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## ***SUPPLEMENTARY MATERIALS***

**A new look at physico-chemical causes of changing climate: Is the seasonal variation in seawater temperature a significant factor in establishing the partial pressure of carbon dioxide in the Earth's atmosphere?**

**Ivan R. Kennedy <sup>1</sup>, John W. Runcie <sup>1</sup>, Shuo Zhang <sup>2</sup> and Raymond J. Ritchie <sup>3</sup>**

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## Supplementary Material

Table A: Astrocal Thermal showing how seasonal variations in pCO<sub>2</sub> correlate inversely with variations in carbonate and calcite solubility. Data are shown graphically in Figure 4

UP		CO2MOD2												
Mauna Loa		Mauna Loa pCO <sub>2</sub> 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 <sup>2+</sup> ][CO <sub>3</sub> <sup>2-</sup> ]		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	9.97E-01	0.994737	0.991999	0.98926	0.986526	0.9837902
pH		8.05	8.05039	8.05077	8.05115	8.05153	8.05192	8.0523	8.05268	8.05306	8.05344	8.05382	8.05419	8.05457
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 <sub>2</sub> ppmv		420	420.575	421.15	421.73	422.3	422.875	423.45	424.025	424.6	425.175	425.75	426.325	426.9
δCO <sub>2</sub>														
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	1722.004	1726.668
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 <sup>2+</sup> ][CO <sub>3</sub> <sup>2-</sup> ]		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 <sub>2</sub> ppmv		420.575	421.15	421.73	422.3	422.875	423.45	424.025	424.6	425.175	425.75	426.325	426.9	427.475
DOWN														
Mauna Loa		Mauna Loa pCO <sub>2</sub> 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	1724.461
c		217.955	217.49	217.025	216.558	216.089	215.619	215.148	214.675	214	213.726	213.349	212.971	212.595
C		1886.734	1891.696	1896.675	1901.67	1906.68	1911.705	1916.746	1921.804	1926.877	1931.967	1937.072	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 <sup>2+</sup> ][CO <sub>3</sub> <sup>2-</sup> ]		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	297.978	297.797	297.6
pCO <sub>2</sub> 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
δCO <sub>2</sub>														
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	1911.088	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	2135.859	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	2228.468	2232.765	2237.067	2241.384	2245.714
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 <sup>2+</sup> ][CO <sub>3</sub> <sup>2-</sup> ]		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		1.016395	1.013887	1.011379	1.00887	1.00636	1.00385	1.001339	0.998828	0.996316	0.993803	0.99129	0.988777	0.986262
pH		8.04872	8.04923	8.04975	8.05026	8.05077	8.05128	8.05179	8.0523	8.05281	8.05331	8.05382	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	297.978	297.797	297.6
pCO <sub>2</sub> 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

with CO2MOD2 (ascending temperature) and CO2MOD3 (descending temperature). Models are run assuming temperature as K, initial pCO<sub>2</sub> values and rates of pCO<sub>2</sub> variations. Alkalinity (Ac, Ab) and dissolved inorganic carbon (C or DIC) is generated in the model thermodynamically.

