Working Group Title: Ocean Carbonate System Intercomparison Forum

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Summary

Recent literature has highlighted several ongoing challenges regarding the consistency of seawater CO_2 measurements with estimates from alternate input pairs. These gaps in our knowledge of the ocean carbonate system are probably related to carbonate constant uncertainties, frequently-unknown concentrations of organic bases in seawater, and unrecognized measurement uncertainties. CO_2 measurement intercomparability is also challenged by the large and growing variety of instruments and approaches used for measurements and the lack of robust assessments or certified reference materials for some methods. While measurement strategies diversify and evolve, the need remains for consistent records of key measurements over time to assess marine CO_2 cycling and its impacts: e.g. dissolved inorganic carbon (DIC) records for anthropogenic carbon storage and changes in the biological pump, partial pressure of CO_2 (pCO_2) records for air-sea CO_2 flux estimates, pH records for ocean acidification (OA) monitoring, and seawater alkalinity (A_T) records for assessing the impacts of OA on carbonate mineral cycling. It is therefore more critical than ever that scientists develop a strategy for identifying and addressing carbonate system intercomparability uncertainties, thus enabling existing and future data to be reconciled into internally-consistent data products with associated uncertainties. We therefore propose a forum between experts in carbonate system parameter measurements, data documentation, and interconversion to debate the nature of the problems, advocate for needed research to resolve these problems, and provide guidance for data product assembly and documentation.

Scientific background and rationale

In principle, any of the commonly-measured seawater carbonate parameter measurements (pH, pCO_2, DIC, A_T, and, as of recently, carbonate ion) can be calculated from any two of the others using carbonate constants (as functions of S, T, and pressure) and knowledge of the chemical properties of all other acid-base systems in the seawater. Moreover, great progress has been made toward standardization of measurement practices through the distribution of Best Practices literature (Dickson et al. 2007; Riebesell et al. 2011) and Certified Reference Materials (Dickson et al. 2003) for key measurements. However, recent literature has highlighted that disagreements remain between direct measurements of carbonate parameters and calculations of these parameters from other measurements (e.g. Kulinski et al., 2014; Chen et al., 2015; Patsavas et al. 2016; Carter et al. 2017; Woosley et al., 2017). These disagreements are comparable in magnitude to, or larger than, the likely decadal changes from climate forcing. Furthermore, there are biases between calculations obtained from different sets of commonly-used carbonate chemistry constants (Woosley et al., 2017). These problems may become more serious in coastal waters with changing salinities and other unidentified acid-base species (Patsavas et al., 2015).

Disagreements between measured and calculated carbonate parameter values and the diversity of measurement types are hampering efforts to combine data sets into unified data products (e.g. Olsen et al. 2016), to interpret existing data products and infer climate signals (e.g. Carter et al., 2017), and to fully utilize measurements from new sensors and measurement platforms to make inferences about the full carbonate system in seawater (e.g. Williams et al., 2017).

