

Pressure Acting on Equilibrium Reactions

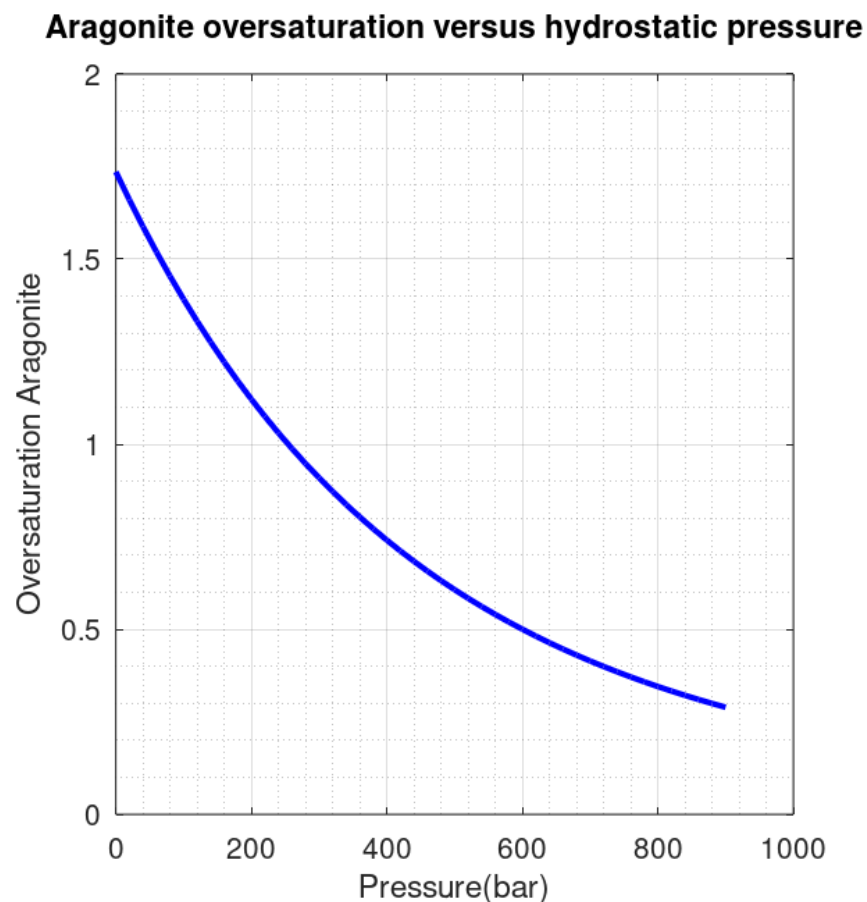
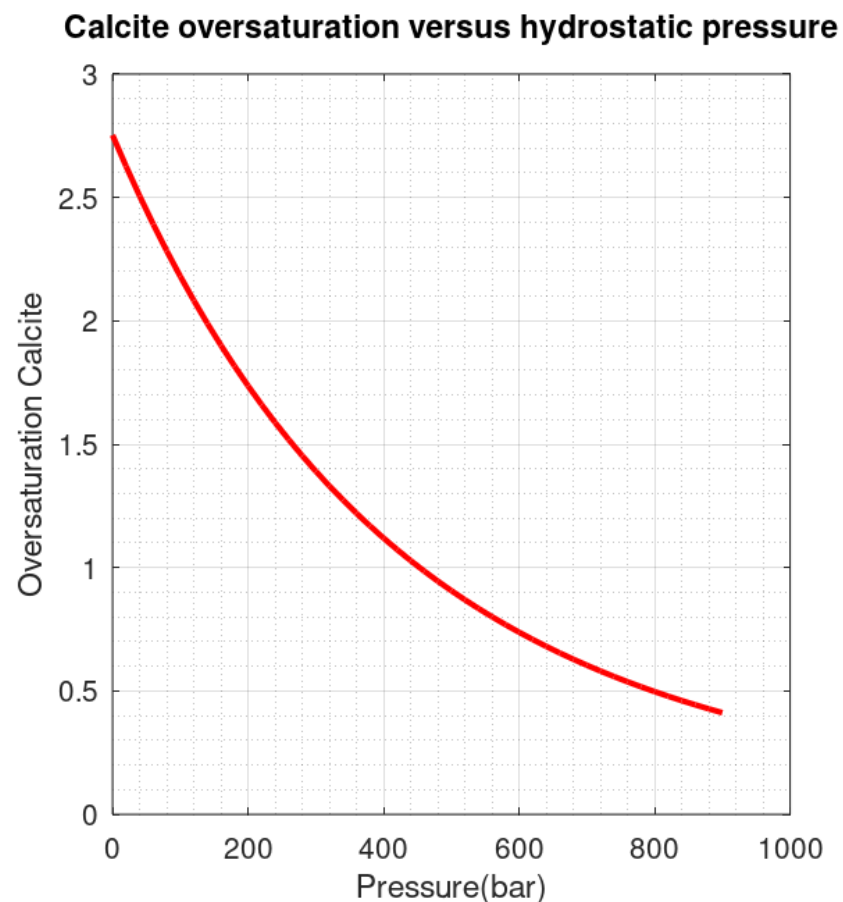


