

Using Kgen to Generate Cross-Verified Apparent Equilibrium Constants (K^*) for Seawater Carbonate Chemistry

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Key Points:

- Kgen is a software package to calculate apparent equilibrium constants for seawater carbonate system calculations
- Kgen accounts for the influences of temperature, pressure, salinity, magnesium concentration, and calcium concentration
- We provide a new implementation of the MyAMI model ('pymyami') to adjust apparent equilibrium constants for changing seawater composition

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Abstract

The state of acid-base equilibria in solutions is calculated using apparent equilibrium constants (K^* 's). The accuracy of these K^* 's is critical for calculations of environmental chemistry, for example the dissociation of dissolved CO_2 in seawater. The K^* 's required to calculate seawater carbonate chemistry are described by empirically determined functions, which are implemented within software packages used to calculate solution carbon speciation. Each of these software packages uses its own implementation of these K^* calculations. This fragmented approach to K^* calculation results in unintended and difficult to resolve discrepancies between outputs calculated by different pieces of software, particularly because of the empirical nature of the K^* functions which are subject to revisions and improvements over time. We present 'Kgen', a collection of software to consistently calculate seawater K^* 's in Python, R, and Matlab. Kgen provides a nearly identical interface for each language and, through use of a Continuous Integration/Continuous Delivery (CI/CD) pipeline, guarantees consistency between languages by automatically cross-checking results from all three implementations. Unifying the approach to K^* calculation in this way provides an extensible platform for verifiable K^* generation, which can be easily integrated into existing carbon speciation calculators to improve consistency of results.

Plain Language Summary

To calculate how various compounds in seawater behave (chemically speaking), it is necessary to calculate what are known as 'apparent equilibrium constants' (denoted by the symbol K^*). These K^* 's are used to determine proportions of compounds which are present in seawater in a variety of forms. Before the work presented here, K^* calculation was done as a necessary aside within other software. This is an issue, because different pieces of software can calculate them in subtly different ways, which leads to differences in the outputs of these packages which are difficult to resolve. In this work, we present a software package called Kgen that is exclusively devoted to generation of K^* 's. The software is co-written in three programming languages (as all three are routinely used for seawater calculations), and we integrate a testing procedure to ensure that all three languages remain consistent. The result is a more coherent approach to K^* generation that can be integrated into existing software.

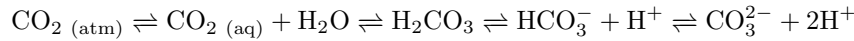
1 Introduction

Many compounds in seawater exist in acid-base equilibria, including fluorine, sulphur, ammonia, nitrite, silica, phosphate, sulphate, boron, and (most importantly) carbon. In solution, each of these compounds exists in an equilibrium state described by one or more equilibrium constants (K 's), which are used to quantify the relative activity of the products and reactants of their dissociation reactions (see Millero (1974), and for an example, see Equation 2). The relative activity of species in these dissociation reactions is dependent on both thermodynamic conditions (temperature and pressure), and the composition of the solution (salinity, concentration of other ions). Equilibrium constants may be derived from thermodynamic first principles for ideal solutions, but the complexity of ion-ion interactions in seawater cause it to diverge from an ideal solution (Huckel & Debye, 1923). To account for this non-ideal behaviour, equilibrium constants in seawater are reframed as 'apparent' equilibrium constants (K^* 's), which are defined in terms of the stoichiometric concentration of individual species (see Equation 3) - and all terms related to activity are integrated into the K^* . We can empirically determine K^* 's at specific solution chemistries and thermodynamic conditions, and K^* 's have been empirically determined across a wide range of seawater salinities and thermodynamic conditions. To calculate these K^* 's between these specifically measured conditions, polynomials that capture the sensitivity of each K^* to temperature and salinity have been

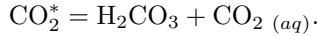
created (Dickson & Goyet, 1994). Any attempt to calculate solution speciation in seawater must begin by defining which equations to calculate K^* 's. Because the K^* equations are empirical, they have been refined and developed over the years, and multiple versions exist (Lewis & Wallace, 1998). Even though carefully-curated sets of 'Best Practices' K^* 's exist (Dickson & Goyet, 1994), this makes it possible for different pieces of software to be using different K^* equations, causing their outputs to deviate in complex and difficult-to-identify ways. To resolve this, we present 'Kgen', a piece of software written synchronously across three programming languages (Python, Matlab, R) that guarantees the provision of consistent K^* values in all three languages, thus removing this source of uncertainty in seawater speciation calculators.

1.1 Carbon in Seawater: The importance of K^* 's

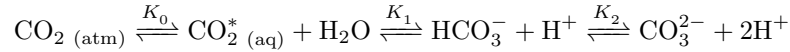
Carbon is present in seawater as four inorganic species: CO_2 (carbon dioxide), H_2CO_3 (carbonic acid), HCO_3^- (bicarbonate), and CO_3^{2-} (carbonate ion), which are related by the acid-base chain:



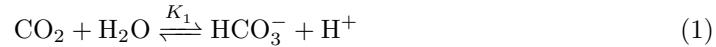
At normal ocean conditions, carbonic acid has a vanishingly small concentration so typically it is incorporated into a single term with aqueous CO_2 as:



We can then express the acid-base chain as:



From which we may write an expression for the equilibrium constants (K_0 , K_1 , and K_2) and apparent equilibrium constants (K^*_0 , K^*_1 , and K^*_2) by taking the ratio of the products and reactants. For example, the equilibrium constant K_1 is given in Equation 2, and the apparent equilibrium constant in Equation 3.



$$K_1 = \frac{\{\text{HCO}_3^-\}\{\text{H}^+\}}{\{\text{CO}_2\}\{\text{H}_2\text{O}\}} \quad (2)$$

$$K_1^* = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2][\text{H}_2\text{O}]} \quad (3)$$

where $\{X\}$ denotes the activity of species X , and $[X]$ denotes the stoichiometric concentration of species X in solution.

Because there are a number of acid-base chains in seawater, each sharing the common ion H^+ , the relationship between the carbonate system and pH is affected by the concentration of numerous other compounds that exist in weak acid-base forms in seawater (such as boron and sulphate). It is therefore necessary to know the K^* 's for multiple species, even if we only seek to determine the state of dissolved carbon in seawater (Zeebe & Wolf-Gladrow, 2001). Carbon is of particular interest because it is the most concentrated weak acid-base system in seawater, and because both ends of the carbon acid-base chain have important environmental implications. The presence of atmospheric CO_2 on the left means that determining the speciation of oceanic carbon is critical in understanding our imminent and long-term climate trajectory, as well as understanding climates of the past. On the right-hand side, carbonate ion concentration is directly proportional to the saturation state of calcium carbonate (Equation 4), which is a key

| Language | Package | Reference | Palaeo-Seawater Method |
|-----------------|----------|-------------------------------|------------------------|
| Microsoft Excel | CO2SYS | Lewis and Wallace (1998) | - |
| Matlab | CO2SYS | Lewis and Wallace (1998) | - |
| Matlab | csys | Zeebe and Wolf-Gladrow (2001) | - |
| R | seacarb | Gattuso and Lavigne (2009) | - |
| R | seacarbx | Raitzsch et al. (2022) | MyAMI look-up-table |
| Python | PyCO2SYS | Humphreys et al. (2022) | - |
| Python | cbsyst | Branson et al. (2023) | Kgen & pymyami |

Table 1. Widely-used software for calculating carbon speciation in seawater.

property for marine calcification (e.g. by foraminifera and corals), and long-term formation and dissolution of calcium carbonate that balances of inputs and outputs of carbon to the ocean.

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}^* \text{ calcite}} \quad (4)$$

Carbon is not the only acid-base sensitive element in seawater of geochemical interest. Boron is another of the key acid-base systems in seawater, partly due to its contribution to alkalinity (Zeebe & Wolf-Gladrow, 2001), but also because the isotopic ratio of borate ($\delta^{11}\text{B}_4$) is used as a proxy for palaeo pH of ancient seawater (Foster & Rae, 2016; Marschall & Foster, 2017). Calculation of pH from boron isotopes requires, among other factors, an estimate of K_B^* (see Equation 5). Quantifying K^* 's therefore has dual importance for the boron isotope community, as K_B^* is required to translate $\delta^{11}\text{B}_4$ to pH (Equation 5), and all K^* 's are needed to calculate palaeo CO_2 from palaeo pH. Partly as a result of this, the boron community is particularly invested in efforts to improve accuracy of K^* 's in past seawater, where major ion chemistry is known to have varied (Dickson & Goyet, 1994).

$$\delta^{11}\text{B}_4 = \frac{\delta^{11}\text{B}_{sw} + (\delta^{11}\text{B}_{sw} - \epsilon) \cdot 10^{pK_B^* - \text{pH}}}{1 + \alpha \cdot 10^{pK_B^* - \text{pH}}} \quad (5)$$

1.2 Calculating K^* 's - Current Approach

The calculation of K^* 's for modern ocean conditions is contained incidentally within multiple software packages designed to calculate carbon speciation in seawater (Table 1). From a user-facing perspective, these software packages all work in broadly the same way. The user must provide two carbonate system parameters, and a variable number of inputs to describe the thermodynamic and compositional properties of seawater - where different to the archetypal standard (25°C, 0 bar, and 35 psu). Some programs accept additional arguments to describe concentrations of other ions in seawater, in particular calcium and magnesium (again where different to the standard modern 10 mmol/kg calcium concentration and 53 mmol/kg magnesium concentration), or specifying which particular expressions and coefficients to use for calculating apparent equilibrium constants. However, the simplicity of these user-facing functions hide a number of complexities and differences between calculation approaches, which have poorly constrained implications for the resulting calculations, and remain opaque to most users.

