**Opinion**

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Has Seasonal Ocean Calcification Been Overlooked as a Cause of the Increasing Keeling Curve? A Thermal Acidifying Calcification Hypothesis

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The Keeling Curve documents a steady rise in partial atmospheric pressure of CO₂ (pCO₂), conventionally attributed to fossil fuel emissions. Here, we propose an alternative cause, the thermal acidifying-calcification (TAC) hypothesis, principles of physical chemistry showing that warming-will induce calcification in surface seawater, driving seasonal and longer-term increases in atmospheric pCO₂. Using thermodynamic modeling and oceanographic data, we estimate that precipitation of ~10 μmol of CaCO₃ per kg of surface seawater annually could release sufficient CO₂ to equilibrate locally with the recent 2 ppmv annual rise in atmospheric pCO₂. Seasonal pH and pCO₂ variations at marine stations (e.g., ALOHA, Hawaii) support this mechanism, challenging the dominant terrestrial photosynthesis- respiration explanation for Keeling oscillations. The TAC process can also explain the decreasing trend in ¹³CO₂ in air because of dilution by the same processes that are driving the longer-term increase in atmospheric pCO₂. To test this hypothesis, we recommend the following program: 1. field validation of CaCO₃ deposition rates, 2. measures of the CO₂ flux and 3. isotopic analysis to test this alternative carbon cycle driver with measures to be taken both in the northern Pacific and in the southern hemisphere on a transect past the Great Barrier Reef.

Keywords: Keeling curve; carbon dioxide; bicarbonate; Mauna Loa; calcite; calcium ions; calcification; carbonic anhydrase; acidification; CaCO₃**Introduction**

Atmospheric carbon dioxide (CO₂) concentrations in the Keeling Curve [1] at Mauna Loa, Hawaii, have risen from ~280 ppmv pre-industrially to 420 ppmv in 2021, with a current annual increase of ~2 ppmv. The Intergovernmental Panel on Climate Change (IPCC) attributes [2] this trend primarily to anthropogenic fossil fuel combustion, with seasonal oscillations linked to

Northern Hemisphere terrestrial carbon cycling [2]. However, the ocean, covering 71% of Earth's surface and exchanging ~90 GtC/year with the atmosphere, may play an underappreciated role. We hypothesize that warming sea surface temperatures enhance CaCO₃ precipitation (calcification), acidifying surface waters and releasing CO₂ via a thermal acid-calcification (TAC) process. This could explain both seasonal pCO₂ fluctuations and the long-term

Keeling trend, potentially reversing the assumed cause-and-effect of atmospheric CO_2 driving ocean acidification. Charles Keeling's sampling location on Mauna Loa, Hawaii, to analyze dry air, is historically significant. This research convinced scientists that CO_2 was increasing, and the cause was human (Figure 1).

Yet CO_2 is the very stuff of plant life on Earth in photosynthesis as well its source of carbon as the structural basis of all living creatures. We are now advised by the United Nations based IPCC that the continuing rise of CO_2 in the Keeling curve shown in Figure 1, is from fossil fuel emissions, threatening global catastrophe from global warming. Such a paradoxical contrast for good and

bad perhaps challenges credibility, given the longevity of life on Earth. Modeling that underpins the TAC process in Figure 2, detailed in Kennedy et al. [3], explains how variations in sea surface temperatures can mediate changes in ocean pH through calcification. This paper extends this work to hypothesize that there will be a net yearly increase in atmospheric CO_2 from global warming. Further, we will detail the policy implications and make suggestions for hypothesis proving research. While CO_2 is a trace gas, now present at a minute pressure of 0.00042 atm, it is much more reactive with water than the primary constituents of air and is coupled to biological action, including human activities.

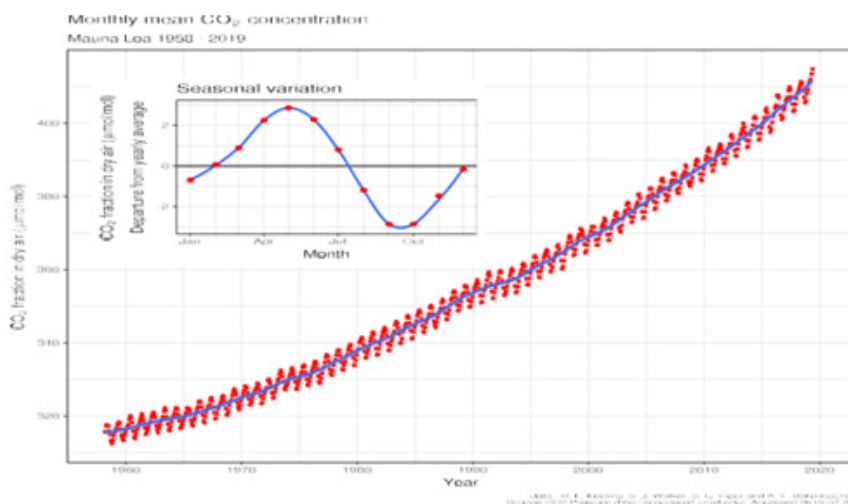


Figure 1: The Keeling curve of atmospheric CO_2 partial pressure at 3200 m on Mauna Loa, Hawaii. Data from Dr. Pieter Tans, NOAA/ESRL and Dr. Ralph Keeling, Scripps Institution of Oceanography. CC BY- SA 4.0, <https://commons.wikimedia.org/w/index.php?curid=40636957>.

