Approaches and tools to manipulate the seawater carbonate chemistry

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Biogeosciences

Technical Note: Approaches and software tools to investigate the impact of ocean acidification

J.-P. Gattuso[1,2] **and H. Lavigne**[1,2]

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[2]Université Pierre et Marie Curie-Paris 6, Observatoire Océanologique de Villefranche,
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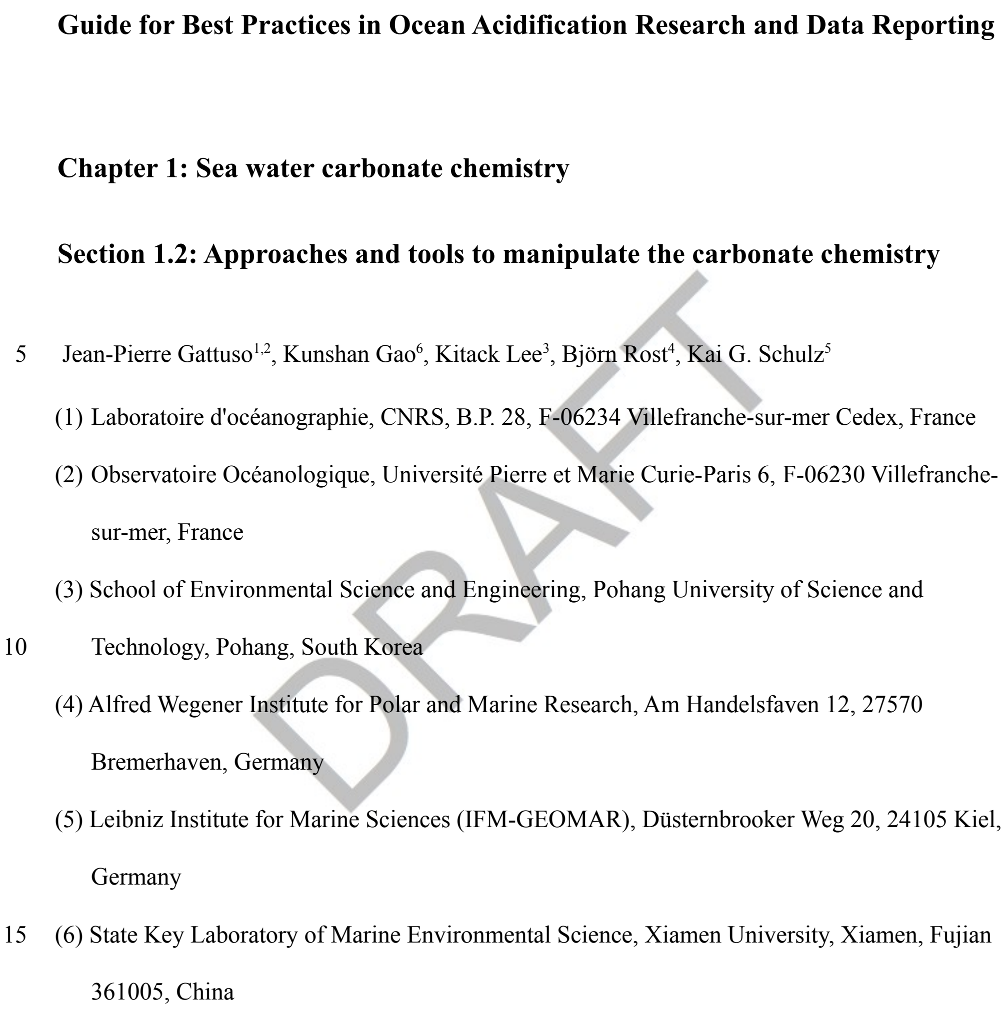

Guide for Best Practices in Ocean Acidification Research and Data Reporting

Chapter 1: Sea water carbonate chemistry

Section 1.2: Approaches and tools to manipulate the carbonate chemistry

Jean-Pierre Gattuso[1,2], Kunshan Gao[6], Kitack Lee[3], Björn Rost[4], Kai G. Schulz[5]

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(3) School of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang, South Korea
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(6) State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, Fujian 361005, China

Introduction

- First purposeful experiments have only been carried out in the 1980s (Agegian, 1985) and most after the late 1990s
- Newcomers with a limited knowledge of the carbonate chemistry and its experimental manipulation; some guidelines could be helpful
- Standardization of measurement of parameters completed (Dickson et al., 2007)
- Perturbation experiments: one of the key approaches; physiological and biogeochemical measurements in seawater with normal or altered chemistry
- Seawater chemistry can be manipulated using different ways

Goals

1. Examine the benefits and drawbacks of various methods used to date
2. Provide simple seacarb functions to assist the design of perturbation experiments
3. Provide guidelines for choosing CO_2 levels
4. Provide other recommendations on the experimental set-up

Outline

- *seacarb* (introduced on Monday)
- Main approaches to set and maintain the initial chemistry
  - Changing DIC at constant AT
    - Gas bubbling
    - Addition of strong acid as well as CO_3^{2-} and/or HCO_3^-
    - Addition of high-CO_2 sea water
  - Changing AT at constant DIC: addition of acid
  - Changing AT and DIC: addition of CO_3^{2-} and/or HCO_3^-
  - Manipulation of $[Ca^{2+}]$
- Guidelines for choosing pCO_2 levels
- Maintaining the chemistry during the expts
- Other recommendations
- Summary and conclusions

Assumptions in following examples

- Atmospheric pCO_2 = 384 μatm
- Target pCO_2 = 793 μatm
- Salinity = 34.9
- Temperature = 18.9°C
- Calculations are done for surface waters
- Concentrations of total phosphate and silicate are assumed to be 0
- Methods to reach the initial carbon chemistry (biological impacts addressed later)

What are we trying to accomplish?

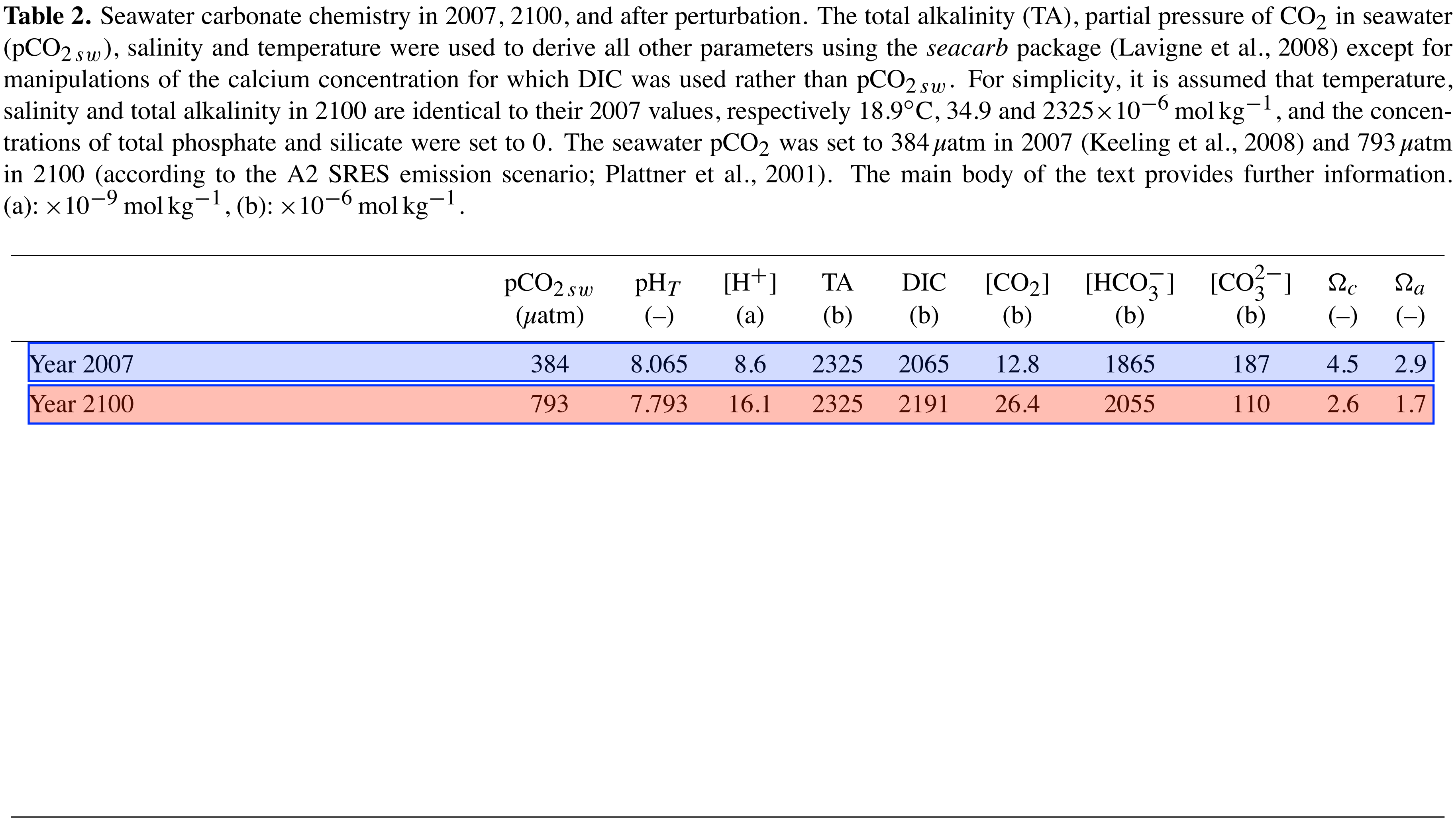


Table 2. Seawater carbonate chemistry in 2007, 2100, and after perturbation. The total alkalinity (TA), partial pressure of CO_2 in seawater ($pCO_{2\,sw}$), salinity and temperature were used to derive all other parameters using the *seacarb* package (Lavigne et al., 2008) except for manipulations of the calcium concentration for which DIC was used rather than $pCO_{2\,sw}$. For simplicity, it is assumed that temperature, salinity and total alkalinity in 2100 are identical to their 2007 values, respectively 18.9°C, 34.9 and 2325×10^{-6} mol kg^{-1}, and the concentrations of total phosphate and silicate were set to 0. The seawater pCO_2 was set to 384 μatm in 2007 (Keeling et al., 2008) and 793 μatm in 2100 (according to the A2 SRES emission scenario; Plattner et al., 2001). The main body of the text provides further information. (a): $\times 10^{-9}$ mol kg^{-1}, (b): $\times 10^{-6}$ mol kg^{-1}.

	$pCO_{2\,sw}$ (μatm)	pH_T (–)	$[H^+]$ (a)	TA (b)	DIC (b)	$[CO_2]$ (b)	$[HCO_3^-]$ (b)	$[CO_3^{2-}]$ (b)	Ω_c (–)	Ω_a (–)
Year 2007	384	8.065	8.6	2325	2065	12.8	1865	187	4.5	2.9
Year 2100	793	7.793	16.1	2325	2191	26.4	2055	110	2.6	1.7

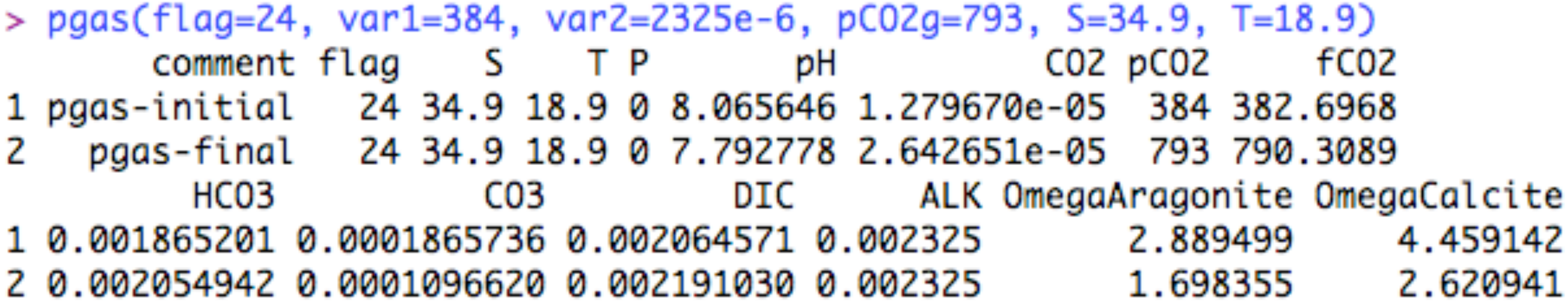
Gattuso & Lavigne (2009)

Changing DIC at constant TA

Gas bubbling

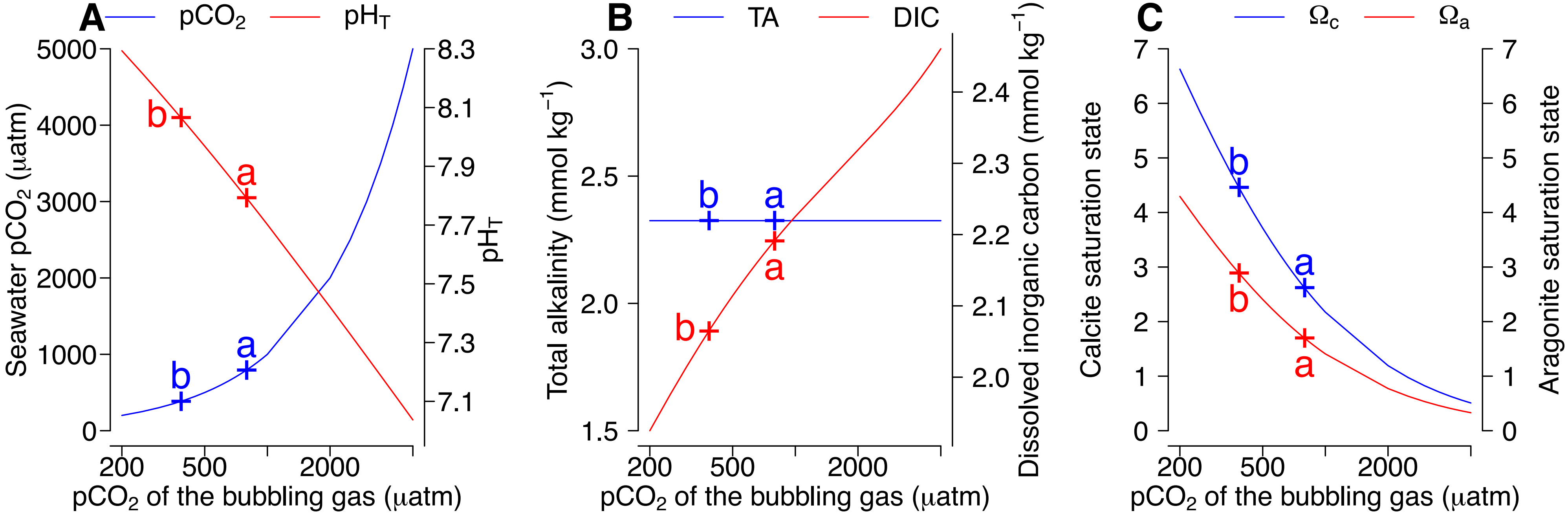
- System open to the atmosphere:
  - TA unaffected
  - If all goes well, pCO_2 reaches the value of the bubbled air
- Example:

  seawater with pCO_2=384 μatm and TA=2325 × 10^{-6} mol kg^{-1} is bubbled with air of pCO_2=793 μatm
- *seacarb* function:



```
> pgas(flag=24, var1=384, var2=2325e-6, pCO2g=793, S=34.9, T=18.9)
      comment flag    S    T P       pH          CO2 pCO2     fCO2
1 pgas-initial   24 34.9 18.9 0 8.065646 1.279670e-05  384 382.6968
2   pgas-final   24 34.9 18.9 0 7.792778 2.642651e-05  793 790.3089
         HCO3          CO3         DIC      ALK OmegaAragonite OmegaCalcite
1 0.001865201 0.0001865736 0.002064571 0.002325       2.889499     4.459142
2 0.002054942 0.0001096620 0.002191030 0.002325       1.698355     2.620941
```

