tutorials and instructional videos on the subject of solution thermodynamics. The web-based modelling tools, augmented by the teaching and training materials, will provide the route to the capacity building so urgently needed in this field.

The work and products of the WG will also help to stimulate future capacity building and research in chemical speciation modelling. Publication of the reviewed database and release of the web tool will focus attention its importance. This will encourage new research efforts in this area, and develop a younger generation of scientists who can maintain and develop the database and modelling tools.

Finally, it is anticipated that the identification of important knowledge gaps in the database will stimulate new research to fill those gaps. History suggests that this is more than an idle hope. A 1981 paper co-authored by two of us (Turner et al., 1981) that identified the dearth of data on the carbonate complexation of trace metals, did indeed stimulate new measurements that now provide the basis for our understanding of this phenomenon in the oceans.

7   Working Group Composition

The WG will have 10 Full Members with the range of expertise needed to address the terms of reference, including speciation modelling, large scale biogeochemical modelling, metal-ligand titration techniques,

chemical-biological interactions and teaching. Importance is attached to ensuring that the modelling tools to be developed are readily accessible to the whole community, thus "users" are in a majority in the WG membership. They represent a broad geographical spread, from Europe, North America, South America, China and New Zealand. Although the applications are not restricted to **GEOTRACES**, we see this project as an important complement to **GEOTRACES** that lies outside that programme's field focus. The Full Members include four members of the **GEOTRACES** SSC (Turner, Hatje, Maldonado, Tagliabue), which will ensure effective coordination. The Associate Members provide additional complementary user expertise, together with experienced modellers (including 2 members of the related SCOR WG 127, see section 9.4) who can contribute to reviewing the database and model development.

7.1 Full members

Name	Gender	Place of Work	Expertise
David Turner (chair)	M	University of Gothenburg, Sweden	Physical chemist, oceanographer and modeller: chemical speciation in seawater
Simon Clegg (vice-chair)	M	University of East Anglia, UK	Modeller: chemical thermodynamic modelling (inc. Pitzer equations), development of web-based tools for research and teaching
Sylvia Sander (vice-chair)	F	University of Otago, New Zealand	User: experimental studies of trace metal speciation, focus on data analysis
Heather Benway	F	Woods Hole Oceanographic Institution, USA	Executive Officer, Ocean Carbon and Biogeochemistry Project Office; expert in communication and outreach.
Arthur Chen	M	National Sun Yat-sen University, Taiwan	User: CO_2 system, estuarine, and marine and hydrothermal biogeochemistry
Andrew Dickson	M	Scripps Institute of Oceanography, USA	Physical chemist and modeller: CO_2 system in seawater, reference materials for measurements
Vanessa Hatje	F	INCT Energy and Environment, Bahia, Brazil	User: trace metal accumulation in marine organisms
Maite Maldonado	F	University of British Columbia, Canada	User: biological oceanographer
Alessandro Tagliabue	M	University of Liverpool, UK	User: development of global biogeochemical models
Rodrigo Torres	M	Centre for the Investigation of the Patagonian Ecosystem (CIEP) , Chile	User: ocean acidification and iron

7.2 Associate members

Name	Gender	Place of Work	Expertise
Eric Achterberg	M	GEOMAR, Kiel, Germany	User: chemical oceanographer, CO_2 system and trace metals
Yuri Artioli	M	Plymouth Marine Laboratory, UK	User: ecosystem modeller, member of the ERSEM group
Giles Marion	M	Desert Research Institute, USA	Modeller: developed the FREZCHEM chemical speciation model for cold water systems (http://frezchem.dri.edu/main.html)
Peter May	M	Murdoch University, Australia	Physical chemist and modeller, author of Joint Expert Speciation System (JESS).
Frank Millero	M	University of Miami, USA	Physical chemist and modeller: many measurements of the thermodynamic properties of seawater, and long experience of applying Pitzer models to marine systems
Stan van den Berg	M	University of Liverpool, UK	User: competitive ligand titrations in seawater
Wolfgang Voigt	M	TU Bergakademie Freiberg, Germany	Physical chemist and modeller: properties of concentrated salt solutions and brines (THEREDA database). May also involve close colleague Helge Moog.
Christophe Völker	M	Alfred Wegener Institute, Germany	User: development of global biogeochemical models
Dewen Zeng	M	Institute of Salt Lakes, China	Physical chemist and modeller: expert in chemical speciation with a background in hydrometallurgy.

