Appendix
Global Carbon Data Management and Synthesis Project

Frank Millero
RSMAS, University of Miami, Miami FL

Table of Contents

1. Abstract 1
2. Project Summary 1
3. Scientific Accomplishments 2
4. Education and Outreach 3
5. Publications and Reports 5
   5.1. Publications by Principal Investigators 5
   5.2. Other Relevant Publications 6

1. Abstract

NOAA's Office of Climate Observations (OCO) funds researchers from NOAA laboratories Pacific Marine Environmental Laboratory (PMEL) and Atlantic Oceanographic and Meteorological Laboratory (AOML), as well as the Carbon Dioxide Information Analysis Center, Princeton University, University of California San Diego and the University of Miami to participate in a project to manage, synthesize and interpret data in an endeavor to understand how the ocean carbon cycle changes over time. NOAA's Office of Climate Observations (OCO) oversees this group project and recognizes the need for proper data management and synthesis.

University of Miami students participate in National Science Foundation (NSF) and NOAA cruises to make pCO_2, TA and pH measurements in the World Oceans. The data is gathered, and submitted to CDIAC in a prescribed format to become part of the global ocean observing system database. As a member of this global carbon data management and synthesis project, Frank Millero, University of Miami participates in national and international planning efforts to evaluate and improve the global ocean observing system. The principal investigators of this multi institutional project gather data and bring it together. They collaborate to discuss and provide tools and methods to manage the data, insure accuracy and facilitate easy access.

2. Project Summary

Most of the approaches used to estimate anthropogenic CO_2 in the oceans are based on assumptions of steady state circulation and constant biology. It is becoming increasingly apparent that these assumptions may not hold in a global change environment. The most important component of an assessment of ocean biogeochemical change, whether of natural or anthropogenic origin, is high-quality observations. The WOCE/JGOFS data set provides an

important point of reference for ocean carbon studies. Many other useful data sets have not been analyzed in such a context, because there has not been a coordinated effort to bring these data together and no data management system to make navigation and exploitation of these data convenient.

The NOAA Office of Climate Observation's Carbon Network (hydrographic sections, underway pCO_2, and CO_2 moorings) is a valuable contribution to the Global Ocean Observing System (GOOS) and Global Climate Observing System (GCOS). It is not sufficient, however, simply to collect and archive the data, if we expect the data to improve our understanding of the global carbon cycle and the role of the ocean in climate change.

Recognizing the need for proper data management and synthesis, NOAA's Office of Climate Observations (OCO) has funded several projects to manage and perform an initial interpretation of the data collected from the Carbon Network. In FY07 several of these projects were merged into one management and synthesis project. The goal of the Global Carbon Data Management and Synthesis Project is to work together with the OCO carbon measurement projects to take the fundamental carbon observations and turn them into products that are useful for scientists and the public for understanding the ocean carbon cycle and how it is changing over time. This effort ranges from ensuring that the observations are of the highest quality and are mutually consistent with each other to combining the observations into a common data set that is available and easy for the community to use and explore to evaluating the time rate of change in global ocean carbon uptake and storage. This project brings together ocean carbon measurement experts, information technology experts and data managers to ensure the most efficient and productive processing possible for the OCO carbon observations.

3. Scientific Accomplishments

By establishing high standards consistent throughout the oceanographic community, measurements can be interpreted and definitions and standards can be established to interpret the changes in the world oceans. As a result of the standardized measurements from the Climate Variability (CLIVAR) and Volunteer Observing Ships (VOS) cruises, several publications have resulted. They are listed in the references below.

Instrumentation on VOS tracks changes in the carbonic acid system in the oceans. The measurements indicate that ocean acidification could play an important role in the basic biological and geochemical processes in future decades (Gledhill et al., 2008).

Onboard measurements on cruises in the Little Bahama Bank examined the distribution of the components of the carbonic acid system. Satellite observations show the presence of extensive whitings in this area. Major changes in the water chemistry inside the whitings versus the surrounding water indicates calcium carbonate precipitation on resuspended carbonate sediments from underlying sediments (Bustos-Serrano, et al. 2009).

In an *Ocean Science* publication, a model is developed that can accurately simulate surface properties of seawater and thereby give a better understanding of seawater chemistry (Marion et al., 2009). Millero and Huang (2009) have made new measurements to expand the equation of state of seawater to a wider range of temperature and absolute salinity. A new equation of state has been used to calculate a number of thermal and caloric parameters. Safarov et al. (2009) present new (p, p. T) measurements for standard seawater samples over the extended temperature interval (T=(273.14 to 468.06)K and for pressure up to p=140 Mpa. The results are used to derive an equation of state of seawater that is valid for higher temperatures and pressures than previously possible. The new equation of state puts all of the physical properties in one equation. This makes it convenient for modelers to calculate various properties of seawater.

