

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

Andrew Dickson (Scripps Institution of Oceanography, San Diego, USA)

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

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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> accumulation and carbonate ion concentration of the mixed layer. *Nature* v. 249, 818–820.

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<sub>2</sub> 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<sub>2</sub> measurements and the associated thermodynamic data that he alludes to when discussing the 1969 GEOSECS test station.

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.*
- (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.  
Sørensen, S.P.L. & Palitzsch, S. (1909) Über die Messung die Wasserstoff-  
ionenkonzentration des Meerwassers, *Biochemische Zeitschrift* v. 24, 387–415.
- (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  $\text{pH} = -\log(m_{\text{H}^+} \gamma_{\text{H}^+})$ , where  $\gamma_{\text{H}^+}$  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).
- (4) In section 3, the manuscript states that: “only 1 part in 600 of the CO<sub>2</sub> 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?
- (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.