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**Salinity/temperature
ranges for seawater
S_A-T-P models**

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Salinity/temperature ranges for application of seawater S_A-T-P models

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Abstract

At the present time, little is known about how broad salinity and temperature ranges are for seawater thermodynamic models that are functions of absolute salinity (S_A), temperature (T) and pressure (P). Such models rely on fixed compositional ratios of the major components (e.g. Na/Cl, Mg/Cl, Ca/Cl, SO_4/Cl , etc.). As seawater evaporates or freezes, solid phases (e.g. $\text{CaCO}_3(\text{s})$ or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$) will eventually precipitate. This will change the compositional ratios, and these salinity models will no longer be applicable. A future complicating factor is the lowering of seawater pH as the atmospheric concentrations of CO_2 increase. A geochemical model (FREZCHEM) was used to quantify the S_A - T boundaries at $P=0.1$ MPa and the range of these boundaries for future atmospheric CO_2 increases. An omega supersaturation model for CaCO_3 minerals based on homogeneous nucleation was extended from 25–40°C to 3°C. CaCO_3 minerals were the boundary defining minerals (first to precipitate) between 3°C (at $S_A=104$ g kg^{-1}) and 40°C (at $S_A=66$ g kg^{-1}). At 2.82°C, calcite(CaCO_3) transitioned to ikaite($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) as the dominant boundary defining mineral for colder temperatures, which culminated in a low temperature boundary of -4.93°C. Increasing atmospheric CO_2 from 385 μatm (in Year 2008) to 550 μatm (in Year 2100) would increase the S_A and t boundaries as much as 11 g kg^{-1} and 0.66°C, respectively. The model-calculated calcite-ikaite transition temperature of 2.82°C is in excellent agreement with ikaite formation in natural environments that occurs at temperatures of 3°C or lower. Furthermore, these results provide a quantitative theoretical explanation (FREZCHEM model calculations) for why ikaite is the solid phase CaCO_3 mineral that precipitates during seawater freezing.

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1 Introduction

At the present time, little is known about how broad salinity and temperature ranges are for seawater thermodynamic models that are functions of absolute salinity (S_A), or practical salinity (S), temperature (T) and pressure (P), such as Feistel (2003, 2008) and Feistel and Marion (2007). Models that are used rely on fixed chemical composition ratios (Na/Cl, Ca/Mg, Cl/HCO₃, etc., Millero et al., 2008). As seawater evaporates or freezes, eventually solid phases such as aragonite (CaCO₃), calcite (CaCO₃), or ikaite (CaCO₃·6H₂O) will precipitate. When precipitation happens, the fixed ratios of various soluble species will change and the seawater salinity (S_A) model will no longer be applicable.

Aragonite and calcite are generally the first solid phase salts that precipitate during seawater evaporation (Pytkowicz, 1973; McCaffrey et al., 1987; Maldonado et al., 1992; Morse et al., 1997, 2007; Zuddus and Mucci, 1998; Hardie, 2003; Millero, 2007). Aragonite and calcite have identical chemical compositions, but differ in their crystal structures and solubilities. How to handle these carbonates with chemical thermodynamic models is problematic because surface seawater is always supersaturated with these minerals. Fortunately, Morse and He (1993) have experimental data that calculates the degree of supersaturation (Ω) at the point where CaCO₃ minerals will start to precipitate from seawater. Unfortunately, these datasets are only defined for 25 and 40°C.

A controversy that dates back a century deals with whether calcite or ikaite precipitates during seawater freezing (Ringer, 1906; Gitterman, 1937; Assur, 1958; Richardson, 1976; Weeks and Ackley, 1982; Marion, 2001; Dieckmann et al., 2008). Recently, for the first time, experimental measurements in Antarctic sea ice discovered ikaite crystals had formed during seawater freezing (Dieckmann et al., 2008). But how supersaturated calcite and saturated ikaite can be integrated into a theoretical model still remains an open question.

