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Date	Total CO ₂	Total Alk
Jan 29, 1990	33.508	2020.15
Oct 01, 1990	33.363	1978.70
Jan 08, 1991		<i>batch not stable</i>
Mar 20, 1991		<i>batch not stable</i>
May 07, 1991		<i>batch not stable</i>
May 22, 1991	38.43	2304.64

BY ANDREW G. DICKSON

STANDARDS FOR OCEAN MEASUREMENTS

ABSTRACT. The Intergovernmental Oceanographic Commission (IOC) has been involved for 50 years in promoting the close coordination needed to ensure comparability of oceanographic measurements. In particular, IOC played a key role in encouraging the development of chemical standards and reference materials for oceanic measurements. This paper briefly reviews this history, and also the early work of the author's laboratory in producing reference materials for oceanic carbon dioxide measurements. The success of the latter program in improving the state of the art of such measurements encouraged others to develop, produce, and distribute additional reference materials for dissolved organic carbon, trace metals, and nutrients. The widespread use of these various reference materials is playing a significant role in ensuring the comparability of ocean data from a variety of laboratories, thus enabling the data to be put to use in global studies.

Salinity /kg	NS
27	A
	B
	B
	B
1	A,C
	C,D
2118.25	B
2055.57	B
0	2001.23
	A
	2000.44
	C,D
6	1998.37
	A
	2012.01
	2013.42
	2025.71
	1985.61
	2011.61
	1996.35
	2020.34
	2015.92
	2016.38
	2005.36
	2003.03
	2013.85
	2115.04
	2021.65

INTRODUCTION

The earliest chemical standard for ocean measurements was the so-called Copenhagen Normal Water (later to become Copenhagen Standard Seawater) introduced by Martin Knudsen working at the Hydrographic Laboratory of the Danish Commission for Marine Research under the auspices of the International Council for the Exploration of the Sea (ICES). It was he who proposed the idea of a single standard to be used by all laboratories for salinity determination, and who agreed in 1908 to accept responsibility for the production, analysis, and distribution of this standard, which he did until his retirement in 1948 (Knudsen, 1925; Culkin, 1978). Before retiring, Knudsen proposed that the International Association for Physical Oceanography (IAPO), which became the International Association for the Physical Sciences of the Oceans (IAPSO) in 1967, assume the responsibility for operating the Standard Seawater Service. The organization agreed, and the Service remained in Copenhagen under the leadership of Frede Herman until he too retired in 1974. It continues to this day in the United Kingdom where it was first transferred to the Institute of Ocean Sciences (directed by Fred Culkin), and subsequently in 1989 to a private company, Ocean Scientific International Ltd, which produces, analyzes, and distributes IAPSO Standard Seawater (<http://oceanscientific.com>). It is experience with this Standard Seawater that has influenced academic oceanographers' views of standards for ocean measurements. This article focuses on efforts to provide standards for oceanic carbon dioxide measurements, initially for expeditions aimed at documenting the role of the ocean in taking up anthropogenic CO₂ from the atmosphere (see also Sabine et al., 2010, in this volume).

ROLE OF THE INTERGOVERNMENTAL OCEANOGRAPHIC COMMISSION

The Intergovernmental Oceanographic Commission (IOC) of the United Nations Educational, Scientific and Cultural Organization (UNESCO) was founded, at least in part, upon the need to understand ocean carbon and the recognition that this was a project that must be addressed at an international and intergovernmental level. At a planning meeting in La Jolla, California, in March 1960, Roger Revelle stated (IOCCP, 2005):

Scientific problems that require nearly simultaneous observations over a wide area or over the entire ocean also demand international co-operation in taking the observations, and close co-ordination to ensure comparability of results. An example is the present attempt to determine the total carbon dioxide content in the atmosphere and the change in this content with time as a result of the input from fossil fuel combustion and the loss to the ocean and biosphere.

At its first meeting in 1961 (IOC, 1962), IOC members again stressed the importance of standardization and intercalibration of oceanographic measurements and “felt that the task of planning new steps in the programme of standardization and intercalibration of methods and equipment should

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be delegated to SCOR because of the essentially scientific nature of this task.” As one of the resolutions from this meeting (Annexe V of IOC, 1962), the Commission tasked SCOR (the Special Committee on Oceanic Research, later to be known as the Scientific Committee on Oceanic Research) to:

Appoint as soon as possible working groups for the purpose of examining, summarizing, and criticizing the present oceanographic methods and equipment in common use to determine where these methods or equipment do not provide universally usable, accurate data, or where such data cannot presently be utilized to the utmost, and to recommend by report to the IOC appropriate steps whereby these methods or equipment should be made universally usable. This may in some cases be accomplished by standardization or by intercalibration, or by such methods as these experts may determine.

This action was taken. Perhaps the most influential of these groups was originally formed as SCOR Working Group 10 on Oceanographic Tables and Standards, reconstituted in 1962 as the Joint Panel on Oceanographic Tables and Standards (JPOTS). The Joint Panel was seen as extremely important and was sponsored jointly by UNESCO, ICES, SCOR, and IAPO (later IAPSO). The work of this group on the development of the Practical Salinity Scale and the associated equation of state for seawater, as well as subsequent work done by SCOR Working Group 127 on the Thermodynamics and Equation of State for Seawater, is the subject of another

article in this issue by Frank Millero (Millero, 2010).