1.3 Calculating K^* 's - The Problem

The core problem underlying K^* calculation is that they can be calculated using any one of multiple empirical equations, and the choice of the 'best' K^* equations has evolved with time in a way that is not immediately apparent even to an expert user. For

modern seawater, it is currently standard practice to use the equations assembled in Dickson and Goyet (1994), which have been implemented in all major carbon chemistry speciation calculators written across multiple platforms (Table 1). Most of these calculation packages jointly implement both the calculation of K^* 's, and their application to calculate the state of the oceanic carbonate system. Throughout the history of these calculators, both the software and our understanding of ocean chemistry have evolved, and typographical errors in coefficients have been introduced and resolved, but not necessarily in concert across all the available packages. There is occasional indirect cross-validation of K^* calculation between these packages by comparing their ability to calculate similar carbon speciation values (Orr et al., 2015), but no continuous checking to ensure that all packages always produce comparable results, and little or no record of how and when changes have been made to the calculation of K^* 's in response to updates in our understanding of the constants used to calculate them. If, for example, a K^* definition were to be revised or modified today, each piece of calculation software would have to be independently updated by a separate team of maintainers, leading to a period in which each software package produces subtly different results, and it is not straightforward for a user to determine which version has been used for a calculation, or indeed which version they are using themselves. This scenario of updating a K^* parameterisation has already arisen, for instance recently Sulpis et al. (2020) published updated parameterisations for K^*_1 and K^*_2 that improve performance at low temperatures, which are now used as the default in PyCO2SYS (Humphreys et al., 2022), but have not been updated in other calculation packages. This will cause deviation in the calculation of carbon parameters between PyCO2SYS and other speciation calculation packages that a casual user will not be aware of.

The challenge of evolving K^* 's is a particularly common occurrence in palaeoseawater calculations, where this lack of synchronisation and validation has caused issues (CenCO2PIP Consortium, 2023). Palaeoseawater requires special consideration because it is necessary to adjust K^* 's to account for secular changes in seawater composition (Millero & Pierrot, 1998; Hain et al., 2015) through time, which affects the strength of ion-ion interactions in the solution. Particular attention has been paid to calcium and magnesium, which show the strongest interaction with the dissolved carbon species, and have both changed over the last 100Myr (Tyrrell & Zeebe, 2004b; Hain et al., 2015; Zeebe & Tyrrell, 2019). Sulphate also deserves special mention, as it features in the definition of pH on the total and seawater scales (as described in Section 2.2.6 below), and is also known to have changed concentration through geological time (Zeebe & Tyrrell, 2019; Weldeghebriel et al., 2022). Our understanding of how to adjust K^* values to account for variations in seawater composition is evolving relatively rapidly, with several proposed approaches that are not uniformly implemented or used by the community.

In summary, the current norms for calculating K^* values create a number of pitfalls which are not always obvious to the end-user:

- The calculation of K^* 's is usually embedded within carbon calculation software, and it is not always clear how they are being performed, or which coefficients are being used.
- Over time, the equations used to calculate K^* 's have evolved, or been refit to new data. There is no standard way to ensure that different pieces of software are using the same coefficients, or whether they adhere to current best practices.
- There are known ambiguities, typographical errors, and programmatic errors in published constants and the implementation of the calculations, but no pipeline presently exists to propagate improvements to all software packages simultaneously to ensure they all produce consistent results.
- It is necessary to account for different pH scales (see Section 2.2.6).

The necessary complexity of K^* calculations, the fragmented nature of the implementation of these calculations in numerous software packages, and the lack of routine cross-checking between existing software packages create the ideal environment for difficult-to-detect errors to emerge, and for the resulting calculations of software packages to differ. We seek to resolve this with a new tool, **Kgen**, which unifies the calculation of K^* 's across the three major software languages - Python, Matlab and R.

2 Kgen: A unified framework for K^* Calculation

Kgen is designed to be a single, definitive source of K^* values in both modern and palaeoseawater, which produces apparent equilibrium constants that are guaranteed to be the same to within 0.01% across all three languages, thus removing a major source of potential error between carbon speciation calculation methods. The overall goal of Kgen is to provide a consistent approach to the calculation of K^* 's for seawater carbonate chemistry calculations that can be used within other software that seeks to calculate ocean carbon speciation. Specifically, we aim to:

1. Separate the generation of K^* 's from their use in carbonate chemistry calculation programs.
2. Standardise and implement the same functions to calculate K^* 's in python, Matlab, and R.
3. Embed automated crosschecking of the K^* 's produced using each language at test conditions to ensure ongoing consistency.
4. Ensure that other software which is required as a dependency of Kgen is portable between languages (for example, to account for changes in seawater composition the MyAMI software package is often used).

The use of Kgen across all three languages is comprehensively described in the on-line documentation, which should be the primary source for users seeking to install and use Kgen. The overall conceptual approach that Kgen employs is described below.

2.1 Equilibrium Constants in Modern and Ancient Seawater

Kgen builds on current state-of-the-art methods for calculating K^* 's in modern and palaeoseawater. Here, we outline the approach we use to deal with the influence of temperature, salinity, pressure, and seawater composition on calculated K^* values.

2.1.1 Temperature and Salinity

Functions for surface ocean K^* 's in terms of temperature and salinity have been calibrated over a number of years and in a number of publications, before being definitively compiled by Dickson and Goyet (1994). Alternative formulations exist for other environments, and there are a number of published alternatives for seawater that use subtly different coefficients, however here we focus on the recommended best practices for seawater in Dickson and Goyet (1994). The same K^* 's were restated in Hain et al. (2015), but with small edits to the order of coefficients. Here we use the following equations for K^* 's:

$$K_0^* = e^{\left(a_0 + \frac{(100 \cdot a_1)}{T} + a_2 \cdot \log\left(\frac{T}{100}\right) + S \cdot \left(a_3 + \frac{a_4 \cdot T}{100} + a_5 \cdot \left(\frac{T}{100}\right)^2\right)\right)} \quad (6)$$

$$K_1^* = 10^{(a_0 + \frac{a_1}{T} + a_2 \cdot \log(T) + a_3 \cdot S + a_4 \cdot S^2)} \quad (7)$$

$$K_2^* = 10^{(a_0 + \frac{a_1}{T} + a_2 \cdot \log(T) + a_3 \cdot S + a_4 \cdot S^2)} \quad (8)$$

$$K_B^* = e^{(a_0 + a_1 \cdot \sqrt{S} + a_2 \cdot S + \frac{1}{T} \cdot (a_3 + a_4 \cdot \sqrt{S} + a_5 \cdot S + a_6 \cdot S^{1.5} + a_7 \cdot S^2) + \log(T) \cdot (a_8 + a_9 \cdot \sqrt{S} + a_{10} \cdot S) + a_{11} \cdot T \cdot \sqrt{S})} \quad (9)$$

$$K_W^* = e^{(a_0 + \frac{a_1}{T} + a_2 \cdot \log(T) + \sqrt{S} \cdot (\frac{a_3}{T} + a_4 + a_5 \cdot \log(t)) + a_6 \cdot S)} \quad (10)$$

$$K_S^* = e^{(a_0 + \frac{a_1}{T} + a_2 \cdot \log(t) + \sqrt{I} \cdot (\frac{a_3}{T} + a_4 + a_5 \cdot \log(T)) + I \cdot (\frac{a_6}{T} + a_7 + a_8 \cdot \log(T)) + \frac{(a_9 \cdot I^{1.5})}{T} + \frac{a_{10} \cdot I^2}{T} + \log(1 - 0.001005 \cdot S))} \quad (11)$$

$$K_F^* = e^{(\frac{a_0}{T} + a_1 + a_2 \cdot \sqrt{S})} \quad (12)$$

$$K_{sp,c}^* = 10^{(a_0 + a_1 \cdot T + \frac{a_2}{t} + a_3 \cdot \log_{10}(T) + \sqrt{S} \cdot (a_4 + a_5 \cdot T + \frac{a_6}{T}) + a_7 \cdot S + a_8 \cdot S^{1.5})} \quad (13)$$

$$K_{sp,a}^* = 10^{(a_0 + a_1 \cdot T + \frac{a_2}{t} + a_3 \cdot \log_{10}(T) + \sqrt{S} \cdot (a_4 + a_5 \cdot T + \frac{a_6}{T}) + a_7 \cdot S + a_8 \cdot S^{1.5})} \quad (14)$$

$$K_{P1}^* = e^{(\frac{a_0}{T} + a_1 + a_2 \cdot \log(T) + \sqrt{S} \cdot (\frac{a_3}{t} + a_4) + S \cdot (\frac{a_5}{T} + a_6))} \quad (15)$$

$$K_{P2}^* = e^{(\frac{a_0}{T} + a_1 + a_2 \cdot \log(T) + \sqrt{S} \cdot (\frac{a_3}{t} + a_4) + S \cdot (\frac{a_5}{T} + a_6))} \quad (16)$$

$$K_{P3}^* = e^{(\frac{a_0}{T} + a_1 + \sqrt{S} \cdot (\frac{a_2}{t} + a_3) + S \cdot (\frac{a_4}{T} + a_5))} \quad (17)$$

$$K_{Si}^* = e^{(\frac{a_1}{T} + a_2 + a_3 \cdot \log(T) + \sqrt{I} \cdot (\frac{a_4}{T} + a_5) + I \cdot (\frac{a_6}{T} + a_7) + I^2 \cdot (\frac{a_8}{T} + a_9) + \log(1 - 0.001005 \cdot s))} \quad (18)$$

Where T is the temperature in degrees Celsius, S is the salinity, and I is the ionic strength as defined in Dickson and Goyet (1994) ($I = \frac{19.924S}{1 - 1.005S}$). Each a_n is a coefficient (Table 2), determined empirically for modern seawater, which will provide a K^* at the specified temperature and salinity at sea surface pressure and modern ocean composition. If using the MyAMI approach in Hain et al. (2015), these a_n coefficients are adjusted to account for changes in palaeoseawater composition.

