Carbonate Geochemistry

Everything useful you need to know about carbonate geochemistry

A Short Course VU March, 2009

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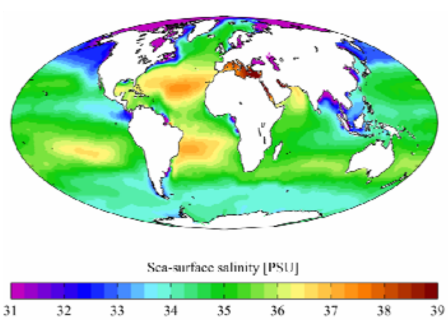
Seawater

- Salinity
  - Concentration of all salts
  - 1000 gms of seawater evaporated to dryness gives 35 gms of salts
  - 35 ppt, gm/kg, psu (practical salinity units)
  - Also defined as conductivity, but does not include non-polar material.



Seawater:cations

- Most Common cations in seawater
- Ca^{2+}
- Mg^{2+}
- Na^{+}
- K^{+}
- Mainly present as uncomplexed form

Anions

- Chloride, Cl^-
- Bicarbonate, carbonate,HCO_3^-, CO_3^{2-}
- Sulfate, SO_4^{2-}

Molality of cations in seawater

- Sodium
  - Concentration = 10,773 ppm= 10773/23= 467 mM = 0.467 M
- Magnesium
  - 1294 ppm = 1294/24 = 55 mM = 0.055 M
- Potassium
  - 399 ppm = 399/39 = 10 mM = 0.010 M
- Calcium
  - 420 ppm = 420/40 = 10 mM = 0.010 M

Anions

- Chloride
  - 19344 ppm = 19344/35.5 = 546 mM = .546 M
- Sulfate
  - 2717 ppm = 2717/94 = 28 mM = 0.028 M
- Bicarbonate
  - 142 ppm = 142/61 = 2.2 mM = 0.0022

Other Important Ions

- Strontium
  - 8 ppm, 8/87.62 = 93 μM = 0.000093 M
- Bromine
  - 67 ppm, 67/80 = 835 μM = 0.000835 M

	Riverwater (mM)	Seawater (mM)
Na	.31	467
Cl	.23	546
Mg	.15	55
SO4	.12	28
Ca	0.37	10
K	0.036	10
HCO3	.87	2

Conservative and non-Conservative

- Elements which generally do not participate in chemical reactions are called conservative
  - Na
  - Cl
  - K
  - Br
- Chemical reactions can include
  - Calcification, photosynthesis, respiration

Non-conservative

- Non-conservative elements include
  - C
  - Ca
  - SO_4^{2-}
  - Mg
  - Sr
  - Fe, NO_3^-, NH_4^-

$$Ca^{2+} + CO_3^{2-} = CaCO_3$$

At equilibrium $K_{sp} = CaCO_3 / [Ca^{2+}]\,[CO_3^{2-}]$

These values have been selected largely from the data bases of the WATEQ family of programs (Plummer et al., 1976; Ball et al., 1980; Runnells and Lindberg, 1981; Nordstrom et al., 1984). They are not necessarily consistent with the free-energy values tabulated in Appendix I.

Reaction	log K	ΔH_r^0 (kJ/mol)
$Al^{3+} + H_2O = AlOH^{2+} + H^+$	−4.987	49.8
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	−10.13	92.0
$Al^{3+} + 3H_2O = Al(OH)_3^0 + 3H^+$	−16.76	138.1
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	−22.16	184.3
$Al^{3+} + F^- = AlF^{2+}$	6.98	4.44
$Al^{3+} + 2F^- = AlF_2^+$	12.60	8.28
$Al^{3+} + 3F^- = AlF_3^0$	16.65	9.04
$Al^{3+} + 4F^- = AlF_4^-$	19.03	9.20
$Al^{3+} + SO_4^{2-} = AlSO_4^+$	3.01	9.0
$Al^{3+} + 2SO_4^{2-} = Al(SO_4)_2^-$	4.90	11.9
$Al(OH)_{3\,amorph} + 3H^+ = Al^{3+} + 3H_2O$	10.8	
$Al(OH)_{3\,gibbsite} + 3H^+ = Al^{3+} + 3H_2O$	8.11	−95.4
$H_2CO_3 = H^+ + HCO_3^-$	−6.35	9.38
$HCO_3^- = H^+ + CO_3^{2-}$	−10.33	15.13
$BaCO_{3\,witherite} = Ba^{2+} + CO_3^{2-}$	−8.56	2.94
$BaSO_{4\,barite} = Ba^{2+} + SO_4^{2-}$	−9.98	26.28
$CaCO_{3\,calcite} = Ca^{2+} + CO_3^{2-}$	−8.48	−10.82
$CaCO_{3\,aragonite} = Ca^{2+} + CO_3^{2-}$	−8.34	−15.54
$CaMg(CO_3)_{2\,dolomite} = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	−17.02	−34.69
$CaSO_4 \cdot 2H_2O_{gypsum} = Ca^{2+} + SO_4^{2-} + 2H_2O$	−4.58	−1.09
$Ca^{2+} + HCO_3^- = CaHCO_3^+$	1.11	
$Ca^{2+} + CO_3^{2-} = CaCO_{3\,(aq)}^0$	3.22	
$Ca^{2+} + SO_4^{2-} = CaSO_{4\,(aq)}^0$	2.23	6.28

