

Supplementary Material

Table A: Astrocal Thermal showing how seasonal variations in pCO₂ correlate inversely with variations in carbonate and calcite solubility. Data are shown graphically in Figure 4

UP		CO2MOD2												
Mauna Loa		Manua Loa pCO ₂ in response to seawater temperature at Hilo, Hawaii												
UP	δT K	1	2	3	4	5	6	7	8	9	10	11	12	13
a		9.843	9.901	9.959	10.018	10.077	10.137	10.198	10.258	10.32	10.382	10.444	10.507	10.57
b		1658.081	1663.553	1669.042	1674.547	1680.069	1685.607	1691.163	1696.735	1702.325	1707.931	1713.554	1719.195	1724.852
c		218.753	218.235	217.716	217.195	216.674	216.151	215.627	215.102	214.576	214.049	213.521	212.992	212.461
C		1886.677	1891.689	1896.717	1901.76	1906.82	1911.895	1916.988	1922.095	1927.221	1932.362	1937.519	1942.694	1947.883
Ac		2095.597	2107.086	2104.474	2108.937	2113.417	2117.909	2122.417	2126.939	2131.477	2136.029	2140.596	2145.179	2149.774
Ab		2190.651	2194.795	2198.954	2203.127	2207.315	2211.518	2215.736	2219.968	2224.216	2228.478	2232.756	2237.049	2241.357
Ksp		4.26E-07	4.26E-07	4.26E-07	4.26E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.28E-07
K [Ca ²⁺][CO ₃ ²⁻]		4.33E-07	4.32E-07	4.31E-07	4.30E-07	4.29E-07	4.28E-07	4.27E-07	4.26E-07	4.25E-07	4.24E-07	4.23E-07	4.22E-07	4.21E-07
Ω		1.016673	1.013928	1.011184	1.008441	1.005698	1.002956	1.000216	0.997473	0.994737	0.991999	0.989261	0.986526	0.9837902
pH		8.05	8.05039	8.05077	8.05115	8.05153	8.05192	8.0523	8.0527	8.0531	8.0535	8.0539	8.0543	8.0547
Temperature K		299.8	299.617	299.433	299.25	299.067	298.883	298.7	298.517	298.333	298.15	297.977	297.793	297.6
pCO ₂ ppmv		420	420.575	421.15	421.75	422.3	422.875	423.45	424.025	424.6	425.175	425.75	426.325	426.9
δCO ₂														
a		9.857	9.914	9.973	10.032	10.091	10.151	10.211	10.272	10.334	10.396	10.458	10.521	10.584
b		1661.826	1667.304	1672.799	1678.31	1683.837	1689.382	1694.943	1700.521	1706.117	1711.729	1717.358	1723.004	1728.668
c		219.442	218.921	218.399	217.875	217.351	216.825	216.298	215.77	215.241	214.711	214.18	213.648	213.115
C		1891.125	1896.139	1901.171	1906.217	1911.279	1916.358	1921.452	1926.563	1931.692	1936.836	1941.996	1947.173	1952.367
Ac		2100.711	2105.146	2109.596	2114.06	2118.539	2123.032	2127.54	2132.061	2136.6	2141.151	2145.718	2150.3	2154.898
Ab		2195.776	2199.92	2204.078	2208.252	2212.44	2216.642	2220.86	2225.092	2229.34	2233.603	2237.88	2242.173	2246.482
Ksp		4.26E-07	4.26E-07	4.26E-07	4.26E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.28E-07
K [Ca ²⁺][CO ₃ ²⁻]		4.34E-07	4.33E-07	4.32E-07	4.31E-07	4.30E-07	4.29E-07	4.28E-07	4.27E-07	4.26E-07	4.25E-07	4.24E-07	4.23E-07	4.22E-07
Ω		1.019875	1.017115	1.014356	1.011598	1.008841	1.006085	1.00333	1.000576	0.997822	0.99507	0.992318	0.989567	0.986818
pH		8.05039	8.05077	8.05115	8.05154	8.05192	8.0523	8.05268	8.05306	8.05344	8.05382	8.05419	8.05457	8.05494
Temperature K		299.8	299.617	299.433	299.25	299.067	298.883	298.7	298.517	298.333	298.15	297.977	297.793	297.6
pCO ₂ ppmv		420.575	421.15	421.75	422.3	422.875	423.45	424.025	424.6	425.175	425.75	426.325	426.9	427.475
DOWN														
Mauna Loa		Manua Loa pCO ₂ in response to seawater temperature at Hilo, Hawaii												
DOWN	δT K	26	25	24	23	22	21	20	19	18	17	16	15	14
a		9.889	9.943	9.998	10.054	10.11	10.166	10.222	10.28	10.338	10.396	10.455	10.514	10.574
b		1658.89	1664.263	1669.652	1675.058	1680.481	1685.92	1691.376	1696.849	1702.338	1707.845	1713.368	1718.908	1724.466
c		217.955	217.49	217.025	216.558	216.089	215.619	215.148	214.675	214	213.726	213.349	212.971	212.591
C		1886.734	1891.696	1896.675	1901.67	1906.68	1911.705	1916.746	1921.804	1926.877	1931.967	1937.172	1942.193	1947.331
Ac		2094.8	2099.243	2103.702	2108.174	2112.659	2117.158	2121.672	2126.199	2130.74	2135.297	2140.066	2144.45	2149.048
Ab		2189.559	2193.735	2197.924	2202.127	2206.344	2210.575	2214.82	2219.08	2223.353	2227.641	2231.943	2236.259	2240.59
Ksp		4.26E-07	4.26E-07	4.26E-07	4.26E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.28E-07
K [Ca ²⁺][CO ₃ ²⁻]		4.32E-07	4.31E-07	4.30E-07	4.29E-07	4.28E-07	4.27E-07	4.26E-07	4.25E-07	4.24E-07	4.23E-07	4.22E-07	4.21E-07	4.20E-07
Ω		1.012961	1.010468	1.007975	1.00548	1.002985	1.00049	0.997993	0.995497	0.99299	0.990501	0.988003	0.985504	0.983004
pH		8.0482	8.04872	8.04923	8.04975	8.05026	8.05077	8.05128	8.05179	8.05229	8.05281	8.05331	8.05382	8.05431
Temperature K		299.8	299.617	299.433	299.25	299.067	298.883	298.7	298.517	298.333	298.15	297.973	297.789	297.6
pCO ₂ ppmv		421.95	422.375	422.8	423.225	423.65	424.075	424.5	424.925	425.35	425.775	426.2	426.625	427.05
δCO ₂														
a		9.899	9.953	10.008	10.064	10.12	10.176	10.233	10.29	10.348	10.406	10.465	10.525	10.584
b		1662.535	1667.914	1673.309	1678.721	1684.15	1689.595	1695.057	1700.535	1706.03	1711.543	1717.072	1722.618	1728.182
c		218.693	218.226	217.758	217.288	216.816	216.343	215.869	215.393	214.916	214.438	213.958	213.478	212.995
C		1891.127	1896.093	1901.075	1906.073	1911.086	1916.114	1921.159	1926.218	1931.294	1936.387	1941.495	1946.621	1951.761
Ac		2099.922	2104.366	2108.825	2113.297	2117.782	2122.281	2126.795	2131.321	2140.419	2140.419	2144.988	2149.574	2154.172
Ab		2194.683	2198.859	2203.048	2207.252	2211.469	2215.7	2219.945	2224.204	2228.465	2232.726	2236.987	2241.248	2245.514
Ksp		4.26E-07	4.26E-07	4.26E-07	4.26E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.27E-07	4.28E-07
K [Ca ²⁺][CO ₃ ²⁻]		4.33E-07	4.32E-07	4.31E-07	4.30E-07	4.29E-07	4.28E-07	4.27E-07	4.26E-07	4.26E-07	4.25E-07	4.24E-07	4.23E-07	4.22E-07
Ω		1.016395	1.013887	1.011379	1.00887	1.00636	1.00385	1.001339	0.998828	0.996316	0.993803	0.99129	0.988777	0.9862628
pH		8.04872	8.04923	8.04975	8.05026	8.05077	8.05128	8.05179	8.0523	8.05281	8.05331	8.05381	8.05432	8.05482
Temperature K		299.8	299.617	299.433	299.25	299.067	298.883	298.7	298.517	298.333	298.15	297.973	297.789	297.6
pCO ₂ ppmv		422.375	422.8	423.225	423.65	424.075	424.5	424.925	425.35	425.775	426.2	426.625	427.05	427.475

