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Revisiting the Carbonate Chemistry of the Sea of Japan (East Sea): from Water Column to Sediment

Pavel Tishchenko [1*], Jing Zhang [2], Galina Pavlova [1], Petr Tishchenko [1], Sergey Sagalaev [1], Mariya Shvetsova [1]

[1] V.I. Il'ichev Pacific Oceanological Institute, Far Eastern Branch, Russian Academy of Sciences, 690041 Vladivostok, Russia; pavlova@poi.dvo.ru (G.P.); eq15@poi.dvo.ru (P.T.); sagalaev@poi.dvo.ru (S.S.); chippers@rambler.ru (M.S.)

[2] Faculty of Science, University of Toyama 3190 Gofuku, Toyama, 930-8555, Toyama, Japan; jzhang@sci.u-toyama.ac.jp (J.Z.)

* Correspondence: tpavel@poi.dvo.ru; Tel.: +7-423-231-3092

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Table S1. Calcium (mmol/kg) and ammonium (uM) in porewater of sediments of JES, obtained on a board of R/V Hakuho Maru at June – July 2010.

St.[1)]	cmbsf[2)]	Depth, m	T, °C	S, ‰	Ca, mmol/kg	NH_4, μM
CR02	0	3549	0.327	34.070	10.01	0.37
CR02	2	3549	0.327	34.070	9.97	38.98
CR02	3.5	3549	0.327	34.070	10.10	11.91
CR02	7	3549	0.327	34.070	10.12	9.20
CR14	0	2652	0.300	34.070	10.01	0.09
CR14	1.5	2652	0.300	34.070	10.10	17.32
CR14	4.5	2652	0.300	34.070	10.03	19.49
CR14	7.5	2652	0.300	34.070	10.06	14.62
CR14	10.5	2652	0.300	34.070	9.97	9.74
CR14	13.5	2652	0.300	34.070	9.97	14.08
CR14	16.5	2652	0.300	34.070	9.88	23.82
CR14	19.5	2652	0.300	34.070	10.20	21.11
CR14	22.5	2652	0.300	34.070	10.05	12.99
CR14	25.5	2652	0.300	34.070	9.91	21.65
CR14	28.5	2652	0.300	34.070	9.92	23.28
CR14	31.5	2652	0.300	34.070	9.89	23.28
CR14	34.5	2652	0.300	34.070	9.91	22.74
CR14	37.5	2652	0.300	34.070	10.04	21.65
CR14	40.5	2652	0.300	34.070	9.85	34.11
CR34	0	554	0.484	34.072	10.01	0.18
CR34	1.5	554	0.484	34.072	10.07	8.46
CR34	4.5	554	0.484	34.072	10.08	7.22
CR34	7.5	554	0.484	34.072	10.23	10.74
CR34	10.5	554	0.484	34.072	10.03	18.16
CR34	13.5	554	0.484	34.072	10.06	26.80
CR34	16.5	554	0.484	34.072	10.06	22.10
CR34	19.5	554	0.484	34.072	10.09	31.99
CR34	22.5	554	0.484	34.072	10.09	28.53
CR41	0	3444	0.318	34.070	10.01	0.91
CR41	1.5	3444	0.318	34.070	9.86	5.22
CR41	4.5	3444	0.318	34.070	10.04	1.68
CR41	7.5	3444	0.318	34.070	9.83	3.17
CR41	10.5	3444	0.318	34.070	9.93	2.72
CR41	13.5	3444	0.318	34.070	9.97	4.28
CR41	16.5	3444	0.318	34.070	9.84	8.34
CR41	19.5	3444	0.318	34.070	9.97	8.52
CR41	22.5	3444	0.318	34.070	9.88	10.19
CR41	25.5	3444	0.318	34.070	10.00	13.46
CR41	28.5	3444	0.318	34.070	9.88	18.71
CR41	31.5	3444	0.318	34.070	9.84	19.48
CR41	34.5	3444	0.318	34.070	9.80	20.26
CR41	37.5	3444	0.318	34.070	9.82	25.76
CR41	40.5	3444	0.318	34.070	9.76	24.77
CR41	43.5	3444	0.318	34.070	9.69	30.39
CR41	46.5	3444	0.318	34.070	9.85	30.57
CR47	0	3614	0.333	34.070	10.01	0.15
CR47	1.5	3614	0.333	34.070	9.97	10.49
CR47	4.5	3614	0.333	34.070	9.88	3.05
CR47	7.5	3614	0.333	34.070	9.76	4.32
CR47	10.5	3614	0.333	34.070	9.85	11.29
CR47	13.5	3614	0.333	34.070	9.76	11.20
CR47	16.5	3614	0.333	34.070	10.01	12.49
CR47	19.5	3614	0.333	34.070	10.03	18.65