| K^* | a_0 | a_1 | a_2 | a_3 | a_4 | a_5 | a_6 | a_7 | a_8 | a_9 | a_{10} | a_{11} |
|-------------|-----------|-----------|----------|----------|------------|-----------|----------|----------|-----------|---------|----------|----------|
| K_0^* | -60.2409 | 93.4517 | 23.3585 | 0.023517 | -0.023656 | 0.0047036 | | | | | | |
| K_1^* | 61.2172 | -3633.86 | -9.67770 | 0.011555 | -0.0001152 | | | | | | | |
| K_2^* | -25.9290 | -471.78 | 3.16967 | 0.01781 | -0.0001122 | | | | | | | |
| K_W^* | 148.9652 | -13847.26 | -23.6521 | 118.67 | -5.977 | 1.0495 | -0.01615 | | | | | |
| K_B^* | 148.0248 | 137.1942 | 1.62142 | -8966.90 | -2890.53 | -77.942 | 1.728 | -0.0996 | -24.4344 | -25.085 | -0.2474 | 0.053105 |
| K_S^* | 141.328 | -4276.1 | -23.093 | -13856 | 324.57 | -47.986 | 35474 | -771.54 | 114.723 | -2698 | 1776 | |
| K_{spA}^* | -171.945 | -0.077993 | 2903.293 | 71.595 | -0.068393 | 0.0017276 | 88.135 | -0.10018 | 0.0059415 | | | |
| K_{spC}^* | -171.9065 | -0.077993 | 2839.319 | 71.595 | -0.77712 | 0.0028426 | 178.34 | -0.07711 | 0.0041249 | | | |
| K_{P1}^* | -4576.752 | 115.525 | -18.453 | -106.736 | 0.69171 | -0.65643 | -0.01844 | | | | | |
| K_{P2}^* | -8814.715 | 172.0883 | -27.927 | -160.340 | 1.3566 | 0.37335 | -0.05778 | | | | | |
| K_{P3}^* | -3070.75 | -18.141 | 17.27039 | 2.81197 | -44.99486 | -0.09984 | | | | | | |
| K_{Si}^* | -8904.2 | 117.385 | -19.334 | -458.79 | 3.5913 | 188.74 | -1.5998 | -12.1652 | 0.07871 | | | |
| K_F^* | 874 | -9.68 | 0.111 | | | | | | | | | |

Table 2. Coefficients used for calculation of K^* 's at standard conditions for modern seawater composition from Dickson and Goyet (1994), and available online.

2.1.2 Pressure

Accounting for changes in pressure is achieved by the following formula (Zeebe & Wolf-Gladrow, 2001).

$$\frac{K_{deep}^*}{K_{surface}^*} = e^{-\left(\frac{\Delta V}{R(T-273.15)}\right)P + \left(0.5 \frac{\Delta \kappa}{R(T-273.15)}\right)P^2} \quad (19)$$

Where:

$$\Delta V = a_0 + a_1 T + a_2 T^2$$

$$\Delta \kappa = b_0 + b_1 T$$

Unfortunately, Equations 6 to 18, and coefficients used in Equation 19 have a history of typographical errors. While we can not preclude the potential of further typographical or other errors here, by using the same coefficients in all three languages we ensure that all three implementations are comparable, and any improvements are simultaneously propagated to all software which uses Kgen. Here we use coefficients from Hain et al. (2015) (Table 3).

| | a_0 | a_1 | a_2 | b_0 | b_1 |
|-------------|--------|---------|------------|----------|------------|
| K^*_0 | 0 | 0 | 0 | 0 | 0 |
| K^*_1 | -25.50 | 0.1271 | 0 | -0.00308 | 0.0000877 |
| K^*_2 | -15.82 | -0.0219 | 0 | 0.00113 | -0.0001475 |
| K^*_B | -29.48 | 0.1622 | -0.002608 | -0.00284 | 0 |
| K^*_W | -20.02 | 0.1119 | -0.001409 | -0.00513 | 0.0000794 |
| K^*_S | -18.03 | 0.0466 | 0.000316 | -0.00453 | 0.00009 |
| K^*_F | -9.78 | -0.0090 | -0.000942 | -0.00391 | 0.000054 |
| K^*_{spC} | -48.76 | 0.5304 | 0 | -0.01176 | 0.0003692 |
| K^*_{spA} | -45.96 | 0.5304 | 0 | -0.01176 | 0.0003692 |
| K^*_{P1} | -14.51 | 0.1211 | -0.000321 | -0.00267 | 0.0000427 |
| K^*_{P2} | -23.12 | 0.1758 | -0.002647 | -0.00515 | 0.00009 |
| K^*_{P3} | -26.57 | 0.2020 | -0.0030420 | -0.00408 | 0.0000714 |
| K^*_{Si} | 0 | 0 | 0 | 0 | 0 |

Table 3. Coefficients used in the pressure correction of K^* 's from Hain et al. (2015) and available online.

2.1.3 Seawater Composition

Palaeoceanographic studies of seawater chemistry need to account for the influence of long-term secular evolution in seawater composition. Solution modelling programs such as PHREEQC (Parkhurst & Appelo, 2013) are not sufficiently accurate in seawater, and a range of other tools and methods have been developed to tackle this problem. Broadly speaking, there are two approaches: use simple sensitivity parameters (Tyrrell & Zeebe, 2004b; Zeebe & Tyrrell, 2019) that modify K^* 's as a linear function of seawater composition, or use a more complex Pitzer speciation model (Hain et al., 2015). The Pitzer ion interaction model adjusts each of the K^* 's using empirical coefficients that describe ion-ion interactions in the solution, and the impact of these interactions on the activities of relevant ions in seawater. All currently available carbonate chemistry speciation programs that provide the facility to account for changing seawater composition have opted to use the MyAMI Pitzer ion interaction from Hain et al. (2015), which is written in Python. MyAMI is designed to account for non-standard seawater calcium and magnesium concentrations by adjusting the coefficients in Equations 6-18. MyAMI can be used in three ways: by directly calling functions, using the command line interface, or using a look-up table of parameters. Both the command line interface and the look-up table approach have been used in previous publications such as Henehan et al. (2019); Rae et al. (2021).

Unfortunately, there are a number of issues with this approach that are not immediately evident to the end user. First, there is a known issue with the published look-up table affecting, in particular, the K^*_B values (CenCO2PIP Consortium, 2023). K^*_B values generated from the look-up table diverge from K^*_B calculated using MyAMI by up to 66%. This look-up table has since been regenerated and can be found in compressed R data published in (Raitzsch et al., 2022), but is formatted slightly differently to the

original. We provide a drag-and-drop replacement for the original table here. While we maintain that Kgen is an overall more effective long-term solution for repeatable K* generation, this corrected look-up table provides a convenient solution to remove the most egregious issues with K*'s in pre-existing scripts that use this method. Second, there is an undocumented difference in the order of parameters returned by MyAMI when using the command line and function-call interfaces, which can lead an unwary user to apply dramatically different correction factors at a given magnesium and calcium concentration. Finally, and more fundamentally, to provide coefficients for input into Equations 6-18, MyAMI runs the underlying Pitzer model across a grid of temperature and salinity conditions at the specified ionic composition of seawater, then fits the relevant K* equation to these gridded data. This is convenient, in that it presents the user with familiar coefficients for ease of use, but is problematic because it assumes that the empirical K* formulation can accurately describe the response to temperature and salinity in modified seawater chemistry. This is fragile because there is no guarantee of linearity or smoothness in the response of these coefficients to calcium and magnesium concentrations. The polynomials used to describe K*'s may also be non-unique, in that different combinations of coefficients may resolve to the same result within a particular domain, but have vastly different predictions outside that domain. Polynomials can also be sensitive, with apparently small changes in the coefficients resulting in a large change in the predicted response. As the look-up table to find coefficients for these polynomials is provided at 0.1 mmol/kg resolution, it is almost always necessary to interpolate the coefficients to the exact magnesium and calcium concentrations of interest, and there is no guarantee that these interpolated coefficients are good predictors of the K*'s. Ultimately, the fact that there are multiple ways to interact with MyAMI that produce significantly different results make it difficult to determine the impact of these complications on the broader literature, in particular because historically code was rarely archived alongside studies so information on exactly *how* the scripts were used has been lost.

We resolve these issues by providing a new version of the MyAMI model in the `pmyami` package, written in Python. `pmyami` is a re-implementation of the MyAMI Specific Ion Interaction Model (Hain et al., 2015) which benefits from:

- Increased speed by 2+ orders of magnitude - due to vectorisation the direct calculation of correction factors (rather than re-fitting the K* functions to gridded parameters).
- Improved transparency, by working with the original parameter tables from Millero and Pierrot (1998) rather than embedding parameter values within the code, which identified and resolved several typographic errors within MyAMI. The correction of these typographic errors result in differences of between 0-3.8% in the correction factors calculated by `pmyami` compared to MyAMI, with no difference in K_w, and the largest difference in K₂.
- Improved flexibility, allowing an expert user to change the concentrations of a greater number of ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Cl⁻, B(OH)₄⁻, HCO₃⁻, CO₃²⁻ and SO₄²⁻).

In addition to these improvements, `pmyami` also changes the output structure from MyAMI. Instead of calculating new coefficients for input into Equations 6-18 at a specified calcium and magnesium concentration, `pmyami` calculates a single multiplicative correction factor ($f_{(T,S,Mg,Ca)}$) for each K* as a direct function of the specified ocean composition:

$$K_x(T, S, Mg, Ca) = K_x(T, S) f_x(T, S, Mg, Ca) \quad (20)$$

This removes the assumption that the functional form of Equations 6-18 remains constant with changes in seawater chemistry, and simplifies the implementation and integration into Kgen.

