

# Preliminary Calculation of CaCO<sub>3</sub> Precipitation in Freezing Sea Water

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## 1 Introduction

It has been mentioned in several studies (e.g. Weeks and Ackley, 1986) that calcium carbonate starts to precipitate from freezing seawater below about  $-2.2$  °C. Here, available thermodynamic data are applied to get a first quantitative estimate. Unfortunately, it was necessary to either extrapolate data outside of the recommended temperature and salinity range or, alternatively, use values for sea water at the freezing point, instead. Interaction with other ions (e.g. mirabilite precipitation) was not considered here.

## 2 Thermodynamic Constants

For the calculations described below, several thermodynamic constants are necessary. When their dependence on temperature and salinity is known, I use  $T$  = temperature in K and  $S$  = salinity in ‰. Square brackets describe concentrations of chemical species in mol/L.

### 2.1 The Solubility Product $K_s$

The solubility product  $K_s$  of CaCO<sub>3</sub> is defined as:

$$K_s = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] \quad (1)$$

Mucci (1983) provides values of  $K_s$  as a function of temperature and salinity:

$$\begin{aligned} pK_s = -\lg K_s = & 171.9065 + 0.077993 T - 2839.319/T - 71.595 \lg(T) \\ & +(0.77712 - 0.0028426 T - 178.34/T)\sqrt{S} \\ & +0.07711 S - 0.0041249 S^{1.5} \end{aligned} \quad (2)$$

Unfortunately, his data are only valid in the salinity range 5...44 ‰. Extrapolation to higher salinities lets  $K_s$  increase by several orders of magnitude which seems unrealistic.

## 2.2 The Henry's Law Coefficient $k_H$

Dissolved  $\text{CO}_2$  is in Henry's Law equilibrium with atmospheric  $\text{CO}_2$ . The Henry's Law coefficient  $k_H$  is taken from Weiss (1974):

$$\begin{aligned}\ln(k_H) &= \ln\left(\frac{p(\text{CO}_2)}{[\text{CO}_2]}\right) \\ &= -58.0931 + 90.5069/(T/100) + 22.2940 \times \ln(T/100) \\ &\quad + S \times (0.027766 - 0.025888 \times (T/100) + 0.0050578 \times (T/100)^2)\end{aligned}\tag{3}$$

where  $p(\text{CO}_2)$  = partial pressure of  $\text{CO}_2$  in atm and  $[\text{CO}_2]$  = concentration of dissolved carbon dioxide in mol/L. The unit of  $k_H$  is mol/(L atm).

## 2.3 Acidity Constants

Acid-base equilibrium constants for  $\text{CO}_2$  are taken from Dickson and Millero (1987):

$$\begin{aligned}pK_{a1} &= -\lg K_{a1} = -\lg\left(\frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]}\right) \\ &= 6320.81/T - 126.3405 + 19.568 \times \ln(T) \\ &\quad + \sqrt{S} \times (-840.39/T + 19.894 - 3.0189 \times \ln(T)) \\ &\quad + 0.00668 \times S\end{aligned}\tag{4}$$

$$\begin{aligned}pK_{a2} &= -\lg K_{a2} = -\lg\left(\frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}\right) \\ &= 5143.69/T - 90.1833 + 14.613 \times \ln(T) \\ &\quad + \sqrt{S} \times (-690.59/T + 17.176 - 2.6719 \times \ln(T)) \\ &\quad + 0.0217 \times S\end{aligned}\tag{5}$$

The ionic product of water  $K_w$  has been taken from Dickson and Riley (1979). However, since their fit function is inconsistent with the data presented in their table, the nonlinear least squares regression was recalculated with the program available at <http://members.aol.com/johnhp71/nonlin.html> yielding the following equation:

$$\begin{aligned}pK_w &= -\lg K_w = -\lg([\text{H}^+][\text{OH}^-]) \\ &= 2.085617 + 3484.584094/T - 0.093326 \times \sqrt{S}\end{aligned}\tag{6}$$