Concentrations of elements are in moles per kilogram (molal)

Ion molal product (IMP) of two elements = the concentration of one times the concentration of the other

For $CaCO_3$ the IMP = 0.011 x 0.0002

The effective molality is called the activity

The activity is only equal to the molality in an infinitely dilute solution

In other solutions the activity is related to the molality through the activity coefficient

So that:

$\alpha = \lambda m$

λ= activity coefficient

Definitions

- K_{sp} = solubility product
- IMP= Ion Molar Product
- IAP = Ion Activity Product
- Activity= molality * activity coefficient
- Activity = effective concentration
- Ionic strength= I= ½ Σ $(m_1c_1^2+m_2c_2^2.m_nc_n^2)$

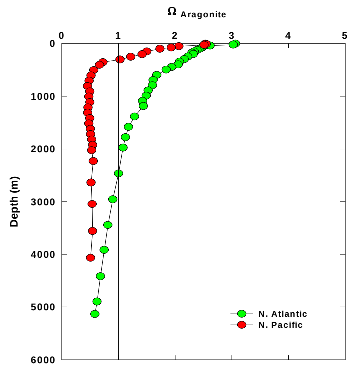
Ionic Strength of Seawater

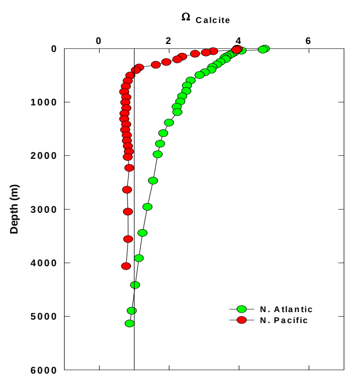
- I = ½(.546*1+ .467*1 + 0.028*4 + 0.01*4 + 0.01*1+ 0.055*4 + 0.002*1)
- Seawater or any solution must remain electrically neutral
- mNa*c^2+ mK*c^2+mCa*c^2+mMg*c^2= mCl-*c^2+mSO4*c^2+mHCO3-*c^2

Thermodynamic Saturation State of $CaCO_3$

$\Omega = [Ca^{2+}]\ [CO_3^{2-}]/Ksp(t,S,P)$

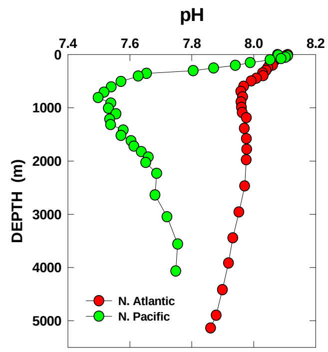
Ω	> 1	**Supersaturation**
Ω	= 1	**Equilibrium**
Ω	< 1	**Under Saturation**