Another complicating factor for the long-term application of ranges for S_A -T-P models

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is the global rise of atmospheric CO₂ concentrations from pre-industrial (1750–1800) concentrations of 280 μatm, to 385 μatm in 2008, and potentially to 550 μatm in 2100 (<http://www.esrl.noaa.gov/gmd/ccgg/trends/>). Such CO₂ trends will affect seawater pH and carbonate mineral solubilities that will alter S_A-T-P applicability boundaries.

5 The specific objectives of this paper were to (1) establish salinity-temperature boundaries for S_A-T-P models at $P=0.1$ MPa (Earth surface pressure), (2) establish the range of these boundaries for future atmospheric CO₂ increases, and (3) reconcile, if possible, the controversy dealing with calcite-ikaite equilibrium during seawater freezing.

2 Methods and materials

10 The S_A-T boundaries for seawater S_A-T-P models will be established with a theoretical chemical thermodynamic model called FREZCHEM (Marion and Kargel, 2008). The composition of seawater will be based on a newly established standard composition based on S_A (Millero et al., 2008). And finally, CaCO₃ supersaturation at precipitation will be integrated into FREZCHEM based on a homogeneous nucleation model (Morse
15 and He, 1993).

2.1 FREZCHEM model

The FREZCHEM model is an equilibrium chemical thermodynamic model parameterized for concentrated electrolyte solutions using the Pitzer approach (Pitzer, 1991, 1995). The model has a temperature range of <-70 to 25°C and a pressure range of 1
20 to 1000 bars (Marion and Farren, 1999; Marion, 2001, 2002; Marion et al., 2003, 2005, 2006, 2008; Marion and Kargel, 2008). The current version of the model is parameterized for the Na-K-Mg-Ca-Fe(II)-Fe(III)-Al-H-Cl-Br-SO₄-NO₃-OH-HCO₃-CO₃-CO₂-O₂-CH₄-Si-H₂O system and includes 95 solid phases including ice, 15 chloride minerals, 35 sulfate minerals, 15 carbonate minerals, five solid-phase acids, three nitrate
25 minerals, six acid-salts, five iron oxide/hydroxides, four aluminum hydroxides, two silica

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minerals, two bromide sinks, and two gas hydrates. Inputs to the model are 1 kg H₂O, individual ion concentrations (Table 1), temperature, and pressure. Outputs include equilibrium compositions, pH, density, water activity, and many other physicochemical properties (Marion and Kargel, 2008). Working copies of previously-published FREZCHEM models are available at the Internet site: <http://frezchem.dri.edu>.

This Pitzer-based model was used in Feistel and Marion (2007) to extend an S_A-T-P model (Feistel, 2003) from S_A=42 g kg⁻¹ to 110 g kg⁻¹ and the cold temperature boundary from -2 to -7°C. This model contains calcite, aragonite, vaterite, and ikaite chemistries. What FREZCHEM currently lacks in addressing the objectives of this paper is how to cope with CaCO₃ supersaturation in seawater, which we will address below.

2.2 Seawater properties

The seawater molalities [moles kg(H₂O)⁻¹, m] that will drive our simulations are taken from Millero et al. (2008) (Table 1). In addition to these ions, we also included B(OH)₃=0.00033 m. Several minor constituents (Sr²⁺, B(OH)₄⁻, F⁻) were excluded from our simulations. Overall, there was a small decrease in the standard S_A from 35.165 g kg⁻¹ (Practical Salinity S=35.00) to the model-used 35.147 g kg⁻¹. Our research efforts will focus exclusively on Absolute Salinity (S_A). To convert S_A to S (Practical Salinity on the 1978 scale), one can use the relationship: S=(35/(35.16504 g kg⁻¹)) S_A=0.995307 S_A/(g kg⁻¹) (Millero et al., 2008).

2.3 CaCO₃ nucleation/supersaturation

There are distinct differences between homogeneous and heterogeneous nucleation and precipitation of CaCO₃ minerals. Homogeneous precipitation of CaCO₃ occurs in the absence of pre-existing solid phases. Heterogeneous precipitation occurs on pre-existing solid phases. Heterogeneous precipitation is relevant where carbonate solid phases are in close contact with supersaturated waters (e.g. in shallow waters or in

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the presence of biotic carbonates). We will focus our attention in this paper primarily on homogeneous CaCO₃ precipitation using the Morse and He (1993) model, but will also discuss two examples of heterogeneous precipitation that can be important in the interpretation of experiments with added crystals, and seawater environments with natural crystals.

