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Discussions

# Comparison of seven packages that compute ocean carbonate chemistry

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## Abstract

To study ocean acidification and the carbon cycle, marine scientists often use two measured or modeled carbonate system variables to compute others. These carbonate chemistry calculations, based on well-known thermodynamic equilibria, are now available from seven public packages: CO2SYS, csys, seacarb, swco2, CO2calc, ODV, and mocsy. We compared results from these packages using common input data and the set of equilibrium constants recommended for best practices. All packages agree within ±0.00025 units for pH and ±0.5 µmol kg$^{-1}$ for $CO_3^{2-}$, and six packages agree within ±0.2 µatm for $p$CO$_2$ in terms of zonal-mean surface values. In the remaining package (csys), the surface $p$CO$_2$ variable is up to 1.4 µatm lower than in other packages, but that is because it is mislabeled. When compared to surface $f$CO$_2$, it differs by less than 0.2 µatm. The csys deviations in $f$CO$_2$, pH, and $CO_3^{2-}$ grow with depth but remain small. Another package (swco2) also diverges significantly but only in warm deep waters as found in the Mediterranean Sea. Discrepancies between packages derive largely from their code for the equilibrium constants. Analysis of the sensitivity of each computed variable to changes in each constant showed the expected dominance of $K_1$ and $K_2$, while also revealing comparable sensitivity to $K_B$, e.g., with the $A_T$–$C_T$ input pair. Best-practice formulations for $K_1$ and $K_2$ are implemented consistently among packages, except those in csys deviate slightly at depth (e.g., 0.5 % larger values at 4000 db) due to its pressure corrections made on the total instead of the seawater pH scale. With more recent formulations for $K_1$ and $K_2$ designed to cover a wider range of salinities, packages disagree more, e.g., by 8 µatm in $p$CO$_2$, 1 µmol kg$^{-1}$ in $CO_3^{2-}$, and 0.006 units in pH under typical surface conditions. These discrepancies stem from packages using different sets of coefficients for the corresponding salinity dependence of the new formulations. Although each set should be equally viable after simple conversions, we show they are fundamentally inconsistent. Despite general agreement between current packages, agreement was much worse with outdated versions, e.g.,

differences reached up to 2.5 µatm in $p\text{CO}_2$, 1.4 µmol kg$^{-1}$ in $\text{CO}_3^{2-}$, and 0.007 units in pH for surface zonal means when using the best-practice constants.

## 1 Introduction

Our ability to assess ocean carbon uptake and associated impacts from ocean acidification relies on an accurate representation of marine carbonate system. Fortunately, the seawater carbonate system is well constrained, allowing any two of its variables to be used to calculate all others, given associated temperature $T$, salinity $S$, pressure $P$, and nutrient concentrations. For example, it is common to measure or simulate two conservative variables, dissolved inorganic carbon $C_\text{T}$ and total alkalinity $A_\text{T}$, and then compute from associated thermodynamics the corresponding pH, partial pressure of carbon dioxide $p\text{CO}_2$, and concentrations of carbonate $\text{CO}_3^{2-}$ and bicarbonate $\text{HCO}_3^-$ ions as well as related buffer factors and saturation states of aragonite $\Omega_\text{A}$ and calcite $\Omega_\text{C}$. It is the $\text{CO}_2$-driven changes in these variables that drive the largest reductions in the ocean carbon sink (Sarmiento et al., 1995; Orr, 2011) and the biological impacts from ocean acidification (Gattuso and Hansson, 2011; Kroeker et al., 2013; Wittmann and Pörtner, 2013).

These equilibrium computations are made with a number of software packages, either those developed and used by individual scientists or, more commonly, those that have already been made available publicly. The latter have become indispensable for many ocean scientists, whether they study marine chemistry or impacts of ocean acidification on marine biota. Yet how packages differ is seldom addressed. Lewis and Wallace (1998) documented differences in basic variables among three existing packages at a time when no such package was available publicly. Provided with the same input, computed output from the three packages differed by 21 µatm for $p\text{CO}_2$, 0.16 units for pH, and 15 µmol kg$^{-1}$ for $\text{CO}_3^{2-}$ as well as $\text{HCO}_3^-$. Packages used different pH scales, different formulations for some of the constants ($K_1$, $K_2$, $K_\text{B}$, and $K_\text{S}$), and different definitions of total alkalinity, all apparently hard-coded. These differences prompted

Lewis and Wallace (1998) to develop a publicly available package, CO2SYS, which provides many options to select from the available pH scales and constants. Since that time, other packages have also been developed and released publicly, yet to this day no study has been published that compares their results. One may assume, given continued efforts to establish and refine procedures for best practices (Dickson and Goyet, 1994; Dickson et al., 2007; Dickson, 2010), that differences among currently available packages are less than what was found 15 years ago. But even that poor level of agreement has not been established. Without a quantitative understanding of the accuracy and precision of these packages, we cannot rigorously compare studies that aim to assess, e.g., air–sea $\text{CO}_2$ fluxes and thresholds associated with ocean acidification.

At this writing, there exist seven publicly available software packages. The first among them is the previously mentioned CO2SYS, but that now exists in four different versions: the original program for DOS (Lewis and Wallace, 1998), two versions as Excel spreadsheets (Pierrot et al., 2006; Pelletier et al., 2007), and most recently a version as MATLAB scripts (van Heuven et al., 2011). Another package, csys, was also written in MATLAB but it was released a decade earlier, already in 2001 as a supplement to the book by Zeebe and Wolf-Gladrow (2001). The development of csys inspired seacarb, an R library (R Development Core Team, 2012) released two years later (Proye and Gattuso, 2003) and since improved with frequent revisions (Lavigne and Gattuso, 2011). About the same time as the release of the two Excel interfaces to CO2SYS, the swco2 package was also released with a similar spreadsheet interface but a distinct library of core routines written in Visual Basic (Hunter, 2007). Three years later, oceanographers saw the release of two new carbonate chemistry packages, CO2calc and ODV, both of which also exploit the core CO2SYS code. While CO2calc provided completely new interfaces for Mac, PC, and iPhone (Robbins et al., 2010), ODV provided carbonate chemistry calculations as an add on to an already widely used visualization and analysis tool (Schlitzer, 2002). Parallel to those developments for the observational community, the Ocean Carbon-Cycle Model Intercomparison Project (OCMIP) provided routines to compute surface $p\text{CO}_2$ and air–sea $\text{CO}_2$

fluxes from simulated $A_T$ and $C_T$ (Orr et al., 1999). Those were adapted to include the full suite of other carbonate system variables (Orr et al., 2005), then later improved and released publicly as the mocsy package (Orr and Epitalon, 2014). With a goal here to assess the consistency of these seven packages, we compared results generated by running them with common sets of constants, pH scales, and input data.

We limit this study to package comparison. For brevity, we avoid redocumenting the associated approaches and algorithms, which are now commonly used and for which abundant literature already exists (e.g., Dickson et al., 2007; Munhoven, 2013). Likewise, we do not address the debate raised by Hoppe et al. (2012) concerning poor agreement between measured $p$CO$_2$ and that computed from $A_T$ and $C_T$, a disaccord found to be worse than in previous studies by marine chemists (e.g., Lueker et al., 2000). Nonetheless, we go beyond simply identifying differences between packages; we also seek to identify their causes. It is hoped that this effort will inspire subsequent package developments and facilitate their validation, while tightening agreement. The ultimate goal is to reach a point where users will no longer need to merely assume that packages provide the same results. Packages can then be legitimately chosen based on convenience, efficiency, functionality, and the level of programming experience of the user. For instance, users without any programming experience may well prefer spreadsheet based programs (CO2SYS, CO2calc, swco2). Users who use ODV for general oceanographic data analysis and visualization can easily compute carbonate system variables using its predefined derived-variable facility. Users with some programming experience may prefer packages that are available in languages that they are already familiar with: MATLAB users will prefer CO2SYS or csys, R users can use seacarb, Visual Basic users may opt for swco2, and users of python or Fortran can use mocsy.

## 2 Methods

To compare all publicly available packages, our approach was to install them in a one location, define common input data and constants, and use those with each package to generate a data archive for centralized analysis.

### 2.1 Packages and reference

All seven publicly available software packages for the ocean carbonate system (Table 1) take two of those system variables as input and compute the others from basic thermodynamics. All packages were first downloaded in November 2012. Our early findings led developers to update two of those packages, seacarb and CO2calc. Results from an older version of each package are included in one of the earlier figures to illustrate the discrepancies associated with running software that is out of date. Subsequent comparison refers only to the latest version of each package.

To compare packages, it was necessary to define a common reference. Although check values exist for most of the equilibrium constants (Dickson et al., 2007), none are available for computed variables. Hence we chose one of the packages as a relative reference, namely CO2SYS, for three reasons: (1) it was the first publicly available package; (2) its core routines already serve as the base code for two other packages (CO2calc and ODV); and (3) its documentation and code reveal the intense effort that its developers have put into ferreting out the right coefficients from the literature and the most appropriate version of formulations for the constants.

However, selecting CO2SYS as the reference requires further specification, because it comes in at least 4 variants: the original for DOS (Lewis and Wallace, 1998), two others both interfaced to Excel (Pelletier et al., 2007; Pierrot et al., 2006), and another for MATLAB (van Heuven et al., 2011). The first two variants may be considered legacy codes because they do not provide options to use formulations for $K_1$ and $K_2$ from Lueker et al. (2000), as recommended for best practices (Dickson et al., 2007). Thus, we reduced our choices for the reference to the latter two versions of CO2SYS (MAT-

LAB code and Pierrot et al.'s Excel version), both of which provide options to use all constants recommended for best practices (with one minor exception). Both versions give essentially identical results (Fig. 1). But they differ significantly from the legacy versions run with the closest substitutes for Lueker et al.'s $K_1$ and $K_2$, namely earlier

5  refits by Dickson and Millero (1987) of the same measured constants from Mehrbach et al. (1973). Finally, the CO2SYS reference also had to be efficient, since all packages needed to be compared with an input data set of nearly 1 million records (Table 2). Thus we chose the MATLAB version of CO2SYS as the reference.

## 2.2 Features

10  The seven packages compute results from the same thermodynamic equilibria, but software features differ, including available input pairs, pH scales, and constants. Package diversity covers all commonly used operating systems: seven packages run on Windows, six packages on Mac OSX, and four packages on Linux (Table 3). Source code is available in four packages in standard programming languages (MATLAB, R,

15  and Fortran 95), thereby allowing code validation and improvements by users on all three operating systems mentioned above. The number of possible input pairs of carbonate system variables varies widely between packages, from 1 to 22 (Table 4). The mocsy package, treats only one input pair $A_T$–$C_T$, the two carbonate system variables carried by models. The CO2SYS package and its derivatives (CO2calc and ODV) al-

20  low the user to select from six commonly measured pairs ($A_T$–$C_T$, $A_T$–pH, $A_T$–$p$CO$_2$, $C_T$–$p$CO$_2$, $C_T$–pH, and pH-$p$CO$_2$); in addition, they allow equivalent pairs where $f$CO$_2$ replaces $p$CO$_2$. The csys package provides 10 more input pairs by allowing pair members to include one or more of the 3 inorganic carbon species: CO$_2^*$, HCO$_3^-$, and CO$_3^{2-}$. Although the two former species can only be calculated, promising new techniques are

25  being developed to measure the latter (Byrne and Yao, 2008; Martz et al., 2009; Easley et al., 2013). Yet despite csys's enhanced number of input pairs, it limits $p$CO$_2$ to be used as input only when combined with pH. The two remaining packages, seacarb and swco2, include the same 16 pairs as csys but also add 4 others, all including $p$CO$_2$.

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Computed variables are affected by the choice of the pH scale and the constants. All packages allow users to work on the total pH scale as recommended for best practices (Table 5) and as used for this comparison. The mocsy package provides only the total scale, while the six others allow for conversion to the free scale. Out of those six, only

5  csys does not allow users to work on the seawater scale. Three packages (CO2SYS, CO2calc, and swco2) also offer the NBS scale. The choice of the pH scale affects the values of the constants for which H$^+$ is part of the equilibrium equation. For $K_1$ and $K_2$, CO2SYS and its derivatives (CO2calc, ODV) offer a large range of choices (Table 6). Yet most of those may now be considered out of date, having been replaced by more

10  recent assessments, often made with the same data. All packages offer the $K_1$ and $K_2$ formulations from Lueker et al. (2000), as recommended for best practices. Four packages also offer the most recent formulations for $K_1$ and $K_2$ that have been proposed as more appropriate for low-salinity waters (Millero, 2010). The formulations for $K_1$ and $K_2$ from the two latter studies are used individually in this comparison to assess associ-

15  ated differences between packages. For the other constants, all packages provide the formulations recommended for best practices, except for $K_F$, a difference shown later to have no consequence.

Some packages also offer additional features. For example, CO2SYS and CO2calc allow users to compute variables at a temperature that differs from that at which the

20  input pair was measured. They also distinguish different components of total alkalinity, including those from total B, P, and Si. The seacarb package provides explicit functions to the user to allow conversion of pH and constants between the free, total, and seawater scales; other packages make such conversions internally, but do not provide user-callable functions. The seacarb package also offers functions to help design

25  perturbation experiments to investigate effects of ocean acidification (Gattuso and Lavigne, 2009).

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### 2.3 Input data

To compare packages, we used two different kinds of input data. A first analysis compared variables computed in each package as a function of latitude and depth using as input the 3-D gridded data products for $A_T$ and $C_T$ from GLODAP (Key et al., 2004) combined with comparable products from the 2009 World Ocean Atlas (WOA2009) for temperature $T$ (Locarnini et al., 2010), salinity $S$ (Antonov et al., 2010), and concentrations of phosphate $PO_4^{3-}$ and silica $SiO_2$ (Garcia et al., 2010). A second analysis focused on comparing packages while separating the effects of physical input variables ($T$, $S$, and $P$) on computed variables. For that, we started with five commonly used input pairs: $A_T$–$C_T$, $A_T$–pH, $A_T$–$pCO_2$, $C_T$–$pCO_2$, and $C_T$–pH. Then for each pair, we computed the other carbonate system variables over ranges of $T$, $S$, and $P$, assuming zero nutrient concentrations. More precisely, all other carbonate system variables were first calculated with one package (seacarb) from $A_T = 2300\,\mu mol\,kg^{-1}$ and $pCO_2 = 400\,\mu atm$ at global average surface conditions ($T = 18\,°C$, $S = 35$, and $P = 0\,db$). Then two surface data sets were produced for each pair (and each package) by varying $T$ and $S$, individually, and recalculating all other carbonate system variables from the fixed input pair. For the first, $T$ wasx52 varied from −2 to 50 °C, while for the second $S$ was varied from 0 to 50. In both cases, pressure was held at 0 db. To assess how packages differ below the surface, we used the same approach, varying pressure between 0 and 10 000 db and maintaining $S = 35$. But pressure corrections are highly sensitive to temperature (Sect. 2.7), so for each package we made two data sets: (1) holding $T = 2\,°C$ (typical of the deep open ocean) and (2) holding $T = 13\,°C$ (typical of deep waters of the Mediterranean Sea).

### 2.4 Best-practices comparison

Comparisons were made using the total pH scale and constants recommended for best practices by Dickson et al. (2007). The equilibrium constant for the solubility of $CO_2$ in seawater $K_0$ is from Weiss (1974). The equilibrium constants $K_1$ and $K_2$ are from

Lueker et al. (2000), who refit the constants determined by Mehrbach et al. (1973) to the total pH scale. The formulation for $K_B$ is from Dickson (1990b) and is also on the total pH scale. Formulations for $K_W$, $K_{1P}$, $K_{2P}$, $K_{3P}$, and $K_{Si}$ are from Millero (1995), who provides equations for the seawater scale, and those are converted to the total scale. The formulation for $K_S$ is from Dickson (1990b) on the free scale (see above). The solubility products for aragonite $K_A$ and for calcite $K_C$ are from Mucci (1983). All are apparent equilibrium constants, given in terms of concentrations, not activities. The only constant for which the formulation was not that recommended by Dickson et al. (2007) is $K_F$, because that best-practices formulation (Perez and Fraga, 1987) is not offered by CO2SYS, CO2calc, and ODV. Instead, we used the $K_F$ formulation by Dickson and Riley (1979) on the total scale, which is offered by all the packages. Dickson et al. (2007) recommend the former but also state that results from the two formulations are in reasonable agreement.