Gas bubbling



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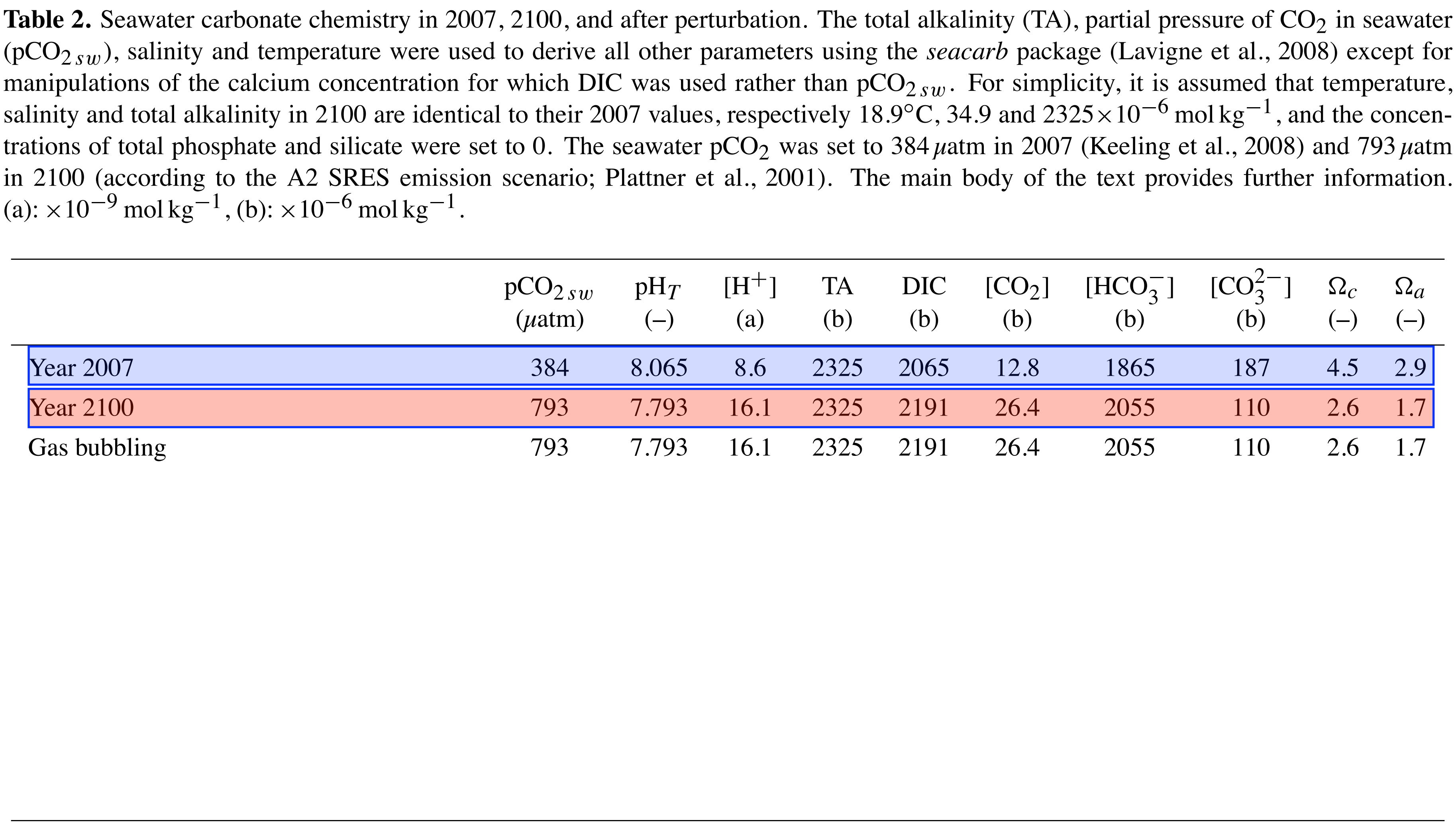

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Gattuso & Lavigne (2009)

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J.-L. Teyssié (IAEA)

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    - controller opens and closes valves when pH (pCO_2) deviates from target value
    - gases (acid/base) delivered until target pH (pCO_2) is reached
    - gases: (1) air and CO_2, (2) CO_2-free air and CO_2 or (3) CO_2-free air, air and CO_2
    - CO_2-free air obtained using molecular sieves or CO_2 scrubbers such as soda lime or NaOH and $Ca(OH)_2$
    - drawback: daily calibration
  - bubbling with premixed gases (purchased or made with mass flow controllers or gas mixing pumps)

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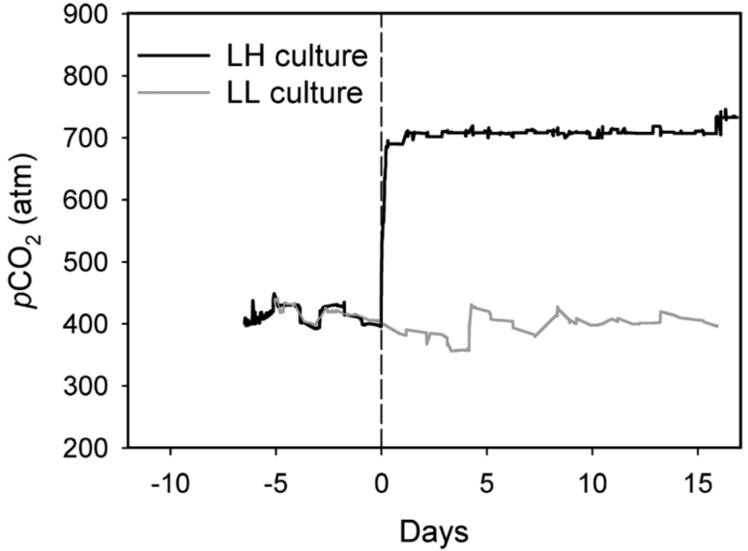

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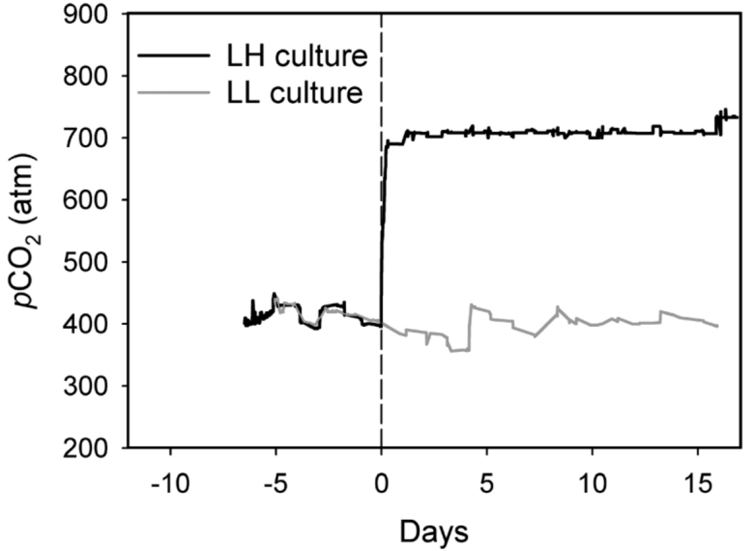

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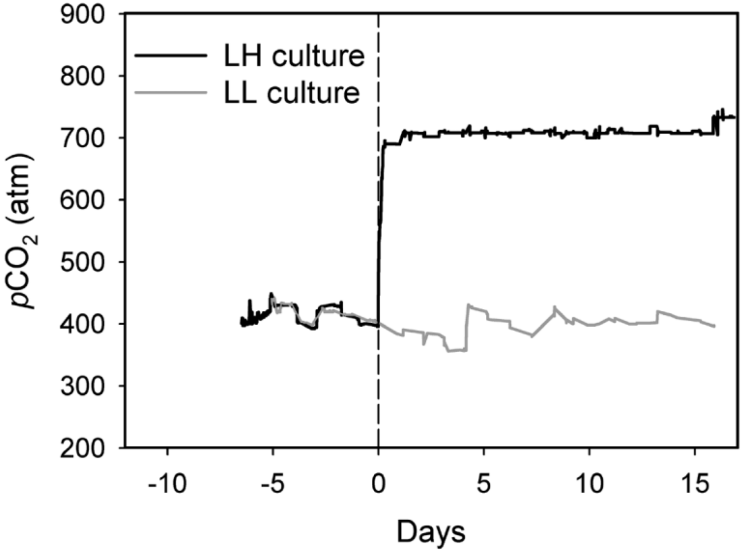
F. Gazeau (CNRS)



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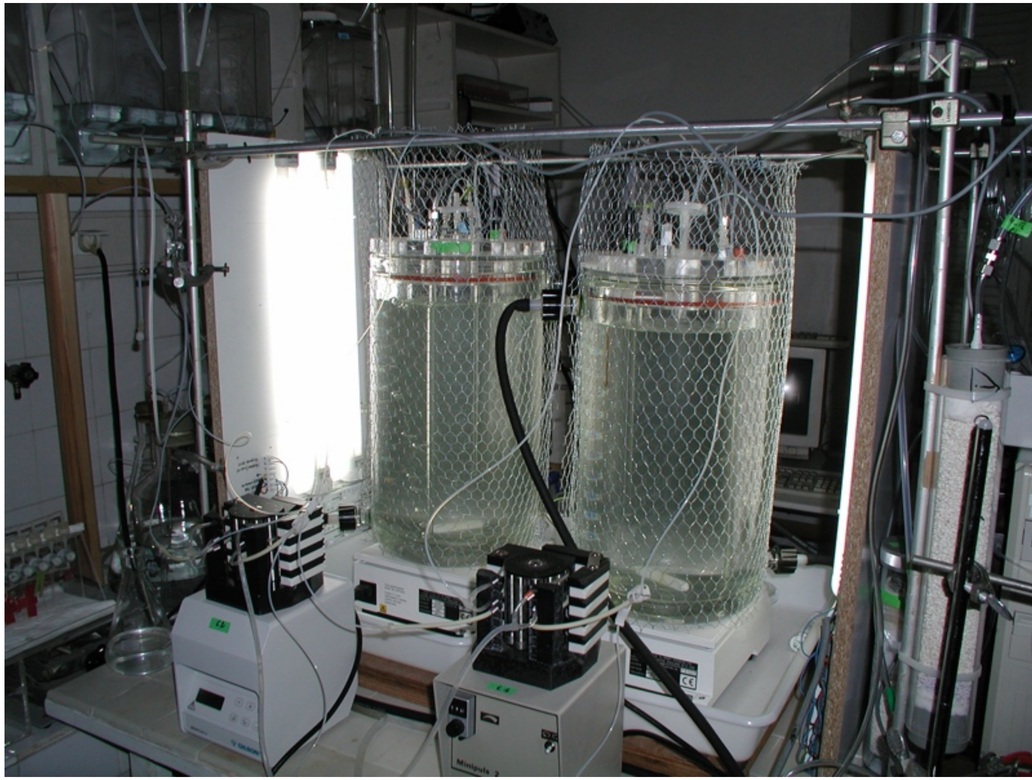

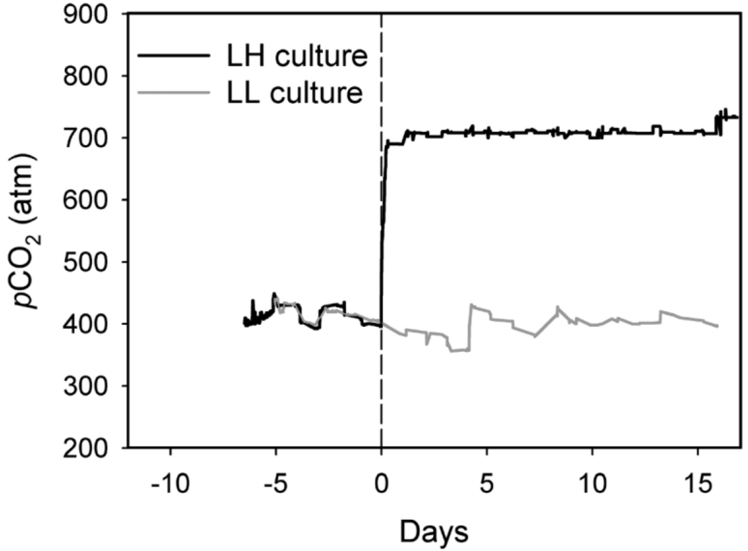

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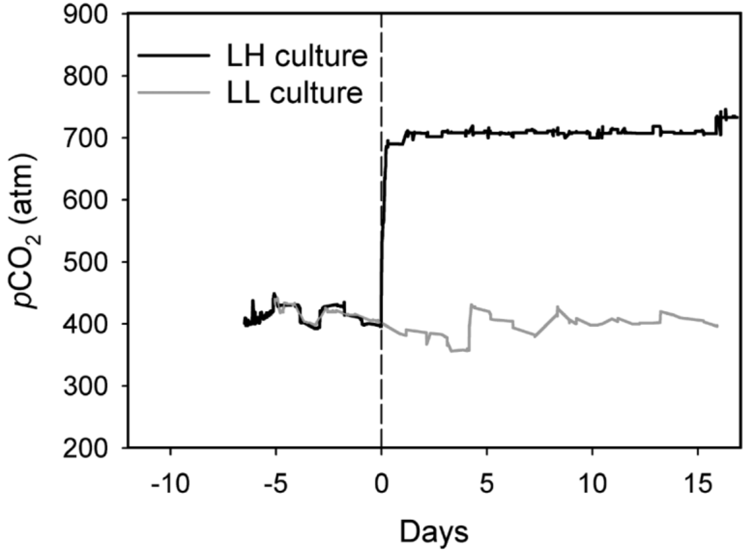

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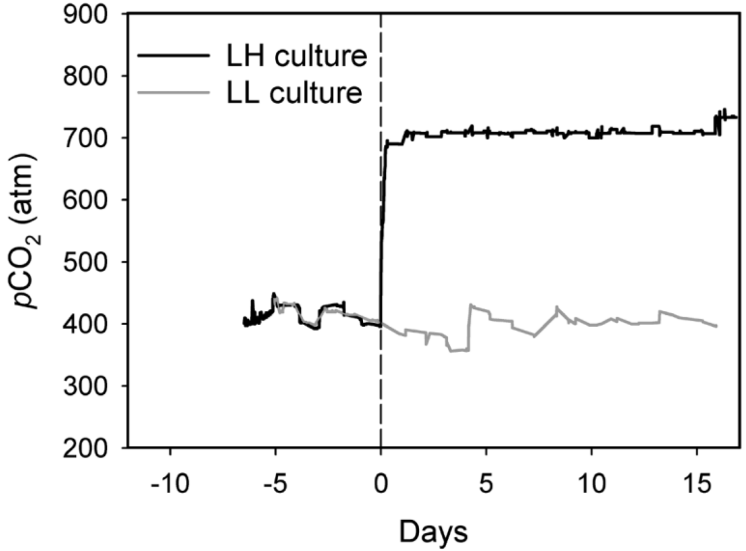


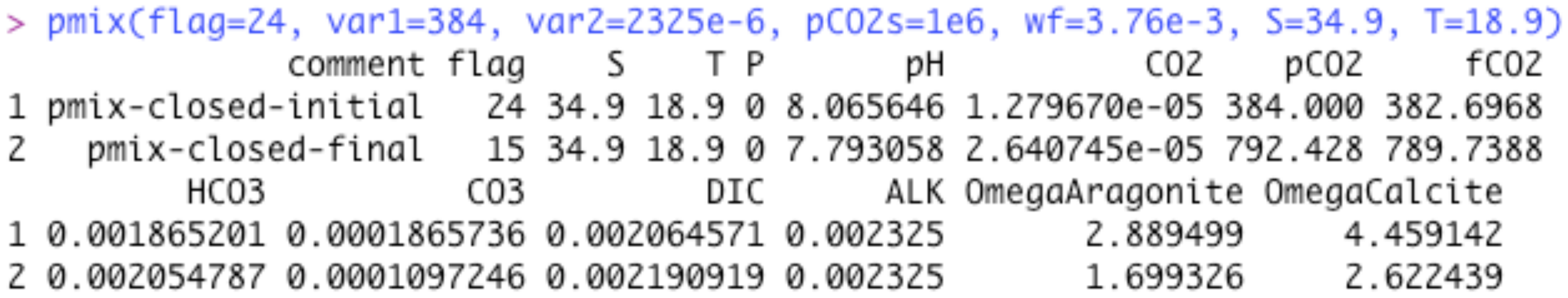
Sciandra et al. (2003)

Addition of high-CO_2 sea water

- Example:

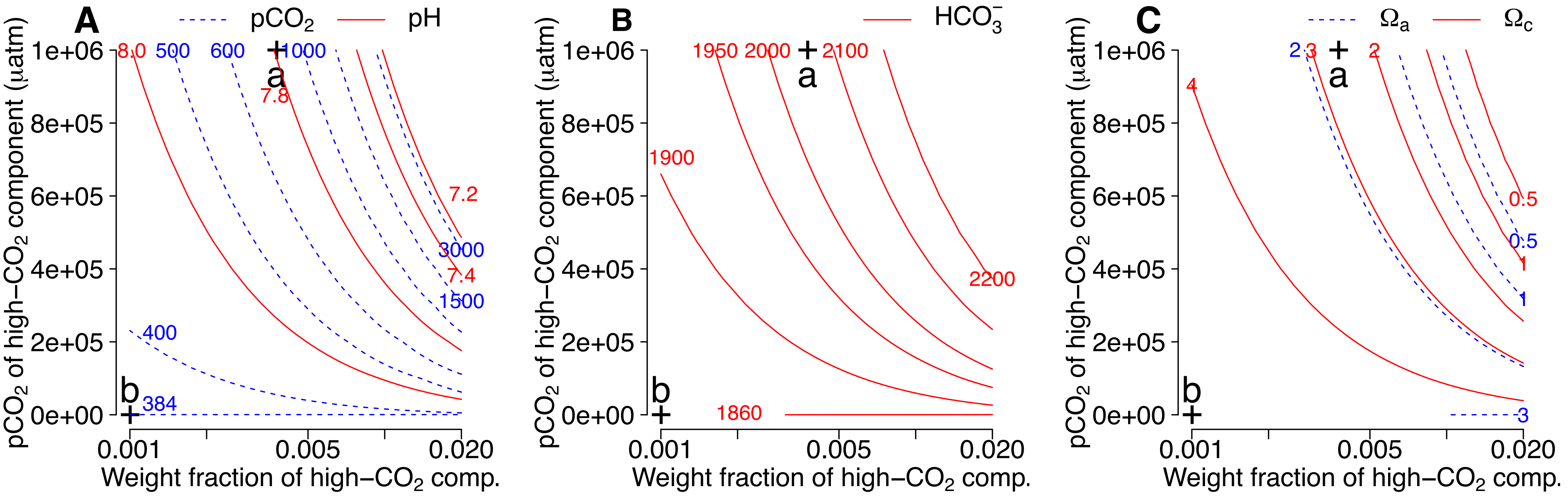
  In a closed system, 0.99624 kg of seawater (pCO_2=384 *µ*atm and AT=2325 *µ*mol kg^{-1}) is mixed with 0.00376 kg of seawater saturated with CO_2 (10^6 *µ*atm) and the same AT