In the seawater literature, it has long been known that seawater is supersaturated with carbonate minerals such as calcite and aragonite (Morse and Mackenzie, 1990; Millero and Sohn, 1992; Millero, 2007; Morse et al., 2007). Traditionally, the degree of supersaturation was described by the omega (Ω) concept:

$$\Omega = \text{IAP} / K \quad (1)$$

where IAP is the calculated ion activity product (e.g. $(a_{\text{Ca}})(a_{\text{CO}_3})$) for a specific mineral (e.g. calcite), and K is the solubility product for the mineral. For example, Ω for calcite at $S_A = 35.147 \text{ g kg}^{-1}$ and $t = 25^\circ\text{C}$ is calculated to be 5.6 with the FREZCHEM model (IAP = 1.856×10^{-8} , $K = 3.312 \times 10^{-9}$). The seawater sample is 5.6-fold supersaturated with respect to calcite. While this is interesting, it provides no clue as to when such a seawater sample would actually start to precipitate a carbonate mineral during the evaporation or freezing process as S_A increases.

John Morse and colleagues (Morse and He, 1993; Morse et al., 2007) have developed an empirical omega model that is geared to estimating the point where carbonate minerals will actually start to precipitate as a function of S and T . In this case, the omega concept is defined as:

$$\Omega(\text{calcite}) = \text{IAP}(\text{CaCO}_3) / K(\text{calcite}) \quad (2)$$

In Eq. (2), the IAP is the value at the point where a “CaCO₃” mineral will start to precipitate, likely either as calcite or aragonite. Despite the fact that Eq. (2) is defined in terms of calcite, the IAP(CaCO₃) only predicts that an undefined CaCO₃ mineral will precipitate. In what follows, we will use:

$$\text{IAP}(\text{CaCO}_3) = \Omega(\text{calcite}) \times K(\text{calcite}) \quad (3)$$

to calculate the $IAP(\text{CaCO}_3)$ at the point where a CaCO_3 mineral will start to precipitate. Effectively, $IAP(\text{CaCO}_3)$ is the equilibrium constant for CaCO_3 minerals in seawater. We will primarily run the FREZCHEM model at a fixed T under the evaporation option, where S_A is steadily increasing because water is being removed, until our model-calculated IAP agrees with the empirical IAP (CaCO_3 equilibrium constant) of Eq. (3) (or another mineral). This means that this calculated salinity (S_A) represents the boundary for our S_A -T-P model because a CaCO_3 (or another) mineral has started to precipitate. We will also run the FREZCHEM model under the freezing option to establish the lower temperature boundary for the S_A -T-P model.

Bear in mind that while Eq. (3) specifically addresses CaCO_3 mineral formation, this concept integrated into the FREZCHEM model does not preclude the possibility that other minerals (with other ions) could precipitate first during the evaporation or freezing process. Where solutions have become supersaturated with respect to specific minerals, the FREZCHEM model selects the solid phase that minimizes the Ca (or other ion) concentration as the most thermodynamically stable mineral. “ CaCO_3 ” as defined in Eq. (3) is the only solid phase in the FREZCHEM model that is allowed to persist at the supersaturated level before precipitating. On the other hand, coping with the degree of supersaturation associated with Eq. (3) required that we remove several carbonate minerals from the FREZCHEM mineral database, including aragonite (CaCO_3), vaterite (CaCO_3), dolomite [$\text{CaMg}(\text{CO}_3)_2$], magnesite (MgCO_3), and hydromagnesite [$3\text{MgCO}_3\text{Mg}(\text{OH})_2\cdot 3\text{H}_2\text{O}$]. These minerals, except for aragonite that is a factor in Eq. (3), do not precipitate from seawater despite their supersaturation. Retention of the latter carbonate minerals in FREZCHEM would lead to their precipitation rather than the supersaturated “ CaCO_3 ” as defined in Eq. (3). As pointed out above, “ CaCO_3 ” likely represents either aragonite or calcite.

