

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

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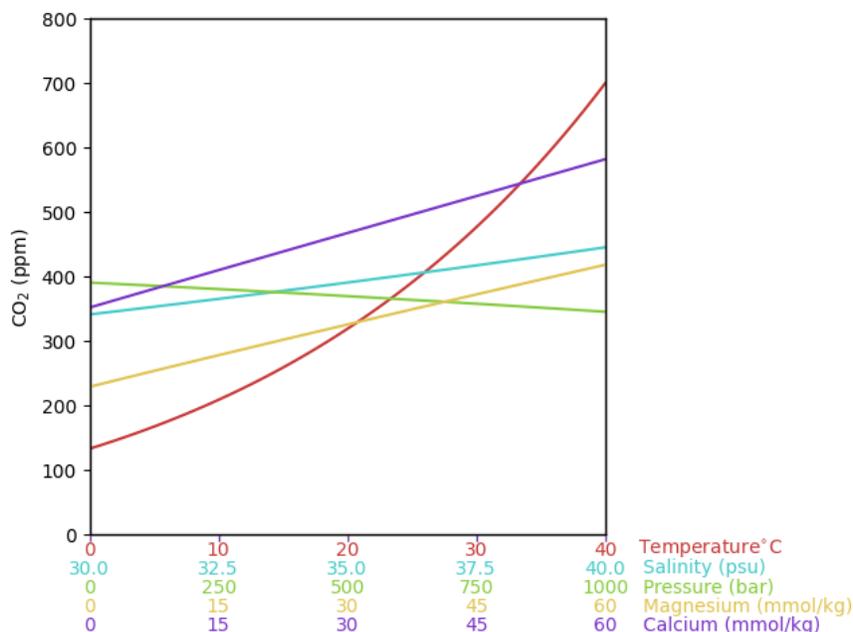
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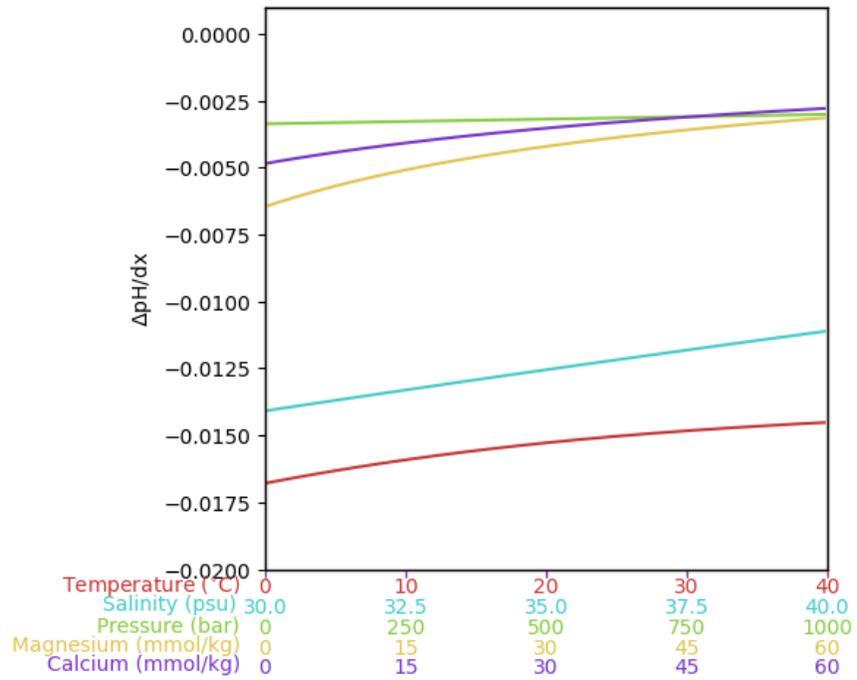
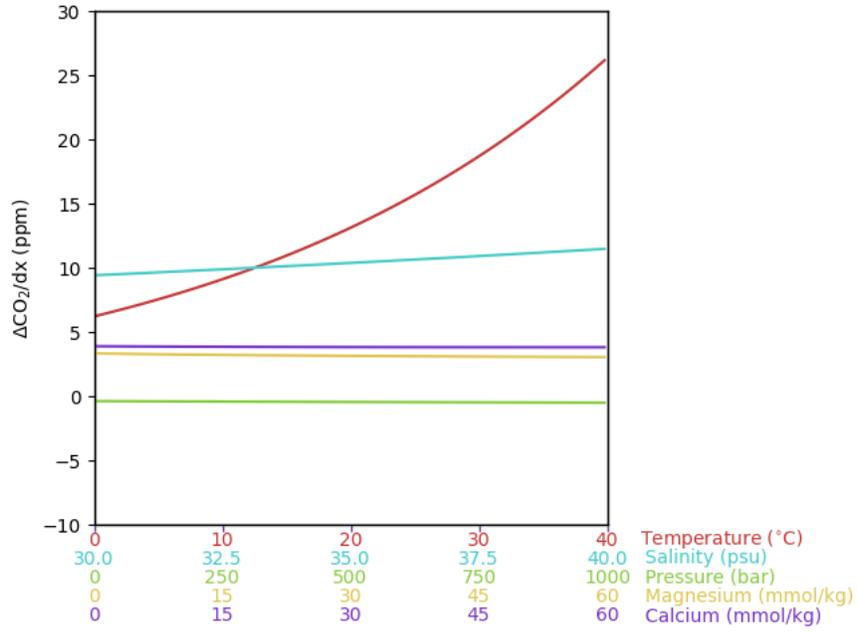
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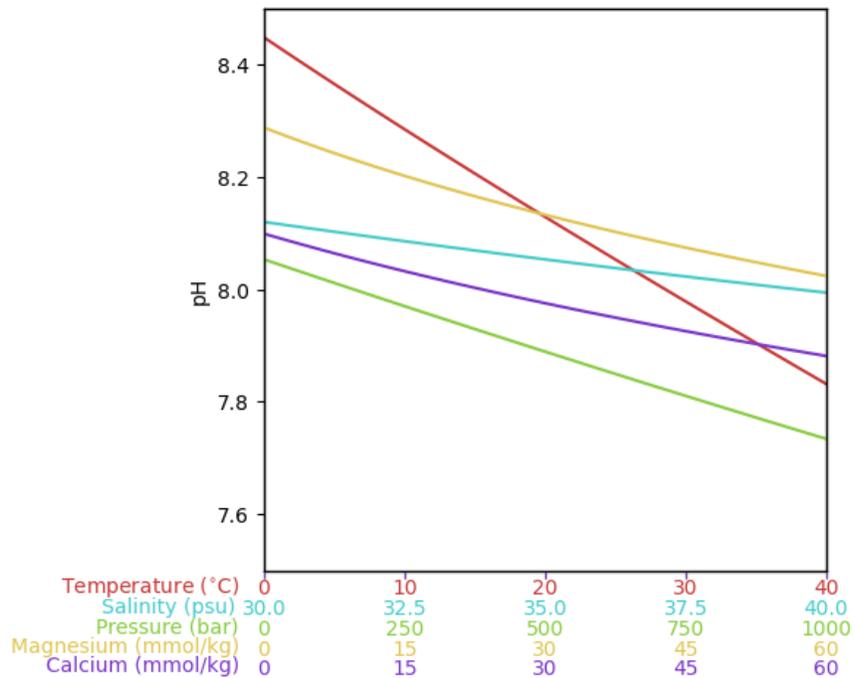
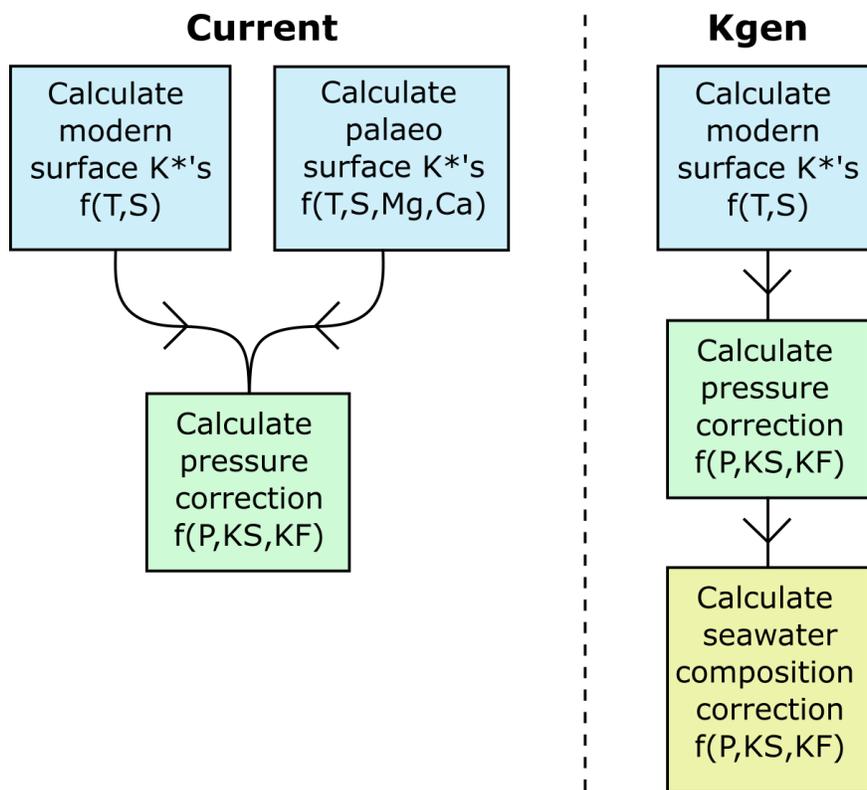
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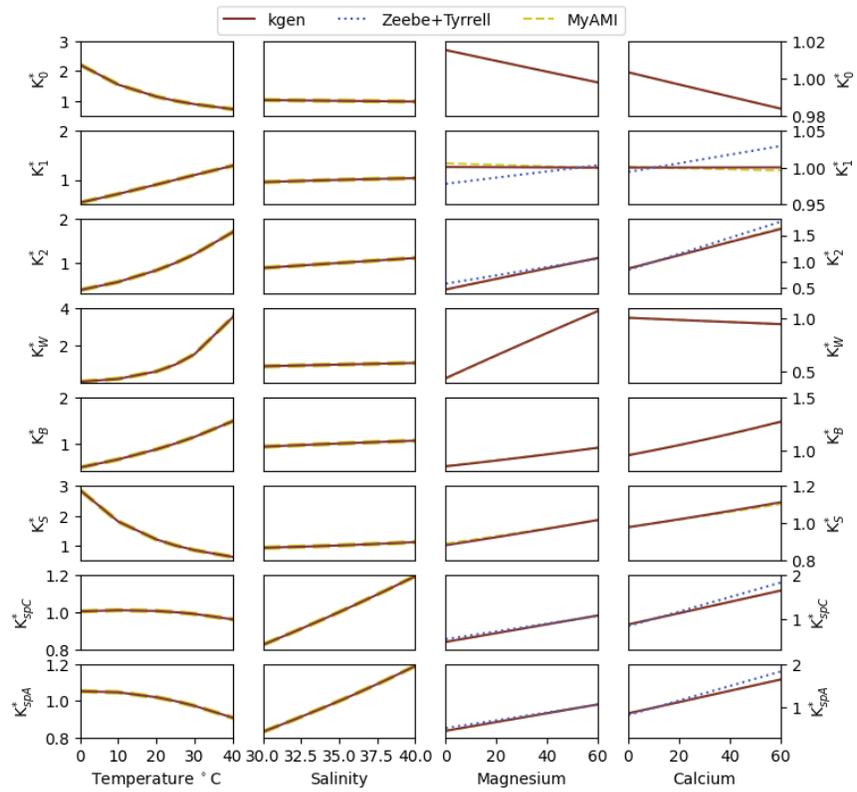
Abstract