CR47	22.5	3614	0.333	34.070	9.79	20.01
CR58	0	2809	0.259	34.070	10.01	0.22
CR58	1.5	2809	0.259	34.070	10.05	5.67
CR58	7.5	2809	0.259	34.070	10.16	5.39
CR58	10.5	2809	0.259	34.070	10.19	5.52
CR58	13.5	2809	0.259	34.070	10.21	17.17
CR58	16.5	2809	0.259	34.070	10.24	21.93

[1]) St. means station number; [2]) cmbsf means depth below seafloor in centimeter.

Table S2 Phosphorus and silica modeled concentrations (uM) in porewater of sediments of JES, obtained on a board of R/V Hakuho Maru at June – July 2010.

St.[1)]	cmbsf[2]	Depth, m	T, °C	S, ‰	[P], μM	Si, μM
CR02	0	3549	0.327	34.070	2.02	90.44
CR02	2	3549	0.327	34.070	4.44	136.78
CR02	3.5	3549	0.327	34.070	2.74	104.29
CR02	7	3549	0.327	34.070	2.58	101.04
CR14	0	2652	0.300	34.070	2.01	90.11
CR14	1.5	2652	0.300	34.070	3.08	110.78
CR14	4.5	2652	0.300	34.070	3.22	113.39
CR14	7.5	2652	0.300	34.070	2.91	107.54
CR14	10.5	2652	0.300	34.070	2.61	101.69
CR14	13.5	2652	0.300	34.070	2.88	106.90
CR14	16.5	2652	0.300	34.070	3.49	118.58
CR14	19.5	2652	0.300	34.070	3.32	115.33
CR14	22.5	2652	0.300	34.070	2.81	105.59
CR14	25.5	2652	0.300	34.070	3.35	115.98
CR14	28.5	2652	0.300	34.070	3.46	117.94
CR14	31.5	2652	0.300	34.070	3.46	117.94
CR14	34.5	2652	0.300	34.070	3.42	117.29
CR14	37.5	2652	0.300	34.070	3.35	115.98
CR14	40.5	2652	0.300	34.070	4.13	130.93
CR34	0	554	0.484	34.072	1.71	90.22
CR34	1.5	554	0.484	34.072	2.23	100.15
CR34	4.5	554	0.484	34.072	2.15	98.66
CR34	7.5	554	0.484	34.072	2.37	102.89
CR34	10.5	554	0.484	34.072	2.84	111.79
CR34	13.5	554	0.484	34.072	3.38	122.16
CR34	16.5	554	0.484	34.072	3.08	116.52
CR34	19.5	554	0.484	34.072	3.70	128.39
CR34	22.5	554	0.484	34.072	3.48	124.24
CR41	0	3444	0.318	34.070	0.91	91.09
CR41	1.5	3444	0.318	34.070	5.22	96.26
CR41	4.5	3444	0.318	34.070	1.68	92.02
CR41	7.5	3444	0.318	34.070	3.17	93.80
CR41	10.5	3444	0.318	34.070	2.72	93.26
CR41	13.5	3444	0.318	34.070	4.28	95.14
CR41	16.5	3444	0.318	34.070	8.34	100.01
CR41	19.5	3444	0.318	34.070	8.52	100.22
CR41	22.5	3444	0.318	34.070	10.19	102.23
CR41	25.5	3444	0.318	34.070	13.46	106.15
CR41	28.5	3444	0.318	34.070	18.71	112.45
CR41	31.5	3444	0.318	34.070	19.48	113.38
CR41	34.5	3444	0.318	34.070	20.26	114.31
CR41	37.5	3444	0.318	34.070	25.76	120.91
CR41	40.5	3444	0.318	34.070	24.77	119.72
CR41	43.5	3444	0.318	34.070	30.39	126.47

