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Proton-controlled mechanism for coupling among proton production/consumption reactions in $CaCO_3$-oversaturated waters or calcifying organism-inhabited seawaters

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ABSTRACT

The $CaCO_3$-oversaturated weakly basic water at around pH=8 was proved by the novel simple equations (e.g. $\log [Ca^{2+}] = -2pH - \log P_{CO_2} + 9.94$) derived from material energetics and proton-controlled mechanism for coupling among proton/hydroxide production/consumption reactions (e.g. $CaCO_3 + H^+ \leftrightarrow HCO_3^- + Ca^{2+}$) in equilibrium with atmospheric carbon dioxide. The cyclic/oscillating variation between pH=8.3 and 8.0 for marine calcifying organism-inhabited paleo and preindustrial seawaters was elucidated by applying the improved proton-controlled mechanism to biochemical reactions in cytoplasts or host tissues of marine calcifying phytoplanktons and phytosymbiont-bearing corals/zooplanktons. It was revealed that photosynthesis enhances biogenic calcification and vice versa, as the thicker growth of $CaCO_3$-made outer casings causes proton production and photosynthesis continuously needs protons to produce $CO_2(aq)$ from major HCO_3^-. The correlation between calcification and photosynthesis creates a number of stationary states with respect to oscillating pH variation. Marine biogenic calcification reaction releases no CO_2 to atmosphere and is no positive feedback to rising atmospheric P_{CO_2} levels.

1. Introduction

It is well known that carbon dioxide uptake of pure water causes acid increase of pH=4-5 under atmospheric carbon dioxide partial pressure 350-400 ppm at room temperature. The oversaturated state with respect to calcium carbonate was, on the other hand, identified to weak base at around pH=8 in equilibrium with atmospheric carbon dioxide [1]. The calcifying organism-inhabited paleo seawater showed around pH=8.3-8.15 in the absence of anthropogenic CO_2 over the past ~400 kyr [2]. The acidification process changes the saturation state of seawaters with respect to solid $CaCO_3$, as it reacts with protons to produce calcium ion and HCO_3^- [1]. The major HCO_3^- species, however, react with calcium ions to produce calcium carbonate and protons. Marine calcifying organisms tolerate rising CO_2 levels and acidic ups at the present time, and might be overcome by falling pH levels of 0.05-0.1 in near future. The in situ $CaCO_3$ dissolution rates were estimated from changes in total alkalinity corrected by contribution from oxidation of organic material and approximately ranged between 45% and 65% for the export production of $CaCO_3$ [3].

The $CaCO_3$ particles-oversaturated water may correspond to the seawater of white bloom-forming coccolithophores and the high density seawater of planktonic foraminifers. The biochemical coupling of marine organisms with atmospheric carbon dioxide and seawater pH may be positive feedback to ocean CO_2 uptake and natural pH variation in absence of anthropogenic CO_2 contribution. The cyclic or oscillating stability between seawater pH=8.3 and 8.0 was observed during paleo and preindustrial ages [2,4]. The real saturation state with respect to $CaCO_3$, and the pH dependence of major stable HCO_3^- species and calcium ions are not yet revealed by exact mechanism that takes proton production/consumption reactions into account. Some biochemical proton production/consumption reactions may become a positive feedback to the cyclic or oscillating stability of seawater pH=8.3-8.0 in equilibrium or stationary state. It has been, on the other hand, recognized over the past decades that marine biogenic calcification derives carbon dioxide release and rising atmospheric CO_2, as introduced in reviews [5,6].

In this work it is for the first time revealed that novel proton-controlled mechanism and material energetics-controlled process of material production derive weak base pH=~8 of calcium carbonate-supersaturated water in equilibrium state. The identified marine proton concentration is variable between pH=8.3 and 8.0 under no anthropogenic impact on seawaters.

The cyclic or oscillating stability of pH was evaluated by applying a coupling among some biochemical enzymatic reactions in cytoplast to proton-controlled mechanism. It is predicted that marine calcareous phytoplanktons of coccolithophores and endosymbiont-bearing reef corals/zooplanktons (e.g. foraminifera) cause changes in ocean pH and atmospheric carbon dioxide, and vice versa. It may be confirmed that marine biogenic calcification derives proton production and no CO_2 production, and positive feedback of ocean CO_2 uptake.