However, the Joint Panel did not confine itself to salinity and to the equation of state alone. In 1986, JPOTS convened a subpanel on standards for CO₂ measurements with the following terms of reference:

1. *Co-ordination and assessment of work done towards preparing CO₂ standards for oceanic measurements*
2. *Development of recommendations for the production and use of such standards*

At almost the same time, two other groups were constituted in related areas. In 1983, SCOR formed Working Group 75 on the Methodology for Carbon Dioxide Measurements, chaired by Charles D. Keeling and C.-S. Wong. In 1984, the Committee on Climatic Changes and the Ocean (CCCCO), originally formed in 1979 and sponsored by IOC and SCOR, decided to establish an Advisory Panel on Carbon Dioxide under the chairmanship of Roger Revelle. This panel recommended an observation program and sampling strategy to determine global ocean CO₂ with an accuracy of 10–20 gigatons of carbon, nearly one order of magnitude better than the data collected by the Geochemical Ocean Sections Study (GEOSECS, a global study of the distribution of chemical tracers in the ocean carried out between 1972 and 1978).

Each of these groups articulated a similar need for standards (or reference materials) for oceanic CO₂ measurements. For example, members of the CCCC Advisory Panel on CO₂ at their 1986 meeting (CCCCO, 1989) noted:

It is essential that the results obtained be as accurate as possible so as to ensure that data collected at different times and by different investigators are as comparable as possible. One approach to assuring this would be the certification and distribution of standard reference materials (SRMs) for alkalinity, dissolved inorganic carbon, and nutrients based on natural seawater samples.

At about the same time, Working Group 75 was writing (UNESCO, 1992):

We recommend that standards be prepared and distributed to all organizations participating in the proposed oceanic carbon program. The constituents for which such standards are needed include partial pressure of CO₂ (P_{CO₂}), dissolved inorganic carbon (DIC), alkalinity, phosphate, nitrate, silicate, and salinity. Salinity standards have been used routinely at sea to calibrate salinometers for many years. We need not further consider these except to note that they serve as a model for developing standards for carbon studies where none presently exist.

Clearly, the work of the JPOTS subpanel on standards for CO₂ measurements was needed! This subpanel (which I chaired) met on three occasions. At its first meeting in Vancouver in 1987, it endorsed a plan that had been formulated by the ICES Marine Chemistry Working Group, and by SCOR Working Group 75 on Methodology for Carbon Dioxide Measurements, to carry out an intercomparison exercise to assess the quality of measurements of total dissolved inorganic carbon and total

alkalinity in seawater (Poisson et al., 1990; UNESCO, 1990). The results from this intercomparison exercise emphasized the need for standards (UNESCO, 1990):

The present situation, therefore, is that it is not yet possible for different laboratories, even those experienced in these measurements, to produce comparable and accurate data on TA, TCO₂, pH and pCO₂ in seawater. There is a clear need for standard reference materials, preferably certified by two laboratories, to be made available for all workers involved in global CO₂ programmes. This intercomparison exercise has shown that it is possible to prepare and store suitable standards which are stable for at least 15 months but to prepare them on a scale sufficient to meet the needs of JGOFS and WOCE necessitates long-term planning and allocation of funds.

The Joint Global Ocean Flux Study (JGOFS) and the World Ocean Circulation Experiment (WOCE) were large international ocean programs that began in the 1980s. WOCE was initiated by CCCO (WCRP, 1986), and JGOFS was launched in 1987 at a planning meeting in Paris under the auspices of SCOR. Two years later, JGOFS became one of the first core projects of the International Geosphere-Biosphere Programme (IGBP). Indeed, once JGOFS was formed, the CCCO Advisory Panel on CO₂ was disbanded and a Joint CCCO/JGOFS CO₂ Panel was constituted. At the first meeting of this CO₂ Panel in The Hague in 1988, one of the conclusions (CO₂ Panel, 1989) underscored earlier recommendations:

The Panel took note of the recommendation of the SCOR WG for an oceanic CO₂ standard. It strongly endorsed this recommendation and the steps being taken in the US and Canada to provide standards. The members believed more work beyond that on-going now was needed to develop, produce and distribute working reference standards on a worldwide basis.

The Joint CCCO/JGOFS CO₂ Panel subsequently formed its own Subpanel on Oceanic CO₂ Standards, Intercalibrations and Quality Assessment to keep the Panel apprised of progress in these areas.

Another important area in which IOC has played a role in the promulgation of the use of standards in marine science has been through the Global Investigation of Pollution in the Marine Environment (GIPME) program established in 1974. GIPME is co-sponsored by IOC, the United Nations Environment Programme (UNEP), and the International Maritime Organization (IMO). Three scientific groups, co-sponsored by UNEP and IOC, conduct the work of this program. Of these, the Group of Experts on Standards and Reference Materials (GESREM), also co-sponsored by the International Atomic Energy Agency (IAEA), deals with the assurance of data quality and comparability of measurements (Calder and Jamieson, 1990; Ibe and Kullenberg, 1995). At their second session in Halifax, Canada, in January 1990, members of GESREM (though largely emphasizing reference materials needed for marine pollution studies) made two recommendations related to oceanographic studies such as JGOFS (IOC, 1991). The Group:

- v. recommended the development of seawater reference materials for determinations of carbon dioxide, based on principles stated by A. Dickson
- vi. [agreed] there was strong support for continuation of the very promising work reported at GESREM-II on seawater reference materials for nutrients, dissolved oxygen and pigments

The work on carbon dioxide is detailed below; the work on nutrients noted at this meeting was that of the National Research Council of Canada. This work was described further at a 1993 GESREM workshop in Miami (IOC, 1993) and ultimately NRC Canada prepared and marketed seawater-based certified reference materials (sold as MOOS-1).