CR41	46.5	3444	0.318	34.070	30.57	126.68
CR47	0	3614	0.333	34.070	0.15	90.18
CR47	1.5	3614	0.333	34.070	10.49	102.59
CR47	4.5	3614	0.333	34.070	3.05	93.66
CR47	7.5	3614	0.333	34.070	4.32	95.18
CR47	10.5	3614	0.333	34.070	11.29	103.55
CR47	13.5	3614	0.333	34.070	11.20	103.44
CR47	16.5	3614	0.333	34.070	12.49	104.99
CR47	19.5	3614	0.333	34.070	18.65	112.38
CR47	22.5	3614	0.333	34.070	20.01	114.01
CR58	0	2809	0.259	34.070	0.22	90.26
CR58	1.5	2809	0.259	34.070	5.67	96.80
CR58	7.5	2809	0.259	34.070	5.39	96.47
CR58	10.5	2809	0.259	34.070	5.52	96.62
CR58	13.5	2809	0.259	34.070	17.17	110.60
CR58	16.5	2809	0.259	34.070	21.93	116.32

[1]) St. means station number; [2]) cmbsf means depth below seafloor in centimeter.

Taking into account the effect of variability of major ions on dissociation constants

Stoichiometric (apparent) constants are used to calculate the carbonate system parameters in seawater and marine pore waters [1] ; the major parameters of the carbonate system being *pH*, *TA* (Total Alkalinity), *DIC* (Dissolved Inorganic Carbon), pCO_2 (partial pressure of CO_2), Ω_c, and Ω_a (saturation degree of seawater with respect to calcite and aragonite, respectively). The effect of the composition of the ionic medium on the stoichiometric constants of carbonic acid and carbonate minerals can be taken into account by empirical equations relating the values of the stoichiometric constants to the prevailing salinity [2]. Such simplification is possible because concentrations of major constituents of seawater exhibit an almost constant ratio to one another throughout the oceans. However, relative concentrations of major constituents are widely variable in pore waters of marine sediments due to diagenetic processes occurring in these often anoxic environments (sulfate reduction, mineral dissolution, and precipitation). Therefore, dissociation constants obtained in seawater, strictly to say, cannot be applied for the description of chemical equilibria in anoxic marine sediments and other seawater environments with anomalous major ion concentrations as it was noted elsewhere [3,4]. An alternative approach is available for the description of chemical equilibria in natural waters of any composition [5–8], it is based on the Pitzer method [9,10].

Here, it is suggested to use a combined approach for the description of the carbonate system in anoxic sediments and in other marine environments with unusual seawater compositions. First of all, it is suggested to use commonly accepted stoichiometric constants of the carbonate system in seawater [2]. Secondly, it is suggested to correct using a constant the additional terms that take into account variations of the concentrations of sulfate, alkalinity, calcium, and magnesium prevailing in the investigated fluids. Applying the Pitzer approach, empirical relations were derived, which can be used to calculate these terms and, thus, reliable stoichiometric equilibrium constants for anoxic marine sediments.

Pitzer method

The basic equations of the ion-interaction model have been presented and discussed in several publications [9,10]. The model starts with a virial expansion of the excess free energy, G^{ex}, of the solution. The expressions for osmotic and activity coefficients are obtained by appropriate derivatives of free energy with respect to the weight of the solution, n_W, and molality of the component, m_i, respectively. Equations (1S)−(4S) give the expressions for the osmotic coefficient and activity coefficients of cations M, anions X, and neutral species, respectively.

$$(\phi-1)=-\frac{\partial G^{ex}/\partial n_W}{RT\Sigma m_i}=(2/\Sigma m_i)[-A^{\phi}I^{3/2}/(1+1.2I^{1/2})+\Sigma\Sigma m_c m_a(B^{\phi}_{ca}+ZC_{ca})$$
$$+1/2\Sigma\Sigma m_c m_{c'}(\Phi^{\phi}_{cc'}+\Sigma m_a\psi_{cc'a})+1/2\Sigma\Sigma m_a m_{a'}(\Phi^{\phi}_{aa'}+\Sigma m_c\psi_{aa'c})+\Sigma\Sigma m_n m_c\lambda_{nc}+ \quad (S1)$$
$$\Sigma\Sigma m_n m_a\lambda_{na}+1/2\Sigma\Sigma m_n m_{n'}\lambda_{nn'}+1/2\Sigma m_n^2\lambda_{nn}+\Sigma\Sigma\Sigma m_c m_a m_n\zeta_{can}]$$

