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Opinion

The Seasonal Keeling Oscillation in Atmospheric pCO_2 is Caused by Variation in Seawater Surface Temperature

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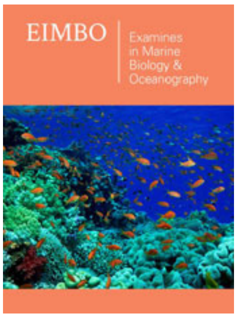

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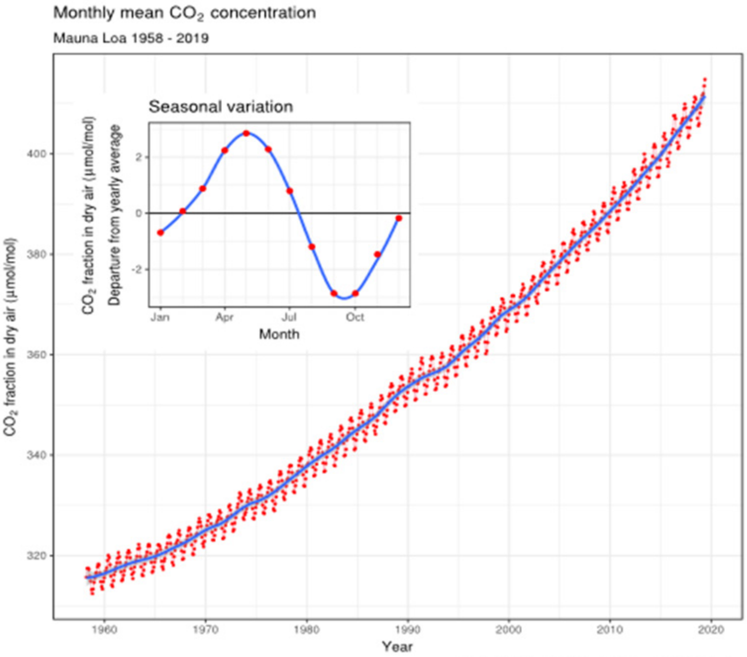
Introduction

Charles Keeling surmised that the seasonal oscillation in the atmospheric CO_2 observed on Mauna Loa shown in Figure 1 and at Point Barron in the arctic [1,2] resulted from seasonally unequal regional variations in photosynthesis and respiration [1]. Here, this assumption is reassessed.



Data : R. F. Keeling, S. J. Walker, S. C. Piper and A. F. Bollenbacher
Scripps CO2 Program (http://scrippsco2.ucsd.edu). Accessed 2019-07-20

Figure 1: The Keeling curve of atmospheric CO_2 partial pressure at 3200m 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, accessed on 12 November 2022.

New data

While this conclusion may be valid for Keeling's early observations made on land in California, we have shown that variation of seasonal sea surface temperature is more likely the cause of this seasonal oscillation [3]. Equilibrium positions of the reactions of dissolved inorganic carbon of CO_2, bicarbonate and carbonate leading to formation of precipitated calcite all shift towards carbonate and calcite formation (Figure 2) peaking in late summer in October and reversing in winter, with calcite being more soluble in colder seawater diminishing until May. The calcification process of calcite or aragonite formation thus favoured in warmer water in summer is usually suggested [4] to involve a charge-neutral stoichiometric reaction between Ca^{2+} ions and bicarbonate as follows in Equation (1).

$$Ca^{2+} + 2HCO_{3-} \Leftrightarrow CaCO_3 + CO_2 + H_2O \quad (1)$$

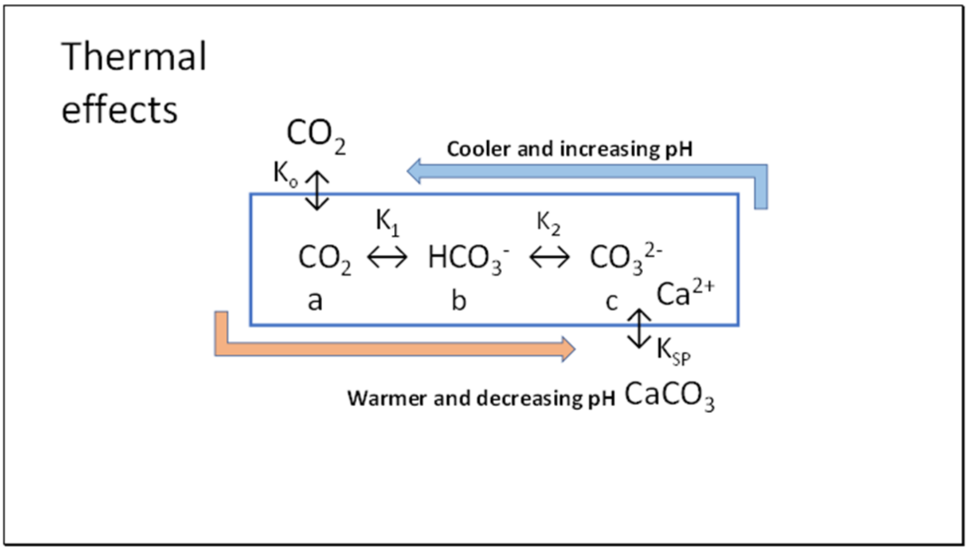


Figure 2: Thermal model showing seasonal displacement of reactions of dissolved inorganic carbon in the mixing zone of seawater. Formation of carbonate and calcite is favoured in warmer seawater [3], with carbonate peaking in October whereas bicarbonate peaks in April at the latitude of Hawaii, where carbonate is minimal

This has the advantage of generating carbonic acid, raising $[CO_2]$ concentration and allowing photosynthesis to occur not possible directly from bicarbonate.

