Towards a quality-controlled and accessible Pitzer model for seawater and related systems

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Abstract (max 350 words)

We elaborate the need for a quality-controlled chemical speciation model for seawater and related natural waters, work which forms the major focus of SCOR Working Group 145. Model development is based on Pitzer equations for the seawater electrolyte and trace components. These equations can be used to calculate activities of dissolved ions and molecules and, in combination with thermodynamic equilibrium constants, chemical speciation. The major tasks to be addressed are ensuring internal consistency of the Pitzer model parameters (expressing the interactions between pairs and triplets of species, which ultimately determines the calculated activities), assessing uncertainties, and identifying important data gaps that should be addressed by new measurements. It is recognised that natural organic matter plays an important role in many aquatic ecosystems, and options for including this material in a Pitzer-based model are discussed. The process of model development begins with the core components which include the seawater electrolyte and the weak acids controlling pH. This core model can then be expanded by incorporating additional chemical components, changing the standard seawater composition and/or broadening the range of temperature and pressure, without compromising its validity. Seven important areas of application are identified: open ocean acidification; micro-nutrient biogeochemistry and geochemical tracers; micro-nutrient behaviour in laboratory studies; water quality in coastal and estuarine waters; cycling of nutrients and trace metals in pore waters; chemical equilibria in hydrothermal systems; brines and salt lakes.

1   Introduction

Ocean composition is changing at an unprecedented rate as a result of anthropogenic pressures, with important implications for the health of the oceans and for economic activities. In a recent survey of global ocean research priorities, ocean acidification and the effects of cumulative stressors were identified as two of the top three areas of concern (Rudd, 2014). Understanding the impacts of ocean acidification on areas of human concern, such as fisheries, is a matter of great urgency. Knowledge of chemical speciation, which describes the distribution of the elements between different chemical forms, is essential to understand how changes in ocean chemistry affect bioavailability of different elements (Tessier and Turner, 1995). For example, the speciation of both carbonate and (micro-nutrient) trace metals are complex functions of natural water composition, pH, temperature and pressure. Changes in ocean chemistry may be small on an annual basis, but are modulated on short time and space scales by physical parameters such as salinity, temperature and irradiance, as well as variations in upwelling and ocean currents. Therefore, these chemical changes need to be measured accurately and consistently across the globe to monitor and understand contemporary processes. In addition, chemical changes need to be modelled accurately to evaluate future scenarios and remediation strategies. These requirements are linked by the need to understand chemical speciation – for example that of carbonate and trace metal micronutrients – both in natural waters and in the reference materials and solutions used for analytical method verification and instrument calibration.

Recognising the importance of chemical speciation modelling, SCOR, the Scientific Committee on Ocean Research of the International Council for Science, created Working Group 145 tasked with establishing a reference seawater chemical speciation model that is user-friendly, and freely available to the marine science community. This paper, which constitutes the first report from the Working Group, describes the approach that will be used and identifies different applications to be supported by this chemical speciation model. These span a variety of aquatic environments, and include measurement, calibration and laboratory studies. Each application has its own requirements for the chemical species to be included, and the physical conditions (temperature and pressure) to be covered. To this end, we have proposed a set of core components that are essential for all marine science applications, followed by the specific requirements for each application. This approach is summarised in Figure 1, where in addition to the core components, seven different groups of application have been identified. The major tasks for the Working Group include: ensuring self-consistency of the chemical speciation model and traceability of its parameters to thermodynamic measurements, establishing quantitatively the uncertainties in the calculated speciation, and identifying important data gaps to be addressed by new measurements.

2   Theory

2.1   Pitzer equations

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 mol per kg seawater), 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.

94

95   The Pitzer model (Pitzer, 1991) is a set of equations to calculate activity coefficients (and
96   hence all forms of chemical equilibria) in aqueous solutions as functions of composition and
97   concentration, temperature and pressure. The equations for water and solute activities, and
98   thermal and volumetric properties, are derived from a single expression for the excess Gibbs
99   energy of the solutions. The equations contain sets of parameters (which are functions of
100   temperature and pressure) of two kinds: "pure" solution parameters whose values are
101   determined by fitting to data for solutions containing single electrolytes (e.g., NaCl,
102   $MgSO_4$); and "mixture" parameters whose values are determined from measurements
103   containing, typically, two different electrolytes with a common ion. (e.g., NaCl and
104   Na_2SO_4).

105

106   The data needed to build a model of a complex mixture, such as seawater, include: solvent
107   and solute activities, apparent molar enthalpies and heat capacities (yielding the variation of
108   the model parameters with temperature), apparent molar volumes and compressibilities (the
109   variation of the parameters with pressure), salt solubilities, liquid/liquid phase partitioning,
110   equilibrium partial pressures of volatile solutes, and others. The model is described in detail
111   by Pitzer (1991), and its application to the chemistry of natural waters by Clegg and
112   Whitfield (1991). For any solution, the major effort in constructing a Pitzer model is the
113   determination of the parameter values; a process that often includes the resolution of
114   differences between inconsistent sets of data, and obtaining approximate values of
115   parameters for which there are no data.

