

# The Influence of David Keeling on Oceanic CO<sub>2</sub> Measurements

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Dave Keeling—only Roger Revelle called him “Charles David” and always in a tone that could command Dave’s attention—had a remarkable influence on the creation of modern understanding of the oceanic CO<sub>2</sub> system. Although Dave resided at an oceanographic institution for almost his entire professional career, the great majority of his work concerned atmospheric measurements; his own account of his work [Keeling, 1998] makes scant reference to his ocean science papers. But those relatively few oceanic papers, and more importantly his intense personal interest and unimpeachable reputation for classic measurement, had enormous impact. It is possible to trace Dave’s influence on oceanic measurement through the course of five decades, and over that time, our understanding has grown enormously. The following is a somewhat personal account, but Dave so influenced the careers of the small group of ocean CO<sub>2</sub> scientists that have led the way that any one of them would write a similar account.

## 1. INTRODUCTION

Today, as the global CO<sub>2</sub> perturbation has grown so large that plans to constrain and dispose of emissions are being considered, there is great demand for monitoring our planet so that the benefits, costs, and risks of trying to constrain this complex system can be calculated. David Keeling’s career laid the foundations for this. The ocean has now absorbed some 500 billion tons of fossil fuel CO<sub>2</sub>, almost all of this within the last century. Continuation of this trend promises to drive our atmosphere and ocean chemistry beyond limits not seen on this planet for geologic time scales, with consequences very difficult to predict accurately. Keeling early on foresaw these issues, and they motivated him for a career spanning over five decades.

Dave’s early passion was for accurate atmospheric CO<sub>2</sub> measurement, but he quickly realized that all of the same,

and many new and more complex, problems lay in accurate observation of the ocean. An account [Keeling, 1968] of his early recognition of this is given in his classic summary of one of the first global sea surface *p*CO<sub>2</sub> maps, and it is worth extracting from that account here:

“The tables, as revised [Buch, 1951] permit the computation of *p*CO<sub>2</sub> from measurements of pH and alkalinity. Buch . . . intercompared procedures under shipboard conditions and was satisfied that they gave comparable results . . . From the time of the expeditions of the *Discovery* [Deacon, 1940] until the International Geophysical Year, 1957–1958, almost all investigators of the carbon system in ocean water relied on pH measurements to determine *p*CO<sub>2</sub>. These investigators, in their optimism for having found a simple measuring routine, failed to note that the new method was scarcely capable of detecting the small changes in pH of surface ocean water that reflect significant changes in *p*CO<sub>2</sub>.”

The problems readily identified by Dave in his 1968 paper, the low buffer capacity of ocean water, the high salt content relative to the standard buffers used for pH calibration, and the complex physical chemistry of seawater, were to plague ocean scientists for more than a decade [Bradshaw

*et al.*, 1981]. It was two decades until the new technologies of scanning spectrophotometry with well-characterized dyes arose that enabled ocean scientists to finally use field pH measurements to constrain the oceanic CO<sub>2</sub> system with the required accuracy [Byrne and Breland, 1989].

The property of  $p\text{CO}_2$  is capable of precise measurement, but the oceanic surface signal varies so enormously in space and time compared to the atmospheric property that integration is very difficult. Accurate measurements of two properties of the aqueous CO<sub>2</sub> system are required to constrain the signal, and attention turned to this problem. The measurement of the primary CO<sub>2</sub> system mass properties of seawater, alkalinity, and TCO<sub>2</sub>, were driven in the 1960s by the elegant titrimetric work of Dyrssen and Sillen [1967]. The stature of Sillen was immense both from his fundamental work on measurement and models of chemical equilibria and also from his classic paper on the geochemical origin of the chemistry of seawater where the long-term buffering of the ocean through silicate weathering was made clear for the first time [Sillen, 1961].

Sillen had taken a sabbatical at Scripps, and he was influential in the work of Edmond [1970] in developing to the next level the titration technique pioneered by Dyrssen and Sillen. Given the eminence of Sillen, and the assertiveness of Edmond, one may have expected Keeling to adopt these procedures so actively espoused within his own Institution. But this was not to be. Rightly concerned over the latent complexity of the seawater system as sensed by a glass electrode [no doubt from his experiences with the  $p\text{CO}_2$  procedures of Buch (above)], and having possession of a gas-extraction/CO<sub>2</sub> measurement laboratory, Dave, together with his student C. S. Wong, established a painstaking gas-extraction/infrared procedure for measurement of TCO<sub>2</sub> [Wong, 1970]. Some years later, this evolved through the efforts of Peter Guenther into a manometric determination of the quantity of extracted CO<sub>2</sub> that was to serve as the unassailable benchmark for decades in resolving the disputes over measurements of the oceanic signal that were to come. Once again, he took his own route, and the conflict between the various ways of measuring the oceanic CO<sub>2</sub> system that he identified was to haunt the field for many years to come. Vestiges of those problems exist today.

## 2. THE SURFACE OCEAN $p\text{CO}_2$ SIGNAL

The use of nondispersive infrared analyzers for atmospheric CO<sub>2</sub> measurements was pioneered by Keeling; but it was a young Taro Takahashi who first adapted this new technology for oceanic measurement [Takahashi, 1961]. The reliable mapping of sea surface  $p\text{CO}_2$  on a global scale could now proceed, and Dave Keeling was in the vanguard. In a se-