## 3 Sea Water at 0 °C

The calculations start with sea water at a temperature of  $T^0 = 273.15$  K and a salinity of  $S^0 = 35$  ‰. The sea water composition is taken from Wilson (1975) with initial chloride and calcium concentrations of  $[\text{Cl}^-]^0 = 0.5612$  mol/L and  $[\text{Ca}^{2+}]^0 = 0.01056$  mol/L, respectively. An initial pH of 7.9 was obtained by assuming a saturated solution of  $\text{CaCO}_3$  ( $K_s = 4.3 \times 10^{-7}$  mol<sup>2</sup>/L<sup>2</sup>) in equilibrium with an atmospheric carbon dioxide partial pressure of  $p(\text{CO}_2) = 3.5 \times 10^{-4}$  atm.

It is useful to define the total alkalinity  $A_T$  to describe the buffer capacity of the solution:

$$A_T = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+]\tag{7}$$

This is a common definition used by oceanographers. Note that the total alkalinity is not affected by uptake or release of  $\text{CO}_2$ . The initial total alkalinity is  $A_T^0 = 6.4 \times 10^{-4}$  mol/L.

## 4 Cooling down the Sea Water

During the freezing process, water ice forms, and the remaining brine increases in salinity. Richardson (1976) has tabulated salinities  $S$  in the temperature range from 0 to  $-52$  °C. After cooling down the sea water from  $T^0$  to a lower temperature  $T$ , the salinity increases from  $S^0$  to  $S$ . The concentration factor is:

$$f = S/S^0 \quad (8)$$

If no carbonate precipitation occurs, the concentration of  $\text{Ca}^{2+}$  and the total alkalinity increase by the same factor as the salinity:

$$A_T = f \times A_T^0 \quad (9)$$

$$[\text{Ca}^{2+}] = f \times [\text{Ca}^{2+}]^0 \quad (10)$$

However, when solid  $\text{CaCO}_3$  precipitates, the concentration of  $\text{Ca}^{2+}$  is reduced to:

$$[\text{Ca}^{2+}] = f \times [\text{Ca}^{2+}]^0 - [\text{CaCO}_3] \quad (11)$$

$\text{CaCO}_3$  precipitates from the supersaturated solution until the solubility product  $K_s$  is reached:

$$K_s = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] \quad (12)$$

$$= (f \times [\text{Ca}^{2+}]^0 - [\text{CaCO}_3]) \times [\text{CO}_3^{2-}] \quad (13)$$

$$\Leftrightarrow [\text{CaCO}_3] = f \times [\text{Ca}^{2+}]^0 - K_s / [\text{CO}_3^{2-}] \quad (14)$$

The lost carbonate must be subtracted from the total alkalinity  $A_T$ :

$$A_T = f \times A_T^0 - 2[\text{CaCO}_3] \quad (15)$$

$$= f \times A_T^0 - 2(f \times [\text{Ca}^{2+}]^0 - K_s / [\text{CO}_3^{2-}]) \quad (16)$$

$$= f(A_T^0 - 2[\text{Ca}^{2+}]^0) + 2K_s / [\text{CO}_3^{2-}] \quad (17)$$

Inserting the equilibrium concentrations of  $[\text{OH}^-]$ ,  $[\text{HCO}_3^-]$ , and  $[\text{CO}_3^{2-}]$  into the definition of  $A_T$  yields an equation that allows the calculation of the solution pH:

$$A_T = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+] = f(A_T^0 - 2[\text{Ca}^{2+}]^0) + \frac{2K_s}{[\text{CO}_3^{2-}]} \quad (18)$$

$$\frac{K_w}{[\text{H}^+]} + \frac{K_{a1} k_H p(\text{CO}_2)}{[\text{H}^+]} \left(1 + \frac{2K_{a2}}{[\text{H}^+]}\right) - [\text{H}^+] = f(A_T^0 - 2[\text{Ca}^{2+}]^0) + \frac{2K_s [\text{H}^+]^2}{K_{a1} K_{a2} k_H p(\text{CO}_2)} \quad (19)$$