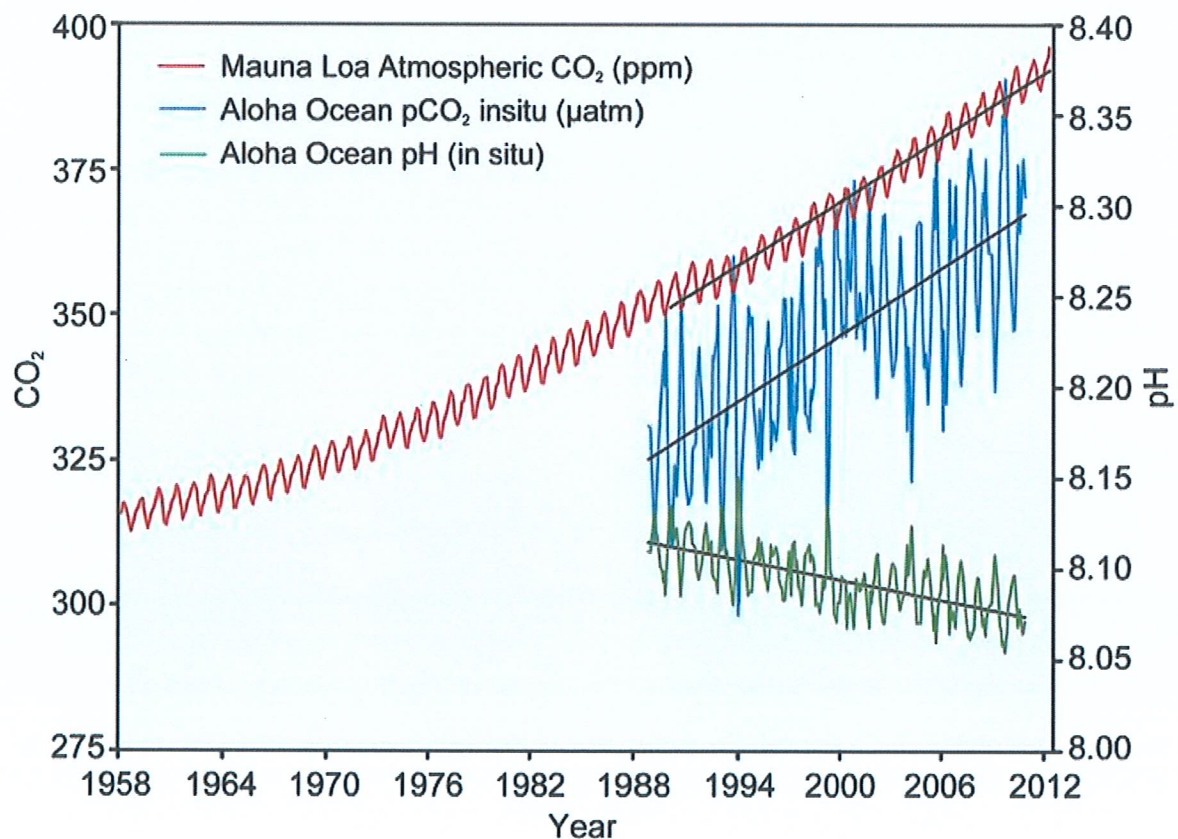
Run

with CO2MOD2 (ascending temperature) and CO2MOD3 (descending temperature). Models are run assuming temperature as K, initial pCO₂ values and rates of pCO₂ variations. Alkalinity (Ac, Ab) and dissolved inorganic carbon (C or DIC) is generated in the model thermodynamically.



Table B. Year 2000 DIC values at Point Barrow, Alaska for atmospheric pCO₂, modelled with Thermal, from temperature data; alkalinity and dissolved inorganic carbon and pH values were generated by model; bold values for Ω represent increased aggregation for calcite

Point Barrow	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
a δT K	22.139	22.139	22.139	22.139	22.139	22.139	20.286	18.189	17.856	19.584	20.704	21.903
b	2944.164	2944.164	2944.164	2944.164	2944.164	2944.164	2890.089	2778.621	2734.484	2802.185	2856.641	2912.173
c	201.358	201.358	201.358	201.358	201.358	201.358	217.458	230.467	227.37	211.768	205.388	199.128
C	3167.661	3167.661	3167.661	3167.661	3167.661	3167.661	3127.833	3027.277	2979.71	3033.537	3082.733	3133.204
Ac	3346.88	3346.88	3346.88	3346.88	3346.88	3346.88	3325.005	3239.555	3189.224	3225.721	3267.417	3310.429
Ab	3418.16	3418.16	3418.16	3418.16	3418.16	3418.16	3400.664	3319.911	3269.732	3258.644	3341	3381.698
Ksp	4.28E-07	4.28E-07	4.28E-07	4.28E-07	4.28E-07	4.28E-07	4.29E-07	4.30E-07	4.30E-07	4.29E-07	4.29E-07	4.28E-07
K [Ca ²⁺][CO ₃ ²⁻]	3.99E-07	3.99E-07	3.99E-07	3.99E-07	3.99E-07	3.99E-07	4.31E-07	4.56E-07	4.50E-07	4.19E-07	4.07E-07	3.94E-07
Ω	0.931524	0.931524	0.931524	0.931524	0.931524	0.931524	1.003477	1.061241	1.04696	0.977122	0.948928	0.921211
pH	8.26	8.26	8.26	8.26	8.26	8.26	8.26	8.26152	8.26259	8.2619	8.2609	8.25991
Temperature K	270.95	270.95	270.95	270.95	270.95	270.95	273.15	275.35	275.35	273.15	272.05	270.95
pCO ₂ ppmv	375.2	375.2	375.2	375.2	375.2	375.2	375.2	366.15	359.45	362.35	366.85	371.35
a δCO_2	22.139	22.139	22.139	22.139	22.139	22.139	19.797	17.863	18.007	19.835	20.967	22.089
b	2944.164	2944.164	2944.164	2944.164	2944.164	2944.164	2830.285	2735.618	2753.301	2831.639	2886.253	2932.06
c	201.358	201.358	201.358	201.358	201.358	201.358	213.706	227.46	228.566	213.503	207.043	200.159
C	3167.661	3167.661	3167.661	3167.661	3167.661	3167.661	3063.788	2980.941	2999.874	3064.977	3114.263	3154.308
Ac	3346.88	3346.88	3346.88	3346.88	3346.88	3346.88	3257.698	3190.538	3210.433	3258.644	3300.338	3332.378
Ab	3418.16	3418.16	3418.16	3418.16	3418.16	3418.16	3333.358	3270.894	3290.948	3334.575	3373.923	3403.647
Ksp	4.28E-07	4.28E-07	4.28E-07	4.28E-07	4.28E-07	4.28E-07	4.29E-07	4.30E-07	4.30E-07	4.29E-07	4.29E-07	4.28E-07
K [Ca ²⁺][CO ₃ ²⁻]	3.99E-07	3.99E-07	3.99E-07	3.99E-07	3.99E-07	3.99E-07	4.23E-07	4.50E-07	4.53E-07	4.23E-07	4.10E-07	3.96E-07
Ω	0.931524	0.931524	0.931524	0.931524	0.931524	0.931524	0.986164	1.047392	1.052484	0.985224	0.956574	0.925978
pH	8.26	8.26	8.26	8.26	8.26	8.26	8.26152	8.26259	8.2619	8.2609	8.25991	8.2592
Temperature K	270.95	270.95	270.95	270.95	270.95	270.95	273.15	275.35	275.35	273.15	272.05	270.95
pCO ₂ ppmv	375.2	375.2	375.2	375.2	375.2	375.2	366.15	359.45	362.35	366.85	371.35	374.35