Additionally, all packages used consistent formulations for total concentrations of boron (Uppström, 1974), sulfur (Morris and Riley, 1966), and $Ca^{2+}$ (Riley and Tongudai, 1967), each proportional to salinity. Six packages compute saturation states for aragonite $\Omega_A$ and calcite $\Omega_C$ from the product of the concentrations of $Ca^{2+}$ and $CO_3^{2-}$ divided by the corresponding apparent solubility product, either for aragonite $K_A$ or calcite $K_C$ (Mucci, 1983), respectively. Only the csys package does not provide output for $\Omega_A$ and $\Omega_C$. To simplify comparison, all figures plot results as an absolute differences, i.e., computed values are shown after subtracting off corresponding results from the reference.

### 2.5 Sensitivity tests

The most extensive comparison was made with the $A_T$–$C_T$ input pair, the only one that is available in all packages. With that pair, packages were also compared in terms of how their computed variables were affected by nutrient concentrations, varying phosphate $PO_4^{3-}$ and silica $SiO_2$ concentrations across the observed range. Additionally, the same pair was used to quantify effects of two important developments since the

best practices were published in 2007. For the first, we quantified effects on computed variables of Lee et al. (2010)'s assessment that the total boron in the ocean may be 4 % larger than considered previously (Uppström, 1974). For the second, we assessed impacts of using Millero (2010)'s new $K_1$ and $K_2$ formulations, which are designed to cover a wider range of input $S$ and $T$ relative to recommended constants (Lueker et al., 2000).

## 2.6 Constants

To better assess the most probable causes of the differences in computed carbonate system variables, we also compared associated constants. For the packages where source code was available (CO2SYS-MATLAB, csys, seacarb, mocsy), we used existing routines or slightly modified versions to output all the constants for the same physical input data ($T$, $S$, and $P$) that we used for computing variables. For swco2, we retrieved its constants using its documented parameter numbers and its routine to extract anything with a parameter number. For other packages where source code was not available, we were able to compute some of the constants from available output variables. Thus with output from CO2calc, we computed its $K_0$, $K_1$, $K_2$, $K_B$, $K_W$, $K_A$, and $K_C$; from ODV output, we computed its $K_0$, $K_1$, $K_2$, $K_A$, and $K_C$.

## 2.7 Pressure correction

Following Millero (1995), all packages correct for the effect of pressure $P$ on each equilibrium constant $K_i$ with the equation

$$\ln\left(K_i^P/K_i^0\right) = -\left(\Delta V_i/RT_k\right)P + \left(0.5\Delta\kappa_i/RT_k\right)P^2, \tag{1}$$

where the left hand side is the ratio between $K_i$ at depth ($P$ in bars) and at the surface ($P$ at 0 bars), $R$ is the gas constant, $T_k$ is temperature in K, $\Delta V_i$ is the partial molal volume, and $\Delta\kappa_i$ is the change in compressibility. For each constant, Millero (1995)

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provided empirical fits, quadratic in temperature:

$$\Delta V_i = a_0 + a_1 T_c + a_2 T_c^2, \tag{2}$$
$$\Delta\kappa_i = b_0 + b_1 T_c + b_2 T_c^2, \tag{3}$$

where $T_c$ is temperature in °C. Some of these original coefficients (Millero, 1995, Table 9) contained typographical errors as identified in the code and documentation of CO2SYS (Lewis and Wallace, 1998, Appendix). Nonetheless, they have persisted in some of the packages as well as in the literature (e.g., Millero, 2007). To help amend this situation, Table 7 lists these coefficients for each constant where known errors have been corrected. To determine the fidelity of packages to this array of coefficients, we studied available source code and evaluated patterns of discrepancies in results, making sensitivity tests to decipher fingerprints characteristic of previous errors.

## 2.8 What is significant?

If software packages with identical input cannot agree to within much less than the measurement precision of a computed variable (e.g., $p\text{CO}_2$), then their varied use would add substantially to the total uncertainty. To avoid this situation, it is necessary for these tools to have a numerical precision that is far superior to the measurement precision. By numerical precision, we mean their agreement, including all coding differences and errors as well as the usually much smaller numerical round-off error. Therefore, we arbitrarily define that cutoff level for numerical precision to be ten times better than the best measurement uncertainty (Dickson, 2010, Table 1.5). A package that agrees with a given variable from the reference package within the numerical cutoff specified in Table 8 will be referred to here as having negligible discrepancy relative to the reference; conversely, a package with a greater difference for a given variable will be considered to have a significant discrepancy.

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## 3 Results

Packages were compared in terms of how computed variables differed with latitude and depth, using global gridded data, and how individual physical variables and chemical choices affected results, using simplified data. Packages were also compared in terms of computational efficiency.

### 3.1 Global gridded data

With gridded data products from GLODAP and WOA2009 as input, 6 out of 7 packages agree well in terms of the global-mean profiles of computed variables (Fig. 2). Five packages agree with CO2SYS within $\pm 0.2\,\mu atm$ for $pCO_2$, $\pm 0.05\,\mu mol\,kg^{-1}$ for $CO_3^{2-}$, and $\pm 0.00025$ units for pH, throughout the water column. The same group of six packages show similar close agreement for surface zonal means at all latitudes (Fig. 3). The remaining package, csys, differs significantly from the others with $pCO_2$ that is up to $1.4\,\mu atm$ lower at the surface and on average up to $2.6\,\mu atm$ lower in subsurface waters. However, those differences shrink by more than a factor of 6 when the csys $pCO_2$ variable is compared to $fCO_2$ in the other packages. Other computed variables in csys agree closely with those from the other 6 packages.

Yet agreement was not always so close. For some perspective, the CO2SYS reference was also compared with older versions of three of the packages: CO2calc (version 1.0.4 revised in 18 June 2013), seacarb (version 2.3.3 revised in 2010), and mocsy, an early precursor developed by Orr et al. (2005) but not released publicly. Discrepancies relative to the same reference used to be larger, e.g., up to twice as much for $pCO_2$ and ten or more times as much for $CO_3^{2-}$ and pH (Fig. 4). With the mocsy precursor, there are significant discrepancies in $pCO_2$ reaching up to $1.5\,\mu atm$ at the surface. Those grow with depth, e.g., reaching $4\,\mu atm$ at $5000\,m$. At the same depth, discrepancies in the other variables reach $0.5\,\mu mol\,kg^{-1}$ in $CO_3^{2-}$ and up to $0.007$ in pH. Subsurface discrepancies are mainly due to two common modeling approximations (Orr and Epitalon, 2014) that are corrected in the first public release of mocsy. With CO2calc v1.0.4, sur-

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face discrepancies reach up to $2\,\mu atm$ in $pCO_2$, up to $1.3\,\mu mol\,kg^{-1}$ in $CO_3^{2-}$, and up to $0.007$ in pH. Those discrepancies are associated with coding errors in the $K_1$ and $K_2$ formulations from Lueker et al. (2000), errors that were corrected in CO2calc version 1.2.0. As for seacarb v2.3.3, there are no significant discrepancies. However, with an even earlier version of seacarb (v2.0.3 released in 2008, not shown), the only package that maintains public access to all previous versions, discrepancies at depth are much larger (e.g., $-7\,\mu mol\,kg^{-1}$ in $CO_3^{2-}$ and $-0.165$ in pH at $4000\,m$), presumably due to errors in the pressure corrections. Thus previous versions of packages often have larger discrepancies, emphasizing the importance for users to keep their carbonate system software up to date.

Although the previous analysis let us assess how discrepancies vary spatially across the global ocean, the realistic gridded input data sets that were exploited did not allow us to isolate how discrepancies vary with individual physical variables and chemical input options. We will now focus on those factors, individually, by exploiting simple artificial input data.

### 3.2 Physical factors

Packages were compared with 5 common input pairs with the same simple data sets where $T$, $S$, and $P$ were varied individually. All packages were compared with the $A_T$–$C_T$ pair. Comparison with 4 other pairs excluded the mocsy package, which is designed to use only $A_T$–$C_T$. Comparison with two of the remaining pairs, $A_T$–$pCO_2$ and $C_T$–$pCO_2$, also excluded the csys package, which does not offer $pCO_2$ as an input variable.

### 3.2.1 $A_T$–$C_T$

With the $A_T$–$C_T$ pair, most packages agree closely at the surface and below. Computed variables from 6 out of 7 packages match tightly across ranges of $T$ and $S$ at surface pressure (Fig. 5). As for the gridded data comparison, the exception is the mislabeled csys $pCO_2$ variable. Although about $1\,\mu atm$ lower than surface $pCO_2$ in other pack-

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ages, it is just 0.1 µatm higher when compared to $f\mathrm{CO_2}$ in the same packages. Other surface variables in csys exhibit negligible discrepancies (e.g., 0.06 µmol kg$^{-1}$ in $\mathrm{CO_3^{2-}}$, and 0.0002 in pH). Away from the surface, the story is slightly more complicated. In the open ocean with its cold deep waters at around 2 °C, pressure corrections in most packages do not add significantly to the discrepancies seen at the surface. At that low temperature, only csys exhibits significant subsurface discrepancies. Those start to become significant when pressures exceed about 2000 db, (excluding the mislabeled $p\mathrm{CO_2}$ comparison). In some isolated regions, deep waters are warmer (e.g., 13 °C for the Mediterranean Sea). Discrepancies there would be larger if due to errors in some coefficients of the pressure-correction, a quadratic function of temperature (Eqs. 2 and 3). Indeed, one of the packages, swco2, exhibits substantial discrepancies with a pressure correction at 13 °C although only negligible discrepancies at 2 °C. For example at 4000 db, its discrepancies at 13 °C reach $-1.5$ µatm for $p\mathrm{CO_2}$, $+0.6$ µmol kg$^{-1}$ for $\mathrm{CO_3^{2-}}$, and $+0.002$ for pH. At the same temperature and pressure, discrepancies in csys are typically two to four times smaller, e.g., 0.8 µatm in $p\mathrm{CO_2}$, $-0.15$ µmol kg$^{-1}$ in $\mathrm{CO_3^{2-}}$, and 0.0003 in pH. Discrepancies in other packages are much smaller still and always negligible.

### 3.2.2 $A_\mathrm{T}$–pH

With the $A_\mathrm{T}$–pH pair (Fig. 6), discrepancies at the surface are similar in magnitude to those found with the $A_\mathrm{T}$–$C_\mathrm{T}$ pair (Fig. 5). The csys package's surface discrepancies for its mislabeled $p\mathrm{CO_2}$ reach up to $-2$ µatm, while they remain negligible for computed $\mathrm{CO_3^{2-}}$ and $C_\mathrm{T}$ except at the highest temperatures and salinities. Surface discrepancies for other packages remain negligible. Below the surface, the largest discrepancies come from csys and swco2. For csys, pressure-correction discrepancies for computed $p\mathrm{CO2}$ and $\mathrm{CO_3^{2-}}$ are similar in shape and magnitude to those with the $A_\mathrm{T}$–$C_\mathrm{T}$ pair (Fig. 5). The pressure correction at 13 °C in swco2 generally leads to discrepancies in $p\mathrm{CO_2}$ and $\mathrm{CO_3^{2-}}$ that are barely significant at 4000 db, whereas discrepancies in $C_\mathrm{T}$

reach $+1$ µmol kg$^{-1}$ at the same depth. With the pressure correction at 2 °C, the swco2 discrepancies are negligible, while the csys discrepancies are not, as already seen for the $A_\mathrm{T}$–$C_\mathrm{T}$ pair. For the other packages, the same low-temperature pressure correction results in negligible discrepancies for all variables.

### 3.2.3 $A_\mathrm{T}$–$p\mathrm{CO_2}$

With the $A_\mathrm{T}$–$p\mathrm{CO_2}$ input pair (Fig. 7), computed variables show discrepancies (relative to CO2SYS) that bear some resemblance to those found with the $A_\mathrm{T}$–$C_\mathrm{T}$ pair (Fig. 5). At the surface, all five packages differ by less than 0.05 µmol kg$^{-1}$ in $C_\mathrm{T}$ and 0.015 µmol kg$^{-1}$ in $\mathrm{CO_3^{2-}}$. Likewise for pH, packages generally agree within 0.0001 unit, although CO2calc exhibits larger variability (within $\pm0.0004$). However, those variations are randomly distributed with a mean near zero, a consequence of CO2calc's limited output precision of only 3 decimal places for pH. The pressure correction when performed at 2 °C does not add significant discrepancies, unlike that performed at 13 °C, for which discrepancies in swco2 grow linearly with pressure, e.g., reaching $+0.7$ µmol kg$^{-1}$ in $C_\mathrm{T}$, $+0.1$ µmol kg$^{-1}$ in $\mathrm{CO_3^{2-}}$, and $+0.0002$ in pH at 4000 db.

### 3.2.4 $C_\mathrm{T}$–pH

With the $C_\mathrm{T}$–pH input pair (Fig. 8), discrepancies generally resemble most those from $A_\mathrm{T}$–pH pair (Fig. 6), while differing more with those from the $A_\mathrm{T}$–$C_\mathrm{T}$ and $A_\mathrm{T}$–$p\mathrm{CO_2}$ pairs (Figs. 5 and 7). With $C_\mathrm{T}$–pH, there is similar agreement for 5 out of 6 packages across ranges of surface $T$ and $S$. Those 5 packages generally agree within 0.05 µatm for $p\mathrm{CO_2}$, 0.007 µmol kg$^{-1}$ for $\mathrm{CO_3^{2-}}$, and 0.1 µmol kg$^{-1}$ in $A_\mathrm{T}$ at surface pressure. As before, only csys exhibits significant discrepancies in $p\mathrm{CO_2}$, largely because it is mislabeled. Surface discrepancies of other variables are negligible in all packages, except for computed $A_\mathrm{T}$ in csys. Those discrepancies, relative to CO2SYS, grow exponentially with $T$ and $S$ but become significant only after reaching $T = 25$ °C and $S = 35$. The pressure correction worsens the csys discrepancy in $\mathrm{CO_3^{2-}}$ until it becomes significant

below 2000 db with the 2 °C pressure correction. Another dissimilarity, relative to previously analyzed pairs, is that with $C_T$–pH, the swco2 package's pressure corrections do not induce substantial discrepancies in computed subsurface $pCO_2$ and $CO_3^{-2}$, even at 18 °C. At that temperature, they do cause significant discrepancies in computed subsurface $A_T$ (e.g., 1 µmol kg$^{-1}$ at 4000 db), but those become negligible with the pressure correction at $T = 2$ °C, as with other input pairs. The same contrast in the temperature sensitivity between the same two packages was apparent with the $A_T$–$C_T$ and $A_T$–pH input pairs (Figs. 5 and 6).

### 3.2.5  $C_T$–$pCO_2$

With the $C_T$–$pCO_2$ pair (Fig. 9), all five packages have negligible surface discrepancies for computed $A_T$ ($\leq \pm 0.1$ µmol kg$^{-1}$), $CO_3^{2-}$ ($\leq \pm 0.01$ µmol kg$^{-1}$), and pH ($\leq \pm 0.003$ units). The pressure correction leads to patterns in discrepancies between packages that are qualitatively similar to those seen with a previously discussed input pair, $C_T$–pH (Fig. 8). Out of the five packages offering both input pairs (excluding csys and mocsy), only swco2 develops significant subsurface discrepancies. Moreover, that exception occurs only for one variable and only with the less realistic pressure correction at 13 °C. At that higher temperature, the swco2 package's discrepancies in computed $A_T$ grow linearly with depth, reaching 1 µmol kg$^{-1}$ at 4000 db. Discrepancies in $A_T$ remain negligible with the low-temperature pressure correction. Discrepancies in other variables are always negligible.