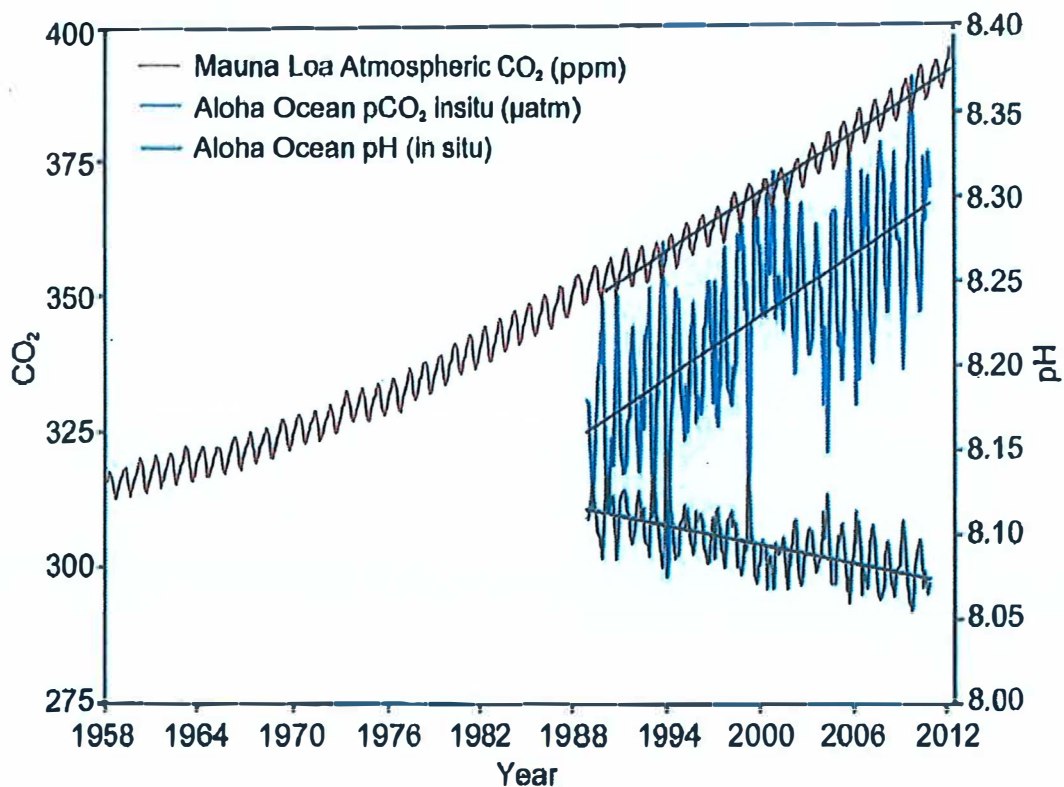


thermo



Table B. Year 2000 DIC values at Point Barrow, Alaska for atmospheric  $p\text{CO}_2$ , modelled with Thermal, from temperature data; alkalinity and dissolved inorganic carbon and pH values were generated by model; bold values for  $\Omega$  represent increased aggregation for calcite

Point Barrow	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
a	22.139	22.139	22.139	22.139	22.139	22.139	22.139	20.286	18.189	17.856	19.584	20.704
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
$K[\text{Ca}^{2+}][\text{CO}_3^{2-}]$	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
$\Omega$	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
$p\text{CO}_2$ 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	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
$K[\text{Ca}^{2+}][\text{CO}_3^{2-}]$	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
$\Omega$	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
$p\text{CO}_2$ 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

May 29, 2022 PLUB 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 B	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 ‰ g/kg		
0665 057 9	1037	096	LABEL	
0666 119 print	1038	083	8	
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 1/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	LOB 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 <sub>a</sub> 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 Ho' mM			1754	048	0
1656	061	=	1755	046	.
1657	119	print	1756	048	0
1658	107	STD 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'			1980	049	1
1804	119	print	1981	052	4
1805	107	STO MEM	1982	056	8
1806	048	0	1983	046	.
1807	052	4	1984	057	9
Get pk2'			1985	054	6
1848	040	(	1986	053	5
1849	040	(	1987	048	0
1850	049	1	1988	050	2
1851	051	3	1989	045	-
1852	057	9	1990	040	(
1853	052	4	1991	049	1
1854	046	.	1992	051	3
1855	055	7	1993	056	8
1856	047	/	1994	052	4
1857	109	RCL MEM	1995	055	7
1858	048	0	1996	046	.
1859	055	7	1997	050	2
1860	041	)	1998	054	6
1861	043	+	1999	047	/
1862	052	4	2000	109	RCL MEM
1863	046	.	2001	048	0
1864	055	7	2002	055	7
1865	055	7	2003	041	)
1866	055	7	2004	045	-
1867	045	-	2005	040	(
1868	048	0	2006	109	RCL MEM
1869	046	.	2007	048	0
1870	048	0	2008	055	7
1871	049	1	2009	110	LOG e
1872	056	8	2010	042	x
1873	052	4	2011	050	2
1874	042	x	2012	051	3
1875	109	RCL MEM	2013	046	.
1876	048	0	2014	054	6
1877	057	9	2015	053	5
1878	043	+	2016	050	2
1879	040	(	2017	049	1
1880	109	RCL MEM	2018	041	)
1881	048	0	2019	043	+
1882	057	9	2020	040	(
1883	113	Square	2021	040	(
1884	042	x	2022	040	(
1885	048	0	2023	049	1
1886	046	.	2024	049	1
1887	048	0	2025	056	8
1888	048	0	2026	046	.
1889	048	0	2027	054	6
1890	049	1	2028	055	7
1891	049	1	2029	047	/
1892	056	8	2030	109	RCL MEM
1893	041	)	2031	048	0
1894	041	)	2032	055	7
Print pk2'			2033	041	)
1935	119	print	2034	045	-
1936	107	STO MEM	2035	053	5
1937	048	0	2036	046	.
1938	053	5	2037	057	9
Get water dissociation lnKw			2038	055	7
1979	040	(	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

