Carbon Isotopes in the Ocean: Ensuring High-Quality Results in the Future

To be convened at the Woods Hole Oceanographic Institution by Ann P. McNichol, Roberta Hansman, Robert Key, and Rolf Sonnerup

Background

Measurements of the carbon isotope composition of oceanic dissolved inorganic carbon ($DI^{13}C$ and $DI^{14}C$) in seawater benefit many oceanographic fields and significantly contribute to climate change investigations on time scales of years to millennia. Isotopic analyses of DIC have been made on a global scale by an international consortium since the 1970's Geochemical Ocean Sections (GEOSECS) era and continued with the 1980's Transient Tracers in the Oceans (TTO) and the South Atlantic Ventilation Experiment (SAVE) programs. Global scale programs (World Ocean Circulation Experiment; Climate and Ocean: Variability, Predictability, and Change; and Global Ocean Ship-Based Hydrographic Investigations Program; WOCE/CLIVAR/GO-SHIP, respectively) commenced in the 1990's and are still continuing. Studies of both ^{13}C and ^{14}C isotopes of DIC provide critical information that has direct application to studies of climate change, oceanic uptake of anthropogenic CO_2, thermocline and abyssal ventilation rates and meridional overturning rates, biological cycling rates, air-sea gas exchange rates, and provide vital calibration tools for ocean models.

Continued monitoring of the oceanic ^{14}C transient in the upper ocean will provide important metrics of ocean models' surface-to-deep exchange rates, and, specifically, deep water formation rates and processes in key locations where continued penetration of anthropogenic CO_2 into the interior and abyssal ocean is occurring (Figure 1; Graven et al 2012). Plans to continue the US GO-SHIP carbon isotope program will provide at least 1000 $DI^{13,14}C$ analyses to the ocean community each year. The return of the atmosphere radiocarbon content to pre-bomb levels (Figure 1) makes it possible to observe the ocean ^{14}C Suess effect, i.e. the decrease in atmospheric ^{14}C from the addition of ^{14}C-free CO_2 from fossil fuel combustion, in the surface ocean again. Katiwala et al. (2018) estimate that changes of -30 to +5 ‰ will be seen in $DI^{14}C$ in the surface 2 km of the ocean over the next two decades. These are easily measurable differences that continued ocean surveys will detect. Observed changes in the ocean $DI^{13}C$ provide a high signal-to-noise method for quantifying ocean uptake of anthropogenic CO_2 (Quay et al. 2003; Sonnerup and Quay 2012; Eide et al. 2017; Quay et al. 2017). Continued monitoring of $DI^{13}C$ will provide a means to better understand the processes causing inter-decadal shifts in the pattern and rate of ocean uptake of atmospheric CO_2.

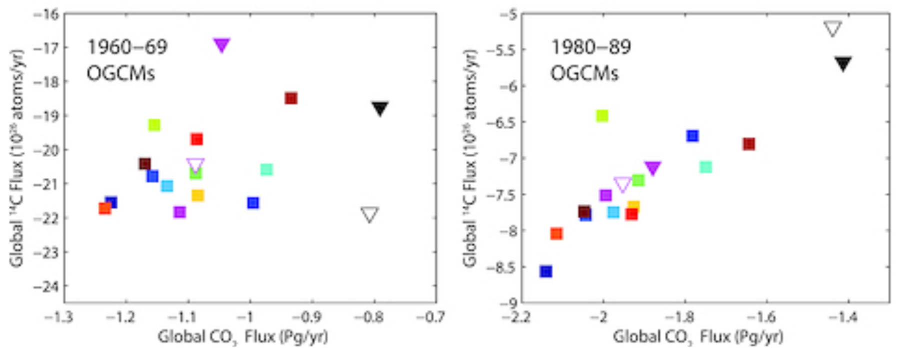

Figure 1. Relationship between global ocean CO_2 and ^{14}C uptake in a collection of ocean models in the 1960s (left) and in the 1980s. Note the linear trend in the more recent data demonstrating control by common factors. Figure adapted from *Graven et al.* [2012].