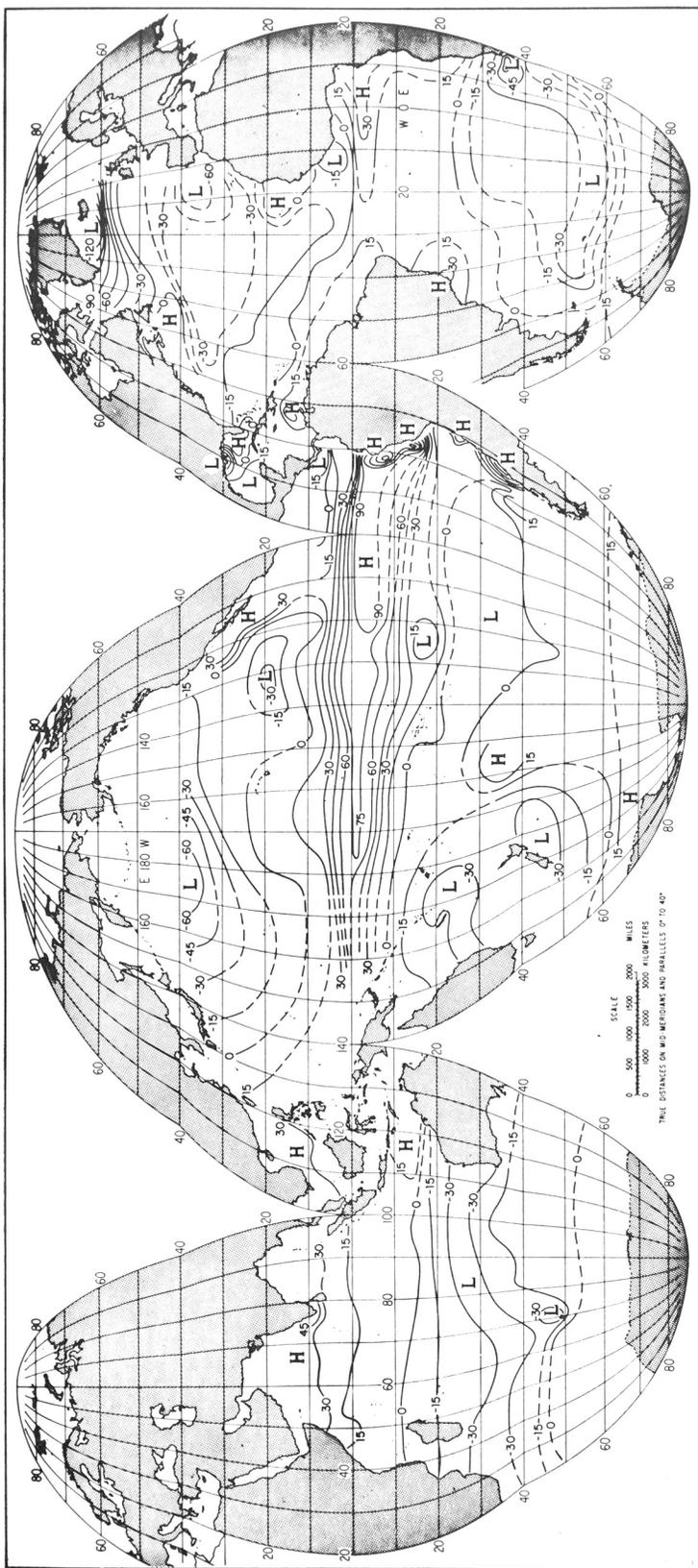
ries of four papers summarized in 1968, he produced the first global picture of ocean surface  $p\text{CO}_2$  (Figure 1), showing the breathing of the sea—the slow transfer of CO<sub>2</sub> between air and water [Keeling, 1968]. In doing so, Dave was intelligently taking advantage of the near-unique Scripps pattern of sending major research vessels out on very large-scale expeditions. These provided platforms for the nonintrusive surface mapping of  $p\text{CO}_2$ , so that this could be accommodated within all manner of geophysical or biological cruises so long as there was a spare berth on board for a skilled assistant to tend to the system.

The dominant seasonal signal of CO<sub>2</sub> in the atmosphere naturally leads to concerns over the validity of such a coarsely sampled system from a ship slowly moving in space and time; it would be decades before the complex oceanic seasonal  $p\text{CO}_2$  signal would be well understood. The data were obtained through the labor of Lee Waterman and others, who painstakingly tended the analyzers through long days at sea, writing numbers on a chart recorder, and meticulously filling in log books. Dave noted that the data were dominantly summer time sampled, so that seasonal bias was present but possibly coherent. The map was hand-drawn and interpolated intuitively.

The dominant equatorial Pacific upwelling signal was massively present, as were the subpolar lows, now known to arise from photosynthetic uptake. The large equatorial Pacific source of CO<sub>2</sub> to the atmosphere continued to fascinate him, and he made sporadic attempts to follow this with the aim of constraining the El Niño-driven changes in atmospheric CO<sub>2</sub>. Dave noted also in his 1968 paper what I take to be the first expression of the correlation with heat flux, as opposed to simple temperature: “ $p\text{CO}_2$  can vary as a result of a (rapid) change in water temperature.” It is true that it had long been recognized that ocean heating and cooling would raise and lower  $p\text{CO}_2$ , but the formal connection between the rate of temperature change and the size of the resulting air–sea disequilibrium had yet to be established.

As far as I know, Dave did not again produce such a global  $p\text{CO}_2$  synthesis; that task was undertaken with amazing skill, insight, and persistence by Taro Takahashi, who in a career spanning five decades has devoted himself to this. Today, the maps of sea surface  $p\text{CO}_2$  are vastly more populated with data (e.g., Plate 1), artfully corrected for seasonality [Takahashi *et al.*, 2002] and are used with wind fields and models in an effort to better constrain CO<sub>2</sub> sources and sinks [Murnane *et al.*, 1999; Sarmiento *et al.*, 2000].

Dave did, however, continue to be engaged in the problem of determining the accuracy of  $p\text{CO}_2$  techniques and measurement throughout his career. He was concerned over the smallest details, for example, ensuring that the distinction between partial pressure and fugacity was kept in mind



**Figure 1.** The hand-drawn 1968 Keeling map of sea surface  $p\text{CO}_2$ , expressed as the departure in ppmv from equilibrium with atmospheric  $\text{CO}_2$ . *H*, indicates high; *L*, low.