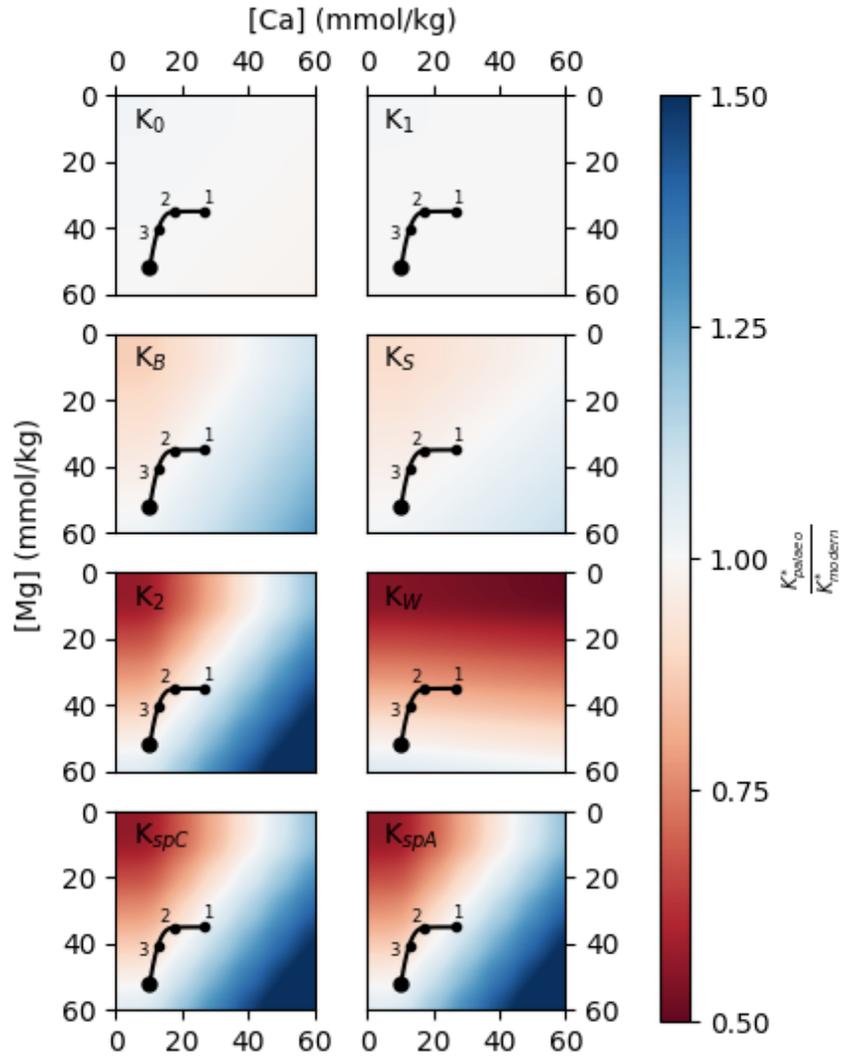
The state of acid-base equilibria in solutions is calculated using apparent equilibrium constants (K^* 's). The accuracy of these K^* 's is critical for calculations of environmental chemistry, for example the dissociation of dissolved CO_2 in seawater. The K^* 's required to calculate seawater carbonate 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.











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.

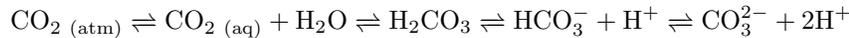
1 Introduction

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

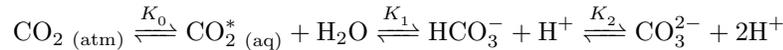
Carbon is present in seawater as four inorganic species: CO_2 (carbon dioxide), H_2CO_3 (carbonic acid), HCO_3^- (bicarbonate), and CO_3^{2-} (carbonate ion), which are related by the acid-base chain:



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:

$$\text{CO}_2^* = \text{H}_2\text{CO}_3 + \text{CO}_2 \text{ (aq)}.$$

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.

$$\text{CO}_2 + \text{H}_2\text{O} \xrightleftharpoons{K_1} \text{HCO}_3^- + \text{H}^+ \quad (1)$$

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

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

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.