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2556 048 0
2557 053 5
2558 041 )
Print lnkb
2599 119 print
2600 047 /
2601 049 1
2602 048 0
2603 110 LOG e
2604 041 )
2605 111 +/-
Print pKb
2646 119 print
2647 107 STO MEM
2648 049 1
2649 057 9
Get R= [HC03-1]/[CO2] Inlg(pH-pK1)
2690 040 (
2691 109 RCL MEM
2692 048 0
2693 051 3
2694 045 -
2695 109 RCL MEM
2696 048 0
2697 052 4
2698 041 )
2699 119 print
2700 064 Inverse
2701 108 LOG 10
2702 119 print
2703 107 STO MEM
2704 049 1
2705 049 1
Get [CO32-1]/[HC03-1]=8
2746 040 (
2747 109 RCL MEM
2748 048 0
2749 051 3
2750 045 -
2751 109 RCL MEM
2752 048 0
2753 053 5
2754 041 )
2755 119 print
2756 064 Inverse
2757 108 LOG 10
Print S
2798 119 print
2799 107 STO MEM
2800 049 1
2801 050 2
Get B(OH)4-
2842 040 (
2843 109 RCL MEM
2844 056 8
2845 055 7
Print previous B(OH)4-
2886 119 print
2887 107 STO MEM
2888 056 8

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2889 054 6
2890 041 )
2891 040 (
2892 040 (
2893 049 1
2894 043 +
2895 040 (
2896 040 (
2897 109 RCL MEM
2898 049 1
2899 057 9
2900 045 -
2901 109 RCL MEM
2902 048 0
2903 051 3
2904 041 )
2905 064 Inverse
2906 108 LOG 10
2907 041 )
2908 041 )
2909 114 1/x
2910 042 x
2911 109 RCL MEM
2912 056 8
2913 056 8
2914 041 )
Print new B(OH)4-
2955 119 print
2956 107 STO MEM
2957 056 8
2958 055 7
2959 109 RCL MEM
2960 056 8
2961 054 6
2962 038 If zero
2963 099 Cosine
2964 040 (
2965 109 RCL MEM
2966 056 8
2967 055 7
2968 045 -
2969 109 RCL MEM
2970 056 8
2971 054 6
2972 041 )
Print d[BOH]4-
3013 119 print
3014 107 STO MEM
3015 056 8
3016 053 5
3017 096 LABEL
3018 099 Cosine
Compute [CO2] from pCO2 and H
[CO2] = Ho'xZ
3099 040 (
3100 109 RCL MEM
3101 048 0
3102 054 6
3103 042 x
3104 109 RCL MEM

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3105	049	1	3438	048	0
3106	056	0	3439	051	3
3107	041	)	Get CaxCO32-		
Print [CO2] mmoles/kg			3480	040	(
3148	119	print	3481	049	1
3149	107	STD 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	STD MEM	3497	041	)
3243	049	1	Print ionic product CaxCO3		
3244	052	4	3538	119	print
Compute CO32- = [HCO3-]x8			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	STD 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	STD 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 show pH			3729	042	x
3436	119	print	3730	109	RCL MEM
3437	107	STD MEM	3731	049	1

