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## ***Interactive comment on “Comparison of seven packages that compute ocean carbonate chemistry” by J. C. Orr et al.***

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### INTRODUCTION

As the authors point out, there is a significant interest in correctly performing the various equilibrium calculations that allow one to link the composition of a seawater system (with respect to the concentrations of all the various acid-base species that are present in the seawater) to the more limited number of composition variables that can be measured by some form of chemical analysis. Furthermore, such calculations (and more particularly the work required to ensure appropriate input data) are of sufficient complexity that many researchers are happy to use a publically available program, rather than develop one for themselves. The question thus arises: are such programs equally “correct”?

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For independent implementations of such calculations to be equivalent, a number of aspects need to be identical: first, the set of species that is considered needs to be the same in the two implementations; second the numerical values of every one of the various equilibrium constants required (usually calculated as functions of salinity, temperature, and pressure) need to be identical over the whole range of salinity, temperature, pressure, being considered; and third, the values for each of the remaining analytical parameters that are themselves inferred from salinity (e.g. total sulfate, total fluoride, total boron, . . .) need to be identical over the whole range of salinity being considered. If these are indeed identical, and if the floating-point arithmetic (e.g., IEEE-754) is implemented appropriately, then it is hard to believe that any noticeable discrepancy need exist. Nevertheless, as the authors point out, discrepancies do exist, even to this day.

The reasons for these discrepancies are often not clear; in this manuscript the authors have – perhaps – done their best to identify likely causes. (In many cases as they have not had access to the original computer code, they infer likely errors rather than confirm them.) The principal difficulty seems to derive from the historical complexity of representing acid-base reactions in seawater media, involving as it does 4 alternate “pH scales” that can be inter-related with varying degrees of sophistication; as well as differing approaches that have been used to extrapolate data for equilibrium constants measured at 1 atm total pressure to higher pressures appropriate to the deep ocean. Thus the key reason for most observed discrepancies – put plainly – is probably that the different independent implementations are ultimately using somewhat different values for the equilibrium constants. The reasons for this vary: on occasion they are a consequence of the proliferation of detectable misprints in the original literature (see e.g., detailed discussions by Lewis & Wallace, 1998); on other occasions they probably reflect errors in introducing pressure corrections to the equilibrium constants, possibly confounded by the difficulties in choosing a pressure-dependent approach to convert constants from one pH scale to another.

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If we are to avoid this in the future, then the community needs access to a clear statement of the chemical model (i.e., indicating all the various species that are being considered) together with their equilibrium relationships; it also needs to agree on an unambiguous statement of the values of the various equilibrium constants (and any salinity-dependent total concentrations) as straightforward functions of salinity, temperature, and pressure. It would then be practical for separate groups to implement subsets of the calculations in a consistent fashion and that are optimized for their aims. It should also be possible to agree on a formal structure for converting between pH scales that would itself be internally consistent. Of course, at present it should be recognized that any agreement as to the “best” values for any of these equilibrium constants (and salinity-dependent total concentrations) is likely to be far more subjective than objective in its basis and open to future change. This is also, of course, equally true for the “pressure corrections” that are used to adjust 1 atm values to higher pressures.

Nevertheless, such a consistency even if achieved would not be sufficient. It is essential to recognize that such a model has inherent uncertainties. These take two forms: first, the model itself may be incomplete – that is there may be other acid-base systems present in the seawater that have been neglected; second, all the various “data” for equilibrium constants and for salinity-dependent total concentrations are necessarily based on experimental measurements and thus are necessarily uncertain. There is a clear need for these various uncertainties to be estimated appropriately and then to be propagated into future such calculations. Indeed, ultimately once such uncertainties are well established, it should provide a clearer rationale for the choice of “recommended” equilibrium constants (those with well-understood, and ideally small, uncertainties).

#### COMMENTS ON THIS MANUSCRIPT

So, though this manuscript certainly does not solve the current problems in a clear way, it does do a good job of outlining the present state of the art in the various computer codes that are widely available. In particular it makes clear that the various codes are

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not equivalent, and that none of them is complete – offering all likely calculations for all likely input data combinations.