96 property for marine calcification (e.g. by foraminifera and corals), and long-term forma-
 97 tion and dissolution of calcium carbonate that balances of inputs and outputs of carbon
 98 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_B^* '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).

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

99 1.2 Calculating K^* 's - Current Approach

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

113 1.3 Calculating K^* 's - The Problem

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

117 modern seawater, it is currently standard practice to use the equations assembled in Dickson
 118 and Goyet (1994), which have been implemented in all major carbon chemistry speci-
 119 cation calculators written across multiple platforms (Table 1). Most of these calculation
 120 packages jointly implement both the calculation of K^* 's, and their application to calcu-
 121 late the state of the oceanic carbonate system. Throughout the history of these calcu-
 122 lators, both the software and our understanding of ocean chemistry have evolved, and
 123 typographical errors in coefficients have been introduced and resolved, but not necessar-
 124 ily in concert across all the available packages. There is occasional indirect cross-validation
 125 of K^* calculation between these packages by comparing their ability to calculate simi-
 126 lar carbon speciation values (Orr et al., 2015), but no continuous checking to ensure that
 127 all packages always produce comparable results, and little or no record of how and when
 128 changes have been made to the calculation of K^* 's in response to updates in our under-
 129 standing of the constants used to calculate them. If, for example, a K^* definition were
 130 to be revised or modified today, each piece of calculation software would have to be in-
 131 dependently updated by a separate team of maintainers, leading to a period in which
 132 each software package produces subtly different results, and it is not straightforward for
 133 a user to determine which version has been used for a calculation, or indeed which ver-
 134 sion they are using themselves. This scenario of updating a K^* parameterisation has al-
 135 ready arisen, for instance recently Sulpis et al. (2020) published updated parameterisa-
 136 tions for K^*_1 and K^*_2 that improve performance at low temperatures, which are now used
 137 as the default in PyCO2SYS (Humphreys et al., 2022), but have not been updated in
 138 other calculation packages. This will cause deviation in the calculation of carbon param-
 139 eters between PyCO2SYS and other speciation calculation packages that a casual user
 140 will not be aware of.

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

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

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

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

174 **2 Kgen: A unified framework for K^* Calculation**

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

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

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

194 **2.1 Equilibrium Constants in Modern and Ancient Seawater**

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

198 **2.1.1 Temperature and Salinity**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

213 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:

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

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

214 Unfortunately, Equations 6 to 18, and coefficients used in Equation 19 have a his-
 215 tory of typographical errors. While we can not preclude the potential of further typo-
 216 graphical or other errors here, by using the same coefficients in all three languages we
 217 ensure that all three implementations are comparable, and any improvements are simul-
 218 taneously propagated to all software which uses Kgen. Here we use coefficients from Hain
 219 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

220
 221 Palaeoceanographic studies of seawater chemistry need to account for the influence
 222 of long-term secular evolution in seawater composition. Solution modelling programs such
 223 as PHREEQC (Parkhurst & Appelo, 2013) are not sufficiently accurate in seawater, and
 224 a range of other tools and methods have been developed to tackle this problem. Broadly
 225 speaking, there are two approaches: use simple sensitivity parameters (Tyrrell & Zeebe,
 226 2004b; Zeebe & Tyrrell, 2019) that modify K^* 's as a linear function of seawater com-
 227 position, or use a more complex Pitzer speciation model (Hain et al., 2015). The Pitzer
 228 ion interaction model adjusts each of the K^* 's using empirical coefficients that describe
 229 ion-ion interactions in the solution, and the impact of these interactions on the activ-
 230 ities of relevant ions in seawater. All currently available carbonate chemistry speciation
 231 programs that provide the facility to account for changing seawater composition have
 232 opted to use the MyAMI Pitzer ion interaction from Hain et al. (2015), which is writ-
 233 ten in Python. MyAMI is designed to account for non-standard seawater calcium and
 234 magnesium concentrations by adjusting the coefficients in Equations 6-18. MyAMI can
 235 be used in three ways: by directly calling functions, using the command line interface, or
 236 using a look-up table of parameters. Both the command line interface and the look-up
 237 table approach have been used in previous publications such as Henehan et al. (2019);
 238 Rae et al. (2021).

239 Unfortunately, there are a number of issues with this approach that are not imme-
 240 diately evident to the end user. First, there is a known issue with the published look-
 241 up table affecting, in particular, the K^*_B values (CenCO2PIP Consortium, 2023). K^*_B
 242 values generated from the look-up table diverge from K^*_B calculated using MyAMI by
 243 up to 66%. This look-up table has since be regenerated and can be found in compressed
 244 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 `pymyami` package, written in Python. `pymyami` 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 `pymyami` compared to MyAMI, with no difference in K^*_w , and the largest difference in K^*_2 .
- Improved flexibility, allowing an expert user to change the concentrations of a greater number of ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Cl^- , $\text{B}(\text{OH})_4^-$, HCO_3^- , CO_3^{2-} and SO_4^{2-}).

In addition to these improvements, `pymyami` 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, `pymyami` 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.

329 The Kgen project is managed through a git repository, augmented with GitHub
 330 actions to automate cross-comparison between the three languages. There are multiple
 331 comparisons made to ensure consistency. The first validates the output from Kgen against
 332 check values given in Zeebe and Wolf-Gladrow (2001). The second runs Kgen in all three
 333 languages to calculate K^* 's for a wide variety of oceanic conditions, then quantifies the
 334 difference between them - with an automatic failure if the difference is greater than 0.01%.
 335 Updated values for parameters or functions can not be merged into the repository with-
 336 out first passing these tests, ensuring ongoing consistency.

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

343 ***2.2.3 Traceable Version Numbering***

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

352 ***2.2.4 Integrating Kgen Into Carbonate Chemistry Solvers***

353 We recommend assimilating Kgen into carbonate chemistry software by treating
 354 it as a dependency. With Python and R this can be managed using your preferred pack-
 355 age manager to specify versions of Kgen compatible with the carbonate chemistry soft-
 356 ware. For Matlab, Kgen can be directly incorporated with the carbonate chemistry pack-
 357 age using the Matlab file exchange. Kgen can run alongside other methodologies of cal-
 358 culating K^* 's (for instance where apparent equilibrium constants appropriate for fresh-
 359 water and seawater are required within the same analysis). Kgen can be integrated into
 360 existing carbonate chemistry software packages in such a way that does not break back-
 361 wards compatibility and K^* 's from a variety of methods can be easily compared.

362 ***2.2.5 Simplified Calculation Sequence***

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

371 ***2.2.6 pH Scales***

372 The primary contribution of Kgen is in providing a central, cross-checked func-
 373 tionality for calculating consistent K^* values. The collection of these calculations in one
 374 place does not, however, address some of the outstanding issues surrounding K^* calcu-
 375 lation.