Considering results from the 5 input pairs together, we can now make several general comments. Only one package (csys) produces significant surface discrepancies, and for the most part only for its computed $pCO_2$, largely because that variable is mislabeled. The same package is the only one to produce significant subsurface discrepancies with the pressure correction at 2 °C, and those also concern other computed variables (e.g., pH and $CO_3^{2-}$). Another package (swco2) also produces significant subsurface discrepancies when the pressure correction is made at higher temperatures,

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which is of concern only for a warm marginal sea such as the Mediterranean. Furthermore, in those isolated warm deep waters, swco2 would produce significant subsurface discrepancies only for computed $A_T$ or for other computed variables when $A_T$ is a member of the input pair.

## 3.3  Chemical Factors

In Sect. 3.2, we compared differences among packages while varying physical input for different input pairs. Here we assess differences due to chemical factors, namely accounting for alkalinity from nutrients and opting for potentially important developments published since the publication of the best practices guide (Dickson et al., 2007).

### 3.3.1  Nutrients

Phosphate and silicate contribute to the total alkalinity when their concentrations are significant. Thus they affect computed carbonate alkalinity $A_C$ when one of the input pairs is $A_T$. One of the packages, csys, neglects nutrient alkalinity, assuming $PO_4^{3-}$ and $SiO_2$ concentrations are always zero. Out of the remaining six packages, four show negligible discrepancies relative to CO2SYS as nutrient concentrations are increased to the maxima observed in the ocean (Fig. 10). Discrepancies for the other 2 packages remain small: for swco2 they reach up to −0.2 µatm in $pCO_2$, +0.07 µmol kg$^{-1}$ in $CO_3^{2-}$, and +0.0002 units in pH; for CO2calc, they remain less than +0.3 µatm in $pCO_2$ and −0.04 µmol kg$^{-1}$ in $CO_3^{2-}$, while for pH they are not significantly different from zero.

These differences between packages are at least 70 times smaller than the actual changes in computed variables attributable to phosphate and silicate alkalinity. With the input pair $A_T$–$C_T$, nutrient alkalinity increases computed $pCO_2$ by 6 µatm for average surface waters in the Southern Ocean and by 12 µatm for average deep waters (below 2000 m); simultaneously, $CO_3^{2-}$ is reduced by about 2 µmol kg$^{-1}$ in the same waters (Orr and Epitalon, 2014).

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### 3.3.2 Total Boron

Relative to the standard formulation for total boron (Uppström, 1974), the new formulation (Lee et al., 2010) represents a 4 % increase of borate alkalinity throughout the ocean. Hence we first assessed whether or not packages gave consistent responses when changing from the standard to the new formulation. For the four packages that allow for the new formulation (CO2SYS, CO2calc, mocsy, and seacarb), their predicted changes agree within 0.15 µatm for $pCO_2$, 0.02 µmol kg$^{-1}$ for $CO_3^{2-}$, and 0.00006 units for pH, i.e., with the $A_T$–$C_T$ pair across observed ranges of $T$, $S$, and $P$ (Fig. 11). With other input pairs, agreement is closer still but the comparison is limited to fewer packages (mocsy treats only $A_T$–$C_T$). Much larger are the actual changes themselves. With the $A_T$–$C_T$ pair, given global average surface conditions ($T = 18°C$, $S = 35$), changing from the standard to the new formulation for total boron increases $pCO_2$ by 5.7 µatm, decreases $CO_3^{2-}$ by 2.1 µmol kg$^{-1}$, and decreases pH by 0.0056 units. Changes are generally smaller with the $A_T$–pH and $A_T$–$pCO_2$ pairs (e.g., −0.3 and −0.4 µmol kg$^{-1}$ for $CO_3^{2-}$, respectively). Conversely, with the $C_T$–pH and $C_T$–$pCO_2$ pairs, changes are negligible for all computed carbonate system variables, except total alkalinity.

### 3.3.3 $K_1$ and $K_2$

The formulations for $K_1$ and $K_2$ from (Lueker et al., 2000) are recommended for best practices (Dickson et al., 2007), but they are intended to be restricted to waters with $S$ between 19 and 43 and $T$ between 2 and 35 °C. For waters with physical conditions outside of those ranges, there are no recommended $K_1$ and $K_2$ formulations. However, formulations exist, such as those from the most recent reassessment by Millero (2010), which are applicable over wider ranges of $S$ (1–50) and $T$ (0–50 °C).

With an analysis analogous to that shown in Fig. 5 (Sect. 3.2.1), we replaced formulations for $K_1$ and $K_2$ from Lueker et al. (2000) with those from Millero (2010) to assess the consistency of computed variables in the four packages that include this

newer option (CO2SYS, CO2calc, seacarb, and mocsy). With the $A_T$–$C_T$ pair, 2 of the 4 packages agree closely at surface pressure across ranges of $T$ and $S$ (Fig. 12). Conversely, CO2calc differs from the CO2SYS reference by up to −12 µatm in $pCO_2$, −1.2 µmol kg$^{-1}$ in $CO_3^{2-}$, and +0.006 units in pH. Discrepancies are also found for seacarb, reaching up to −20 µatm in $pCO_2$, ±0.2 µmol kg$^{-1}$ in $CO_3^{2-}$, and −0.0025 units in pH. However, seacarb's discrepancies at the surface are inconsistent with its negligible subsurface discrepancies. Pressure corrections alter CO2calc's discrepancies by less than +1 µatm in $pCO_2$, −0.05 µmol kg$^{-1}$ in $CO_3^{2-}$, and −0.001 units in pH, changes that are notably less than its surface discrepancies. Overall, even though fewer packages offer the Millero (2010) formulations for $K_1$ and $K_2$, the resulting differences between packages reach levels that are orders of magnitude larger than with the Lueker et al. (2000) formulations.

### 3.4 Computational efficiency

This study is primarily focused on assessing the accuracy and the precision of the different packages that compute carbonate system variables. Another concern, relevant for users with large data sets, is computational efficiency. To assess differences in computation time between packages, we chose to use the global gridded data set described in Sect. 3.1. With nearly 1 million grid points of input data, the computational time needed to compute all carbonate system variables varies by more than a factor of 3000 between packages (Table 2). The slowest of the seven packages (seacarb) required more than 1 day while the fastest (mocsy) needed 30 s. Except for seacarb, packages based on spreadsheets are generally slower than those run by directly calling routines with programming languages (Fortran 95, MATLAB, Visual Basic). The latter are usually coded so that the equilibrium calculations are made one time for each set of input data, whereas spreadsheets often repeat the same set of calculations for each computed variable (each cell). Fortunately, even with the slowest of the packages shown in Table 2, the computational time is trivial for most observational analysis

efforts, because the number of samples is much smaller. Hence developers of most packages have not concerned themselves with computational efficiency. Nonetheless, for very large data sets and for models, which may have millions of grid cells to be treated every time step, computational efficiency is critical.

## 4  Discussion

To diagnose why computed variables differ between packages, we computed their sensitivities to each constant, assessed errors in individual constants, and used both to assign causes.

### 4.1  Sensitivity to individual constants

A computed variable $y$ is affected by errors in all input variables (including constants as well as members of the input pair), each denoted here as $x_i$ (for $i = 1, 2, \ldots n$). Thus, we calculated the sensitivity ratio as the relative change of $y$ to the relative change in each $x_i$, namely $\partial y/y : \partial x_i/x$. These sensitivity ratios were determined numerically in three successive steps. First, we calculated variables with seacarb under our standard conditions ($S = 35$, $T = 18\degree C$, $P = 0$ db, and zero nutrients, along with $C_T = 2058.185$ and $A_T = 2300\,\mu mol\,kg^{-1}$). Then, we increased each input variable by 1 % ($\partial x_i/x = 0.01$), individually, and recalculated output variables with seacarb for each perturbation. Finally, we took the difference between the first and second computations to obtain the proportional change in the computed variable $\partial y/y$.

Table 9 shows these sensitivity ratios for each variable and constant. Sensitivities of computed variables to input $A_T$, $C_T$, $K_0$, and $K_1$ are much like those from Dickson and Riley (1978) who used the same approach, but with different software, input data, and values for constants. Yet our sensitivities to $K_2$ differ. Although only $\sim 30$ % smaller for computed $CO_2^*$, $pCO_2$, and $H^+$, they are 7 times larger for $CO_3^{2-}$ as well as $\Omega_A$ and $\Omega_C$. The former moderate reductions occur because the $K_2$ from Lueker et al.

(2000) at standard conditions is 30 % greater than Dickson and Riley's ($pK_2 = 9.115$). Conversely, our seven-fold greater sensitivity of $CO_3^{2-}$ to $K_2$ is inconsistent with the previous study. Further investigation suggests our results are accurate because (1) our code for this 3-step numerical calculation treats $K_2$ exactly as other constants (in a loop), (2) numerical derivatives have been verified by computing analytical solutions to the derivatives (by hand) in other pairs where such calculations are feasible, and (3) results are written directly to the electronic (LaTeX) version of Table 9, reducing room for transcription error.

With the $A_T$–$C_T$ input pair, the sensitivities to $K_1$ and $K_2$ generally dominate, as expected from Dickson and Riley (1978). There is a similarly large sensitivity to $K_0$ when computing $pCO_2$ and $fCO_2$. The sensitivities to other constants have not been discussed previously. Here we find a surprisingly large sensitivity to $K_B$, even surpassing that to $K_1$ for computed $H^+$, $HCO_3^-$, $CO_3^{2-}$, $\Omega_A$, and $\Omega_C$, i.e., with the $A_T$–$C_T$ input pair. The sensitivity to $K_W$ is also significant but remains 14 to 26 times smaller than that for $K_B$. The sensitivity to other constants remain small (absolute values less than 0.001), except for the solubility products $K_A$ and $K_C$ which are inversely proportional to $\Omega_A$ and $\Omega_C$ (large negative sensitivities of $-1$). Sensitivities differ with other input pairs as shown by Dickson and Riley (1978).

These sensitivities are fundamental to the classic propagation of relative errors that has already been applied to the carbonate system (Dickson and Riley, 1978; Dickson et al., 2007). In that, the uncertainty $u$ of computed variable $y$ is expressed as

$$\frac{u(y)}{y} = \sqrt{\sum_{i=1}^{n} \left( \frac{\partial y/y}{\partial x_i/x} \right)^2 \left( \frac{u(x_i)}{x} \right)^2}, \tag{4}$$

where the left-hand side is the relative error in $y$, a function of the right-hand side's individual relative errors of each input variable and constant ($u(x_i)/x$) multiplied by the square of the associated sensitivity term $\left( \partial y/y \right) / \left( \partial x_i/x \right)$ (Table 9). Hence to assess the relative importance of each input variable, we need not only its sensitivity but also

its error. For the case where relative errors for each of the constants are assumed to be similar (Table 8), then it is largely the sensitivity term which determines the relative contribution of each constant to the overall error. Yet numerical errors in computed constants are neither identical nor entirely negligible in all packages.

## 4.2 Errors in equilibrium constants

In order to identify sources of error, equilibrium constants were plotted in the same manner as computed variables. By characterizing errors graphically, we were able to use patterns in discrepancies to help isolate problems and eventually identify their causes, particularly in packages where source code was available. For packages without source code, we attempted to reproduce error patterns by making temporary modifications to another package where source code was available.

### 4.2.1 $K_0$, $K_1$, and $K_2$: best practices

The constants that have the greatest potential to cause the differences in computed variables seen in Figs. 5–6 are $K_0$, $K_1$, and $K_2$ (Table 9), simply because of their prominence in the fundamental equilibria. For $K_0$, all packages have negligible discrepancies relative to CO2SYS across ranges of $T$ and $S$, and all packages agree with the check value from Dickson et al. (2007) (Table 11). For $K_1$ and $K_2$ with the Lueker et al. (2000) formulation, the story is almost the same, except that the csys package exhibits small discrepancies (Fig. 13). All packages agree at the surface, but csys's discrepancies slowly increase with depth, e.g., reaching values that are 0.5 % larger than other packages at 4000 db. These discrepancies are caused by csys's pressure correction that is made on the total instead of the seawater pH scale.

Qualitatively, the patterns in csys's increasing discrepancies with depth for $pK_1$ and $pK_2$ resemble those already seen for computed $pCO_2$, $CO_3^{2-}$, and pH (e.g., Fig. 5). To demonstrate, quantitatively, that $pK_1$ and $pK_2$ are responsible, we computed ratios between csys's three inorganic carbon species as a function of its $K_1$ and $K_2$, while

relating those to the same ratio and constants in CO2SYS. Using the definition of $K_1$ for package $p$ and for the reference $r$, we can divide the first by the second and rearrange to obtain

$$\frac{[HCO_3^-]}{[CO_2^*]}\bigg|_p = \frac{(K_1)|_p}{(K_1)|_r} \cdot \frac{[HCO_3^-]}{[CO_2^*]}\bigg|_r. \tag{5}$$

This equation is applicable when $[H^+]$ does not differ between packages (e.g., $A_T$–pH and $C_T$–pH input pairs). Likewise for $K_2$

$$\frac{[CO_3^{2-}]}{[HCO_3^-]}\bigg|_p = \frac{(K_2)|_p}{(K_2)|_r} \cdot \frac{[CO_3^{2-}]}{[HCO_3^-]}\bigg|_r, \tag{6}$$

and for the product $K_1K_2$

$$\frac{[CO_3^{2-}]}{[CO_2^*]}\bigg|_p = \frac{(K_1K_2)|_p}{(K_1K_2)|_r} \cdot \frac{[CO_3^{2-}]}{[CO_2^*]}\bigg|_r. \tag{7}$$

With the $A_T$–pH pair, these derived ratios overlap with corresponding ratios directly determined from csys's computed $CO_2^*$, $HCO_3^-$, and $CO_3^{2-}$ (not shown). Thus subsurface discrepancies in csys's computed variables are largely due to errors in the formulations for pressure corrections to $K_1$ and $K_2$. Likewise, it follows from Eqs. (5) and (6) that packages without discrepancies in the $[HCO_3^-]/[CO_2^*]$ and $[CO_3^{2-}]/[HCO_3^-]$ ratios must have essentially identical $K_1$'s and $K_2$'s. Hence swco2's discrepancies in individual carbonate system variables (Fig. 6) do not come from errors in $K_1$ and $K_2$. Therefore only csys exhibits problems that can be traced back to its implementation of the Lueker et al. (2000) formulations for $K_1$ and $K_2$.

### 4.2.2 $K_1$ and $K_2$: alternative for low salinities

Section 3.3.3 detailed the large discrepancies among packages, in terms of computed variables, that were generated simply by replacing the Lueker et al. (2000) formulations for $K_1$ and $K_2$ with those from Millero (2010), i.e., the most recent alternative for low salinity waters and the one based on the greatest number of measurements. Hence the implementation of the Millero (2010) formulations must be done inconsistently between the different packages. Indeed, four of the seven packages offer that new option, but two of them show significant surface discrepancies in $K_1$ and $K_2$ relative to those computed by CO2SYS (Fig. 14). And patterns of those discrepancies are qualitatively consistent with patterns of computed variables found with the same option (Fig. 12). A comparison of the source code in the three packages where it is available revealed that the implemented formulations are strictly identical; however, the sets of coefficients differ. More precisely, Millero fit 551 measurements of $K_1$ and 590 measurements of $K_2$ on the seawater pH scale to basic equations of the form

$$pK_i - pK_i^0 = A_i + B_i/T_k + C_i \ln(T_k), \tag{8}$$

where $pK_i^0$ was from his previous fit of the same form for pure water (Millero et al., 2006), $T_k$ is the absolute temperature, and $A_i$, $B_i$, and $C_i$ are functions of salinity:

$$A_i = \alpha_0 S^{0.5} + \alpha_1 S + \alpha_2 S^2,$$
$$B_i = \alpha_3 S^{0.5} + \alpha_4 S, \tag{9}$$
$$C_i = \alpha_5 S^{0.5}.$$

Millero (2010) provides a set of the six $\alpha$ coefficients for each of $K_1$ and $K_2$ on the original seawater pH scale but also on the free and total scales, i.e., by making analogous fits after converting the measured constants to each of those other scales (Millero, 2010, equations 9 to 12).