[Weiss *et al.*, 1982]. With one of his very few students, he reinvestigated the problem [Lueker *et al.*, 2000] of the validity of the thermodynamic constants that were so bravely addressed in planning the Geosecs program. The conclusion, that the calculation of  $p\text{CO}_2$  from analyses of  $\text{TCO}_2$  and alkalinity could result in an uncertainty in  $f\text{CO}_2$  of 1%, was classic precise Keeling science.

### 3. THE GEOSECS ERA AND THE USE OF CHEMICAL TRACERS

#### 3.1. The Pre-Geosecs Period

The use of tracers, initially conceived of as radioisotopes but soon broadened to accommodate a wide variety of chemical species with a definable half-life, to investigate ocean mixing and transport processes on a large scale was first seriously tackled by the astonishingly creative geochemical team at the Lamont Geological Observatory [Broecker *et al.*, 1960, 1961]. Dave Keeling had been hired at Scripps by the legendary Roger Revelle, and the classic paper by Revelle and Suess [1957] outlining the challenge of mankind's "great geophysical experiment" was very much on Keeling's mind, although the styles of Revelle and Keeling could not have been more different. Thus, it was natural for him to tackle the tracer problem with the aim of coupling the information on the physical circulation with the strictures on observing and constraining the oceanic CO<sub>2</sub> system.

This challenge was met in partnership with Bert Bolin [Keeling and Bolin, 1967, 1968] in two exhaustively detailed papers which utilized the box model approach pioneered by Riley [1951]. The papers, highly formalistic and almost impossible to read, nonetheless contain some inimitable Keeling phrases that give clues as to his views on measurement needs and the then-dismissive attitude of the larger ocean science community to the problem he saw as central. For example, "The complicated electrochemical property, pH, and quotients of chemical concentrations such as 'specific' alkalinity are therefore unacceptable as tracers" and "Because of its chemical bivariance, the inorganic carbon system poses a more difficult problem in evaluating chemical transport than tracers such as salinity and oxygen. This perhaps explains the reluctance of oceanographers to give carbon, the element most intimately and fundamentally involved in organic processes in the oceans, the same degree of attention that they have devoted to the related tracers, oxygen and phosphorus."

The final words of the 1968 paper are telling, "Particularly important is the need to increase drastically the accuracy of observations of (the) inorganic carbon system. We conclude that present routine measurements of pH, not more accu-

rate than  $\pm 0.01$ , are of little value for general ocean circulation studies. Also, more information on organic carbon is needed." The words were prescient.

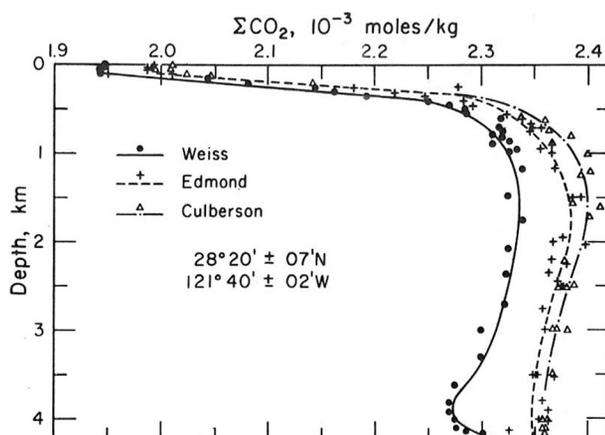
We thus had the situation wherein the same volume of a distinguished journal (*Tellus*, XIX), two separate papers from distinguished teams expressed deep concern for the lamentable state of oceanic CO<sub>2</sub> observations that derived from pH measurements. One provided advocacy for the adoption of far more sophisticated electrochemical procedures [Dyrssen and Sillen, 1967], and one expressed strong doubts that "complicated electrochemical properties" [Keeling and Bolin, 1967] could provide an answer. At issue was not some nicety, but critical decisions as to how to measure the ocean that were to haunt the field for the next dozen years.

#### 3.2. The Geosecs Period, 1967–1979

The Geosecs program was a major expeditionary effort to provide the first global snapshot of the evolving tracer field in the ocean. It was a period of extraordinary creativity and energy. The bomb radiocarbon and tritium signals had already penetrated the oceanic thermocline and were providing the first glimpse of transient tracers. In preparation, a 4000-m-deep test station in the Pacific was occupied in 1969 and a second Atlantic station in 1970 [Turekian, 1970]. The results of the analysis of the inorganic CO<sub>2</sub> system gave cause for concern [Takahashi *et al.*, 1970]. A team of eight investigators had measured the full suite of ocean CO<sub>2</sub> system properties ( $p\text{CO}_2$ , pH, alkalinity, and  $\text{TCO}_2$ ) on identical water samples, and the accuracy and precision were far from satisfactory.

Figures 2 and 3 show the results of the  $\text{TCO}_2$  and TA measurements; presumably, these were of higher quality than any that had gone before, for the stakes were high and the teams prepared. But the deep water alkalinity values diverged on average by about 50  $\mu\text{mol/kg}$ , and the  $\text{TCO}_2$  values by a similar amount. The strictures raised by Keeling and Bolin were all too painfully true. In an extraordinarily creative effort at compromise Takahashi *et al.* [1970] suggested that the entire data set could be reconciled "if a 30% error in the second apparent dissociation constant of carbonic acid ( $K_2'$ ) is assumed." The pH data were indeed accurate to only  $\pm 0.01$  as feared by Keeling and Bolin, and the ensemble of complex CO<sub>2</sub> system equations embedded in the paper spoke eloquently to the "complicated electrochemical properties." Interestingly Keeling's student, Wong, was not invited to participate in the cruise, although he was included as a coauthor in the subsequent paper.

