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A new look at physico-chemical causes of changing climate: Is the seasonal variation in seawater temperature a significant factor in establishing the partial pressure of carbon dioxide in the Earth's atmosphere?

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Abstract: Seasonal oscillations in the partial pressure of carbon dioxide (pCO_2) in the Earth's atmosphere stronger in northern latitudes are assumed to show that terrestrial photosynthesis exceeds respiration in summer reducing the pCO_2, but increasing in winter when respiration exceeds photosynthesis. We disagree, proposing that variations in the temperature of the surface mixing zone of seawater also regulate the atmospheric pCO_2, thermodynamically. We show that carbonate (CO_3^{2-}) concentrations will therefore increase in summer with $CaCO_3$ (calcite or aragonite) becoming less soluble, so calcium and carbonate ions are predicted to aggregate more while CO_2 concentration falls in warmer seawater, thermodynamically favoring lower atmospheric pCO_2. In winter, these physical processes are reversed, redissolving suspended calcite thus increasing carbonate alkalinity; carbonate concentration lessens as bicarbonate and soluble CO_2 increase, raising the pCO_2 in air. Our numerical computation shows that thermal fluctuations in equilibria favor absorption from air of more than one mole of CO_2 per square meter in summer, coinciding with calcite formation maximizing in warmer water, potentially augmenting limestone reefs if there is a trend for increasing temperature . Another assumption we challenge is that upwelling from deeper water is the sole cause of increases in dissolved inorganic carbon (DIC) and alkalinity in surface waters, particularly in the southern hemisphere. Instead, calcite dissolution is favored as water temperature falls near the surface. It is well established that the seasonal summer decline in atmospheric CO_2 coincides in fertile seawater with higher rates of biotic calcification and acidity, allowing increased CO_2 capture by photosynthesis. However, its reversal in winter is proposed to be also a result of the cyclic dissolution of calcite as temperature falls, facilitated by biogenic respiration now exceeding photosynthesis; this can mutually provide the CO_2 needed to convert carbonate ion alkalinity from calcite dissolution with bicarbonate increasing. Physical reasons why this oscillation is more obvious in the northern hemisphere include greater seasonal variations in water temperature (ca. 7.1 ^oC) being almost twice that in the cooler southern hemisphere (ca. 4.7 ^oC) and the greater depth of the surface mixing zone of seawater in the southern oceans. Evidence from $^{13}CO_2$ fluxes between surface seawater and air is also assessed to test this hypothesis but questions remain regarding the regional rates of inorganic precipitation and dissolution of $CaCO_3$ in the mixing zone. In summary, rapid biogenic calcification is favored by summer photosynthesis, but slower abiogenic calcification is more likely in warmer water.

Keywords: CO_2; Keeling curve; Mauna Loa; carbonates; ocean pH; chemical potential; acidification 1

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1. Introduction

It is well understood that CO_2 levels in the Earth's atmosphere have increased at about half the rate at which fossil fuels have been combusted globally [1]. The conclusion was reached in the Inter-governmental Panel for Climate Change report of 2001 [2] that these observations are directly related, with only half of the CO_2 emissions being reabsorbed by surface biological or physical processes, generating imbalances in the rates of the emission and absorption processes. Particularly for the northern hemisphere, it was assumed that imbalances between photosynthesis and respiratory processes cause oscillations of CO_2 levels (pCO_2) recorded in air of several ppmv [3,4] above 3000 m on Mauna Loa in Hawaii, shown in Figure 1. These seasonal oscillations in pCO_2 extend to the top of the troposphere as observed using spectral occultation from space [5]. By comparison, at Cape Grim, Tasmania in the southern hemisphere only relatively small oscillations are observed, assumed to be a result of less vegetation on land or ocean and limitations on nutrients in seawater.

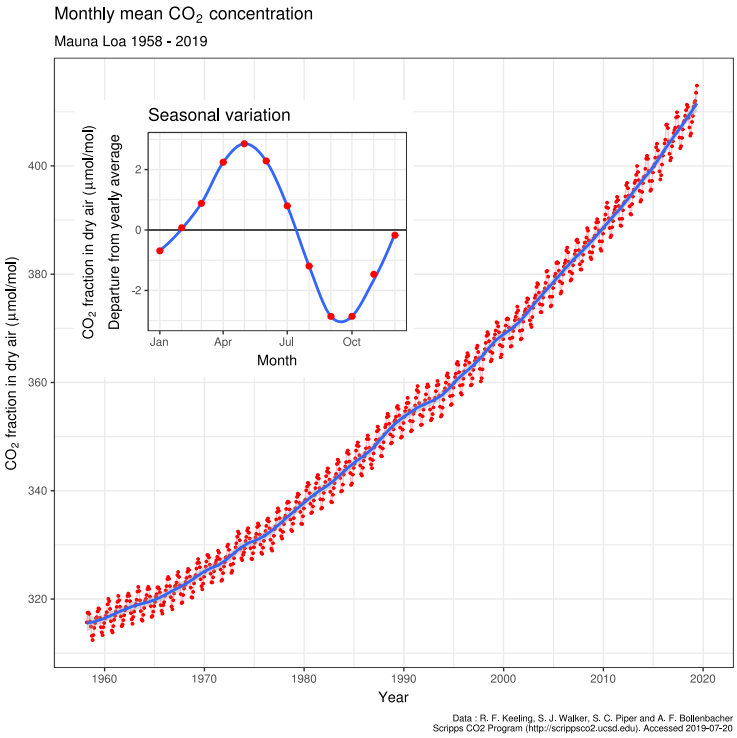

Figure 1. The Keeling curve of atmospheric CO_2 partial pressure at 3200 m on Mauna Loa, Hawaii. Data from Dr. Pieter Tans, NOAA/ESRL and Dr. Ralph Keeling, Scripps Institution of Oceanography. CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=40636957.

Seasonal assessments using observational platforms in the southern latitudes show significant daily variations in carbonate chemistry with some biological activity in subpolar latitude with more nutrients [6]. Also, it has been recognized that the pH of the

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seawater surface has been falling [7,8], claimed to be a result of the absorption and reaction of CO_2 in surface seawater with carbonate ions, increasing carbonic acid concentration. However, other processes may be at work. More recently, it was concluded that variability in ocean circulation and convection is also an important factor in exchange of CO_2 by the ocean [9], explaining some of the variation seen in the annual rise in oceanic CO_2. Here we will not consider such macroscopic processes. Rather, to help resolve issues of such global complexity, we focus on the mechanistic thermodynamics of interactions occurring at the boundary layers of air and land water. We advance a proposition capable of being tested that seasonal variations in temperature play an important role in establishing rates of abiotic exchange of inorganic carbon between the atmosphere and the surface.

2. Background

2.1 Chemistry of CO_2 in seawater

An important fact regarding CO_2 dissolved in seawater (Fig. 2) is its small quantity near pH 8 by comparison with the much larger content of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ; together these carbonic species indicate the total capacity to evolve CO_2 by strong acidification (designated as dissolved inorganic carbon or $C = \{[CO_2]+ [HCO_3^-] + [CO_3^{2-}]\}$). Another key concept is that of alkalinity due to inorganic carbon ($A_c = \{[HCO_3^-] + 2[CO_3^{2-}]\}$) indicating the total equivalents of acidity needed for neutralization, releasing CO_2. Insights into thermodynamic concepts such as chemical potential and fugacity may help clarify environmental behavior of CO_2. At equilibrium the matching of chemical potentials means that no work is required for a chemical species to move reversibly from one phase to another. However, fluctuations in environmental conditions ensure that conditions of non-equilibrium predominate and spontaneous fluxes of chemical species like CO_2 from one location to another are favored as irreversible processes. These factors (C and Ac) impose strong constraints on chemical equilibria, although this may be less rigorous in an open system like seawater because of gaseous diffusion.

In Figure 2 illustrating seawater chemistry, CO_2 molecules exist in all phases, attempting to equilibrate but responding to fluctuations in environmental states of temperature and pressure. The chemical potential of CO_2 (μ_{CO2}) is related to the quantum state of the molecule, mainly concerned [10] with activated translation and rotation at environmental temperatures. At equilibrium between phases, the change in the configurational quantum state from any change in the number density of the molecule is the same for all phases. Then no translational or rotational work is needed to move molecules from one phase to another.

The expression of gas pressures as parts per million by volume (pCO_2 in ppmv) is not ideal for thermodynamic descriptions. We can express the average pressure of CO_2 in the Earth's atmosphere by the ideal gas law, indicating the number density (N) of molecules per unit volume. In Figure 1, the pressure is given as µatoms of CO_2 per mole of air (i.e. 6.023×10^{23} molecules), equivalent to ppmv. However, the idea of a heterogeneous mole of air made up of a total of 6.022×10^{23} different molecules is not useful in thermodynamic terms. The mean partial pressure (p_i) of each gas per molecule can be given in terms of its number density (N) and the temperature (T).

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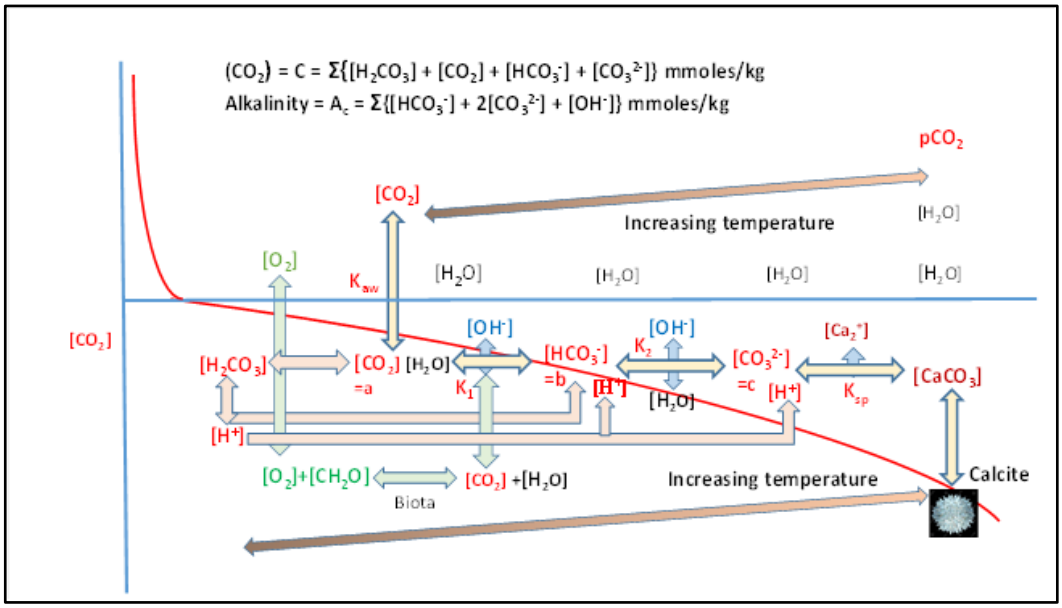

Figure 2. Fluctuating equilibria controlling absorption and emission of CO_2 and calcite dissolution. Reactions indicate the direct reaction of CO_2 plus water to form bicarbonate at pH 8. Temperature sensitive equilibrium constants shown (K_0, K_1, K_2, K_{sp}) all favour calcite formation in summer and CO_2 emissions in winter.

$$p_i = N_i kT \quad (1)$$

Since the total atmospheric pressure is regulated by the gravitational weight of the air per unit area, in equation (1) containing Boltzmann's constant per molecule (k) the number density (N per unit volume) and the temperature (T) must therefore have an inverse relationship. When warming, molecules migrate to lower number density at higher action or quantum states with greater entropy and lower chemical potential, expressed as more negative from zero at absolute zero. This decrease also applies to gas molecules dissolved in water −they will tend to escape to the air as temperature rises, a process captured in the term *fugacity* that means fleeing tendency. This is a more accurate thermodynamic concept for gases in multiphase systems, fugacity (f) being an expression with the same dimensions as partial pressure but corrected to a value expressing ideal behavior. This property in the gas phase is given as follows, where x_i is the mole fraction ($N_i/\Sigma N_i$) multiplied by the total pressure (p_t), with its correction factor (ϕ).

$$f_{CO2} = x_i \phi p_t \quad (2)$$

Like chemical potential, at equilibrium the fugacity must have the same value for all phases, indicating they all support the same vapor pressure, even though the concentrations in each phase will differ, an effect of different chemical environments on chemical potential. In fugacity theory a further correction (Z-factor) is applied to the concentration in each phase ($C_i/Z_i = f_i$) required to generate the fugacity held in common [11]. For CO_2 in the atmosphere its fugacity (adjusted from Dickson et al. [12]) for a partial pressure of 400×10^{-6} atm (400 ppmv) is 398.743×10^{-6} atm or 40.403 Pa, given 1 atm is 101,325 Pa, with a temperature and pressure sensitive Z-factor of about 0.025 for $[CO_2]$ at 10^{-5} molal concentration (10 μmolal) in seawater. This difference between fugacity and partial pressure is so small that the departure from ideality (0.3143%) can be neglected in the

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modelling carried out in this study. The fugacity is assumed to be equal to the partial pressure in atmospheres or pascals. The assumptions in our model regarding pressures and concentrations and even the field measurements possible are all subject to much larger variations, making such absolute accuracy unnecessary.