With the Millero (2010) formulation, the two packages with internally consistent results are CO2SYS and mocsy (Fig. 14). Both use the coefficients for his formulation on

the seawater scale. In seacarb though, it is more complicated. At the surface, seacarb uses Millero's set of coefficients on the total scale to compute $K_1$ and $K_2$; conversely, below the surface seacarb uses Millero's coefficients for the seawater scale and then converts the resulting constants to the total scale after making the pressure correction (as is appropriate). Although the two approaches should yield equivalent results, seacarb's constants computed for the surface differ from those calculated by CO2SYS. Conversely, below the surface, the two packages agree. Because seacarb's formulations and coefficients are strictly identical to those published by Millero (2010), which we have verified closely, the surface discrepancies imply an inconsistency between Millero's sets of coefficients for the total and seawater scales. Both sets should yield the same results for $K_1$ and for $K_2$, e.g., once the results from the seawater set are converted back to the total scale. Yet they do not. Indeed when $K_1$ and $K_2$ were computed separately from Millero's published sets of coefficients, we found similar patterns of surface discrepancies as between seacarb and CO2SYS (Fig. 15). Patterns matched exactly when we also accounted for the differences in $K_F$. That is, Millero converted $pK_1$ and $pK_2$ on the measured seawater scale to the total scale using $K_F$ from Perez and Fraga (1987), whereas for this study all packages use $K_F$ from Dickson and Riley (1979). In summary, seacarb shows surface discrepancies (relative to CO2SYS) primarily because it uses Millero's coefficients on the total scale, which are inconsistent with those on the seawater scale, and secondly because the $K_F$ used by Millero is inconsistent with that used in this study.

The second package that differs substantially from CO2SYS is CO2calc, but only for $K_2$. Although CO2calc's main code was taken from CO2SYS, the CO2calc developers included the Millero (2010) $K_1$ and $K_2$ formulations themselves, before they were available in CO2SYS. Lacking the CO2calc source code, we studied discrepancy patterns and with sensitivity tests found that they come from a different number of significant figures in one of the coefficients. More precisely, Fig. 15 compares the constants computed from the published set of coefficients (Millero, 2010, Tables 2 and 3) to those computed with the unpublished yet more precise set of coefficients used by Millero, i.e.,

his spreadsheet for the same publication (F. J. Millero, personal communication 2013). Only the $\alpha_5$ coefficient differs, having one additional significant figure in the spreadsheet (Table 10). The difference between constants computed with the published coefficients and those computed with unpublished coefficients (Fig. 15) (seawater scale, spreadsheet coefficients) match the pattern and magnitude of the differences between CO2calc and CO2SYS (Fig. 14). Hence CO2calc developers appear to have used the set of coefficients (seawater scale) from Millero's spreadsheet. Given their greater precision and their consistency with original results (Millero, 2010, Fig. 3), it appears that the other package developers should also adopt this more precise set of coefficients designed for the seawater scale, and they should avoid using the sets of coefficients on the total and free scales based on inconsistencies identified in the previous paragraph and in Fig. 15.

Future work is needed though to assess if the number of significant figures of some of these seawater-scale coefficients from the spreadsheet still need to be extended further. The case for need of further improvement comes from our sensitivity tests that compared the analogous sets of coefficients on the total scale (for which the spreadsheet provides much greater precision). That scale's published $\alpha_1$ for $K_1$ had to be extended from 4 to 5 significant figures, while corresponding $\alpha_5$'s for both $K_1$ and $K_2$ had to be extended from 4 to 6 significant figures before the results matched those computed with the unpublished spreadsheet coefficients. The much worse agreement among packages found when changing from the Lueker et al. (2000) to the Millero (2010) formulations for $K_1$ and $K_2$ emphasizes the danger of applying conclusions from one comparison to cases with different sets of constants.

### 4.2.3 $K_B$ and $K_W$: principal non-carbonate alkalinity constants

Previous comparison revealed substantial discrepancies in subsurface variables computed from the swco2 package (Fig. 5–6), which are not due to $K_1$ and $K_2$ (Figs. 13). These discrepancies occur only when $A_T$ is a member of the input pair or when $A_T$ is computed, suggesting that they stem from the need in these cases to correct from total

to carbonate alkalinity. Moreover, carbonate alkalinity itself was ruled out previously. Hence the next most likely cause of these discrepancies is the correction for borate alkalinity. Indeed, comparison of $K_B$ computed by the different packages does reveal discrepancies for swco2 (Fig. 16). Furthermore, swco2's divergence from CO2SYS increases linearly with depth, consistent with discrepancies in computed variables. Although we do not have access to the code for swco2, this discrepancy is consistent with a sign error in its $a_2$ pressure correction coefficient for $K_B$. This same error was only identified and corrected in other packages (e.g., in csys and seacarb) in 2010, whereas the current version of swco2 (v2) dates from 2007. Because the $a_2$ coefficient is multiplied by the square of $T_c$ (Eq. 2), the swco2 discrepancies associated with the pressure correction of $K_B$ are about two orders of magnitude smaller and become negligible when carried out at 2 °C rather than 13 °C.

Discrepancies in the pressure correction for $K_B$ are also evident with csys, although its divergence from CO2SYS (at most $\Delta pK$ of 0.002) is 15 times less than for swco2. Inspection of the csys source code found no discrepancies in the related pressure-correction coefficients, but did reveal two other relatively minor code differences that could potentially contribute to the small divergence. First, pressure corrections for $K_B$ and most other constants are designed to be effected on the seawater scale (Millero, 1995). Conversely, csys makes the $K_B$ correction on the total scale. All other packages, convert $K_B$ from the total to the seawater scale, make the pressure correction, and then reconvert $K_B$ back to the total scale. Second, the value of the gas constant $R$ used by csys in the pressure correction is 83.131 bar cm$^{-3}$ mol$^{-1}$ K$^{-1}$ instead of the recommended value of 83.14472 (Dickson et al., 2007). The other packages use values for $R$ that are consistent to the third decimal place with the recommended value. However, sensitivity tests with seacarb show that these small differences in $R$ have virtually no effect on computed results.

For related reasons, $K_W$ in csys diverges significantly from CO2SYS, whereas in other packages it does not. These csys package's discrepancies for $K_W$ are larger than for $K_B$, and they occur at surface conditions as well as at depth. Surface discrepancies

reach up to $\Delta pK = 0.06$ at high temperatures and at low salinities. Perusal of the csys code reveals that its formulation for $K_W$ corresponds exactly to that given by (Dickson and Goyet, 1994), which is identical to that from (Dickson et al., 2007). Furthermore, csys's computed $K_W$ at $T = 25°C$, $S = 35$, $P = 0$ db matches the best-practices' check value (Fig. 16). Nonetheless, the other packages prefer to use a more sophisticated formulation. The formulation for $K_W$ is that from Millero (1995), on the seawater scale, for which the best-practice approach subtracts 0.015 as a simple way to convert to the total scale (Dickson and Goyet, 1994; Dickson et al., 2007, Chap. 5, footnote 5). The other packages use the same formulation but do not impose the simple constant offset. Instead, they use the more rigorous, classic approach to convert between the two scales (e.g., Millero, 2010, Eq. 6), resulting in an offset that varies with [HF]. For example, with $K_F$ from Perez and Fraga (1987) the offset ranges from 0 to 0.032 across observed ocean temperatures and salinities; with $K_F$ from Dickson and Riley (1979), it ranges from 0 to 0.024.

All packages but csys also use the variable-offset approach. Another reason for that is to defer the seawater-to-total scale conversion until after the pressure correction, which for $K_W$ (and most other constants) should be done on the original seawater scale. In contrast, csys makes the $K_W$ pressure correction on the total scale, explaining a portion of the discrepancy seen in Fig. 16. A greater part of that discrepancy stems from csys's $a_0$, $a_1$, and $a_2$ pressure correction coefficients for $K_W$, which are intended for fresh water. Conversely, the other packages use the seawater specific coefficients. The three freshwater coefficients from Millero (1983) were erroneously published in a table for seawater by the same author (Millero, 1995, Table 9). Although that artifact was identified in the documentation to CO2SYS (Lewis and Wallace, 1998, Appendix), it was buried among many others, perhaps explaining why other packages have been slow to make this correction. In the seacarb package this error was corrected in its version 2.3.4, released in 2010.

### 4.2.4 $K_F$ and $K_S$: constants to change pH scales

For $K_F$, two packages diverge substantially from CO2SYS under surface conditions, and one of those also exhibits discrepancies at depth. At the surface, csys and seacarb deviate substantially from CO2SYS for salinities below 20, a divergence that grows exponentially to $\Delta pK_F = -0.025$ as salinity approaches zero. Their identical discrepancies suggests that both have the same problem. Inspection of their code reveals that the source of the problem is an incorrect formulation for the ionic strength, which is necessary for the formulation of $K_F$ chosen for this comparison (Dickson and Riley, 1979), i.e., the same as recommended by Dickson and Goyet (1994). Immediately adjacent to the incorrect formulation in both packages, there is another equation that computes the ionic strength correctly, as recommended for best practices, but that equation is not used.

In addition, the divergence for csys grows with depth, e.g., starting with near-zero $\Delta pK_F$ at surface pressure ($T = 13°C$ and $S = 35$) and reaching $\Delta pK_F = -0.015$ at 4000 db. Study of the csys code and follow-up sensitivity tests reveal that this discrepancy is due entirely to an error in the conversion of $K_F$ from the total to the free scale. The conversion between the two scales is straightforward using the classic approach

$$\left[H^+\right]_T = \left[H^+\right]_F \left(1 + S_T/K_S\right). \tag{10}$$

where $S_T$ is the total sulfur concentration and $K_S$ the equilibrium constant for bisulfate. The csys package properly incorporates this conversion in the formulation for $K_F$, but the pressure correction for $K_S$ is done afterwards; the other packages do it beforehand. Hence the pH-scale conversion of $K_F$ is inexact below the surface. That inconsistency explains virtually all of csys's subsurface discrepancy in $K_F$ (Fig. 17). Other issues were also identified in the csys code, including an erroneous value for $R$ and the $K_F$ pressure correction being effected on the total scale instead of the free scale. The effect of former is entirely negligible, while the latter slightly compensates the lack of pressure effect on $K_S$ (e.g., $\Delta pK_F = +0.002$ at 10 000 db). Although these $\Delta pK$'s are

generally larger than for other constants, they produce only minor consequences. They imply errors in $K_F$ of up to several percent, but $K_F$ is only important when converting between the seawater and total scales, a small difference to start with (e.g., 0.01 pH unit for average seawater).

For $K_S$, all packages essentially agree ($\Delta pK_S$'s always less than 0.0002). There are visible differences for $K_S$ computed from the different packages that merit further investigation (e.g., positive excursions under surface conditions for swco2 and a growing negative divergence with depth for csys) but they are quite small. Given the negligible consequences, we leave their resolution to the package developers.

### 4.2.5   $K_A$ and $K_C$: solubility products

For $K_A$, the situation is similar at the surface but not at depth (Fig. 17). Under surface conditions, no packages have significant discrepancies. Although CO2calc appears to have discrepancies larger than other packages (average $\Delta pK_A \sim 0.0002$), they remain quite small; moreover, they may be exaggerated because we had to calculate them from computed variables with limited output precision (2 decimal places for $CO_3^{2-}$). Pressure-correction discrepancies are negligible in all packages but one, swco2. At 4000 db, the discrepancy for 13 °C water reaches $\Delta pK_A = 0.015$, thereby biasing $K_A$ to be 3.4 % too low and $\Omega_A$ to be 3.4 % too high. However, for more usual deep waters at 2 °C, those discrepancies are reduced by a factor of 7. The form of the swco2 discrepancy curve, quadratic with pressure, suggests an error in the $b_1$ pressure-correction coefficient. Without access to the swco2 source code, we made sensitivity tests with seacarb that confirmed that there is a sign error in swco2's $b_1$ coefficient for $K_A$. It should be +0.0003692 as in all other packages. The other swco2 pressure-correction coefficients for $K_A$ appear to be correct.

### 4.2.6   Constants for phosphoric and silicic acids

Constants for phosphoric and silicic acid enter into the calculations only when nutrient concentrations are significant and $A_T$ is a member of the input pair. Under those conditions, $A_T$ must be corrected for nutrient alkalinity to provide an accurate estimate of $A_C$, as needed to compute other variables. For $K_{1P}$, $K_{2P}$, and $K_{3P}$, two packages (seacarb and mocsy) agree with results from CO2SYS across ranges of $T$, $S$, and $P$ (Fig. 18). Two other packages (CO2calc and ODV) do not provide these constants as output, nor could they be calculated from available variables.

The two remaining packages, csys and swco2, diverge significantly from CO2SYS, with discrepancies for each being consistent across all three constants. For csys, surface discrepancies in these nutrient constants have the same form and magnitude as already seen for csys's $K_W$ (Fig. 16). The cause is also identical, the 0.015 constant offset proposed for best practices (Dickson et al., 2007) to convert from the seawater to the total scale; the other packages employ the more rigorous variable offset, which varies with $T$ and $S$. For swco2, discrepancies under surface conditions remain constant across ranges of $T$ and $S$. They are attributable to using the equations for $K_{1P}$, $K_{2P}$, and $K_{3P}$ exactly as given by Dickson et al. (2007), i.e., with 0.015 subtracted from the constant term in each equation (to convert from the seawater to the total scale), but also applying the more rigorous, variable pH-scale correction afterwards. Effectively, swco2 errs by making both corrections instead of just one. The best remedy would be to remove the constant offset and keep the variable correction.

Away from the surface, only one package exhibits pressure-correction discrepancies in $K_{1P}$, $K_{2P}$, and $K_{3P}$, and those remain quite small. The results for csys demonstrate the minor error ($\Delta pK = 0.002$ over 10 000 db) that is associated with making pressure corrections on the total scale instead of the seawater scale, as intended by Millero (1995) and performed in all other packages. At very high pressures (10 000 db), that error partly compensates for taking the simplified approach (−0.015 offset) to change pH scales. Although this small discrepancy is only obvious when other errors are com-

pletely negligible, it is also detectable in csys's previous results for $K_1$, $K_2$, and $K_B$ (Figs. 13 and 16).

For $K_{Si}$, only the swco2 package reveals any discrepancies relative to CO2SYS (Fig. 16). Out of the other packages, two agree with $K_{Si}$ from CO2SYS (seacarb and mocsy), two do not provide $K_{Si}$ as output (CO2calc and ODV), and one does not compute $K_{Si}$ (csys). Discrepancies for $K_{Si}$ in swco2 under surface conditions are identical to those for its $K_W$, $K_{1P}$, $K_{2P}$, $K_{3P}$. The constant positive excursion of 0.006 is due to correcting $K_{Si}$ from the seawater to the total scale two times, as mentioned for $K_{1P}$, $K_{2P}$, and $K_{3P}$. Below the surface, swco2's discrepancy for $K_{Si}$ grows linearly with pressure, just as does its discrepancy for $K_B$ (Sect. 4.2.3). The cause is identical, a sign error in the $a_2$ pressure correction coefficient: it should be $-0.002608$ instead of $+0.002608$. As for $K_B$, discrepancies in swco2's pressure correction for $K_{Si}$ are lower when carried out at 2 °C rather than at 13 °C (e.g., $\Delta p K_{Si}$'s of 0.007 and 0.015, respectively, at 4000 db).