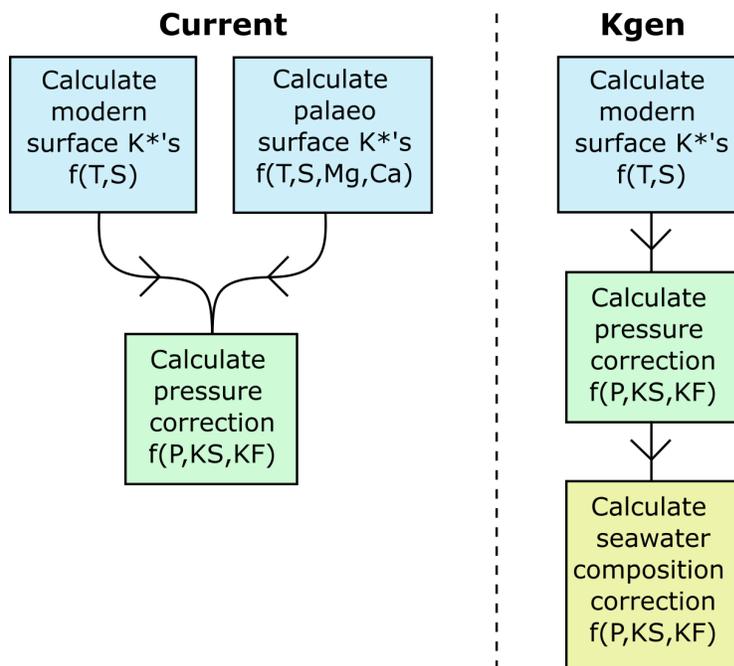


Figure 1. The pathways for calculation of K^* 's for carbonate chemistry software. The current, two step paradigm is shown on the left, and is branched depending on whether K^* 's are required for modern or palaeo seawater. Kgen linearises this workflow into three separate steps.

376 pH can be expressed on a variety of scales: the NBS scale, the free scale, the total
 377 scale, or the seawater scale. The free scale is the simplest, as it accounts only for free
 378 hydrogen ions, while the total scale accounts for hydrogen sulphate, and the seawater
 379 scale accounts for both hydrogen sulphate and hydrogen fluoride. The motivation behind
 380 these scales is practical in nature, in that, while we might typically be interested
 381 in free hydrogen ion concentration, pH measurement apparatus may respond more closely
 382 to the combined influence of free hydrogen ions, hydrogen sulphide, and hydrogen fluoride.
 383

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

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

397 **3 Results: Kgen Performance**

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

401

3.1 Comparison

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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)).

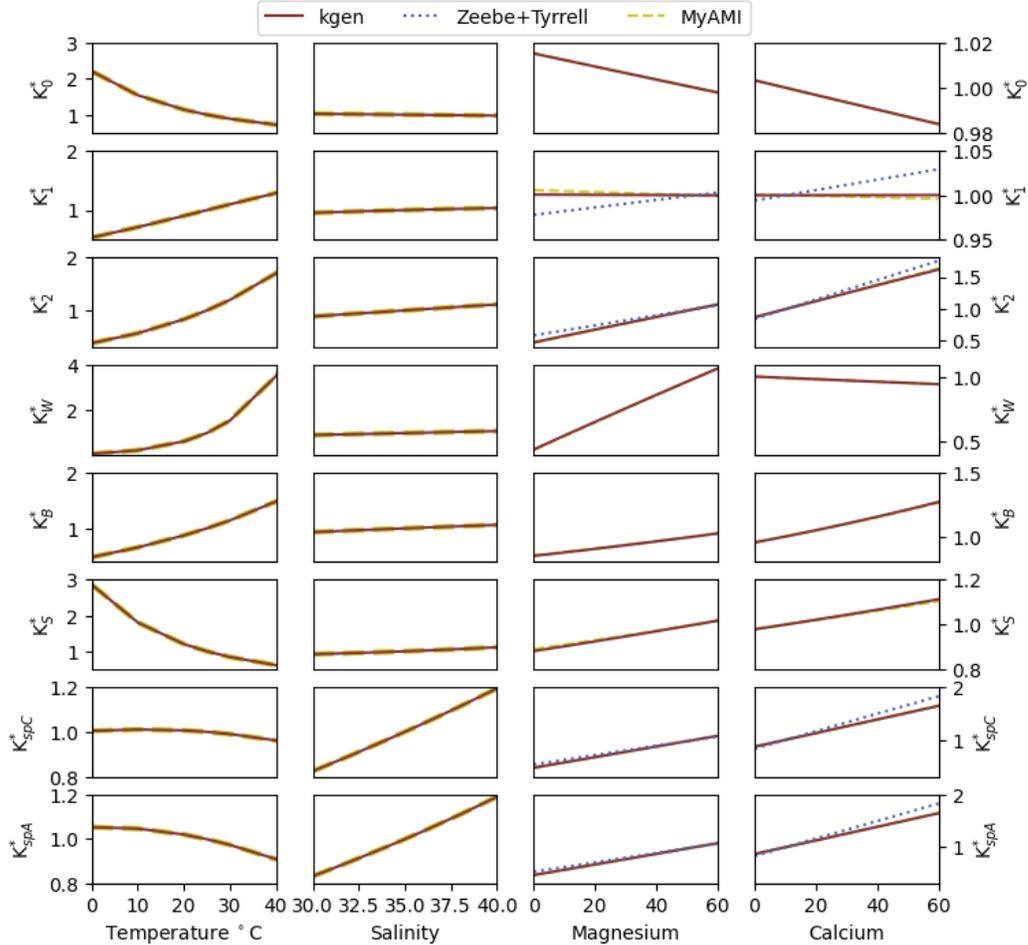


Figure 2. The sensitive of K^* 's to temperature, salinity, magnesium concentration and calcium concentration using three different methods. Each K^* is shown in a row and each control in a column. There is generally good agreement between the three methods. The largest offsets are between the sensitivity 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.

409

410

411

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-

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

414 **3.2 K* Properties**

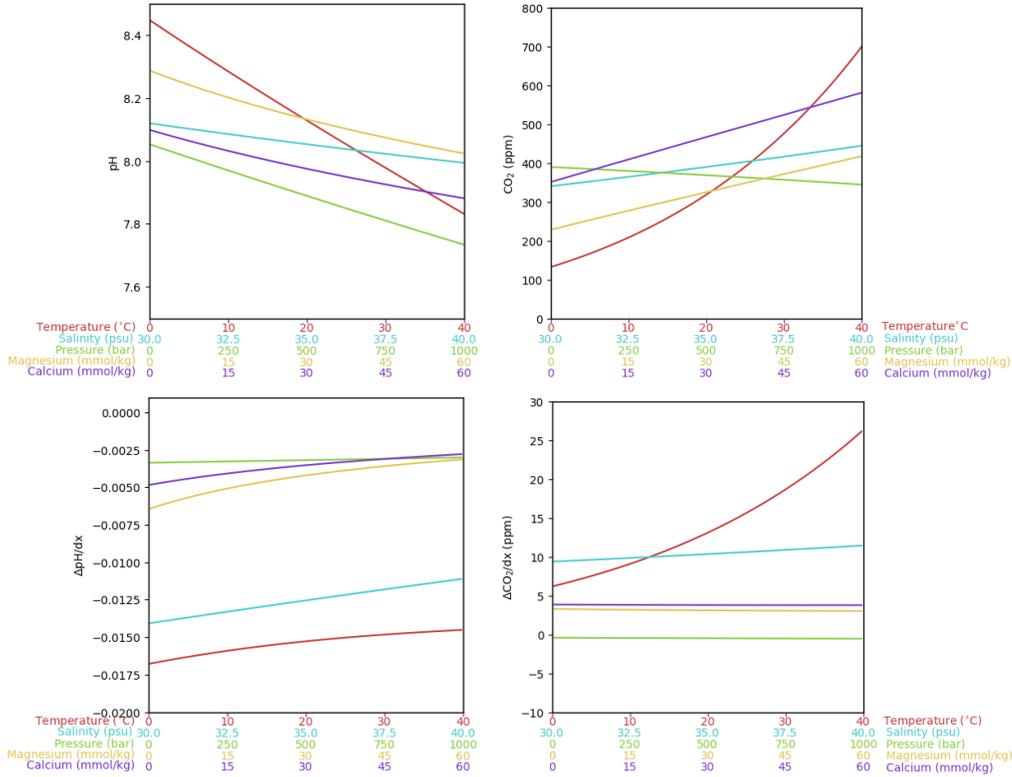


Figure 3. The sensitivity of pH and CO₂ to each individual factor (temperature, salinity, pressure, magnesium concentration, and calcium concentration) is shown above at a reference condition of DIC=2000μmol/kg and alkalinity=2300μmol/kg, and standard modern seawater conditions.

