Comments on "A short history of ocean acidification science in the 20th century: a chemist's view."

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I very much enjoyed this somewhat personal view of the development of ocean acidification science through the 20th century. I feel it will be a useful addition to the literature, and am happy to see it published.

Thank you for the kind words. I will see if I can attend to most, if not all, of these helpful comments.

I have one significant suggestion for the author's consideration, and a few more minor comments.
The more significant suggestion is that Dr. Brewer consider the interesting series of papers addressing what has come to be known as "ocean acidification" that were published in the early 1970s. In hindsight, there were hints (as I recollect – I do not have access to the book at this time) in, Broecker, W.S., Li, Y.H. & Peng, T.H. (1971), Carbon dioxide – Man's unseen artifact, in *Impingement of Man on the Oceans*, ed. Hood, D.W., John Wiley & Sons, 287–324.

The reviewer is correct that these articles appeared and the choice of how many papers to cite in a review not intended to be encyclopedic is difficult. I too do not have a copy of the 1971 Broecker/Li/Peng book chapter and was thus reluctant to cite it blind. But the early contributions by Broecker and colleagues were so powerful and influential that, although they do not directly address modern concerns over biological impact, they should be cited. I have added the reference.

As an aside a difficult choice was whether to cite the many early papers in the 1920s and 30s by K. Buch on ocean pCO_2 observations and the use of the chemical constants. I elected not to cite these since growth trends and biogeochemical impacts were not addressed, and the results hint at considerable inaccuracies due to the unfortunate technical limitations of the times.

Then two articles appeared in 1973, each of which (though flawed) alluded to likely changes in carbonate equilibria and potential implications for marine organisms:
Fairhall, A.W. (1973) Accumulation of fossil CO_2 in the atmosphere and the sea. *Nature* v. 245, 20–23 (*Erratum* Nature v. 246, 106)
Zimen, K.E. & Altenhein, F.K. (1973) The future burden of industrial CO_2 on the atmosphere and oceans. *Naturwissenschaften* v. 60, 198–199.

Interestingly, neither of these articles was written by an ocean scientist; perhaps why they were neglected? However, they sparked some controversy at the time:
Whitfield, M. (1974) Temperature, fossil CO_2 accumulation and carbonate ion concentration of the mixed layer. *Nature* v. 249, 818–820.

My apologies here. The 1974 Whitfield paper and its antecedents were described in some detail in the oral presentation of this paper given at the 2012 "High CO2 Ocean" meeting. This was inadvertently left out of this manuscript and has now been rightfully inserted.

Skirrow, G. & Whitfield, M. (1975) The effect of increases in the atmospheric carbon dioxide content on the carbonate ion concentration of surface ocean water at 25 °C. *Limnology & Oceanography* v. 20, 103–108.
Fairhall, A.W. & Erickson, J.L. (1975) Future impact of fossil CO_2 on the sea. *Nature* v. 254, 273–274.

I would be interested in Dr. Brewer's take on why these various papers disagreed so on what he refers to as "quite simple calculations". I suspect, in part, it reflects the degree of uncertainty in the community about the quality of ocean CO_2 measurements and the associated thermodynamic data that he alludes to when discussing the 1969 GEOSECS test station.

I am unsure of how to reply here. The debate at the time was intense over what procedures were reliable, over what data could be useful, and there was lack of comprehension over what proved to be the rapid increase in the CO2 emissions rate. In 1969 at the time of the GEOSECS test station there was considerable naiveté over the technical chemistry issues. The results shown here were certainly bracing and controversial.

My more minor comments are:
(1) In equation 1 of this manuscript, the impression is given that the potential of the cell is dependent solely on the hydrogen electrode. This is not so, as I recollect Sørensen used a calomel reference electrode and thus may have written as he did in subsequent papers (the Nernst factor 0.0577 is for 18 °C):

$$\frac{\pi - \pi_0}{K} = \log\left(\frac{1}{C_H}\right)$$

I suspect the form of equation 1 used came from Jensen's paper in *J. Chem Ed.*

The reviewer is correct that the form of Equation 1 is taken from Jensen's paper, and I have modified the manuscript to acknowledge this. The choice I made for this narrative history form was an attempt to communicate to as large an audience as possible, and I am reliably informed that chemical equations often do not help in this matter. So with some considerable difficulty I reduced the formalism to only the simplest equation; and with remarkable restraint the only equation in the entire manuscript.

(2) Sørensen did carry out seawater pH measurements, though I would not really refer to them as significant. He calibrated indicator dyes for use in seawater, and reports a variety of measurements on seawater samples.

Sörensen, S.P.L. & Palitzsch, S. (1909) Über die Messung die Wasserstoffionenkonzentration des Meerwassers, *Biochemische Zeitschrift* v. 24, 387–415.

I will add this as a brief comment. Thank you.

(3) The comment “The term pH applies only to aqueous solutions” is not strictly true. See the comment below from the IUPAC Compendium of Analytical Nomenclature (1997)

Procedures analogous to those on which a practical pH scale for aqueous solutions have been based can be used to establish operational acidity scales in certain nonaqueous and mixed solvent media. A universal pH scale relating proton activity uniformly to the aqueous standard reference state is not possible, but separate scales for each medium can be achieved and will fulfill most of the requirements, such that the notional definition is ${}_{s}pH = - \log (m_{H\,s}\,{}_{s}\gamma_{m,H})$, where ${}_{s}{}_{s}\gamma_{m,H}$ is referred to the standard state in each particular medium s. The 'normal scale length of pH' in each solvent and solvent mixture is determined by the autoprotolysis constant (see section 3.2.3.5).

I see that this point is technically correct and I will change the wording to reflect this.

(4) In section 3, the manuscript states that: “only 1 part in 600 of the CO_2 and organic carbon that had at one time been in circulation in the atmosphere and ocean is now buried in sedimentary rocks. . . .”; is this ratio not inverted?

Good point and this legendary paper is worth expanding on. The full quote is:“ Carbon plays a significant part in the chemistry of sea water and in the realm of living matter. The amount now buried as carbonates and organic carbon in sedimentary rocks is about 600 times as great as that in today’s atmosphere, hydrosphere, and biosphere. If only 1/100 of this buried carbon were suddenly added to the present atmosphere and ocean, many species of marine organisms would probably be exterminated.”
This material is now added to the text.

(5) It is possible, though unlikely, that the Russian pH measurements were on the “NBS pH scale” as we now know it. Although the work on defining pH buffers started at NBS in the 1940s, a key aspect to the NBS scale was adoption of the 1960 Bates-Guggenheim convention for the treatment of the limiting activity coefficient of chloride ion in the buffer solutions. I suspect the Russians used similar buffers, though with this aspect defined differently. Certainly, I doubt this distinction makes any real difference to the likely uncertainty of the Russian measurements.

It is hard to make such distinctions in a paper for general reading. How about “likely using an early form of the buffers which were already forming the basis of what later became the fully developed form of the widely used NBS scale.”