ESTABLISHMENT OF AN OCEANIC CO₂ REFERENCE MATERIAL LABORATORY AT SCRIPPS

Funded by NSF

In 1989, the US National Science Foundation (NSF) funded, as a pre-JGOFS activity, a proposal submitted by Charles Keeling and I (at the Scripps Institution of Oceanography) entitled: “The carbon dioxide system in sea water: The certification of standard reference materials for the quality control of oceanic measurements.” As noted above, there was by this time a substantial clamor for such standards, which our work could potentially address. In our proposal we wrote:

In this proposal we outline a plan to establish the capacity to perform the necessary chemical analyses required to certify standard reference materials for

the CO₂ system in sea water. We shall establish procedures which yield highly precise and accurate determinations of C_T and A_T; we will also prepare such standards and test them for long term reliability. We shall lay particular stress on the use of appropriate primary standards to control the various laboratory procedures. In addition to determining C_T and A_T for such standards, we shall cross-check our estimates of accuracy by examining the thermodynamic consistency of measurements of C_T, A_T, P(CO₂), and a measure of the hydrogen ion concentration, pH. Our research will thus provide standard reference materials for C_T and A_T that can also be used to check the performance of sea-going instruments used to measure P(CO₂) and pH.

Once the necessary preliminary work is complete, we propose to act as a central laboratory to certify such standard reference materials. We believe that the appropriate distribution agency for such standards should be the I.A.P.S.O. Standard Sea Water Service in Wormley, England. We suggest that our role, after developing suitable calibrating procedures, will be to certify batches of these standards which will then be distributed by the Standard Sea Water Service. Standard materials from other sources could also be certified if the need arose. Procedures, and reports of certification would follow closely the general approach for disseminating standard reference materials used by the U.S. National Bureau of Standards with whom we plan to consult closely.

Clearly, these goals have not yet all been achieved—and might never

be! Nevertheless, the story of how we proceeded, and of our successes and failures, may provide a useful tale.

First Batches

We began in 1989 by preparing our first (prototype) batch of reference material. This batch was based on low-nutrient surface seawater collected about 100 miles (160 km) off the California coast. This water was passed in sequence through: a carbon filter intended to reduce the amount of organics (however, as I describe later, this step was not a success), a 5 μm filter, a 0.2 μm filter, and a flow-through UV sterilizer, into a 200 L polythene drum. A saturated mercuric chloride solution was added (0.1 mL L⁻¹) to kill microbes in the water, and the contents of the drum were recirculated through the 0.2-μm filter and the UV sterilizer for about 48 hours, so as to assure sterility and to equilibrate the whole volume with atmospheric CO₂ levels. The water was bottled using gravity feed to fill the various containers, flow being controlled by a solenoid valve operated from a foot switch. The samples were bottled in borosilicate glass bottles made from Schott Duran glass with ground glass stoppers sealed with Apiezon-L grease.

This approach benefited greatly from prior experience within the oceanographic community, and especially within Keeling’s laboratory at Scripps. Wong (1970) first described the collection of samples in Pyrex glass bottles, their preservation with mercuric chloride, and the use of Apiezon-L grease to seal the stoppers. The Keeling laboratory successfully used this approach over the subsequent years. Also, tests performed by Poisson et al. (1990) indicated that

Pyrex containers were suitable for the storage of intercalibration samples.

Furthermore, the Carbon Dioxide Research Group at Scripps under Keeling's direction had begun in 1978 to effect a major improvement in measurements of dissolved inorganic carbon by collecting samples at sea that were analyzed later in a carefully controlled shore laboratory environment. Samples collected on the GEOSECS Indian Ocean Expedition, the Atlantic Transient Tracers in the Ocean Expedition, and on subsequent cruises in selected areas to create time series showed that the dissolved inorganic carbon content of a seawater sample could be measured with an imprecision of $0.7 \mu\text{mol kg}^{-1}$. The procedure used in the Keeling laboratory, which was also used to analyze our first batch of reference materials, was ultimately used to analyze numerous seawater samples as part of the WOCE/JGOFS CO_2 Program (Guenther et al., 1994).

In this analysis, a weighed seawater sample was acidified with phosphoric acid, then the CO_2 evolved was extracted under vacuum and condensed in a trap cooled by liquid nitrogen. The water and CO_2 were subsequently separated by sublimation, and the CO_2 was transferred into a mercury column manometer that had been developed originally to calibrate gases for Keeling's CO_2 in air program (Guenther and Keeling, 1986). There, its volume, temperature, and pressure were controlled and measured. The total amount of dissolved inorganic carbon in the original sample was calculated from the virial equation of state for CO_2 gas. Figure 1 shows the results for Batch 1.