415 To evaluate the sensitivity of pH and CO₂ to temperature, salinity, pressure, mag-
 416 nesium concentration, and calcium concentration, we prescribe a standard set of condi-
 417 tions 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.,
 418 are shown in Figure 3, alongside the second derivative of each parameter (e.g. the sen-
 419 sitivity of $\frac{\partial pH}{\partial T}$ to temperature). From this we find that pressure is the strongest driv-
 420 ing factor of pH and CO₂ across the range found in the ocean (only one tenth of which
 421 is shown in Figure 3), followed by temperature, while the influence of other factors is more
 422 muted. Pressure is the only parameter which has a negative correlation to CO₂. The sen-
 423 sitivity of pH and CO₂ to salinity, pressure, magnesium concentration, and calcium con-
 424 centration is almost constant across their range, whereas the influence of temperature
 425 is much more nonlinear, with a much greater sensitivity of CO₂ to temperature at higher
 426 temperatures. The lower subplots in Figure 3 allow us to express the sensitivity of pH
 427 and CO₂ to each individual factor quantitatively and, for modern ocean conditions, get
 428 some sense of the uncertainty stemming from each parameter - though it is important
 429 to note that (as described above) these are partial derivatives, and the combinative ef-
 430 fects of parameters may be different to treating each factor independently. In particu-

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

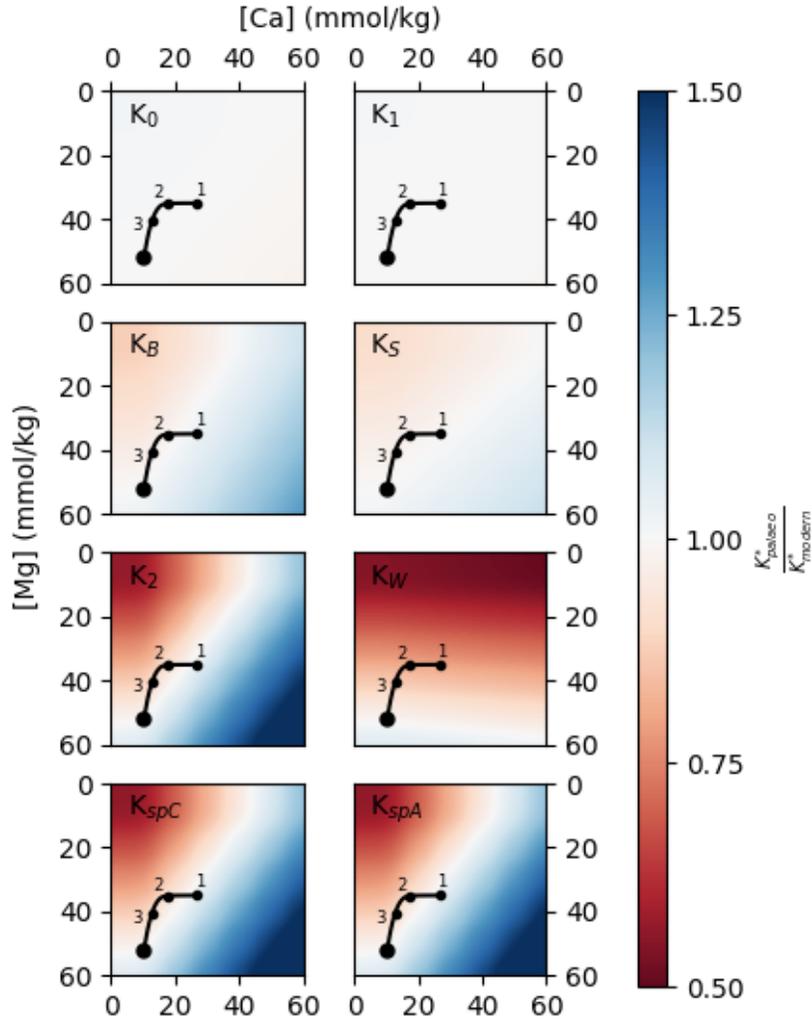


Figure 4. Each subplot shows a single K^* , normalised to the modern day K^* across a range of seawater calcium and magnesium concentrations. Lighter colours indicate that the K^* at these conditions are similar to the modern ocean, warmer colours indicate higher K^* , and cooler colours indicate lower 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.

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

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

449 4 Summary

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

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

459 Kgen is already in use within cbsyst (Branson et al., 2023), a carbonate chemistry
 460 library written in python which is applicable to both modern and palaeo seawater com-
 461 positions, alongside a number of convenience functions for calculating the carbon sys-
 462 tem from boron speciation and isotopes. We are currently exploring the best way of in-
 463 tegrating Kgen into existing carbonate chemistry software packages (seacarb/seacarbX
 464 for R, and CO2SYS for Matlab).

465 5 Open Research

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

471 References

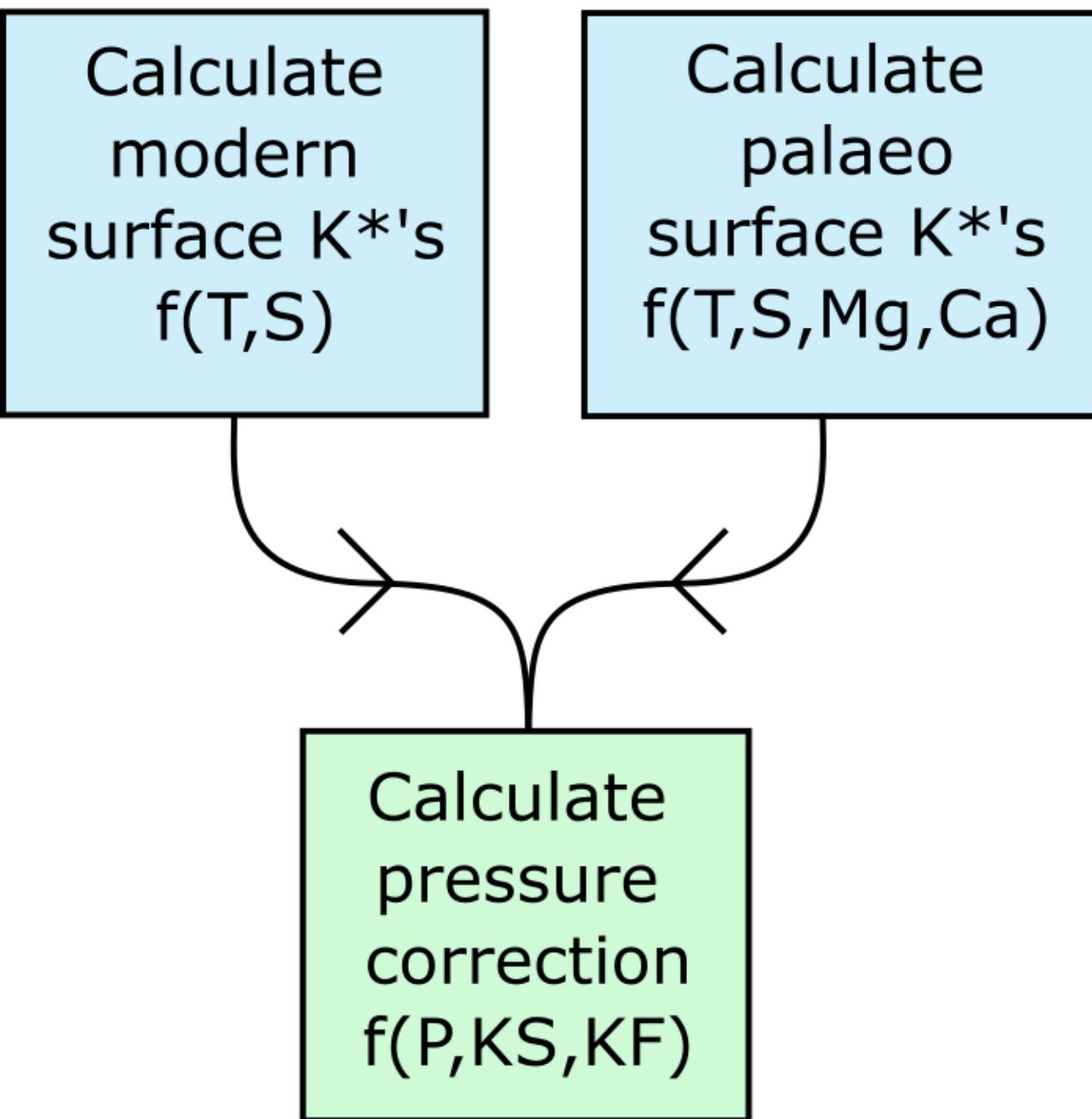
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Figure 1.