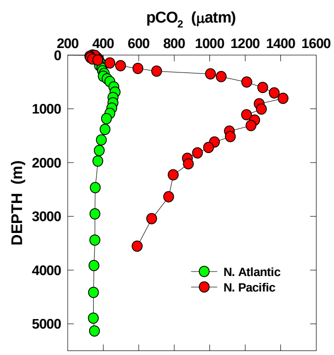


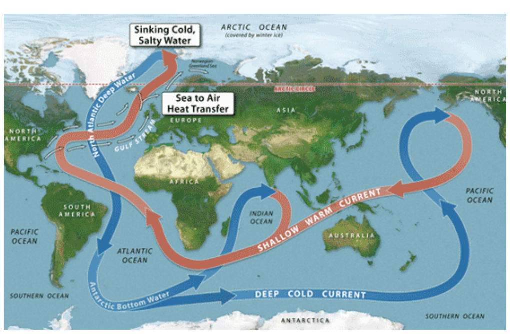


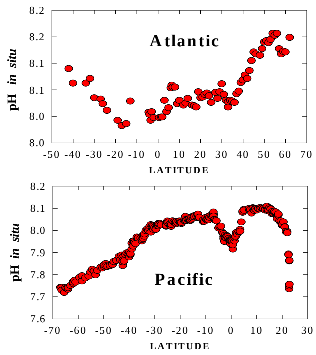
Water

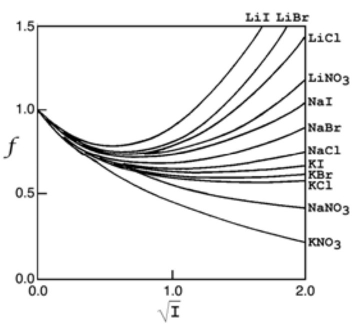
- $H_2O = H^+ + OH^-$
- $K_{H2O} = 10^{-14} = [H^+][OH^-]/ H_2O$
- pK = negative log = 14


pH
7.4
7.6
7.8
8.0
8.2
0
1000
2000
3000
4000
5000
DEPTH (m)
N. Atlantic
N. Pacific


pCO2 (µatm)
200
400
600
800
1000
1200
1400
1600
0
1000
2000
3000
4000
5000
DEPTH (m)
N. Atlantic
N. Pacific


Sinking Cold, Salty Water
ARCTIC OCEAN
(covered by winter ice)
ARCTIC CIRCLE
Sea to Air Heat Transfer
North Atlantic Deep Water
GULF STREAM
NORTH AMERICA
EUROPE
ASIA
AFRICA
SOUTH AMERICA
PACIFIC OCEAN
ATLANTIC OCEAN
INDIAN OCEAN
AUSTRALIA
SHALLOW WARM CURRENT
DEEP COLD CURRENT
Antarctic Bottom Water
SOUTHERN OCEAN
ANTARCTICA





$$\log \gamma_i = \frac{-Az^2\sqrt{I}}{1+\sqrt{I}}$$

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1+Ba_0\sqrt{I}}$$

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1+Ba_0\sqrt{I}} + bI$$

TABLE 2.1 PARAMETERS FOR THE DEBYE–HUCKEL EQUATION AT 1 ATMOSPHERE PRESSURE (ADAPTED FROM MANOV ET AL., 1943; KLOTZ, 1950; TRUESDELL AND JONES, 1974)

T(°C)	A	$B(\times 10^8)$	Ion	$a_0(\times 10^{-8})$	b
0	0.4883	0.3241	Ca^{2+}	5.0	0.165
5	0.4921	0.3249	Mg^{2+}	5.5	0.20
10	0.4960	0.3258	Na^+	4.0	0.075
15	0.5000	0.3262	K^+, Cl^-	3.5	0.015
20	0.5042	0.3273	SO_4^{2-}	5.0	−0.04
25	0.5085	0.3281	HCO_3^-, CO_3^{2-}	5.4	0.0
30	0.5130	0.3290	NH_4^+	2.5	
40	0.5221	0.3305	Sr^{2+}, Ba^{2+}	5.0	
50	0.5319	0.3321	Fe^{2+}, Mn^{2+}, Li^+	6.0	
60	0.5425	0.3338	H^+, Al^{3+}, Fe^{3+}	9.0	

$$K_H = \frac{\{H_2CO_3^o\}}{pCO_2} = 10^{-1.46}$$ 1

$$K_1 = \frac{\{HCO_3^-\}\{H^+\}}{\{H_2CO_3^O\}} = 10^{-6.35}$$ 2

$$K_2 = \frac{\{CO_3^-\}\{H^+\}}{\{HCO_3^{2-}\}} = 10^{-10.33}$$ 3

$$H_2O + pCO2 \rightleftarrows H_2CO_3^o$$

$$K_H = \frac{\{H_2CO_3^o\}}{pCO_2} = 10^{-1.46}$$

$$H_2CO_3^o \rightleftarrows HCO_3^- + H^+$$

$$K_1 = \frac{\{HCO_3^-\}\{H^+\}}{\{H_2CO_3^O\}} = 10^{-6.35}$$

$$\log K*_1 = -356.3094 - .06091964T + 21834.37/T + 126.8339\log T - 1684915/T^2$$