116

117   The principal Pitzer chemical speciation model of seawater is that of Millero and co-
118   workers at the University of Miami (Millero and Roy, 1997;Millero and Pierrot,
119   1998;Waters and Millero, 2013). Using many of the same data sources, Clegg and Whitfield
120   (1995) also developed a seawater model, including the protonation of dissolved ammonia.
121   The model of Millero and co-workers is applicable primarily to major ions in seawater
122   (from 0 to 50°C, and 0 to >40 salinity) containing the species H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+},
123   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 use of the
124   model to calculate pH, and some of the problems concerning pH scales that still need to be
125   addressed, are discussed by Waters and Millero (2013). There is, as yet, no comprehensive
126   evaluation of the uncertainties in model-calculated speciation arising from uncertainties in
127   the thermodynamic measurements upon which they are based. The data for trace metal
128   activities and complexation in seawater – which are important for understanding their
129   behaviour and fate – are best described as patchy, and the effects of pressure on activities
130   are only well characterised for aqueous solutions of some of the major seawater electrolytes
131   (eg. NaCl). This limits the accuracy of calculations of chemical speciation in the subsurface
132   ocean.

133

134   The parameters that comprise the Pitzer models developed for seawater are drawn from
135   many sources, include data up to a century old, and are often not optimised for solutions of
136   seawater but rather for modelling brines, e.g. Harvie et al. (1984). To our knowledge, the
137   number of new studies yielding the activities and other data needed to improve the model
138   have been in decline for many years, though the need to quantitatively understand ocean
139   biogeochemistry, especially carbonate chemistry, has increased significantly. Furthermore,
140   there is no comprehensive evaluation relating the capabilities of speciation models, and the
141   measurements upon which they are based, to current and future needs in chemical
142   oceanography as exemplified in current programs such as the international GEOTRACES
143   Programme (Henderson et al., 2007).

144

145 The matrix of Pitzer parameters for major ions in seawater – of the composition noted above
146 but excluding Sr^{2+} and boric acid – is considerable: 36 sets of cation-anion interactions, and
147 potentially 210 ternary or "mixture" parameters that express the interactions between two
148 dissimilar ions of one charge type, and one of the opposite charge type. Some of these can
149 be neglected if all the interacting species are at very low concentration. Nevertheless, the
150 large numbers of interactions and the fact that they can vary with both temperature and
151 pressure emphasises the need to (1) assess the completeness and reliability of the model, (2)
152 validate its basis in measured thermodynamic properties (including analyses to relate the
153 uncertainties in the output quantities of the model to those of the fundamental data – for
154 each interaction – upon which it is based); and (3) establish the sets of measurements still
155 needed to adequately characterise the behaviour of seawater, estuarine and other natural
156 waters encountered worldwide.

157

158 When Pitzer equations are used to calculate activity coefficients, the stability constants used
159 for the chemical equilibria are *thermodynamic constants K*, which are functions of
160 temperature and pressure only. However, many practical applications make use of
161 *stoichiometric constants K** (sometimes also called conditional constants), which are
162 expressed in terms of concentrations and are thus functions of temperature, pressure and
163 solution composition. This dependence on solution composition – via the activity
164 coefficients γ – limits the practical value of stoichiometric constants. Taking the
165 dissociation of HF as an example, and using square brackets to represent concentrations:

166

167 $K^* = [H^+][F^-]/[HF] = K \cdot (\gamma_{HF} / \gamma_{H+} \gamma_{F-})$ 　　　　　　　　　　(1)

168

169 Values of the stoichiometric constant K^* measured in normal seawater can be used only for
170 solutions of seawater composition and for the salinity, or salinities, for which K^* has been
171 determined. Any variations from seawater composition – such as might be found in
172 enclosed seas, pore waters, and some estuaries – will lead to changes in the values of the
173 three activity coefficients in the equation above and therefore a change in K^*.

174

175 Models based on the Pitzer equations are used to calculate chemical speciation at
176 equilibrium, although there is of course no guarantee that a particular system is at
177 equilibrium. In marine environments, the different redox couples that are present are, in
178 general, not in equilibrium with each other. The Pitzer equations can be used to examine
179 this phenomenon by calculating the equilibrium speciation in the two oxidation states of a
180 redox couple: combining measured total concentrations and the standard potential for the
181 couple allows the degree of disequilibrium to be established. Such calculations can also be
182 used to establish the relative oxidising or reducing power of different redox couples at in
183 situ conditions. A knowledge of the equilibrium speciation may also contribute to the
184 analysis of rate processes in places where complexation of a metal ion affects the rate of
185 oxidation (Santana-Casiano et al., 2005).

186 **2.2　Natural Organic Matter (NOM)**

187 The Pitzer equations are applicable to reactions involving relatively simple chemical species
188 whose chemical composition and structure are well defined. Natural organic matter (NOM)
189 in natural waters, including seawater, falls outside this definition since it is a polydisperse
190 material comprising a mixture of many different molecular structures (Koch et al., 2005).
191 Modelling of NOM in seawater is currently restricted to its complexation of trace metals;
192 the available information is derived from competitive ligand exchange cathodic stripping

193 voltammetry (CLE-CSV) titrations (section 6.1), which are summarised as the
194 "concentrations" and "stability constants" of one or more ligand classes. This operational
195 summary cannot be applied in conditions that depart from those used in the titration,
196 although in many cases a broad agreement between different studies has been observed. An
197 alternative strategy worthy of investigation is the use of modelling approaches for
198 freshwater NOM, following extensive laboratory studies of extracted material. Three
199 modelling approaches have been developed: the Windermere Humic Acid Model (WHAM)
200 (Tipping et al., 2011); the Stockholm Humic Model (SHM) (Gustafsson, 2001); and the
201 NICA-Donnan model (Koopal et al., 2005). All three approaches explicitly recognise the
202 polydisperse nature of NOM, and also explicitly treat the development of charge due to
203 ionisation and complexation reactions. The model codes developed for these approaches in
204 fresh waters use simple extended Debye-Hückel equations for the calculation of activity
205 coefficients. These equations are not adequate for use in seawater. However, the WHAM
206 formulation has recently been combined with a Pitzer model (Ulfsbo et al., 2015), providing
207 the basis to test this approach for NOM modelling in seawater.