8   Working Group Contributions

David Turner contributes a broad-based understanding of the field, with experience in chemical speciation modelling, and also in field-based biogeochemistry as Chief Scientist on 3 JGOFS cruises. He also contributes experience as a former WG co-chair (WG109, co-sponsored with IUPAC).

Simon Clegg (modeller) has long experience in applying Pitzer equations both to seawater and atmospheric aerosols, and has an extensive knowledge of the data upon which they are based. His experience in developing the *E-AIM* modelling website (section 2.2) will also make an important contribution to the WG.

Sylvia Sander (user) is expert in competitive ligand titrations, which are used to characterize metal-organic binding in seawater: there is a clear need for improved speciation modelling in this area. As one of the leaders of WG139, she will be able to ensure that the two WG:s complement each other effectively.

Heather Benway (capacity building) is an essential link to the Ocean Carbon and Biogeochemistry Programme, for which she is Executive Officer. She also brings a strong record of outreach and community involvement and will contribute greatly to the teaching and training elements of the web-based speciation tools.

Arthur Chen (user) contributes a wide expertise in marine, estuarine and hydrothermal biogeochemistry and the application of speciation modelling to these systems.

Andrew Dickson (modeller) is an expert in laboratory measurement and modelling of chemical speciation; and also in the development of standard materials, calculation methods and documentation for the marine CO_2 system.

Vanessa Hatje (user) contributes expertise in the study of the trace metal content of marine organisms, an area where improved chemical speciation modelling is needed.

Maite Maldonado (user) contributes expertise in the study of chemical-biological interactions, most particularly the uptake of trace metals by microorganisms. Understanding uptake processes is dependent on good chemical speciation models.

Alessandro Tagliabue (user) contributes expertise in global biogeochemical modelling where there is a clear need for improved descriptions of (particularly) iron speciation.

Rodrigo Torres (user) contributes expertise in studies of ocean acidification and its consequences for iron biogeochemistry

9 Relationships to Other Programmes and SCOR Working Groups

9.1 GEOTRACES

The data generated by the **GEOTRACES** programme, as exemplified by the recently released Intermediate Data Product, is a game-changer in marine biogeochemistry. **GEOTRACES** involves simultaneous sampling for key trace elements and supporting parameters with an accuracy, coverage and resolution far beyond that previously available for trace elements. However, the marine biogeochemistry community currently lacks readily available tools for complementing the **GEOTRACES** data with state of the art calculations of chemical speciation. This proposal aims to fill that gap.

9.2 Global change programmes

The need to understand the effects of climate change and other anthropogenic forcings on marine biogeochemistry is inherent in a number of international programmes such as **IMBER** and **SOLAS**, large scale models such as the **European Regional Seas Ecosystem Model**, and national programs such as the Ocean Acidification Programme in the UK (**UKOARP**, see below). This will continue as a priority within the Future Earth programme now under development. Within these programmes there is an increasing focus on multi-stressors, i.e. the way in which different forcings combine synergistically or antagonistically to produce a net effect. An understanding of chemical speciation is of key importance here. Iron, which is now known to be a limiting nutrient in large areas of the ocean, is one example. The proposed WG is highly relevant to these ongoing and future studies.

9.3   UK national programmes

Both the **UKOARP** and the Shelf Sea Biogeochemistry Programme (**SSB**) have been contacted, and common interests identified. A UK-hosted workshop in 2015 is likely to be attractive to **SSB**, and co-funding is possible. This will be requested later in 2014 when the announcement of opportunity for such 'added value activities' is made.

9.4   SCOR WG 127

The thermodynamic equation of state for seawater, 2010, was produced by this WG. It is a Gibbs function (an equation) from which the thermodynamic properties of seawater are calculated. Most relevant to this WG is the fact that the osmotic coefficient, and also the density, of seawater can be calculated from TEOS 2010. These are important constraints for the speciation models, and should be adhered to.

