Chemical Speciation Models Including the Propagation of Uncertainties: Application to the Marine ‘Total’ pH Scale

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Abstract

- Accurate chemical speciation models of natural waters are needed to calculate pH, and carbonate and trace metal speciation.
- In a combined experimental/modelling project we are developing such a model, using the Pitzer equations.
- Results: models with full propagation of uncertainties; assessment of accuracy against current data for artificial seawater; insights into the total pH scale needed for future development.

Background

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- But: (1) measurement of speciation for every natural water of interest is impractical; (2) the marine pH scale is problematic for salinities < 20 and is limited to seawater stoichiometries. These restrictions are severely limiting.

Motivation

- Models of solute activities and speciation, for waters of arbitrary composition, are essential for addressing the difficulties identified above.
- The promise of such models has long been understood; but they have not been widely adopted for various reasons including a lack of quantified uncertainties and exclusion of the Tris buffer solutions used to define pH.

Vision and Timeline

- Free community access to documented, state of the art, user-friendly software for chemical speciation calculations of pH, acid-base, and trace metal equilibria in natural waters, including uncertainty estimates.
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Accurate speciation models of seawater and other natural waters are needed to calculate pH, carbonate and trace metal speciation. pH is a key variable, but the marine 'total' scale is only defined for natural waters of seawater stoichiometry and for salinities of 20 and above. Lower salinities remain problematic. Speciation models will be important for extending the pH scale, as well as being needed for practical applications.

In a combined experimental/modelling project we are developing such models, using the Pitzer equations. Uniquely, they include full propagation of uncertainties, and identify the key interactions that contribute most to any calculated model output. This guides our experimental program to improve the model.

We have assessed model accuracy against current data for artificial seawater and gained insights into the total pH scale that is required for its extension.

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Experiments

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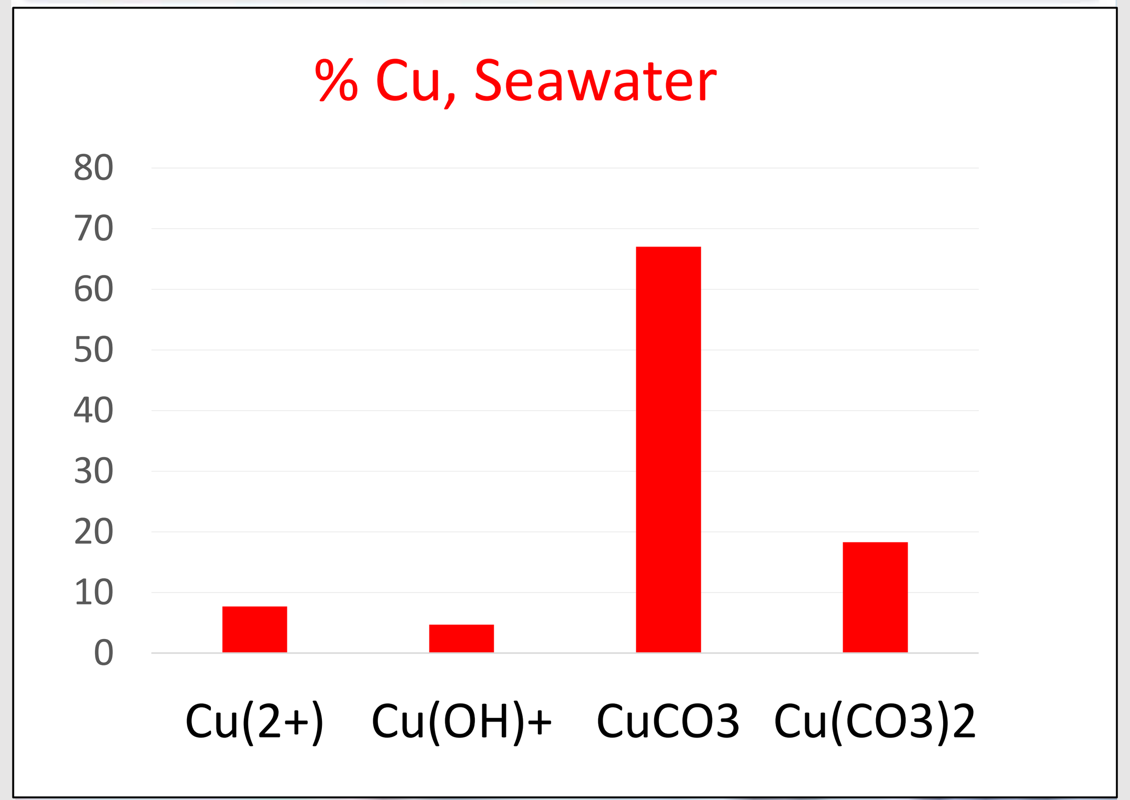
Speciation of an element or component controls its tendency to react, affecting: biological (nutrient) availability; toxicity; and shell-building by marine organisms (CO_3^{2-}). A **quantitative understanding of speciation is important** for understanding ocean change, biogeochemical cycles, and in marine environmental management. However, **measurement of speciation** for every natural water of interest **is impractical**, leading to a need for models.