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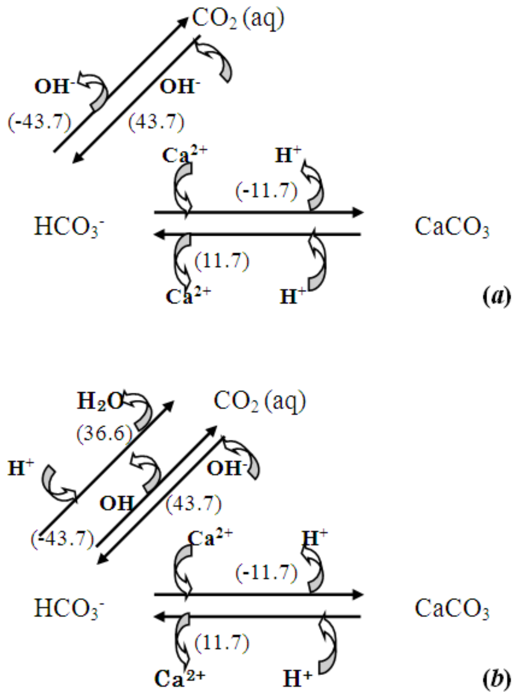
2. Theoretical

The proton-controlled mechanism is build up from realistically exact reactions of proton/hydroxide production and consumption, and material energetics-controlled process of material production.

2.1. $CaCO_3$-oversaturated water

$CaCO_3$-oversaturated water is in equilibrium with atmosphere. Unstable hydrated carbon dioxides CO_2 (aq) in equilibrium with atmospheric carbon dioxide are likely attacked by hydroxides in water. A number of energetically stable bicarbonates HCO_3^- become major in water, but both CO_2(aq) and carbonates CO_3^{2-} (i.e. conjugate base of stable major HCO_3^-) are unstable and minor at physiological pH < ~8.5 (Supplementary (*a*)). Minor unstable CO_3^{2-} is produced by acid dissociation of HCO_3^- at physiological pH < ~8.5 to arrive at equilibrium state through energetically controlled production pathway. The major HCO_3^- reacts with calcium ion to produce calcium carbonate and proton; the oversaturated $CaCO_3$ is attacked by protons and produces both calcium ion and HCO_3^- ($CaCO_3 + H^+ \leftrightarrow HCO_3^- + Ca^{2+}$) [1].

The $CaCO_3$ production/dissolution is caused by chemical reaction along with proton production/consumption and hardly takes place with no change of chemical species via e.g. $Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$ between pH=~7.5 and ~8.5. The saturation state of $CaCO_3$-oversaturated waters, therefore, be relevantly expressed by solubility product of $[Ca^{2+}][HCO_3^-]$ and not by much smaller $[Ca^{2+}][CO_3^{2-}]$. The proton-controlled mechanism and material energetics for the coupling among the proton/hydroxide production/consumption equilibrium reactions, as shown in Scheme 1a, can reproduce the observed proton-concentration pH=~8 of $CaCO_3$-overersaturated water in equilibrium with atmospheric carbon dioxide [1], as shown below.



Scheme 1. Proton-controlled mechanism and material energetics applied to (***a***) $CaCO_3$-supersaturated waters in equilibrium with atmospheric CO_2, and (***b***) Marine calcified organism-inhabited seawaters. As photosynthesis continuously consumes CO_2 (aq), it is always produced from major HCO_3^- ($HCO_3^- + H^+ \rightarrow CO_2$ (aq) $+ H_2O$) to approach a stationary state in (***b***). Starting material of calcification as well as photosynthesis is stable major HCO_3^- and not unstable minor CO_3^{2-}. The figures in brankites are standard affinity (kJ/mol) at 300 K and 1 atm.