Some samples from this first batch of

prototype reference materials were also sent in February 1990 to Richard Feely of the Pacific Marine Environmental Laboratory of the National Oceanic and Atmospheric Administration (NOAA/PMEL) to test on a cruise. The results were encouraging (see Figure 2). The

shipboard analyses, made using an extraction/coulometric method, showed stable values over a period of more than six weeks; however, they had a mean of 2012.6, a significant deviation from the value of $2020.3 \mu\text{mol kg}^{-1}$ obtained at Scripps. Buoyed by these successes, we

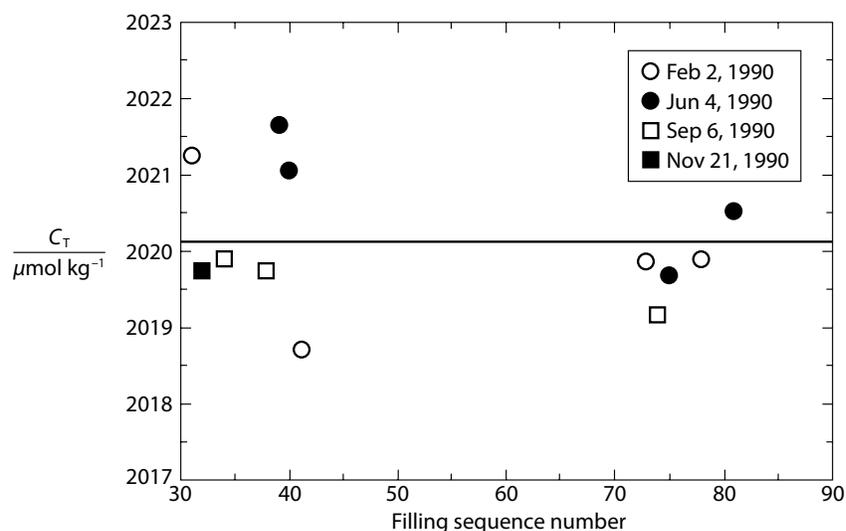


Figure 1. Total dissolved inorganic carbon results measured using vacuum extraction and mercury manometry on bottles from Batch 1 (bottled January 29, 1990). The different symbols indicate different extraction dates (noted on figure).

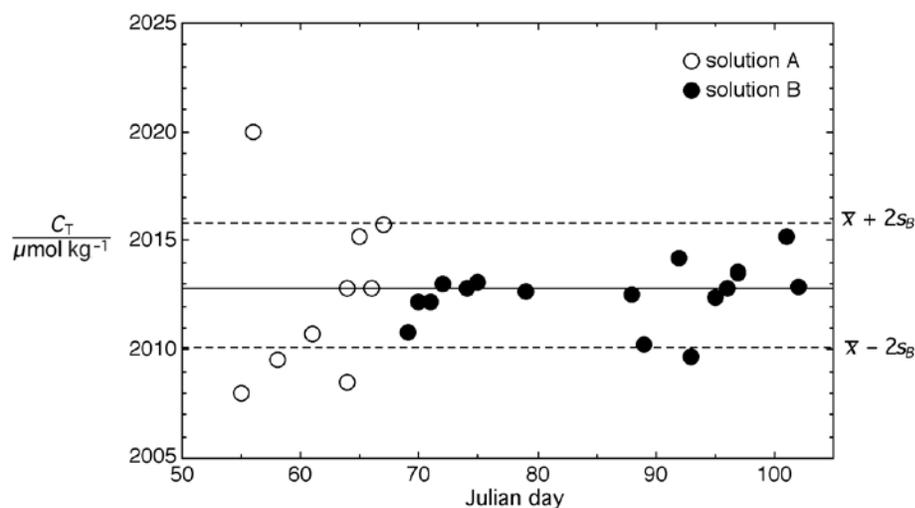


Figure 2. Control chart obtained by NOAA/PMEL during a cruise in 1990. The annotations A and B refer to the use of different batches of coulometric solution. The standard deviation s_B ($1.4 \mu\text{mol kg}^{-1}$) was calculated from the results using solution B.

prepared Batch 2 on October 1, 1990. This batch was again monitored to assess its stability and then distributed to 14 laboratories, seven in the United States and seven in Europe and Canada, for use in a collaborative study of the extraction/coulometric method for the determination of total dissolved inorganic carbon (Dickson, 1992).

Figure 3 shows the results of this first study, in which each laboratory calibrated its coulometer system independently. The need for a reliable calibration standard was clear. The weighted mean from the results of the 12 laboratories shown (i.e., omitting laboratories F and N whose data were outside the scale of the graph) was almost identical to the certified value obtained by extraction/manometry, and the individual sets of measurements were mostly of good precision—the pooled

standard deviation for all 12 laboratories was $1.6 \mu\text{mol kg}^{-1}$ —suggesting that this procedure showed promise. (Indeed, it has since become the recommended approach for the high-quality determination of dissolved inorganic carbon in seawater [DOE, 1994; Dickson et al., 2007].)

Problems!