pH is a fundamental variable in many speciation reactions. However, the **marine "total" pH scale is limited to waters of seawater stoichiometry** and was initially defined for salinities of ≥20 (DelValls and Dickson, 1998) so as to limit the **influence of some inherent assumptions**. An extension (Muller et al., 2017) to salinity of 5 is **problematic**, as we have discovered very recently.

Challenges: To model speciation generally, and to address some of the problems specific to **pH**, which is the **driver of many equilibria**.



e.g., $HCO_3^-{}_{(aq)} \leftrightarrow H^+{}_{(aq)} + CO_3^{2-}{}_{(aq)}$

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Speciation models, based on the Pitzer equations (Pitzer, 1991) have been developed over many years by Millero (e.g., Waters and Millero, 2013). The promise of such models is well understood, but they have not been widely adopted because of: **complexity, lack of quantified uncertainties, they are incomplete w.r.t. some key interactions (notably for 'Tris' pH buffer solutions) , and there are no fully documented and validated computer codes available.**

Approach

We are addressing these obstacles in a project that combines two elements:

1. **Experimental measurements:** to extend the models to **include Tris buffers**. These experiments, typically yielding activities of dissolved Tris, or activity products of H^+ and Cl^-, are used to determine interaction parameters in the Pitzer model.
2. **Model development:** to **include quantified uncertainties** in model outputs; assess, document, and improve the model, and **develop codes for public use**.

Benefits

pH: Ability to **define pH in buffer solutions** for natural waters of non-seawater stoichiometry; **extend 'total' pH scale to lower salinities**, linking the operationally defined pH-as-measured to total H^+ concentration.

Carbonate chemistry: Calculate **speciation for many different natural waters**, inc. fresh waters.

Trace metals: Models **provide a framework** to which trace metal speciation can be added.