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3 Results

In Fig. 1 are the experimental data that depict $\Omega(\text{calcite})$ as a function of S_A at 25 and 40°C (Morse and He, 1993; Morse et al., 2007). The S values of the original data were converted to S_A values (Fig. 1) by $S_A = 1.004715 (\text{g kg}^{-1}) S$. We fit a linear equation to these data, which is given by:

$$\Omega(\text{calcite}) = -14.6128 + 0.098043T + 0.129602S_A (T \text{ in } K) \quad (4)$$

where r^2 (coefficient of determination) = 0.922, and SE (standard error) = 0.54 (Steel et al., 1997). The three coefficients in Eq. (4) (and Fig. 1) are all statistically significant at the <1% chance of a Type I error (Steel et al., 1997). Extrapolation of the equation to 0°C is also depicted in Fig. 1. The equation fits to data at 25 and 40°C seem reasonably good. The extrapolation to lower temperatures will be discussed below.

Now given an equation that allows one to calculate $\Omega(\text{calcite})$ as a function of S_A and T (Eq. 4), we can estimate the IAP(CaCO_3) of Eq. (3). Next, we ran the FREZCHEM model under the evaporation process, at a fixed T and a starting $S_A = 35.147 \text{ g kg}^{-1}$, until the model-calculated IAP equilibrated with IAP(CaCO_3) of Eq. (3) to form carbonates, or other minerals. This process allowed us to place S_A and T limits where solid phase minerals start to form. The results of these calculations for Year 2008 with $\text{CO}_2 = 385 \mu\text{atm}$ are given in Fig. 2 (solid lines). As an example, for a temperature of 20°C with initial $S_A = 35.147 \text{ g kg}^{-1}$, we evaporated the solution with FREZCHEM until CaCO_3 started to precipitate at $S_A = 83.1 \text{ g kg}^{-1}$, which sets the boundary limit for an S_A -T-P model at $T = 20^\circ\text{C}$ and $S_A = 83.1 \text{ g kg}^{-1}$. Similar calculations established the boundary between 3 and 40°C (Fig. 2). Aragonite is likely the dominant CaCO_3 mineral between 8 and 40°C, and calcite is likely the dominant CaCO_3 mineral between 3 and 8°C (Morse et al., 2007). Note that in this temperature range of 3–40°C, the boundary increases with decreasing temperature because the solubility of CaCO_3 minerals increases with decreasing temperatures.

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At a temperature of 2.82°C, the FREZCHEM model predicts that ikaite should start precipitating instead of CaCO₃. Because ikaite solubility decreases with decreasing temperature, the slope of the curve changes from that for CaCO₃ solubility (Fig. 2).

Now to establish the lower temperature limit, we needed to extend the calculations to the point where minerals start precipitating at cold temperatures. If we start at 25°C with $S_A=35.147\text{ g kg}^{-1}$, then lowering temperature will eventually reach the “ice line” in Fig. 2 at $t=-1.9^\circ\text{C}$. Ice formation, per se, does not limit the range of S_A -T-P models because relatively pure ice forms concentrating all solution phase constituents equally, therefore leaving ratios such as Ca/Mg unchanged. But as temperature continues to changes below -1.9°C , the freezing process will follow the ice line changing rapidly in S_A until it hits the ikaite line at -4.93°C with $S_A=87.3\text{ g kg}^{-1}$ (Fig. 2). The lower t-limit for all phases that lead to ice formation is -4.93°C .

The atmospheric CO₂ has changed historically from 280 μatm in pre-industrial years, to 385 μatm in 2008, and potentially to 550 μatm by 2100 (<http://www.esrl.noaa.gov/gmd/ccgg/trends/>). This process results in a decrease in seawater pH (at $S_A=35\text{ g kg}^{-1}$, $t=25^\circ\text{C}$) from 8.38 in pre-industrial years, to 8.27 in 2008, and to 8.14 in 2100 (Fig. 3). These pH values were estimated with the FREZCHEM model that defines $\text{pH}=-\log_{10}(\text{H}^+)$, where the parentheses define H⁺ activity. In contrast, had we estimated pH using the seawater scale (SWS) (Millero, 2001) that defines $\text{pH}(\text{SWS})=-\log_{10}[\text{H}^+ + \text{HSO}_4^- + \text{HF}]$, where the brackets define concentrations, then the corresponding pH values are 8.13, 8.02, and 7.88, respectively, about 0.25 pH units lower than the pH values in Fig. 3. Either scale can be used to define pH in seawater. But, caution must be used to assure consistency in how the pH options are defined and subsequent applications to H⁺ equilibria. See Millero (2001) for more details on pH scale variability.