The chemical properties (e.g. $[Ca^{2+}]$, $[HCO_3^-]$ and $[CO_2(aq)]$) of $CaCO_3$-oversaturated water are expressed as a function of master variables, atmospheric P_{CO2} and physiological pH (Supplementary (*b*)) by using proton-controlled mechanism (Scheme 1a), as follows:

$$\log [Ca^{2+}] = -2pH - \log P_{CO2} + \alpha,$$

$$\log [HCO_3^-] = pH + \log P_{CO2} + \beta,$$

$$\log X_{sp} = -pH + \alpha + \beta$$

and

$$\log [CO_2(aq)] = \log P_{CO2} + \gamma$$

Here Xsp stands for the product $[Ca^{2+}][HCO_3^-]$. The last equation was derived from atmosphere-water equilibrium equation between atmospheric CO_2 and hydrated CO_2 (i.e. CO_2 (aq)). Both $[Ca^{2+}]$ and Xsp are variable along with falling and rising pH levels. Here minor unstable CO_3^{2-} produced from acid dissociation reaction of major stable HCO_3^- (Supplementary (*a*)) shows the much more small contribution to proton production/consumption was deleted out for simplicity at physiological pH < ~8.5. Parameters α, β and γ were defined by the standard Gibbs free energies G^o, i of chemical species i and evaluated from standard Gibbs free energy difference, ΔG^o.

The simple equation $pH = (-\log [Ca^{2+}] - \log P_{CO2} + \alpha)/2$ (α = 9.94 calculated at 300 K and 1 atm) derived from proton-controlled mechanism (Supplementary (*b*)) reproduced the observed pH=~8 of $CaCO_3$-oversaturated water by using experimental data of Ca^{2+} concentrations under P_{CO2} 350-400 ppm at room temperature (Supplementary (*c*) and [1]).

2.2. Reversible chemical reactions controlled by proton/hydroxide production/consumption

Water CO_2 uptake is first enhanced via real nucleophilic reaction of hydroxide to unstable hydrated carbon dioxide CO_2(aq) to produce stable major bicarbonates,

$CO_2(aq) + OH^- \leftrightarrow HCO_3^-$. Ao = 43.6 kJ/mol

Here Ao stands for standard affinity. As the produced OH^- by the acid-base dissociation reaction of water is consumed, water CO_2 uptake causes acid increase. The collision between CO_2 (aq) and water molecules produces few protons owing to material energetics (supplemental (*d*)). Since the large magnitude of $[HCO_3^-]/[CO_2(aq)]$ is controlled by material energetics, ocean CO_2 uptake is around one hundred times enhanced (Supplemental (*a*)) at physiological pH. CO_2(aq) in equilibrium with atmospheric CO_2 (g) is more unstable, compared with CO_2 (g): $CO_2(aq) = CO_2(g)$ Ao = 8.5 kJ/mol.

Spontaneous recovery of pH=~8.0 from more acid or more base, and simultaneous calcification/decalcification and proton production/consumption may take place in calcium carbonate-oversaturated water.

An equilibrium equation between calcification and dissolution in calcium carbonate-oversaturated water,

$CaCO_3 + H^+ \leftrightarrow HCO_3^- + Ca^{2+}$, Ao = 11.7 kJ/mol

is dynamical via the ups and downs of proton concentrations. Proton attack may bring about $CaCO_3$ dissolution because of small but positive Ao. The "overbasic" pH peak and supersaturated $CaCO_3$ were observed at pH > ~8 during sodium hydroxide titration to aqueous calcium ion solutions [1]. The observed peaks were caused by the slow production rate of both $CaCO_3$ and proton because of negative standard affinity of forward calcification. The spontaneous prompt pH-increase was observed along with acid-attack dissolution of supersaturated $CaCO_3$. An equilibrium pH was observed at around pH=8 (Figure 1 of [1] and Supplementary (*c*)). The dissolution reaction via proton consumption owing to protonation of CO_3^{2-} at solid $CaCO_3$ surface takes place at the oversaturated $CaCO_3$-water interface (Figure 4 of [1]). The backward calcification occurs via the Ca^{2+}-inspired deprotonation of major stable HCO_3^-, as the acid dissociation constant pKa (= -log Ka) of Ca^{2+}-inspired HCO_3^- is equal to ~2, but that of HCO_3^- to ~10.