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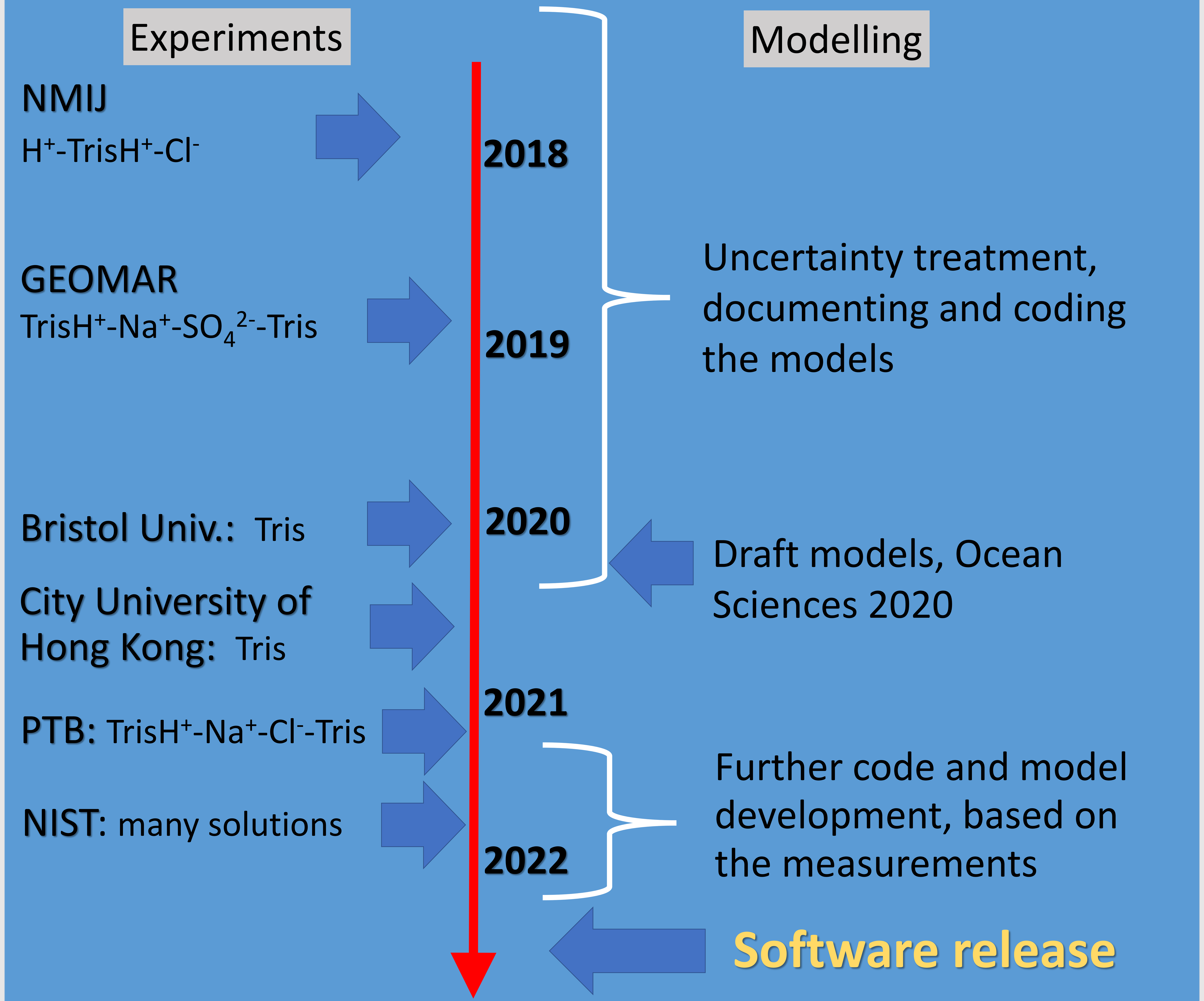