We have the following equalities for concentrations (C) and fugacity of CO_2.

$$[C_{air}]/Z_{air} = [C_{sw}]/Z_{sw} = f_{CO2} \approx pCO_2 \quad (3)$$

$$[C_{sw}]/Z_{sw} = f_{CO2} \approx pCO_2 \quad (4)$$

The condition of equal fugacity for air and seawater is expressed quantitatively by the Henry's Law coefficient (K_0) that gives the ratio of the molal concentration [CO_2] in solution to pressure of CO_2 (atm) in the atmosphere, assuming equilibrium between the phases.

$$K_0 = [CO_2]_{aq}/[pCO_2]\ atm \quad (5)$$

Obviously, the Henry coefficient (Ko) is synonymous with the Z_{sw} factor for the seawater phase; by contrast, the partition coefficient is given by the ratio of molal concentrations.

$$[C_{air}]/[C_{sw}] = Z_{air}/Z_{sw} = K_{aw} \quad (6)$$

It is important to understand that the Henry coefficient is not a partition or phase distribution function that indicates a ratio between the amount of substance in each phase (equation 6); instead, it is a means to indicate the concentration in water that sustains a certain pressure of a gaseous substance in the atmosphere at equilibrium. This definition has special significance for the processes modelled in this paper.

The Henry's coefficient can also be expressed as the inverse of equation (5), but Sander [13] in his comprehensive review for atmospheric scientists preferred the form given; multiplying the pCO_2 by K_0 obtains the molal concentration of CO_2 dissolved in water. For convenience in modelling of chemical species expressed as mmoles per kg of seawater, the Henry coefficient is usually estimated to give mM concentrations of CO_2 in solution.

2.2 Effects of temperature on physical K values

Regarding daily or seasonal oscillations in the abiotic equilibria shown in Figure 2, changes in temperature must be considered. The Clausius-Clapeyron equation [14] describes the strong effect of temperature on positions of chemical equilibrium, suggesting temperature effects on the concentration of CO_2 in warmer seawater. These fluctuating equilibria are also affected by the reduced pCO_2 in air subject to surface convective forces - or displacement by water vapor that can reach 10% of air volume under extreme conditions. Under warmer air conditions, the lower number density at constant pressure shown by equation (4) will give a lower chemical potential equilibrating with a lower concentration of CO_2 in seawater. The Henry coefficient is reduced at warmer temperature, while K_1 and K_2 governing formation of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) increase. Importantly for the hypotheses in this paper, the equilibrium shift in dissolved inorganic carbon away

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from CO_2 and toward increased carbonate is also accentuated by higher temperature, shown conversely by decreasing pK values. This process of carbon transport is further enhanced by a decrease in the solubility product (K_{sp}) with increasing temperature, reducing the amount of soluble carbonate needed in solution for precipitation; the relatively high stable concentration of calcium ions (Ca^{2+}, ca. 400 ppm or 10 mM) in sea water will lead to precipitation of crystalline calcite ($CaCO_3$) or at least small aggregates as carbonate increases to the point where its ionic product with calcium ions exceeds the current solubility product. For precipitation of calcium ions it is important to observe that the concentration of calcium ions (Ca^{2+}) in seawater has been estimated by Berner [15] with its activity only 20% of its molal concentration (ca. 10 mM). In this article, we will assume an activity of 0.20 for Ca^{2+} as estimates to allow ease in recognizing the variation in solubility with temperature.

The chemical potentials controlling equilibria for reactions between CO_2, bicarbonate, carbonate and calcite will be perturbed by increases in seawater temperature, increasing the equilibrium ratios of HCO_3^-/CO_2 and CO_3^{2-}/HCO_3^-, whilst decreasing the activity of hydroxyl ions, lowering pH. The ionic saturation product for the precipitation of $CaCO_3$ ($[Ca^{2+}]x[CO_3^{2-}]$) may also exceed the temperature-sensitive solubility product (K_{sp}). It is well established that the solubilities in seawater of anhydrous $CaCO_3$ and $MgCO_3$, counter-intuitively, decline with increasing temperature [16-19]; this property will cause accelerated formation of calcite or aragonite in late summer if carbonate ions are near saturation with respect to their solubility product with Ca^{2+} ions. This is particularly the case in the northern oceans where Keeling's observations were made. In principle, these feedbacks to increases in temperature could extract CO_2 into water, diminishing its pressure in the atmosphere at all altitudes in summer, explaining the well-known oscillations in pCO_2 noted at Mauna Loa in Hawaii [20]. The magnitude of the oscillation is predicted to be a direct function of the seasonal variation in seawater temperature.

The increasing trend in atmospheric CO_2 since the 19th century is also predicted to be a cause of the increasing acidity of the ocean's surface water [21], with the current anthropogenic emissions of CO_2 mainly responsible. A temperature-based oscillation in atmospheric pCO_2 would require that CO_2 is transported rapidly through the sea surface; this process is subject to rates of boundary layer dispersion as well as longer times for temperature variation − suggested as about a 3-month lag in the oscillation at Mauna Loa. The oscillation is much shorter at Point Barrow in northern Alaska where the surface freezes, holding seawater temperature constant until the thaw in June. The sea's surface pH is a function of the increasing atmospheric CO_2 activity, but also of all inputs of acidity and alkalinity into the ocean.

While warm water contains less dissolved CO_2, it is obvious that a loss of dissolved inorganic carbon (C) can be accentuated if carbonate ions precipitate with calcium ions (Ca^{2+}), reducing alkalinity (Ac). In principle, it should be possible to simultaneously withdraw CO_2 from the atmosphere while the solubility product of calcium carbonate is exceeded by the actual product of its ionic concentrations. For data collected from Mauna Loa and elsewhere [3,4] there is a striking seasonal oscillation in the ppmv of CO_2 relative to nitrogen, oxygen and argon. These air samples are dehydrated before gas analysis although daily evaporation of water will also partly control the number density of CO_2 in the atmosphere at the surface.

Based on these conjectures relying on variations in chemical potential, a testable thermodynamic hypothesis will be proposed. The focus in this article is on abiotic processes, though not to the exclusion of important biogenic processes such as calcification producing protons and soluble CO_2 as described by McConnaughey and Whelan [22].

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Thermal Hypothesis : Seawater temperature sufficiently affects chemical equilibria that its seasonal variations cause reversible exchanges between inorganic carbon of atmospheric CO_2 and calcite in seawater (Fig. 3).

This thermal hypothesis is illustrated in Figure 3 for seasonal oscillations in seawater surface temperature. Because of variation in positions of equilibrium at equalized Gibbs potential, DIC alkalinity not only increases in winter as calcite dissolves but the extra alkalinity is more predominantly carried in bicarbonate rather than in carbonate, requiring consumption of dissolved CO_2.

Seasonal assessments using observational platforms in the southern hemisphere show significant daily variations in carbonate chemistry with some biological activity in sub-polar latitude with more nutrients [6]. Also, it has been recognized that the pH of the seawater surface has been falling [7,8], claimed to be a result of the absorption and reaction of CO_2 in surface seawater with carbonate ions, increasing carbonic acid concentration. However, other processes may be at work. More recently, it was concluded that variability in ocean circulation and convection is also an important factor in exchange of CO_2 by the ocean [9], explaining some of the variation seen in the annual rise in oceanic CO_2. Here we will not consider such macroscopic processes. Rather, to help resolve issues of such global complexity, we focus on the mechanistic thermodynamics of interactions occurring at the boundary layers of air and land water. We advance a proposition capable of being tested that seasonal variations in temperature play an important role in establishing rates of abiotic exchange of inorganic carbon between the atmosphere and the surface.

Calcification by photosynthetic marine organisms is also favored by this scheme. The following equation (7) from McConnaughey and Whelan [22] emphasizing proton formation is favored by the variations in Figure 3.

$$Ca^{2+} + HCO_3^- \leftrightarrow CaCO_3 + H^+ \quad (7)$$

They also explain that the acidifying protons are needed to generate soluble CO_2 needed for photosynthesis.

$$HCO_3^- + H+ \leftrightarrow CO_2 + H_2O \quad (8)$$

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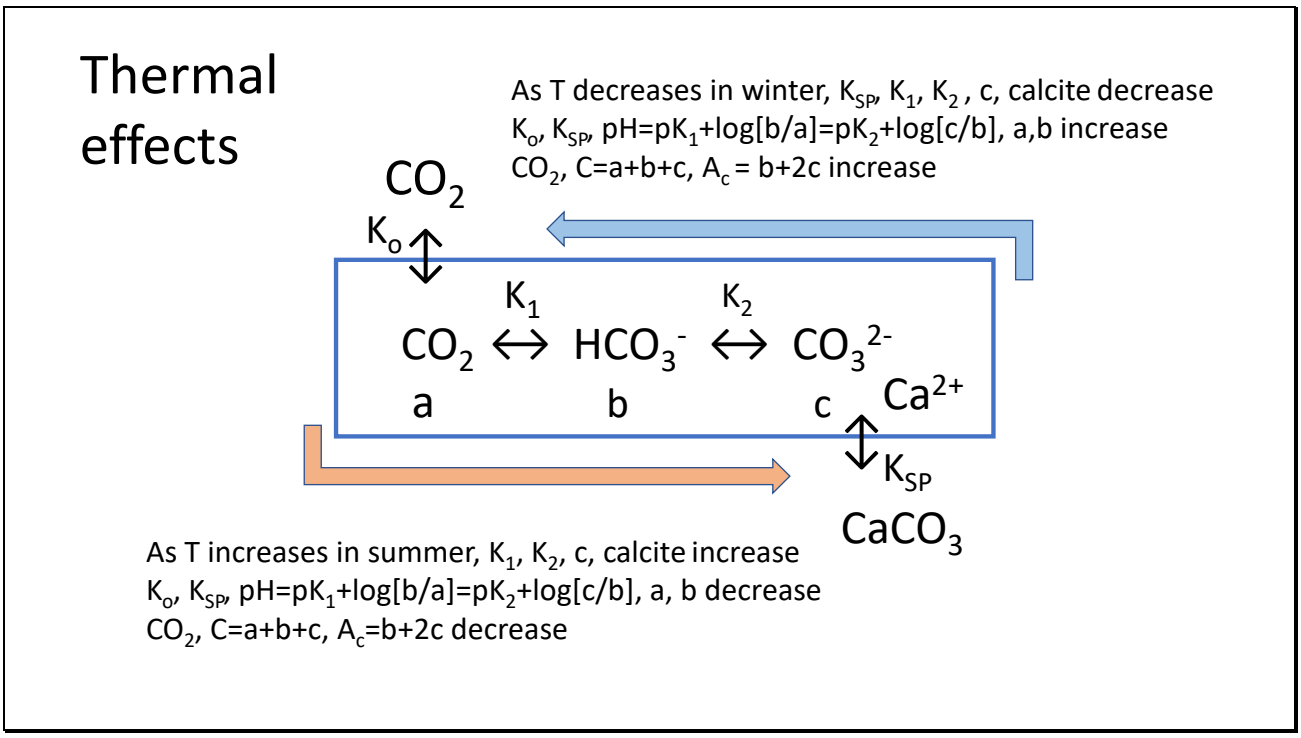

Figure 3. Variations in thermodynamic constants with temperature are proposed to favour precipitation of $CaCO_3$ in summer coupled with absorption of CO_2 from the atmosphere. In winter, the process is reversed, for example dissolving calcite (x moles) and releasing CO_2 (y moles), with calcite dissolution in colder water exceeding CO_2 emissions ($x > y$).