2.3. Application of proton-controlled mechanism to coupling of marine calcifying organisms with ocean pH

The reactions and pathways of proton production/consumption outside and inside the cytoplasts of marine calcareous phytoplanktons and endosymbiont-bearing zooplanktons must be identified from view of fundamental chemical biology and material energetics. The calcifying organisms-inhabited seawaters may be identified on the basis of $CaCO_3$-oversaturated water; the variation between pH=8.3 and 8.0 may come from many stationary states during the paleo and preindustrial ages [2,4].

The proton-controlled mechanism is applied to marine calcifying organism-inhabited seawaters. The normalized concentrations of RCa (=$[Ca^{2+}]/[Ca^{2+}]_0$) and $RHCO_3$ (=$[HCO_3^-]/[HCO_3^-]_0$), and the normalized product of concentrations Ca^{2+} and HCO_3^- RXsp (=$[Ca^{2+}][HCO_3^-]/([Ca^{2+}]_0[HCO_3^-]_0)$) are evaluated by,

$$\log RCa = -2pH - \log P_{CO2} + \alpha - \log [Ca^{2+}]_0,$$

$$\log RHCO_3 = pH + \log P_{CO2} + \beta - \log [HCO_3^-]_0$$

and

$$\log RXsp = - pH + \alpha + \beta - \log (Xsp)_0,$$

where the suffix zero of $[C]_0$ or $(Xsp)_0$ (=$[Ca^{2+}]_0[HCO_3^-]_0$), stands for a reference state at (pH_0, P_{CO20}). The (pH, P_{CO2}) dependence of RCa (Figure 1), $RHCO_3$ and RXsp was evaluated between 190 ppm and 750 ppm at pH=8.5-7.5, where the reference state of paleo atmosphere P_{CO2} 280 ppm and paleo ocean pH=8.15 was four times observed at around interglacial age during the past ~100 kyr-cyclic 400 kyr [2]. Here RCa = 2 means that $[Ca^{2+}]$ is two times increased at P_{CO2}=380 ppm and pH=7.93 in comparison with $[Ca^{2+}]_0$ at 280 ppm and 8.15. Since pH coefficient *a* of RCa (= -*a* pH + *b*) is equal to ~2 at RCa < ~0.9 and ~15 at RCa > ~2.5, the decalcification or thinner growth of $CaCO_3$-produced shells/skeletons is much more enhanced along with falling pH levels at pH < ~7.9 (Figure 1). While RCa decreases with rising pH levels at a given P_{CO2}, calcification/ thicker growth takes place. The serious change of RCa 0.9 to 2.5 (i.e. a green or upper line to a rose pink or lower line in Figure 1) may take place under pH decrease of ~8.0 to ~7.9: it may suggest that ocean acid attack to calcifying organism will take place in near future, as mentioned later. The small change of $RHCO_3$ between 0.7 and 1.0 may, however, not relevant to characterize the time-courses of chemical properties of calcifying organism-inhabited seawaters. The past, present and near future oceans are characterized from the temporal dependence of the identified P_{CO2} and pH. The coupling of marine calcifying phytoplanktonic coccolitho-phores, and phytosymbiont-bearing corals or foraminifera with the marine proton concentration and marine chemical properties may be relevantly revealed by applying biochemical proton production/consumption reactions to proton-controlled mechanism and material energetics.

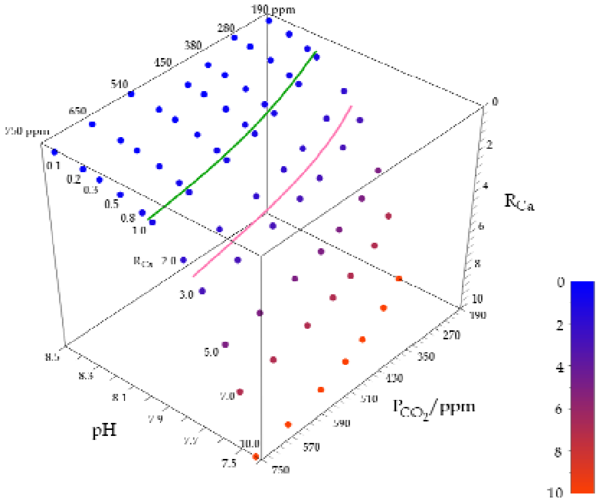


Figure 1. The normalized RCa (= $[Ca^{2+}]/[Ca^{2+}]_0$) by a specified reference state was evaluated for the master variables of atmospheric P_{CO2} and ocean pH. The reference state was identified at the four times observed P_{CO2} 280 ppm and pH=8.15 of the four interglacial ages during the past ~400 kyr. The normalized isoconcentrations of RCa 0.1-10 were evaluated between pH=7.5 and 8.5 at the past, present and future P_{CO2}=190-750 ppm. The green and rose pink lines correspond to RCa = 0.9 and 2.5, respectively.