Changing S_A , especially lower values, will have a major influence on the relationship of CO₂ and pH (Fig. 3). The Baltic Sea is a classic case where seawater S_A is highly variable, from below 1 g kg⁻¹ in the coastal lagoons, over 8–12 g kg⁻¹ in the central Gotland Sea, to about 25 g kg⁻¹ at the Danish Straits, with significant temporal variability.

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ity from the daily to the decadal (climatological) time scales (see e.g. online figures of Feistel et al., 2008). In addition, brackish Baltic seawater contains anomalously high CaCO_3 concentrations (Rohde, 1966; Millero and Kremling, 1976; Feistel and Weinreben, 2008).

5 A decreasing pH due to increasing atmospheric CO_2 will cause CaCO_3 minerals to increase in solubility, which will increase the salinity-temperature boundaries by up to 11 g kg^{-1} and 0.66°C by 2100 (dashed lines, Fig. 2). Also, interestingly, the model predicts that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) should be the boundary precipitating mineral between 0 and 6°C in 2100 (Fig. 2). We also made an approximation of where gypsum should
10 start to first precipitate, which is at $S_A = 109.5 \text{ g kg}^{-1}$, $t = 2.95^\circ\text{C}$, and $\text{CO}_2 = 450 \mu\text{atm}$.

4 Discussion

Our efforts have resulted in placing S_A -T boundaries for using S_A -T-P models at $P = 0.1 \text{ MPa}$, which was the primary purpose of this paper. But Figs. 1 and 2 deal with homogeneous nucleation of CaCO_3 . McCaffrey et al. (1987) estimated that CaCO_3
15 starts precipitating from seawater at 1.8-fold brine concentration at a temperature of $\approx 31^\circ\text{C}$. Those experiments were made at the Morton Bahamas solar salt production facility on Great Inagua Island in the Bahamas and represent heterogeneous nucleation because of the shallow depths that likely contain CaCO_3 mineral nucleation sites. Multiplying 1.8×35 leads to a salinity of 63 g kg^{-1} at the point where CaCO_3 starts to
20 precipitate. This result compares to a salinity of 73 g kg^{-1} at 31°C under homogeneous nucleation (Fig. 2). Gitterman (1937) examined CaCO_3 formation resulting from seawater freezing where his experimental aqueous solutions ($S_A = 33.34 \text{ g kg}^{-1}$) were likely seeded with calcite crystals (Marion, 2001). His first experimental point, after freezing started at -1.8°C , was at -3.5°C where CaCO_3 was clearly precipitating. Because he
25 seeded the aqueous phase with CaCO_3 crystals, this represents heterogeneous nucleation. The brine concentration factor between -1.8 and -3.5°C is 2.0-fold, which represents a maximum concentration factor because CaCO_3 could have started pre-

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5 precipitating at any temperature between -1.8 and -3.5°C . The point is that heterogeneous nucleation at a temperature that could be as low as -3.5°C still led to a lower brine concentration than was the case for ikaite that precipitated at a temperature of -4.9°C under homogeneous precipitation (Fig. 2). Heterogeneous nucleation in the presence of CaCO_3 minerals will reduce the applicability range of S_A -T-P models. Unfortunately, the data to place a broad range on heterogeneous nucleation is relatively limited. Fortunately, homogeneous nucleation (Fig. 2) is more realistic for the bulk of Earth seawater.