Current



Kgen

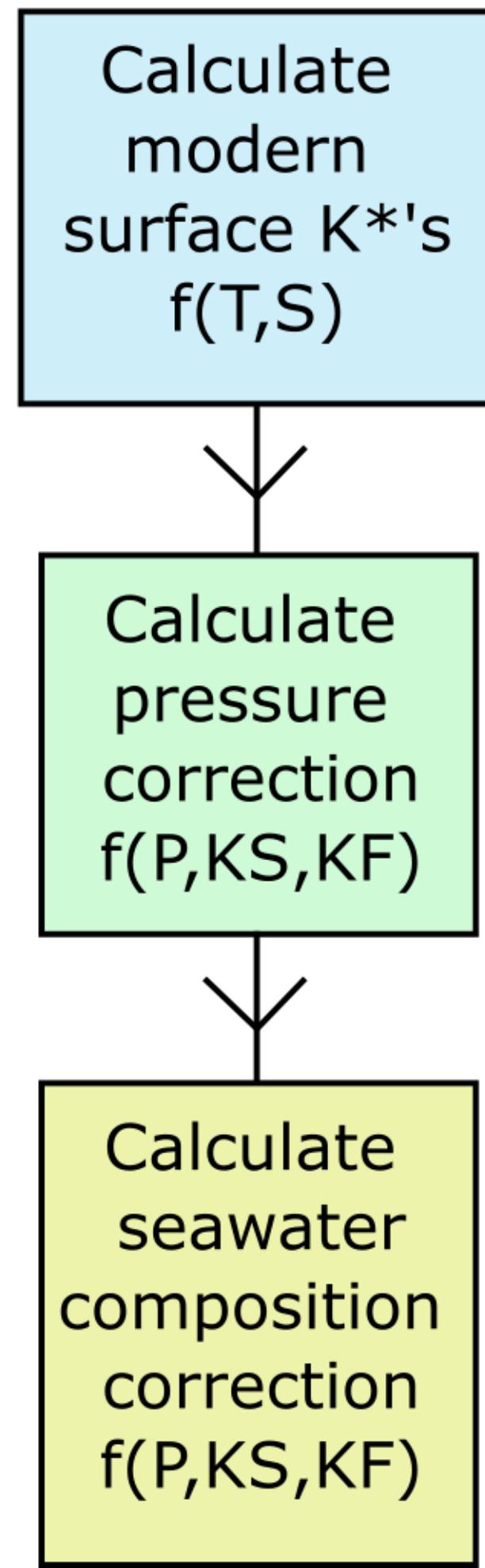


Figure 2.