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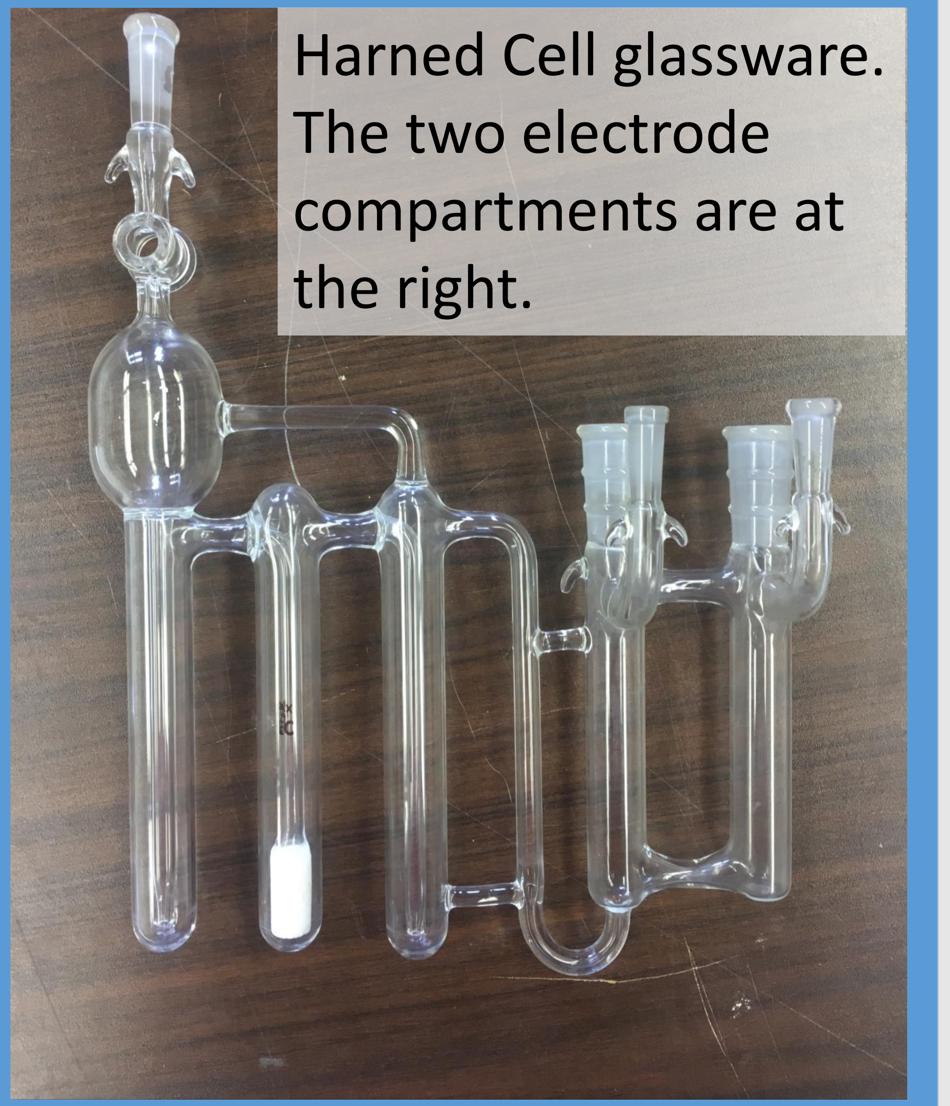
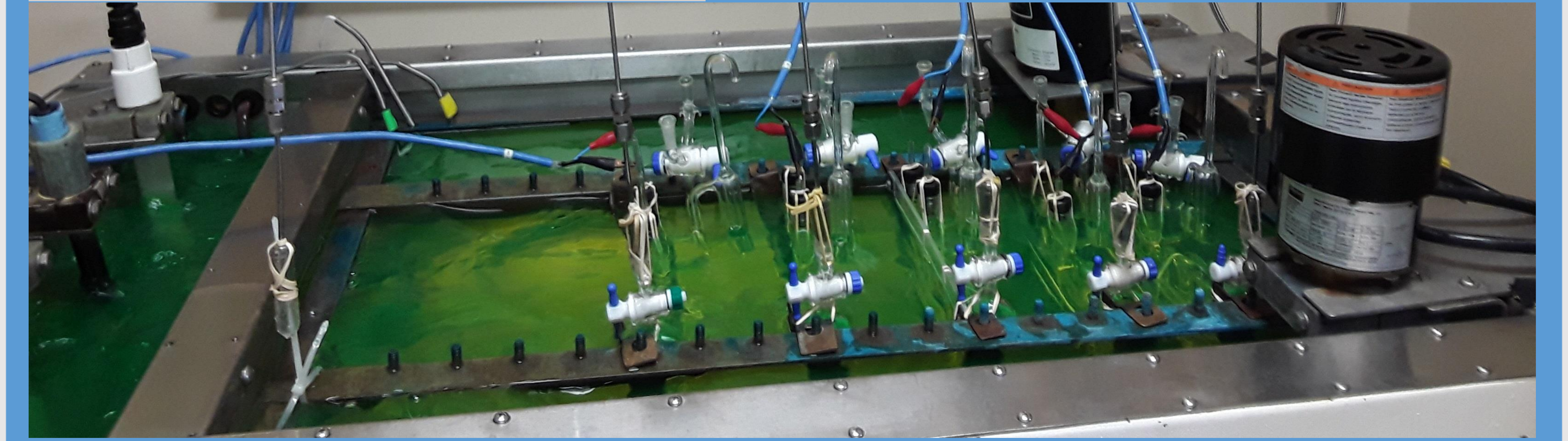
- Designed to **support model development** (and not measurements on seawater directly, for example).
- The speciation model describes solution behaviour in terms of both **thermodynamic equilibrium constants** (e.g., $HSO_4^- = H^+ + SO_4^{2-}$, $HCO_3^- = H^+ + CO_3^{2-}$), and **interactions between pairs and triplets of solute species** (e.g., $H^+ – Cl^-$, $H^+ – Na^+ –$ Cl-, Tris – Na^+).
- Solubility experiments (Lodeiro et al., 2020) and Harned Cell measurements of HCl activity products to **quantify interaction parameters** over a range of temperatures
- Focused on the **model of Tris pH buffer** in solutions containing the ions of seawater, to obtain the benefits described in the Motivation section.
- Participants: GEOMAR – solubility measurements; NMIJ (Japan), PTB (Germany), NIST (USA) – Harned Cells.