These problems were to plague the program for some time. The enormous number of samples to be processed required shipboard analysis, and the titrimetric techniques of-



**Figure 2.** The  $\text{TCO}_2$  profile measured at the Geosecs 1969 test station [Takahashi *et al.*, 1970]. The titrimetric and pH data, dependent on glass electrode techniques, lie to the right of the data cluster. The gas chromatographic data are to the left. The spread of values in the profile is about  $50 \mu\text{mol/kg}$ —approximately a factor of 10 worse than desired for reasonably constraining the  $\text{CO}_2$  system. A failure to preserve the samples for shore-based analysis with  $\text{HgCl}_2$  meant that the samples analyzed in the Keeling laboratory were not available for comparison.

ferred the primary way of accomplishing this. Therefore, the Geosecs expedition set off and in 1972–1973 executed the major Atlantic Ocean survey [Craig and Turekian, 1976], closely followed by the 1973–1974 Pacific Ocean survey [Craig and Turekian, 1980]. The troublesome titrimetric procedures were adopted, but with critical checks and balances provided by discrete  $p\text{CO}_2$  measurements [Takahashi *et al.*, 1976]. The wisdom of providing some redundancy in measurement was to become abundantly clear.

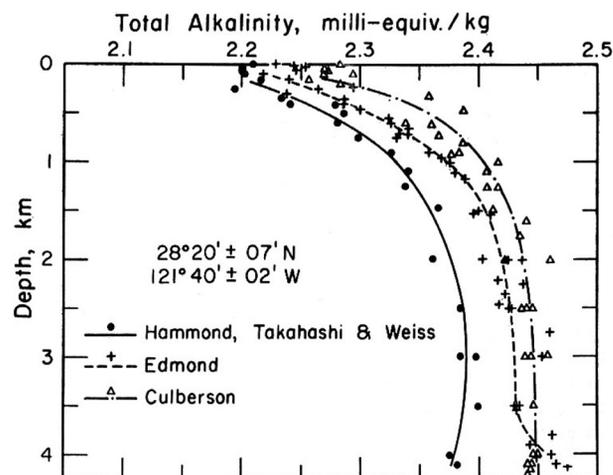
The cost of the skilled human labor involved in making the thousands of measurements over many, many months at sea should not be underestimated. It was thus with great care and respect that the outcome of the Atlantic and Pacific Ocean  $\text{CO}_2$  surveys was examined. The problems, foreseen by Keeling, had not gone away [Takahashi, 1977], and the discrepancy between  $p\text{CO}_2$  observed and computed had, if anything, grown worse. The titrator results yielded  $p\text{CO}_2$  values up to 20% higher than those obtained by direct measurement. Despite this, expeditionary work in the Indian Ocean proceeded in 1978.

### 3.3. The Post-Geosecs Period

By 1979, a full 10 years had passed since the creation of the Geosecs program, and the situation was critical since major publication of the results was being unconscionably

delayed. An emergency meeting, held at Scripps in December 1979 was called to address these concerns. I had been advised for a long time to stay out of these controversies, but that was no longer possible, and Dave Keeling had provided strong behind the scenes support. In a series of papers [Brewer, 1978; Brewer and Goldman, 1976; Brewer *et al.*, 1975], I had uncovered the unrecognized effects of nitrogen oxidation state changes on the alkalinity, observed this process experimentally, and used the information to extract a tentative fossil fuel  $\text{CO}_2$  signal from a Geosecs Atlantic leg on which I had served as co-chief scientist. The work was not without controversy, and validation/resolution of the Geosecs  $\text{CO}_2$  results was essential.

In preparation for the 1979 meeting, I had uncovered some surprises and became keenly aware of the Keeling concerns over (unspecified) complexity. The much heralded titrimetric work of Edmond [1970] was misleading. It contained a diagram showing the potential influence of a great many minor constituents of seawater ( $\text{HSO}_4^-$ , HF, etc.) on the determination of  $\text{TCO}_2$  and alkalinity, leading many to believe that these corrections had been applied. But no such steps had been taken; the numerical treatment had ignored these components—the diagram was simply an illustration, not an implemented procedure. In addition, a hero of Geosecs, the technical leader Arnold Bainbridge (who had briefly worked in the Keeling laboratory), had died suddenly. He alone had had knowledge of exactly what numerical procedure



**Figure 3.** The alkalinity profile measured at the 1969 Geosecs test station [Takahashi *et al.*, 1970]. The determination of alkalinity necessarily involves a titration procedure. The spread of values obtained was approximately  $50 \mu\text{eq/kg}$ , much as was observed for the  $\text{TCO}_2$  determination. Taken together, these two results gave serious concern as to whether the aims of the program could be achieved.

had been implemented for the titration algorithms that had driven thousands of measurements at sea over a decade of controversy, and he had left no detailed record.

The only recourse was to reverse engineer the software written in Fortran (and some machine code for the micro-processors for instrument control) for the state-of-the-art shipboard computer system that was the Geosecs' pride and joy. I volunteered to undertake that task and took home a large binder of printout, generously loaned by Bainbridge's deputy Bob Williams. Within a few hours, I had narrowed the search to a few lines of code that looked most unusual, and I wisely sought help from my colleague Alvin Bradshaw.

The end result [Bradshaw *et al.*, 1981] was surprising. Arnold Bainbridge had apparently been aware of the deficiencies in the paper of Edmond's [1970] and had crafted some remedies, but he had done so without telling anyone. The Swedish team of Hansson and Jagner [1973] had already published a very nice improvement to the titrimetric technique, but there is no evidence that Bainbridge was aware of this. For example, his equations contained representations of the presence of, e.g., HSO<sub>4</sub><sup>-</sup> and HF, but not of the obvious CO<sub>3</sub><sup>-</sup> and OH<sup>-</sup>.