The ad hoc approach they have taken: comparing results to those obtained using the MATLAB version of CO2SYS, is reasonable and justified in section 2.1. However, it does leave open the possibility that that code is itself imperfect, and that its imperfections have been adopted (possibly unknowingly) by other codes with which it agrees. Another difficulty they have is in distinguishing between the existence of small (but real) errors, and problems with comparing floating point answers, particularly when the number of significant figures is limited (e.g., CO2calc). They are fairly honest about this (though perhaps do not recognize all the places it could have happened) and have, I believe, addressed the difficulty conscientiously. In a number of cases, they try to explicitly link discrepancies in computed values to inferred discrepancies in the various data that are enshrined in the various codes; to the extent these discrepancies cannot be directly identified (due to lack of access to the internal code) the reasons for such discrepancies, though plausible, may not be proven.

I did wonder at the added value of using the GLODAP data as an exercise strategy for comparing the codes over a range of conditions; it certainly makes clear those codes that are slow, but does not seem to have added much more than a carefully structured examination of the S, T, p space might have done.

The discussion of difficulties with making “correct” pressure adjustments to the various equilibrium constants is salutary. It points out how much this area depends on a single paper by Frank Millero in 1995, and on Ernie Lewis’s interpretation of how to implement them in his version of CO2SYS, as well as his extensive work on tracking down typographic errors (see Appendix in Lewis & Wallace, 1998). It is certainly a good thing that the authors include the various coefficients used in these adjustments in their Table 7, so others have them all in one place, however it might be a good time to revisit this and to assess the likely uncertainty resulting from such adjustments. It was interesting to note that the authors choose to present data for a “new” set of K1 and K2 in Table 10,

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noting that the published values for these coefficients and the values in a spreadsheet of Prof. Millero differ. I would point out that if the authors wish to assess whether or not the values published for the total hydrogen ion scale are equivalent to those for an alternate pH scale, the best approach is to look at the ratio  $K1/K2$  which should remain independent of the choice of pH scale. If this is not true, there is certainly a problem .

. .

It was interesting to see how the authors used sensitivity analyses to better discriminate between alternate hypotheses as to the likely sources of errors. I would like to point out, however, that the sensitivity coefficients in Table 9 are themselves function of the composition of the solution, and thus it would be clearer to indicate that in the Table legend. (I shall reconsider my earliest work in the light of the comments here – may need to pull my PhD back out) – but wonder if the apparent differences are not (at least in part) due to my decision in 1978 to use carbonate alkalinity directly, rather than total alkalinity. The sensitivity factors with respect to calculations involving AT are bound to be different, and also to change with the exact conditions being considered – as noted above.)

## CONCLUSIONS

The authors should be encouraged to submit a revised version of this manuscript for publication in Biogeosciences; it is a valuable statement of the current state-of-the-art for these calculations. Nevertheless, I feel the authors should be encouraged to elaborate further on my key points from my introduction. That is to try to answer the question: “How do we move forward from here?” (I repeat my opinions below.)

First, the marine CO<sub>2</sub> community is in dire need of a clear and unambiguous statement of what might comprise a correct calculation model; ideally this would be based on a particular numerical implementation of an agreed set of constants including appropriate pressure corrections (and perhaps even pH scale adjustments). Ideally this statement would also include estimates of the standard uncertainty for each of the parameters contained in the model. Of course, if “better” constants were to come along

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in the future, they could be slotted in relatively straightforwardly. There is also an urgent need for a computational tool that takes such a model and implements error propagation appropriately, i.e. including the uncertainties in all of the parameters that contribute to the calculation of a particular value. A variety of other more focused computational tools could also be based on such a model statement. These separate computational tools could, of course, be optimized individually for particular purposes but must be shown to be correct. It would be valuable if the authors were to provide their opinions on how this might be done reliably.

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