Fig.1 Calcite/Aragonite oversaturation($T=4^{\circ}\text{C}$; salinity = 35; ppmCO₂ = 410; prec. CaCO₃ = 0). Data are reported as text in the following.

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Temp = temperature in degree Celsius (°C)
CO2 = ppmv, parts per million in volume of CO2 in dry air
pptF = fraction of CaCO3(calcite) which precipitates, ratio to complete precipitation(when omega=1)
Pres = pressure in bar x 100
Saln = salinity in grams of disolved salts per kg of solution
pHfr. pHtot pHsws = different pH scales, free, total and seawater
pOH = -log10[OH-]
H2CO3 HCO3 CO3 = concentrations in millimol/kg-solution
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DIC = Dissolved Inorganic Carbon in mmol/kg-soln
 Alk = alkalinity in mmol/kg-soln Alk = 2*CO3+HCO3+OH+BOH4-H
 Ca++ CaCO3 = concentrations in mmol/kg-soln
 sovr1 sovr2 = Calcite and aragonite overasaturation (omega)
 pH2O = water vapour pressure above sea level
 Cout = mmol/kg-soln of carbon absorbed(-) or outgassed (+) from the first iteration

Temp	CO2	pptF	Pres	Saln	pHfr.	pHtot	pHsws	pOH	H2CO3	HCO3-	CO3--	DIC	Ca++	Alk	CaCO3	over1	over2	pH2O	Cout
4.00	410	0.00	0.00	35.0	8.112	8.075	8.067	6.041	0.0219	2.109	0.1153	2.246	10.280	2.400	0.000	2.753	1.736	0.0079	0.00
4.00	410	0.00	0.50	35.0	8.089	8.053	8.046	6.039	0.0219	2.112	0.1134	2.247	10.280	2.400	0.000	2.448	1.553	0.0079	-0.00
4.00	410	0.00	1.00	35.0	8.066	8.032	8.025	6.037	0.0219	2.115	0.1116	2.249	10.280	2.400	0.000	2.180	1.392	0.0079	-0.00
4.00	410	0.00	1.50	35.0	8.044	8.010	8.004	6.036	0.0219	2.118	0.1098	2.250	10.280	2.400	0.000	1.944	1.249	0.0079	-0.00
4.00	410	0.00	2.00	35.0	8.021	7.989	7.983	6.034	0.0219	2.121	0.1081	2.251	10.280	2.400	0.000	1.736	1.122	0.0079	-0.00
4.00	410	0.00	2.50	35.0	7.999	7.968	7.962	6.032	0.0219	2.124	0.1064	2.252	10.280	2.400	0.000	1.553	1.009	0.0079	-0.01
4.00	410	0.00	3.00	35.0	7.977	7.947	7.942	6.031	0.0219	2.126	0.1048	2.253	10.280	2.400	0.000	1.391	0.909	0.0079	-0.01
4.00	410	0.00	3.50	35.0	7.954	7.925	7.921	6.029	0.0219	2.129	0.1032	2.254	10.280	2.400	0.000	1.247	0.820	0.0079	-0.01
4.00	410	0.00	4.00	35.0	7.932	7.904	7.901	6.028	0.0219	2.131	0.1017	2.255	10.280	2.400	0.000	1.120	0.741	0.0079	-0.01
4.00	410	0.00	4.50	35.0	7.910	7.883	7.881	6.027	0.0219	2.133	0.1002	2.256	10.280	2.400	0.000	1.007	0.670	0.0079	-0.01