To make the seawater composition corrections available outside of python, we provide two approaches: a polynomial approximation of the correction factors, and a mechanism to call the full python implementation of pymyami (which can be imported in the case of Matlab, or used via the reticulate platform in R). The approximation method uses a high-dimensional polynomial to estimate a correction factor as a function of temperature, salinity, and magnesium and calcium concentration ($f_{(T,S,Mg,Ca)}$) natively in each language. This is useful in cases where speed is paramount (e.g. uncertainty propagation using random sampling methods such as Monte Carlo), but these approximations are only accurate to within 0.2% of the directly calculated values. This inaccuracy is small given the relative scale of other uncertainties in palaeo-oceanographic reconstructions, so the approximation method is likely to be sufficient for most purposes. However, we would caution users to avoid the approximation in cases where a very high level of precision is required.

2.2 Practicalities: Usability and Automated Consistency Checking

As well as providing state-of-the-art K^* calculation, Kgen brings a number of key considerations which are designed to make the process of K^* calculation as painless and reliable as possible for the end-user.

2.2.1 Consistent Interface

Implementations of Kgen in python, R, and Matlab provide user-facing functions with the same naming scheme and input arguments, allowing straightforward migration between languages. Kgen provides two main functions for calculating a single K^* :

```
calc_K(name,temp_c,sal,p_bar,magnesium,calcium)
```

or multiple K^* 's

```
calc_Ks(names,temp_c,sal,p_bar,magnesium,calcium)
```

These combine lower-level functions to calculate the K^* for modern seawater, apply a pressure correction factor created with the function

```
calculate_pressure_correction(name,temp_c,p_bar)
```

followed by, if necessary, a correction for seawater composition calculated by pymyami

```
calculate_seawater_correction(name,temp_c,sal,magnesium,calcium)
```

The primary source of documentation for code is online, however here we list these functions here to demonstrate the benefit of having consistently named functions and function arguments.

2.2.2 Automated Consistency Checking

Each implementation of Kgen performs three sequential actions (as shown in Figure 1). First, required apparent equilibrium constants are determined for surface ocean seawater at the prescribed temperature and salinity. Second, a multiplicative pressure correction is determined. Third, a multiplicative seawater composition correction is determined. The externally available functions of Kgen reflect these three actions.

The Kgen project is managed through a git repository, augmented with GitHub actions to automate cross-comparison between the three languages. There are multiple comparisons made to ensure consistency. The first validates the output from Kgen against check values given in Zeebe and Wolf-Gladrow (2001). The second runs Kgen in all three languages to calculate K^* 's for a wide variety of oceanic conditions, then quantifies the difference between them - with an automatic failure if the difference is greater than 0.01%. Updated values for parameters or functions can not be merged into the repository without first passing these tests, ensuring ongoing consistency.

Versioning uses the semantic naming scheme (X.Y.Z), with consistency between all three languages guaranteed at the X.Y level, and bug fixes for individual languages incrementing the Z version number. Each increase in version number triggers an automated GitHub action which stores an indicative value how much each K^* has changed between versions. This framework has been implemented for python, R, and Matlab, but is extensible, and open to future implementations of Kgen in other languages.

2.2.3 Traceable Version Numbering

The semantic version numbering scheme of Kgen, e.g. '1.0.0', is in the form of [major release].[K value update].[minor patch] across all three software languages. We guarantee that all versions of the software that share the same [major release].[K value update] numbers will produce quantitatively identical K values, regardless of the language. Whenever there is a change in the underlying code that causes a change in K values, these will be recorded and described in the online manual. Thus, as long as a user states which version of Kgen was used in a calculation, it will be possible to exactly reproduce that calculation by installing a legacy version of Kgen.

2.2.4 Integrating Kgen Into Carbonate Chemistry Solvers

We recommend assimilating Kgen into carbonate chemistry software by treating it as a dependency. With Python and R this can be managed using your preferred package manager to specify versions of Kgen compatible with the carbonate chemistry software. For Matlab, Kgen can be directly incorporated with the carbonate chemistry package using the Matlab file exchange. Kgen can run alongside other methodologies of calculating K^* 's (for instance where apparent equilibrium constants appropriate for freshwater and seawater are required within the same analysis). Kgen can be integrated into existing carbonate chemistry software packages in such a way that does not break backwards compatibility and K^* 's from a variety of methods can be easily compared.

2.2.5 Simplified Calculation Sequence

The current procedure to calculate K^* 's proceeds along one of two paths, depending on whether the target is modern or ancient seawater. These two pathways are illustrated in Figure 1. If the target is modern seawater, we proceed along the left hand path - using Equations 6-18 (or analogous equations) to calculate modern, surface seawater K^* 's. A pressure correction is applied to adjust K^* 's to be appropriate for depth. If the target is ancient seawater, then the calculation is more involved. Coefficients for Equations 6-18 must first be estimated for the palaeo seawater composition, then the calculation proceeds as before. The pressure correction step remains the same.

2.2.6 pH Scales

The primary contribution of Kgen is in providing a central, cross-checked functionality for calculating consistent K^* values. The collection of these calculations in one place does not, however, address some of the outstanding issues surrounding K^* calculation.

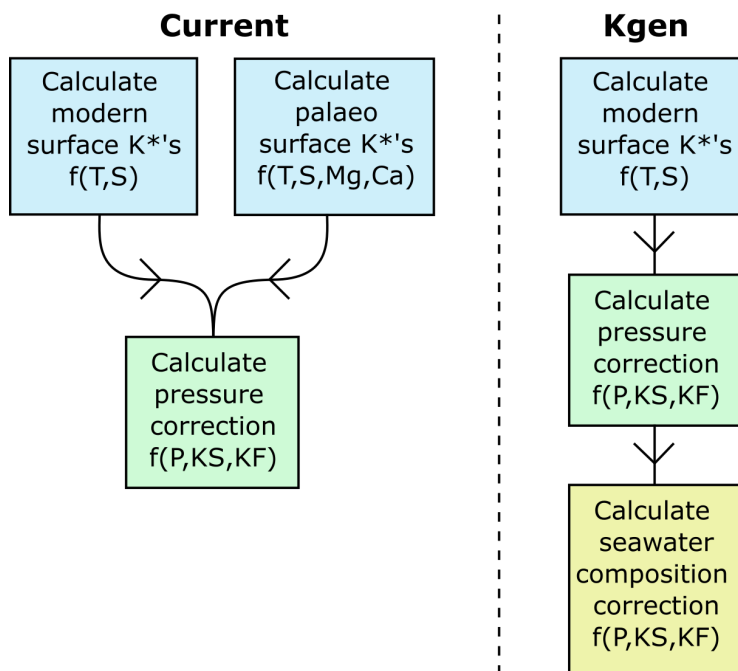


Figure 1. The pathways for calculation of K^* 's for carbonate chemistry software. The current, two step paradigm is shown on the left, and is branched depending on whether K^* 's are required for modern or palaeo seawater. Kgen linearises this workflow into three separate steps.

pH can be expressed on a variety of scales: the NBS scale, the free scale, the total scale, or the seawater scale. The free scale is the simplest, as it accounts only for free hydrogen ions, while the total scale accounts for hydrogen sulphate, and the seawater scale accounts for both hydrogen sulphate and hydrogen fluoride. The motivation behind these scales is practical in nature, in that, while we might typically be interested in free hydrogen ion concentration, pH measurement apparatus may respond more closely to the combined influence of free hydrogen ions, hydrogen sulphide, and hydrogen fluoride.

When calculating pH of a palaeo ocean, it would seem sensible to use the free scale - as there is no pristine preserved seawater on which modern analytical equipment can be used. However, as carbonate system programs (and the equations which govern K^* 's) were originally targeted at modern seawater, most equations are given on the total pH scale - or are converted to be on an approximate total scale. We adopt this convention here, reporting almost all K^* 's on the total scale.

There are some important exceptions though. K^*_{sulphate} and K^*_{fluoride} are used in the definition of the total and seawater pH scales. They are therefore given on the free scale to avoid producing a self referential scale. The other major exception is in the calculation of the pressure correction for K^* 's, which understood to have been given on the seawater scale (Rae, 2011). To perform this pressure correction, we convert all K^* 's to the seawater scale, apply the correction, then convert them all back to the total scale (in line with CO2SYS (Lewis & Wallace, 1998) and PyCO2SYS (Humphreys et al., 2022)).

3 Results: Kgen Performance

The primary result of this paper is the Kgen software library itself. We take this opportunity to analyse the output of Kgen at a variety of conditions, both to validate our approach, and to illustrate various properties of the K^* 's.

3.1 Comparison

We have validated the K^* 's produced by Kgen against K^* 's from MyAMI and the sensitivity parameter approach of Zeebe and Tyrrell (2019) (see Figure 2). We find that MyAMI and Kgen produce identical K^* 's across profiles for temperature and salinity. MyAMI, Kgen (using pymyami), and the sensitivity parameter approach illustrated in Zeebe and Tyrrell (2019) show broad agreement, with the most notable discrepancies being in K^*_{1} , K^*_{2} , K^*_{spC} , and K^*_{A} . The differences are mostly minor, with the exception of K^*_{1} , which behaves differently (as previously noted in (Hain et al., 2018)).