Seawater pH can provide an example of these problems and why it is urgent that they be addressed. One of the main symptoms of OA is the ocean pH decrease, however, direct detection of OA based on ocean pH measurements was not feasible prior to the development of the highly-precise spectrophotometric methods (Clayton and Byrne, 1993; see the review of Dickson, 2015). The lack of a certified pH seawater reference material is an additional ongoing challenge for pH measurements. Also, seawater pH has been measured with a variety of methods—and reported on a small collection of pH scales at a range of temperatures and pressures—over the last several decades. The pH measurement approaches used include potentiometric measurements and spectrophotometric measurements made with several different dyes and different batches of dyes, all with differing concentrations of impurities that affect the measured pH (Yao et al., 2008; Liu et al., 2011). The recent emergence (Liu et al. 2011) and independent replication (DeGrandpre et al., 2014) of purified m-Cresol dyes and dye coefficients and formulae raised the possibility that pH measurements would be brought in line with other carbonate system measurements. However, pH calculated from other measured parameters such as DIC and A_T) has been observed to still have a pH-dependent offset from spectrophotometrically measured pH along many cruises, even when purified dyes are used (Patsavas et al., 2015; Williams et al., 2017; Carter et al., 2017). This is thought likely to be the result of gaps in our understanding of how to calculate carbonate system properties from one another (e.g. various measurements and their calibrations, K constants, and the concentrations of borate and other minor seawater acid-base pairs). As a result of these pH issues and the infrequency with which seawater pH was measured, discrete water column pH measurements were completely absent in the first effort synthesizing a globally consistent CO_2 data product, GLODAPv1 (Key et al., 2004). Instead, the mismatch between calculated and measured pH was made apparent with the introduction and quality assessment of water column pH data in regional data products such as CARINA (Velo et al., 2010) and the most recent version of GLODAP (v2: Olsen et al., 2016). During recent years, the number of seawater pH measurements available has increased by orders of magnitude following the development of inexpensive, low-power, pressure-tolerant, sometimes reagent-free pH sensors (see: Wendy Schmidt Ocean Health XPRIZE), and their implementation on biogeochemical profiling floats and other sensor platforms (Johnson et al. 2016; 2017). Now, a float observing strategy is under consideration for implementation as a global array, and related strategies are being developed for other moored and autonomous platforms (see: the supportive United Nations document). Any limitations to the interchangeability of pH with other carbonate parameters will directly limit the utility of sensor measurements for observing air-sea carbon fluxes (from $p CO_2$ calculations) and carbon storage (from DIC calculations). Essentially random measurement errors and offsets are mitigated by the large number of profiling floats that would compose such a global array, but systematic errors from carbonate parameter calculations would result in significant biases.

These are problems with solutions. The ideal solution to the problems for intercomparability of future measurements would be to identify the remaining factors limiting carbonate measurement comparability and address them through carefully planned and agreed upon research among independent research laboratories. If successful, it may eventually be possible to counter the biases in historical data with carefully considered adjustments based on the findings from this research. Whether or not complete carbonate system intercomparability is attainable, an improved understanding of the biases inherent in various approaches for constraining the carbonate system should allow information from these approaches to be appropriately interpreted. This Working Group proposal aims to make progress on these issues by assembling a team of experts to identify the remaining unknown aspects (including measurement uncertainties) of the carbonate system in seawater, the terms in the equations for carbonate parameter interconversion where these uncertainties have the greatest influence, and the research efforts most likely to reduce these uncertainties. Further, the experts would provide guidance on how best to proceed with data assembly and documentation. Finally, the working group will consider how best to encourage adoption of the proposed improvements by both established and emerging laboratories internationally.

These efforts are in service of the NSF "Big 10" objectives of Growing Convergence Research (unifying diverse carbonate system measurements), Harnessing the Data Revolution (allowing the creation of data products with consistent formatting and well-constrained uncertainties, needed for machine learning), and Navigating the New Arctic (by reconciling sensor based measurement—that are emerging as a dominant observational strategy for the seasonally ice-covered Arctic—with the existing global hydrographic record).

Terms of reference

The working group will pursue the following goals through discussion, debate, and writing peer-reviewed articles:

1. Identify and quantify the remaining unknowns for describing seawater CO_2 chemistry (e.g., uncertainties in measurements, CO_2 system calculations and constants, and organic base concentrations);
   a. estimate the magnitudes of these uncertainties, and thereby determine how important each unknown is to address;
   b. outline and advocate for research that could fill the most important gaps in our understanding;
2. Review measurement reporting practices (e.g., reporting of pH scales, reference temperatures, uncertainty, and measurement methods);
   a. debate whether standardized reporting practices would be appropriate, and develop and advocate standardized reporting practices if so;
3. Review the current state of reference materials for seawater CO_2 system measurements, and identify which seawater CO_2 parameters need more viable or available reference materials;
   a. make recommendations for making such materials more viable or available;
   b. make recommendations for how to best use reference materials to characterize measurement uncertainties;

The metrics for the success of these efforts will be publication of 1-2 peer-reviewed white papers on the Working Group's findings, and citation of such papers in research proposals and papers.