Harned Cell glassware. The two electrode compartments are at the right.

Above: Close up of Harned Cell showing Pt H^+ electrode (right) and Ag/AgCl Cl^- electrode (left)

Below: 5 Harned Cells in a temperature-controlled water bath in Andrew Dickson's lab. at Scripps.



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- The models, based on the work of Millero and co-workers (2013, 2017), will **be released in autumn 2022** to the community.
- The models will be developed over time. The **initial focus** is on solutions containing the **ions of standard seawater**, and those present in the **Tris buffers** used to define the marine 'total' pH scale.
- The models usable directly from the web, and as downloaded programs with Python, Matlab, or R interfaces.

Test drive the draft models here:
tinyurl.com/WG145model

EXAMPLE: Calculate the change in pH of the a Tris buffer of salinity 35 which contains 20 mol% less SO_4^{2-} than normal seawater.

STEPS

1. Goto the 'pH of Tris buffers' page at the above site.
2. Enter "-20" in the "Vary SO_4^{2-} by (%):" box.
3. Press "Submit"

RESULTS: Here is the top part of the results page from the calculation.

- Temperature: 25.00 °C, Salinity: 35.00, Pressure: 1.0 atm (fixed)
- Buffer composition has been altered as follows:

```
Na   by -2.624% (by changing Na2SO4)
SO4  by -20.000% by removing Na2SO4
```

- This changes the calculated pH from 8.059 ± 0.0082 to 8.079 (ΔpH = 0.01980)