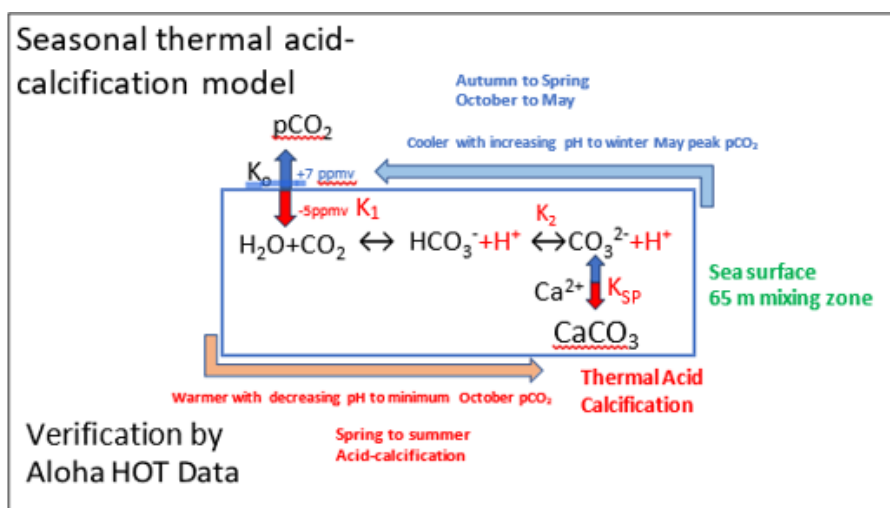


Figure 2: Thermal acid-calcification model for seasonal and longer-term generation of the Keeling curve. The Thermal model (<https://doi.org/10.3390/thermo2040028>), showed calcification is favored by increase in temperature giving decreasing pH values in summer, reversing in cooler conditions to more alkaline pH in winter. Note that precipitation of CaCO_3 in spring to summer removes CO_3^{2-} that is replaced from HCO_3^- with more acidity, provided by absorption of CO_2 from air up to October. However, as the pH falls the steady state concentration of $[\text{CO}_2]$ increases favoring photosynthesis.

At the surface layer of the atmosphere and within the oceans, CO_2 is produced and destroyed through chemical and biological processes affected by temperature, pH and atmospheric pressure. These processes will also be affected by the concentration of other molecules, particularly salts in the seawater solution. The various quasi-equilibria reached will be continually changing with temperature and concentration, affecting the amount of CO_2 released to the air from the ocean. Consideration of the TAC hypothesis requires an understanding of mixing zone chemistry and must not be confused between short term surface CO_2 cycling and the more static reservoir of dissolved inorganic carbon in the deeper ocean. The TAC hypothesis only makes sense with proper consideration of the dynamic nature of such ocean chemistry, an open system that includes abiotic and biotic components, all subject to kinetic effects of seasonal or longer term variation of temperature.

Our hypothesis for CO_2 cycling in the global ecosystem (Figure 2) may seem counterintuitive, given CaCO_3 is less soluble in warmer water. This scientific fact is consistent with CO_2 being absorbed from the atmosphere into surface seawater in spring and summer, to form calcite or slightly more soluble aragonite. This feature of warming is a property of the calcium ion, given the solubility of calcium sulphate also decreases as temperature increases. This solubility behavior, known as retrograde, is uncommon: dissolution of most salts increases with temperature. The retrograde solubility of calcium sulphate is also responsible for its precipitation in the hottest zones of heating systems and for its contribution to the formation of scale in boilers together with the precipitation of calcium carbonate whose solubility also decreases when CO_2 outgasses from hot water or otherwise can escape out of the system (https://en.wikipedia.org/wiki/Calcium_sulfate). The ocean is a vast reservoir of carbon, and the amount converted to carbon dioxide and transferred slowly to the atmosphere, are affected by abiotic as well as biotic processes. Perhaps half of the O_2 emitted to the atmosphere, and CO_2 absorbed from the atmosphere, are from phytoplankton, marine biota that underpin many food chains and cycle CO_2 into O_2 .