4.00	410	0.00	5.00	35.0	7.888	7.862	7.860	6.026	0.0219	2.136	0.0988	2.256	10.280	2.400	0.000	0.907	0.607	0.0079	-0.01
4.00	410	0.00	5.50	35.0	7.867	7.841	7.840	6.026	0.0219	2.138	0.0974	2.257	10.280	2.400	0.000	0.817	0.551	0.0079	-0.01
4.00	410	0.00	6.00	35.0	7.845	7.820	7.819	6.026	0.0219	2.140	0.0961	2.258	10.280	2.400	0.000	0.738	0.500	0.0079	-0.01
4.00	410	0.00	6.50	35.0	7.823	7.800	7.799	6.026	0.0219	2.142	0.0948	2.258	10.280	2.400	0.000	0.667	0.455	0.0079	-0.01
4.00	410	0.00	7.00	35.0	7.802	7.779	7.778	6.026	0.0219	2.144	0.0936	2.259	10.280	2.400	0.000	0.604	0.414	0.0079	-0.01
4.00	410	0.00	7.50	35.0	7.781	7.758	7.758	6.026	0.0219	2.145	0.0924	2.260	10.280	2.400	0.000	0.548	0.378	0.0079	-0.01
4.00	410	0.00	8.00	35.0	7.759	7.738	7.737	6.027	0.0219	2.147	0.0912	2.260	10.280	2.400	0.000	0.497	0.345	0.0079	-0.01
4.00	410	0.00	8.50	35.0	7.738	7.717	7.717	6.028	0.0219	2.149	0.0901	2.261	10.280	2.400	0.000	0.452	0.316	0.0079	-0.01
4.00	410	0.00	9.00	35.0	7.717	7.697	7.697	6.029	0.0219	2.150	0.0890	2.261	10.280	2.400	0.000	0.412	0.289	0.0079	-0.02

The effect of pressure on equilibrium constants is of paramount importance; sinking down into the depths of the oceans, pressure increases by 1 atm with every 10 meters. As the intermolecular distances between water molecules decrease slightly, the density of liquid water increases accordingly. Therefore, interionic interaction and equilibrium constants become progressively altered in relation to the pressure itself. The effects become noticeable when pressure reaches hundreds of bars; pH and solubility of calcium carbonate alter to such an extent that aragonite oversaturation, and calcite at greater depths, disappear and, if formed, these salt readily re-dissolve.

As discussed in Section 4.4 on water density, we recall that water pressure is measured in 'bars' (1 atm = 1.01325 bar; 1 bar = 0.1 Mpa), and that the surface pressure of the sea is assumed to be zero.

The effect of pressure on equilibrium constants can be calculated (Millero 1995) according to a second order polynomial expression of the natural logarithm of the ratio between $K_{i,P}$ (the value of i-esimal constant at pressure P) and $K_{i,0}$ (the value of i-esimal constant at reference zero pressure P)

$$\log\left(\frac{K_{i(P)}}{K_{i,0}}\right) = -\frac{\Delta V_i}{R^* T} P + \frac{\Delta K_i}{2 \cdot R^* T} P^2 \quad \log = \log_e \quad T [K] \quad P = \text{bar}$$