## 5 Conclusions

To assess the consistency of carbonate chemistry software packages, we have compared computed variables from the seven publicly available distributions, identifying discrepancies and their causes. Packages generally agree when using the set of constants recommended for best practices (Dickson et al., 2007). The small discrepancies that do exist become significant in two packages and generally derive from a few constants. The only exception is csys's computed $p\text{CO}_2$, which is about 1 µatm too low at the surface because it mislabels $f\text{CO}_2$ as $p\text{CO}_2$. When compared to $f\text{CO}_2$ in other packages, there is little disagreement. The csys package also has small errors in computed variables associated with pressure corrections of $K_1$, $K_2$, and $K_B$, which are carried out on the total scale instead of the seawater pH scale (leading to 0.5 % greater values at 4000 db).

Pressure corrections do not contribute other significant differences when packages compute variables in the cold waters that pervade the deep ocean. For isolated warm

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deep waters though, such as found in the Mediterranean Sea, the swco2 package produces significant discrepancies, e.g., when $p\text{CO}_2$ and $\text{CO}_3^{2-}$ are computed from the $A_T$–$C_T$ input pair. Those discrepancies derive from a sign error in a pressure-correction coefficient for $K_B$. Similar sign errors in swco2's pressure-correction coefficients for $K_A$ and $K_C$ also cause $\Omega_A$ and $\Omega_C$ to be underestimated by 3 % at 4000 db when at 13 °C but only 0.5 % when at 2 °C.

Computed variables in the remaining packages (CO2calc, ODV, mocsy, and seacarb) do not differ significantly from CO2SYS, when used with the same set of constants recommended for best practices. Although significant discrepancies in some of those constants were identified, e.g., overestimates in $K_F$ for $S < 10$ in both seacarb and csys (reaching +6 % at S=0) due to an error in ionic strength equation, much larger errors in $K_F$ would be needed to significantly alter computed variables. Furthermore, if the best-practices set of constants are considered together, they should not be used at such low salinities nor at very low temperatures. That is, the associated formulations for $K_1$ and $K_2$ (Lueker et al., 2000) are not designed to be used in estuaries ($S < 19$) nor in the ocean's coldest waters ($T < 2$ °C), which comprise 11 % of its global surface area and 42 % of its global volume, based on an annual climatology (Locarnini et al., 2010).

Consequently, we also compared packages changing only the formulation for $K_1$ and $K_2$ to one designed for low-salinity and lower temperature waters (Millero, 2010). Out of the four packages where that newer option is available, mocsy agreed with the CO2SYS reference, whereas CO2calc and seacarb differed significantly, e.g., with surface $p\text{CO}_2$ lower by 5 and 7 µatm, respectively (at $S = 35$ and $T = 18$°C). The seacarb package differs because it uses the set of published coefficients to compute the salinity-dependence of $K_1$ and $K_2$ on the total scale; conversely, CO2SYS and mocsy use another set to compute those constants on the seawater scale, later converting to the total scale. Although results from both approaches should be the same, they are not, indicating a fundamental inconsistency between the two published sets of coefficients. The CO2calc package differs for another reason. Although it uses the set of coefficients

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for the seawater scale, one of its coefficients contains an additional significant figure. The latter comes from the unpublished spreadsheet provided by Millero that was used with the same publication (Millero, 2010). Unfortunately, some of the other published coefficients still appear to lack 1 or 2 significant figures, based on our tests with the spreadsheet coefficients on the total scale, for which there is much greater precision. Once this issue is resolved, the Millero (2010) formulations for $K_1$ and $K_2$ may well serve as better alternatives for low salinity waters.

This comparison of computed variables, constants, and source code from the different packages leads us to make several recommendations for both developers and users. Developers would facilitate future validation and improvements by providing computed constants as output and, if possible, by releasing their source code. Developers would enhance reproducibility by providing access to all older versions of their package along with a detailed history of changes. Developers are encouraged to offer the option, if not already available, to use the revised total boron to salinity ratio (Lee et al., 2010), which now appears preferable. Users would facilitate reproducibility by citing in their publications not only the name of the package but also its version number. Larger differences were found here between versions of one package than between all up-to-date packages. Users should use the best-practices set of constants (Dickson et al., 2007) by default, reporting exceptions along with rationale. Although our focus has been on public packages, it is just as necessary to validate privately developed code. To facilitate such validation, we provide a subset of the data that was produced for this comparison in the Supplement.

**Supplementary material related to this article is available online at http://www.biogeosciences-discuss.net/11/5327/2014/ bgd-11-5327-2014-supplement.zip.**

## References

Antonov, J. I., Seidov, D., Boyer, T. P., Locarnini, R. A., Mishonov, A. V., Garcia, H. E., Baranova, O. K., Zweng, M. M., and Johnson, D. R.: World Ocean Atlas 2009, Volume 2: Salinity, edited by: Levitus, S., Atlas NESDIS 69, NOAA, US Government Printing Office, Washington DC, 184 pp., 2010. 5335, 5381

Byrne, R. H. and Yao, W.: Procedures for measurement of carbonate ion concentrations in seawater by direct spectrophotometric observations of Pb (II) complexation, Mar. Chem., 112, 128–135, 2008. 5333

Cai, W.-J. and Wang, Y.: The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia, Limnol. Oceanogr., 43, 657–668, 1998. 5373

Dickson, A. G.: Standard potential of the reaction: $AgCl(s) + 1/2H_2(g) = Ag(s) + HCl(aq)$, and the standard acidity constant of the ion $HSO_4^-$ in synthetic seawater from 273.15 to 318.15 K, Chemical Thermodynamics, 22, 113–127, 1990a. 5373, 5396

Dickson, A. G.: Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K, Deep-Sea Res., 37, 755–766, 1990b. 5336, 5373

Dickson, A. G.: The carbon dioxide system in seawater: equilibrium chemistry and measurements, in: Guide to Best Practices for Ocean Acidification Research and Data Reporting, edited by: Riebesell, U., Fabry, V. J., Hansson, L., and Gattuso, J.-P., Publications Office of the European Union, 17–40, 2010. 5330, 5338

Dickson, A. G. and Goyet, C.: Handbook of methods for the analysis of the various parameters of the carbon dioxide system in seawater; version 2, ORNL/CDIAC-74, ORNL, 1994. 5330, 5355, 5356, 5396

Dickson, A. G. and Millero, F.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, Deep-Sea Res., 34, 1733–1743, 1987. 5333, 5373, 5380

Dickson, A. G. and Riley, J. P.: The effect of analytical error on the evaluation of the components of the aquatic carbon-dioxide system, Mar. Chem., 6, 77–85, 1978. 5347, 5348

Dickson, A. G. and Riley, J. P.: The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base, I. The ionic product of water – $K_W$, Mar. Chem., 7, 89-99, 1979. 5336, 5352, 5355, 5356, 5373, 5396

Dickson, A. G., Sabine, C. L., and Christian, J. R.: Guide best practices for ocean $CO_2$ measurements, PICES Special Publication 3, 191 pp., 2007. 5330, 5331, 5332, 5335, 5336, 5344, 5345, 5348, 5349, 5354, 5355, 5358, 5359, 5361, 5390

Easley, R. A., Patsavas, M. C., Byrne, R. H., Liu, X., Feely, R. A., and Mathis, J. T.: Spectrophotometric Measurement of Calcium Carbonate Saturation States in Seawater, Environ. Sci. Technol., 47, 1468–1477, 2013. 5333

Garcia, H. E., Locarnini, R. A., Boyer, T. P., Antonov, J. I., Zweng, M. M., Baranova, O. K., and Johnson, D. R.: World Ocean Atlas 2009, Volume 4: Nutrients (Phosphate, Nitrate, Silicate), edited by: Levitus, S., Atlas NESDIS 71, NOAA, US Government Printing Office, Washington DC, 398 pp., 2010. 5335, 5381

Gattuso, J.-P. and Hansson, L. (Eds.): Ocean Acidification, Oxford Univ. Press, Oxford, UK, 2011. 5329

Gattuso, J.-P. and Lavigne, H.: Technical Note: Approaches and software tools to investigate the impact of ocean acidification, Biogeosciences, 6, 2121–2133, doi:10.5194/bg-6-2121-2009, 2009. 5334

Goyet, C. and Poisson, A.: New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity, Deep-Sea Res., 36, 1635–1654, 1989. 5373

Hansson, I.: A new set of acidity constants for carbonic acid and boric acid in sea water, Deep-Sea Res., 20, 461–478, 1973a. 5373

Hansson, I.: The determination of dissociation constants of carbonic acid in synthetic sea water in the salinity range of 20–40 ‰ and temperature range of 5–30 °C, Acta Chemica Scandanavia, 27, 931–944, 1973b.

Hoppe, C. J. M., Langer, G., Rokitta, S. D., Wolf-Gladrow, D. A., and Rost, B.: Implications of observed inconsistencies in carbonate chemistry measurements for ocean acidification studies, Biogeosciences, 9, 2401–2405, doi:10.5194/bg-9-2401-2012, 2012. 5331

5363

Hunter, K. A.: XLCO2 – Seawater CO2 Equilibrium Calculations Using Excel Version 2, University of Otago, New Zealand, available at: http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2/, 2007. 5330, 5368

Key, R. M., Sabine., C. L., Lee, K., Wanninkhof, R., Bullister, J., Feely, R. A., Millero, F. J., Mordy, C., and Peng, T.-H.: A Global Ocean carbon climatology: results from Global Data Analysis Project (GLODAP), Global Biogeochem. Cy., 18, GB4031, doi:10.1029/2004GB002247, 2004. 5335, 5381

Khoo, K. H., Ramette, R. W., Culberson, C. H., and Bates, R. G.: Determination of hydrogen ion concentrations in seawater from 5 to 40 °C: standard potentials at salinities from 20 to 45 ‰, Anal. Chem., 49, 29–34, 1977. 5373

Kroeker, K. J., Kordas, R. L., Crim, R., Hendriks, I. E., Ramajo, L., Singh, G. S., Duarte, C. M., and Gattuso, J.-P.: Impacts of ocean acidification on marine organisms: quantifying sensitivities and interaction with warming, Glob. Change Biol., 19, 156–159, 2013. 5329

Lavigne, H. and Gattuso, J.-P.: seacarb: seawater carbonate chemistry with R. R package version 2.4.2, The Comprehensive R Archive Network, 2011. 5330, 5368

Lee, K., Kim, T.-W., Byrne, R. H., Millero, F. J., Feely, R. A., and Liu, Y.-M.: The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans, Geochim. Cosmochim. Ac., 74, 1801–1811, doi:10.1016/j.gca.2009.12.027, 2010. 5337, 5345, 5361, 5390

Lewis, E. and Wallace, D. W. R.: Program Developed for $CO_2$ System Calculations, ORNL/CDIAC-105, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn., 38 pp., 1998. 5329, 5330, 5332, 5338, 5355, 5368

Locarnini, R., Mishonov, A., Antonov, J., Boyer, T., Garcia, H., Baranova, O., Zweng, M., and Johnson, D.: World Ocean Atlas 2009, Volume 1: Temperature, edited by: Levitus, S., Atlas NESDIS 68, NOAA, US Government Printing Office, Washington DC, 184 pp., 2010. 5335, 5360, 5381

Lueker, T. J., Dickson, A. G., and Keeling, C. D.: Ocean $p$CO$_2$ calculated from dissolved inorganic carbon, alkalinity, and equations for $K_1$ and $K_2$: validation based on laboratory measurements of $CO_2$ in gas and seawater at equilibrium, Mar. Chem., 70, 105–119, 2000. 5331, 5332, 5333, 5334, 5336, 5337, 5340, 5345, 5346, 5347, 5349, 5350, 5351, 5353, 5360, 5373, 5391, 5392, 5393

Martz, T. R., Jannasch, H. W., and Johnson, K. S.: Determination of carbonate ion concentration and inner sphere carbonate ion pairs in seawater by ultraviolet spectrophotometric titration, Mar. Chem., 115, 145–154, 2009. 5333

5364

Mehrbach, C., Culberson, C. H., Hawley, J. E., and Pytkowicz, R. M.: Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, Limnol. Oceanogr., 18, 897–907, 1973. 5333, 5336, 5373

Millero, F. J.: The thermodynamics of the carbonate system in seawater, Geochim. Cosmochim. Ac., 43, 1651–1661, 1979. 5373

Millero, F. J.: Influence of pressure on chemical processes in the sea, in: Chemical Oceanography, edited by: Riley, J. P. and Chester, R., 1–88, Academic Press, New York, 1983. 5355

Millero, F. J.: Thermodynamics of the carbon dioxide system in the oceans, Geochim. Cosmochim. Ac., 59, 661–677, 1995. 5336, 5337, 5338, 5354, 5355, 5358, 5373, 5395, 5397

Millero, F. J.: The marine inorganic carbon cycle, Chem. Rev., 107, 308–341, 2007. 5338

Millero, F. J.: Carbonate constants for estuarine waters, Mar. Freshwater Res., 61, 139–142, doi:10.1071/MF09254, 2010. 5334, 5337, 5345, 5346, 5351, 5352, 5353, 5355, 5360, 5361, 5373, 5377, 5391, 5393, 5394

Millero, F. J., Graham, T. B., Huang, F., Bustos-Serrano, H., and Pierrot, D.: Dissociation constants of carbonic acid in seawater, Mar. Chem., 100, 80–94, doi:10.1016/j.marchem.2005.12.001, 2006. 5351, 5373

Mojica Prieto, F. J. and Millero, F. J.: The values of $pK_1 + pK_2$ for the dissociation of carbonic acid in seawater, Geochim. Cosmochim. Ac., 66, 2529–2540, 2002. 5373

Morris, A. and Riley, J.: The bromide/chlorinity and sulphate/chlorinity ratio in sea water, Deep-Sea Res., 13, 699–705, 1966. 5336

Mosley, L. M., Peake, B. M., and Hunter, K. A.: Modelling of pH and inorganic carbon speciation in estuaries using the composition of the river and seawater end members, Environ. Modell. Softw., 25, 1658–1663, 2010. 5368

Mucci, A.: The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure, Am. J. Sc., 283, 780–799, 1983. 5336, 5373, 5396

Munhoven, G.: Mathematics of the total alkalinity–pH equation–pathway to robust and universal solution algorithms: the SolveSAPHE package v1.0.1, Geosci. Model Dev., 6, 1367–1388, doi:10.5194/gmd-6-1367-2013, 2013. 5331

Orr, J. C.: Recent and future changes in ocean carbonate chemistry, in: Ocean Acidification, edited by: Gattuso, J.-P., and Hansson, L., chap. 3, 41–66, Oxford Univ. Press, 2011. 5329

Orr, J. C. and Epitalon, J.-M.: Improved routines to model the ocean carbonate system: mocsy 1.0, Geosci. Model Dev. Discuss., submitted, 2014. 5331, 5339, 5344, 5368

5365

Orr, J. C., Najjar, R., Sabine, C. L., and Joos, F.: Abiotic-HOWTO. Internal OCMIP Report, LSCE/CEA Saclay, Gif-sur-Yvette, France, 25 pp., 1999. 5331

Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., Feely, R. A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R. M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R. G., Plattner, G.-K., Rodgers, K. B., Sabine, C. L., Sarmiento, J. L., Schlitzer, R., Slater, R. D., Totterdell, I. J., Weirig, M.-F., Yamanaka, Y., and Yool, A.: Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, Nature, 437, 681–686, doi:10.1038/nature04095, 2005. 5331, 5339, 5383

Pelletier, G., Lewis, E., and Wallace, D.: CO2SYS.XLS: A calculator for the $CO_2$ system in seawater for Microsoft Excel/VBA, Wash. State Dept. of Ecology/Brookhaven Nat. Lab., Olympia, WA/Upton, NY, USA, 2007. 5330, 5332, 5368

Perez, F. F. and Fraga, F.: Association constant of fluoride and hydrogen ions in seawater, Mar. Chem., 21, 161–168, 1987. 5336, 5352, 5355, 5373, 5394

Pierrot, D., Lewis, E., and Wallace, D. W. R.: MS Excel Program Developed for CO2 System Calculations, Tech. rep., Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., US DOE, Oak Ridge, Tenn., 2006. 5330, 5332, 5333, 5368, 5373

Proye, A. and Gattuso, J.-P.: Seacarb, an R package to calculate parameters of the seawater carbonate system, 2003. 5330