3732	053	5	Get new C=[CO2+HCO3-+Co32-]=a+b+c
3733	041	)	Add W-mmolescale/ite/kg=d(pCO2)
3734	043	+	3989 040 (
3735	109	RCL MEM	3990 109 RCL MEM
3736	056	8	3991 048 0
3737	055	7	3992 056 8
3738	043	+	3993 043 +
3739	040	(	3994 109 RCL MEM
3740	109	RCL MEM	3995 056 8
3741	048	0	3996 057 9
3742	050	2	3997 045 -
3743	111	+/-	3998 048 0
3744	064	Inverse	3999 046 .
3745	110	LOG e	4000 048 0
Print Kw			4001 048 0
3786	119	print	4002 048 0
3787	114	1/x	4003 041 )
3788	042	x	4004 119 print
3789	040	(	4005 107 STO MEM
3790	109	RCL MEM	4006 048 0
3791	048	0	4007 056 8
3792	052	4	Get next [CO2] = a using KH
3793	111	+/-	4048 040 (
3794	064	Inverse	4049 109 RCL MEM
3795	108	LOG 10	4050 048 0
3796	041	)	4051 054 6
3797	041	)	4052 042 x
3798	045	-	4053 109 RCL MEM
3799	040	(	4054 049 1
3800	109	RCL MEM	4055 056 8
3801	048	0	4056 041 )
3802	052	4	Print next [CO2] = a
3803	111	+/-	4097 119 print
3804	064	Inverse	4098 107 STO MEM
3805	108	LOG 10	4099 049 1
3806	041	)	4100 051 3
3807	041	)	Compute z=K2/(K1a)=c/b^2;b=HCO3-,c=CO3
Print alkalinity = Ac+Ab			Solve quadratic Ax^2+Bx+C=0
3848	119	print	Set Ab^2+Bb+C=0
3849	107	STO MEM	c=b^2K2/aK1=(A-b)/2
3850	048	0	A=2Z, B=1, C=-Ac
3851	049	1	Solve Ab^2+Bb+C=0 equating c's
3852	040	(	2Zh^2+b-A=0
3853	109	RCL MEM	x=-B+- (B^2-BZA)^0.5/4Z
3854	057	9	4421 040 (
3855	057	9	4422 040 (
3856	043	+	4423 109 RCL MEM
3857	109	RCL MEM	4424 048 0
3858	055	7	4425 053 5
3859	056	8	4426 111 +/-
3860	043	+	4427 064 Inverse
3861	109	RCL MEM	4428 108 LOG 10
3862	049	1	4429 041 )
3863	056	8	4430 047 /
3864	041	)	4431 040 (
Print and stow next pCO2			4432 109 RCL MEM
3905	119	print	4433 048 0
3906	107	STO MEM	4434 052 4
3907	049	1	4435 111 +/-
3908	056	8	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 $c=2b^2=(Ac-b)/2$			4848	109	RCL MEM
So $22b^2+b-A=0$ 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

Get DG			1010	057	9
0906	040	(	1011	045	-
0907	109	RCL MEM	1012	109	RCL MEM
0908	049	1	1013	049	1
0909	048	0	1014	050	2
0910	110	LOG e	1015	041	)
0911	042	x	Print TDS		
0912	056	8	1056	119	print
0913	046	.	1057	107	STO MEM
0914	051	3	1058	049	1
0915	049	1	1059	051	3
0916	052	4	1060	040	(
0917	042	x	1061	109	RCL MEM
0918	109	RCL MEM	1062	049	1
0919	049	1	1063	051	3
0920	049	1	1064	047	/
0921	041	)	1065	109	RCL MEM
0922	111	+/-	1066	049	1
Print DG			1067	049	1
0963	119	print	1068	041	)
0964	107	STO MEM	Print DS		
0965	049	1	1109	119	print
0966	050	2	1110	107	STO MEM
Get TDS			1111	049	1
1007	040	(	1112	052	4
1008	109	RCL MEM	1113	002	HALT
1009	048	0	Input Keq1		
ENTHALPY/CAL 13/10/22			0268	096	LABEL
Temperature 1			0269	076	L
0080	096	LABEL	0270	107	STO MEM
0081	075	K	0271	048	0
0082	107	STO MEM	0272	053	5
0083	048	0	0273	119	print
0084	049	1	0274	002	HALT
0085	119	print	Input Keq2		
0086	002	HALT	0315	096	LABEL
Temperature 2			0316	077	M
0127	096	LABEL	0317	107	STO MEM
0128	084	T	0318	048	0
0129	107	STO MEM	0319	054	6
0130	048	0	0320	119	print
0131	050	2	0321	002	HALT
0132	119	print	Execute program		
0133	002	HALT	0362	096	LABEL
pk1			0363	088	X
0174	096	LABEL	0364	109	RCL MEM
0175	080	P	0365	048	0
0176	107	STO MEM	0366	051	3
0177	048	0	0367	111	+/-
0178	051	3	0368	064	Inverse
0179	119	print	0369	108	LOG 10
0180	002	HALT	Print and stow K1		
Input pk2			0410	119	print
0221	096	LABEL	0411	107	STO MEM
0222	081	Q	0412	048	0
0223	107	STO MEM	0413	053	5
0224	048	0	0414	109	RCL MEM
0225	052	4	0415	048	0
0226	119	print	0416	052	4
0227	002	HALT			