Now, of course, things started to go wrong. Batch 3 bottled at the beginning of 1991 and sent almost immediately for use on R/V *Meteor* (WOCE Section A09) and on R/V *Discoverer* (WOCE Section P16N) was not stable, despite being filtered, preserved, and bottled using methods similar to those used for Batches 1 and 2. The CO_2 analysts on A09 (Doug Wallace and Ken Johnson) reported that they measured high and noisy values for total dissolved inorganic

carbon on this batch at sea, although the few bottles they had remaining from Batch 2 (bottled four months previously) remained stable. In addition, the samples also behaved strangely, foaming in the stripping-cell of the extraction unit. Furthermore, the partial pressure of carbon dioxide ($p\text{CO}_2$) in a gas sample in equilibrium with the seawater, measured in the reference material bottles, was high ($\sim 700 \mu\text{atm}$ at 20°C). Our measurements on bottles stored at Scripps also showed an increase in total dissolved inorganic carbon of about $4.5 \mu\text{mol kg}^{-1}$ (over a seven-week period) together with a simultaneous decrease in total alkalinity of about $8 \mu\text{mol kg}^{-1}$. The agreement between replicates also got worse.

Our initial conclusion (based on the report of substantial bottle-to-bottle variation observed at sea) was that the bottles from Batch 3 had been contaminated in some way. We thus bottled another batch (Batch 4) at the end of March 1991 using more stringent bottle-cleaning procedures. Furthermore, we increased the mercury concentration to about 14 ppm (0.025% saturated mercuric chloride). Unfortunately, these measures did not help. Initial measurements on this batch showed a similar trend with time (increasing total dissolved inorganic carbon, decreasing total alkalinity), but at three times the rate that had been observed for Batch 3!

Another feature of this batch was the presence of substantial systematic residual patterns in data from total alkalinity titrations performed in a closed-cell titration system (see SOP 3 in DOE, 1994). These residuals suggested the probable presence of unidentified organic acids, and it was clear that the amount of these was increasing with

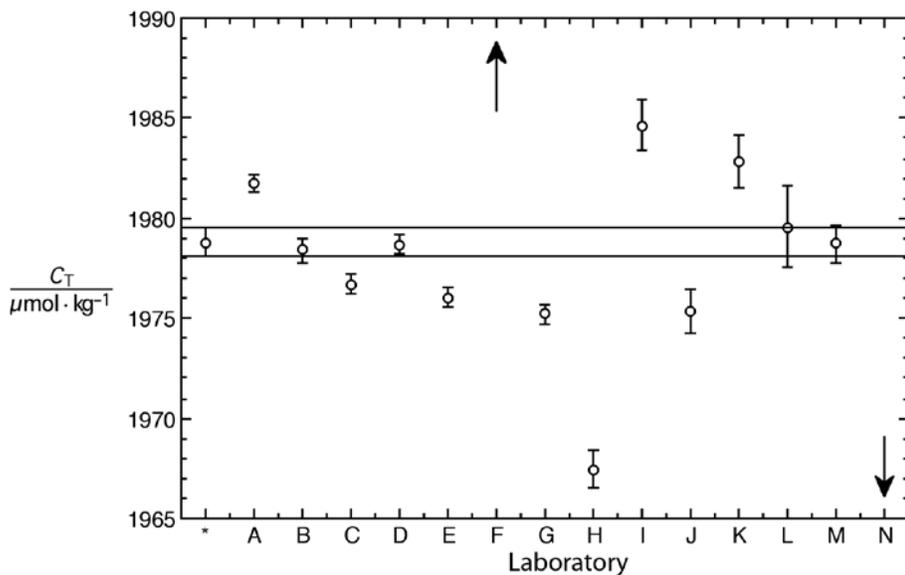


Figure 3. Results obtained by the participating laboratories from the analysis of reference material Batch 2. (The results for laboratories F and N lie off the graph as drawn.) Open circles represent the mean values; the error bars represent the 95% confidence interval for these mean values. The band across the graph is the 95% confidence interval based on the mean value obtained by vacuum extraction/manometry.

time. A small batch (Batch 5) bottled in early May also showed the same features; again, the rate of change had increased so that now changes of about $10 \mu\text{mol kg}^{-1}$ occurred in total dissolved inorganic carbon over a 10-day period, and total alkalinity decreased by about $25 \mu\text{mol kg}^{-1}$ over the same period. We initially suspected that these acids were being produced by the bacterial decomposition of organic material present in our initial seawater. (Later work implicated the carbon filter that was being used ostensibly to remove organic material, and this filter was removed from the system beginning with Batch 10.)

We also arranged to get our stored bottles of seawater analyzed for mercury by plasma emission spectroscopy at the University of Arizona. These analyses confirmed that we had indeed added mercury to our batches in the quantities that we believed we had, and that the mercury had not been removed to the walls of our bottling apparatus. We thus hypothesized that we had somehow cultivated a colony of mercury-tolerant bacteria that was now contaminating every batch. It seemed likely that this colony could be resident in our bottling system, which was left with poisoned seawater at all times in the tubing, reservoir, and pump, and that it would have had little opposition to getting established, competing bacteria having been killed by the mercury. Some number of months later, David Karl of the University of Hawaii examined a few bottles from Batch 4 to assess whether there were bacteria living in them. His conclusion was that there were, indeed, active bacteria present in the samples, capable of breaking down ^{14}C -labelled glucose and producing $^{14}\text{CO}_2$. At the

time of his experiments, however, their metabolic rate was quite low.