NCCARF Plot of Aloha Station Data
National Climate Change Research Facility
Australian Government

Chemical Oceanography and Marine Carbon Cycle

Steven Emerson

- **Publisher:** Cambridge University Press
- **Online publication date:** September 2012
- **Print publication year:** 2008
- **Online ISBN:** 9780511793202
- **DOI:** <https://doi.org/10.1017/CB09780511793202>

Carbonate Chemistry

Emerson S. and Hedges pp. 101-133

Appendix 4.2 equations were employed in CO2MOD2 THERMAL

$$K_{P,3} = \frac{[\text{PO}_4^{3-}] \times [\text{H}^+]}{[\text{HPO}_4^{2-}]} \quad (4A1.6)$$

$$K_W = [\text{OH}^-] [\text{H}^+] \quad (4A1.7)$$

4A1.2

The following Matlab function program finds the root of the cubic equation for $[\text{H}^+]$ in terms of $A_{\text{C\&B}}$ and DIC resulting from the combination of the equations in 4A1.1 (a) and (b) above (Zeebe and Wolf-Gladrow, 2000). Input values are temperature, salinity, depth, $A_{\text{C\&B}}$ and DIC and the outputs are f_{CO_2} , pH, $[\text{CO}_2]$, $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$. Units and equilibrium constants used are indicated in the comment statements, which are preceded by a % sign.

```
function [fco2, pH, co2, hco3, co3] = co3eq (temp, s, z, alk, dic)
% Function to calculate fCO2, HCO3, and CO3 from ALK and DIC as a
% f(temp,sal,Z)
% temp = temp(deg C),
% sal = salinity(ppt), depth = z(m), alk = ALK(microeq/kg),
% dic = DIC(micromol kg-1)
% HCO3, CO3, and CO2 are returned in mol kg-1, fCO2 in atm
% This program uses the equations in Zeebe and Wolf-Gladrow (2000) and
% Matlab's root finding routine
% checked for fCO2 against Luecker et al. (2000), May 2002;
% Depth dependence has not been checked
t = temp + 273.15;
Pr = z/10;
alk = alk * .000001;
dic = dic * .000001;
R = 83.131;
% Calculate total borate (tbor) from chlorinity
tbor = .000416 * s / 35.0;
% Calculate Henry's Law coeff, KH (Weiss, 1974)
U1 = -60.2409 + 93.4517 * (100/t) + 23.3585 * log(t/100);
U2 = s * (.023517 - .023656 * (t/100) + .0047036 * (t/100) ^ 2);
KH = exp(U1 + U2);
% Calculate KB from temp & sal (Dickson, 1990)
KB = exp((-8966.9 - 2890.53 * s ^ 0.5 - 77.942 * s + 1.728 * s ^ 1.5
- 0.0996 * s ^ 2)/t ... + 148.0248 + 137.1942 * s ^ 0.5 + 1.62142 * s
- (24.4344 + 25.085 * s ^ 0.5 + ... 0.2474 * s) * log(t) + 0.053105 * s ^ 0.5 * t);
% Calculate K1 and K2 (Luecker et al., 2000)
K1 = 10^(-(3633.86/t - 61.2172 + 9.67770 *
log(t) - 0.011555 * s + 0.0001152 * s ^ 2));
K2 = 10^(-(471.78/t + 25.9290 - 3.16967 *
log(t) - 0.01781 * s + 0.0001122 * s ^ 2));
% Pressure variation of K1, K2, and KB (Millero, 1995)
dvB = -29.48 + 0.1622 * temp - .002608 * (temp)^2;
dv1 = -25.50 + 0.1271 * temp;
dv2 = -15.82 - 0.0219 * temp;
dkB = -.00284;
dk1 = -.00308 + 0.0000877 * temp;
```

```

dk2 = +.00113 -.0001475 * temp;
KB = (exp( -(dvB/(R*t))*Pr + (0.5 * dkB/(R*t))*Pr^2)) * KB;
K1 = (exp( -(dv1/(R*t))*Pr + (0.5 * dk1/(R*t))*Pr^2)) * K1;
K2 = (exp( -(dv2/(R*t))*Pr + (0.5 * dk2/(R*t))*Pr^2)) * K2;
% temperature dependence of Kw (DoE, 1994)
KW1 = 148.96502-13847.26/t-23.65218*log(t);
KW2 = (118.67/t-5.977 + 1.0495*log(t))*s ^ .5-0.01615*s;
KW = exp(KW1 + KW2);
% solve for H ion (Zeebe and Wolf-Gladrow, 2000)
a1 = 1;
a2 = (alk + KB + K1);
a3 = (alk*KB-KB*tbor-KW + alk*K1 + K1*KB + K1*K2-dic*K1);
a4 = (-KW*KB + alk*KB*K1-KB*tbor*K1-KW*K1 + alk*K1*K2
+ KB*K1*K2-dic*KB*K1-2*dic*K1*K2);
a5 = (-KW*KB*K1 + alk*KB*K1*K2-KW*K1*K2-KB*tbor*K1*K2-2*dic*KB*
K1*K2);
a6 = -KB*KW*K1*K2;
p = [a1 a2 a3 a4 a5 a6];
r = roots(p);
h = max(real(r));
% calculate the HCO3, CO3 and CO2aq using DIC, Alk and H +
format short g;
hco3 = dic/(1 + h/K1 + K2/h);
co3 = dic/(1 + h/K2 + h*h/(K1*K2));
co2 = dic/(1 + K1/h + K1*K2/(h*h));
fco2 = co2 / KH;
pH = -log10(h);
% calculate B(OH)4- and OH
BOH4 = KB*tbor/(h + KB); OH = KW/h;
% recalculate DIC and Alk to check calculations
Ct = (hco3 + co3 + co2)*1e6;
At = (hco3 + 2*co3 + BOH4 + OH-h)*1e6;

```

Appendix 4.2 Equations for calculating the equilibrium constants of the carbonate and borate buffer system

Constants are based on the “total” pH scale, pH_T (Dickson, 1984, 1993). Values are first presented at 1 atm pressure and then equations are given for calculating the pressure effect on K . T is temperature in either degrees Kelvin (T), or degrees centigrade (T_C). Salinities are on the practical salinity scale. Equilibrium constants for the equilibria other than K_H , K'_1 , K'_2 , K'_B , and K'_W given in Appendix 4A1.1(c) can be found in DoE (1994) and in Zeebe and Wolf-Gladrow (2000).