There is poor appreciation of the role of calcification, which is the focus of this paper. This largely biological process, one favored by warming, gave the massive carbonate deposits including the white cliffs of Dover formed from biological calcification in the oceans millions of years ago, and the modern Great Barrier Reef visible even from outer space, but there is little understanding of the associated ocean abiotic chemistry and how this might affect atmospheric CO_2 . Remarkably, limestone as a geochemical product of calcification is inherently biological in its formation. It is frequently assumed that the isotopic composition of the carbon

in CO_2 of air distinguishes its origin as from the ocean, forests or fossil fuels. This error in part a consequence of ignoring important aspects of ocean chemistry, failing to distinguish between carbon that is from deep ocean upwellings versus carbon from the mixed uppermost layer of the ocean where temperature, salinity, and density are relatively uniform due to mixing driven by wind, waves, and convection.

The mixed layer is distinct from deeper waters where stratification (e.g. the thermocline) limits vertical mixing. The depth of the mixed layer will vary by location, season, and in particular conditions affecting the transport of energy and matter. A decreasing trend in $\delta^{13}\text{C}$ in the atmosphere is claimed to indicate an anthropogenic source of carbon. By contrast, our TAC process could drive an equivalent $\delta^{13}\text{C}$ reduction through dilution of air with $^{12}\text{CO}_2$ enriched from surface seawater. The TAC hypothesis is primarily concerned with the redistribution of dissolved inorganic carbon (DIC) between carbonate, bicarbonate and CO_2 forms, directly relevant to the formation of the biosphere's great carbonate deposits. The TAC hypothesis considers both inorganic and biological processes. Phytoplankton operate at environmental temperatures in surface waters, their small size relative to surface area preventing warming by cellular metabolism. It is relevant that the enzyme carbonic anhydrase in surface seawater can increase the rate of interconversion between inorganic bicarbonate and CO_2 in water by orders of magnitude, having also been shown to catalyze the dissolution of calcite in seawater in winter. This is an area for future research not specifically discussed in this paper.

Thermodynamic Modeling

We modelled seawater carbonate equilibria in Figure 2 using temperature-dependent constants (Henry's coefficient K_0 , dissociation constants for H^+ of K_1 and K_2 , and solubility product K_{sp} for CaCO_3) using the proven algorithms summarized by Emerson and Hedges [4], such as from Mucci [5]. All these reactions are reversible and two involve either the release or the absorption of acidity as hydrogen ions (H^+) (Figure 2). Our assumptions included a mixed layer depth of approximately 65 meters, representing the average seasonal mixing zone in the North Pacific where TAC-driven calcification and CO_2 outgassing occur, with salinity of 35 psu and atmospheric pCO_2 of 420 ppmv. Any process of strong acidification of surface seawater will raise the concentration of carbon dioxide as $[\text{CO}_2]$ available to marine algae, including phytoplankton, for photosynthesis. Bicarbonate cannot be a direct substrate for Rubisco, although the presence of the enzyme carbonic anhydrase speeds up its interconversion to hydrated CO_2 . Our modeling analysis confirmed [3,6] that CaCO_3 precipitation is strongly favored by warmer temperatures, shown below in Table 1.

Table 1a: Outputs of estimated variation with temperature of equilibrium constants used for modeling surface seawater at pCO_2 air 420 ppmv.

Temperature		$K_0 = Z_{\text{sw}}$	$\text{p}K_1$	$\text{p}K_2$	$K_w \times 10^{14}$	$\text{p}K_w$	$K_{\text{sp}} \times 10^{-7}$ $2 \cdot [\text{Ca}^{2+}][\text{CO}_3]$	$\mu\text{molar CO}_2$ in seawater
K	C							
278.15	5	0.05213	6.042	9.292	0.855	14.07	4.309	21.90
283.15	10	0.04388	5.984	9.203	1.443	13.84	4.317	18.43
288.15	15	0.03746	5.931	9.118	2.380	13.62	4.315	15.73
293.15	20	0.03241	5.882	9.035	3.839	13.42	4.300	13.61
298.15	25	0.02839	5.837	8.955	6.063	13.22	4.272	11.92

Results varying with temperature estimated with Emerson polynomials in Supplementary Materials

Table 1b: Van't Hoff equation outputs of standard enthalpy, Gibbs energy and entropy changes for the K_1 and K_2 equilibria.