2.4. Cyclic change in ocean ph and thicker/thinner growth $CaCO_3$-made shell during paleo ages

As the atmospheric P_{CO2} and calcareous organism-inhabited seawater pH were identified for the paleo, preindustrial and modern ages by stable isotope technique [2,4,7], the seawater of interest is pointed out by an identified coordinate in the three-dimensional coordinates of P_{CO2}, pH and RCa (Figure 1). The RCa or RXsp that identifies thicker or thinner growth is evaluated from seawater pH and atmospheric P_{CO2} in equilibrium/stationary state of the past and present oceans. The RCa or RXsp of near future oceans may be predicted by temporal dependence of P_{CO2} and pH, although temporal dependence of calcium ion concentrations in oceans was not identified over the paleo and preindustrial ages. But the $CaCO_3$-dissolution rates were determined from the in situ experiment or estimation [3,8].

The temporal dependence of ocean pH and atmospheric P_{CO2} during the past 400 kyr did four times show the around 100 kyr cycle of glacial-interglacial age [2]. The four glacial-interglacial ~100 kyr cycles were mainly determined by earth precession and tilt target [9]. The normalized calcium ion concentrations (RCa) in stationary state of planktonic foraminifer-inhabited oceans were evaluated from the proton-controlled mechanism by using the pH and P_{CO2} data during the past 400 kyr: they showed the small change of 0.9 to 1.1 for the data of pH=8.35-8.15 [2] and P_{CO2}=195-280 ppm identified from the bubbles of Vostok Antarctic ice core [4,9], as shown by a green box of Figure 2. The paleo oceans of four glacial-interglacial ages were, therefore, characteristic of steady stable ecosystem of foraminifera over the past 400 kyr.

The estimated RCa(model) from the observed $CaCO_3$-made shell weights, W_{fora}, of similarly sized fossil foraminifera (Table 1 of [2], Supplementary (***e***)) roughly reproduced the evaluated ~100 kyr-cyclic RCa by proton-controlled mechanism, as shown in Figure 3. The rough agreement between RCa(model) and RCa confirmed that thicker/thinner growth of foraminifera shells took place according to the proton-controlled mechanism. The higher atmospheric P_{CO2} is a negative feedback to thicker growth/calcification at pH=8.35-8.15 under P_{CO2} < ~290 ppm. The thicker growth or calcification is not a positive feedback of P_{CO2} increase. The temporal dependence of size-normalized shell weight data for paleo foraminifera reconstructed the same results during the past 50 kyr but without pH data [10]. The calcification (i.e. increased weight of planktonic foraminifer shells) and decalcification (i.e. their decreased weight) correspond respectively to the decrease and increase in RCa (Figure 3). The calcification acts as no CO_2 production and is not a positive feedback to rising atmospheric P_{CO2} levels. The observed faster ocean acidification brought about the faster thinner growth of foraminifer shells i.e. the faster increase in RCa (Figure 3). The marine calcifying organisms showed a slowly thicker growth (i.e. slow decrease of RCa) along with the slow pH increase; the slow change in RCa may come from negative affinity for forward calcification.