4A2.1. Values at 1 atmosphere

(a) The Henry's Law constant for CO_2 in seawater ($\text{mol kg}^{-1}\text{atm}^{-1}$), Eq. (4.14)

Source: From Weiss (1974) as reported in DoE (1994).

$$\begin{aligned}\ln K_H &= \frac{9345.17}{T} - 60.2409 + 23.3585 \ln \left(\frac{T}{100} \right) \\ &+ S \left[0.023517 - 0.00023656T + 0.0047036 \left(\frac{T}{100} \right)^2 \right] \\ &= -3.5617 \quad (T_C = 25 \text{ (} T = 298.15 \text{)}, S = 35). \quad (4A2.1)\end{aligned}$$

(b) The first (Eq. (4.11)) and second (Eq. (4.9)) dissociation constants for carbonic acid in seawater (mol kg⁻¹)

Mehrbach's constants are given on the total pH scale (Luecker *et al.*, 2000).

$$\begin{aligned}\text{p}K'_1 &= \frac{3633.86}{T} - 61.2172 + 9.6777 \ln(T) - 0.011555S + 0.0001152S^2 \\ &= 5.847 \quad (T_C = 25, S = 35) \quad (4A2.2)\end{aligned}$$

$$\begin{aligned}\text{p}K'_2 &= \frac{471.78}{T} + 25.9290 - 3.16967 \ln(T) - 0.01781S + 0.0001122S^2 \\ &= 8.966 \quad (T_C = 25, S = 35). \quad (4A2.3)\end{aligned}$$

(c) Boric acid in seawater, mol kg⁻¹ (Eqs. (4.19 and 4.20))

Based on Dickson (1990) as reported in DoE (1994).

$$B_T = [\text{B(OH)}_3] + [\text{B(OH)}_4^-] = 4.16 \times 10^{-4} \quad (S = 35) \quad (4A2.4)$$

$$\begin{aligned}\ln K_B &= \frac{-8966.90 - 2890.53S^{1/2} - 77.942S + 1.728S^{3/2} - 0.0996S^2}{T} \\ &+ 148.0248 + 137.1942S^{1/2} + 1.62142S \\ &- \left(24.4344 + 25.085S^{1/2} + 0.2474S \right) \ln(T) + 0.053105S^{1/2}T \\ &= -19.7964 \quad (T_C = 25, S = 35). \quad (4A2.5)\end{aligned}$$

(d) The dissociation constant of water, mol² kg⁻¹

From Dickson and Riley (1979) as reported in DoE (1994).

$$\begin{aligned}\ln K_W &= 148.96502 - \frac{13847.26}{T} - 23.6521 \ln(T) \\ &+ \left(\frac{118.67}{T} - 5.977 + 1.0495 \ln(T) \right) S^{1/2} - 0.01615S \\ &= -30.434 \quad (T_C = 25, S = 35). \quad (4A2.6)\end{aligned}$$

4A2.2 The pressure dependence (from Millero, 1995)

The effect of pressure can be calculated from the molal volume, ΔV , and compressibility, $\Delta \kappa$, changes for any given reaction

$$\ln \frac{K_P}{K_0} = - \left(\frac{\Delta V}{RT} \right) P + \left(\frac{0.5 \Delta \kappa}{RT} \right) P^2, \quad (4A2.7)$$

Table 4A2.1. Parameters for calculating the effect of pressure change on carbonate buffer system reactions and values of equilibrium constants at $P = 0$ and 300 bar

Constant	a_0	a_1	$a_2 \times 10^3$	$b_0 \times 10^3$	$b_1 \times 10^3$	$P = 0$	$P = 300$	K^{300}/K^0
pK'_1	25.50	-0.1271	0.0	3.08	-0.0877	5.847	5.726	1.32
pK'_2	15.82	0.0219	0.0	-1.13	0.1475	8.966	8.883	1.21
pK'_B	29.48	-0.1622	2.608	2.84	0.0	8.598	8.455	1.39
pK'_W	25.60	0.2324	-3.6246	5.13	0.0794	13.217	13.106	1.43

where K_P and K_0 are equilibrium constants for the reaction of interest at pressure P and at 0 bars (1 atm), respectively. P is pressure in bars, $R = 83.131 \text{ (cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}\text{)}$ and T is in degrees Kelvin. The molar volume ($\text{cm}^3 \text{ mol}$) and compressibility can be fit to equations of the form ($S = 35$)

$$-\Delta V = a_0 + a_1 T_C + a_2 T_C^2; \quad (4A2.8)$$

$$-\Delta \kappa = b_0 + b_1 T_C, \quad (4A2.9)$$

where T_C is now temperature in degrees C. Values for the coefficients a and b are presented in Table 4A2.1 along with calculated differences in pK' and K' at two different pressures ($T_C = 25^\circ \text{C}$, $S = 35$).

References

- Broecker, W. S. and T.-H. Peng (1982) *Tracers in the Sea*. Palisades, NY: EIDIGIO Press.
- Dickson, A. G. (1981) An exact definition of total alkalinity and a procedure for estimation of alkalinity and total inorganic carbon from titration data. *Deep-Sea Res.* **28A**(6), 609–23.
- Dickson, A. G. (1984) pH scales and proton-transfer reactions in saline media such as sea water. *Geochim. Cosmochim. Acta* **48**, 2299–308.
- Dickson, A. G. (1990) Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 298.15 K. *Deep-Sea Res.* **37**, 755–66.
- Dickson, A. G. (1993) pH buffers for sea water media based on the total hydrogen ion concentration scale. *Deep-Sea Res.* **40**, 107–18.
- Dickson, A. G. and F. J. Millero (1987) A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Res.* **34**, 1733–43.
- Dickson, A. G. and J. P. Riley (1979) The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base I. The ionic product of water (K_w). *Mar. Chem.* **7**, 89–99.
- DoE (1994) *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water*, version 2 (ed. A. G. Dickson and C. Goyet). ORNL/CDIAC-74.
- Emerson, S. (1995) Enhanced transport of carbon dioxide during gas exchange. In *Air-Water Gas Transfer. Selected papers from the Third International Symposium on Air-Water Gas Transfer July 24–27, 1995 Heidelberg University* (ed. B. Jahne and E. C. Monahan), pp. 23–36. Hanau: AEON Verlag.