Temperature		pK_1	ΔH° kJ/mol	ΔG° kJ/mol	ΔS° kJ/K	pK_2	ΔH° kJ/mol	ΔG° kJ/mol	ΔS° kJ/K/mol
K	C								
278.15	5	6.042	17.490	32.301	-0.053	9.292	26.837	49.672	-0.081
283.15	10	5.984				9.203			
288.15	15	5.931	16.273	32.698	-0.057	9.118	26.751	50.152	-0.081
293.15	20	5.882				9.035			
298.15	25	5.837	15.059	33.160	-0.061	8.955	26.771	50.900	-0.082

Estimates made with pK results from (a) using software in Supplementary Materials

All the reaction equilibria in seawater are displaced by warming, acidifying the water, as shown in Figure 2. The equilibrium between CO_2 concentration and $p\text{CO}_2$ in air favors a lower concentration $[\text{CO}_2]$ in water in summer, compared to winter, when it is greatest (Table 1). Our results even confirmed that the formation of CaCO_3 as calcite is predicted to increase in summer as water becomes warmer (Table 1b) and K_{sp} decreases. Thus, we predict more limestone formation in summer if the carbonate concentration reaches a sufficient level, caused by warming. The decline in average pH values in surface seawater to about 8.05 from pH 8.20 would explain the increased $p\text{CO}_2$ in the atmosphere of 140 ppmv since the industrial revolution as a matter of dynamic equilibrium. If caused by calcification, this would require a simultaneous equivalent deposition of limestone as sediment, though only a global increase of about 10 μmoles per kg of surface seawater, or a net 1 mg per kg each year, a function of increasing temperature. This is a key prediction of our TAC hypothesis that can be tested experimentally in seawater.

An important feature of CaCO_3 formation needing explanation is acidification. Removal of CO_3^{2-} ions by precipitation displaces the equilibrium to generate even more acidification by extra H^+ than that from dissolving CO_2 alone in forming bicarbonate and carbonate. Each precipitation of a μmole of carbonate will reduce pH values by an equivalent amount. Even if calcite is not visibly formed, the fact that much of the surface layer in oceans are measured to be supersaturated with CO_3^{2-} ions suggests that the activity of Ca^{2+} ions is diminished by binding to CO_3^{2-} ions when the sea is warmer. Warmer water also dissociates water clusters, diminishing the shielding of Ca^{2+} ions from negatively charged carbonate and thus promoting acidification from bicarbonate dissociating a proton (H^+), forming carbonate. This process of calcification is important for much photosynthetic life in the ocean since it raises the concentration of CO_2 , equivalent to a fugacity equal to 7 ppmv $p\text{CO}_2$ in air for each fall of 0.01 pH units, an output of our thermal model [3,6].

This is our acid-calcification thermal (TAC) hypothesis. It is sufficient to explain the seasonal changes in pH and $p\text{CO}_2$. The Km concentration value for the enzyme absorbing CO_2 known as Rubisco, the most common protein on Earth, is about the same as that of the concentration $[\text{CO}_2]$ in air and seawater, so any increased value speeds up photosynthesis. Without calcification, much photosynthetic life in seawater would cease for lack of sufficient CO_2 for Rubisco from bicarbonate, explained by McConnaughey and Whelan [7]. We emphasize here the abiotic thermodynamic responses shown in Table 1, but calcite formation is promoted by

phytoplankton taking advantage of these responses, contributing significantly to the net accumulation of CaCO_3 equivalent to the net emission of CO_2 to the atmosphere, that we have discussed previously. For example, coccolithophores excrete platelets of calcite to their surface, having benefited from increased $[\text{CO}_2]$ from acidification for their rate of photosynthesis. Once sedimented, these oil- containing exoskeletons may contribute to future fossil carbon products.

Data Sources

Seasonal $p\text{CO}_2$ and pH data were sourced from the ALOHA Station [8] and WHOT measurements [9]. Keeling Curve data were obtained from NOAA/ESRL and Scripps Institution of Oceanography.

Seasonal and Long-Term CO_2 Dynamics

The Keeling Curve on Mauna Loa exhibits a 6 ppmv seasonal oscillation, peaking in late winter and troughing in October (Figure 1). We claim this reflects ocean outgassing rather than terrestrial plant growth cycles. In the TAC model (Figure 2), warming in spring- summer drives CaCO_3 precipitation, lowering pH and raising seawater equilibrium $p\text{CO}_2$, peaking in summer. CO_2 emits to the atmosphere in autumn-winter, exceeding spring reabsorption, yielding a net annual increase of ~ 2 ppmv.

Thermodynamic Support

Table 1a shows equilibrium constants shifting with temperature: The Henry coefficient (K_h) is almost halved by over a 20°C increase in temperature. The pK values near pH 6 and 9 where $[\text{CO}_2]$ and $[\text{HCO}_3^-]$ or $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ respectively are of equal concentration both decline with temperature at a similar rate, showing K_1 and K_2 values increase (i.e., more acid). The solubility product shows a maximum near 285 K, being less soluble in seawater either warmer or colder than this temperature (Table 1b). This facilitates the solubility system Ω factor as $[(\text{Ca}_2^+) \times (\text{CO}_3^{2-}) / K_{sp}]$ reaching an activity quotient greater than 1.0, signaling precipitation [3]. Van't Hoff analysis (Table 1b) to measure changes in equilibrium constants (K_2/K_1) from variations in enthalpy (ΔH) showed that all reactions favored in summer are endothermic, absorbing heat at higher temperatures, cooling surface seawater. In winter when the reverse reactions are favored there will be a tendency to warm seawater slightly, these thermal effects being a good demonstration of Le Chatelier's principle. When environmental conditions force reaction in one direction, natural processes tend to oppose such changes.