The constant value R^* is given by $R^* = 83.14472 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$ (corrected from the original value of 83.131, reported in Zeebe, 2001 slightly biased) whereas ΔV_i is the molal volume change, and ΔK_i the compressibility change. They are in turn deconvoluted in terms of a second order polynomial which, strictly speaking, is only valid for Salinity = 35, but can be acceptable in a wider range, say 20-50.

$$\Delta V_i = a_0 + a_1 T_c + a_2 T_c^2 \quad T = [^\circ \text{C}]$$

$$\Delta K_i = b_0 + b_1 T_c \quad T = [^\circ \text{C}]$$

The values for the a_i and b_i parameters are taken from Zeebe, 2001 and are reported here for each of the reactions, where T_c indicates the temperature in $^\circ \text{C}$, P the pressure in bar, and T the absolute temperature ($T = T_c + 273.15$) and finally $R^* = 83.14472$.

	a0	a1	a2	b0	b1
K1(P)	-25.50	0.1271	0.0	$-3.08 \cdot 10^{-3}$	$0.0877 \cdot 10^{-3}$
K2(P)	-15.82	-0.0219	0.0	$1.13 \cdot 10^{-3}$	$-0.1475 \cdot 10^{-3}$
KB(P)	-29.48	0.1622	$2.608 \cdot 10^{-3}$	$-2.84 \cdot 10^{-3}$	0.0
KW(P)	-25.60	0.2324	$-3.6246 \cdot 10^{-3}$	$-5.13 \cdot 10^{-3}$	$0.0794 \cdot 10^{-3}$
KS(P)	-18.03	0.0466	$0.3160 \cdot 10^{-3}$	$-4.53 \cdot 10^{-3}$	$0.0900 \cdot 10^{-3}$
KF(P)	-9.780	-0.0090	$-0.942 \cdot 10^{-3}$	$-3.91 \cdot 10^{-3}$	$0.054 \cdot 10^{-3}$
KSP,cal(P)	-48.76	0.5304	0.0	$-11.76 \cdot 10^{-3}$	$0.3692 \cdot 10^{-3}$
KSP,ara(P)	-46.00	0.5304	0.0	$-11.76 \cdot 10^{-3}$	$0.3692 \cdot 10^{-3}$

The effect of pressure alters the values for every equilibrium constant, and must therefore be properly accounted for in the program flow. Greater detail on this can be found by inspecting the program script.

Oversaturation of CaCO₃

Generally speaking, in heterogeneous reactions, reactants are in different phases, like solids, liquid solutions or gaseous mixtures. One of the most relevant of such reactions is the formation or dissolution of calcium carbonate (solid/solution), according to its oversaturation value, indicated by Ω and discussed elsewhere.

Once formed biologically by calcifying organisms or by inorganic route, and with a density greater than 1, it eventually sinks into the dark abyss. Due to increasingly high pressure, solid CaCO₃ begins to dissolve below a certain depth, referred to as the saturation horizon where Ω is exactly equal to 1. Dissolution of the solid is not instantaneous, and the downward flux continues to a depth where the solid particles of calcium carbonate are completely dissolved. This depth is called the carbonate compensation depth. If the sea bottom does not reach such a depth, it becomes undissolved carbonate sediment. The two crystallographic forms of CaCO₃, calcite and aragonite, have different solubility products, the former being less soluble. Therefore, the saturation horizon and the compensation depth for aragonite are at a higher level compared to calcite. Most calcifying organisms (e.g. Coccolithophores) produce calcite, whilst coral reefs are made of aragonite.

Solving the equilibria involved in CaCO₃ formation with the algorithm described the oversaturation profiles at different depths can be calculated. Some of the results can be seen in the graph in Figure . The curious reader, intent on modifying input parameters and looking for new results (in a “see what happens” procedure) is re-directed to the script.

In Fig. 1 oversaturation Ω , is plotted against pressure being temperature fixed at 4°C, which is the overall temperature for the ocean's depths below the thermocline (about 300 meters). Below $\Omega=1$ (light blue area) carbonates begin their dissolution process.