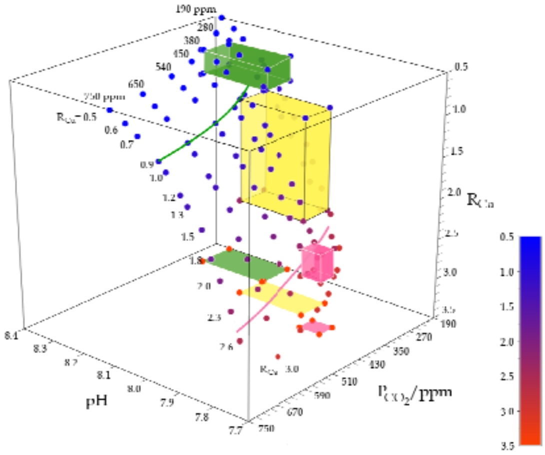


Figure 2. The paleo oceans during the past 400 kyr are identified in a green box of P_{CO2} 195 ppm-280 ppm, pH=8.35-8.15 and RCa=0.85-1.1, the preindustrial and industrial oceans during the past 1710 yr-1990 yr are in a yellow box of P_{CO2}=275-350ppm, pH=8.15-7.95 and RCa=1.15-2.35, and the nearly future oceans may be estimated in a rose pink box of P_{CO2}=355-395ppm, pH=7.9-7.85 and RCa=2.6-2.85. For instance RCa=2 means that $[Ca^{2+}]$ is equal to the twice magnitude of reference concentration $[Ca^{2+}]_0$ at P_{CO2} 280 ppm and pH 8.15, as mentioned in Figure 1 and text.

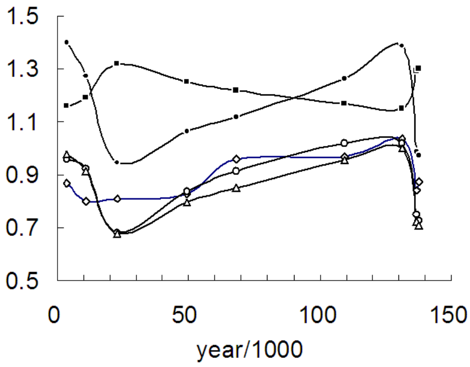


Figure 3. The around 100 kyr-cyclic dependence of P_{CO2} 195 ppm-280 ppm, pH=8.35-8.15 and RCa=0.85-1.1 during the past 400 kyr. The ~100 kyr-cyclic RCa (model) was estimated from the age dependence of paleo planktonic foraminifera shells weight, Wfor (Table 1 in Ref. [2]) as mentioned in text and Supplementary (*c*)). The temporal variations of RCa (model) reconstructed that of the evaluated RCa by proton-controlled mechanics and using the data of P_{CO2} and pH. ●: P_{CO2}/200, ■: pH - 7, ○: RCa, ◊: RCa (model), Δ: RXsp.

2.5. Oscillating but stable ph and thicker/thinner growth of preindustrial and modern oceans

The coral reef oceans at preindustrial to modern age is located at RCa=1.15-2.35 between a green or upper line at RCa 0.9 and a rose pink or lower line at RCa 2.5 (Figure 1), as shown by a yellow box of Figure 2. The ~50 yr-periodic oscillating variation in RCa evaluated from proton-controlled mechanism was similar to that of pH between the identified 8.15 and 7.95 by boron isotopic technique [7,8] under the gradually increased P_{CO2} of 270 ppm to 315 ppm between 1710 yr and 1950 yr of preindustrial to modern, as shown in Figure 4. The phases of oscillating temporal dependence of pH and RCa were opposing to each other under the granularly increasing P_{CO2} (Figure 4). The coral reef seawaters in yellow box are not yet dangerous for marine ecosystem of reef corals, as they may tolerate ocean acid attack. The ups and downs of RCa or RXsp correspond respectively to falling and rising pH levels (i.e. the thicker growth for pH increase and the thinner growth for pH decrease) under steady increase of 270 ppm to 315 ppm (Figure 4). Since the reef corals alternatively repeated thinner growth and thicker growth under gradually increased P_{CO2} over the past 1710 yr-1950 yr, marine calcification/decalcification corresponds to no carbon dioxide release/sink; the observed oscillating stability of ocean pH does not always need the P_{CO2} ups and downs. The alternate increase and decrease in RCa came from alternate falling and rising pH levels under increased P_{CO2}, as 2pH is much larger than positive-logP_{CO2}. Biochemical or enzymatic proton production/consum- ption reactions control seawater pH under the influence of atmospheric CO_2 and vice versa, as shown in Scheme 1b of the partially improved proton-controlled mechanism. The enzymatic reaction of major HCO_3^- species with protons continuously produces a profusion of unstable CO_2(aq) species, as they are consumed for photosynthesis. The continuous consumption of protons may enhance thicker shell-growth because of proton production along with calcification. $CaCO_3$-supersaturated waters in the absence of marine calcifying organisms are, however, static at pH=~8 in equilibrium with atmosphere, as no continuous consumption of protons takes place via photosynthesis (Scheme 1a).