208 **3   Core components and conditions**

209 **3.1   The seawater electrolyte**

210 The basis of any speciation model that aims to predict activity coefficients accurately is the
211 background electrolyte that determines the physicochemical properties of seawater, and the
212 chemical environment experienced by trace species. On a molar concentration basis, seven
213 chemical elements account for 99.9% of the dissolved species in seawater. Models of the
214 seawater electrolyte normally include the eleven elements whose concentrations exceed 1
215 μmol kg^{-1} and constitute a constant or near-constant proportion of salinity. These are, in
216 order of descending concentration, chlorine (Cl), sodium (Na), magnesium (Mg), sulphur
217 (S), calcium (Ca), potassium (K), (inorganic) carbon (C), bromine (Br), boron (B),
218 strontium (Sr) and fluorine (F).
219
220 The definition of the core speciation model also includes the ranges of the three master
221 variables temperature, salinity and pressure. A temperature range of 0 - 50°C and a salinity
222 range of 0 – 50 correspond to the ranges of many speciation models, although the most
223 complete data collection is usually at 25°C. Information on pressure dependence is often
224 limited, so the core speciation model that the Working Group will consider is initially for 1
225 atmosphere pressure.

226 **3.2   pH**

227 The practical scales used by chemical oceanographers to measure pH are summarised by
228 Waters and Millero (2013). The complexities of these scales, and the difficulty of defining
229 pH, arise because neither the concentration nor the activity of H$^+$ can be measured directly
230 and independently of other quantities (Dickson, 1984). On the *total* scale, the H$^+$ associated
231 with SO$_4^{2-}$ (as HSO$_4^-$) is included in the pH, so that:
232

233 $$pH_T = -\log_{10}\left([H^+] + \left[HSO_4^-\right]\right) = -\log_{10}\left\{[H^+]\left(1 + \left[SO_4^{2-}\right]/K^*_{HSO_4}\right)\right\} \qquad (2)$$

234

235 The *seawater* pH scale also includes the H$^+$ bound to F$^-$ (as HF), so that
236

237 $$pH_{SWS} = -\log_{10}\left([H^+] + \left[HSO_4^-\right] + [HF]\right) = -\log_{10}\left\{[H^+]\left(1 + \left[SO_4^{2-}\right]/K^*_{HSO_4}\right) + \left[F^-\right]/K^*_{HF}\right\} \qquad (3)$$

5

238

239   In the above equations the stoichiometric dissociation constants K^*_{HSO4} (for reaction HSO_4^-

240    $\leftrightarrow H^+ + SO_4^{2-}$) and K^*_{HF} ($HF \leftrightarrow H^+ + F^-$) vary with temperature, pressure, and salinity.

241   More generally, they vary with chemical composition which affects pH in natural waters

242   whose composition differs from that of normal seawater.

243

244   The total and seawater pH scales have been adopted for the following practical reason: the

245   artificial seawater solutions used for the characterisation of pH buffers and pH indicators

246   must contain a relatively high concentration of sulphate in order to match the major ionic

247   composition of natural seawater. However, glass and hydrogen pH electrodes respond only

248   to the free H^+ in solution, while analytical hydrogen ion concentrations obtained from

249   measurements on these scales include both H^+ and HSO_4^-. This difference is significant: -

250    $\log_{10}[H^+]$ and pH_T at salinity 35 and 25°C differ by 0.128 pH units, while the difference

251   between pH_T and pH_{SWS} is only 0.005 units. The accuracy with which the free H^+

252   concentration can be determined from pH_T and pH_{SWS} is currently limited by the accuracy

253   with which K^*_{HSO4} is known (Waters and Millero, 2013). Waters and Millero recommend

254   further work to resolve discrepancies between measured and modelled activity coefficients

255   in seawater-like solutions containing sulphate.

256

257   Figure 2 shows concentrations of the principal species controlling pH in a salinity 35

258   seawater at 25°C, calculated using an ion-interaction speciation model (Clegg and

259   Whitfield, 1995). It is clear, from the relatively high concentrations of carbonate and borate,

260   that seawater pH is largely controlled by equilibria involving these species.

261   **3.3   Weak acids**

262   The chemical species in the model include the weak acids that are involved in defining the

263   pH and alkalinity of seawater. These are clearly illustrated in the open-ended definition of

264   total alkalinity A_T (Dickson, 1981):

$$A_T=[HCO_3^-]+2[CO_3^{2-}]+[B(OH)_4^-]+[OH^-]+[HPO_4^{2-}]+2[PO_4^{3-}]+[SiO(OH)_3^-]+[NH_3]+....$$

265                $$-[H^+]-\left[HSO_4^-\right]-[HF]-[H_3PO_4] - \cdots \tag{4}$$

266   The core chemical species in the model have been selected based on a significant

267   contribution (> 1 µmol kg^{-1}) to A_T in the open ocean. This includes all the species in

268   Equation 4, with the exception of the weak base ammonia.

269   **4   The CO$_2$ system**

270   **4.1   Limitations of current calculation programmes**

271   A number of software packages are freely available for carrying out calculations on the CO_2

272   system, and are based on stoichiometric constants parameterised as a function of salinity,

273   temperature and pressure (Orr et al., 2015). However, the use of salinity as a master variable

274   carries the drawback that these calculations are not applicable to waters of different

275   compositions. This is a particular problem at lower salinities where major ion composition

276   of the seawater/freshwater mixture does not correspond simply to diluted seawater.