One topic frequently debated today is the potential hazard for coralline reefs of the rising concentrations of CO₂, through the reduction of ocean pH and carbonate ion concentration. The effect of this, is however compensated for by an increase in oversaturation in warmer areas of oceans, where calcifying organisms and coral reefs prosper. Global warming, estimated at about 1°C from the beginning of the twentieth century to the present day, also favours oversaturation and thereby counteracts the effects of increasing CO₂ content by anthropogenic emissions. Therefore the two figures should be considered together to gain a complete picture.

Here as follows the program script to obtain graphics of fig.1 and text thereafter.

```
clear;clc;
global SO4 KS K1 K2 Kw K7 K8 H2CO3 HCO3 CO3 OH F KF KB B BOH4 Ksp1 pptF Mg Sr Na K Cl Br H HT
global Hsws Ca Ca1
% No Mg(OH)+ or Ca(OH)+ formation because they seem to be negligible effects
function y = neut(pH) % ==> pH free scale, i.e. chemical true scale, always used if not otherwise stated !!
    global SO4 KS K1 K2 Kw K7 K8 H2CO3 HCO3 CO3 OH F KF KB B BOH4 Ksp1 pptF Mg Sr Na K Cl Br H HT
    global Hsws Ca Ca1
    H = 10^(-pH);Ca = Ca1;
    HCO3 = K1*H2CO3/H;
    CO3 = K2*HCO3/H;
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% --> HERE AS FOLLOWS THE 6 PARAMETERS. THEY CAN BE VARIED IN A REASONABLE RANGE*
Tc = 4;          % temperature in Celsius (°C)          *
ppmCO2 = 410;    % parts per million (in volume) of CO2 in the atmosphere *
P = 0;          % pressure in atm. P=0 means ambient pressure, 1 atm.      *
S = 35;         % salinity, in grams of salts in 1 kg of solution          *
pptF = 0;       % fraction of CaCO3 which actually precipitates           *
pH2O = 100;     % H2O vapour pressure in %saturation at sea level         *
%*****
% standard seawater composition for salinity = 35 g/Kg-soln
Cli = 0.54586;  % Cl- Mol/kg(solution)
Nai = 0.46906;  % Na+ Mol/kg(solution)
Mgi = 0.05282;  % Mg++ Mol/kg(solution)
Cai = 0.01028;  % Ca++ Mol/kg(solution)
SO4i = 0.02824; % SO4-- Mol/kg(solution)
Ki = 0.01021;  % K+ Mol/kg(solution)
Bri = 0.00084;  % Br- Mol/kg(solution)
Sri = 0.00009;  % Sr++ Mol/kg(solution)
Fi = 0.00007;  % F- Mol/kg(solution)
Bi = 0.00042;  % B(OH)3 + B(OH)4- Mol/kg(solution)
R = 8.314;R1 = 83.131;j = 0;

% ----> For/Endfor cycle for one of the six above parameters Tc, ppmCO2, P, S, pptF, pH2O
for P = 0 :50:900 % modify line to cycle over other parameters

T = Tc + 273.15;
Cl = Cli*S/35;Na = Nai*S/35;Mg = Mgi*S/35;Ca = Cai*S/35;SO4 = SO4i*S/35;
K = Ki*S/35;Br = Bri*S/35;Sr = Sri*S/35;F = Fi*S/35;B = Bi*S/35;Ca1 = Ca;Mg1 = Mg;