Isotopic measurements of DIC are contributing to our understanding of biogeochemical and paleoceanographic processes as well. Shah Walter et al. (2018) used $DO^{13,14}C$ and $DI^{13,14}C$ distributions in pore fluids of crustal rock to show that microbial oxidation may account for at least 5% of DOC loss in the open ocean. A study of isotopic fractionation in archaeal lipids as a proxy for past changes in $DI^{13}C$ required a good record of $DI^{13}C$ in the water column. The results of this study suggest that $\delta^{13}C$ in archaeal lipids may be a useful pCO_2 paleobarometer (Hurley et al. 2019). Models describing ocean circulation in the past rely on not only sediment records, but also an ability to reasonably simulate the pre-Industrial ocean distributions of $DI^{13}C$ and $DI^{14}C$ (Muglia et al. 2018).

Until recently, only a few laboratories had the ability to make the precise isotope measurements necessary for studying ocean circulation and the uptake of anthropogenic carbon. Technological advances have changed how both the stable and radiocarbon measurements are being made and are making it easier for more laboratories to collect and analyze the ^{13}C and ^{14}C of DIC. Advances in accelerator technologies have reduced the sample size required to accurately measure radiocarbon and, in some cases, allow the measurement to be made on CO_2 gas rather than graphite. Consequently, new methods are being developed (Bryant et al. 2013; Gao et al. 2014; Gospodinova et al. 2016; Casacuberta et al. 2019). Optical techniques now allow shipboard analysis of $DI^{13}C$ analysis sufficiently that shipboard measurement techniques are already being used (Su et al. 2019; Deng et al. submitted). Robust, documented protocols exist for the collection and analysis of samples collected as part of the GO-SHIP program (McNichol et al. 1994; McNichol et al. 2010; https://www.go-ship.org/HydroMan.html) and these novel methods need to be compared to this standard.

At present, **there are no recognized standards or reference materials for carbon isotopes in seawater.** The community relies on the use of internationally recognized isotope standards from IAEA and NIST to ensure the basic isotope measurements are robust and uses laboratory standards to evaluate any fractionation or introduction of extraneous carbon during the extraction of CO_2 from seawater. Carbonate material certified for its stable isotope or radiocarbon content (e.g. IAEA and NIST standards) can be added to distilled water and then extracted from the solution. In this method, the solid is never fully dissolved until the acid that is part of the overall method is added to the solution. This method benefits from having a traceable value to compare a result with but suffers from using a different matrix than the sample, i.e. it is not seawater. Laboratories also collect larges batches of seawater to use as secondary standards. This method provides a reference material whose matrix is the same as the samples being analyzed but does not have a traceable value with which to compare. As the methods for measuring $DI^{13,14}C$ continue to expand and improve, it will be important to establish best practices and define reference materials, certified or not, that can be used to ensure that results produced throughout the ocean community are intercomparable and comparable to results produced in the past and those that will be produced going forward.

Existing comparisons

There are few published comparisons of $DI^{13}C$ and $DI^{14}C$ measured in different laboratories although informal comparisons have been made in the past. From its inception in the early 1990's, the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS), one of the leading laboratories making this measurement, has relied on deep water comparisons with historic ^{14}C data (primarily GEOSECS) to check the accuracy of their measurements (Figure 2).

In response to the designation of DI^{13}C as an essential ocean variable by the Global Ocean Observation System (GOOS), a DI^{13}C comparison exercise was conducted (Cheng et al. 2019). The results demonstrated that it was possible to achieve a between-lab reproducibility of 0.06‰, close to the ±0.05‰ accuracy/uncertainty goal identified by GOOS. This level of reproducibility was obtained only by using an external standard measured by each participating laboratory in conjunction with the samples to correct each laboratories' results. The study found that there were a number of different methods used by participating laboratories to ensure their results were comparable over time within the laboratory, ranging from internally prepared or collected liquid standards to carbonate minerals. The paper resulting from this comparison concluded, "Therefore, we recommend strongly that the δ^{13}C measurement community work together rapidly to establish a procedure for the preparation and distribution of liquid or soluble CRMs [certified reference materials] for δ^{13}C-DIC."