277   Compared with seawater, river waters generally have high Mg, Ca and borate

278   concentrations relative to Na, Cl and SO4. Furthermore, river waters are typically high in

279   organic ligands of various molecular sizes. This material can contribute to alkalinity, as

280 noted above, and its decomposition in estuaries can cause substantial changes in the CO_2
281 system (Cai, 2011;Chen et al., 2013;Yang et al., 2013).
282

283 The interpretation of measured alkalinity, and its use in calculations of CO_2 equilibria in
284 natural waters, requires identification of all the relevant weak acids (i.e. those that
285 contribute more than ca. 1 µmol kg^{-1} to the alkalinity), and their degrees of dissociation at
286 the temperature, salinity and pressure of interest. This presents an analytical challenge in
287 many estuarine and brackish waters where natural organic matter can make a significant
288 contribution to alkalinity (Hernandez-Ayon et al., 2007;Kulinski et al., 2014). Complete
289 modelling of the CO_2 system in such waters will also require a treatment of the acid-base
290 chemistry of this material. Overall, there is a great deal to be gained by integrating
291 calculations of the carbon dioxide system, and pH, into a Pitzer model of chemical
292 speciation.

4.2 Calcium carbonate solubility

294 An aspect of ocean acidification that has received a great deal of attention is the
295 concomitant increase in the solubility of calcium carbonate, and its consequences for
296 calcifying marine organisms. A large number of experiments have been carried out
297 exposing different calcifying (and non-calcifying) marine organisms to reduced pH. These
298 experiments show a range of results, and that, at least in the short term, not all calcifying
299 organisms are negatively affected (Dupont and Poertner, 2013). It is, however, clear that
300 oceanic pH is falling and that organisms that precipitate the more soluble forms of calcium
301 carbonate will be greatly affected. Corals, for example, precipitate aragonite, which is the
302 most soluble pure form of calcium carbonate, although high magnesium calcites can have
303 even higher solubilities (Haese et al., 2014). Projections show that aragonite will become
304 undersaturated in large parts of the ocean during the next century. As for the CO_2 system
305 equilibria in solution, the solubility products of calcite and aragonite are currently available
306 as functions of salinity, temperature and pressure (Millero, 2007). Incorporation of these
307 equilibria into a Pitzer framework would enable improved calculations of the solubility
308 products of calcite and aragonite in waters whose composition differs from standard
309 seawater.

4.3 Buffers for pH measurement

311 The recognition of ocean acidification as "the other CO_2 problem" has highlighted the need
312 for precise and accurate pH measurements in seawater. Two methods are currently
313 recognised as meeting these requirements: glass electrodes calibrated in artificial seawater
314 buffers; and indicator spectrophotometry (Dickson et al., 2007), also calibrated against
315 buffer solutions. The most widely used buffer for this purpose is "tris" (2-amino-2-
316 hydroxymethyl-1,3-propanediol), although alternative buffers such as 2-aminopyridine,
317 morpholine (tetrahydro-l,4-isoxazine) and bis (2-amino-2-methyl-l.3-propanediol) can be
318 used when the pH departs significantly from the normal seawater range (Dickson, 1993).
319 The pH values assigned to these buffers are available as functions of salinity and
320 temperature, and have been derived by least-squares fitting pH values determined from a
321 large number of potentiometric measurements in cells without liquid junctions (DelValls
322 and Dickson, 1998). As yet, these measurements cover a limited salinity range (20 – 40). An
323 alternative approach, to fitting the buffer pH values to semi-empirical functions of salinity
324 and temperature, is to derive Pitzer parameters for the interactions of these two buffers with
325 the components of seawater. This would then allow these important pH buffers to be

326 incorporated into the planned unified model of seawater, and also facilitate the treatment of
327 low salinity buffer solutions.

4.4 Sulphonephthalein indicators

329 Indicator spectrophotometry has gained wide acceptance as the method of choice for
330 measurements of seawater pH. These measurements require the stoichiometric stability
331 constant of the indicator dye at the salinity and temperature of the measurement. This is
332 currently achieved by laboratory measurements of these constants under a range of
333 conditions, followed by least squares fitting of the data to semi-empirical functions of
334 salinity and temperature (Liu et al., 2011). As with the pH buffers, an alternative approach
335 to fitting the indicator pH values to semi-empirical functions of salinity and temperature is
336 to derive Pitzer parameters for the interactions of the relevant indicators with the
337 components of seawater. This would allow these important indicators to be incorporated
338 into the planned unified seawater model. The most important indicators are m-cresol purple,
339 phenol red and thymol blue, which are used for pH measurements; and also bromocresol
340 green and bromocresol purple which are used for the determination of alkalinity by the
341 single point method.

5 Trace metals: micronutrients and geochemical tracers

343 The key role of trace metals in ocean science has been recognised in the development of the
344 GEOTRACES programme (Henderson et al., 2007), which is coordinating a global survey
345 of key trace elements and isotopes in the ocean. GEOTRACES focuses on the behaviour of
346 trace metals as micronutrients and as tracers for ocean processes; this division of roles is not
347 exclusive: some trace metals such as Cd and Mn fall into both categories.