R Development Core Team: R: A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, Vienna, Austria, ISBN 3-900051-07-0, 2012. 5330

Riley, J. and Tongudai, M.: The major cation/chlorinity ratios in sea water, Chem. Geol., 2, 263–269, 1967. 5336

Robbins, L. L., Hansen, M. E., Kleypas, J. A., and Meylan, S. C.: CO2calc: a user-friendly carbon calculator for Windows, Mac OS X, and iOS (iPhone), USGS Open-File Report, 2010–1280, 17, 2010. 5330, 5368

Roy, R. N., Roy, L. N., Vogel, K. M., Porter-Moore, C., Pearson, T., Good, C. E., Millero, F. J., and Campbell, D. M.: The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45 °C, Mar. Chem., 44, 249–267, 1993. 5373

Sarmiento, J. L., Le Quéré, C., and Pacala, S.: Limiting future atmospheric carbon dioxide, Global Biogeochem. Cy., 9, 121–137, 1995. 5329

Schlitzer, R.: Interactive analysis and visualization of geoscience data with Ocean Data View, Comput. Geosci., 28, 1211–1218, 2002. 5330, 5368

5366

Uppström, L. R.: The Boron/Chlorinity Ratio of Deep-Sea Water from the Pacific Ocean, in: Deep-Sea Research and Oceanographic Abstracts, 21, 161–162, Elsevier, 1974. 5336, 5337, 5345, 5390

van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E., and Wallace, D. W. R.: MATLAB program developed for $CO_2$ system calculations, ORNL/CDIAC-105b, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., US DOE, Oak Ridge, Tenn., doi:10.3334/CDIAC/otg.CO2SYS_MATLAB_v1.1, 2011. 5330, 5332, 5368

Weiss, R. F.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Mar. Chem., 2, 203–215, 1974. 5335, 5373

Wittmann, A. C. and Pörtner, H.-O.: Sensitivities of extant animal taxa to ocean acidification, Nature Climate Change, 3, 995–1001, 2013. 5329

Zeebe, R. E. and Wolf-Gladrow, D. A.: $CO_2$ in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier, Amsterdam, 346 pp., 2001. 5330, 5368

**Table 1.** Carbonate system software packages.

| Package | Language | Version | Reference |
|---|---|---|---|
| CO2SYS[a] | DOS | 1.05 | Lewis and Wallace (1998) |
| CO2SYS[b] | Excel | 14 | Pelletier et al. (2007) |
| CO2SYS[a] | Excel | 2.1 | Pierrot et al. (2006) |
| CO2SYS[a] | MATLAB | 1.1 | van Heuven et al. (2011) |
| CO2calc[c] | Visual Basic | 1.2.0 | Robbins et al. (2010) |
| csys[d] | MATLAB | 3 | Zeebe and Wolf-Gladrow (2001) |
| ODV[e] | C++ | 4.5.0 | Schlitzer (2002) |
| mocsy[f] | Fortran 95 | 1.2 | Orr and Epitalon (2014) |
| seacarb[g] | R | 2.4.8 | Lavigne and Gattuso (2011) |
| swco2[h] | Excel | 2 | Hunter (2007); Mosley et al. (2010) |
| swco2[h] | Visual Basic | 2 | Hunter (2007) |

[a] http://cdiac.ornl.gov/oceans/co2rprt.html
[b] http://envsci.rutgers.edu/~reinfelder/aquaticnotes/co2sys.xls
[c] http://pubs.usgs.gov/of/2010/1280/
[d] http://www.soest.hawaii.edu/oceanography/faculty/zeebe_files/CO2_System_in_Seawater/csys.html
[e] http://odv.awi.de/
[f] http://ocmip5.ipsl.jussieu.fr/mocsy
[g] http://cran.r-project.org/package=seacarb
[h] http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2/

**Table 2.** Computational time needed to process global 3-D GLODAP gridded data product.

| Package | Total time | Run time | Write time |
|---|---|---|---|
| seacarb (R) | 1665.3 | | |
| swco2 (Excel) | 897.1 | | |
| CO2calc | 91.2 | | |
| ODV | 73.3 | | |
| swco2 (Visual Basic) | 28.0 | | |
| csys (MATLAB) | 7.7 | | |
| CO2SYS (MATLAB) | 5.9 | 5.5 | 0.4 |
| mocsy (Fortran 95) | 0.5 | 0.2 | 0.3 |

[a] Time in minutes required to treat 958 557 unmasked records
[b] All packages run on a 2.0 GHz Intel Pentium dual-core T4200 under Linux or Windows Vista.

**Table 3.** Operating system and code details for each package.

| OS & details | CO2SYS | | | CO2calc | ODV | csys | seacarb | swco2 | mocsy |
|---|---|---|---|---|---|---|---|---|---|
| | DOS | Excel | Matlab | | | | | | |
| Linux/Unix | | | • | | • | • | • | | • |
| Windows | • | • | • | • | • | • | • | • | • |
| Mac OS | | • | • | • | • | • | • | | • |
| iPhone | | | | • | | | | | |
| Public source code | • | • | • | | | • | • | | • |
| User programmable | | | • | | | • | • | •[b] | • |
| Required software | E[c] | M[a] | | | | M[a] | R | E[c] | F95[d] |

[a] Package works with MATLAB (commercial software) or octave (free software)

[b] Spreadsheet interface is not code; Core library is callable (Visual Basic) but not modifiable

[c] Package works with Excel (commercial) or LibreOffice (free and open source)

[d] Fortran 95 code, which is also callable via python

**Table 4.** Available input pairs for each package.

| Pair | CO2SYS | | | CO2calc | ODV | csys | seacarb | swco2 | mocsy |
|---|---|---|---|---|---|---|---|---|---|
| | DOS | Excel | Matlab | | | | | | |
| $A_T$–$C_T$ | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| $A_T$–$pCO_2$ | ● | ● | ● | ● | ● | ● | ● | ● | |
| $A_T$–pH | ● | ● | ● | ● | ● | ● | ● | ● | |
| $A_T$–$CO_3^{2-}$ | | | | | | ● | ● | ● | |
| $A_T$–$CO_2^*$ | | | | | | ● | ● | ● | |
| $A_T$–$HCO_3^-$ | | | | | | ● | ● | ● | |
| $C_T$–$pCO_2$ | ● | ● | ● | ● | ● | ● | ● | ● | |
| $C_T$–pH | ● | ● | ● | ● | ● | ● | ● | ● | |
| $C_T$–$CO_3^{2-}$ | | | | | | ● | ● | ● | |
| $C_T$–$CO_2^*$ | | | | | | ● | ● | ● | |
| $C_T$–$HCO_3^-$ | | | | | | ● | ● | ● | |
| $pCO_2$–pH | ● | ● | ● | ● | ● | ● | ● | ● | |
| $pCO_2$–$CO_3^{2-}$ | | | | | | ● | ● | ● | |
| $pCO_2$–$HCO_3^-$ | | | | | | ● | ● | ● | |
| pH–$CO_3^{2-}$ | | | | | | ● | ● | ● | |
| pH–$CO_2^*$ | | | | | | ● | ● | ● | |
| pH–$HCO_3^-$ | | | | | | ● | ● | ● | |
| $CO_3^{2-}$–$CO_2^*$ | | | | | | ● | ● | ● | |
| $CO_3^{2-}$–$HCO_3^-$ | | | | | | ● | ● | ● | |
| $CO_2^*$–$HCO_3^-$ | | | | | | ● | ● | ● | |

[1] CO2SYS, CO2calc, and ODV also allow input pairs containing $fCO_2$ instead of $pCO_2$
[2] seacarb and swco2 include user callable functions to convert between $pCO_2$ and $fCO_2$

**Table 5.** Available pH scales for each package.

| pH scale | CO2SYS | | | CO2calc | ODV | csys | seacarb | swco2 | mocsy |
|---|---|---|---|---|---|---|---|---|---|
| | DOS | Excel | Matlab | | | | | | |
| NBS | ● | ● | ● | ● | | | | ● | |
| Free | ● | ● | ● | | ● | ● | ● | ● | |
| Total | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| Seawater | ● | ● | ● | ● | ● | | ● | ● | |
| Convert pH between scales | | | ● | | | | ● | ● | |
| Convert K's between scales | ● | | | | | | ● | | |

[1] All packages convert pH and K's between scales, internally
[2] Some packages have user-callable routines to make these conversions between scales

**Table 6.** Available constants for each package.

| Constant | CO2SYS | | | CO2calc | ODV | csys | seacarb | swco2 | mocsy |
|---|---|---|---|---|---|---|---|---|---|
| | DOS | Excel[a] | Matlab | | | | | | |
| $K_1$ and $K_2$ | | | | | | | | | |
| (Lueker et al., 2000) | | • | • | • | • | • | • | • | • |
| (Roy et al., 1993) | • | • | • | • | • | • | • | • | |
| (Goyet and Poisson, 1989) | • | • | • | • | | | | • | |
| (Hansson, 1973a, b)[b] | • | • | • | • | | | | • | |
| (Mehrbach et al., 1973)[b] | • | • | • | • | | | | | |
| (Millero, 1979) | • | • | • | • | | | | • | |
| (Mojica Prieto and Millero, 2002) | | • | • | | | | | • | |
| (Cai and Wang, 1998) | | • | • | | | | | | |
| (Millero et al., 2006) | | • | • | • | | | • | • | |
| (Millero, 2010) | | • | • | • | | | • | | • |
| $K_0$ (Weiss, 1974) | • | • | • | • | • | • | • | • | • |
| $K_B$ (Dickson, 1990b) | • | • | • | • | • | • | • | • | • |
| $K_F$ (Perez and Fraga, 1987) | | | | | | | • | | • |
| $K_F$ (Dickson and Riley, 1979) | • | • | • | • | • | • | • | • | • |
| $K_W$ (Millero, 1995) | • | • | • | • | • | • | • | • | • |
| $K_S$ (Dickson, 1990a) | • | • | • | • | • | • | • | • | • |
| $K_S$ (Khoo et al., 1977) | • | • | • | • | • | • | • | • | • |
| $K_{1P}, K_{2P}, K_{3P}$ (Millero, 1995) | • | • | • | • | • | • | • | • | • |
| $K_{Si}$ (Millero, 1995) | • | • | • | • | • | | • | • | • |
| $K_A$ (Mucci, 1983) | • | • | • | • | • | | • | • | • |
| $K_C$ (Mucci, 1983) | • | • | • | • | • | | • | • | • |

[a] Excel version of CO2SYS from Pierrot et al. (2006)
[b] refit by Dickson and Millero (1987)

**Table 7.** Coefficients used in Eqs. (2) and (3) to correct for effect of pressure on equilibrium constants.

| $K$ | $a_0$ | $a_1$ | $a_2$ | $b_0$ | $b_1$ | $b_2$ |
|---|---|---|---|---|---|---|
| $K_1$ | −25.50 | 0.1271 | 0 | −0.00308 | $0.877 \times 10^{-4}$ | 0 |
| $K_2$ | −15.82 | −0.0219 | 0 | 0.00113 | $-1.475 \times 10^{-4}$ | 0 |
| $K_B$ | −29.48 | 0.1622 | −0.002608 | −0.00284 | 0 | 0 |
| $K_W$ | −20.02 | 0.1119 | −0.001409 | −0.00513 | $0.794 \times 10^{-4}$ | 0 |
| $K_S$ | −18.03 | 0.0466 | 0.000316 | −0.00453 | $0.900 \times 10^{-4}$ | 0 |
| $K_F$ | −9.78 | −0.0090 | −0.000942 | −0.00391 | $0.540 \times 10^{-4}$ | 0 |
| $K_C$ | −48.76 | 0.5304 | 0 | −0.01176 | $3.692 \times 10^{-4}$ | 0 |
| $K_A$ | −46.00 | 0.5304 | 0 | −0.01176 | $3.692 \times 10^{-4}$ | 0 |
| $K_{1P}$ | −14.51 | 0.1211 | −0.000321 | −0.00267 | $0.427 \times 10^{-4}$ | 0 |
| $K_{2P}$ | −23.12 | 0.1758 | −0.002647 | −0.00515 | $0.900 \times 10^{-4}$ | 0 |
| $K_{3P}$ | −26.57 | 0.2020 | −0.003042 | −0.00408 | $0.714 \times 10^{-4}$ | 0 |
| $K_{hs}$ | −14.80 | 0.0020 | −0.000400 | 0.00289 | $0.540 \times 10^{-4}$ | 0 |
| $K_n$ | −26.43 | 0.0889 | −0.000905 | −0.00503 | $0.814 \times 10^{-4}$ | 0 |
| $K_{Si}$ | −29.48 | 0.1622 | −0.002608 | −0.00284 | 0 | 0 |

**Table 8.** Desired measurement and numerical uncertainties.

| | Uncertainties | | |
| --- | --- | --- | --- |
| Variable | Measurement | Numerical | Units |
| $A_T$ | 1 | 0.1 | $\mu mol\,kg^{-1}$ |
| $C_T$ | 1 | 0.1 | $\mu mol\,kg^{-1}$ |
| $pCO_2$ | 1 | 0.1 | $\mu atm$ |
| $CO_3^{2-}$ | 1 | 0.1 | $\mu mol\,kg^{-1}$ |
| pH | 0.003 | 0.0003 | |
| $pK_0$ | 0.002 | 0.0002 | |
| $pK_1$ | 0.01 | 0.001 | |
| $pK_2$ | 0.02 | 0.002 | |
| $pK_i$ (other) | 0.01 | 0.001 | |

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**Table 9.** Ratio of relative change between output and input variables $(\partial y/y)/(\partial x/x)$.

| | Input | | | | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Output | $A_T$ | $C_T$ | $K_0$ | $K_1$ | $K_2$ | $K_B$ | $K_W$ | $K_S$ | $K_F$ | $K_A$ | $K_C$ |
| $CO_2^*$ | −9.5 | 11.7 | | −0.92 | 0.63 | 0.28 | 0.02 | | | | |
| $HCO_3^-$ | −0.7 | 1.7 | | 0.01 | −0.03 | 0.02 | | | | | |
| $CO_3^{2-}$ | 8.8 | −7.4 | | −0.05 | 0.30 | −0.24 | −0.01 | | | | |
| $H^+$ | −8.8 | 9.8 | | 0.06 | 0.66 | 0.26 | 0.01 | | | | |
| $pCO_2$ | −9.5 | 11.7 | −0.99 | −0.92 | 0.63 | 0.28 | 0.02 | | | | |
| $fCO_2$ | −9.5 | 11.7 | −0.99 | −0.92 | 0.63 | 0.28 | 0.02 | | | | |
| $\Omega_A$ | 8.8 | −7.4 | | −0.05 | 0.30 | −0.24 | −0.01 | | | −0.99 | |
| $\Omega_C$ | 8.8 | −7.4 | | −0.05 | 0.30 | −0.24 | −0.01 | | | | −0.99 |

[1] Percent change in ouput ($dy/y$) computed from a 1 % change in input ($dx/x$).
[2] Missing values indicate changes of less then 0.001 %.

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**Table 10.** Coefficients from Millero (2010) for $K_1$ and $K_2$ formulations (seawater scale).

| | $K_1$ | $K_2$ |
|---|---|---|
| $\alpha_0$ | 13.4038 | 21.3728 |
| $\alpha_1$ | 0.03206 | 0.1218 |
| $\alpha_2$ | $-5.242 \times 10^{-5}$ | $-3.688 \times 10^{-4}$ |
| $\alpha_3$ | $-530.659$ | $-788.289$ |
| $\alpha_4$ | $-5.8210$ | $-19.189$ |
| $\alpha_5$ | $-2.0664$ | $-3.374$[a] |

[a] Value is $-3.3738$ in Millero's spreadsheet (F. J. Millero, personal communication 2013).