$$\ln\gamma_M=\frac{1}{RT}\frac{\partial G^{ex}}{\partial m_M}=z_M^2F+\Sigma m_a(2B_{Ma}+ZC_{Ma})+\Sigma m_c(2\Phi_{Mc}+\Sigma m_a\psi_{Mca})$$
$$+1/2\Sigma m_a m_{a'}\psi_{Maa'}+z_M\Sigma\Sigma m_c m_a C_{ca}+2\Sigma m_n\lambda_{nM}+\Sigma\Sigma m_n m_a\zeta_{Man} \quad (S2)$$

$$\ln\gamma_X=\frac{1}{RT}\frac{\partial G^{ex}}{\partial m_X}=z_X^2F+\Sigma m_c(2B_{Xc}+ZC_{Xc})+\Sigma m_a(2\Phi_{Xa}+\Sigma m_c\psi_{Xac}$$
$$+1/2\Sigma m_c m_{c'}\psi_{Xcc'}+|z_M|\Sigma\Sigma m_c m_a C_{ca}+2\Sigma m_n\lambda_{nX}+\Sigma\Sigma m_n m_c\zeta_{Xcn} \quad (S3)$$

$$\ln\gamma_{\mathrm{n}}=2m_{\mathrm{n}}\lambda_{\mathrm{n,n}}+2\Sigma m_c\lambda_{\mathrm{n,c}}+2\Sigma m_a\lambda_{\mathrm{n,a}}+\Sigma\Sigma m_c m_a\zeta_{\mathrm{n,c,a}} \quad (S4)$$

The parameters appearing in Equations (1S)−(4S) are defined as follows:

$$F=f^{\gamma}+\Sigma\Sigma m_c m_a B'_{ca}+\Sigma\Sigma m_c m_{c'}\Phi'_{cc'}+\Sigma\Sigma m_a m_{a'}\Phi'_{aa'} \quad (S5)$$

$$f^{\gamma}=-A^{\phi}\cdot\left[I^{1/2}/(1+1.2\cdot I^{1/2})+\frac{2}{1.2}\cdot\ln(1+1.2\cdot I^{1/2})\right] \quad (S6)$$

$$B_{MX}=\beta^0_{MX}+\beta^1_{MX}\cdot g(\alpha_1 I^{1/2})+\beta^2_{MX}\cdot g(\alpha_2 I^{1/2}) \quad (S7)$$

$$g=2[1-(1+x)\exp(-x)]/x^2 \quad (S8)$$

$$Z=\Sigma m_i|z_i| \quad (S9)$$

$$B^{\phi}_{ca}=B_{ca}+IB'_{ca} \quad (S10)$$

$$\Phi^{\phi}_{cc'}=\Phi_{cc'}+I\Phi'_{cc'} \quad (S11)$$

Here "a", "c", and "n" are cations, anions, and neutral species, respectively. A^{ϕ} is the Debye–Hueckel limiting slope with numerical values calculated according to an empirical equation suggested by Clegg and Whitfield [7]. For non-associated electrolytes α_1 and α_2 take values of 2 and 0, respectively, whereas for 2-2 electrolytes the optimized values of α_1 and α_2 are 1.4 and 12 kg$^{1/2}$ mol$^{-1/2}$, respectively. B' and Φ' are the ionic strength derivatives of B and Φ, I is ionic strength, and β^0_{MX} ,. β^1_{MX} , β^2_{MX} , C_{MX} , Φ_{ij} , ψ_{ijk} , λ_{ni} , ξ_{nca} are measurable empirical constants (Pitzer parameters). Note that in equations (1S) - (4S) non-measurable terms containing virial coefficients of individual ions are omitted. Fortunately, these terms cancel out for electro-neutral combinations of ions and therefore have no effect on the calculations carried out below. In our calculations, we assumed that the original composition of pore waters

prior to diagenetic alteration is the same as in seawater (Table S3). Pitzer parameters applied in our calculations were taken from the literature, which is listed in Tables S4 and S5.