This equation is multiplied by  $[\text{H}^+]^2$ :

$$K_w [\text{H}^+] + K_{a1} k_H p(\text{CO}_2) [\text{H}^+] + 2K_{a1} K_{a2} k_H p(\text{CO}_2) - [\text{H}^+]^3 = f(A_T^0 - 2[\text{Ca}^{2+}]^0) [\text{H}^+]^2 + \frac{2K_s}{K_{a1} K_{a2} k_H p(\text{CO}_2)} [\text{H}^+]^4 \quad (20)$$

This is a fourth-order polynomial of the type

$$a[\text{H}^+]^4 + b[\text{H}^+]^3 + c[\text{H}^+]^2 + d[\text{H}^+] + e = 0 \quad (21)$$

with the coefficients:

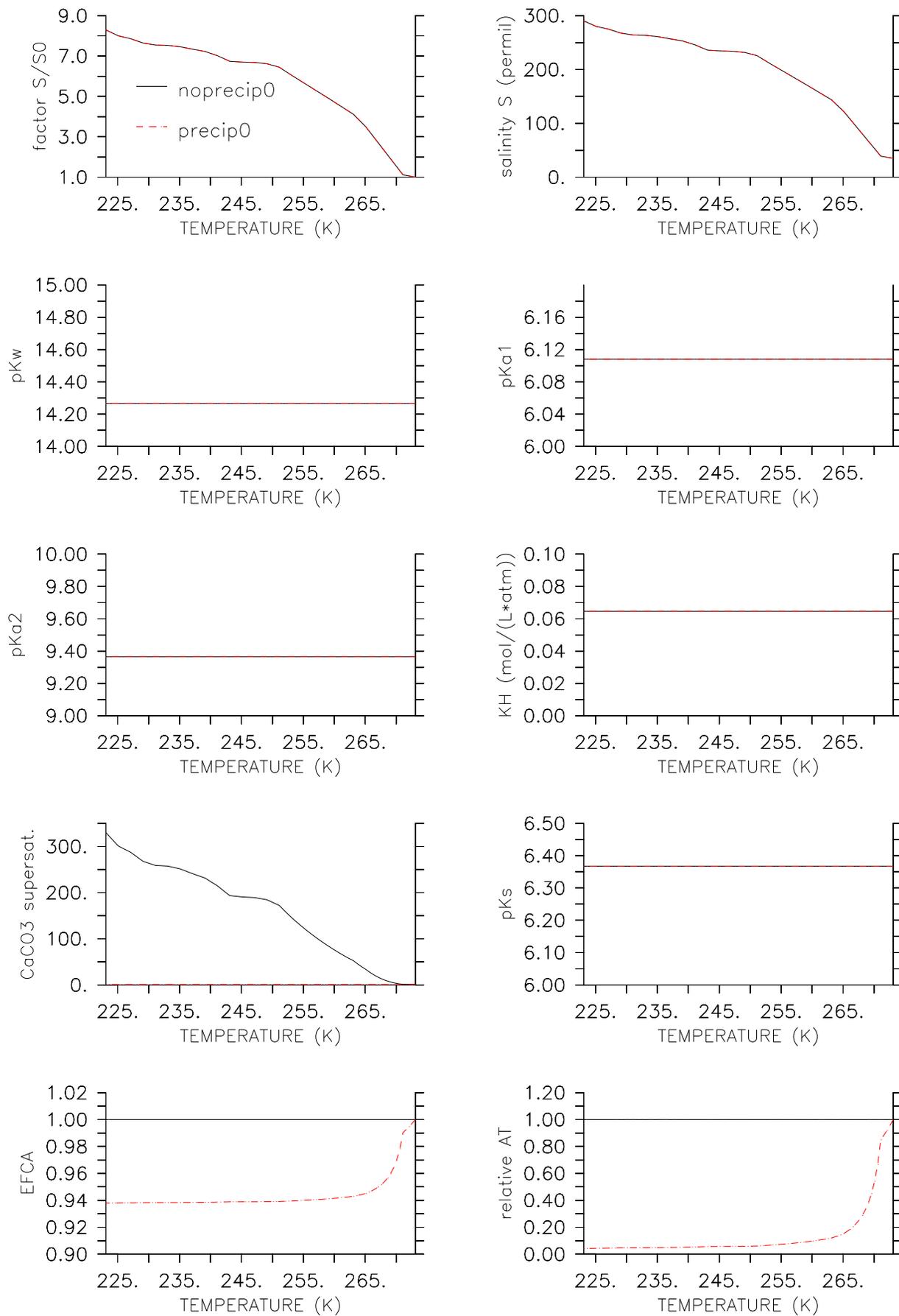


Figure 1: Calculated thermodynamic data. EFCA is the calcium enrichment factor. A value of e.g. 0.94 shows that 6 % of the Ca have precipitated as CaCO<sub>3</sub>. The relative total alkalinity (relative AT =  $A_{T,rel}$ ) is defined as the ratio of  $A_T$  with (Eqn. 15) and without (Eqn. 9) carbonate precipitation. See text for further details.