5.1 Micro-nutrients

349 It is now recognised that the bioavailability of iron is a key factor in determining primary
350 production and/or phytoplankton community structure in large areas of the ocean (Turner
351 and Hunter, 2001). The thermodynamically stable oxidation state in oxic waters, Fe(III), is
352 poorly soluble with a solubility of the order of 10^{-11} mol L^{-1} in seawater in the absence of
353 organic ligands (Liu and Millero, 2002). However, strong organic complexation can
354 maintain significantly higher concentrations. While organic complexation by (as yet) not
355 fully characterised ligands dominates the speciation of Fe(III), there is continuing interest in
356 defining the inorganic complexation and solubility as essential supporting information.
357 There is also considerable interest in Fe(II), both as a component of anoxic waters, and as
358 metastable Fe(II) produced by photochemical reduction in surface waters. The speciation of
359 this metastable Fe(II) and its effects on Fe oxidation rates are key factors determining the
360 bioavailability of Fe in sunlit surface waters.
361
362 While much attention has been focused on Fe in recent years, several other metals are
363 essential for biological processes. A recent review gives the generalised ranking of trace
364 metal content in phytoplankton as Fe ≈ Zn > Mn ≈ Ni ≈ Cu >> Co ≈ Cd (Twining and
365 Baines, 2013). While all these metals act as micronutrients, some can also have toxic effects
366 at elevated concentrations (Cd, Ni, Cu, Zn, see also section 7.2). Four of these metals (Fe,
367 Zn, Cu and Cd) are obligatory core parameters on GEOTRACES cruise sections, which are
368 providing extensive new information on these metals, both in terms of dissolved (< 0.2 μm)
369 concentrations and CLE-CSV titration data (see section 6.1). Chemical speciation modelling
370 will provide an excellent tool to help extract full value from these unique global datasets.

371   **5.2   Tracers of ocean processes**

372   Manganese is present as insoluble MnO_2 at equilibrium in oxic seawater. However,
373   relatively slow oxidation rates result in dissolved Mn concentrations at the nM level. This
374   slow oxidation has led to the use of Mn as a tracer for releases from anoxic environments,
375   where Mn is present as dissolved Mn(II), and from hydrothermal systems where significant
376   amounts of reduced Mn are released into the surrounding waters (German et al., 1999). The
377   speciation of dissolved Mn has been considered to be dominated by weakly complexed
378   Mn(II), but recent work indicates that Mn(III) may also be present at significant
379   concentrations (Luther et al., 2015).
380
381   In surface waters, Al has been used as a tracer for dust input, which is a major source of Fe
382   to the ocean. The strong correlation between dissolved Al and silicic acid has prompted
383   suggestions of biological control of Al distributions (van Hulten et al., 2014). However,
384   for example in the Mediterranean Sea, the correlation between Al and Si could be explained
385   purely by vertical transport of biogenic particles (Rolison et al., 2015).
386
387   The lanthanides series are a powerful set of tracers because of their coherent and predictable
388   behaviour. Lanthanides have been used in many studies to investigate redox conditions (Liu
389   et al., 1988;Sholkovitz and Schneider, 1991), particulate exchange and scavenging
390   processes (Andersson et al., 2008), water mass transport (Scher and Martin, 2004;Haley et
391   al., 2008) and identification of benthic sources of pore fluid (Abbott et al., 2015). More
392   recently, the lanthanides' widespread use in high-technology processes and products is
393   increasing their environmental occurrence. For example, lanthanides are now being used as
394   tracers of wastewater-derived contaminants in the marine environment (Hatje et al.,
395   2014;Hatje et al., 2016).
396
397   The close relationship between the depth profiles of Cd and phosphate concentrations makes
398   Cd an attractive candidate as a proxy for phosphate concentrations in palaeoceanography,
399   although the relationship shows significant variation (Debaar et al., 1994).

400   **6   Micronutrients: complexation and laboratory experiments**

401   **6.1   CLE-CSV titrations**

402   The most widely used method for characterising the organic complexation of trace metals in
403   seawater is currently Competitive Ligand Exchange (CLE), although direct electrochemical
404   measurements by Anodic Stripping Voltammetry (ASV) are also used, e.g. Sinoir et al.
405   (2016). CLE involves the addition of a competing ligand which has two properties: it forms
406   a complex that competes for trace metals with the natural unknown ligands present in the
407   sample; and it forms a complex with the target trace metal that adsorbs on a mercury
408   electrode and can thus be detected by Cathodic Stripping Voltammetry (CSV). The methods
409   of fitting the CLE/CSV and ASV titration data accurately have been improved significantly
410   in recent times (Pizeta et al., 2015). However, to enable accurate CLE characterisation of
411   the complexation of the trace metal with unknown ligands, it is essential to quantify the
412   complexation of the metal by the added competing ligand, as well as competition reactions
413   with other metals.
414
415   For CLE measurements, the most commonly used added ligands are SA (salicylaldoxime),
416   which complexes with Cu and Fe (Campos and van den Berg, 1994;Buck et al.,
417   2007;Abualhaija and van den Berg, 2014); NN (1-nitroso-2-naphthol), which complexes

9

418 with Fe (Aldrich and van den Berg, 1998); APDC (aminopyrrolidinedithiocarbamate),
419 which complexes with Zn (van den Berg, 1985); and DHN (dihydroxynaphthalene), which
420 complexes with iron (van den Berg, 2006). Other relevant ligands are TAC (2-(2-
421 thiazolylazo)-p-cresol), which has been used as competing ligand for the determination of
422 Fe organic complexation in seawater (Croot and Johansson, 2000;Sander et al., 2015); and
423 DMG (dimethyglyoxime), which has been used for determinations of Co and Ni
424 complexation (van den Berg et al., 1991;Ellwood and van den Berg, 2001).