Observational Evidence

ALOHA data reveal a pH decline of 0.003 units per year [8] and larger seasonal swings of 0.04 units, with maximum seawater $p\text{CO}_2$ coinciding with minimum pH (Figure 3) [8]. The ALOHA or HOT data in particular shows this seasonal variation in pH values of 0.04 units in seawater, with matching between minimum pH and maximum fugacity of CO_2 in surface seawater (Figure 3). Our modeling indicates that absorption of CO_2 alone is unable to explain the decreased pH value abiotically from this cause. Significant calcification removing more CO_2 from the atmosphere is needed to explain the additional $[\text{H}^+]$ increase and pH changes involved. TAC hypothesis confirmation needs a field demonstration that additional CaCO_3 precipitation is occurring each year, with more formed in summer than is decalcified in winter, in agreement with the K_{sp} predictions. Obviously, the extent of this process will be a function of the seasonal variation in surface seawater temperature.

We have expressed this according to the Ψ (psi) equation, following a similar suggestion by Smith [10] investigating whether the oceans were a net source or a sink for CO_2 , showing variation with depth rather than seasonal variations in temperature. Published data (Figure 4) confirms higher seawater $p\text{CO}_2$ than for air in autumn-winter, supporting net emission. The ALOHA or HOT data in particular shows this seasonal variation in pH values of 0.04 units in seawater, with matching between minimum pH and maximum fugacity of CO_2 in surface seawater (Figure 3). Our modeling indicates that absorption of CO_2 alone is unable to explain the decreased pH value abiotically from this cause. Significant calcification removing more CO_2 from the atmosphere is needed to explain the additional $[\text{H}^+]$ increase and pH changes involved, consistent with our TAC hypothesis. Its confirmation needs field demonstrations that additional CaCO_3 precipitation occurs each year if global temperature increases, with more formed in summer than is decalcified in winter, in agreement with the K_{sp} predictions.

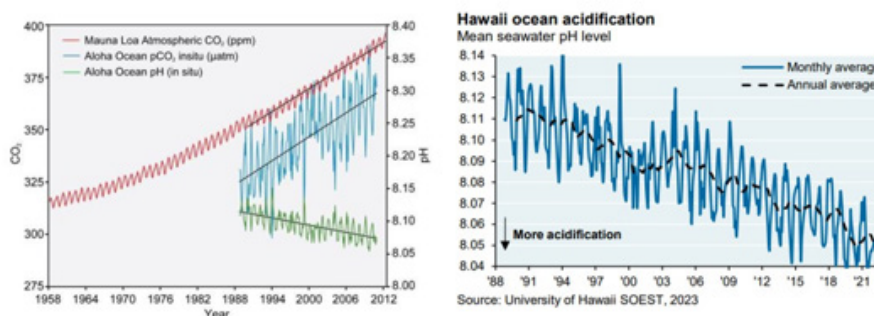


Figure 3: NCCARF Plot of ALOHA Station Data, National Climate Change Research Facility, Australian Government and more recent data from the University of Hawaii.

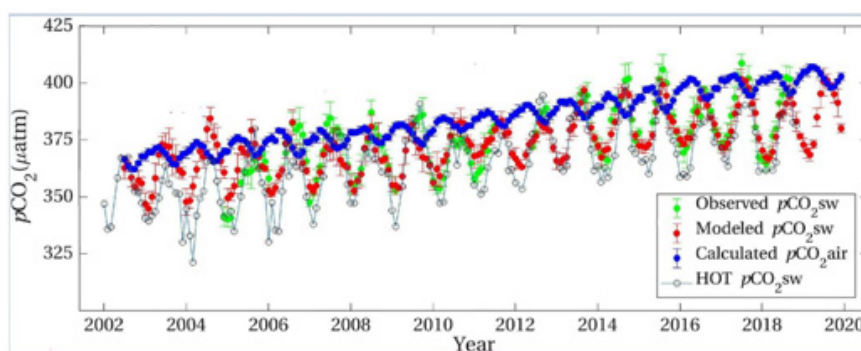


Figure 4: Seasonal WHOT non-equilibrium oscillations in simultaneous $p\text{CO}_2$ measurements in seawater and air showing converse values supporting transfer of CO_2 to air in autumn through winter and, less strongly, from air to seawater in spring and summer. Peak and minimum seawater surface temperatures were 1-2 months after mid-summer and mid-winter with ranges of over 4 K, supporting the Figure 2 TAC model [3]; Credit figure Chen et al. <https://doi.org/fmars.2021.636881>.