The Pitzer method treats strong electrolytes as fully dissociated in solution. In this case, the Pitzer parameters are derived from measurable non-ideal properties such as mean activity coefficients of salts, osmotic coefficients, heat dilutions, and capacity heats. However, when species reveal strong interactions in the solutions (weak acids, poor soluble salts, formation of complexes between ions) then appropriate accurate Pitzer parameters cannot be derived from experimental data due to the fact that species cannot coexist anymore with each other under moderate concentrations. For such strong interactions, the Pitzer and ion-pairing models are complementary as demonstrated by Whitfield [8,10–12]. These are interactions between hydrogen and sulfate ions and between carbonate anions and calcium and magnesium cations, respectively. The "free" activity coefficients of hydrogen and carbonate ions ($(\gamma_H)_f$, $(\gamma_{CO3})_f$) were calculated using equations (2S) and (3S) without taking into account the strong and specific interactions. The "total" activity coefficients were then obtained by the following relations:

$$\gamma_H = (\gamma_H)_f / (1 + m_{SO_4} / K^*_{HSO_4}) \quad \text{(S12)}$$

$$\gamma_{CO_3} = (\gamma_{CO_3})_f / (1 + m_{Ca} / K^*_{CaCO_3} + m_{Mg} / K^*_{MgCO_3}) \quad \text{(S13)}$$

where $K^*_{HSO_4}$ is the stoichiometric dissociation constant of HSO_4^- in seawater [13]. Thermodynamic stability constants (K_{MX}) for ion pairs of $CaCO_3$ [14] and $MgCO_3$ [8] were converted into stoichiometric constants valid for seawater (K^*_{MX}) applying the following equation:

$$K^*_{MX} = K_{MX} (\gamma_M \gamma_X / \gamma_{MX}) \quad \text{(S14)}$$

Effect of Pore Water Composition on Carbonate System Constants

Early diagenetic processes significantly change the composition of pore waters. The concentrations of major ions are strongly affected by sulfate reduction, formation/dissociation of carbonate minerals, formation of clay minerals, and ionic exchange [15]. Microbiological oxidation of organic matter or methane by sulfate consumes sulfate ions and produces an equivalent amount of dissolved bicarbonate. Formation/dissociation of carbonate minerals changes calcium, magnesium, and bicarbonate concentrations in pore waters. Dissolved magnesium is also bound in clay minerals and other authigenic silicate phases formed during the alteration of volcanic ash and oceanic basement [16,17]. Moreover, the weathering of silicates in anoxic marine sediments may affect the calcium and bicarbonate concentrations [18]. Due to charge balance constraints, the variations of these ion concentrations are not independent, but follow the relation:

$$2 \cdot \Delta m_{SO_4} + \Delta m_{HCO_3} = 2 \cdot \Delta m_{Ca} + 2 \cdot \Delta m_{Mg} \quad \text{(S15)}$$

The dissociation constants of carbonic acid and solubility products of calcium carbonates in a large number of different pore waters with variable compositions were evaluated. In these calculations, the concentrations of dissolved sulfate and Ca were diminished and the total alkalinity increased following the stoichiometry and charge balance constraints defined above. Moreover, the reduced concentration of dissolved Mg was explored for the effects of Mg concentrations on the stability constants. Finally, the salinities of the pore fluids were varied between 30 and 40 and the temperatures between 0° and 30°C.

For each of the generated pore fluid compositions, the activity coefficients of CO_2, H^+, HCO_3^-, CO_3^{-2}, Ca^{+2} and a_{H_2O} was calculated using the Pitzer approach. Moreover, the logarithms of the non-ideal part of the stoichiometric dissociation con-

stants of carbonic acid (K^*_{1sw} and K^*_{2sw}) and the ionic products of calcium carbonate (IP_{sw}) for sea water were evaluated which are defined by the following equations

$$\log(k_1) = \log(K^*_{1sw}) - \log(K^o_1) - \log(1 - S/1000) \quad \text{(S16)}$$

$$\log(k_2) = \log(K^*_{2sw}) - \log(K^o_2) - \log(1 - S/1000) \quad \text{(S17)}$$

$$\log(k_S) = \log(IP_{sw}) - \log(IP^o_{sw}) - \log(1 - S/1000) \quad \text{(S18)}$$