Although a comprehensive account of calcification is discussed, no mention is made of any role for variation in temperature. The thermodynamic stoichiometry of reactions (7) and (8) may be questioned, although the overall reaction favoring emission of CO_2 is qualitatively correct. Recent data from Zarkogiannis et al. [23] showed that planktonic foraminifera from the central Atlantic Ocean had larger, denser shells in cooler water compared to tropical, possible a result of reduced competition for calcification. However, according to Raven et al. [24] it is unlikely that biogenic calcification has a thermal factor given the rapid diffusion of heat in marine organisms because of their high ratio of surface to volume, unless some special internal metabolic apparatus exists. We will show that higher temperatures favor proton and carbonate formation from bicarbonate by increased K_1 and K_2 values and calcite precipitation as a result of decreased K_{sp}. Thus, in warmer climates, abiotic calcification is predicted to be favored as part of our proposal.

Consistent with this hypothesis, the possible effect of summer warming on precipitating calcite is shown in Figure 4, showing increasing values for the Omega supersaturation based on calcium ion concentration as temperature rises, as carbonate alkalinity.

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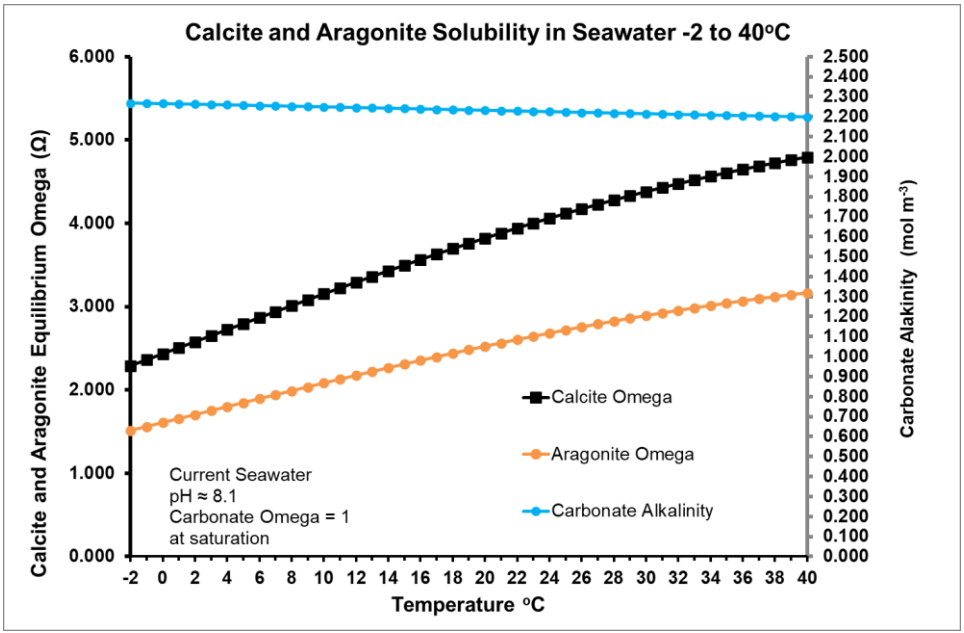

Figure 4. Estimated variation of calcite and aragonite solubility in seawater from -2- 40 °C for year 2022 CE and Keeling pCO_2 of 421 ppm

3. Materials and Methods

3.1 Modelling strategy

To perform numerical modelling of the control of fluctuating partial pressure of CO_2 by the physico-chemical seawater environment it is essential to define certain principles. First, these must include a definition for conservation of mass related to seawater. Such a constraint must still have flexible limits, given there are multiple sources for intermediates such as CO_2. The expression in Figure 2 relating inorganic carbon includes the dissolved forms of CO_2 but it allows fluctuations in atmospheric CO_2 under colder conditions when $[CO_2]_{sw}$ as defined by the larger Henry coefficient. So, the conservation of mass is defined within the limits given in the following equation. Note that variations in solid calcium carbonate as crystals has an indeterminate value thermodynamically, with unit activity as anhydrous calcite. For modeling, we usually refer to calcite because the method to estimate solubility is for this anhydrous product, although the more soluble hydrated form of aragonite could also be involved.

$$C_T = (CO_2)_{atmosphere} + [CO_2]_{sw} + [HCO_3^-]_{sw} + [CO_3^{2-}]_{sw} + [CaCO_3]_{solid} \quad (9)$$

Second, for the model we designate as Thermal, we need to define the set of fluctuating functions that define positions of the interacting equilibria. None of these K values following are constant in the environment.

K_o = $[CO_2]/f_{CO2} \approx [CO_2]/[pCO_2, atm]$ relating the CO_2 dissolved in seawater and air

K_B = $[B(OH)_4^-][H^+]/[B(OH)_3]$ for borate alkalinity

$K_w = [H^+][OH^-]$ for dissociation of water

$K_1 = [H^+][HCO_3^-]/[CO_2]$ for interconversion of CO_2 and bicarbonate

$K_2 = [H^+][CO_3^{-\Omega 2-}]/[HCO_3^-]$ for interconversion of bicarbonate and carbonate

$K_{sp} = [Ca^{2+}][CO_3^{2-}]$ as solubility product of calcite or anhydrous $CaCO_3$

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Equations to calculate bicarbonate, carbonate (and even pCO_2) are given in terms of these equilibrium (K) values and hydrogen ion concentrations [12], but these equations can rely on a constant total value for dissolved CO_2, bicarbonate and carbonate, suitable for a confined laboratory sample of given volume and composition, but not for the open environment.

Third, the initial conditions for each model must be defined. For the Thermal model, these include variables such as regional seawater temperature, pH in the mixing layer, pCO_2 and others that may be held constant, such as salt concentration (3.50 g/kg) and calcium ions (varying relatively little from 10 mM) or the overall longer term annual trend rate for increasing pCO_2 from various sources. Variables such as $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]x[CO_3^{2-}]$ are outputs from the above K functions, responding to changes in temperature, alkalinity, pH and pCO_2.

The chemical reactions considered in this article are illustrated in Figure 2. The concentrations of dissolved CO_2, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) are calculated as mmoles per kg sea-water following oceanographic practice, with CO_2 gas pressure corresponding to ppmv expressed in atmospheres. In tables and graphs, the use of μmoles per kg for output is preferred and ppmv for ease of reading. For calculations, each meter depth (cubic meter) is assumed to contain about 1000 (near 1025) kg of seawater per square meter of surface, so approximately 1000 times molal values are given for each meter of depth, or some 65 times this amount for the surface mixed layer. The chemistry at greater depths is regarded as unchanging in the time scale of the study and is not considered relevant. This depth is regarded as representative of the mixed layer although it is recognized as varying from 20-30 m near the equator up to 100-200 m at high latitudes such as near Cape Grim Tasmania where convective and turbulent overturning occurs in much larger parcels of water [1].

3.2 Software

The model program coding called Thermal generated for this study is given in Supplementary Material. The algebraic logic of the programmable Texas Instruments SR52 was chosen for modelling purposes, because of its simplicity and ease of use. Rewriting this code given in Supplementary materials in higher level languages such as R, Mathematica, Python or Java is suggested for those interested in repeating this study, particularly for easier graphical illustration. There are at least 10 computing packages available for calculating key inorganic properties of DIC in seawater [25] based on the principle of setting input pairs of variables to particular values and then calculating all other values of interest.

The relevant literature is highly valued by us for its role in forming hypotheses and by supplying suitable algorithms for calculating changes with temperature in thermodynamic constants for seawater. These authors include Wells [15], Saruhashi [26], Pales [3], Gieskes [27], Pytkowicz [28], Mehrbach et al. [29], Ingle [30], Plath et al. [12], Mucci [16], Dickson and Millero [31], DoE [32], Millero [33], Millero et al. [34], Bailey et al. [35] and Watson et al. [36]. The methods described by Dickson and Millero were relied on for algorithms to calculate fluctuations in equilibrium constants with temperature, used in programming. The equation of Mucci [17] based on earlier research [12,18,29,30] was employed to establish the temperature dependence of the stoichiometric solubility constants of calcite. The values estimated for K_{sp} near $4.2x10^{-7}$ for calcite employed in the Thermal model, are two orders of magnitude larger than those given in textbooks for fresh water. Without the clear ideas expressed in these papers this article would not have been possible.

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To simplify numerical computation, the concentrations of intermediates were routinely abbreviated as is customary: [CO_2] as *a*, [bicarbonate] *b* and [carbonate] as *c*. A flow sheet for the Thermal model is shown in Figure 5. Periodic variations in values (mM) for carbonic alkalinity (A_c) and total inorganic carbon (C_T) were provided by reiteration in coding, allowing for changes in temperature or in emission reducing C, or absorption of CO_2 or variation in calcite content (varying A_c). Changes in factors such as pCO_2, concentration of CO_2, bicarbonate and carbonate can be programmed with versatility. For example, being able to calculate equilibrium constants with variations in temperature [31] enables [CO_2] and pCO_2 to be estimated from inputs of alkalinity, pK and pH values alone. Alternatively, pCO_2 and temperature changes can be used to generate values for alkalinity (A_c) and dissolved inorganic carbon (DIC) compounds (C). Given likely time delays in equilibration for atmospheric pCO_2 values with seawater [CO_2], the Henry coefficient was adjusted to 0.85 times its equilibrium value to allow the product of [Ca^{2+}] and [CO_3^{2-}] to exceed 1.0 for comparisons during cooling or warming processes.

Although the variations in equilibrium constants with temperature are regarded as accurate, environmental systems rarely reach equilibrium. While equilibrium is likely in the short term for carbonic reactants dissolved in seawater, it is difficult to predict the extent of disequilibrium where inorganic carbon passes from one phase to another at the water surface or in formation or dissolution of anhydrous calcite. In the Thermal model, where CO_2 passes from seawater to air, any disequilibrium can be simulated numerically by adjusting the value of the Henry's coefficient downwards so that the concentration in solution is slightly elevated reflecting for the lag time involved.

3.3 Solving Thermal carbonic concentrations

A key element in the programming was the use of a standard quadratic equation solution to find approximate values of bicarbonate concentration (b) as variations in pCO_2 and [CO_2] or alkalinity (A_c) occurred. This solution is based on the equality that $K_2/K_1 = ac/b^2$; $A_c = b+2c$, then equating the two relations with carbonate ion (c) as follows, solving bicarbonate or b as estimates for current new inputs of CO_2 (a) or alkalinity (A_c).

$$\text{Carbonate} = c = (K_2/K_1 a)b^2 = (A_c - b)/2 \,.$$

Then

$$(2K_2/K_1 a)b^2 + b - A_c = 0 \qquad (10)$$

This allows bicarbonate (b) to be obtained from the quadratic solution $x = \{-b \pm (b_q^2 - 4ac)^{1/2}\}/2a$, taking care not to confuse the quadratic factor b_q (+1) in equation (10) with the b for bicarbonate in the solution; in fact $x = [HCO_3^-] = b$ from solving the equation.

Each reiteration recalculated all constants and DIC species at the new temperature allowing direct computation of $a=[CO_2]$ from the Henry coefficient, estimating b and c using the new K_1 and K_2 values and then pH, total DIC (C) and alkalinity (A_c and A_t) before estimating CO_2 vented to the atmosphere with an equivalent transfer of calcite, recalculating a and the new value of bicarbonate (b) using a quadratic equation with the new alkalinity value Ac. This operation was regarded as occurring in an open system, with calcite dissolving and CO_2 being transferred within the water column more freely.

A preliminary analysis of the variation in key constants involved in modelling defined variations with temperature as shown in Table 1. The Henry coefficient varies strongly with temperature

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favoring a lower gas concentration in seawater $[CO_2]_{sw}$ compared to the equilibrium air pressure pCO_2 (atm) as temperature rises. Thus, the fugacity of CO_2 in solution increases with temperature. Note the wider range of values between 278 and 298 K for the Henry coefficient (K_0) in seawater compared to its equivalent Z_{air} coefficient changing CO_2 concentration in air proportional to temperature as predicted by the ideal gas equation, estimated using equation (4) for number density as moles per liter. The decreasing pK_1 and pK_2 values with increasing temperature means that the respective K_1 and K_2 values increase with temperature, increasing the equilibrium ratios of bicarbonate to CO_2 and of carbonate to bicarbonate.