Working plan

The OCSIF team will meet to make progress on its terms of reference at two separate 2-day-long meetings associated with OCB summer workshops in the summers of 2019 and 2020. Between each of these meetings, spaced by ~1 year, the Working Group will collaborate remotely to build upon and publish their findings from these meetings.

Throughout:

Prior to the first meeting and throughout the duration of the Working Group, OCSIF would aim to increase the Working Group's visibility by hosting sessions and town halls at major international research conferences. This will serve both to increase awareness of relevant research, and to generate enthusiasm and involvement from the community.

Year 1:

The first meeting would begin with a review of the evidence for carbonate system intercomparability problems, as well as a summary of the various uncertainties that have been proposed to account for these problems, and a round-table discussion of what research is thought to be most likely to clarify these issues (ToR 1,1a,1b). The meeting would then commence preliminary discussions on how best to assemble consistent data products from diverse measurements (ToR 2,2a), given what was discussed earlier. The final part of the meeting would involve planning the work involved in writing a review paper designed to articulate the Working Group's current understanding of the likely uncertainties involved in computing CO_2 parameters from other measurements (see Deliverables - part b) together with specific recommendations where practical. It is intended that this paper be written and submitted within the 12 months immediately following the meeting. Collaboration will be maintained remotely through E-mail correspondence and, if deemed appropriate by OCSIF members, free online collaboration software such as Slack or Google documents. Once specific values have been agreed on for the various likely uncertainties, it will be practical to start (as a group) on the work required to produce the second proposed manuscript.

Year 2:

The second meeting would occur 1 year after the first. The format of this meeting is expected to be similar to the first, beginning with a refresher on the major issues and including an update on research and new results that have come to light in the intervening year and the work done by Working Group members towards the papers proposed in the "Deliverables". The team would then decide whether to break into two groups to discuss the remaining topics sequentially (1 group) or in parallel (2 groups): the two topics would be (1) considering what additional research is likely needed to address the remaining uncertainties (ToR 1,1a,1b) and (2) brainstorming new efforts aimed at establishing carbonate measurement and data reporting best-practices, as well as identifying issues that may have prevented more complete adoption of past and ongoing best-practices guidelines (ToR 3,3a,3b). The working group would conclude in plenary by planning authorship of documents summarizing the findings of the group's 2nd meeting. These include meeting summary documents as well as the 1-2 manuscripts proposed in the deliverables, and started in the first intersession. If one manuscript is planned, it will detail progress made and findings regarding ToR 1. If a second manuscript is planned, it will describe progress made toward ToR 2 and 3.

Deliverables in service of OCB research and observational priorities

The expected deliverables from the activities of the proposed Working Group are:

(a) Reports to OCB on the details of the meetings that were held.

(b) A series of papers (submitted, e.g., to Frontiers in Marine Science under their topic "Best Practices in Ocean Observing"). These will comprise:

> An initial methodological paper that primarily focuses on assessing the likely uncertainties of the manifold factors contributing to the overall uncertainty of computed results for the CO_2 system for a particular sample of seawater. Once these have been assessed and documented, it will be possible to use them in conjunction with publicly available computational software that propagates such uncertainties so as to estimate uncertainties in calculated values. This paper will document the degree to which the careful assessment of uncertainties does indeed provide an explanation for previously noted discrepancies, and to identify if additional contributions to uncertainty still remain to be found. Ideally, as more and more data are examined carefully, it may become practical to identify potential biases in one or more of the parameters, to suggest potential adjustments, and to modify the estimated uncertainty appropriately.
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> A second white-paper that makes explicit recommendations for CO_2 system measurement and reporting best practices that build upon the community experience to date, and that aim to address those issues that are believed to have compromised wholesale adoption of previous "best practice" guides.