9.5   SCOR WG 139

The current SCOR WG, entitled "Organic Ligands – A Key Control on Trace Metal Biogeochemistry in the Ocean", addresses the experimental characterisation of interactions between trace metals and natural organic matter in the ocean. There is a strong focus on the use of competitive ligand titrations, from which stability constants and concentrations are derived for a small number of "ligands". Our proposal complements WG 139 by providing (i) a chemical speciation model for all other interactions affecting the trace metal in question; (ii) a chemical speciation model for the titrations that are frequently used to characterise the trace metal – natural organic interactions; and (iii) a framework for including the experimentally derived "ligand" concentrations and stability constants in a chemical speciation model. The leadership of WG 139 has confirmed that this proposal does not overlap WG139.

References

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S. L. Clegg and M. Whitfield (1995) A chemical model of seawater including dissolved ammonia, and the stoichiometric dissociation constant of ammonia in estuarine water and seawater from -2° to 40°C. *Geochim. et Cosmochim. Acta* **59**, 2403-2421.

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A. S. Wexler and S. L. Clegg (2002) Atmospheric aerosol models for systems including the ions H^+, NH_4^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, Br^-, and H_2O. *J. Geophys. Res.-Atmos.* **107**, D14, Art. No. 4207.

Appendix: Key Publications of Full Members

David Turner

(1) Z. Abbas, A. Ulfsbo and **D.R. Turner** (2013) Monte Carlo simulation of the dissociation constants of CO_2 in 0 to 1 molal sodium chloride between 0 and 25 degrees C. *Mar. Chem.* 150, 1-10.

(2) E. Breitbarth, J.Gelting, J. Walve, L.J. Hoffmann, **D.R. Turner**, M. Hassellöv and J. Ingri (2009). Dissolved iron (II) in the Baltic Sea surface water and implications for cyanobacterial bloom development. *Biogeosciences* **6**, 2397-2420.

(3) P.L. Croot, K. Andersson, M. Öztürk and **D.R. Turner** (2004). The distribution and speciation of iron along 6°E in the Southern Ocean. *Deep-Sea Res. II* **51**, 2857-2879

(4) **D.R. Turner** and K.A. Hunter, eds (2001). *The Biogeochemistry of Iron in Seawater*. 2001, John Wiley, Chichester, 396pp

(5) **D.R. Turner**, M. Whitfield, and A.G. Dickson (1981). The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atmosphere pressure. *Geochim. Cosmochim. Acta*, **45**, 855-881.

Simon Clegg:

(1) C. S. Dutcher, X. Ge, A. S. Wexler, and **S. L. Clegg** (2013) An isotherm-based thermodynamic model of multicomponent aqueous solutions, applicable over the entire concentration range. *J. Phys. Chem. A.* **117**, 3198-3213.

(2) **S. L. Clegg** and A. S. Wexler (2011) Densities and apparent molar volumes of atmospherically important electrolyte solutions. 2. The systems H^+-HSO_4^--SO_4^{2-}-H_2O from 0 to 3 mol kg^{-1} as a function of temperature and H^+-NH_4^+-HSO_4^--SO_4^{2-}-H_2O from 0 to 6 mol kg^{-1} at 25 ^oC using a Pitzer ion interaction model, and NH_4HSO_4-H_2O and $(NH_4)_3H(SO_4)_2$-H_2O over the entire concentration range. *J. Phys. Chem. A* **115**, 3461-3474.

(3) **S. L. Clegg** and J. H. Seinfeld (2006) Thermodynamic models of aqueous solutions containing inorganic electrolytes and dicarboxylic acids at 298.15 K. II. Systems including dissociation. *J. Phys. Chem. A* **110**, 5718-5734.

(4) A. S. Wexler and S. L. Clegg (2002) Atmospheric aerosol models for systems including the ions H^+, NH_4^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, Br^-, and H_2O. *J. Geophys. Res.-Atmos.* **107**, D14, Art. No. 4207. (*Extended Aerosol Inorganics Model*: http://www.aim.env.uea.ac.uk/aim/aim.php)

 (5) **S. L. Clegg** and M. Whitfield (1995) A chemical model of seawater including dissolved ammonia, and the stoichiometric dissociation constant of ammonia in estuarine water and seawater from -2° to 40^oC. *Geochim. et Cosmochim. Acta* **59**, 2403-2421.

Sylvia Sander

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