This thermodynamic behavior increasing carbonate activity in summer in seawater is central to the main hypothesis given in this article. The variation in the dissociation of water (K_w) is also significant, contributing to the large variation in K_0. True neutrality in seawater at pH 7.0 appears to occur only near 280 K, coinciding with a maximum value for K_{sp}. Clusters of water molecules are larger in colder water, with reduced ionization shown by the ten-fold reduction in dissociation constant; this means that hydrogen ion activity measured as pH 7 is associated with a higher activity of hydroxyl ions in warmer water. The estimates [10] given for chemical potential in air (μ_{CO2} in J/molecule) are expected to be equal at each temperature to the seawater chemical potential, only necessary if in equilibrium.

Thermal

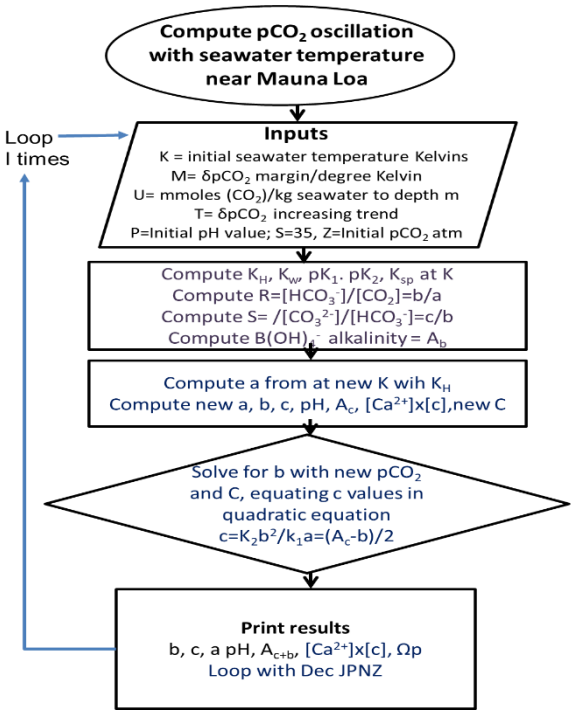

Figure 5. Flow diagrams for Thermal programs, generating changes in pCO_2 in response to changes in temperature. A copy of the code is provided as Supplementary Material or directly from the corresponding author.

The values generated using the program for K_o, K_1, K_2 and K_W at 25 ^oC, with a salt concentration index of 35‰ and 1 atm pressure are almost identical with those in the comparison made by Orr et al. [24] of the ten packages available that compute ocean carbonate chemistry.

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Table 1. Variation with temperature of key constants for modelling in seawater

Temperature K	C	$K_o=Z_{sw}$	pK_1	pK_2	K_w x10^{14}	K_{sp} x10^7 $[Ca^{2+}][CO_3^{2-}]$	Z_{air}	μ_{CO2} x10^{27} J	µM CO_2
278.15	5	0.05213	6.042	9.292	0.855	4.309	0.04382	-9.1660	21.90
283.15	10	0.04388	5.984	9.203	1.443	4.317	0.04304	-9.3482	16.34
288.15	15	0.03746	5.931	9.118	2.380	4.315	0.04230	-9.5307	15.73
293.15	20	0.03241	5.882	9.035	3.839	4.300	0.04158	-9.7135	12.20
298.15	25	0.02839	5.837	8.955	6.063	4.272	0.04088	-9.8966	11.92

4. Results

A preliminary model run (see Supplementary Material for programming details) tested how the pCO_2 pressures generated in the atmosphere might vary with monthly seawater temperature at Hilo, Hawaii (Big Island). However, the result in Table 2 of just over 1 ppm variation of pCO_2 in this temperature range of 2.2 ºC is too small to support a hypothesis that variations of 7 ppmv are possible. This possibility may have been considered previously by researchers in this area, then dismissed. Further, the model was run with constant pH − unnatural for the environment. Thus, some other variable factors need to be included before a thermodynamic explanation for the Keeling oscillation can be obtained. However, the observation in Table 2 that the relative ratio (Ω) of the saturation product for calcite ($[Ca^{2+}]x[CO_3^{2-}]$) over the solubility product (K_{sp}) exceeded 1.0 (shown bolded) at the warmest temperatures was a useful finding, helping to justify proceeding with this Thermal hypothesis. An early estimate for Ca^{2+} ion activity in seawater near 0.2 [15] has been assumed in this model analysis, but an exact value is not required since only the relative seasonal variation with temperature is needed.

4.1 Testing the Thermal Hypothesis

This hypothesis makes the novel proposition that changes in the temperature of seawater simultaneously affect chemical equilibria so that seasonal variations (Fig. 1) can cause reversible exchanges between inorganic carbon in atmospheric CO_2 and calcite in seawater, with a flux of inorganic carbon from seawater to the atmosphere in winter and its reabsorption forming calcite in summer. The hypothesis is tested in the knowledge that other factors including biota may also affect the CO_2 pressure and the formation or dissolution of calcite. A primary test of the hypothesis can be conducted in a computer model to examine covariation of these thermodynamic factors, successfully performed here. Other tests can be conducted in the laboratory, or the field using tools such as ^{14}C-labelled calcite to test variation in solvation discussed later. Table 2 shows variations in temperature and concentrations of intermediates suggesting precipitation of calcite for the relative ratio Ω greater than 1.0, as occurs in steps 5-12. No change in alkalinity was programmed, which is only possible if no acids are absorbed, giving constant pH value. Only slight changes in the solubility product occurs with change in temperature, slightly lower in summer when carbonate concentration reaches its maximum, facilitating calcite formation in this season

Thermal model: This numerical model outlined in Figure 3 first recalculates the effect of fluctuations in temperature on all equilibrium constants for the reactions in Figure 2 − the Henry's

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coefficient (K_o) for pCO_2, constants for reversible formation of bicarbonate (K_1) and carbonate (K_2) as well as the solubility product (K_{sp}) for calcite ($CaCO_3$). The intensity of the trend with temperature will be related to the rates of processes such as decreases in chemical potential or increases in entropy of CO_2 with temperature [10], as well as the rate of decreased solubility of calcite [27,34].

Table 2. Thermal modelling Jan-Dec showing DIC intermediates between CO_2 and calcite vary significantly with changes in regional seawater temperature at constant pH

CO2TIT1 Testing effect of temperature at constant pH and alkalinity Hilo Hawaii sea T									NOAA temperature data at website seatemperature				
a	CO_2	10.704	10.747	10.805	10.704	10.591	10.479	10.396	10.269	10.193	10.269	10.382	10.591
b	HCO_3^-	1740.338	1742.206	1744.689	1740.338	1735.337	1730.031	1726.513	1720.154	1716.958	1720.154	1725.879	1735.337
c	CO_3^{2-}	214.831	213.897	212.655	214.831	217.331	219.847	221.744	224.923	226.521	224.923	222.061	217.332
C	Sum	1965.873	1966.85	1968.149	1965.873	1963.259	1960.632	1958.652	1955.337	1953.672	1955.337	1958.322	1963.259
Ab	Borate+	2261.501	2261.215	2260.834	2261.501	2262.266	2263.034	2263.612	2264.579	2265.065	2264.579	2263.708	2262.266
Ksp		4.27E-07	4.27E-07	4.28E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.26E-07	4.26E-07	4.26E-07	4.27E-07	4.27E-07
K $[Ca^{2+}][CO_3^{2-}]$		4.25E-07	4.24E-07	4.2105747	4.25E-07	4.3E-07	4.35E-07	4.39E-07	4.45E-07	4.49E-07	4.45E-07	4.4E-07	4.3E-07
Ω	**Ratio**	**0.995306**	**0.990746**	**0.984688**	**0.995306**	**1.007539**	**1.019878**	**1.029202**	**1.044875**	**1.052774**	**1.044875**	**1.030762**	**1.007539**
pH		8.05	8.05	8.05	8.05	8.05	8.05	8.05	8.05	8.05	8.05	8.05	8.05
Temperature K		297.95	297.8	297.6	297.95	298.35	298.75	299.05	299.55	299.8	299.55	299.1	298.35
Total pCO2 ppmv		375.114	375.189	375.284	375.114	374.906	374.683	374.506	374.192	374.026	374.192	374.475	374.906
Ac		2170	2170	2170	2170	2170	2170	2170	2170	2170	2170	2170	2170

Run with Titrate (CO_2TIT1), allowing pCO_2 values to be calculated from pH, pK values and alkalinity (Ac). Results shown are modelled for seawater temperature variation at Hilo Hawaii from 24.45 ºC in March to 26.65 ºC in September.

However, this initial version of the Thermal model held pH constant. There is no reason pH need be constrained and the Thermal program was revised to allow pH variation.

4.2 Oscillation of pCO_2 on Mauna Loa

The model output in Figure 6 and Table 3 using the revised coding allowing pH variation shows how the intermediate equilibria are predicted to shift in seawater during cooling from the warmest seawater temperature of 299.8 K (26.65 ºC) in September to 297.6 K (24.45 ºC) in March, as measured nearby in Hilo, Hawaii. As a result of shifts in the equilibria with temperature varying 2.2 ºC, carbonate is predicted to decrease 6.2 µmoles per kg seawater, with bicarbonate and CO_2 increasing by 71 and 0.77 µmoles per kg respectively during cooling from September to April, dissolving calcite. The flux of CO_2 to the atmosphere from dissolving 2.5615 µmoles calcite per kg for each of 13 cooling temperature periods is predicted to be 2.1645 moles per square meter, emitted from some 65 tonnes of well-mixed seawater; this could occur more intensively from a lower volume nearer the surface. Calcite solubility increases as shown by the decline in the ratio for relative saturation (Ω) from 1.019 to 0.987 as seawater cools.

For simplicity, the model assumes that the variations of temperature and pCO_2 are periodic, but the results given are not designed as functions varying with time but as functions of change in temperature. The intention was to illustrate the effect of temperature variation on the scale of thermodynamic properties. However, the range of pCO_2 values and seawater temperatures do match those typically observed in the region, with the model calibrated to give a change of pCO_2 in air of 7 ppmv at Mauna Loa for each half-year; this included a longer-term superimposed upward trend of 1.8 ppmv per annum as shown in the Keeling curve (Fig. 1).

These predictions may need adjustment to local conditions and the oscillation in pCO_2 may be associated with a larger seasonal temperature range given the CO_2 mixing ratio in the atmosphere is derived from a larger area around Mauna Loa. For example, using the same program with a 5 ºC

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range between 292 and 297 K assuming the same dissolution rate for calcite to be emitted as CO_2, bicarbonate and [CO_2] increased by 107.8 and 1.6 μmoles per kg of seawater with carbonate decreasing from 296.3 to 261.3 μmoles per kg, about six times greater than the range of 2.2 ºC at Hilo. This demonstrates the sensitivity to temperature, including a lower winter and summer temperatures. Earlier research [35] on the effect of variation of temperature on the pressure of CO_2, perhaps perversely, claimed that warmer seawater from Woods Hole released more CO_2. However, that experiment used a closed system and observation was clearly a short-term result consistent with operation of the Henry's coefficient, reducing the amount of dissolved CO_2. In the field over a longer time span, the model predicts the now obvious alternative that CO_2 can flow reversibly *en masse* through an open system, becoming first carbonate and then mainly calcite, as seawater warms in a system near calcite saturation.

A role for marine biota in achieving the rates of these thermal adjustments in DIC cannot be excluded, provided sufficient growth nutrients exist. For example, precipitation of calcium carbonate by phytoplankton during photosynthesis is a normal function of their metabolism [22]. In Figure 2, alkalization as hydroxyl ion formation is shown as occurring during photosynthesis mainly in summer, by extraction of the substrate CO_2 from bicarbonate ions. In winter, this process is reversed, possibly increasing the rate of calcite dissolution. However, the model in Figure 3 proposes that the DIC equilibria shift towards carbonate and proton formation favouring calcification in summer, generating the higher CO_2 activity needed for photosynthesis while increasing the rate of calcification including that of the more soluble aragonite compared to calcite.