May 29, 2022 PLUS TREND 0.15 umoles			Input pH value	
CO2MOD2 includes borate	0802	096	LABEL	
Models Mauna Loa oscillation	0803	080	P	
Inputs pH, pCO2 T to compute C and A	0804	107	STO MEM	
Varies H,K1,K2,Kw,Kc with T & salt S	0805	048	0	
C=[CO2+HCO3-+CO32-] total C mmoles/kg	0806	051	3	
A=[HCO3-+2CO32-+OH--H++B(OH4)-]	0807	119	print	
DIC alkalinity = Ac	0808	002	HALT	
140 moles CO2/m^2 dCO2=1=0.3333 m/m^2	Label	pK1o		
Iterations of increment,say 12/demi yr	0849	096	LABEL	
Adjust Ko solubility at 1532	0850	078	N	
Ionic product calcite 0.198x0.7=0.17	0851	107	STO MEM	
Ionic product CO32- x0.85	0852	048	0	
0520 096 LABEL	0853	052	4	
0521 073 I	0854	119	print	
0522 107 STO MEM	0855	002	HALT	
0523 048 0	Label	pK2o		
0524 048 0	0896	096	LABEL	
0525 119 print	0897	079	0	
0526 002 HALT	0898	107	STO MEM	
Margin, 0.000001 atm for d(pCO2)/month	0899	048	0	
0567 096 LABEL	0900	053	5	
0568 077 M	0901	119	print	
0569 107 STO MEM	0902	002	HALT	
0570 057 9	Label	Henry's constant Kaw		
0571 057 9	0943	096	LABEL	
0572 119 print	0944	072	H	
0573 002 HALT	0945	107	STO MEM	
Input pCO2 trend 0.00000015 (0.15 ppm)	0946	048	0	
0614 096 LABEL	0947	054	6	
0615 084 T	0948	119	print	
0616 107 STO MEM	0949	002	HALT	
0617 055 7	Input	lowest temperature K		
0618 056 8	0990	096	LABEL	
0619 119 print	0991	075	K	
0620 002 HALT	0992	107	STO MEM	
{CO2-calcite} U mmoles/kg 65 depth	0993	053	5	
0661 096 LABEL	0994	055	7	
0662 085 U	0995	119	print	
0663 107 STO MEM	0996	002	HALT	
0664 056 8	Input	salinity S %o g/kg		
0665 057 9	1037	096	LABEL	
0666 119 print	1038	083	S	
0667 002 HALT	1039	107	STO MEM	
Alkalinity=[HCO3-]+2[CO32-]+B(OH)4-+OH	1040	048	0	
0708 096 LABEL	1041	057	9	
0709 065 A	1042	119	print	
0710 107 STO MEM	1043	002	HALT	
0711 048 0	Input	pCO2 atmospheres		
0712 049 1	1084	096	LABEL	
0713 119 print	1085	090	Z	
0714 002 HALT	1086	107	STO MEM	
Label C[CO2+HCO3-+CO32-] mmol/kg	1087	049	1	
0755 096 LABEL	1088	056	8	
0756 067 C	1089	119	print	
0757 107 STO MEM	1090	002	HALT	
0758 048 0	Execute			
0759 056 8	1131	096	LABEL	
0760 119 print	1132	088	X	
0761 002 HALT	1133	096	LABEL	

1134	104	Hyperbol	1428	057	9
Recall iterations to set To			1429	043	+
Establish temperature gradient			1430	040	(
1215	040	(	1431	057	9
1216	109	RCL MEM	1432	051	3
1217	053	5	1433	052	4
1218	055	7	1434	053	5
1219	043	+	1435	046	.
1220	040	(	1436	049	1
1221	109	RCL MEM	1437	055	7
1222	048	0	1438	047	/
1223	048	0	1439	109	RCL MEM
Divide by I/dT			1440	048	0
1264	042	x	1441	055	7
1265	053	5	1442	041	)
1266	046	.	1443	043	+
1267	048	0	1444	040	(
1268	047	/	1445	109	RCL MEM
1269	049	1	1446	048	0
1270	050	2	1447	055	7
1271	041	)	1448	042	x
1272	041	)	1449	049	1
Print and stow current T			1450	101	EE
1313	119	print	1451	050	2
1314	107	STD MEM	1452	111	+/-
1315	048	0	1453	041	)
1316	055	7	1454	110	LOG e
Get Bt =total borates			1455	042	x
1357	096	LABEL	1456	050	2
1358	115	Sine	1457	051	3
1359	040	(	1458	046	.
1360	048	0	1459	051	3
1361	046	.	1460	053	5
1362	052	4	1461	056	8
1363	049	1	1462	053	5
1364	054	6	1463	041	)
1365	042	x	1464	043	+
1366	040	(	1465	040	(
1367	109	RCL MEM	1466	109	RCL MEM
1368	048	0	1467	048	0
1369	057	9	1468	057	9
1370	047	/	1469	042	x
1371	051	3	1470	040	(
1372	053	5	1471	048	0
1373	041	)	1472	046	.
1374	041	)	1473	048	0
1375	119	print	1474	050	2
1376	107	STD MEM	1475	051	3
1377	056	8	1476	053	5
1378	056	8	1477	049	1
Get pK _o Henry's coefficient repCO2			1478	055	7
1419	040	(	1479	045	-
1420	048	0	1480	040	(
1421	045	-	1481	049	1
1422	054	6	1482	101	EE
1423	048	0	1483	050	2
1424	046	.	1484	111	+/-
1425	050	2	1485	042	x
1426	052	4	1486	109	RCL MEM
1427	048	0	1487	048	0

1488	055	7	1704	054	6
1489	041	)	1705	055	7
1490	042	x	1706	048	0
1491	048	0	1707	046	.
1492	046	.	1708	055	7
1493	048	0	1709	047	/
1494	050	2	1710	109	RCL MEM
1495	051	3	1711	048	0
1496	054	6	1712	055	7
1497	053	5	1713	045	-
1498	054	6	1714	054	6
1499	043	+	1715	050	2
1500	040	(	1716	046	.
1501	049	1	1717	048	0
1502	101	EE	1718	048	0
1503	050	2	1719	056	8
1504	111	+/-	1720	043	+
1505	042	x	1721	040	(
1506	109	RCL MEM	1722	109	RCL MEM
1507	048	0	1723	048	0
1508	055	7	1724	055	7
1509	041	)	1725	110	LOG e
1510	113	Square	1726	042	x
1511	042	x	1727	057	9
1512	048	0	1728	046	.
1513	046	.	1729	055	7
1514	048	0	1730	057	9
1515	048	0	1731	052	4
1516	052	4	1732	052	4
1517	055	7	1733	041	)
1518	048	0	1734	045	-
1519	051	3	1735	040	(
1520	054	6	1736	048	0
1521	041	)	1737	046	.
1522	041	)	1738	048	0
1523	041	)	1739	049	1
Adjust solubility factor			1740	049	1
Print lnK'o function			1741	056	8
1604	119	print	1742	042	x
1605	064	Inverse	1743	109	RCL MEM
1606	110	LOG e	1744	048	0
1607	042	x	1745	057	9
1608	049	1	1746	041	)
1609	101	EE	1747	043	+
1610	051	3	1748	040	(
1611	042	x	1749	109	RCL MEM
1612	048	0	1750	048	0
1613	046	.	1751	057	9
1614	056	8	1752	113	Square
1615	048	0	1753	042	x
Print Ha' mM			1754	048	0
1656	061	=	1755	046	.
1657	119	print	1756	048	0
1658	107	STO MEM	1757	048	0
1659	048	0	1758	048	0
1660	054	6	1759	049	1
Get pK1'			1760	049	1
1701	040	(	1761	054	6
1702	040	(	1762	041	)
1703	051	3	1763	041	)

```

Print pk1'
1804 119 print
1805 107 STO MEM
1806 048 0
1807 052 4
Get pk2'
1848 040 (
1849 040 (
1850 049 1
1851 051 3
1852 057 9
1853 052 4
1854 046 .
1855 055 7
1856 047 /
1857 109 RCL MEM
1858 048 0
1859 055 7
1860 041 )
1861 043 +
1862 052 4
1863 046 .
1864 055 7
1865 055 7
1866 055 7
1867 045 -
1868 048 0
1869 046 .
1870 048 0
1871 049 1
1872 056 8
1873 052 4
1874 042 x
1875 109 RCL MEM
1876 048 0
1877 057 9
1878 043 +
1879 040 (
1880 109 RCL MEM
1881 048 0
1882 057 9
1883 113 Square
1884 042 x
1885 048 0
1886 046 .
1887 048 0
1888 048 0
1889 048 0
1890 049 1
1891 049 1
1892 056 8
1893 041 )
1894 041 )
Print pk2'
1935 119 print
1936 107 STO MEM
1937 048 0
1938 053 5
Get water dissociation lnKw
1979 040 (