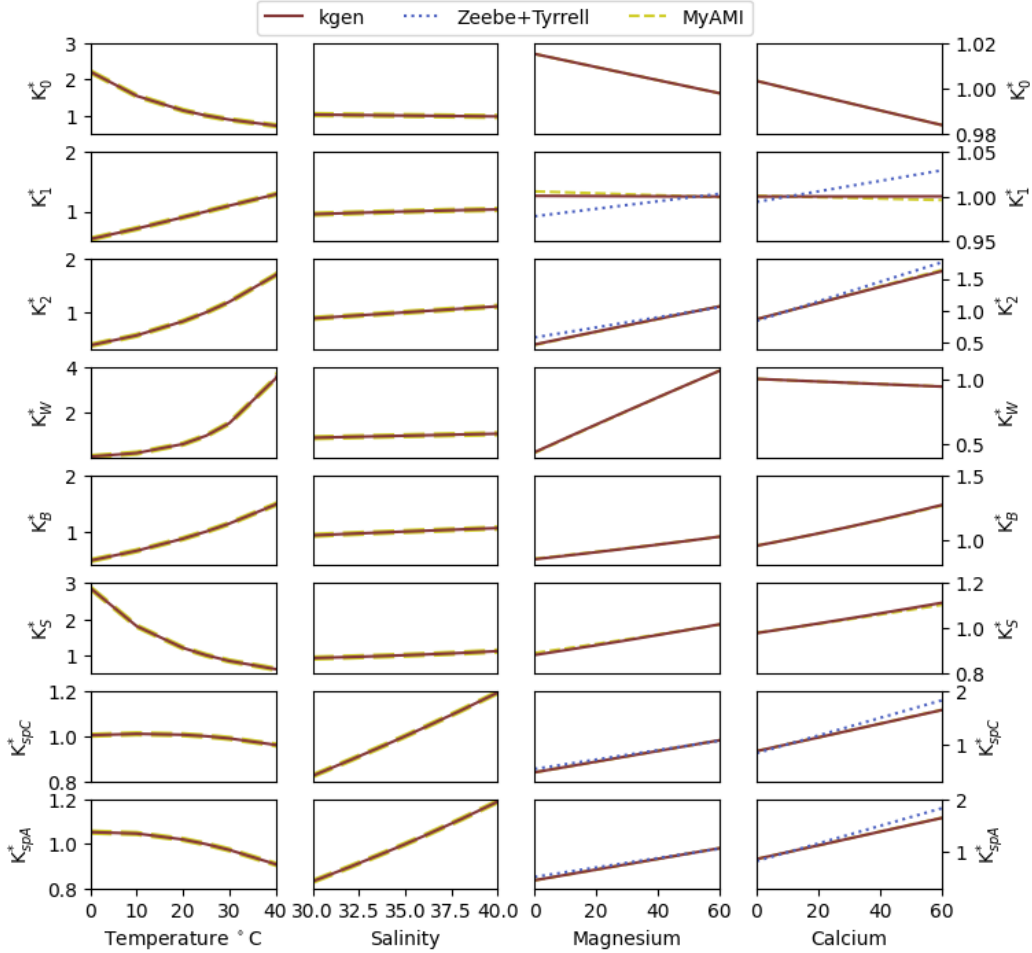


Figure 2. The sensitive of K^* 's to temperature, salinity, magnesium concentration and calcium concentration using three different methods. Each K^* is shown in a row and each control in a column. There is generally good agreement between the three methods. The largest offsets are between the sensitivity parameter approach (Zeebe & Tyrrell, 2019) and the Pitzer model approach in particular for K^*_{1} . pymyami and MyAMI diverge only slightly, as a result of correction of typographical errors.

The dominant factor driving differences between K^* 's is the chosen approach (Pitzer ion model vs sensitivity parameters). The sensitivity parameter style approach of Zeebe and Tyrrell (2019) gives noticeably different results to the pitzer ion model approach demon-

strated in Hain et al. (2015) and here. Differences between MyAMI and pymyami are much smaller, and are driven by small typographical corrections to MyAMI.

3.2 K* Properties

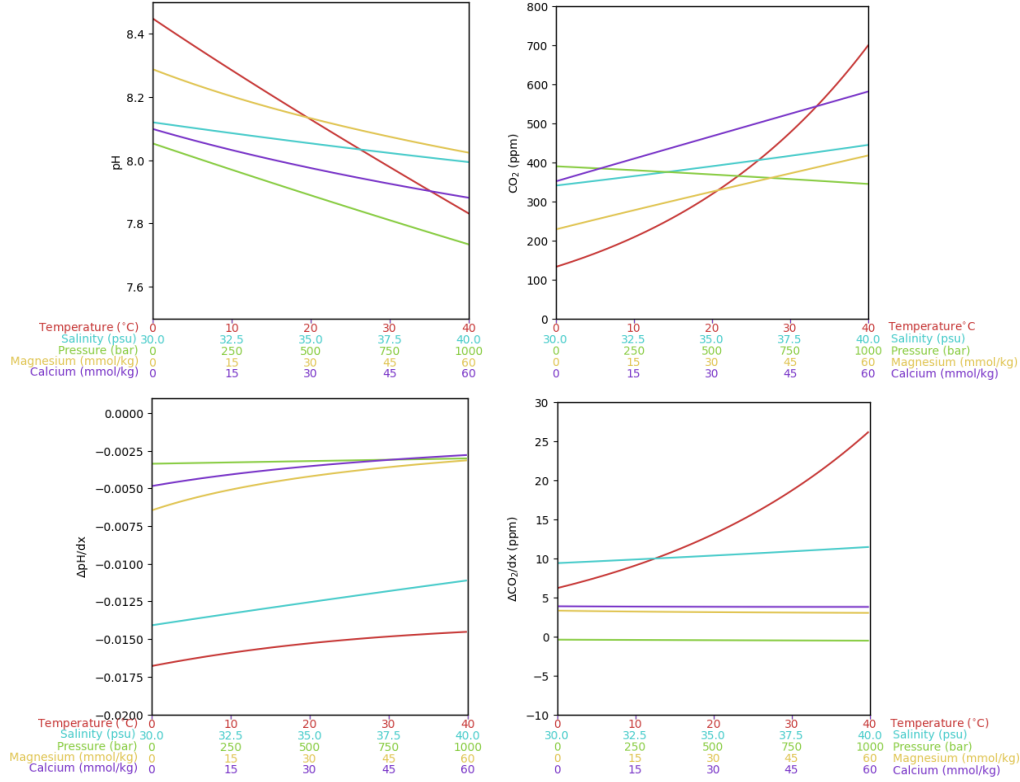


Figure 3. The sensitivity of pH and CO₂ to each individual factor (temperature, salinity, pressure, magnesium concentration, and calcium concentration) is shown above at a reference condition of DIC=2000 μ mol/kg and alkalinity=2300 μ mol/kg, and standard modern seawater conditions.

To evaluate the sensitivity of pH and CO₂ to temperature, salinity, pressure, magnesium concentration, and calcium concentration, we prescribe a standard set of conditions then vary each parameter independently. The estimates of $\frac{\partial pH}{\partial T}$, $\frac{\partial pH}{\partial S}$, $\frac{\partial CO_2}{\partial T}$ etc., are shown in Figure 3, alongside the second derivative of each parameter (e.g. the sensitivity of $\frac{\partial pH}{\partial T}$ to temperature). From this we find that pressure is the strongest driving factor of pH and CO₂ across the range found in the ocean (only one tenth of which is shown in Figure 3), followed by temperature, while the influence of other factors is more muted. Pressure is the only parameter which has a negative correlation to CO₂. The sensitivity of pH and CO₂ to salinity, pressure, magnesium concentration, and calcium concentration is almost constant across their range, whereas the influence of temperature is much more nonlinear, with a much greater sensitivity of CO₂ to temperature at higher temperatures. The lower subplots in Figure 3 allow us to express the sensitivity of pH and CO₂ to each individual factor quantitatively and, for modern ocean conditions, get some sense of the uncertainty stemming from each parameter - though it is important to note that (as described above) these are partial derivatives, and the combinative effects of parameters may be different to treating each factor independently. In particu-

lar, we know that seawater calcium and magnesium concentrations have inversely varied across the Cenozoic (Weldeghebriel et al., 2022).

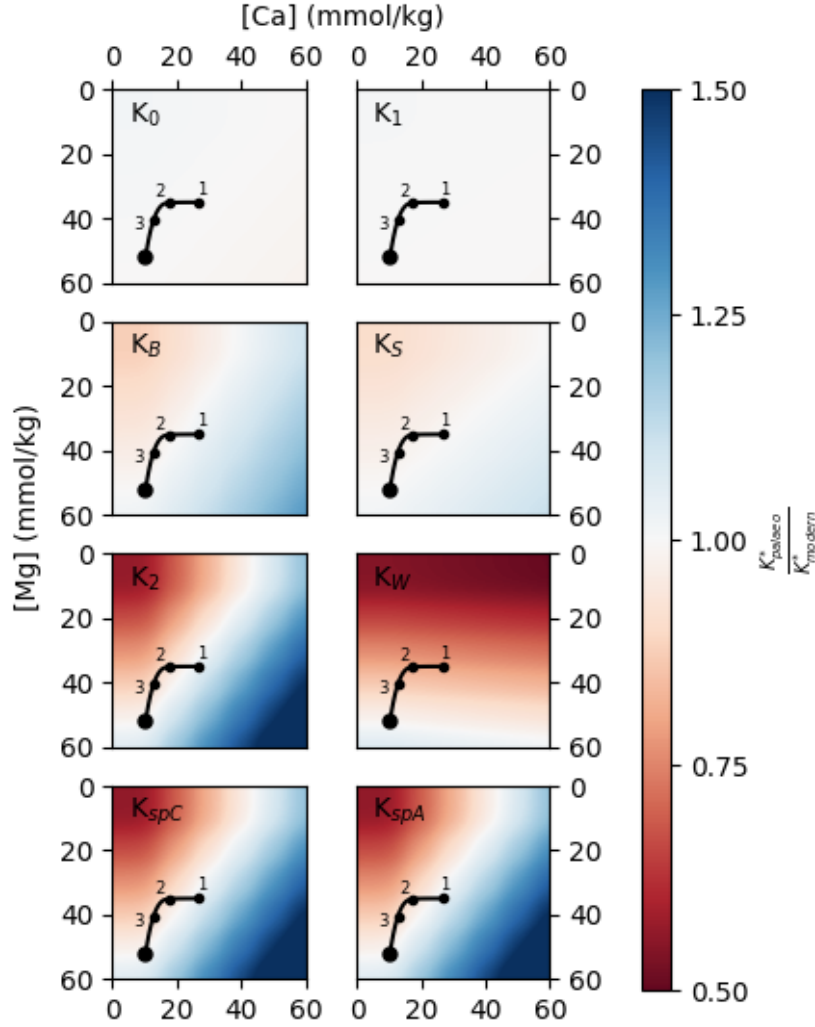


Figure 4. Each subplot shows a single K^* , normalised to the modern day K^* across a range of seawater calcium and magnesium concentrations. Lighter colours indicate that the K^* at these conditions are similar to the modern ocean, warmer colours indicate higher K^* , and cooler colours indicate lower K^* . The evolution of calcium and magnesium concentration over the Cenozoic is plotted in black, with keypoints 1. 100Ma, 2. Eocene (56Ma), 3. Miocene (14Ma), and the large point representing modern seawater.