- *seacarb* function:



```
> pmix(flag=24, var1=384, var2=2325e-6, pCO2s=1e6, wf=3.76e-3, S=34.9, T=18.9)
              comment flag    S    T P       pH          CO2    pCO2     fCO2
1 pmix-closed-initial   24 34.9 18.9 0 8.065646 1.279670e-05 384.000 382.6968
2   pmix-closed-final   15 34.9 18.9 0 7.793058 2.640745e-05 792.428 789.7388
         HCO3          CO3         DIC      ALK OmegaAragonite OmegaCalcite
1 0.001865201 0.0001865736 0.002064571 0.002325       2.889499     4.459142
2 0.002054787 0.0001097246 0.002190919 0.002325       1.699326     2.622439
```

Mixing with high-CO_2 sea water



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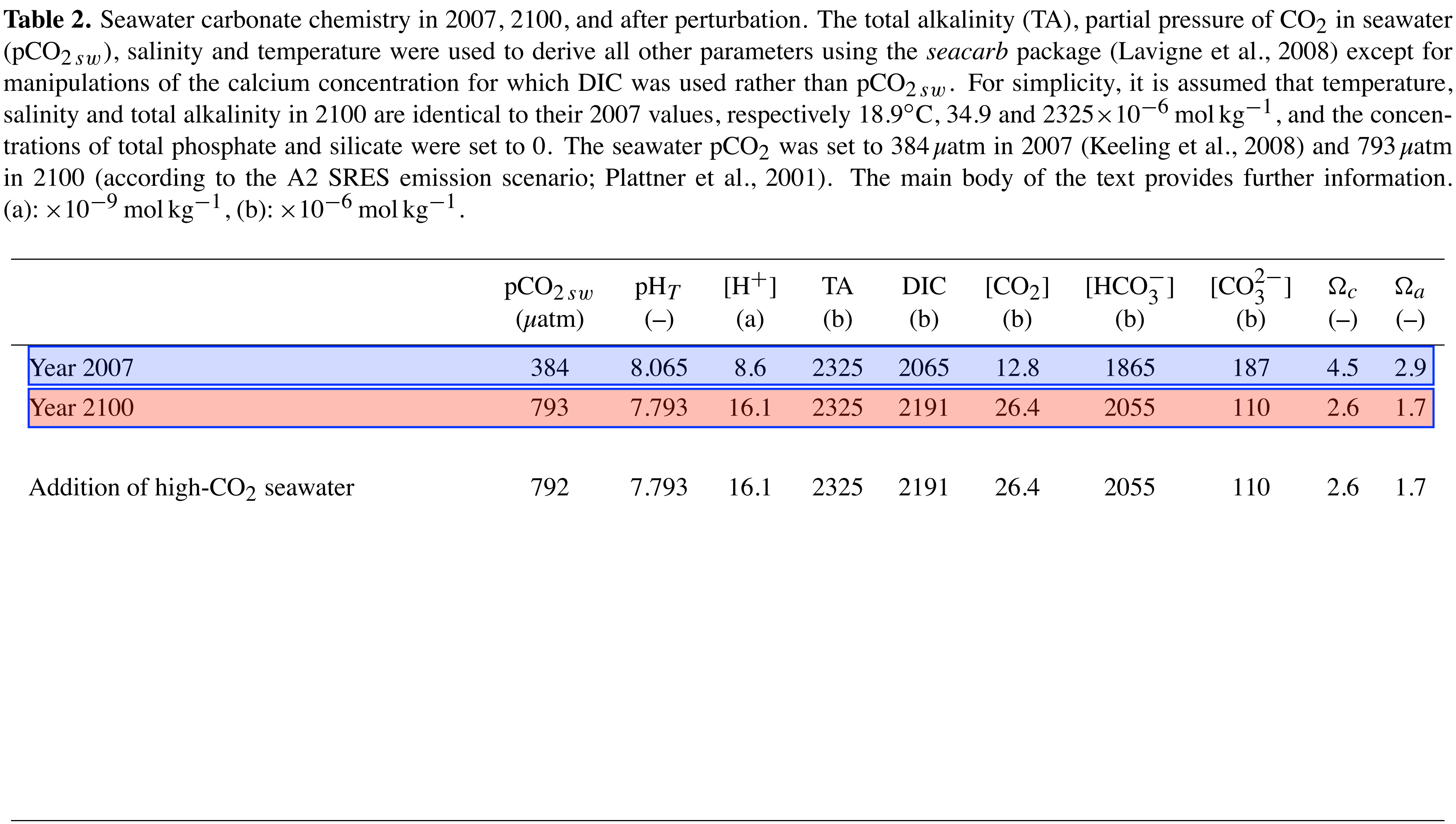

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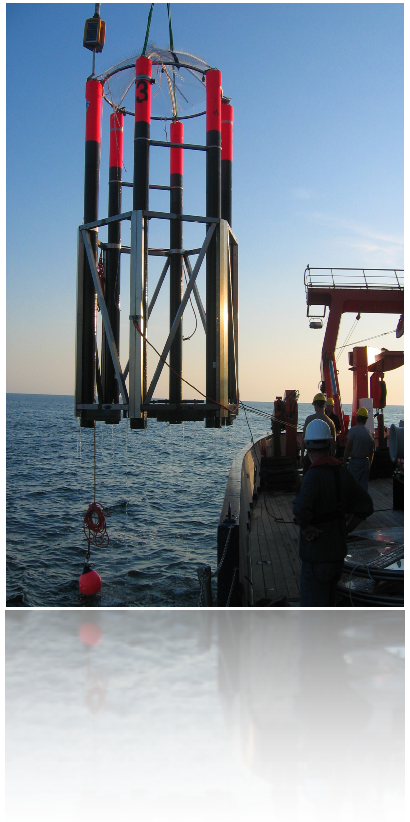
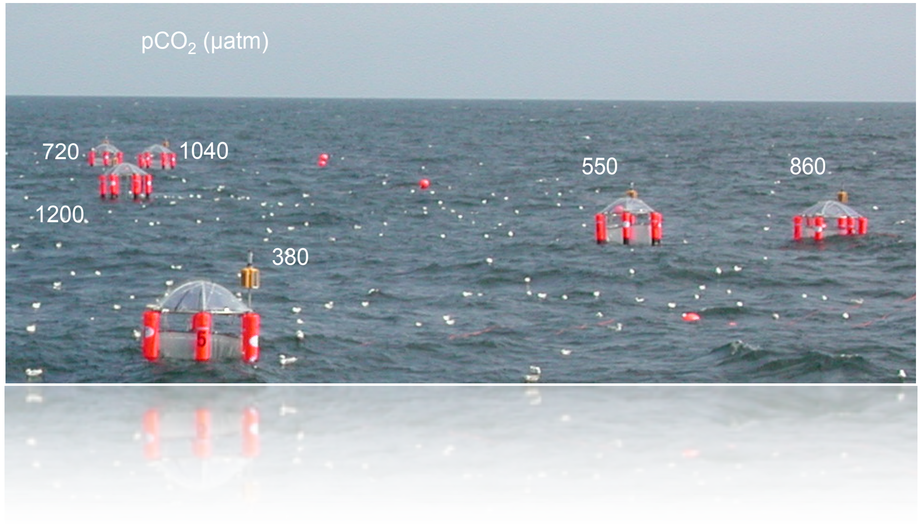
Gattuso & Lavigne (2009)

Addition of high-CO_2 sea water

- Can be recommended
- Used only twice (?):
  - lab expts (McGraw et al., unpubl.)
  - mesocosm expts: 100 l in 60 m^3 (Schulz et al., unpubl.)
- not easy to precisely adjust to target values

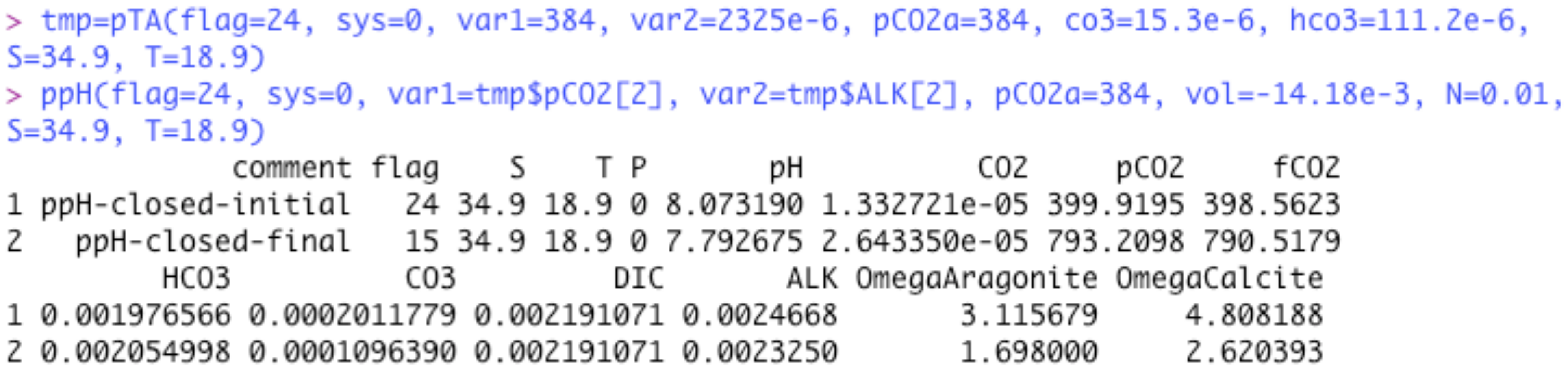


Andrea Ludwig, IFM-GEOMAR



Addition of HCO_3^- and/or CO_3^{2-} as well as acid

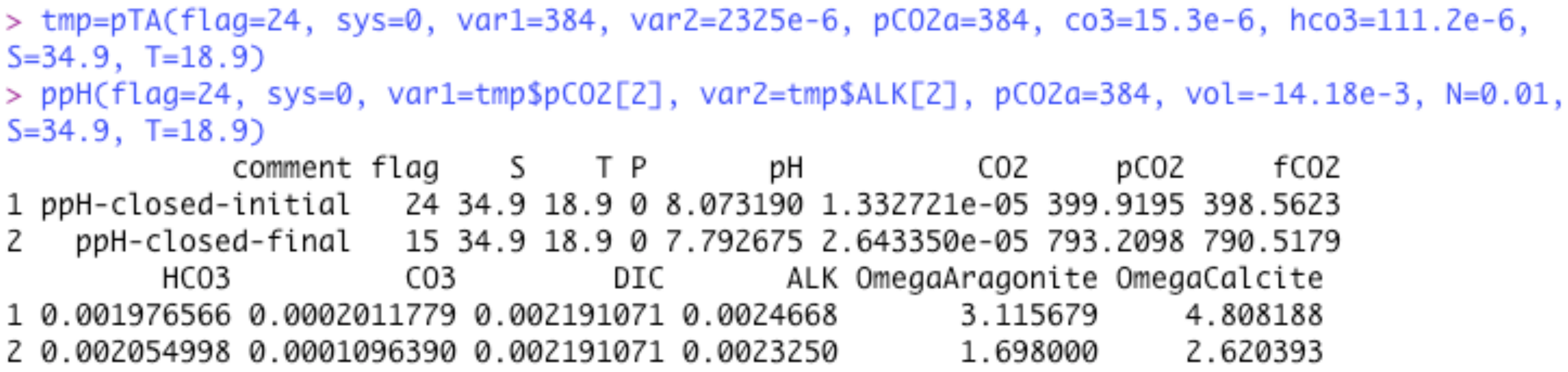
- Two steps:
  - addition of HCO_3^- and/or CO_3^{2-} to elevate DIC to the desired level
  - addition of acid (at constant DIC) to cancel out the increase in AT
- Adding 15.3 x 10^{-6} mol kg^{-1} of CO_3^{2-} and 111.2 x 10^{-6} mol kg^{-1} of HCO_3^- increases DIC, adding 14.18 ml of HCl 0.01N restores AT to its initial value of 2325 x 10^{-6} mol kg^{-1} and all final carbonate parameters are on the target values



```
> tmp=pTA(flag=24, sys=0, var1=384, var2=2325e-6, pCO2a=384, co3=15.3e-6, hco3=111.2e-6,
S=34.9, T=18.9)
> ppH(flag=24, sys=0, var1=tmp$pCO2[2], var2=tmp$ALK[2], pCO2a=384, vol=-14.18e-3, N=0.01,
S=34.9, T=18.9)
             comment flag    S    T P       pH          CO2     pCO2     fCO2
1 ppH-closed-initial   24 34.9 18.9 0 8.073190 1.332721e-05 399.9195 398.5623
2   ppH-closed-final   15 34.9 18.9 0 7.792675 2.643350e-05 793.2098 790.5179
         HCO3          CO3         DIC       ALK OmegaAragonite OmegaCalcite
1 0.001976566 0.0002011779 0.002191071 0.0024668       3.115679     4.808188
2 0.002054998 0.0001096390 0.002191071 0.0023250       1.698000     2.620393
```