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+$$

$$K_2 = \frac{\{CO_3^-\}\{H^+\}}{\{HCO_3^{2-}\}} = 10^{-10.33}$$

$$K_H = \frac{\{H_2CO_3^o\}}{pCO_2} = 10^{-1.46}$$

Take logs

$$\log\{H_2CO_3^o\} = -1.46 + \log pCO_2$$

$$K_H = \frac{\{H_2CO_3^o\}}{pCO_2} = 10^{-1.46}$$

$$K_1 = \frac{\{HCO_3^-\}\{H^+\}}{\{H_2CO_3^O\}} = 10^{-6.35}$$

Combine

$$\{H_2CO_3^O\} = K_H\, pCO_2$$

$$\frac{K_H K_1 pCO_2}{H^+} = \{HCO_3^-\}$$

$$\log\{HCO_3^-\} = -7.81 + \log pCO_2 + pH$$

$$\frac{K_H K_1 pCO_2}{H^+} = \{HCO_3^-\}$$

$$K_2 = \frac{\{CO_3^-\}\{H^+\}}{\{HCO_3^{2-}\}} = 10^{-10.33}$$

Combine

$$\frac{K_H K_1 K_2\, pCO_2}{2H^+} = \{CO_3^-\}$$

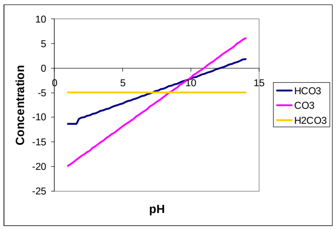
Take logs

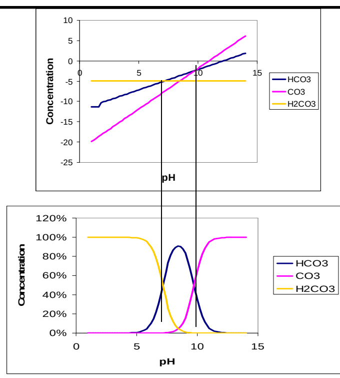
$$\log\{CO_3^-\} = -18.34 + \log pCO_2 + 2pH$$

$$\log\{H_2CO_3^o\} = -1.46 + \log pCO_2$$

$$\log\{HCO_3^-\} = -7.81 + \log pCO_2 + pH$$

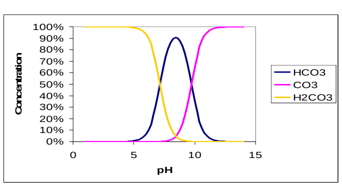
$$\log\{CO_3^-\} = -18.34 + \log pCO_2 + 2pH$$

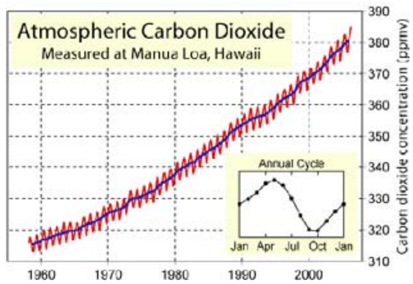


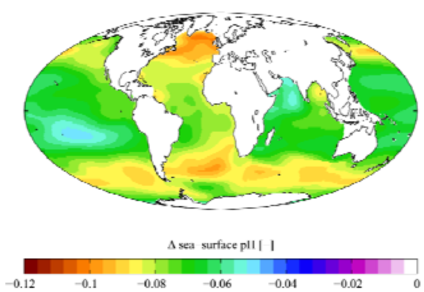


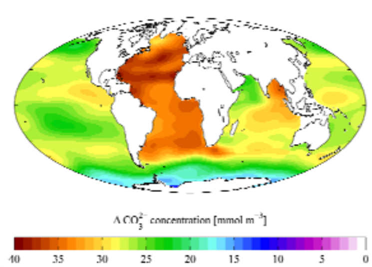
$$DIC = mH_2CO_3^o + mCO_3^{2-} + mHCO_3^-$$

Bjerrum Diagram




Atmospheric Carbon Dioxide
Measured at Manua Loa, Hawaii
Annual Cycle
Jan Apr Jul Oct Jan
390
380
370
360
350
340
330
320
310
Carbon dioxide concentration (ppmv)
1960 1970 1980 1990 2000


Δ sea surface pH [ ]
−0.12 −0.1 −0.08 −0.06 −0.04 −0.02 0


Δ CO_3^{2-} concentration [mmol m^{-3}]
40 35 30 25 20 15 10 5 0

Oxygen Isotopes