To evaluate the likely magnitude of the combined effect of magnesium and calcium, we can calculate the impact of various combinations of calcium and magnesium concentration on each K^* (as depicted in Figure 4). Most K^* 's show a diagonal sensitivity pattern (meaning the influence of magnesium and calcium are compensatory to one another) - the exception is K^*_W , which is more strongly dependent on magnesium than calcium. We find the influence of magnesium and calcium concentration is strongest on K^*_2 , K^*_W , K^*_{spC} , K^*_{spA} , and weakest on K^*_0 and K^*_1 .

The trajectory of magnesium and calcium concentration across the Cenozoic (Zeebe & Tyrrell, 2019) is shown on top of the sensitivity in Figure 4 in a black line. As magnesium concentration has generally increased over the Cenozoic while calcium concentration has generally fallen, their compensatory effect means the K^* 's are very similar to their value during the earliest Cenozoic. It is somewhat inherent in the nature of magnesium and calcium to be inversely correlated (Tyrrell & Zeebe, 2004a), which is beneficial to us as it means that palaeo K^* 's are unlikely to be far away from their modern day value by changes in seawater composition. That said, transiently during the Eocene, Oligocene, and Miocene, K^* 's were generally higher than present day values.

4 Summary

We provide Kgen, a multilanguage approach to calculation of apparent equilibrium constants (K^* 's). Kgen resolves discrepancies between previous software packages which calculate K^* 's, and provides a mechanism for ongoing consistency through automated crosschecking of generated K^* 's across a wide range of conditions.

In addition to the direct benefits Kgen brings, we also believe the Kgen repository provides a convenient programming language comparison as applied to geochemistry. Kgen attempts to improve clarity in the equations which underlie the calculation of apparent equilibrium constants and how these influence chemical speciation, in particular as related to atmospheric CO_2 calculations.

Kgen is already in use within cbsyst (Branson et al., 2023), a carbonate chemistry library written in python which is applicable to both modern and palaeo seawater compositions, alongside a number of convenience functions for calculating the carbon system from boron speciation and isotopes. We are currently exploring the best way of integrating Kgen into existing carbonate chemistry software packages (seacarb/seacarbX for R, and CO2SYS for Matlab).

5 Open Research

The software generated during this project is managed through our GitHub repository, which each release of Kgen archived using Zenodo. Two alpha release versions have been archived already, Kgen v0.2.0 (Whiteford et al., 2023a), and Kgen v0.3.0 (Whiteford et al., 2023b). Kgen v1.0.0 will stabilise alongside the publication of this manuscript and similarly be available through GitHub and archived on Zenodo.

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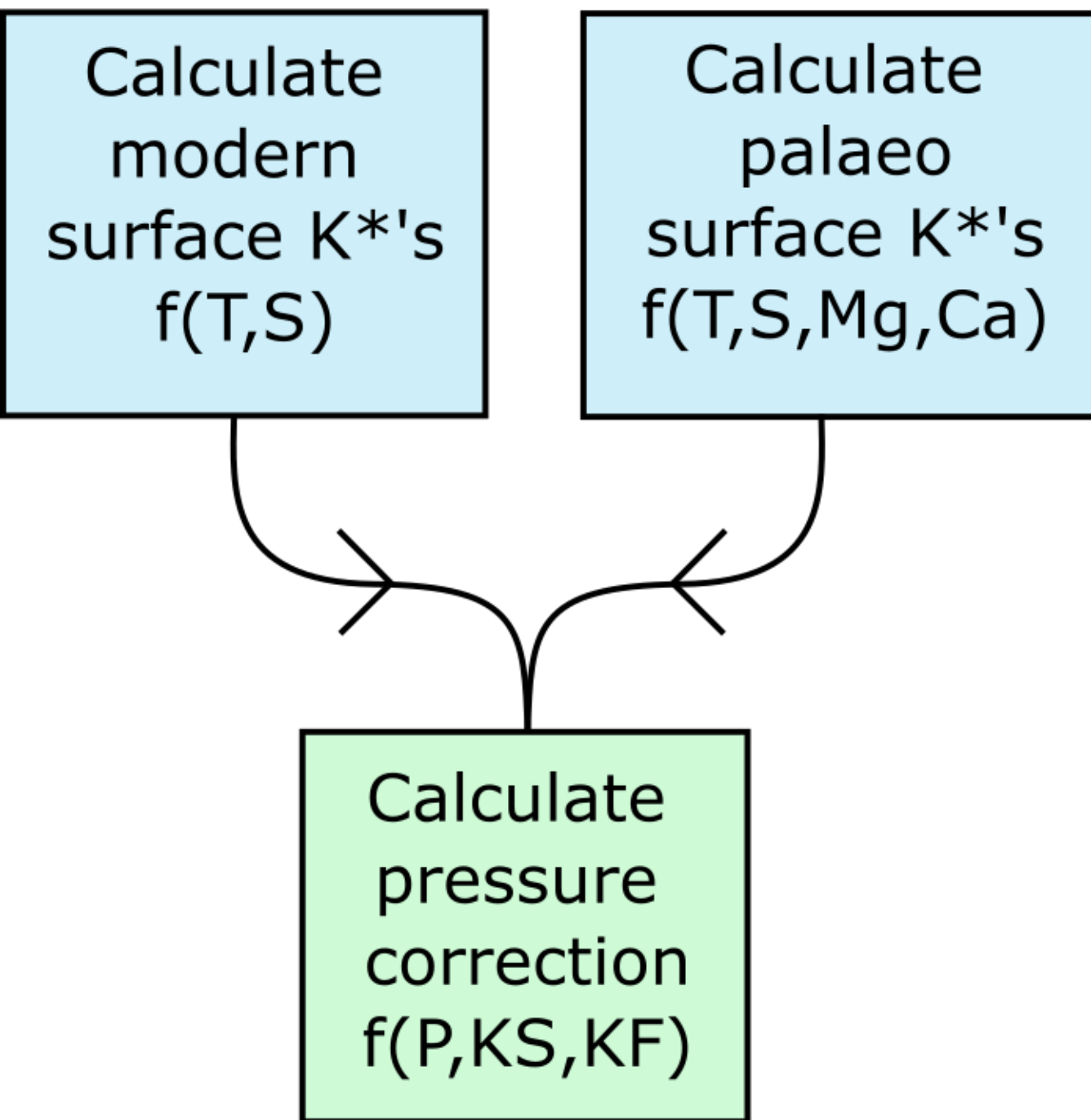
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Figure 1.

Current



Kgen

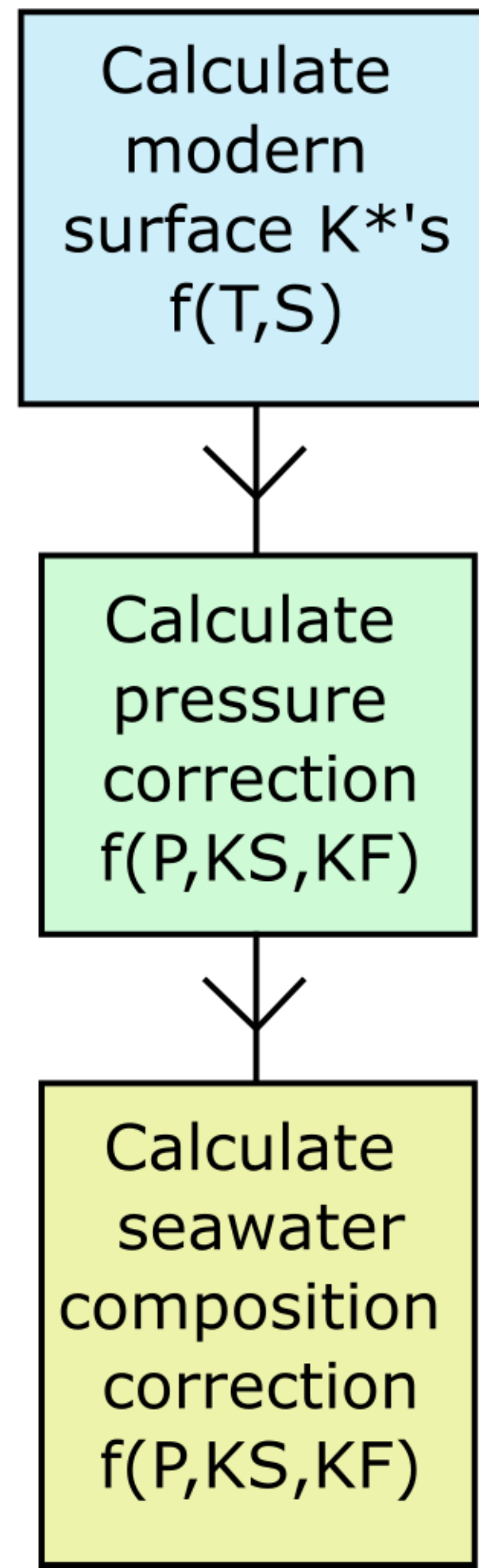


Figure 2.