Obviously, the extent of this process will be a function of the seasonal variation in surface seawater temperature (Figure 4). The 18-year seasonal WHOT data of Chen et al. shown in Figure 4 [9] confirms this seasonal variation in fugacity of CO_2 in the northern

Pacific, even showing that values in surface seawater exceed that in air for several months each year, speeding up transfer when the greatest differences occur between the phases at highest temperature.

Isotopic Considerations

Our model assumes calcification across the ocean's mixed layer that we define as above 65 meters in depth. Our model does not consider carbon from upwellings. The ocean's dissolved inorganic carbon (DIC) is more usually, at least in climate models, treated as a uniform pool with a $\delta^{13}\text{C}$ of $\sim 0\text{‰}$ to $+2\text{‰}$ (from marine carbonate equilibrium), averaged across depths to include surface layers and upwellings. The IPCC and others assume CO_2 absorbed into surface waters reflects this, acting as a sink that slightly raises atmospheric $\delta^{13}\text{C}$ (counteracting fossil fuel's -25‰ pull). Outgassing, they argue, is minimal and isotopically neutral, so fossil fuels dominate the observed -6.5‰ to -8.5‰ shift. If surface waters—where TAC's calcification happens—have a distinct $\delta^{13}\text{C}$ content from that in deep oceans, and if warming drives outgassing from this surface layer, the IPCC's assumption needs revision. In particular, surface processes, not only calcification but also photosynthesis by phytoplankton, would enrich ^{12}C in outgassed CO_2 , lowering atmospheric $\delta^{13}\text{C}$ delta more than deep ocean signatures suggest, mimicking fossil fuels. Note the equivalence predicted for CaCO_3 formation and net CO_2 emission. This hypothesis proposes a self-regulating system for control of atmospheric CO_2 by surface seawater pH that needs testing.

Key Future Research to Test the TAC Hypothesis

Three research projects are proposed to test the TAC hypothesis and associated modeled processes.

a) Field Validation of CaCO_3 Deposition Rates

Objective: Test the TAC prediction of an annual CaCO_3 deposition of $\sim 10 \mu\text{mol/kg}$ in surface seawater, linked to the 2 ppmv atmospheric CO_2 increase.

Approach: Conduct nearshore sediment core analyses and direct measurements of surface calcification rates in key ocean regions. We suggest this research be focused on both the northern Pacific at Aloha, Hawaii, and at the Great Barrier Reef that is the largest coral reef ecosystem, and on the western margin of the South Pacific. There is a need to quantify seasonal and yearly limestone accumulation in the mixed layer ($\sim 65 \text{ m}$ depth) from biotic and abiotic sources.

Why: Confirms the model's core claim that calcification drives CO_2 emissions stoichiometrically. Current estimates lack empirical backing, making this a critical gap.

b) Seasonal CO_2 Flux Measurements

Objective: Verify TAC's explanation of Keeling Curve oscillations via ocean outgassing rather than terrestrial cycles.

Approach: Deploy high-frequency pCO_2 sensors in surface seawater and air across seasons, focusing on marine-dominated regions (e.g., central Pacific and Great Barrier Reef). Correlate with

temperature, pH, and calcification rates.

Why: Challenges the photosynthesis-respiration narrative. Data showing peak seawater pCO_2 driving atmospheric rises (autumn-winter in each hemisphere) would support TAC.

c) Isotopic Analysis of CO_2 Sources

Objective: Distinguish ocean-derived CO_2 from fossil fuel emissions using isotopic fingerprints ($^{13}\text{C}/^{12}\text{C}$ ratios).

Approach: Measure $\delta^{13}\text{C}$ in atmospheric CO_2 near marine stations during peak outgassing (autumn-winter in both hemispheres) and compare to fossil fuel signatures. Assess whether TAC's predicted enrichment from seawater holds up.

Why: The IPCC consensus argues fossil fuels explain the isotopic shift. Robust data could bolster TAC's claim of a significant ocean source.

Implications

The IPCC attributes the Keeling rise to fossil fuel emissions, approaching 10 GtC/year; oceans are considered a sink for about half of this. The TAC model suggests a natural source: warming-induced calcification releases $\sim 4.26 \text{ GtC per year}$ (2 ppmv), though this needs regional adjustments for emissions on land and sea [10] amplified by ocean feedback. The seasonal oscillations (Figure 1), traditionally tied to terrestrial processes of photosynthesis and respiration, align better with marine temperature cycles near Mauna Loa (Figure 4). If the TAC Hypothesis and processes shown in Figures 2&5 were validated, then the logical conclusion is that ocean warming—regardless of cause—drives CO_2 increases in air, challenging widespread mitigation strategies focused solely on emissions as futile. The predicted net CaCO_3 deposition ($\sim 1 \text{ mg/kg}$ surface seawater/year) is small but testable, including via sediment analysis.