The uncertainty in ΔpH is ± 8.76E-04

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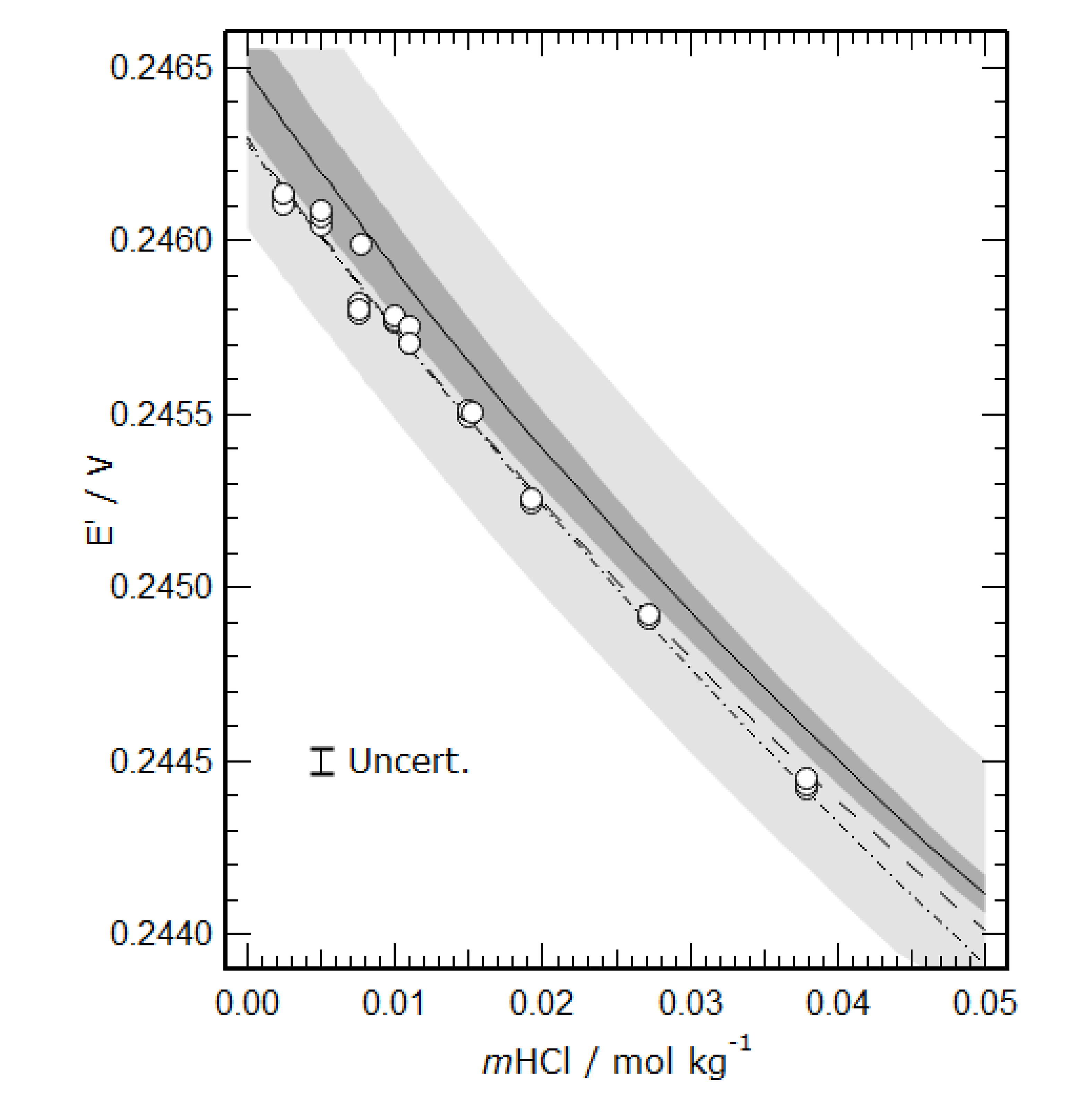
First Results

Results (pH)

1. The model can **predict EMFs of the TrisH⁺/Tris buffers, and acidified seawaters**, used to define the marine 'total' pH scale. Here's are example of the determination of the standard electromotive force *E** (salinity 35, 25 °C) used in the definition of the pH of Tris buffer:



Above: model-calculated (dashed line) and empirical fit (dash-dot) of data agree. *E** is the intercept at *m*HCl = 0. Data of Dickson (1990). Shaded areas show model uncertainties

2. A first calculation of the **"difference term" inherent in the total pH scale** that relates pH-as-measured to ($[H^+] + [HSO_4^-]$) suggests that the existing **total scale can readily be extended to lower salinities** (from the current 20). Quantifying this term, which is *not* shown here, is **key to extending the scale to freshwater**, to non-seawater stoichiometries, and relating model-calculated speciation to measurements.

3. Our examination of the results of Muller et al. (2018) have identified flaws in the data, casting into doubt their extension of the pH scale from 20 to 5 salinity. We calculate that their pH are too low by up to about 0.01 pH units.