The model results shown in Figure 6 follow the observations for pCO_2 at 3200 m altitude on Mauna Loa very closely. The model assumes the actual monthly seawater regional temperatures measured at Hilo, generating the corresponding range of pCO_2 observations. It predicts corresponding values for alkalinity (A_c), total dissolved inorganic carbon (C) and individual activities of CO_2 (a), bicarbonate (b), carbonate (c), the pH value as well as the saturation of calcite (Fig. 4). The close quantitative correspondence of the pCO_2 and the temperature pattern and the feasibility of the inorganic process, even for such a narrow temperature range, suggests that the assumption of the oscillation being caused exclusively by imbalances between photosynthesis and respiration, mainly on land, should be rejected. Particularly in a maritime region where rates of processes vary little from temperature changes, biological processes on land for cycling carbon may be near balance, at the warm low latitudes of the Hawaiian Islands.

The full data set from testing this hypothesis in the Thermal model is also given as Supplementary Material. The primary data shown in Figure 6 unsurprisingly all give linear responses, since they are equal differentials in temperature. The actual time course of temperature for seawater at Hilo could be modelled, possibly giving a closer correspondence with time in field data, but with no material advantage. The testing of the physical hypothesis in the model shows it is consistent with the proposal. Experimental confirmation by actual laboratory and field studies under appropriate conditions is strongly recommended.

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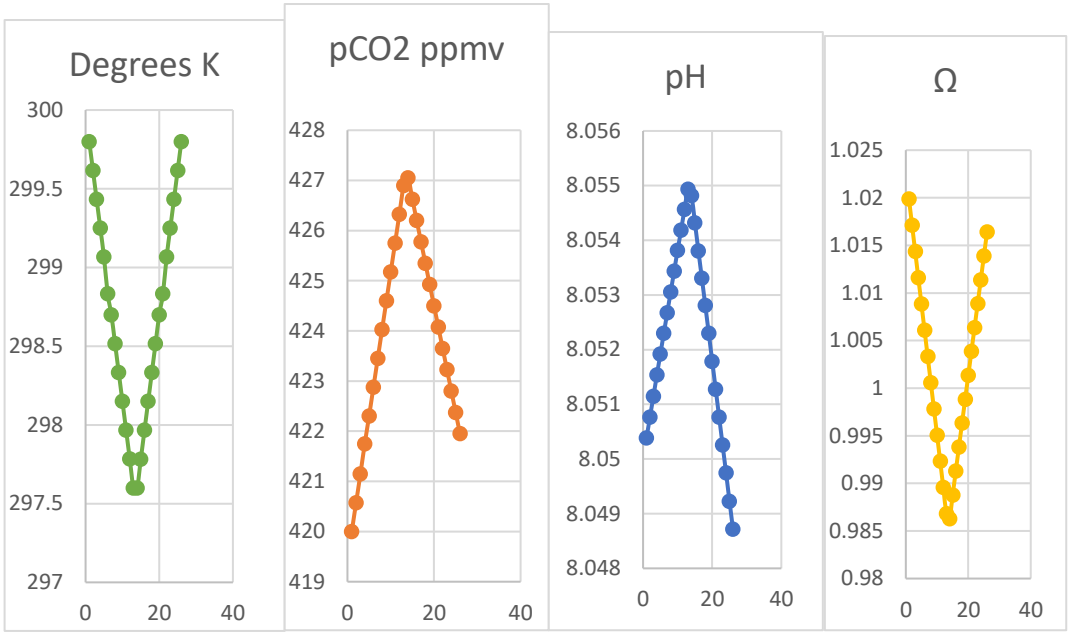

Figure 6. Variations from October to the following September in seawater temperature, pH and saturation (Ω) for calcite at Hilo and pCO2 on Mauna Loa for 26 periods per year (x-axis, temperature x time); only for temperature is the original condition regained. The x-axis indicates 26 iterations in temperature for 4.4 ºC variation in 12 months. Note that all factors other than temperature are asymmetrical caused by the ongoing trend in pCO_2 value; solubility of calcite increases 0.3% annually unless temperature increases.

We can also conclude from this analysis that the ocean surface layer must tend to equilibrate with the CO_2 level of the atmosphere, responding strongly to changes in surface temperature. This should be confirmed by satisfactory laboratory and marine field studies. Oscillations highly similar to that observed on Mauna Loa can be simulated. Greater variations in temperature more typical of middle latitudes in the Pacific ocean would magnify the variations shown in Figure 6.

Data shown in Figure 6 is also as the complete dataset in Table 3, for a 12-month period of 26 two-week periods commencing in October at the maximum water temperature. The scale is not time, but the segmented temperature. Two sets of data are shown, one for the effect of variation in temperature and a second for data generated after addition of a slug of CO_2. Full details of the program is given as listed in Supplementary Materials available on-line. Note from Table 3 that during the onset of winter that concentrations of both bicarbonate and CO_2 increase together with carbonate alkalinity (A_c) and DIC (C) while carbonate decreases, proportional to the temperature difference. In the subsequent summer season, all these results are reversed.

Although temperatures taken at Hilo were employed in the model, in fact the variation in pCO_2 in Hawaii obviously would be influenced by the seawater temperature covering a much larger area of seawater.

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Table 3. Thermal program model showing how seasonal variations in pCO_2 correlate inversely the variations in carbonate and calcite solubility. Data are shown graphically in Figure 4

UP	I=12,M=0.0000005,U=0.0025615,T=0.000000075,P=8.05,S=35,Z=0.00042								CO2MOD2					
	Mauna Loa		Manua Loa pCO_2 in response to seawater temperature at Hilo, Hawaii											
	UP	δT K	1	2	3	4	5	6	7	8	9	10	11	12	13
a			9.843	9.901	9.959	10.018	10.077	10.137	10.198	10.258	10.32	10.382	10.444	10.507	10.57
b			1658.081	1663.553	1669.042	1674.547	1680.069	1685.607	1691.163	1696.735	1702.325	1707.931	1713.554	1719.195	1724.852
c			218.753	218.235	217.716	217.195	216.674	216.151	215.627	215.102	214.576	214.049	213.521	212.992	212.461
C			1886.677	1891.689	1896.717	1901.76	1906.82	1911.895	1916.988	1922.095	1927.221	1932.362	1937.519	1942.694	1947.883
Ac			2095.597	2107.086	2104.474	2108.937	2113.417	2117.909	2122.417	2126.939	2131.477	2136.029	2140.596	2145.179	2149.774
Ab			2190.651	2194.795	2198.954	2203.127	2207.315	2211.518	2215.736	2219.968	2224.216	2228.478	2232.756	2237.049	2241.357
Ksp			4.26E-07	4.26E-07	4.26E-07	4.26E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.28E-07
K $[Ca^{2+}][CO_3^{2-}]$			4.33E-07	4.32E-07	4.31E-07	4.30E-07	4.29E-07	4.28E-07	4.27E-07	4.26E-07	4.25E-07	4.24E-07	4.23E-07	4.22E-07	4.21E-07
Ω			1.016673	1.013928	1.011184	1.008441	1.005698	1.002956	1.000216	9.97E-01	0.994737	0.991999	9.89E-08	0.986526	0.9837902
pH			8.05	8.05039	8.05077	8.05115	8.051537	8.05192	8.0523	8.05E+00	8.05306	8.05344	8.05E+00	8.05419	8.05457
Temperature K			299.8	299.617	299.433	299.25	299.067	298.833	298.7	2.99E+02	298.333	298.15	2.98E+02	297.7833	297.6
pCO2 ppmv			420	420.575	421.15	421.75	422.3	422.875	423.45	424.025	424.6	425.175	425.75	426.325	426.9
		δCO2													
a			9.857	9.914	9.973	10.032	10.091	10.151	10.211	10.272	10.334	10.396	10.458	10.521	10.584
b			1661.826	1667.304	1672.799	1678.31	1683.837	1689.382	1694.943	1700.521	1706.117	1711.729	1717.358	1723.004	1728.668
c			219.442	218.921	218.399	217.875	217.351	216.825	216.298	215.77	215.241	214.711	214.18	213.648	213.115
C			1891.125	1896.139	1901.171	1906.217	1911.279	1916.358	1921.452	1926.563	1931.692	1936.836	1941.996	1947.173	1952.367
Ac			2100.711	2105.146	2109.596	2114.06	2118.539	2123.032	2127.54	2132.061	2136.6	2141.151	2145.718	2150.3	2154.898
Ab			2195.776	2199.92	2204.078	2208.252	2212.44	2216.642	2220.86	2225.092	2229.34	2233.603	2237.88	2242.173	2246.482
Ksp			4.26E-07	4.26E-07	4.26E-07	4.26E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.28E-07
K $[Ca^{2+}][CO_3^{2-}]$			4.34E-07	4.33E-07	4.32E-07	4.31E-07	4.30E-07	4.29E-07	4.28E-07	4.27E-07	4.26E-07	4.25E-07	4.24E-07	4.23E-07	4.22E-07
Ω			1.019875	1.017115	1.014356	1.011598	1.008841	1.006085	1.00333	1.000576	0.997822	0.99507	0.992318	0.989567	0.986818
pH			8.05039	8.05077	8.05115	8.05154	8.05192	8.0523	8.05268	8.05306	8.05344	8.05382	8.05419	8.05457	8.05494
Temperature K			299.8	299.617	299.433	299.25	299.067	298.833	298.7	298.517	298.333	298.15	297.9777	297.783	297.6
pCO2 ppmv			420.575	421.15	421.75	422.3	422.875	423.45	424.025	424.6	425.175	425.75	426.325	426.9	427.475
DOWN	I=12,M=0.0000005,U=0.0025615,T=0.000000075,P=8.0482,S=35,Z=0.00042195								CO2MOD3					
	Mauna Loa		Manua Loa pCO_2 in response to seawater temperature at Hilo, Hawaii											
	DOWN	δT K	26	25	24	23	22	21	20	19	18	17	16	15	14
a			9.889	9.943	9.998	10.054	10.11	10.166	10.222	10.28	10.338	10.396	10.455	10.514	10.574
b			1658.89	1664.263	1669.652	1675.058	1680.481	1685.92	1691.376	1696.849	1702.338	1707.845	1713.368	1718.908	1724.466
c			217.955	217.49	217.025	216.558	216.089	215.619	215.148	214.675	214	213.726	213.349	212.771	212.291
C			1886.734	1891.696	1896.675	1901.67	1906.68	1911.705	1916.746	1921.804	1926.877	1931.967	1937.172	1942.193	1947.331
Ac			2094.8	2099.243	2103.702	2108.174	2112.659	2117.158	2121.672	2126.199	2130.74	2135.297	2140.066	2144.45	2149.048
Ab			2189.559	2193.735	2197.924	2202.127	2206.344	2210.575	2214.82	2219.08	2223.353	2227.641	2231.943	2236.259	2240.59
Ksp			4.26E-07	4.26E-07	4.26E-07	4.26E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.28E-07
K $[Ca^{2+}][CO_3^{2-}]$			4.32E-07	4.31E-07	4.30E-07	4.29E-07	4.28E-07	4.27E-07	4.26E-07	4.25E-07	4.24E-07	4.23E-07	4.22E-07	4.21E-07	4.20E-07
Ω			1.012961	1.010468	1.007975	1.00548	1.002985	1.00049	0.997993	0.995497	0.99299	0.990501	0.988003	0.985504	0.983004
pH			8.0482	8.04872	8.04923	8.04975	8.05026	8.05077	8.05128	8.05179	8.05229	8.05281	8.05331	8.05382	8.05431
Temperature K			299.8	299.617	299.433	299.25	299.067	298.833	298.7	298.517	298.333	298.15	297.783	297.967	297.6
pCO2 ppmv			421.95	422.375	422.8	423.225	423.65	424.075	424.5	424.925	425.35	425.775	426.2	426.625	427.05
		δCO2													
a			9.899	9.953	10.008	10.064	10.12	10.176	10.233	10.29	10.348	10.406	10.465	10.525	10.584
b			1662.535	1667.914	1673.309	1678.721	1684.15	1689.595	1695.057	1700.535	1706.03	1711.543	1717.072	1722.618	1728.182
c			218.693	218.226	217.758	217.288	216.816	216.343	215.869	215.393	214.916	214.438	213.958	213.478	212.995
C			1891.127	1896.093	1901.075	1906.073	1911.086	1916.114	1921.159	1926.218	1931.294	1936.387	1941.495	1946.621	1951.761
Ac			2099.922	2104.366	2108.825	2113.297	2117.782	2122.281	2126.795	2131.321	2140.419	2140.419	2144.988	2149.574	2154.172
Ab			2194.683	2198.859	2203.048	2207.252	2211.469	2215.7	2219.945	2224.204	2232.765	2232.765	2237.067	2241.384	2245.714
Ksp			4.26E-07	4.26E-07	4.26E-07	4.26E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.28E-07
K $[Ca^{2+}][CO_3^{2-}]$			4.33E-07	4.32E-07	4.31E-07	4.30E-07	4.29E-07	4.28E-07	4.27E-07	4.26E-07	4.26E-07	4.25E-07	4.24E-07	4.23E-07	4.22E-07
Ω			1.016395	1.013887	1.011379	1.00887	1.00636	1.00385	1.001339	0.998828	0.996316	0.993803	0.99129	0.988777	0.9862628
pH			8.04872	8.04923	8.04975	8.05026	8.05077	8.05128	8.05179	8.0523	8.05281	8.05331	8.05381	8.05432	8.05482
Temperature K			299.8	299.617	299.433	299.25	299.067	298.833	298.7	298.517	298.333	298.15	297.783	297.967	297.6
pCO2 ppmv			422.375	422.8	423.225	423.65	424.075	424.5	424.925	425.35	425.775	426.2	426.625	427.05	427.475

Run with CO2MOD2 (ascending temperature) and CO2MOD3 (descending temperature). Models assume temperature as K, initial pCO_2 values and rates of pCO_2 variations. Alkalinity (Ac, Ab) and dissolved inorganic carbon (C or DIC) is generated in the model thermodynamically.

