European Journal of Chemistry 1 (4) (2010) 246-251

EurJChem European Journal of Chemistry EurJChem

Journal homepage: www.eurjchem.com

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

Kazuhiko Ichikawa

Graduate School of Environmental Earth Science, Hokkaido University, Sapporo, JP-060-0810, Japan

**Corresponding author at: Graduate School of Environmental Earth Science, Hokkaido University, Sapporo, JP-060-0810, Japan. Tel.: +81.11.761.5456; fax: +81.11.761.5456.E-mail address: ichikawa@ees.hokudai.ac.jp (K. Ichikawa).*

ARTICLE INFORMATION

Received: 03 March 2010
Received in revised form: 21 July 2010
Accepted: 25 July 2010
Online: 31 December 2010

KEYWORDS

Acid attack
Calcifying organism
Phytosymbiont
Proton mechanism
$CaCO_3$-oversaturated water pH
Seawater pH

ABSTRACT

The $CaCO_3$-oversaturated weakly basic water at around pH=8 was proved by the novel simple equations (e.g. log $[Ca^{2+}] = -2pH - \log P_{CO2} + 9.94$) 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_{CO2} levels.

Supplementary Materials

(*a*) Energetically controlled relative concentrations: stable major HCO_3^- species, compared with unstable minor $CO_2(aq)$ and CO_3^{2-} species at physiological pH < ~8.5

Since the magnitude of $[HCO_3^-]/[CO_2(aq)]$ is controlled by material energetics, water/seawater CO_2 uptake is around one hundred times enhanced. The ratio is equal to ~40 at pH 8 for NaCl/$NaNO_3$-dissolved waters at I = ~0.1M [S1], and ~120 at pH 8 for seawaters at I = ~0.7M [S2, S3].

Minor CO_3^{2-} is in equilibrium with major HCO_3^- via reversible acid-dissociation reaction, i.e. $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ ($\Delta Go = 59.3$ kJ mol^{-1}): $[HCO_3^-]/[CO_3^{2-}]$ is equal to ~2×10^2 at I = ~0.1M and pH 8 [S1]), and to ~10 at I = ~0.7M at pH 8 for seawater [S2, S3].

(*b*) $CaCO_3$-oversaturated waters at pH < ~8.5

In $CaCO_3$-supersaturated waters at less than around pH 9 and I = ~0.1M at 300 K and 1 atm

$HCO_3^- + Ca^{2+} = CaCO_3 + H^+$, $\Delta Go = 11.7$ kJmol-1 (1)

where ΔGo stands for Gibbs free energy difference and $Ka = [H^+]/\{[HCO_3^-][Ca^{2+}]\}$.

$CO_2\ (aq) + OH^- = HCO_3^-$ 43.7 (2)

where $Knucl = [HCO_3^-]/\{[CO_2\ (aq)][OH^-]\} = \{[HCO_3^-]/[CO_2\ (aq)]\}\{Kneut\ [H^+]\}$.

$H^+ + OH^- = H_2O$, 79.9 (3)

where $Kneut = 1/\{[H^+][OH^-]\}$ and

$[Ca^{2+}] = [H^+]/\{Ka[HCO_3^-]\} = \{ Ka\ Knucl/ Kneut \}^{-1} [H^+]^2 [CO_2\ (aq)]^{-1}$.

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online) © 2010 EURJCHEM
DOI:10.5155/eurjchem.1.4.246-251.156

$CO_2 = CO_2(aq)$,   8.5   (4)

where $[CO_2\ (aq)] = k_H P_{CO2}$ owing to Henry`s Law and $k_H = 3.3810^{-2}$ M atm^{-1} at 300 K and 1 atm.

Thus,

$pCa = -\log[Ca^{2+}] = 2pH - pPCO2 - 9.94$

$[HCO_3^-] = [H^+]/\{ [Ca^{2+}]\ Ka \}$

$pHCO_3 = -\log[HCO_3^-] = -pKa + pH - pCa = pH + pPCO2 + 7.88$

$pXsp = -\log [HCO_3^-][Ca^{2+}] = pHCO_3 + pCa = pH - 2.03$

$pCO_2 = -\log [CO_2(aq)] = pPCO2 + 1.47$

Here $pPCO2 = -\log PCO2$.

(*c*) Figure S1.