425

426 In addition to modelling the chemistry of the added ligands, attention needs to be paid to the
427 buffers added to control pH in the CSV measurements. Optimal buffers are those near the
428 natural pH of the water. While the carbonate system acts as the major pH buffer in seawater,
429 sample deaeration undertaken during the CSV analysis disrupts this function, so that an
430 additional buffer is needed. As well as buffering close to the natural pH of seawater, the
431 added buffer must have only weak interactions with the trace metals being studied, so that it
432 does not act as an additional competing ligand. The two buffers that are most commonly
433 used are EPPS (4-(2-hydroxyethyl)-1-piperazinepropanesulphonic acid) and HEPES (4-(2-
434 hydroxyethyl) piperazine-1-ethanesulphonic acid), however phosphate buffer is becoming
435 more popular as it can be cleaned very efficiently to remove any traces of organic ligands
436 and trace metals. A quantitative understanding of these buffers' chemistry in seawater
437 would allow the buffering effect to be calculated more accurately, thus providing a better
438 definition of the chemical conditions of the complexation titrations.

439 **6.2   Model ligands for laboratory experiments**

440 Model organic chelators are used in culture media to ensure that the inorganic trace metal
441 concentrations stay constant during culturing. Furthermore, the use of these chelators, in
442 conjunction with chemical equilibrium modelling, allows the researcher to manipulate the
443 inorganic concentration of a given trace metal while maintaining the inorganic
444 concentrations of the remaining bioactive trace elements unchanged. This design is
445 especially suitable for controlled physiological studies investigating the response of
446 phytoplankton to limiting or toxic trace metal concentrations. The most common general
447 model chelator in culture studies is EDTA (ethylenediaminetetraacetic acid) (Price et al.,
448 1988;Sunda et al., 2005). However, the chelator of choice may vary depending on the
449 research question. For example, if Cu is the metal of interest, one might use DTPA
450 (diethylene triamine pentaacetic acid) instead of EDTA, given that DTPA is a stronger
451 chelator of Cu than EDTA.

452

453 Limiting growth in cultures by manipulation of a specific trace metal is often challenging,
454 and requires the use of well-chosen metal chelators. For example, siderophores, such as
455 DFB (desferrioxamine B) and DFE (desferrioxamine E), are often used to significantly
456 reduce the concentrations of inorganic Fe in the culture media, and thus induce Fe limitation
457 in phytoplankton with extremely low Fe requirements (Strzepek et al., 2011). Similarly, Cu
458 specific chelators, such as Cyclam (1,4,8,11-tetraazacyclotetradecane) and Cyclen (1,4,7,10-
459 tetraazacyclododecane) are frequently used to induce Cu limitation in phytoplankton
460 cultures (Semeniuk, 2014). In addition, these organic ligands are frequently used in uptake
461 experiments (Semeniuk et al., 2015), as they are believed to mimic naturally occurring
462 strong organic ligands of Fe and Cu in seawater. Naturally occurring thiols such as
463 glutathione, cysteine and thiourea are known to strongly bind Cu and other chalcophilic
464 metals (Laglera and van den Berg, 2003). Chemical modelling that includes these organic
465 chelators will greatly enhance our understanding of the chemical speciation of the trace
466 metals in laboratory growth and uptake media, as well as in situ oceanic conditions.

7 Coastal and estuarine systems

7.1 Estuaries and groundwater discharge

Estuaries are where the river water meets seawater, and where the mixture interacts with the land, oceans, atmosphere, sediments and biota. The freshwater end members are typically richer in major nutrients (nitrate, nitrite, ammonia, phosphate and silicate) compared with ocean waters, hence biological productivities are generally high in estuaries. River waters subject to anthropogenic influence frequently have high concentrations of micronutrients and toxic elements (Liu et al., 2010), while permafrost degradation affects the chemistry of Arctic rivers and coastal seas through the mobilisation of organic matter (Semiletov et al., 2016). Furthermore, submarine groundwaters with unique chemical compositions discharge into many estuaries and coastal waters (Zhang and Mandal, 2012). In the case of eutrophication, the pH and dissolved oxygen concentration are both lowered following organic matter breakdown, with consequences for acid-base and redox reactions. Moreover, when riparian tidal freshwater lands and oligohaline marshes are inundated by seawater, competition by major cations such as Mg and Ca can result in the release of trace metals from particulate matter (Wang et al., 2012;Zhang and Mandal, 2012).

7.2 Contaminant discharge

The United Nations Environmental Programme (UNEP, 2013) has highlighted the phenomenon of "global chemical intensification": in many parts of the world, the anthropogenic inputs of metals to the ocean are estimated to be far greater than non-anthropogenic inputs, and the way in which this affects global biogeochemical cycles and ecosystem diversity is as yet poorly understood. Islam and Tanaka (2004) and Davies (1978) noted that the 10 most significant contaminant elements in marine waters are, in order of decreasing toxicity Hg, Cd, Ag, Ni, Se, Pb, Cu, Cr, As and Zn. Four of these (Cd, Ni, Cu and Zn) are classified as key micro-nutrients (Twining and Baines, 2013), and Se and Cr can in addition act as micronutrients.

Specific examples of contaminant discharge include run-off from metal mines, their associated mine tailings, and also naturally occurring acid rock drainage springs. The metals that are commonly found at elevated concentrations (micromolar to millimolar) in mine runoff include Fe, Cu, Zn (Brown et al., 2005;Braungardt et al., 2007), and depending on the ore formations, may also include Cd, Ni, Ag, Au, As. High acidity (pH<1) is associated with the oxidation of iron pyrites and the subsequent formation of sulphuric acid. High acidity also mobilises metals and prevents their removal by precipitation and scavenging.