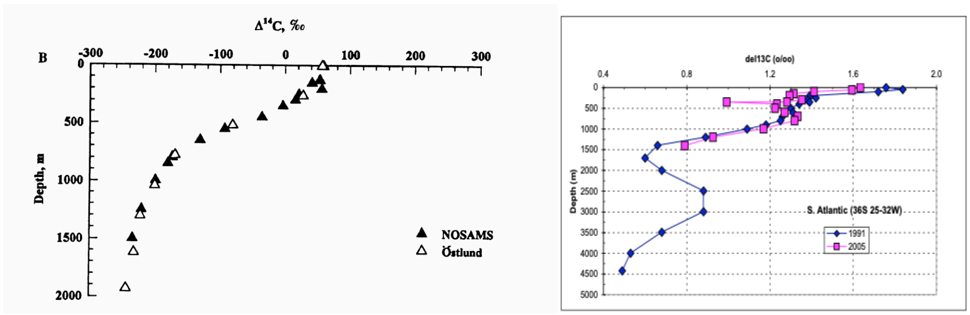

Figure 2. Differences observed in DI^{14}C (left)and DI^{13}C (right) profiles collected at the same or similar locations over many years. While changes are expected in the surface values over time, no differences are expected at depth. (DI^{14}C, McNichol et al. 1994; DI^{13}C, unpublished data)

There are even fewer studies of the comparability of DI^{14}C measurements. Secondary standards at NOSAMS usually consist of large seawater batches collected over the years on cruises of opportunity. New laboratories making DI^{14}C measurements will often arrange a laboratory comparison with NOSAMS or another laboratory to evaluate the accuracy of their methods. An early attempt by NOSAMS in the 1990s to use Dickson certified reference seawater (Dickson 2010) as an isotope standard failed when the batch was determined to have been contaminated with radiocarbon from spiking experiments. More recent work indicates that the Dickson CRM is no longer contaminated but this episode does point to the additional care required when establishing a reference material for natural level radiocarbon. Just as with DI^{13}C, it is past time to establish protocols and reference materials for the community. These protocols should include required details of data handling and reporting.

Proposed Activities

We propose convening a workshop to define methods of best practice for the measurement of DI^{13}C and DI^{14}C with the goal of guaranteeing data comparability of all measurements across laboratories and over time. We will assemble researchers from laboratories making DI^{13}C and/or DI^{14}C measurements to discuss the different methods in use, recommend best practice protocols, and decide on the best source of reference materials. A US National Research Council committee recognized the need for carbon isotopic standards (NRC 2002), yet little was done to make it a reality.

Our plan is to host a two-day workshop at the Woods Hole Oceanographic Institution (WHOI), possibly in connection with a scheduled OCB meeting. A preliminary agenda is shown in Table 1. Participants will be selected from the US and international community of researchers measuring carbon isotopes in the ocean. Potential invitees/laboratories include Wei-Jun Cai (University of Delaware), Paul Quay (University of Washington), Jeff Chanton/Katy Sparrow (Florida State University), Xiaomei Xu/Ellen Druffel (University of California, Irvine), Douglas Wallace (Dalhousie University), JR Toggweiler (Geophysical Fluid Dynamics Laboratory), Nuría Casacuberta (ETH, Switzerland), Heather Graven (Imperial College, England), Yuichuro Kumamoto (JAMSTEC, Japan), Brett Walker/Jennifer Walker (University of Ottawa, Canada) and others. Not only will it be important to ensure the workshop does not get too large, it will also be important to ensure that we attract the broadest representation of researchers possible. To that end, prior to selecting attendees, we will solicit interest in the workshop in venues such as the OCB newsletter and EOS. The workshop will benefit from the expertise of staff at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) housed at WHOI. The NOSAMS laboratory has analyzed DI^{13,14}C on over 30,000 seawater samples collected as part of the US WOCE/CLIVAR/GO-SHIP programs.