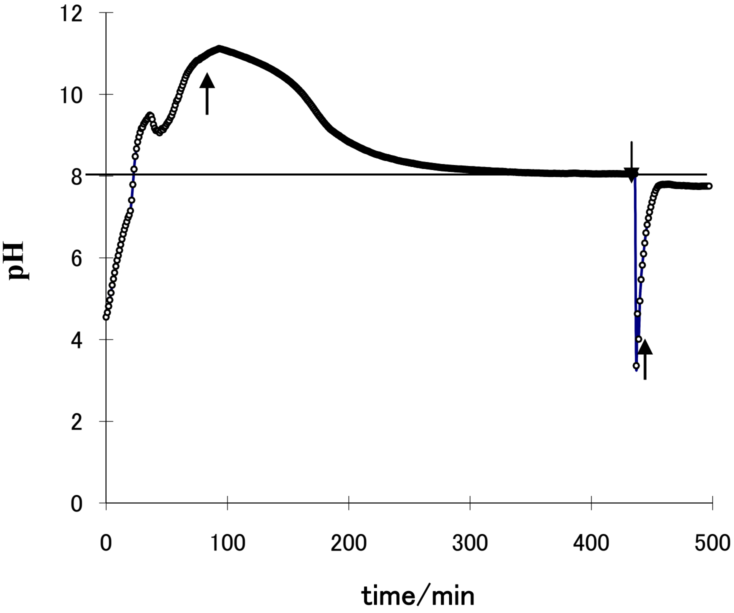

Figure S1 For the $CO_2/CO_2(aq)$-HCO_3^--CO_3^{2-}-Ca^{2+}-$CaCO_3$ system the time evolution of proton concentration was measured during the 0.05 M NaOH titration into 5 mM Ca^{+2}-including 0.1M NaCl [S4]. An overbasic pH peak and $CaCO_3$ precipitation were appeared between pH 8 and 9.5 during the sodium hydroxide titration. After the NaOH or HNO_3 addition was stopped at the up arrows, the spontaneous recovery from basic to physiological or from acidic to physiological was observed. At a down arrow HNO_3 was quickly added to the solution until pH ~ 4.

(*d*) No real reactions somewhat different from material energetics-controlled proton production/consumption reactions

It has been sometimes recognized that acidification of waters/seawaters in equilibrium with atmosphere mainly originates from acid dissociation reaction of dissolved carbon dioxide molecules $CO_2(aq)$ as follows,

$CO_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+$.   Ao = -36.6 kJ mol^{-1}

The forward reaction or proton formation is actually rejected from view of material energetics, e.g. negative standard affinity Ao [S5]. The chemical nucleophilic reaction of hydroxide ion to $CO_2(aq)$ is actual as mentioned in text, and the consumption of hydroxide ions causes water acidification under dissociation reaction of water molecules.

It is now recognized in the published articles [S3, S6-S8] that dissolution of oversaturated $CaCO_3$ or thinner growth of outer casings of calcifying organisms was caused by the decreased concentration of minor CO_3^{2-} via a reaction,

$CO_2(aq) + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^-$. Ao = 23.0 kJ mol^{-1}

The above discussion was, however, built up from incorrect identification that production and dissolution of $CaCO_3$ are mainly controlled by $Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$ at pH < ~8.5. The chemical nucleophilic reaction for HCO_3^- production, $CO_2(aq) + OH^- \leftrightarrow HCO_3^-$, is major because of larger Ao = 43.6 kJ mol^{-1}, as mentioned in text. The production and dissolution of $CaCO_3$ are controlled by a chemical reaction, as mentioned in text. Minor CO_3^{2-} is produced via reversible acid-dissociation reaction of major HCO_3^- from view of material energetics at pH < ~8.5.

(*e*) Evaluation of RCa by using the observed weight W_{fora} of fossil planktonic foraminifera.

Under equilibrium or stationary state of surface foraminifera-inhabited seawaters $[Ca^{2+}]$ is inversely proportional to the observed weight W_{fora} of fossil planktonic foraminifera. Here RCa(model) was estimated from 11.6/W_{fora} because of the reference weight 11.6g at PCO2 ~280ppm and pH ~8.15 (see Table 1 of [S9]). The data of W_{fora} were measured from average weight of 50 foraminifera collected for identified age during the past 400kyr (private communication of Börbel Hönisch 2008).

S1. e.g. Manahan, S.E. *Environmental chemistry,* Lewis Pub., Tokyo (1994).
S2. Zeebe, R. E.; Wolf-Gladrow, D. CO_2 in Seawater: Equilibrium, Kinetics, Isotopes, *Elsevier Oceanography Series 65*, 2-53 (Elsevier 2000).
S3. Fabry, V. J.; Seibel, B. A.,; Feely, R. A.; Orr, J. C. Impacts of ocean acidification on marine fauna and ecosystem processes *ICES J. Marine Sci.* 2008, *65*, 414- 432.
S4. Ichikawa, K. Buffering Dissociation/formation reaction of biogenic calcium carbonate, *Chemistry European J.* 2007, *13*, 10176-10181.
S5. e.g., Prigogine, I.; Defay, R.; Everett, D. H. Chemical Thermodynamics (Longman, London, 1973).
S6. Barker, S.; Higgins, J. A.; Elderfield, H. (2003), The future of the carbon cycle: review, calcification response, ballast and feedback on atmospheric CO_2, Phil. *Trans. R. Soc. Lond.*2003, *A 361*, 1977-1999.
S7. Riebesell, U. Effect on CO_2 enrichment on marine phytoplankton (review), *J. Oceanography* 2004, *60*, 719-729
S8. Orr, J. C. *et al.* Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms *Nature* 2005, *437*, 681-686.
S9. Hönisch, B.; Hemming, N. G. Surface ocean pH responses to variation in pCO_2 through two full glacial cycles, *Earth and Planetary Science Letters* 2005, *236*, 305-314.