```

```

1980 049 1
1981 052 4
1982 056 8
1983 046 .
1984 057 9
1985 054 6
1986 053 5
1987 048 0
1988 050 2
1989 045 -
1990 040 (
1991 049 1
1992 051 3
1993 056 8
1994 052 4
1995 055 7
1996 046 .
1997 050 2
1998 054 6
1999 047 /
2000 109 RCL MEM
2001 048 0
2002 055 7
2003 041 )
2004 045 -
2005 040 (
2006 109 RCL MEM
2007 048 0
2008 055 7
2009 110 LOG e
2010 042 x
2011 050 2
2012 051 3
2013 046 .
2014 054 6
2015 053 5
2016 050 2
2017 049 1
2018 041 )
2019 043 +
2020 040 (
2021 040 (
2022 040 (
2023 049 1
2024 049 1
2025 056 8
2026 046 .
2027 054 6
2028 055 7
2029 047 /
2030 109 RCL MEM
2031 048 0
2032 055 7
2033 041 )
2034 045 -
2035 053 5
2036 046 .
2037 057 9
2038 055 7
2039 055 7

```

2040	043	+	2139	048	0
2041	040	(	2140	055	7
2042	109	RCL MEM	2141	055	7
2043	048	0	2142	057	9
2044	055	7	2143	057	9
2045	110	LOG e	2144	051	3
2046	042	x	2145	042	x
2047	049	1	2146	109	RCL MEM
2048	046	.	2147	048	0
2049	048	0	2148	055	7
2050	052	4	2149	041	)
2051	057	9	2150	045	-
2052	053	5	2151	040	(
2053	041	)	2152	050	2
2054	041	)	2153	056	8
2055	042	x	2154	051	3
2056	109	RCL MEM	2155	057	9
2057	048	0	2156	046	.
2058	057	9	2157	051	3
2059	064	Inverse	2158	049	1
2060	113	Square	2159	057	9
2061	041	)	2160	047	/
2062	041	)	2161	109	RCL MEM
2063	045	-	2162	048	0
2064	048	0	2163	055	7
2065	046	.	2164	041	)
2066	048	0	2165	045	-
2067	049	1	2166	040	(
2068	054	6	2167	109	RCL MEM
2069	049	1	2168	048	0
2070	053	5	2169	055	7
2071	042	x	2170	108	LOG 10
2072	109	RCL MEM	2171	042	x
2073	048	0	2172	055	7
2074	057	9	2173	049	1
2075	041	)	2174	046	.
2076	119	print	2175	053	5
2077	107	STD MEM	2176	057	9
2078	048	0	2177	053	5
2079	050	2	2178	041	)
2080	064	Inverse	2179	043	+
2081	110	LOG e	2180	040	(
2082	119	print	2181	048	0
2083	107	STD MEM	2182	046	.
2084	054	6	2183	055	7
2085	049	1	2184	055	7
Get calcite pKs for solubility product			2185	055	7
2126	040	(	2186	049	1
2127	049	1	2187	050	2
2128	055	7	2188	045	-
2129	049	1	2189	040	(
2130	046	.	2190	048	0
2131	057	9	2191	046	.
2132	048	0	2192	048	0
2133	054	6	2193	048	0
2134	053	5	2194	050	2
2135	043	+	2195	056	8
2136	040	(	2196	052	4
2137	048	0	2197	050	2
2138	046	.	2198	054	6

2199	042	x		2259	046	.
2200	109	RCL MEM		2260	053	5
2201	048	0		2261	041	)
2202	055	7		2262	041	)
2203	041	)		2263	041	)
2204	045	-			Print pKs calcite	
2205	040	(		2304	119	print
2206	049	1		2305	107	STD MEM
2207	055	7		2306	049	1
2208	056	8		2307	054	6
2209	046	.		2308	111	+/-
2210	051	3		2309	064	Inverse
2211	052	4		2310	108	LOG 10
2212	047	/			Print Ks calcite solubility product	
2213	109	RCL MEM		2351	119	print
2214	048	0		2352	107	STD MEM
2215	055	7		2353	049	1
2216	041	)		2354	055	7
2217	041	)			Get lnKb boric acid	
2218	042	x		2395	040	(
2219	040	(		2396	040	(
2220	109	RCL MEM		2397	048	0
2221	048	0		2398	045	-
2222	057	9		2399	056	8
2223	064	Inverse		2400	057	9
2224	113	Square		2401	054	6
2225	041	)		2402	054	6
2226	041	)		2403	046	.
2227	043	+		2404	057	9
2228	040	(		2405	048	0
2229	048	0		2406	045	-
2230	046	.		2407	109	RCL MEM
2231	048	0		2408	048	0
2232	055	7		2409	057	9
2233	055	7		2410	064	Inverse
2234	049	1		2411	113	Square
2235	049	1		2412	042	x
2236	042	x		2413	050	2
2237	109	RCL MEM		2414	056	8
2238	048	0		2415	057	9
2239	057	9		2416	048	0
2240	041	)		2417	046	.
2241	045	-		2418	053	5
2242	040	(		2419	051	3
2243	048	0		2420	045	-
2244	046	.		2421	109	RCL MEM
2245	048	0		2422	048	0
2246	048	0		2423	057	9
2247	052	4		2424	042	x
2248	049	1		2425	055	7
2249	050	2		2426	055	7
2250	052	4		2427	046	.
2251	057	9		2428	057	9
2252	042	x		2429	052	4
2253	040	(		2430	050	2
2254	109	RCL MEM		2431	043	+
2255	048	0		2432	109	RCL MEM
2256	057	9		2433	048	0
2257	091	Exponent		2434	057	9
2258	049	1		2435	091	Exponent