— kgen Zeebe+Tyrrell - - - MyAMI

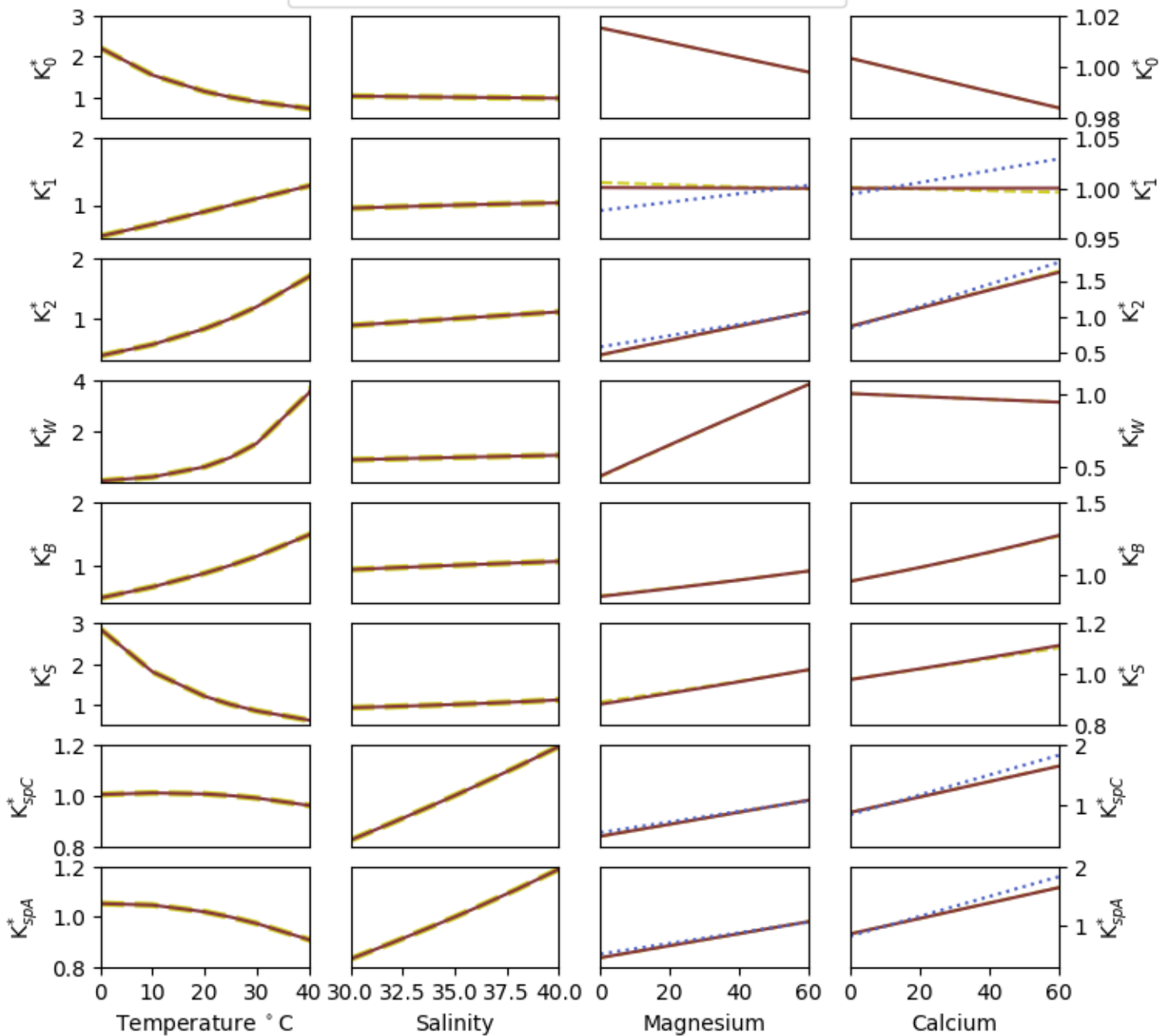


Figure 3a.

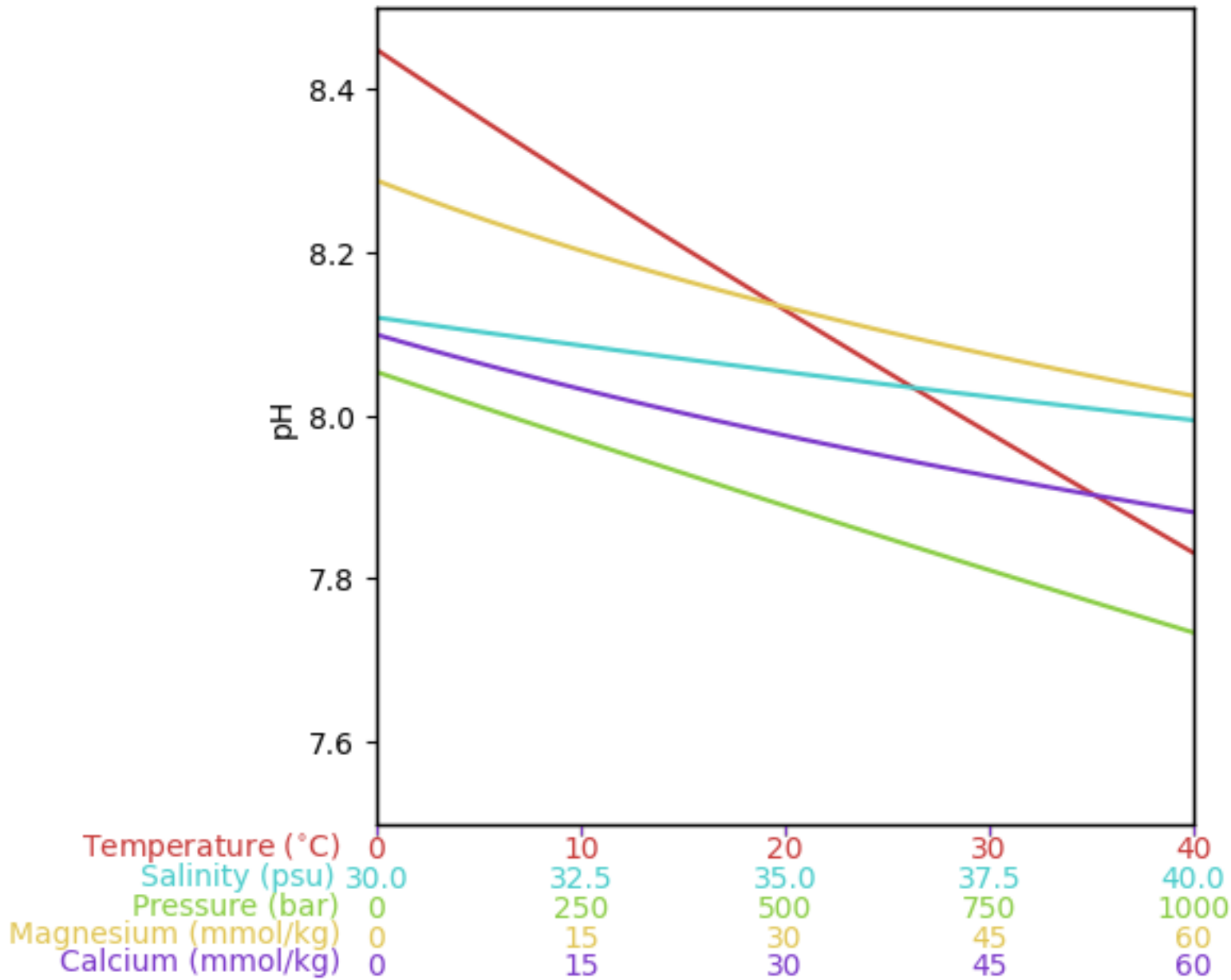


Figure 3b.