As a result of our suspicions of a bacterial infection in our bottling apparatus, we disassembled the bottling system completely, replaced

all tubing, fittings, and even the pump vane assembly, rinsed the remainder of the system thoroughly with 6 mol L^{-1} hydrochloric acid (a suggestion of Peter Williams here at Scripps) and deionized water, and then reassembled a clean, dry system. When we disassembled the system, we discovered a small amount of slime in some of the fittings, strengthening the case for biological contamination of the bottling apparatus. (This cleaning practice is now followed for every batch we prepare.)

By this time (April 1991), there was significant urgency to find a way to prepare stable materials for use in conjunction with the carbon measurements that were to be made as part of a joint WOCE/JGOFS Global CO_2 Survey being carried out on cruises of the WOCE Hydrographic Program (the plan originally developed by the CCCO Advisory Panel on CO_2). In addition to our grant from NSF, we

now received additional funds from the US Department of Energy (DOE) to provide reference materials to assist with the quality control of measurements on this survey.

In an almost desperate attempt to

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ensure that the reference materials were stable, our next batch, Batch 6, was made from inorganic salts: sodium chloride, sodium bicarbonate, and deionized water, and still higher mercury levels (50 ppm) were added to help sterilize it. This batch was prepared in some haste in order to load crates of the reference material on R/V *Thomas Washington* in preparation for a series of cruises in the Pacific (WOCE Sections P17C, P17S, P16S, and P16C), and for shipping for use on a NOAA cruise on R/V *Baldrige* in the South Atlantic (WOCE Section A16S). Our subsequent laboratory monitoring showed that this batch was stable, and we prepared a further batch based on sodium chloride a few weeks later before returning to further experiments with natural seawater, culminating in a stable Batch 10. Indeed, with one unexplained exception—Batch 39—we have had excellent results since that time.

Development of a Suitable Method for the Certification of Alkalinity

From the beginning, the extraction/manometric method developed in the Keeling laboratory had all the hallmarks of being suitable for consideration as a primary method for the certification of reference materials. “A primary method of measurement is a method having the highest metrological qualities, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units” (Milton and Marschal, 2001). However, when we started to prepare reference materials in 1990, there was no equivalently well-understood procedure for the determination of total alkalinity, and this parameter was typically measured using the awkward closed-cell approach described by Bradshaw et al. (1981). A significant amount of work in our laboratory in the early 1990s thus went into addressing this deficiency even while we continued to produce and distribute seawater certified for total dissolved inorganic carbon.

Our work resulted in two independent yet complementary analytical methods. First, we developed a simpler, yet quicker and more precise, method for the determination of alkalinity using a two-stage, open-cell, potentiometric titration approach. Second, we implemented in our laboratory a highly accurate coulometric titration procedure for hydrochloric acid that had been developed at the US National Bureau of Standards (see Dickson et al., 2003). The combined overall uncertainty for this determination is thus (when performed with due attention to detail) about $1.2 \mu\text{mol kg}^{-1}$ (Dickson, 2007).

As a result, all batches of reference materials starting with Batch 33 (bottled in February 1996) have been certified for total alkalinity as well for total dissolved inorganic carbon. In 1996, we also analyzed samples of stored materials from earlier batches to provide information on their alkalinity. These results, together with all the other results on our reference materials, are available at <http://andrew.ucsd.edu/co2qc/batches.html>.

Distribution and Use of Reference Materials

Since the beginning, we have distributed our oceanic carbon reference materials widely. Our DOE funding enabled us to provide materials to all laboratories that were participating in the WOCE/JGOFS Global CO₂ Survey (free to US laboratories, for the cost of shipping alone to our various international collaborators), and

and handling charge). Nevertheless, the demand continued. After 10 years, we had distributed over 23,500 bottles and now, after 20 years, this number has grown to more than 56,000 bottles shipped to 33 countries. Indeed, in the past year alone, we shipped over 6,500 bottles all over the world!

Measurements made on reference materials while at sea were used extensively to ascertain data quality on the various cruises in the WOCE/JGOFS Global CO₂ Survey (see, for example, Johnson et al., 1998, and Millero et al., 1998) and are felt to have contributed substantially to the overall high quality of the resultant data set. A further indication that the use of reference materials has improved oceanographic data quality can be seen by examining the degree of agreement between measurements for deep water masses obtained

“ THE WIDESPREAD USE OF THESE REFERENCE MATERIALS IS PLAYING A SIGNIFICANT ROLE IN ENSURING BOTH THE COMPARABILITY OF OCEAN DATA COLLECTED BY A VARIETY OF LABORATORIES AND USE OF THE REFERENCE MATERIALS IN A VARIETY OF GLOBAL STUDIES. ”

we did so. By the end of 1997 (when that survey and the associated DOE funding came to an end), we had distributed over 17,500 bottles of reference material to scientists in 25 countries.