2436	049	1	2496	052	4
2437	046	.	2497	050	2
2438	053	5	2498	045	-
2439	042	x	2499	040	(
2440	049	1	2500	050	2
2441	046	.	2501	052	4
2442	055	7	2502	046	.
2443	050	2	2503	052	4
2444	056	8	2504	051	3
2445	045	-	2505	052	4
2446	109	RCL MEM	2506	052	4
2447	048	0	2507	043	+
2448	057	9	2508	109	RCL MEM
2449	113	Square	2509	048	0
2450	042	x	2510	057	9
2451	048	0	2511	064	Inverse
2452	046	.	2512	113	Square
2453	048	0	2513	042	x
2454	057	9	2514	050	2
2455	057	9	2515	053	5
2456	054	6	2516	046	.
2457	041	)	2517	048	0
2458	047	/	2518	056	8
2459	109	RCL MEM	2519	053	5
2460	048	0	2520	043	+
2461	055	7	2521	109	RCL MEM
2462	043	+	2522	048	0
2463	049	1	2523	057	9
2464	052	4	2524	042	x
2465	056	8	2525	048	0
2466	046	.	2526	046	.
2467	048	0	2527	050	2
2468	050	2	2528	052	4
2469	052	4	2529	055	7
2470	056	8	2530	052	4
2471	043	+	2531	041	)
2472	109	RCL MEM	2532	042	x
2473	048	0	2533	040	(
2474	057	9	2534	109	RCL MEM
2475	064	Inverse	2535	048	0
2476	113	Square	2536	055	7
2477	042	x	2537	110	LOG e
2478	049	1	2538	041	)
2479	051	3	2539	043	+
2480	055	7	2540	109	RCL MEM
2481	046	.	2541	048	0
2482	049	1	2542	055	7
2483	057	9	2543	042	x
2484	052	4	2544	109	RCL MEM
2485	050	2	2545	048	0
2486	043	+	2546	057	9
2487	109	RCL MEM	2547	064	Inverse
2488	048	0	2548	113	Square
2489	057	9	2549	042	x
2490	042	x	2550	048	0
2491	049	1	2551	046	.
2492	046	.	2552	048	0
2493	054	6	2553	053	5
2494	050	2	2554	051	3
2495	049	1	2555	049	1

2556	048	0	2889	054	6
2557	053	5	2890	041	)
2558	041	)	2891	040	(
Print lnkb			2892	040	(
2599	119	print	2893	049	1
2600	047	/	2894	043	+
2601	049	1	2895	040	(
2602	048	0	2896	040	(
2603	110	LOG e	2897	109	RCL MEM
2604	041	)	2898	049	1
2605	111	+/-	2899	057	9
Print pKb			2900	045	-
2646	119	print	2901	109	RCL MEM
2647	107	STO MEM	2902	048	0
2648	049	1	2903	051	3
2649	057	9	2904	041	)
Get R= [HCO3-]/[CO2] lnlg(pH-pK1)			2905	064	Inverse
2690	040	(	2906	108	LOG 10
2691	109	RCL MEM	2907	041	)
2692	048	0	2908	041	)
2693	051	3	2909	114	1/x
2694	045	-	2910	042	x
2695	109	RCL MEM	2911	109	RCL MEM
2696	048	0	2912	056	8
2697	052	4	2913	056	8
2698	041	)	2914	041	)
2699	119	print	Print new B(OH)4-		
2700	064	Inverse	2955	119	print
2701	108	LOG 10	2956	107	STO MEM
2702	119	print	2957	056	8
2703	107	STO MEM	2958	055	7
2704	049	1	2959	109	RCL MEM
2705	049	1	2960	056	8
Get [CO32-]/HCO3-]=S			2961	054	6
2746	040	(	2962	038	If zero
2747	109	RCL MEM	2963	099	Cosine
2748	048	0	2964	040	(
2749	051	3	2965	109	RCL MEM
2750	045	-	2966	056	8
2751	109	RCL MEM	2967	055	7
2752	048	0	2968	045	-
2753	053	5	2969	109	RCL MEM
2754	041	)	2970	056	8
2755	119	print	2971	054	6
2756	064	Inverse	2972	041	)
2757	108	LOG 10	Print d[BOH]4-		
Print S			3013	119	print
2798	119	print	3014	107	STO MEM
2799	107	STO MEM	3015	056	8
2800	049	1	3016	053	5
2801	050	2	3017	096	LABEL
Get B(OH)4-			3018	099	Cosine
2842	040	(	Compute [CO2] from pCO2 and H		
2843	109	RCL MEM	[CO2] = Ho'xZ		
2844	056	8	3099	040	(
2845	055	7	3100	109	RCL MEM
Print previous B(OH)4-			3101	048	0
2886	119	print	3102	054	6
2887	107	STO MEM	3103	042	x
2888	056	8	3104	109	RCL MEM

3105	049	1	3438	048	0
3106	056	8	3439	051	3
3107	041	)	Get CaxCO32-		
Print [CO2] mmoles/kg			3480	040	(
3148	119	print	3481	049	1
3149	107	STO MEM	3482	046	.
3150	049	1	3483	054	6
3151	051	3	3484	053	5
Compute [HCO3-] = [CO2]xR			3485	101	EE
3192	040	(	3486	051	3
3193	109	RCL MEM	3487	111	+/-
3194	049	1	3488	042	x
3195	049	1	3489	109	RCL MEM
3196	042	x	3490	049	1
3197	109	RCL MEM	3491	053	5
3198	049	1	3492	042	x
3199	051	3	3493	049	1
3200	041	)	3494	101	EE
Print HCO3-			3495	051	3
3241	119	print	3496	111	+/-
3242	107	STO MEM	3497	041	)
3243	049	1	Print ionic product CaxCO3		
3244	052	4	3538	119	print
Compute CO32- = [HCO3-]xS			3539	047	/
3285	040	(	3540	109	RCL MEM
3286	109	RCL MEM	3541	049	1
3287	049	1	3542	055	7
3288	050	2	3543	041	)
3289	042	x	Print insolubility ratio		
3290	109	RCL MEM	3584	119	print
3291	049	1	Compute C=[CO2]+[HCO3-]+[CO32-]		
3292	052	4	3625	040	(
3293	041	)	3626	109	RCL MEM
Print [CO32-]			3627	049	1
3334	119	print	3628	051	3
3335	107	STO MEM	3629	043	+
3336	049	1	3630	109	RCL MEM
3337	053	5	3631	049	1
Get pH			3632	052	4
3378	040	(	3633	043	+
3379	040	(	3634	109	RCL MEM
3380	109	RCL MEM	3635	049	1
3381	048	0	3636	053	5
3382	052	4	3637	041	)
3383	043	+	Print total carbon C		
3384	040	(	3678	119	print
3385	109	RCL MEM	3679	107	STO MEM
3386	049	1	3680	048	0
3387	052	4	3681	056	8
3388	047	/	Compute alkalinity including borate		
3389	109	RCL MEM	3722	040	(
3390	049	1	3723	109	RCL MEM
3391	051	3	3724	049	1
3392	041	)	3725	052	4
3393	108	LOG 10	3726	043	+
3394	041	)	3727	040	(
3395	041	)	3728	050	2
Print and stow pH			3729	042	x
3436	119	print	3730	109	RCL MEM
3437	107	STO MEM	3731	049	1

```

3732 053 5
3733 041 )
3734 043 +
3735 109 RCL MEM
3736 056 8
3737 055 7
3738 043 +
3739 040 (
3740 109 RCL MEM
3741 048 0
3742 050 2
3743 111 +/-
3744 064 Inverse
3745 110 LOG e
Print Kw
3786 119 print
3787 114 1/x
3788 042 x
3789 040 (
3790 109 RCL MEM
3791 048 0
3792 052 4
3793 111 +/-
3794 064 Inverse
3795 108 LOG 10
3796 041 )
3797 041 )
3798 045 -
3799 040 (
3800 109 RCL MEM
3801 048 0
3802 052 4
3803 111 +/-
3804 064 Inverse
3805 108 LOG 10
3806 041 )
3807 041 )
Print alkalinity = Ac+Ab
3848 119 print
3849 107 STD MEM
3850 048 0
3851 049 1
3852 040 (
3853 109 RCL MEM
3854 057 9
3855 057 9
3856 043 +
3857 109 RCL MEM
3858 055 7
3859 056 8
3860 043 +
3861 109 RCL MEM
3862 049 1
3863 056 8
3864 041 )
Print and stow next pCO2
3905 119 print
3906 107 STD MEM
3907 049 1
3908 056 8