**Table 11.** Check values vs. computed equilibrium constants ($pK$'s) at $T = 25\,°C$, $S = 35$, $P = 0$.

| | $pK_0$ | $pK_1$ | $pK_2$ | $pK_B$ | $pK_W$ | $pK_S$[1] | $pK_F$[1] |
|---|---|---|---|---|---|---|---|
| Check value | 1.5468 | 5.8472 | 8.966 | 8.5975 | 13.217 | 0.999 | 2.627 |
| swco2 | 1.54680 | 5.84720 | 8.96600 | 8.59750 | 13.2204 | 0.9987 | 2.6261 |
| mocsy | 1.54680 | 5.84720 | 8.96600 | 8.59750 | 13.2173 | 0.9987 | 2.6261 |
| CO2SYS | 1.54681 | 5.84715 | 8.96595 | 8.59747 | 13.2204 | 0.9987 | 2.6261 |
| csys | 1.54681 | 5.84715 | 8.96595 | 8.59747 | 13.2173 | 0.9987 | 2.6260 |
| seacarb | 1.54681 | 5.84715 | 8.96595 | 8.59747 | 13.2206 | 0.9987 | 2.6260 |
| CO2calc | 1.54681 | 5.85643 | 8.97522 | 8.59697 | 13.2200 | | |
| ODV | 1.54681 | 5.84715 | 8.96595 | | | | |

[1] free scale (all other pKs are on total scale)

**Table 11.** Continued.

|  | $pK_C$ | $pK_A$ | $pK_{1P}$ | $pK_{2P}$ | $pK_{3P}$ | $pK_{Si}$ |
|---|---|---|---|---|---|---|
| Check value |  |  | 1.61 | 5.962 | 8.79 | 9.39 |
| swco2 | 6.3693 | 6.1883 | 1.6220 | 5.9715 | 8.799 | 9.394 |
| mocsy | 6.3693 | 6.1883 | 1.6120 | 5.9618 | 8.789 | 9.384 |
| CO2SYS | 6.3693 | 6.1883 | 1.6150 | 5.9649 | 8.793 | 9.387 |
| csys | 6.3693 | 6.1883 | 1.6119 | 5.9618 | 8.789 |  |
| seacarb | 6.3693 | 6.1883 | 1.6152 | 5.9652 | 8.7927 | 9.3872 |
| CO2calc | 6.3696 | 6.1884 |  |  |  |  |
| ODV | 6.3693 | 6.1883 |  |  |  |  |

**Fig. 1.** Differences (Δ) between the 4 versions of CO2SYS relative to the reference (MATLAB code) for variables computed from $C_T$ and $A_T$. Differences are shown across ranges of $T$ (left), $S$ (center), and $P$ (right) for $p$CO$_2$ (top), CO$_3^{2-}$ (middle), and pH (bottom). The two most recent versions (MATLAB and Pierrot's Excel version) are run with constants recommended for best practices (BP). The two legacy codes (DOS and Pelletier's Excel version) do not offer the same $K_1$ and $K_2$, so we used an earlier refit by Dickson and Millero (1987) of the same data (DM87).

**Fig. 2.** Global-mean vertical profiles of variables computed from gridded data products for $C_T$ and $A_T$ from GLODAP (Key et al., 2004) combined with $T$, $S$, and nutrients from the 2009 World Ocean Atlas (WOA2009) (Locarnini et al., 2010; Antonov et al., 2010; Garcia et al., 2010). Results are shown for each software package after subtracting off corresponding results from the reference (CO2SYS-MATLAB). The csys package does not provide results for $R$ and $\Omega_A$ (bottom center and right).
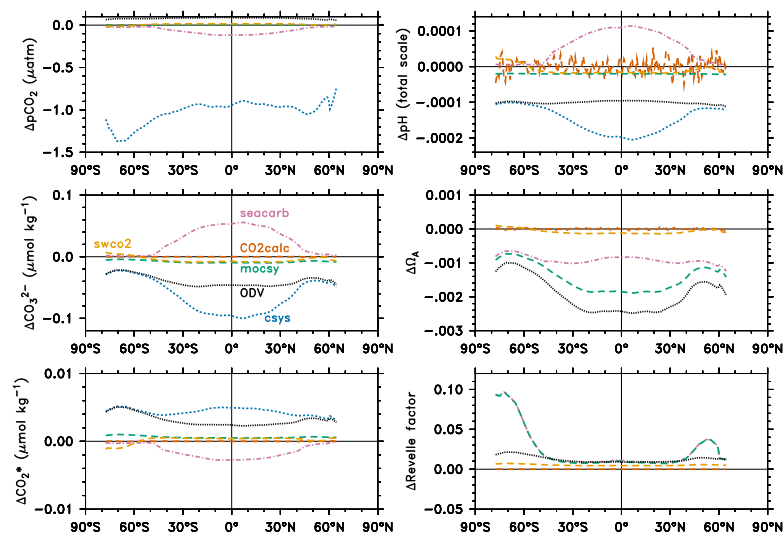
**Fig. 3.** Global zonal-mean surface values for variables computed from GLODAP $C_T$ and $A_T$ as in Fig. 2. Curves are shown for each package and variable after subtracting off corresponding results for the CO2SYS reference. The csys packages does not provide results for $\Omega_A$ and $R$ (middle right and bottom right).
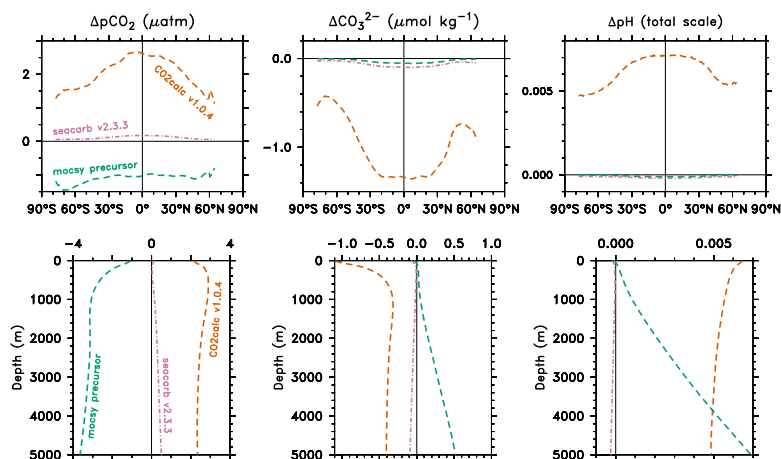
**Fig. 4.** Global zonal-mean surface values (top) and global-mean vertical profiles (bottom) from outdated versions of packages for $p\mathrm{CO}_2$ (left), $\mathrm{CO}_3^{2-}$ (middle), and pH (right) as computed from GLODAP $C_\mathrm{T}$ and $A_\mathrm{T}$ as in Figs. 2 and 3. The three older versions include CO2calc (v1.0.4), seacarb (v2.3.3), and mocsy (non public precursor from Orr et al., 2005). As before, results are shown after subtracting off corresponding results from the same CO2SYS reference.
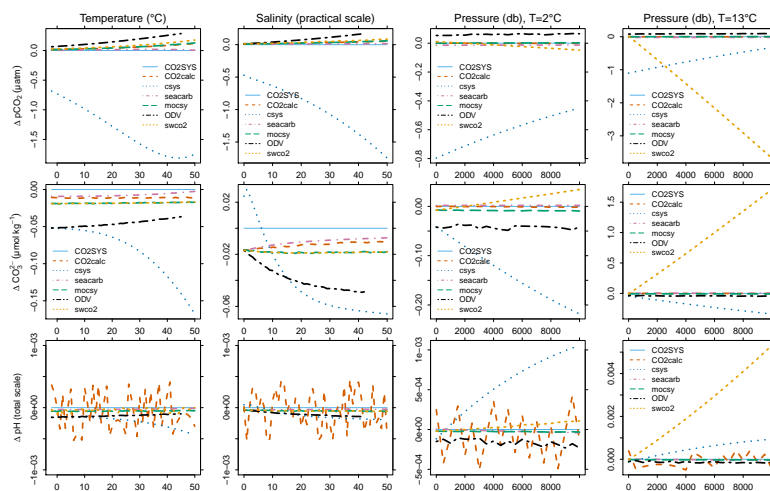
**Fig. 5.** Variables computed from $A_\mathrm{T}$–$C_\mathrm{T}$ for each package minus corresponding results from CO2SYS. The computed $p\mathrm{CO}_2$ (top), $\mathrm{CO}_3^{2-}$ (middle), and pH (bottom) are shown across ranges of $T$ (column 1), $S$ (column 2), and $P$ when $T = 2\,°\mathrm{C}$ (column 3), and when $T = 13\,°\mathrm{C}$ (column 4). For each range, there is one curve per package and per variable.
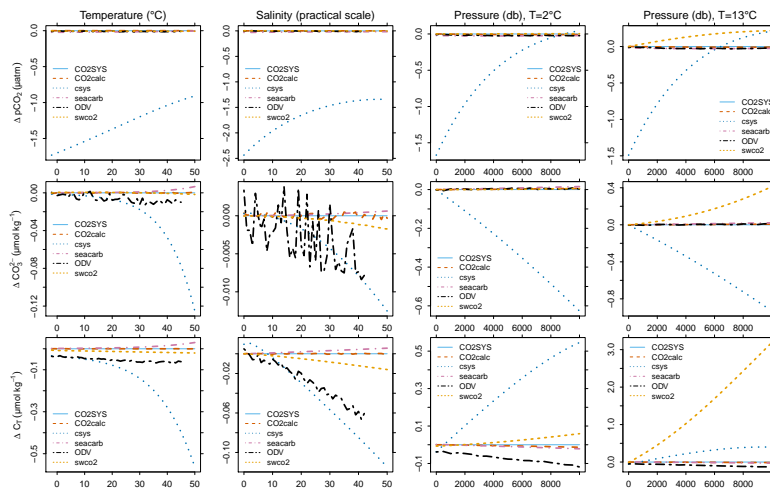
**Fig. 6.** Variables computed from $A_T$–pH with each package minus corresponding results from CO2SYS. Shown are computed $pCO_2$ (top), $CO_3^{2-}$ (middle), and $C_T$ (bottom) across ranges of $T$ (column 1), $S$ (column 2), and $P$ when $T = 2\,°C$ (column 3) and when $T = 13\,°C$ (column 4).
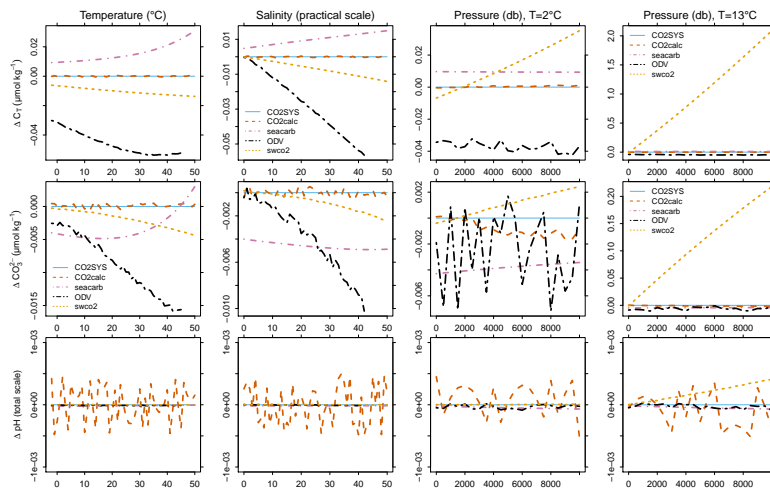
**Fig. 7.** Variables computed from $A_T$–$pCO_2$ with each package minus corresponding results from CO2SYS. Shown are computed $C_T$ (top), $CO_3^{2-}$ (middle), and pH (bottom) across ranges of $T$ (column 1), $S$ (column 2), and $P$ when $T = 2\,°C$ (column 3) and when $T = 13\,°C$ (column 4) for each of the six software packages. Packages not included are mocsy, which allows only the $A_T$–$C_T$ pair, and csys, which does not allow $pCO_2$ as an input variable.
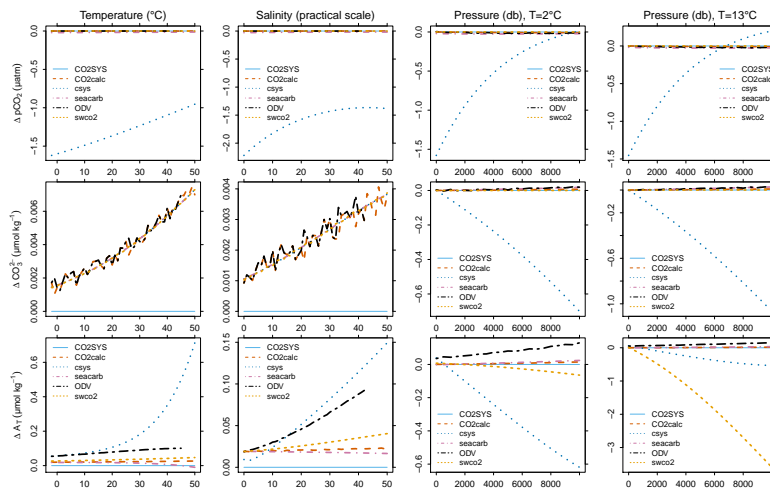
**Fig. 8.** Variables computed from $C_T$–pH with each package minus corresponding results from CO2SYS. Shown are computed $pCO_2$ (top), $CO_3^{2-}$ (middle), and $A_T$ (bottom) across ranges of $T$ (column 1), $S$ (column 2), and $P$ when $T = 2\,°C$ (column 3) and when $T = 13\,°C$ (column 4) for the six software packages.
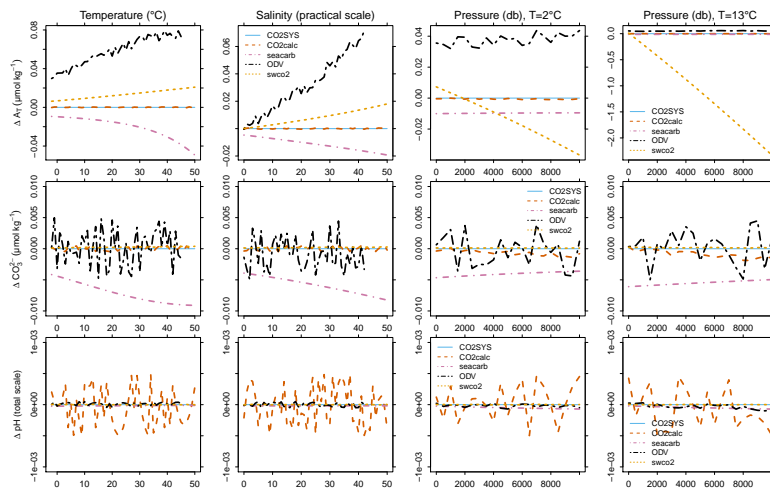
**Fig. 9.** Variables computed from $C_T$–$pCO_2$ with each package minus corresponding results from CO2SYS. Shown are computed $A_T$ (top), $CO_3^{2-}$ (middle), and pH (bottom) across ranges of $T$ (column 1), $S$ (column 2), and $P$ when $T = 2\,°C$ (column 3) and when $T = 13\,°C$ (column 4) for six software packages.
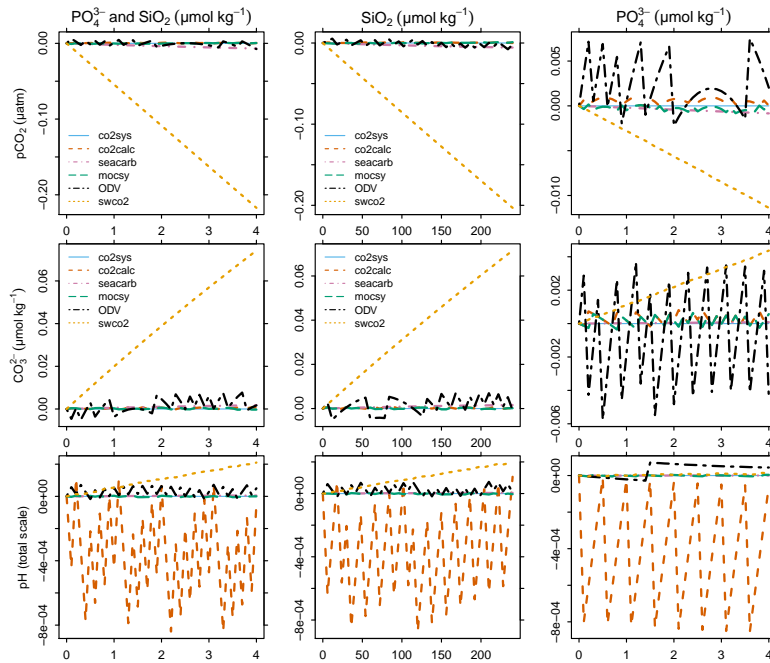
**Fig. 10.** Effect of nutrients on variables computed from $C_T$–$A_T$ with each package minus results for CO2SYS. Shown are effects on computed $p$CO$_2$ (top), CO$_3^{2-}$ (middle), and pH (bottom) across the observed oceanic ranges of PO$_4^{3-}$ (right), SiO$_2$ (center), and their combined effect (left) for six software packages. Results for csys are not included as it assumes that nutrient concentrations are always zero.