Capacity building for the broader OCB community

The Working Group (OCSIF) will be engaged in capacity building for many distinct aspects of seawater CO_2 chemistry science. OCSIF will aim to improve capacities related to:

1. SOP updates: The carbonate measurement community relies on Standard Operating Procedures (SOPs) for measurement and calculation best practices. Iterating on SOPs will be a priority as OCSIF discussions and activities reveal the need for SOP updates.
2. Uncertainty estimation: In order to be meaningfully interpreted, CO_2 measurements require accurate and well-estimated uncertainties. The first-order OCSIF goal of estimating the uncertainties for several key gaps in our understanding of seawater CO_2 chemistry will have direct impacts on our interpretation of measured and calculated seawater CO_2 chemistry values. An improved understanding of how comparable measurements are to the true seawater chemistry and to one another will broadly improve the capacity of the oceanographic community to make correct

inferences based on seawater CO_2 measurements. A likely research item will be the organization of an update to the inter-laboratory comparison exercise of Bockmon and Dickson (2015).

3. Reference material diversity, availability, affordability, and viability: Reference materials for DIC and A_T measurements have had large positive impacts on the quality of the carbonate chemistry measurements since their introduction in the early 90s. OCSIF will examine whether this impact can be extended by encouraging development of additional reference materials for other seawater carbonate measurements (e.g. spectrophotometric pH over a broad pH range), or with a wider range of carbonate chemistry states than are current readily available, and that are more inexpensively available (perhaps more efficiently distributed) to laboratories globally.
4. Data product development: OCSIF plans to debate the metadata requirements for data products that combine measurements made using a range of approaches. The goal for this debate is to create guidelines that will assist members of the community working to compile such data products, and thus resolve challenging questions that are limiting data product development capacities. This will have direct synergies with the Global Data Analysis Project (GLODAPv2), Global Ocean-Ship Based Hydrographic Investigations Program (GO-SHIP), Southern Ocean Carbon Climate Observations and Modeling (SOCCOM), and Surface Ocean CO_2 Atlas (SOCAT) collaborations by providing guidance for documenting and presenting carbonate data to encourage measurement intercomparability.

Budget and justification

Budget	Cost	Quantity	Per meeting	Meetings	Needed	Total cost
Domestic Travel	$550	9*	1	2	18	9900
International Travel	$1000	3	1	2	6	6000
Hotel	$150	12*	2	2	48	7200
Room rental and setup	$250	1	2	2	4	1000
Per Diem or catering	$50	12*	2	2	48	2400
Publication fees	$1500	1	1	2	2	3000
Total						$29,500

* Dr. Easley will seek funding to attend through her institution.

US Domestic travel funds ($550 per person per meeting) are requested for 9 working group participants to travel two OCB Summer Workshop meetings each. International travel funds are requested (at $1000 per person per meeting) for 3 working group participants at two meetings each. Per diem or catering fees are requested for each person for each day of the two meetings (at $50 each, 48 person-days total). Similarly, hotel rooms will be needed for each person for each day (at $150 each, 48 total). A room will be needed for discussions at WHOI for 2 meetings of 2 days each (at $250 per day, 4 total). Finally, publication fees are requested for two publications ($1500 each, 2 total). These requests sum to a total request of $29,500.

References

Carter, B. R., R. A. Feely, N. L. Williams, A. G. Dickson, M. B. Fong, and Y. Takeshita (2017), Updated methods for global locally interpolated estimation of alkalinity, pH, and nitrate, *Limnol. Oceanogr. Methods*, doi:10.1002/lom3.10232.

Chen, B., Cai, W.-J., and Chen, L. (2015) The marine carbonate system of the Arctic Ocean: assessment of internal consistency and sampling considerations, summer 2010. *Mar. Chem. 176, 174-188.* doi: 10.1016/j.marchem.2015.09.007.

Clayton, T. D., and R. H. Byrne (1993), Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results, *Deep Sea Res. Part I Oceanogr. Res. Pap.*, 40(10), 2115–2129, doi:10.1016/0967-0637(93)90048-8.