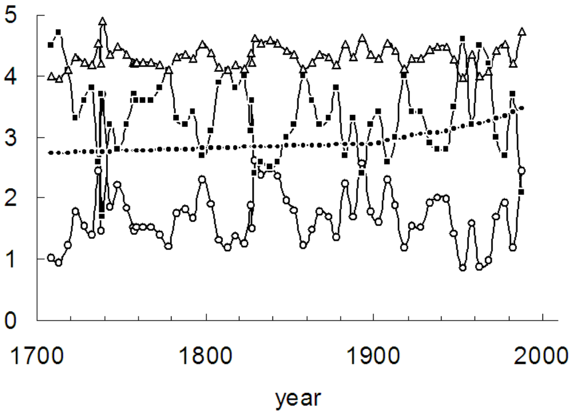


Figure 4. Temporal variations of the falling/rising pH levels and RCa/RXsp increase/decrease were identified under the increased P_{CO2} during 1710 yr-1990 yr. The minima and maxima of the observed pH derived the maxima and minima of RCa or RXsp, respectively. RCa and RXsp were evaluated by proton-controlled mechanics and using the data of P_{CO2} and pH. ●: P_{CO2}/100, ■: 10 (pH=7.8) + 1, ○: RCa, Δ: RXsp + 3.

2.6. Anthropogenic ocean acidification at recent age and in near future

In coral reefs between 1950 yr and 1990 yr the temporal variation of pH showed some abnormal behavior of oscillating but falling levels under increase of 320 ppm to 350 ppm (Figure 4), and may cause ocean acidification and thinner growth of coral skeletons. If the nearly future P_{CO2} and pH become by 15 ppm larger than present P_{CO2}=350-380 ppm and by ~0.1 lower than present seawater pH=8.0-7.95, RCa in the calcifying organism-inhabited oceans ranges between 2.6-2.85 (a rose pink box in Figure 2). Since the evaluated RCa=2.5-2.6 at P_{CO2}=350-365 ppm and pH=7.9 corresponds to ~60%-decreased weight of outer casings of marine calcifying organisms, the pH decrease of ~0.1 might eat away at $CaCO_3$-

made skeletons/shells. The $CaCO_3$-made outer casings protect the calcifying planktonic organisms located at the basis of marine food chain. The proton-controller mechanism gives serious caution that seawater pH downs are caused by dissolution of anthropogenic acidic molecules (e.g. H_2S, SO_X and NO_X gases) in atmosphere in addition to anthropogenic carbon dioxide. It may be pointed out that the marine calcifying organisms at their infant age are in serious danger by the pH decrease of ~0.1.

2.7. Proton production/consumption in biogenic reactions of calcifying organisms in their inhabited seawaters

One of biogenic reactions of calcifying organisms is enzymatic production reaction of starting material HCO_3^- for calcification or photosynthesis. The carbonic anhydrase CA [11,12] of reef-building corals plays an important role as catalyst of nucleophilic reaction (Scheme 1) similar to the human and mollusk CA [13]. Ocean CO_2-uptake is accelerated via enzymatic conversion of CO_2 (aq) to HCO_3^- material energetics and dissolved inorganic carbon (DIC) concentration is effectively increased. As the acidic dissociation equilibrium constant pKa of water molecule coordinated by CA active center-mimicking organic zinc [14,15] showed the great decrease of pure water pKa=~14 to zinc-coordinated water molecule pKa=7-8 (pKa for mollusk nacrain enzyme and CA is around 7). Since these water molecules are efficiently deprotonated to produce hydroxide at physiological pH < ~8.5, the HCO_3^- production rate becomes faster.