0417	111	+/-	Get mean Keq		
0418	064	Inverse	0712	040	(
0419	108	LOG 10	0713	040	(
Print and stow K2			0714	109	RCL MEM
0460	119	print	0715	048	0
0461	107	STD MEM	0716	053	5
0462	048	0	0717	043	+
0463	054	6	0718	109	RCL MEM
Get DH=-[ln(K2/K1)xR/(1/T2-1/T1)]			0719	048	0
0504	040	(	0720	054	6
0505	109	RCL MEM	0721	041	)
0506	048	0	0722	047	/
0507	054	6	0723	050	2
0508	047	/	0724	041	)
0509	109	RCL MEM	Print mean Keq		
0510	048	0	0765	119	print
0511	053	5	0766	107	STD MEM
0512	041	)	0767	049	1
Print K2/K1			0768	048	0
0553	119	print	Get mean T		
0554	107	STD MEM	0809	040	(
0555	048	0	0810	040	(
0556	055	7	0811	109	RCL MEM
Get (1/T1-1/T2)= -(1/T2-1/T1)			0812	048	0
0597	040	(	0813	049	1
0598	109	RCL MEM	0814	043	+
0599	048	0	0815	109	RCL MEM
0600	049	1	0816	048	0
0601	114	1/x	0817	050	2
0602	045	-	0818	041	)
0603	109	RCL MEM	0819	047	/
0604	048	0	0820	050	2
0605	050	2	0821	041	)
0606	114	1/x	Print mean T		
0607	041	)	0862	119	print
0608	119	print	0863	107	STD MEM
0609	107	STD MEM	0864	049	1
0610	048	0	0865	049	1
0611	056	8	Get DG		
0612	040	(	0906	040	(
0613	109	RCL MEM	0907	109	RCL MEM
0614	048	0	0908	049	1
0615	055	7	0909	048	0
0616	110	LOG e	0910	110	LOG e
0617	042	x	0911	042	x
0618	056	8	0912	056	8
0619	046	.	0913	046	.
0620	051	3	0914	051	3
0621	049	1	0915	049	1
0622	052	4	0916	052	4
0623	047	/	0917	042	x
0624	109	RCL MEM	0918	109	RCL MEM
0625	048	0	0919	049	1
0626	056	8	0920	049	1
0627	041	)	0921	041	)
Print DH			0922	111	+/-
0668	119	print	Print DG		
0669	107	STD MEM	0963	119	print
0670	048	0	0964	107	STD MEM
0671	057	9	0965	049	1

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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  $f_{\text{CO}_2}$ , 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 (DoB, 1994)
KW1 = 148.96502 - 13847.26/t - 23.65218*log(t);
KW2 = (118.67/t - 5.977 + 1.0495*log(t))^2 * .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*(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 DoB (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 DoB (1994).

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
$pK'_3$	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 ( $T_C = 25^\circ \text{C}$ ,  $S = 35$ ).

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