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Ocean Science
Discussions

Interactive comment on "Salinity/temperature ranges for application of seawater S_A-T-P models" *by* G. M. Marion et al.

Anonymous Referee #3

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A multi-component chemical equilibrium model for aqueous solutions (called FREZCHEM) is applied to estimate the precipitation of calcite ($CaCO_3$) and ikaite ($CaCO_3.6H_2O$) over a temperature range of –5° to 40°C and salinity range of 0 to 120 gm/kg. The effect of increasing pCO2 on the precipitation of carbonate crystals and pH of solutions are also presented. The information presented are useful for predicting the formation of the crystalline phases and resulting changes in chemical compositions, that may occur in natural aqueous media (such as seawater, brines etc.) in response to environmental changes.

However, this MS needs additional explanations and clarifications before the results are fully accepted. My comments are itemized below.

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1) Title of the paper does not fully reflect the contents.

While the main message of this MS is on the precipitation of carbonate minerals in aqueous media, this is not shown in the title. I might suggest " Precipitation of solid calcium carbonate phases and its effect on salinity based on seawater chemical models".

2) "Thermodynamic" Model?

"Thermodynamic" refers to a system that is reversible. While the aqueous reaction model used in this study is a reversible equilibrium model, the reactions described by Eq. (1) through (4) are only for the precipitation of pure CaCO3 (calcite). Since seawaters contain high concentrations of Mg++, the thermodynamic equilibrium phase is a magnesian calcite which contains several mole % of Mg. The rate of nucleation and growths depends greatly on the conditions (as reported in a number of old papers) and may reflect this aspect. Additionally, the rates of dissolution of (pure biogenic) calcite and aragonite are subject of great interest from the point of views of ocean acidification and paleo-oceanography. Therefore, "spontaneous" precipitation should be differentiated clearly from the "thermodynamic" equilibria as well as from "dissolution" reactions.

3) Unify the pressure units.

Three different pressure units are used in this MS: MPa (line 9, page 2 and elsewhere), uatm (line 16 in page 2 and elsewhere) and bars (line 8 in page 5). Since this reduces the readability of this MS, these units should be unified. Since uatm are commonly used for the atmospheric CO2, a conversion factor (1 uatm = 0.1013 Pa) and an example may be given: e. g. 385 uatm = 39.01 Pa.

4) Page 10: Extrapolation of Eq. (4) to lower temperature and high salinity should be justified more strongly.

The authors extended an expression (Eq. 4) that has been fitted to a limited T-Sal range of experimental data, and the method is briefly described in page 10. Since this extrapolation constitutes the main contribution of this MS, the method should be more clearly explained and defended.

a) When the temperature was changed from 3°C to 40°C (line 11), was pCO2 in seawater changed or kept constant at 385 uatm? If the pCO2 was kept constant at salinity of 35, then the total concentration of CO2 in solution (= (CO2)aq + HCO3$^-$ + CO3$^=$) should change from about 2206 umol/kg at 3°C to 1900 umol/kg at 40°C. While this causes only a small change of 0.013 gm/kg in salinity, this deviates from the chemical conditions listed in Table 1. Similarly, when the salinity is increased from 35.147 to 83.1 under a constant pCO2, the total CO2 concentration would change. Changes occurred in the chemical system during your manipulation should be more carefully explained.

b) It appears that that authors accepted the linear fit obtained for temperatures of 25°C and 40°C and salinity of 35 to 70, and extrapolated to 0°C and 120 salinity. Can the authors provide stronger explanations justifying this assumption?

5) Page 11, line 7: Focus on the seawater property rather than atmospheric CO2.

Although atmospheric pCO2 has increased, it is by no means in equilibrium with surface seawater everywhere over the global oceans. Therefore, I would suggest the following change in line 7: “The corresponding increases in pCO2 in surface ocean water results in a decrease in pH ....”.

6) Page 12, line 8: A typo? Should it be 550 uatm rather than 450 uatm?

7) Page 12, lines 15 and 19: What is the phase of CaCO3?

If the observation was made in the Bahamas, the crystalline phase may be more like aragonite rather than calcite.

8) Figure 2 caption: Define pCO2 in seawater.

Since the plot pertains to seawater properties, define pCO2 in seawater as 350 uatm and 550 uatm respectively rather than by “year”. If the authors are willing, define

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whether the variable is pCO2 or fCO2.

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