Since photosynthesis needs a large amount of carbon dioxide species as its starting material, they are produced from major HCO_3^- by proton-accelerated dehydration reaction via electrostatic molecular recognition between major HCO_3^- and H^+ in host cytoplast,

$$HCO_3^- + H^+ \rightarrow CO_2(aq) + H_2O. \quad Ao = 36.6\ kJ/mol$$

This reaction is necessary for the calcifying organisms of phytoplanktons and phytosymbionts in seawaters, associated with cyclic/oscillating stability between pH=8.3 and 8.0, as shown in Scheme 1b. The calcification to fix $CaCO_3$-made outer casings, on the other hand, produces protons and seawater pH decreases. The simultaneous photosynthesis-inspiring calcification and calcification-inspiring photosynthesis are much more relevant for the calcifying organisms of phytoplanktons and phytosymbionts.

The CO_2(aq) production for photosynthesis continually consumes protons but thicker growth of skeletons/shells supply protons. The correlation between calcification and photosynthesis creates a number of stationary states owing to the oscillating variation of seawater pH=~8.3-~8.0 [8]. Photosynthesis enhances biogenic calcification and vice versa, as the thicker growth of $CaCO_3$-made outer casings causes proton production and photosynthesis continuously needs protons to produce CO_2(aq) from major HCO_3^-. Since $CaCO_3$-supersaturated water has no function of photosynthesis, on the other hand, the water becomes static at steady pH=~8 under equilibrium with atmosphere.

The CO_2(aq)-concentrating process may take place in cytoplast [16,17]. Calcification in vesicles can enhance photosynthesis in the chloroplast of calcareous phytoplanktons (e.g. coccolithophores) and vice versa [18-21]. The endosymbiont-bearing protests (e.g. foraminifera) sequester chloroplasts and have many calcifying vacuoles of $CaCO_3$ stores [22]. As a profusion of endosymbiotic phytoplanktonic alga (zooxanthellae) carry out the enzymatic conversion of HCO_3^- to CO_2(aq) and proton consumption in the host coral's tissues [23,24], the photosynthesis of alga enhances thicker growth rate of reef coral's skeletons.

3. Conclusion

The stable major species of HCO_3^- react with calcium ions to produce calcium carbonate and protons. The oversaturated $CaCO_3$ reacts with protons to produce calcium ion and HCO_3^-. The $CaCO_3$-supersaturated weakly basic water at around pH=8 was expressed by novel simple equation, $\log [Ca^{2+}] = -2pH - \log P_{CO2} + 9.94$ derived by proton-controlled mechanism for coupling among proton production/consumption reactions in equilibrium with atmospheric carbon dioxide.

The cyclic/oscillating variation between pH=8.3 and 8.0 for marine calcifying organism-inhabited paleo and preindustrial seawaters was elucidated by applying the improved proton-controlled mechanism to biochemical reactions in cytoplasts or host tissues of marine calcifying phytoplanktons and phytosymbiont-bearing corals/zooplanktons. The simple equations expressed as function of P_{CO2} and pH can characterize the past, present and nearly future seawaters (e.g. $\log RCa = -2pH - \log P_{CO2} + 12.75$, where normalized RCa ($=[Ca^{2+}]/[Ca^{2+}]_0$) by the reference state at paleo atmosphere P_{CO2}=280 ppm and paleo ocean pH=8.15 which were four times observed at around interglacial age). The cyclic or oscillating stability of calcium concentrations or fossil-shell weights during paleo and preindustrial ages was revealed from the novel simple equation and the observed temporal dependence of P_{CO2} and pH. Since the thicker growth of $CaCO_3$-made shells/skeletons causes proton production, marine biogenetic calcification in cytoplast enhances photosynthesis that continuously needs protons to produce CO_2(aq) from major HCO_3^-. The biogenic calcification gives no production of CO_2 and is no positive feedback to atmospheric P_{CO2} increase. The photosynthesis consumes protons and inspires their thicker growth. The correlation between calcification and photosynthesis creates a number of stationary states along with seawater pH variation. The possible many stationary states under increasing partial pressure of CO_2 brought about the many observed calcification response patters of marine calcifying planktons [25].

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Supplementary material

Supporting information for this article is available on the WWW under http://www.eurjchem.com or from author.

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