In Figure 5 we present our current estimates of CO_2 cycling globally, per square meter of the Earth's surface. These numbers will be justified in more detail in an article in preparation. The key statistic is the 0.7 increase in atmospheric carbon dioxide measured as moles per meter squared per year, from surface ocean waters as an output from our modeling. In all of this it is important to consider the total ocean reserve of carbon as the IPCC modeling does, and CO_2 cycling as a distinct process within the global ecosystem. In this way it is possible to calculate a global budget for CO_2 as we have done. It may not always be realized by physicists, who perhaps dominate discussions concerning the physical basis of climate change, that CO_2 is continually produced and destroyed naturally near the Earth's surface. Indeed, chemistry is much more complicated and reactive than the radiative climate models that currently dominate thinking.

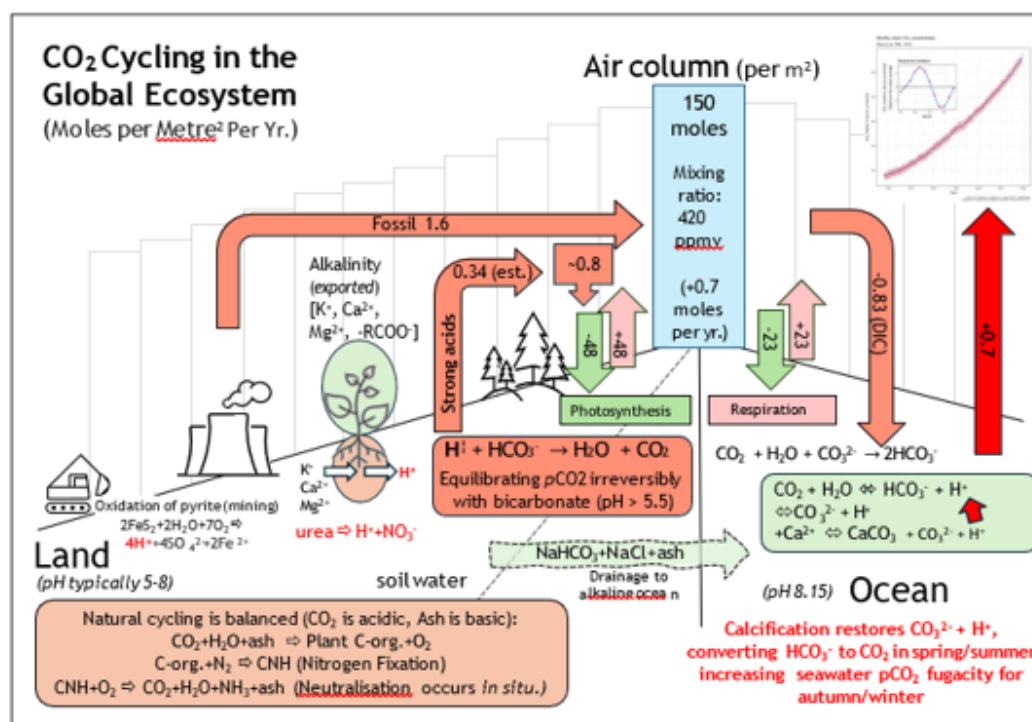


Figure 5: Rates per square meter in global carbon cycling between land water, the atmosphere, and the ocean, illustrating the pH-acidification hypothesis. Emissions and absorptions shown are average moles per square meter of the Earth, for a mixing ratio of 420 ppmv in 2021 shown in the central column bridging land and ocean. The land acidification values are derived elsewhere [11], assuming photosynthesis is equal to respiration. The terrestrial area of Earth is $1.48 \times 10^{14} \text{ m}^2$, the ocean's area is $3.62 \times 10^{14} \text{ m}^2$, $5.101 \times 10^{14} \text{ m}^2$ in total., represented as a mean value in the central air column.