4.2 Larger oscillations at Point Barrow, Alaska

The oscillation in pCO_2 measured by Keeling and colleagues on the northern coast of Alaska at Point Barrow is even more striking in its magnitude than at Mauna Loa (Table 3). The seawater temperature is almost constant for seven months of the year controlled by the effects of ice in brine (Fig. 7). The pCO_2 stays constant on a plateau during the winter period, only falling in late summer from July to December as seawater warms a total of 4.4 ºC. This pattern is claimed to represent stronger photosynthesis on the tundra in summer but it is also easily explained as a thermodynamic

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response to seawater temperature. The precise correspondence between temperature and changes in pCO_2 is striking, corresponding to the plateau effect. The variation in seawater temperature is twice that observed at Hilo nearest Mauna Loa, explaining the characteristic steeper gradient of pCO_2 in the summer months and a doubling of its magnitude.

The Thermal program was employed to model the effects of changes in temperature (Fig. 7). As for Mauna Loa, results were output twice at each stage shown in Supplementary Materials, once for each change in temperature and again when alkalinity was reduced from formation of calcite in warming water with atmospheric CO_2 declining or the in reverse when temperature to cooling. The primary data also show that the ratio of the corrected ionic product $(Ca^{2+}).(CO_3^{2})$ and the solubility product or the saturation constant (Ω) only exceeds 1.0 in the three summer months, suggesting that $CaCO_3$ is augmenting at the same time as the pCO_2 is falling. The result shown in Figure 7 is consistent with the longer-term trend for 1974-2009 [4] at Point Barrow.

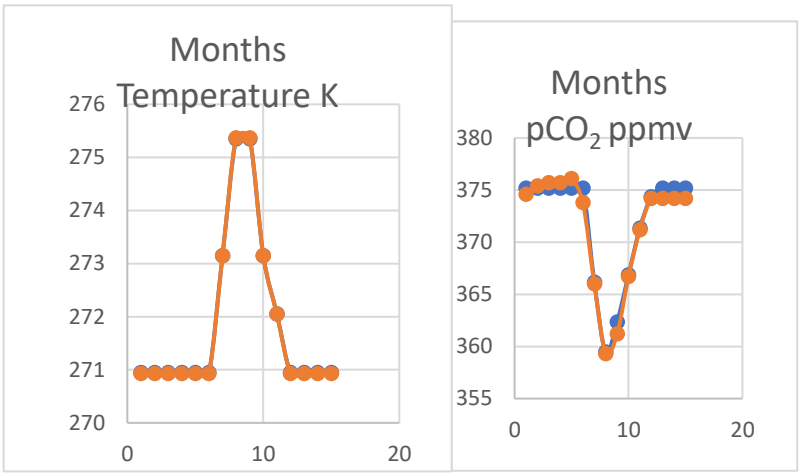

Figure 7. Coupled temperature (left) and pCO_2 (right) oscillations January to December at Point Barrow, Alaska showing a plateau in winter months falling in summer, consistent with modelled reduced solubility shown in Supplementary Materials. Thus, calcite is predicted to be dissolved when seawater is colder from November to June.

Using temperature data from Point Barrow as shown in Supplementary Materials, the model was run at a higher pH value of 8.26 consistent with Arctic conditions [37], automatically generating a much higher alkalinity under the much lower temperatures at Barrow. This is predicted to occur at the lower seawater temperature at Point Barrow near freezing. It is not certain, however, that calcite is the proper crystalline form of calcium carbonate formed under frigid conditions [37,38], where crystalline ikaite [38] may be formed; this is a hydrated form of crystalline $CaCO_3$ with a K_{sp} ten times less (ca. $6x10^{-8}$), showing it could be more easily precipitated with less alkalinity. Ikaite is regarded as too soluble to precipitate at warmer temperatures [38]. Takahashi and Olafsson [39] showed that at the onset of summer there is a rapid onset of photosynthesis at the thaw consuming nutrients of nitrate and phosphate rapidly but the consumption of CO_2 they observed of 100 μmoles per kg corresponding to Redfield values for nutrients only accounts for about half the diminution in pCO_2 in air per square meter that continues to decline after the nutrients are exhausted, rising again as seawater freezes.

4.3 Comparing Cape Grim, Tasmania and sites at Mauna Loa and Point Barrow

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Although similar seasonal oscillations in pCO_2 for greenhouse gases have been observed in the southern hemisphere at Cape Grim on the north-western corner of Tasmania [1], these are lower than the annual trend curve for increasing CO_2, in contrast to those in the northern hemisphere, particularly in the Pacific basin. The mean seawater temperature near Cape Grim is lower at 14.8 °C than at Hilo, Hawaii where it is 28.4 °C, but higher than at Point Barrow near freezing (Fig. 7).

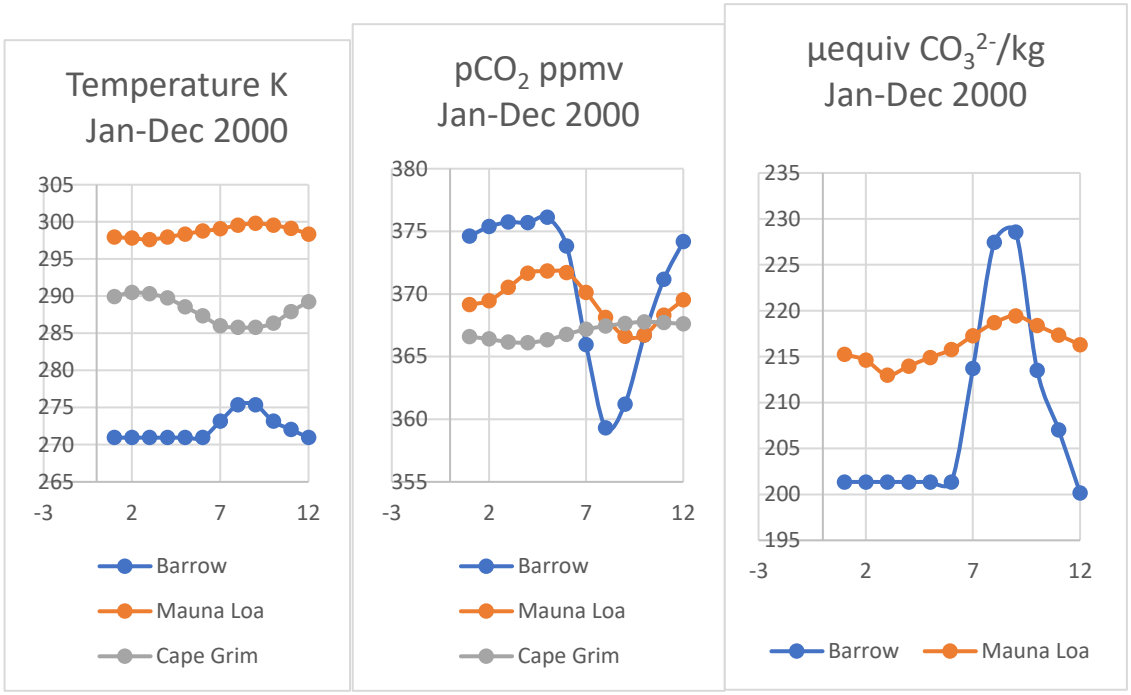

Figure 8. Comparison of actual data recorded for seawater temperature and pCO_2 and carbonate estimated in Astrocal Thermal for seawater at Point Barrow, Mauna Loa (Keeling et al., 2009) and near Cape Grim (CSIRO) at Smithton, Tasmania.

4. Discussion

In 2003, Zeebe and Westbroek [40] defined a simple model for the $CaCO_3$ saturation states of the ocean, demonstrated by actual inorganic precipitation as shown in 'whitings', or as by biogenic shallow water precipitation with settling under gravity or as of low precipitation, remaining effectively in solution. Their analysis applied to past and present saturation states was very useful, pointing to a predominance of the latter. However, there was no discussion of seawater temperature and its effect on these states. In this article, we draw attention to what might be considered a fourth active state preserving mass but defined by oscillation in temperature. Restricted to the mixing zone, it presents an intermediate condition of variable augmentation, probably insufficient to be called precipitating and settling under gravity with some degree of variable buoyancy. The extent of augmentation of calcite in summer or dissolution at a maximum would be little more than 1% of the DIC, near analytical sensitivity. Yet this would be sufficient to explain the scale of seasonal oscillation in the atmosphere of some 2 moles of CO_2 moles per m^2 of the Earth's surface.

4.1 Deciphering the Station ALOHA data set

Estimates of the calculated pCO_2 either directly by equilibrated gas phase infra-red measurements [41] or by calculation using formulae show major variation in values where biotic activity is likely to be

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high, as in coastal sampling. Nevertheless, the Station ALOHA dataset (see section 3. In Supplementary Materials, NCCARF replot for 1989-2010 data) show peaks in [CO_2] in seawater in late summer, with minimum pH values at the same time as the atmospheric pCO_2 is minimal. Peak pCO_2 in air occurs in late winter, although there is a preceding small pause in solar mid-winter. In our Thermal model, inputs of carbonate from dissolution of calcite resulted in equivalent increases in DIC alkalinity (A_c) in winter. The input in terms of dissolved carbonate against pCO_2 of the atmosphere takes into account a surface layer of 65 m with about 65,000 kg of seawater. Each iteration increased pCO_2 of 0.5 ppmv per iteration, equal to 2.5615 μmoles CO_3^{2-} assuming that each 1 ppmv in air was equivalent to 0.333 moles of CO_2 of 140 moles total per square meter. Millero [33] pointed out the difficulties of obtaining accurate pH values in seawater, stressing the need for measurements to be performed under environmental conditions of temperature and pressure where samples were taken.