Addition of HCO_3^- and/or CO_3^{2-} as well as acid

- Two steps:
  - addition of HCO_3^- and/or CO_3^{2-} to elevate DIC to the desired level
  - addition of acid (at constant DIC) to cancel out the increase in AT
- Adding 15.3×10^{-6} mol kg^{-1} of CO_3^{2-} and 111.2×10^{-6} mol kg^{-1} of HCO_3^- increases DIC, adding 14.18 ml of HCl 0.01N restores AT to its initial value of 2325×10^{-6} mol kg^{-1} and all final carbonate parameters are on the target values



```
> tmp=pTA(flag=24, sys=0, var1=384, var2=2325e-6, pCO2a=384, co3=15.3e-6, hco3=111.2e-6,
S=34.9, T=18.9)
> ppH(flag=24, sys=0, var1=tmp$pCO2[2], var2=tmp$ALK[2], pCO2a=384, vol=-14.18e-3, N=0.01,
S=34.9, T=18.9)
              comment flag    S    T P       pH          CO2     pCO2     fCO2
1 ppH-closed-initial   24 34.9 18.9 0 8.073190 1.332721e-05 399.9195 398.5623
2   ppH-closed-final   15 34.9 18.9 0 7.792675 2.643350e-05 793.2098 790.5179
         HCO3          CO3         DIC       ALK OmegaAragonite OmegaCalcite
1 0.001976566 0.0002011779 0.002191071 0.0024668       3.115679     4.808188
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Addition of HCO_3^- and/or CO_3^{2-} as well as acid

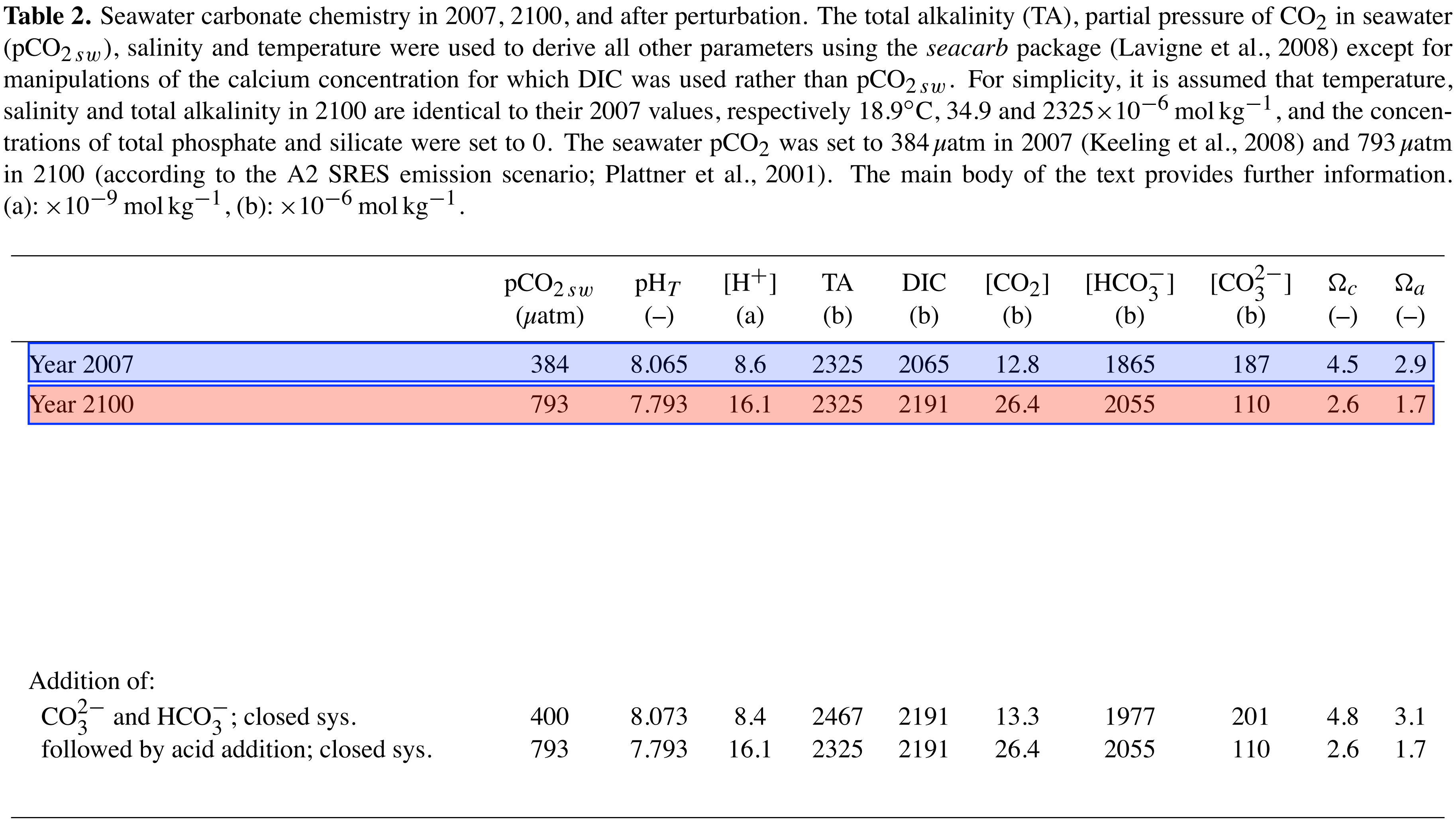


Table 2. Seawater carbonate chemistry in 2007, 2100, and after perturbation. The total alkalinity (TA), partial pressure of CO_2 in seawater ($pCO_{2\,sw}$), salinity and temperature were used to derive all other parameters using the *seacarb* package (Lavigne et al., 2008) except for manipulations of the calcium concentration for which DIC was used rather than $pCO_{2\,sw}$. For simplicity, it is assumed that temperature, salinity and total alkalinity in 2100 are identical to their 2007 values, respectively 18.9°C, 34.9 and 2325×10^{-6} mol kg^{-1}, and the concentrations of total phosphate and silicate were set to 0. The seawater pCO_2 was set to 384 µatm in 2007 (Keeling et al., 2008) and 793 µatm in 2100 (according to the A2 SRES emission scenario; Plattner et al., 2001). The main body of the text provides further information. (a): $\times 10^{-9}$ mol kg^{-1}, (b): $\times 10^{-6}$ mol kg^{-1}.

	$pCO_{2\,sw}$ (µatm)	pH_T (–)	$[H^+]$ (a)	TA (b)	DIC (b)	$[CO_2]$ (b)	$[HCO_3^-]$ (b)	$[CO_3^{2-}]$ (b)	Ω_c (–)	Ω_a (–)
Year 2007	384	8.065	8.6	2325	2065	12.8	1865	187	4.5	2.9
Year 2100	793	7.793	16.1	2325	2191	26.4	2055	110	2.6	1.7
Addition of:										
CO_3^{2-} and HCO_3^-; closed sys.	400	8.073	8.4	2467	2191	13.3	1977	201	4.8	3.1
followed by acid addition; closed sys.	793	7.793	16.1	2325	2191	26.4	2055	110	2.6	1.7

Gattuso & Lavigne (2009)

Addition of HCO_3^- and/or CO_3^{2-} as well as acid

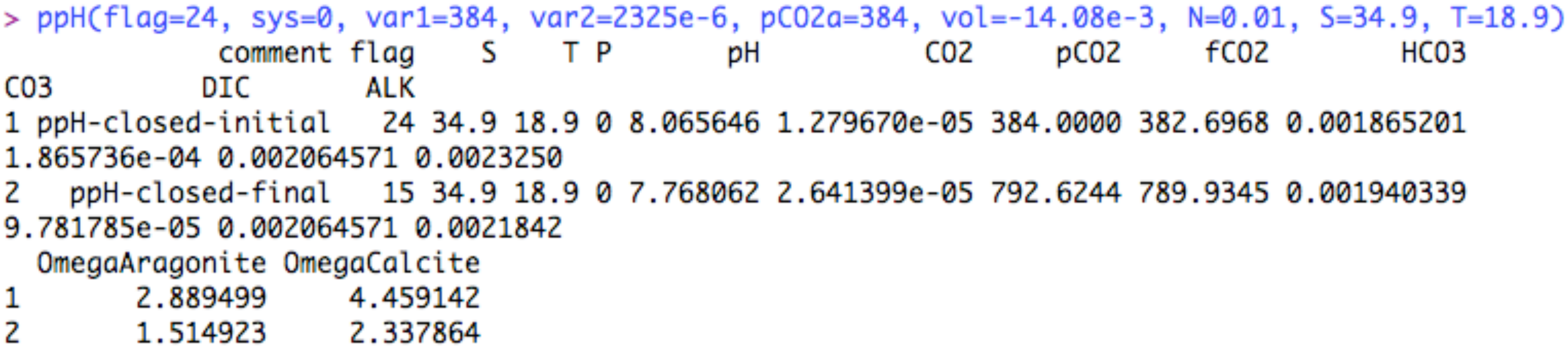
- Recommended
- Not frequently used (Borowitzka, 1981)
- Very precise control of the carbonate chemistry
- Cannot be used in flow-through systems

Addition of HCO_3^- and/or CO_3^{2-} as well as acid

- Recommended
- Not frequently used (Borowitzka, 1981)
- Very precise control of the carbonate chemistry
- Cannot be used in flow-through systems

Addition of strong acid or base

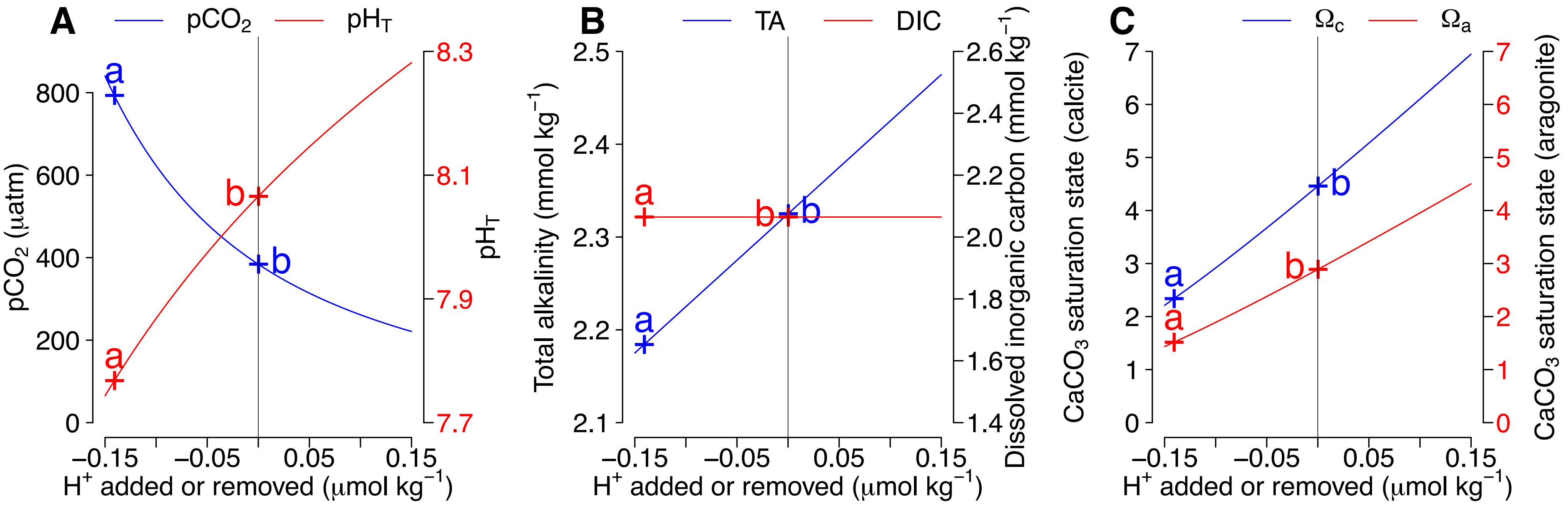
- System closed to the atmosphere:
  - dissolved inorganic carbon (DIC) unchanged
  - TA decreases following addition of acid and increases following addition of a base
- System open to the atmosphere:
  - TA decreases following addition of acid and increases following addition of a base
  - DIC is modified through air-water CO_2 exchange
- Example: Addition of 14.08 ml of 0.01 N HCl to 1 kg seawater (pCO_2=384 μatm and TA=2325 μmol kg^{-1}) in a closed system:



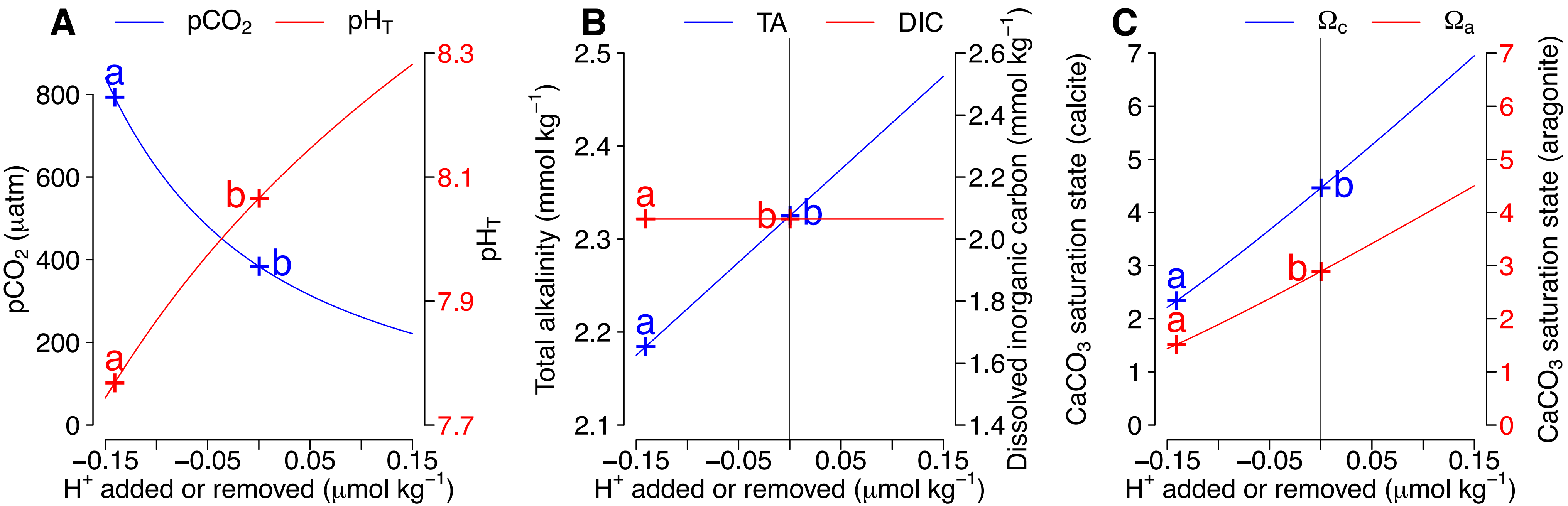
```
> ppH(flag=24, sys=0, var1=384, var2=2325e-6, pCO2a=384, vol=-14.08e-3, N=0.01, S=34.9, T=18.9)
             comment flag    S    T P       pH          CO2     pCO2     fCO2        HCO3
CO3         DIC       ALK
1 ppH-closed-initial   24 34.9 18.9 0 8.065646 1.279670e-05 384.0000 382.6968 0.001865201
1.865736e-04 0.002064571 0.0023250
2   ppH-closed-final   15 34.9 18.9 0 7.768062 2.641399e-05 792.6244 789.9345 0.001940339
9.781785e-05 0.002064571 0.0021842
  OmegaAragonite OmegaCalcite
1       2.889499     4.459142
2       1.514923     2.337864
```

Changing AT at constant DIC

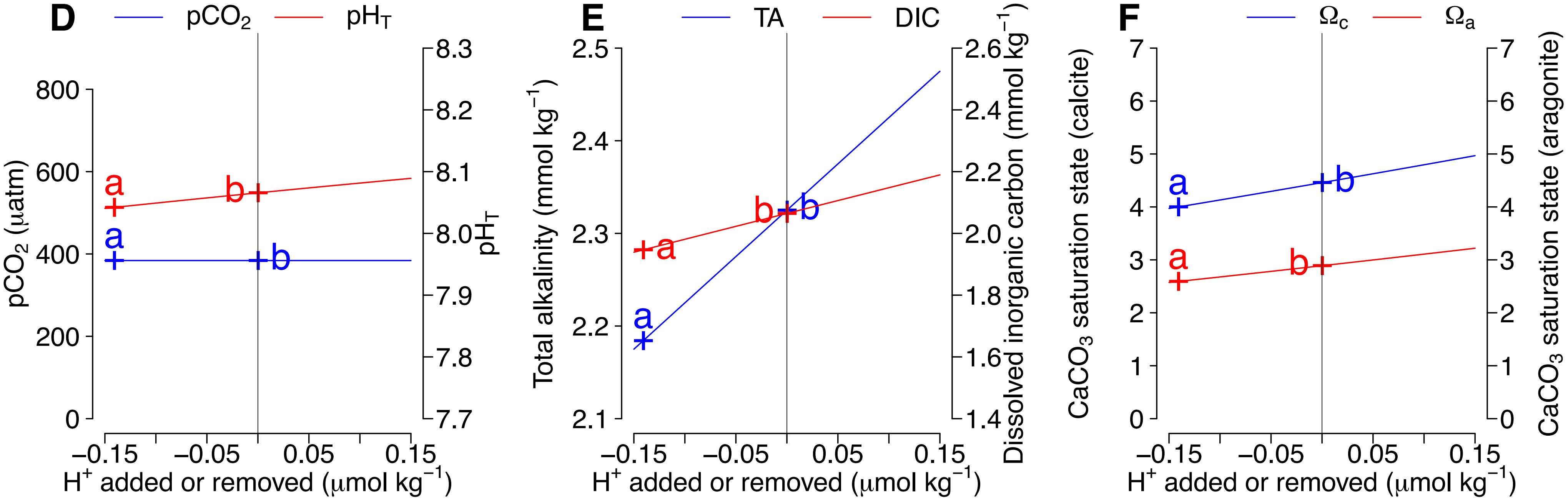
Addition of strong acid or base



Addition of strong acid or base



Addition of strong acid or base



Addition of acid

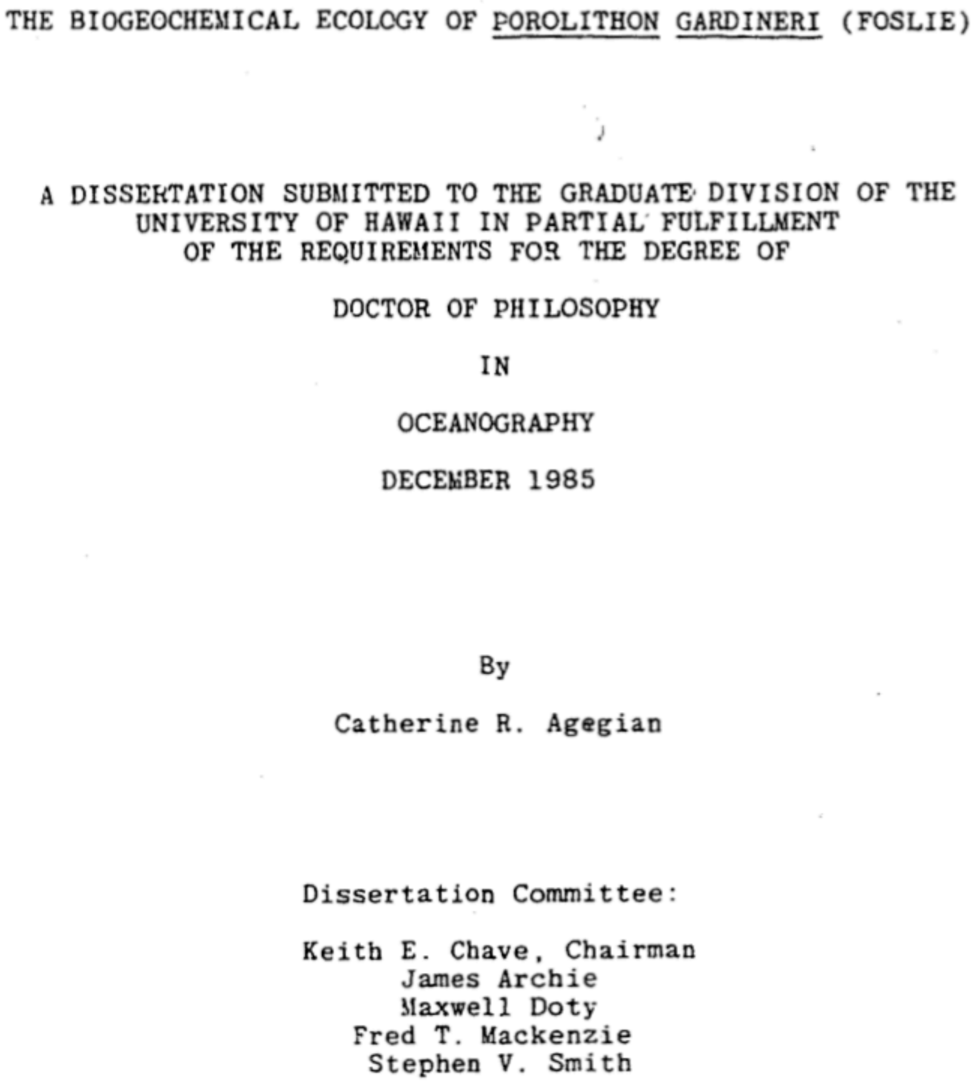
Table 2. Seawater carbonate chemistry in 2007, 2100, and after perturbation. The total alkalinity (TA), partial pressure of CO_2 in seawater ($pCO_{2\,sw}$), salinity and temperature were used to derive all other parameters using the *seacarb* package (Lavigne et al., 2008) except for manipulations of the calcium concentration for which DIC was used rather than $pCO_{2\,sw}$. For simplicity, it is assumed that temperature, salinity and total alkalinity in 2100 are identical to their 2007 values, respectively 18.9°C, 34.9 and 2325×10^{-6} mol kg^{-1}, and the concentrations of total phosphate and silicate were set to 0. The seawater pCO_2 was set to 384 µatm in 2007 (Keeling et al., 2008) and 793 µatm in 2100 (according to the A2 SRES emission scenario; Plattner et al., 2001). The main body of the text provides further information. (a): $\times 10^{-9}$ mol kg^{-1}, (b): $\times 10^{-6}$ mol kg^{-1}.

	$pCO_{2\,sw}$ (µatm)	pH_T (–)	$[H^+]$ (a)	TA (b)	DIC (b)	$[CO_2]$ (b)	$[HCO_3^-]$ (b)	$[CO_3^{2-}]$ (b)	Ω_c (–)	Ω_a (–)
Year 2007	384	8.065	8.6	2325	2065	12.8	1865	187	4.5	2.9
Year 2100	793	7.793	16.1	2325	2191	26.4	2055	110	2.6	1.7
Acid addition; closed sys.	793	7.768	17.1	2184	2065	26.4	1940	98	2.3	1.5
Acid addition; open sys.	384	8.042	9.1	2184	194	12.8	1767	167	4	2.6

Gattuso & Lavigne (2009)

Addition of acid

- Not recommended
- Often used (Bouxin, 1926)
- Can be used with a pH-stat in flow-through systems



THE BIOGEOCHEMICAL ECOLOGY OF *POROLITHON GARDINERI* (FOSLIE)

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

OCEANOGRAPHY

DECEMBER 1985

By

Catherine R. Agegian

Dissertation Committee:

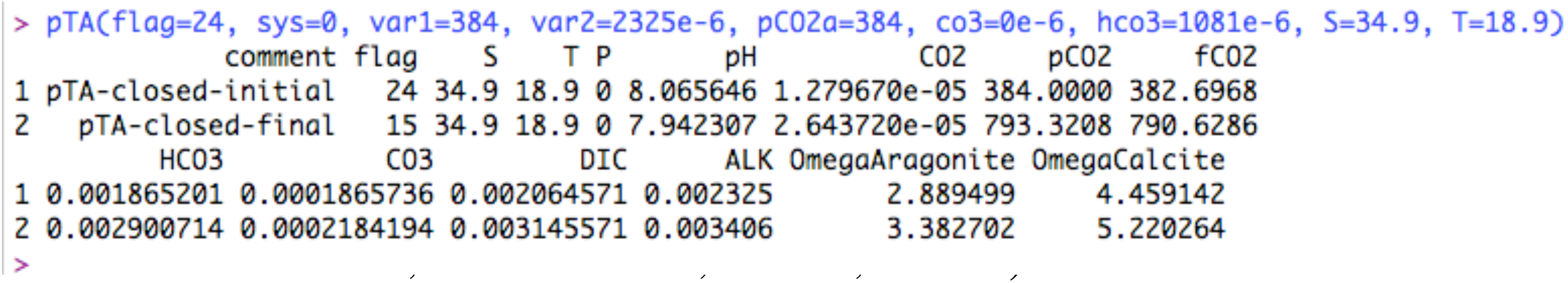
Keith E. Chave, Chairman
James Archie
Maxwell Doty
Fred T. Mackenzie
Stephen V. Smith

Changing AT and DIC

Addition of HCO_3^- and/or CO_3^{2-}

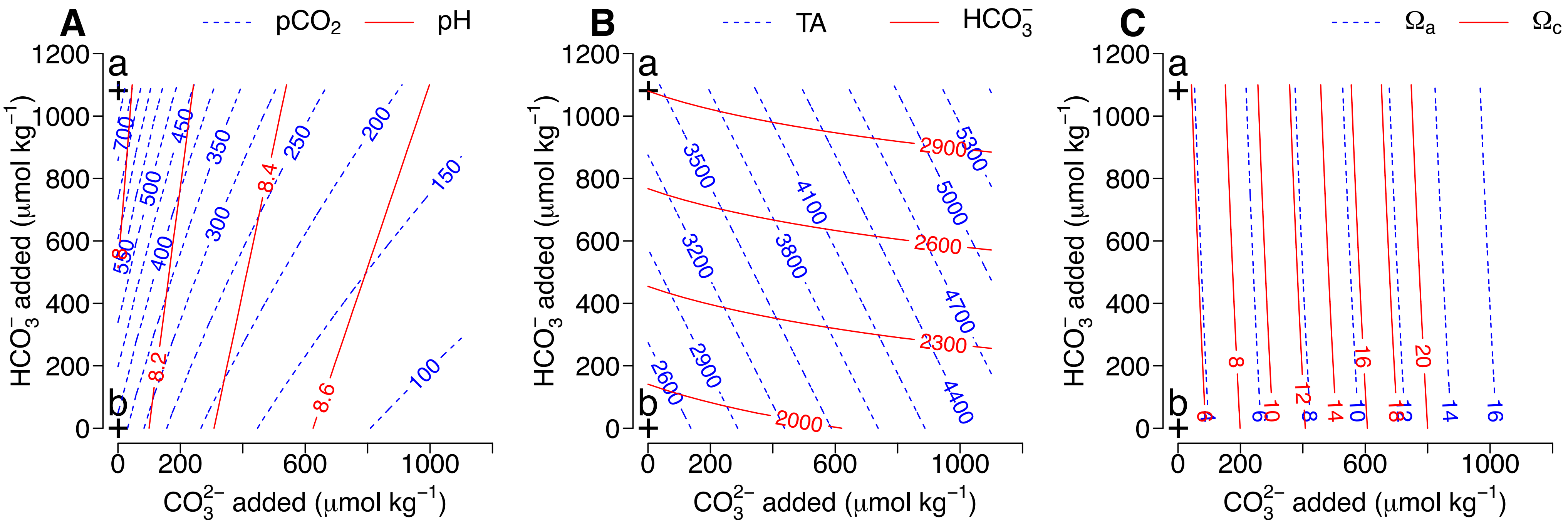
- System closed to the atmosphere:
  - TA increases by 2 x $\Delta[CO_3^{2-}]$ and 1 x $\Delta[HCO_3^-]$
  - DIC increases by 1 x $\Delta[CO_3^{2-}]$ and 1 x $\Delta[HCO_3^-]$
- System open to the atmosphere:
  - re-equilibration with atmosphere impacts DIC but not TA
- Example:

  HCO_3^- (1081×10^{-6} mol kg^{-1} is added to seawater (pCO_2=384 μatm and AT=2325×10^{-6} mol kg^{-1}) in a closed system

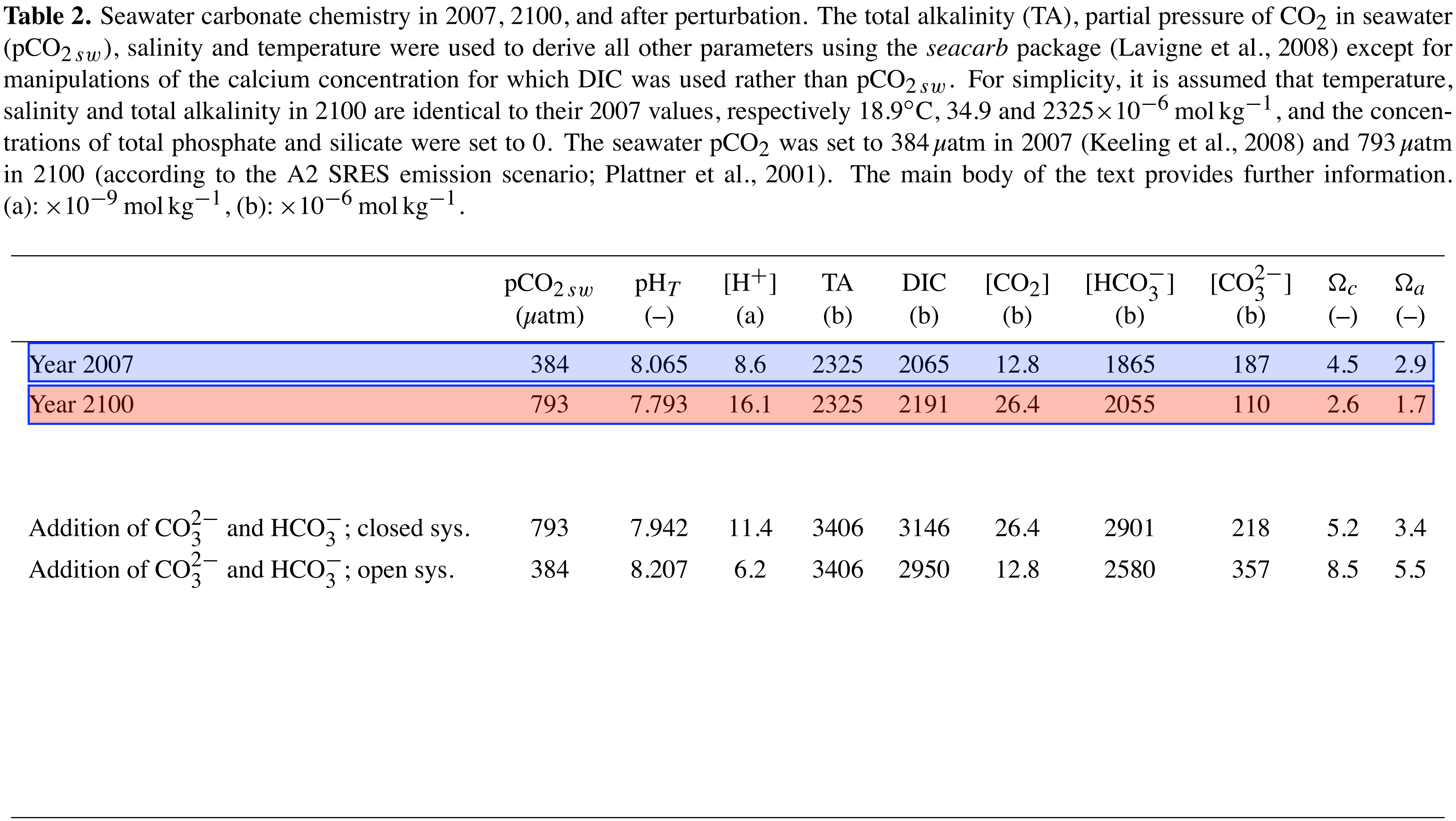