% CO2 + H2O <==> H2CO3 (Weiss 1994)
LnK0 = 9345.17/T - 60.2409 + 23.3585*log(T/100) + S*(0.023517 - 0.00023656*T + 0.0047036*(T/100)^2);

% H2CO3 <==> H+ + HCO3-
% --> Waters, Millero, Woosley (Mar. Chem., 165, 66-67, 2014) [H+]=free scale
LnK1 = -log(10)*(6320.813/T + 19.568224*log(T) -126.34048 + 5.592953*S^0.5 + 0.028845*S - (6.388e-5)*S^2 + (-
225.7489*S^0.5 - 4.761*S)/T -0.8715109*S^0.5*log(T));
% HCO3- <==> H+ + CO3--
% --> Waters, Millero, Woosley (Mar. Chem., 165, 66-67, 2014) [H+]=free scale

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LnK2 = -log(10)*(5143.692/T + 14.613358*log(T) - 90.18333 + 13.396949*S^0.5 + 0.12193009*S - (3.8362e-4)*S^2 + (-
472.8633*S^0.5 - 19.03634*S)/T - 2.1563270*S^0.5*log(T));

% H2O <==> H+ + OH- (DOE 1994) % pH = pH(SWS) !!
LnKw = 148.9802 - 13847.26/T - 23.6521*log(T) + (118.67/T - 5.977 + 1.0495*log(T))*S^0.5 - 0.01615*S;

% HSO4- <==> H+ + SO4--
I = 19.924*S/(1000 - 1.005*S); % ionic strength, useful for KS and KF calculations
LnKS = -4276.1/T + 141.328 - 23.039*log(T) + (-13856/T + 324.57 - 47.986*log(T))*I^0.5 + (35474/T - 771.54 +
114.723*log(T))*I - 2698/T*I^1.5 + 1766/T*I^2 + log(1-0.001005*S);

% HF <==> H+ + F-
LnKF = 1590.2/T - 12.641 + 1.525*I^0.5 + log(1-0.001005*S); % pH = pH free NO conversion to total

% CaCO3calcite <==> Ca++ + CO3--
LogKspCal = -171.9065 - 0.077993*T + 2839.319/T + 71.595*log10(T) + (-0.77712 + 0.0028426*T + 178.34/T)*S^0.5 -
0.07711*S + 0.0041249*S^1.5;
LnKspCal = LogKspCal*log(10);

% CaCO3aragonite <==> Ca++ + CO3--
LogKspAra = -171.945 - 0.077993*T + 2903.293/T + 71.595*log10(T) + (-0.068393 + 0.0017276*T + 88.135/T)*S^0.5 -
0.10018*S + 0.0059415*S^1.5;
LnKspAra = LogKspAra*log(10);

% B(OH)3 + H2O <==> H+ + B(OH)4-
LnKB = (-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;

% The log(K) are modified according to hydrostatic pressure (on the sea surface P=0)
LnK1P = LnK1 + (25.5 - 0.1271*Tc)/R1/T*P + 0.5*(-3.08e-3 + 0.0877e-3*Tc)/R1/T*P^2;
LnK2P = LnK2 + (15.82 + 0.0219*Tc)/R1/T*P + 0.5*(1.13e-3 - 0.1475e-3*Tc)/R1/T*P^2;
LnKwP = LnKw + (25.6 - 0.2324*Tc + 3.6246e-3*Tc^2)/R1/T*P + 0.5*(-5.13e-3 + 0.0794e-3*Tc)/R1/T*P^2;
LnKBP = LnKB + (29.48 - 0.1622*Tc - 2.608e-3*Tc^2)/R1/T*P + 0.5*(-2.84e-3)/R1/T*P^2;
LnKspCalP = LnKspCal + (48.76 - 0.5304*Tc)/R1/T*P + 0.5*(-11.76e-3 + 0.3692e-3*Tc)/R1/T*P^2;
LnKspAraP = LnKspAra + (46 - 0.5304*Tc)/R1/T*P + 0.5*(-11.76e-3 + 0.3692e-3*Tc)/R1/T*P^2;
LnKSP = LnKS + (18.03 - 0.0466*Tc - 0.3160e-3*Tc^2)/R1/T*P + 0.5*(-4.53e-3 + 0.09e-3*Tc)/R1/T*P^2;
LnKFP = LnKF + (9.78 + 0.009*Tc + 0.942e-3*Tc^2)/R1/T*P + 0.5*(-3.91e-3 + 0.054*Tc)/R1/T*P^2;