— kgen ···· Zeebe+Tyrrell - - - MyAMI

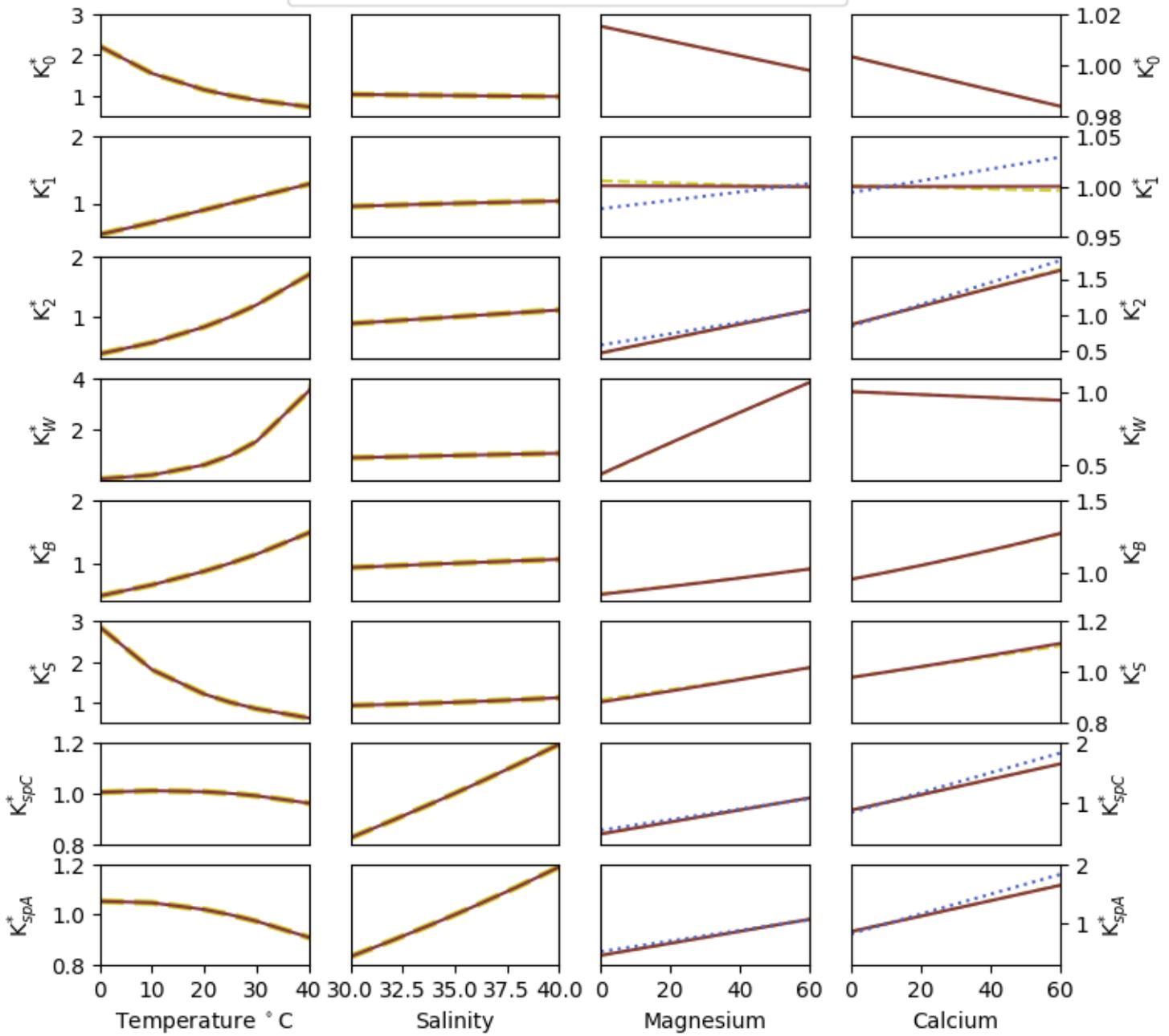
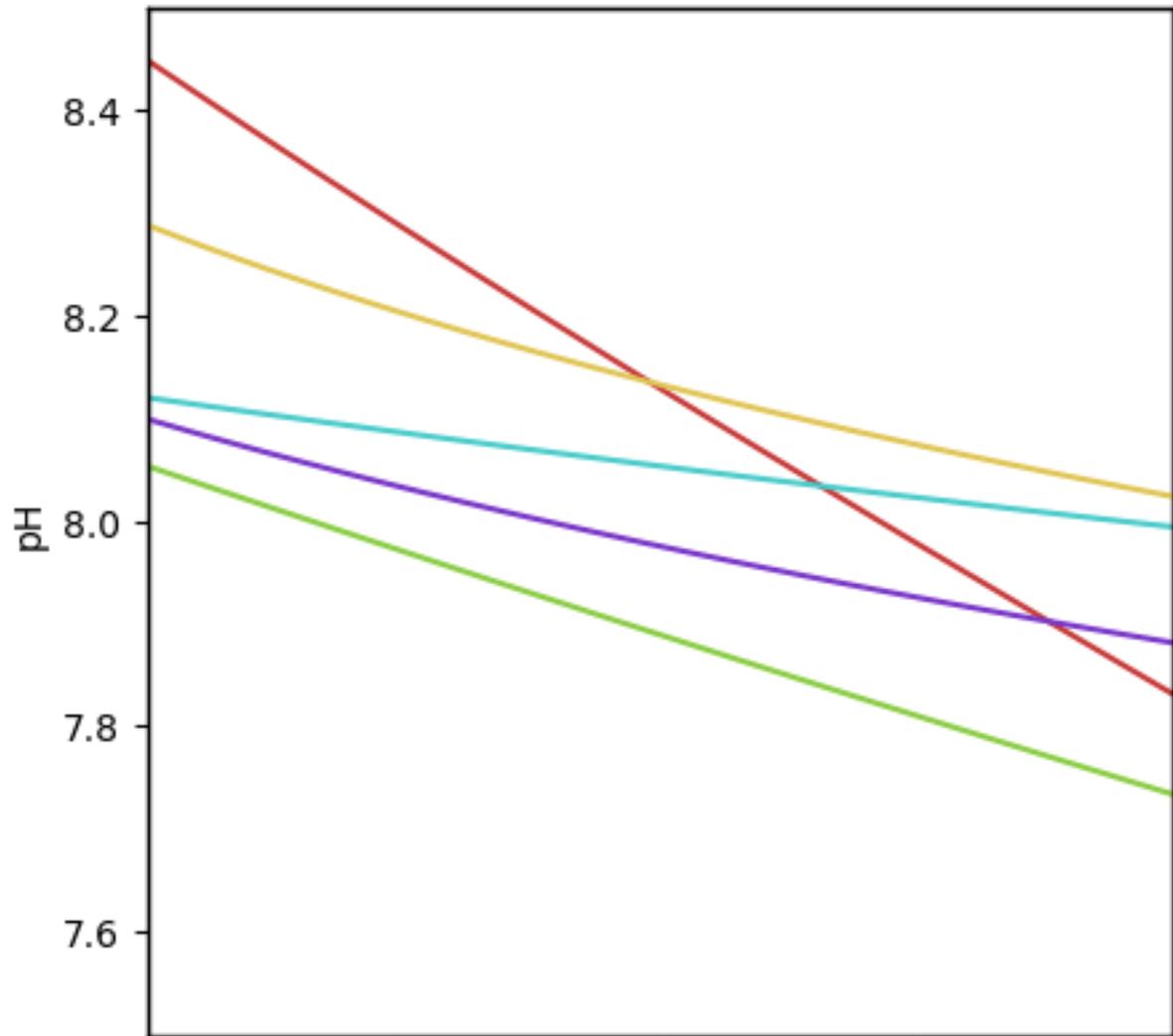
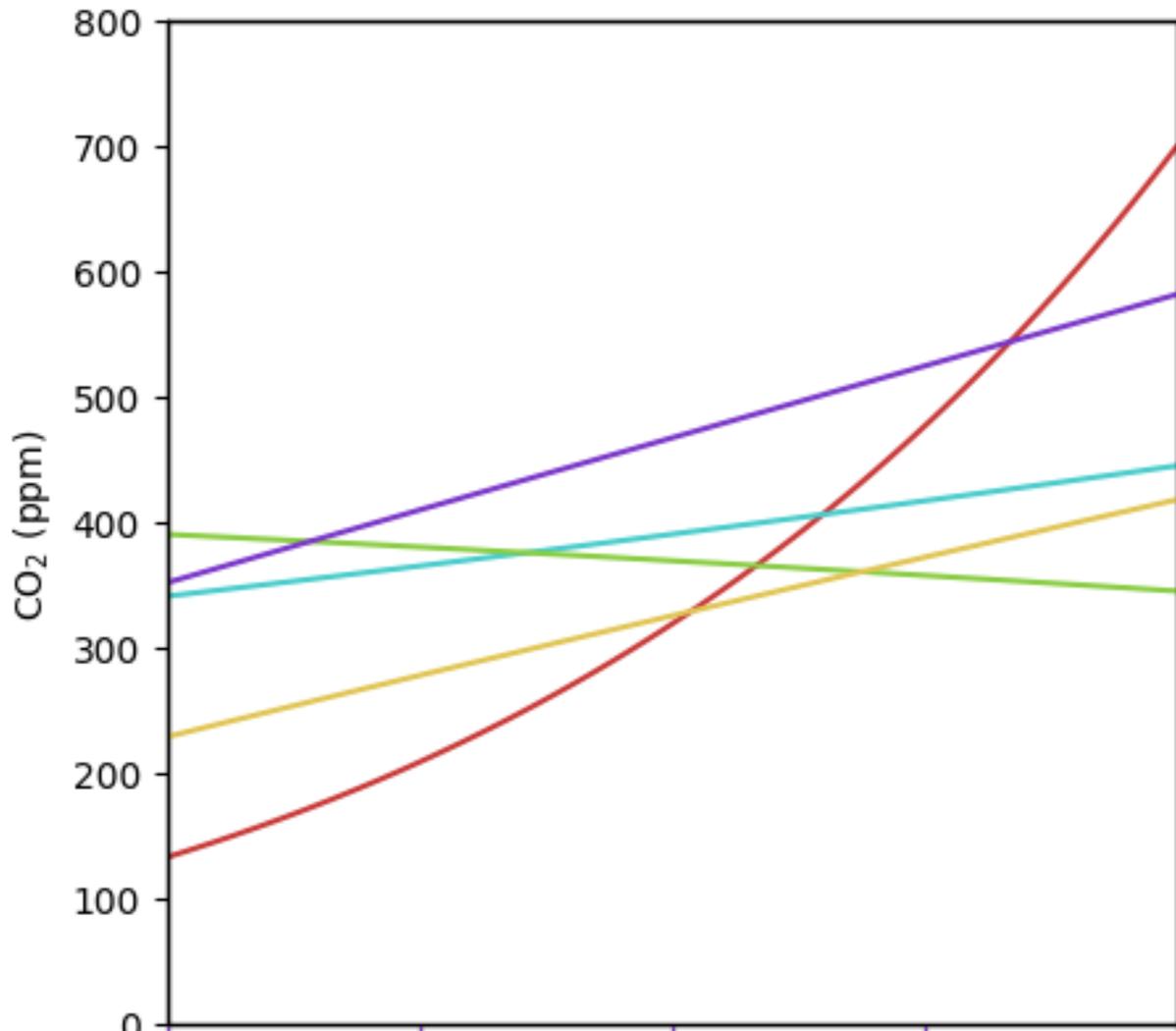


Figure 3a.