It is clear from the subtropical Station ALOHA dataset that biogenic processes at the sampling sites dominate when the pCO_2 from seawater data is compared to the atmospheric pCO_2. This result reflecting the [CO_2] activity as potential pCO_2 in seawater reaches a maximum in midsummer when the atmospheric pCO_2 value approaches its least value, with maximum pH values. Minimum values in seawater of [CO_2] or fCO_2 in midwinter may reflect consumption of CO_2 as H_2CO_3 reacting with carbonate from dissolving calcite at the lower temperature, shown in equation (11).

$$\begin{aligned} CaCO_3 &\rightarrow Ca^{2+} + CO_3^{2-} \\ H_2CO_3 + CO_3^{2-} &\rightarrow 2HCO_3^- \end{aligned} \qquad (11)$$

This is consistent with the highest pH values in the ALOHA dataset on removal of CO_2 as carbonic acid The high CO_2 concentration just as the spring-summer photosynthesis increases ensures that the pH value will be lowered in spring. As shown in this article, the general correlation is that each change of 10 ppm in pCO_2 corresponds to a pH change of 0.01 units, although the biotic variations in these factors are greater than those predicted for abiotic reactions (Fig. 6). Just as biotic photosynthesis increases in early summer, there could also be a rapid decrease in pH value as CO_2 is released as carbonic acid from the bicarbonate pool and calcite clusters augment with sufficient warming.

$$\begin{aligned} 2HCO_3^- &\Rightarrow H_2CO_3 + CO_3^{2-} \\ &\Rightarrow H_2O + CO_2 \\ Ca^{2+} + CO_3^{2-} &\Rightarrow CaCO_3 \end{aligned} \qquad (12)$$

This biological pH shift will contribute to increased carbonate ion activity in summer and in the solubility index (Ω), as is predicted for abiotic processes in summer. It may be difficult to quantitatively separate the thermodynamic effects of the two calcification processes, biotic and abiotic, with both contributing to a depletion of atmospheric CO_2 in summer as calcite or aragonite is precipitated, an issue to be further discussed. For rapid transfer of CO_2 from the atmosphere, the rate of increase in fugacity of CO_2 in seawater should be greatest as the pCO_2 in the atmosphere is maximal, consistent with the rapidly falling pH, just as the predicted equilibrium value in Figure 6 reaches a maximum. A test of this scheme requires sufficient dissolved CO_2, possibly augmented by respiration in seawater of organic carbon. However, direct correlation between field data for seawater and thermodynamic properties would be impossible, given the significant time lags from each process. Still, it is noteworthy that the pCO_2 at Mauna Loa falls slightly just before midwinter as CO_2 is consumed to convert carbonate to bicarbonate, as is required in the

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Thermal model and equation (11). It is proposed also that CO_2 within the surface seawater layers could be sufficiently mobile by diffusion between the mixing zone and water slightly deeper. Given a difference in chemical potential caused by the variation in surface temperature its diffusion will be accelerated. A variation of less than 2% in the chemical potential of $[CO_2]$ for 5 ^oC difference (Table 1) could cause a significant flow of dissolved CO_2 sufficient to overcome this difference. Given that chemical potential is a logarithmic function of concentration, this temperature difference would require a doubling of the CO_2 concentration. Alternatively, as mentioned previously, in winter respiration fueled by organic carbon fixed in the previous summer can provide the CO_2 required.

4.2 Interpreting stoichiometry of reaction between bicarbonate and calcium ions

Smith [42] and others have questioned the stoichiometry of the qualitative calcification reaction (13) as stated in [22].

$$Ca^{2+} + 2HCO_3^- \Rightarrow CaCO_3 + CO_2 + H_2O \quad (13)$$

In effect, equation (13) links photosynthesis to the formation of $CaCO_3$ so that carbonic acid yields carbohydrate plus oxygen. An extensive analysis of field data suggested that the following equation was more appropriate.

$$Ca^{2+} + (1 + \Psi)HCO_3^- + (1 - \Psi)OH^- \Rightarrow CaCO_3 + (1 + \Psi)CO_2 + (1 + \Psi)H_2O \quad (14)$$

The Ψ factor was found [42] to be around 0.6. If 100 μmol per kg of calcite was precipitated from water with known values of C and A_c and then returned to that water's starting pCO_2. This precipitation reduces alkalinity by 200 μmoles per kg and the pCO_2 of the water at a given temperature rises, then degasses to reach the previous value. That is, the system is constrained by equilibrium with pCO_2.

By comparison, a similar approach with respect to the effect of variation in temperature, a factor not considered by Smith is materially different. The need to allow for the extra alkalinity A_c requires the temperature induced increase in bicarbonate and decrease in carbonate be included. The decrease in the carbonate in colder water as K_2 decreases is equated to Ψ, but sufficient CO_2 must react to convert all the dissolved carbonate from calcite plus the diminished carbonate in the seawater pool to bicarbonate. Carbon dioxide could be rapidly diffusible from lower in the seawater profile, responding to a thermodynamic force, effectively consuming $(2 + \Psi)$ molecules of CO_2 to vent one to the atmosphere and converting carbonate to bicarbonate.

$$Ca^{2+} + 2(1 + \Psi)HCO_3^- <=> CaCO_3 + \Psi CO_3^{2-} + (1 + \Psi)CO_2 + (1 + \Psi)H_2O \quad (15)$$

As shown, reaction (15) indicates the summer process releasing CO_2. However, paradoxically the reaction consuming CO_2 in winter that we propose also raises the $[CO_2]$ concentration in seawater and thus the pCO_2 in the atmosphere more likely results from a mutualistic or even symbiotic process between biotic and abiotic reactions. The CO_2 required in winter to absorb the alkalinity (A_c) converting carbonate to bicarbonate is proposed to be from biogenic oxidation of organic carbon or detritus in the oxic zone near the surface or from anaerobic respiration with inorganic sulfate as the most prevalent oxidant in deeper seawater. This process of generation of carbonic acid naturally reduces the pH value of seawater but its consumption in converting carbonate to bicarbonate restores the pH value as more alkaline.

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The magnitude of (1 + Ψ) for the Thermal model corresponds to the variation in temperature. If there is no variation in temperature as examined by Smith [42], the ratio of bicarbonate to carbonate is less affected and consequently less CO_2 is required to allow for a change in in alkalinity. The Ψ factor is by no means a constant as Smith shows but varies to some extent with environmental conditions such as seawater depth as well as the presence of other buffering systems, such as borates or phosphates. If a mutual relationship between bioorganic and inorganic processes is responsible for much of the seasonal oscillation it is not surprising that this proposal has been slow in its understanding. These seasonal reactions in winter and summer involve consumption and release of CO_2 in seawater could also be responsible for the larger seasonal excursions in seawater pH values. Although the summer reaction with decreasing A_c alkalinity generates decreased pH values, this will be accentuated by the significant release of CO_2 as calcite augments. In winter the increased pH value observed in the modelling from October to May will also be greater as a result of the consumption of CO_2 generated biogenically. This conclusion is consistent with 'snapshot' ALOHA Station data that show a maximum in [CO_2] and lowest pH in seawater in summer, favoring photosynthesis and a minimum in [CO_2] and maximum pH in winter; this suggests the consumption of CO_2 in the reverse reaction with carbonate by equation (15) and significant escape to the atmosphere with a thermodynamic potential for [CO_2] supporting a higher atmospheric pCO_2.

4.3 Absence of similar data in the southern hemisphere

As at Mauna Loa, it is widely claimed that the smaller oscillation is consistent with less photosynthesis in the southern hemisphere, with greater ocean surface but less area of littoral zones. However, the regularity of the close correlation between maximum temperature and minimum pCO_2 values as well as the estimates for maximum concentrations of carbonate (Fig. 7) suggesting saturation and calcite formation is striking. A predominance of photosynthesis over respiration in late summer in warmer water may seem reasonable, but this is a weak hypothesis difficult to disprove. Little specific evidence from measurement of photosynthesis either from surface or satellite data in support can be cited, or on the tundra near Point Barrow. Despite the expectation that the large close of global industry during the Covid-19 pandemic, no clear effect on the progress of the signals from Mauna Loa or Point Barrow has been reported. A more precise physico-chemical explanation producing such regular phenomena at multiple sites should be preferred, consistent with Occam's principle.

The smaller magnitude of the oscillation at Cape Grim needs a physical explanation. Despite the Earth receiving more insolation in the southern hemisphere summer being closer to the sun at aphelion, it receives less in the southern hemisphere winter; the range of southern ocean surface temperatures from Ceres satellite data [43] is about 4.7 ^oC versus 7 ^oC in the northern ocean. Isolation at the top of the atmosphere is less variable in the northern hemisphere and of higher average intensity. This is consistent with the range in pCO_2 and hence calcite precipitation being twice as much comparing Barrow with Mauna Loa, but the air temperature range at Cape Grim is about the same as near Barrow, although Cape Grim is considerably warmer. Other factors such as the poise of carbonate concentration with respect to saturation (Ω) may be involved to explain the hemispheres differences. Given that the northern hemisphere ocean basins are significantly warmer but oscillating more strongly in temperature near freezing in polar conditions as at Point Barrow, there may be an inherent inability to concentrate the base level of carbonate in the southern hemisphere. Such repeated freezing and thawing is an effective means of increasing concentration of solutes as the proportion of liquid water declines.

The mixing layer in the Southern Ocean extending to Antarctica is buffeted with higher wind speeds and its surface convection is therefore deeper than in the northern Pacific Ocean [1]. As shown in Table 2,

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calcite is more soluble at lower temperatures so accumulation of a higher alkalinity at Point Barrow is possible. It is proposed that the absence of strong seasonal oscillations in pCO_2 at Cape Grim is explained by the relative absence of a seasonal calcite-CO_2 cycle rather than a small disparity between photosynthesis and respiration. Field experimentation is warranted to test the thermal variation hypothesis near Cape Grim, examining the scale of any reversible calcite formation that is predicted to be smaller than at Hilo or Point Barrow.

4.3 Weighing the available evidence

The thermal hypothesis regarding variations in pCO_2 we present in this article is novel. Furthermore, the demonstration that all the key equilibrium constants vary seasonally in a manner supporting its main thesis of calcite formation and CO_2 absorption in warmer waters reducing alkalinity in summer and a seasonal reversal dissolving calcite increasing alkalinity and releasing CO_2 in winter is also novel; no published cases drawing attention to this inorganic thesis are known to the authors. These predictions are consistent with the global field results reported by Takahashi et al. [44] who found that widespread observations of the ocean surface show lower alkalinity in summer, particularly in the northern hemisphere as at Point Barrow, as expected if calcite is precipitated. Other measurements reported by Takahashi et al. such as reduced DIC and increased Ω in summer also agree with the Thermal model's prediction. However, their lower calculated pH values in winter are at variance with the predicted result in Figure 5, where pH is more alkaline as anticipated in a solution with more alkalinity. This suggests a possible flaw in either the calculation or the Thermal model such as respiration in winter that should be investigated.

Assessment of seasonal carbonate cycles in the Southern Ocean differ from those in the northern hemisphere oceans [6]. Below the Antarctic circumpolar current the annual mean pH observed with Argo robots is 0.03 units lower and the pCO_2 of seawater higher. Winter upwelling of DIC and alkalinity may be in part a temperature effect, signaling dissolution of calcite. This novelty regarding thermal effects is despite demonstrated understanding of the physical chemistry of the DIC inorganic reactions involved, published widely in IPCC reports. The key omission is failure to understand how the individual chemical reactions can couple in a concerted manner to achieve this result. Variations in these constants including the Henry coefficient with temperature is likely to be critical information in explaining large scale releases or absorption of CO_2 as ocean currents move between different latitudes. While the proposal regarding inorganic calcite precipitation from seawater in summer is novel this will be no surprise to chemical engineers who deal with serious scaling from $CaCO_3$ precipitation from hard waters, just as observed in kitchen kettles.

This possibility does not exclude significant biological reactions forming $CaCO_3$ in summer and releasing net CO_2 in winter of even greater magnitude, but only if sufficient nutrients for biota are available. A significant scale for the difference between biotic CO_2 assimilation in summer by photosynthesis and its respiratory emission in the colder season lacks quantitative evidence. All plants respire 24 hours a day and there is a large respiratory burden for biosynthesis during the growing season. Respiration by plants in winter should be much diminished, given the lower rate of dry matter accumulation. Whether the excess of respiratory formation of CO_2 in winter over assimilation by photosynthesis required in winter is sufficient to explain the oscillation has not been determined.

The second novel demonstration in this article is how dependent inorganic calcite formation is on absolute temperature. The mean temperature of the Earth's surface is close to 288 K in a zone where seasonal oscillation in inorganic calcite is likely, although regional variation in total alkalinity (A) and DIC content (C) can mean that precipitation is still possible across a wider range of temperatures. Although

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the solubility product for calcite and other forms of $CaCO_3$ is only slightly responsive to temperature (Table 2), the strong seasonal shifts of the DIC reactions towards increasing $[CO_2]$ in winter and carbonate in summer for thermodynamic reasons is the main basis of the thermal hypothesis.