10 What is perhaps most intriguing about the theoretical model calculations is that the model predicts a transition from CaCO_3 (probably calcite) to ikaite at a temperature of 2.82°C (Fig. 2). Natural occurrences of ikaite appear to have water temperatures of 3°C or lower (Pauley, 1963; Bischoff et al., 1993; Larsen, 1994; Omelon et al., 2001), which is in excellent agreement with our model calculation. In the Dieckmann et al. (2008) paper that recently identified ikaite formation in sea ice, great care was taken to keep the temperature of the isolated ikaite crystals between 0 and 2°C during sample analyses because ikaite easily decomposes at higher temperatures forming calcite crystals (Omelon et al., 2001; Dieckmann et al., 2008). At the transition temperature of 2.82°C , the $\Omega(\text{calcite})$ value is 25.9 , meaning that calcite is 25.9 -fold supersaturated. The fact that this high $\Omega(\text{calcite})$ value accurately predicts the transition from CaCO_3 to ikaite at 3°C is strong support for the broad-range equation for $\Omega(\text{calcite})$ (Eq. 4, Fig. 1), which we extended from 25 – 40°C to 3°C . Furthermore, this result argues in favor of ikaite formation during the freezing process, which, as we mentioned earlier, has been controversial for over a century (Ringer, 1906; Gitterman, 1937; Assur, 1958; Richardson, 1976; Weeks and Ackley, 1982; Marion, 2001; Dieckmann et al., 2008). The fact that the theoretical FREZCHEM model can quantitatively predict CaCO_3 mineral formation in seawater across a broad range of S_A -T values is a major step forward in geochemical modeling.

25 A limitation, at present, is that the equation for estimating $\Omega(\text{calcite})$ is based on seawater S_A that works well for seawater compositions, but may not work for other

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salt assemblages. For example, calcite precipitation in seawater requires high Ω values (high supersaturation) (Figs. 1–2), which is due to seawater inhibitory components such as Mg^{2+} , orthophosphate, and organic matter (Pytkowicz, 1973; Bischoff et al., 1993; Morse et al., 2007). Other saline waters with different compositions (e.g. exceedingly low or high Mg^{2+} , orthophosphate, and organic matter) would likely respond quite differently with respect to calcite precipitation. Another limitation is how to deal with pressure effects. The S_A -T data used to estimate the omega values (Fig. 1) were based on a single set of experiments that were done at $P=0.1$ MPa (Morse and He, 1993). Nevertheless, as formulated in this paper, we can accurately simulate surface properties of seawater, which by itself is a major improvement in understanding seawater chemistry.

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Table 1. Initial ion composition of the seawater sample ($S_A=35.147 \text{ g kg}^{-1}$).

| Cation | Initial molality | Anion | Initial molality |
|------------------|------------------|---|------------------|
| Na ⁺ | 0.48 606 | Cl ⁻ | 0.56 577 |
| Mg ²⁺ | 0.05 474 | SO ₄ ²⁻ | 0.02 926 |
| Ca ²⁺ | 0.01 066 | Br ⁻ | 0.00 087 |
| K ⁺ | 0.01 058 | HCO ₃ ⁻ +2CO ₃ ²⁻ | 0.00 228* |

* equivalents/kg(H₂O), everything else are moles/kg(H₂O).

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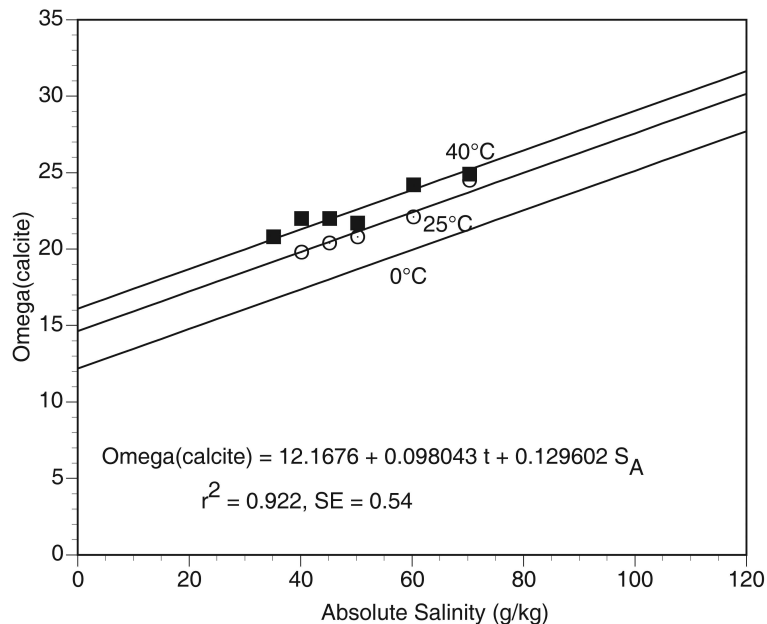