```
> pTA(flag=24, sys=0, var1=384, var2=2325e-6, pCO2a=384, co3=0e-6, hco3=1081e-6, S=34.9, T=18.9)
            comment flag    S    T P       pH          CO2     pCO2     fCO2
1 pTA-closed-initial   24 34.9 18.9 0 8.065646 1.279670e-05 384.0000 382.6968
2   pTA-closed-final   15 34.9 18.9 0 7.942307 2.643720e-05 793.3208 790.6286
         HCO3          CO3         DIC      ALK OmegaAragonite OmegaCalcite
1 0.001865201 0.0001865736 0.002064571 0.002325       2.889499     4.459142
2 0.002900714 0.0002184194 0.003145571 0.003406       3.382702     5.220264
>
```

Addition of carbonate and/or bicarbonate



Addition of HCO_3^- and/or CO_3^{2-}



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	$pCO_{2\,sw}$ (μatm)	pH_T (–)	$[H^+]$ (a)	TA (b)	DIC (b)	$[CO_2]$ (b)	$[HCO_3^-]$ (b)	$[CO_3^{2-}]$ (b)	Ω_c (–)	Ω_a (–)
Year 2007	384	8.065	8.6	2325	2065	12.8	1865	187	4.5	2.9
Year 2100	793	7.793	16.1	2325	2191	26.4	2055	110	2.6	1.7
Addition of CO_3^{2-} and HCO_3^-; closed sys.	793	7.942	11.4	3406	3146	26.4	2901	218	5.2	3.4
Addition of CO_3^{2-} and HCO_3^-; open sys.	384	8.207	6.2	3406	2950	12.8	2580	357	8.5	5.5

Gattuso & Lavigne (2009)

Addition of HCO_3^- and/or CO_3^{2-}

- Not recommended
- Often used to investigate the physiological response to changes in the carbonate chemistry (Swift & Taylor, 1966; Marubini & Thake, 1999)
- Langdon et al. (2000) used it, together with additions of Ca^{2+}, to increase the $CaCO_3$ saturation state.

Manipulation of $[\mathrm{Ca}^{2+}]$

- Manipulating $[\mathrm{Ca}^{2+}]$ is not technically altering the carbonate chemistry *per se*
- Has been used in the context of ocean acidification because some calcifying organisms, such as corals, respond to the calcium carbonate saturation state of seawater (Ω):

$$\Omega = \frac{[\mathrm{Ca}^{2+}]_{\mathrm{sw}} \times [\mathrm{CO}_3^{2-}]_{\mathrm{sw}}}{K^*_{\mathrm{sp}}}$$

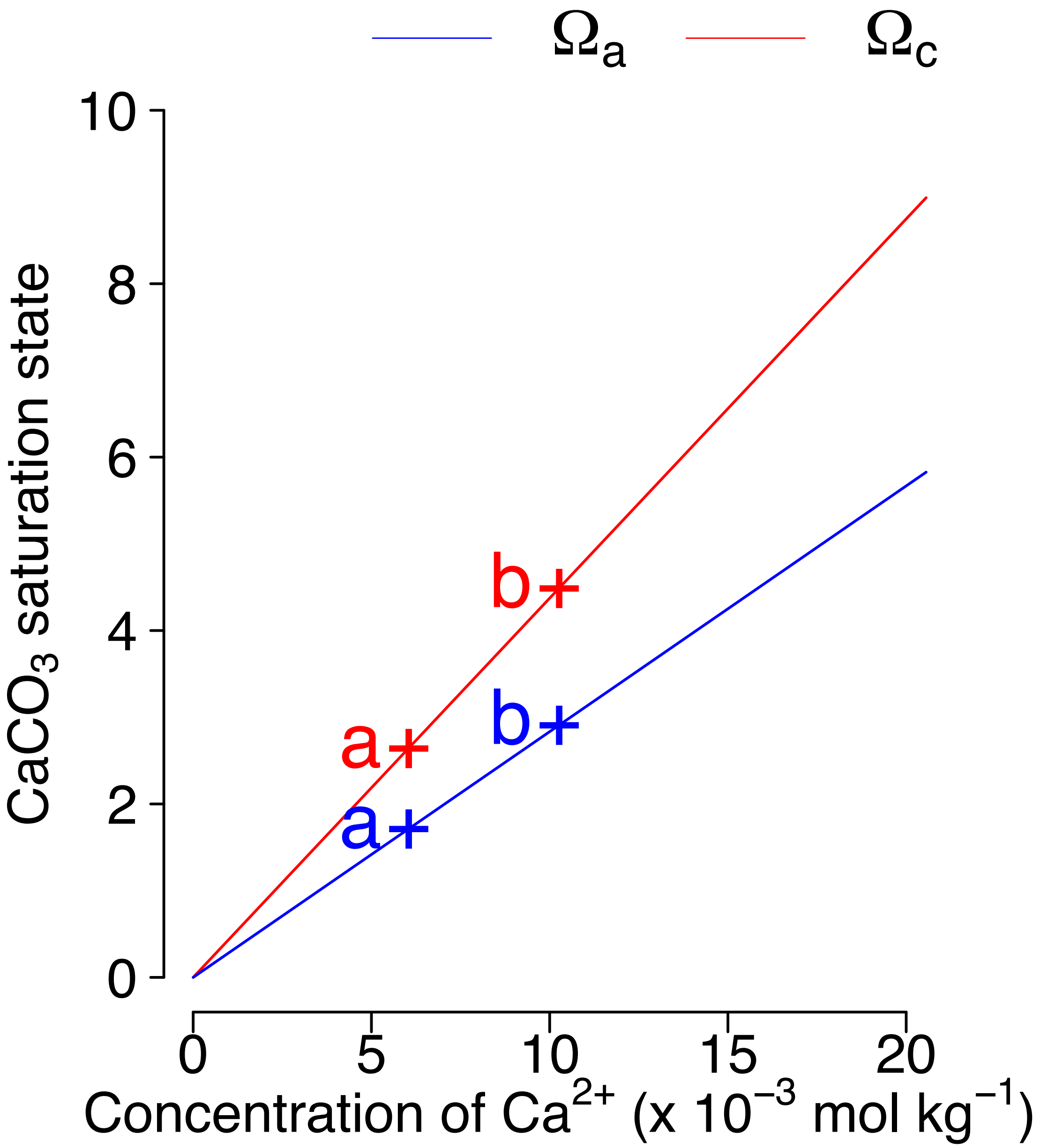
- Example:

artificial seawater is made with a known TA (2303×10^{-6} mol kg^{-1}) and DIC (2054×10^{-6} mol kg^{-1}); $[\mathrm{Ca}^{2+}]$ is set to 5.98×10^{-3} mol kg^{-1}

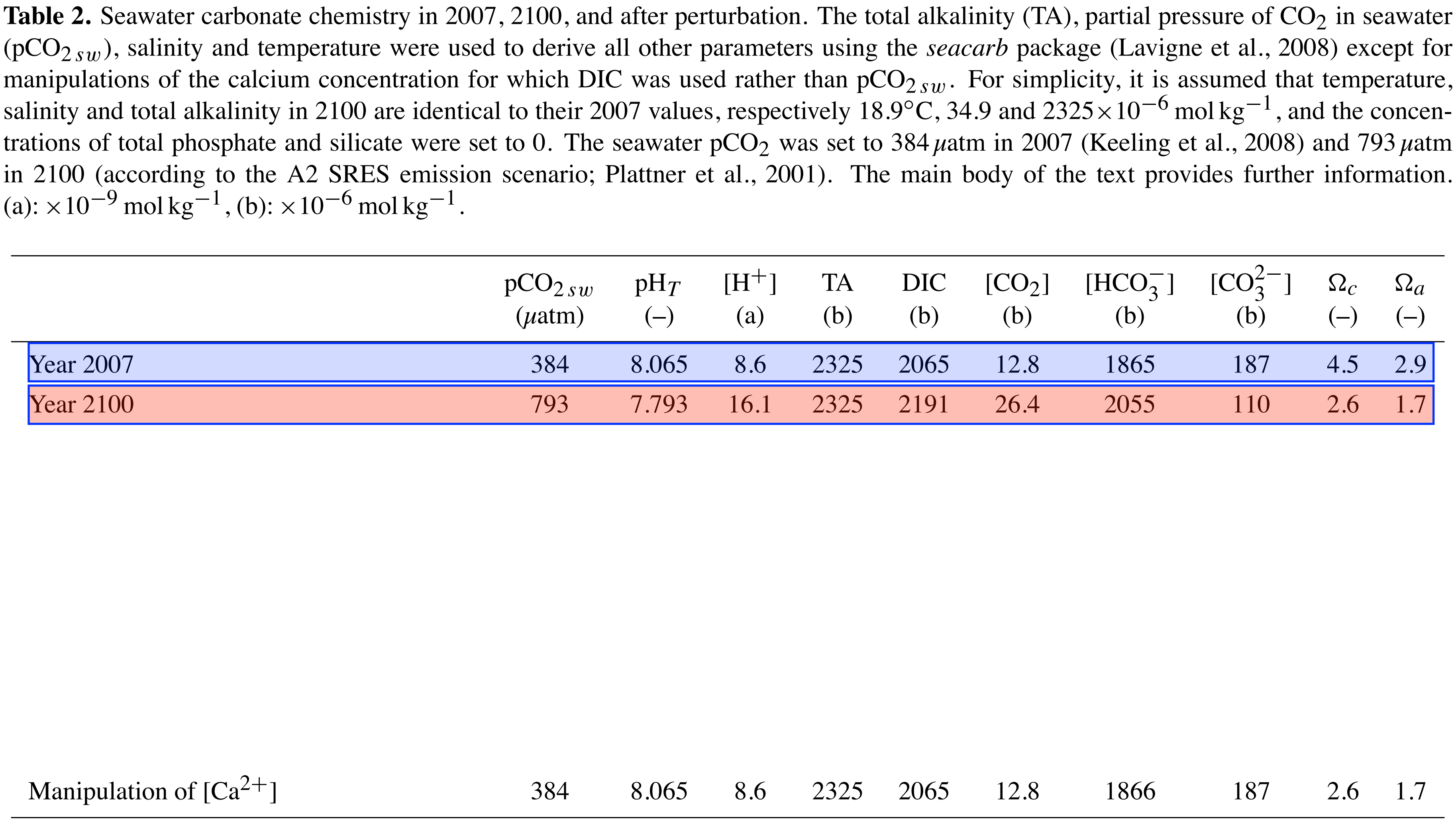
- *seacarb* function:

```
pCa(flag=15, var1=2303e-6, var2=2054e-6, Ca=5.98e-3, S=34.6, T=18.1)
```

Manipulation of the calcium concentration



Manipulation of $[Ca^{2+}]$



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	$pCO_{2\,sw}$ (μatm)	pH_T (–)	$[H^+]$ (a)	TA (b)	DIC (b)	$[CO_2]$ (b)	$[HCO_3^-]$ (b)	$[CO_3^{2-}]$ (b)	Ω_c (–)	Ω_a (–)
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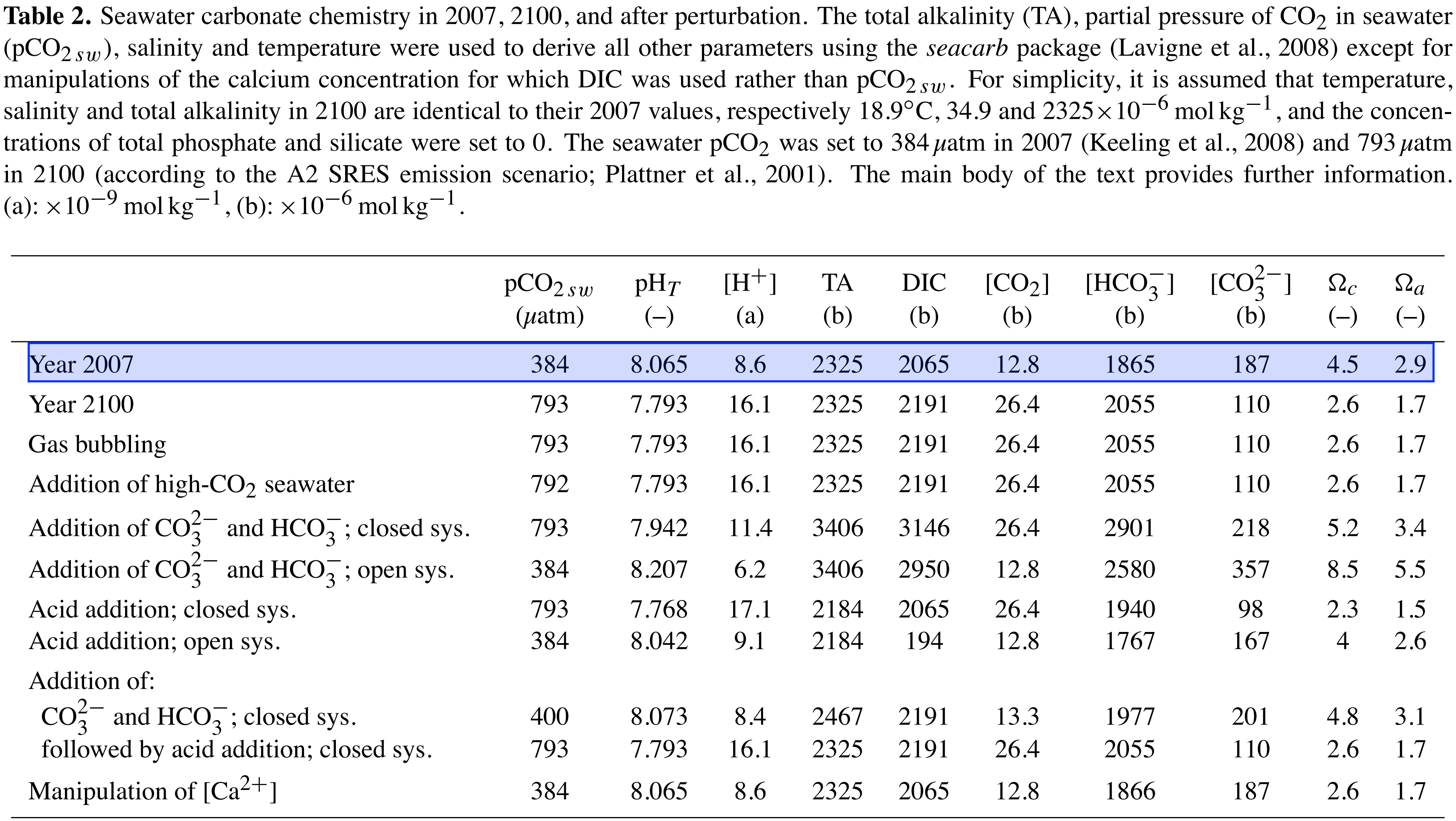
Manipulation of $[Ca^{2+}]$	384	8.065	8.6	2325	2065	12.8	1866	187	2.6	1.7

Gattuso & Lavigne (2009)

Manipulation of [Ca^{2+}]

- Not recommended for OA perturbation experiments
- Sometimes used to investigate the physiological response of corals (Gattuso et al., 2000) and coccolithophores (Trimborn, 2007) to lower rates of calcification.
- Also used to replenish Ca^{2+} during long-term experiments with calcifiers (Langdon et al., 2000).

Summary



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	$pCO_{2\,sw}$ (µatm)	pH_T (–)	$[H^+]$ (a)	TA (b)	DIC (b)	$[CO_2]$ (b)	$[HCO_3^-]$ (b)	$[CO_3^{2-}]$ (b)	Ω_c (–)	Ω_a (–)
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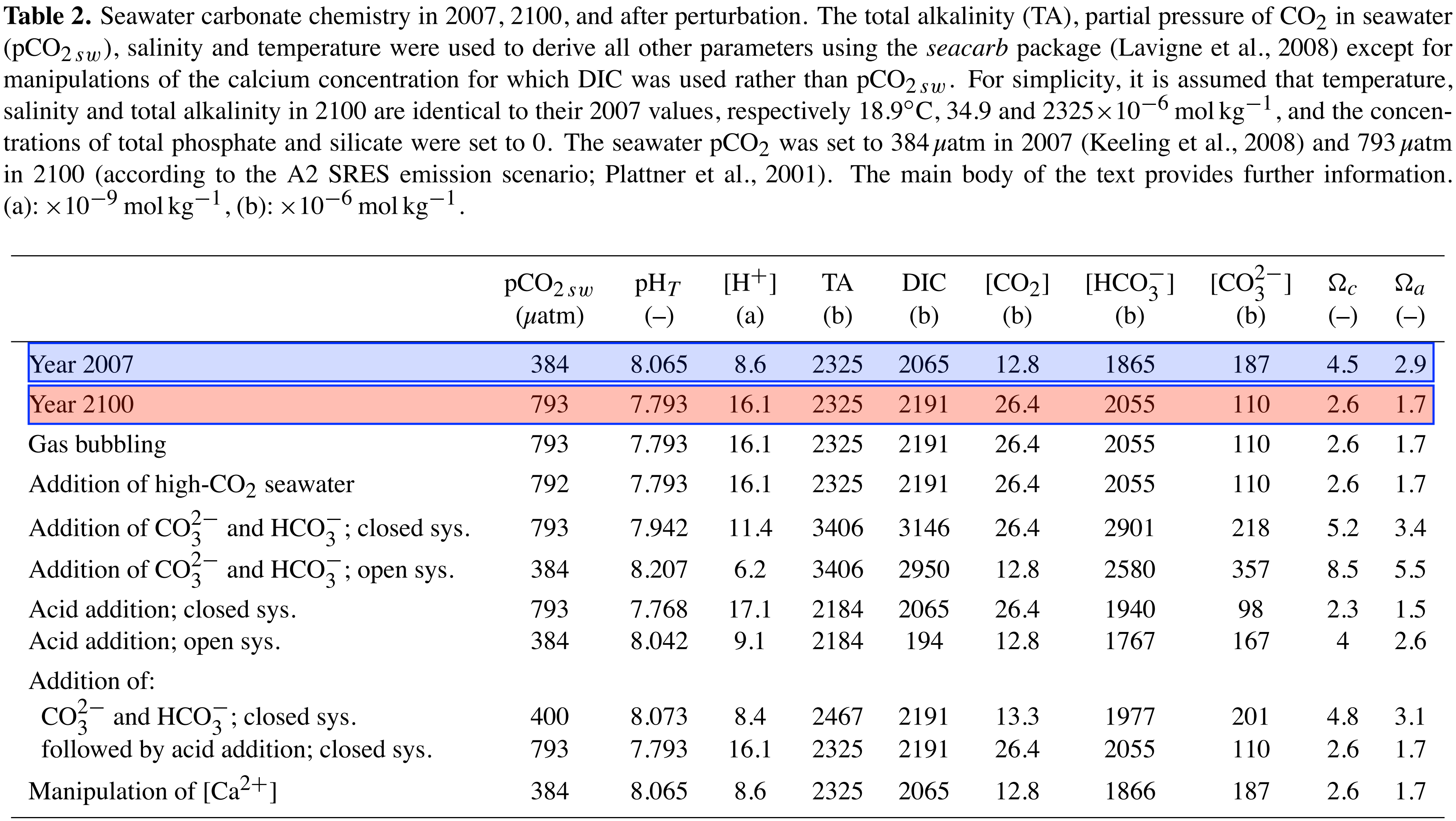
Gattuso & Lavigne (2009)

Summary



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	$pCO_{2\,sw}$ (μatm)	pH_T (–)	$[H^+]$ (a)	TA (b)	DIC (b)	$[CO_2]$ (b)	$[HCO_3^-]$ (b)	$[CO_3^{2-}]$ (b)	Ω_c (–)	Ω_a (–)
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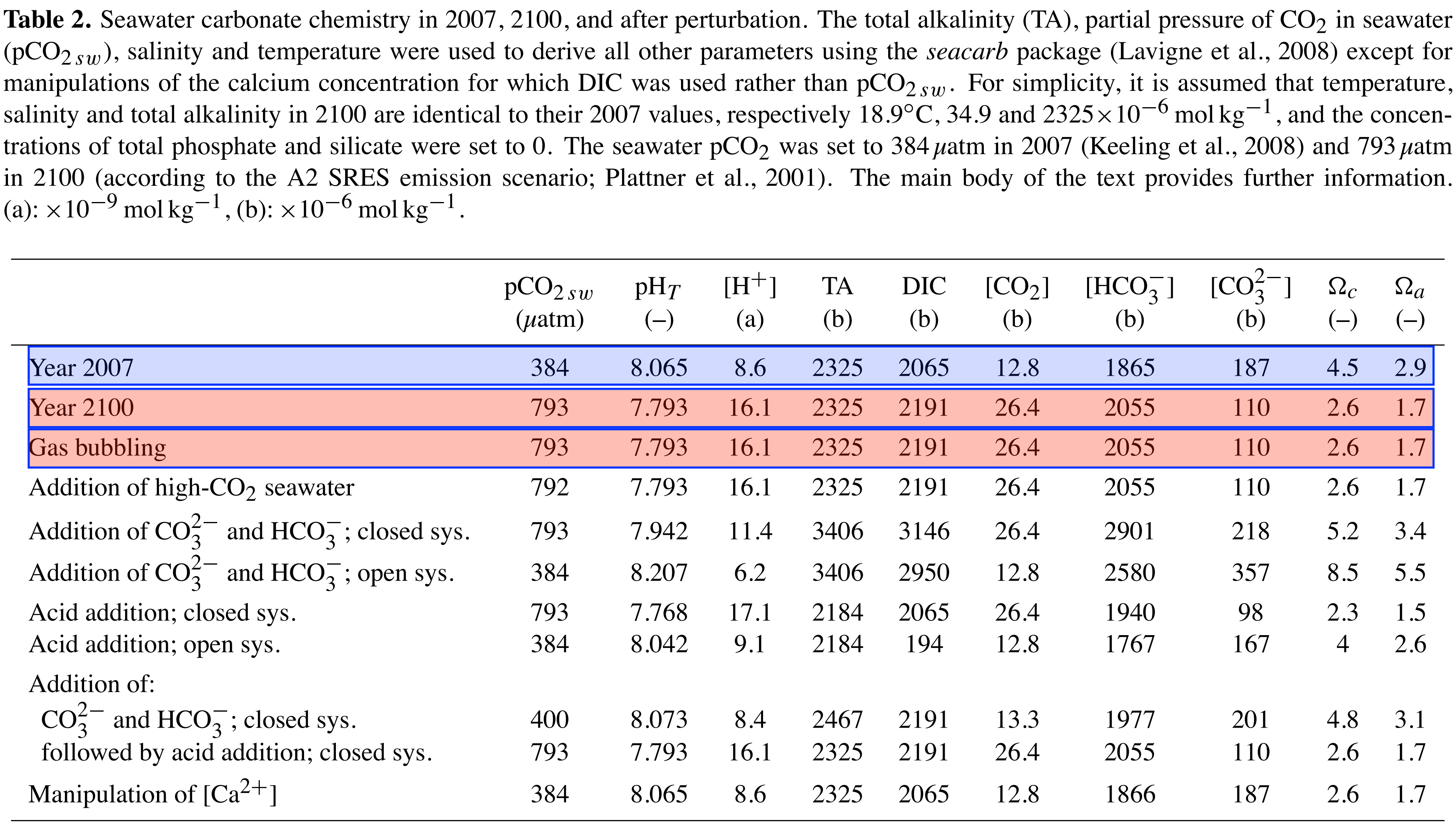
Gattuso & Lavigne (2009)

Summary



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	$pCO_{2\,sw}$ (µatm)	pH_T (–)	$[H^+]$ (a)	TA (b)	DIC (b)	$[CO_2]$ (b)	$[HCO_3^-]$ (b)	$[CO_3^{2-}]$ (b)	Ω_c (–)	Ω_a (–)
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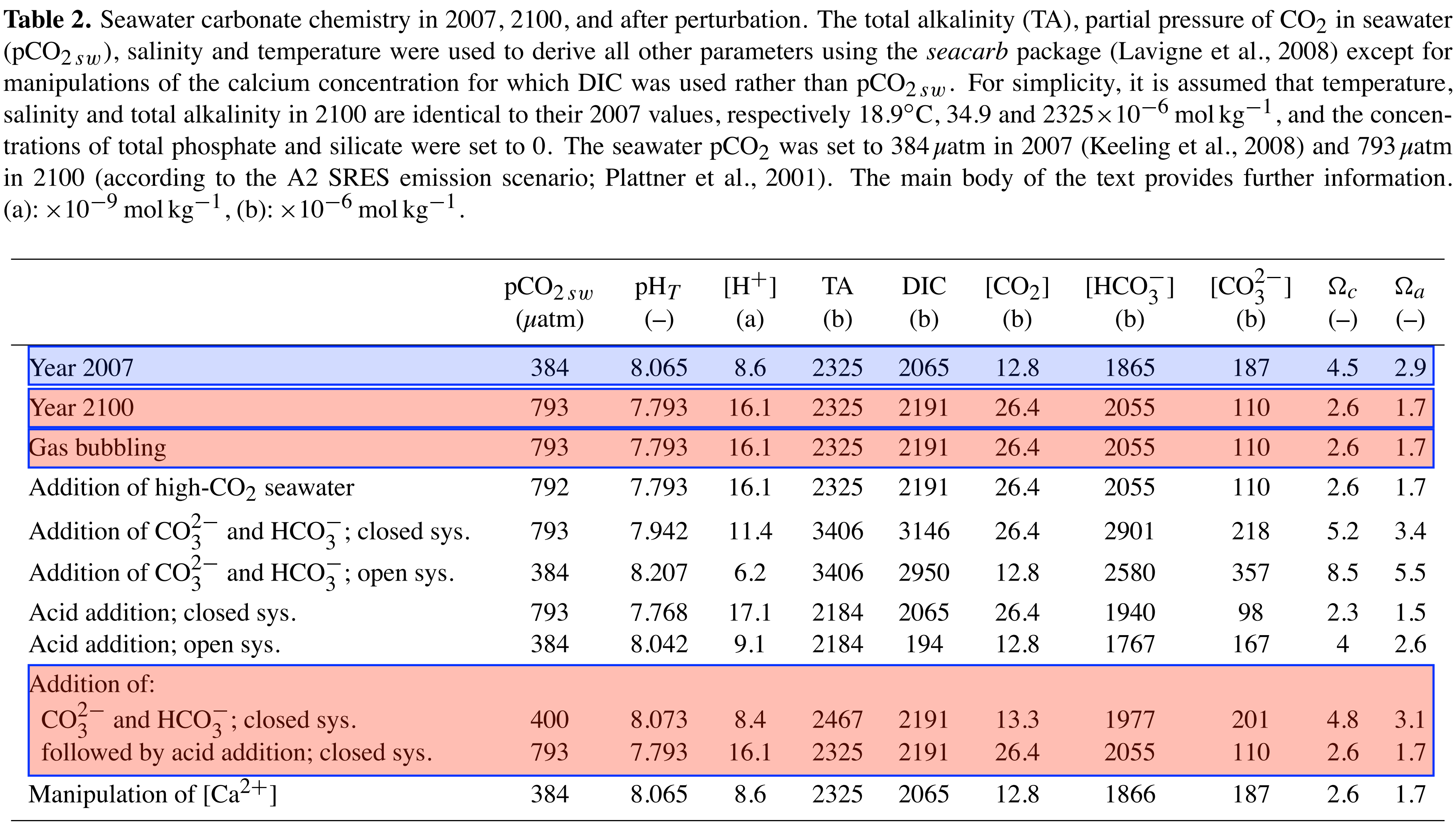
Gattuso & Lavigne (2009)

Summary



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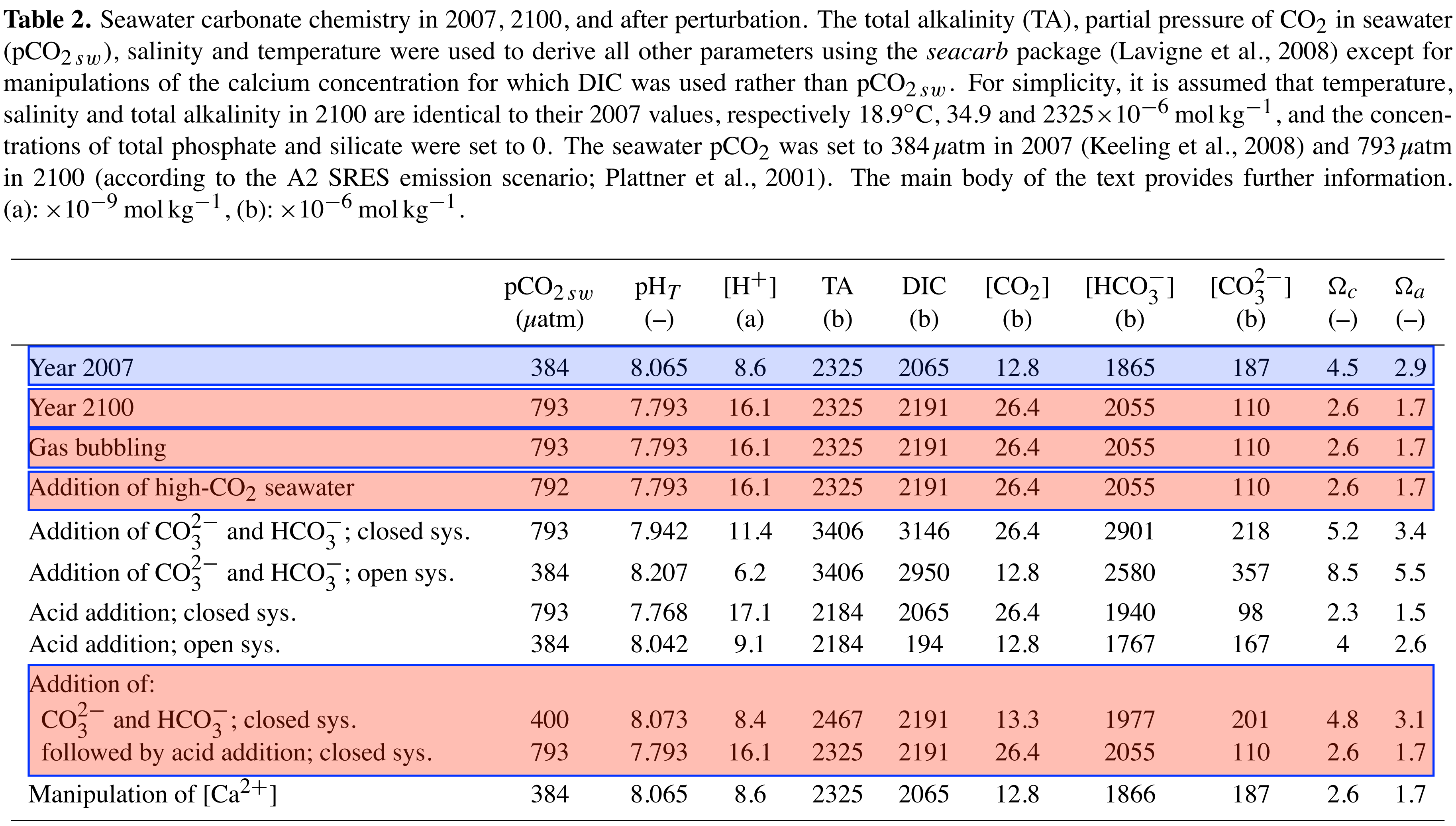

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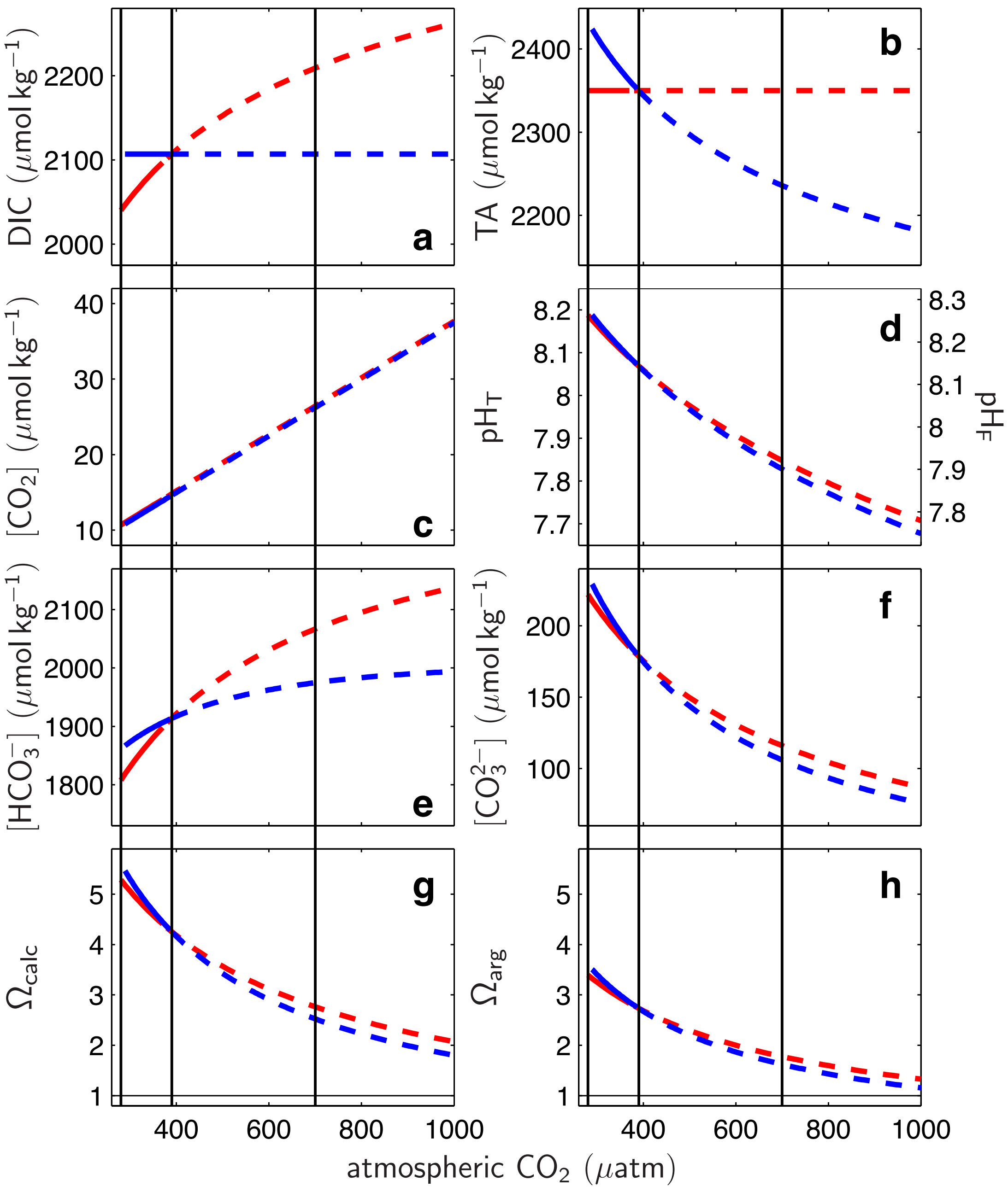
Gattuso & Lavigne (2009)

Comparative effects of acid addition and gas bubbling

Addition of acid

Gas bubbling

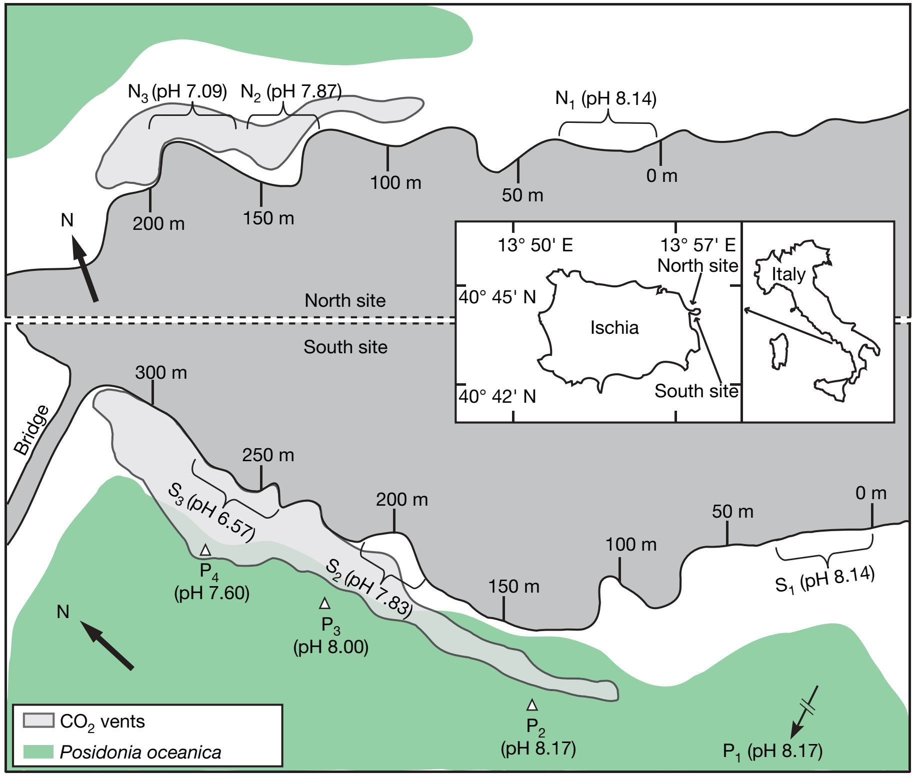


Schulz et al. (2009)

Conclusion

Approach	Target values reached?	Ease of use	Relative cost
Acid addition	No (only pCO2)	***	*
Acid addition and restoration of TA	Yes	*	*
Gas bubbling	Yes	***	***
Mixing with high-CO_2 seawater	Yes	**	*
Addition of HCO_3^- and/or CO_3^{2-}	No	**	*
Calcium manipulation	No (only Ω)	*	*

Naturally acidified site: Ischia island (Italy)



Hall-Spencer et al. (2008); Martin et al. (2008)

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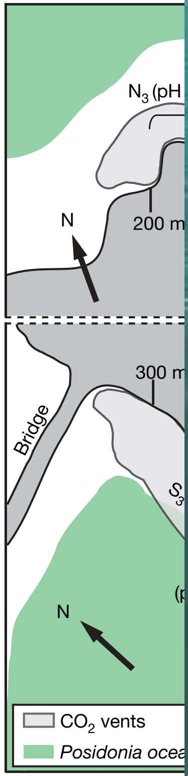

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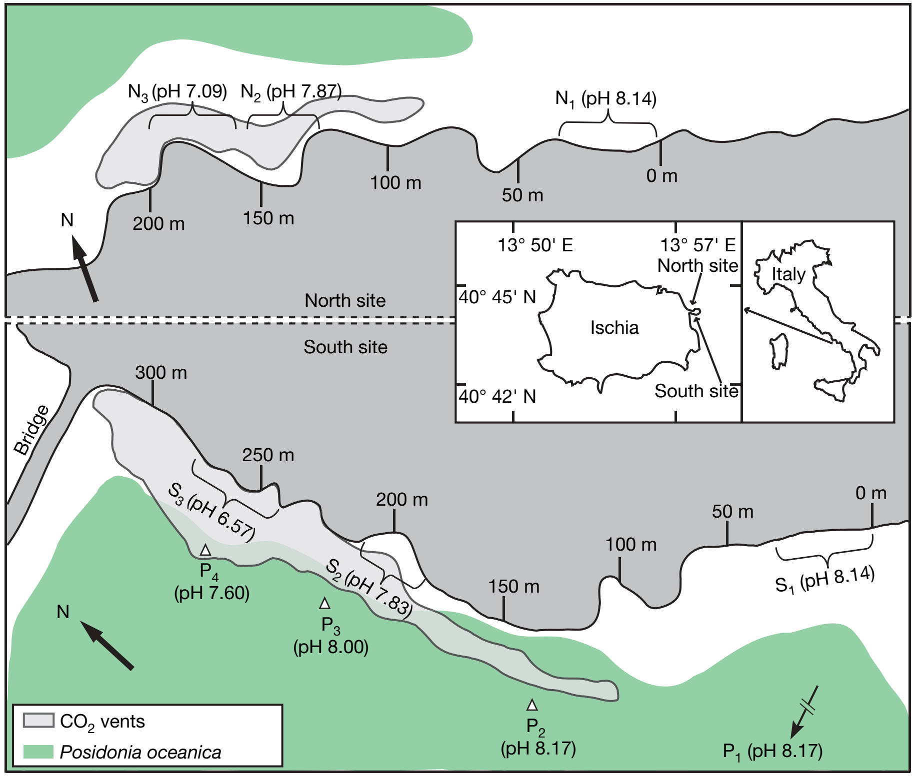


30% reduction in biodiversity at mean pH 7.8

Algae	**pH 8.2**	**pH 7.8**	**pH 6.6**
Green	15	12	4
Red	20	11	3
Brown	17	13	11
Total	**52**	**36**	**18**
Fauna			
Sponges	8	7	1
Cnidarians	8	4	2
Annelids	4	3	0
Crustaceans	5	3	2