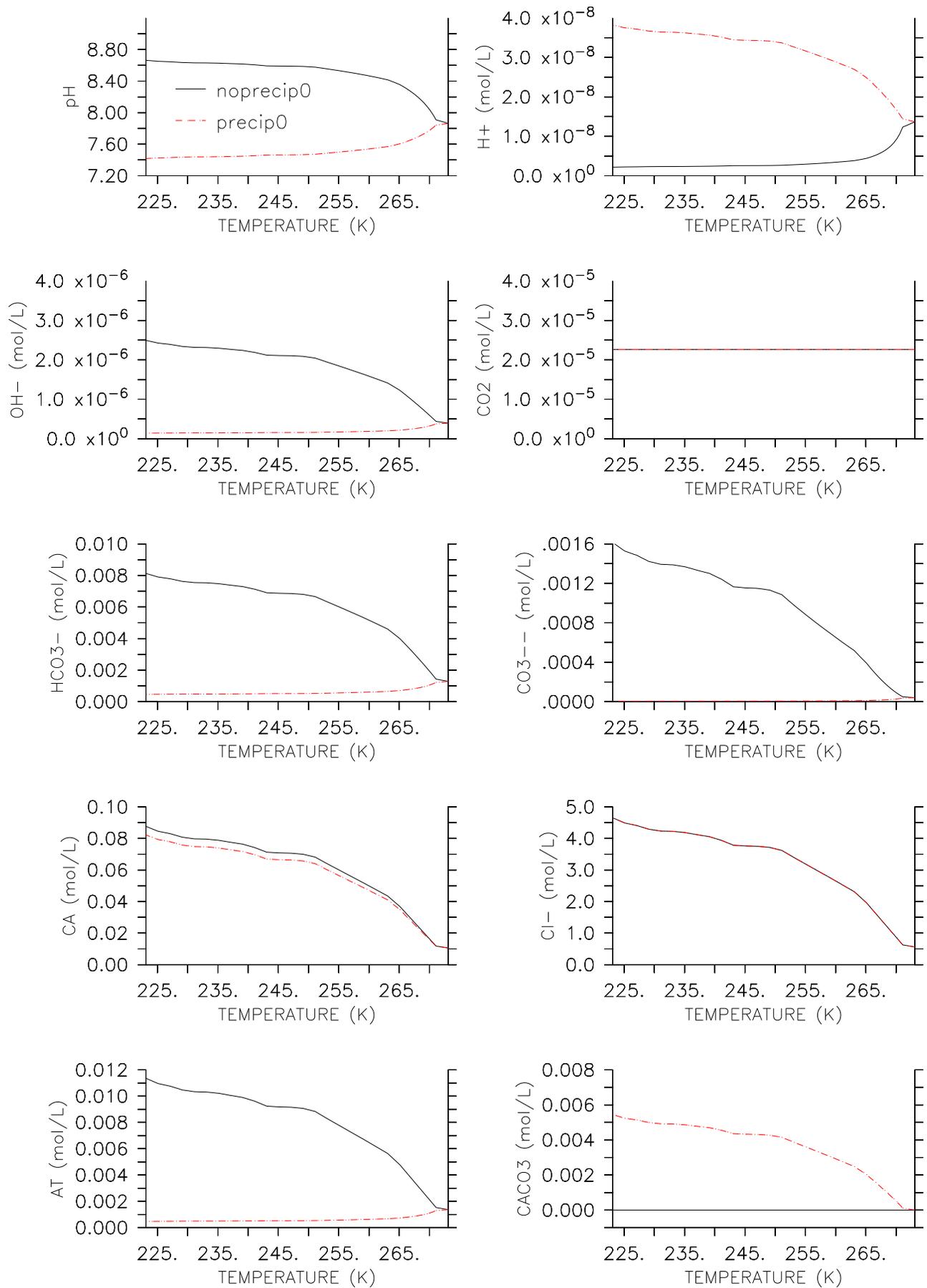


Figure 2: Calculated concentrations. See text for details.

$$a = \frac{2 K_s}{K_{a1} K_{a2} k_H p(\text{CO}_2)} \quad (22)$$

$$b = 1 \quad (23)$$

$$c = f(A_T^0 - 2[\text{Ca}^{2+}]^0) \quad (24)$$

$$d = -K_w - K_{a1} k_H p(\text{CO}_2) \quad (25)$$

$$e = -2 K_{a1} K_{a2} k_H p(\text{CO}_2) \quad (26)$$

If there was no precipitation,  $[\text{CaCO}_3]$  could be set to zero in equation (15), and two of the coefficients would be different:

$$a = 0 \quad (27)$$

$$c = f A_T^0 \quad (28)$$

Solving the polynomial yields  $[\text{H}^+]$ , and resubstitution into the equilibrium equations yields the concentrations of all other species.

## 5 Results

Equilibrium concentrations in freezing sea water have been calculated from 273.15 K down to 223.15 K using the procedure described above. The results are shown in Figs. 1 and 2. Two different scenarios were calculated: PRECIP0 and NOPRECIP0, i.e. one with carbonate precipitation and one without. The suffix 0 indicates that thermodynamic data at 0 °C (and sea-water salinity) were used for  $K_w$ ,  $K_{a1}$ ,  $K_{a2}$ ,  $k_H$ , and  $K_s$ . The main findings are:

- About 80 % of the total alkalinity  $A_T$  is lost throughout the temperature range  $-25 \dots -5$  °C (see subfigure “relative AT”). The relative amount of carbonate precipitation equals  $1 - A_{T,\text{rel}}$ .
