

**Improved routines to model the ocean carbonate system: mocsy 1.0**  
**J. C. Orr & J.-M. Epitalon**  
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The existence of carefully evaluated computer code for use in ocean carbon cycle models is clearly desirable, and this code goes beyond that used in the Ocean Carbon Model Intercomparison Project (OCMIP) both in terms of the number of carbonate system variables it computes, and in the careful evaluations provided by this manuscript. I thus feel it is appropriate for publication. Nevertheless, I feel it can be improved in a few key areas.

As with the companion paper (Orr *et al.*, Biogeosciences Discussions 11, 5327–5397, 2014) this manuscript looks carefully at a number of potential discrepancies that arise when computing ocean carbonate chemistry. However, it too seemingly ignores the elephant in the room: the calculations themselves can, in principle, be done as accurately as machine precision allows, however, the real uncertainties in the various calculations are due to uncertainties in the input data – in this context, the various equilibrium constants and estimates of salinity-dependent concentrations.

As the manuscript notes, both in praising the work of Lewis & Wallace (1998) and in commenting on the paper by Millero (2010), these are all susceptible to error. Such errors take two potential forms: errors (typographical?) in the values for the various coefficients in the fitting equations representing the equilibrium constants, and uncertainties in the original data that is being represented. Although, it may well be that such uncertainties are not the largest contribution to the overall uncertainty in ocean carbon cycle models, I feel it might be useful for the authors to consider the implications of such errors on the calculated quantities such as  $p\text{CO}_2$  or even  $\Omega_{\text{arag}}$ , possibly in the way they have considered the implications of choosing alternate total boron estimates.

*Other more specific comments*

The discussion throughout refers to the  $p\text{CO}_2$ . Insofar as the Weiss (1974) formulation relates  $[\text{CO}_2]$  to the  $\text{CO}_2$  fugacity, rather than to its partial pressure I was wondering just how the one was converted to the other? (Of course it is practical to use the alternate coefficients in Weiss & Price (1980) to get an equilibrium constant that relates directly to  $p\text{CO}_2$ .)

How is  $p\text{CO}_2$  calculated at pressure? Is the Weiss (1974) approach to high-pressure  $\text{CO}_2$  solubility used? (I don't think it is mentioned either in Millero (1995) or in Orr et al. 2014, Table 7.)

Finally, does mocsy allow for computation of the more common form used for the atmosphere:  $x(\text{CO}_2)$  in dry air?

The use of the particular chemical formulae  $\text{PO}_4^{3-}$  and  $\text{SiO}_2$  to represent the terms *total (dissolved inorganic) phosphate* and *total (dissolved inorganic) silicate* is potentially misleading, especially as a later discussion focuses on the contribution of various such species to total alkalinity. I recommend choosing an alternate notation

The decision to use an analytical expression for the Revelle Factor, whether that of Frankignoulle (1994) or of Egleston *et al.* (2010), implies – I believe – that the contributions of phosphate species and silicate to alkalinity are ignored. This may well explain the deviations from CO2SYS shown in Figs. 1 & 2.

It is – I feel – misleading to refer to the various equilibrium constants as *apparent constants*. This term appeared originally in the biochemical literature as a synonym for conditional constant (a concentration quotient that applies only when the concentration of one of more reactants or products is fixed at a particular constant value); it was then adopted by Pytkowicz in the 1960s to describe what had earlier been referred to as *incomplete* constants (as they were a combination of concentration terms and  $10^{-\text{pH}}$ : believed to be the activity of hydrogen ion). Thus it is not (as the m/s states on p. 2882) because “these equilibria use concentrations instead of activities”. I would prefer to say “concentration quotients” if I am making clear that these are not standard equilibrium constants (with a reference state of pure water), otherwise I feel that “equilibrium constants” is sufficiently correct and clear.

I note the authors say both “total boron” (p. 2882 line 16) and “total borate” (p. 2882 line 24), I’d prefer they used one only.

The authors choose to talk about discrepancies both in relative terms (Figs. 1 & 2) as well as in absolute terms (other figures). I found this confusing, and wonder at the value of using absolute discrepancies without, at least, indicating how large the original number is.

On p. 2886 the authors write “Hence the  $A_T$  minus  $C_T$  increases, as must then the buffer capacity.” I am not sure that this is very clear. I assume this is referring to the fact that the Revelle factor has a maximum when  $A_T \approx C_T$  and thus as one moves away from this the Revelle factor decreases.

Although I think it was Zeebe & Wolf-Gladrow who coined the phrase “practical alkalinity” I am not sure it bears repeating here. If the contribution of phosphate and silicate alkalinities is larger than the likely error in alkalinity, then it is not strictly either practical or an alkalinity.

It is incorrect to write the *water alkalinity* as is done in (4); rather it should include the hydrogen sulfate and hydrogen fluoride terms – which should be removed from (7):

$$A_w = [\text{OH}^-] - [\text{H}^+]_F - [\text{HSO}_4^-] - [\text{HF}] .$$

The grouping ( $[\text{H}^+]_F + [\text{HSO}_4^-] + [\text{HF}]$ ) is a form of total concentration of hydrogen ion in the seawater; and the water alkalinity is a measure of the difference from acid-base neutrality. Note that in many representations this grouping is represented as  $[\text{H}^+]$ , strictly this should be thought of as being on the so-called sea water scale.

Fig. 1: The close correspondence between the relative deviation in  $[\text{H}^+]$  and in  $[\text{CO}_2^*]$  suggests a slight discrepancy in  $K_1$ ; the mismatch between the error in  $[\text{CO}_2^*]$  and that in  $p\text{CO}_2$  suggests a slight discrepancy in  $K_0$ . As was noted above, the growing discrepancy in the Revelle factor suggests to me that nutrients may not have been considered when calculating it (either in CO2SYS or in mocsy).

Why is a mean a useful parameter to plot in Figs. 1 and 2? I would have thought that the maximum discrepancy would have been the one most of interest.

Fig. 3: I am not sure that absolute deviations are superior to relative ones here. Certainly I found the scale difference between  $p\text{CO}_2$  and the corresponding concentration of unionized  $\text{CO}_2$  to be odd.

Fig.4: Shouldn't the last line of the legend say . . . (1) Uppström (1974) and . . . ?