Molluscs	29	17	6
Echinoderms	6	6	0
Fish	9	9	0
Total	**69**	**49**	**11**

Hall-Spencer et al. (2008); Martin et al. (2008)

Guidelines for the pCO_2 levels

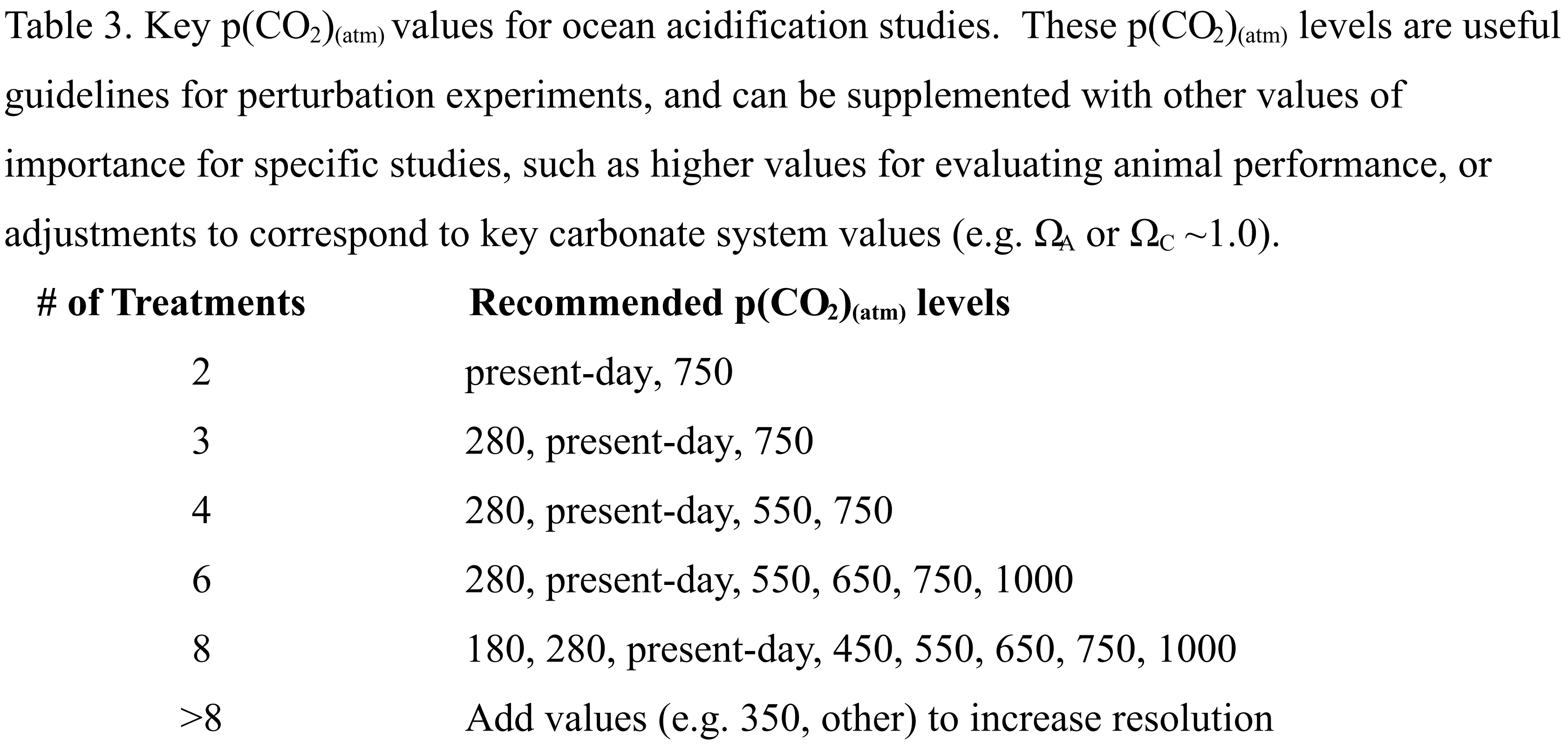


Table 3. Key $p(CO_2)_{(atm)}$ values for ocean acidification studies. These $p(CO_2)_{(atm)}$ levels are useful guidelines for perturbation experiments, and can be supplemented with other values of importance for specific studies, such as higher values for evaluating animal performance, or adjustments to correspond to key carbonate system values (e.g. Ω_A or Ω_C ~1.0).

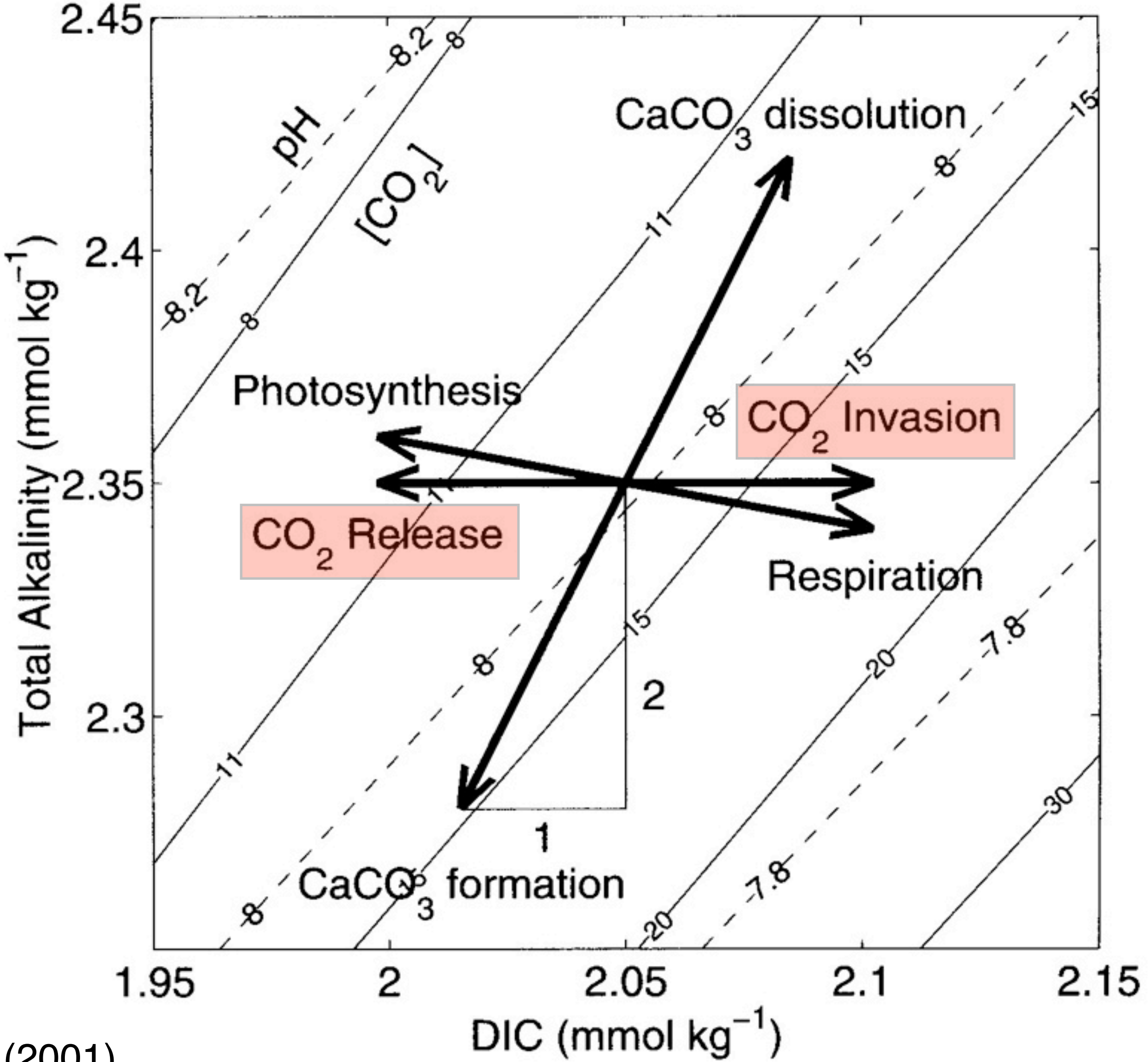
# of Treatments	**Recommended $p(CO_2)_{(atm)}$ levels**
2	present-day, 750
3	280, present-day, 750
4	280, present-day, 550, 750
6	280, present-day, 550, 650, 750, 1000
8	180, 280, present-day, 450, 550, 650, 750, 1000
>8	Add values (e.g. 350, other) to increase resolution

Barry et al. (2009, *Guide for Best Practices...*)

The initial chemistry is set.
What are the next complications?

Impact of CO_2 invasion and evasion in open systems

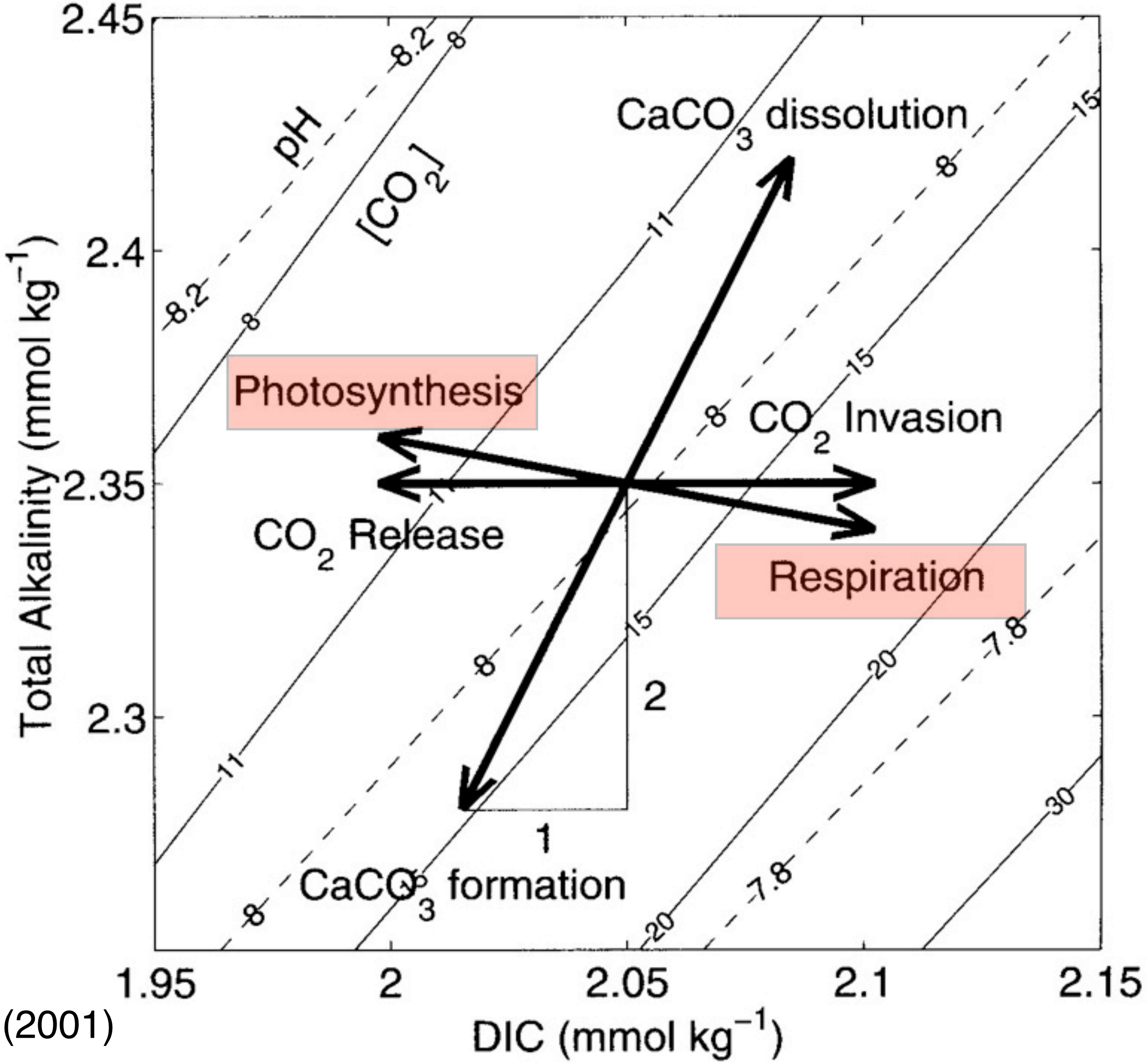
No change in the charge balance: $\Delta TA = 0$



Zeebe & Wolf-Gladrow (2001)

Impact of photosynthesis and respiration

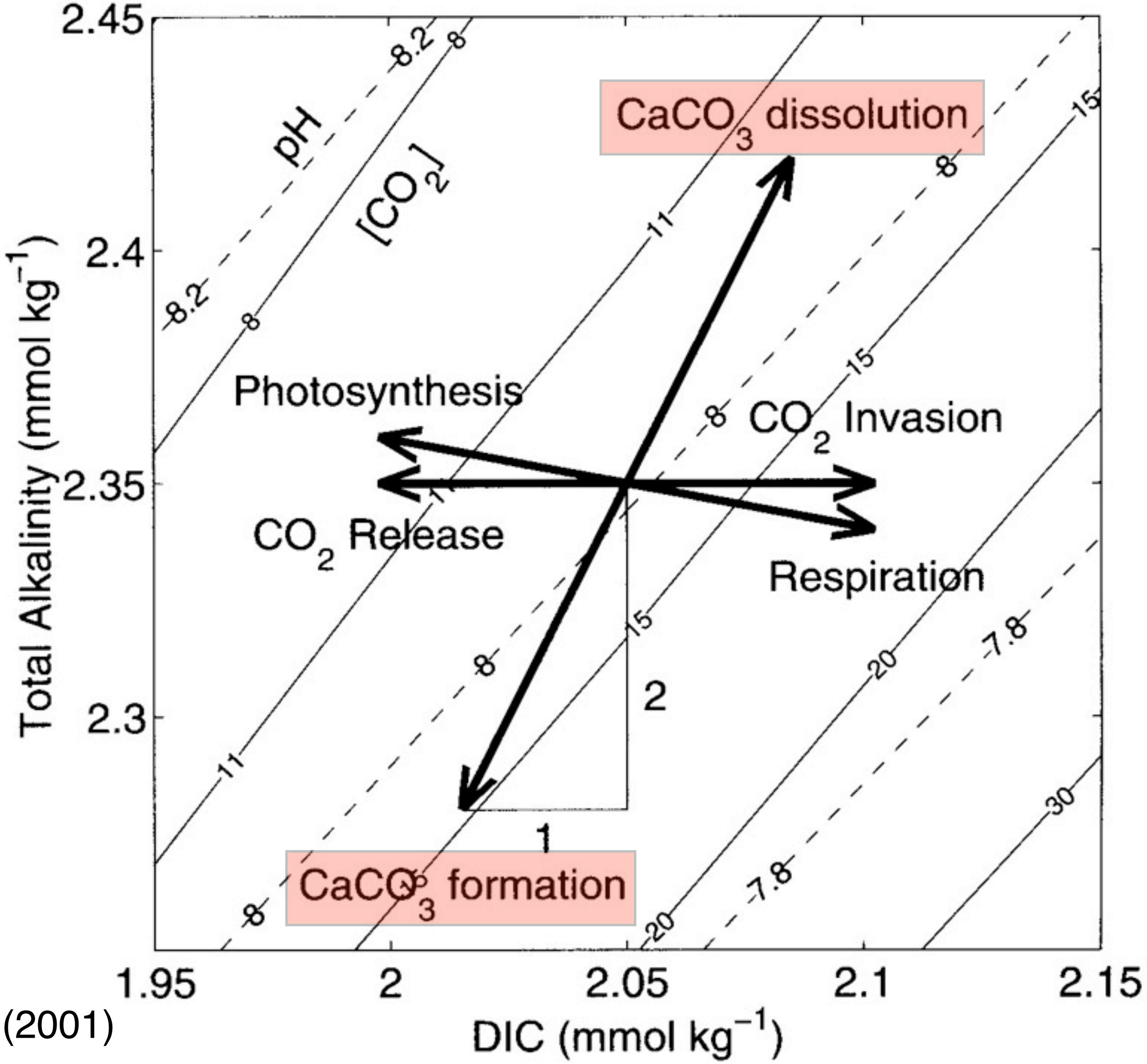
$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ \underset{\text{phot.}}{\overset{\text{resp.}}{\leftrightharpoons}} C_{106}H_{263}O_{110}N_{16}P + 138O_2; \frac{\Delta DIC}{\Delta TA} = \frac{-106}{+18} = \frac{-1}{+0.17}$$



Zeebe & Wolf-Gladrow (2001)

Impact of precipitation and dissolution of CaCO3

$$\mathrm{Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 + CO_2 + H_2O}; \frac{\Delta \mathrm{DIC}}{\Delta \mathrm{TA}} = \frac{-1}{-2}$$



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  - residence time (flow rate) in flow-through systems
- Ex. dilute phytoplankton batch cultures (Fiorini et al., in revision):
  - 6 to 9 generations
  - final cell number: 8000 to 40000 cells/ml
  - shifts in pH and DIC never higher than 0.07% and 1.7%
  - Average change in pCO_2 of 17%
  - TA decreased by 34 µmol kg^{-1}

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- Filtration:
  - significantly shifts the carbonate chemistry
  - manipulations must be done after filtration. If that is not possible, the carbonate chemistry must be measured again after filtration
  - gentle pressure filtration through a cartridge should be used to avoid cell rupture, which would increase AT

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- Autoclaving:
  - severely changes the carbonate chemistry: most of the DIC is lost and AT has been reported to change as well
  - should also be performed prior to manipulating the carbonate chemistry
  - it is recommended to sample for DIC and AT before and after autoclaving in order to ascertain the impact of the operating procedure on the carbonate chemistry

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- Gas bubbling:
  - one must ascertain that equilibrium has been reached before starting an experiment
  - required time to equilibrium depends on biomass to volume ratio, p(CO_2), gas flow rate, bubble size, volume and shape of the flask and temperature. May require several days.
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- Extra care with calcifying organisms (decreased TA and [Ca^{2+}]).

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- pH buffers cause large deviations from the natural carbonate chemistry because they increase AT. Pairs such as pH-DIC or pCO2-DIC should be used.
- Depending on chemical form and concentration, inorganic nutrient addition (P and Si) can change AT and must be included in carbonate chemistry calculations. Furthermore, changes in inorganic nutrient concentrations and speciation during the experiment have an impact on AT (Brewer and Goldman, 1976; Wolf-Gladrow et al., 2007). One may need to measure phosphate, ammonium and silicate (see *Guide for Best Practices*...)

Isotopic labelling of dissolved inorganic carbon

- Labelling the DIC pool with ^{13}C or ^{14}C is a carbonate chemistry manipulation in itself
- Requires the same precautions during preparation and handling as described earlier and should be the last step in the preparation of an experiment
- Furthermore, depending on the amount of ^{13}C- or ^{14}C-sodium salts added, AT can change significantly
- Obviously, bubbling must not be used and no headspace allowed.

epoca-project.eu

Guide for Best Practices in Ocean Acidification Research and Data Reporting

The need for standardised protocols and reporting of data is crucial for meaningful comparisons and collaboration within the field of ocean acidification. EPOCA organised this fall, together with the International Ocean Carbon Coordination Project (IOCCP,) the US Ocean Carbon and Biogeochemistry Program (OCB), and the Kiel Excellence Cluster 'The Future Ocean', an international research workshop on best practices for ocean acidification research (19-21 November 2008 in Kiel, Germany; chair: Ulf Riebesell). The following topics were covered: seawater carbonate chemistry, experimental design of perturbation experiments, measurements of CO2-sensitive processes and data reporting

Svalbard 2010 campaign

The Svalbard 2010 pelagic mesocosm experiment is the second large-scale EPOCA field study in Ny-Ålesund. More information (restricted area).

EPOCA Svalbard blog

EPOCA's first large-scale perturbation experiment took place from 28 April to 10 June 2009 in Ny-Alesund, Svalbard. For more information visit the blog.

News

- EPOCA will release a special introductory guide for policy advisers and decision makers
- Seacarb gets updated to v. 2.2
- Ocean acidification : impact on key organisms of oceanic

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- Héloïse Lavigne
- Kunshan Gao, Kitack Lee, Björn Rost and Kai Schulz
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