The global rate of inorganic precipitation and dissolution of $CaCO_3$ is not well established. Although biotic calcification is probably more rapid while sufficient nutrients (P, N, etc.) for growth are available, the relative contribution of the two modes of calcification to geological limestone formation is unclear. However, Burton and Walter [45] demonstrated significant rates of aragonite and calcite precipitation from supersaturated seawater as a function of increasing temperature, with the former predominant above 5 ºC, some four times greater at 25 ºC at the same saturation. Their data suggests a rate of laboratory precipitation of about 1 mole of $CaCO_3$ per fortnight per g of crystal seeds, each 3 g shown to exhibit about 1 m^2 of surface area. About 50 µg of crystal seeds per kg of seawater (i.e. 0.5 µmoles $CaCO_3$) could be sufficient to explain the absorption of 2 moles of CO_2 in the summer season. Concern [46] that particulate inorganic carbon might decrease with increasing pCO_2 providing negative feedback affecting CO_2 uptake by the ocean is one indication how much this gap in knowledge on rates of calcite precipitation is.

Conversely, a study of dissolution of calcite above the 100% saturation horizon [47] was considered as contrasting with the conservative paradigm of pelagic $CaCO_3$ at shallow water depths, with $11.1x10^{12}$ moles C estimated to be dissolved annually in the Atlantic Ocean, an area of $1.065x10^{12}$ m^2. The oscillation of 2 moles per m^2 recycling as an upper limit for the Keeling oscillation is not unreasonable in this context. Gattuso et al. [48] found in association with corals that inorganic calcification of aragonite increased nearly 3-fold when its saturation increased from 98% to 390%, however they failed to consider the effects of oscillating temperature in their study. Buitenhuis et al. [49] estimated global ocean primary production as about 13 moles C per m^2 annually, in which an annual oscillation in both hemispheres of 1-2 moles per m^2 can readily be accommodated.

Neither of these properties related to seasonal shifts in equilibria including for the solubility product for calcite has previously been considered in reviews of the seasonal oscillation in the Keeling curve, although Feely et al. [50] observed significant seasonal variations in saturation ratios in surface calcite and aragonite in the northern hemisphere, with a maximum in summer. Despite $[CO_2]_{sw}$ being predicted to be lower in summer from venting to the atmosphere by the large change in the Henry coefficient K_o, the variations in constants K_1 and K_2 allow $[CO_3^{2-}]$ to increase in summer despite the lower $[CO_2]$. In winter, negative feedback changes in constants K_2 and K_1 ensures that $[CO_2]$ increases sufficiently to support a higher atmospheric pCO_2. The maximum of DIC measured in seawater at 6 m depth in winter is also consistent with the model of calcite dissolution, although the authors suggested that this observation was a result of the entrainment of high subsurface waters. Their results do not prove this conclusion compared to the effect of the decline in water temperature in winter on $CaCO_3$ solubility. Although capable software allowing most aspects of the complex inorganic chemistry of carbon to be understood, modelling programs have generally failed to predict correctly the significant abiotic seasonal oscillation in calcite concentrations. Too many of the calculations related to concentrations of DIC intermediates and pH rely on formulae that may fail to consider the subtle changes in alkalinity and total DIC resulting from precipitation and dissolution of calcite.

This article pays less attention to the scale and important role of biological effects on pCO_2 such as those considered in Fransner et al. [51], studying the effect of nutrients on pCO_2 drawdown in the Gulf of Bothnia in the northern Baltic Sea. However, their observation that primary production needed to reproduce the observed drop in pCO_2 exceeded that they estimated in their study by up to 400%. Rather than adopting their hypothesis-saving suggestion that organic carbon production was underestimated,

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significant absorption of CO_2 in crystalline $CaCO_3$ would better explain their observations. To some extent, there may be confusion regarding the use of estimated 'pCO_2' values using pH and alkalinity (A_t) or DIC (C_T) calculated using formulae based on estimates of [CO_2]. These show discrepancies between predicted and actual atmospheric pCO_2 values that probably only partly result from the lack of equilibrium between CO_2 in seawater and air. Furthermore, we have earlier remarked how the seasonal oscillation in pCO_2 and hence of calcite in seawater at Point Barrow is best explained by a combination of biotic and abiotic processes, allowing initial rapid CO_2 assimilation by the unusually high nutrient loads (N and P) in melting Arctic seawater. A combination of unlinked biotic and abiotic processes must also ensure measurements of intermediates cannot match any simple model. The IPCC report [3] concludes that the relatively minor seasonal oscillation in pCO_2 in the southern hemisphere (Figure 7b) may result from a poorer nutrient status in the Southern Ocean, particularly in iron, therefore supporting less photosynthetic activity than the ocean of northern latitudes.

This conclusion is consistent with the greater prevalence of land masses above the equator with greater runoff from rainfall into surrounding littoral zones. However, the saturation index for precipitation of calcite is also favored in northern latitudes given the greater prevalence of runoff from rivers of calcium and DIC into the northern ocean basins. The alkalinity and total DIC is known to be greater in northern oceans, particularly nearer the pole. Much greater river runoff also decreases the salt content of northern ocean surface waters, leading to a significant decrease in the solubility product of $CaCO_3$, meaning calcite is likely to be formed at a lower concentration of carbonate ions. These factors governing abiotic calcite formation also favor pCO_2 oscillation in the northern hemisphere atmosphere. Depending on the relative rates of biotic and abiotic processes regionally, the extent to which particular factors regulate these processes may vary but the common causes may mean they are indistinguishable. Apart from the much deeper surface mixing zones in the southern oceans that may also minimize carbonate activity preventing precipitation, the fact that southern oscillation pCO_2 is so small from either cause is logical.

4.4 Ambivalence of the anticorrelation with $^{13}CO_2$

The lessening ^{13}C-content of atmospheric CO_2 is regarded as evidence for its source, either biological as in fossil fuels. DIC species in the ocean's surface layer are enriched in this stable isotope, enhanced by the biological pump transferring metabolised carbon to greater depths deposited in the ocean. It is claimed that CO_2 in the atmosphere is not derived from the surface layer of the ocean as evidence shows atmospheric CO_2 has a declining heavy isotope content. This fact is used as strong evidence that increases in the Keeling curve show fossil fuels are the main source of the new CO_2 in air. This may be substantially true for the ocean, but soil carbon is also depleted in ^{13}C-content, given its predominantly biological source with this store of carbon claimed to be twice that in the atmosphere as CO_2. To the extent that significant increases in release of soil carbon from human activity are possible, this logical proof of the fossil emissions source of CO_2 becomes less convincing.

Furthermore, the anticorrelation of the ^{13}C content of the atmosphere with the pCO_2 of the atmosphere, with the heavy isotope at its lowest value in the northern winter is not necessarily proof as has been claimed [52] that the source of elevated CO_2 is mainly terrestrial respiration, although it is superficially consistent with the hypothesis. Depleted CO_2 from seawater is also possible if its source is from seawater respiration of organic detritus, likely fixed the previous summer. Depletion of ^{13}C is also by no means exclusive to biological systems like photosynthesis. Yumol et al. [53] show how CO_2 hydration can deplete

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gaseous carbon -29.7‰ potentially resulting in the summer season, enriching air with $^{13}CO_2$. Wanninkhof [54] claimed much lower enrichment Although Becker et al. [55] did not interpret their excellent results over 4 years for transects of 10 bands of longitude in the North Atlantic as indicating abiotic calcite formation in summer and dissolution in winter, their $^{13}CO_2$ results are consistent with this hypothesis. The three mol CO_2 per m^2 they claimed was exchanged with the atmosphere and surface water is similar to that modelled in this paper. The peak ^{13}C in [CO_2] in summer and the declining value in the winter season is consistent with the abiotic model presented here. Dissolution and fractionation of the lighter versions of carbonate, and bicarbonate as calcite is dissolved in winter must result in a lower enrichment in the [CO_2] pool in the surface layer.

The claims by Henzler et al. [56] that $CaCO_3$ nucleation in supersaturated seawater is likely to be predominantly classical with simple ions or ion pairs a majority is not disputed by our temperature variation hypothesis, given that though carbonate ions must increase in summer at warmer temperature seawater still contains mainly free ions of carbonate, carbonate increasing or declining only some 10% in our modelling. Their thermodynamic data was estimated at 298 K with no temperature variation included in their calculations. Broecker and Peng [57] pointed out the uncertainties in using ^{13}C depletion as a means to calculate CO_2 uptake by the ocean from fossil carbon is problematical, given inaccuracy in the available data set. Tans et al. [58] also question the uncertainty in such calculation. The diminution of the heavy isotope in air to fossil fuels is attributed to Quay et al. [59].

4.5 A corollary to the thermal hypothesis

The broad issue regarding changes in the pH value of the ocean has only been recognized more recently [38,43] in the IPCC's program for climate change. The data for Ocean Station ALOHA referred to above are relevant in this context, showing the progressive decrease in pH, considered of particular concern to marine ecosystems. It is clear from the Thermal program and other models such as CO2MODSYS [25] that the hydrogen ion activity is the key connecting factor for the marine system, effectively determining the ratio of dissolved CO_2 to both bicarbonate and carbonate − as well as any other chemical system for which pK values can be written, such as for borates in seawater and phosphates on land. Although the Thermal models have been written for seawater systems, they should be applicable to aquatic land systems despite greater variability. As a consequence, can the pCO_2 of the atmosphere be proposed to be a global result of the generalized pH value of the Earth's surface, whether land or sea? For CO_2 in the atmosphere, clearly the bicarbonate-carbonate buffering system on land and sea is critical in establishing its activity. This will be examined in a companion article (Kennedy et al., unpublished). Extending the principle of applying thermodynamics to our understanding, a second hypothesis now seems obvious.

pH Hypothesis for pCO_2 control: From observations made in testing Hypothesis 1, the pCO_2 in the regional and global atmospheres is predicted to be strongly regulated by the pH value of surface seawater and of the land's surface. This hypothesis will be tested in a separate article investigating thermodynamic control.

5. Conclusion

This paper tests a novel thermodynamic hypothesis regarding physical control of atmospheric pCO_2 by temperature rather than biological processes alone. Venting of CO_2 to the atmosphere or its

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reabsorption should be controlled by the chemical potential of its seasonal concentration in seawater whereas the composition of seawater samples could be dominated by regional or local biotic and abiotic processes, a function of nutrients, solar radiation and other environmental factors. The factual nature of the increasing Keeling curve is beyond dispute [60] but a better understanding of how it is generated is essential. In this article the focus is strongly on thermodynamic effects of temperature with environmental acidity or pH value to be considered in a separate article. This article shows that many of the observations made on seawater regarding analyses on the DIC and its alkalinity [61] assuming biotic processes can equally well be explained by inorganic processes governed by variations in temperature.

Obviously, these hypotheses regarding the strong tendency to equilibrium driven thermodynamically lend themselves to further rigorous testing in both laboratory and field. There is clearly a role for modelling of the kind shown in this article to obtain better understanding of datasets taken under specific times and environments. Critical factors include causes of variation of calcite precipitation and dissolution with changes in temperature. The implications of inorganic processes are much broader than explaining the seasonal oscillations in the progressive Keeling curve of increasing pCO_2.

Too little regard has been paid to the cyclic nature of temperature variation globally, when predicting trends in climate [62]. This neglect is made more acute given the potential effect of such environmental frequencies in phase on fluctuations in chemical potentials. This paper's main thesis is that short term variations in the pCO_2 in air is a simple but inevitable result of changes in temperature, largely independent of the rate of accumulation of biomass. If so, as this paper shows in theory, CO_2 is thermodynamically bound to distribute in particular ways between the air and Earth's surface. This viewpoint is offered for experimental testing and as guidance for regulating CO_2 in the atmosphere. We call for critical experimental tests of this thermal hypothesis to be conducted as soon as possible.

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Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, 1. Table S1. Astrocal Thermal showing seasonal variation in pCO_2 correlated inversely with variations in carbonate and calcite solubility. 2. Table SB: Year 2000 DIC values for Point Barrow Alaska. 3. NCCARF plot of ALOHA Station Data. 4. The Thermal (CO2MOD2) Texas Instruments SR52 Program for Windows Emulator. Inputs and Outputs are as shown in line numbers. Contact ivan.kennedy@sydney.edu.au for further explanation.

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Data Availability Statement: All data generated is included in the text, or in Supplementary Material, using algorithms from Emerson and Hedges [63]. The CO2/HCO3-/CO32- calculator used for Figure 4 is an Excel routine (RJR), based on the work of Dickson and Millerno [32] and Millerno [34] and is available on request. As atmospheric CO_2 varies the Excel routine includes an ongoing fit to the Keeling Curve (Fig.1), allowing variation in temperature, salinity and pH.

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