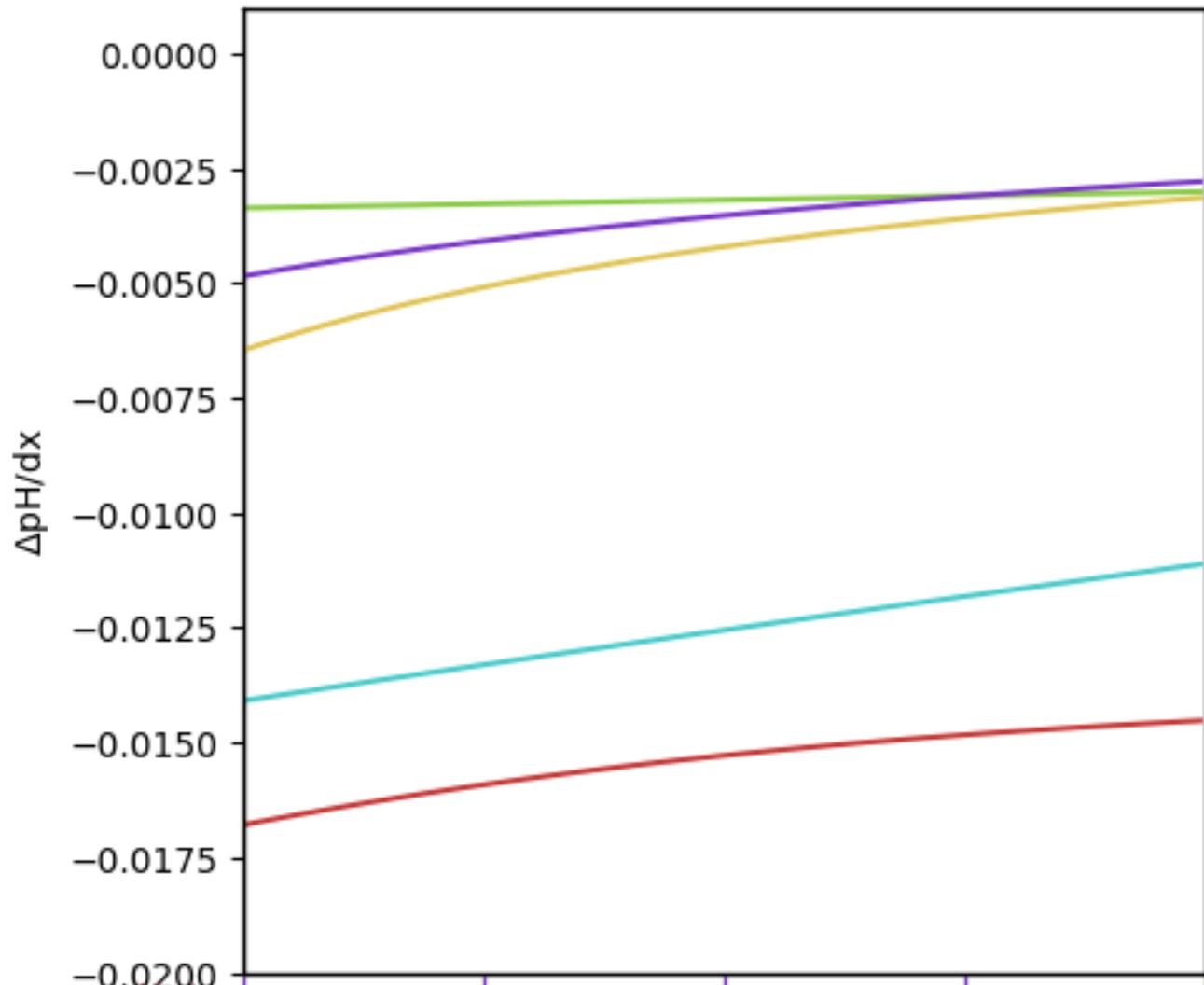
Temperature (°C)	0	10	20	30	40
Salinity (psu)	30.0	32.5	35.0	37.5	40.0
Pressure (bar)	0	250	500	750	1000
Magnesium (mmol/kg)	0	15	30	45	60
Calcium (mmol/kg)	0	15	30	45	60

Figure 3b.



Temperature° C
 Salinity (psu)
 Pressure (bar)
 Magnesium (mmol/kg)
 Calcium (mmol/kg)

Figure 3c.



Temperature (°C)	0	10	20	30	40
Salinity (psu)	30.0	32.5	35.0	37.5	40.0
Pressure (bar)	0	250	500	750	1000
Magnesium (mmol/kg)	0	15	30	45	60
Calcium (mmol/kg)	0	15	30	45	60

Figure 3d.

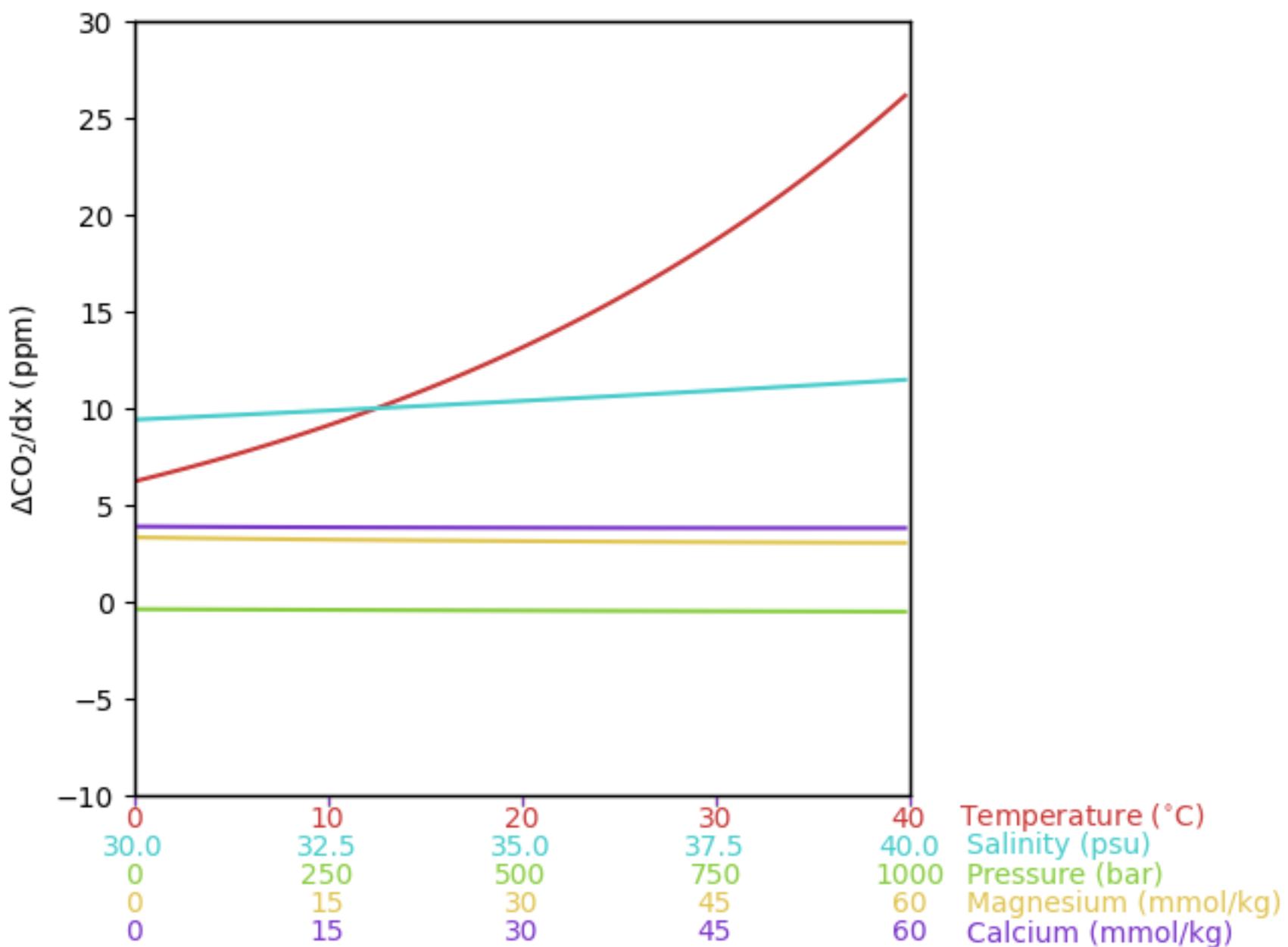


Figure 5.