- The effect on Ca is small. The loss of Ca relative to Cl is about 6 % or less. This results from the large calcium-to-carbonate ratio in sea water. This is consistent with the results of Hall and Wolff (1998) who could not detect any Ca depletion in Antarctic sea-salt aerosol.
- Precipitation of  $\text{CaCO}_3$  has a large effect on total alkalinity  $A_T$  but only a small effect on pH.

## References

- Dickson, A. G. and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, *Deep-Sea Res. A*, 34, 1733–1743, 1987.
- Dickson, A. G. and Riley, J. P.: 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, 1979.
- Hall, J. S. and Wolff, E. W.: Causes of seasonal and daily variations in aerosol sea-salt concentrations at a coastal Antarctic station, *Atmos. Environ.*, 32, 3669–3677, 1998.
- Mucci, A.: The solubility of calcite and aragonite in seawater at various salinities, temperatures and one atmosphere total pressure, *Am. J. Sci.*, 283, 780–799, 1983.
- Richardson, C.: Phase relationship in sea ice as a function of temperature, *J. Glaciol.*, 17, 507–519, 1976.
- Weeks, W. F. and Ackley, S. F.: The growth, structure, and properties of sea ice, in: *The Geophysics of Sea Ice*, NATO ASI Series, Vol. 186, edited by Untersteiner, N., pp. 9–164, Plenum Press, NY, 1986.
- Weiss, R. F.: Carbon dioxide in water and seawater: The solubility of a non-ideal gas, *Mar. Chem.*, 2, 203–215, 1974.
- Wilson, T. R. S.: Salinity and the major elements of sea water, in: *Chemical Oceanography*, Vol. 1, 2nd Ed., edited by Riley, J. P. and Skirrow, G., pp. 365–413, Academic Press, 1975.