Industrial discharges are also potential sources of inorganic contaminants, including those from metallurgical industry (metals), fertiliser industry (N, P), and desalination plants (metals). Furthermore, domestic waste water treatment operations discharge inorganic contaminants into receiving waters, and the growth of aquaculture in coastal zones is associated with increasing pollution by inorganic compounds.

8 Pore waters

Pore waters are aqueous solutions that occupy the pore spaces between particles in sediments and can often be considered in equilibrium with the sediments. Diagenetic reactions within sediments and at the sediment-pore water interface control, among others, the recycling of nutrients, carbon, trace elements and contaminants, the dissolution of

512 carbonates, the flux of organic matter to benthic communities and the burial of several
513 elements; see for example (Berner, 1980;Klinkhammer, 1980;Klinkhammer et al., 1982).
514 Pore water studies have provided a link between water column transport processes and
515 sedimentary accumulation by showing evidence for the release of metals associated with the
516 degradation of organic matter (Sholkovitz et al., 1989).
517
518 Chemical changes across redox interfaces in marine systems can have a profound impact on
519 metal solubility and bioavailability. At these oxic-anoxic interfaces, changes in oxidation
520 state, as well as complexation with reduced sulphur species and formation of insoluble
521 sulphides, are common. In coastal areas, redox interfaces are found in anoxic sediments, in
522 anoxic basins and fjords, as well as in sewage outfalls. In the open ocean, oxic-anoxic
523 interfaces are less common, but changes in trace metal solubility and speciation are often
524 observed in oxygen minimum zones. Thus, water columns with oxic-anoxic interfaces have
525 an impact on the cycling of trace metals in the global ocean.
526
527 Knowledge of biogeochemical processes in marine sediments and benthic fluxes of pore
528 water is essential for understanding the global carbon cycle and climate (Berner,
529 1980;Siegenthaler and Sarmiento, 1993;Ridgwell and Hargreaves, 2007). Moreover, pore
530 water is a key exposure route for metal contaminants to organisms associated with the
531 sediments, in particular infauna (Chapman et al., 2002). Knowledge of metal speciation in
532 pore waters is necessary for the development of predictions of bioavailability and for
533 reliable risk assessment strategies. This knowledge could be incorporated in biotic ligand
534 models to derive better-founded quality criteria for marine environments.

535 **8.1 Sulphides**

536 The need to model chemistry in anoxic pore waters, and to understand the chemical
537 processes occurring at the oxic/anoxic boundary, focuses attention on redox reactions and
538 on the chemistry of reduced oxidation states . The most abundant of these are NH_3, Fe(II),
539 Mn(II) and sulphide. The most challenging of these species for chemical modelling is
540 sulphide. In the last 2 decades, metal sulphide speciation in aquatic systems has become of
541 great interest, due to the discovery of nanomolar levels of sulphide in oxic seawater (Luther
542 and Tsamakis, 1989). Sulphides become stable in oxic conditions by forming complexes
543 with trace elements, especially with Hg, Cu (Dyrssen, 1988;Luther and Tsamakis, 1989);
544 and Pb (Bura-Nakic et al., 2007). These metal (M) - sulphide species in oxic waters include
545 simple MHS^+ (or $M(HS)_2^0$ complexes), but also higher-order unprotonated clusters
546 (multinuclear oligomers) with high stability constants (Rozan et al., 2000). In the case of Cu
547 and Zn, the resulting metal-sulphide species are resistant to oxidation in oxic waters and
548 include a mixture of dissolved metal-sulphide complexes and active metal-sulphide
549 nanoparticles (Rozan et al., 1999;Sukola et al., 2005).

550 **9 Hydrothermal systems**

551 Hydrothermal venting occurs in two forms: as hot (up to 450°C), or diffuse venting (5-
552 100°C). Hot vents are mainly found close to mid ocean ridges, subduction zones and arcs;
553 whilst diffuse venting also occurs off axis and in areas with mild tectonic activity. Recently,
554 it has been argued that seafloor venting may provide a significant source of the bio-essential
555 Fe, Cu, and Zn, as well as other metals, due to their stabilization with organic ligands and
556 nanoparticulate sulphides (Sander and Koschinsky, 2011;Yucel et al., 2011;Nishioka et al.,
557 2013). These results place new constraints on submarine metal vent fluxes worldwide,
558 including an indication that the majority of Fe supplied to hydrothermal plumes should

559 come from entrainment of diffuse flow (German et al., 2015). Submarine hydrothermal
560 venting has recently been suggested to have the potential to impact ocean biogeochemistry
561 at the global scale (Tagliabue et al., 2010;Sander and Koschinsky, 2011;Wu et al.,
562 2011;Fitzsimmons et al., 2014). This is the case because processes active in hydrothermal
563 plumes are so vigorous that the residence time of seawater cycling through hydrothermal
564 plumes is comparable to the residence time of deep-water mixing by thermohaline
565 circulation.