Calculated activity coefficients and k - values were combined into delta(log K) values, which can be used to determine stability constants valid for anoxic pore fluids:

$$\Delta\log(K_1) = \log(\gamma_{CO_2}) + \log(a_{H_2O}) - \log(\gamma_H) - \log(\gamma_{HCO_3}) - \log(k_1) \quad \text{(S19)}$$

$$\Delta\log(K_2) = \log(\gamma_{HCO_3}) - \log(\gamma_H) - \log(\gamma_{CO_3}) - \log(k_2) \quad \text{(S20)}$$

$$\Delta\log(K_s) = -\log(\gamma_{CO_3}) - \log(\gamma_{Ca}) - \log(k_S) \quad \text{(S21)}$$

Some results of these calculations are presented in Figure S1. When sulfate ions are replaced by bicarbonate ions, the ionic strength of the solution is diminished and, therefore, the activity coefficients of ions are increased. Coevally, the specific interactions between calcium and bicarbonate ions are enhanced due to the increase in bicarbonate concentrations. Because of these opposing effects, the solubility of calcium carbonate minerals changes only insignificantly upon sulfate reduction. In contrast, sulfate concentrations have a strong effect on the first and second stoichiometric dissociation constant of carbonic acid due to the strong association between hydrogen and sulfate ions. With decreasing temperature the association becomes weaker and changes in the $\Delta\log K$ are diminished. A decrease in dissolved Ca and Mg concentrations, as induced by carbonate precipitation processes, causes a decrease in the stoichiometric dissociation constants of carbonic acid and the ionic products of calcium carbonate (Fig. 2). The effect is caused by the diminished ionic strength of the pore fluids altered by carbonate precipitation.

The results of our simulations were fitted using the following equations:

$$\begin{aligned}\Delta\log(K_1) &= (0.0014566\cdot \mathrm{Cl}-[\mathrm{SO_4}])\cdot[-144.188+1.10614\cdot T-0.00216\cdot T^2 + \\ &(4.7793-0.034532\cdot T+0.00006366\cdot T^2)\cdot \mathrm{Cl}]+(0.0032833\,\mathrm{Cl}-[\mathrm{Mg}]-[\mathrm{Ca}])\times \\ &(-2.444-0.01688\cdot T+(3.689+0.01271\cdot T)\cdot \mathrm{Cl}^{1/2}/(1+\mathrm{Cl}^{1/2}))\end{aligned} \quad \text{(S22)}$$

$$\begin{aligned}\Delta\log(K_2) &= (0.0014566\cdot \mathrm{Cl}-[\mathrm{SO_4}])\cdot[-141.594+1.09368\cdot T-0.002149\cdot T^2 + \\ &(3.9943-0.02936\cdot T+0.00005497\cdot T^2)\cdot \mathrm{Cl}]+(0.0032833\cdot \mathrm{Cl}-[\mathrm{Mg}]-[\mathrm{Ca}])\times \\ &\{128.139-30.411\cdot \ln(T)+[-157.692+36.570\cdot \ln(T)]\cdot \mathrm{Cl}^{1/2}/(1+\mathrm{Cl}^{1/2})\}+ \\ &(0.0032833\cdot \mathrm{Cl}-[\mathrm{Mg}]-[\mathrm{Ca}])^2\cdot\{4042.88-787.32\cdot \ln(T)+[-4689.1+ \\ &908.44\cdot \ln(T)]\cdot \mathrm{Cl}^{1/2}/(1+\mathrm{Cl}^{1/2})\}\end{aligned} \quad \text{(S23)}$$

$$\begin{aligned}\Delta\log(K_s) &= (0.0032833\cdot \mathrm{Cl}-[\mathrm{Mg}]-[\mathrm{Ca}])\cdot\{157.55-37.817\cdot \ln(T)+ \\ &[-187.70+44.197\cdot \ln(T)]\cdot \mathrm{Cl}^{1/2}/(1+\mathrm{Cl}^{1/2})\}+(0.0032833\cdot \mathrm{Cl}-[\mathrm{Mg}]-[\mathrm{Ca}])^2\times \\ &\{5778.6-1165.47\cdot \ln(T)+[-6836.8+1376.21\cdot \ln(T)]\cdot \mathrm{Cl}^{1/2}/(1+\mathrm{Cl}^{1/2})\}\end{aligned} \quad \text{(S24)}$$

In relations (22S)–(24S), T is the temperature on the Kelvin scale, Cl is chlorinity expressed as a mass fraction in ‰ and [SO_4], [Mg] and [Ca] are the concentrations of sulfate, magnesium, and calcium in mol/kg-sw, "molinity" [7].