DeGrandpre, M. D., R. S. Spaulding, J. O. Newton, E. J. Jaqueth, S. E. Hamblock, A. A. Umansky, and K. E. Harris (2014), Considerations for the measurement of spectrophotometric pH for ocean acidification and other studies, *Limnol. Oceanogr. Methods,* 12(12), 830–839, doi:10.4319/lom.2014.12.830.

Dickson, A. G., J. D. Afghan, and G. C. Anderson (2003), Reference materials for oceanic CO_2 analysis: a method for the certification of total alkalinity, *Mar. Chem.*, *80*(2–3), 185–197, doi:10.1016/S0304-4203(02)00133-0.

Dickson, A. G., M.F. Camões, P. Spitzer, P. Fisicaro, D. Stoica, R. Pawlowicz, and R. Feistel (2015), Metrological challenges for measurements of key climatological observables. Part 3: seawater pH. *Metrologia*, *53*(1), R26.

Johnson, K. S., et al. (2016), Deep-Sea DuraFET: A pressure tolerant pH sensor designed for global sensor networks. *Analytical chemistry*, *88*(6), 3249-3256.

Johnson, K. S., et al. (2017), Biogeochemical sensor performance in the SOCCOM profiling float array. *Journal of Geophysical Research: Oceans*, *122*(8), 6416-6436.

Key, R. M., A. Kozyr, C. L. Sabine, K. Lee, R. Wanninkhof, J. L. Bullister, R. A. Feely, F. J. Millero, C. Mordy, and T.-H. Peng (2004), A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), *Global Biogeochem. Cycles*, *18*(4), 1–23, doi:10.1029/2004GB002247.

Liu, X., M. C. Patsavas, and R. H. Byrne (2011), Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements, *Environ. Sci. Technol.*, *45*(11), 4862–4868, doi:10.1021/es200665d.

Olsen, A. et al. (2016), The Global Ocean Data Analysis Project version 2 (GLODAPv2) – an internally consistent data product for the world ocean, *Earth Syst. Sci. Data*, *8*(2), 297–323, doi:10.5194/essd-8-297-2016.

Orr, J. C., J. M Epitalon, A.G. Dickson, and J.P. Gattuso (2018), Routine uncertainty propagation for the marine carbon dioxide system. *Marine Chemistry*, *207*, 84-107.

Patsavas, M. C., R. H. Byrne, R. Wanninkhof, R. A. Feely, and W.-J. Cai (2015), Internal consistency of marine carbonate system measurements and assessments of aragonite saturation state: Insights from two U.S. coastal cruises, *Mar. Chem.*, *176*, 9–20, doi:10.1016/j.marchem.2015.06.022.

Riebesell U., Fabry V. J., Hansson L. & Gattuso J.-P. (Eds.), 2011 Guide to best practices for ocean acidification research and data reporting. Luxembourg, Publications Office of the European Union, 258pp. (EUR 24872 EN). doi: 10.2777/66906.

Velo, A., F. F. Pérez, X. Lin, R. M. Key, T. Tanhua, M. De La Paz, A. Olsen, S. Van Heuven, S. Jutterström, and A. F. Ríos (2010), CARINA data synthesis project: pH data scale unification and cruise adjustments, *Earth Syst. Sci. Data*, *2*, 133–155, doi:10.3334/CDIAC/otg.CARINA.SO.V1.0.

Williams, N. L. et al. (2017), Calculating surface ocean pCO_2 from biogeochemical Argo floats equipped with pH: An uncertainty analysis, *Global Biogeochem. Cycles*, *31*(3), 591–604, doi:10.1002/2016GB005541.

Woosley, R. J., F. J. Millero, and T. Takahashi (2017), Internal consistency of the inorganic carbon system in the Arctic Ocean, *Limnol. Oceanogr. Methods*, *15*(10), 887–896, doi:10.1002/lom3.10208.

Yao, W., X. Liu, and R. H. Byrne (2007), Impurities in indicators used for spectrophotometric seawater pH measurements: Assessment and remedies, *Mar. Chem.*, *107*(2), 167–172, doi:10.1016/j.marchem.2007.06.012.