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The models, while state-of-the-art and yielding important insights, are drafts. Further development is a long-term project. The most pressing items are:

1. Apply accumulated experimental measurements **to improve model of pH buffers**
2. **Improve uncertainty treatment**, which currently takes a simplified (and overly conservative) approach
3. Develop community-requested **user interface** and **model features**

For more information:
Simon Clegg, David Turner (Chair of WG 145), Andrew Dickson
(email addresses on title page)

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- First, we have an accumulation of experimental data that will be used to improve the model, mainly for the calculation of pH and properties of the buffers used to define the scale.
- Next, the focus will be acid-base and carbonate equilibria in standard seawater of all salinities, and natural waters containing the ions of seawater.

Contributors and References

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Abstract

- Accurate chemical speciation models of natural waters are needed to calculate pH, and carbonate and trace metal speciation.
- In a combined experimental/modelling project we are developing such a model, using the Pitzer equations.
- Results: models with full propagation of uncertainties; assessment of accuracy against current data for artificial seawater; insights into the total pH scale needed for future development.

Background

- Solute speciation is central to trace metal chemistry, the marine carbonate system, and the behaviour of dissolved organic matter. pH is a primary variable.
- But: (1) measurement of speciation for every natural water of interest is impractical; (2) the marine pH scale is problematic for salinities < 20 and is limited to seawater stoichiometries. These restrictions are severely limiting.

Motivation and Approach

- Models of solute activities and speciation, for waters of arbitrary composition, are essential for addressing the difficulties identified above.
- The promise of such models has long been understood; but they have not been widely adopted for various reasons including a lack of quantified uncertainties and exclusion of the Tris buffer solutions used to define pH.

Vision and Timeline

- Free community access to documented, state of the art, user-friendly software for chemical speciation calculations of pH, acid-base, and trace metal equilibria in natural waters, including uncertainty estimates.
- We began with the formation of the SCOR Working Group 45 in March 2015, and will continue until at least 2022 (software release).

Contributors and References

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National Metrological Institute of Japan – Igor Maksimov and Toshiaki Asakai; GEOMAR (Kiel) – Pablo Lodeiro and Eric Achterberg; City University of Hong Kong – Tian Xiaomeng and Chak K. Chan; University of Bristol – Florence Gregson and Jonathan Reid; Physikalisch-Technische Bundesanstalt (PTB, Braunschweig) – Frank Bastkowski and Steffen Seitz.

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Lodeiro, P., Turner, D.R., et al., 2021. Solid–liquid equilibria in aqueous solutions of Tris, Tris-NaCl, Tris-TrisHCl, and Tris-$(TrisH)_2SO_4$ at temperatures from 5 to 45 °C. *J. Chem. Eng. Data*, 66, 437-455.

Humphreys, M.P., Waters, J.F., et al., 2021. Chemical speciation models based upon the Pitzer activity coefficient equations, including the propagation of uncertainties: artificial seawater from 0 to 45 ^{o}C. Submitted to *Mar. Chem*.

Clegg, S.L., Humphreys, M.P., et al., 2021. Chemical speciation models based upon the Pitzer activity coefficient equations, and including the propagation of uncertainties. II. The pH of Tris buffer in artificial seawater at 25 ^{o}C. In Preparation for *Mar. Chem*.

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Experiments

- The speciation model contains parameters for the interactions of ions (these determine the activity coefficients needed to calculate speciation).
- The parameters are determined from measurements of activities in simple aqueous solutions containing the species of interest.
- Colleagues at 6 institutions have contributed experimental measurements.

Modelling

- The models, based on the work of Millero and co-workers (2013, 2017), will be released to the community in autumn 2022.
- How will I do calculations? A: on the web, or with downloaded programs that have Python, Matlab, or R interfaces. Test drive a draft version now!

Key First Results

- The model predicts EMFs of the $TrisH^+$/Tris buffers, and acidified seawaters, used to define the marine pH scale, and the effect of variations in composition.
- The first calculation of the "difference term" that relates pH-as-measured to the true [H+] + [HSO4-]: quantifying this is key to extensions of the scale.
- Problems in the recent extension to the scale (5 to 20 salinity) have been identified.

The Future

- First, we have an accumulation of experimental data that will be used to improve the model, mainly for the calculation of pH and properties of the buffers used to define the scale.
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