The workshop is planned as an in-person event but there will be opportunities to participate remotely. Additionally, should it be required due to COVID-19, it will be possible to conduct the workshop virtually. If funded, plans will be made for both options—a hybrid in-person/virtual event and an entirely virtual event.

Products

An important part of this meeting will be the production of documents summarizing the group recommendations. Recommendations will address proper sampling protocols, storage procedures, appropriate secondary standards, standard reporting procedures, and other issues brought up at the meeting. Our intention is to provide GO-SHIP and the international community with a "Best Practices" protocol detailing the best ways to handle DI^{13,14}C samples from shipboard to reporting/publication as well as to publish articles in the American Geophysical Union's *EOS* newsletter and the Oceanography journal. We plan to present the findings at OCB 2022 and at Ocean Sciences 2022. We view this meeting as the start of a process to provide standard reference materials and protocols to the ocean sciences isotope community. Follow-up will include calls to prepare and standardize reference materials as well as conduct round-robin trials to assess the performance of laboratories making isotopic measurements.

Budget justification

OCB funds will be used to support the travel and per diem of up to 20 participants in the proposed workshop at a cost of $28,260. The funds will be use to provide a travel allowance, two nights of hotel accommodations, a nominal stipend to cover the cost of dinners, and funds for on campus breakfast and lunch catering for a combination of 20 domestic and international participants. Of this sum, funds are also requested for publication costs. Supported attendees will be expected to contribute to the documents that will be prepared at and after the workshop.

Table 1. Proposed agenda for $DI^{13,14}C$ Workshop

2 day meeting
~20 participants

Day 1.
Morning seminars

- Introduction
    1. The need for standard isotopic methods for $DI^{13}C$ and $DI^{14}C$
    2. Results from prior inter-laboratory comparisons

- Collection/preservation methods
    1. Summary of historical approaches
    2. Novel and small volume techniques

- Methods for analysis
    1. Traditional
    2. New

- Standards
    1. Historical and current inter-laboratory standards
    2. Possibilities/strategies for standards going forward
    3. Procedures for reporting uncertainties

- Afternoon—breakout groups/discussion
    - Groups:
        - Sample collection
        - Novel analytical techniques
        - Establishment of standards
        - Uncertainty reporting, standard practices

Day 2.

- Morning seminars.
    - Reports from breakout groups.
    - Data management
- Afternoon—breakout groups/discussion/preparation of recommendations

References

Bryant C.L., S.F. Henley, C. Murray, R.S. Ganeshram, and R. Shanks (2013) Storage and hydrolysis of seawater samples for inorganic carbon isotope analysis. *Radiocarbon 55*, 401-409. http://dx.doi.org/10.1017/S0033822200057520

Casacuberta, N., Castrillejo, M., Wefing, A.-M., Bollhalder, S., & Wacker, L. (2019). High Precision 14C Analysis in Small Seawater Samples. *Radiocarbon*, *00*(00), 1–12. https://doi.org/10.1017/rdc.2019.87

Cheng, L., Normandeau, C., Bowden, R., Doucett, R., Gallagher, B., Gillikin, D. P., … Wallace, D. W. R. (2019). An international intercomparison of stable carbon isotope composition measurements of dissolved inorganic carbon in seawater. *Limnology and Oceanography: Methods*, *17*(3), 200–209. https://doi.org/10.1002/lom3.10300

Dickson, A.G. (2010) Standards for ocean measurements. *Oceanography 23*, 34-47.