9.1   High temperature venting (> 100°C)

567 Since hot hydrothermal vents expel fluid at temperatures between 100 and 450°C,
568 depending on vent activity and depth, these fluids are highly reactive and far from
569 thermodynamic equilibrium with the surrounding seawater. Besides their high temperature,
570 they exhibit extreme pH values (less than 3 or greater than 9), are highly reduced and may
571 have a very different ionic composition to that of standard seawater. In fact, the fluid
572 composition is defined by the underlying bedrock, pressure and temperature, and may
573 reflect phase separation. Once the venting fluids encounter cold oxygenated seawater,
574 precipitation reactions occur instantly, resulting in the commonly seen black (or white)
575 smokers. While the chemical signature of hot hydrothermal vents can be followed in the
576 hydrothermal plume over thousands of kilometres, the temperature will only be > 300°C for
577 seconds or millimetres after discharge. Most chemical reactions with the seawater will occur
578 at temperatures between 4 and 300°C. Taking samples that are representative of in-situ
579 conditions is almost impossible as samples will undergo spontaneous degassing upon the
580 release of pressure and cooling. Thus, to fully understand the reactions and processes
581 occurring at depth in the presence of high temperature and pressure, it is essential to model
582 the speciation of the fluid at in situ conditions.

9.2   Low temperature venting (< 100°C)

584 Shallow vents are of great importance for the supply of micro- and macro-nutrients to the
585 photic zone. The majority of shallow vents are characterized by diffuse venting rather than
586 hot vents, making them an interesting field of research and a natural laboratory to link
587 speciation with biological uptake and toxicity (Klevenz et al., 2012;Kleint et al., 2015). For
588 the vast majority of chemical tracers enriched in vent fluids, net fluxes to the oceans are
589 modified as these tracers are incorporated into Fe-rich polymetallic sulphide and
590 oxyhydroxide particles that sink to the seafloor at or close to mid ocean ridges (Mottl and
591 McConachy, 1990;German et al., 1991;Kadko, 1993). Since diffuse vent fluids have
592 undergone modification in the sub-seafloor and are composed of more than 90% seawater,
593 they have had time to partially equilibrate with ambient seawater. However, often they are
594 still exposed to reducing conditions. The mixing zone for diffuse venting is in the order of
595 metres. Beyond that mixing zone, minor ions still undergo reactions that need to be
596 modelled to understand the chemistry and biological uptake in the vicinity of these diffuse
597 vents.

10   Salt lakes and brines

599 Brines, i.e. natural waters with substantially higher ionic strengths than seawater, are
600 formed in two ways: during ice formation in polar waters where salt rejection increases the
601 salt content of the remaining water; and during evaporation in salt lakes.

10.1 Polar brines

Polar regions are subject to intensive research activities, as they are particularly sensitive to rising temperatures and increasing atmospheric CO_2 concentrations, whilst at the same time playing a key role in global biogeochemical cycles and climate. Ocean acidification adds another stressor to these rapidly changing ecosystems (Orr et al., 2005). Polar regions experience extremes in primary productivity. In the Southern Ocean, low productivity is common in extensive regions with low iron supply, while high productivity is observed in regions with substantial iron supply from sediments (South Georgia) or ice melt (Nielsdottir et al., 2012). Whereas iron supply over a large part of the Arctic is considered sufficient to sustain primary productivity (Klunder et al., 2012), the macro-nutrient concentrations may become exhausted following ice retreat. The freezing of sea ice results in brines with high salinity (100 or more), with freezing points well below that of normal seawater (ca. -1.8°C). These are conditions that are not included in chemical speciation models for seawater. In particular, the carbonate system in the polar oceans is not adequately described at sub-zero temperatures and salinities greater than 50. In order to improve our mechanistic understanding of the dynamics of polar carbonate chemistry, and to allow quantification of CO_2 fluxes across the atmosphere–ice–seawater interfaces, Pitzer based chemical speciation models covering these conditions will be valuable.

10.2 Salt lakes

Salt lakes are systems with very high ionic strength, the record being held by Don Juan Pond (Antarctica), which contains 3.72 mol kg^{-1} $CaCl_2$ and 0.5 mol kg^{-1} NaCl (Marion, 1997). The major focus in modelling of salt lakes and brines is the accurate prediction of precipitation equilibria as a function of temperature and composition (e.g., (Harvie et al., 1984;Vančina et al., 1986;Greenberg and Møller, 1989;Vančina et al., 1997), with two major areas of application. The first is in understanding the evolution of past environments. An example is the modelling of evaporite sequences (layers of different salts accumulated over time) to infer the temperatures, concentrations, and compositions in the water body at the time of deposition. This type of work is can be used to link the evolution of the water body to long term climate variations. The second area concerns the modelling of future scenarios. Interest here is focused on water bodies that are saturated, or close to saturation, by one or more salts in response to changes in inflow/outflow and evaporation. Such changes can be due to human activities. The Dead Sea, for example, is decreasing in volume, resulting in salt precipitation

11 Concluding remarks

This paper outlines the programme of work for the development of a quality-controlled chemical speciation model for seawater and related systems, including descriptions of the different applications that can benefit from the model. Ensuring accessibility by the marine science community will be addressed in a future publication. SCOR Working Group 145 welcomes comments on the proposed programme of work. Comments can be sent to the corresponding author.

Conflict of Interest

14

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979   **Figure legends**
980
981   **Figure 1:** Schematic diagram showing the core components and conditions, and seven
982   groups of additional components and conditions with associated applications for the Pitzer
983   chemical speciation model proposed by the SCOR WG 145. These conditions and
984   applications cover the majority of problems biogeochemists face in describing the chemical
985   speciation of elements in marine and estuarine environments. Each set of additional
986   components, conditions and applications, is discussed in the text section indicated by the
987   number shown in the diagram.
988
989   **Figure 2:** **C**oncentrations of the principal species controlling pH in salinity 35 seawater at
990   25°C, calculated using an ion-interaction speciation model (Clegg and Whitfield, 1995).
991

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Figure 01.JPEG

Figure 1