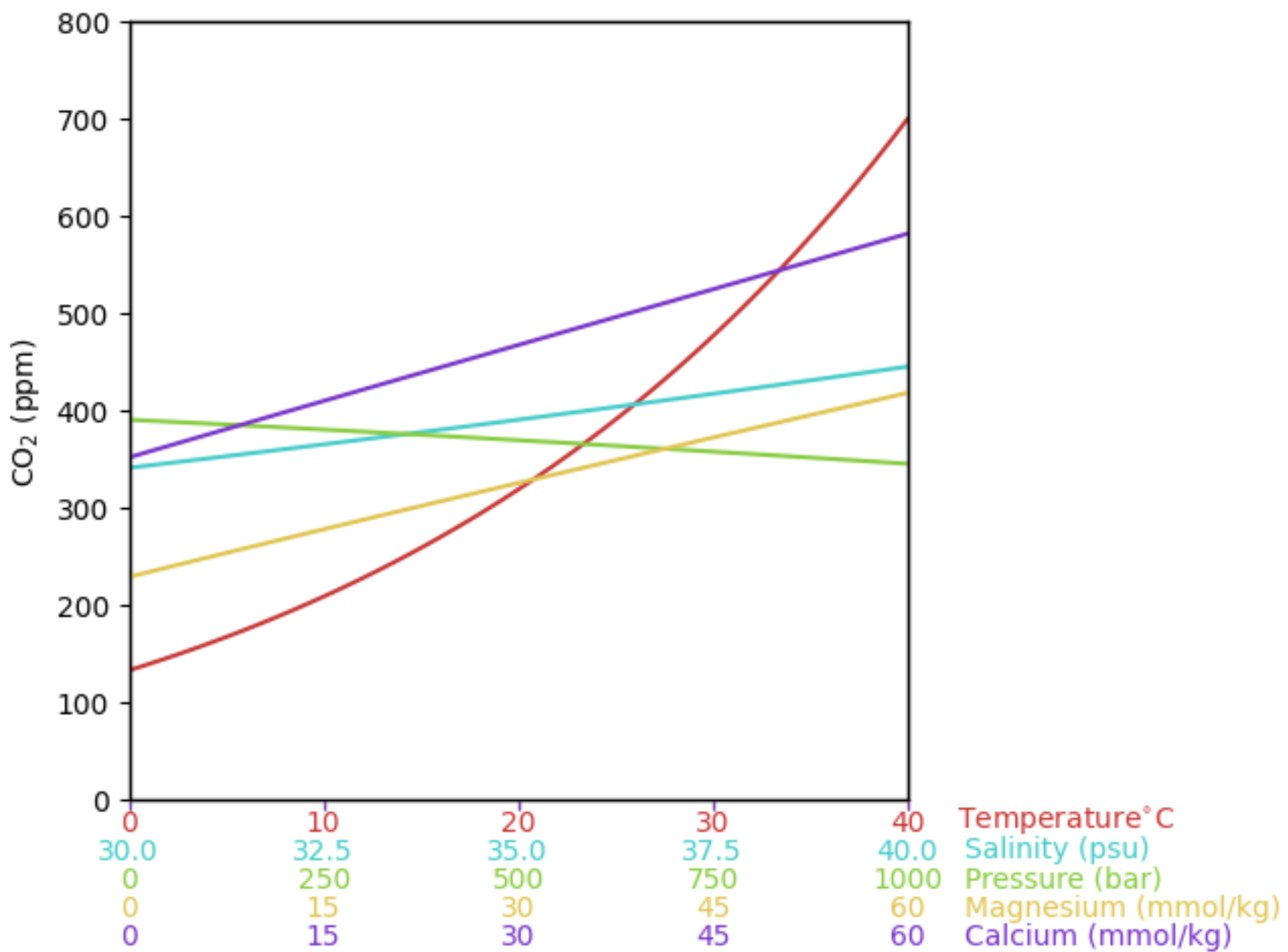
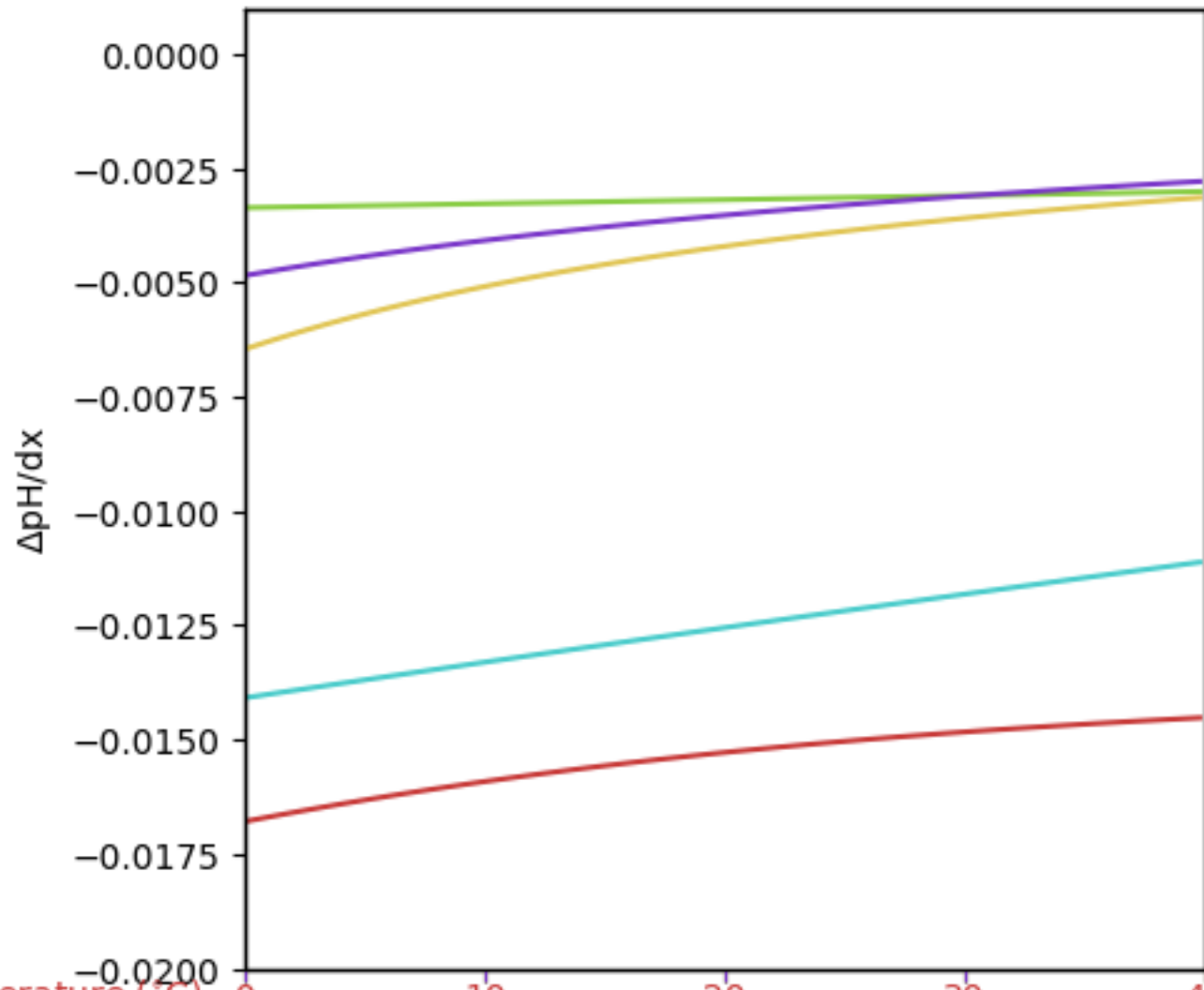


Figure 3c.



Temperature ($^{\circ}C$)

Salinity (psu)

Pressure (bar)

Magnesium (mmol/kg)

Calcium (mmol/kg)

Figure 3d.

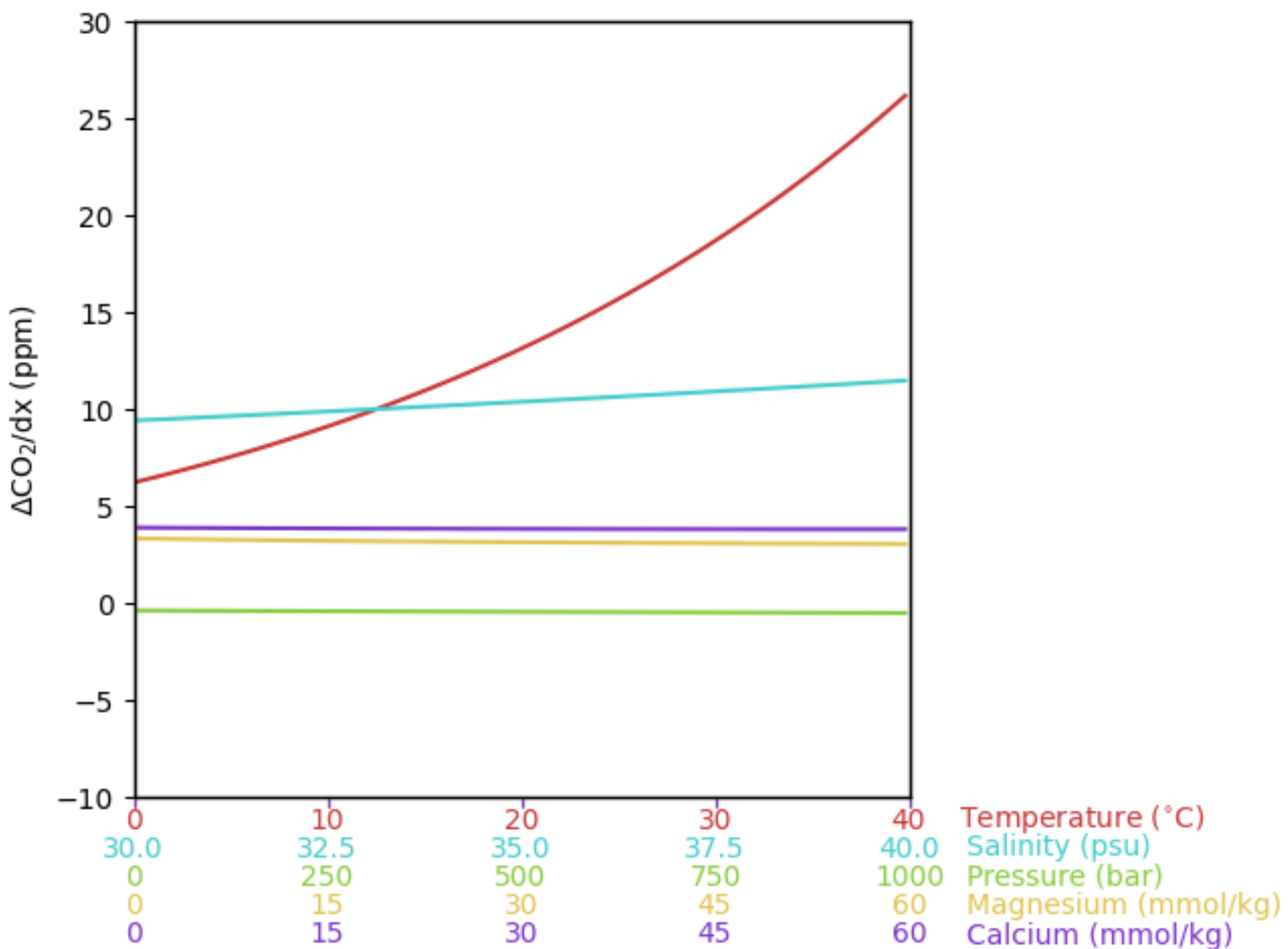


Figure 5.