However, to explain the published ALOHA dataset [5], we concluded [3] that the stoichiometry of this process must occur as shown in Equation (2), emphasizing the close connection between inorganic and biological reactions involving seasonal cycling of CO_2. It was also concluded that the Ψ factor [6] is a variable combining the range of the seasonal temperature variation affecting the extent of calcification as well as biological factors. An important factor is the acidification shown for summer reducing the pH value of the system in summer and therefore raising the fugacity for CO_2 (fCO_2). This explains the highest values of pCO_2 recorded by equilibrating a large sample of seawater with an air bubble in summer when the pCO_2 in air just above the surface as recorded by Chen et al. [7] in the ALOHA samples is lowest. Just when the seawater is warmest, this facilitates a rapid transfer of CO_2 from seawater to air continuing until late winter as the pCO_2 in air reaches its peak. While equilibrium between different forms of DIC in seawater should be rapid with changes as temperature changes, equilibrium between CO_2 is highly transient.

$$Ca^{2+} + 2(1+\Psi)\left(HCO_{3^-} + H^+\right) <=> CaCO_3 + \Psi CO_3^{2-} + (1+\Psi)(CH_2O + O_2) + 2(1+\Psi)H^+ \quad (2)$$

It is the consumption of Ca^{2+} ions in this calcification process within organisms that causes acidification and the potential for generation of CO_2 from bicarbonate preserving charge balance, thus made available for photosynthesis. Reaction (1) does not explain the increase in fugacity of CO_2 in summer, which peaks as the pCO_2 in air is least. The methods developed by Chen et al. [7] and Sutton et al. [8] include adjustments for variations in air humidity with temperature that vary pCO_2. Standard methods for measuring CO_2 involve analysis of dehydrated air, tending to overestimate its pressure particularly in summer. Their data [7] show that the fugacity of CO_2 in seawater exceeds that in air in mid-summer when pCO_2 in air is minimal, facilitating diffusion between the two phases at a maximum rate. Chen et al. [7] were more concerned with defining the rate of increase in seawater CO_2 fugacity as the longer term trend in pCO_2 in air shown in Figure 1 increases.

Key Factors

The key factors that contribute to the oscillation being caused by emission and absorption of CO_2 by the ocean surface, particularly where there is a high range in seasonal temperature in the northern hemisphere are several. These include:

i. Reactions in Figure 2 from CO_2 to carbonate have been shown as endothermic, absorbing heat in the conversion to calcite in summer, in agreement with Le Chatelier's principle tending to reverse summer warming.

ii. Our modelling [3] based on algorithms of Emerson & Hedges [9] showed that the magnitude of seasonal temperature variation in seawater affects the extent of formation of carbonate and calcite from bicarbonate in summer, or its diminution in winter in the reverse reaction.

iii. The pH change in summer is towards acidification, raising the fugacity of CO_2 in seawater; as autumn and winter proceed, the pH change is alkaline, as calcite and carbonate decline and bicarbonate and $[CO_2]$ in solution increase in colder water, consuming protons.

iv. To the extent allowed by nutrients particularly of nitrogen and phosphate, photosynthesis is favoured by the calcification reaction shown on the right-hand side of Reaction (2).

We concluded [3] that explaining the extent of the oscillation requires a combination of seasonal inorganic and biological reactions and that the respective contributions of these two causes of carbon cycling probably varies locally. Even the contribution of biological factors assisting reaction rates such as extracellular carbonic anhydrase [10] needs assessment. In general, our conclusion that variation in seawater temperature is the fundamental cause of seasonal oscillation in the Keeling curve shown in Figure 1 is consistent with the global climatological distributions of pH, pCO_2, total CO_2, alkalinity, and $CaCO_3$ saturation in the global surface ocean analysed by Takahashi et al. [11].

Conclusion

The ALOHA dataset between 1990 and 2009 [5] has been used to show that the pH of the ocean surface water is declining as the Keeling curve for increasing pCO_2 from anthropogenic sources increases. For every change of pH of 0.01 units, pCO_2 increases almost 10ppmv. In the modern era since 1750, pH values have probably declined about 0.15 units, while the pCO_2 in the global atmosphere has increased about 140ppmv. Every square meter of the Earth's surface now has about 140 moles of CO_2 above it in the troposphere. We are also investigating the extent to which increases of atmospheric CO_2 are caused by declining pH values on land surfaces as a result of significant acidification by export of alkaline agricultural produce [5] and the application of excess reduced nitrogen fertilisers, tending to form nitric acid. This has not been considered significant by the IPCC panels as a source compared to emission from fossil fuels. However, we claim that acidification releases stoichiometric quantities of CO_2, particularly from neutral or mildly alkaline soils with high levels of bicarbonate (HCO_3^-) and the scale of this source must be determined if the pCO_2 trend in Figure 1 is to be mitigated.

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