Conclusions

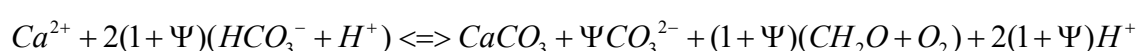
The TAC hypothesis offers a plausible alternative to the fossil fuel-driven Keeling curve narrative, emphasizing ocean calcification as a CO₂ source. Field measurements of CaCO₃ deposition and isotopic fluxes are critical next steps. This work underscores the need to revisit natural carbon cycle feedback in a warming climate. The thermal acid-calcification (TAC) hypothesis proposes that warming-induced calcification in the ocean's surface mixed layer (65 m) contributes significantly to the Keeling Curve's observed 2 ppmv annual increase in atmospheric pCO₂ (4.26 GtC/year). Our thermodynamic modeling indicates that temperature-driven shifts in carbonate equilibria release CO₂ at rates consistent with this rise, potentially augmented by biotic processes if nutrient sources of nitrogen and phosphorus are available, while fossil emissions may be fully absorbed by oceanic and terrestrial sinks shown in Figure 5. Seasonal pCO₂ oscillations, conventionally linked to terrestrial carbon cycling, correlate with marine outgassing patterns at

stations such as ALOHA, suggesting this oceanic driver.

The observed decline in atmospheric $\delta^{13}\text{C}_{\text{CO}_2}$ compared to a standard (-6.5‰ to -8.5‰) could reflect dilution by processes favoring net 12CO₂ emission, caused by calcification processes in the mixed layer. Validation requires field measurements—CaCO₃ deposition rates in warmed surface water, seasonal CO₂ fluxes, and $\delta^{13}\text{C}$ profiles—at key sites (e.g., northern Pacific, Great Barrier Reef). These data could be used to test TAC's premise that warming amplifies natural carbon feed backs, offering an alternative perspective on the global carbon cycle and its response to global warming from whatever cause.

To quantify temperature's role in CO₂ release from acid calcification, we employ the Psi (Ψ) equation, adjusting stoichiometry to the range of seasonal thermal variations:

The Ψ Equation



The Ψ parameter scales CO_2 production with temperature range (e.g., 5-10°C annually near Mauna Loa), reflecting increased calcification under warmer conditions as opposed to depth-dependent gradients [10]. To the extent in summer that temperature increases, the decreased pH value from the release of H^+ ions increases the steady state concentration of $[\text{CO}_2]$, increasing its fugacity in seawater. Modeling showed that CaCO_3 precipitation was accompanied by ΨCO_3^{2-} of carbonate formation from bicarbonate, required to preserve the alkalinity of dissolved inorganic carbon. Given that phytoplankton are unable to generate an increased temperature from that of seawater by metabolism, because of their large surface area compared to their radial dimension, the equilibria shown in Figure 2 are dominated by varying seawater temperature as discussed elsewhere [3], whether considered biotic or abiotic. This dynamic seasonal and longer-term process, reversible by season, contrasts with static equilibrium models (e.g. K_0 reduction over 20°C, Table 1a), emphasizing thermal energy's influence on pCO_2 .

Observational data from ALOHA or WHOT [8,9] corroborate this — seasonal pH decreases (ca. 0.04 units) and pCO_2 increases align with elevated temperatures, driving CO_2 outgassing. The estimated $\sim 0.7 \text{ mol per m}^2 \text{ CO}_2$ release (ca. 2 ppmv rise) hinges on this temperature-dependent mechanism, with biotic catalysis (e.g., carbonic anhydrase) potentially enhancing rates, though abiotic processes seeking equilibrium predominate in our current modeling framework, shown in Figure 2.

Acknowledgments

Our seasonal modeling depended on published algorithms [4] that reveal thermodynamic equilibrium constants for seawater change with temperature. The values estimated for K_{sp} near 4.2×10^{-7} for calcite employed in our thermal model are two orders of magnitude larger than those often given in textbooks for fresh water, with those for more soluble aragonite lower. The maturity of this physical chemistry research by dedicated oceanographers and their excellent analytical results made verification of our modeling predictions possible, using real world data from the northern Pacific [9,10].

We also acknowledge the assistance that peer reviewers and the editor of *Thermo* [6,7] provided. Our deciphering of the enigma of the ALOHA data [9,10] depended on knowing the strong seasonal non-equilibrium for the fugacity of CO_2 in surface seawater and the atmosphere, a function of temperature and pH value. Publishing this hypothesis in *Advances in Oceanography and Marine Biology*, even as an Opinion, could seem a low bar for reviewing. Indeed, one key member of our team (JM) prefers not to be listed as a coauthor for

an article in this journal. The hypothesis presented here depends entirely on peer reviewed publications by the authors and others. Readers are free to form their own opinion regarding its validity for experimental testing.

Corresponding author (IRK) however welcomes AOMB's acceptance of this testable hypothesis by its editorial panel, claiming it as a plausible alternative cause for the increasing Keeling curve. It signals the urgent need for a fresh approach to research on the link between CO_2 and climate change. To delay publication of an article potentially disruptive to the current IPCC global warming paradigm would be a failure in professional diligence. We acknowledge the essential contribution Jennifer Marohasy has made in helping bring forward this publication by emphasizing that the seasonal oscillation as a product of thermal conditions must also apply to global warming as a source of increasing pCO_2 longer than seasonal.

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