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% The K(eq) values are calculated from their logarithms.
K1 = exp(LnK1P);K2 = exp(LnK2P);K0 = exp(LnK0);Kw = exp(LnKwP);Ksp1 = exp(LnKspCalP);
Ksp2 = exp(LnKspAraP);KS = exp(LnKSP);KF = exp(LnKFP);KB = exp(LnKBP);
% CO2 fugacity is introduced, according to Koertzinger (pag 65 Zeebe and Gladrow 2001)
fCO2 = ppmCO2*exp(101325*((-1636.75 + 12.0408*T - 3.27957e-2*T^2 + 3.16528e-5*T^3)*1e-6 + 2*(57.7 -
0.118*T)*1e-6)/R/T);
% H2O vapour pressure is calculated for seawater, Weiss and Price 1980
LnpH2O = 24.4543 - 6745.09/T - 4.8489*log(T/100) - 0.000544*S;
% CO2 fugacity is corrected according to water vapour partial pressure
fCO2 = fCO2*(1 - exp(LnpH2O)*pH2O/100);
H2CO3 = K0*fCO2*1e-6;

[pH,fval,info] = fzero(@neut,[0,14]); % call to fzero

CaCO3 = (Ca1 - Ca)*1000;
DIC = (H2CO3+HCO3+CO3)*1000; % Dissolved Inorganic Carbon in mmol/kg-soln
Alk = 1000*(2*CO3+HCO3+OH+BOH4-H); % Total Alkalinity mmol/kg-soln
OverSatCal = Ca*CO3/Ksp1; % Oversaturation of CaCO3 (calcite form)
OverSatAra = Ca*CO3/Ksp2; % Oversaturation of CaCO3 (aragonite form)
if Cini == 0;Cini = 1000*(H2CO3 + HCO3 + CO3) + CaCO3;end %DIC iniziale
Cout = Cini - 1000*(H2CO3 + HCO3 + CO3) - CaCO3; %CO2 outgassed during the for/endfor cycles

% The results are displayed.
if Tc<10;T1 = ['|',num2str(Tc,'%2f')];else T1 =['|',num2str(Tc,'%1f')];endif
T1 = [T1,'|',num2str(ppmCO2,3),'|',num2str(pptF,'%2f'),'|',num2str(P/100,'%2f'),'|',num2str(S,'%1f')];
T1 = [T1,'|',num2str(pH,'%3f'),'|',num2str(-log10(HT),'%3f'),'|',num2str(-log10(Hsws),'%3f'),'|',num2str(-
log10(OH),'%3f')];
T1 = [T1,'|',num2str(H2CO3*1000,'%4f'),'|',num2str(HCO3*1000,'%3f'),'|',num2str(CO3*1000,'%4f')];
T1 = [T1,'|',num2str(DIC,'%3f'),'|'];
if Ca>0.01;T1 = [T1, num2str(Ca*1000,'%3f')];else;T1 = [T1, num2str(Ca*1000,'%4f')];endif
T1 = [T1,'|',num2str(Alk,'%3f'),'|',num2str(CaCO3,'%3f'),'|',num2str(OverSatCal,'%3f')];
T1 = [T1,'|',num2str(OverSatAra,'%3f'),'|',num2str(exp(LnpH2O),'%4f'),'|',num2str(Cout,'%2f')];
disp(T1);
++j;
x(j) = P;y1(j) = OverSatCal;y2(j) = OverSatAra; % modify line to plot other variables
endfor
disp(T2);

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```
subplot(1,2,1)
plot(x,y1,'r','LineWidth',2);grid on;grid minor on;xlabel('Pressure(bar)');ylabel('Oversaturation Calcite');hold on;
title('Calcite oversaturation versus hydrostatic pressure')
subplot(1,2,2)
plot(x,y2,'b','LineWidth',2);grid on;grid minor on;xlabel('Pressure(bar)');ylabel('Oversaturation Aragonite');
title('Aragonite oversaturation versus hydrostatic pressure')
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