It was very confusing, and it was clear that a complete rewrite from first principles of the protonation sequence of seawater was required and that a major recomputing of each titration curve of the entire global data set would then have to be carried out. In the course of this, we uncovered several new effects, including the contribution of phosphate to both the alkalinity and total CO<sub>2</sub> determinations. The Keeling warnings of complexity had come to pass—the appendix to the paper of Bradshaw *et al.* [1981] considered 17 interacting chemical complexes in addition to the normal H<sub>2</sub>O and CO<sub>2</sub> system constants. When this recalculation was complete, it was clear that the inconsistencies pointed out by Takahashi [1975] were entirely correct and could very largely be resolved with the new chemical models; these included for the first time the influence of phosphate on the computed TCO<sub>2</sub> and the effects of silicate. A full decade after the test cruise, the problem had been solved [Bradshaw *et al.*, 1981], and the results were published in the Geosecs series of atlases.

### 3.4. The TTO Cruises and Beyond

The Geosecs program had left a major gap in North Atlantic observations due to early technical flaws. It was agreed that this should be remedied as soon as possible. With the apparent success in resolving the CO<sub>2</sub> system measurements, this was to be a primary focus of the cruise. The acronym TTO stood for Transient Tracers in the Ocean, a reference to the power of the information provided by the growing

number of chemical species with a specified input history [Broecker and Peng, 1982].

Keeling had long argued that the CO<sub>2</sub> increase itself could be used as its own tracer. In a long discussion, Keeling [1982] noted, "Why not regard the dissolved inorganic carbon (DIC) in ocean water also as a transient tracer...?" and "...we have achieved for several hundred pairs of samples a precision of  $\pm 0.5 \mu\text{mol kg}^{-1}$  for each pair." The earlier detection of the fossil fuel signal [Brewer, 1978] based upon the Geosecs titrimetric data was still viewed with suspicion, although the basic equations derived are in use in only slightly modified form to this day. So it was natural to turn to Keeling for the reference method even though that was "so tedious that the cost of a single analysis is comparable to that of a radiocarbon analysis."

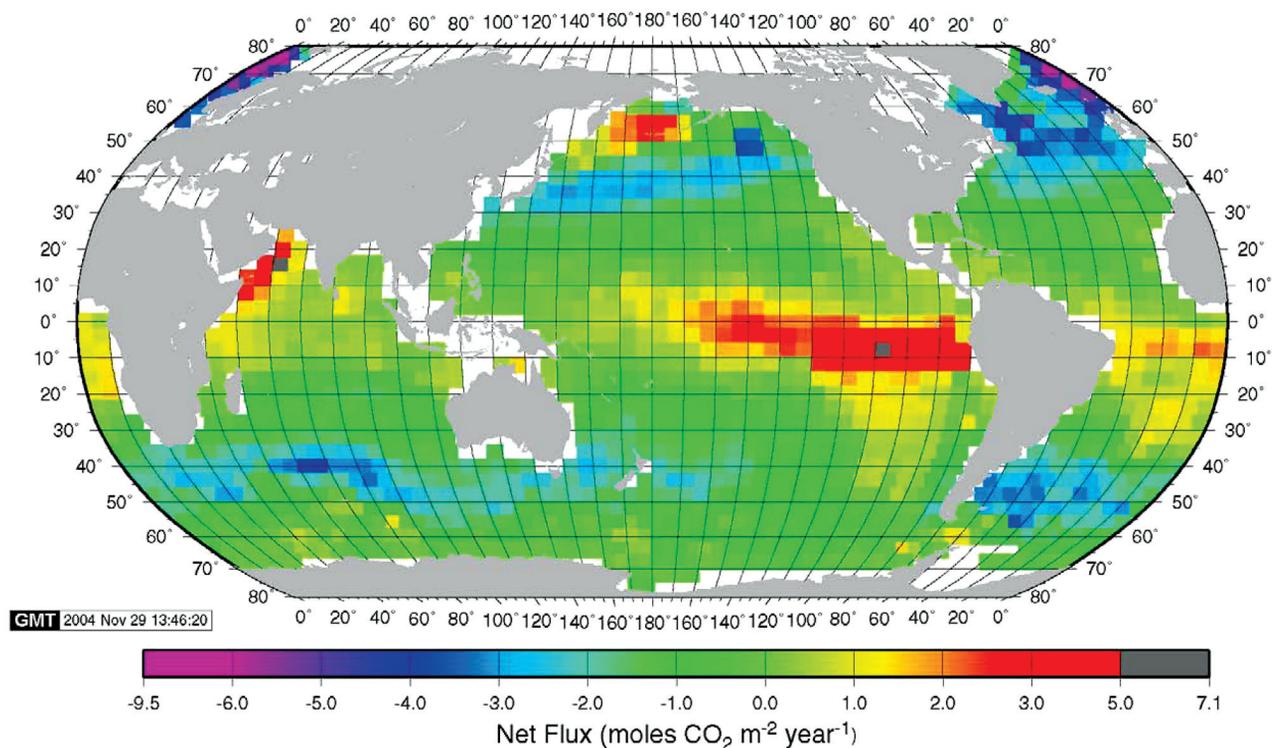
The tediousness and cost were real; but so was the problem, and so funds were awarded to the Keeling laboratory for measurement of a select subset of samples from the TTO North Atlantic survey. The results (Figure 4) were rewarding. The TTO program had in 1981 occupied 250 hydrographic stations, providing unprecedented coverage of the North Atlantic using the same titrator systems that had created the Geosecs data set, but with the new chemical models implemented. The mean deep water difference in TCO<sub>2</sub> between the Keeling "tedious" data and the rapid shipboard analysis was only +4  $\mu\text{mol/kg}$ . This finally achieved the goal set in 1967, and the high precision alkalinity results were also verified. Such was the stature of the Keeling measurement protocol that no one doubted the result.