Eide, M., Olsen, A., Ninnemann, U. S., and Eldevik, T. (2017). A global estimate of the full oceanic 13C Suess effect since the preindustrial. *Global Biogeochemical Cycles*, *31*(3), 492–514. https://doi.org/10.1002/2016GB005472

Gao, P., Xu, X., Zhou, L., Pack, M. A., Griffin, S., Santos, G. M., … Liu, K. (2014). Rapid sample preparation of dissolved inorganic carbon in natural waters using a headspace-extraction approach for radiocarbon analysis by accelerator mass spectrometry. *Limnology and Oceanography: Methods*, *12*(APR), 174–190. https://doi.org/10.4319/lom.2014.12.174

Gospodinova, K., McNichol, A. P., Gagnon, A., & Walter, S. R. S. (2016). Rapid extraction of dissolved inorganic carbon from seawater and groundwater samples for radiocarbon dating. *Limnology and Oceanography-Methods*, *14*(1), 24–30. https://doi.org/10.1002/lom3.10066

Graven, H. D., Gruber, N., Key, R., Khatiwala, S., & Giraud, X. (2012). Changing controls on oceanic radiocarbon: New insights on shallow-to-deep ocean exchange and anthropogenic CO2 uptake. *J. Geophys. Res.*, *117*(C10), C10005. https://doi.org/10.1029/2012JC008074

Hurley, S. J., Close, H. G., Elling, F. J., Jasper, C. E., Gospodinova, K., McNichol, A. P., and Pearson, A. (2019). CO2-dependent carbon isotope fractionation in Archaea, Part II: The marine water column. *Geochimica et Cosmochimica Acta*, *261*, 383–395. https://doi.org/10.1016/j.gca.2019.06.043

Khatiwala, S., Graven, H., Payne, S., and Heimbach, P. (2018). Changes to the air-sea flux and distribution of radiocarbon in the ocean over the 21st century. *Geophys. Res. Lett.*, *45*(11), 5617–5626. https://doi.org/10.1029/2018GL078172

McNichol, A.P., Jones, G.A., Hutton, D.L., Gagnon, A.R., & Key R.M (1994) The rapid preparation of seawater SCO2 for radiocarbon analysis at the National Ocean Sciences AMS facility. *Radiocarbon, 36(2)*, 237-246.

McNichol, A.P., P.D. Quay, A.R. Gagnon, and J.R. Burton (2010) Collection and measurement of Carbon Isotopes in Seawater DIC. In GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. IOCCP Report No. 14, ICPO Publication Series No. 134.

Muglia J., L.C. Skinner, and A. Schmittner (2018) Weak overturning circulation and high Southern Ocean nutrient utilization maximized glacial ocean carbon. *Earth and Planetary Science Letters 496*, 47-56.

National Research Council (2002) Chemical Reference Materials: Setting the standards for ocean science. The National Academies Press.

Quay, P., Sonnerup, R., Westby, T., Stutsman, J., and McNichol, A. (2003). Changes in the 13C/12C of dissolved inorganic carbon in the ocean as a tracer of anthropogenic CO2 uptake. *Global Biogeochemical Cycles*, *17*(1), 4-1-4–20. https://doi.org/10.1029/2001GB001817

Quay, P., Sonnerup, R., Munro, D., and Sweeney, C. (2017). Anthropogenic CO2 accumulation and uptake rates in the Pacific Ocean based on changes in the 13C/12C of dissolved inorganic carbon. *Global Biogeochemical Cycles*, *31*(1), 59–80. https://doi.org/10.1002/2016GB005460

Shah Walter, S. R., Jaekel, U., Osterholz, H., Fisher, A. T., Huber, J. A., Pearson, A., … Girguis, P. R. (2018). Microbial decomposition of marine dissolved organic matter in cool oceanic crust. *Nature Geoscience*, *11*(5), 334–339. https://doi.org/10.1038/s41561-018-0109-5

Sonnerup, R. E., and Quay, P. D. (2012). 13C constraints on ocean carbon cycle models. *Global Biogeochemical Cycles*, *26*(2). https://doi.org/10.1029/2010GB003980

Su, J., Cai, W.-J., Hussain, N., Brodeur, J., Chen, B., & Huang, K. (2019). Simultaneous determination of dissolved inorganic carbon (DIC) concentration and stable isotope (δ13C-DIC) by Cavity Ring-Down Spectroscopy: Application to study carbonate dynamics in the Chesapeake Bay. *Marine Chemistry*, *215*(March), 103689. https://doi.org/10.1016/j.marchem.2019.103689