Starting in 1998, we began to charge \$30 per 500 mL bottle for the reference materials (in addition to a shipping

where two separate cruises intersect. For cruises where reference materials are available, measurements of total dissolved inorganic carbon in deep water now often agree to within $2 \mu\text{mol kg}^{-1}$ (Sabine et al., 1999; Lamb et al., 2002; Wanninkhof et al., 2003). This agreement is in sharp contrast to the problems

with earlier oceanic carbon data sets, where ad hoc adjustments of as much as 15–20 $\mu\text{mol kg}^{-1}$ were sometimes applied so as to attain reasonable data compatibility (see, for example, Gruber et al., 1996, and Gruber, 1998).

Such high-quality CO_2 data sets made possible the real science of JGOFS by providing a resource for synthesis and modeling that enables a coherent global view of the oceanic carbon cycle. Thus, high-quality, global pictures of the ocean's carbon cycle, such as those of Sabine et al. (2004) and Feely et al. (2004), are now practical, based on data from a wide variety of laboratories. Indeed, it is hoped that it will now be possible to resolve changes on shorter time periods as a result of the high-quality data that are now almost routine (Feely et al., 2005).

Problems Found and Lessons Learned

Looking back at the ambitious goals spelled out in our original proposal and in later proposals (NSF has supported us continually since the beginning), it is humbling to see how slowly we have achieved them despite continuous activity over the past 20 years. For example, we are only now (in 2010) distributing pH reference materials on a regular basis. These materials are based on a tris buffer in synthetic seawater (DeValls and Dickson, 1998; Nemzer and Dickson, 2005), prepared in 40 L quantities, and certified using hydrogen electrodes. We have not yet managed to certify our seawater-based reference materials for pH, though we continue to wrestle with achieving a sufficient understanding of the spectrophotometric pH method (Clayton and Byrne,

1993) to assure us that we do indeed have a calibration of this method for which we understand the overall uncertainty. We have—as yet—done nothing toward the calibration of seawater $p\text{CO}_2$ measurements, though our reference materials have been used to assess the quality of discrete measurements of this quantity (Neill et al., 1997). Nor have we made progress in certifying reference materials for ^{13}C levels in the total dissolved carbon, although preliminary work carried out about 15 years ago indicated that these samples were ideal for this purpose.

A careful study of CO_2 thermodynamics carried out by Tim Leuker in Keeling's laboratory (Leuker et al., 2000) showed that—at least at $p\text{CO}_2$ values less than 500 μatm —the techniques used to certify our reference materials for total dissolved inorganic carbon and for total alkalinity were consistent with the preferred equilibrium constants for CO_2 dissociation in seawater. However, this was no longer true at higher $p\text{CO}_2$ values, and to date these observations have not been explained satisfactorily.

So, why are so many things left undone? Ultimately, the reason has been lack of time and/or of sufficiently trained personnel. In some ways, we have been victims of our own success. The relentless need to produce and certify new batches of reference materials in order to supply the demands of the oceanographic community has kept the skilled personnel assigned to this task busy, leaving little extra time for further related projects. We are now producing about eight batches of seawater reference material (1100 bottles in each batch) per year, as well as an additional two to three batches of tris buffer.

Also, the skills required to develop new approaches to certify these reference materials at the accuracy desired take time to acquire. I am fortunate in having had some truly excellent and experienced technical staff involved with this project over the years, but although some were (and are) superb analysts, they have not had formal training in either chemical metrology or in formal quality-control procedures.

An early ambition of this program was to have the reference materials themselves prepared outside the university, for example, at Ocean Scientific International Ltd (OSIL), which prepares and distributes IAPSO Standard Seawater. OSIL prepared one test batch (Batch 24) using clean bottles and shipping crates that we sent them together with water they collected from the North Atlantic. The overall cost was higher than doing the work in house, and we did not pursue this as a viable way forward at that time. (Now that Europe is heavily involved in ocean acidification research activities, it may well be desirable to revisit this.) We had also hoped to work more with the US National Institute of Standards and Technology (NIST) to improve our approach to reference material production, and in particular certification. I met on a number of occasions with staff from NIST. It was clear that, although they could and did provide good advice, it was not likely that NIST would consider preparing reference materials for what they considered a niche market.

Another area we hope to address as we move forward is to see if we can package the reference materials differently. The use of glass bottles (which are returned to our laboratory and cleaned

for reuse) brings with it—in addition to the undoubted advantage that it works—additional shipping costs for such heavy containers, and because the bottles are rigid, requires containers significantly larger than might be needed to provide an adequate sample size for analysis. We are therefore investigating the potential of flexible packaging made from a trilaminate film.

CONCLUSIONS

The success of our reference material program for ocean CO₂ measurements has led to a clear recognition within the oceanographic community of both the benefits and the costs of developing chemical reference materials explicitly for oceanographic science. Each of them can be substantial (in our own case, NSF has invested about \$3.5M between 1989 and 2010). Nevertheless, the oceanographic community has come to appreciate the value of such reference materials as a way of ensuring comparability

acidification studies (Dickson, 2010).

An early companion program, based at the University of Miami and also supported by NSF since about 1998, produces reference materials for dissolved organic carbon in seawater (see <http://www.rsmas.miami.edu/groups/biogeochem/CRM.html>). Dennis Hansell leads this effort and—as with our program—the demand for these materials has grown over the years.