```

```

Get new C=[CO2+HCO3-+Co32-]=a+b+c
Add U-mmolescalcite/kg=d(pCO2)
3989 040 (
3990 109 RCL MEM
3991 048 0
3992 056 8
3993 043 +
3994 109 RCL MEM
3995 056 8
3996 057 9
3997 045 -
3998 048 0
3999 046 .
4000 048 0
4001 048 0
4002 048 0
4003 041 )
4004 119 print
4005 107 STD MEM
4006 048 0
4007 056 8
Get next [CO2] = a using KH
4048 040 (
4049 109 RCL MEM
4050 048 0
4051 054 6
4052 042 x
4053 109 RCL MEM
4054 049 1
4055 056 8
4056 041 )
Print next [CO2] = a
4097 119 print
4098 107 STD MEM
4099 049 1
4100 051 3
Compute z=K2/(K1a)=c/b^2;b=HCO3-,c=CO3
Solve quadratic Ax^2+Bx+C=0
Set Ab^2+Bb+C=0
c=b^2K2/aK1=(A-b)/2
A=2Z, B=1, C=-Ac
Solve Ab^2+Bb+C=0 equating c's
2Zb^2+b-A=0
x=-B+- (B^2-BZA)^0.5/4Z
4421 040 (
4422 040 (
4423 109 RCL MEM
4424 048 0
4425 053 5
4426 111 +/-
4427 064 Inverse
4428 108 LOG 10
4429 041 )
4430 047 /
4431 040 (
4432 109 RCL MEM
4433 048 0
4434 052 4
4435 111 +/-
4436 064 Inverse

```

4437	108	LOG 10	4653	049	1
4438	041	)	4654	041	)
4439	041	)	4655	047	/
4440	047	/	4656	040	(
4441	109	RCL MEM	4657	052	4
4442	049	1	4658	042	x
4443	051	3	4659	109	RCL MEM
4444	041	)	4660	057	9
Print Z			4661	056	8
4485	119	print	4662	041	)
4486	107	STO MEM	4663	041	)
4487	057	9	Print and stow b		
4488	056	8	4704	119	print
Get new DIC alkalinity			4705	107	STO MEM
4529	040	(	4706	049	1
4530	109	RCL MEM	4707	052	4
4531	049	1	Compute y=C-a=b+c		
4532	052	4	4748	040	(
4533	043	+	4749	109	RCL MEM
4534	050	2	4750	048	0
4535	042	x	4751	056	8
4536	109	RCL MEM	4752	045	-
4537	049	1	4753	109	RCL MEM
4538	053	5	4754	049	1
4539	043	+	4755	051	3
4540	050	2	4756	041	)
4541	042	x	Print y=b+c=C-a		
4542	109	RCL MEM	4797	119	print
4543	056	8	4798	107	STO MEM
4544	057	9	4799	057	9
4545	045	-	4800	055	7
4546	048	0	Compute pH		
4547	046	.	4841	040	(
4548	048	0	4842	040	(
4549	041	)	4843	109	RCL MEM
4550	119	print	4844	048	0
4551	107	STO MEM	4845	052	4
4552	055	7	4846	043	+
4553	057	9	4847	040	(
Solve $c = Zb^2 = (Ac - b)/2$			4848	109	RCL MEM
So $2Zb^2 + b - A = 0$ to solve			4849	049	1
4634	040	(	4850	052	4
4635	040	(	4851	047	/
4636	049	1	4852	109	RCL MEM
4637	043	+	4853	049	1
4638	040	(	4854	051	3
4639	056	8	4855	041	)
4640	042	x	4856	108	LOG 10
4641	109	RCL MEM	4857	041	)
4642	057	9	4858	041	)
4643	056	8	Print and stow pH		
4644	042	x	4899	119	print
4645	109	RCL MEM	4900	107	STO MEM
4646	055	7	4901	048	0
4647	057	9	4902	051	3
4648	041	)	Compute $c = [CO_3^{2-}]$		
4649	041	)	4943	040	(
4650	064	Inverse	4944	109	RCL MEM
4651	113	Square	4945	049	1
4652	045	-	4946	052	4

4947	113	Square	Get [Ca2+][CO32-] product
4948	042	x	5281 040 (
4949	109	RCL MEM	5282 049 1
4950	057	9	5283 046 .
4951	056	8	5284 054 6
4952	041	)	5285 053 5
Print c			5286 101 EE
4993	119	print	5287 051 3
4994	107	STO MEM	5288 111 +/-
4995	049	1	5289 042 x
4996	053	5	5290 109 RCL MEM
Compute C=a+b+c			5291 049 1
5037	040	(	5292 053 5
5038	109	RCL MEM	5293 042 x
5039	049	1	5294 049 1
5040	051	3	5295 101 EE
5041	043	+	5296 051 3
5042	109	RCL MEM	5297 111 +/-
5043	049	1	5298 041)
5044	052	4	5299 119 print
5045	043	+	5300 107 STO MEM
5046	109	RCL MEM	5301 057 9
5047	049	1	5302 054 6
5048	053	5	5303 040 (
5049	041	)	5304 109 RCL MEM
Print and stow C			5305 057 9
5090	119	print	5306 054 6
5091	107	STO MEM	5307 047 /
5092	048	0	5308 109 RCL MEM
5093	056	8	5309 049 1
Compute A=b+2c			5310 055 7
5134	040	(	5311 041)
5135	109	RCL MEM	Print Omega solubility
5136	049	1	5352 119 print
5137	052	4	5353 109 RCL MEM
5138	043	+	5354 048 0
5139	040	(	5355 048 0
5140	050	2	5356 039 Dec JPNZ
5141	042	x	5357 104 Hyperbol
5142	109	RCL MEM	5358 049 1
5143	049	1	5359 107 STO MEM
5144	053	5	5360 048 0
5145	041	)	5361 048 0
5146	041	)	5362 039 Dec JPNZ
Print alkalinity Ac			5363 104 Hyperbol
5187	119	print	5364 040 (
5188	107	STO MEM	5365 053 5
5189	048	0	5366 046 .
5190	049	1	5367 048 0
Compute and print Ac+Ab			5368 047 /
5231	040	(	5369 049 1
5232	109	RCL MEM	5370 050 2
5233	048	0	5371 041)
5234	049	1	5372 064 Inverse
5235	043	+	5373 117 SUM MEM
5236	109	RCL MEM	5374 048 0
5237	056	8	5375 055 7
5238	055	7	5376 040 (
5239	041	)	5377 109 RCL MEM
5240	119	print	5378 048 0

5379	055	7	5384	055	7
5380	119	print	5385	041	)
5381	045	-	5386	038	If zero
5382	109	RCL MEM	5387	115	Sine
5383	053	5	5388	002	HALT