## 4. THE ESTABLISHMENT OF OCEAN TIME SERIES

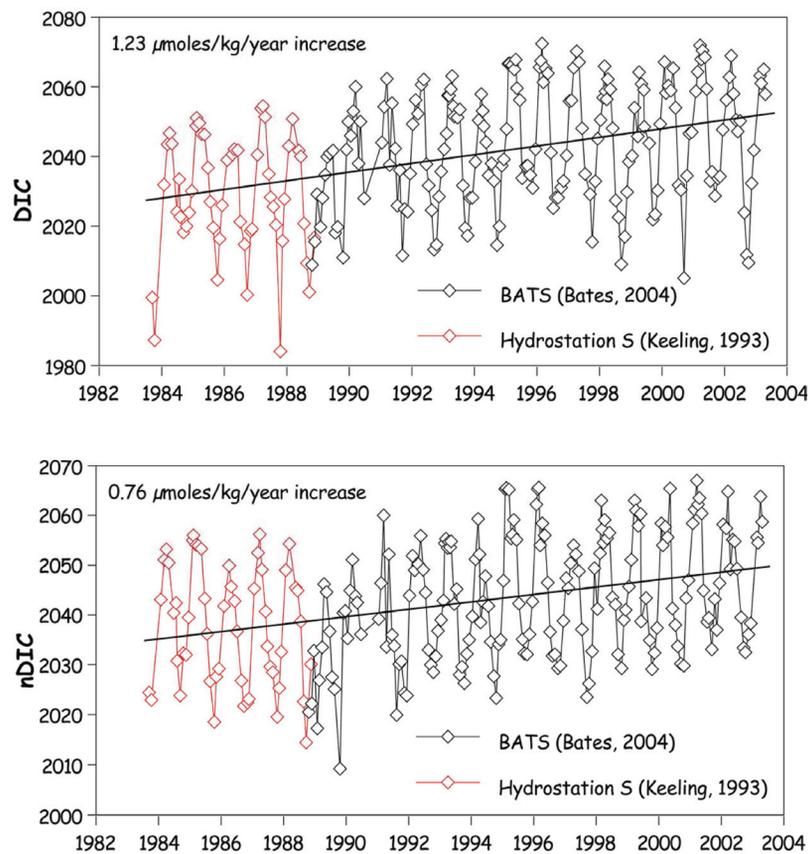
The 1981 TTO and immediate successor South Atlantic program (SAVE) were the last of the style of science begun in the Geosecs period. Things had to change, and the largely abiological tracer approach would have to compete with the vigorous new discipline of global biogeochemical cycles. New techniques were appearing, fresh and eager young scientists were bubbling up, and ocean modeling was racing ahead. Moreover, public and policy interests in the growing CO<sub>2</sub> problem were reaching to high levels, and different questions were being asked.

I had taken a 2-year position at the National Science Foundation late in 1981 [Brewer, 2000] and was asked to serve on a *National Academy of Science* [1983] report on "Changing Climate." The assembled team of scientists, economists, and policy figures had little knowledge of, or tolerance for, the arcane details of CO<sub>2</sub> system measurement above. They wanted answers about the rising ocean CO<sub>2</sub> uptake if (to my absolute astonishment) this could be proven. I went back to my office and funded a proposal from Keeling, who was re-

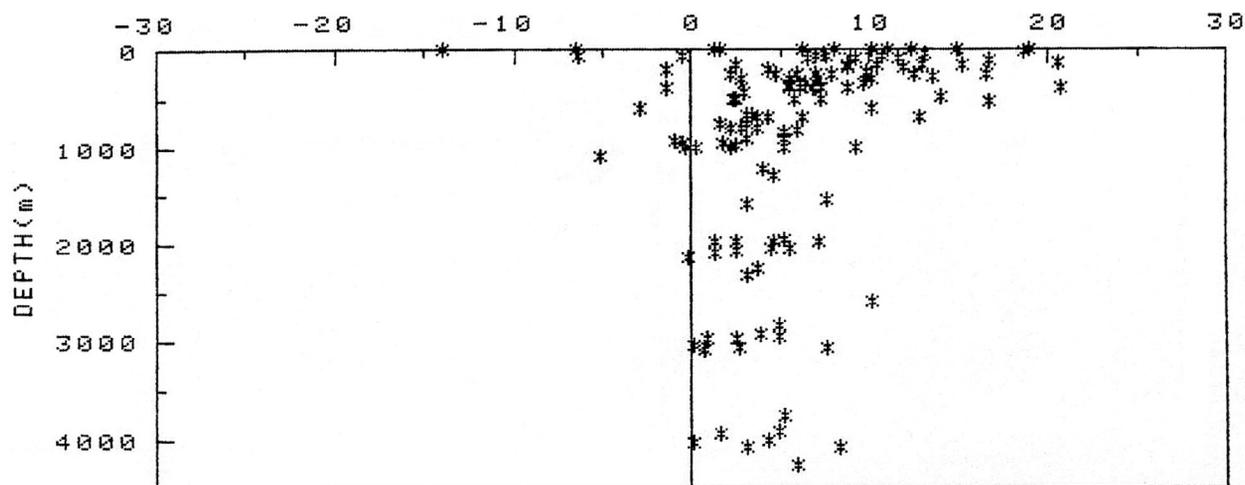
### Mean Annual Air-Sea Flux for 1995 (NCEP 41-Yr 10 Meter Wind, 1,744K, W-92)



**Plate 1.** Net sea-air CO<sub>2</sub> flux over the global oceans for a reference year 1995 representing a 1960–2004 climatological mean for non-El Niño years [Takahashi *et al.*, 2002]. The map is constructed on the basis of about 1.75 million surface ocean water  $p\text{CO}_2$  measurements, excluding the equatorial Pacific data (10°N–10°S) during El Niño periods. The sea-air CO<sub>2</sub> transfer rates are estimated using the (wind speed)<sup>2</sup> dependence of Wanninkhof [1992] and the NCEP 42-year mean wind speeds corrected to 10 m above sea surface. The yellow-orange color indicates that the seawater is a source for atmospheric CO<sub>2</sub> and the blue-magenta color indicates a sink for atmospheric CO<sub>2</sub>. The net ocean uptake flux of CO<sub>2</sub> from the air in 1995 is estimated to be about 1.5 ± 0.3 Pg C/year. Note that the correlation of the large-scale features with the 1968 map of Keeling are preserved as deviations from atmospheric equilibrium, even though the absolute value of the atmospheric signal has increased by approximately 60 ppm.