Fig. 1. The experimental data for supersaturation $\Omega(\text{calcite})$ (Morse and He, 1993; Morse et al., 2007) necessary for homogeneous nucleation of CaCO_3 in seawater at 25°C (circles) and 40°C (squares), and an extrapolation to 0°C.

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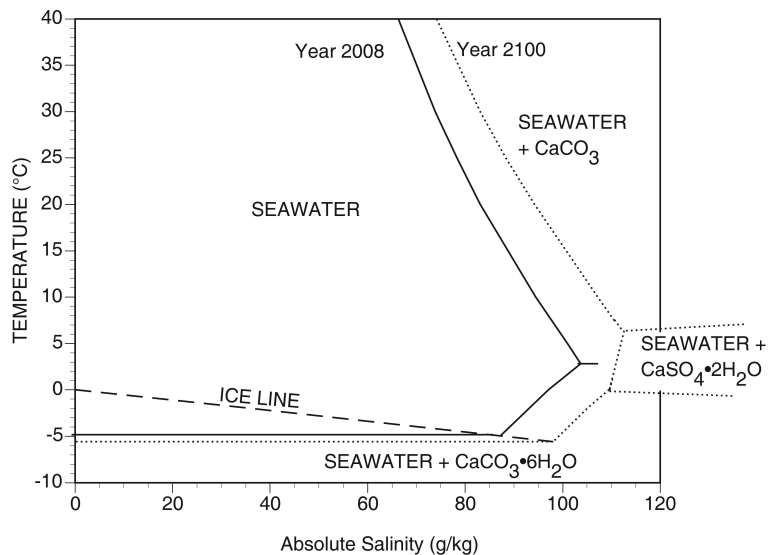


Fig. 2. The boundaries for S_A -T-P models in Year 2008 (solid lines) and potentially in Year 2100 (dashed lines).

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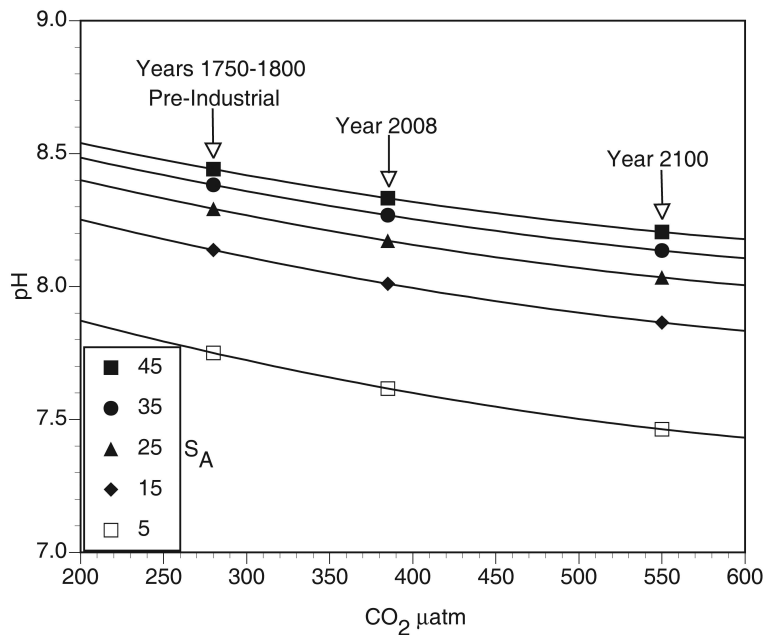


Fig. 3. Model calculated seawater pH values as a function of CO₂ μatm for S_A values of 5–45 g kg⁻¹ at 25°C.

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