Spectroscopic measurements of the pH in NaCl brines were made by Millero et al. (2009) in an article in Geochimica et Cosmochimica Acta. In another publication, South Pacific Ocean waters were examined on the P18 CLIVAR (Climate Variability and Predictability) cruise to determine the effect of composition on the density of the waters (Millero et al., 2009).

Wilson et al. (2009) examine the contribution of fish to the marine inorganic carbon cycle. Considering estimates of global fish biomass, an estimate has made that suggests that marine fish contribute 3 to 15% of total oceanic carbonate production. This is significant because the oceans' calcium carbonate controls the delicate pH balance of seawater. These finding highlight how little is known about some aspects of the marine carbon cycle, which is undergoing rapid change as a result of global CO_2 emissions.

Millero (2010) published a paper on the carbonate constants for estuarine waters. Another by Millero and DiTrolio (2010) will be published in October on the effects of ocean acidification due to CO_2 dissolution in *Elements*.

A RSMAS cruise report on the pH and total alkalinity measurements in the Pacific Ocean P18 was prepared and the data was sent to CDIAC for standardization of all measurements (Millero et al., 2008d). CDIAC has prepared a report from all the participating investigators on the chemical data obtained during the *R/V Knorr* Repeat Hydrography Cruises in the North Atlantic Ocean during 2003. The report is a compilation of all the data obtained during the cruise and briefly describes the methods of obtaining data consistent with community standards, issues with the data and the resulting quality data.

4. Education and Outreach

The R/V *Walton Smith* is used by the University of Miami Department of Marine Science to provide undergraduate students with at sea experience in marine chemistry. The pCO_2 data collected during these cruises are used by the students in exercises designed to introduce them to the collection and analysis of oceanographic data, and the preparation of a cruise data report.

Investigators presented public lectures, and are members of national and international steering committees. Numerous students have participated in this project and have been partially supported by NOAA grants to Frank J. Millero.

Chairman
Mareva Chanson; Ph.D., 2009
Michael Trapp; Ph.D., 2009
Héctor Bustos Serrano, Ph.D., in progress
Jason Waters, Ph.D., in progress
Ryan Woosley, Ph.D., in progress
Benjamin Ditrolio, Ph.D., in progress

Committee Member
Jonathan Blanchard, Ph.D., 2009
Derek Manzello, Ph.D., in progress
Edward Mager, Ph.D., in progress
Corrine Hartin, Ph.D., in progress
María E. González, Ph.D., 2009 (outside Committee Member, Universidad Nacional de Colombia, Bogotá, Columbia)
Andreas Felix Hofmann, Ph.D., 2009 (outside Committee Member, Utrecht University, The Netherlands)
Remy Okazaki, Ph.D., in progress

Short Term Visiting International Scholars
Gabriele Lando, 2008-09
Andres Suarez, 2008-09
Giuseppe Manfredi, 2009-10

Undergraduate Fellowships
Alexander Abrams, University of Miami, 2006-2008
Nancy Williams, University of Miami, 2006-2008
W. Schultz, University of Miami, 2009

National and International Committees

GEOC Medal Committee Chair	2008
SCOR Working Group 127	2006-9
AMLC Honorary Medal Committee,	2008
The National Academies Committee on the Development of an integrated Science Strategy for Ocean Acidification Monitoring, Research and Impacts Assessment	2009-10

Invited Lecturer:

Presentation at Symposium in Honor of Frank J. Millero's 70th Birthday, F.J. Millero and R.J. Woosley, Hydrolysis of Al(III) in NaCl solutions: A model for Fe(III), 237th ACS National Meeting, Salt Lake City, UT, March 22-26, 2009.

Invited Lecturer, F.J. Millero, "The Carbon Dioxide System in the Oceans", University of Messina, Messina, Italy, July 9, 2009.

Committee Member:
- SCOR WG 127 meeting Berlin September 2-6, 2008;
- IAPWS meeting, Berlin, September 7-11, 2008;
- SCOR/IAPSO WG 127, 2006-present;
- GEOC Medal Committee, 2006-2007; Chair 2008;
- AMLC Honorary Medal Committee, 2008;
- UM Internal Committee for the Graduate Program Review in Chemistry, 2008.