**Plate 2.** The interannual variability of surface seawater dissolved inorganic carbon ( $\mu\text{mol/kg}$ ) in the ocean near Bermuda as determined initially by Keeling from March 1983 to September 1988. The units of “nDIC” in the lower panel refer to the data normalized to a salinity of 35. These data were obtained at Hydro Station S. The data from 1988 to the present were obtained by N. Bates [Bates, 2004] at the Bermuda Atlantic Times Series (BATS) site. The unquestioned accuracy of the initial Keeling observations led to the wide acceptance of these elegant observations.



**Figure 4.** The difference (in  $\mu\text{mol/kg}$ ) between titrimetric measurements of  $\text{TCO}_2$  in seawater, and the gas extraction/manometric data of Keeling, as achieved during the TTO program in 1981 [Brewer *et al.*, 1985]. The agreement is about one order of magnitude improved over that obtained during the 1969 Geosecs test cruise (Figure 2). The increased difference in the upper ocean values has not yet been satisfactorily explained. From Brewer *et al.* [1986].

questing support for a set of surface ocean measurements from somewhere on a remote South Pacific island. The basis for this was that the seasonal signal and biological effects were small, potentially allowing for easier recovery of the fossil fuel  $\text{CO}_2$  invasion signal.

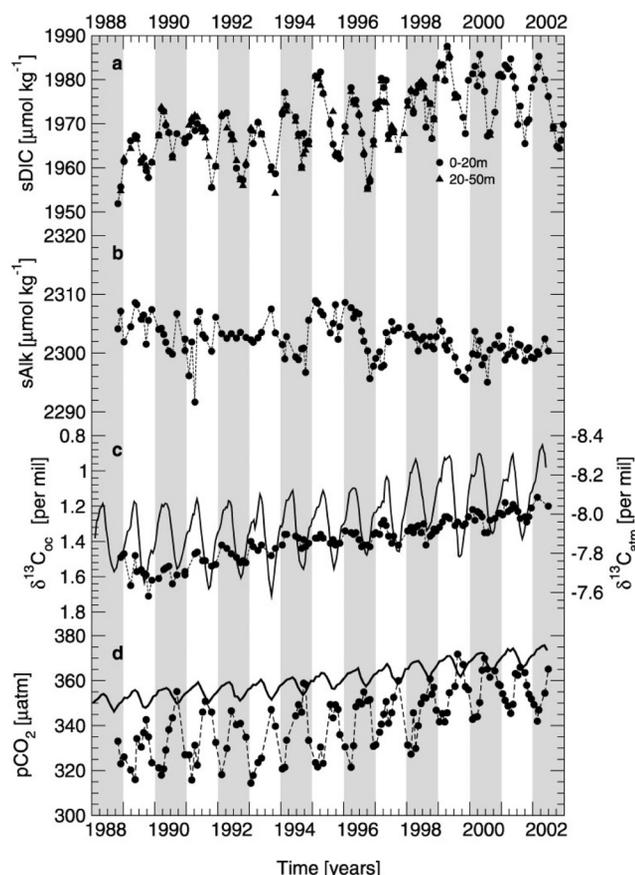
It appeared to me that this would result in a fragmentary and isolated data set, with none of the essential linked observations of ocean biogeochemical cycles. I strongly suggested to Dave that he carry out the work at Bermuda, where there was a long established time series station with excellent supporting work. I had already carried out some early titrimetric  $\text{CO}_2$  work there and was well aware that the seasonal signal had a strong biological component superimposed upon the thermal signal. In retrospect, this decision to confront the issue of biogeochemical cycles rather than avoiding them [Brewer, 1986] marked a significant turning point in the growth of “biogeochemical cycles” as a widely adopted ocean theme which more formally emerged later in the Joint Global Ocean Flux Program [Brewer, 2003].

Dave Keeling did not have a mean bone in his body, but neither did he have a practical one, and it was with bewilderment that he received this news. The negotiations went on for some considerable time as, with slowly diminishing disbelief, he came to the realization that work at a well-established time series site might be useful. With reluctance, he engaged in discussions with the staff of the Bermuda Biological Station and quickly became enamored of their efforts and the strong support he received. The results (Plate 2) were absolutely convincing, and they unequivocally set the

standard for ocean time series measurements which continue to this day [Bates, 2001].

The establishment, nurturing, and modeling of atmospheric time series work was Dave’s ultimate contribution. Thus, one might have expected him to apply the same passion to oceanic time series because from 1983 onward, he was in a formidable position to do so. But that did not occur due largely to the pressure of other work; thus, the exceptionally productive time series stations that became established at Bermuda (BATS) and Hawaii (HOT) under the aegis of the Joint Global Ocean Flux Study (JGOFS) proceeded for a decade largely without Dave’s active participation, although his background presence was of constant value. By this time, it is clear what progress in oceanic  $\text{CO}_2$  measurement has been made. We may contrast the results in Figure 2 with those in Figure 5: the 1969 confusion over a spread of as much as  $50 \mu\text{mol/kg}$  at a single station has been replaced by the ability to detect a time change of surface ocean  $\text{CO}_2$  concentrations of  $1.6 \pm 5.8 \mu\text{mol/kg/year}$  superimposed upon a complex natural background signal. This would not be possible without Dave’s early work.