These equations can be used to determine the log *K* values for any anoxic pore water sample given the concentrations of dissolved sulfate, Mg and Ca. Subsequently, the concentration constants for the carbonate system in anoxic porewaters (K^*_{pw}) can be calculated as the sum of the concentration constants valid for seawater (K^*_{sw}) and the log *K* values:

$$\log(K^*_{1pw}) = \log(K^*_{1sw}) + \Delta\log(K_1) \quad \text{(S25)}$$

$$\log(K^*_{2pw}) = \log(K^*_{2sw}) + \Delta\log(K_2) \quad \text{(S26)}$$

$$\log(IP^*_{pw}) = \log(IP^*_{sw}) + \Delta\log(K_s) \quad \text{(S27)}$$

Where "*IP*" means Ionic Product. With these new constants, it is now possible to calculate reliable pH values and other parameters of the carbonate system in anoxic pore fluids and seawater with anomalous concentrations of sulfate, alkalinity, and alkaline earth metals.

Alteration of the composition of pore water would change not only the constants of the carbonate system at pressure 1 atmosphere but also their pressure dependence. However, we consider this effect to be of secondary order, and in further calculations of the carbonate system at in situ pressure, we will carry out the procedure as is generally accepted for seawater [1] without any consideration of the effect variation of composition pore water on the pressure dependence of the constants.

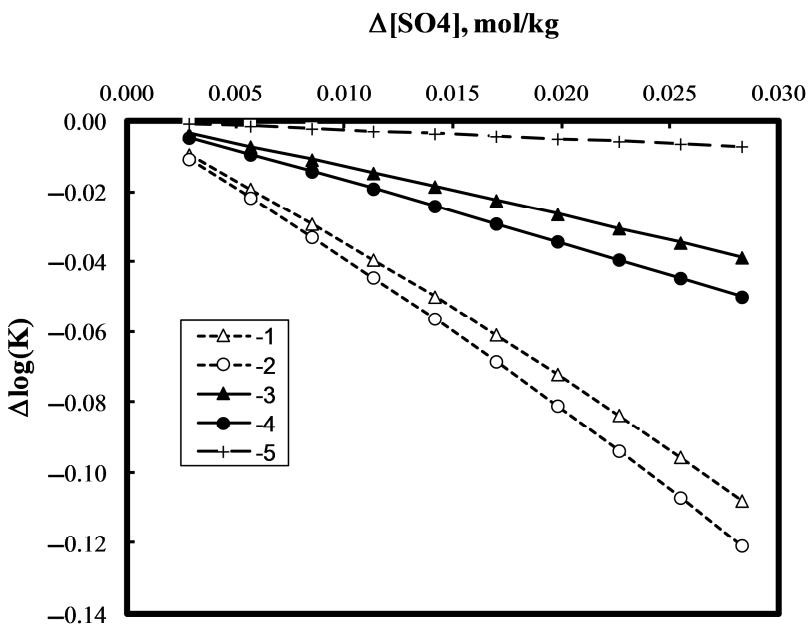

Figure S1. Effect of sulfate reduction (decreasing sulfate concentrations and increasing carbonate alkalinity) on the stability constants of the carbonate system in seawater (salinity = 35). Symbols indicate changes in the logarithm of the first dissociation constant (**1**,**3**) and the second dissociation constant (**2**,**4**) at 25°C and 0°C, respectively; **5** – changes in log(Ks) at 0°C.