5. Publications and Reports

5.1. Publications by Principal Investigators

Carbonate System Refereed Journal Articles (with full and partial support from NOAA).

Gledhill, D. K., R. Wanninkhof, F. J. Millero, M. Eakin, 2008: Ocean Acidification of the greater Caribbean region 1996-2006. J. Geophys. Res. **113**, C10031, Doi: 10.1029/2007JC004629.

Bustos-Serrano, H., J. W. Morse, and F. J. Millero, 2008: The formation of whitings on the Little Bahama Bank. Mar. Chem., **113**, 1-8, 2009, doi:10.1016/j.marchem.2008.10.006.

Marion, G. M., F. J. Millero, and R. Feistel, 2009: Precipitation of solid phase calcium carbonates and their effect on application of seawater SA-T-P models. Ocean Sci., **5**, 285-291, 2009, www.ocean-sci.net/5/285/2009/.

Millero, F. J., and F. Huang, 2009: The density of seawaters as a function of salinity (5 to 70 g kg^{-1}) and temperature (273.15 to 363.15K). Ocean Sci., **5**, 91-100.

Millero, F. J., B. Ditrolio, A.F. Suarez, and G. Lando, 2009: Spectroscopic measurements of pH in NaCl. Geochem. Cosmochim. Acta, **73**, 3109-3114.

Millero, F. J., F. Huang, N. Williams, J. Waters and R. Woosley, 2009. The effect of composition on the density of South Pacific Ocean waters. Mar. Chem., **114**, 56-62.

Safarov, J., F. Millero, R. Feistel, A. Heintz, and E. Hassel, 2009: Thermodynamic properties of standard seawater: Extensions to high temperatures and pressures. Ocean Sci. **6**, 689-722.

Wilson, R. W., F. J. Millero, J. R. Taylor, P. J. Walsh, V. Christensen, S. Jennings, and M. Grosell, 2009: Contribution of fish to the marine inorganic carbon cycle. Science, **323**, 359-362, DOI: 10.1126/science.1157972.

F.J. Millero, Carbonate constants for estuarine waters, Mar. Freshwater Res., 61, 139-142, DOI: 10.1071/MF09254, 2010.

Millero, F.J. and B. DiTrolio, The effects of ocean acidification due to CO_2 dissolution, Elements, 6(5), in press to be published October 2010.

Woosley, R. and F.J. Millero, The hydrolysis of Al(III) in NaCl solutions-A model for M(II), M(III) and M(IV) ions, Aquat. Geochem., **16**, 317-324, DOI: 10.1007/s10498-009-9075-2, 2010.

5.2. Other Relevant Publications

Reports:

Millero, F. J., R.J. Woosley, J.F. Waters, M. Chanson, N.L. Williams, R. Okazaki, A. Suarez, G. Lando, C.A. Moore, 2008: Global Ocean Repeat Hydrography Study: pH and Total Alkalinity Measurements in the Pacific Ocean P18 15th December 2007-18/21 January 2008-23 February 2008, University of Miami Technical Report, No. RSMAS-2008-03, 2008.

Feely, R. A., C.L. Sabine, F.J. Millero, A.G. Dickson, R. A. Fine, C.A. Carlson, J. Toole, T.M. Joyce and W.M. Smethie, 2008: Carbon Dioxide, Hydrographic and Chemical Data Obtained During the *R/V Knorr* Repeat Hydrography Cruises in the North Atlantic Ocean: CLIVAR CO_2 Sections A20_2003 (22 September-20 October, 2003) and A22_2003 (23 October-13 November 2003), ORNL/CDIAC-153, NDP-089.

R. A. Feely, R. A., C. L. Sabine, F. J. Millero, A. G. Dickson, R. A. Fine, J. L. Bullister, D. A. Hansell, C. A. Carlson, B. M. Sloyan, A. P. McNichol, R. M. Key, R. H. Byrne, and R. Wanninkhof, 2009: Carbon dioxide, hydrograhic and chemical data obtained during the R/V Roger Revelle and Thomas Thompson repeat hydrography cruises in the Pacific Ocean: CLIVAR CO_2 sections P16S_2005 (6 January-19 February, 2005) and P16N_2006 (13 February-30 March, 2006, ORNL/CDIAC-155 NDP-090.

IOC, SCOR and IAPSO, 2010: The international thermodynamic equation of seawater - 2010: Calculation and use of thermodynamic properties. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56, UNESCO (English). Available from http://www.TEOS-10.org