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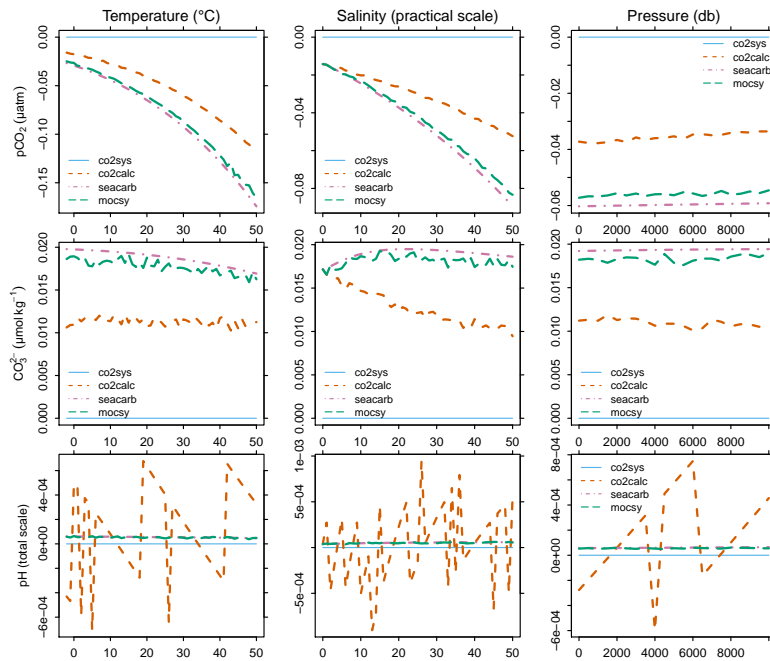
**Fig. 11.** Effect of increased total boron on variables computed from $C_T$–$A_T$. Shown are the effects of the increased boron (Lee et al., 2010 minus Uppström, 1974) on computed $p$CO$_2$ (top), CO$_3^{2-}$ (middle), and pH (bottom) across ranges of $T$ (left), $S$ (center), and $P$ (right). The Lee et al. (2010) formulation is included in 3 packages (CO2SYS, seacarb, and mocsy). The recommendation to use the Uppström (1974) formulation by Dickson et al. (2007) came before the Lee et al. (2010) study.

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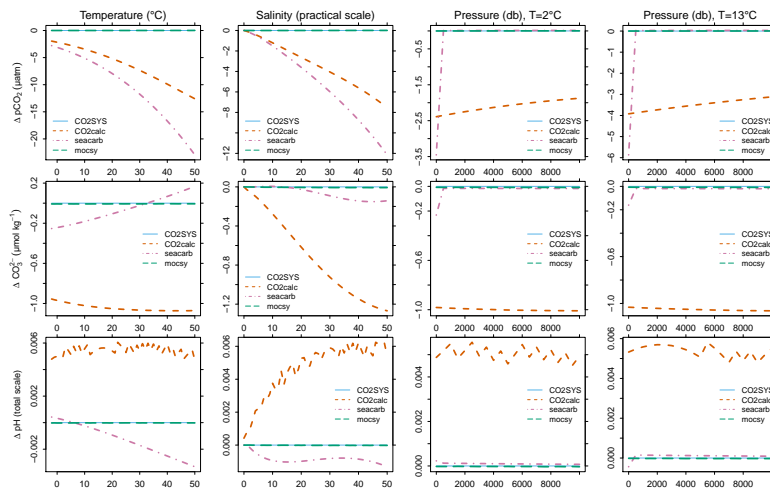
**Fig. 12.** Variables computed from $C_T$–$A_T$ with each package minus corresponding results from CO2SYS, as in Fig. 9 but with $K_1$ and $K_2$ from Millero (2010) instead of from Lueker et al. (2000). Shown are computed $p\mathrm{CO}_2$ (top), $\mathrm{CO}_3^{2-}$ (middle), and pH (bottom) across ranges of $T$ (column 1), $S$ (column 2), and $P$ when $T = 2\,^{\circ}$C (column 3) and when $T = 13\,^{\circ}$C (column 4). Only four packages (CO2SYS, CO2calc, seacarb, and mocsy) include this newer option.
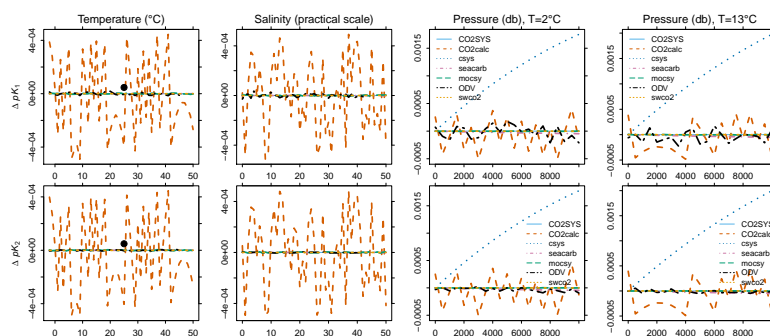
**Fig. 13.** The $pK_1$ (top) and $pK_2$ (bottom) computed with each package minus corresponding values for CO2SYS. Formulations are those recommended for best practices, namely $K_1$ and $K_2$ from (Lueker et al., 2000). Constants were computed across the same ranges of $T$ (column 1), $S$ (column 2), and $P$ when $T = 2\,^{\circ}$C (column 3) and when $T = 13\,^{\circ}$C (column 4) as used in previous figures. Constants from CO2calc and ODV were not directly available but are estimated from variables computed with the $A_T$–$C_T$ pair. The filled black circles indicate the check values (Table 11).
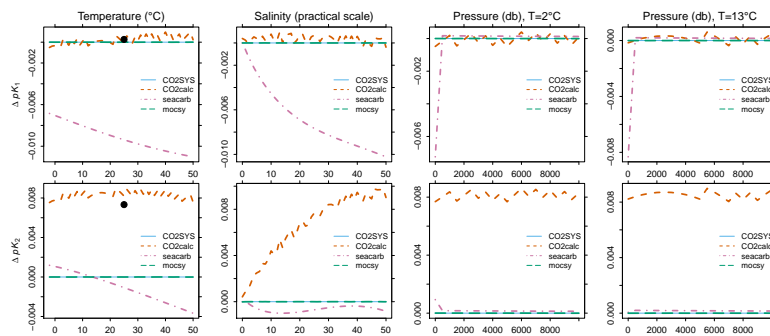
**Fig. 14.** The $pK_1$ (top) and $pK_2$ (bottom) computed in each of four packages minus corresponding values for CO2SYS, as in Fig. 13 except that formulations are from Millero (2010), not Lueker et al. (2000). The filled black circles indicate the check values (Table 11).
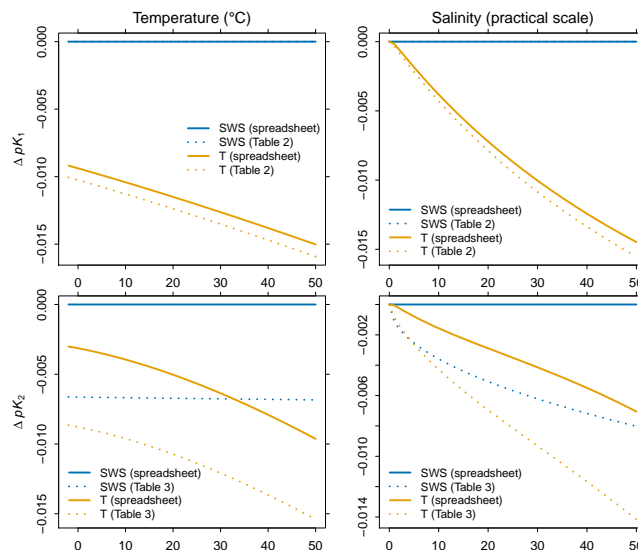
**Fig. 15.** Relative differences between four formulations for $pK_1$ (top) as well as $pK_2$ (bottom), i.e., between values computed from four different sets of coefficients from Millero (2010) over ranges of $T$ (left) and $S$ (right). Two sets of coefficients are from Millero's (2010) Tables 2 and 3, i.e., for the total scale ($T$, orange dotted line) and the seawater scale (SWS, blue dotted line). The two other sets, also on the $T$ and SWS scales (solid lines), have greater precision, coming from the spreadsheet used for calculations in the same publication (F. J. Millero, personal communication 2013). For consistent comparison, both SWS curves were converted to the total scale using the standard approach (Millero, 2010, Eqs. 11 and 12) and $K_F$ from Perez and Fraga (1987). Curves are shown after subtracting values from the preferred formulation (spreadsheet coefficients for the SWS scale converted to the $T$ scale).
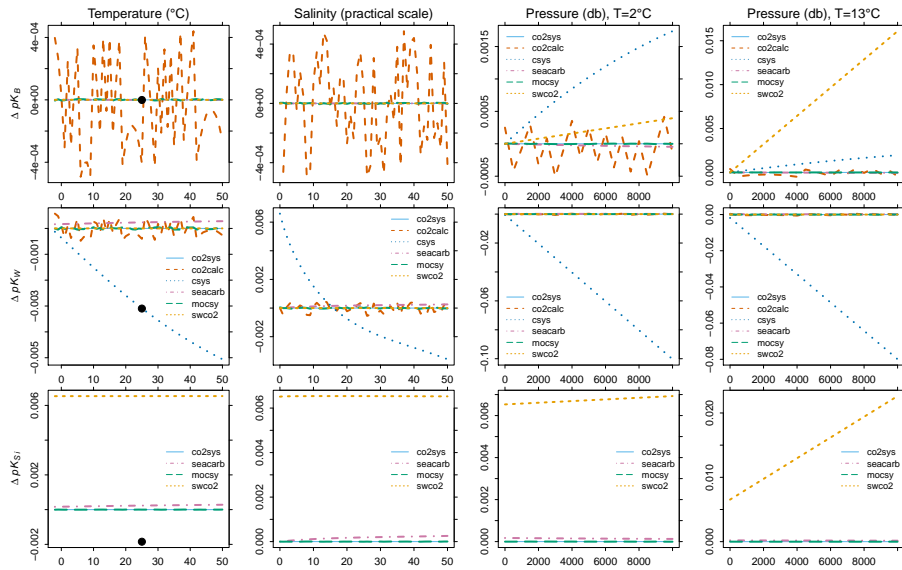
**Fig. 16.** The $pK_B$ (top), $pK_W$ (middle) and $pK_{Si}$ (bottom) computed from each package minus corresponding values from CO2SYS. Formulations are from Millero (1995), as recommended for best practices. The filled black circles indicate the check values (Table 11).
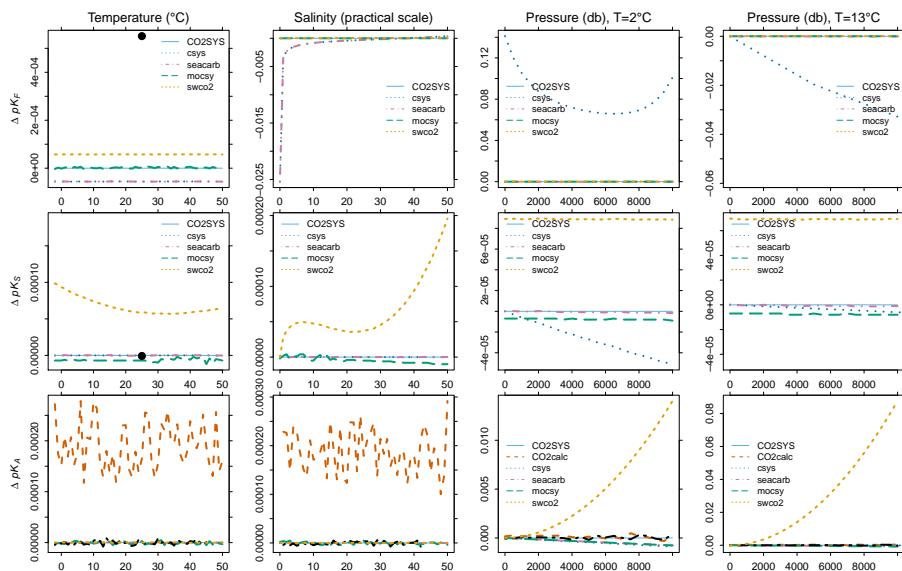
**Fig. 17.** The $pK_F$ (top), $pK_S$ (middle) and $pK_A$ (bottom) computed from each package minus corresponding values from CO2SYS. The formulation for $K_F$ is from Dickson and Riley (1979) as recommended by Dickson and Goyet (1994), with all packages on the free scale. The formulation for $K_S$ is from Dickson (1990a) and on the free scale, while that for $K_A$ is from Mucci (1983) with no scale, as recommended for best practices. The filled black circles indicate check values (Table 11).
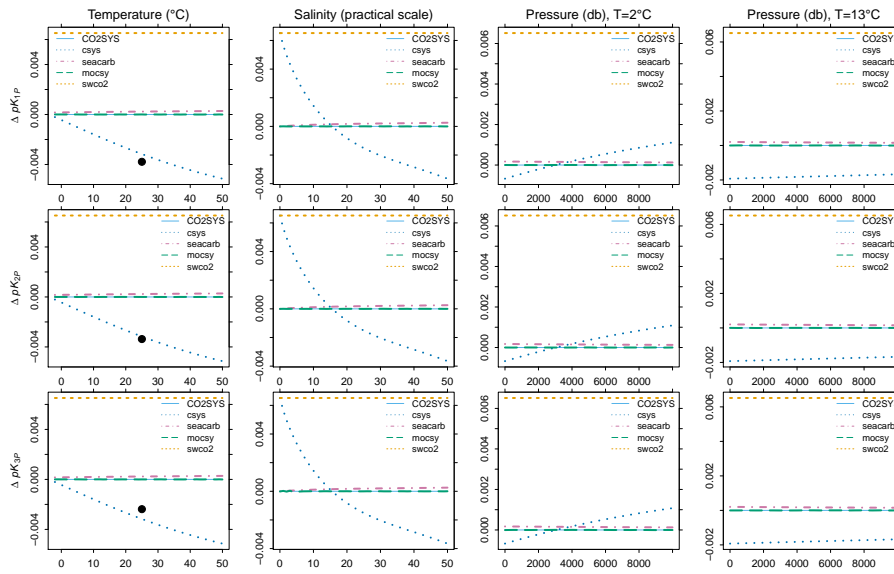
**Fig. 18.** The $pK_{1P}$ (top), $pK_{2P}$ (middle) and $pK_{3P}$ (bottom) computed from each package minus corresponding values from CO2SYS. Formulations are from Millero (1995), as recommended for best practices. Constants are computed across the same ranges of $T$ (column 1), $S$ (column 2), and $P$ when $T = 2\,^{\circ}C$ (column 3) and when $T = 13\,^{\circ}C$ (column 4) as used in previous figures. The filled black circles indicate the check values (Table 11).