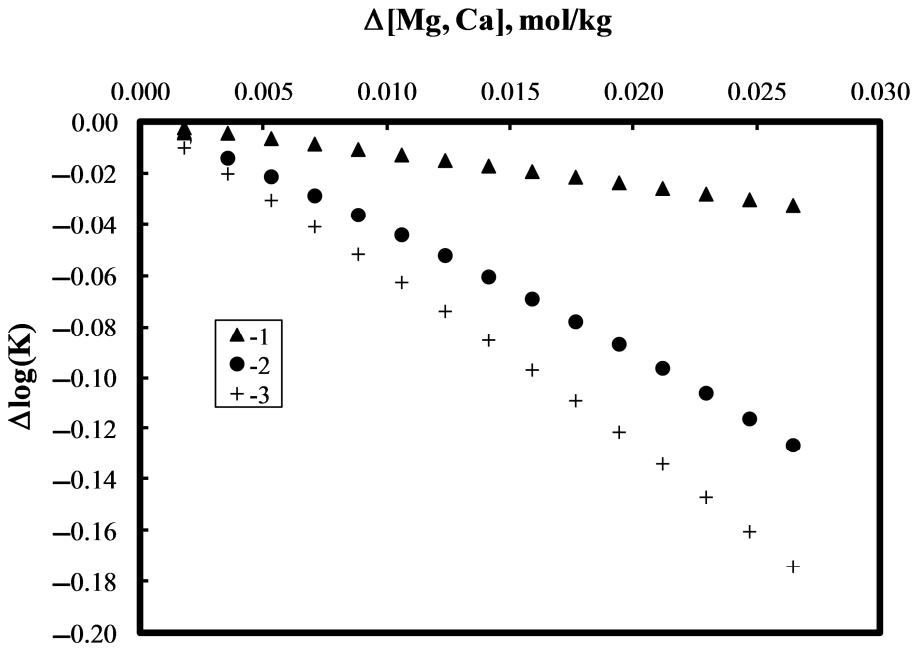

Figure S2. Effect of carbonate precipitation (decreasing calcium, magnesium, and carbonate alkalinity) on the stability constants of the carbonate system in seawater (salinity = 35, temperature = 0°C). Symbols indicate changes in the logarithm of the first (**1**) and the second (**2**) dissociation constants and solubility of calcium carbonate (**3**).

Table S3. The composition of seawater at S=35.

Salt	Molality
NaCl	0.42522
Na_2SO_4	0.02927
KCl	0.01058
$NaHCO_3$	0.00240
$CaCl_2$	0.01074
$MgCl_2$	0.05475

Table S4. References of Pitzer parameters which take into account interactions between cations and anions for individual electrolyte solutions used in the modeling calculations.

Cation (i)	anion(j)	Ref.	Cation	Anion	Ref.
Ca	SO4	[5]	Mg	Cl	[22]
Ca	HCO3	[5]	Mg	SO4	[23]
Na	SO4	[6]	Mg	HCO3	[24]
H	Cl	[9]	K	Cl	[25]
Na	Cl	[19]	K	SO4	[26]
Na	HCO3	[20]	K	HCO3	[27]
Na	CO3	[21]	Ca	Cl	[28]
K	CO3	[21]	-	-	-

Table S5. References of Pitzer parameters which take into account interactions in ternary electrolyte solutions (i, j, k – peces) used in the modeling calculations.

(i)	(j)	(k)	Ref.	(i)	(j)	(k)	Ref.
K	HCO3	Cl	[5]	H	Ca	Cl	[8]
Na	K	CO3	[5]	HCO3	Cl	Na	[20]
CO3	HCO3	K	[5]	Na	CO3	Cl	[21]
Na	HCO3	K	[5]	CO3	SO4	Na	[21]
H	K	Cl	[5]	Na	Cl	CO2	[29]
H	K	SO4	[5]	Na	SO4	CO2	[30]
HCO3	Cl	Mg	[5]	K	Cl	CO2	[30]
HCO3	SO4	Na	[5]	K	SO4	CO2	[30]
HCO3	SO4	Mg	[5]	Mg	Cl	CO2	[30]
CO3	SO4	K	[5]	Mg	SO4	CO2	[30]
CO3	HCO3	Na	[5]	Ca	Cl	CO2	[30]
H	Na	Cl	[8]	H	Cl	CO2	[31]
H	Na	SO4	[8]	Na	HCO3	CO2	[31]
H	Mg	Cl	[8]	-	-	-	-

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