In 2001, the National Research Council (NRC) Ocean Studies Board convened a Committee on Reference Materials for Ocean Science. The committee was charged with the following tasks (National Research Council, 2002):

- Compile from available sources a list of important oceanographic research questions that may benefit from chemical reference standards
- Create a comprehensive list of reference materials currently available for oceanic studies

- Determine the most appropriate approaches for the development and future production of reference materials for ocean sciences

A variety of recommendations were made as to the need for reference materials for ocean sciences (Box 1), and since that time there have been a number of significant developments. NSF supported a multi-investigator collaboration to follow up on recommendations 6 and 7 (Box 1) and develop oceanic reference materials for trace metals at natural concentration levels (Johnson et al., 2007). As suggested by the NRC committee, two large samples—one of surface water and one of deep water—were collected and bottled. Consensus values have now been assigned to these SAFe (Sampling and Analysis of Fe) Reference Samples, and additional samples are being prepared (<http://www.geotraces.org/Intercalibration.html#Standards>).

The lessons learned from this work are being implemented in planning for GEOTRACES, an international study of the marine biogeochemical cycles of trace elements and their isotopes. The international GEOTRACES project (GEOTRACES Planning Group, 2006), learning from the experiences of earlier projects such as WOCE and JGOFS, formed a Standards and Intercalibration Committee from the outset to ensure appropriate quality control for the project, including, if needed, the production and distribution of additional reference materials.

In Japan, there has also been recent work focused on the measurement of nutrients and of ocean CO₂ parameters. An International Workshop on Chemical Reference Materials in Ocean

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of ocean CO₂ results in space and time (see, for example, Key et al., 2004; Sabine et al., 2005; Bates, 2007), and reference materials are now used widely for ocean CO₂ measurements, as well as being recommended to ensure interlaboratory comparability for a variety of ocean

- Identify and prioritize the reference materials needed to study the identified research questions
- Determine for each priority analyte whether reference materials and/or analytic methods should be standardized

Science was held in Tsukuba, Japan, from October 29–November 1, 2007, in conjunction with the BERM-11 meeting (Biological and Environmental Reference Materials). A follow-up meeting was held in Paris, France, from February 10–12, 2009 (UNESCO, 2009; Aoyama, 2010). Ota et al. (2010) described a facility built by Kanso Technos that is dedicated to the production and bottling of sterile seawater. This facility contains a “walk-in” autoclave and a suite of clean rooms for sample preparation. This facility has been used to prepare large batches (up to 6,000 bottles at a time) of sterilized natural seawater, which is being investigated primarily for use as a reference material for nutrients in seawater. In addition, this system is being used to investigate whether it is practical to prepare reference materials for the oceanic CO₂ system that have been sterilized by autoclaving, thus providing the added benefit that they do not contain mercuric chloride (Murata, 2010).

As a result of the positive discussions and collaborations from these first two workshops, the participants decided to approach IOC and ICES to form a study group with sponsorship from these two organizations. This effort was successful, and the study group held its first meeting from March 23–24, 2010. In the coming years, this group plans to continue collaborative testing of the candidate reference materials, as well as to work with the National Metrology Institute of Japan to certify these materials. Thus, it is apparent that IOC continues, 50 years on, to have a keen interest in enabling international standardization and intercalibrations on into the future. Many thanks!

BOX 1. RECOMMENDED REFERENCE MATERIALS FOR OCEAN SCIENCE

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MATERIALS RECOMMENDED FOR CONTINUED AVAILABILITY

Currently Available Materials

1. Standard Seawater (Ocean Scientific International Ltd.)
2. Reference Materials for Ocean CO₂ (NSF via Dr. A. Dickson)
3. Reference Materials for Dissolved Organic Carbon (NSF via Dr. D. Hansell)
4. Various Standard Reference Materials from NIST

MATERIALS RECOMMENDED FOR DEVELOPMENT

Seawater-Based Reference Materials

5. One certified for the nutrient elements: nitrogen (as NO₃), phosphorus (as PO₄), and silicon (as Si(OH)₄).
6. One with concentrations of metals corresponding to oceanic deep water, certified for total iron concentration.
7. One with concentrations of metals corresponding to open-ocean surface water with an information value for total iron concentration.

Certified Reference Materials for Radionuclides

8. An acidic solution containing ²³⁸U and ²³⁵U with daughters in secular equilibrium through ²²⁶Ra and ²²³Ra.
9. An acidic solution containing ²³²Th with daughters in secular equilibrium through ²²⁴Ra.
10. An acidic solution containing ²¹⁰Pb with daughters in secular equilibrium through ²¹⁰Po.

Solid Matrix-Based Reference Materials*

11. Freeze-dried culture of the diatom *Thalassiosira pseudonana*
12. Freeze-dried culture of the dinoflagellate *Scrippsiella trochoidea*
13. Freeze-dried culture of the haptophyte *Emiliana huxleyi*
14. Open-ocean, carbonate-rich sediment
15. Open-ocean, silicate-rich sediment
16. Open-ocean, clay mineral-rich sediment
17. Coastal, carbonate-rich sediment
18. Coastal, silicate-rich sediment
19. Coastal, clay mineral-rich sediment
20. Deltaic sediment (that has not contacted seawater)

* Each of these solid reference materials should be certified for both inorganic and organic carbon concentrations, total nitrogen concentration, δ¹³C of both the inorganic and organic carbon components, and δ¹⁵N for the total nitrogen component.

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