Dave is most widely known for his atmospheric time series work at the Hawaii Mauna Loa observatory. Thus, it is natural that he should eventually return to the oceanic signal off Hawaii. With establishment of the HOT time series station within the JGOFS program, and an elegant and complete data set, new opportunities, fully supported by first class biogeochemical studies [Karl and Lukas, 1996] opened up. In one of Dave’s last first authored papers, he provided



**Figure 5.** From Keeling *et al.* [2004]. The time series record of surface ocean CO<sub>2</sub> properties at the JGOFS Hawaii Time Series Station (HOT). These CO<sub>2</sub> measurements were made in the Scripps laboratory, and in modeling the results, he was returning to his fundamental passion for understanding the changing CO<sub>2</sub> status of our world.

a characteristically thorough analysis of the observations made there by his laboratory [Keeling *et al.*, 2004].

The key to this transformation in data assuredness from the Geosecs days was the deliberate break away from the “complicated electrochemical properties” for determination of TCO<sub>2</sub>, as advocated by Keeling and Bolin in 1967 (although this technique remains essential for the determination of alkalinity). But the overly tedious method of Wong [1970] used for, e.g., the early Bermuda time series measurements was not the answer. The credit for that goes to K. M. Johnson and colleagues who took the gas stripping step and combined this with coulometric detection of the extracted CO<sub>2</sub> [Johnson *et al.*, 1985, 1987, 1993]. This technique was very rapidly adopted and developed into a precise tool by David Chipman and Taro Takahashi at Lamont, and it is now used

worldwide; the correspondence with the Keeling laboratory measurements is now universally accepted.

## 5. COMPLETING THE PICTURE

This story would not be complete without recognition of Dave’s legendary passion for accuracy that pervaded all his undertakings. One aspect of this was his strong support of Andrew Dickson at Scripps, who laudably provided the first authoritative standards for seagoing TCO<sub>2</sub> and alkalinity measurements in the form of a standard seawater bottle akin to the long time “IAPSO Standard Sea Water” used for salinity calibration [Dickson, 1990; Dickson *et al.*, 2003]. Although these standards have proved invaluable in tracing the imprint of the fossil fuel signal on ocean waters worldwide, in the matter of TCO<sub>2</sub>, it is the parentage in the Keeling calibration world that gave the initial credibility.

The smallest details did not escape Keeling’s attention. But nor did some of the larger issues that were overlooked by many. The last sentence of the 1967 Keeling and Bolin paper reads “Also, more information on organic carbon is needed.” That comment was prescient.

In the Geosecs period of 1967–1979, the problems with determination of the oceanic CO<sub>2</sub> system were so large that this topic could be safely neglected. With the creation of more rigorous procedures [Brewer *et al.*, 1986], the problem could no longer be ignored. The discrepancy shown in Figure 4 had to be accounted for, and the influence of acidic moieties in marine dissolved organic matter [Bradshaw and Brewer, 1988] on the titrimetric procedure (absolutely no one doubted the Keeling results!) was offered as one possible explanation. That, together with controversial reports of dissolved organic matter distributions closely correlated with oxygen utilization [Sugimura and Suzuki, 1988], lead to a renewed attack on the oceanic dissolved organic matter problem. The technique issues were resolved [Sharp *et al.*, 1995], and for the first time, a correct local mass balance of the carbon budget could be obtained [Peltzer and Hayward, 1996]. It is worth commenting that Peltzer was, however briefly, one of Keeling’s students. The global contribution of the dissolved organic signal to the ocean water column carbon budget is about 10%—once again, Dave was proven, many years later, to be correct.

David Keeling will be sorely missed, for his influence has been so profound. His strictures on accurate observation and reporting were legendary, often reaching well beyond the world of science. I once had a call from a Capitol Hill staffer who asked to meet with me. They were baffled. There had been a flap over the continued provision of support for accurately prepared gas standards. Thinking this was a small matter, the staff had dismissed it speedily. They vastly under-

estimated Dave's tenacity in pursuing this, and months later, the standards were preserved in a manner that satisfied the highest standards of measurement. The legacy depends on Dave's lifelong courage in speaking up for honest science.

*Acknowledgments.* I must also acknowledge a more personal debt for Dave's many kindnesses over the years. I first met Dave when he spoke at the spring 1968 AGU meeting in Washington, D. C. The meeting took place amid the riots arising from the assassination of Martin Luther King Jr., and a curfew held the scientific participants in close proximity. I nervously went up to Dave after his talk—the only one of a large audience who did so. I shall never forget his courtesy to a young scientist, and I recall it every time I first meet with someone early in their career. Dave insisted on giving me two papers which I still treasure, not, I was amazed to find, of his own work, but on longer range issues. One was a paper on the finiteness of our energy resources; it remarked that the scale, rapidity, and sophistication of our extractive procedures was now so advanced that should some catastrophe occur, it would be very difficult for a machine-based civilization ever again to arise upon this planet. The second was on the personal tragedies that would increasingly be felt as the natural world around us changed as a result of our industrial activities. Although these themes rarely arose in his scientific writing, they appeared time and again in conversations. At Dave's last scientific talk at this Chapman Conference, his final figure was the famous King Hubbert curve showing the astonishing rise and inevitable fall of our fossil fuel resource extraction and the impact this would have on our world. He always had the big picture in mind. Financial support was provided by The David and Lucile Packard Foundation and by the U.S. Department of Energy (grant DE-FC26-00NT4092). I thank A. Dickson and K. Caldeira for helpful comments on the manuscript.

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